Gmelin Handbook of Inorganic Chemistry

8th Edition

Gmelin Handbook Volumes on Radium and Actinides

Ac	Actinium*			– 1942
	Actinium Suppl. Vol. 1			– 1981
Np, Pu ...	Part A1, I	(New Suppl. Series Vol. Nr. 7a)	(Elements)	– 1973
	Part A1, II°	(New Suppl. Series Vol. Nr. 7b)		– 1974
	Part A2°	(New Suppl. Series Vol. Nr. 8)		– 1973
	Part B1°	(New Suppl. Series Vol. Nr. 31)	(Metals)	– 1976
	Part B2*	(New Suppl. Series Vol. Nr. 38)	(Alloys)	– 1976
	Part B3*	(New Suppl. Series Vol. Nr. 39)		– 1977
	Part C°	(New Suppl. Series Vol. Nr. 4)	(Compounds)	– 1972
	Part D1°	(New Suppl. Series Vol. Nr. 20)	(Chemistry in Solution)	– 1975
	Part D2°	(New Suppl. Series Vol. Nr. 21)		– 1975
	Index			– 1979
Pa	Protactinium Main Volume*			– 1942
	Protactinium Suppl. Vol. 1°	(Element)		– 1977
	Protactinium Suppl. Vol. 2°	(Metal. Alloys. Compounds. Chemistry in Solution)		– 1977
Ra	Radium Main Volume*			– 1928
	Radium Suppl. Vol. 1*	(History. Cosmochemistry. Geochemistry)		– 1977
	Radium Suppl. Vol. 2	(Element. Compounds)		– 1977
Th	Thorium Main Volume*			– 1955
	Thorium Suppl. Vol. C1*	(Compounds with Rare Gases, Hydrogen, Oxygen)		– 1978
	Thorium Suppl. Vol. C2*	(Ternary and Polynary Oxides)		– 1976
U	Uranium Main Volume*			– 1936
	Uranium Suppl. Vol. A1*	(Uranium Deposits)		– 1979
	Uranium Suppl. Vol. A2°	(Isotopes)		– 1980
	Uranium Suppl. Vol. A3*	(Technology. Uses)		– 1981
	Uranium Suppl. Vol. A4	(Irradiated Fuel. Reprocessing)		– 1982 (present volume)
	Uranium Suppl. Vol. C1*	(Compounds with Rare Gases and Hydrogen. Uranium-Oxygen System)		– 1977
	Uranium Suppl. Vol. C2*	(U_3O_8 and UO_3 Oxides. Hydroxides and Oxide Hydrates. Peroxides)		– 1978
	Uranium Suppl. Vol. C3*	(Ternary and Polynary Oxides)		– 1975
	Uranium Suppl. Vol. C7°	(Compounds with Nitrogen)		– 1981
	Uranium Suppl. Vol. C8*	(Compounds with Fluorine)		– 1980
	Uranium Suppl. Vol. C9	(Compounds with Chlorine, Bromine, Iodine)		– 1979
	Uranium Suppl. Vol. C11	(Compounds with Selenium, Tellurium, and Boron)		– 1981
	Uranium Suppl. Vol. C14	(Compounds with P, As, Sb, Bi, Ge)		– 1981
	Uranium Suppl. Vol. D2	(Solvent Extraction)		– 1982
	Uranium Suppl. Vol. E1	(Coordination Compounds)		– 1979
	Uranium Suppl. Vol. E2°	(Coordination Compounds)		– 1980

* Completely or ° in part in German

Gmelin Handbuch der Anorganischen Chemie

Achte völlig neu bearbeitete Auflage

BEGRÜNDET VON Leopold Gmelin

ACHTE AUFLAGE BEGONNEN im Auftrag der Deutschen Chemischen Gesellschaft
von R. J. Meyer

FORTGEFÜHRT VON E. H. E. Pietsch und A. Kotowski
Margot Becke-Goehring

HERAUSGEGEBEN VOM Gmelin-Institut für Anorganische Chemie
der Max-Planck-Gesellschaft zur Förderung der Wissenschaften
Direktor: Ekkehard Fluck

Springer-Verlag Berlin Heidelberg GmbH 1982

Gmelin-Institut für Anorganische Chemie
der Max-Planck-Gesellschaft zur Förderung der Wissenschaften

KURATORIUM (ADVISORY BOARD)

Dr. J. Schaafhausen, Vorsitzender (Hoechst AG, Frankfurt/Main-Höchst), Dr. G. Breil (Ruhrchemie AG, Oberhausen-Holten), Dr. G. Broja (Bayer AG, Leverkusen), Prof. Dr. G. Fritz (Universität Karlsruhe), Prof. Dr. N. N. Greenwood (University of Leeds), Prof. Dr. R. Hoppe (Universität Gießen), Prof. Dr. R. Lüst (Präsident der Max-Planck-Gesellschaft, München), Dr. H. Moell (BASF-Aktiengesellschaft, Ludwigshafen), Prof. Dr. E. L. Muetterties (University of California, Berkeley, California), Prof. Dr. H. Nöth (Universität München), Prof. Dr. A. Rabenau (Max-Planck-Institut für Festkörperforschung, Stuttgart), Prof. Dr. Dr. h.c. mult. G. Wilke (Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr)

DIREKTOR (DIRECTOR)
Prof. Dr. Dr. h.c. Ekkehard Fluck

STELLVERTRETENDER DIREKTOR (DEPUTY DIRECTOR)
Dr. W. Lippert

HAUPTREDAKTEURE (CHIEF EDITORS)

Dr. K.-C. Buschbeck, Ständiger Hauptredakteur

Dr. H. Bergmann, Dr. H. Bitterer, Dr. H. Katscher, Dr. R. Keim, Dipl.-Ing. G. Kirschstein, Dipl.-Phys. D. Koschel, Dr. U. Krüerke, Dr. H. K. Kugler, Dr. E. Schleitzer-Rust, Dr. A. Slawisch, Dr. K. Swars, Dr. B. v. Tschirschnitz-Geibler, Dr. R. Warncke

MITARBEITER (STAFF)

Z. Amerl, D. Barthel, Dr. N. Baumann, I. Baumhauer, Dr. K. Beeker, Dr. W. Behrendt, Dr. L. Berg, Dipl.-Chem. E. Best, M. Brandes, E. Brettschneider, E. Cloos, Dipl.-Phys. G. Czack, I. Deim, Dipl.-Chem. H. Demmer, R. Dombrowsky, R. Dowideit, Dipl.-Chem. A. Drechsler, Dipl.-Chem. M. Drößmar, M. Engels, Dr. H.-J. Fachmann, Dr. J. Faust, I. Fischer, Dr. R. Froböse, J. Füssel, Dipl.-Ing. N. Gagel, Dipl.-Chem. H. Gedschold, E. Gerhardt, Dr. U. W. Gerwarth, M.-L. Gerwien, Dipl.-Phys. D. Gras, Dr. V. Haase, H. Hartwig, B. Heibel, Dipl.-Min. H. Hein, G. Heinrich-Sterzel, H.-P. Hente, H. W. Herold, U. Hettwer, U. Hilberger, Dr. I. Hinz, Dr. W. Hoffmann, Dipl.-Chem. K. Holzapfel, Dipl.-Chem. W. Karl, H.-G. Karrenberg, Dipl.-Phys. H. Keller-Rudek, I. Knauss, Dipl.-Phys. E. Koch, Dr. E. Koch, Dipl.-Chem. K. Koeber, Dipl.-Chem. H. Köttelwesch, R. Kolb, E. Kranz, Dipl.-Chem. I. Kreuzbichler, Dr. A. Kubny, Dr. P. Kuhn, M. Langer, M.-L. Lenz, Dr. A. Leonard, Dipl.-Chem. H. List, H.Mathis, E. Meinhard, Dr. P. Merlet, K. Meyer, M. Michel, K. Nöring, C. Pielenz, E. Preißer, I. Rangnow, Dipl.-Phys. H.-J. Richter-Ditten, Dipl.-Chem. H. Rieger, E. Rieth, Dr. J. F. Rounsaville, E. Rudolph, G. Rudolph, Dipl.-Chem. S. Ruprecht, D. Schädle, V. Schlicht, Dipl.-Chem. D. Schneider, Dr. F. Schröder, Dipl.-Min. P. Schubert, A. Schwärzel, Dipl.-Ing. H. M. Somer, E. Sommer, Dr. P. Stieß, M. Teichmann, Dr. W. Töpper, U. Trautwein, Dipl.-Ing. H. Vanecek, Dipl.-Chem. P. Velić, Dipl.-Ing. U. Vetter, Dipl.-Phys. J. Wagner, R. Wagner, Dipl.-Chem. S. Waschk, Dr. G. Weinberger, Dr. H. Wendt, Dr. B. Wöbke, K. Wolff, Dr. A. Zelle, U. Ziegler

FREIE MITARBEITER (CORRESPONDENT MEMBERS OF THE SCIENTIFIC STAFF)

Dr. I. Kubach, Prof. Dr. P. F. Linde, Prof. Dr. Y. Marcus, Dr. K. Rumpf, Dr. R. C. Sangster, Dr. R. P. Taylor, Dr. U. Trobisch

EM. WISSENSCHAFTLICHES MITGLIED
(EMERITUS MEMBER OF THE INSTITUTE)
Prof. Dr. Dr. E. h. Margot Becke

AUSWÄRTIGE WISSENSCHAFTLICHE MITGLIEDER
(CORRESPONDENT MEMBERS OF THE INSTITUTE)
Prof. Dr. Hans Bock
Prof. Dr. Dr. Alois Haas, Sc. D. (Cantab.)

Gmelin Handbook of Inorganic Chemistry

8th Edition

U
Uranium

Supplement Volume A4

Behavior of Uranium Fuels in Nuclear Reactors. Reprocessing of Spent Nuclear Fuels

With 173 illustrations

AUTHORS

Helmut Aßmann, Kraftwerk Union AG, Erlangen

Erich Merz, Kernforschungsanlage, Jülich

Aristides Naoumidis, Kernforschungsanlage, Jülich

Hubertus Nickel, Kernforschungsanlage, Jülich

Heinz Stehle, Kraftwerk Union AG, Erlangen

Gilbert N. Walton, Department of Chemical Engineering and Chemical Technology, Imperial College, London University, London, U.K.

CHIEF EDITORS

Karl-Christian Buschbeck, Gmelin-Institut,
Frankfurt am Main

Cornelius Keller, Supervising scientific coordinator
for the Uranium Supplement Volumes,
Schule für Kerntechnik, Kernforschungszentrum Karlsruhe

System Number 55

Springer-Verlag Berlin Heidelberg GmbH 1982

LITERATURE CLOSING DATE: END OF 1979
IN MANY CASES MORE RECENT DATA HAVE BEEN CONSIDERED

Library of Congress Catalog Card Number: Agr 25-1383

ISBN 978-3-662-06016-2 ISBN 978-3-662-06014-8 (eBook)
DOI 10.1007/978-3-662-06014-8

Originally published by Springer-Verlag, Berlin · Heidelberg · New York 1981
Softcover reprint of the hardcover 8th edition 1981

Preface

The present volume A 4 of the "Uranium" series of the Gmelin Handbook deals with two very important technological aspects of the nuclear fuel cycle:

- the behavior of fuel elements during burnup in a nuclear reactor, and
- the reprocessing of spent fuel to recover the non-fissioned uranium and newly created materials.

The useful lifetime of a fuel element in a nuclear reactor depends strongly on the change of its chemical and physical properties during irradiation. Properties like thermal conductivity, swelling, creep, and oxygen-to-metal ratio are strongly affected by the intense neutron field and the energetic fission products. Furthermore, the high temperature gradient in a fuel element also produces alterations of the initial fuel, such as densification or U:Pu segregation. All of these effects are thoroughly discussed for the different kinds of fuels to be used in modern nuclear reactors today or in the future. The vast amount of very often contradictory results in sometimes difficultly obtainable literature has been summarized to create a compendium in this field with the two sections, on oxide and on carbide and nitride fuels, respectively.

The chapters on reprocessing of spent fuels deal only with fuel elements of the uranium-thorium fuel cycle and with those containing fuel highly enriched in ^{235}U. The treatment of UO_2 and $(U,Pu)O_2$ has already been given in the transuranic element series.

Due to the vast amount of literature published within the topics of this book, only selected and important papers have been mentioned here. For other references see the "General References" etc. in this book. The literature is evaluated for the period up to the end of 1979, in many cases more recent literature has been considered.

I thank the authors from industry and the nuclear research centers for their excellent collaboration. I thank also the Gmelin Institute, with Prof. Dr. Y. Marcus, who translated the originally German text into English, Dr. K. C. Buschbeck as the supervising editor and Prof. Dr. Dr. h.c. E. Fluck as director, for its support and encouragement.

Frankfurt am Main
December 1981

Cornelius Keller

Table of Contents

1 The Behavior of Uranium Fuels in Nuclear Reactors

1.1 Oxide Fuels

H. Aßmann, H. Stehle
Kraftwerk Union AG
Erlangen, Bundesrepublik Deutschland

General References:

Bibliographies and Discussions of the Literature

W. E. Bost, Irradiation of UO_2, A Literature Search, TID-3559 [1960] 1/23 [167 Refs.]; N.S.A. **15** [1961] No. 14808.

B. J. Seddon, Uranium Ceramics Data Manual Properties of Interest in Reactor Design, DEG-120-R [1960] 1/68; N.S.A. **15** [1961] No. 4280.

B. J. Seddon, Physical Properties of Some Plutonium Ceramic Compounds, A Data Manual, TRG-1601-R [1968] 1/54; N.S.A. **22** [1968] No. 43651.

M. Bloomfield, Irradiation of Plutonium Fuels, A Selected Bibliography, NAA-SR-Memo-6271 [1961] 1/14 [187 Refs.]; N.S.A. **15** [1961] No. 18557.

W. Uhlmann, Radiation Effects on Solid-Based Nuclear Fuel Materials, A Bibliography, VDIT-16.1 [1961]/VDIT-16.5.4 [1965] 1/775 [20 Repts., 2 Index-Repts., 1601 Refs.].

G. Neuer, R. Brandt, G. Haufler, Literaturstudie über die Wärmeleitfähigkeit und den Emissionsgrad von festem UO_2, IRS-SB-3 [1973] 1/217 [277 Refs.]; N.S.A. **30** [1974] No. 27343; C.A. **82** [1975] No. 116968.

J. Richter, H. E. Schmidt, H. A. Tasman, Bibliography on Heat Transport in Nuclear Fuels and Related Phenomena, EUR-5119.e [1974] 1/216 [2236 Refs. about oxides].

Reviews

J. D. Eichenberg, P. W. Frank, T. J. Kisiel, B. Lustman, K. H. Vogel, Effects of Irradiation on Bulk Uranium Dioxide, TID-7546 [1958] 616/716; N.S.A. **12** [1958] No. 9446; C.A. **1958** 9905.

J. A. L. Robertson, A. S. Bain, A. H. Booth, J. Howieson, W. G. Morison, R. F. S. Robertson, Behavior of Uranium Oxide as a Reactor Fuel, Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 6, pp. 655/76.

W. K. Barney, Irradiation Effects in UO_2, Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 6, p. 67.

H. H. Hausner, J. F. Schumar, Nuclear Fuel Elements, Reinhold, New York 1959, pp. 1/420.

J. Belle, Uranium Dioxide, Properties and Nuclear Applications, U.S. At. Energy Commission, Washington, D.C., 1961, pp. 1/726; C.A. **1961** 23110.

J. A. L. Robertson, A. S. Bain, J. R. MacEwan, M. J. F. Notley, UO_2 Performance, The Importance of Temperature Distribution, Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 395/404.

L. E. J. Roberts, P. Brock, J. R. Findlay, B. R. T. Frost, L. E. Russell, J. B. Sayers, E. Wait, The Behavior of UO_2 and $(U, Pu)O_2$ Fuel Materials Under Irradiation, Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 464/71.

T. J. Pashos, D. R. de Halas, D. L. Keller, L. A. Neimark, Irradiation Behavior of Ceramic Fuels, Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 472/84.

R. B. Holden, Ceramic Fuel Elements, Gordon and Breach, New York 1966, pp. 1/244; C.A. **68** [1968] No. 45422.

B. T. Bradburg, B. R. T. Frost, Radiation Effects in Ceramic Fuels in: G. J. Dienes, Studies in Radiation Effects on Solids, Vol. 2, Gordon and Breach, New York 1967, pp. 159/279.

M. D. Freshley, Irradiation Behavior of Plutonium Fuels in: O. J. Wick, Plutonium Handbook, A Guide to the Technology, Vol. 2, Gordon and Breach, New York 1967, pp. 643/706.

J. A. L. Robertson, Irradiation Effects in Nuclear Fuels, Gordon and Breach, New York 1968, pp. 1/320; C.A. **70** [1969] No. 25049.

B. R. T. Frost, Studies of Irradiation Effects in Ceramic Fuels at Harwell in: O. L. Kruger, Ceramic Nuclear Fuels, Columbus, Ohio, 1969, pp. 225/43.

M. T. Simnad, Fuel Element Experience in Nuclear Power Reactors, Gordon and Breach, New York 1971, pp. 1/620; C.A. **76** [1972] No. 67165.

R. Farnmakes, Proceedings of the Conference on Fast Reactor Fuel Element Technology, New Orleans 1971, pp. 267/738.

G. B. Greenough, J. S. Nairn, J. B. Sayers, Uranium Dioxide Fuel in the Mark II Gas-Cooled Reactor [AGR], Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 10, pp. 141/52.

W. H. Zinn, W. P. Chernock, M. H. Bleiberg, H. M. Ferrari, T. Stern, M. F. Lyons, G. J. Walke, Development of Improved Light Water Reactor Fuels, Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 10, pp. 121/36.

M. F. Lyons, R. F. Boyle, J. H. Davies, V. E. Hazel, T. C. Rowland, UO_2 Properties Affecting Performance, Nucl. Eng. Design **21** [1972] 167/99.

M. D. Freshley, A Comparison of Pellet and VIPAC Nuclear Fuels, Nucl. Eng. Design **21** [1972] 264/78.

British Nuclear Energy Society, Nuclear Fuel Performance Proceedings of the International Conference, London 1973, Sessions 1 to 7.

M. Taube, Plutonium. A General Survey, Kernchemie in Einzeldarstellungen, Vol. 4, Verlag Chemie, Weinheim/Bergstr. 1974, pp. 169/81.

IAEA, Behavior and Chemical State of Irradiated Ceramic Fuels, Proceedings of a Panel, Vienna 1972 [1974], pp. 1/437.

IAEA, Thermodynamics of Nuclear Materials Proceedings of the 4th Symposium, Vienna 1974 [1975], Vol. 1, pp. 1/469, Vol. 2, pp. 1/534.

J. E. Harris, E. C. Sykes, Physical Metallurgy of Reactor Fuel Elements Proceedings of an International Conference, Berkeley, U.K., 1973 [1975], pp. 1/474.

H. Stehle, H. Aßmann, F. Wunderlich, Uranium Dioxide Properties for LWR Fuel Rods, Nucl. Eng. Design **33** [1975] 230/60.

K. D. Reeve, Ceramics as Nuclear Reactor Fuels, Ceramurgia Intern. **1** [1975] 59/71 [178 Refs.].

D. R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 1/624; INIS Atomindex **8** [1977] No. 284120.

P. E. MacDonald, L. B. Thompson, MATPRO-Version 09, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, TREE-NUREG-1005 [1976] 1/402; INIS Atomindex **8** [1977] No. 321147.

D. L. Hagrman, G. A. Reyman, R. E. Mason, MATPRO-Version 11 – Rev. 1, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, NUREG-CR-0497-Rev. 1 [1980] 1/513; TREE-1280 – Rev. 1 [1980] 1/513.

ANS [American Nuclear Society], Water Reactor Fuel Performance Topical Meeting, St. Charles, Illinois, 1977.

IAEA, Nuclear Power and Its Fuel Cycles Proceedings of an International Conference, Salzburg 1977, Vol. 2.

The European Nuclear Conference, Hamburg 1979; Trans. Am. Nucl. Soc. **31** [1979]; CONF-790519 [1979).

ANS [American Nuclear Society], Topical Meeting on LWR Fuel Performance, Portland 1979.

ANS [American Nuclear Society], Winter Meeting, San Francisco 1979; Trans. Am. Nucl. Soc. **33** [1979]; CONF-791103 [1979).

IAEA, International Symposium on Water Reactor Fuel Elements Fabrication with Special Emphasis on Its Effects on Fuel Performance; Prague 1978 [1979].

Characterization and Quality Control of Nuclear Fuels Proceedings of a Conference, Karlsruhe 1978; J. Nucl. Mater. **81** [1979] 1/286.

F. Garzarolli, R. v. Jan, H. Stehle, The Main Causes of Fuel Element Failures in Water Cooled Power Reactors, At. Energy Rev. **17** No. 1 [1979].

K. D. Reeve, Ceramic Nuclear Fuels – Status and Recent Developments, Mater. Sci. Monogr. **6** [1980] 807/22 [110 Refs.]; C.A. **93** [1980] No. 55952.

Introduction and Survey

This chapter summarizes what is known, as of 1978, concerning the behavior of the nuclear fuels UO_2 and UO_2-PuO_2 under irradiation in water cooled power reactors and in fast breeder reactors. Some sections have been updated (especially Sections 1.1.2, 1.1.3, 1.1.4, 1.1.7, and 1.1.8), to include more recent results published until 1980. The approximately 1 000 references to the literature present a selection of the most important publications in this area. The literature of the last ten years was given priority in the selection.

By far the largest amount of nuclear fuel is employed today in light water reactors (LWR) – pressurized water reactors (PWR) and boiling water reactors (BWR) – and in heavy water reactors. This fuel involves pressed and sintered pellets of UO_2 containing slightly enriched uranium (^{235}U content up to ca. 4 wt%) or of natural uranium. Beside this basic fuel, in some LWRs are employed also the fuels UO_2-PuO_2 (thermal Pu-recycling, Pu content ca. 4 wt%) and UO_2-Gd_2O_3 (Gd_2O_3 content up to ca. 6 wt%), where the Gd serves as a burnable neutron absorber. The behavior of these two kinds of fuel under irradiation is very similar to that of pure UO_2, and they need not be discussed separately. The Pu content of the UO_2-PuO_2 fuel for fast breeder reactors (FBR) ranges from 15 to 30 wt%. The properties of the LWR and FBR fuels are treated together, as long as phenomena specific for Pu-containing fuels do not require a separate discussion. Chapter 3.2.4 (pp. 180/6) of "Uran" Erg.-Bd. A3, 1981, deals with fuel for high temperature reactors (coated fuel particles, ThO_2-UO_2). Vibrationally compacted fuel is not dealt with here specifically.

The behavior of UO_2 and UO_2-PuO_2 under conditions of stationary operation and operation under variable load typical for a power reactor is described systematically in the following. The behavior in cases of design accidents and hypothetical accidents is not discussed. In certain cases, however, the discussion will go beyond that range of parameters, which occurs under normal operation conditions, in order to deal in a complete manner with the dependence of the physical properties on, e.g., the temperature. Properties are therefore described in many cases, which can be regarded as material properties of irradiated fuels, and which permit extrapolation to different operational conditions or even to different fuels.

The behavior of nuclear fuels under irradiation is determined by the following phenomena:

(1) Effects of the fission fragments in the crystal lattice

A short-circuit like diffusion occurs in the spike of the fission fragment, so that many diffusion-controlled processes at low temperatures (e.g., creep, sintering) suffer "fission-induced" acceleration in a nuclear reactor. The formation of lattice defects in the fuel, on the contrary, has a less noticeable effect.

(2) Mechanical behavior

The elastic properties and the fracture of the fuel in the reactor may be extrapolated from the properties of the non-irradiated material. However the rate of creep at temperatures below ca. 1 000 °C is accelerated under irradiation and is essentially temperature independent.

(3) Thermal behavior

The thermal conductivity, which is practically unaffected by radiation above 500 °C, is an extremely important quantity for the description of the behavior of the fuel in the reactor, since it determines the temperature level and gradients in the fuel pellet. Further parameters which are important are thermal expansion and specific heat.

(4) Behavior of the fission products and their release

The nuclear fission products (FP) can be classified as: (a) solid and volatile fission products, and (b) fission gases (Kr, Xe). The first category may be homogeneously dispersed, or may occur in finely or coarsely dispersed nonmetallic and metallic phases. A redistribution and a partial release of these FPs may result from a temperature gradient. The fission gases (FG) behave in a very complicated manner. The FGs formed in the fuel matrix separate out as FG bubbles. The size of these bubbles depends on the one hand on the aggregation of further FG atoms brought in by diffusion, and on the other on a redissolution mechanism caused by the fission fragments. Bubbles migrate either isotropically by diffusion, or they may be directed by temperature gradients. Transport of the FGs to the grain boundaries and the development of continuous grain boundary porosity leads to the release of the FG from the fuel. This release may occur at high temperatures also from the migration of bubbles along temperature gradients.

(5) Radiation-induced dimensional changes (densification and swelling)

The densification of irradiated fuel results from the interaction of fission fragments and pores at low and intermediate temperatures. The initial pore volume is transformed into lattice vacancies in this process. The vacancies migrate to the grain boundaries, and cause a macroscopically noticeable densification of the polycrystalline material.

The swelling of the fuel is determined by those fission products that are not released. It is maximal at intermediate temperatures, at which a major portion of the fission gases occur as bubbles. The radiation induced dimensional changes of the fuel are an additive result of the "densification" and "swelling" phenomena, which are essentially unaffected by external forces. The swelling of the fuel may, therefore, be compensated by a "taylor-made" porosity to some extent.

(6) Restructuring

A certain crack pattern of the fuel pellet is generated by the thermal stresses in it. At high temperatures a redistribution of the initial porosity results, and grain growth occurs. At very high temperatures, columnar grain growth and the formation of a central void may occur.

(7) Changes in the stoichiometry, redistribution of the oxygen and uranium/plutonium

The mean valency of the fission products is lower than that of uranium or plutonium in the fuel. It is necessary to consider the formation of new oxide phases, the alteration of the O/U or O/Pu ratios of the fuel matrix and the loss of oxygen, e.g., by reaction with the cladding, for arriving at the oxygen balance. Oxygen transport may result from solid or gas diffusion as well as thermodiffusion. Similar mechanisms are effective for the demixing of uranium and plutonium in FBR fuels.

(8) Interaction with the cladding

A more or less regular oxide layer forms on the interior surface of Zircaloy cladding tubes (LWR fuel rods) as well as steel cladding tubes (FBR fuel rods), that has essentially no effect on the operational behavior. Zircaloy cladding tubes, which are tension-stressed by the thermal expansion of the fuel pellets during fast power increases (power ramps), may suffer from microcracking by means of stress corrosion. Iodine or iodine compounds are probably the effective chemical species in this process. This phenomenon is described as "pellet-clad-interaction (PCI)". Caesium plays a similar role in the observed grain boundary corrosion of austenitic steel cladding tubes of FBR fuels.

(9) Behavior in defective fuel rods

Oxidic fuel is in principle very corrosion-resistant against water and sodium (or NaK). Continued operation till the next planned fuel element change is a well rehearsed and safe process for dealing with water cooled defective fuel rods.

In summary, it may be stated that oxidic fuels fulfill their task excellently, due to their stable behavior under irradiation. This is confirmed by the low liability for developing defects shown by LWR fuel rods in practice.

1.1.1 Effects of the Fission Fragments in the Crystal Lattice

General Reference

H. Matzke, Lattice Defects and Irradiation Damage in ThO_2, UO_2, and $(U,Pu)O_2$, Plutonium and Other Actinides 1975, Proc. 5th Intern. Conf., Baden-Baden 1975 [1976], pp. 801/31 [227 Refs.]; C.A. **85** [1976] No. 100623.

1.1.1.1 Properties of the Fission Fragment Spike

Fission fragments are the high-energetic, highly ionized daughter atoms formed in fission, immediately after the fission event. Fission products are these daughter atoms after they have given off their kinetic energy. Blank, Matzke [1, 2] and Ronchi [3] have studied the fission fragment spike both theoretically and experimentally. Some 95% of the energy of the fission fragment is transformed into electronic stopping power, and only a minor portion causes lattice defects, e.g., through displacement cascades. Theoretical estimates have been presented by Kinchin, Pease [4] and by Linhard, Scharff [5].

The following relationships describe the thermoplastic stress field of the fission fragment spike in a ceramic fuel [1, 2]:

the temperature distribution $T = \bar{T} + T_0 \exp(-x)$, (1)
the pressure distribution $p = -BT_0 \exp(-x)$, (2)

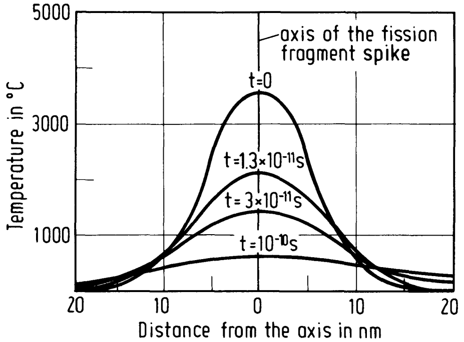
where

$$T_0 = (dE/dl)/(4\, c_p \rho k(t + t_0));\; x = r^2/4k\,(t + t_0);\; B = (4/3)\, G\alpha(1 + \mu)/(1 - \mu). \quad (3)$$

$\bar{T}$ is the mean temperature of the fuel, (dE/dl) is the electronic stopping power per unit of length, c_p is the specific heat, ρ is the theoretical density, k is the thermal diffusivity, G is the shear modulus, μ is Poisson's ratio, α is the coefficient of thermal expansion, r is the radial distance from the axis of the spike, and $t_0 \approx 10^{-11}$ s is the time, during which the electronic stopping power is transformed into heat, and only after which thermal and mechanical effects may be observed.

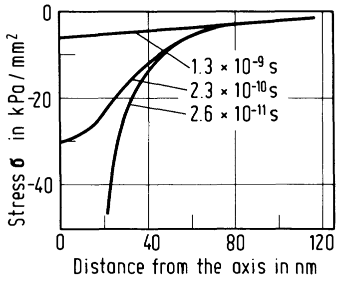
Fig. 1-1 shows the radial temperature distribution 20 nm below a free surface [3]. Only for distances smaller than 10 nm is there an appreciable temperature distortion. **Fig. 1-2** shows the radial stress distribution of a fission fragment spike in the interior of a crystal lattice [1]. A typical fission fragment spike is considered nowadays to be a cylindrical tube having a diameter of 10 nm and a length of 6 μm. Surface traces of fission fragments are shown in **Fig. 1-3** [3]. The fission fragments that emerge from the surface cause sputtering effects. Bessonov [6] has summarized the observations of this phenomenon.

Fig. 1-1



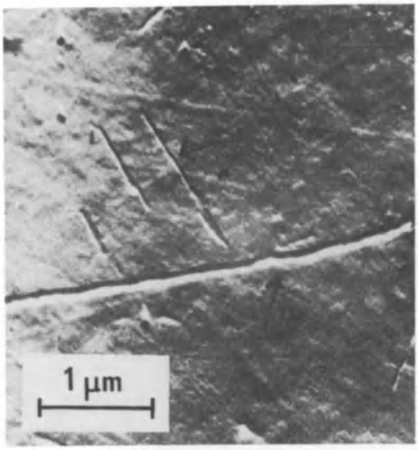
Radial temperature distribution in a fission fragment spike in UO_2, 20 nm below a free surface, after various times [3].

Fig. 1-2



Radial stress distribution in a fission fragment spike in a UO_2 lattice after various times [1].

Fig. 1-3



Traces of fission fragment spikes in UO_2 [3].

The direct effects of the fission fragments have been considered in various mechanistic models for fission-induced processes. The most important examples are:

(1) Radiation-induced creep, according to Malygin et al. [7] (see 1.1.2.3),
(2) Redissolution of fission gases, according to Blank, Matzke [2] (see 1.1.4.2),
(3) Fission-induced densification, according to Aßmann, Stehle [8, 9] (see 1.1.5.1).

References for 1.1.1 on pp. 10/1

1.1.1.2 Increased Self-Diffusion

A further effect of the fission fragments is the acceleration of diffusion processes. In the case of athermal self-diffusion of the metal atoms in the UO_2 lattice at low temperatures, the diffusion constant obeys, according to Clough [10] and Perrin [11, 12], the expression

$$D^* \approx 1 \times 10^{-29} F \quad cm^2/s$$

where F is the fission rate in fissions $\cdot$ $cm^{-3} \cdot s^{-1}$. Direct measurements of Höh, Matzke [13] in UO_2 at 900 °C with $F = 1 \times 10^{13}$ fissions $\cdot$ $cm^{-3} \cdot s^{-1}$ gave

$$D^* = (1.5 \pm 0.6) \times 10^{-16} \quad cm^2/s.$$

A theoretical deduction of the vacancy diffusion coefficient $D_v^* = D^*/C$ (C is the concentration of vacancies) was presented by Stehle et al. [14]:

$$D_v^* = (8/3\pi^2)\ D_v^M \tau F \Omega_f^M \tag{4}$$

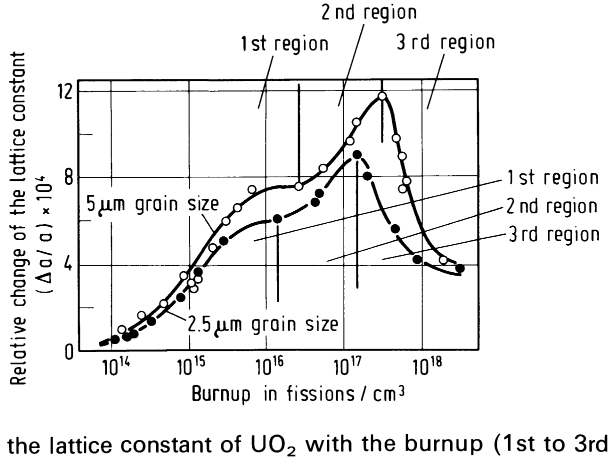
where D_v^M is the vacancy diffusion coefficient in molten UO_2, and Ω_f^M ($\approx 10^{-16} cm^3$) is the volume of the fission fragment spike that is temporarily molten, for the duration τ ($\approx 10^{-11}$ s).

1.1.1.3 Formation and Annealing of Lattice Defects

Radiation damage in the crystal lattice of UO_2 (and PuO_2) was studied experimentally by investigating changes of the lattice constants during self-irradiation (PuO_2) [15 to 17], irradiation with α particles [16], and nuclear fission [18 to 20], as well as by recovery measurements. Lattice constant [16 to 18] and electrical resistance measurements (e.g., [22]) showed the progress of the recovery process during annealing.

The worst lattice damage occurs through the recoil of the ^{235}U daughter nucleus resulting from the decay of the ^{239}Pu, while the α particle has only 1/5 of this effect. Nuclear fission, too, has only 1/4 of this effect [16], where, however, the high fission rate (e.g., 10^{13} fissions $\cdot$ $cm^{-3} \cdot s^{-1}$) must be considered. When UO_2 is irradiated to up to ca. 10^{19} fissions/cm^3, two regions of

Fig. 1-4



The change of the lattice constant of UO_2 with the burnup (1st to 3rd regions) [18].

increasing and one region of decreasing lattice constants are noted (**Fig. 1-4**), which can be interpreted according to Kirihara, Nakae et al. [18, 19] as follows:

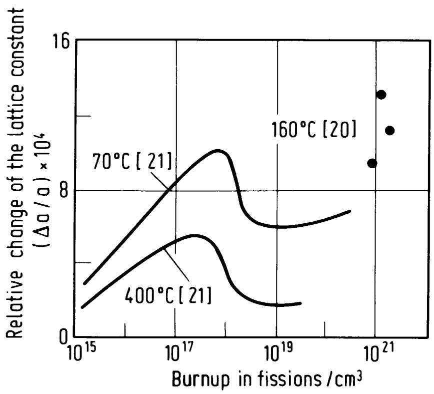
1st region: The concentration of primary defects increases and becomes saturated according to first order kinetics.

2nd region: Secondary defects (e.g., caused by cluster formation of primary defects) increase according to second order kinetics, while the concentration of primary defects decreases.

3rd region: Mobile interstitial atoms are annealed at excess vacancies, and the total concentration of defects decreases.

At an irradiation dose above 10^{20} fissions/cm^3 the lattice constant increases again, according to Kosenkov et al. [20] (see **Fig. 1-5**, together with the results of Roberts et al. [21]). A possible cause could be the formation of compounds from fission products and UO_2.

Fig. 1-5

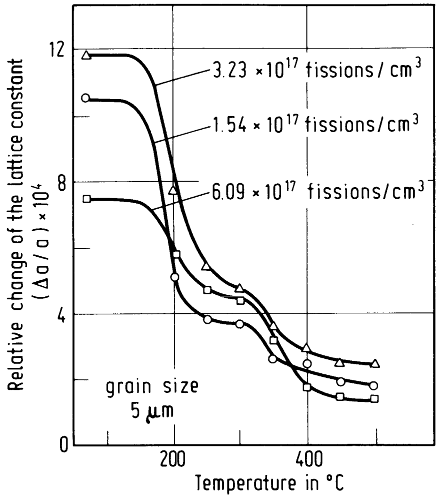


The change of the lattice constants of UO_2 with the burnup at intermediate and high burnup values [20, 21].

In the dose range from 4×10^{15} to 6×10^{17} fissions/cm^3 Nakae et al. [18] have found that the annealing curves show one annealing stage between 200 and 250 °C and another between 300 and 400°C (see for example **Fig. 1-6**, p. 10). Generally, the results show an important annealing stage around 600°C and complete annealing at 1000°C.

Studies by Vollath [22] of annealing processes, by measurements of the electrical conductivity, which were made on quenched UO_2 samples that had been irradiated by fast neutrons, yielded self-consistent results. Table 1/1 presents the recovery stages, their activation energies, and their interpretation in terms of defect removal [23].

Fig. 1-6



Annealing curves for the lattice constant of UO_2 at various burnup values [18].

Table 1/1
Recovery Stages in UO_{2-x}, UO_2, and UO_{2+x}, According to Vollath [22].

recovery stage	temperature in °C	activation energy in kJ/mol	interpretation
A	150 to 250	84 to 105	migration of O-interstitials (only in UO_{2+x})
B	390	138	redistribution of defects in neutron-irradiated and quenched UO_2 through migration of O-interstitials
C	430	167	recombination of near O-Frenkel pairs
D	580 to 600	230	elimination of U-Frenkel pairs through migration of U-vacancies in irradiated UO_2
E	700 to 830	264	migration of O-vacancies in UO_2 and UO_{2-x} after neutron irradiation and quenching

References for 1.1.1:

[1] H. Blank (Phys. Status Solidi A **10** [1972] 465/78). – [2] H. Blank, H. Matzke (Radiat. Eff. **17** [1973] 57/64). – [3] C. Ronchi (J. Appl. Phys. **44** [1973] 3575/85). – [4] G. H. Kinchin, R. S. Pease (Rept. Progr. Phys. **18** [1955] 1). – [5] J. Linhard, M. Scharff (Phys. Rev. [2] **124** [1961] 128/30).

[6] V. A. Bessonov (At. Energ. [USSR] **37** [1974] 52/6; Soviet At. Energy **37** [1974] 730/4). – [7] V. B. Malygin, Yu. K. Bibilashvili, I. S. Golovnin (At. Energ. [USSR] **42** [1977] 8/13; Soviet At. Energy **42** [1977] 6/11; C.A. **86** [1977] No. 112675). – [8] H.

Stehle, H. Aßmann (J. Nucl. Mater. **52** [1974] 303/8). – [9] H. Aßmann, H. Stehle (Nucl. Eng. Design **48** [1978] 49/67). – [10] D. J. Clough (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 321/35).

[11] J. S. Perrin (J. Nucl. Mater. **39** [1971] 175/82). – [12] J. S. Perrin (J. Nucl. Mater. **42** [1972] 101/4). – [13] A. Höh, H. Matzke (J. Nucl. Mater. **48** [1973] 157/64). – [14] H. Stehle, H. Aßmann, F. Wunderlich (Nucl. Eng. Design **33** [1975] 230/60). – [15] M. H. Rand, A. C. Fox, R. S. Street (Nature **195** [1962] 567/8).

[16] R. P. Turcotte (Plutonium 1975 Other Actinides Proc. 5th Intern. Conf., Baden-Baden 1975 [1976], pp. 851/9). – [17] I. I. Kapshukov, L. V. Sudakov, E. V. Shimbarev, A. Ya. Baranov, G. N. Yakovlev (Plutonium 1975 Other Actinides Proc. 5th Intern. Conf., Baden-Baden 1975 [1976], pp. 861/9; C.A. **85** [1976] No. 168465). – [18] N. Nakae, A. Harada, T. Kirihara (J. Nucl. Mater. **71** [1978] 314/9). – [19] T. Kirihara, N. Nakae, H. Matsui, M. Tamaki (Plutonium 1975 Other Actinides Proc. 5th Intern. Conf., Baden-Baden 1975 [1976], pp. 903/13). – [20] V. M. Kosenkov, V. I. Kuzmin, I. G. Lebedev, V. D. Shushakov (At. Energ. [USSR] **37** [1974] 139/43; Soviet At. Energy **37** [1974] 837/41).

[21] L. E. J. Roberts, P. Brock, J. R. Findlay, B. R. T. Frost, L. E. Russell, J. B. Sayers, E. Wait (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 464/70; C.A. **65** [1966] 6665). – [22] D. Vollath (Plutonium 1975 Other Actinides Proc. 5th Intern. Conf., Baden-Baden 1975 [1976], pp. 843/50). – [23] H. Blank (Plutonium 1975 Other Actinides Proc. 5th Intern. Conf., Baden-Baden 1975 [1976], pp. 873/4).

1.1.2 Mechanical Behavior

General References:

G. Engelhardt, H. Hoffmann, Mechanische Eigenschaften von UO_2 [Literaturübersicht], KFK-729 [1968]; EUR-3729.d [1968]; EURFNR-528 [1968] 1/54 [62 Refs.]; N.S.A. **23** [1969] No. 8302.

W. Blum, B. Ilschner, Mechanische Eigenschaften oxidkeramischer Stoffe [Literaturrecherche], Ber. Deut. Rheol. Ges. **31** [1967] 19/64 [213 Refs.].

H. Stehle, H. Aßmann, F. Wunderlich, Uranium Dioxide Properties for LWR Fuel Rods, Nucl. Eng. Design **33** [1975] 230/60.

P. E. MacDonald, L. B. Thompson, MATPRO-Version 09, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, TREE-NUREG-1005 [1976] 40/90.

D. R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 333/72.

D. L. Hagrman, G. A. Reymann, MATPRO-Version 11, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, NUREG-CR-0497 [1979] 49/82, 154/64; TREE-1280 [1979] 49/82, 154/64.

1.1.2.1 Elastic Behavior

An isotropic polycrystalline material has only two independent elastic constants. Given Young's modulus, E, and Poisson's ratio, μ, the shear modulus is obtained as $G = (E/2\mu) + \frac{1}{2}$. The main quantities that affect the elasticity are the temperature and the porosity.

For UO_2 Olsen [1] recommended in the MATPRO-Version 09 handbook the following expression for E, which was derived from a statistical evaluation of the measurements of numerous authors [2 to 8]:

For $\Theta \leq 2000\,°C$

$$E = 2.26 \times 10^5 \, (1 - 1.131 \times 10^{-4} \Theta)(1 - 2.62\,P) \pm 0.037 \times 10^5 \;\; N/mm^2 \tag{1 a}$$

and for $\Theta > 2000\,°C$

$$E = 7 \times 10^2 N/mm^2, \tag{1 b}$$

where Θ is the temperature in °C and P is the volume fraction of the pores. In MATPRO-Version 11, Hagrman et al. [103] recommend the following relationship for Young's modulus of stoichiometric UO_2 below the melting temperature:

$$E_S = 2.334 \times 10^5 \, (1 - 1.0915 \times 10^{-4} T) \; (1 - 2.752\,P), \tag{1 c}$$

where T is the temperature in K and P the volume fraction of the pores. Stehle et al. [9] also dealt with the temperature and porosity dependencies of E in the light of the available literature [4, 5, 7, 8, 10 to 17], and arrived at the expression:

$$E = 2.29 \times 10^5 \; - \; 2.01\,T \; - \; 5.87 \times 10^5\,P \; N/mm^2, \tag{2}$$

where T is the temperature in K. The influence of the irradiation and of the burnup is small, and may be neglected in practice, as has been shown by Baranov et al. [18] by means of measurements in a reactor.

Poisson's ratio μ has the value 0.316 with negligible temperature and porosity dependencies [1, 4, 5, 9, 19, 103]. For 80% UO_2 – 20% PuO_2 these quantities have the following values, according to MATPRO-Version 09 [1, 4, 20]:

$$E = 2.52 \times 10^5 \, (1 - 7.843 \times 10^{-4} \Theta)(1 - 2.03\,P) \;\; N/mm^2 \text{ for } \Theta \leq 1275\,°C \tag{3a}$$

and

$$E = 7 \times 10^2 \;\; N/mm^2 \text{ for } \Theta > 1275\,°C \tag{3b}$$

while the value of μ is 0.276 [20, 103].

For nonstoichiometric fuel or fuel which contains PuO_2 Young's modulus below the melting temperature, as proposed in MATPRO-Version 11 [103], is:

$$E = E_S \exp\,(-Bx) \; (1 + 0.05f), \tag{3c}$$

where $B = 1.34$ for hyperstoichiometric fuel or 1.75 for hypostoichiometric fuel; x is the magnitude of the deviation from stoichiometry in $MO_{2 \pm x}$ fuel, and f is the PuO_2 content of the fuel (weight fraction).

1.1.2.2 Plastic Behavior and Behavior upon Fracture

According to Evans et al. [21] and Cannon et al. [22], three temperature regions may be discerned in the behavior of UO_2 upon fracture:

(1) $T < T_c$: brittleness; elastic deformation up to the fracture stress, which is lower than the yield strength; transcrystalline fracture [21 to 25].

(2) $T_c < T < T_t$: elastic-plastic behavior; elastic deformation, followed by plastic fracture; the yield strength is lower than the fracture stress [21 to 25].

(3) $T > T_t$: plastic fracture (intercrystalline).

T_c and T_t are the transition temperatures between these regions.

The fracture strength σ_F in region (1) depends on the temperature and on the porosity. According to Igata, Domoto [16]:

$$\sigma_F = 105.4\ (1-2.90\,P)\ \mathrm{N/mm^2} \tag{4}$$

The temperature dependence may be expressed by

$$\sigma_F = \sigma_{F_0} \pm AT \tag{5}$$

Table 1/2 shows the parameters σ_{F_0} and A evaluated by Stehle et al. [9] from data in [21, 22, 26]. Olsen recommends in the MATPRO-Version 09 handbook [27] the following expression, based on his evaluation of the literature [22, 23, 26, 28, 29]:

for $273\,K < T < 773\,K$

$$\sigma_F = 156\ (1-2.62\,P)^{1/2} \exp[-(380/1.987\,T)]\ \mathrm{N/mm^2} \tag{6a}$$

and for $773\,K < T < 2273\,K$

$$\sigma_F = 143\ \mathrm{N/mm^2} \tag{6b}$$

The temperature 500 °C (= 773 K) is thus the transition temperature T_c under irradiation. Not considered in this relationship are the increase of T_c with augmenting rates of deformation and grain size, obtained outside of a reactor [22], and its decrease with augmenting porosity [30]. In the MATPRO-Version 11 handbook [104] the following recommendation is given for $273\,K < T \leqq 1000\,K$:

$$\sigma_F = 170\ (1-2.62\,P)^{1/2} \exp\,(-1590/8.314\,T)\ \mathrm{N/mm^2}, \tag{6c}$$

and for $T > 1000\,K$: $\sigma_F = \sigma_F\ (1000\,K)$.

The second transition temperature T_t is related to the rate of deformation $\dot{\varepsilon}$ as follows [22]:

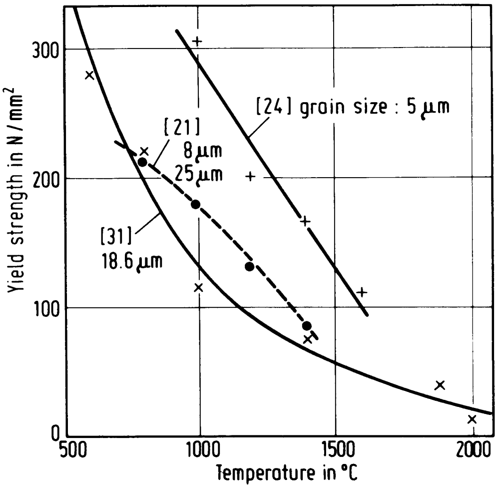
$$\dot{\varepsilon} = 2.41 \times 10^{11} \exp[-(96000/1.987\,T_t)]\ \mathrm{h^{-1}} \tag{7}$$

The yield strength of UO_2 is shown in **Fig. 1-7**, p. 14, as a function of the temperature, according to measurements of Evans, Davidge [21], Guerin [24], and Byron [31].

Table 1/2
Constants of Eq. (5) for the Temperature Dependence of the Fracture Strength of UO_2 (96% of theoretical density) [9].

σ_{F_0} in $\mathrm{N/mm^2}$	A in $\mathrm{N \cdot mm^{-2} \cdot K^{-1}}$	grain size in μm	Ref.
150.7	0.028	8	[21]
98.5	0.027	8	[22]
108.5	0.025	15	[22]
24.5	0.31	8	[26]
65.6	0.14	15	[26]

Fig. 1-7



Yield strength of UO_2 as a function of the temperature [21, 34, 31].

1.1.2.3 Creep Behavior

General References:

J. R. Matthews, Mechanical Properties and Diffusion Data for Carbide and Oxide Fuels, Ceramics Data Manual Contribution, AERE-M-2643 [1974] 1/28 [75 Refs.]; C.A. **82** [1975] No. 91466.

M. S. Seltzer, A. H. Clauer, B. A. Wilcox, A Review of Creep Behavior of Ceramic Nuclear Fuels, Reactor Technol. **14** [1971] 99/135; BMI-1906 [1971] 1/72 [93 Ref.]; N.S.A. **25** [1971] No. 49566.

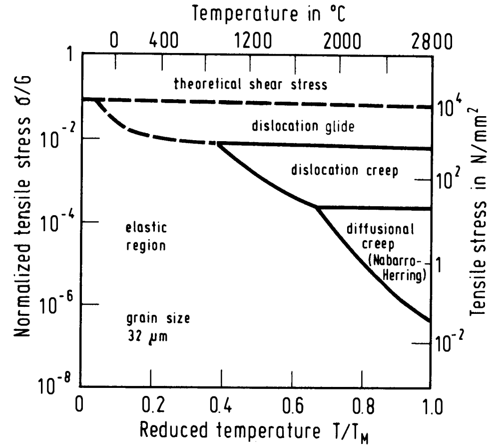
J. Gittus, Irradiation-Induced Deformation, in: J. Gittus, Creep, Viscoelasticity, and Creep Fracture in Solids, Applied Science Publisher, London 1975, pp. 203/68.

W. Dienst, Irradiation Induced Creep of Nuclear Fuels, J. Nucl. Mater. **65** [1977] 1/8.

E. R. Gilbert, In-Reactor Creep of Reactor Materials, Reactor Technol. **14** [1971] 258/85 [105 Refs.].

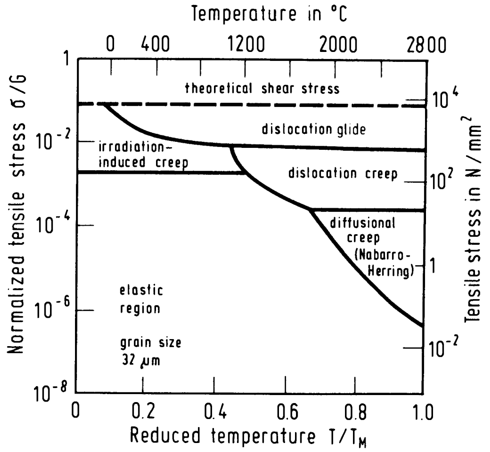
In order to describe the creep mechanisms predominant in various temperature and stress regions, Ashby [32] recommends the use of so-called "deformation maps", in which also the limits for elastic and fracture deformations are delineated. Such deformation maps for UO_2 out-of-pile and in-pile are shown in **Fig. 1-8** and **1-9**, respectively. A somewhat modified depiction was selected in **Fig. 1-10** and **1-11**, p. 16, for UO_2-PuO_2 [34].

Fig. 1-8



Deformation map for UO_2, out-of-pile [33].

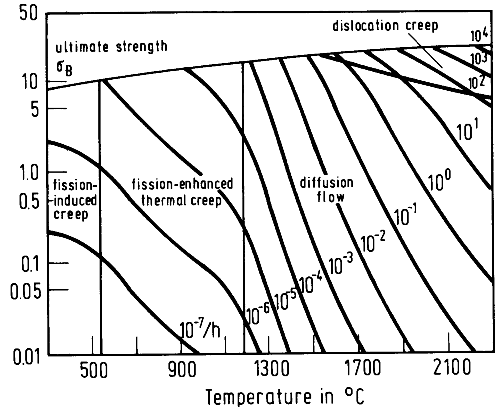
Fig. 1-9



Deformation map for UO_2, in-pile, at a burnup rate of 5% per year [33].

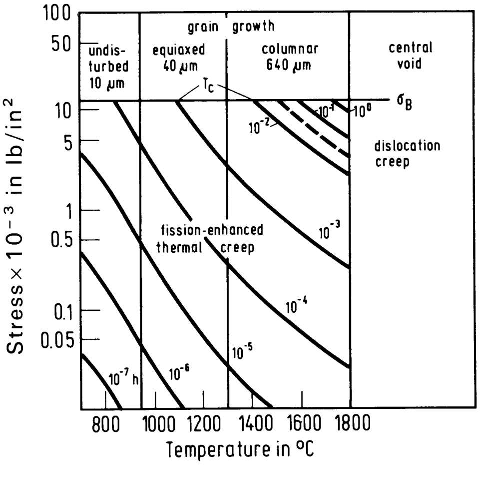
References for 1.1.2 on pp. 27/9

Fig. 1-10



Deformation map for UO_2-PuO_2 (20 to 25% PuO_2, 96% of the theor. density) at a fission rate of 1.2×10^{13} fissions · cm^{-3} · s^{-1} at low or intermediate power [34].

Fig. 1-11



Deformation map for UO_2-PuO_2 at high power (completely restructured fuel) [34].

The following creep mechanisms may be effective in the reactor:

(1) Viscous creep (diffusion controlled flow) at high temperatures and low stresses.

(2) Dislocation creep at high temperatures and stresses.

(3) Thermal creep accelerated by fission events at intermediate temperatures.

(4) Fission induced creep at low temperatures.

Theoretical Models

(1) Viscous creep (thermally activated)

There are essentially three models: (a) stress-directed lattice diffusion, according to Nabarro [35] and Herring [36]; (b) stress-directed grain boundary diffusion, according to Coble [37]; and (c) grain boundary gliding, according to Gifkin et al. [38 to 41]. Common to these models is the linear dependence of the steady-state creep on the stress. The grain size dependence found for UO_2 (prop. $1/d^2$) is consistent with mechanism (a). A supplement of the theory required for very small stresses was provided by Burton, Reynolds [42 to 44].

(2) Dislocation creep (thermally activated)

There are again three models, which have in common with case (1) the fact, that the temperature dependence of the creep is determined by the vacancy diffusion. These models are: (a) dislocation climb out of a piling-up of dislocations before a blocked one, according to Weertman [45]; (b) climb and dissolution of dislocations in dislocation loops, according to Weertman [46]; and (c) climb of jogged screw dislocations according to Barrett, Nix [47]. In model (c) the diffusion of vacancies from supersaturated to subsaturated regions leads to the climb of jogs. The steady-state creep rate follows the relationship

$$\dot{\varepsilon} = A\sigma^{3.5}\sinh\,(b(x)\sigma/RT)\;\exp(-Q(x)/RT), \qquad (8)$$

where A is a structural factor, σ is the stress, and the parameter b(x) and the effective activation energy Q(x) for the creep of UO_{2+x} are both stoichiometry- (i.e., x-) dependent. This latter fact is explainable by the stoichiometry dependence of the self-diffusion. According to the theory of Lidiard [48] and Matzke [49] the diffusion coefficient of uranium in UO_{2+x} is proportional to the square of x. Up to intermediate values of the stress, the approximation $\sinh(b(x)\sigma/RT) \approx b(x)\sigma/RT$ is valid, so that an effective exponent of 4.5 of the stress results, as for model (b). For high stresses this exponent rises steeply.

(3) Radiation-enhanced and fission-induced creep

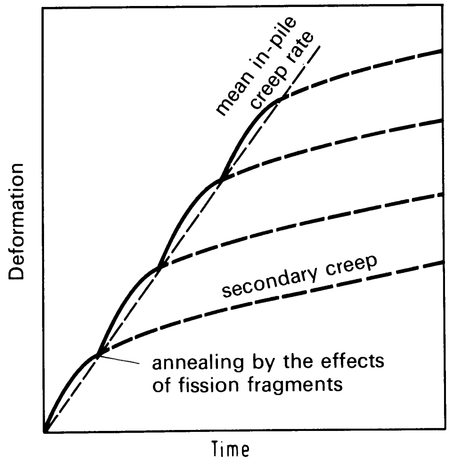
A survey of the possible creep mechanisms is included in the above-mentioned general reference of Gilbert and Dienst. It contains:

(a) Relaxation of elastic stress by the effects of the lattice defects generated by the fission fragments [50 to 52].

(b) Acceleration of dislocation sliding through the purely thermal action of the fission fragments [53]. Radiation effects keep the UO_2 in the primary creep state, **Fig. 1-12**, p. 18.

(c) Modified Nabarro-Herring creep [54]. Point defects formed under irradiation anneal at clusters of defects, that replace the grains in the original creep model.

Fig. 1-12



Maintainance of primary creep by means of the thermal effect of the fission fragments [53].

(d) Stress-oriented formation and growth of dislocation loops [54 to 57].

(e) Diffusional creep by means of the migration of vacancies between properly oriented dislocation loops [58].

(f) Radiation accelerated dislocation climb. Gilbert (see general references) discusses numerous theoretical treatments. The climb of jogs in screw dislocations [59] or of piled-up edge dislocations over obstacles [60, 61] may be of importance. In this case the stress dependence has the following form:

$$\dot{\varepsilon} = A\sigma^2 (B_1\sigma^2 + B_2) \qquad (9)$$

The parameter B_1 is temperature dependent, while B_2 describes the athermal portion of the creep. At low temperatures $B_1\sigma^2$ may be neglected compared with B_2.

(g) Radiation-induced creep caused by the climb of dislocation loops by means of absorption of interstitials, according to Solomon [62]. The interstitials formed under irradiation precipitate at low temperatures ($\lesssim$500 °C) in dislocation loops. If such loops are sufficiently large, to escape resolution due to fission fragment effects, they grow and climb by absorbing further interstitials. Steady-state creep follows, if the concentration of vacancies in the surroundings of the dislocation loop, acting as a sink, has reached an equilibrium value, as have also the absorption of interstitials and the climb of the dislocation loops. According to Solomon, not only the fission fragments, but also other high energy particles, such as fast neutrons, may be the energy source for this mechanism. Therefore he designated it as "radiation-induced".

(h) Fission-accelerated creep, as primary creep in the volume of the fission fragment track, was discussed by Malygin et al. [63]. This model permits the description of the fission-accelerated creep of UO_2 (as also that of UO_2-PuO_2, UC, UN) on the basis of (mostly thermal) material properties and creep parameters, that are evaluated in thermal creep experiments in the primary creep region. The following relationship holds:

$$\dot{\varepsilon}_{irr} = A\frac{v\sigma\exp(-Q/RT)}{v-V_fF[1-\exp(-v/kV_fF)](k-1)} + \frac{2\alpha v\sigma V_fF}{2V_fF+v} \tag{10}$$

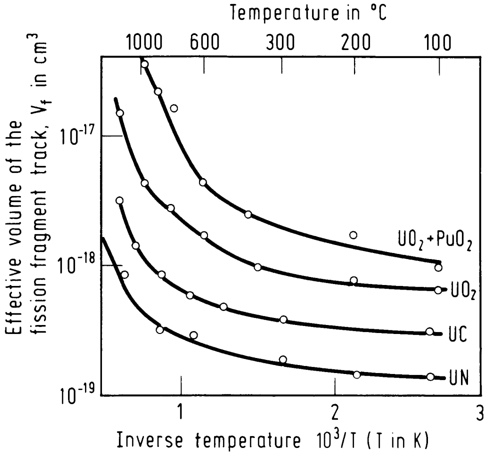
where the previously unidentified symbols have the following meanings (with numerical values valid for UO_2): A = structure factor, $k = \dot{\varepsilon}_{primary}/\dot{\varepsilon}_{steady\text{-}state} = 5$, while $v = 10^{-2}\,s^{-1}$ and $\alpha = 10^{-5}$ are parameters in the equation for primary creep. As a special case of a more general expression [64]

$$\dot{\varepsilon}_{primary} = \varepsilon_0 - \alpha\ln(1+vt) \tag{11}$$

is valid, where ε_0 is the initial deformation. The effective volume of the fission fragment track, V_f, may be calculated from the thermal properties of the fuel. **Fig. 1-13** shows V_f as a function of the temperature of the fuel for various nuclear fuels. Equation (10) thus describes the dependence of the creep rate on the temperature, the stress and the fission rate.

At high temperatures the second term of equation (10) is small, while at low ones the first term may be neglected. At temperatures around 1 000 °C both terms must be considered.

Fig. 1-13



Effective volume of the fission fragment track V_f as a function of the temperature [63].

Experimental Results

(1) Methods and kinds of measurements

Types of samples and experiments: the pulling and squeezing of spiral springs [62, 65, 67], the bending of rods [67, 68], and the pressing of discs and pellets [68 to 80]. Stresses were applied as weights [65], as the force of a spring [66, 67], and as gas pressure [69, 71, 72, 74 to 80]. The deformation was measured: inductively [65, 66, 74 to 80], with a pneumatic

Table 1/3
Techniques and Parameters of Creep Experiments on UO_2 and UO_2-PuO_2 under Irradiation. TD = theoretical density.

technique	composition	samples		O/M ratio	fission rate in 10^{13} fissions $\cdot cm^{-3} \cdot s^{-1}$	temperature range in °C	stress range in N/mm^2	authors
		grain size in µm	density (%TD)					
compression of spiral spring	UO_2	8 to 10	97.5	–	0.08 to 0.17	525 to 880	6.0 to 12.5	Sykes, Sawbridge [66]
compression of disc	UO_2	30 to 40	95	–	11.8	400 to 600	7.8 to 17.7	Bruchlacher, Dienst [69]
three-point bending	UO_2	8 to 10	96 to 97	2.0005	0.82 to 1.60	595 to 630	26.4 to 30.5	Clough [67]
tension of spiral spring	UO_2	22	96	2.000	0.26	103	37.9	Solomon, Gebner [65]
compression	UO_2	27	98	2.003	0.4, 1.2	1110 to 1215	6.9 to 27.6	Perrin [70]
compression and bending	UO_2	10 to 15	97 to 98	2.000 to 2.005	0.14 to 0.70	775 to 1250	8 to 42	Clough [68]
tension of spiral spring	UO_2	22	96	2.000	0.2 to 1.5	80 to 200	14.5, 20.0	Solomon [62]
compression	UO_2	12 to 15	–	2.00 to 2.01	0.06	1100 to 1300	29.4, 39.2	Miloserdin et al. [72]
compression	UO_2-22% PuO_2	3 to 5	95	1.98	0.7 to 1.2	910 to 1125	13.8	Perrin [71]
compression	UO_2-22% PuO_2	3 to 5	93	1.975	3.8	350, 600	27.6, 55.2	Robinson et al. [74]
compression	UO_2-15% PuO_2	–	98	1.93 to 2.00	1 to 6	700 to 900	26.5	Combette, Milet [92]
compression	UO_2-15% PuO_2	–	86 93.5	1.98	5 to 10	300 to 1000	15, 40	Dienst [93]

transducer [71, 74], with a microwave-resonator or an acustic sensor [72, 73], or with a micrometer [68, 84]. Table 1/3 is a summary of all creep experiments on UO_2 and UO_2-PuO_2 in reactors, giving the experimental techniques used and the parameters measured.

(2) Creep of UO_2 under irradiation

(a) Dependence on stress and fission rate.

Below 1 000 °C, for stresses in the range 10 to 50 N/mm^2, and for a fission rate in the range 3×10^{12} to 1×10^{14} fissions $\cdot$ $cm^{-3}\cdot s^{-1}$, the creep rate is as a first approximation proportional to the stress [62, 65 to 69] and to the fission rate [62, 75], according to all the experimental results:

$$\dot{\varepsilon} \sim \sigma F \tag{12}$$

This relationship is often employed for normalizing the results of different authors.

In the temperature range 1 100 to 1 300 °C, and for stresses in the range 10 to 40 N/mm^2, the occurrence of radiation-accelerated creep was assumed prior to 1977. The irradiation factor is between 2 and 3 [70, 72, 81, 82] at a fission rate of 1.2×10^{13} fissions $\cdot$ $cm^{-3}\cdot s^{-1}$. According to a proposal of Solomon et al. [83], expression for the creep rate is [82]

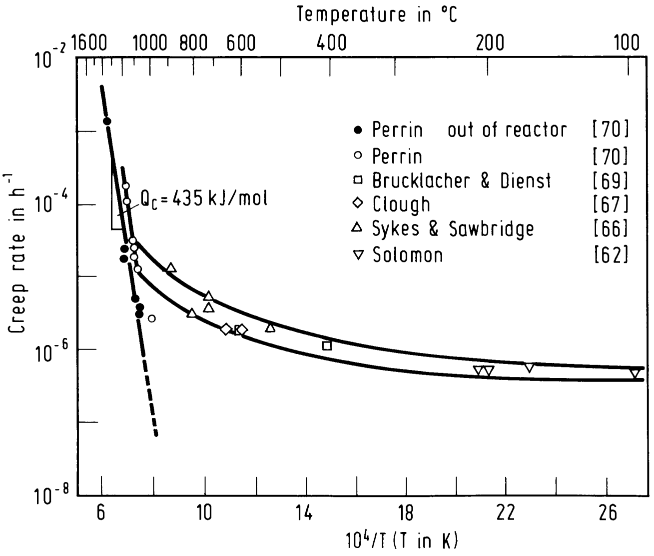
$$\dot{\varepsilon}_{irr} \sim (C_1 + C_2F)\sigma \exp(-Q/RT) \tag{13}$$

where C_1 and C_2 are constants.

(b) Temperature dependence

The results normalized to a stress of 24 N/mm^2 and a fission rate of 1.2×10^{13} fissions $\cdot cm^{-3}\cdot s^{-1}$ [62, 65 to 67, 69, 70] are presented in **Fig. 1-14** as an Arrhenius diagram, ac-

Fig. 1-14



Temperature dependence of the radiation-enhanced creep of UO_2 (stress: 24 N/mm^2, fission rate: 1.2×10^{13} fissions $\cdot cm^{-3}\cdot s^{-1}$) according to [9].

References for 1.1.2 on pp. 27/9

cording to Stehle et al. [9]. Below about 1100 °C, the values show neither a uniform mechanism of thermal activation nor a purely athermal one.

The complicated temperature dependence is generally described by means of additive terms for thermally-activated and for radiation-induced creep. Solomon et al. [83] were the first to summarize the results of Perrin [70] and of Bohaboy et al. [85, 86], including also the dependencies on density and grain size. Brucklacher et al. [87, 88] found at low temperatures (250 to 500 °C) a mild temperature dependence, with an "effective energy of activation" of 21.77 kJ/mol. Olsen [81, 82] and Mason in the MATPRO-Version 11 [105] took this into account, and proposed the following creep equation:

$$\dot{\varepsilon}_{irr} = \frac{(A_1 + A_2F)\sigma \exp(-Q_1/RT)}{(D-A_3)G^2} + \frac{A_4\sigma^{4.5}\exp(-Q_2/RT)}{D-A_5} + A_6\sigma F\exp(-Q_3/RT)\ \mathrm{s}^{-1} \qquad (14a)$$

$$\sigma_{trans} = 1.6547\times 10^{7}\cdot G^{-0.5714}\ \mathrm{Pa} \qquad (14b)$$

For applied stresses σ higher than σ_{trans} (equation 14b), σ_{trans} should be used instead of σ in the first term of equation 14a. For equation 14a the following parameters are defined and recommended by Mason [105] (with the ranges of applicability according to Olsen [82]):

$A_1 = 0.3919$, $A_2 = 1.31\times 10^{-19}$, $A_3 = 87.7$, $A_4 = 2.0391\times 10^{-25}$, $A_5 = 90.5$, $A_6 = 3.72264 \times 10^{-35}$.

$\dot{\varepsilon}_{irr}$ = steady-state creep rate (in s^{-1})
σ = stress (in Pa), from 7×10^6 to 110×10^6 Pa
F = fission rate (in fissions $\cdot m^{-3}\cdot s^{-1}$), from 8.4×10^{17} to 1.18×10^{20} fissions $\cdot m^{-3}\cdot s^{-1}$
T = temperature (in K), from 713 to 2073 K
D = relative density (in % of theoretical density), from 92 to 98%
G = grain size (in μm), from 4 to 35 μm
R = universal gas constant ($8.314\,J\cdot K^{-1}\cdot mol^{-1}$)
$Q_3 = 2.177\times 10^4\ J\cdot mol^{-1}$.

For the values of Q_1 and Q_2 Manson [105] recommended the following expressions:

$$Q_1 = 17884.8\left\{\exp\left[\frac{-20}{\log(O/U-2)} - 8\right] + 1\right\}^{-1} + 72124.23, \qquad (14c)$$

$$Q_2 = 19872.0\left\{\exp\left[\frac{-20}{\log(O/U-2)} - 8\right] + 1\right\}^{-1} + 111543.5, \qquad (14d)$$

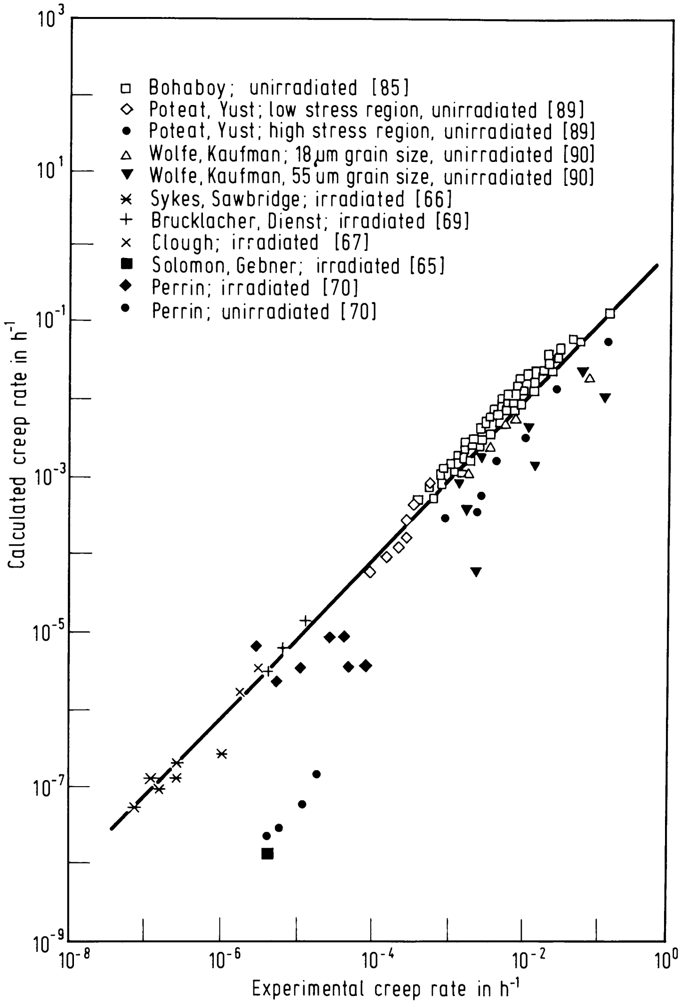
where Q_1 and Q_2 are given in $J\cdot mol^{-1}$ and O/U is the O:U ratio in the oxide.

Fig. 1-15 shows a comparison of the creep rate according to eq. (14) with the results of many authors [42, 43, 65 to 67, 69, 70, 83, 85, 89, 90], as reported in [82].

Application of the above mentioned theory of Malygin et al. [63] also yields good agreement between the measured and the calculated values. **Fig. 1-16**, p. 24, shows this for the acceleration factor of radiation-induced creep in the temperature range 1150 to 1300°C (data from [70] and [72]). **Fig. 1-17**, p. 24, shows a comparison of measured [62, 70, 71, 75, 88] and calculated creep rates for the temperature range 150 to 1250°C for various fuels and fission rates.

Clough [68, 91] considers the creep rate under irradiation to be purely athermal for temperatures below about 1200 °C. His results at 450 °C and in the region 775 to 1200 °C indicate this. He traces all the deviating results back to the irradiation-induced sintering of fabrication pores (see Section 1.1.5, p. 70). Only at doses beyond about 10^{26} fissions/cm^3 are

Fig. 1-15



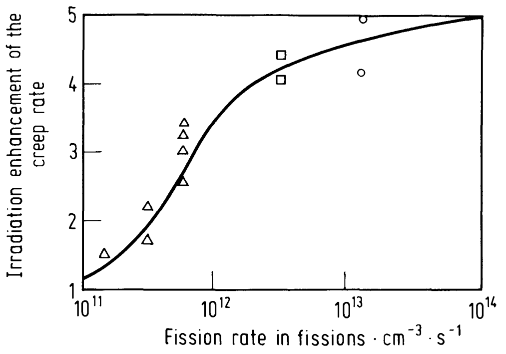
Comparison of the measured creep rate and that calculated by fitting for UO_2, in-pile and out-of-pile, according to [82].

the effects of this in-pile sintering sufficiently small compared with the creep effect. For the range of viscous creep (e.g., $\sigma < 60\ \mathrm{N/mm^2}$ for a grain size $G = 5\ \mu m$) the following equation is proposed:

$$\dot{\varepsilon}_{irr} = [2.65\times10^{10}\sigma/G^2(D-88)]\ \exp(-376.8/RT) + BF\sigma\ h^{-1} \qquad (15)$$

(the symbols and units as for eq. (14)). According to the measurements of various authors, $B = 5.0\times10^{-21}$, Clough [68]; $B = 5.3\times10^{-21}$, Solomon [62]; $B = 5.14\times10^{-21}$, Brucklacher, Dienst [69].

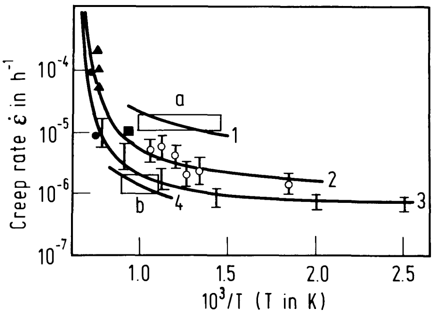
Fig. 1-16



The factor for the irradiation-induced enhancement of the creep of UO$_2$. Comparison between theory [63] and experiments [70, 72] according to [63] (Temperature range: about 1150 to 1300°C).

○: Perrin [70]; △, □: Miloserdin et al. [72]; solid line: theory [63].

Fig. 1-17



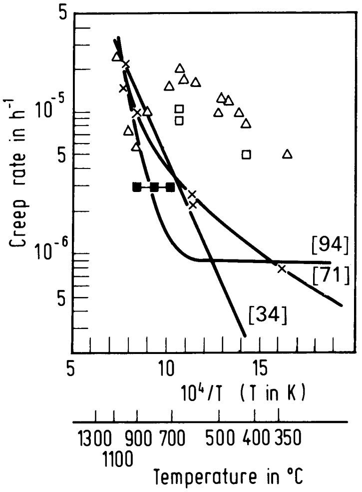
Temperature dependence of the creep rate of different fuels under irradiation. A comparison between theory and experiment, according to [63].

Theoretical values:	Experimental values:
1 UO$_2$; 2.5×10^{14} fissions · $cm^{-3} \cdot s^{-1}$	a [75] UO$_2$; [62] UO$_2$; ● [70] UO$_2$
2 UO$_2$; 1.2×10^{14} fissions · $cm^{-3} \cdot s^{-1}$	Φ [88] UO$_2$-PuO$_2$ (15% PuO$_2$)
3 UO$_2$-PuO$_2$; 1.2×10^{14} fissions · $cm^{-3} \cdot s^{-1}$	■, ▲ [71, 88] UO$_2$-PuO$_2$ (22% PuO$_2$)
4 UN; 2.5×10^{14} fissions · $cm^{-3} \cdot s^{-1}$	b [75] UN.

(3) Creep of UO_2-PuO_2 under irradiation

For applications in fast breeder reactors, UO_2-PuO_2 has a typical PuO_2 content of 25%. For such fuels, too, in the temperature range 300 to 1100 °C, for stresses <40 N/mm^2, and fission rates between 0.7 to 6×10^{13} fissions $\cdot$ cm$^{-3} \cdot$ s^{-1}, a stress and fission rate dependence of the creep rate according to eq. (12) could be obtained. The temperature dependence is as complicated as in the case of UO_2. The data of various authors [34, 71, 92 to 94] are summarized in **Fig. 1-18**, and there exist further data of Robinson et al. [74]. The data show a broad scatter band, partly due to differences in the density, the plutonium content, the stoichiometry, and the degree of the micro-homogeneity of the material, which is mostly produced by means of the mixing of UO_2 and PuO_2 powders, pressing and sintering. While Perrin [71] finds between 910 and 1125 °C a strongly irradiation-accelerated creep (by a factor of 40), Combette et al. [92] determined that the creep is purely athermal between 700 and

Fig. 1-18



Temperature dependence of the irradiation-induced creep of UO_2-PuO_2 (15 to 25% PuO_2, stress: 13.9 N/mm^2, fission rate: 1.2×10^{13} fissions $\cdot$ cm$^{-3} \cdot$ s^{-1}), according to [92].

authors	% PuO_2	O/M	% of theoretical density
[34] Roberts, Voglewede	22 to 25	1.97	95%
[71] Perrin	22	1.98	95% ×
[94] Roberts, Wrona	22 to 25	1.97	95%
[93] Brucklacher, Dienst	15	1.98	93.5% □ , 86% △
[92] Combette et al.	15	2.00	98% ■

900°C (as was found by Clough [68] for UO_2 between 450 and 1200°C). The creep expression is

$$\dot{\varepsilon}_{irr} = 1.81 \times 10^{-20} \sigma F \qquad (16)$$

The creep rate of UO_2-PuO_2 is thus higher by a factor of about 3.5 than that of UO_2 under comparable conditions.

The observations in [68] and [92], made on fuels of high densities, 97 to 98% of the theoretical, indicate that in other cases densification phenomena may play a role. Brucklacher et al. [87] and Dienst [93] find between 350 and 650°C as weak a temperature dependence as found for UO_2, and also an anomalous minimum of the creep rate at 900°C, which is interpreted as a contraction occurring as a result of fission-induced sintering, superimposed on the other effects. Dienst [93] treats the PuO_2 particles in the UO_2 matrix as an "effective porosity", due to their relatively high plasticity, and concludes that the data may be interpreted without specific consideration of the effect of the plutonium content on the properties of the UO_2 matrix.

Olsen [82] and Manson [105] recommend in the MATPRO handbook, on the basis of the data of Evans et al. [95] and Routbort et al. [96] out-of-pile and mainly of those of Perrin [71] in-pile, the following creep expression:

$$\begin{aligned}\dot{\varepsilon}_{irr} = {} & (B_1 + B_2F)G^{-2} \exp(-Q_1/RT)\sigma \exp(B_1P) \exp(B_4C) \\ & + (B_5 + B_6F)\sigma^{4.5} \exp(-Q_2/RT) \exp(B_7P) \exp(B_4C)\end{aligned} \qquad (17)$$

B_1 to B_7 are constants, Q_1 and Q_2 are activation energies, C is the PuO_2 concentration, while the other symbols are the same as used previously. No purely athermal term is included in eq. (17).

Primary and Transient Creep

Primary creep of UO_2 at high temperatures has already been observed by Scott et al. [6], Armstrong, Irving [97, 98] and Burton, Reynolds [42]. Irradiation-induced primary creep of UO_2 and UO_2-PuO_2 could be found by Dienst [93] up to irradiation doses of 3 to 5×10^{19} fissions/cm^3 (sometimes even up to 10^{20} fissions/cm^3) [62, 88, 99 to 101].

The time dependence of the deformation by creep is described by means of the expression

$$\dot{\varepsilon}_{primary} = Kt^m \qquad (18)$$

where $0.5 \leq m \leq 0.9$. The exponent m was found to be independent of the stress and the fission rate [102]. The parameter K depends on the stress, the temperature, the fission rate and the density of the fuel. Primary creep ranges generally up to 10%, in some specific cases only up to 1%, of the creep deformation. Dienst [93] concluded from the data in the literature, that primary creep is only weakly affected by the irradiation; doubtless, however, thermal densification effects and fission-induced densification also play some role.

Manson [105] recommends the following expression for the transient creep, when the fuel first experiences stress, usually during initial irradiation, or when a higher stress than in any other period is applied:

$$\dot{\varepsilon}_t = \dot{\varepsilon}_{irr}[2.5 \exp(-1.40 \times 10^{-6} t) + 1], \qquad (19)$$

where $\dot{\varepsilon}$ is the steady-state creep rate which is finally reached after the transient creep (see equation 14).

References for 1.1.2:

[1] C. S. Olsen (TREE-NUREG-1 005 [1976] 40/51). – [2] M. O. Marlowe, A. I. Kaznoff (J. Am. Ceram. Soc. **53** [1970] 90/9). – [3] A. R. Hall (J. Nucl. Mater. **37** [1970] 314/23). – [4] A. Padel, C. de Novion (J. Nucl. Mater. **33** [1969] 40/51). – [5] R. J. Forlano, A. W. Allen, R. J. Beals (J. Am. Ceram. Soc. **50** [1967] 93/6; C.A. **66** [1967] No. 90692).

[6] R. Scott, A. R. Hall, I. Williams (J. Nucl. Mater. **1** [1959] 39/48; C. A. **1959** 21227). – [7] J. B. Wachtman, W. E. Tefft, D. G. Lam, R. P. Stinchfield (WADC-TR-59-278 [1959] 1/81; N.S.A. **14** [1960] No. 19443). – [8] J. Belle, B. Lustman (TID-7546 [1957] 442/515; N.S.A. **12** [1958] No. 9439; WAPD-184 [1957] 1/140; C.A. **1958** 3496). – [9] H. Stehle, H. Aßmann, F. Wunderlich (Nucl. Eng. Design **33** [1975] 230/60). – [10] O. L. Anderson (Phys. Rev. [2] **144** [1966] 553/7).

[11] J. B. Wachtman, W. E. Tefft, D. G. Lam, C. S. Apstein (Phys. Rev. [2] **122** [1961] 1754/9; C.A. **1961** 19393). – [12] F. Gatto (Alluminio **19** [1950] 19). – [13] R. M. Spriggs (J. Am. Ceram. Soc. **44** [1961] 628). – [14] R. C. Rossi (J. Am. Ceram. Soc. **51** [1968] 433/9). – [15] N. Claussen (Ber. Deut. Keram. Ges. **44** [1967] 267/70).

[16] N. Igata, K. Domoto (J. Nucl. Mater. **45** [1972/73] 317/22). – [17] D. J. Bowers, W. A. Hedden, M. J. Snyder, W. H. Duckworth (BMI-1117 [1956] 1/28; N.S.A. **11** [1957] No. 7601). – [18] V. M. Baranov, Yu. K. Bibilashvili, I. S. Golivnin (At. Energ. [USSR] **40** [1976] 37/40; Soviet At. Energy **40** [1976] 37/9). – [19] J. B. Wachtman, M. L. Wheat, H. J. Anderson, J. C. Bates (J. Nucl. Mater. **16** [1965] 39/41). – [20] A. W. Nutt, A. W. Allen, J. H. Handwerk (J. Am. Ceram. Soc. **53** [1970] 205/10).

[21] A. G. Evans, R. W. Davidge (J. Nucl. Mater. **33** [1969] 249/60). – [22] R. F. Cannon, J. T. A. Roberts, R. J. Beals (J. Am. Ceram. Soc. **54** [1971] 105/12). – [23] J. T. A. Roberts, Y. Ueda (J. Am. Ceram. Soc. **55** [1972] 117/24). – [24] Y. Guerin (J. Nucl. Mater. **56** [1975] 61/75). – [25] C. R. Tottle (ANL-7070 [1965] 1/31; N.S.A. **20** [1966] No. 15029).

[26] F. P. Knudsen, H. S. Parker, M. D. Burdick (J. Am. Ceram. Soc. **43** [1960] 641/7). – [27] C. S. Olsen (TREE-NUREG-1 005 [1976] 81/90). – [28] J. Katanić-Popović, V. Petrović (Phys. Sintering **5** [1973] 95/105). – [29] M. Burdick, H. Parker (J. Am. Ceram. Soc. **39** [1956] 181/7). – [30] J. T. A. Roberts, B. J. Wrona (J. Nucl. Mater. **41** [1971] 23/38).

[31] J. F. Byron (J. Nucl. Mater. **27** [1968] 48/53). – [32] M. F. Ashby (Acta Met. **20** [1972] 887/97). – [33] J. Gittus (Creep, Viscoelasticity, and Creep Fracture in Solids, Applied Science Publisher, London 1975, pp. 203/68). – [34] J. T. A. Roberts, J. C. Voglewede (J. Am. Ceram. Soc. **56** [1973] 472/5). – [35] F. R. N. Nabarro (Rept. Conf. Strength Solids, Bristol, U.K., 1947 [1948], p. 75).

[36] C. Herring (J. Appl. Phys. [London] **21** [1950] 437/45). – [37] R. L. Coble (J. Appl. Phys. [London] **34** [1963] 1679/82). – [38] R. C. Gifkins, K. U. Snowden (Nature **212** [1966] 916/7). – [39] R. C. Gifkins, K. U. Snowden (Trans. AIME **239** [1967] 910/5). – [40] R. C. Gifkins (J. Am. Ceram. Soc. **51** [1968] 69/72).

[41] M. F. Ashby, R. Raj, R. C. Gifkins (Scripta Met. **4** [1970] 737). – [42] B. Burton, G. L. Reynolds (Acta Met. **21** [1973] 1073/8). – [43] B. Burton, G. L. Reynolds (Acta Met. **21** [1973] 1641/7). – [44] B. Burton, G. L. Reynolds (Phil. Mag. [8] **29** [1974] 1359/70). – [45] J. Weertman (J. Appl. Phys. [New York] **26** [1955] 1213).

[46] J. Weertman (ASM [Am. Soc. Metals] Trans. Quart. **61** [1968] 681). – [47] C. R. Barrett, W. D. Nix (Acta Met. **13** [1965] 1247/58). – [48] A. B. Lidiard (J. Nucl. Mater. **19** [1966] 106/8). – [49] H. Matzke (J. Phys. [Paris] **34** [1973] Suppl. No. 11/12, pp. C9-317/C9-325). – [50] S. T. Konobeevsky (At. Energ. [USSR] **9** [1960] 194/200; Soviet J. At. Energy **9** [1961] 707/14).

[51] J. A. Brinkmann, H. Wiedersich (Am. Soc. Testing Mater. Spec. Tech. Publ. No. 380 [1965] 3). – [52] R. G. Anderson, R. Hargreaves (TRG-1975-S [1973] 1/9; C.A. **79** [1973] No. 99550). – [53] W. R. D. Wilson, J. A. Walowit, J. N. Anno (BMI-1857-C [1969] 20;

N.S.A. **23** [1969] No. 20546). – [54] D. Brucklacher, W. Dienst, F. Thümmler (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 343/68). – [55] R. V. Hesketh (Phil. Mag. [8] **7** [1962] 1417).

[56] R. V. Hesketh (BNL-50083 [1967] 389). – [57] M. F. Ashby (Scripta Met. **6** [1972] 1231). – [58] M. F. Ashby (TR-4 [1971] 1/16; AD-719905 [1971] 1/16; N.S.A. **25** [1971] No. 42900). – [59] G. R. Piercy (J. Nucl. Mater. **26** [1968] 18/50). – [60] J. A. Tesk, Che-Yu Li (Trans. Am. Nucl. Soc. **12** [1969] 133).

[61] S. D. Harkness, J. A. Tesk, Che-Yu Li (Nucl. Appl. Technol. **9** [1970] 24/30). – [62] A. A. Solomon (J. Am. Ceram. Soc. **56** [1973] 164/71). – [63] V. B. Malygin, Yu. K. Bibilashvili, I. S. Golovnin, K. V. Naboichenko (At. Energ. [USSR] **42** [1977] 8/13; Soviet At. Energy **42** [1977] 6/11; C.A. **86** [1977] No. 112675). – [64] J. Li (Acta Met. **11** [1963] 1269/70). – [65] A. A. Solomon, R. H. Gebner (Nucl. Technol. **13** [1972] 177/84).

[66] E. C. Sykes, P. T. Sawbridge (RD-B-N-1489 [1969] 1/14; N.S.A. **24** [1970] No. 12487). – [67] D. J. Clough (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 321/42). – [68] D. J. Clough (J. Nucl. Mater. **65** [1977] 24/36). – [69] D. Brucklacher, W. Dienst (J. Nucl. Mater. **36** [1970] 244/7). – [70] J. S. Perrin (J. Nucl. Mater. **39** [1971] 175/82).

[71] J. S. Perrin (J. Nucl. Mater. **42** [1972] 101/4). – [72] J. V. Miloserdin, K. V. Naboichenko, I. S. Golovnin, Yu. K. Bibilashvili, T. S. Men'shikova, P. A. Mandryka, K. G. Bobkov, N. I. Arlamenkov et al. (At. Energ. [USSR] **35** [1973] 371/5; Soviet At. Energy **35** [1973] 1065/9; C.A. **80** [1974] No. 90011). – [73] P. Combette, C. Milet (J. Nucl. Mater. **65** [1977] 37/47). – [74] R. A. Robinson, S. J. Basham, J. S. Perrin (Nucl. Eng. Design **24** [1973] 242/9). – [75] D. Brucklacher, W. Dienst (J. Nucl. Mater. **42** [1972] 285/96).

[76] W. Dienst (J. Nucl. Mater. **61** [1976] 185/91). – [77] D. Brucklacher, W. Dienst (J. Nucl. Mater. **36** [1970] 244/7). – [78] H. E. Häfner, H. Nill (Kerntechnik **13** [1971] 454/7). – [79] H. E. Häfner (Nucl. Technol. **34** [1977] 69/74). – [80] H. E. Häfner (J. Nucl. Mater. **65** [1977] 65/71).

[81] C. S. Olsen (Steady-State Creep Model for UO_2, CONF-751101-16 [1975] 1/5; N.S.A. **33** [1976] No. 5892; C.A. **84** [1976] No. 157002). – [82] C. S. Olsen (TREE-NUREG-1005 [1976] 51/80). – [83] A. A. Solomon, J. L. Routbort, J. C. Voglewede (Fission-Induced Creep of UO_2 and Its Significance to Fuel-Element Performance, ANL-7857 [1971] 1/19; N.S.A. **26** [1972] No. 15561). – [84] R. W. Stratton (Nucl. Eng. Intern. **17** [1972] 100/3). – [85] P. E. Bohaboy, R. R. Asamoto, A. E. Conti (GEAP-10054 [1969] 1/52; N.S.A. **24** [1970] No. 10156).

[86] P. E. Bohaboy, R. R. Asamoto (Compressive Creep Characteristics of Ceramic Oxide Nuclear Fuels: Part I: Uranium Dioxide, Am. Ceram. Soc. Nucl. Div., Pittsburg 1968). – [87] D. Brucklacher, W. Dienst, F. Thümmler (Reaktortagung, Karlsruhe 1973, Tagungsber. pp. 413/6). – [88] D. Brucklacher (Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 118/22; C.A. **84** [1976] No. 127808). – [89] L. E. Poteat, C. S. Yust (ORNL-P-2371 [1965] 1/16; N.S.A. **20** [1966] No. 46191). – [90] R. A. Wolfe, S. F. Kaufman (WAPD-TM-587 [1967] 1/132; N.S.A. **22** [1968] No. 4871).

[91] D. J. Clough (AERE-R-6627 [1970]). – [92] P. Combette, C. Milet (J. Nucl. Mater. **65** [1977] 37/47). – [93] W. Dienst (J. Nucl. Mater. **65** [1977] 1/8). – [94] J. T. A. Roberts, B. J. Wrona (ANL-7945 [1972] 1/39; N.S.A. **26** [1972] No. 53545; C.A. **78** [1973] No. 78694). – [95] S. K. Evans, P. E. Bohaboy, R. A. Laskiewitz (GEAP-13732 [1971] 1/36; N.S.A. **26** [1972] No. 12741).

[96] J. L. Routbort, N. A. Javed, J. C. Voglewede (J. Nucl. Mater. **44** [1972] 247/59). – [97] W. M. Armstrong, W. R. Irvine (J. Nucl. Mater. **9** [1963] 121/7). – [98] W. M. Armstrong, W. R. Irvine (J. Nucl. Mater. **12** [1964] 261/70). – [99] D. J. Clough (J. Nucl. Mater. **56** [1975] 279/86). – [100] A. A. Solomon (Relation Between Primary and Steady-State Creep of UO_2 at Elevated Temperature and Under Neutron Irradiation, AED-CONF-74-350-004

[1974]; Deform. Ceram. Mater. Proc. Symp., Washington, D.C., 1974 [1975], pp. 313/24; C.A. **84** [1976] No. 10158).

[101] A. A. Solomon (Trans. Am. Nucl. Soc. **23** [1976] 176). – [102] A. A. Solomon (ANL-RDP-13 [1973] Paper 6.4). – [103] D. L. Hagrman, E. T. Laats, C. S. Olsen (NUREG-CR-0497 [1979] 49/64; TREE-1280 [1979] 49/64). – [104] C. S. Olsen (NUREG-CR-0497 [1979] 154/64; TREE-1280 [1979] 154/64). – [105] R. E. Mason (NUREG-CR-0497 [1979] 64/83; TREE-1280 [1979] 64/83).

1.1.3 Thermal Behavior

General References:

IAEA, Thermal Conductivity of Uranium Dioxide, Tech. Rept. Ser. Intern. At. Energy Agency No. 59 [1966].

H. Marchandise, Conductibilité Thermique du Bioxyde d'Uranium, EUR-4568.f [1970] 1/158.

G. Neuer, R. Brand, G. Haufler, Wärmeleitfähigkeit und Emissionsgrad von festem UO_2, Literaturstudie, IRS-SB-3 [1973] 1/217 [277 Refs.]; N.S.A. **30** [1974] No. 27343; C.A. **82** [1975] No. 116968.

A. B. G. Washington, Preferred Values for the Thermal Conductivity of Sintered Ceramic Fuel for Fast Reactor Use, TRG 2236 (D) [1973] 1/91 [131 Refs.].

J. Richter, H. E. Schmidt, H. A. Tasman, Bibliography on Heat Transport in Nuclear Fuels and Related Phenomena, EUR-5119.e [1974] 1/215 [2235 Refs. about Oxides].

R. O. Lokken, E. L. Courtright, Review of the Effects of Burnup on the Thermal Conductivity of UO_2, BNWL-2270 [1976] 1/15.

P. E. MacDonald, L. B. Thompson, MATPRO-Version 09, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, TREE-NUREG-1005 [1976] 9/39.

D. R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 113/44.

D. L. Hagrman, G. A. Reymann, R. E. Mason, MATPRO-Version 11-Rev. 1, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, NUREG-CR-0497-Rev. 1 [1980] 9/48 m; TREE-1280-Rev. 1 [1980] 9/48 m.

The thermal behavior of a nuclear fuel is of particular importance, when its behavior inside a nuclear reactor is considered. Firstly, it is the purpose of the fuel to produce heat and to conduct it to the coolant outside, and secondly, many important properties of the fuel depend on the temperature level and the temperature profile.

1.1.3.1 Thermal Conductivity and Conductivity Integral of UO_2

Thermal conduction in UO_2 is a complex physical process. The thermal conductivity depends therefore on many parameters, e.g.: the temperature, the density (porosity), the stoichiometry (the O/U ratio), impurities or additives, the duration of irradiation, i.e., burnup.

Three mechanisms contribute to the heat conduction in the UO_2 lattice: phonon conduction (lattice conduction), photon conduction (radiation), and electronic conduction. Up to temperatures around 1300 °C, the phonon conduction predominates, but it diminishes with increasing temperatures [1]. At higher temperatures UO_2 becomes a semiconductor [2 to 4], and the increasing electronic conduction leads to increasing thermal conductivities. Photon conduction is of minor importance [5, 6].

References for 1.1.3 on pp. 36/9

Many models describe the dependence of the thermal conductivity on the porosity, e.g., those of Loeb [7], Kämpf, Karsten [8], Maxwell-Eucken [9, 10], Fricke [11], Biancheria [12], Marino [13], Stora [14], Nazare et al. [15], and Ondracek, Schulz [16]. They have been considered in detail in the review of Neuer et al. (see General References), which also discussed thoroughly the various methods for measuring the thermal conductivity (see also [17 to 19]).

The conductivity integral, which had first been mentioned in the literature by Lewis [20], and the application of which for thermal calculation has been thoroughly discussed in [21, 22], is of particular interest.

The steady-state temperature distribution in a cylindrical body is given by the heat conduction equation

$$(1/r)(d/dr)(r\lambda dT/dr) + q = 0 \tag{1}$$

where r is the radius, λ the thermal conductivity, T the temperature, and q an axially symmetrical heat source density. Axial heat flow is neglected here. This is sufficiently well justified technically, except at the ends of the fuel rods and for other disturbances.

For a constant heat source density, a double integration of eq. (1) leads to

$$\int_{T_0}^{T_c} \lambda(T)dT = q'/4\pi \quad (W/cm) \tag{2}$$

where q' is the linear power ("rod power"), T_0 is the surface temperature and T_c is the central temperature. The usefulness of the conductivity integral arises from its following properties:

(1) It is directly connected with the linear fuel rod power, which can be determined calorimetrically.

(2) The central temperature is independent of the diameter of the UO_2.

(3) The integrated thermal conductivity is a characteristic property of the material, which is independent of the geometry.

(4) The thermal conductivity is obtained by derivation according to the upper limit.

(5) The integrated thermal conductivity may be additively normalized to any desired lower limit.

(6) The integrated thermal conductivity may be utilized directly for the interpretation of thermally activated phenomena, such as grain growth or the formation of a central void.

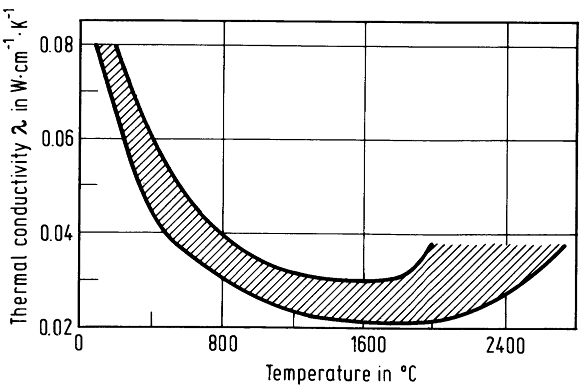
(7) The integrated thermal conductivity may be utilized for the calculation of the central temperature of a fuel rod, for given power and boundary conditions.

Experimental Results

(1) The temperature dependence of the thermal conductivity

A compilation of 242 data curves is found in the work of Touloukian [17]. The 30 studies which were published between 1954 and 1972 are reviewed by Neuer et al. [109]. **Fig. 1-19** shows the ranges of the data obtained for stoichiometric UO_2 (O/U = 2.005 ± 0.005, density > 92% of the theoretical (TD)) normalized to 100% TD. The figure includes the data of Daniel et al. [23], Feith [24], Stora et al. [25], Vogt et al. [26], Godfrey et al. [27], Nishijima et al. [28], Schmidt et al. [29], Ainscough, Wheeler [30], Kruger [31], Asamoto et al. [32], Gibby [33],

Fig. 1-19



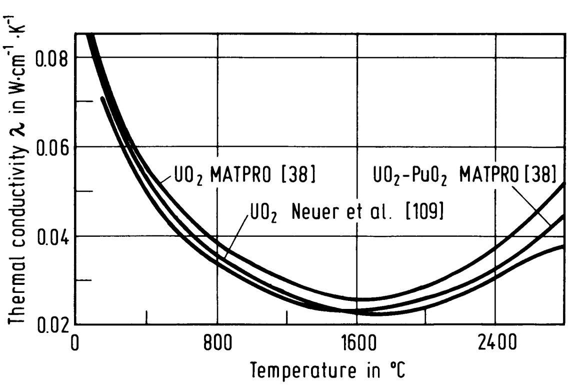
The temperature dependence of the thermal conductivity of $UO_{2.005\pm0.005}$, corrected to the theoretical density [109]. Range of the results according to [23 to 34].

and Weilbacher [34]. For such UO_2 Neuer et al. [109] propose the following expression, which is the mean of the results of [25, 27, 34, 36]:

$$\lambda(T) = (4.39 + 0.0216\,T)^{-1} + 11.2\times10^{-4}\,T\exp(-114/RT) - 4.18\times10^{3}\exp(-317/RT) \qquad (3)$$

where T is in K and $R = 0.008314\ \text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. This function is shown in **Fig. 1-20**.

Fig. 1-20



The thermal conductivity as a function of the temperature for UO_2 [38, 109] and UO_2-PuO_2 (5 to 30% PuO_2) [38]. The curves are valid for the stoichiometric composition and are corrected to the theoretical density.

In 1967 a multi-participant experiment was conducted by the USAEC, in which six laboratories carried out measurements on samples derived from the same substance [35, 36]. The results were discussed in great detail in the review of Neuer et al. (see General References on p. 29). The values given by Godfrey et al. [27] and Stora et al. [25] have already in 1965 been recommended by an IAEA commission in Vienna [37]. The multi-participant experiment confirmed these results up to 1 400 °C, and yielded also reliable values for higher temperatures.

A further evaluation of the literature was undertaken by Olsen and Reymann within the framework of the MATPRO-Version 09 handbook [38]. This evaluation considered 476 data points due to Goldsmith, Douglas [39], Van Craeynest, Stora [40], Hetzler et al. [41], Godfrey et al. [27], Bates [36], Lucks, Deem [42], Christensen et al. [43], Fayl, Hansen [44], and Stora et al. [25].

An up-dated evaluation according to MATPRO-Version 11 (Rev. 1) [110] is reported at the end of this section (see p. 34). A modified Loeb formula [7, 40, 45] (see pp. 30 and 33) served for the normalization to a constant density. The result is:

$$\lambda = \lambda_0 (1-\beta P) \tag{4a}$$

$$\beta = 2.58-0.58\times10^{-3}\Theta \tag{4b}$$

where Θ is in °C and λ_0 is the thermal conductivity at a porosity $P = 0$.

Literature data [33, 41, 46 to 52] for UO_2-PuO_2 mixed oxides (5 to 30% PuO_2) are also evaluated in the MATPRO-Version 09 handbook [38]. The following relationships are proposed:

$$\lambda = (1-\beta(1-D))(1-\beta(1-0.95))^{-1}(K_1(K_2+\Theta)^{-1} + K_3\exp(K_4\Theta)) \tag{5a}$$

for $0\,^\circ C \leq \Theta \leq 1\,650\,^\circ C$

$$\lambda = (1-\beta(1-D))(1-\beta(1-0.95))^{-1}(K_5 + K_3\exp(K_4\Theta)) \tag{5b}$$

for $1\,650\,^\circ C \leq \Theta < 2\,840\,^\circ C$

where $D = 1-P$ (fraction of the theoretical density). Table 1/4 gives the constants K_1 to K_5. For UO_2-PuO_2 the transition temperature is 1 550 °C rather than 1 650 °C. The resulting curves have been inserted in Fig. 1-20 for the sake of comparison.

The conductivity integrals of UO_2 and UO_2-PuO_2 have the following temperature dependencies, according to [38]:

$$\int_0^{\Theta} \lambda(\Theta)d\Theta = K_1 \ln(K_2+\Theta) + K_6\exp(K_4\Theta) - K_7 \qquad (0 \leqq \Theta \leqq \Theta') \tag{6a}$$

$$\int_{\Theta'}^{\Theta_m} k(\Theta)d\Theta = K_5\Theta + K_6\exp(K_4\Theta) - K_8 \qquad (\Theta' \leqq \Theta \leqq \Theta_m) \tag{6b}$$

where Θ' is the "transition temperature" (1 650 and 1 550 for UO_2 and UO_2-PuO_2 (20% PuO_2), respectively), Θ_m is the melting temperature; the constants are given in Table 1/4.

Theoretical interpretations of the observed temperature dependence of the thermal conductivity have been presented by Bates [53], Christensen [54], Viskana [55], De Halas [56], Stoddard, McCormick [57], Moore, McElroy [58], Schmidt [59], Weilbacher [34], and Müller [60].

Table 1/4
Constants for Expressing the Thermal Conductivity (Eq. 5a, b) and the Integrated Heat Conductivity (Eq. 6a, b) of UO_2 and UO_2-PuO_2 (20% PuO_2), as a Function of the Temperature [38].

constant	UO_2	UO_2-PuO_2
K_1	40.4	33.0
K_2	464	375
K_3	1.216×10^{-4}	1.540×10^{-4}
K_4	1.867×10^{-3}	1.710×10^{-3}
K_5	1.91×10^{-2}	1.71×10^{-2}
K_6	6.513×10^{-2}	9.006×10^{-2}
K_7	248.1	195.7
K_8	32.93	27.78

(2) The effect of the porosity

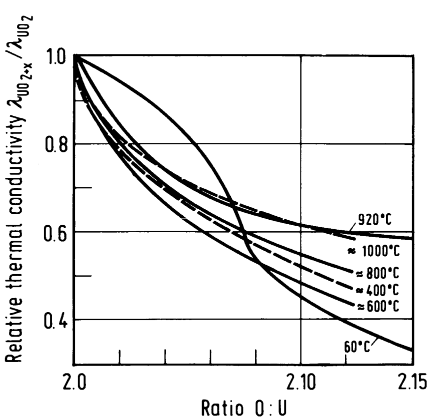
Neuer et al. (see in General References, p. 29) reviewed a large number of single measurement data, which appeared in the literature. Systematic studies, by means of direct or indirect methods (e.g., employing structural zones in irradiated fuel) have been made by Ross [61], Vogt et al. [26], Notley, MacEwan [62], Aragones, Guerrero [63], MacEwan et al. [45], Asomoto et al. [64], Van Craeyest, Stora [40], Stora [65], Moore, McElroy [58], and Goldsmith, Douglas [39, 66].

The evaluation of the literature concerning the effects of the porosity leads to expression (4), for which Neuer et al. recommended somewhat modified constants ($\beta = 2.5 - 0.5 \times 10^{-3}\Theta$).

(3) Other material-dependent effects

There is general agreement among the authors (e.g. [22, 27, 39, 61, 66 to 68]), that the thermal conductivity of UO_2 diminishes with increasing O:U ratios (**Fig. 1-21**). Additives act

Fig. 1-21



Relative thermal conductivity $\lambda(UO_{2+x})/\lambda(UO_2)$ as a function of the O:U ratios [109].

in the same direction (e.g. [67, 69, 70]), as long as they do not form a continuous phase (e.g., cermets [71]). The grain size has no appreciable effect, as was found from measurements on single crystals and on polycrystalline material (e.g. [34, 40, 58]).

In the most recent MATPRO-Version 11 (Rev. 1) [110] the following equation for the thermal conductivity of solid unirradiated UO_2 and UO_2-PuO_2 as a function of temperature, density, oxygen-to-metal (0:M) ratio, and plutonium content of the fuel is recommended:

$$\begin{aligned}\lambda = {} & (D(1 + (6.5-0.00459T')(1-D))^{-1})\ (C_v(A + BT'')^{-1}(1 + 3e_{th})^{-1}) \\ & + 5.2997\times10^{-3}\,T\exp(-13358/T)\ (1 + 0.169(13358/T) + 2)^2,\end{aligned} \tag{7a}$$

where λ = thermal conductivity (in $W \cdot m^{-1} \cdot K^{-1}$), D = fraction of theoretical density, C_v = phonon contribution to the specific heat at constant volume (in $J \cdot kg^{-1} \cdot K^{-1}$),

$$\begin{aligned}C_v = {} & 296.7\ (535.285^2T^{-2}\ (\exp(535.285/T)-1)^{-2}\cdot\exp(535.285/T)\ (1-C) \\ & + 237.4\ (571^2T^{-2}\ (\exp(571/T)-1)^{-2}\cdot\exp(571/T)\cdot C)\end{aligned} \tag{7b}$$

where C is the PuO_2 content of the fuel (ratio of weight of PuO_2 to total weight)

e_{th} = linear strain caused by thermal expansion when the temperature is above 300 K (see eq. 9a, 9b).
T = fuel temperature (in K)
T′ = fuel temperature if less than 1364 K. For temperatures above 1834 K the porosity factor, $D(1 + (6.5-0.00459T')\ (1-D))^{-1}$, is equal to 1 and for temperatures in the range 1364 to 1834 K the factor is found by interpolation as described in [110].
T″ = fuel temperature if less than 1800 K. For temperatures above 2300 K, T″ is equal to 2050 K and for temperatures in the range 1800 to 2300 K, T″ is found by interpolation as explained in [110].
A = a factor proportional to the point defect contribution to the phonon mean free path (in m · s/kg).
A = 0.339 + 11.1 × absolute value (2.0 − 0:M ratio).
B = a factor proportional to the phonon-phonon scattering contribution to the phonon free path ($m \cdot s \cdot kg^{-1} \cdot K^{-1}$).
B = 0.06867 + (1 + 0.6238 × plutonium content of fuel).

The first term of eq. 7a represents the phonon contribution to specific heat and the second term represents the electronic (electron-hole) contribution.

(4) The effect of irradiation

A comparison of data obtained after irradiation with those obtained before it (e.g. [23, 61, 72], cf. also the reviews by Bradbury, Frost [73]), of data obtained directly under irradiation (e.g. [72]) and of indirect measurements (e.g. [74 to 77]), leads to the conclusion that below 500 °C the thermal conductivity is lowered, as a result of the formation of lattice defects on irradiation, but that above 500 °C, up to the melting point, there is no noticeable effect. Neither do grain growth nor dendritic grain growth alter the thermal conductivity. According to Schulz [78], UO_2-PuO_2 samples, which were doped with simulated fission products corresponding to a 150 MWd/kg(U + Pu) burnup, showed above 800 °C no change in thermal conductivity relative to undoped samples.

1.1.3.2 Thermal Expansion and Specific Heat Capacity

Burdick, Parker [79], Conway et al. [80, 81], Christensen [82], Hoch, Momin [83] report results of linear thermal expansion measurements on non-irradiated UO_2. Sheets [84] reported the results of Lambertson, Handwerk [85], Bell, Makin [86], and Murray, Thackray [87]. Regression analysis by Olsen [88] of the data [79, 80, 85 to 87] leads to the expression:

$$\Delta L/L = -4.972\times10^{-4} + 7.107\times10^{-6}\Theta + 2.581\times10^{-9}\Theta^2 + 1.114\times10^{-13}\Theta^{13} \quad (8a)$$

The effect of the irradiation on the thermal expansion coefficient is generally considered as negligible. Olsen [88] also gave an averaged expression for pure PuO_2, obtained from the data of Tokar et al. [89] and of Brett, Russell [90]:

$$\Delta L/L = -3.9735\times10^{-4} + 8.4955\times10^{-6}\Theta + 2.1513\times10^{-9}\Theta^2 + 3.7143\times10^{-16}\Theta^3 (8b)$$

The thermal expansion of the mixed oxides UO_2-PuO_2 is obtained from the weighted average of expressions (8a) and (8b), according to Olsen's recommendation [88].

While in MATPRO-Version 09 [88] the data were fitted with a polynominal, in MATPRO-Version 11 (Rev. 1) [111] a correlation based on more physical grounds is recommended for UO_2:

$$\Delta L/L = 1.0\times10^{-5}\,T - 3.0\times10^{-3} + 4.0\times10^{-2}\exp(-6.9\times10^{-20}/kT), \quad (9a)$$

and for PuO_2:

$$\Delta L/L = 9.0\times10^{-6}\,T - 2.7\times10^{-3} + 7.0\times10^{-2}\exp(-7.0\times10^{-20}/kT), \quad (9b)$$

where k denotes Boltzmann's constant (1.38×10^{-23} J/K).

For UO_2-PuO_2 the contributions from each constituent are to be combined in proportion to their weight fractions.

The first two terms in eq. 9a, b describe low temperature thermal expansion whereas the last term describes the contribution from Schottky defects [113]. The O:M ratio is not included. When the departure from stoichiometry (O:M ratio) is greater than 0.2 there is clearly an effect, however this is not relevant for the in-reactor behavior of the fuel.

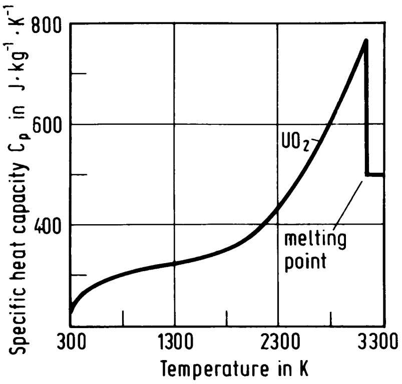
The specific heat capacity, or its integral over the temperature, i.e., the enthalpy, were measured by Moore, Kelley [91], Ogard, Leary [92, 93], Hein et al. [94], Leibowitz et al. [95], and Frederickson, Chasanov [96]. Measurements at low temperatures were carried out by Huntzicker, Westrum [97] and Grønvold et al. [98]. Affortit [99] examined the effect of the stoichiometry of the UO_2 on its specific heat capacity. The data were evaluated by Hein et al. [100], Engel [101], Conway, Hein [102], Kerrisk, Clifton [103], as well as by Olsen [104]. From regression analysis of the data in [91 to 96], Kerrisk, Clifton [103] obtained the following relationship for the temperature dependence of C_p, except the factor (O:M)/2, which has been recommended by Olsen [104] and refined by Reymann [112]:

$$\begin{aligned} C_p = {} & K_1\Theta^2 \exp(\Theta/T)T^{-2}(\exp(\Theta/T)-1)^{-2} + K_2T \\ & + ((O/M)/2)(K_3E_D/RT^2)\exp(-E_D/RT) \end{aligned} \quad (10)$$

where C_p is in $J\cdot kg^{-1}\cdot K^{-1}$ and T in K. The values of the constants Θ, E_D and K_1, K_2, and K_3 are given in Table 1/5. Approximately the same relationship was given in "Bureau of Mines Bulletin No. 605" [105]. **Fig. 1-22**, p. 36, shows the functional relationship expressed by eq. (10).

The same relationship (10), but with different constants (given in Table 1/5), was used by Reymann [112] for PuO_2, based on his evaluation of the data of Ogard, Leary [92], Gibby et al.

Fig. 1-22



Specific heat capacity of stoichiometric UO_2 as a function of the temperature [112].

[106, 107], Leibowitz et al. [108], and Kruger, Savage [114]. For UO_2-PuO_2 the specific heat capacity is found by combining the contributions of the constituents as described for $\Delta L/L_0$.

Table 1/5
Constants for Expressing the Specific Heat Capacity (Eq. 10) of UO_2 and PuO_2 as a Function of the Temperature [112].

constant	UO_2	PuO_2	units
K_1	296.7	347.4	$J \cdot kg^{-1} \cdot K^{-1}$
K_2	2.43×10^{-2}	3.95×10^{-4}	$J \cdot kg^{-1} \cdot K^{-2}$
K_3	8.745×10^{7}	3.860×10^{7}	J/kg
Θ	535.285	571.000	K
E_D	1.577×10^{5}	1.967×10^{5}	J/mol
R	8.3143	8.3143	$J \cdot mol^{-1} \cdot K^{-1}$

References for 1.1.3:

[1] R. Peierls (Ann. Physik [5] **3** [1929] 1055/101). – [2] R. A. Wolfe (WAPD-270 [1963] 1/20; N.S.A. **17** [1963] No. 36305). – [3] R. K. Willardson, J. W. Moody, H. L. Goering (J. Inorg. Nucl. Chem. **6** [1958] 19/33). – [4] J. L. Bates, C. A. Hinman, T. Kawada (J. Am. Ceram. Soc. **50** [1967] 652/6). – [5] L. Genzel (Z. Physik **135** [1953] 177/95).

[6] F. Engelmann, H. E. Schmidt (Nucl. Sci. Eng. **24** [1966] 317/21). – [7] A. L. Loeb (J. Am. Ceram. Soc. **37** [1954] 96/9). – [8] H. Kämpf, G. Karsten (Nucl. Appl. Technol. **9** [1970] 288/300). – [9] J. C. Maxwell (A Treatise of Electricity and Magnetism, 3rd Ed., Vol. 1, Oxford Univ. Press, Oxford 1904, p. 440). – [10] A. Eucken (Die Wärmeleitfähigkeit keramischer feuerfester Stoffe, VDI [Ver. Deut. Ing.] Forschungsh. No. 353 [1932]).

[11] H. Fricke (Phys. Rev. [2] **24** [1924] 575/87). – [12] A. Biancheria (Trans. Am. Nucl. Soc. **9** [1966] 15). – [13] G. P. Marino (J. Nucl. Mater. **38** [1971] 178/90). – [14] J. P. Stora

(Nucl. Technol. **17** [1973] 225/33). – [15] S. Nazare, G. Ondracek, F. Thümmler (in: H. H. Hausner, Modern Developments in Powder Metallurgy, Vol. 5, Plenum, New York 1971, pp. 171/86).

[16] G. Ondracek, B. Schulz (J. Nucl. Mater. **46** [1973] 253/8). – [17] Y. S. Touloukian, E. H. Buyco (Thermal Conductivity of Nonmetallic Solids, Thermophysical Properties of Matter, Vol. 2, IFI-Plenum, New York 1970, pp. 1/1649; C.A. **74** [1971] No. 131 307). – [18] R. P. Tye (Thermal Conductivity, Academic, London-New York 1969, pp. 1/376; C.A. **74** [1971] No. 131 308). – [19] A. M. Ross (A Literature Survey on the Measurement of Thermal Conductivity of Several Solids Including Uranium Dioxide, AECL-585 [1958] 1/42; CRFD-762 [1958] 1/42; N.S.A. **12** [1958] No. 10679). – [20] W. B. Lewis (AECL-478 [1957] 9; DM-44 [1957] 1/21; N.S.A. **11** [1957] No. 11 490).

[21] J. Belle (Uranium Dioxide, Properties and Nuclear Applications, U.S. Government Printing Office, Washington 1961, p. 576). – [22] J. A. L. Robertson, A. M. Ross, M. J. F. Notley, J. R. MacEwan (J. Nucl. Mater. **7** [1962] 225/62; C.A. **59** [1963] 8324). – [23] J. L. Daniel, J. Matolich, H. W. Deem (HW-69945 [1962] 1/39; N.S.A. **17** [1963] No. 11 258). – [24] A. D. Feith (GE-TM-63-9-5 [1963]). – [25] J. P. Stora, B. de Bernardy de Sigoyer, R. Delmas, P. Deschamps, B. Lavaud, C. Ringot (CEA-R-2586 [1964]; EURAEC-1095 [1964] 1/117; N.S.A. **19** [1965] No. 7982).

[26] J. Vogt, L. Grandell, U. Runfors (Ab. Atomenergie Rapp. RMB-527 [1964]). – [27] T. G. Godfrey, W. Fulkerson, T. G. Kollie, J. P. Moore, D. L. McElroy (ORNL-3556 [1964] 1/72; N.S.A. **18** [1964] No. 27965). – [28] T. Nishijima, T. Kawada, A. Ishihata (J. Am. Ceram. Soc. **48** [1965] 31/4). – [29] H. E. Schmidt, J. Richter, M. van den Berg (Proc. 6th Conf. Therm. Conduct. Dayton, Ohio, 1966, pp. 527/45). – [30] J. B. Ainscough, M. J. Wheeler (Brit. J. Appl. Phys. **19** [1968] 859/68).

[31] O. L. Kruger (ANL-7513 [1964] 93/100). – [32] R. R. Asamoto, F. L. Anselin, A. E. Conti (J. Nucl. Mater. **29** [1969] 67/81). – [33] R. L. Gibby (J. Nucl. Mater. **38** [1971] 163/77). – [34] J. C. Weilbacher (High Temp.-High Pressures **4** [1972] 331/8). – [35] J. B. Conway, A. D. Feith (GEMP-715 [1969] 1/76; GEMP-715-Add. [1970]; N.S.A. **24** [1970] No. 10158).

[36] J. L. Bates (High Temperature Thermal Conductivity of Round Robin, Uranium Dioxide, ORNL-1431 [1970]). – [37] IAEA (Thermal Conductivity of Uranium Dioxide, Tech. Rept. Ser. Intern. At. Energy Agency No. 59 [1966]). – [38] C. S. Olsen, G. A. Reymann (TREE-NUREG-1005 [1976] 15/28). – [39] L. A. Goldsmith, J. A. M. Douglas (TRG-Report-2103-Add. [1971/72] 1/4; N.S.A. **26** [1972] No. 43418). – [40] J. C. Van Craeynest, J. P. Stora (J. Nucl. Mater. **37** [1970] 153/8).

[41] F. J. Hetzler, T. E. Lamin, K. J. Perry, E. L. Zebroski (GEAP-4879 [1967] 1/32; N.S.A. **22** [1968] No. 19625). – [42] C. F. Lucks, H. W. Deem (BMI-1448-Rev. [1960] 1/104; N.S.A. **14** [1960] No. 21883). – [43] J. A. Christensen, A. J. Bush, H. M. Ferrari, R. J. Allio (Trans. Am. Nucl. Soc. **7** [1964] 391). – [44] G. Fayl, K. Hansen (RISO-269 [1972] 1/35; N.S.A. **27** [1973] No. 7818). – [45] J. R. McEwan, R. L. Stonte, M. F. Notley (J. Nucl. Mater. **24** [1967] 109/12).

[46] M. Serizawa, H. Hiromitsu, Y. Yokouchi, M. Koizumi (J. Nucl. Mater. **34** [1970] 224/6; C.A. **72** [1970] No. 104707). – [47] R. L. Gibby (BNWL-704 [1968] 1/43; N.S.A. **22** [1968] No. 38619). – [48] R. L. Gibby (BNWL-927 [1969] 1/25; N.S.A. **23** [1969] No. 14393). – [49] L. A. Goldsmith, J. A. M. Douglas (J. Nucl. Mater. **43** [1972] 225/33). – [50] H. E. Schmidt (Forsch. Ingenieurw. Ver. Deut. Ing. [VDI] **38** [1972] 149/51).

[51] H. E. Schmidt (High Temp.-High Pressures **3** [1971] 345). – [52] J. C. Van Craeynest, J. C. Weilbacher (J. Nucl. Mater. **26** [1968] 132/6). – [53] J. L. Bates (Nucleonics **19** [1961] 8316). – [54] J. A. Christensen (WCAP-2531 [1963]). – [55] R. Viskanta (Nucl. Sci. Eng. **21** [1965] 13/9).

[56] D. R. DeHalas (Nucleonics **21** [1963] 92/4). – [57] J. A. Stoddard, N. J. MacCormick (Nucl. Sci. Eng. **39** [1970] 126/9). – [58] J. P. Moore, D. L. McElroy (J. Am. Ceram. Soc. **54** [1971] 40/6). – [59] H. E. Schmidt (J. Nucl. Mater. **39** [1971] 234/7). – [60] E. M. Müller (Atomwirtsch. Atomtech. **15** [1970] 434/5).

[61] A. M. Ross (AECL-1096 [1960]; CRFD-817 [1960] 1/61; N.S.A. **15** [1961] No. 5417). – [62] M. J. F. Notley, J. R. MacEwan (AECL-2230 [1965] 1/33; N.S.A. **19** [1965] No. 22962). – [63] M. Aragones, H. Guerrero (AECL-2564 [1966] 1/45; N.S.A. **20** [1966] No. 39446). – [64] R. R. Asomoto, F. L. Anselin, A. E. Conti (GEAP-5493 [1968] 1/52; N.S.A. **22** [1968] No. 41097). – [65] J. P. Stora (Trans. Am. Nucl. Soc. **13** [1970] 137).

[66] L. A. Goldsmith, J. A. M. Douglas (J. Nucl. Mater. **47** [1973] 31/42). – [67] V. C. Howard, T. F. Gulvin (IG-Report-51 [1961] 1/22; N.S.A. **15** [1961] No. 16179). – [68] J. A. L. Robertson (AECL-1123 [1960] 1/19; N.S.A. **15** [1961] No. 4334). – [69] R. M. Powers, Y. Cavallaro, J. P. Mathern (SCNC-317 [1960] 1/128; N.S.A. **15** [1961] No. 27601). – [70] J. A. L. Robertson (AECL-1037 [1960]; CRFD-933 [1960] 1/17; N.S.A. **14** [1960] No. 24546).

[71] G. W. Cunningham, D. E. Kizer, S. J. Paprocki (Plansee Proc. 4th Seminar, Reutte/Tyrol 1961 [1962], pp. 483/506). – [72] D. J. Clough, J. B. Sayers (AERE-R-4690 [1964] 1/75; N.S.A. **19** [1965] No. 11776). – [73] B. T. Bradbury, B. R. T. Frost (Radiation Effects in Ceramic Fuels, in: G. J. Dienes, Studies in Radiation Effects on Solids, Gordon & Breach, New York 1967, pp. 159/279). – [74] R. C. Hawkings, J. A. C. Robertson (AECL-1733 [1963]; CRDC-1143 [1963] 1/114; N.S.A. **17** [1963] No. 32661). – [75] M. G. Balfour, J. A. Christensen, H. M. Ferrari (WCAP-2933 [1966]).

[76] J. P. Stora, P. Chenebault (CEA-R-3618 [1968] 1/114; N.S.A. **23** [1969] No. 9154). – [77] J. A. Gyllander (AE-411 [1971] 1/71; N.S.A. **25** [1971] No. 22203). – [78] B. Schulz (KFK-1400 [1971] 247/51; N.S.A. **26** [1972] No. 30214). – [79] M. D. Burdick, H. S. Parker (J. Am. Ceram. Soc. **39** [1956] 181/7). – [80] J. B. Conway, R. M. Fincel, R. A. Hein (Trans. Am. Nucl. Soc. **6** [1963] 153).

[81] J. B. Conway, R. M. Fincel, R. A. Hein (GE-TM-63-6-6 [1963]). – [82] J. A. Christensen (J. Am. Ceram. Soc. **46** [1963] 607/8). – [83] M. Hoch, C. A. Momin (High Temp.-High Pressures **1** [1969] 401/7). – [84] H. D. Sheets (in: J. Belle, Uranium Dioxide, Properties and Nuclear Applications, United States At Energy Commission, Washington, D.C., 1961, pp. 192/5). – [85] W. A. Lambertson, J. H. Handwerk (ANL-5053 [1956] 1/48; N.S.A. **11** [1957] No. 2221).

[86] I. P. Bell, S. M. Makin (RDB-C-TN-70 [1954] 1/17; N.S.A. **9** [1955] No. 1266). – [87] P. Murray, R. W. Thackray (Harwell Energy Res. Estab. HERE-M-M-22 [without data]). – [88] C. S. Olsen (TREE-NUREG-1005 [1976] 34/40). – [89] M. Tokar, A. W. Nutt, T. K. Keenan (Nucl. Technol. **17** [1973] 147/52). – [90] N. H. Brett, L. E. Russell (Plutonium 1960 Proc. 2nd Intern. Conf. Plutonium Met., Grenoble 1960 [1961], pp. 397/410).

[91] G. E. Moore, K. K. Kelley (J. Am. Chem. Soc. **69** [1947] 2105/7). – [92] A. E. Ogard, J. A. Leary (Thermodyn. Nucl. Mater. Proc. Symp., Vienna 1967 [1968], pp. 651/65). – [93] A. E. Ogard, J. A. Leary (LA-4494-MS [1970] 43). – [94] R. A. Hein, L. H. Sjodahl, R. Szwarc (J. Nucl. Mater. **25** [1968] 99/102). – [95] L. Leibowitz, L. W. Mishler, M. G. Chasanov (J. Nucl. Mater. **29** [1969] 356/8).

[96] D. R. Frederickson, M. G. Chasanov (J. Chem. Thermodyn. **2** [1970] 623/9). – [97] J. J. Huntzicker, E. F. Westrum (J. Chem. Thermodyn. **3** [1971] 61/76). – [98] F. Grønvold, N. J. Kveseth, A. Sveen, J. Tichi (J. Chem. Thermodyn. **2** [1970] 665/79). – [99] C. Affortit, J. Marcon (Rev. Intern. Hautes Temp. Refract. **7** [1970] 236/41). – [100] R. A. Hein, P. N. Flagella, J. B. Conway (J. Am. Ceram. Soc. **51** [1968] 291/2).

[101] T. K. Engel (J. Nucl. Mater. **31** [1969] 211/4). – [102] J. B. Conway, R. A. Hein (J. Nucl. Mater. **15** [1965] 149/50). – [103] J. F. Kerrisk, D. G. Clifton (Nucl. Technol. **16** [1972] 531/5). – [104] C. S. Olsen (TREE-NUREG-1005 [1976] 9/15). – [105] C. E. Wicks, F. E.

Block (Thermodynamic Properties of 65 Elements, Their Oxides, Halides, Carbides, Nitrides, U.S. Bur. Mines Bull. No. 605 [1963]).

[106] R. L. Gibby, L. Leibowitz, J. F. Kerrisk, D. G. Clifton (J. Nucl. Mater. **50** [1974] 155/61). – [107] R. L. Gibby (HEDL-TME-73-19 [1973] 1/36; N.S.A. **27** [1973] No. 25086). – [108] L. Leibowitz, D. F. Fischer, M. G. Chasanov (ANL-8042 [1974] 1/19; N.S.A. **30** [1974] No. 773). – [109] G. Neuer, R. Brand, G. Haufler (IRS-SB-3 [1973] 1/217; N.S.A. **30** [1974] No. 27343). – [110] D. L. Hagrman (NUREG-CR-0497-Rev. 1 [1980] 23/48; TREE-1280-Rev. 1 [1980] 23/48).

[111] G. A. Reymann (NUREG-CR-0497-Rev. 1 [1980] 48d/48m; TREE-1280-Rev. 1 [1980] 48d/48m). – [112] G. A. Reymann (NUREG-CR-0497 [1979] 9/23; TREE-1280 [1979] 9/23). – [113] P. J. Baldock, W. E. Spindler, T. W. Baker (J. Nucl. Mater. **18** [1966] 305/13). – [114] O. L. Krüger, H. Savage (J. Chem. Phys. **45** [1968] 4540/4).

1.1.4 Behavior of the Fission Products and Release of Fission Gases

General References:

J. Belle, Uranium Dioxide, Properties and Nuclear Applications, U.S. Government Printing Office, Washington, D.C., 1961, pp. 477/572.

B. G. Childs, Fission Product Effects in Uranium Dioxide, Review Article, J. Nucl. Mater. **9** [1963] 217/44 [61 Refs.].

F. A. Nichols, Kinetics of Diffusional Motion of Pores in Solids, J. Nucl. Mater. **30** [1969] 143/65 [60 Refs.].

J. A. L. Robertson, Keynote Address, Introductory Survey on Swelling and Gas Release, Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 219/21 [44 Refs.].

M. V. Speight, Effects of Fission Gas in Fuels During Irradiation, Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 222/30, [65 Refs.].

IAEA, Behavior and Chemical State of Irradiated Ceramic Fuels, Proceedings of a Panel, Vienna 1972 [1974], pp. 1/437 [30 papers].

IAEA, Thermodynamics of Nuclear Materials, Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1, pp. 3/250, Vol. 2, pp. 145/302.

C. E. Beyer, C. R. Hann, Prediction of Fission Gas Release from UO_2 Fuel, BNWL-1875 [1974] 1/54, 38 [88 Refs.]; N.S.A. **31** [1975] No. 24926.

P. E. MacDonald, L. B. Thompson, MATPRO-Version 09, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, TREE-NUREG-1005 [1976] 140/8.

D. R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 172/332.

G. T. Lawrence, A Review of the Diffusion Coefficient of Fission-Product Rare Gases in Uranium Dioxide, J. Nucl. Mater. **71** [1978] 195/218 [49 Refs.].

K. H. Neeb, Zum Verhalten von Spaltprodukten im Kernbrennstoff von Leichtwasserreaktoren, in: F. Baumgärtner, Chemie der nuklearen Entsorgung, Thiemig-Taschenbuch, Vol. 65, Thiemig, München 1978, pp. 56/88.

D. L. Hagrman, G. A. Reymann, MATPRO-Version 11, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, NUREG-CR-0497 [1979] 165/202; TREE-1280 [1979] 165/202.

C. Ronchi, H. Matzke, J. v. d. Laar, H. Blank, Fission Gas Behavior in Nuclear Fuels, Proceedings of the Workshop held at the Joint Research Centre, Karlsruhe Establishment [European Institute for Transuranium Elements], Germany, October 26 – 27, 1978, Eur. Appl. Res. Rept. **1** [1979] 1/350.

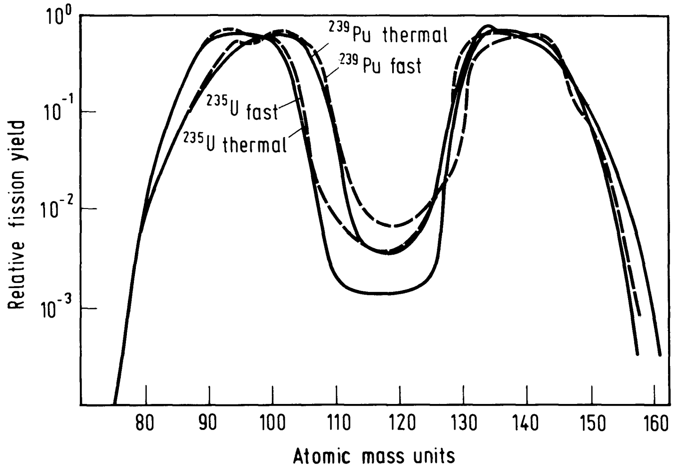
Consultants' Symposium on Rare Gases in Metals and Alkali Halides, Harwell, U.K.A.E.A., September 10 to 14, 1979:

C. R. A. Catlow, Theory of Fission Gas Migration in UO_2, Radiat. Eff. **53** [1980] 127/31.
A. B. Lidiard, Theory of Diffusion of Rare Gases in Solids, Radiat. Eff. **53** [1980] 133/9.
H. Matzke, Gas Release Mechanisms in UO_2: A Critical Review, Radiat. Eff. **53** [1980] 219/42.
J. A. Turnbull, A Review of Irradiation Induced Resolution in Oxide Fuels, Radiat. Eff. **53** [1980] 243/9.

Concentration of the Fission Products

The concentration of the various fission product elements in an irradiated fuel depends on its composition (e.g., the Pu-content), on the neutron spectrum, on the fission rate, and on the amount of burnup. It is necessary to consider decay chains in this connection. **Fig. 1-23** shows fission product concentrations at equilibrium for 10% burnup (relative to the number of metal atoms), according to Davies, Ewart [1]. For further quantitative data see, e.g., references [2 to 7].

Fig. 1-23



Fission yield spectra of ^{235}U and ^{239}Pu [1].

1.1.4.1 Solid and Volatile Fission Products

The behavior of the fission products has been studied since the early sixties. Already the studies of Bleiberg et al. [8, 9] and of Daniel et al. [10] have shown that for burnups up to 4×10^{21} fissions/cm^3 (160 MWd/kg(U); 10^{20} fissions/cm^3 correspond to 4 MWd/kg(U), assuming 200 MeV per fission) no change of the cubic lattice structure of UO_2 occurs. The radial distribution of the fission products in UO_2 pellets was reported by Bates et al. [11 to 13] and by Anselin [14]; the first review was published by Childs [15] in 1963. More recent examinations of the state of knowledge concerning the behavior of the fission products were conducted at two IAEA conferences in Vienna, in 1972 [16] and in 1974 [17].

Fission Products in the Fuel

The fission products in UO_2 and in UO_2-PuO_2 may be classified according to their chemical and physical behavior as follows [18]:

1) Those forming soluble oxides: Sr, Zr, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd.

2) Those forming insoluble oxides: Ba, Sr (as zirconate), Mo (according to the oxygen potential of the fuel).

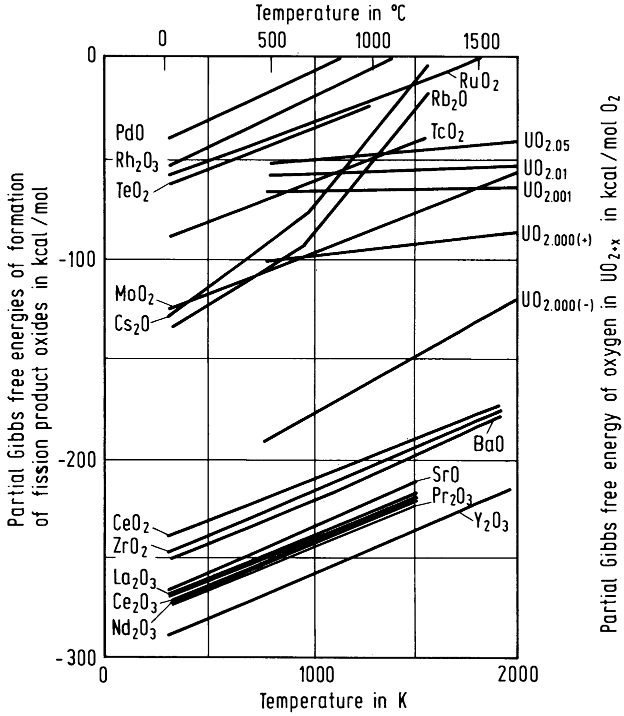
3) Elemental metals: Ru, Rh, Pd, and Mo (partly).

4) Volatile ones: Br, I, Rb, Cs, Se, Te.

5) Noble gases: Kr, Xe (these are treated in Section 1.1.4.2, p. 45). He and tritium are relatively rare fission products formed in ternary fissions.

Whether fission products occur as the oxides or as the elements depends on the free energy of formation of the oxides (**Fig. 1-24**), compared with the partial molar free energy of the oxygen in the oxide fuel. It is seen in Fig. 1-24 that BaO, ZrO_2, SrO, and the oxides of the rare earths are stable relative to technical grade UO_2 in a thermodynamical sense.

Fig. 1-24



Gibbs free energies of formation of fission product oxides and partial Gibbs free energy of the oxygen in UO_2 of various stoichiometries (according to [234]).

References for 1.1.4 on pp. 65/70

A different classification can be made according to the metallographically observed phases of the fission products (cf. e.g. [19, 20]):

1) Homogeneous distribution or very finely dispersed precipitates. The oxides of the rare earths, with the exception of Ce, and those of Y and Zr, which are thermodynamically very stable, occur in homogeneous or quasihomogeneous dispersion [21].

2) Grey phases (nonmetallic inclusions). The grey phases have high Ba and low Ce and Sr concentrations [19 to 22], while the concentration of Zr is variable [19, 21, 23]. They are essentially oxides and zirconates [24, 25], and contain also variable amounts of Nd, Mo, Ru, and Tc (up to 9%) [21].

3) White phases (metallic inclusions). Metallic inclusions are the major fraction (70%) of all inclusions. Their size is generally 5 to 6 µm [19, 20, 25] (in extreme cases up to 1 mm [25]), they are located at grain boundaries or near voids, and have melting points between about 1 800 and 1 900 °C [25]. The composition of the white phases corresponds to that calculated from the fission concentrations of the elements shown in Table 1/6 (according to [25 to 27] in [28]), except for Mo, which occurs partly as the oxide at elevated oxygen potential of the fuel.

Table 1/6
Composition of Metallic Inclusions in Irradiated Oxidic Nuclear Fuels [28].

group	components	main components	position
I	U,Ru,Rh,Pd	Pd	central void
	U,Pu,Te,O(?)	Te	near surface
II	Mo,Tc,Ru,Rh,Pd	Mo,Ru	whole fuel
	Tc,Ru,Rh	Ru	columnar grains
	Pd,Te,Sn,Sb	Pd	non-restructured zone
	Pd,Mo,Sn	Pd	
	Ba,Sr,Mo,Zr,O	Ba,Mo	whole fuel,
	Ba,Mo,O		crack
	Ba,Ce,O		whole fuel
	Ba,Fe,O		whole fuel
	Ba, Mo, Nb,O	Ba	central void
	Cs, Mo,O		near surface, crack
III	Pd,Mo		near surface
	Pd,Fe		near surface
	Pd,Fe,Ni		near surface
	Pd,Fe,Mo	Pd,Mo	near surface
	Pd,Fe,Mo,Tc	Pd,Mo	near surface
	Fe,Cr,Ni	Fe(75%)	near surface
	Ba,Mo,Fe,O		near surface
	Cs,Te,O(?)		near surface
	Cr,Te,O(?)		near surface
	Cs,Cr,O		surface, crack

Numerous studies deal with the analysis and spatial distribution of the white phases. A hexagonal phase containing Mo-Ru-Tc-Rh-Pd and a face-centered-cubic phase containing U-Pu-Ru-Rh-Pd were isolated [25]. Also reported are intermetallic compounds of the type MN_3 (M = U, Pu; N = Rh, Pd) [19, 29]. Extensive microprobe studies, e.g., those of Kleykamp [30], Bazin et al. [31], and Friskney, Simpson [38], as well as gamma spectrometric studies, e.g., those of Conteson et al. [32] and Powell [33], have been published. The results from [30] are shown in Table 1/7. A special sampling technique (microdrilling) is described in [34].

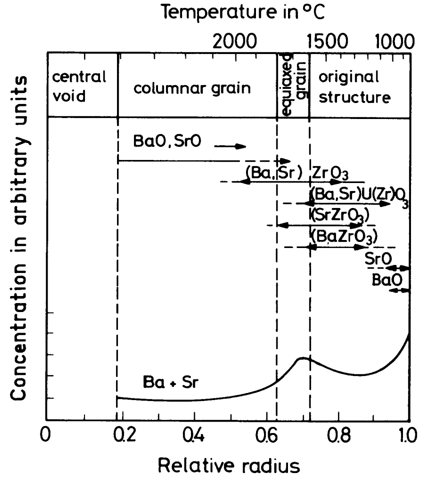
Table 1/7
Analysis of Metallic Fission Product Phases in Irradiated Oxidic Fuel [30].

fuel	composition in %					Ref.
	Mo	Ru	Tc	Rh	Pd	
UO_2	60	24	16			[26]
UO_2	55	22	17	6		[21]
$(U_{0.8}Pu_{0.2})O_2$	43	32	16	7	2	[25]
$(U_{0.8}Pu_{0.2})O_2$	21	48	17	12	2	[27]

An important factor concerning the spatial distribution of the fission products is the behavior of their precursors in the decay chains. For example, the precursors of Mo are the relatively immobile Zr and Nb isotopes.

Further insight into the behavior of the fission products was obtained, e.g., by Schmitz et al. [29], Götzmann, Hofmann [35], Conte et al. [36], and Kerolas et al. [37], from studies on fuels containing simulated fission products. Koizum, Satoh [39] studied the system UO_2-Ba-Sr-Zr and found at 1 500 °C the compounds $(Ba, Sr)ZrO_3$ and $(Ba, Sr)UO_3$. **Fig. 1-25** presents their model for the radial distribution of Ba and Sr in the fuel.

Fig. 1-25



Chemical compounds and concentration profiles of barium and strontium in irradiated fuel, model of [39].

References for 1.1.4 on pp. 65/70

Potter [40] presents a survey of what was known in 1972 concerning the phase diagrams of the systems U-Pu-O-fission products. Of particular interest is the system U-O-Cs, that had been investigated by Cordfunke [41]. A preliminary phase diagram of this system at low oxygen partial pressures is shown in "Uran" Erg.-Bd. C3, 1975, on p. 51. The behavior of Cs as a fission product was studied in detail also by Adamson, Aitken [42].

The Behavior of Volatile Fission Products

The mobility of the fission products must always be considered relative to their chemical form. Typically volatile fission products, such as I and Cs, may be relatively immobile as certain compounds under suitable conditions, as is, for example, the thermodynamically very stable CsI. However, during irradiation of the fuel in the reactor this compound may decompose [43 to 45].

In colder fuel zones Cs is often found in oxide phases [23, 46]. Between 500 and 1 000 °C there exist [42] at least two different Cs-U(Pu)-O compounds (for the systems Cs-U-O and Cs-U(Pu)O see in "Uran" Erg.-Bd. C3, 1975, pp. 50/4): $Cs_2U(Pu)O_4$ at O:U $\geq$2.009, $Cs_2U(Pu)O_3$ at O:U $<$2.009 (hypothetically, according to [42]). The formation of Cs_2UO_4 in mixed oxide fuel rods in the breeding zone as a consequence of Cs and O migration may cause local volume increases [47, 48], which are significantly larger than the effects of fission product swelling (see Section 1.1.5.2, p. 80). The compound Cs_2MoO_4 is important for the transport of the elements Cs, Mo, and O [42], that is observable in porous regions in the fuel and in the void space between the fuel and the cladding [23].

The axial distribution of Cs in mixed oxide fuel rods was studied by Swailos, Geithoff [49], Phillips et al. [50, 51], and Karnesky et al. [52]. Further investigations of the caesium uranate system and of the migration of Cs, Mo, and other fission products, from both thermodynamic and kinetic viewpoints, were carried out by Johnson et al. [53 to 56], O'Hare, Hoekstra [57], and Osborne et al. [58]. The various aspects of the migration of Cs may be summarized as follows, according to Bramman, Powell [59]:

1) Even at low burnup, there occurs a major migration of Cs to the cold periphery of the fuel (concentration up to 100 times that in the center).

2) An axial migration occurs to both the hotter rod end (at low axial temperature gradients) and the colder one (at high gradients) [49].

3) Very little Cs is found in the fuel rod plenum (a fuel-free space at the end of the rod for the uptake of fission gases).

As volatile fission products must be classified the halogens I and Br, in the compounds CsI, RbI, CsBr, and RbBr, as well as Te and Se, in the form of Cs_2Te and Cs_2Se, with vapor pressures of about 10^{-3} bar at 1 000 K and 1 bar at 2 000 K [60].

Less volatile, but still sufficiently mobile to suffer concentrations shifts in the fuel rod, and even to be released from the fuel, are Mo and Ba in oxide form [60, 61]. A diffusion controlled precipitation of Mo and Ba at the surface of the fuel is reported in [61]. While Phillips et al. [62] found an appreciable migration of Nb in UO_2-PuO_2 fuel rods, Swailos, Geithoff [49] state that practically neither Nb nor Ce, Pr, Ru, and Rh are mobile. The behavior of Ba and Sr is reported by Friskney, Simpson [63].

Many publications deal with the behavior of the radioactive fission products (such as ^{131}I, ^{133}I, ^{132}Te, ^{137}Cs). Their release from the fuel is discussed in particular by Friskney, Simpson [64] and Turnbull, Friskney [65, 66]. For a quantitative description of the release of unstable fission products see Section 1.1.4.3, p. 51 (models for intermediate temperatures).

The diffusion behavior of metallic Cs, Ag, and Sr in layered fuel particles is discussed by Brown, Faircloth [67]. The release of fission-produced Cs, Sr, and Ba may be diminished by the additions of SiO_2 and Al_2O_3 to the UO_2 [68, 69]. For the retention of Ba also ZrO_2 may be used, as an "interior getter" [70].

1.1.4.2 Behavior of the Fission Gases in the Fuel

Robertson [71] surveyed what had been known on the behavior of fission gases in 1973, a subject that had been studied since the fifties. Recently a critical review of gas release mechanisms in UO_2 was given by Matzke [234]. Noteworthy milestones in understanding the behavior of the fission gases in the fuel are:

1957: Booth [72] – measurement of the release of the fission gases; its interpretation as the diffusion of single gas atoms; introduction of the radius of an equivalent sphere for the description of the porous structure of a fuel pellet.

1960: Lewis [73] – observation of the resolution of the fission gases.

1960: MacEwan, Lawson [74] – recognition of the migration of pores along a temperature gradient as a factor contributing to the release of the fission gases.

1963: Barnes, Mazey [75] – observation of bubble migration (in metals).

1964: MacEwan, Stevens [76] – the interpretation of the decrease of the fission gas release rate with increasing burnup in terms of interactions of its atoms with lattice defects (defect trap model).

1965: Whapham, Sheldon [77] – observation of the resolution of fission gas bubbles under irradiation.

1966: Notley, McEwan [78] – the recognition that the transient fission gas release during power excursions occurs by means of grain boundary bubbles.

1967: Cornell, Banister [79] – the finding that the mean bubble migration rate varies with bubble size.

1967: Matzke, Davies [80] – the finding that fission gases diffuse by means of triple vacancies (one U-vacancy and two O-vacancies).

1969: Bellamy, Rich [81] – the recognition that grain boundary pore growth leads to fission gas release.

1969/71: Nelson [84], Turnbull, Cornell [98, 99] – quantitative data on resolution of bubbles, theory of atomic collision aspect.

1971: Turnbull, Cornell [87, 88] – consideration of heterogeneous nucleation of bubbles.

1974/78: Tucker [162, 235 to 238] – observation of grain boundary bubbles, quantitative treatment.

1977/79: Baker [239 to 241] – radial bubble distribution in pin, transmission microscopy.

1977/79: Turnbull, Friskney, Speight [66, 167, 242] – high-temperature high-burnup isothermal in-pile release experiments.

1979: Johnson et al. [243] – observation of gas bubble morphology by scanning electron microscopy.

1979: Kleykamp [244] – measurements of radial Xe-profiles by electron microprobe analysis.

1979: Zimmermann [245] – simultaneous measurement of gas in pores and gas in matrix.

The state of the analytical treatment of the behavior of the fission gases in the fuel was summarized in 1973 by Speight [82]. The following aspects were considered: 1) Formation of bubbles, 2) stability, growth, and migration of intragranular bubbles, and 3) migration of large bubbles along temperature gradients.

The Formation and Growth of Bubbles

Homogeneous nucleation is treated in the model proposed by Greenwood et al. [83], and plays some role also in those of Nelson [84], Whapham [85], and Dollins, Ocken [86]. The density of bubble nuclei should decrease at increasing temperatures, if nucleation is homogeneous. This decrease should be around an order of magnitude between 900 and 1 200 °C, according to Whapham [85].

Heterogeneous nucleation results, according to Turnbull [87] and Cornell [88], from spontaneous generation in the fission fragment track. The bubble nucleus contains [87] about four gas atoms, and each fission fragment forms some five nuclei. Heterogeneous nucleation is favored by the observation with an electron microscope [87] of linearly arranged fission gas bubbles (**Fig. 1-26**), and by the small temperature dependence, a factor of 4 between 800 and 1 600 °C, of the bubble concentration observed by Cornell [88] (**Fig. 1-27**).

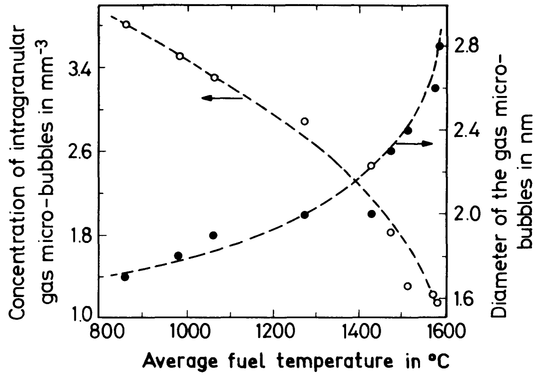
Olander reviewed the theoretical studies of bubble growth [89]. Some simplifying assumptions that have been used in the models are:

(1) All the gas occurs in the bubbles, none in the matrix.
(2) Resolution mechanisms involving the fission fragments are neglected.
(3) All the bubbles have the same size.
(4) The bubbles are in mechanical equilibrium with the matrix.
(5) The gas density corresponds either to that of closest packing or to that of an ideal gas.

Fig. 1-26

Electron-microscope pictures of intragranular fission gas microbubbles [87].

Fig. 1-27



Concentrations and diameters of intragranular fission gas bubbles as a function of the average fuel temperature [88].

The model of Eyre, Bullough [90] employs all these five simplifications, that of Markworth [91, 92] only simplifications (2) to (5), while fission-induced resolution is recognized (and assumptions (3) to (5) are kept) in those of Nelson [84], Pati et al. [93, 94], and Marlowe [95]. The giving up of simplification (4) entails the consideration of vacancies, for which Greenwood et al. [83], Gulden, Kaae [96], and Harrison [97] made theoretical contributions, in the latter two cases involving the effects of mechanical stresses.

In order to analyse the distribution of bubble sizes, it is necessary to take account not only of the mechanisms of the creation and growth of bubble nuclei, but also mechanisms of bubble resolution due to fission fragment effects. These effects are:

(1) Complete spontaneous resolution of small bubbles due to the effect of a single fission fragment. The model of Turnbull [87], that describes the data of Cornell [88], leads to a bubble size distribution which is the result of the dynamic equilibrium between their generation, growth, and resolution. The mean lifetime of such bubbles is of the order of one hour.

(2) The knocking out of gas atoms from a large bubble due to the effect of a fission fragment. According to Turnbull and Cornell [98], this mechanism takes place for bubble sizes larger than about 2.4 nm (cf. also [99 to 100]).

Dollins and Ocken [86] arrive at mean lifetimes of the bubbles as a function of their sizes differing from those of [87, 88].

A complete mathematical treatment of the Turnbull model was undertaken by Speight [102], who reported the bubble size distribution as a function of the burnup. According to this Turnbull-Speight model, the processes of nucleation, bubble growth, and bubble resolution occur simultaneously. At low fission rates and high temperatures there is a broad distribution of the bubble sizes and the concentration of the bubbles is low. On the contrary, at high fission rates and low temperatures, the size distribution is narrow, but the concentration of bubbles is again low, due to the strong effect of the resolution on the state of the equilibrium.

Ross [103] and Nelson [84] presented mechanisms for the shrinkage of gas bubbles in the fuel. In both models it is assumed that gas atoms are knocked out of the gas bubble by fission fragments. The continuous change in the radius of the fission gas bubbles (or gas filled closed sinter pores) obeys, according to Ross [103], the expression

$$\Delta r = r_0 - r = (3/2)k \cdot T \cdot n \cdot B \tag{1}$$

where r_0 is the initial radius, B is the burnup, k and T have their usual meanings, and $n \approxeq 5 \times 10^{11}$ Xe atoms per $cm^3 \cdot bar \cdot MWd/t(U)$ is a parameter. From this follows that a pore with $r_0 = 0.25\,\mu m$ at $T = 473$ K will disappear after about 500 MWd/t(U). According to Nelson [84] the mean lifetime of a bubble of $r_0 = 5\,\mu m$ is about 10^5 s. Another model, which deals mechanistically with the effect of fission fragments on fission gas bubbles, was presented by Blank, Matzke [104]. Further theoretical treatments of bubble growth may be found in the studies of Markworth [92] and Speight [105].

Bubble Migration

There are essentially two different mechanisms for bubble migration:

(1) stochastic movement of fission gas bubbles in the fuel matrix, and
(2) migration of fission gas bubbles along temperature gradients.

Greenwood, Speight [106] presented in 1963 the first model for the coalescence of stochastically migrating fission gas micro-bubbles under isothermal conditions. Gruber [107] extended this model in 1967 by means of computer calculations to include non-analytic solutions of the migration equations. Olander [108] summarized these studies. The migration and coalescence of fission gas bubbles, and the relation between fission gas behavior and fuel swelling, was discussed also in several theoretical papers by Dollins, Nichols, Ocken and Warner [86, 109 to 114] as well as in one by Cornell, Speight et al. [115].

Observations of bubble migration were made by Cornell, Bannister [79], who injected gas atoms into foils, and by Gulden [116], who generated the bubbles by annealing of a fuel, that had been irradiated at low temperatures. Contrary to this, Turnbull [117] found at temperatures ≤1 500 °C no indication of the mobility of bubbles that had been generated by irradiation at higher temperatures. This was confirmed by Baker [118, 119]. Gas micro-bubbles with diameters from 1 to 4 nm have often facets with crystallographically definable morphology. The migration velocities of such bubbles may be lower by several orders of magnitude than those of spherical bubbles, according to Shewmon [120] and Beeré [121], since the rate of formation of new facet-steps may be rate-determining. The different results of Gulden [116] and Baker [118, 119] may be further due to the fact that in the former case a precipitation of solid fission products could be found in most of the bubbles, while in the latter one the surfaces of the bubbles were clean.

It appears, thus, that below 1 500 °C it is the diffusion of dissolved gas atoms, and not the stochastic migration and coalescence of fission gas micro-bubbles, that is responsible for bubble growth. Above 1 700 °C the bubbles are spherical, and have an appreciably enhanced mobility.

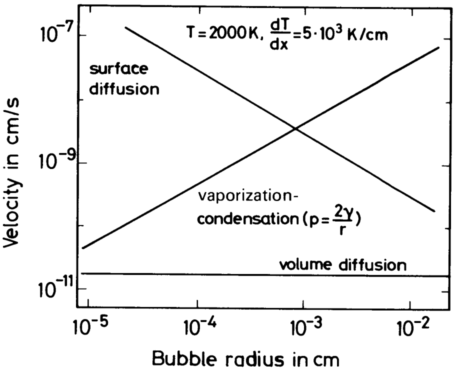
Nichols [122] surveyed the possible mechanisms of the mobility of pores and bubbles in a solid. The migration velocity of a bubble along a temperature gradient, v_B, may be expressed as follows:

$$v_B = (D_B/kT)(4\pi r^3/3\Omega)(Q^*/T)\ (dT/dx)_B \tag{2}$$

where D_B is the "bubble diffusion coefficient", r is the bubble radius, Ω is the volume of the matrix atoms, Q^* is the heat of transport and $(dT/dx)_B$ is the temperature gradient at the position of the bubble. The transfer of matrix atoms to the colder side of a bubble causes the movement of the bubble in the temperature gradient. **Fig. 1-28** [18] shows the velocity as a function of the radius of the bubble for the following three mechanisms:

(1) volume diffusion ($D_B \sim r^{-3}$),
(2) surface diffusion ($D_B \sim r^{-4}$), and
(3) vaporization-condensation ($D_B \sim r^{-2}$).

Fig. 1-28

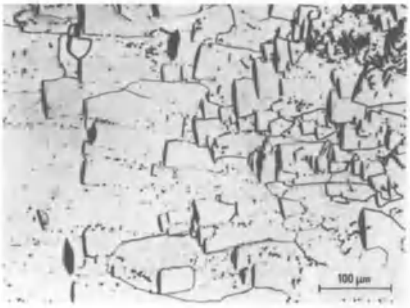


Velocities of bubble migration according to the three transport mechanisms as a function of the bubble radius [18].

Weeks et al. [123] have calculated migration velocities. The larger bubbles and pores migrate at high temperatures by means of a vaporization-condensation process. **Fig. 1-29** [124] shows the typical appearance of lenticular pores, which migrate towards higher temperatures, and leave behind them columnar grains (grain boundaries not visible), as well as pearl-string-like micropores at the edges of their track. The basic mechanism of this phenomenon had first been presented by MacEwan, Lawson [125]. The effects of the crystal orientation were treated in [126, 127], and the effect of the gas-filling in [128]. Further theoretical papers were published by Sens [129], De Halas, Horn [130], Speight [131], and Nichols [132, 133]. However, experimental studies by Oldfield et al. [134, 135] showed the observed migration velocities to be lower than the theoretically predicted ones. This may be explained by the effect of impurities on the crystal growth [136].

Experiments simulating the migration of large pores along temperature gradients were made by Ronchi, Sari [137], Kikuchi, Tobita [138], and Kawamata et al. [139]. Lenticular pores occur [137] only if the pressure of the gas in them is lower than the equilibrium pressure of the solid phase. The pore migration velocity is then proportional to $T^{-5/2}$, as was also derived theoretically by Clement [140]. According to this model, the velocity of the migration of He-filled pores along a temperature gradient is controlled by the kinetics of the vaporization-condensation process at the pore surface.

Fig. 1-29



Lenticular pores, that migrate towards higher temperatures (left) [124].

1.1.4.3 The Release of Fission Gases

Experimental

There are essentially three types of experiments for examining the release of fission gases:

(1) Annealing of pre-irradiated samples (for the experimental arrangement see, e.g., [141, 142]).
(2) Measurement during the irradiation (for the experimental arrangement see, e.g., [143, 144]).
(3) The puncturing of irradiated fuel rods.

Models for Low Temperatures ($\lesssim$1 000 °C)

Since the mobility of the fission gas atoms by means of thermally activated processes is small at low temperatures, the fission gases can emerge from the fuel only by means of one or more of the following mechanisms:

(1) Irradiation-enhanced diffusion,
(2) recoil of the fission fragments, and
(3) knock-out of gas atoms by the fission fragments.

Mechanisms (2) and (3) are treated in [144 to 149]; they are effective only near the surface. Also fuel atoms may be knocked out, together with the fission gas atoms. The layer plated out on the cladding may affect the integral of the fission gas release [150].

In the model of Shiba et al. [151] (pseudo-recoil model) the fission gas atoms are temporarily held back in traps (lattice defects produced by the fission fragments). According to Yamagishi, Tanifuji [152] the "pseudo-recoil" process is, in fact, a "self-knock-out" mechanism: when a fission fragment spends its energy near the UO_2 surface, it knocks surface atoms out, together with which it is released from the lattice. In the model of Szuta [153], an "intermediate state" of the fission gas (high energy fission fragments) is assumed, which explains the fission-rate dependence of the fission gas release.

Release measurements of Shiba [154] with UO_{2+x} ($0 \leq x \leq 0.62$) show that the release increases up to a maximum at $x = 0.2$, falls to a sharp minimum at $x = 0.25$, and then rises again for increasing values of x. More or less "ideal" UO_2 and U_4O_9 crystals thus possess at low temperatures a lower fission gas release ability than crystals with more lattice defects.

Models for Intermediate Temperatures (1 000 to 1 600 °C)

A survey of what had been known prior to 1963 was published by Childs [15]. The simplest explanation for the temperature dependence of the fission gas release is that the fission gas atoms diffuse through the matrix and emerge at surfaces adjacent to the surroundings. The fuel is regarded as an assembly of spheres of equal sizes, having an equivalent radius, a, defined by

$$a = 3V/A \tag{3}$$

where V is the total volume and A the total surface area. Often a is treated as just an empirical parameter. There are two variants of the equivalent radius model:

(a) Simple diffusion model

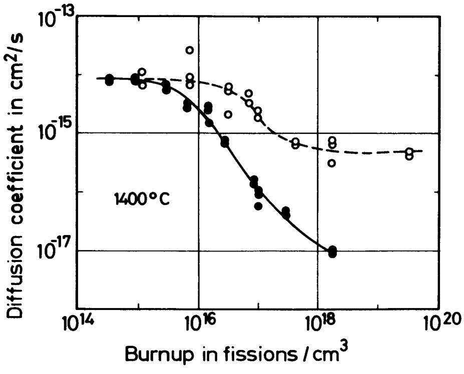
According to Booth [72], the fractional release, f, of stable noble gas isotopes is for $f \leq 0.57$ the following function of the duration of the irradiation, t:

$$f = 4\,(D't/\pi)^{1/2} - 1.5\,D't \tag{4a}$$

where $D' = D/a^2$ and D is the diffusion constant of noble gas atoms in the fuel, provided their rate of generation and the temperature are constant. Three experimental facts indicate that this model is oversimplified:

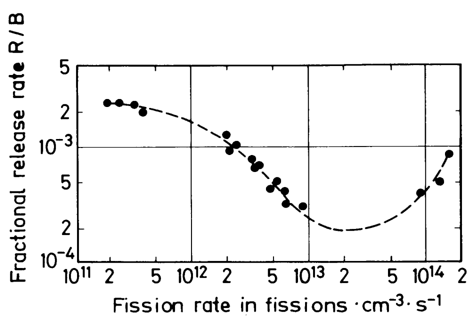
- the $t^{1/2}$ law is not always obeyed,
- D and therefore D′ depend on the burnup, as is shown in **Fig. 1-30** [155], and
- the release depends in a complicated way on the fission rate, as is seen in **Fig. 1-31**, p. 52 [156].

Fig. 1-30



Diffusion coefficient of the noble gas atoms in sintered UO_2-pellets (90% of the theoretical density) and in single crystals as a function of the burnup [155]. ---○--- polycrystalline, 90% of theoretical density, —●— single crystal.

Fig. 1-31



Fractional release rate R/B of ^{85}Kr as a function of the fission rate (R = release rate, B = generation rate) [156].

The fractional release obtained by annealing after irradiation is given by

$$f = 6\,(D't/\pi)^{1/2} \qquad (4b)$$

Radioactive fission gas isotopes (and generally, active fission products) may be treated only under steady-state conditions by simple expressions, such as

$$R/B = 3\,(D'/\lambda)^{1/2} \qquad (4c)$$

where R is the release rate, B the rate of generation (R/B is thus the fractional release rate) and λ the decay constant [157].

(b) Diffusion mechanisms with traps and resolution

Olander [157] classifies the traps for fission gases as follows:

1. Natural disturbances:
   (a) grain boundaries,
   (b) dislocation lines,
   (c) closed pores, generated during manufacture,
   (d) impurities in the matrix.

2. Irradiation-induced disturbances:
   (a) vacancy clusters (in particular in fission fragment tracks),
   (b) dislocation loops (condensation of interstitials),
   (c) fission gas micro-bubbles
   (d) precipitated fission products (e.g., noble metals).

Further aspects are the "stability" of the traps against thermally activated processes and against fission fragment effects, and the "depth" of the traps.

An example for this variant of the model is that of Speight [105], which was discussed also by Frost [158]. Two kinds of traps are considered: intragranular fission gas micro-bubbles, and intergranular fission gas bubbles at the grain boundaries. Both kinds of bubbles submit to fission-induced redissolution. This model was used for practical fuel rod layout, in spite of the many parameters which are difficult to estimate (see Collins, Hargreaves [159, 160]). The following mechanisms were considered:

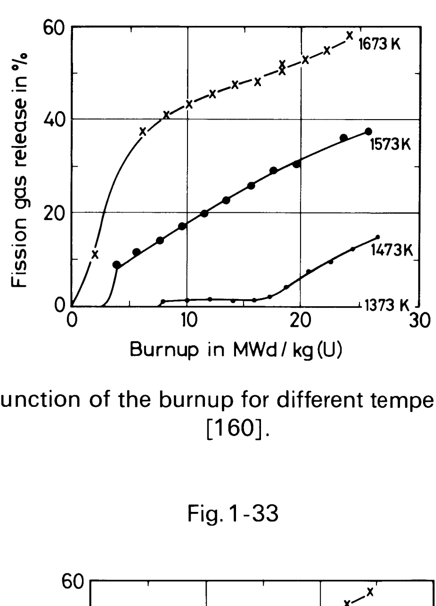
(1) Diffusion of gas atoms from the interior of the grain to its boundary, including the effects of intragranular micro-bubbles.

(2) Resolution processes by means of fission fragments.

(3) Grain growth as an additional process for the collection of gas atoms.

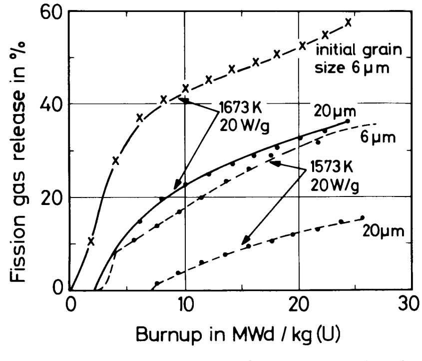
The fission gas release calculated according to the model is shown in **Fig. 1-32** for various temperatures and in **Fig. 1-33** for various grain sizes of the UO_2. This model is considered together with the swelling and the migration of fission products generally in the

Fig. 1-32



Fission gas release as a function of the burnup for different temperatures (model calculations) [160].

Fig. 1-33

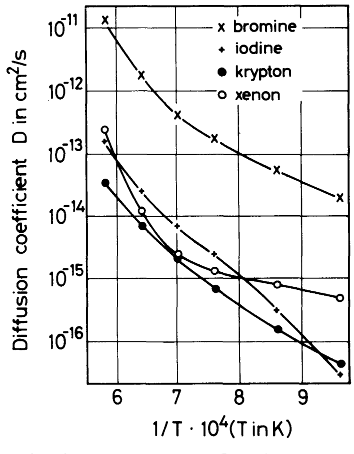


Fission gas release as a function of the burnup for different grain sizes and temperatures (model calculations) [160].

References for 1.1.4 on pp. 65/70

reviews of Frost [158], Findlay [161], and Turnbull, Tucker [162]. Several more papers from the Berkeley Nuclear Laboratories "school", (Central Electricity Generating Board, UK, = CEGB), provide experimental confirmation and material for possible supplementary considerations of the model. Turnbull, Tucker [163] calculated the fission gas release for temperature gradients of short duration, and found that only minimal amounts of gas are released thereby from the fuel matrix. A model for the morphology and growth rate of the grain boundary porosity in irradiated UO_2 was constructed by Beeré, Reynolds [164]. The model predicts fission gas release after an incubation time of about 3.4×10^6 s for thermal gas diffusion (1600 °C) or of 2.4×10^7 s for athermal gas diffusion. The following gas release comes in individual outbursts, the mean time between outbursts being 3.5×10^5 s, respectively 1.6×10^6 s, for the two above-mentioned conditions. Also Tucker, Turnbull [165] regard the pore morphology and changes in it under irradiation. Several experimental studies by Friskney, Turnbull et al. [64, 166 to 168] report the release rates of individual fission gas isotopes and their temperature and grain size dependencies. **Fig. 1-34** [168] shows the diffusion constants of Kr and Xe, compared with those of Br and I, derived from the results. Grain boundary diffusion is of relative minor importance for the fission gases (contrary to iodine [64]).

Fig. 1-34



Fission product release from single crystals of UO_2. Calculated diffusion constants in Arrhenius plots [168].

The modeling and experimental work at CEGB has been continued up to now (1981). According to Tucker [235 to 238], fission gas release depends on the following sequential but interrelated processes: (1) Diffusion of gas atoms to the grain boundaries. (2) Passage of gas atoms to pores on grain edges. (3) Growth of interconnected grain edge porosity results in fission gas release.

The coalescence of grain boundary bubbles is treated mathematically by a simple diffusion model in [235]. As shown in scanning electron micrographs of UO_2 fracture surfaces (**Fig. 1-35**) the small fission gas pores on the grain boundaries are discrete and are randomly spaced. They remain discrete until they all coalesce with their neighbors by simple overlapping. Further

Fig. 1-35

Scanning electron micrograph of a fracture surface of UO_2 irradiated at 1 750 °C to an exposure of 0.13% FIMA [235].

calculations on the migration of grain edge bubbles lead to the conclusion that a bubble tends to migrate preferentially towards those of its neighbors that contain the lowest fission gas pressure, a process which dominates over random migration [236].

An important step in the understanding of fission gas behavior in UO_2 was the experimental work of Baker [239 to 241], who observed intragranular fission gas bubbles by electron microscopy and came to the following conclusions [241]:

(1) Intragranular fission gas bubbles nucleate heterogeneously in UO_2.

(2) The bubbles have clean surfaces and are faceted.

(3) The bubble size increases slightly and the bubble density decreases slightly with irradiation temperature.

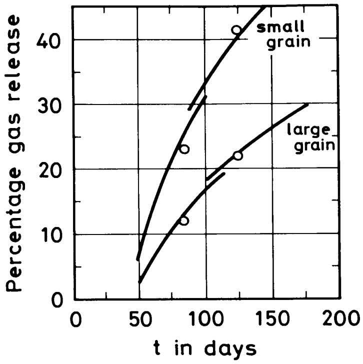
(4) There is no evidence for appreciable mobility of gas bubbles, at least up to 1 600 °C.

(5) At irradiation temperatures below 1 500 °C only a small fraction of the gas is present as intragranular bubbles. The majority of the gas is in solution.

(6) The dominant mechanism leading to the release of gas by its transfer to grain boundaries is the diffusion of single atoms.

Tucker and Turnbull [242, 246] refined their model, taking into account the effect of open grain edge porosity on the resolution of fission gas. With increasing fraction of grain surfaces occupied by tunnels the resolution parameter is reduced. **Fig. 1-36**, p. 56, [242] shows a comparison of gas release at 1450 °C with that predicted by this model.

Fig. 1-36



Comparison of measured and predicted values of gas release for specimens of UO_2 isothermally irradiated in sealed capsules at 1 450 °C [242].

A model of the release of unstable gaseous and volatile fission products was developed by Tucker and White [247, 248]. Friskney, Turnbull [249] measured the release rates for unstable rare gases ^{88}Kr, ^{87}Kr, ^{85m}Kr, ^{133}Xe, ^{138}Xe for samples of polycrystalline small-grained and large-grained UO_2 in the temperature range 700 to 1 550 °C. Interpretation is in terms of simple diffusion of gas atoms and their halogen precursors. Diffusion coefficients calculated for Kr, Xe, and I are similar in magnitude and temperature dependency; the coefficient for Br is about 200 times higher.

Another working group in Great Britain which delivered many papers on theoretical and experimental aspects of fission gas release is with UKAEA, especially AERE Harwell. Starting with the analysis of observations of fission gas bubble distributions in the fuel [250] and with the modelling of bubble nucleation and fission-induced resolution in the fuel [251] by Wood, this author and Matthews developed a simple operational gas release model (and swelling model) for intragranular gas [252] and for grain boundary gas [253]. This model can be extended to the fission gas behavior during transient heating under hypothetical accident situations [254, 255]. Greatley and Hargreaves [256], UKAEA, measured the fission gas release of UO_2 during irradiation in the Windscale Advanced Gas-Cooled Reactor. The results lend support to current theories of the mechanism of fission gas release.

A further "school of thought" concerning fission gas behavior is the Bettis Atomic Power Laboratory, USA. The state of knowledge up to 1971 was reviewed by Nichols, Warner [110]. Dollins, Nichols published in 1977 a model [114] for the release of and the swelling by fission gases, for temperatures below 1 700 °C, covering also the temperature range below 1 200 °C, for which Dollins [113] had already proposed a model in 1976. The most important characteristics of the model are:

(1) The fission gas micro-bubbles are generated homogeneously at low temperatures (two atoms form one nucleus), and are mobile even at temperatures below 1 300 °C, but they move randomly even in the presence of large temperature gradients [113].

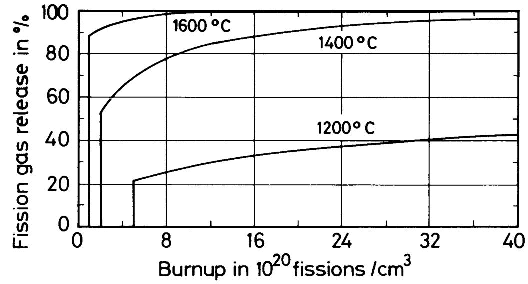
(2) The model describes the size and concentration of gas bubbles in the interior of the grains, as well as at their boundary surfaces, edges, and corners.

(3) Resolution mechanisms are considered even for grain boundary bubbles.

(4) When the gas bubble swelling at the edges and corners of the grains reaches 5%, mutually connected and branched gas tunnels are formed.

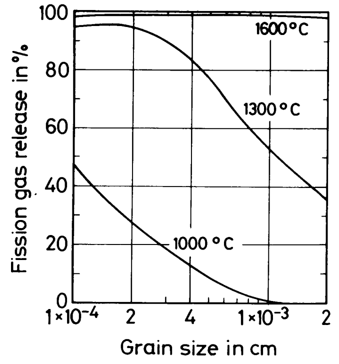
This model is a further development of the BUBL-codes, previously developed by Nichols, Warner [110] and their many coworkers, extensively discussed in [157]. **Fig. 1-37** shows predictions for the fractional fission gas release as a function of the burnup. **Fig. 1-38** shows the calculated grain size dependence, as an example of one of the parameters of the model. **Fig. 1-39**, p. 58, compares values calculated from the model with the experimental results of Zimmermann [169].

Fig. 1-37



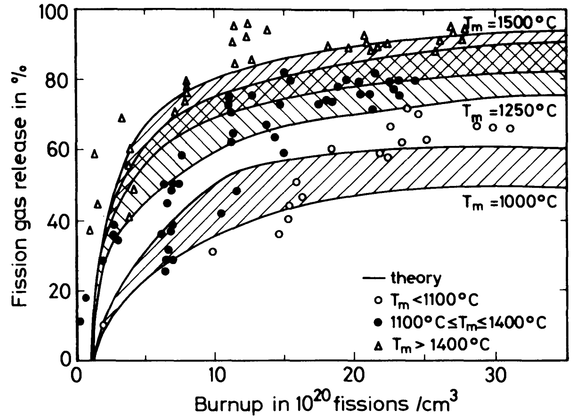
Fission gas release as a function of the burnup for different temperatures (fission rate: 10^{13} fissions · cm^{-3} · s^{-1}, temperature gradient: 1000 K/cm, grain size: 10 µm, pressure: 138 bar) (model calculation) [114].

Fig. 1-38



Fission gas release as a function of the grain size for different temperatures (fission rate: 10^{13} fissions · cm^{-3} · s^{-1}, burnup: 10^{21} fissions/cm^3, temperature gradient: 1000 K/cm) (model calculation) [114].

Fig. 1-39



A comparison between theory [114] and experimental data for the fission gas release [169] in UO_2-PuO_2. The boundary curves correspond to the upper and lower grain sizes, 5×10^{-3} cm and 1×10^{-4} cm, respectively. T_m is the mean fuel temperature.

A further microstructure-dependent model for fission gas release (and swelling) in UO_2 fuel which incorporates the relevant physical properties (fission gas diffusion, bubble and grain boundary movement, intergranular bubble formation and interlinkage) was developed by Notley and Hastings [257 to 259]. Recently Kidson [260] published a generalized analysis of the "equivalent sphere model" introduced by Booth in 1957 [72]. This model has been generalized to describe the behavior of the m members of a radioactive chain during k cycles of reactor operation. The expressions obtained for the concentration of the species in the equivalent sphere and the cumulative fractional release from the sphere include, as special cases, all results previously considered as well as some new predictions.

Another mechanistic model is that of Ronchi and Matzke [170 to 172]. It starts from the following differential balance of the fission gas concentration:

$$dc_{\text{in solution}} = dc_{\text{generation}} + dc_{\text{resolution}} - dc_{\text{intragranular bubbles}} - dc_{\text{grain boundary bubbles}} \qquad (5)$$

It presents a set of linear differential equations that must be solved numerically. The following quantities are determined:

(1) the concentration of fission gases in the matrix, as a result of a dynamical equilibrium,

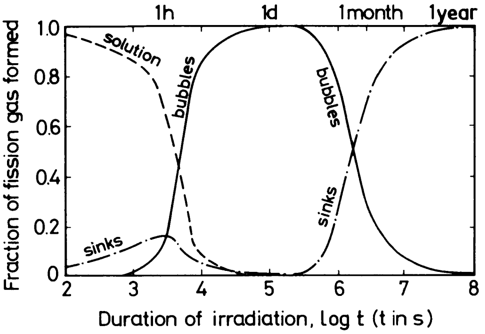
(2) the concentration of fission gases in intragranular micro-bubbles,

(3) the concentration of fission gases at grain boundaries,

(4) local swelling caused by bubble growth.

A comparison between the theory and experimental results (UO_2-PuO_2 fuel rods for fast breeders) shows that the portion of fission gas calculated to be at the grain boundaries (3) practically equals the released fission gas. **Fig. 1-40** shows the time dependence calculated for portions (1) to (3), expressed as a fraction of the fission gas formed.

Fig. 1-40



Balance of the occurrence of fission gases at a fuel temperature of 1500°C (model calculation), in matrix (solution), micro-bubbles, and grain boundaries (sinks) [171].

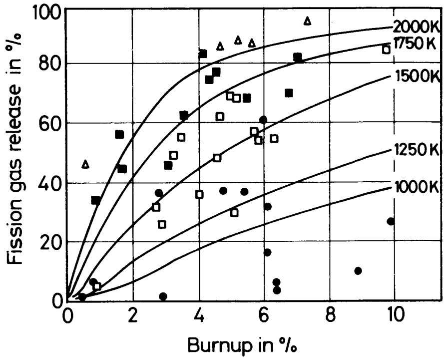
Three categories of fission gases have been distinguished in the study of fission gas behavior and the swelling of oxide nuclear fuels by Zimmermann [18]:

(1) released fission gas (**Fig. 1-41**),

(2) fission gas in pores, which may be released on grinding of the fuel (**Fig. 1-42**a and b, p. 60) and

(3) fission gas in the lattice, the remainder after subtracting the fission gas categories (1) and (2) (**Fig. 1-43**, p. 60, and 1-**44**, p. 61).

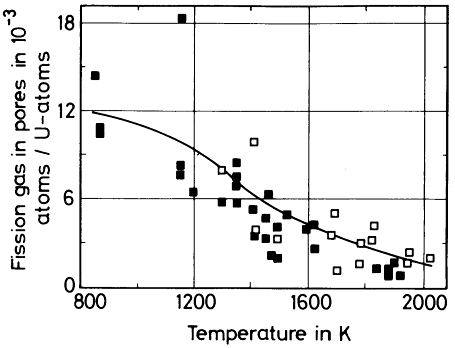
Fig. 1-41



Dependence of the fission gas release from UO_2 on the burnup [18].

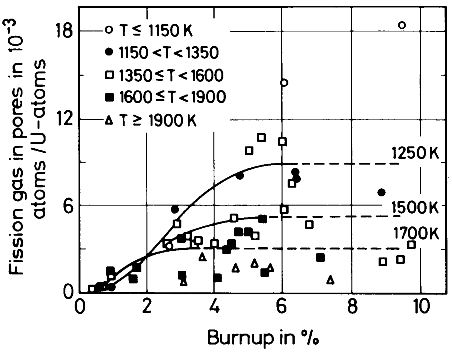
References for 1.1.4 on pp. 65/70

Fig. 42a



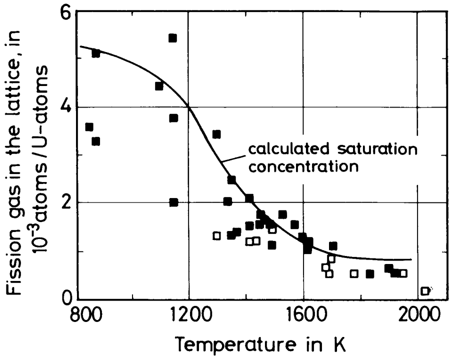
Concentration of the fission gas in pores in UO_2 as a function of the temperature for burnup values >3% [18]. □ without contact to cladding, ■ with contact to cladding.

Fig. 1-42b



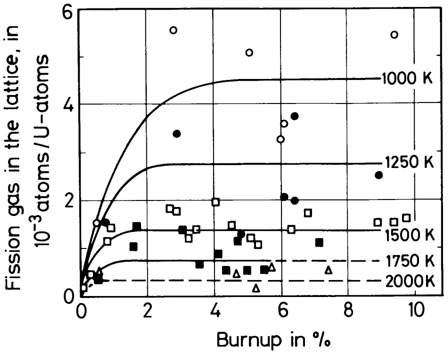
Concentration of the fission gas in pores in UO_2 as a function of the burnup [18].

Fig. 1-43



Concentration of fission gas in the lattice of UO_2 as a function of the temperature at burnup values >3% [18]. □ without contact to cladding, ■ with contact to cladding.

Fig. 1-44



Concentration of fission gas in the lattice of UO_2 as a function of the burnup [18].

Zimmermann describes the release of the fission gas as a two-step process: (a) release from the lattice unto the grain boundaries, and (b) release from the grain boundaries. The first part (a) is calculated according to the model of Booth (eq. 4a), with the empirical parameter

$$D' = 1.3\times10^{-7}\exp(-78/RT) - 1.38\times10^{-24}F \qquad (6)$$

(D' is in s^{-1}, the activation energy is in kJ/mol, the fission rate F in fissions $\cdot cm^{-3}\cdot s^{-1}$). The relative release from the grain boundaries R_G is expressed by

$$R_G = K(D_G t)^{1/2}P^n \qquad (7)$$

where K is a structure factor, D_G is the effective transport coefficient for the release of fission gases from the grain boundaries to free surfaces in cm^2/s, and P is the concentration of fission gas in pores. The experimental result for D_G is

$$D_G = 9\times10^{-11} + 1.5\times10^{-6}\exp(-100/RT) \qquad (8)$$

and the parameter n was found to equal $10^{-4}T$. The relative total release is $f\cdot R_G$, where f is given by eq. (4a).

The model of Hering et al. [173] consists of two parts: (a) steady-state fission gas release, and (b) transient fission gas release. Based on the findings of Zimmermann [18], the release is treated as a two-step process, but the release from the grain boundary is considered in a refined manner. At a steady state the release follows the relationship

$$df(t)/dt = K_1(T)\cdot K_2(B,T)\cdot K_3(P_{op},B)\cdot g(t) \qquad (9)$$

where $K_1(T)$ describes the dependence of the gas transport along the grain boundaries on the temperature, $K_2(B, T)$ describes the burnup and temperature dependencies of the release through a "breakaway" mechanism, $K_3(P_{op}, B)$ deals with the effect of the open porosity P_{op}, that decreases as a consequence of post-sintering during burnup (see Section 1.1.5, p. 70), and g(t) is the concentration of fission gases at the grain boundaries at time t. The part of the model, that deals with the transient release of fission gases, assumes that the release is caused by the formation of additional cracks. These cracks arise from grain boundary separations caused by power transients.

Another model is proposed in the MATPRO-Version 09 [174]. This model, developed by Weisman et al. [175], leads to an expression of the following form:

$$F = 1-(1-k')(1-\exp(-kt))/kt \tag{10}$$

where F is the portion of the fission gas released, while k and k′ are temperature- and density-dependent parameters, respectively. This model is valid for a constant power level, but it may be modified to apply to time-dependent power levels [174]. The data base for the calibration of the model is an extensive literature survey by Beyer, Hahn [176]. These authors selected carefully such results which were obtained with representative and well characterized samples and operating conditions. Fortysix experiments from seven different sources [177 to 183] were utilized for the evaluation of the parameters k and k′.

A refined version of this analytical fission gas release model was presented in MATPRO-Version 11 [261]. The fission gas released to the fuel free volume (F) is a fraction released from the grain boundaries (F′) times the sum of the fission gas stored at the grain boundaries during previous time steps (S) and the fission gas that reaches the grain boundaries during a time increment (Δn):

$$F = F'(S + \Delta n) \tag{11}$$

The rate of fission gas transport from the interior of the grain to the grain boundary is

$$dn/dt = k'(B + k''C) \tag{12}$$

where n is the fission gas released from the grain interior to the grain surfaces, t is the time, C is the fission gas trapped at defects in the interior of the grain.

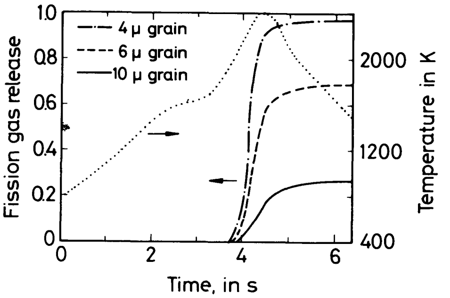
$$B = dn/dt + dC/dt \tag{13}$$

is the fission gas birth rate, k′ is the probability of direct release from the fuel grains and depends on the temperature, k″ is the probability per unit time of release of fission gases from grain defect traps and depends on temperature and burnup, F is a function of temperature, burnup, fuel density, and grain size of the fuel. The relationships are reported in [261].

There are numerous alternative models for the release of fission gases. Reference is made, e.g., to the studies of Rest [183], Johnson, Hofman [185] (two-zone model), and Beyer, Hahn [186, 187] (three-zone model). General agreement exists, that the release increases with increasing temperature and burnup, but decreases with increasing fuel density. There are, however, contradictory statements in the literature about the effects of other factors.

Some further aspects of the release of fission gases are discussed below, e.g., its dependence on the properties of the fuel and on the operating conditions. Only an indirect effect of the density (by the temperature distribution) in the range 10.42 to 10.74 g/cm^3 is claimed in [188]. A transient fission gas release was observed even for downward power excursions in closed fuel rods [78], but this effect was absent in ventilated rods [189]. The diffusion constant of Kr is different by a factor of 2 in single- and polycrystalline fuels in the temperature range 1 400 to 1 600 °C [190]. That of ^{133}Xe increased at 1 250 °C from 5×10^{-11} to 4.5×10^{-7} cm^2/s for grain sizes varying from 20 to 100 μm, but the activation energy did not change [191, 192]. Additions of Nb_2O_5 or La_2O_3 up to 1 mol% affect the fission gas release only indirectly, through the grain size of UO_2 [193]. Doping UO_2 with Cr_2O_3 does not markedly change the fission gas release of the fuel [262]. A high hydrostatic pressure (600 to 1 000 bar) may repress the formation of intra- and inter-granular fission gas bubbles [194]. A strong dependence of the release of fission gas on the grain size was observed by Griesmeyer et al. [195] (**Fig. 1-45**) for rapid temperature transients. For the fission gas behavior during fast thermal transients under hypothetical accident conditions see also [254, 255, 263 to 265].

Fig. 1-45



Fission gas release for fast temperature transients for different grain sizes (model calculation) [195].

Model for High Temperatures (≳1600 °C)

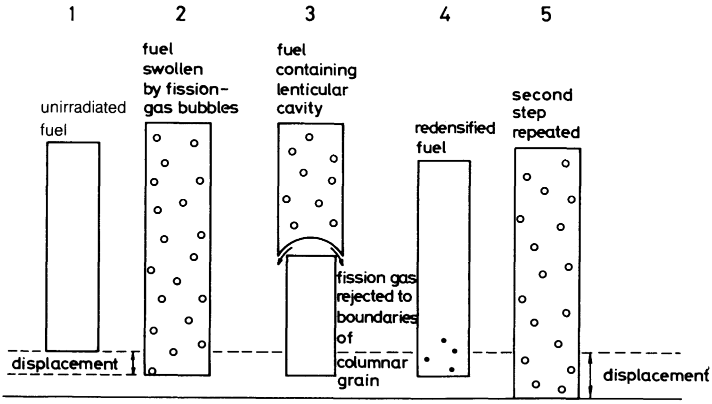
A model for the release of fission gas and the swelling at higher temperatures was proposed by a group of authors at the Battelle Columbus Laboratories, USA [196 to 198]. **Fig. 1-46** shows the individual steps of the mechanism:

(1) – (2) The build-up of a population of intragranular micro-bubbles without fission gas release.

(3) – (4) The migration of lenticular pores through the matrix along the temperature gradient towards higher temperatures, whereby the fission gas is collected from the micro-bubbles and is transported thereby.

(5) Renewed formation of a micro-bubble population.

Fig. 1-46



Schematic representation of the individual steps in fission gas release by flushing with migrating lenticular pores. The temperature gradient is positive in the upward direction [28, 197].

The sources for the pores, that are lenticular for energetic reasons, are large stable fission gas bubbles, sinter-pores, and crack surfaces. The model is based on high-temperature irradiation experiments of Hilbert et al. [197], Chubb et al. [198], Doi et al. [199], and Nelson et al. [200, 201]. Simulation experiments with non-irradiated samples were made by Lawson, MacEwan [202], Oldfield et al. [203], and Ronchi, Sari [137].

The Diffusion Coefficient of Fission Gases

A recent review of the diffusion coefficients of fission gases in UO_2 was published by Lawrence [204]. Previous surveys had been published by Belle [205], Childs [15], Matzke [206], and Turnbull [207].

Lawrence [204] surveyed all the experimental investigations of the diffusion coefficients of noble gases due to fission in UO_2, finding a considerable scatter of the values. Deviations due to differing sample properties and experimental conditions were examined. The most important results were tabulated for the following types of experiments: annealing after irradiation [142, 205 to 225], determination during the irradiation [148, 149, 221, 226 to 228], and miscellaneous experiments [206, 229 to 233].

The diffusion of noble gases in UO_2 depends strongly on the stoichiometry and on the burnup. The diffusion coefficient varies by a factor of 10^4 in the O:U range from 1.997 to 2.020 [142]. Fig. 1-30 (p. 51) shows the results of MacEwan, Stevens [155] concerning the dependence on burnup.

Lawrence [204] normalized the reported data to zero burnup and to the stoichiometric composition $UO_{2.000}$, and obtained the following "diffusion coefficient for fission-generated noble gases in UO_2":

$$D = 7.6\times10^{-6}\exp(-304/RT)\ (\mathrm{cm}^2/\mathrm{s}) \qquad (14)$$

(the activation energy is in kJ/mol).

In his review paper [234] Matzke stressed the point that the better definition of terms for the diffusion of rare gases in UO_2 is necessary in order to avoid obvious disagreements of the results and their interpretation. The following definitions for diffusion coefficients of rare gases in UO_2 are recommended: D for intrinsic diffusion of single gas atoms in the undamaged UO_2 lattice; possibly affected by deviations from stoichiometry and accumulation of fission products in solution. $D_{\mathrm{trap}}^{\mathrm{lab.}}$ for diffusion in the presence of traps, but in the absence of irradiation. $D_{\mathrm{trap}}^{\mathrm{lab.}} = f(nvt)$ between about 10^{16} and 10^{20} nvt. At higher nvt, saturation is indicated with a very low diffusion coefficient. $D_{\mathrm{trap}}^{\mathrm{in\text{-}pile}}$ for diffusion in the presence of both traps and irradiation, describing gas mobility between fission gas bubbles. $D_{\mathrm{eff}} = D_{\mathrm{trap}}^{\mathrm{in\text{-}pile}}\, b/(g+b)$ describing effective mobility including precipitation in bubbles. b = resolution probability; g = capture probability. D_{bubble} for diffusion of the bubble itself, describing gas transport in the absence of resolution. It proceeds via surface or volume diffusion of matrix atoms, U being rate-controlling, or via evaporation-condensation. The order of magnitude of the first three coefficients is:

$$D_{\mathrm{trap}}^{\mathrm{lab.}} < D_{\mathrm{trap}}^{\mathrm{in\text{-}pile}} < D. \qquad (15)$$

References for 1.1.4:

[1] J. H. Davies, F. T. Ewart (J. Nucl. Mater. **41** [1971] 143/55). – [2] L. Burris, I. G. Dillon (ANL-5742 [1957] 1/57; N.S.A. **11** [1957] No. 10719). – [3] L. E. Weaver, P. O. Strom, P. A. Killeen (USNRDL-TR-633 [1963] 1/41; N.S.A. **17** [1963] No. 39985). – [4] C. A. Anderson (LA-3383 [1965] 1/24; N.S.A. **20** [1966] No. 9970). – [5] M. E. Meek, B. F. Rider (APED-5398-A-Rev. [1968] 1/62; N.S.A. **23** [1969] No. 34784).

[6] H. Holleck, H. Kleykamp (KFK-1181 [1970] 1/66; EURFNR-836 [1970] 1/66; N.S.A. **25** [1971] No. 28690). – [7] W. Batey, K. Q. Bagley (J. Brit. Nucl. Energy Soc. **13** [1974] 49/61). – [8] M. L. Bleiberg, R. M. Berman, B. Lustman (WAPD-T-1455 [1962] 1/142; N.S.A. **17** [1963] No. 11270). – [9] M. L. Bleiberg, R. M. Berman, B. Lustman (Radiat. Damage Reactor Mater. Proc. Symp., Venice 1962 [1963], pp. 319/428; C.A. **60** [1964] 10151). – [10] R. C. Daniel, M. L. Bleiberg, H. B. Meieran, W. Yeniscavich (WAPD-263 [1962] 1/290; N.S.A. **16** [1962] No. 33524).

[11] J. L. Bates, J. A. Christensen, W. E. Roake (Nucleonics **20** [1962] 88/90). – [12] J. L. Bates (Trans. Am. Nucl. Soc. **7** [1964] 389/90). – [13] J. L. Bates (BNWL-58 [1965] 1/26; N.S.A. **19** [1965] No. 34740). – [14] F. Anselin (GEAP-5583 [1969] 1/37; N.S.A. **24** [1970] No. 14965). – [15] B. G. Childs (J. Nucl. Mater. **9** [1963] 217/44).

[16] IAEA (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974]; IAEA-PL-463 [1974]). – [17] IAEA (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1/2; IAEA-SM-190 [1975]). – [18] H. Zimmermann (KFK-2467 [1977] 1/102; INIS Atomindex **9** [1978] No. 354633). – [19] D. R. O'Boyle, F. L. Brown, J. E. Sanecki (J. Nucl. Mater. **29** [1969] 27/42). – [20] G. Camozzo (EUR-4613 [1971] 1/46; BNWL-tr-80 [1972]1/36; N.S.A. **26** [1972] No. 18114).

[21] B. M. Jefferey (J. Nucl. Mater. **22** [1967] 33/40). – [22] B. T. Bradbury, J. T. Demant, P. M. Martin, D. M. Poole (J. Nucl. Mater. **17** [1965] 227/36). – [23] H. Kleykamp (KFK-1727 [1973] 75/105). – [24] F. Anselin, W. E. Baily (Trans. Am. Nucl. Soc. **10** [1967] 103). – [25] J. I. Bramman, R. M. Sharpe, D. Thom, G. Yates (J. Nucl. Mater. **25** [1968] 201/15).

[26] B. T. Bradbury, J. T. Demant, P. M. Martin (Proc. Brit. Ceram. Soc. **7** [1967] 311/29). – [27] D. R. O'Boyle, F. L. Brown, A. D. Dwight (J. Nucl. Mater. **35** [1970] 257/66). – [28] D. R. Olander (TID-26711-P1 [1976] 172/98). – [29] F. Schmitz, G. Dean, M. Housseay, F. de Keroulas, J. C. van Craeynest (Proc. Conf. Fast Reactor Fuel Fuel Elements, Karlsruhe 1970, pp. 396/410). – [30] H. Kleykamp (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 157/66; IAEA-PL-463/8 [1974]; C.A. **82** [1975] No. 78275).

[31] J. Bazin, M. Perrot, N. Vignesoult (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 201/10; IAEA-PL-463/9d [1974]; C.A. **82** [1975] No. 91560). – [32] G. de Conteson, J. Monier, N. Vignesoult (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974]. pp. 191/200; IAEA-PL-463/9c [1974]; C.A. **82** [1975] No. 78276). – [33] H. J. Powell (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 379/92; IAEA-PL-463/21 [1974]; C.A. **82** [1975] No. 78282). – [34] W. Jennison, M. L. Clark (TRG-Report-1163 [1965] from [33]). – [35] O. Götzmann, P. Hofmann (KFK-1610 [1972] 1/173).

[36] M. Conte, M. Mouchnino, F. Schmitz (CEA-CONF-2011 [1971] 1/38; N.S.A. **26** [1972] No. 56582). – [37] F. de Keroulas, D. Calais, F. Schmitz (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 167/77; IAEA-PL-463/9a [1974]; C.A. **82** [1975] No. 91456). – [38] C. A. Friskney, K. A. Simpson (J. Nucl. Mater. **57** [1975] 341/7). – [39] M. Koizumi, M. Satoh (J. Nucl. Mater. **51** [1974] 90/4). – [40] P. E. Potter (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 115/55; IAEA-PL-463/7 [1974]; C.A. **82** [1975] No. 65711).

[41] E. H. P. Cordfunke (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1, pp. 185/92; IAEA-SM-190/6 [1975]; C.A. **84** [1976] No. 23471). – [42] M. G. Adamson, E. A. Aitken (Trans. Am. Nucl. Soc. **17** [1973] 195/6). – [43] J. B. Ainscough (TRG-Report-1937 [1970] 1/16; N.S.A. **25** [1971] No. 4888). – [44] D. A. Collins, R. Taylor, A. E. McIntosh, W. B. Roys (TRG-Report-1332 [1967] 1/28 from [43]; N.S.A. **21** [1967] Nr. 35852). – [45] A. W. Castleman, I. N. Tang (J. Inorg. Nucl. Chem. **32** [1970] 1057/64).

[46] H. Kleykamp (KFK-1736 [1973] 84/101). – [47] D. Brucklacher, W. Dienst (Fuels and Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 147/61; C.A. **82** [1975] No. 36226). – [48] J. D. B. Lambert, L. A. Neimark, R. V. Strain (Trans. Am. Nucl. Soc. **17** [1973] 193). – [49] E. Smailos, D. Geithoff (KFK-1648 [1972] 1/68). – [50] J. R. Phillips, G. R. Waterbury, N. E. Vanderborgh (J. Inorg. Nucl. Chem. **36** [1974] 17/23).

[51] J. R. Phillips, G. R. Waterbury, N. E. Vanderborgh, T. K. Marshall (Anal. Chem. **47** [1975] 71/5). – [52] R. A. Karnesky, R. D. Legget, S. A. Castain, J. W. Weber (HEDL-SA-970-S [1975]; CONF-751101-82 [1975] 1/21; INIS Atomindex **7** [1976] No. 269026). – [53] I. Johnson, C. E. Johnson (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1, p. 73/82; IAEA-SM-190-43 [1975] 99; C.A. **84** [1976] No. 51130). – [54] C. E. Johnson, I. Johnson (Trans. Am. Nucl. Soc. **23** [1976] 149/50). – [55] C. E. Johnson, I. Johnson (ANL-8122 [1974] 36).

[56] C. E. Johnson, I. Johnson (ANL-75-48 [1975] 20). – [57] P. A. G. O'Hare, H. R. Hoekstra (J. Chem. Thermodyn. **6** [1974] 251). – [58] D. W. Osborne, H. E. Flotow, H. R. Hoekstra (J. Chem. Thermodyn. **6** [1974] 179). – [59] J. I. Bramman, H. J. Powell (J. Brit. Nucl. Soc. **14** [1975] 63/75). – [60] D. Cubicciotti, J. E. Sanecki (J. Nucl. Mater. **78** [1978] 96/111).

[61] N. Oi, I. Tanabe (J. Nucl. Mater. **25** [1968] 288/95). – [62] J. R. Phillips, J. R. Netuschil, J. N. Quintana, G. R. Waterbury (J. Inorg. Nucl. Chem. **37** [1975] 1337/40). – [63] C. A. Friskney, K. A. Simpson (J. Nucl. Mater. **57** [1975] 121/2). – [64] C. A. Friskney, K. A. Simpson (J. Nucl. Mater. **57** [1975] 341/7). – [65] J. A. Turnbull, C. A. Friskney (J. Nucl. Mater. **58** [1975] 31/8).

[66] J. A. Turnbull, C. A. Friskney (J. Nucl. Mater. **71** [1978] 238/48). – [67] P. E. Brown, R. L. Faircloth (J. Nucl. Mater. **59** [1976] 29/41). – [68] K. Hilpert, H. W. Nürnberg (JUEL-953-AC [1973]; Diss. Univ. Bonn 1973, pp. 1/239; C.A. **80** [1974] No. 151735). – [69] R. Förthmann, H. Grübmeier, H. Kleykamp, A. Naoumidis (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1, p. 147/62; IAEA-SM-190/35 [1975] 147/71; C.A. **84** [1976] No. 36487). – [70] R. Odoj, K. Hilbert, H. W. Nürnberg, R. Förthmann, A. Naoumidis (J. Nucl. Mater. **60** [1976] 216/22).

[71] J. A. L. Robertson (Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., [1975], pp. 219/21). – [72] A. H. Booth (AECL-496 [1957]; CRDC-721 [1957] 1/23; N.S.A. **12** [1958] No. 399). – [73] W. B. Lewis (AECL-964 [1960]; DM-58 [1960] 1/49; N.S.A. **14** [1960] No. 8662). – [74] J. R. MacEwan, V. B. Lawson (AECL-994 [1960] 1/25; CRFD-915 [1960] 1/25; N.S.A. **14** [1960] No. 15975). – [75] R. S. Barnes, D. J. Mazey (Proc. Roy. Soc. [London] A **275** [1963] 47/57).

[76] J. R. MacEwan, W. H. Stevens (J. Nucl. Mater. **11** [1964] 77/93). – [77] A. D. Wapham, B. E. Sheldon (Nucl. Appl. **2** [1966] 122/30). – [78] M. J. F. Notley, J. R. MacEwan (Nucl. Appl. **2** [1966] 477/80). – [79] R. M. Cornell, G. H. Bannister (Proc. Brit. Ceram. Soc. **7** [1967] 355/62). – [80] H. Matzke, J. A. Davies (J. Appl. Phys. **38** [1967] 805/8).

[81] R. G. Bellamy, J. B. Rich (J. Nucl. Mater. **33** [1969] 64/76). – [82] M. V. Speight (Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 222/30). – [83] G. W. Greenwood, A. J. E. Foreman, D. E. Rimmer (J. Nucl. Mater. **4** [1959] 305/24). – [84] R. S. Nelson (J. Nucl. Mater. **31** [1969] 153/61). – [85] A. D. Wapham (Phil. Mag. [8] **23** [1971] 987/1009).

[86] C. C. Dollins, H. Ocken (J. Nucl. Mater. **45** [1972/73] 150/62). – [87] J. A. Turnbull (J. Nucl. Mater. **38** [1971] 203/12). – [88] R. M. Cornell (J. Nucl. Mater. **38** [1971] 319/28). – [89] D. R. Olander (TID-26711-P1 [1976] 227/35, 261/2). – [90] B. L. Eyre, R. Bullough (J. Nucl. Mater. **26** [1968] 249/66).

[91] A. J. Markworth (J. Appl. Phys. **40** [1969] 1986/8). – [92] A. J. Markworth (J. Nucl. Mater. **43** [1972] 341/2). – [93] S. R. Pati (Trans. Am. Nucl. Soc. **14** [1971] 580/1). – [94] M. J. Dapht, S. R. Pati, D. R. O'Boyle (Trans. Am. Nucl. Soc. **15** [1972] 212/3). – [95] M. O. Marlowe (GEAP-12148 [1970] 1/22; N.S.A. **25** [1971] No. 30032).

[96] T. D. Gulden, J. L. Kaae (J. Nucl. Mater. **32** [1969] 168/70). – [97] J. W. Harrison (J. Nucl. Mater. **23** [1967] 139/53). – [98] J. A. Turnbull, R. M. Cornell (J. Nucl. Mater. **41** [1971] 156/60). – [99] J. A. Turnbull, R. M. Cornell (J. Nucl. Mater. **36** [1970] 161/8). – [100] J. A. Turnbull, R. M. Cornell (J. Nucl. Mater. **37** [1970] 355/7).

[101] R. M. Cornell, J. A. Turnbull (J. Nucl. Mater. **41** [1971] 87/90). – [102] M. V. Speight (J. Nucl. Mater. **38** [1971] 236/8). – [103] A. M. Ross (J. Nucl. Mater. **30** [1969] 134/42). – [104] H. Blank, H. Matzke (Radiat. Eff. **17** [1973] 57/64). – [105] M. V. Speight (Nucl. Sci. Eng. **37** [1969] 180/5).

[106] G. W. Greenwood, M. V. Speight (J. Nucl. Mater. **10** [1963] 140/4). – [107] E. E. Gruber (J. Appl. Phys. **38** [1967] 243/50). – [108] D. R. Olander (TID-26711-P1 [1976] 243/9, 261/2). – [109] H. R. Warner, F. A. Nichols (Nucl. Appl. Technol. **9** [1970] 148/66). – [110] F. A. Nichols, H. R. Warner (Proc. Conf. Fast Reactor Fuel Elem. Technol., New Orleans 1971, pp. 267/89; C.A. **77** [1972] No. 108321).

[111] C. C. Dollins, H. Ocken (Nucl. Appl. Technol. **9** [1970] 141/7). – [112] C. C. Dollins (Trans. Am. Nucl. Soc. **16** [1973] 118/9). – [113] C. C. Dollins (J. Nucl. Mater. **60** [1976] 107/10). – [114] C. C. Dollins, F. A. Nichols (J. Nucl. Mater. **66** [1977] 143/57). – [115] R. M. Cornell, M. V. Speight, B. C. Masters (J. Nucl. Mater. **30** [1969] 170/8).

[116] M. E. Gulden (J. Nucl. Mater. **23** [1967] 30/6). – [117] J. A. Turnbull (J. Nucl. Mater. **62** [1976] 325/8). – [118] C. Baker (CEGB-RD-B-N-4003 [1977] 1/14). – [119] C. Baker (J. Nucl. Mater. **71** [1977] 117/23). – [120] L. E. Willertz, P. G. Shewman (Met. Trans. **1** [1970] 2217).

[121] W. Beeré (J. Nucl. Mater. **45** [1972/73] 91/5). – [122] F. A. Nichols (J. Nucl. Mater. **30** [1969] 143/65). – [123] R. W. Weeks, R. O. Scattergood, S. R. Pati (J. Nucl. Mater. **36** [1970] 223/9). – [124] D. R. Olander (TID-26711-P1 [1976] 266 [Fig. from J. R. MacEwan, V. B. Lawson, Atomic Energy of Canada, Ltd.]). – [125] J. R. MacEwan, V. B. Lawson (J. Am. Ceram. Soc. **45** [1962] 42/6).

[126] W. Dietz, J. Biersack (Phys. Status Solidi **32** [1969] 247/61). – [127] W. Oldfield, A. J. Markworth (Mater. Sci. Eng. **4** [1969] 353). – [128] B. N. Bhat, R. A. Swalin (Acta Met. **20** [1972] 1387/96). – [129] P. F. Sens (J. Nucl. Mater. **43** [1972] 293/307). – [130] D. R. De Halas, G. R. Horn (J. Nucl. Mater. **8** [1963] 207/20).

[131] M. V. Speight (J. Nucl. Mater. **13** [1964] 207/9). – [132] F. A. Nichols (J. Nucl. Mater. **22** [1967] 214/22). – [133] F. A. Nichols (J. Nucl. Mater. **27** [1968] 137/46). – [134] W. Oldfield, J. B. Brown (Mater. Sci. Eng. **6** [1970] 361). – [135] W. Oldfield, A. J. Markworth (Scripta Met. **6** [1972] 757).

[136] J. P. Hirth, G. M. Pound (J. Chem. Phys. **26** [1957] 1216/24). – [137] C. Ronchi, C. Sari (J. Nucl. Mater. **50** [1974] 91/7). – [138] A. Kikuchi, T. Tobita (JAERI-M-5722 [1974] 1/17). – [139] H. Kawamata, H. Kaneko, H. Furnya, M. Koizumi (J. Nucl. Mater. **68** [1977] 48/53). – [140] C. F. Clement (J. Nucl. Mater. **68** [1977] 63/8).

[141] H. Matzke, F. Springer (Radiat. Eff. **2** [1969] 11). – [142] W. Miekeley, F. W. Felix (J. Nucl. Mater. **42** [1972] 297/306). – [143] T. B. Burley, M. D. Freshley (Nucl. Appl. Technol. **9** [1970] 233). – [144] R. M. Carroll, J. G. Morgan, R. B. Perez, O. Sisman (Nucl. Sci. Eng. **38** [1969] 143/55). – [145] M. D. Rogers (J. Nucl. Mater. **16** [1965] 298/305).

[146] G. Nilsson (J. Nucl. Mater. **20** [1966] 215/30). – [147] M. D. Rogers (J. Nucl. Mater. **22** [1967] 103/5). – [148] R. M. Carroll, O. Sisman (Nucl. Sci. Eng. **21** [1965] 147/58). – [149] R. Soulhier (Nucl. Appl. **2** [1966] 138/41). – [150] C. M. Fleck, H. Böck, H. Erber (Atomkernenergie **20** [1972] 51/4).

[151] K. Shiba, M. Handa, S. Yamagashi, T. Fukuda, Y. Takahashi, T. Takaaki, S. Omori, A. Kondo (J. Nucl. Mater. **48** [1973] 253/63; C.A. **80** [1974] No. 55068). – [152] S. Yamagishi, T. Tanifuji (J. Nucl. Mater. **59** [1976] 243/56). – [153] M. Szuta (J. Nucl. Mater. **58** [1975] 278/84). – [154] K. Shiba (J. Nucl. Mater. **57** [1975] 271/9). – [155] J. R. MacEwan, W. H. Stevens (J. Nucl. Mater. **11** [1964] 77/93).

[156] R. M. Carroll, O. Sisman, R. B. Perez (Nucl. Sci. Eng. **32** [1968] 430/1). – [157] D. R. Olander (TID-26711-P1 [1976] 287/330). – [158] B. R. T. Frost (Nucl. Appl. Technol. **9** [1970] 128/40). – [159] D. A. Collins, R. Hargreaves (Nucl. Fuel Perform. Proc. Intern. Conf., London 1973, pp. 50.1/50.5). – [160] R. Hargreaves, D. A. Collins (J. Brit. Nucl. Soc. **15** [1976] 311/8).

[161] J. R. Findlay (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 211/20). – [162] J. A. Turnbull, M. O. Tucker (Phil. Mag. [8] **30** [1974] 47/63). – [163] J. A. Turnbull, M. O. Tucker (J. Nucl. Mater. **50** [1974] 53/6). – [164] W. Beeré, G. L. Reynolds (J. Nucl. Mater. **47** [1973] 51/7). – [165] M. O. Tucker, J. A. Turnbull (Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 325/30).

[166] J. A. Turnbull, C. A. Friskney (J. Nucl. Mater. **58** [1975] 31/8). – [167] J. A. Turnbull, C. A. Friskney, F. A. Johnson, A. J. Walter, J. R. Findlay (J. Nucl. Mater. **67** [1977] 301/6). – [168] C. A. Friskney, J. A. Turnbull, F. A. Johnson, A. J. Walter, J. R. Findlay (J. Nucl. Mater. **68** [1977] 186/92). – [169] H. Zimmermann (Nucl. Technol. **28** [1976] 127/33). – [170] C. Ronchi, H. Matzke (J. Nucl. Mater. **45** [1972/73] 15/28).

[171] C. Ronchi, H. Matzke (Fuels and Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 57/70; IAEA-SM-173/40 [1974]). – [172] H. Matzke (Plutonium 1975 Other Actinides Proc. 5th Intern. Conf., Baden-Baden 1975 [1976], pp. 801/31). – [173] W. Hering et al. (private communication, to be published). – [174] G. A. Reymann (TREE-NUREG-1005 [1976] 140/8). – [175] J. Weisman, P. E. MacDonald (Trans. Am. Nucl. Soc. **12** [1969] 900/1).

[176] C. E. Beyer, C. R. Hann (BNWL-1875 [1974] 1/38). – [177] J. P. Stora, P. Chenebault (CEA-R-3618 [1968] 1/114; N.S.A. **23** [1969] No. 9154). – [178] J. A. Ainscough (HPR-129 [1971] 1/75; N.S.A. **26** [1972] No. 8563). – [179] E. de Meulemeester, N. Hoppe, G. de Conteson, M. Watteau, (J. Nucl. Mater. **11** [1964] 92.1/92.15). – [180] M. J. F. Notley, R. DesHaies, J. R. MacEwan (AECL-2662 [1966] 1/75; N.S.A. **21** [1967] No. 40693).

[181] M. J. F. Notley, J. R. MacEwan (AECL-2230 [1965] 1/33; N.S.A. **19** [1965] No. 22962). – [182] M. J. F. Notley, A. S. Bain, S. Ananthakrishnan, G. W. Parry (AECL-1676 [1962]; CRFD-1117 [1962] 1/57; N.S.A. **17** [1963] No. 18854). – [183] J.-C. Janvier, B. de Bernardy de Sigoyer, R. Delmas (CEA-R-3358 [1967] 1/78; N.S.A. **22** [1968] No. 26092). – [184] J. Rest (Trans. Am. Nucl. Soc. **23** [1976] 171/2). – [185] D. L. Johnson, G. L. Hofman (Trans. Am. Nucl. Soc. **19** [1974] 138).

[186] C. E. Beyer, C. R. Hann (Trans. Am. Nucl. Soc. **19** [1974] 139/40). – [187] C. E. Beyer, R. O. Meyer (Trans. Am. Nucl. Soc. **23** [1976] 172/3). – [188] M. J. F. Notley, J. R. MacEwan (Nucl. Appl. **2** [1966] 117/22). – [189] W. B. Bremsner, A. B. G. Washington (J. Brit. Nucl. Eng. Soc. **12** [1973] 449/54). – [190] J. R. Findlay, F. A. Johnson (Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 231/7).

[191] J. Klima, M. Podest, V. Vins (Jaderna Energie **20** [1974] 224/9). – [192] J. Klima, M. Podest, V. Vins (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 221/4). – [193] J. C. Killeen (J. Nucl. Mater. **58** [1975] 39/46). – [194] Y.

Iwano, N. Oi (J. Nucl. Sci. Technol. [Tokyo] **12** [1975] 763/6). – [195] J. M. Griesmeyer, W. G. Steele, D. Okrent, S. H. Chien, A. R. Wassam (Trans. Am. Nucl. Soc. **23** [1976] 174).

[196] R. L. Ritzman, A. J. Markworth, W. Oldfield, W. Chubb (Nucl. Appl. Technol. **9** [1970] 167/87). – [197] R. F. Hilbert, V. W. Storhok, W. Chubb, D. L. Keller (J. Nucl. Mater. **38** [1971] 26/34). – [198] W. Chubb, V. W. Storhok, D. L. Keller (J. Nucl. Mater. **44** [1972] 136/52). – [199] A. Doi, K. Inone, N. Hockkyo (J. Nucl. Sci. Technol. [Tokyo] **9** [1972] 505/11). – [200] R. C. Nelson, D. H. Coplin, M. F. Lyons, B. Weidenbaum (GEAP-4572 [1964] 1/58).

[201] R. C. Nelson, M. F. Lyons, B. Weidenbaum (Trans. Am. Nucl. Soc. **7** [1964] 91). – [202] V. B. Lawson, J. R. MacEwan (AECL-994 [1960]; CRFD-915 [1960] 1/25; N.S.A. **14** [1960] No. 15975). – [203] W. Oldfield, A. J. Markworth, J. B. Brown (Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 242/8). – [204] G. T. Lawrence (J. Nucl. Mater. **71** [1978] 195/218). – [205] J. Belle (Uranium Dioxide, Properties and Applications, U.S. Government Printing Office, Washington, D.C., 1961, pp. 493/518, 657/66).

[206] H. Matzke (Lect. Summer School Phys. Ionized Gases, Hercegnovi, Yugoslavia, 1970). – [207] J. A. Turnbull (Central Electricity Generating Board, U.K., RD-B-N 2406 [1972]). – [208] A. H. Booth, G. T. Rymer (AECL-692 [1958]; CRDC-720 [1958] 1/30; N.S.A. **13** [1959] No. 573). – [209] J. Belle (Proc. 2nd U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 6, pp. 569/89). – [210] R. Lindner, H. Matzke (Z. Naturforsch. **13a** [1958] 794/6).

[211] J. Belle (WAPD-MRP-82 [1959] 1/89; N.S.A. **14** [1960] No. 4130). – [212] R. Lindner, H. Matzke (Z. Naturforsch. **14a** [1959] 582/4). – [213] R. Lindner, H. Matzke (Z. Naturforsch. **14a** [1959] 1074/7). – [214] A. B. Auskern (WAPD-TM-185 [1960] 1/10; C.A. **1960** 11734). – [215] W. H. Stevens, J. R. MacEwan, A. M. Ross (TID-7610 [1960] 7/22; from [204]; C.A. **1961** 24453).

[216] G. Long, D. Davies, J. R. Findlay (TID-7610 [1960] from [204]). – [217] J. Belle, A. B. Auskern, W. A. Bostrom, F. S. Susko (Proc. 4th Intern. Symp. Reactivity Solids, Amsterdam 1960 [1961], pp. 452/66; C.A. **58** [1963] 3913). – [218] D. F. Toner, J. L. Scott (Symposium on Radiation Effects in Refractory Fuel Compounds, Am. Soc. Testing Mater. Spec. Tech. Publ. No. 306 [1961/62] 86/99; C.A. **58** [1963] 5225). – [219] R. H. Barnes, M. Kangilaski, J. B. Melehan, F. A. Rough (BMI-1533 [1961] 1/42; N.S.A. **15** [1961] No. 29691). – [220] D. Davies, G. Long (AERE-R-4347 [1963] 1/14; N.S.A. **17** [1963] No. 32563).

[221] J. B. Melehan, R. H. Barnes, J. E. Gates, F. A. Rough (BMI-1623 [1963] 1/53; N.S.A. **17** [1963] No. 22216). – [222] G. Jackson, D. Davies, P. Biddle, M. Waterman (AERE-R-4714 [1964] 1/61; N.S.A. **19** [1965] No. 18532). – [223] F. Felix, T. Lagerwall, P. Schmeling, K. E. Zimen (Proc. 3rd U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1964 [1965], Vol. 11, pp. 363). – [224] G. Long, W. P. Stanaway, D. Davies (AERE-M-1251 [1964] 1/12; N.S.A. **18** [1964] No. 14453). – [225] G. Frigerio, T. Gerevini (J. Nucl. Mater. **16** [1965] 76/8).

[226] A. Schurenkamper, B. Souhlier (CEA-R-2588 [1964]; EURAEC-1094 [1964]). – [227] R. M. Carroll, O. Sisman (J. Nucl. Mater. **17** [1965] 305/12). – [228] J. R. Findlay, M. Waterman (from [161]). – [229] R. Kelly, H. Matzke (J. Nucl. Mater. **17** [1965] 179/91). – [230] H. Matzke (Nucl. Appl. **2** [1966] 131/7).

[231] J. C. Clayton, S. Aronson (WAPD-276 [1963] 1/29; N.S.A. **18** [1964] No. 4183). – [232] J. C. Carter, E. J. Driscoll, T. S. Elleman (Phys. Status Solidi A **14** [1972] 673/80). – [233] R. M. Cornell (Phil. Mag. [8] **19** [1969] 539/54). – [234] H. Matzke (Radiat. Eff. **53** [1980] 219/42). – [235] M. O. Tucker (J. Nucl. Mater. **74** [1978] 34/40).

[236] M. O. Tucker (J. Nucl. Mater. **75** [1978] 282/7). – [237] M. O. Tucker (J. Nucl. Mater. **78** [1978] 17/23). – [238] M. O. Tucker (J. Nucl. Mater. **79** [1979] 199/205, 206/13).

– [239] C. Baker (J. Nucl. Mater. **66** [1977] 283/91). – [240] C. Baker (J. Nucl. Mater. **75** [1978] 105/9).

[241] C. Baker (Eur. Appl. Res. Repts. Nucl. Sci. Technol. Sect. **1** [1979] 19/30). – [242] J. A. Turnbull, M. V. Speight (Eur. Appl. Res. Repts. Nucl. Sci. Technol. Sect. **1** [1979] 109/26). – [243] F. A. Johnson, F. T. Ewart, B. M. Sharpe (Eur. Appl. Res. Repts. Nucl. Sci. Technol. Sect. **1** [1979] 59/63). – [244] H. Kleykamp (J. Nucl. Mater. **84** [1979] 109/17). – [245] H. Zimmermann (Eur. Appl. Res. Repts. Nucl. Sci. Technol. Sect. **1** [1979] 35/44).

[246] M. O. Tucker, J. A. Turnbull (J. Nucl. Mater. **83** [1979] 278/85). – [247] M. O. Tucker, R. J. White (J. Nucl. Mater. **87** [1979] 1/10). – [248] M. O. Tucker, R. J. White (J. Nucl. Mater. **98** [1981] 157/66). – [249] C. A. Friskney, J. A. Turnbull (J. Nucl. Mater. **79** [1979] 184/98). – [250] M. H. Wood (J. Nucl. Mater. **82** [1979] 257/63).

[251] M. H. Wood (J. Nucl. Mater. **82** [1979] 264/70). – [252] M. H. Wood, J. R. Matthews (J. Nucl. Mater. **91** [1980] 35/40). – [253] J. R. Matthews, M. H. Wood (J. Nucl. Mater. **91** [1980] 241/56). – [254] M. H. Wood (J. Nucl. Mater. **78** [1978] 58/63). – [255] J. R. Matthews, M. H. Wood (J. Nucl. Mater. **84** [1979] 125/36).

[256] C. J. Greatley, R. Hargreaves (J. Nucl. Mater. **79** [1979] 235/45). – [257] M. J. F. Notley, I. J. Hastings (AECL-5838 [1979] 1/39; INIS Atomindex **11** [1980] No. 528689). – [258] I. J. Hastings, M. J. F. Notley (Trans. 5th Intern. Conf. Struct. Mech. React. Technol., Amsterdam 1979, Paper C1/3, pp. 1/7). – [259] M. J. F. Notley, I. J. Hastings (Nucl. Eng. Design **56** [1980] 163/75). – [260] G. V. Kidson (J. Nucl. Mater. **88** [1980] 299/308).

[261] R. E. Mason (NUREG-CR-0497 [1979] 165/85; INIS Atomindex **10** [1979] No. 477203). – [262] J. C. Killeen (J. Nucl. Mater. **88** [1980] 177/84). – [263] E. E. Gruber (Nucl. Technol. **35** [1977] 617/34). – [264] R. G. Esteves, A. R. Wazzan, D. Okrent (Nucl. Eng. Design **45** [1978] 343/82). – [265] R. J. DiMelfi, L. W. Deitrich (Nucl. Technol. **43** [1979] 328/37).

1.1.5 Changes in Dimensions Induced by Irradiation (Densification and Swelling)

General References:

H. Ocken, A Review of Irradiation-Induced Densification in Uranium Dioxide Fuel, EPRI-SR-15 [1975] 1/32.

D. L. Hagrman, G. A. Reymann, MATPRO-Version 11, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, NUREG-CR-0497 [1979] 83/98 [Densification], 98/125 [Swelling].

D. R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 193/96, 199/262 [Swelling].

M. D. Freshley, D. W. Brite, J. L. Daniel, P. E. Hart, Irradiation-Induced Densification of UO_2 Pellet Fuel, J. Nucl. Mater. **62** [1976] 138/66.

H. Aßmann, H. Stehle, Thermal and In-Reactor Densification of UO_2, Mechanisms and Experimental Results, Nucl. Eng. Design **48** [1978] 49/67.

M. D. Freshley, D. W. Brite, J. L. Daniel, P. E. Hart, Irradiation-Induced Densification and PuO_2 Particle Behavior in Mixed-Oxide Pellet Fuel; Meeting: Characterization and Quality Control of Nuclear Fuels, Karlsruhe 1978; J. Nucl. Mater. **81** [1979] 63/92.

T. C. Rowland, M. O. Marlowe, R. B. Elkins, Fission Product Swelling in BWR Fuels, NEDO-20702 [1974].

H. Zimmermann, Untersuchungen zum Schwellen und Spaltgasverhalten in oxidischem Kernbrennstoff unter Neutronenbestrahlung, KFK-2467 [1977] 1/102 [162 Refs.].

C. Ronchi, H. Matzke, J. v. d. Laar, H. Blank, Fission Gas Behavior in Nuclear Fuels – Proceedings of the Workshop Held in Joint Research Centre, Karlsruhe Establishment

(European Institute for Transuranium Elements), Germany, October 26–27, 1978. Session I: Microscopic and Local Swelling, Eur. Appl. Res. Repts. Nucl. Sci. Technol. Sect. 1 No. 1 [1979] 17/106.

1.1.5.1 Irradiation-Induced Densification

Already in 1958 has it been reported by Barney [1] that loose UO_2 particles sinter in the reactor at 500 °C. This effect was also reported afterwards by Bleiberg et al. [2] and Marlowe [3]. Aitken [4] has supposed already in 1962, that at low temperatures athermal sintering is operative when the material is irradiated, and that fission fragments affect the kinetics more than do fast neutrons. Irradiation induced sintering, produced by the solar wind on the surface of the moon, was used in 1969 as an explanation of the structure seen in photographs made by Surveyor V of this surface [5]. Horn, Gulley [6] used a reactor as a sintering furnace for raw UO_2-PuO_2, where, however, thermally activated sintering was of greater importance. Stevens [7], too, considered the thermal densification in a reactor.

The fission-induced dissolution and shrinkage of fission gas bubbles and/or sinter-pores were reported in 1966 by Whapham [8], Ross [9], and Bellamy, Rich [10], and later by Turnbull, Cornell [11, 12].

A shortening of the length of the fuel column was observed by Knudsen [13], List, Knudsen [14], and Locke [15] for UO_2, and by Bini et al. [16] and Mikailoff et al. [17] for UO_2-PuO_2. Greenough et al. [18] found a decrease in the diameter of fuel pellets. The temperature dependence of the densification is reported in [15].

The densification of fuel pellets in the reactor has become an intensively studied phenomenon since 1972, when collapsing of the cladding was found in several pressurized water reactors (Beznau-1, Ginna, Point Beach-1, H. B. Robinson-1, and Zorita-2). The American report WASH-1236 [19] presents a review of this (a summary is given in [39]). In boiling water reactors this effect was much weaker (because of the higher density of the fuel and the lower system pressure), and has never led to clad collapsing into axial gaps [20].

Theoretical Models for Thermally Activated and Irradiation-Induced Densification

Table 1/8 surveys the characteristics of the various models and their applicability for thermally activated effects and for irradiation effects.

The model presented by Coble [21] for final stage sintering is the most frequently used one for the description of the dimensional behavior of ceramic sinters at high temperatures. Idealized pore and grain structures are considered in this model, which Aßmann et al. [22] developed further, to include realistic microstructures of the sinters.

Marlowe [23, 24] replaced the thermal diffusion coefficient in the model of Coble by a fission-rate dependent athermal diffusion coefficient, in order to describe the irradiation induced densification, and obtained a relationship between the fuel density and the burnup. This relationship described the dependence of the densification on the pore structure indirectly, but did not include any temperature dependence.

Table 1/8
Comparison of Various Densification Models with Respect to the Temperature and Microstructure Dependence of the Densification Rate.

authors	model	temperature dependence	microstructure dependence	remarks
Coble [21]	final stage of thermally activated sintering	thermally activated diffusion and grain growth	grain size dependence, pore structure described by constant factor	idealized pore structure, intergranular pores
Aßmann et al. [22]	final stage of thermally activated sintering	thermally activated diffusion and grain growth	grain size and pore size distribution dependence	realistic pore structure
Marlowe [23, 24]	irradiation-induced densification through irradiation-enhanced diffusion	independent at low temperature, irradiation-enhanced diffusion	same as Coble model [21]	replaces thermal diffusion coefficient of Coble model by irradiation-enhanced diffusion coefficient
Aßmann, Stehle [25 to 30]	superposition of thermally-activated and irradiation-induced densification by means of interaction between fission fragments and pores	thermal vacancy concentration and diffusion, when vacancy mobility controls rate; independent if fission-induced vacancy formation and mobility control it	grain size and pore size distribution dependence	four temperature regions (Fig. 1-49, p. 75); separate models for fission-induced densification by fine and coarse pores
Carlson [32]	irradiation-induced shrinking of closed gas-filled pores	through the gas law for the pore gas	no dependence on grain or pore size	constant rate of decrease of pore radius
MacEwen, Hastings [33]	irradiation-induced densification by annealing of interstitials at pores	thermally activated annealing of interstitials at pores	dependent on size distribution of intergranular pores	intergranular pores are practically stable

Table 1/8 [continued]

authors	model	temperature dependence	micro-structure dependence	remarks
Lindman [35]	superposition of the Coble [21] and Marlowe [23, 24] models	independent at low temperatures, irradiation enhanced diffusion	according to Coble model [21]	thermal diffusion coefficient of Coble model is additively combined with irradiation-induced diffusion coefficient
Dollins, Nichols [37]	combination of Aßmann-Stehle [25 to 30], MacEwen, Hastings [33] and own model for swelling and gas release [38]	thermal diffusion of vacancies	dependent on grain size and size of intergranular pores	main effect: interaction of fission fragments and pores according to Aßmann-Stehle model

A series of partial models were constructed by Aßmann, Stehle [25 to 30], starting from an atomistic point of view. According to these models, the densification follows a two step mechanism in the intermediate temperature range which is of main interest:

(1) Production of an excess of vacancies by means of the effect of the fission fragments on the pores (athermal process).

(2) Migration of these vacancies to sinks which are effective for the densification, e.g., grain boundaries (thermally activated process).

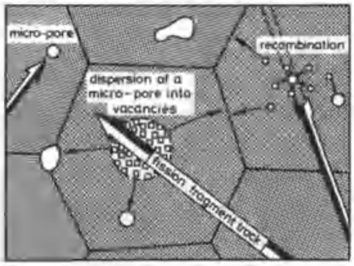
Fig. 1-47, p. 74, shows that micropores may be dispersed as vacancies by a single fission fragment. Some of the vacancies diffuse away but the majority of them recombine to a new pore. Coarse pores retain their identity when affected by a fission fragment (**Fig. 1-48**, p. 74), their radius decreasing in a quasi-continuous manner. The distinction between fine and coarse pores sets in at a diameter of about 0.1 μm.

The following relationship results from the fine-pore model of Stehle, Aßmann [29] for conditions typical for LWR's, describing the relative volume change of the fuel [25]:

$$\Delta V/V_0 = -P_0^f\,[1-\exp(-\eta\,\Omega_f F t)] \qquad (1)$$

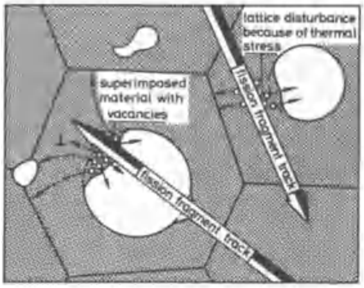
where P_0^f is the fine porosity (initial value), $\eta \approx 0.2\%$ is the fraction of the vacancies which escape to the grain boundary per hit, and Ω_f is the "volume" of the fission fragment track, $\approx 10^{-15}\,cm^3$. One sees that the fine porosity may vanish (e.g., for $F = 10^{13}$ fissions$\cdot cm^{-3}\cdot s^{-1}$) in a matter of hours.

Fig. 1-47



Densification by means of an interaction of fission fragments with pores (micro-pores) [25, 29].

Fig. 1-48



Densification by means of an interaction of fission fragments with pores (coarse pores) [25, 26].

A subsequent review of the work of Aßmann and Stehle [30] shows that all the partial models are particular cases of a general model. This overall model includes also the thermally activated densification, for all pore sizes. The differential equation [30]

$$dr/dt = [(D_v^{th} + D_v^{irr})R/r(R-r)] - [(1/2ga)(2\gamma\Omega D/rkT) + (1/3)\lambda\omega F(C_s-C_T)]/ \\ [(1/2ga)D_v^{th} + (D_v^{th} + D_v^{irr})R/r(R-r) + (1/3)\lambda\omega F] \qquad (2)$$

is valid for the rate of change of the pore radius r, the meaning and values of the other symbols being given in Table 1/9. The Arrhenius diagram, **Fig. 1-49**, obtained from these values, shows four temperature regions I to IV, the physical meaning of which is shown in Table 1/10, p. 76. The regions III and IV are of practical importance. The main part of the volume of LWR fuels is densifying according to region III. The relationship

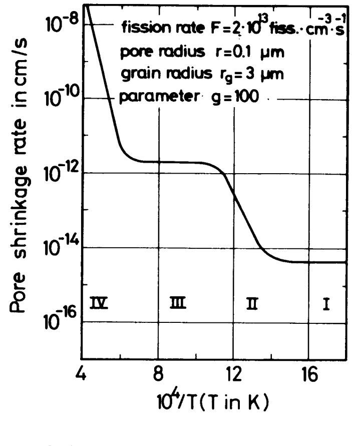
$$\Delta V/V_0 = -\sum_i P_{oi}\,[1-(1-\lambda\omega Ft/3\,r_{oi})^3] \qquad (3)$$

Table 1/9
Values and Meanings of the Quantities in Equations (2) to (5) [30].

$D_v^{th} = 0.125 \exp(-26700/T)$ cm^2/s	thermal vacancy diffusion coefficient in UO_2
$D_v^{irr} = 10^{-30}$ F cm^2/s	irradiation-induced vacancy diffusion coefficient in UO_2
$D = 0.09 \exp(-53400/T)$ cm^2/s	self-diffusion coefficient of uranium in $UO_{2.01}$
$D(x) = D(x/0.01)^2$	self-diffusion coefficient of uranium in UO_{2+x} according to [31]
$C_T = D/D_v^{th}$	thermal vacancy concentration
$C_s = 0.002$	saturation value of C_T in UO_2
r (e.g., $= 10^{-5}$ cm)*	pore radius
r_g (e.g., $= 30 \times 10^{-5}$ cm)*	grain radius; $R = r_g + r$
$g = 100$	numeric parameter of the model from [30]
$\gamma = 6 \times 10^{-5}$ J/cm^2	surface tension of UO_2
$\Omega = 4.1 \times 10^{-23}$ cm^3	vacancy volume in UO_2
$a = 5.47 \times 10^{-8}$ cm	lattice constant of UO_2
$\lambda = 6 \times 10^{-4}$ cm	length of fission fragment track
$\omega = 5 \times 10^{-19}$ cm^3	UO_2 volume corresponding to the model in [30]
F (e.g., $= 2 \times 10^{13}$ fissions $\cdot cm^{-3} \cdot s^{-1}$)*	fission rate
T in K	absolute temperature
t in s	time
$\lambda = 1.38 \times 10^{-23}$ J/K	Boltzmann's constant

* These quantities are variables, the numerical values given were used in the sample calculations.

Fig. 1-49



Arrhenius plot for the pore shrinking rate in UO_2 (model calculation, coarse pores) [30].

Table 1/10
Temperature Regions of the Thermally Activated and Fission-Induced Densification of UO_2 (Fission Rate 2×10^{13} fissions $\cdot$ $cm^{-3} \cdot s^{-1}$) [30].

region	temperature	vacancy formation	vacancy migration
I	$\lessapprox$450 °C	athermally	athermally
II	450 → 750 °C	athermally	thermally, determines densification rate
III	750 → 1 300 °C	athermally, determines densification rate	thermally
IV	$\gtrapprox$1 300 °C	thermally	thermally

is obtained, where P_{oi} is the pore volume fraction of the i-th pore size group, with mean radius r_{oi}, and summation is carried out over all the groups [25]. The corresponding relationship in region IV (thermal activation) is

$$\Delta V/V_0 = -\sum_i P_{oi}\, 6\Omega\gamma D(x)t/kT r_{oi}^3 \tag{4}$$

(the symbols are defined in Table 1/9, p. 75). The diffusion coefficient depends on the O:U ratio in UO_{2+x} according to Matzke [31] as $D(x) \sim x^2$, which leads to a strong dependence of the densification in region IV on the stoichiometry.

Carlson [32] considers the shrinking of closed gas filled pores by means of irradiation induced transplantation of gas atoms from the pore into the matrix (see, e.g., Ross [9]) and the trapping of fission gas atoms as a competing process, and obtains the relationship:

$$\Delta D = -4.37 \times 10^{-5}\, B + 9.45 \cdot 10^{-13}\, B^2 T \tag{5}$$

where ΔD is the decrease in the diameter of the pore, B is the burnup in MWd/t(M) ($\leq$30 MWd/kg(M)), and T is the absolute temperature, 1 000 to 1 450 K.

In the model of MacEwen and Hastings [33] it is assumed that Frenkel-defects are produced by the fission fragments in the matrix, and that interstitials are annealed at the pores. Speight [34], however, shows that the kinetics of the densification cannot be explained by this mechanism.

A variant, based on the method of Marlowe [23, 24], has been proposed by Lindman [35]. It is assumed, according to Reynolds et al. [36], that the surface tension of the fuel is diminished by the absorption of fission products during burnup.

Dollins, Nichols [37] combine the models of Stehle, Aßmann [26, 29] and of MacEwen, Hastings [33] with their own model for swelling and release of fission gas [38]. It is indicated that the densification effect is caused essentially by the interaction of fission fragments with the pores.

Besides the more or less mechanistic models discussed above there are numerous so-called "analytical models" which describe the densification by means of formulas (see, e.g., MATPRO Handbook [40, 131] and [41 to 44]). A chronological listing of the "analytical models" employed in the USA was published by Meyer [45]. Ocken [46] reviewed this problem in 1975.

Experimental Studies

Experimental results concerning fuel densification are obtained by the following methods:

(1) Studies of irradiated fuel rods:

- (a) column length measurements (e.g., radiographically),
- (b) fuel density measurements (see, e.g., [47]),
- (c) ceramography of the fuel.

(2) Experimental capsules monitored instrumentally (e.g., with recording of length and temperature).

It is possible to judge the predictions according to the various models (Table 1/11 [27]) by comparing them with the experimental results.

The studies of Ferrari et al. [48], Chubb et al. [49], Hanevik et al. [50], and Carlson [32] show the great influence the pore size has on the densification. As seen in **Fig. 1-50**, p. 78, [49], a large fraction of fine porosity causes strong densification. On the other hand, fuels with coarse pores are stable against densification, as found by Heal et al. [53] and Rigdon et al. [52]. Brucklacher, Dienst [53] show that below 1250°C sintering processes are accelerated by irradiation. The kinetics of the densification was described by Collins, Hargreaves [54] and Rolstad et al. [55] by means of empirical expressions. The relationships given in [45, 55] were incorporated by Mason into the MATPRO Handbook [40].

Banks [56] studied the changes in the fuel density by measurements made on irradiated fuel samples. Above 1200°C the swelling caused by gaseous fission products predominated.

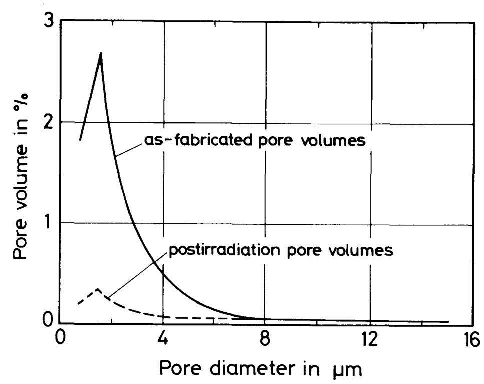
Table 1/11
Predictions of the Densification Model of [27].

total porosity and pore size distribution	most important parameter in all regions; large pores are more stable than small ones; micropores eliminated rapidly in region III*)
temperature	controlling parameter in regions II and IV
fission rate	important parameter in regions I and II; no fission rate dependence in regions III and IV
grain size	smaller densification for large grain sizes, mainly in region II
pore form	spherical pores are most stable, because of smallest surface-to-volume ratio
grain growth	independent mechanism, indirect dependence through grain size
pore localization (intragranular, at grain boundaries)	stronger densification of grain-boundary pores because of shorter vacancy diffusion distances; otherwise stabilization because of accumulation of fission gas
nonhomogeneous fission density (mixed oxide UO_2-PuO_2)	less densification because of smaller fission rate in the UO_2 matrix

---

*) The pore size of larger pores will increase if they act as sinks for the vacancies from smaller pores; this mechanism does not contribute to densification.

Fig. 1-50



The change in the pore size distribution in UO_2 under irradiation [49].

The largest changes in the dimensions were found between 1 000 and 1 100 °C (overlap of pore shrinking and matrix swelling, see Section 1.1.5.3). Below 1 100 °C a temperature dependence of the changes of the dimensions could be discerned (and be described by means of a formal "activation energy" of 21.7 kJ/mol). Banks and Clough [132] examined micropore shrinkage in UO_2 irradiated below 1100°C using optical and scanning electron microscope techniques. They showed that in the temperature range 400 to 1000 °C densification is mainly due to the in-reactor shrinkage of micropores smaller than 2 µm in diameter.

Extensive experimental studies are discussed by Chernock et al. [57, 58], Yario et al. [59], and Harkness et al. [60]. The results confirm many of the aspects of the model of Aßmann, Stehle. Besides the dependence of the densification on the microstructure (grain size and pore size), the following temperature dependence was found: between 430 and 750 °C the densification increases with the temperature; below these temperatures, and in a certain range above them, the temperature dependence is unimportant.

Further experimental results are given in [62 to 71]. Couteson et al. [64] and Buescher, Horn [65] deal with the relationship between thermal and irradiation-induced densifications.

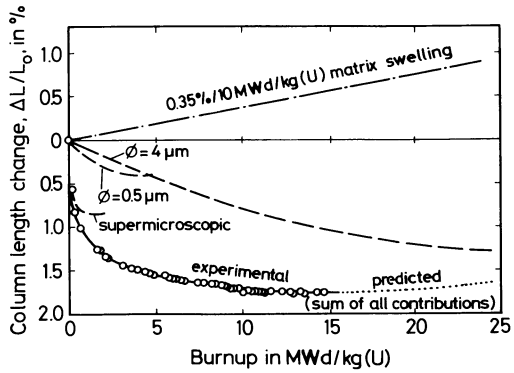
Stehle et al. [27] could describe surprisingly well the results of a densification experiment with continuous columnar length measurements by means of their densification model, with suitable fitting of the parameters (**Fig. 1-51**). Aßmann et al. [67] could confirm the temperature dependence of the densification in the range 1 000 to 1 200 °C by means of irradiation experiments under isothermal conditions.

Two irradiation programs, which were carried out in the USA with the participation of many companies and institutes from all over the world, yielded a broad data base. The results of the UO_2 program were published in 1976 by Freshley et al. [70]. The program for UO_2-PuO_2 (up to 6% PuO_2 content) was concluded in 1978 [71].

The studies on 20 UO_2 and 13 UO_2-PO_2 fuel types showed:

The densification can be correlated with the microstructure. The largest densification occurs with those fuels that combine the smallest pore sizes, the largest fraction of pores with

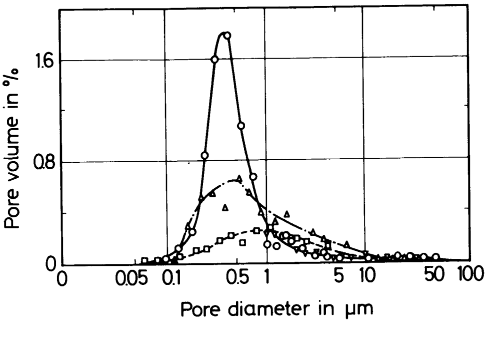
Fig. 1-51



Continuous column length change of an experimental unstable UO_2 fuel (IFA 418, rod 3). A comparison with the theory. $\Delta L/L = {}^1/_3\, \Delta V/V_0$ [27]. $\Delta V/V_0 = 1.1 \times 10^{-4} B - 2.55[1 - \exp(-6.0 \times 10^{-3} B)] - 1.25[1 - (1 - 2.3 \times 10^{-4} B)^3] - 4.00[1 - (1 - 2.66 \times 10^{-5} B)^3]$. B = burnup in MWd/kg(U).

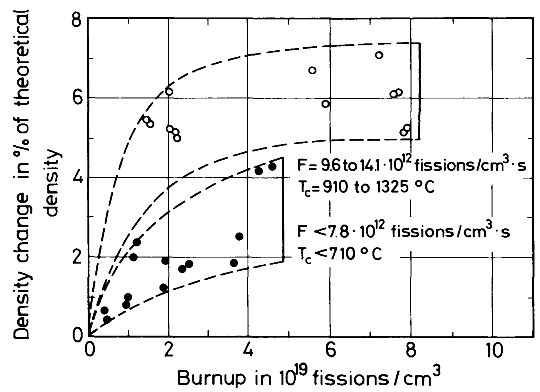
diameters <1 µm, the smallest grain size, and the lowest density. Densification is connected with a strong diminution of the volume fraction of those pores that have diameters <1 µm (see **Fig. 1-52**). It leads to a shifting of the pore size distribution. The densification depends also on the fission rate (9.6 to 14.1×10^{12} fissions · cm^{-3} · s^{-1}), the fuel temperature (910 to 1325 °C central temperature), and the burnup (maximally 8.25×10^{19} fissions/cm^3). **Fig. 1-53**, p. 80, shows an example.

Fig. 1-52



The effect of the irradiation on the distribution of pore sizes of an unstable UO_2 fuel [70].
△–·–△ burnup 520 MWd/kg(U); 6.6×10^{12} fissions · cm^{-3} · s^{-1}; Δρ in % D = 2.14,
□---□ burnup 943 MWd/kg(U); 12.0×10^{12} fissions · cm^{-3} · s^{-1}; Δρ in % D = 5.06,
▽·····▽ burnup 3313 MWd/kg(U); 11.6 × 10^{12} fissions · cm^{-3} · s^{-1}; Δρ in % D = 5.22,
○——○ as fabricated.

Fig. 1-53



The density change of numerous UO_2 fuel variants, as a function of the burnup at different temperatures and fission rates [70].

The relationship between the densification behavior and the individual parameters of the microstructure is less clear for UO_2-PuO_2 fuels than for UO_2 ones, because of the more complex microstructure of the former. The densification process is superimposed by homogenization processes.

The relationship between irradiation-induced and thermally activated densification (annealing outside the reactor) was discussed in both programs. Such correlations were important at the time, since a desire existed to be able to predict the densification behavior of a fuel in a reactor.

1.1.5.2 Swelling by Fission Products

Experimental Results

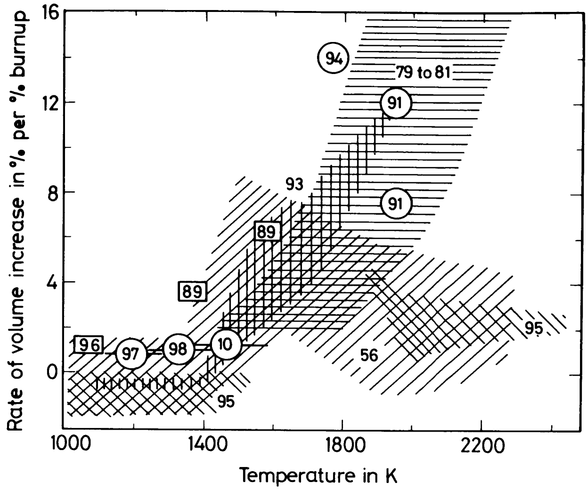
Summaries of the published data on fission product swelling were presented by Rowland et al. [72], Stephany [73] (MATPRO-Version 09), Mason [131] (MATPRO-Version 11) and Zimmermann [74] (see also the General References on p. 70/1.

Table 1/12 [73] surveys the results on swelling rates of UO_2 and UO_2-PuO_2. **Fig. 1-54** shows an evaluation of the literature according to Zimmermann [74]. For the swelling of UO_2-PuO_2 mixed oxide see also [133, 134]. The swelling of UO_2 (in a cermet fuel) was first reported in 1958 by Barney, Wemple [75].

Remarks Concerning Table 1/12 (p. 81)

The first systematic studies on the burnup dependence of the swelling of UO_2 were made by Bleiberg et al. at the Bettis Laboratory on plate-like fuel elements [76, 77] and on fuel rods [78]. For the plates a swelling rate of only 0.16% per 10^{20} fissions/cm^3 was observed in the first

Fig. 1-54



The rate of volume increase of UO_2 and UO_2-PuO_2 as a function of the fuel temperature at low burnup values (evaluation of the literature, the numbers being the relevant references) [74]. □= $(U,Pu)O_2$, ○= UO_2.

Table 1/12
Literature Survey of Swelling Rates, According to [73].

authors	swelling rate in % per 10^{20} fissions/cm^3	fuel temperature in °C	remarks
Bleiberg et al. [76, 77]	0.7 (0.4)	1000 to 2000	UO_2 plateform fuel elements
Berman et al. [78]	0.82	900 to 1700	UO_2, fuel rods
Chubb et al. [81]	3 to 15	1450 to 2250	UO_2, isothermal
Rowland et al. [72, 85]	0.4 (max.)	1200 to melting temperature	UO_2, BWR fuel rods
Lyons et al. [86]			
Baroch, Rigdon [87]	1.10	1850 to melting temperature	UO_2, PWR fuel rods
Duncan et al. [88]	0.23 (max.)	540 to melting temperature	UO_2-PuO_2
Grando et al.	2.6	1580	UO_2-PuO_2
[89]	1.5	1365	UO_2
Collins, Hargreaves [54]	0.17 to 0.33	1125	UO_2, isothermal
Turnbull [91]	4.0	1750	UO_2, isothermal
Nelson, Zebroski	0.12	1400	UO_2-PuO_2
[92]	0.2 to 0.3	1800	UO_2-PuO_2
	0.20	2200	UO_2-PuO_2

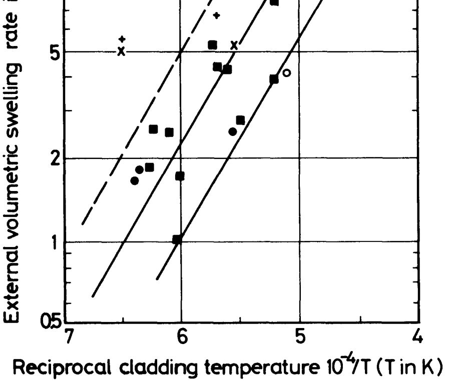
phase of the experiment. This is to be ascribed to the densification effect, as we know today. A new evaluation by Rowland et al. [72] of the results with these plates yielded a value of 0.4% per 10^{20} fissions/cm^3, rather than the 0.2% appearing in the original evaluation.

The temperature dependence of the swelling was studied by Chubb et al. [79 to 82] with UO_2 and UO_2-PuO_2 in W-Rh capsules in the range 1 200 to 1 900 °C (cladding temperature; the central temperature is estimated to be ca. 300 °C higher). The rate of the increase in volume was plotted in an Arrhenius-type diagram (**Fig. 1-55** [83]). **Fig. 1-56**, p. 83, shows that at high temperatures too the increase in the volume is linear with the burnup [84].

Further results were obtained with BWR fuel rods [72, 85, 86], PWR fuel rods [87], Fast Breeder fuel rods (UO_2-PuO_2) [88, 89], and AGR (Advanced Gas-Cooled Reactor) fuel rods [90] (not included in Table 1/12). Collins, Hargreaves [54] concluded from an evaluation of the literature that the swelling rate below 1125 °C is in the range 0.17 to 0.33% per 10^{20} fissions/cm^3.

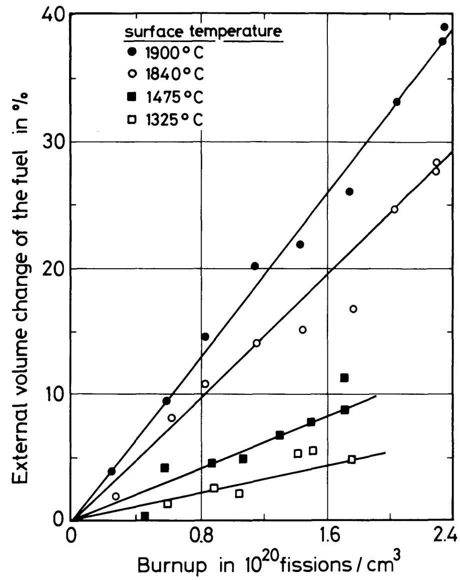
High swelling rates were found at a fuel temperature of 1 750 °C (isothermal conditions) [91], smaller ones in experiments with strong radial retaining forces [92].

Fig. 1-55



The rates of the volume increase of UO_2 and UO_2-PuO_2 as a function of the cladding temperature (W-Re capsules) [83].

Fig. 1-56



The rate of volume increase of UO_2 at high temperatures [84].

Remarks concerning Fig. 1-54 (p. 81)

The measured rates of volume increase are valid for low burnup (<1 %), in particular the higher values at high temperatures [93, 94]. The strong scatter of the values in this temperature range is due essentially to the different operational conditions the samples were exposed to. A large temperature gradient at the same central temperature reduces the swelling rate, since more fission gas release occurs. Hastings et al. [95] found the largest increases in the volume at temperatures near 1 500 °C. Some values could be obtained at lower temperatures from the extrapolation of results from creep experiments [96 to 98].

Volume increase rates between 0.5 and 2.0% per % burnup, at burnup values below 5% and in the temperature range 500 to 1 000 °C, were found for cermets consisting of UO_2 and stainless steel [99 to 103]. Proschk et al. [104] determined the changes in the diameters of UO_2 cores in coated fuel particles (for the HTR) in the temperature range 900 to 1 300 °C and the burnup range 0.5 to 52.5% (!). The core diameter increases linearly with the burnup for small burnups, and reaches a saturation value at higher ones (ca. 1.5 to 2%). Killeen [94] found that Nb_2O_5 and La_2O_3 additives (up to 1 mol%) had no effect on the rate of swelling of UO_2 at low burnups (up to 0.1 %).

Values of the swelling by means of solid fission products [105 to 109] are summarized in Table 1/13 [73, 131]. Olander [109] gave the following expression:

$$\Delta V/V = (\sum_i Y_i(V_i/V_U)-1) \cdot (\text{burnup}) \qquad (6)$$

where Y_i is the yield of the ith fission product, V_i is its partial molar volume in the relevant chemical form, V_U is the partial molar volume of uranium in UO_2, and the index i extends over all the solid fission products. The following values should be used:

$V_U = 40.93 \times 10^{-24}$ cm³/UO₂-"molecule",
$V_{\text{soluble fission products}} = 40.93 \times 10^{-24}$ cm³/molecule,
$V_{\text{metallic inclusions}} = 14.73 \times 10^{-24}$ cm³/atom, and
$V_{\text{other fission products}} = 31.1 \times 10^{-24}$ cm³/fission product atom.

No cognizance is made here of the migration of the fission products.

Table 1/13
Summary of the Literature Data Concerning Swelling due to Solid Fission Products [73, 131].

authors	swelling rate (solid fission products) in % per 10^{20} fissions/cm³	
Anselin [105]	0.13 to 0.54	calculated
	0.35	measured
Wait [106]	0.21	
Whapham, Sheldon [107]	0.20	
Harrison, Davies [108]	0.46 to 0.39	flux 10^{12} to 10^{15} $n \cdot cm^{-2} \cdot s^{-1}$
Olander [109]	0.12 ± 50%	

Mechanistic and Empirical Models

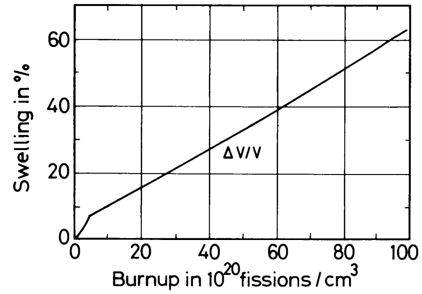
What had been known about swelling prior to 1970 was reviewed by Hilbert et al. [84], Frost [110], and Nichols, Warner [111, 112]. The latter authors describe fundamental models for the swelling by fission gas bubbles, which have been employed in the BUBL code and the GRASS code (see [113, 114]). The model of Greenwood, Speight [115] has been employed in the CYGRO code [116] and the FIGRO code [117]. A series of simple semiempirical models [118 to 120] is based mainly on the data from the Batelle Columbus Laboratory [81 to 84]. The empirical model characterized in Table 1/14 is recommended in the MATPRO Handbook [73].

Table 1/14
Temperature Dependence of the Swelling Rate According to [73].

central temperature in °C	swelling rate in %/% burnup	swelling rate in % per 10^{20} fissions/cm³
$T \leqq 1400$	1.0	0.28
$1400 < T \leqq 1800$	$1 + 0.00575\,(T - 1400)$	0.92 at 1800 °C
$1800 < T \leqq 2200$	$3.3 - 0.004\,(T - 1800)$	0.476 at 2200 °C
$T > 2200$	1.7	0.476

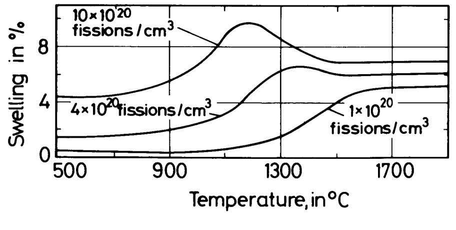
Dollins et al. [38, 121 to 124] developed stagewise improved models, which described also the interplay of swelling and fission gas release. The predictions of the model [38] are shown in **Fig. 1-57** (dependence on the burnup), **Fig. 1-58** (dependence on the temperature), and **Fig. 1-59**, p. 86 (dependence on the grain size). Below about 500 °C the swelling is caused by intragranular fission gas microbubbles. Above about 600 °C the fission gas migrates to the grain boundaries, and periodically self-annealing tunnels are formed. Above 1 200 °C the elimination of fission gas predominates. Maximal swelling occurs in both the Dollins-Ocken model and the mechanistic models of Nichols, Warner [111], Nelson [125], and Matzke, Ronchi [126] at intermediate temperatures. The interrelationship between the behavior of fission gas bubbles and microscopic swelling at low temperatures has been discussed by Ronchi [135, 136] and Blank [137].

Fig. 1-57



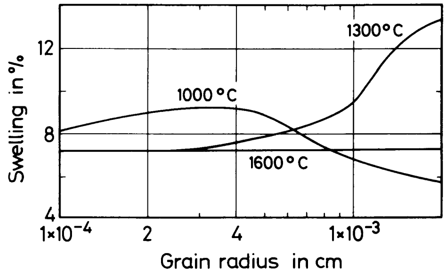
Swelling of UO_2 as a function of the burnup (fission rate: 10^{13} fissions·cm^{-3}·s^{-1}, temperature 1200°C, temperature gradient: 1000 K/cm, grain size: 10 μm, pressure: 138 bar) according to model calculations [38].

Fig. 1-58



Swelling of UO_2 as a function of the temperature for various amounts of burnup. (Model calculation; boundary conditions as in Fig. 1-57) [38].

Fig. 1-59



The dependence of the swelling of UO_2 on the grain size at different temperatures (fission rate: 10^{13} fissions · cm^{-3} · s^{-1}; burnup: 10^{20} fissions/cm^3, temperature gradient: 1000 K/cm) [38].

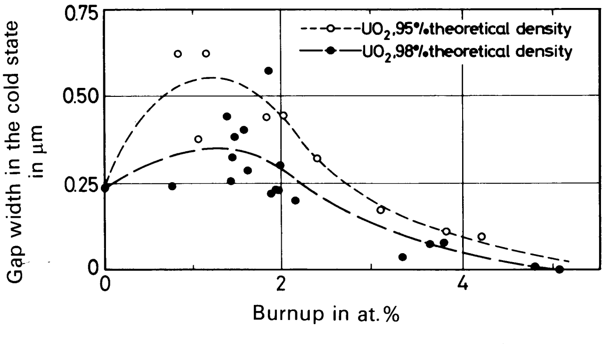
1.1.5.3 The Superposition of Swelling, Densification, and Other Deformative Phenomena

The dimensional behavior of fuel pellets is determined by the interplay of the following deformative phenomena:

(1) Plastic deformation/creep (see Sections 1.1.2.2, 1.1.2.3, pp. 12 and 14);
(2) Cracking and relocation of the fragments (see Sections 1.1.2.2, 1.1.6.1, pp. 12 and 95);
(3) Densification by means of pore shrinking (see Section 1.1.5.1, p. 71);
(4) Irradiation-induced swelling (see Section 1.1.5.2, p. 80).

The two last named phenomena have in common, that they proceed primarily without the presence of a mechanical stress applied from the outside. The effect of the superposition of (3) and (4) on the gap between the fuel pellets and their cladding was examined first by Bellamy, Rich [10] (**Fig. 1-60**). The densification predominates at the beginning, but at high

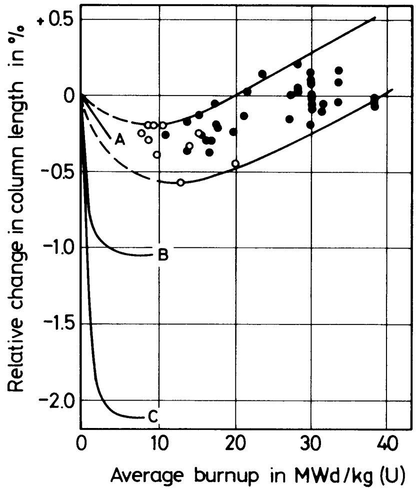
Fig. 1-60



Mean width of the gap between the fuel pellets and the cladding [10].

burnup the swelling gains the upper hand. This relationship was found also by Skinner et al. [90] and Collins, Hargreaves [54], and is described in the papers of Kuzmin, Lebedev [127], Hargreaves, Collins [128], and Stehle et al. [27] (**Fig. 1-61**).

Fig. 1-61



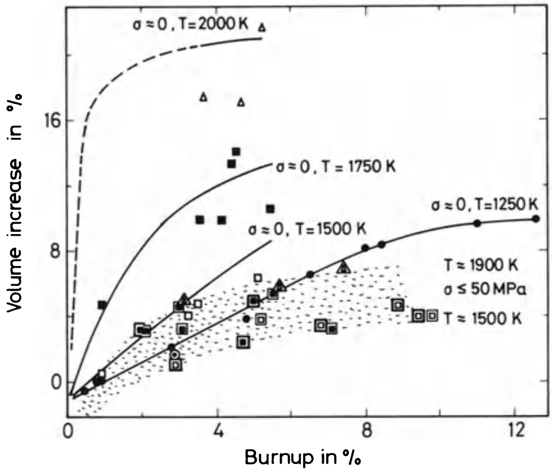
Column length change in UO_2 as a function of the burnup [27].
● = KWO, ○ KWL and KRB, 93% of theoretical density. A, B, C: 92% of theoretical density (different microstructure), from [48].

Aßmann, Manzel [129] defined a "matrix swelling rate" S as the relative volume change rate of the initially ideally densely packed matrix, and determined this quantity experimentally for UO_2 under the typical LWR irradiation conditions. In general agreement with [74, 127, 128], the following values were found for the matrix swelling rate at temperatures below 1300 °C:

$$S = 0.4 \pm 0.06\% \text{ per } 10^{20} \text{ fissions/cm}^3, \text{ equivalent to}$$
$$S = 1.0 \pm 0.15\% \text{ per } 10 \text{ GWd/t(U)}$$

The volume changes of UO_2 in LWR fuel rods may be predicted from the additive superposition of matrix swelling and densification. **Fig. 1-62**, p. 88, shows the results of numerous series of experiments by Zimmermann [74, 130]. It includes also experiments where retaining forces were present. Table 1/15 shows the values for the swelling rates recommended by Zimmermann.

Fig. 1-62



Volume increase of UO_2 as a function of the burnup [74].

temperature in K	pressure in MPa ≈ 0	 ≤ 2	 25 to 50
< 1350	●	◉	
1350 to 1600	□	⧈	⧈
1600 to 1900	■	▣	▣
≥ 1900	△	◬	

Table 1/15
Dependence of the Swelling Rate on Burnup and Power Density, According to [74].

burnup in %	integral swelling rate in %/% burnup at power densities of ≤ 50 W/g	 150 to 200 W/g	 > 200 W/g
≤ 2	1	2.5	3.5
> 2	1	1	0.65

References for 1.1.5:

[1] W. K. Barney (Proc. 2nd U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 6, pp. 677/80). – [2] M. L. Bleiberg, R. M. Berman, B. Lustman (Radiat. Damage Reactor Mater. Proc. Symp., Venice 1962 [1963], pp. 319/428). – [3] M. O. Marlowe (Am. Ceram.

Soc. Bull. **51** [1972] 388). – [4] E. A. Aitken (Am. Soc. Testing Mater. Spec. Tech. Publ. No. 306 [1962] 123/9). – [5] A. C. Damask (Radiat. Eff. **1** [1969] 95/100).

[6] G. R. Horn, R. L. Gulley (Trans. Am. Nucl. Soc. **11** [1968] 112). – [7] E. G. Steven (Trans. Am. Nucl. Soc. **11** [1968] 130/1). – [8] A. D. Whapham (Nucl. Appl. **2** [1966] 123/30). – [9] A. M. Ross (J. Nucl. Mater. **30** [1969] 134/42). – [10] R. G. Bellamy, J. B. Rich (J. Nucl. Mater. **33** [1969] 64/76).

[11] J. A. Turnbull, R. M. Cornell (J. Nucl. Mater. **36** [1970] 161/8). – [12] J. A. Turnbull, R. M. Cornell (J. Nucl. Mater. **37** [1970] 355/7). – [13] P. Knudsen (RISO-M-1350 [1971] 1/32; N.S.A. **25** [1971] No. 32844). – [14] F. List, P. Knudsen (Nucl. Technol. **20** [1973] 103/8). – [15] D. H. Locke (Nucl. Eng. Intern. **17** [1972] 1015/7).

[16] A. Calza Bini et al. (Proc. Intern. Meeting Fast Reactor Fuel Fuel Elem., Karlsruhe 1970, pp. 520/37). – [17] H. Mikailoff, J. Bloch, M. Conte (CEA-N-1254 [1970] 1/32; N.S.A. **24** [1970] No. 36995). – [18] G. B. Greenough, J. S. Nairn, J. B. Sayers (Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 10, pp. 141/52). – [19] Regulatory Staff USAEC (Technical Report on Densification of Light Water Reactor Fuels, WASH-1236 [1972] 1/167). – [20] D. C. Ditmore, R. B. Elkins (NEDM-10735 [1972] 1/48; N.S.A. **28** [1973] No. 1543).

[21] R. L. Coble (J. Appl. Phys. **32** [1961] 787/92). – [22] H. Aßmann, G. Maier, H. Stehle (Reaktortagung, Nürnberg 1975, Meeting Report, pp. 391/4). – [23] M. O. Marlowe (NEDO-12440 [1973] 1/31). – [24] M. O. Marlowe (Trans. Am. Nucl. Soc. **17** [1973] 166/9). – [25] H. Aßmann, H. Stehle (Reaktortagung, Karlsruhe 1973, Meeting Report, pp. 409/12).

[26] H. Stehle, H. Aßmann (J. Nucl. Mater. **52** [1974] 303/8). – [27] H. Stehle, H. Aßmann, F. Wunderlich (Nucl. Eng. Design **33** [1975] 230/60). – [28] H. Aßmann, H. Stehle (Atomwirtsch. Atomtech. **21** [1976] 239/41). – [29] H. Stehle, H. Aßmann (J. Nucl. Mater. **61** [1976] 326/9). – [30] H. Aßmann, H. Stehle (Nucl. Eng. Design **48** [1978] 49/67).

[31] H. Matzke (Plutonium 1975 Other Actinides Proc. 5th Intern. Conf., Baden-Baden 1975 [1976], pp. 801/31). – [32] M. C. Carlson (Nucl. Technol. **22** [1974] 335/59). – [33] S. R. MacEwen, I. J. Hastings (Phil. Mag. [8] **31** [1975] 135/43). – [34] M. V. Speight (Phil. Mag. [8] **32** [1975] 1101/5). – [35] N. Lindman (J. Nucl. Mater. **71** [1977] 73/7).

[36] G. L. Reynolds, W. B. Beeré, P. T. Sawbridge (J. Nucl. Mater. **41** [1971] 112/4). – [37] C. C. Dollins, F. A. Nichols (J. Nucl. Mater. **78** [1978] 326/35). – [38] C. C. Dollins, F. A. Nichols (J. Nucl. Mater. **66** [1977] 143/57). – [39] W. H. Culbert (Nucl. Safety **14** [1973] 356/61). – [40] R. E. Mason (NUREG-CR-0497 [1979] 83/98).

[41] Regulatory Staff USAEC (Technical Report on Densification of General Electric Reactor Fuels, WASH-1331 [1973] 1/73). – [42] USAEC (Densification of General Electric Reactor Fuels, NP-19906 Suppl. No. 1 [1973] 1/41). – [43] M. G. Andrews (CENPD-118-Rev. 1 [1974] 1/122). – [44] Exxon Nuclear Co. (Densification Effects on Exxon Nuclear Pressurized Water Reactor Fuel, XN-209-Suppl. 4-Rev. 1 [1974] 1/28). – [45] R. O. Meyer (NUREG-0085 [1976] 1/78; INIS Atomindex **8** [1977] No. 290586).

[46] H. Ocken (PB-245996 [1975]; EPRI-SR-15 [1975] 1/32). – [47] D. A. Banks, J. Prestwood (J. Phys. E **7** [1974] 794/7). – [48] H. M. Ferrari, E. Roberts, J. Scott (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 54.1/54.4). – [49] W. Chubb, A. C. Hott, B. M. Argall, G. R. Kilp (Nucl. Technol. **26** [1975] 486/95). – [50] A. Hanevik, K. D. Knudsen, P. Arnesen (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 89.1/89.4).

[51] T. J. Heal, J. E. Littlechild, R. H. Watson (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 52.1/52.4). – [52] M. A. Rigdon, T. P. Papazoglou, C. J. Baroch, M. H. Montgomery (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 59.1/59.4). – [53] D. Brucklacher, W. Dienst (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 60.1/60.3). – [54] D. A. Collins, R. Hargreaves (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 50.1/50.5). – [55] E.

Rollstad, A. Hanevik, K. K. Knudsen (Enlarged Halden Program Group Meeting Computer Control Fuel Res. 4./7.6.1974 from [40]).

[56] D. A. Banks (J. Nucl. Mater. **54** [1974] 97/107). – [57] W. P. Chernock, R. N. Duncan, S. D. Harkness (Proc. Am. Power Conf. **36** [1974] 234/40). – [58] W. P. Chernock, M. G. Andrews, S. D. Harkness (Trans. Am. Nucl. Soc. **20** [1975] 215/6). – [59] W. R. Yario, S. T. Ziegler, T. E. Hollowell, S. D. Harkness (Trans. Am. Nucl. Soc. **18** [1974] 123). – [60] S. D. Harkness, S. R. Pati, M. G. Andrews, W. P. Chernock (Progress in Nuclear Energy, Nuclear Energy Maturity, Proc. 1st Eur. Nucl. Conf., Paris 1975, Vol. 3, Part I, pp. 1/21).

[61] J. V. Sharp, A. J. E. Foreman (AERE-R-5786 [1968]). – [62] J. P. Stora, M. Bruet (CEA-CONF-3390 [1975] 1/7). – [63] J. P. Stora, M. Bruet (Trans. Am. Nucl. Soc. **22** [1975] 206/7). – [64] G. de Conteson, G. Lestiboudois, N. Vignesoult (Trans. Am. Nucl. Soc. **20** [1975] 216/9). – [65] B. J. Buescher, G. R. Horn (Trans. Am. Nucl. Soc. **22** [1975] 205/6).

[66] M. Uchida, K. Yanagisawa, M. Ichikawa (JAERI-M-6904 [1977] 1/23). – [67] H. Aßmann, G. Kaspar, H. Zimmermann (Reaktortagung, Mannheim 1977, Meeting Report, pp. 486/9). – [68] M. D. Freshley, S. Goldsmith (Trans. Am. Nucl. Soc. **18** [1974] 122). – [69] D. W. Brite, J. L. Daniel, N. C. Davis, M. D. Freshley, P. E. Hart (EEI-EPRI Fuel Densification Project, Final Report, PB-243218 [1975] 1/116). – [70] M. D. Freshley, D. W. Brite, J. L. Daniel, P. E. Hart (J. Nucl. Mater. **62** [1976] 138/66).

[71] M. D. Freshley, D. W. Brite, J. L. Daniel, P. E. Hart (Irradiation-Induced Densification and PuO_2 Particle Behavior in Mixed-Oxide Pellet Fuel, Meeting, Charakterisierung und Qualitätskontrolle von Kernbrennstoffen, Karlsruhe 1978, J. Nucl. Mater. **81** [1979] 63/92). – [72] T. C. Rowland, M. O. Marlowe, R. B. Elkins (NEDO-20702 [1974]). – [73] W. P. Stephany (TREE-NUREG-1005 [1976] 91/110). – [74] H. Zimmermann (KFK-2467 [1977] 1/102). – [75] W. K. Barney, B. D. Wemple (KAPL-1836 [1958] 1/40; N.S.A. **12** [1958] No. 8825).

[76] M. L. Bleiberg, R. M. Berman, B. Lustman (WAPD-T-1455 [1962] 1/142; N.S.A. **17** [1963] No. 11270). – [77] R. C. Daniel, M. L. Bleiberg, H. B. Meieran, W. Yeniscavich (WAPD-263 [1962] 1/290; N.S.A. **16** [1962] No. 33524). – [78] R. M. Berman, H. B. Meieran, P. W. Patterson (WAPD-TM-629 [1967] 1/118; N.S.A. **21** [1967] No. 39660). – [79] W. Chubb (Trans. Am. Nucl. Soc. **12** [1969] 76). – [80] R. F. Hilbert, V. W. Storhock, W. Chubb, D. C. Keller (Trans. Am. Nucl. Soc. **14** [1971] 582/3).

[81] W. Chubb, V. W. Storhock, D. L. Keller (Nucl. Technol. **18** [1973] 231/56). – [82] W. Chubb, D. L. Keller (BMI-1918 [1971] B98/B112). – [83] R. F. Hilbert, W. J. Zielenbach, D. E. Lozier, R. B. Clark, V. W. Storhock (BMI-1918 [1971] B2/B43). – [84] R. F. Hilbert, V. W. Storhock, W. Chubb, D. L. Keller (J. Nucl. Mater. **38** [1971] 26/34). – [85] T. C. Rowland, M. O. Marlowe, R. B. Elkins (Trans. Am. Nucl. Soc. **18** [1974] 124).

[86] M. F. Lyons, T. C. Rowland, D. T. Weiss (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 68.1/68.18). – [87] C. J. Baroch, M. A. Rigdon (Intern. Conf. Nucl. Fuel Perform., London 1973. pp. 58.1/58.4). – [88] R. N. Duncan, D. A. Cantley, K. J. Perry, R. C. Nelson (Proc. Conf. Fast Reactor Fuel Elem. Technol., New Orleans 1971, pp. 291/309). – [89] C. Grando, M. Montgomery, A. Strasser (Proc. Conf. Fast Reactor Fuel Elem. Technol., New Orleans 1971, pp. 771/84). – [90] J. Skinner, K. A. Bradshaw, R. D. Stacey (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 10.1/10.4).

[91] J. A. Turnbull (J. Nucl. Mater. **50** [1974] 62/8). – [92] R. C. Nelson, E. L. Zebroski (Trans. Am. Nucl. Soc. **9** [1966] 412/3). – [93] K. S. B. Rose, J. Williams, G. Potts (J. Nucl. Mater. **51** [1974] 195/8). – [94] J. C. Killeen (J. Nucl. Mater. **58** [1975] 39/46). – [95] I. J. Hastings, D. H. Rose, M. H. Schankula (J. Am. Ceram. Soc. **58** [1975] 74).

[96] P. Combette, C. Milet (J. Nucl. Mater. **65** [1977] 37/47). – [97] D. Brucklacher, W. Dienst (Experimental Results on the Mechanical Interaction between Oxide Fuel and Cladding, Fast Reactor Fuel Fuel Elem. Proc. Symp., Brussels 1973 [1974] from [74]). – [98] D. J.

Clough (J. Nucl. Mater. **65** [1977] 24/36). – [99] J. D. B. Lambert (High Temperature Nuclear Fuels, Met. Soc. Conf. Proc. **42** [1966/68] from [74]). – [100] D. G. Freas, J. H. Saling, J. E. Gates, D. I. Keller, R. F. Dickerson (BMI-1529 [1961] 1/25; N.S.A. **15** [1961] No. 26610).

[101] B. R. T. Frost, L. H. Cope, J. D. B. Lambert, H. Lloyd, W. Long, J. E. Manson, P. G. Mardon (Proc. 3rd U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 170/7). – [102] J. D. B. Lambert (Nucl. Energy **8** [1967] 106/11). – [103] J. D. B. Lambert (Proc. Brit. Ceram. Soc. **7** [1967] 331/42). – [104] E. Proschk, K. Knotik, A. Strigl (J. Nucl. Mater. **66** [1977] 263/72). – [105] F. Anselin (GEAP-5583 [1969] 1/37; N.S.A. **24** [1970] No. 14965).

[106] E. Wait (unpublished work, quoted in: J. B. Ainscough, Some Limiting Aspects of UO_2 Performance, TRG-Report-1937 [1969] 1/16; N.S.A. **25** [1971] No. 4888). – [107] A. D. Whapham, B. E. Sheldon (AERE-R-4970 [1966]; Nucl. Appl. **2** [1966] 123/30; N.S.A. **20** [1966] No. 37255). – [108] J. W. Harrison, L. M. Davies (J. Nucl. Mater. **27** [1968] 239/40). – [109] D. R. Olander (Fundamental Aspects of Nuclear Fuel Elements, TID-26711-P1 [1976] 193/6). – [110] B. R. T. Frost (Nucl. Appl. Technol. **9** [1970] 128/40).

[111] F. A. Nichols, H. R. Warner (Proc. Conf. Fast Reactor Fuel Elem. Technol., New Orleans 1971, pp. 267/89). – [112] H. R. Warner, F. A. Nichols (Nucl. Appl. Technol. **9** [1970] 148/66). – [113] R. B. Poeppel (Proc. Conf. Fast Reactor Fuel Elem. Technol., New Orleans 1971, pp. 311/26). – [114] J. W. Dias, R. B. Poeppel (ANL-7992 [1973] 1/26; N.S.A. **28** [1973] No. 23514). – [115] G. W. Greenwood, M. V. Speight (J. Nucl. Mater. **10** [1963] 140/4).

[116] E. Duncombe, J. E. Meyer, W. A. Coffman (WAPD-TM-583 [1966] 1/93; N.S.A. **21** [1967] No. 1963). – [117] I. Goldberg, L. L. Lynn, C. D. Sphar (WAPD-TM-618 [1966] 1/52; N.S.A. **21** [1967] No. 14116). – [118] Y. H. Sun, D. Okrent (UCLA-ENG-7591 [1975] 1/38 from [73]; INIS Atomindex **7** [1976] No. 273717). – [119] V. A. Bauer (Nucl. Technol. **13** [1972] 65/70). – [120] S. S. Bupara, R. L. Jentgen (BMI-1918 [1971] B85/B98).

[121] C. C. Dollins, H. Ocken (Nucl. Appl. Technol. **9** [1970] 141/7). – [122] C. C. Dollins, H. Ocken (J. Nucl. Mater. **45** [1972/73] 150/62). – [123] C. C. Dollins (J. Nucl. Mater. **49** [1973/74] 10/20). – [124] C. C. Dollins (J. Nucl. Mater. **60** [1976] 107/10). – [125] R. C. Nelson (Trans. Am. Nucl. Soc. **9** [1966] 412/3).

[126] H. Matzke, C. Ronchi (Phys. Met. React. Fuel Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 259/65). – [127] V. I. Kuz'min, I. G. Lebedev (At. Energ. [USSR] **38** [1975] 11/5; Soviet At. Energy **38** [1975] 10/4). – [128] R. Hargreaves, D. A. Collins (J. Brit. Nucl. Soc. **15** [1976] 311/8). – [129] H. Aßmann, R. Manzel (J. Nucl. Mater. **68** [1977] 360/4). – [130] H. Zimmermann (J. Nucl. Mater. **75** [1978] 154/61).

[131] R. E. Mason (NUREG-CR-0497 [1979] 98/125; TREE-1280 [1979] 98/125). – [132] D. A. Banks, D. J. Clought (Nucl. Energy **18** [1979] 195/200). – [133] H. Zimmermann (Nucl. Technol. **41** [1978] 408/10). – [134] H. Zimmermann (Eur. Appl. Res. Repts. Nucl. Sci. Technol. Sect. **1** No. 1 [1979] 35/44). – [135] C. Ronchi (Eur. Appl. Res. Repts. Nucl. Sci. Technol. Sect **1** No. 1 [1979] 45/58).

[136] C. Ronchi (Eur. Appl. Res. Repts. Nucl. Sci.Technol. Sect. **1** No. 1 [1979] 211/230). – [137] H. Blank (Eur. Appl. Res.Repts. Nucl. Sci. Technol. Sect. **1** No. 1 [1979] 231/45).

1.1.6 Restructuring

General References:

R. E. Mason, in: D. L. Hagrman, G. A. Reymann, R. E. Mason, MATPRO-Version 11-Rev. 1, A Handbook of Materials Properties for Use in the Analysis of Light Water Reactor Fuel Rod Behavior, NUREG-CR 0497 – Rev. 1 [1980] 136/48; TREE-1280 – Rev. 1 [1980] 136/48.

D. R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 265/83.

The concept "restructuring" concerns essentially the following:

(a) formation and eventual annealing of cracks in fuel pellets,
(b) grain growth, and
(c) redistribution of the initial porosity.

Superposed on these processes are the phenomena already discussed above, of swelling, densification, fission gas bubble formation and migration, and the precipitation of solid fission products. In the case of UO_2-PuO_2 fuel a redistribution of the actinides can also take place, which is discussed in Section 1.1.7 (p. 106).

Phenomenological Description of the Structural Zones

If UO_2 or UO_2-PuO_2 is irradiated under such conditions that high central temperatures (near the melting point) occur, and thereby also large temperature gradients, then even after short irradiation periods (less than 10 h) certain structural zones may be discerned in the fuel.

Fig. 1-63 shows the UO_2 structure (according to Stehle [1]) in a fuel rod that has been operated at such a high power level that brought it to partial melting. The following structural zones are discernable:

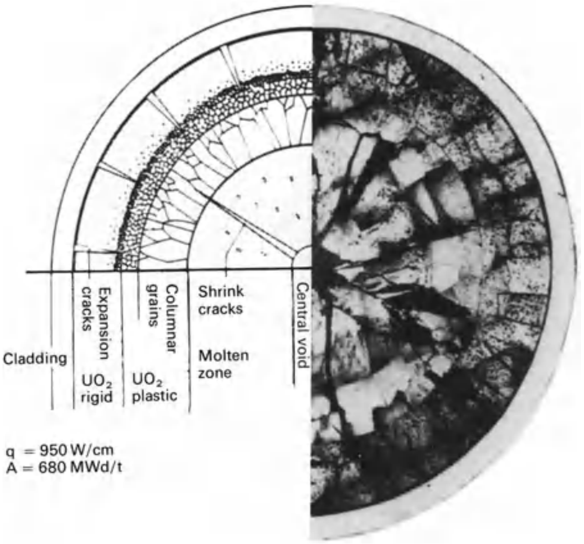
(1) The external zone, having a nearly unchanged microstructure and preferentially radial cracks.
(2) A zone with equiaxed grain growth.
(3) A zone with columnar grain growth and eventually cracks due to shrinking (in the cooled state).
(4) Melted zone, also with radial cracks.
(5) Central void.

At lower power levels the radii of the individual zones are respectively smaller and the cracks are further spread apart.

De Halas, Horn [2] interpret the structural zones as resulting from a certain series of events: e.g., central melting or formation of columnar grains. According to Bradbury [3] these latter are formed according to two mechanisms: (a) accumulation of micropores, and (b) migration of large pores in the temperature gradient. A review of the subject of restructuring was published in 1963 by Robertson et al. [4]. The results of post-irradiation studies are described in detail by Hausner et al. [5 to 7] as are also results of thermal simulation experiments outside of a reactor (see also [8 to 10]).

Bain et al. [11 to 13] report structural changes in UO_2, that was exposed to central melting in the reactor. A summary of such observations and a discussion of the relevant transport processes were published by Christensen [14] (see Table 1/16). Rosenbaum et al. [15] survey the methods for the examination of the structure of irradiated fuels.

Fig. 1-63



UO_2 structure in a highly powered fuel rod [1].

Table 1/16

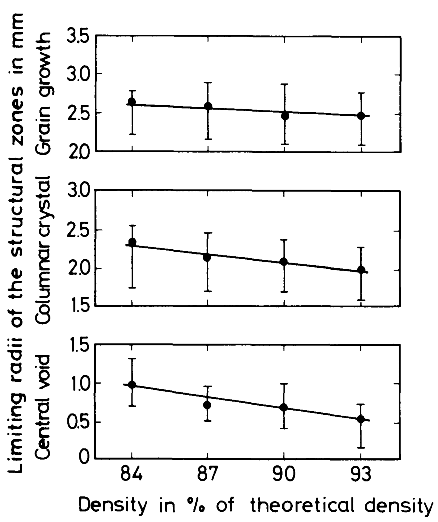
Description of the Structural Zones in Oxidic Nuclear Fuels (small burnup, high fuel rod power level). (Observations are made on $(U_{0.75}, Pu_{0.25})O_2$; initial density: 94% of theoretical; 830 W/cm, 6×10^{18} fissions/cm^3. Valid also for other oxidic fuels with modified temperatures and dimensions [14]).

temperature in °C	grain morphology	grain size in µm	pore morphology	approximate pore size in µm
900 to 1200	equiaxed, initial state	20	randomly arranged spherical pores	5
1200 to 1700	equiaxed, grain growth	20 to 40	radial migration or spherical grain boundary pores	5
1700 to ca. 2000	columnar grains	20 × 20	lenticular pores	3 × 50
2000 to melting point	radially extended	150 × 600	randomly arranged spherical pores	10 to 30
molten layer, outer region	radially extended	150 × 600	no pores	–
molten layer, center	radially extended	–	randomly arranged tubular pores	20 × 100

Already in 1972 have the redistribution of the porosity and its effect on the temperature profile in the fuel been treated analytically [16, 17]. Experimental results for a UO_2-PuO_2 fuel for Fast Breeder Reactors have been reported in [18 to 23, 88].

According to [16] and [19] the "residual porosity" is still 5% in the columnar grain zone. The radial distribution of porosity is reported by Hofmann et al. [24], by Ondracek, Schulz [22], and by Kummerer [23]. The limiting radii of the individual structural zones are shown in **Fig. 1-64** according to [23]. Bober, Schumacher [25] review the transport phenomena occurring during the restructuring.

Fig. 1-64



Limiting radii of the individual structural zones in UO_2-PuO_2, as a function of the fuel density [27]. Power level of fuel rod: 400 to 550 W/cm; burnup: 6 to 47 MWd/kg(U+Pu); the structural zones have completely formed already after 6 MWd/kg(U+Pu).

Extensive programs of studying the structural and the thermal behavior of UO_2 and UO_2-PuO_2 have been carried out at the Nuclear Research Center Karlsruhe (KFK), in connection with the "Fast Breeder Project". A summary of the irradiation experiments at FR2, Karlsruhe, BR2, Mol, and DFR, Dounray, is presented by Hofmann [26]. A representative selection from the KFK reports concerning, as an example, the "UO_2-PuO_2 fuel rod capsule irradiation by the research group FR2-5a" is:

(1) KFK 1886 (1975) [27], including a documentation of the post-irradiation examinations. **Fig. 1-65** shows a typical etched section micrograph.

Fig. 1-65

Typical section micrograph of an irradiated UO_2-PuO_2 pellet [27].

(2) KFK 2134 (1975) [28], containing a pore volume analysis.

(3) KFK 2477 (1977) [29], containing a theoretical analysis by means of models of the restructuring.

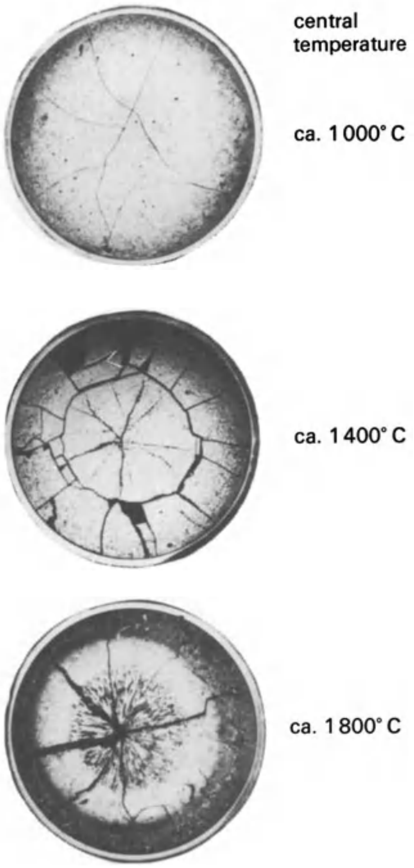
All the experimental studies concerning restructuring involve a strong dependence of the diffusion constant in UO_2 on the stoichiometry. In many of the older experiments, the necessity to control the oxygen activity in the experimental environment was not taken into account.

1.1.6.1 Crack Patterns and Relocation

Diameter changes of the pelletized fuel in the nuclear reactor are determined not only by the swelling and densification but to a large part also by the changes in the crack structure. As a consequence of thermal stresses in the fuel pellet, a typical crack pattern is formed, dependent on the power level of the fuel rod. During the operation of the reactor both annealing and new formation of cracks take place, dependent on the power history of the fuel. Since the fuel pellets are inserted into the cladding tube with some "filling-in clearance", the pellet fragments after the cracking may shift outwards. This phenomenon is called "relocation".

The dependence of the cracking behavior and of the shifting of the fragments on the temperature distribution in the fuel has been known since the beginning of the 60's already [30].

Fig. 1-66

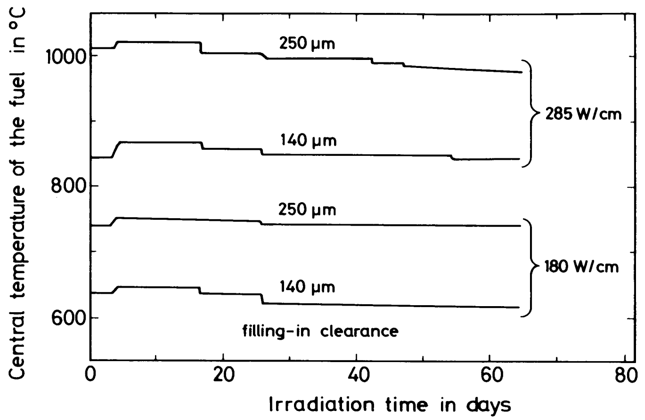


Typical crack patterns in UO_2 [31].

Fig. 1-66 [31] shows typical cracking patterns of UO_2, that was irradiated at various fuel rod power levels. A series of studies deal with the formation, spreading, and annealing of cracks in the fuel [26, 32 to 37]. It is assumed that both lattice diffusion [34] and grain boundary diffusion [35] are rate controlling for the annealing of the cracks. Komatsu et al. [36] and Koizumi et al. [38] analyzed the crack structure (both peripheral cracks and radial cracks). The number of radial cracks increases as a function of the fuel rod power level and the number of reactor shut-offs. Dienst et al. [28] determined the widths and volumes of radial cracks in UO_2-PuO_2 fuel as a function of the fuel density and the burnup. At the start of the irradiation the cracks widen because of the densification of the fuel; at higher burnups the cracks close-up again, because of the swelling, by means of an evaporation-condensation mechanism.

Of greater importance than the crack pattern itself is the shifting outwards of the pellet fragments, the relocation. Experimental investigations of this are reported, e.g., in [39 to 41].

Fig. 1-67



The variation of the central temperature of UO_2-pellets as a function of the duration of the irradiation [48].

That the pellet fragments shift outwards, thus decreasing the gap between pellet and cladding, may be concluded from measurements of the temperature. The central temperature falls either immediately at the start of the irradiation, as may be concluded from [42 to 44], or after some initial increase, as reported in [45 to 48]. An example for such a temperature course is shown in **Fig. 1-67**, taken from Märkl, Stehle [48]. The initial increase in the temperature may be traced back to the densification phenomenon.

Brzoska, Wunderlich [49] conducted a literature evaluation [50 to 54]. The closure of the gap between the pellet and the cladding was studied as a function of the irradiation time by means of analyses of microphotographs of etched sections. **Fig. 1-68**, p. 98, shows the result from which a simple relocation model was derived (see also [55]):

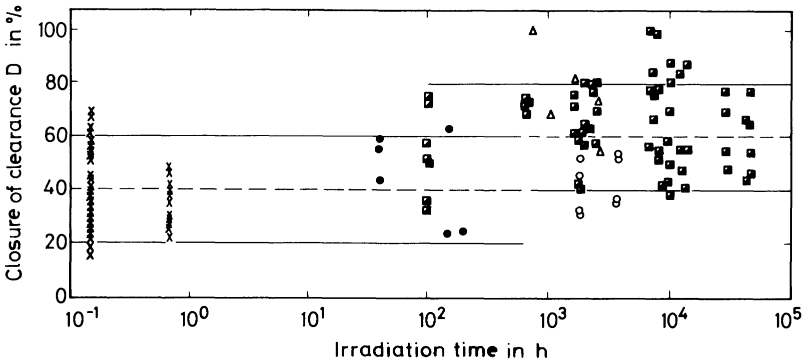
(1) 40 ± 20% of the gap closure occurs already at the initial start-up of the reactor.

(2) 60 ± 20% of the gap closure occurs after 500 h or 400 MWd/t(U) burnup or more than 5 power cycles.

Other empirical models present more or less continuous courses of the relocation, and take various parameters, e.g., the initial gap and power level of the rod into account [56 to 59].

Consequences of fuel cracking and relocation for the thermal behavior of LWR fuel rods are discussed in [89]. A mechanical analysis of crack patterns in fast reactor fuel pellets is presented in [90]. In [91] the results of out-of-pile simulation experiments to study the kinetics and mechanics of pellet fragment relocation are reported.

Fig. 1-68



Closure of the clearance between the fuel pellet and the cladding as a function of the duration of the irradiation ("gap-closure") [49].

Diametrical clearance: 0.50 to 4.97% of the pellet diameter, heat rating: 128 to 925 W/cm. × AECL 2588 [50], ● GEAP 5748 [51], ○ CEA-R-3358 [52], △ BN-7310-02 [53], ◪ XN-73-17 [54].

1.1.6.2 Grain Growth

Theoretical Models

The growth rate of the grain diameter dD/dt may, for energetic reasons, be set proportional to its inverse, i.e.:

$$dD/dt = (k/D)\exp(-Q/RT) \qquad (1\,a)$$

From this follows the parabolic law:

$$D^2 - D_0^2 = 2k\exp(-Q/RT)\cdot t \qquad (1\,b)$$

where D and D_0 are the diameter, respectively the initial diameter, k is a constant, Q the activation energy, T the absolute temperature, R the gas constant and t the time.

Equation (1 b) expresses the grain growth of pure metals very well. Oxide fuels, however, always contain pores in the grains, at the grain boundaries, and at grain boundary triple points, which inhibit the grain growth. The rate reducing effect of grain boundary pores is described in the model of Kingery, Francois [60] by means of an additional factor (k′/D), so that the expression

$$dD/dt = (k/D)(k'/D) \qquad (2\,a)$$

holds. Integration then leads to

$$D^3 - D_0^3 = k_0'\exp(-Q'/RT)\cdot t \qquad (2\,b)$$

Nichols [61] showed that expression (2 b) is valid, provided that pore migration occurs via the evaporation-condensation mechanism (see 1.1.6.3, p. 102), and that the gas pressure in the pores is in equilibrium with the surface tension. In the case of a radius-dependent gas pressure in the pore the relationship

$$D^4 - D_0^4 = k_0'' \exp(-Q''/RT) \cdot t \tag{3}$$

is obtained, where Q″ is the heat of vaporization of the fuel.

Ainscough et al. [62] propose a model, according to which the inhibitory effect of the pores may be expressed as

$$dD/dt = (k/D) - (1/D_m) \tag{4}$$

where D_m is a constant. This means that grain growth ceases when the maximal grain size D_m is attained. The integral form of the grain growth law is hence:

$$D_m^2 \ln [(D_m - D_0)/(D_m - D)] - D_m(D - D_0) = k_0^* t. \tag{5}$$

Ainscough et al. [62] found empirically, that the effect of irradiation may be taken into account by modifying equation (4):

$$dD/dt = k[(1/D) - (1 + 2000\,\Omega\, F\ t)/D_m^\circ)] \tag{6}$$

where $\Omega = 4.1 \times 10^{-23}$ cm³ is the mean volume of a fission track, F t is the burnup in fissions/cm³, and D_m° is the limiting grain size without irradiation.

Experimental Results

Studies summarizing the experimental results have been published by Lyons et al. [63], MacEwan, Hayashi [64], Ainscough et al. [62], and Olsen [65]. The dependence of the grain growth on the following factors is discussed in [64]: (1) porosity, (2) impurities, (3) stoichiometry, (4) compressive stress, and (5) irradiation.

The available data [64, 66 to 69] have been compared in [63] with the cubic law of equation (2b), and with the exception of the data of [66] and [68] there exists good agreement between the model and the data.

It had been customary in the older studies to stay with the parabolic law, and to express the apparent deviations by means of a fractional exponent of the time (e.g. $t^{0.8}$). A wrong time dependence leads, however, to a physically incorrect activation energy.

Stehle [67] was the first to describe his experimental results with a linear time dependence and a cubic law:

$$D^3 - D_0^3 = 7.5 \times 10^{11} \exp(-364/RT) \cdot t \quad (\text{in } \mu m^3/h) \tag{7}$$

($R = 8.314 \times 10^{-3}$ kJ · mol⁻¹ · K⁻¹ in eqs. (7) to (11), the activation energies are in kJ/mol). Nichols [61] reevaluated the data of MacEwan [70] and obtained the relationship

$$D^3 - D_0^3 = 8.57 \times 10^{14} \exp(-519/RT) \cdot t \quad (\text{in } \mu m^3/h) \tag{8}$$

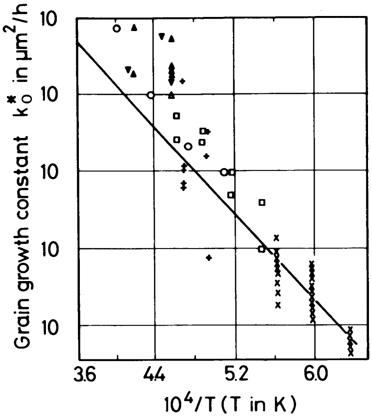
The following expression:

$$D^4 - D_0^4 = 6.18 \times 10^{13} \exp(-387/RT) \cdot t \quad (\text{in } \mu m^4/h) \tag{9}$$

is proposed in the MATPRO-Version 09 handbook [65]. It is shown there, however, that the expression due to Ainscough et al. [62] is suitable too. The latter authors determined both from their own data and from an evaluation of data in the literature the following parameters of eq. (5) (see **Fig. 1-69** and 1-**70**, p. 100):

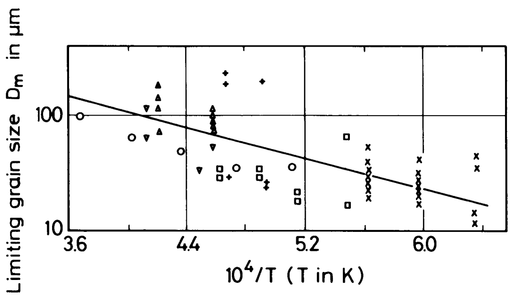
$$k_0^* = 5.24 \times 10^7 \exp(-112/RT) \quad (\text{in } \mu m^2/h) \tag{10a}$$
$$D_m = 2.23 \times 10^3 \exp(-32/RT) \quad (\text{in } \mu m) \tag{10b}$$

Fig. 1-69



Grain growth constant k_0^* according to eq. (10a) and the data required for the calculation [62]. ×, + [62]; ○ [64]; □ [67]; △ [71]; ▽ [72].

Fig. 1-70



Limiting grain size D_m according to eq. (10b) and the data required for the calculation [62], ×, + [62]; ○ [64]; □ [67]; △ [71]; ▽ [72].

In the MATPRO-Version 11 (Rev. 1) handbook [92] the following relationship for equiaxed grain growth of UO_2 and UO_2-PuO_2 is proposed:

$$D^4 - D_0^4 = [1.0269 \times 10^{-13} t \cdot \exp(-35873.2/T)]/[(1.0 - 5.746 \times 10^{-6} B)^2 T] \quad (11)$$

where D = grain diameter, in m, at the end of a time interval; D_0 = grain diameter, in m, at beginning of the time interval; t = time interval in s; T = temperature in K; B = burnup in MWs/kg.

A grain growth relationship with the exponent 5/2 has been given already in 1967 by MacEwan, Hayashi [64], and was recently again (1978/79) proposed by Hastings et al. [73, 93, 94]. In [93] they give the expression:

$$D^{5/2} - D_0^{5/2} = 4.68 \times 10^9 \exp(-320/RT) \cdot t \text{ (in } \mu m^{5/2}/h). \tag{12}$$

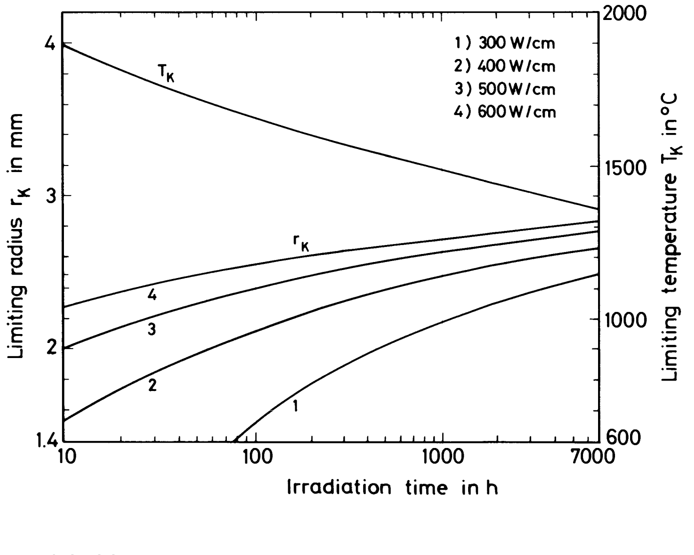
According to [94] the apparent activation energy for grain growth depends on the fuel type and varies from 150 kJ/mol for early AU powder to 360 kJ/mol for pellets from the ADU process.

The interrelationship of grain growth and fission gas bubble migration is considered in [95]. In this paper equations are developed that describe equiaxed grain growth in oxide fuel which contains gas bubbles on the grain boundaries.

Jimenez, Elbel [29], using $D_0 = 5 \mu m$ as the initial value and $D = 25 \mu m$ as the final value, calculated according to Stehle's [67] grain growth expression (eq. (7)) the limiting radius r_k and temperature T_k for the grain growth as a function of the duration of the irradiation t (in h) (**Fig. 1-71**). According to Olander [74] the following holds for T_k

$$1/T_k = 3.7 \times 10^{-5} \log t + 4.2 \times 10^{-4} \text{ (in } K^{-1}) \tag{13}$$

Fig. 1-71



Limiting radii r_k and limiting temperatures T_k of the zone with regular grain growth in UO_2 as a function of the duration of the irradiation for various fuel rod power levels (fuel boundary temperature: 1000 °C) [29].

References for 1.1.6 on pp. 104/6

1.1.6.3 Pore Migration, Columnar Grain Growth, Central Void

The mechanism of the migration of large pores in a temperature gradient has already been dealt with in Section 1.1.4.2 (see p. 48). More recent contributions to the theory of the movement of lenticular pores are presented in [96] for UO_2 and in [97] for UO_2-PuO_2. In the following the resulting restructuring will be dealt with.

Olander [74] showed that it is possible to describe measured pore distributions [75] by means of a model (**Fig. 1-72**), provided that the following analytical procedure is followed:

(1) Assumption of an evaporation-condensation mechanism for pore migration in a temperature gradient.

(2) Setting-up a porosity balance equation.

(3) Consideration of the interplay of the temperature profile and the kinetics of the porosity redistribution.

Several authors presented their numerical analysis according to this method [75 to 77].

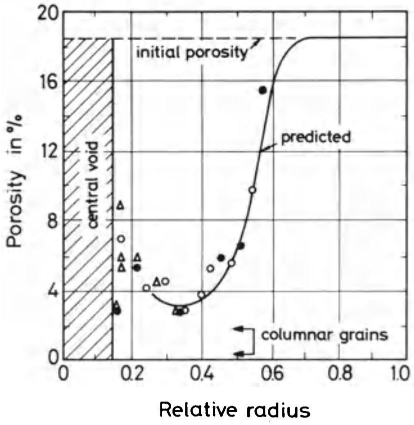
Christensen [78] found as a result of irradiating UO_2 that contained artificial pores that:

(1) Large voids and cracks may disperse into small lenticular pores.

(2) Pore migration results also in the flushing of fission products and in their accumulation at the center of the fuel (see also [79]).

Hinman, Christensen [80] report experimental results concerning the formation of the central void. Meyer [81] proposes a model, according to which sintering processes are favored over gas-phase transport at high temperatures. This model was included into the computer code LIFE-II, and is able to describe experimental results [82, 83] remarkably well. It may be compared with the models of Lackey et al. [75] and Kämpf et al. [84]. It is also meaningful for the redistribution of the actinides (see Section 1.1.7, p. 106).

Fig. 1-72



Comparison between the predicted and the measured distribution of the porosity in a UO_2-PuO_2 fuel rod (power level of fuel rod: 450 W/cm, burnup: 0.7%, VIPAC fuel).

Most authors [10, 17, 61, 76, 78] consider the migration of pores in the temperature gradient as constituting the mechanism of columnar grain growth. It has, however, been shown [85] in simulation experiments with UO_2 having 95% of the theoretical density, that columnar grain growth is possible even without the presence of lenticular pores. Thermal stress and the reduction of the grain boundary energy are considered as the driving forces.

Olander [74] has shown how to calculate according to Nichols [85] the temperature T_s at the outer edge of the dendritic crystal zone as a function of the duration t (in h) of the irradiation. The result is:

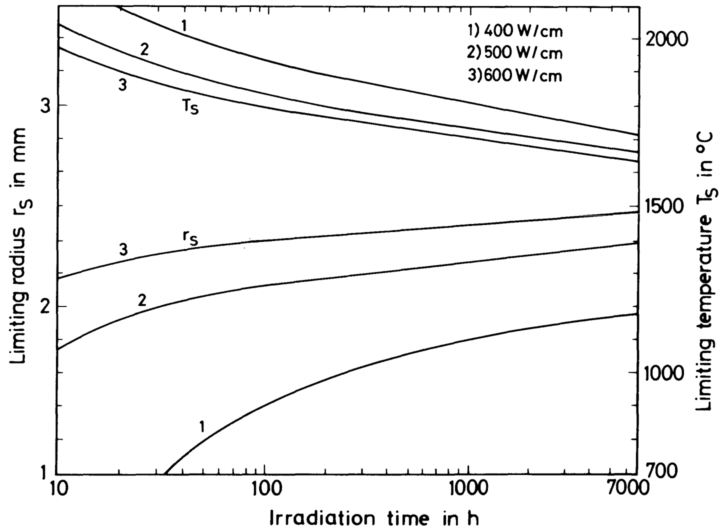
$$1/T_s = 3.4\times10^{-5}\log\ t + 4.2\times10^{-4}\ K^{-1} \tag{14}$$

Christensen [17] presented a similar expression.

Also Jimenez, Elbel [29] have calculated r_s and T_s (**Fig. 1-73**). It is seen that the boundary temperature T_s decreases during burnup. Columnar grain formation occurs mainly at the beginning of the irradiation, and the boundary radius r_s increases rather slowly after the initial restructuring, in particular at high rod power levels. The calculated values of r_s agree well with those obtained from micrographs of etch sections.

Columnar grain formation does not have an appreciable effect on the heat conduction, as was found in [86] for the temperature range 1700 to 2150 °C. Neither was there found a difference for the grain sizes 10 and 100 μm [87].

Fig. 1-73



Limiting radii r_s and limiting temperatures T_s of the region with columnar grain growth in UO_2 as a function of the duration of the irradiation for various power levels of the fuel rod (fuel rod boundary temperature: 1000 °C) [29].

References for 1.1.6 on pp. 104/6

References for 1.1.6:

[1] H. Stehle (Atomwirtsch. Atomtech. **15** [1970] 450/4). – [2] D. R. de Halas, G. R. Horn (HW-SA-2650 [1962] 1/36). – [3] B. T. Bradbury (Trans. Brit. Ceram. Soc. **62** [1963] 159/70). – [4] J. A. L. Robertson, A. S. Bain, J. R. MacEwan, M. J. F. Notley (Proc. 3rd U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 395/404). – [5] H. Hausner (CONF-553-10 [1964]; Am. Ceram. Soc. 66th Ann. Meeting Incl. Symp. Nucl. Space Appl., Chicago 1964, pp. 1/13).

[6] H. Hausner, R. C. Nelson (GEAP-4535 [1964] 1/55). – [7] H. Hausner, R. C. Nelson, M. F. Lyons, B. Weidenbaum (GEAP-4667 [1965] 1/46). – [8] J. M. Kerr, E. N. Harbinson, C. R. Johnson (Trans. Am. Nucl. Soc. **8** [1965] 386/7). – [9] W. P. Chernock, C. E. Burdg, E. I. Veil, G. Zuromsky, J. J. Koziol (CEND-2863-217 [1964] 1/45; EURAEC-1191 [1974]; N.S.A. **18** [1964] No. 45001). – [10] J. R. MacEwan, J. B. Lawson (J. Am. Ceram. Soc. **45** [1962] 42/6).

[11] A. S. Bain, M. Aragones, H. Guerrero (AECL-2289 [1965] 1/22). – [12] A. S. Bain (Trans. Am. Nucl. Soc. **9** [1966] 27/8). – [13] A. S. Bain (AECL-2588 [1966] 1/79). – [14] J. A. Christensen (Ceram. Nucl. Fuels Proc. Intern. Symp., Washington, D.C., 1969, pp. 109/25). – [15] H. S. Rosenbaum, U. E. Wolff, T. E. Lannin (Electron Microsc. Struct. Mater. Proc. 5th Intern. Mater. Symp. Struct. Prop. Mater. Tech. Appl. Electron. Microsc., Berkeley, Cal., 1971 [1972], pp. 1017/26; C.A. **77** [1972] No. 121132).

[16] W. J. Lackey, F. J. Homan, A. R. Olsen (ORNL-TM-3762 [1972]). – [17] J. A. Christensen (Trans. Am. Nucl. Soc. **15** [1972] 214/5). – [18] R. F. Hilbert, T. J. Black, B. F. Rubin, J. D. Stephen (Trans. Am. Nucl. Soc. **15** [1972] 750/2). – [19] J. A. Christensen, G. R. Horn, L. A. Lawrence (Trans. Am. Nucl. Soc. **15** [1972] 215/6). – [20] J. D. B. Lambert, L. A. Neimark (Trans. Am. Nucl. Soc. **17** [1973] 170/2).

[21] D. Geithoff (Fuel Fuel Elem. Fast React. Proc. Symp., Vienna 1973 [1974], Vol. 1, pp. 39/56). – [22] G. Ondracek, B. Schulz (EURFNR-1181 [1974] 112-12/17). – [23] K. Kummerer (Reaktortagung, Nürnberg 1975, Meeting report, pp. 403/6). – [24] H. Hofmann, W. Hellriegel, K. Spieler (Reaktortagung, Bonn 1971, Meeting report, pp. 574/7). – [25] M. Bober, G. Schumacher (KFK-1887 [1973] 1/23).

[26] H. Hoffmann (J. Nucl. Mater. **54** [1974] 9/23). – [27] K. Kummerer, P. Weimar (KFK-1886 [1975] 1/199; N.S.A. **32** [1975] No. 23626). – [28] W. Dienst, O. Goetzmann, B. Schulz (KFK-2134 [1975] 1/40). – [29] J. L. Jimenez, H. Elbel (KFK-2477 [1977] 1/21). – [30] A. S. Bain, J. A. L. Robertson, A. Ridal (AECL-1192 [1961] 1/58).

[31] S. Aas (Nucl. Eng. Design **21** [1972] 237/53). – [32] A. S. Bain (Trans. Am. Nucl. Soc. **6** [1963] 352/3). – [33] G. G. Trantina, J. T. A. Roberts (Fract. Mech. Ceram. Proc. Symp., Pennsylvania State Univ. 1973 [1974], Vol. 2, pp. 779/90; C.A. **85** [1976] No. 168469). – [34] B. Bandyopadhyay, C. R. Kennedy (J. Am. Ceram. Soc. **60** [1977] 48/50). – [35] J. T. A. Roberts, B. J. Wrona (J. Am. Ceram. Soc. **56** [1973] 297/9).

[36] J. Komatsu, Y. Yokouchi, T. Kajiyama, T. Terunuma, M. Koizumi (PNCT-831-73-01 [1973] 18/38). – [37] C. R. Kennedy, F. L. Yaggee, J. C. Voglwede, D. S. Kupperman, B. J. Wrona, W. A. Ellingson, E. Johanson, A. G. Evans (ANL-76-110 [1976] 1/50; INIS Atomindex **8** [1977] No. 324142). – [38] M. Koizumi, H. Furuya, Y. Yokouchi, M. Kajiyama, T. Toshihiro (PNCT-831-73-01 [1973] 84/8). – [39] D. H. Geithoff (Reaktortagung, Berlin 1970, Meeting report, pp. 462/5). – [40] L. A. Lawrence, J. A. Christensen (Trans. Am. Nucl. Soc. **14** [1971] 146).

[41] R. Duncan, P. G. Smerd, H. Knaab, R. Manzel (Trans. Am. Nucl. Soc. **18** [1974] 250). – [42] G. Testa, F. Doria, P. Grillo, A. Nobili, P. L. Rotoloni (Nucl. Appl. Technol. **7** [1969] 550/60). – [43] W. E. Baily, C. N. Craig, E. L. Zebrosky (Trans. Am. Nucl. Soc. **9** [1966] 40). – [44] A. Calza Bini, G. Cosoli, G. Filacchioni, M. Lanchi, A. Nobili, U. Rocca, P. L. Rotoloni

(Trans. Am. Nucl. Soc. **17** [1973] 166). – [45] L. A. Lawrence (Trans. Am. Nucl. Soc. **17** [1973] 173/4).

[46] F. E. Panisko, J. A. Christensen, A. E. Avave (Trans. Am. Nucl. Soc. **15** [1972] 765/6). – [47] M. Gärtner, P. Dewes (Reaktortagung, Nürnberg 1975, Meeting report, pp. 326/9). – [48] H. Märkl, H. Stehle (KWU Plutonium Fuel Recycle, Miami Beach, Florida 1977; CONF-770554 [1977]). – [49] B. Brzoska, F. Wunderlich (Reaktortagung, Nürnberg 1975, Meeting report, pp. 330/3). – [50] A. S. Bain (AECL-2588 [1966] 1/79; N.S.A. **21** [1967] No. 25737).

[51] C. N. Craigh, G. R. Hull, W. E. Baily (GEAP-5748 [1969] 1/42; N.S.A. **23** [1969] No. 47341). – [52] J. C. Janvier, B. de Bernardy de Sigoyer, R. Delmas (CEA-R-3358 [1967] 1/78; N.S.A. [1968] No. 26092). – [53] E. de Meulemester, N. Hoppe, G. de Contenson, M. Watteau (Intern. Conf. Nucl. Fuel Perform., London 1973, pp. 92.1/92.15; BN-7310-02 [1973] 1/27). – [54] K. P. Galbraith (XN-73-17 [1973] 1/45 from [49]). – [55] H. Stehle, H. Aßmann, F. Wunderlich (Nucl. Eng. Design **33** [1975] 230/60).

[56] D. S. Dutt, R. B. Baker, S. A. Chastain (Trans. Am. Nucl. Soc. **17** [1973] 175). – [57] R. A. Proebstle, R. B. Elkins, M. O. Marlowe, E. B. Johannson, G. A. Potts, R. Stijovic, T. C. Rowland (Trans. Am. Nucl. Soc. **18** [1974] 121/2). – [58] J. P. Stora, C. Hueber (Trans. Am. Nucl. Soc. **22** [1975] 208/9). – [59] N. Hoppe, P. Verbeek (Trans. Am. Nucl. Soc. **24** [1976] 175/7). – [60] W. D. Kingery, B. Francois (J. Am. Ceram. Soc. **48** [1965] 546/7).

[61] F. A. Nichols (J. Appl. Phys. **37** [1966] 4599/602). – [62] J. B. Ainscough, B. W. Oldfield, J. O. Ware (J. Nucl. Mater. **49** [1973/74] 117/28). – [63] M. F. Lyons, D. H. Coplin, B. Weidenbaum (GEAP-4411 [1963] 1/53; N.S.A. **18** [1964] No. 18345). – [64] J. R. MacEwan, J. Hayashi (Proc. Brit. Ceram. Soc. **7** [1967] 245/72). – [65] C. S. Olsen (TREE-NUREG-1005 [1976] 110/27).

[66] T. R. Padden (Proc. 2nd U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 6, pp. 569/86). – [67] H. Stehle (Ber. Deut. Keram. Ges. **40** [1963] 129). – [68] B. Weidenbaum (GEAP-3771-5 [1962]; GEAP-3771-6 [1963]). – [69] J. D. Eichenberg, P. W. Frank, T. J. Kisiel, B. Lustmann, K. H. Vogel (WAPD-183 [1957] 1/192; N.S.A. **12** [1958] No. 3907). – [70] J. R. MacEwan (AECL-1184 [1961] 1/15; CRFD-999 [1961]; N.S.A. **15** [1961] No. 16044).

[71] H. Hausner (GEAP-4315 [1963] 1/49; N.S.A. **18** [1964] No. 2221). – [72] H. Hausner (GEAP-4689 [1965]; EURAEC-1836 [1965] 1/26; N.S.A. **21** [1967] No. 28836). – [73] M. J. F. Notley, I. J. Hastings (80th Ann. Meeting Am. Ceram. Soc., Detroit 1978, Paper 30-N-78). – [74] D. R. Olander (Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 273/83). – [75] W. J. Lackey, F. J. Homan, A. R. Olsen (Nucl. Technol. **16** [1972] 120/42).

[76] P. F. Sens (J. Nucl. Mater. **43** [1972] 293/307). – [77] C. S. Rim, H. Fenech (Trans. Am. Nucl. Soc. **12** [1969] 103/4). – [78] J. A. Christensen (Trans. Am. Nucl. Soc. **8** [1965] 44/5). – [79] J. L. Bates (BNWL-58 [1965] 1/26). – [80] C. A. Hinman, J. A. Christensen (HEDL-SA-337 [1972] 1/14).

[81] R. O. Meyer (J. Nucl. Mater. **50** [1974] 11/24). – [82] R. O. Meyer, E. M. Butler, D. R. O'Boyle (ANL-7929 [1972] 1/32; N.S.A. **26** [1972] No. 48312). – [83] R. O. Meyer, E. M. Butler, D. R. O'Boyle (ANL-7929–Suppl. 1 [1973]). – [84] H. Kämpf, H. Elbel, F. Depisch (KFK-1575 [1972] 1/60; N.S.A. **27** [1973] No. 16837). – [85] F. A. Nichols (J. Nucl. Mater. **22** [1967] 214/22).

[86] M. G. Balfour, H. M. Ferrari (Met. Soc. Conf. Proc. **42** [1966] 223/35). – [87] M. Aragones, H. Guerrero (AECL-2564 [1966] 1/45). – [88] R. Paris, J. M. Horspool, R. G. Bellamy (Proc. Intern. Conf. Fast Breeder React. Fuel Perform., La Grange Park 1979, pp. 133/42). – [89] J. T. Maki, J. E. Meyer (PB-299392 [1978] 1/121). – [90] R. M. Guha, J. L. Head, J. R. Matthews (Trans. 4th Intern. Conf. Struct. Mech. React. Technol., San Francisco

1977 [1978], Abstr. C2.7, p. 1; INIS-mf-4470 [1977] C2.7; INIS Atomindex **9** [1978] No. 408712).

[91] C. R. Kennedy, R. A. Christensen, R. F. Eilbert (EPRI-NP-1106 [1979] 1/87). – [92] R. E. Mason (NUREG-CR-0497 [1979] 136/48). – [93] I. J. Hastings, J. A. Scoberg, K. MacKenzie (J. Nucl. Mater. **82** [1979] 435/8). – [94] I. J. Hastings, J. A. Scoberg, K. MacKenzie, W. Walden (AECL-6411 [1979] 1/34). – [95] W. L. Baldewicz, A. R. Wazzan, D. Okrent (Nucl. Technol. **46** [1979] 263/7).

[96] C. F. Clement (J. Nucl. Mater. **68** [1977] 63/8). – [97] C. F. Clement, M. W. Finnis (J. Nucl. Mater. **75** [1978] 115/24).

1.1.7 Changes in the Stoichiometry, Redistribution of Oxygen and Uranium/Plutonium

General References

H. Holleck, H. Kleykamp, Zur Stöchiometrieverschiebung in einem oxidischen Brennelement bei hohem Abbrand, KFK-1181 [1970] 1/72 [62 Refs.].

C. E. Johnson, I. Johnson, P. E. Blackburn, C. E. Crouthamel, Effects of Oxygen Concentration on Properties of Fast Reactor Mixed-Oxide Fuel, Reactor Technol. **15** [1972/73] 303/38 [90 Refs.].

IAEA, Behavior and Chemical State of Irradiated Ceramic Fuels, Proceedings of a Panel, Vienna 1972 [1974], pp. 1/437 [30 papers].

IAEA, Thermodynamics of Nuclear Materials, Proceedings of a Symposium, Vienna 1974 [1975], 2 Vol.; in particular Vol. 1, pp. 3/143.

D. R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 145/71.

W. Breitung, Verdampfungskinetik von oxidischen Kernbrennstoffen und ihr Einfluß auf die Spaltstoffentmischung in Reaktorbrennstäben und auf den Brennstoffdampfdruck unter Störfallbedingungen, KFK-2240 [1976] 1/142 [61 Refs.].

IAEA, Thermodynamics of Nuclear Materials, Proceedings of a Symposium, Jülich 1979 [1980], Vol. 1; in particular pp. 357/438.

The chemical state of the fuel in the nuclear reactor is affected by changes in its composition resulting from (a) the nuclear fission, and (b) the redistribution of the oxygen and the fissile material. The last-mentioned phenomena are especially observed, when large burnups, high temperatures, and large temperature gradients occur.

Two processes ought to be considered in respect of the O:M (M = U, Pu) ratio:

(1) a change in the stoichiometry, and
(2) redistribution of the oxygen in the volume of the fuel.

In the case of UO_2-PuO_2 mixed oxides for fast breeder reactors, the following additional phenomenon plays an important role:

(3) redistribution of the fissile material in the fuel volume.

In the cases (2) and (3) one deals essentially with a radial change in the fuel composition caused by transport processes in the steep temperature gradient. The extent of the redistribution is determined by:

a) the thermodynamic relationships of the system,
b) the transport mechanism.

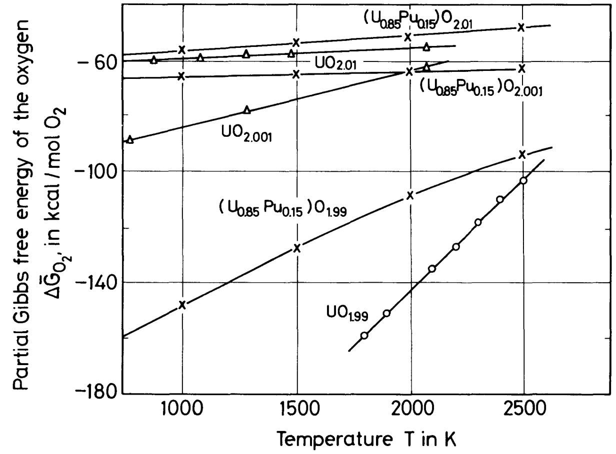
Thermodynamic Data Base

The partial Gibbs free energy of the oxygen $\Delta\bar{G}_{O_2}$ – also termed oxygen potential – (where $\Delta\bar{G}_{O_2}$ = RT ln p_{O_2}; p_{O_2} is the partial pressure of oxygen, R the gas constant, T the absolute temperature) is of central importance for the chemical behavior of the oxidic fuel $(U_{1-y}Pu_y)O_{2\pm x}$ (general formula, with $0 \leq y \leq 1$, $x \ll 1$). This quantity has been determined with solid-state electrolytes [1 to 4], or from vapor pressure measurements [4 to 6]. The thermodynamic data base for UO_2 is reported comprehensively in [5, 7 to 12]; that for UO_2-PuO_2 and PuO_2 may be found in [2 to 4] and [6, 13 to 15], respectively.

Holleck, Kleykamp [12] show, on the basis of a literature evaluation, that $\Delta\bar{G}_{O_2}$ depends on the following factors:

(1) the temperature (see **Fig. 1-74**),
(2) the O:M ratio (see **Fig. 1-75**, p. 108), i.e., on x, and
(3) the Pu:(U + Pu) ratio (see **Fig. 1-76**, p. 108) i.e., on y.

Fig. 1-74



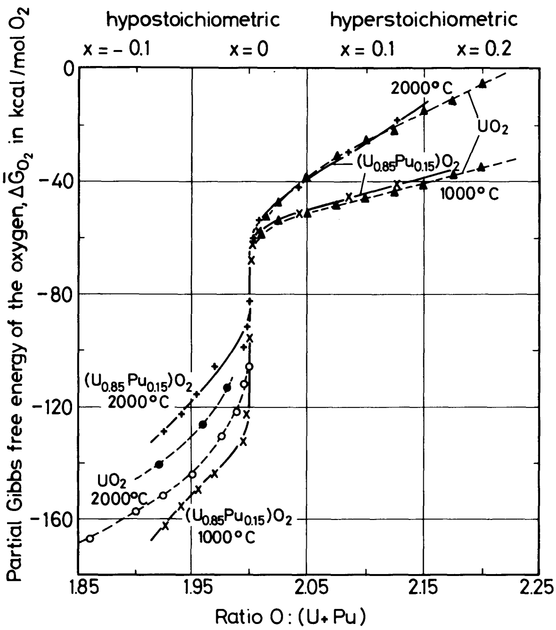
Partial Gibbs free energy of the oxygen in $UO_{2\pm x}$ and $(U_{0.85}$-$Pu_{0.15})O_{2\pm x}$ as a function of the temperature [12]. × Rand, Markin [4]; ○ Pattoret [7]; △ Perron [9].

Fig. 1-77, p. 109, shows some important interrelationships between $\Delta\bar{G}_{O_2}$, the temperature, the O:M ratio, the valencies of U and Pu (for P:(U + Pu) = 0.15), and the composition of CO_2/CO gas mixtures in equilibrium with $(U_{0.85}Pu_{0.25})O_{2\pm x}$ according to Holleck, Kleykamp [12].

The results of more recent measurements of $\Delta\bar{G}_{O_2}$ for $(U_{1-y},Pu_y)O_{2\pm x}$ with $y = 0, 0.15, 0.23$, and 0.31 by a thermogravimetric method and using CO_2/CO gas mixtures are reported by Chilton, Edwards [87] and shown in **Fig. 1-78**, p. 109. The values for $UO_{2\pm x}$ are compared with results from Markin et al. [8] and Aukrust et al. [88].

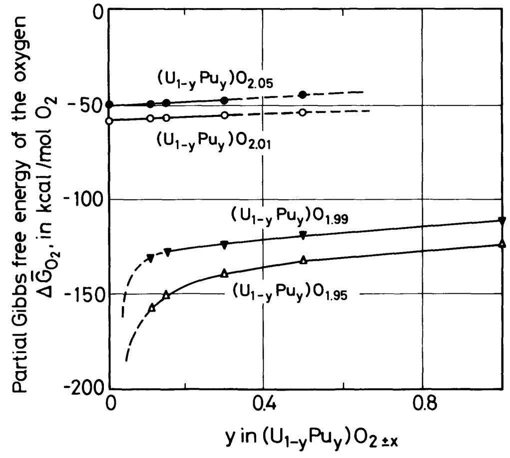
The oxygen potential $\Delta\bar{G}_{O_2}$ of hyperstoichiometric $(U_{1-y},Pu_y)O_{2-x}$ with y between 0.1 and 0.4 was measured by Woodley [89].

Fig. 1-75



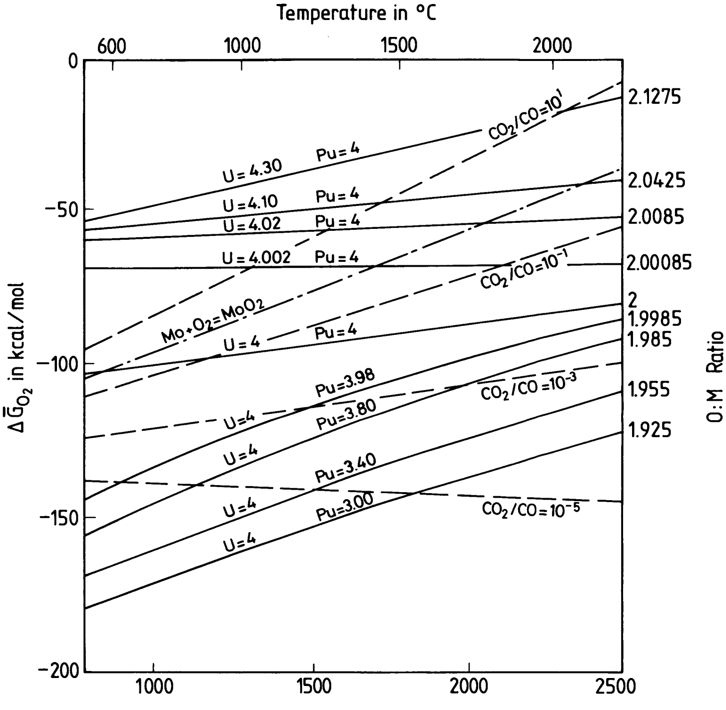
Partial Gibbs free energy of the oxygen in UO_2 and UO_2-PuO_2 as function of the O : (U + Pu) ratio at 1 000 and 2 000 °C [12]. ×, + Rand, Markin [4]; ○ Pattoret [7]; ● Aitken [5]; ▲ Perron [9].

Fig. 1-76



Partial Gibbs free energy of the oxygen in $(U_{1-y},Pu_y)O_{2\pm x}$ as a function of the U : Pu ratio at 1 000 °C [12].

Fig. 1-77



Partial Gibbs free energy of the oxygen in mixed oxide as a function of temperature and for different U and Pu valencies. The O:M ratio is valid for a Pu:(U+Pu) ratio of 0.15. Different CO_2/CO ratios are indicated by dashed lines [12].

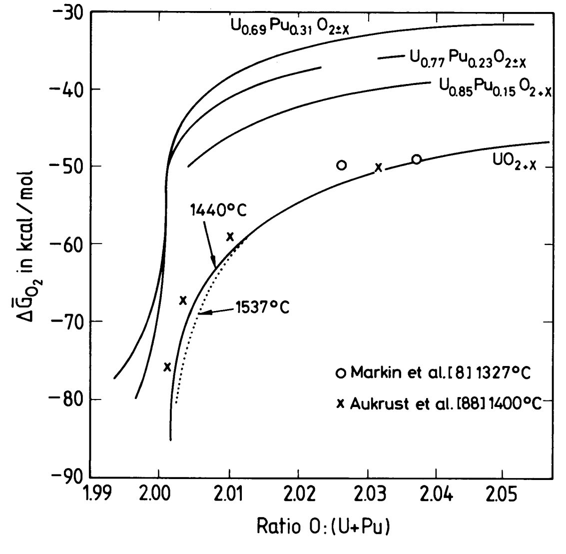


Fig. 1-78

Partial Gibbs free energy of the oxygen in $(U_{1-y}Pu)O_{2\pm x}$ as a function of the O:M ratio [87].

1.1.7.1 Changes in the Stoichiometry

During the fission of a uranium or a plutonium nucleus, two oxygen atoms are set free in the primary step. The mean valency of the fission products is, however, somewhat smaller than that of U or Pu, so that a net amount of oxygen is, in fact, set free during burnup, and its chemical potential increases.

Three factors ought to be taken into account in the oxygen balance:

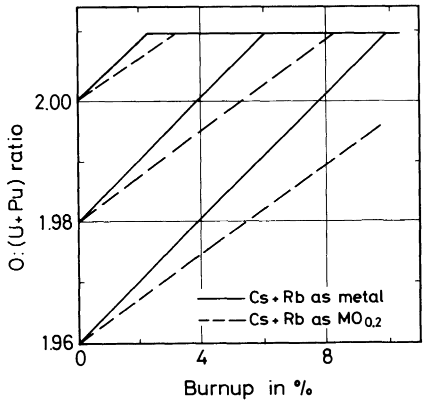
(1) the formation of new oxidic phases of the fission products,
(2) the change in the O:M ratio of the fuel matrix, and
(3) a loss of oxygen, e.g., by means of a reaction with the cladding.

Fuel in Steel Cladding (Fast Breeder Reactors)

In this fuel rod system, part (3) is negligible as a first approximation. Calculations of the oxygen balance in UO_2-PuO_2 mixed oxides have been carried out in [12, 16 to 18]. Tables 1/17 and 1/18 show the results for $(U_{0.85}Pu_{0.15})O_{2\pm x}$ with initial values of $-0.1 \leq x \leq 0.03$ for 1 000 and 2 000 K, respectively [12]. The shift in the stoichiometry is strongly affected by the discontinuous change in the valency of the fission product cations.

Mo and Tc play a special role in this respect (see Tables 1/17 and 1/18). Johnson et al. [19] showed that the rate of change of the stoichiometry slows-up at that point, where Mo is oxidized to MoO_2. According to Findlay [18] the fission products Cs, Rb, and Nb must also be considered besides Mo and Tc. He calculated the course of the O:M ratio in the fuel matrix shown in **Fig. 1-79** as a function of the burnup. A buffering of all the oxygen sets in at O:M = 2.01, the rate at which this ratio is reached being dependent on the chemical state of the elements Rb and Cs.

Fig. 1-79



The variation of the O:(U + Pu) ratio in the fuel matrix of $(U,Pu)O_{2\pm x}$ in steel cladding [18].

Table 1/17

Average Final Stoichiometry of $(U_{0.85}Pu_{0.15})O_{2\pm x}$ as a Function of the Initial Stoichiometry and of the Oxygen Balance (model calculation). Burnup: 10%; temperature of irradiation: 1 000 K. The oxygen balance is given as the number of atoms for 10 fissions. The following is valid at 1 000 K: $^{f}\Delta G^{\circ}\langle MoO_2\rangle = \Delta\overline{G}_{O_2}\,[(U_{0.85}\text{-}Pu_{0.15})O_{2.000}]$ [12].

initial stoichiometry	available oxygen	consumption of oxygen for the oxidation					oxide fraction		final stoichiometry
		R.E.*, Zr, Sr, Ba	$\leq UO_{2.000}$	Mo	Tc	$>UO_{2.000}$	Mo	Tc	
$MO_{1.900}$	19.00	14.74	4.26	0	0	0	0	0	$MO_{1.947}$
$MO_{1.940}$	19.40	14.74	4.66	0	0	0	0	0	$MO_{1.992}$
$MO_{1.950}$	19.50	14.74	4.50	0.26	0	0	6.5%	0	$MO_{2.000}$
$MO_{1.960}$	19.60	14.74	3.60	1.26	0	0	31.5%	0	$MO_{2.000}$
$MO_{1.970}$	19.70	14.74	2.70	2.26	0	0	56.5%	0	$MO_{2.000}$
$MO_{1.980}$	19.80	14.74	1.80	3.26	0	0	81.5%	0	$MO_{2.000}$
$MO_{1.990}$	19.90	14.74	0.90	4.00	0	0.26	100%	0	$MO_{2.003}$
$MO_{2.000}$	20.00	14.74	0	4.00	0.63	0.63	100%	54.3%	$MO_{2.007}$
$MO_{2.010}$	20.10	14.74	0	4.00	1.26	0.20	100%	100%	$MO_{2.012}$
$MO_{2.020}$	20.20	14.74	0	4.00	1.26	0.30	100%	100%	$MO_{2.023}$
$MO_{2.030}$	20.30	14.74	0	4.00	1.26	0.40	100%	100%	$MO_{2.034}$

---

* R.E. = rare earth elements

Table 1/18

Average Final Stoichiometry of $(U_{0.85}\text{-}Pu_{0.15})O_{2\pm x}$ as a Function of the Initial Stoichiometry and of the Oxygen Balance (model calculation). Burnup: 10%; temperature of irradiation: 2000 K. The oxygen balance is given as the number of atoms for 10 fissions. The following is valid at 2000 K: ${}^{f}\Delta G^{\circ}\langle MoO_2\rangle = \Delta\overline{G}_{O_2}\,[(U_{0.85}\text{-}Pu_{0.15})O_{2.003}]$ [12].

initial stoichiometry	available oxygen	consumption of oxygen for the oxidation				oxide fraction Mo	final stoichiometry
		R.E.*, Zr, Sr, Ba	$\leq UO_{2.003}$	Mo	$>UO_{2.003}$		
$MO_{1.900}$	19.00	14.74	4.26	0	0	0	$MO_{1.947}$
$MO_{1.940}$	19.40	14.74	4.66	0	0	0	$MO_{1.992}$
$MO_{1.950}$	19.50	14.74	4.76	0	0	0	$MO_{2.003}$
$MO_{1.960}$	19.60	14.74	3.87	0.99	0	24.8%	$MO_{2.003}$
$MO_{1.970}$	19.70	14.74	2.97	1.99	0	49.8%	$MO_{2.003}$
$MO_{1.980}$	19.80	14.74	2.07	2.99	0	74.8%	$MO_{2.003}$
$MO_{1.990}$	19.90	14.74	1.17	3.99	0	99.8%	$MO_{2.003}$
$MO_{2.000}$	20.00	14.74	0.27	4.00	0.99	100%	$MO_{2.014}$
$MO_{2.010}$	20.10	14.74	0	4.00	1.36	100%	$MO_{2.025}$
$MO_{2.020}$	20.20	14.74	0	4.00	1.46	100%	$MO_{2.036}$
$MO_{2.030}$	20.30	14.74	0	4.00	1.56	100%	$MO_{2.047}$

* R.E. = rare earth elements

Fuel in Zircaloy Cladding (Water Cooled Reactors)

It is necessary to note for UO_2 fuels in water-cooled reactors that in the course of the burnup an increasing fraction of the fissions occurs in the bred-in plutonium. Thereby the "oxygen release" per fission is somewhat enlarged, since the fission products of Pu are slightly more "noble" than those of U. Considering this phenomenon, according to [22], 5×10^{20} atoms/cm^3 of "excess oxygen" are produced after a burnup of 50 MWd/kg(U) in UO_2 fuel rods of light water reactors. The "oxygen release" is always larger in a fuel rod containing Pu as a fissile material (in particular that of a fast breeder reactor).

The loss of oxygen to the cladding plays a decisive role in Zircaloy clad fuel rods. The Zircaloy cladding takes up oxygen, forming an oxide layer, at 400 °C and realistic oxygen partial pressures [20]. This process should cause a stabilization of the O:M ratio in the fuel between 2.000 and 1.995. This is confirmed by the results of Adamson et al. [21] and Garzarolli, Manzel [22] for irradiated fuel rods.

1.1.7.2 Redistribution of Oxygen

Olander [23] reviewed the models proposed in the literature concerning the redistribution of the oxygen. Three models are discussed:

(1) The Markin-Rand-Roberts model: a mechanistic gas transport model.

(2) The Aitken model: a phenomenological model, which considers both gas transport and solid state diffusion.

(3) The Bober-Schumacher model: a mechanistic thermodiffusion model (solid state diffusion).

Experimental results of oxygen redistribution are reported in [24 to 30], and are presented in Table 1/19 [23]. Oxygen transport occurs in hyperstoichiometric fuel ($x > 0$) in the direction of the hotter zone, and in hypostoichiometric fuel ($x < 0$) in the direction of the colder zone.

Table 1/19
Summary of the Experiments Concerning Redistribution of Oxygen in $UO_{2\pm x}$ and $(U,Pu)O_{2\pm x}$ According to [23].

authors	fuel	geometry	oxygen enrichment
Christensen [24]	UO_{2+x}	radial	hot zone
Fryxell, Aitken [25]	UO_{2-x}	axial	cold end (no redistribution in $UO_{2.000}$)
Evans et al. [26]	$(U,Pu)O_{2-x}$	axial	cold end
Jeffs [27]	$(U,Pu)O_{2+x}$	radial	hot zone (no redistribution in $(U,Pu)O_{2.000}$)
Adamson [28]	UO_{2+x}	axial	hot end
Adamson, Carney [29, 30]	$(U,Pu)O_{2+x}$	axial	hot end

(1) Mechanistic Redistribution Model (Gas Transport)

Rand et al. [1, 4] propose a model, that is based on the attainment of a thermodynamic equilibrium among CO_2, CO, and O_2 in the temperature gradient by means of diffusion in the gaseous phase involving pores and cracks in the fuel. The transport of oxygen is the result of the diffusion of CO_2 and CO in opposite directions. These gases are formed from carbon impurities in the fuel. In hyperstoichiometric fuels the CO_2 diffuses to the hotter zone, releases an oxygen atom to the solid, and the CO formed diffuses back to the colder zone. The CO_2:CO ratio is constant, despite the temperature gradient, and its value is determined by the initial stoichiometry.

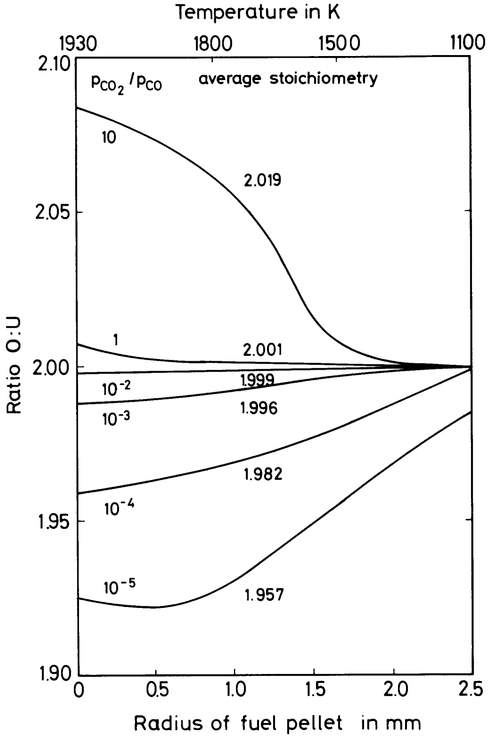
According to Holleck, Kleykamp [12] the partial Gibbs free energy of oxygen in a mixture of CO_2 and CO is given by

$$\Delta\overline{G}_{O_2} = -135000 + 41.50T + 9.15T\log(p_{CO_2}/p_{CO}) \qquad (1)$$

($\Delta\overline{G}_{O_2}$ in cal/mol, T is the absolute temperature, p_{CO_2} and p_{CO} are the partial pressures of the indicated species).

This expression permits the calculation of the local stoichiometry in a UO_2 pellet along the radial temperature profile. **Fig. 1-80**, p. 114, shows the results of such a calculation [4]. **Fig. 1-81**, p. 114, compares the measured data of Christensen [24] with the calculated results, according to Perron [9]. Jeffs [27], too, could interpret his data well by means of this model.

Fig. 1 – 80



Dependence of the local stoichiometry on the radius of the fuel pellet or on the radial temperature profile (model calculation) (from [12], according to [4]).

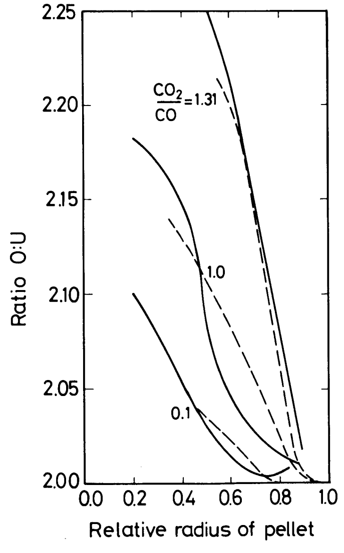


Fig. 1-81

Comparison between the calculated and the measured O : U profiles in UO_2, that are established in the temperature profile ([9, 24]). —— exper. [24], ---- calc. [9].

(2) Phenomenological Redistribution Model

If the model described above is employed for hypostoichiometric fuel, the following difficulty is met. Such a fuel corresponds to a small CO_2:CO ratio, so that a very slow gas transport and practically no oxygen redistribution are expected. This is, however, contrary to the observations.

Aitken et al. [31 to 34] therefore construct a model that permits various transport mechanisms. Based on the thermodynamics of irreversible processes, the following relationship between x, the deviation of the stoichiometry, and T, the temperature, is proposed:

$$\ln x = (Q^{\ddagger}/RT) + C \qquad (2)$$

$Q^{\ddagger}$ is an effective "heat of transport", that can describe several superimposed transport mechanisms. The constant C depends on the initial stoichiometry. Aitken et al. [33] showed that for the hypostoichiometric fuel $(U_{1-y}Pu_y)O_{2+x}$ $(x < 0)$ the following is valid:

$$Q^{\ddagger} = -125\,\text{kJ/mol for } -0.02 < x < 0 \qquad (3a)$$

$$Q^{\ddagger} = -A/x^2\,\text{kJ/mol for } -0.10 < x < 0.02 \qquad (3b)$$

$$A = 0.59 \text{ to } 0.096\,\text{kJ/mol.} \qquad (3c)$$

The fewer obstacles (e.g., pores) for solid-state transport are present, the higher is the value of the parameter A. The comparison between model and experiment led Aitken [31] to the following predictions concerning the predominant mechanisms for the redistribution of oxygen:

(1) UO_{2+x} $(x < 0)$:

UO_2 transport in the gas phase and oxygen transport in the solid.

(2) $(U_{1-y}Pu_y)O_{2+x}$ $(x < 0)$:

CO_2/CO transport mechanism in the gas phase and oxygen transport in the solid.

(3) UO_{2+x} $(x \geq 0)$, $(U_{1-y}Pu_y)O_{2+x}$ $(x > 0)$:

CO_2/CO transport mechanism in the gas phase.

(3) Mechanistic Thermodiffusion Model

The thermodiffusion model has already in 1971 been considered by Bober et al. [35] as an explanation for experimentally observed demixing processes (demixing of U and Pu in the UO_2-PuO_2 mixed oxide). Later it was applied to the redistribution of the oxygen. Observations on hypostoichiometric mixed oxide fuels having a density 100% of the theoretical led Bober, Schumacher [36] to the conclusion that in this case a thermodiffusion mechanism should be effective for the oxygen redistribution. The quantitative treatment of the model, that is based on the thermodynamics of irreversible processes, is given in [36 to 40]. The model was widened by Sari, Schumacher [41], to include also hyperstoichiometric mixed oxides.

According to this model, oxygen vacancies migrate in the hypostoichiometric fuel with an "effective heat of transport" $Q_v^{\ddagger}$, while oxygen interstitials migrate with an "effective heat of transport" $Q_i^{\ddagger}$ in the hyperstoichiometric fuel. The migration takes place in the temperature gradient, obeying the relationships:

$$\text{hypostoichiometric: } (1/x)(\text{grad } x/\text{grad } T) = -Q_v^{\ddagger}/RT^2 \qquad (4a)$$

$$\text{hyperstoichiometric: } (1/x)(\text{grad } x/\text{grad } T) = -Q_i^{\ddagger}/RT^2. \qquad (4b)$$

For $(U_{0.8}Pu_{0.2})O_{2+x}$ Sari, Schumacher [41] present the following empirical expressions:

$$Q_v^{+} = -3.96\times10^{3} + 2.37\times10^{3}v_{Pu} - 3.56\times10^{2}v_{Pu}^{2} \text{ kJ/mol} \tag{5a}$$

$$Q_i^{+} = -3.5\times10^{31}\exp(-17v_U) \text{ kJ/mol} \tag{5b}$$

where v_{Pu} and v_U are the mean valencies of Pu and U in the mixed oxide. For $x < 0$

$$v_U = 4;\ v_{Pu} = 4+2x/y \tag{6a}$$

and for $x > 0$

$$v_U = 4 + 2x/(1-y);\ v_{Pu} = 4 \tag{6b}$$

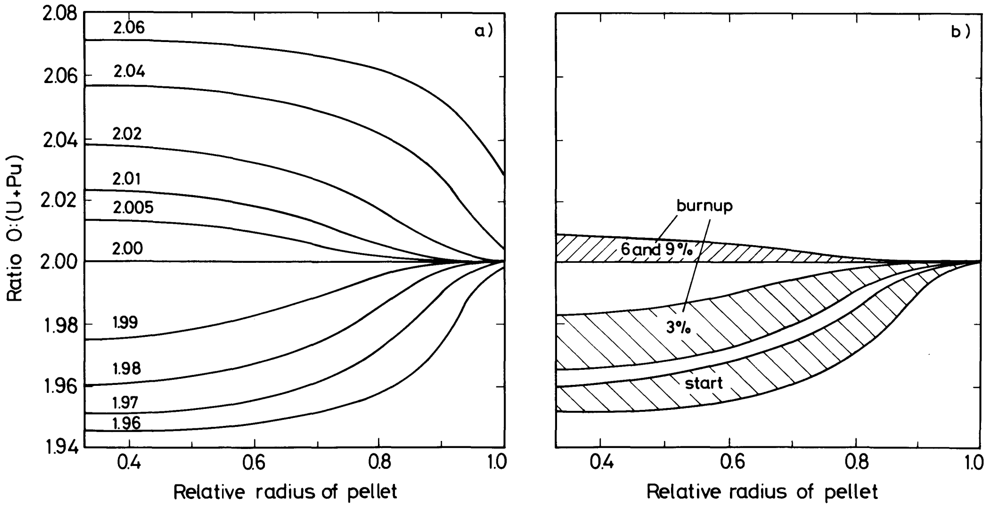
are valid for $(U_{1-y}Pu_y)O_{2+x}$ fuels.

The negative value of $O_v^{\pm}$ means that the net flow of oxygen vacancies is against the direction of the temperature gradient, i.e., there exists an oxygen transport towards the lower temperatures. In the hyperstoichiometric fuel the oxygen is transported in the opposite direction. The negative value of $O_i^{\pm}$ is related to the effect of the thermoelectrical potential gradient [40, 41]. **Fig. 1-82**a and b show some results from model calculations [41]. In the range above 6% burnup (Fig. 1-82b) a stabilization of the O:M ratio is effected by the buffering action of the Mo.

(4) Further Theoretical and Experimental Studies

Johnson, Blackburn, and their coworkers [19, 42, 43] published reviews on the effects of the stoichiometry of UO_2-PuO_2 pellets for fast breeder reactors. The last-mentioned paper describes the physical basis for a computer model [44] for the calculation of the oxygen distribution (and the redistribution of fissile material). Reference is made there to theoretical studies of the oxygen potential made by Blackburn [45].

Fig. 1-82



Radial oxygen distribution a) for various mean O:(U+Pu) ratios; b) for various burnup values, for an initial mean ratio O:(U+Pu) = 1.97 to 1.98 (model calculations) [41].

The model of Johnson and Blackburn [43] considers the following mechanisms for the transport:

(1) Diffusion of oxygen vacancies.

a) For a strongly hypostoichiometric fuel the concentration of the vacancies is large, and diffusion is determined by the gradient of the oxygen potential.

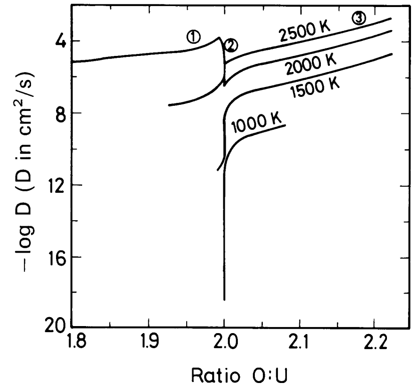
b) For a weakly hypostoichiometric fuel the concentration of the vacancies sinks, at a given temperature, below some critical value and becomes rate controlling for the diffusion.

(2) Diffusion of oxygen interstitials.

This diffusion is determined by the oxygen potential.

Fig. 1-83 presents the results from semiempirical model calculations of the self-diffusion coefficient of the oxygen in UO_{2+x} ($x > 0$ or $x < 0$) [43].

Fig. 1-83



Self-diffusion coefficient of the oxygen in UO_{2+x} as a function of the O:U ratio (model calculation) [43]. ① Activity dependent lattice diffusion, ② vacancy concentration dependent lattice diffusion, ③ activity dependent interstitial diffusion.

The Markin-Rand-Roberts model has met not only agreement [46] but also criticism. Leitnacker, Spear [47] express doubts concerning the CO_2/CO transport mechanism. Adamson, Aitken, and Rand [48] present an extensive comment thereon, and summarize all the positive arguments for their case.

A selection of further papers is found in [49 to 51, 90 to 94].

References for 1.1.7 on pp. 121/3

1.1.7.3 Redistribution of Uranium and Plutonium in a Mixed Oxide

Olander [52] and Breitung [53] present comprehensive discussions of the published models concerning the redistribution of fissile material in UO_2-PuO_2 mixed oxide fuels. It is explained by means of two basic mechanisms:

(1) thermodiffusion of plutonium [54 to 61] (Soret effect), and

(2) vapor transport (e.g., as UO_3): a) along cracks in the fuel (crack models), and b) in migrating pores (pore migration models).

In fuel melts, processes analogous to zone refining may also contribute to the redistribution of fissile material [55].

(1) Thermodiffusion Model

Bober, Schumacher [62, 63] reviewed what was known concerning the thermodiffusion mechanism. The Pu concentration profile that sets in is determined by means of a differential equation. The important physical quantities which appear in this equation are the self-diffusion coefficient of the plutonium in the fuel, D_{Pu}, and the "effective heat of transport" Q^{+}_{Pu}. The former quantity has been expressed as a function of the temperature as follows:

$D_{Pu} = 0.046 \exp(-418/RT)$ cm²/s [64], and
$D_{Pu} = 0.34 \exp(-464/RT)$ cm²/s [65] (R in $kJ \cdot mol^{-1} \cdot K^{-1}$).

In a more exact consideration, D_{Pu} must be replaced by the chemical interdiffusion coefficient $D_{Pu/U} = y\,D_{Pu} + (1-y)D_U$, where, as before, y is the mole fraction of Pu in the fissile material. According to [66] for $(U_{0.8}Pu_{0.2})O_2$ at 3.5% burnup $D_{Pu/U} = 1 \times 10^{-5} \exp(-255/RT)$ and at 10% burnup $D_{Pu/U} = 1 \times 10^{-5} \exp(-222/RT)$ cm²/s.

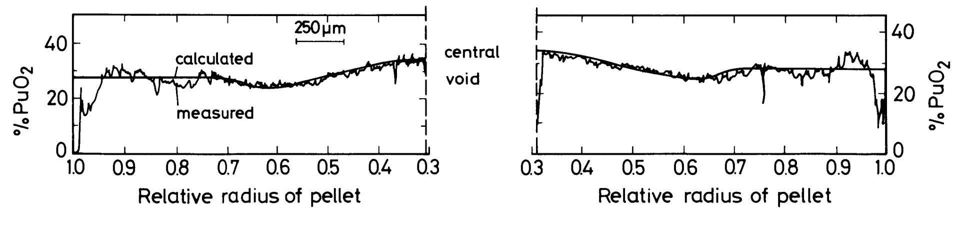
Rather different values have been reported in the literature for Q^{+}_{Pu}: −35 kJ/mol [61], −146 kJ/mol [65], and −240 kJ/mol [58]. Bober et al. [63] found by parameter fitting the value −126 kJ/mol for a fuel with an initial ratio O:U = 1.95. With this value the Pu distribution could be approximated well, except at the rim, as seen in **Fig. 1-84** [63].

There are two phenomena which indicate that another mechanism must be effective besides thermodiffusion:

a) For a weakly hypostoichiometric fuel (e.g., O:U = 1.99), more Pu is found in the center than is expected from the thermodiffusion model [67].

b) For a strongly hypostoichiometric fuel (e.g., O:U = 1.90), the demixing process is inverted, i.e., the uranium migrates to the center.

Fig. 1-84



Comparison between the measured and the calculated diametrical distribution of plutonium after 6.8% burnup (initial Pu valency: 3.67; Bober, Schumacher model [63]).

(2) Vapor Transport (Crack Models and Pore Migration Models)

In a hypostoichiometric mixed oxide fuel having O:M <1.96 uranium migrates from the hot to the cold zone, while for O:M >1.96 it is the plutonium that migrates in this direction. These facts have been explained in the model of Rand, Markin [4] on the basis of the partial pressures of UO_3 and PuO above the mixed oxide. This turning point corresponds to the O:M ratio at which the mixed oxide evaporates congruently, as also shown by Meyer et al. [69]. These authors [70, 71] construct a model which considers both radial cracks and migrating pores as transport routes. Olander [72 to 74], however, argues on geometrical reasons, that a uniform consideration of these two routes is not justified. These two authors disputed in [75] and [76] about the kinetics and the effectivities of these two transport routes.

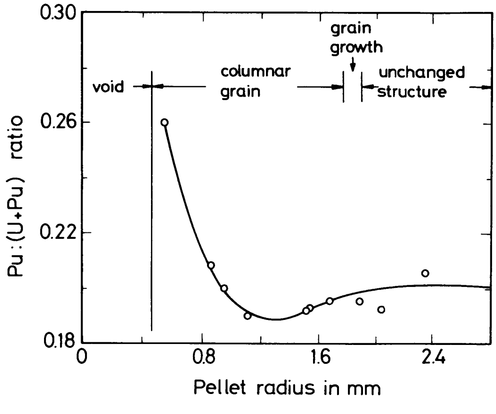
In order to let the redistribution process come to an end in the case of an inhibited equilibrium, most models assume a mechanism that inhibits the vapor transport. O'Boyle, Meyer [70, 71, 77, 78] regard the annealing of the cracks by means of sintering effects as such a mechanism. Experimental results could be interpreted well by means of the model of Blackburn, Johnson [43, 44], as seen in **Fig. 1-85**. The reason for the agreement between the measured data and the values calculated from the model is not the choice of the proper transport mechanism – diffusion of metal oxide vapors along cracks – but the observed diminution of the transport cross section with time.

Adamson, Aitken [79, 80] propose the back diffusion of Pu through the solid as a process that is counter current to the vapor diffusion along cracks.

Breitung [53] dismisses the crack model in principle, since one may not reckon with a lasting presence of these transport routes because of the restructuring of the fuel.

The basis for the model of Lackey et al. [81, 82] is the pore migration mechanism, according to which the evaporation of the fuel on the hotter side and its condensation on the colder side of a pore causes its migration in a temperature gradient. It is assumed herein that the

Fig. 1-85



Comparison between the measured and the calculated radial distribution of plutonium in irradiated UO_2-PuO_2 fuel (Blackburn-Johnson model, [43]). Initial state: density 87.2% of theoretical, O:(U + Pu) = 1.988. Irradiation: power 436 W/cm, burnup 4.7%. ○ measured, – calculated.

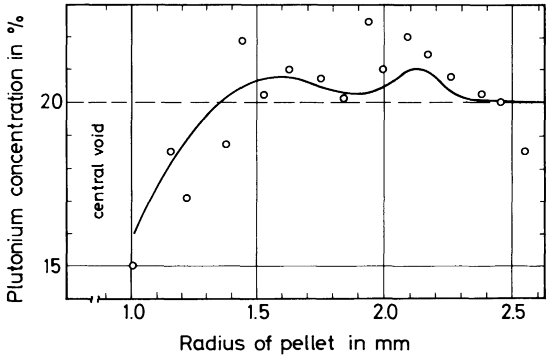
References for 1.1.7 on pp. 121/3

concentration of Pu behind the pore is identical with that in the gas phase. According to [53, 73, 74], however, the composition at this location is that which corresponds to the congruently melting mixed oxide.

The model of Breitung [53] is a pore migration model. The pore which migrates by means of an evaporation-condensation mechanism accumulates Pu at its hotter side. The ability of the pore to transport Pu in a fuel rod, that has given radial temperature and O : M profiles, depends on the radial position, and generally diminishes in the direction of the center of the fuel rod. Some of the Pu, which the pore took up at its starting place, is thus redeposited along its route, so that a zone relatively poor in Pu remains at its origin.

The pore migration mechanism, which is highly effective already at the beginning of the irradiation, has superimposed on it the thermodiffusion mechanism which gains more slowly in effectivity. A successful interpretation of the measured data is possible if both processes are considered, as shown in **Fig. 1-86**, for $(U_{0.8}Pu_{0.2})O_{1.90}$ as an example (data due to [68], calculation due to [53]).

Fig. 1-86



Comparison between the measured (Mouchnino [68]) and the calculated (Breitung [53]) demixing of uranium and plutonium in highly hypostoichiometric fuel $(U_{0.8}Pu_{0.2})O_{1.90}$.

A strong radial redistribution of fissile material caused by pore migration may be suppressed when one of the following conditions is applicable:

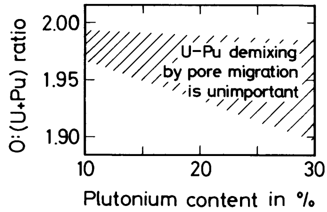
(1) A relationship exists between the O:M ratio and the Pu content that falls within the hatched area in **Fig. 1-87** [53].

(2) The density of the fuel is larger than 95% of the theoretical.

Concerning the operational conditions, it may be said that the contribution of thermodiffusion is small as long as the power level of the rod is kept below 350 W/cm.

At very high power levels of the fuel rod, where central melting occurs, a massive axial redistribution of fissile materials takes place [83]. Some peculiarities that are encountered are an unsymmetrical radial redistribution of fissile material [84] and a fine structure of the concentration of fissile material at the cold rim of the fuel, which depends on the burnup [85].

Fig. 1-87



The ranges of the O:(U + Pu) ratios and contents of plutonium, in which the U-Pu demixing by means of pore migration is unimportant [53].

References for 1.1.7:

[1] M. H. Rand, L. E. J. Roberts (Thermodyn. Proc. Symp., Vienna 1965 [1966], Vol. 1, p. 3). – [2] T. L. Markin, E. J. McIver (Plutonium 1965 Proc. 3rd Intern. Symp., London 1965 [1967], pp. 845/57). – [3] T. L. Markin (Chem. Eng. Progr. Symp. Ser. **63** No. 80 [1967] 43). – [4] M. H. Rand, T. L. Markin (Thermodyn. Nucl. Mater. Proc. Symp., Vienna 1967 [1968] pp. 637/50). – [5] E. A. Aitken, H. C. Brassfield, R. E. Fryxell (Thermodyn. Proc. Symp., Vienna 1965 [1966], Vol. 2, p. 435).

[6] L. M. Atlas, G. J. Schlehman (Thermodyn. Proc. Symp., Vienna 1965 [1966], Vol. 2, p. 407). – [7] A. Pattoret, J. Drowart, S. Smoes (Thermodyn. Nucl. Mater. Proc. Symp. Vienna 1967 [1968], p. 613). – [8] T. L. Markin, V. J. Wheeler, R. J. Bones (J. Inorg. Nucl. Chem. **30** [1968] 807). – [9] P. O. Perron (J. Nucl. Mater. **27** [1968] 237/8). – [10] R. Szwarc, R. E. Latta (J. Am. Ceram. Soc. **51** [1968] 264/8).

[11] T. L. Markin, R. J. Bones (AERE-R-4042 [1962] 1/38; N.S.A. **16** [1962] No. 22043). – [12] H. Holleck, H. Kleykamp (KFK-1181 [1970] 1/74). – [13] T. L. Markin, R. J. Bones, E. R. Gardner (AERE-R-4724 [1964]). – [14] M. H. Rand, D. T. Livey, P. Feschotte, H. Nowotny, K. Seifert, R. Ferro (At. Energy Rev. **4** Special Issue No. 1 [1966]). – [15] D. R. Messier (J. Am. Ceram. Soc. **51** [1968] 710/3).

[16] J. H. Davies, F. T. Ewart, R. G. Taylor (AERE-R-6264 [1969] 1/14). – [17] F. T. Ewart, J. H. Davies (J. Nucl. Mater. **41** [1971] 143/55). – [18] J. R. Findlay (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1974 [1975], pp. 31/9). – [19] C. E. Johnson, I. Johnson, P. E. Blackburn, C. E. Crouthamel (Reactor Technol. **15** [1972/73] 303/38). – [20] D. W. Shannon (Role of the Oxidation Rate on the Hydriding of Zirconium Alloys in Gas Atmospheres Containing Hydrogen, HW-76562-Rev. [1963] 1/29; N.S.A. **17** [1963] No. 36225).

[21] M. G. Adamson, E. A. Aitken, S. K. Evans, J. H. Davies (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1, pp. 59/72). – [22] F. Garzarolli, R. Manzel (High Burnup UO_2 Performance in LWR's, Trans. Am. Nucl. Soc. **31** [1979] 162/3). – [23] D. R. Olander (Fundamental Aspects of Nuclear Reactor Fuel Elements, TID-26711-P1 [1976] 160/6, 170/1). – [24] J. A. Christensen (BNWL-536 [1967] 1/107; N.S.A. **22** [1968] No. 11088). – [25] R. E. Fryxell, E. A. Aitken (J. Nucl. Mater. **30** [1969] 50/6).

[26] S. K. Evans, E. A. Aitken, C. N. Craig (J. Nucl. Mater. **30** [1969] 57/61). – [27] A. T. Jeffs (AECL-3690 [1970] 1/18). – [28] M. G. Adamson (J. Nucl. Mater. **38** [1971] 213/6). – [29] M. G. Adamson, R. F. A. Carney (AERE-R-6830 [1972] 1/27; C.A. **78** [1973] No. 65892). – [30] M. G. Adamson, R. F. A. Carney (AERE-R-6831 [1972], from [23]).

[31] E. A. Aitken (J. Nucl. Mater. **30** [1969] 62/73). – [32] E. A. Aitken, S. K. Evans (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970, p. 772; Nucl. Met. **17** II [1970] 772). – [33] E. A. Aitken, M. G. Adamson, S. K. Evans, T. E. Ludlow (GEAP-12254 [1971] 1/16; N.S.A. **26** [1972] No. 23212). – [34] S. K. Evans, E. A. Aitken (GEAP-14036 [1975]). – [35] M. Bober, C. Sari, G. Schumacher (J. Nucl. Mater. **39** [1971] 265/84).

[36] M. Bober, G. Schumacher (Advan. Nucl. Sci. Technol. **7** [1973] 121/81). – [37] M. Bober, G. Schumacher (KFK-1887 [1973] 1/20). – [38] M. Bober, S. Dorner, G. Schumacher (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 221/32). – [39] M. Bober, G. Schumacher (J. Nucl. Mater. **49** [1974] 322/4). – [40] C. Sari, G. Schumacher (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1, pp. 73/82).

[41] C. Sari, G. Schumacher (Reaktortagung, Düsseldorf 1976, Meeting Report, pp. 546/9). – [42] C. E. Johnson, I. Johnson, P. Blackburn, J. E. Battles, C. E. Crouthamel (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1974 [1975], pp. 1/30). – [43] P. E. Blackburn, C. E. Johnson (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1, pp. 17/33). – [44] P. E. Blackburn, C. E. Johnson (Trans. Am. Nucl. Soc. **17** [1973] 196/7). – [45] P. E. Blackburn (J. Nucl. Mater. **46** [1973] 244/52).

[46] D. R. Olander (J. Nucl. Mater. **47** [1973] 113/6). – [47] J. M. Leitnaker, K. E. Spear (J. Nucl. Mater. **45** [1972] 195/200). – [48] M. G. Adamson, E. A. Aitken, M. H. Rand (J. Nucl. Mater. **50** [1974] 217/22). – [49] M. Trotabas, F. de Keroulas, J. P. Gatesoupe (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 315/24). – [50] I. Johnson, C. E. Johnson, C. E. Crouthamel, C. A. Seils (J. Nucl. Mater. **48** [1973] 21/34).

[51] D. D. Marchant, H. K. Bowen (Mass Transp. Phenomena Ceram., Cleveland, Ohio, 1974; AED-Conf-74-247-006 [1974]; Mater. Sci. Res. **9** [1975]). – [52] D. R. Olander (TID-26711-P1 [1976] 166/71). – [53] W. Breitung (KFK-2240 [1976] 1/142). – [54] P. E. Novak, T. A. Lauritzen, R. Protsik, J. H. Davies, E. L. Zebroski (ANL-7120 [1965] 392/9). – [55] M. G. Chasanov, D. F. Fischer (ANL-7703 [1970] 1/30; N.S.A. **25** [1971] No. 16597).

[56] M. G. Adamson, E. A. Aitken (Trans. Am. Nucl. Soc. **14** [1971] 179/80). – [57] A. A. Bauer, H. Beisswenger, G. Giacchetti, E. Patrassi, G. Schumacher, R. Theisen (ANL-7120 [1965] 400/1). – [58] H. Beisswenger, M. Bober, G. Schumacher (Plutonium Reactor Fuel Proc. Symp., Brussels 1967, pp. 273/82; C.A. **68** [1968] No. 45285). – [59] K. Wirtz (J. Am. Chem. Soc. **90** [1968] 3098/9). – [60] M. Bober, C. Sari, G. Schumacher (Trans. Am. Nucl. Soc. **12** [1969] 603).

[61] N. G. Demas, R. Natesh, C. W. Maynard (Trans. Am. Nucl. Soc. **14** [1971] 593). – [62] M. Bober, G. Schumacher (KFK-1904 [1974] 1/24). – [63] M. Bober, G. Schumacher (KFK-2200 [1975] 149/91). – [64] F. Schmitz, R. Lindner (Radiochim. Acta **1** [1973] 218). – [65] M. Bober, G. Schumacher, D. Geithoff (J. Nucl. Mater. **47** [1973] 187/97).

[66] E. M. Butler, R. O. Meyer (J. Nucl. Mater. **47** [1973] 229/40). – [67] M. Bober, H. Kleykamp, G. Schumacher (Nucl. Technol. **26** [1975] 172/82). – [68] M. Mouchnino (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 325/35). – [69] R. O. Meyer, D. R. O'Boyle, E. M. Butler (J. Nucl. Mater. **47** [1973] 265/7). – [70] R. O. Meyer, E. M. Butler, D. R. O'Boyle (Trans. Am. Nucl. Soc. **15** [1972] 216/7).

[71] R. O. Meyer, E. M. Butler, D. R. O'Boyle (ANL-7929 [1972] 1/32; N.S.A. **26** [1972] No. 48312). – [72] D. R. Olander (J. Nucl. Mater. **47** [1973] 251/4). – [73] D. R. Olander (J. Nucl. Mater. **49** [1973/74] 21/34). – [74] D. R. Olander (J. Nucl. Mater. **49** [1973/74] 35/44). – [75] R. O. Meyer (J. Nucl. Mater. **52** [1974] 326/8).

[76] D. R. Olander (J. Nucl. Mater. **52** [1974] 329/30). – [77] D. R. O'Boyle, R. O. Meyer (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 41/66). – [78] R. O. Meyer (J. Nucl. Mater. **50** [1974] 11/24). – [79] M. G. Adamson, E. A. Aitken (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 225/35). – [80] E. A. Aitken, S. K. Evans, M. G. Adamson, T. E. Ludlow (GEAP-12229 [1971] 1/23).

[81] W. J. Lackey, F. J. Homan, A. R. Olsen (CONF-720420-3 [1971] 1/62; ORNL-RM-3762 [1972]). – [82] W. J. Lackey, F. J. Homan, A. R. Olsen (Nucl. Technol. **16** [1972] 120/41). – [83] G. Schumacher (INR-4/70-27 [1970] 1/102; NP-18556 [1970] 1/102; N.S.A. **25** [1971] No. 8138). – [84] D. Geithoff (KFK-1887 [1973] 39/56). – [85] P. Weimar, H. Kleykamp (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 1, pp. 550/3).

[86] D. C. Hata, D. F. Washburn, R. A. Karnesky, R. B. Baker (Trans. Am. Nucl. Soc. **24** [1976] 149/50). – [87] G. R. Chilton, J. Edwards (Intern. Symp. Thermodyn. Nucl. Mater., Jülich 1979, Vol. 1, pp. 357/68; IAEA-SM-236-43-Vol. 1 [1980] 357/68; INKA-CONF-79-003-28[1979] 1/18; INIS Atomindex **10** [1979] No. 468712). – [88] E. Aukrust, T. Førland, K. Hagemark (Thermodyn. Nucl. Mater. Proc. Symp., Vienna 1962, p. 713). – [89] R. E. Woodley (HEDL-SA-1532 [1978] 1/16; CONF-7810143-1 [1978] 1/16; INIS Atomindex **10** [1979] No. 461787). – [90] A. Moreno, C. Sari (EUR-5971 [1978] 1/23; INIS Atomindex **10** [1979] No. 423798).

[91] L. A. Lawrence (HEDL-SA-1749-FP [1979] 1/21; CONF-790602-75 [1979] 1/21; INIS Atomindex **11** [1980] No. 500292). – [92] L. Lawrence, R. D. Leggett (HEDL-SA-1760-FP [1979] 1/21). – [93] F. T. Ewart, C. M. Mari, S. Fourcaudot, H. Matzke, F. Toci (Intern. Symp. Thermodyn. Nucl. Mater., Jülich 1979, Vol. 1, pp. 369/83; IAEA-SM-236-07-Vol. 1 [1980] 369/83; INKA-CONF-79-003-006 [1979] 1/5; INIS Atomindex **10** [1979] No. 460459). – [94] R. Ducroux, M. Fromont, A. Pattoret (Intern. Symp. Thermodyn. Nucl. Mater., Jülich 1979, Vol. 1, pp. 385/404; IAEA-SM-236-89-Vol. 1 [1980] 385/404).

1.1.8 Interaction with the Cladding

General References:

C. E. Johnson, I. Johnson, P. E. Blackburn, C. E. Crouthamel, Effects of Oxygen Concentration on Properties of Fast Reactor Mixed-Oxide Fuel, Reactor Technol. **15** [1973] 303/38 [90 Refs.].

R. W. Ohse, M. Schlechter, The Role of Caesium in Chemical Interaction of Austenitic Steels with Uranium-Plutonium Oxide Fuels, Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1974 [1975], pp. 299/314 [105 Refs.].

F. Thümmler, H. Kleykamp, P. Hofmann, Der Einfluß chemischer Faktoren auf das Bestrahlungsverhalten von Oxidbrennstoff, Meeting: Charakterisierung und Qualitätskontrolle von Kernbrennstoffen, Karlsruhe 1978, J. Nucl. Mater. **81** [1979] 215/30 [37 Refs.].

F. Garzarolli, R. von Jan, H. Stehle, The Main Causes of Fuel Element Failures in Water Cooled Power Reactors, At. Energy Rev. **17** Special Issue No. 1 [1979] [130 Refs.].

S. Aas, Mechanical Interaction between Fuel and Cladding, Nucl. Eng. Design **21** [1972] 237/53 [59 Refs.].

B. Cox, J. C. Wood, Iodine Induced Cracking of Zircaloy Fuel Cladding, A Review, in: C. S. Tedmon, Corrosion Problems in Energy Conversion and Generation, Electrochem. Soc., Baltimore 1974, pp. 257/321 [48 Refs.].

D. H. Locke, Pellet Cladding Interaction for Water Reactors: Experience, Testing, and Evaluation. Summary Report on the Specialist Meeting, Vienna, June 27th to July 1st, 1977, At. Energy Rev. **15** [1977] 779/92.

D. Cubicciotti, R. L. Jones, B. C. Syrett, Stress Corrosion Cracking of Zircaloys, EPRI-NP-1329 [1980] 1/161; INIS Atomindex **11** [1980] No. 543474.

H. Stehle, R. von Jan, H. Knaab, LWR Fuel Behavior During Operational and Overpower Transients, ANS-ENS Topical Meeting on Reactor Safety Aspects of Fuel Behavior, Sun Valley, ID, August 2nd to 6th, 1981.

1.1.8.1 Interior Corrosion in Zircaloy Cladding

The interior surface of Zircaloy cladding tubes that contain oxidic nuclear fuel is, in principle, oxidized to form a ZrO_2 layer. At normal LWR operational temperatures the temperature of the cladding is so low, that no appreciable diffusion of oxygen into it occurs.

In no case ZrO_2 layers thicker than ca. 12 μm were found, and this value is attained only at a burnup of above 40 MWd/kg(U) [1]. In the case of a UO_2 fuel in BWR fuel rods (Zircaloy-2 cladding), a thickness of the oxide only slightly more than 5 μm was found [1, 2] at a burnup of about 30 MWd/kg(U). In the case of PWR fuel rods (Zircaloy-4 cladding) this value was attained only at a burnup of ca. 40 MWd/kg(U) [1]. A mixed oxide fuel (UO_2-PuO_2 with 6.6% PuO_2 content) in Zircaloy cladding follows this behavior too [3, 4]. For information on the chemical interaction between UO_2-PuO_2 with Zircaloy see [127].

As the burnup increases and at elevated fuel rod power levels a multilayered structure is built up. Fuel particles often stick to the ZrO_2 layer of the cladding by means of special layers. Bazin et al. [5, 6] found an intermediate layer composed of Zr, U, Cs, and O. For the individual elements the following average concentrations (in wt%) were determined by microanalysis: Zr 45%, U 37%, Cs 4%, O 20%. Cubicciotti et al. [7 to 9] (see also [124]) used a scanning electron microscope and an energy dispersive X-ray analyzer to examine the depositions on the interior surface of the cladding. Three kinds of deposits on the ZrO_2 basis layer could be observed phenomenologically:

(1) sharply defined straight bands at the locations of cracks in the pellets,
(2) massive deposits at the contact points with the pellets, and
(3) circular deposits distributed randomly.

The compounds Cs_2UO_4, Cs_2Te, and CsI could be identified with varying degrees of certainty. The deposits of type (2) were demonstrated to contain only Cs and U, forming a ceramic double layer with a higher U content at the fuel side. Particles of UO_2 sticking to the cladding appear to be cemented to it by means of the same material. Cubicciotti, Sanecki [9] propose Cs_2O (m.p. ca. 730 K) as the transporting species for the major part of the deposit, since Johnson [10] found only Cs and Cs_2O on vaporization of Cs_2UO_4 (cf. "Uran" Erg.-Bd. C3, p. 52).

1.1.8.2 Interior Corrosion in Steel Cladding

The system, consisting of oxidic fuel and austenitic steel (e.g., DIN 1.4970, AISI 316), is thermodynamically stable, as was confirmed by isothermal out-of-pile compatibility experiments [11, 12]. The fission products and the released oxygen are responsible for the interior corrosion of the cladding under irradiation.

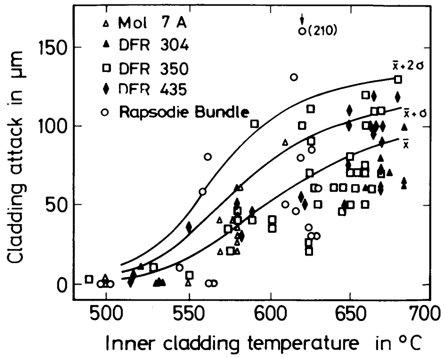
Two kinds of attack on the cladding were observed [11 to 17]:

(1) homogeneous attack, causing uniform oxidation at low temperatures (<700 °C), and
(2) attack at grain boundaries at higher temperatures, caused by oxygen and fission products.

The main factors for the interior corrosion of the cladding are the oxygen potential in the fuel rod and the temperature of the cladding, while, e.g., the composition of the cladding and the state of the material have only a minor effect [18, 19].

According to Thümmler [16] (see **Fig. 1-88**) reactions with the steel cladding start at 500 °C and reach saturation between 650 and 700 °C, yielding reaction zones of maximal

Fig. 1-88



Statistical evaluation of the maximal depth of attack of the austenitic steel cladding of BWR fuel rods as a function of the temperature [16].

thickness of about 150 µm [11, 12, 20]. At intermediate and low temperatures the corrosion of the cladding follows a parabolic time dependence, but at higher temperatures rather a linear one [11].

Both post-irradiation studies and out-of-pile experiments were conducted in order to find which fission products are responsible for the attack on the cladding (Table 1/20, p. 126, [16]). It was found, in fact, that only the elements Cs(Rb), I(Br), and Te(Se) are reactive towards austenitic steel (see also Ohse, Schlechter [21, 22] and Aubert et al. [23]).

A recent publication by Bradbury et al. [17] deals with the corrosion mechanism of the interior surface of the cladding of fast breeder fuel rods in terms of models. The corrosion is described as a series of numerous individual steps, and the following aspects, among others, are considered. The oxide layer consists essentially of Cr_2O_3, so that the metal matrix layer directly beneath it and the grain boundaries of lower layers are depleted in chromium. Spinel phases are therefore formed at the interface between the Cr_2O_3 layer and the metal [24], which are decomposed by the effects of Cs and oxygen [25 to 27].

Two processes are considered for the corrosion of the cladding by caesium:

(1) Direct attack on that part of the surface, that is not yet covered by an oxide layer, with the formation of caesium chromates [28]. Although caesium seems to play the decisive role, the cooperative effects of tellurium [29] or iodine [17] as corrosive fission products cannot be disregarded.

(2) A corrosion mechanism that depends on the depletion of chromium in the steel. When this depletion is sufficiently advanced the austenite turns into the ferritic state, in which (a) the chromium diffusion is enhanced, and (b) the solubility of the carbon is lower. Chromium carbides (e.g., $Cr_{23}C_6$) may form at the grain boundaries, in particular in non-stabilized steels. When $Cr_{23}C_6$ reacts with caesium and oxygen Cs_2CrO_4 is formed, carbon is released, and $Cr_{23}C_6$ may be formed anew. The carbon thus acts as a catalyst for the grain boundary corrosion.

Table 1/20
Fission Products that Reduce the Compatibility between the Cladding and a Mixed Oxide Fuel [16].

Fission products or fission product compounds examined:
Cs, Rb, I, Br, Te, Se, Ru, Rh, Pd, Sb, Sn, In, Cd, Mo,
BaO, SrO, ZrO_2, CeO_2, Nd_2O_3, MoO_3

Fission products considered dangerous (20% burnup)

	Cs	I	Te
reactions:	at O:M >2.00	at O:M ≷2.00 stronger than at O:M >2.00	depends little on O:M
formation of:	Cs chromates; decomposition of austenite into ferrite and Ni-martensite	Cr iodide (ferrite, martensite)	Cr tellurides, Ni tellurides
attack on cladding:	preferentially along grain boundaries, depth 120 µm at 700 °C	preferentially along grain boundaries, partly holewise	at <700 °C areawise, at >700 °C at grain boundaries

1.1.8.3 Cooperative Mechanical and Chemical Interactions

A special form of the interaction between the fuel and the cladding may under certain circumstances occur in fuel rods with Zircaloy cladding. This is stress corrosion cracking (SCC), in which fission products act as agressive media, while simultaneously a mechanical stress, caused by the different thermal expansions of fuel and cladding, is effective. This type of interaction is designated as PCI (pellet clad interaction).

Garzarolli et al. [30] survey the PCI phenomenon. In an irradiation program ("High Performance UO_2 Program") in 1964 [31], small cracks, like pinholes, were found in the cladding, in the neighborhood of which high local concentrations of iodine are present. A connection with SCC became evident, when Rosenbaum et al. [32, 33] showed that such an iodine-induced process occurs in Zircaloy even outside the reactor.

Mechanical Interaction between Fuel and Cladding

In numerous earlier studies the mechanical aspect of PCI was over-emphasized or even considered exclusively. Aas [34] reviewed the mechanical aspects in 1972, while the various observations and analyses have been published in [34 to 83, 128]. The following phenomena are discussed in detail:

(1) Axial deformation of the cladding, including its dependence on the length, form, and density of the fuel pellets [34, 39, 43 to 45, 50, 56].

(2) Radial deformation of the cladding by means of
- thermal expansion of the fuel [45, 52, 57 to 59],
- opening of cracks in the pellet surface [60 to 62], and
- fuel swelling [59].

(3) Extension caused by so-called "ridges" in the cladding [61, 63 to 65].

(4) The "ratchetting effect": the repeated irreversible "dragging" of the cladding along with the fuel column during changes in the power level [46, 48, 66].

An interaction theory based on the friction between the fuel and the cladding was constructed by Gittus [67 to 72]. The mechanical interaction between the fuel and the cladding is treated by many computer models (see [73 to 81]). Simulation experiments with fuel rods outside the reactor are described in [82, 83].

For the mechanical interaction between UO_2-PuO_2 and the steel cladding of fast breeder reactor fuel rods, [84 to 88, 129] should be consulted.

Stress Corrosion Cracking (SCC) Arising from Pellet/Clad Interaction (PCI)

Some knowledge about the mechanism of the PCI phenomenon was obtained in laboratory studies, but mainly it was obtained in so-called "ramp tests" in the reactor. A clear distinction between power ramps and power cycles must be made in this connection, since the latter do not lead to the PCI phenomenon. According to Holzer, Stehle [89, 90], a power ramp is defined as the first rise of the local rod power above the previous steady state, while a power cycle is defined as repeated changes without exceeding the previously reached limits of the power level, to which the rod had been conditioned. The latter case occurs in the typical day/night cycle of a power station.

Garzarolli et al. [30] discuss in detail the parameters of the reactor operation, on which the probability of a PCI effect depends:

(1) burnup,
(2) upper level of the rod power, after the power ramp,
(3) ramp height, i.e., the power jump caused by the ramp,
(4) rate of the power change, and
(5) duration of the higher power level.

PCI defects have been observed in all types of light water reactors [31, 90] as well as in heavy water/natural uranium reactors [91].

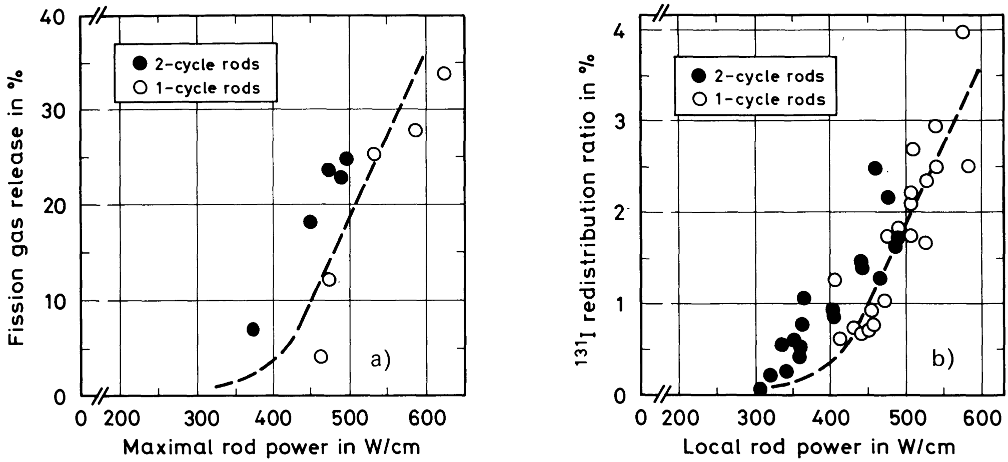
Ramp tests with the combinations "irradiated cladding-new fuel" [31, 92] and "new cladding-irradiated fuel" [93], as well as many other irradiation experiments (e.g., [52, 94 to 96]) showed that the PCI is connected with SCC by means of fission products (see also [6, 97, 98]).

Garzarolli et al. [99], Fuhrman et al. [100], and Cubicciotti, Sanecki [9] showed that the PCI phenomenon is evidently accompanied by an increase in the release of fission gas. An enhanced redistribution of volatile fission products (Cs, I, Te, etc.) occurs simultaneously. This is also evident from the results shown in **Fig. 1-89**a, b, p. 128, for fission gas and ^{131}I behavior according to Vogl et al. [130, 131] and Sontheimer et al. [132].

The following substances may produce SCC:

(1) iodine or iodides (ZrI_4) [101],
(2) cadmium (low fission yield) [102],
(3) caesium in the liquid state if it has a low oxygen content and is contaminated with iron [103, 104].

Fig. 1-89



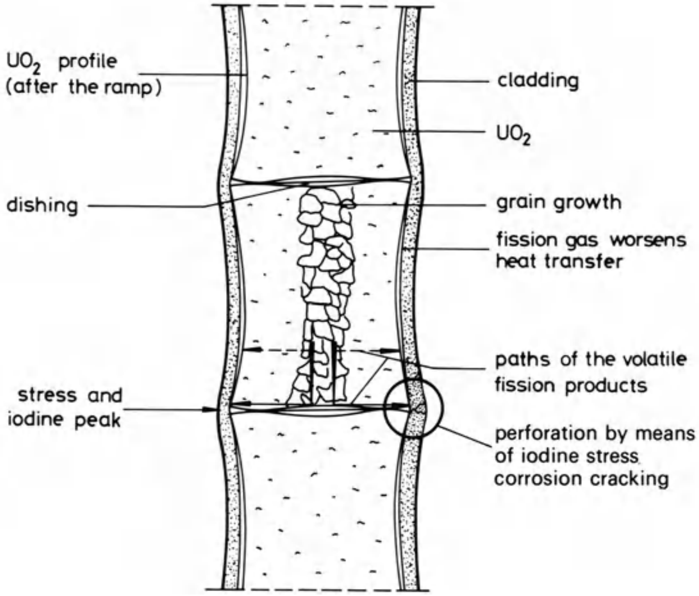
Results of ramp experiments. a) Fission gas release due to power ramping [131, 132]. b) Ratio of ^{131}I concentration at position of pellet interface to pellet average after power ramping [131, 132].

Further potential agents are: caesium compounds, Te, Se, Sb, As, Ag, Cd, In, Sn, Pb. Iodine and iodine compounds are considered nowadays as the materials which are definitely responsible for the chemical aspects of the PCI phenomenon. The iodine SCC of Zircaloy has been intensively studied during recent years (see, e.g., [9, 99, 100, 105 to 114]). Cox, Wood reviewed in 1974 what was then known about this subject [106]. In 1980 a review was given by Cubicciotti et al. [133].

According to present day knowledge, the PCI phenomenon may be described as follows (**Fig. 1-90**): The power ramp is accompanied by a rise of the central temperature of the fuel, above its stationary value. The diabolo form of the fuel pellet, which is due to the thermal expansion, becomes even more emphasized because of this circumstance. Tensile stresses in the cladding are thereby caused, which are enhanced at the pellet/pellet interfaces and perhaps also at locations where cracks occur in the pellets. A transient release of fission gases and of volatile fission products accompanies the temperature increase, in particular when grain growth (dependent on the temperature level) occurs at the same time. The release of the volatile fission products takes place preferentially at the pellet/pellet interfaces or through radial cracks. The transient release of the fission gases decreases the heat transfer between pellet and cladding. This may lead to an increased central temperature and therefore to thermal feed back [112] which further increases the UO_2 temperature.

The SCC leads to a finely branched perforation, eventually with limited ductile rupture or deformation lines (X shaped markings) on the exterior surface. Fission products break through this "primary defect" (as does any filling gas, such as He, the fuel rod may contain), and water vapor finds its way in. Thereby "secondary defects" (hydriding failures) are caused, sometimes at locations far from the primary PCI defect.

Fig. 1-90



Schematic description of the PCI phenomenon in LWR fuel rods [144].

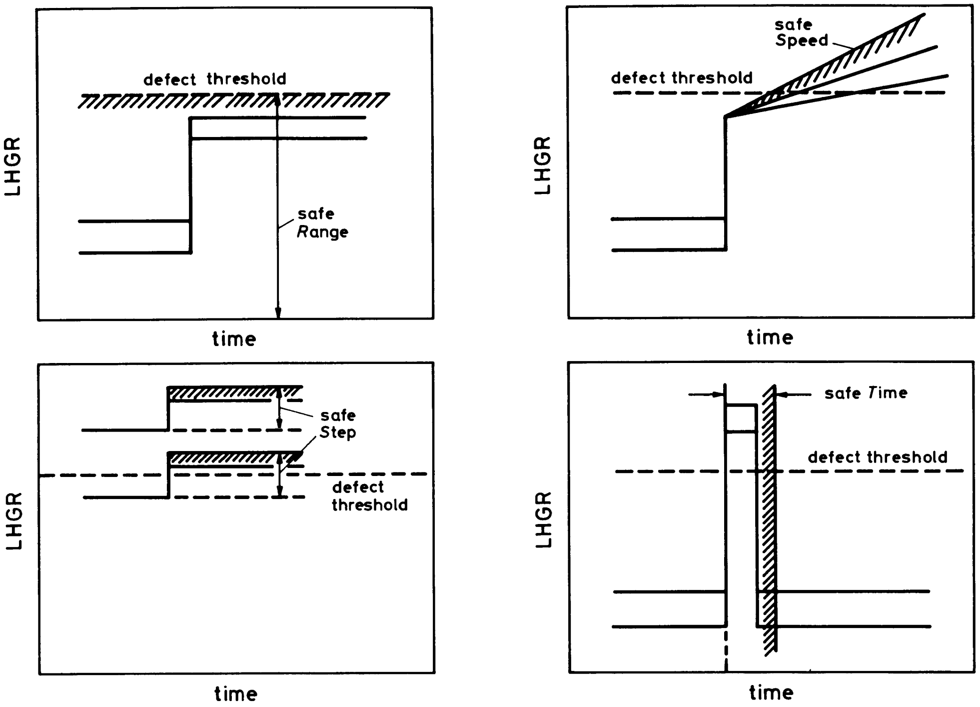
SCC takes place only when the critical fission product concentration and the critical tensile stress are exceeded simultaneously and for a certain time interval.

An experimental strategy which converts the SCC criteria into operational parameters by evaluating "safe values" for the overpower range, overpower step, speed, and time, respectively, was proposed by Vogl et al. [131, 134]. The meaning of this so-called RSST approach (Range, Step, Speed, Time) is outlined in **Fig. 1-91**, p. 130 [131]. The defect threshold separates the range where a possibility of PCI failure exists from the "safe range" where at least one of the requirements to create SCC (stress, strain, iodine concentration) is not fulfilled.

Extensive reviews of all the activities in this field, summaries of what is known about the PCI phenomenon, and detailed discussions were the result of international meetings between 1977 and 1981:

(1) ANS Topical Meeting on Water Reactor Fuel Performance, St. Charles, Illinois, USA, 1977 [89, 100, 115 to 126],
(2) IAEA Specialists Meeting on PCI for Water Reactors, Vienna, June 27 to July 1, 1977, with the following sessions:

Fig. 1-91



RSST approach in the ramp test strategies [131, 134]. (LHGR = linear heat generation rate).

(a) PCI failure experience and observation
(b) Mechanisms of PCI failure
(c) Cladding and fuel characteristics with respect to PCI behavior
(d) Fuel pin modelling with respect to PCI behavior
(e) Ways of avoiding PCI defects and general discussion.

A summary report of this meeting was given by Locke [135].

(3) KTG/ENS/JRC Meeting on Ramping and Load Following Behavior of Reactor Fuel, Petten, Holland, 30.11.–1.12.1978 (KTG = Kerntechnische Gesellschaft e.V.; ENS = European Nuclear Society; JRC = Joint Research Centre of the Commission of the European Communities) [90, 136 to 143].

(4) IAEA Specialists Meeting on Power Ramping and Power Cycling of Water Reactor Fuel and its Significance to Fuel Rod Behavior, Arles, France, May 1979.

(5) IAEA Specialists Meeting on Water Reactor Fuel Element Performance Computer Modelling, Blackpool, England, March 16th to 21st, 1980, with the following sessions:

(a) Input data and assumptions
(b) Fuel element performance computer models
(c) Comparison of predictions with fuel element performance data

(d) Probabilistic modelling and code applications

(6) IAEA Specialists Meeting on Pellet-Cladding Interaction in Water Reactors, Risø, Denmark, Sept. 22nd to 26th, 1980 [145] with the following sessions:

(a) PCI experience

(b) Effect on PCI of operational strategies and alternative fuel designs

(c) Mechanistic studies

(d) PCI failure criteria.

(7) Enlarged Halden Program Group Meetings, e.g., Lillehammer, Norway, June 1st to 6th, 1980, and Fredrikstad and Hankø, June 14th to 19th, 1981. These meetings are annual meetings where the results and their evaluation as well as modelling work of the participants of the Halden Program are presented and discussed. These programs are currently being continued.

For further contributions to this item at other conferences see [146 to 150].

References for 1.1.8:

[1] R. Manzel, W. Dörr (Am. Ceram. Soc. Bull. **59** [1980] 601/3, 616). – [2] F. H. Megerth, C. P. Ruiz, U. E. Wolf (GEAP-10371 [1971] 1/230). – [3] W. R. Smalley (WCAP-3385-56-Pt. I [1971] 1/122; N.S.A. **26** [1972] No. 35438). – [4] W. R. Smalley (WCAP-3385-57 [1974] 1/177; N.S.A. **30** [1974] No. 25824). – [5] J. Bazin, J. J. Jouan, N. Vignesoult (Trans. Am. Nucl. Soc. **20** [1975] 235/7).

[6] J. Bazin, J. Jouan, N. Vignesoult (Nucl. Energy Maturity Proc. Eur. Nucl. Conf., Paris 1975 [1976], Vol. 3, Pt. I, pp. 123/39). – [7] D. Cubicciotti, J. E. Sanecki, R. V. Strain, S. Greenberg, L. A. Neimark, C. E. Johnson (Top. Rept. Electr. Power Res. Inst. Proj. RP-455-1 [1976]). – [8] J. T. A. Roberts, E. Smith, N. Fuhrman, D. Cubicciotti (Nucl. Technol. **35** [1977] 131). – [9] D. Cubicciotti, J. E. Sanecki (J. Nucl. Mater. **78** [1978] 96/111). – [10] I. Johnson (ANL-75-48 [1976] p. 18).

[11] O. Götzmann, P. Hofmann, F. Thümmler (J. Nucl. Mater. **52** [1974] 33/50). – [12] O. Götzmann, P. Hofmann (KFK-1803 [1973] 1/29; N.S.A. **28** [1973] No. 20403). – [13] C. E. Johnson, I. Johnson, P. E. Blackburn, C. E. Crouthamel (Reactor Technol. **15** [1973] 303/38). – [14] C. E. Johnson, I. Johnson, P. E. Blackburn, J. E. Battles, C. E. Crouthamel (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1974 [1975], pp. 1/30). – [15] W. Batey, K. Q. Bagley (J. Brit. Nucl. Eng. Soc. **13** [1974] 49/61).

[16] F. Thümmler, H. Kleykamp, P. Hofmann (J. Nucl. Mater. **81** [1979] 215/30). – [17] M. H. Bradbury, S. Pickering, W. H. Whitlow (J. Nucl. Mater. **78** [1978] 272/80). – [18] O. Götzmann, P. Hofmann (J. Nucl. Mater. **59** [1976] 192/8). – [19] L. Schäfer, P. Hofmann (J. Nucl. Mater. **67** [1977] 88/96). – [20] P. Hofmann (KFK-1831 [1974] 1/116 [219 Figs.]).

[21] R. W. Ohse, M. Schlechter (J. Nucl. Mater. **78** [1978] 299/314). – [22] R. W. Ohse, M. Schlechter (Reaktortagung, Berlin 1974, Meeting Report, pp. 368/71). – [23] M. Aubert, D. Calais, R. Le Benze (J. Nucl. Mater. **60** [1976] 279/90). – [24] O. Götzmann, P. Hofmann (KFK-1619 [1972] 1/173; N.S.A. **27** [1975] No. 11522). – [25] P. S. Maiya, D. E. Busch (Met. Trans. A **6** [1975] 409/15; C.A. **82** [1975] No. 174216).

[26] J. E. Antill, K. A. Peakall, E. F. Smart (AERE-R-7797 [1974]). – [27] J. E. Antill, K. A. Peakall, E. F. Smart (J. Nucl. Mater. **56** [1975] 47/60; C.A. **83** [1975] No. 86763). – [28] C. T. Walker (J. Nucl. Mater. **74** [1978] 358/62). – [29] D. Calais, M. Conte, F. d'Keroulas, R. Le Benze (J. Nucl. Mater. **78** [1978] 287/97). – [30] F. Garzarolli, R. von Jan, H. Stehle (At. Energy Rev. **17** No. 1 [1979]).

[31] J. H. Davies, H. S. Rosenbaum, J. S. Armijo, R. A. Proebstle, T. C. Rowland, J. R. Thompson, E. L. Esch, G. Romeo, D. R. Rutkin (NEDO-21551 [1977]). – [32] H. S. Rosenbaum (Electrochem. Technol. **4** [1966] 153/6). – [33] H. S. Rosenbaum, J. H. Davies, J. Q. Pon (GEAP-5100-5 [1966] 1/43; N.S.A. **21** [1967] No. 34250). – [34] S. Aas (Nucl.

Eng. Design **21** [1972] 237/53). – [35] A. S. Bain, J. A. L. Robertson, A. Ridal (AECL-1192 [1961] 1/58; N.S.A. **15** [1961] No. 17365).

[36] A. Ridal, A. S. Bain, J. A. L. Robertson (AECL-1199 [1961] 1/21; N.S.A. **15** [1961] No. 17366). – [37] M. F. Lyons, F. A. Comprelli, V. A. Hazel, H. E. Townsend (GEAP-3739 [1961] 1/94). – [38] M. J. F. Notley (AECL-1598 [1962] 1/25). – [39] M. J. F. Notley, W. D. C. Fitzgimmons (AECL-1664 [1962] 1/18). – [40] R. D. MacDonald, A. S. Bain (AECL-1685 [1962] 1/32).

[41] V. E. Hazel, M. F. Lyons, F. A. Comprelli (GEAP-4088 [1962] 1/42; N.S.A. **18** [1964] No. 7288). – [42] M. J. F. Notley, H. Harvey (AECL-1846 [1962] 1/36). – [43] M. J. F. Notley, A. S. Bain, J. A. L. Robertson (AECL-2143 [1964] 1/25). – [44] A. S. Bain (AECL-2276 [1965] 1/45; N.S.A. **20** [1966] No. 2415). – [45] A. S. Bain (AECL-2587 [1966] 1/65; N.S.A. **21** [1967] No. 5013).

[46] E. Duncombe, J. E. Meyer, W. A. Coffman (WAPD-TM-583 [1966] 1/93). – [47] J. E. McCauley, R. C. Daniel, H. B. Meieran, J. T. Engel (WAPD-TM-595 [1966] 1/105). – [48] J. T. Engel, H. B. Meieran (WAPD-TM-631 [1967] 1/151). – [49] G. Kjaerheim, E. Rolstad (HPR-80 [1967] 1/85). – [50] A. T. Jeffs (AECL-2674 [1967] 1/29).

[51] G. Kjaerheim, E. Rolstad (HPR-107 [1969] 1/36). – [52] H. Mogard, S. Aas, S. Jungkrans (Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 10, pp. 273/87). – [53] G. Testa, F. Doria, P. Grillo, A. Nobili, P. L. Rotoloni (Nucl. Appl. Technol. **7** [1969] 550/60; C.A. **72** [1970] No. 27403). – [54] G. Kjaerheim, E. Rolstad (Nucl. Appl. Technol. **7** [1969] 347/60). – [55] C. N. Spalaris (Nucl. Sci. Eng. **17** [1963] 381/91).

[56] R. R. Asomoto, K. J. Perry, E. L. Zebroski (GEAP-5284 [1966] 1/49). – [57] J. C. Janvier, B. de Bernardy de Sigoyer, R. Delmas (CEA-R-3358 [1967] 1/78; N.S.A. **22** [1968] No. 26092). – [58] A. S. Bain (AECL-1827 [1963] 1/40). – [59] M. F. Lyons, R. F. Boyle, J. H. Davies, V. E. Hazel, T. C. Rowland (Nucl. Eng. Design **21** [1972] 167/99). – [60] J. H. Gittus, D. A. Howe, H. Hughes (Nucl. Appl. Technol. **9** [1970] 40/6).

[61] J. H. Gittus (TRG-Report-1547 [1967] 1/24; N.S.A. **22** [1968] No. 50844). – [62] V. E. Hazel, O. E. Wolf (GEAP-5404-Sect. 9 [1966]). – [63] J. Veeder (AECL-2660 [1967] 1/21). – [64] H. J. Gittus, H. Hughes (TRG-MEMO-3986-S [1967]). – [65] M. J. F. Notley (Nucl. Appl. Technol. **9** [1970] 195/204).

[66] A. S. Bain, J. Christie, A. R. Daniel (AECL-1895 [1964] 1/70; CRFD-1179 [1964]; N.S.A. **18** [1964] No. 22523). – [67] J. H. Gittus (TRG-2757-S [1976] 1/42; INIS-Atomindex **7** [1976] No. 263401). – [68] J. H. Gittus (Nucl. Eng. Design **18** [1972] 69/82). – [69] J. H. Gittus (Nucl. Eng. Design **30** [1974] 293/5). – [70] J. H. Gittus (Wear **30** [1974] 393/4).

[71] J. H. Gittus (Phil. Mag. [8] **31** [1975] 317/29). – [72] J. H. Gittus (Nucl. Eng. Design **32** [1975] 358/62). – [73] B. M. Ma (Nucl. Eng. Design **7** [1968] 181/93). – [74] J. H. Gittus (Nucl. Eng. Design **28** [1974] 252/6). – [75] S. Levy, J. P. D. Wilkinson (2nd Intern. Conf. Struct. Mech. React. Technol., Berlin 1973, Paper D1/5).

[76] Y. R. Rashid (Nucl. Eng. Design **29** [1974] 22/32). – [77] P. Royl, A. Watanabe, A. Agrawal (2nd Intern. Conf. Struct. Mech. React. Technol., Berlin 1973, Paper C3/1). – [78] T. R. Hsu, A. W. M. Bertels, S. Banerjee, W. C. Harrison (AECL-5233 [1976] 1/67; INIS Atomindex **8** [1977] No. 299641). – [79] J. J. M. Too, T. R. Hsu, A. W. M. Bertels (Fuel Elem. Anal. Sel. Papers Natl. Congr. Pressure Vessels Piping, San Francisco 1975, pp. 23/35; C.A. **87** [1977] No. 30664). – [80] J. J. Thompson (EUR-4820-Vol. 2-Pt. C [1972] 195/208).

[81] F. Wunderlich, I. Distler, H.-P. Fuchs, W. Hering (Reaktortagung, Mannheim 1977, Meeting Report, pp. 469/72). – [82] B. J. Wrona, J. T. A. Roberts (Trans. Am. Nucl. Soc. **16** [1973] 77). – [83] J. F. Whatham (Nucl. Eng. Design **26** [1974] 423/31). – [84] C. M. Cox, F. J. Homan (Nucl. Appl. Technol. **9** [1970] 317/25). – [85] B. F. Rubin, T. J. Black, W. K. Appleby, J. D. Stephen, R. F. Hilbert (Nucl. Technol. **16** [1972] 89/99).

[86] I. Johnson, C. E. Johnson (Trans. Am. Nucl. Soc. **17** [1973] 194/5). – [87] D. Brucklacher, W. Dienst (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, p. 147/61). – [88] H. Plitz, G. Senski (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 2, p. 47/65; C.A. **82** [1975] No. 36224). – [89] R. Holzer, D. Knödler, H. Stehle (Pellet Clad Interaction: Experience, Testing and Evaluation, A KWU Review, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977). – [90] R. Holzer, H. Stehle (J. Nucl. Mater. **87** [1979] 227/35).

[91] J. A. L. Robertson (Eng. J. Can. **1972** Nov./Dec., p. 9). – [92] R. D. MacDonald, D. G. Hardy, C. E. L. Hunt (Trans. Am. Nucl. Soc. **17** [1973] 216/7). – [93] J. H. Davies, J. S. Armijo, R. A. Proebstle (Am. Ceram. Soc. Meeting, San Francisco 1976 from [26]). – [94] K. D. Knudsen, E. Rolstad, A. Hanevik, K. Svanholm (Trans. Am. Nucl. Soc. **15** [1972] 222/3). – [95] S. Aas, K. D. Olshausen, K. Videm (Nucl. Fuel Perform. Proc. Intern. Conf., London 1973, pp. 55.1/55.6).

[96] P. Knudsen, K. Bryndum (Trans. Am. Nucl. Soc. **19** [1974] 140). – [97] M. Chagrot, C. Ringot, H. Vidal (Nucl. Fuel Perform. Proc. Intern. Conf., London 1953, pp. 91.1/91.4). – [98] J. Delafosse, G. Listiboudois, G. de Conteson, M. Watteau (NUCLEX [Intern. Fachmesse Kerntech. Ind.], Basel 1975 [1976], 1/10; CEA-CONF-3377 [1976] 1/10). – [99] F. Garzarolli, R. Manzel, M. Peehs, H. Stehle (Kerntechnik **20** [1978] 27/31). – [100] N. Fuhrman, V. Pasupathi, L. V. Corsetti (PCI Observation in a Combustion Engineering PWR (Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 262/72; C.A. **89** [1978] No. 137292).

[101] D. Cubicciotti, J. H. Davies (Nucl. Sci. Eng. **60** [1976] 314/9). – [102] W. T. Grubb (Nature **265** [1977] 36/7). – [103] B. Syrett, D. Cubicciotti, R. L. Jones (in: Zirconium in the Nuclear Industry, ASTM Spec. Tech. Publ. No. 633 [1977] 281/94; C.A. **88** [1978] No. 178938). – [104] J. C. Wood, B. A. Surette, I. M. London, J. Baird (J. Nucl. Mater. **57** [1975] 155/79). – [105] K. Videm, L. Lunde (Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 274/81; C.A. **89** [1978] No. 154262).

[106] B. Cox, J. C. Wood (Iodine Induced Cracking of Zircaloy Fuel Cladding, A Review, Corros. Probl. Energy Convers. Gener. Papers Symp., New York 1974, pp. 275/321; C.A. **84** [1976] No. 51064). – [107] A. Garlick (J. Nucl. Mater. **49** [1973/74] 209/24). – [108] C. C. Busby, R. P. Tucker, J. E. McCauley (J. Nucl. Mater. **55** [1975] 64/82). – [109] J. C. Wood (Nucl. Technol. **23** [1974] 63/79). – [110] M. Aubert, D. Calais, R. Le Benze (J. Nucl. Mater. **60** [1976] 279/90).

[111] M. Peehs, H. Stehle, E. Steinberg (Out-of-Pile Testing of Iodine Stress Corrosion Cracking in Zircaloy Tubing Under the Aspect of the PCI-Phenomenon, 4th Intern. Conf. Zirconium Nucl. Ind., Stratford-upon-Avon, England, 1978). – [112] F. Wunderlich, F. Garzarolli (Reaktortagung, Hannover 1978, Meeting Report, pp. 525/8). – [113] J. T. A. Roberts, F. E. Gelhaus, H. Ocken, N. Hoppe, S. T. Oldberg, G. R. Thomas, D. Franklin (EPRI-NP-737-SR [1978] 1/141; INIS Atomindex **9** [1978] No. 408630). – [114] D. Cubicciotti, S. M. Howard, R. L. Jones (J. Nucl. Mater. **78** [1978] 2/16). – [115] D. G. Hardy, A. S. Bain, R. R. Meadowcroft (Performance of CANDU Development Fuels in the NRU Reactor Loops, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 198/206; C.A. **89** [1978] No. 137288).

[116] S. Junkrans, O. Varmild (ASEA-ATOM Research on PCI, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 219/29; C.A. **89** [1978] No. 137053). – [117] J. H. Davies, H. S. Rosenbaum, J. S. Armijo, R. A. Proebstle, T. C. Rowland, J. R. Thompson, E. L. Esch, G. Romeo, D. R. Rutkin (Irradiation Tests to Characterize the PCI Failure Mechanism; Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 230/42; C.A. **89** [1978] No. 154261). – [118] P. Knudsen, C. Bagger, M. Fishler (Characterization of PWR Power Ramp Tests, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 243/52; C.A. **89** [1978] No. 137290). – [119] T. P.

Papazoglou, H. H. Wilson (Fuel Rod Power Ramp Experiments, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 253/61; C.A. **89** [1978] No. 137291). – [120] K. Videm, L. Lunde (Stress Corrosion Cracking of Zircaloy Fuel Cladding Tubes Under Power Ramps and In-Laboratory Tests, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 274/81; C.A. **89** [1978] No. 154262).

[121] A. Garlick, J. G. Gravenor (A Criterion and Mechanism for Power Ramp Defects, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 305/14; C.A. **89** [1978] No. 137295). – [122] J. C. Wood, D. G. Hardy (Characteristics and Interpretation of Power Ramping Defects, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 315/24; C.A. **89** [1978] No. 137296). – [123] W. T. Grubb, M. H. Morgan (Cadmium Embrittlement of Zircaloy-2, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 295/304; C.A. **89** [1978] No. 137294). – [124] D. Cubicciotti, J. S. Sanecki, R. V. Strain, S. Greenberg, L. A. Neimark, C. E. Johnson (The Nature of Fission-Product Deposits Inside LWR Fuel Rods, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 282/94; C.A. **89** [1978] No. 137293). – [125] E. Smith, G. V. Ranjan (A Criterion for Failure of Zircaloy Cladding in a Water Reactor Fuel Rod Subjected to Power Ramps, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, pp. 337/45; C.A. **89** [1978] No. 137298).

[126] H. Mogard (Suppressing PCI Induced Defects by Lightly Undulating the Bore Surface of the Fuel Cladding, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illionois, 1977, pp. 325/36; C.A. **89** [1978] No. 137297). – [127] J. S. Waddington, G. Roberts, I. K. Dickson (J. Am. Ceram. Soc. **60** [1977] 377/80). – [128] J. P. Gatesoupe, Y. Guerin, C. Courtois, J. Truffert (Intern. Conf. Fast Breeder Reactor Fuel Perform., La Grange Park, Ill., 1979, pp. 246/57). – [129] R. Verma, V. K. Mahajan (J. Nucl. Mater. **79** [1979] 252/4). – [130] W. Vogl, W. Hering, M. Peehs, J. C. Lavake (5th Intern. Conf. Struct. Mech. Reactor Technol., Berlin 1979, Paper D2-5, pp. 1/8; SMIRT-5 [1979] D2-5.1/8; INKA-CONF-79-321-111 [1979] D2-5.1/8; INIS Atomindex **12** [1981] No. 588928).

[131] W. Vogl, R. von Jan, H. Stehle (Nucl. Eng. Design **65** [1981] 307/12). – [132] F. Sontheimer, W. Vogl, H. Knaab (Paper Presented Enlarged Halden Programme Group Meeting, Lillehammer, Norway, 1980, personal communication). – [133] D. Cubicciotti, R. C. Jones, B. C. Syrett (EPRI-NP-1329 [1980] 1/161; INIS Atomindex **11** [1980] No. 543474). – [134] H. Stehle, R. von Jan, H. Knaab (LWR Fuel Behavior During Operational and Overpower Transients, ANS-ENS Topical Meeting on Reactor Safety Aspects of Fuel Behavior, Aug. 2nd to 6th, 1981, Sun Valley, ID, 1981). – [135] D. H. Locke (At. Energy Rev. **15** [1977] 779/92; INIS Atomindex **9** [1978] No. 360844).

[136] G. R. Thomas (J. Nucl. Mater. **87** [1979] 215/26). – [137] G. Lestiboudois, J. Delafosse, P. Morize, R. Atabek, G. DeConteson (J. Nucl. Mater. **87** [1979] 236/46). – [138] A. Garlick, R. Sumerling, A. Stuttard, G. G. Bond, D. A. Howl, W. N. Fox, D. Cordall, R. M. Cornell (EUR-6623 [1979] 127/58; INIS Atomindex **12** [1981] No. 578177). – [139] S. Junkrans, H. Nerman (J. Nucl. Mater. **87** [1979] 247/50). – [140] P. Bouffioux, J. Van Vliet, P. Deramaix, M. Lippens (J. Nucl. Mater. **87** [1979] 251/8).

[141] K. Videm, L. Lunde, T. Hollowell, K. Vilpponen, C. Vitanza (J. Nucl. Mater. **87** [1979] 259/67). – [142] J. H. Gittus, D. A. Howl (J. Nucl. Mater. **87** [1979] 268/73). – [143] M. Peehs, F. Garzarolli, R. Hahn, E. Steinberg (J. Nucl. Mater. **87** [1979] 274/82). – [144] H. Aßmann, H. Stehle (J. Nucl. Mater. **81** [1975] 19/30). – [145] IAEA (Specialists Meeting Pellet-Cladding Interact. Water Reactors, Vienna 1981, pp. 1/296; IWGFPT-8 [1981] 1/296).

[146] M. Peehs, H. Stehle, E. Steinberg (ASTM Zirconium Conf., Stratford-upon-Avon 1978; ASTM-STP-681 [1979]). – [147] W. Hering (6th Intern. Conf. Struct. Mech. Reactor Technol., Paris 1981, Paper D1-4; SMIRT-6 [1981]). – [148] M. Peehs, W. Jung, H. Stehle, E. Steinberg (6th Intern. Conf. Struct. Mech. Reactor Technol., Paris 1981, Paper C2–4; SMIRT-6 [1981]). – [149] H. Bairiot, S. Junkrans, J. F. Marin, D. O. Pickman, H. G.

Weidinger (ANS Top. Meeting Reactor Safety Aspects Fuel Behavior, Sun Valley, ID, 1981). – [150] M. Peehs, G. Kaspar (Experimental Investigations of the Cesium and Iodine Exhalation from Irradiated UO_2, AERE, Harwell, U.K., 1981).

1.1.9 Behavior of Oxide Nuclear Fuels in Defective Fuel Rods

General References:

D. H. Locke, Defected Zircaloy Fuel, A World Review of the Experience Obtained in the Operation of Land Based Power Reactors with Defected Zircaloy Clad Fuel, Nucl. Eng. Intern. **14** [1969] 648/52.
D. H. Locke, The Behavior of Defective Reactor Fuel, Nucl. Eng. Design **21** [1971] 318/30.
D. H. Locke, Defective Fuel Behavior in Water Reactors, Water Reactor Fuel Performance, ANS Top. Meeting, St. Charles, Illinois, 1977, Session I, pp. 28/37.
F. Garzarolli, R. Manzel, H. Stehle, The Behavior of Defective Fuel Rods Under Continued Reactor Operation, Kerntechnik **20** [1978] 463/6.
H. Kleykamp, Das chemische Verhalten defekter Mischoxid-Brennstäbe unter Bestrahlung, Reaktortagung, Mannheim 1977, Meeting Report, pp. 510/3.

1.1.9.1 Water Cooled Fuel Elements

The behavior of defective fuel rods in water cooled reactors has been studied since the late 50's [1 to 4]. Already since that time has the good behavior of the defective rods been known. This is due to the choice of the chemically very stable oxide as the nuclear fuel. Locke [5 to 7] published a series of reviews, and a more recent survey paper is due to Garzarolli et al. [8].

A perforation of the cladding may have the following consequences for the behavior of the oxidic nuclear fuel [8]:

(1) Release of fission products into the coolant (see also [9, 10, 31, 32])
  – contamination of the primary coolant system.
(2) Oxidation of the fuel (e.g., UO_2 to U_3O_8)
  – decrease of thermal conductivity, increase of central temperature,
  – increases in volume and diameter.
(3) Flushing out and loss of fuel through the defect in the cladding
  – contamination of the primary coolant system.

The release of fission products to the coolant is a complicated function of the operational parameters [8]. The following release mechanisms may be distinguished systematically [8]:

a) slow or sudden release of stored fission products during the process of clad perforation,
b) steady-state release of fission products from existing fuel failures during constant power operation of a reactor,
c) fission product spiking during shut-down [9], and
d) moderately increased release rate during nonsteady operation of a plant [10].

The rate of oxidation of the fuel depends on the following factors:

a) time elapsed since the perforation,
b) size of the defect,
c) temperature of the fuel, and
d) coolant chemistry.

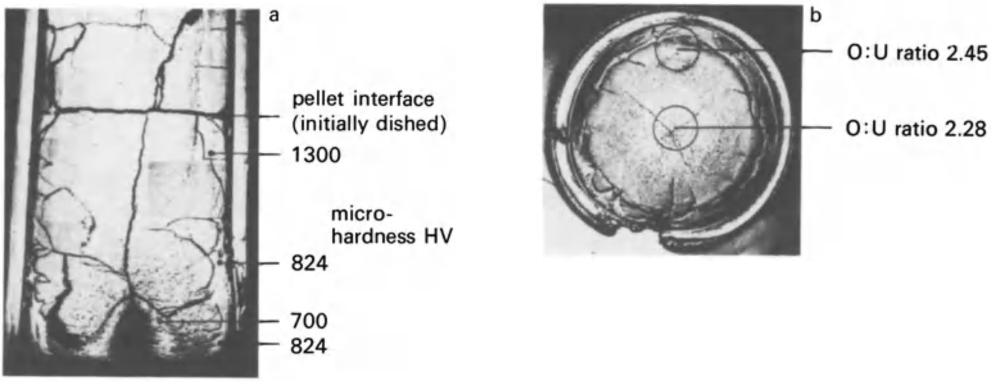
References for 1.1.9 on p. 138

Blackburn et al. [11, 12] reported rates of oxidation as a function of the partial pressure of the oxygen (see also [13]). Accordingly, stronger oxidation should be expected in boiling water reactors (e.g., 0.2 ppm oxygen in the water) than in pressurized water reactors (e.g., only 0.005 ppm oxygen in the water, due to the diminished radiolysis of the water because of the addition of H_2). Such an effect was not found, however, according to [8].

The oxidation of the fuel near a defect in the cladding leads after a few days to an O : M ratio of about 2.1, while after one year values above 2.4 are attained (Fig. 1 in [14]).

Fig. 1-92 shows that the oxidation of the fuel is stronger at its edge than at its center. Layers of U_3O_8 were found on the surface of the fuel, the thickness of which varied according to the size of the defect, the power level or the central temperature of the fuel rod, and the distance from the defect, having values between 10 μm and 1 mm [8].

Fig. 1-92



Etched section micrographs of a defect LWR fuel rod: a) longitudinal section, b) cross section [14]

Oxidation of the fuel leads to a decrease in the thermal conductivity, hence to an increase in the central temperature (see Section 1.1.3.1, p. 29). From this result restructurings, which are not observed under normal operation: columnar grain growth and possibly the formation of a central void (see Section 1.1.6.3, p. 102). These phenomena, as also accelerated equiaxed grain growth, were observed in defective fuel rods at lower temperatures than in non-defective fuel rods. The reasons, therefore, should be sought in the enhanced self-diffusion in hyperstoichiometric UO_{2+x} [15]. An accelerated grain growth was found in such UO_{2+x} also in out-of-pile experiments [16].

The increase of the diameter of the pellet because of the oxidation of the fuel is generally small. Garzarolli et al. [8] estimated an increase of the diameter by 20 μm for a layer thickness of 100 μm of the U_3O_8.

UO_2 has an excellent corrosion resistance against the coolant water, and only a minimal leaching of the fuel results [8, 13, 17]. As a consequence of chemical reactions and mechanical erosion by the coolant, the following fuel losses from the fuel rod were noted after one year of operation in the defective state:

a) pinhole: 10^{-3} g
b) hole with a diameter of 5 to 10 mm: 1 g
c) crack (20 to 50 mm long, 5 mm wide): 10 g

The quantities cited are orders of magnitude only. No increase of the effect with the power level was noted up to a power of about 500 W/cm.

In the literature, an effect designated as "water logging" was discussed [18 to 20], in particular for fuel of relatively low density (80% of the theoretical). When the reactor is shutdown water may be sucked-in into the void space of the fuel rod, including open pores of the fuel. On fast increase of power in the reactor a water vapor pressure may buildup, causing rupture of the cladding. This effect does not occur with fuels having realistic properties for water cooled reactors ($>$ 94% of theoretical density), and has never been observed in power reactors of this kind.

The behavior of UO_2-PuO_2 in Zircaloy cladding tubes relative to defects has been studied by Freshley [21]. The results were similar to those for UO_2.

1.1.9.2 **Sodium Cooled Fuel Elements** (NaK Coolant)

The behavior of UO_2-PuO_2 fuel in fast breeder reactors relative to defects in the fuel rod cladding has been studied essentially only since the early 70's. Geithoff [22] reported the flushing of fuel from defective fuel rods in irradiation experiments in the Dounray Fast Reactor (experiment DFR-435; for post-irradiation studies see [23]). Contrary to the experience in previous irradiation experiments (Mol-7A [24], FR2 [25]), where the fuel remained practically completely within the cladding, in the case of DFR-435 fuel losses amounting to between 3 and 5 g per defective rod were observed. The mechanism of the flushing was assumed to be mechanical without appreciable cooperation from chemical reactions. Vibrations of the fuel rods and turbulence of the coolant should be the causes for this effect.

The chemical interaction between the fuel and the coolant is reported in [25, 26] for Mol 7-A, in [27] for DFR-435, in [28] for FR-2 and in [29] for Vadia-I.

Kleykamp [30] discussed the chemical behavior of defective mixed oxide fuel rods under irradiation. The intrusion of the coolant into the interior of the fuel rod has the following consequences:

(1) Fuel-coolant-cladding reactions.

Depending on the temperatures of the fuel and of the cladding, two kinds of oxidic reaction layers are found between the fuel and the cladding:

a) Layered oxidic and metallic phases of the components of the cladding, with small amounts of Na-K-Ba-U oxides at the surface of the fuel as well as Na-K chromate and manganate.
b) Oxidic Na-K-Cs-Ba-Mo-U phases between the fuel and the cladding.

Since the layers have a smaller density than the fuel has, increases of the diameter of the fuel rod occur, but these are insignificant.

(2) Changes in the stoichiometry of the fuel.

A multi-phase alkali metal-alkaline earth metal-uranium (plutonium)-molybdenum oxide is formed by the reaction of the sodium and the potassium on the mixed oxide fuel. The O:(U + Pu) ratio is thereby reduced from 2.00 to 1.96.

References for 1.1.9 on p. 138

(3) Enhanced axial redistribution of fissile material.

The central temperature becomes elevated because of the poor heat conductivity of the reaction layers that are formed. As a consequence, an enhanced vaporization of uranium oxides towards the ends of the fuel rods takes place.

(4) Precipitation of fuel and fission products.

Besides the well known precipitation of Mo, Tc, Ru, Rh, and Pd, in the case of a defect a multi-phase actinide-platinum metal precipitate is formed (intermetallic compound), which is insoluble in nitric acid (problems are encountered in the reprocessing of the irradiated fuel).

References for 1.1.9:

[1] J. T. Stiefel, H. Feinroth, G. M. Odenham (WAPD-TM-390 [1963] 1/67; N.S.A. **17** [1963] No. 40348). – [2] H. M. Ferrari, R. J. Allio (Nucl. Appl. **2** [1966] 492/7). – [3] C. N. Spalaris (Trans. Am. Nucl. Soc. **4** [1961] 146/8). – [4] S. Naymark, C. N. Spalaris (Proc. 3rd U. N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1964 [1965], Vol. 11, pp. 425/35, Paper Nr. 233). – [5] D. H. Locke (Nucl. Eng. Intern. **14** [1969] 648/52).

[6] D. H. Locke (Nucl. Eng. Design **21** [1971] 318/30). – [7] D. H. Locke (Fuel Rod Power Ramp Experiments, Water React. Fuel Perform. ANS Top. Meeting, St. Charles, Illinois, 1977, Session I, pp. 28/37). – [8] F. Garzarolli, F. Manzel, H. Stehle (Kerntechnik **20** [1978] 463/6). – [9] K. H. Neeb, E. Schuster (Siemens Forsch. Entwicklungsber. **8** [1979] 92/7). – [10] E. Schuster, A. Kersting, K. H. Neeb (Reaktortagung, Mannheim 1977, Meeting Report, pp. 817/20).

[11] P. E. Blackburn, J. Weissbart, E. A. Gulbransen (J. Phys. Chem. **62** [1958] 902/8). – [12] P. E. Blackburn, J. Weissbart, E. A. Gulbransen (Westinghouse Res. Rept. No. 100FF942-R2-Rev. [1957] from [13, p. 393]; AECU-3674 [1975] 1/22; N.S.A. **12** [1958] No. 8382). – [13] J. Belle (Uranium Dioxide, Properties and Nuclear Application, Naval Reactors Division of Reactor Development USAEC, Washington 1961, 1/726, 377/430; C. A. **1961** 23110). – [14] H. Stehle, H. Aßmann, F. Wunderlich (Nucl. Eng. Design **33** [1975] 230/60). – [15] H. Matzke (Plutonium 1975 Proc. 5th Intern. Conf. Plutonium Other Actinides, Baden-Baden 1975 [1976], pp. 801/31).

[16] I. Amato, R. L. Colombo, A. M. Protti (J. Am. Ceram. Soc. **46** [1963] 407). – [17] J. T. Bittel, L. H. Sjodahl, J. F. White (J. Am. Ceram. Soc. **52** [1969] 446/51). – [18] J. D. Eichenberg, P. W. Frank, T. J. Kisiel, B. Lustman, K. H. Vogel (TID-7546 [1958] 616/7; N.S.A. **12** [1958] No. 9417). – [19] A. J. Mooradian, G. M. Allison, J. F. Palmer (Nucleonics **18** No. 1 [1960] 81/5). – [20] B. Lustman (WAPD-T-1939 [1966] 1/49; CONF-660531-1 [1966]; N.S.A. **20** [1966] No. 40387).

[21] M. D. Freshley (Nucl. Technol. **15** [1972] 209/28). – [22] D. Geithoff (Reaktortagung, Nürnberg 1975, Meeting Report, pp. 455/8). – [23] K. Kummerer, D. Geithoff, P. Weimar (KFK-1522 [1972] 1/213; N.S.A. **27** [1973] No. 26785). – [24] D. Freund (KFK-1376 [1972] 1/82; N.S.A. **26** [1972] No. 52382). – [25] H. Kleykamp (KFK-1736 [1973] 631/701).

[26] H. Kleykamp (Reaktortagung, Karlsruhe 1973, Meeting Report, pp. 299/302). – [27] H. Kleykamp (in: W. Dienst, O. Götzmann, H. Kleykamp, H. Zimmermann, KFK-2218 [1976] 45/74). – [28] H. Kleykamp, H. Späte (Project Fast Breeder, KFK-1275/2 [1975] 112.21/112.23). – [29] H. Kleykamp, H. Späte (Project Fast Breeder, KFK-1276/2 [1976] 112.13/112.17). – [30] H. Kleykamp (Reaktortagung, Mannheim 1977, Meeting Report, pp. 510/3).

[31] S. Jacobi, K. Letz, G. Schmitz (Nucl. Eng. Design **44** [1977] 125/34). – [32] E. Schuster, F. Garzarolli, A. Kersting, K. H. Neeb, H. Stehle (Nucl. Eng. Design **64** [1981] 81/5).

1.2 Carbide and Nitride Nuclear Fuels

A. Naoumidis, H. Nickel,
Kernforschungsanlage Jülich
Jülich, Bundesrepublik Deutschland

1.2.1 Introduction

Uranium monocarbides and mononitrides, their solid solutions, and the corresponding uranium-plutonium compounds, are potential ceramic nuclear fuels and breeding materials. Higher burnups (at higher heat rating), and thereby also more favorable fuel cycle costs, may be attained with these materials than with metallic fuels, because of the high dimensional stability under irradiation of the ceramics.

Characteristic properties of uranium and plutonium monocarbides and mononitrides and their solid solutions are high thermal conductance, high density, and a high ability to retain gaseous fission products. The thermal conductivity of these compounds is from 4 to 10 times higher than that of uranium dioxide. Therefore, with these materials significantly higher linear heat rates may be produced, than with the oxide fuels.

The following advantages, among others, result from these facts, when carbide or nitride fuel and breeding material are employed in, e.g., a Na-cooled fast breeder reactor:

a) Fuel rods having larger diameters may be employed because of the higher heat conductivity. This leads to diminished fabrication costs, and to lower neutron losses in metallic cladding and structural material.

b) The fuel temperature is lower compared with oxide fuels in spite of the higher specific power. Therefore appreciable separation of fissile and fertile materials and release of fission gases during the irradiation process can be avoided.

c) The operating temperature is well below the thermal load limit of these fuels. The operational safety potential in thereby raised, because of the smaller significance of the negative Doppler effect.

d) The smaller fission gas release in carbide and nitride fuels allows a smaller gas plenum in the fuel rod without an increase in the internal pressure.

e) The ca. 30, resp. 40%, higher density of the monocarbide, resp. mononitride, fuels relative to the oxide fuels, may, at a smaller enrichment, lead to larger breeding rates, shorter fuel doubling times, and longer core operation times.

The following disadvantages of carbide fuels (UC and (U,Pu)C) compared with the oxidic fuels must be noted too:

a) High chemical reactivity towards oxygen and humidity in the air, which leads to higher fabrication costs, e.g., the use of an inert atmosphere.

b) A relatively high swelling rate, which limits the burnup.

These disadvantages are not as important for the mononitrides as they are for the monocarbides. On the other hand, higher neutron losses, caused by the (n,p) reaction of the nitrogen, must be taken into account.

Caspersson et al. [1] calculated the nuclear data for a 500 MW_e Na-cooled fast breeding reactor from the properties of oxide, carbide, and nitride fuels (Table 1/21).

References for 1.2.1 on p. 142

Table 1/21
Nuclear Performance Comparison of Various Fuels for a 500 MW_e LMFBR Core.

parameter	fuel type		
	$(U, Pu)O_2$	(U, Pu)C	(U, Pu)N
peak heavy metal burnup in MWd · kg (mean/max.)	65/100	50/78	47/51
fissile Pu in kg	1225	1181	1201
fissile Pu enrichment in %	15.6	12.4	12.5
reactor breeding ratio	1.20	1.42	1.35
peak neutron-flux in $10^{15} n \cdot cm^{-2} \cdot s^{-1}$	7.6	7.9	8.1
Doppler coefficient/T, dk/dT	−0.0070	−0.0075	−0.0074
relative absorption cross section of the non-metal	8.1	0.8	249.0
full power days per refueling cycle	156	218	205

The development of uranium and plutonium monocarbides and mononitrides to become useable nuclear fuels is the result of intensive worldwide efforts. On the one hand, basic research provides the physical, mechanical, and chemical properties required for the use of these ceramic fuels in reactors. On the other, national and international projects test in irradiation experiments the suitability and the load limits of the various fuel element designs.

The application of these high-power fuels to other reactor types has also been proposed and examined. In the sixties, EURATOM was concerned with UC in its ORGEL (*org*anique *e*au *l*ourde) project, *A*tomic *E*nergy *C*anadian *L*imited (AECL) and the USAEC in connection with the development of a *h*eavy *w*ater moderated *o*rganic *c*ooled *r*eactor (HWOCR). The requirements on the fuel of this reactor type were summarized by Falk et al. [2] (Table 1/22).

Table 1/22
Operational Conditions of the Fuel Elements of the Heavy Water Organic Cooled Reactor (HWOCR).

	HWOC reactor	U-305AL
cladding and fuel	SAP*-UC	SAP*-UC or Zircaloy-UO_2
coolant	Santowax OM + 10% HB**	Santowax OM + 10 up to 30% HB HB-40 with 22 to 33 wt% HB
fuel enrichment (% ^{235}U)	1.3	1.5
peak unperturbed neutron-flux in $n \cdot cm^{-2} \cdot s^{-1}$	2.8×10^{14}	2.4×10^{14}
peak specific power in MW/MTU	48.1	46.8
peak fuel temperature in °C	1150	1100
peak cladding temperature in °C	465	455
bulk average power density in MW/m^3	0.116	0.112

* SAP = *S*intered *A*luminium *P*roduct

** HB = high boiler polymers, produced also by the radiation damage of o-, m-, and p-terphenyl (the Santowax)

UC and UN were considered also as fuels in a thermionic reactor [3 to 5]. The most significant fuel development work in this area was done by *G*ulf *G*eneral *A*tomic (GGA) in San Diego and by the *C*onnecticut *A*dvanced *N*uclear *E*ngineering *L*aboratory (CANEL), within the framework of the *S*ystems for *N*uclear *A*uxilary *P*ower (SNAP-50) project.

For the sake of completeness it is necessary to mention also the ROVER project operated by the *L*os *A*lamos *S*cientific *L*aboratory (LASL), the aim of which was the development and testing of nuclear rocket fuels. A UC-ZrC solid solution in a graphite carrier was used as fuel.

The main direction of development and application of the high power fuels, however, has been, for nearly two decades, the liquid metal fast breeder reactor (LMFBR). Almost all the nuclear research centers in the industrialized nations have made some efforts in this area. The most important contributions have been provided by teams from the following establishments (in alphabetical order):

- *A*tomic *E*nergy *R*esearch *E*stablishment (AERE), Harwell, England
- *A*rgonne *N*ational *L*aboratory (ANL), Argonne, Ill., USA
- *B*atelle *M*emorial *I*nstitute (BMI), Columbus, Ohio, USA
- *C*entre d'*E*tudes *N*ucléaires (CEN), Fontenay-aux-Roses, France
- *E*idgenössisches *I*nstitut für *R*eaktorforschung (EIR), Würenlingen, Switzerland
- *E*uropäisches *I*nstitut für *T*ransurane (EIT), Karlsruhe, F. R. Germany
- *J*apan *A*tomic *E*nergy *R*esearch *I*nstitute (JAERI), Tokai, Japan
- *K*ern*f*orschungszentrum *K*arlsruhe (KfK), Karlsruhe, F. R. Germany
- Kurchatov Institute of Atomic Energy, Moscow, USSR
- *L*os *A*lamos *S*cientific *L*aboratory (LASL), Los Alamos, New Mexico, USA
- *U*nited *N*uclear *C*orporation (UNC) or, since 1972, *G*ulf *U*nited Nuclear Fuel Corporation (GU), Elmsford, NY, USA.

The results of these teams have been published in reports from the individual research centers, in the technical literature, and in the proceedings of technical meetings, such as the Transactions of the *A*merican *N*uclear *S*ociety (ANS) or the Compacts of the annual German Reactor Meetings (Reaktortagung) of the Deutsches Atomforum (DAtF) and the Kerntechnische Gesellschaft (KTG). The contributions to important conferences were, furthermore, published in book form [6 to 17].

It is not the aim of this presentation to evaluate systematically the extensive literature. The data are presented in a readily surveyed form in two chapters. The first part (Section 1.2.2, from p. 142) deals with the physical, mechanical, and chemical properties of UC, (U,Pu)C, UN, (U,Pu)N, and the corresponding carbide nitrides before irradiation. Special attention is given to the thermal conductivity, the self-diffusion, and the compatibility of the various fuels with the cladding material. The second part (Section 1.2.3, from p. 191) examines the various effects arising in the fuel from irradiation. Here, too, the changes in the physical and chemical properties are presented first, and then effects such as swelling, fission gas release, and the behavior of the solid fission products and plutonium, important for the fuel rod design, are discussed.

The units (for temperature, pressure, etc.) used in the original publications have been replaced in the present chapter by the units valid nowadays. The values of the burnup, however, have not been changed, and this quantity is reported in the following units:

a) at. % or % FIMA, i.e., % *f*ission of *i*nitial heavy *m*etal *a*toms
b) MWd/t, i.e. megawatt × days/tons heavy metal
c) 10^{20} fissions/cm^3.

References for 1.2.1 on p. 142

Table 1/23 correlates these three units for UC and UN.

Table 1/23
Correlation of Burnup Units.

material	% FIMA	fissions/cm^3	MWd/t
UC	1	3.28×10^{20}	8220
	0.305	10^{20}	2500
	1.22	4.0×10^{20}	10000
UN	1	3.41×10^{20}	8150
	0.293	10^{20}	2390
	1.23	4.18×10^{20}	10000

References for 1.2.1:

[1] S. A. Caspersson, R. C. Noyes, A. Vitti (Advan. React. Phys. Des. Econ. Proc. Intern. Conf. Atlanta, Georgia, 1974 [1975], pp. 125/34; AED-Conf-74-394-038 [1974]; C.A. **84** [1976] No. 10174). – [2] E. D. Falk, R. E. Forester, W. B. Wolfe, R. J. Sulivan (AI-CE-75 [1968]). – [3] IEEE (Thermionic Conversion Spec. Conf., Monterey, Cal., 1969; TID-25287 [1969]). – [4] IEEE (Thermionic Conversion Spec. Conf., San Diego, Cal., 1971; Conf-711038 [1971]; N.S.A. **26** [1972] No. 18121, 18379). – [5] Kernforschungsanlage Jülich GmbH (Proc. Intern. Conf. Thermionic Electr. Power Generation, Jülich, Germany, 1972; CONF-720613-P2 [1972].

[6] IAEA (Radiat. Damage Reactor Mater. Part Proc. Symp., Venice 1962 [1963]; C.A. **60** [1964] 10167, 8867). – [7] L. E. Russell et al. (Carbides Nucl. Energy Proc. Symp., Harwell, UK, 1963 [1964] Vol. 1/2, pp. 1/966; C.A. **64** [1966] 13710). – [8] J. T. Waber, P. Chiotti, W. N. Mine (Compounds Interest Nucl. Reactor Technol., Proc. Symp., Boulder, Colo., 1964; Inst. Mining Met. Petrol Eng. Inst. Metals Div. Spec. Rept. Ser. No. 13 [1964] 1/798; Nucl. Met. **10** [1964] 1/798; CONF-506 [1964]; N.S.A. **19** [1965] No. 7441). – [9] A. E. Kay, M. B. Waldron (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 1/1114). – [10] A. N. Holden (High Temperature Nuclear Fuels, Gordon and Breach, New York 1968, pp. 1/528; Met. Soc. Conf. **42** [1966/68]; C.A. **70** [1969] No. 25048).

[11] K. E. Horton et al. (Plutonium Fuel Technol. Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1968]). – [12] K. Kummerer, F. Thümmler (Karbidische Kernbrennstoffe für schnelle Brutreaktoren, KFK-1111 [1969] 1/399; EUR-4315 [1969]; N.S.A. **24** [1970] No. 17226; EURFNR-722 [1970] 1/492; N.S.A. **24** [1970] No. 38542). – [13] M. Dalle Donne, K. Kummerer, K. Schroeter (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970). – [14] W. N. Miner (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Acitinides, Santa Fe 1970; Nucl. Met. **17** [1980] pt. 1/2). – [15] R. Farmakes (Proc. Conf. Fast Reactor Fuel Elem. Technol., New Orleans 1971).

[16] IAEA (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974] Vol. 1/2). – [17] J. Leary, H. Kittle (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 1/694; CONF-771008 [1977]).

1.2.2 Properties in the Non-Irradiated State

For a detailed discussion of the physical properties of the pure uranium compounds see "Uranium" Suppl. Vol. C7, 1981 (Nitrides), and C12 (Carbides).

1.2.2.1 Mechanical Properties

1.2.2.1.1 Creep Behavior

The long lifetime of fuel rods in the reactor can be limited by the swelling rate of the fuel and on the resulting mechanical interaction between the fuel and the cladding. It is generally known that the swelling of the fuel is directly related to its plasticity, to its creep, and to its fracture characteristics. Therefore the creep behavior of high density single phase carbide and nitride materials was studied in out-of-pile experiments, as a function of the temperature and of the stress.

1.2.2.1.1.1 Carbides

The steady-state creep behavior of uranium carbides has been reviewed by Seltzer et al. [1]. Most of the high temperature creep experiments had been conducted in vacuum, between 10^{-4} and 10^{-6} Torr, on UC under applied mechanical pressure [2 to 7, 9, 20]. Only a few tensile creep measurements have been reported [8]. Samples consisting of coarse-grained arc-melted polycrystalline material were employed for the determination of the creep behavior, except for two experiments made on single crystals [4, 10]. The results for hyper-, respectively hypostoichiometric carbides are summarized in **Fig. 1-93**, respectively 1-**94**, p. 145. Killey et al. [9] conducted creep experiments on arc-melted polycrystalline (120 μm grain size) hyperstoichiometric UC (4.81 to 5.18 wt% C) in the temperature range from 1 225 to 1 600 °C under stresses of 1 500 to 10000 lb/in^2 (10 to 70 N/mm^2). The creep behavior of hyperstoichiometric carbides, obtained from the experimental results, could be described well by eq. (1).

$$\dot{\varepsilon} = A''\sigma^n \exp(-\Delta H''/RT) \qquad (1)$$

where $\dot{\varepsilon}$ is the creep rate, σ the stress, and, at low temperatures and stresses,

$A'' = 2.28\times10^{-2}$ $\quad n = 1.79\pm0.67$ $\quad \Delta H'' = 68.6\pm23.4$ kcal/mol (287 ± 98 kJ/mol),

and at high temperatures (>1 300 °C) and high stresses (>6000 lb/in^2 or >42 Nmm^2)

$A'' = 1.13\times10^{-1}$ $\quad n = 4.18\pm1.36$ $\quad \Delta H'' = 141.6\pm21.6$ kcal/mol (590 ± 90 kJ/mol).

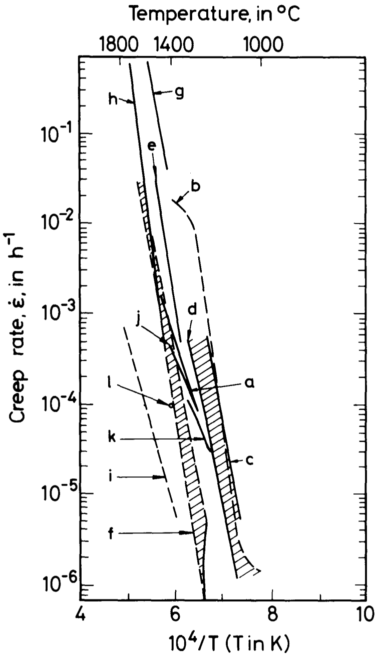
The creep rate of hyperstoichiometric UC is several orders of magnitude lower than that of the hypostoichiometric material at similar stress and temperature ranges. The high activation enthalpies for creep and the exponents of the stress in eq. (1) are in agreement with numerous models of creep processes. In all of these the diffusion of the uranium atoms controls the motion of the dislocations.

Creep tests on single crystals at different orientations showed, on the basis of metallographic examination, that {110} {100} is the slip system at ≤1 400 °C [1]. Between 1 300 and 1 500 °C and at a stress of 6000 lb/in^2 (42 N/mm^2) the slip plane becomes increasingly wavy.

Information on the creep rate controlling process could sometimes be obtained from the effect of the composition on this property. Norreys [5], Killey et al. [9, 10], and Magnier et al. [2] found that the creep rate of uranium carbides decreased with increasing carbon content. Norreys [5] observed at 1 300 °C and 6000 lb/in^2 a plastic deformation of 25% in 30 h in a UC sample having 4.7 wt% C, whereas samples having 4.9 and 5.2 wt% C under similar conditions strained less than 2%. This difference could be explained by the presence of free uranium along the grain boundaries in the hypostoichiometric material.

References for 1.2.2.1 on p. 152

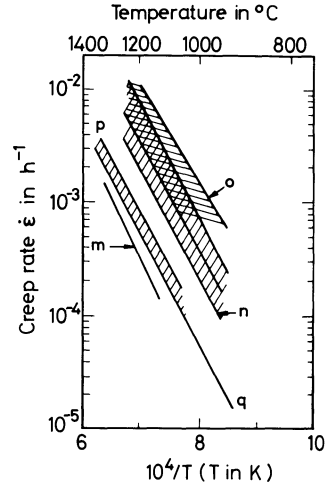
Fig. 1-93



Summary of creep rate measurements on hyperstoichiometric carbides. Symbols on curves are explained in the table below.

symbol	material	carbon content in wt%	stress, in MN/m^2	preparation of sample	Ref.
a	UC	4.9	–	sintered	[6]
b	UC	4.8 to 4.97	–	sintered	[9]
c	$U_{0.85}Pu_{0.15}C$	4.9	20	sintered	[9]
d	UC	4.83	–	sintered	[13]
e	$U_{0.79}Pu_{0.21}C$	5.1	–	sintered	[11]
f	UC	5.2 to 5.6	–	arc-cast	[14]
g	UC	4.88	–	arc-cast	[12, 41, 42]
h	UC	5.05	–	arc-cast	[12, 41, 42]
i	$U_{0.9}Zr_{0.1}C+W$	5.73	–	arc-cast	[12, 41, 42]
j	UC	4.9	–	arc-cast	[5]
k	UC	5.2	–	arc-cast	[7]
l	UC	5.2	34	arc-cast	[19]

Fig. 1-94



Summary of creep rate measurements on hypostoichiometric carbides. Symbols on curves are explained in the table below.

symbol	material	carbon content in wt%	stress in MN/m^2	preparation of sample	Ref.
m	UC	4.5	–	sintered	[6]
n	UC	4.6 to 4.8	20	sintered	[9]
o	$U_{0.85}Pu_{0.15}C$	4.6 to 4.8	20	sintered	[9]
p	UC	4.4 to 4.6	–	sintered	[14]
q	UC	4.6 to 4.8	–	arc-cast	[10]

Seltzer et al. [12, 41, 42] determined the stationary creep behavior of UC samples having various C/U ratios and of samples containing additives such as W and ZrC. The additives decrease the creep rate by several orders of magnitude.

The study of Hall [13] concerning sintered UC and (U,Pu)C showed only a minor effect of Pu on the creep rate, in agreement with Tokar's work [11]. On the contrary, even small amounts of Ni residues, from its use as a sintering aid, had an appreciable effect. Matthews [14] expressed this effect by means of eq. (2):

$$\dot{\varepsilon} = A \exp[BW + (CW + Q + (\beta RT + \alpha)\sigma)/RT] \quad (2)$$

The parameters in this equation have the following values:

parameter	A	B	C	Q	α	β
units	h^{-1}		MJ/mol	MJ/mol	MJ/MPa·mol	MPa^{-1}
for UC	6.21×10^{14}	226.3	−1.219	−0.594	9.024×10^{-3}	−0.6055
for (U,Pu)C	3.21×10^{15}	224.8	−2.051	−0.612		

W is the wt% of Ni and the stress σ is in MPa.

Besides the steady-state creep Singh [15] determined also the primary creep behavior of $(U_{0.8}Pu_{0.2})C$. The dependence of the primary creep rate $\dot{\varepsilon}_p$ on the time t and the stress σ is given in eq. (3), where A and m are temperature-dependent parameters:

$$\dot{\varepsilon}_p = A\,\sigma\,t^{m-1} \tag{3}$$

The value of m varies from 0.1 to 0.3 over the temperature range from 1 573 to 1 873 K, that of A, at a stress of 7.0 MPa, from $2.14\times10^{-4}\,MPa^{-1}\cdot h^{-1.9}$ to $6.43\times10^{-4}\,MPa^{-1}\cdot h^{-1.7}$ over the same temperature range. These studies also show that the steady-state creep rate of $(U_{0.8}Pu_{0.2})C$ may be related to the stress and the temperature by eq. (4):

$$\dot{\varepsilon} = 1.03\times10^{-19}\,\sigma^{(3\pm0.5)}\exp[-(296\pm30)/RT] \tag{4}$$

with (296 ± 30) in kJ/mol.

The mechanism of steady-state creep of mixed carbides is assumed to be controlled by the climb of dislocations, with the simultaneous diffusion of uranium in the bulk.

1.2.2.1.1.2 Nitrides, Carbide Nitrides

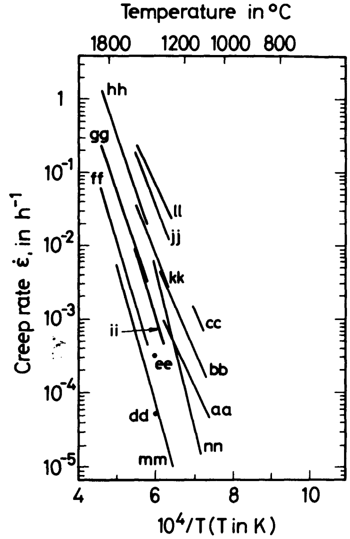
Routbort, Singh [16] published an extensive review of the stationary creep of uranium nitride. It is necessary to evaluate the data for the creep behavior of UN critically, since although the studies have been performed either under defined N_2 partial pressures, or in vacuum, the single phase region of UN is narrow, as is that of UC. Furthermore, the dependence of the composition of UN_{1-x} on the pressure and the temperature has not been completely clarified. Therefore for the creep data shown in **Fig. 1-95** it must be assumed that in several of the experiments a shift of the N:U ratio occurred during the measurement, as a consequence of a temperature variation. It is therefore also difficult to use these data to establish an effect of pores and of the grain size on the steady-state creep.

The higher melting point (2490 °C for UC and 2839 °C for UN) and the higher elasticity constant of the nitride lead to expect a higher creep resistance of the nitride than of the carbide. Uchida, Ichikawa [17], however, found that UN creeps faster than UC. Both the grain size and the density were kept constant during the experiments, and the dependence of the modulus of elasticity on the porosity and on the temperature is similar for the two materials. Hence the higher creep rate of UN must be attributed to the composition change during the measurement.

The presence of impurities affects the rate of deformation of UN. Fassler et al. [6] observed a reduction in the creep rate, in the region of the stationary creep, when the oxygen content was increased from 400 to 2600 ppm.

Uchida, Ichikawa [17] studied also the creep behavior of U(C,N) mixed crystals. The change of the creep rate with the composition shows two characteristics: the creep rate increases rapidly from UC to $UC_{0.78}N_{0.22}$, and the value for $UC_{0.28}N_{0.72}$ is notably low (Fig. 1-

Fig. 1-95



The steady-state creep rates of UN, (U,Pu)N, and (U,Pu)(C,N). The symbols on the curves refer to the following table.

symbol	material	stress in MPa	oxygen content in ppm	Ref.
aa	UN	11	2600	[6]
bb	UN	54.4	2600	[6]
cc	UN	41	400	[6]
dd	UN	17	–	[19]
ee	UN	34	–	[19]
ff	UN	20.4	400	[18]
gg	UN	27	400	[18]
hh	UN	34	400	[18]
ii	UC	41	1100	[17]
jj	UN	41	2100	[17]
kk	$UC_{0.28}N_{0.72}$	41	2100	[17]
ll	$UC_{0.78}N_{0.22}$	41	2200	[17]
mm	$(U_{0.85}Pu_{0.15})(C_{0.65}N_{0.85})$	7.6	–	[21]
nn	$(U_{0.85}Pu_{0.15})(C_{0.65}N_{0.85})$	44	–	[21]

95). The minimum in the creep rate coincides with the maximum in the Young's modulus at the composition $UC_{0.2}N_{0.8}$ [22, 43]. The heat of solution of UC in UN, too, plays some role in the deformation behavior, because of its relation to the binding energies [23].

De Novion et al. [21] determined the compressive creep properties of (U,Pu)(C,N). The creep rates found were higher than that of UC and lower than that of UN [17].

1.2.2.1.2 Elastic Properties

The published data concerning the elastic properties of UC and UN has been summarized by Routbort, Singh [16]. The elastic moduli M of the polycrystalline material depend strongly on the type and the fraction of the pores. The effect of the porosity may be described by means of eq. (5):

$$M = M_0 (1 + AP) \qquad (5)$$

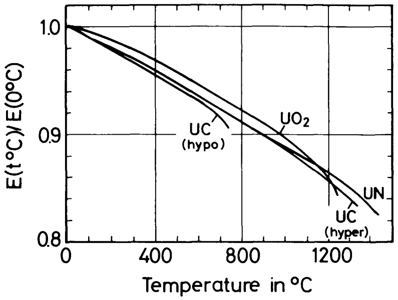
where P is the fraction of the pores. For small, spherical, and closed pores the constant A should be independent of the material. Since this independence has only seldom been observed, it is concluded that generally A depends on both the type and the distribution of the pores. The elastic moduli of UC [3, 22, 23, 26, 28, 43] and UN [22 to 27, 38] have been determined as a function of the porosity (Table 1/24). The effect of the temperature on the E modulus of various ceramic fuels is shown in **Fig. 1-96** [28]. The linearity of the decrease in the cases of UC and UN vanishes, once the temperature has attained the plasticity limits of these materials.

Table 1/24
The Dependence of the Elastic Moduli of UN and UC on the Porosity at 25 °C.

material	Young's modulus E in GPa	shear modulus G in GPa	bulk modulus M in GPa	Poisson's ratio ν	Ref.
UN	262.0 (1 − 2.21 P)	103.7 (1 − 2.22 P)	184.2 [P = 0]	0.263 [P = 0]	[24]
	266.8 (1 − 2.72 P)	103.9 [P = 0]	205.9 [P = 0]	0.284 (1 − 1.31 P)	[22]
	229.0 (1 − 4.08 P)	–	–	–	[25]
	217 [P = 0.04]	99.4 [P = 0.04]		0.1	[38]
calculated from data on single crystals	265.0	104.0	191.5	0.272	[27]
UC	225 (1 − 2.3 P)	87.3 [P = 0]	176.8 [P = 0]	0.284 (1 − 1.17 P)	[22, 43]
calculated from data on single crystals	211.0	82.9	157.5	0.28	[28]

Matthews [14] proposed eqs. (6a) and (6b) for the calculation of the porosity and temperature dependencies of the Young's moduli (E) of UC and $(U_{0.8}Pu_{0.2})C$, respectively, and eqs. (7a) and (7b) for the corresponding dependencies of the shear moduli G. The moduli

Fig. 1-96



The variation of the elastic moduli of UC, UO_2, and UN with the temperature.

may be determined with an accuracy of about 1 % up to 1 200 °C. The equations for E and G, both in GPa may be employed up to the melting points of the materials, albeit with a larger margin of error, and a greater effect of the porosity.

UC:

$E = 215\ (1-2.3\ P)[1-0.92\times10^{-4}\ (T-298)]$ (6a)

$G = 94.3\ (1-2.3\ P)[1-0.92\times10^{-4}(T-298)]/[1-0.44\times10^{-4}(T-298)]$ (6b)

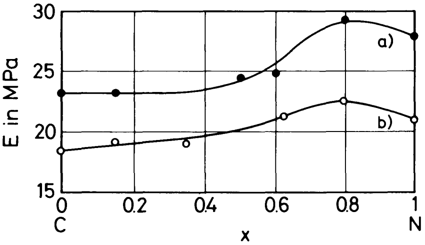
$(U_{0.8}Pu_{0.2})C$:

$E = 202\ (1-1.54\ P)[1-0.92\times10^{-4}(T-298)]$ (7a)

$G = 78.5\ (1-1.54\ P)[1-0.92\times10^{-4}(T-298)]/[1-0.44\times10^{-4}(T-298)]$ (7b)

Young's modulus of uranium and $(U_{0.85}Pu_{0.15})$ carbide nitrides ("carbonitrides") varies with the nitrogen content according to Padel et al. [43] at room temperature as shown in **Fig.1 - 97**.

Fig. 1-97



Young's moduli of carbide nitrides ("carbonitrides") of uranium (upper curve) and of $(U_{0.85}Pu_{0.15})$ (lower curve) according to Padel et al. [43]. Shown are extrapolated values for $UC_{1-x}N_x$ having 100% of the theoretical density and of $(U_{0.85}Pu_{0.15})C_{1-x}N_x$ having 70% of the theoretical density.

References for 1.2.2.1 on p. 152

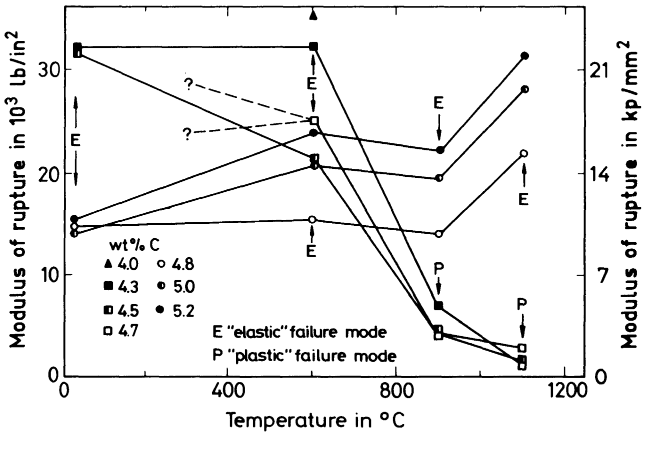
1.2.2.1.3 Strength

Rough, Chubb [29] determined the compression strength rigidity of UC up to 51 100 lb/in^2 (≈350 MPa). The strength increases with the carbon content of the material up to a maximal value at 60 at.% C.

Taylor, McMurtry [23] determined the modulus of rupture of sintered UC and UN between 25 and 1600 °C. Whereas the modulus of rupture of UC diminishes from 23000 lb/in^2 (≈160 MPa) at 25 °C to 10000 lb/in^2 (≈70 MPa) at 1000 °C, it rises again to 19300 lb/in^2 (≈135MPa) at 1200 °C. For UN having 80% of the theoretical density it increases from 10500 lb/in^2 (≈73 MPa) at room temperature to 19300 lb/in^2 (≈135 MPa) at 1200 °C, probably as a consequence of a sintering process during the measurement.

Carniglia [30] determined the modulus of rupture of arc-cast samples of UC having various C contents as a function of the temperature up to 1100 °C (**Fig. 1-98**). From these and some unpublished results, Matthews [14] compared the strength of a few ceramic uranium compounds, Table 1/25. It is necessary to point out, however, that the strength depends heavily on how the samples have been prepared, so standard deviations of ±10% are expected for the values given.

Fig. 1-98



The modulus of rupture of arc-cast U-C alloys up to 1100 °C, according to Carniglia [30].

Table 1/25
Fracture Strength of Ceramic Uranium Compounds, According to Matthews [14].

compound	UO_2	$(U,Pu)O_2$	UC_{1-x}	UC_{1+x}
σ_f in MPa	150	100	100	210

1.2.2.1.4 Hardness

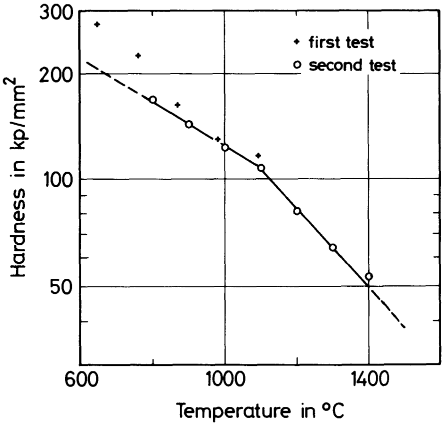
Several authors determined the hardness of carbide and nitride fuels. Dubuisson et al. [31] reported for stoichiometric UC values between 7 and 8 GPa (with a 30 kg weight). These hardness values agreed well with those of most other authors [29, 32 to 35]. Only Barnes et al. [36] found significantly lower values: 4 to 5 GPa, for samples which must have been incompletely converted (1 100 °C in vacuum). Single crystals, in the {100} orientation, showed appreciably lower values than the polycrystalline materials, at room temperature, but at 500 °C the measured hardness values of both material types were similar [35].

The hardness of carbide fuels increases steadily up to a C content of 8 wt% [29, 31], but decreases with increasing temperatures [20, 32, 33, 35]. Hypostoichiometric UC ($C < 4.3$ wt%) becomes plastic above 800 °C. Among the uranium carbides U_2C_3 has the greatest hardness [34]. Additions of Mo ($\approx$25 wt%) and Si ($\approx$0.4 wt%) raise the hardness of hypostoichiometric UC [35].

Microhardness measurements on PuC [37] yielded at room temperature a value of 8.45 ± 0.25 GPa. More recent measurements of Tokar [11] on various mixed carbides between room temperature and 1 000 °C showed different temperature dependences of the hardness of mixed carbides having different compositions. The highest value of the hardness at 1 000 °C, above 2.0 GPa, is exhibited by $U_{0.47}Pu_{0.53}C_{1.03}$.

Measurements on sintered UN gave values of the microhardness of 8.0 to 8.6 GPa [28, 40], whereas Speidel, Keller [38] reported a value of 6.0 ± 0.3 GPa. These authors also gave the temperature dependence (**Fig. 1-99**). Single crystals of UN above 1 000 °C have a hardness lower by 30% than that of hot-pressed material [39].

Fig. 1-99



Effect of the temperature on the hardness of UN (100 kp/mm^2 $\hat{=}$ 0.981 GPa).

References for 1.2.2.1 on p. 152

References to 1.2.2.1:

[1] M. S. Seltzer, J. S. Perrin, A. H. Clauer (Reactor Technol. **14** [1971] 99/135). – [2] P. Magnier, M. Marchal, A. Accary (Proc. Brit. Ceram. Soc. **7** [1967] 141/58). – [3] R. Chang (J. Appl. Phys. **33** [1962] 858/63). – [4] R. Chang (in: C. Klingsberg, Physics and Chemistry of Ceramics, Gordon and Breach, New York-London 1963, pp. 275/85). – [5] J. J. Norreys (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], pp. 435/44).

[6] M. H. Fassler, F. J. Guegel, M. A. DeCrescente (PWAC-482-Pt. 1 [1965] 1/17; N.S.A. **20** [1966] No. 4396). – [7] D. E. Stellrecht, M. S. Farkas, D. P. Moak (J. Am. Ceram. Soc. **51** [1968] 455/8). – [8] D. E. Stellrecht, D. P. Moak (in: D. L. Keller, W. Chubb, BMI-1859 [1969] 1/74; N.S.A. **23** [1969] No. 25020). – [9] N. M. Killey, E. King, H. J. Hedger (J. Brit. Nucl. Energy Soc. **10** [1971] 65/72). – [10] N. M. Killey (J. Nucl. Mater. **41** [1971] 178/86).

[11] M. Tokar (J. Am. Ceram. Soc. **56** [1973] 173/7). – [12] M. S. Seltzer, T. R. Wright, D. P. Moak (J. Am. Ceram. Soc. **58** [1975] 138/42). – [13] A. R. Hall (AERE-R-7326 [1973/74]). – [14] J. R. Matthews (AERE-M-2643 [1964]). – [15] R. N. Singh (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 257/66).

[16] J. L. Routbort, R. N. Singh (J. Nucl. Mater. **58** [1975] 78/114). – [17] M. Uchida, M. Ichikawa (J. Nucl. Mater. **49** [1973/74] 91/7). – [18] R. R. Vandervoort, W. L. Barmore, C. F. Cline (Trans. AIME **242** [1968] 1466/7). – [19] D. E. Stellrecht, D. P. Moak (BMI-1886 [1974] 94). – [20] Y. Guerin, B. Amice, C. de Novion, J. M. Lefevre (J. Nucl. Mater. **58** [1975] 1/10).

[21] C. de Novion, B. Amice, A. Groff, Y. Guerin, A. Padel (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970, Part 1). – [22] A. Padel, C. de Novion (J. Nucl. Mater. **33** [1969] 40/51). – [23] K. M. Taylor, C. H. McMurtry (ORO-400 [1961] 1/94; N.S.A. **15** [1961] No. 27510). – [24] H. L. Whaley, W. Fulkerson, R. A. Potter (J. Nucl. Mater. **31** [1969] 345/50). – [25] T. Honda, T. Kikuchi (J. Nucl. Sci. Technol. **6** [1969] 221/2).

[26] J. L. Routbort (J. Nucl. Mater. **40** [1971] 17/27). – [27] M. Guinan, C. F. Cline (J. Nucl. Mater. **43** [1972] 205/6). – [28] A. R. Hall (J. Nucl. Mater. **37** [1970] 314/25). – [29] F. A. Rough, W. Chubb (BMI-1488 [1960] 1/64; N.S.A. **15** [1961] No. 7680). – [30] S. C. Carniglia (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 403/26).

[31] J. Dubuisson, A. Houyvet, E. Le Boulbin, R. Lucas, C. Moranville (Proc. 2nd U.N. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 6, pp. 151/60). – [32] M. C. Regan, H. J. Hedger (Plansee Proc. 4th Seminar, Reutte/Tyrol, Austria, 1961 [1962], pp. 420/30). – [33] D. J. Brown, J. J. Stobo (Brit. Ceram. Soc. Trans. **62** [1963] 177/82). – [34] D. I. Sinizer (Uranium Carbides Reactor Fuel Mater. Proc. Symp., Germantown, Mass., 1961; TID-7614 [1961] 4/31). – [35] North American Aviation Inc. (Ann. Tech. Progr. Rept. NAA-SR-9999 [1964]).

[36] E. Barnes, W. Munro, R. W. Thackray, J. Williams, P. Murray (in: H. M. Finniston, J. P. Howe, Progress in Nuclear Energy, Vol. V, Metallurgy and Fuels, Pergamon, New York-Oxford-Paris 1956). – [37] O. L. Kruger (Compounds Interest Nucl. Reactor Technol. Proc. Symp., Boulder, Colo., 1964; Inst. Mining Met. Petrol Eng. Inst. Metals Div. Spec. Rept. Ser. No. 13 [1964], pp. 387/94). – [38] E. O. Speidel, D. L. Keller (BMI-1633 [1963] 1/67; EURAEC-706 [1963]; N.S.A. **17** [1963] No. 30906). – [39] R. W. Endebrock, E. L. Foster, D. L. Keller (BMI-1690 [1964] 1/24; N.S.A. **19** [1965] No. 6242). – [40] P. E. Evans, T. J. Davis (J. Nucl. Mater. **10** [1963] 43/55).

[41] M. S. Seltzer, T. R. Wright, E. O. Speidel (J. Nucl. Mater. **55** [1975] 327/34). – [42] T. R. Wright, M. S. Seltzer (NASA-CR-134588 [1974]; N-74-21177 [1974] 1/100; N.S.A. **31** [1975] No. 23159). – [43] A. Padel, A. Groff, C. de Novion (J. Nucl. Mater. **36** [1970] 297/303).

1.2.2.2 Thermal Properties

1.2.2.2.1 Coefficient of Thermal Expansion

1.2.2.2.1.1 Carbides

Knowledge of the coefficient of linear expansion of a solid fuel is significant for

a) the determination of the maximal central temperature of a fuel rod, the carbidic fuel of which is connected to the metallic cladding via, e.g., a He filled gap, and

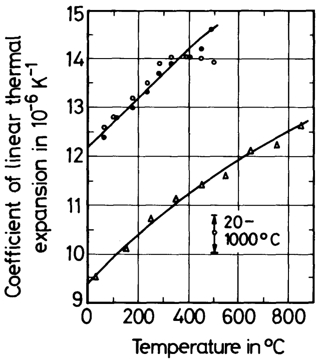
b) the estimation of the thermal and mechanical behavior of the fuel during temperature transients.

The data available for UC, PuC, (U,Pu)C, as well as for U_2C_3, Pu_2C_3, and $(U,Pu)_2C_3$ have been critically evaluated by Andrew, Latimer [1]. According to Méndes-Peñalosa, Taylor [2] the coefficient of linear expansion of melted UC, having a C-content of 4.7 to 5.05 wt%, may be represented between 20 and 2000 °C by equation (1):

$$(L_T - L_0)/L_0 = -2.01\times10^{-4} + 1.004\times10^{-5}\,t + 1.17\times10^{-9}\,t^2 \quad (t \text{ in } {}^\circ\mathrm{C}) \qquad (1)$$

The measurements by other authors [3 to 10] show that the values obtained over the whole temperature range for sintered UC agree with those of arc-cast UC within ±10%. Data from the Battelle Memorial Institute [11] are shown in **Fig. 1-100**. According to these data, the coefficient of linear expansion of melted UC samples is in good agreement with eq. (1), but the values determined for sintered samples are higher by about 30%, independently of the composition. The addition of 5 to 15 mol% WC to UC has no effect on the thermal expansion of uranium carbide up to 1600 °C [12].

Fig. 1-100



Thermal expansion of uranium monocarbide (BMI [11]).

heating	cooling	form	composition in wt% C	density in g/cm^3
□		sintered	4.8	10.84
△		melted	4.8	13.60
○	●	sintered	4.6	12.87

References for 1.2.2.2.1 on p. 155

The coefficient of thermal expansion of single-phase arc-cast PuC, having a ratio C:Pu = 0.85, may be expressed, according to Ogard et al. [13], by equation (2) between 25 and 900°C:

$$(L_T - L_0)/L_0 = -4.0\times10^{-4} + 8.3\times10^{-6}t + 3.0\times10^{-9}t^2 \quad (t \text{ in } ^\circ\text{C}) \qquad (2)$$

The mean α values for PuC determined from the lattice parameters by Pallmer [14] and Rand, Street [15] for the temperature range 20 to 600°C, resp. 20 to 700°C, are in good agreement with those of Ogard et al. [13]. The expansion coefficient measured by Russel [16] between 25 and 1000°C for sintered $PuC_{0.96}$, 12.4×10^{-6}/K, seems to be less accurate, because of the use of samples having small dimensions. A mean α value of $(10.8\pm0.2)\times10^{-6}$/K is given in a summary by Ogard, Leary [17], and the value given by Reshetnikov et al. [18] is also within these limits.

Stahl, Strasser [19] determined the same coefficients of expansion, within ±5%, for (U,Pu)C as for the monocarbide (Table 1/26). This is true independently of the plutonium concentration (from 5 to 20 wt%), the C/M ratio, or the presence of a small amount of Ni (about 0.1 wt%), added as a sintering aid. This result agrees with the studies of Ogard et al. [13] made on $(U_{0.87}P_{0.13})C$, and those of Bocker et al. [20] made on $(U_{0.8}Pu_{0.2})C_{0.95}$.

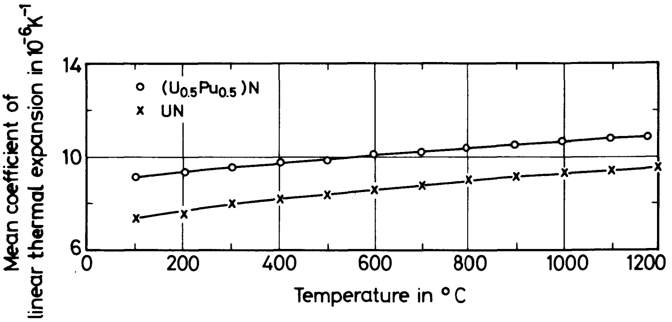
Table 1/26
The Thermal Expansion of $(U_{0.95}Pu_{0.05})C_{0.98}$ + 0.1 wt% Ni, According to Stahl, Strasser [19].

temperature in °C	expansion in %	$\alpha_m\times10^{-6}$ in K^{-1}
200	0.150	8.6
400	0.382	10.2
600	0.627	10.9
800	0.883	11.4
1000	1.221	11.9
1200	1.422	12.1
1400	1.678	12.7

1.2.2.2.1.2 Nitrides, Carbide Nitrides

The coefficient of thermal expansion of UN was measured by Speidel, Keller [21]. The value of α increases from 7.4×10^{-6}/K at 100°C to 9.4×10^{-6}/K at 1200°C, in good agreement with the work of Taylor, McMurtry [22]. These values, and those reported by Keller [23] for $(U_{0.5}Pu_{0.5})N$ are shown in **Fig. 1-101**. The latest measurements reported by Battelle Institute [24] for $(U_{0.8}Pu_{0.2})N$ are about 0.2×10^{-6}/K below the values of α shown in Fig. 1-101. Ihara et al. [25] determined the coefficient of thermal expansion of UN, U(C,N), and (U,Ce)(C,N), the latter serving for the simulation of (U,Pu)(C,N). Up to 1600°C the coefficient was temperature independent for all the samples. Its values are 6.91×10^{-6}/K for UN and 9.17×10^{-6}/K for $U(C_{0.36}N_{0.63})$. These data lead to a nearly linear dependence of the coefficient of expansion on the composition in the entire composition range of UC-UN solid solutions. The values for $(U_{0.8}Ce_{0.2})(C,N)$ mixed crystals are between 9 and 10×10^{-6}/K, and increase with the carbon content of the material.

Fig. 1-101



Coefficient of thermal expansion of $(U_{0.5}Pu_{0.5})N$ and of UN [23].

References for 1.2.2.2.1:

[1] J. F. Andrew, T. W. Latimer (LA-6037-MS [1975] 1/17; N.S.A. **33** [1976] No. 15177). – [2] R. Méndez-Peñalosa, R. E. Taylor (J. Am. Ceram. Soc. **47** [1964] 101/2). – [3] M. A. DeCrescente, A. D. Miller (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 342/57). – [4] A. C. Secrest, E. L. Foster, R. F. Dickerson (BMI-1309 [1959] 1/17; N.S.A. **13** [1959] No. 4692). – [5] A. B. Tripler, M. J. Snyder, W. H. Duckworth (BMI-1313 [1959] 1/55; N.S.A. **13** [1959] No. 8908).

[6] H. S. Kalish, J. Crane (UNC-5033 [1962] 1/22; N.S.A. **16** [1962] No. 33483). – [7] G. A. Meerson (At. Energ. [USSR] **9** [1960] 387). – [8] W. Chubb, R. F. Dickerson (Bull. Am. Ceram. Soc. **41** [1962] 564). – [9] J. Crane, E. Gordon (UNC-5080 [1964] 1/80; N.S.A. **18** [1964] No. 39828). – [10] A. Accary, R. Caillat (in: H. H. Hausner, J. F. Schumar, Nuclear Fuel Elements, Reinhold, New York 1959, pp. 257/66).

[11] F. A. Rough, W. Chubb (BMI-1441 [1960] 1/22; N.S.A. **14** [1960] No. 18107; BMI-1488 [1960] 1/64; N.S.A. **15** [1961] No. 7680). – [12] D. P. Moak, S. S. Nelson, E. L. Foster, D. L. Keller (BMI-1732 [1965]). – [13] A. E. Ogard, C. C. Land, J. A. Leary (LA-2768 [1962] 1/21; N.S.A. **17** [1963] No. 6662; J. Nucl. Mater. **15** [1965] 43/8). – [14] P. G. Pallmer (HW-72245 [1962] 1/12; N.S.A. **16** [1962] No. 15180). – [15] M. H. Rand, R. S. Street (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 108/12).

[16] L. E. Russell (AERE-R-1230 [1963]). – [17] A. E. Ogard, J. A. Leary (LA-4415 [1970] 1/6; N.S.A. **24** [1970] No. 44785). – [18] F. G. Reshetnikov, V. V. Argamonov, M. G. Gorvich, V. I. Kutaitsev, V. K. Kuznetsova, V. I. Bagrova, O. A. Alekseev, N. T. Chebotarev, N. I. Kuzin (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 751/67). – [19] D. Stahl, A. Strasser (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 373/91). – [20] S. Bocker, R. Boucher, R. Lorenzelli, C. Milet (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970, Part 1, pp. 113/9).

[21] E. O. Speidel, D. L. Keller (BMI-1633 [1963] 1/67; EURAEC-706 [1963]; N.S.A. **17** [1963] No. 30906). – [22] K. M. Taylor, C. H. McMurtry (ORO-400 [1961] 1/94; N.S.A. **15** [1961] No. 27510). – [23] D. L. Keller (BMI-1837 [1968] 1/85; N.S.A. **22** [1968] No. 28777). – [24] C. A. Alexander, J. S. Ogden, W. N. Pardue (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970, Part 1, pp. 95/103). – [25] S. Ihara, M. Suzuki, Y. Akimoto (J. Nucl. Mater. **39** [1971] 311/4).

1.2.2.2.2 Thermal Conductivity

The thermal conductivity λ of a nuclear fuel is one of the most important parameters of high power fuels, since it determines the relationship between the power x, the surface temperature T_s and the central temperature T_c according to

$$x = 4\pi \int_{T_s}^{T_c} \lambda \, dT \qquad (1)$$

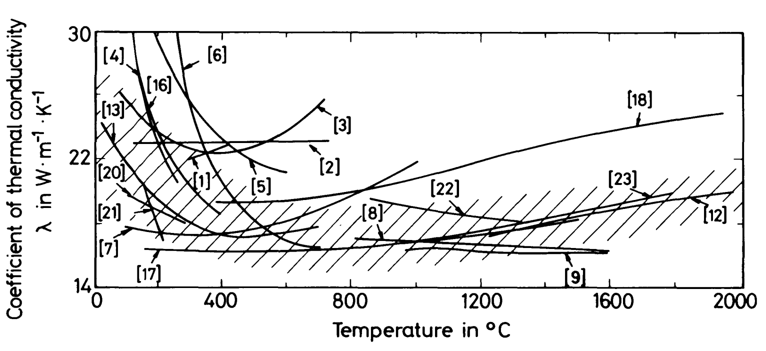
The aim of all the studies of the thermal conductivity of nuclear fuels is to permit the calculation of the temperature profile of a fuel rod, and in particular the central temperature to be expected under given operational conditions.

1.2.2.2.2.1 Carbides

Many studies [1 to 34] had the determination of the thermal conductivity of carbide fuels (UC, PuC, (U,Pu)C) as their aim. The results published during various periods were summarized in the reviews of Regan, Hedger (1961) [25], Leary, Johnson (1968) [1], Schmidt (1969) [14], Fulkerson et al. (1970) [26], Washington (1973) [27], Sheth, Leibowitz (1974) [28], and Lewis, Kerrisk (1976) [29]. These authors tried also to interpret the large differences between the measured values and to work out suitable suggestions.

Fig. 1-102 summarizes the thermal conductivity of uranium monocarbide as a function of the temperature, according to Schmidt [14]. All the thermal conductivity curves measured for UC and (U,Pu)C between room temperature and 300 °C, with the exception of those given by Leary et al. [1] and by Pearlman et al. [2], decrease with increasing temperatures. However, the values measured by Secrest et al. [3], Böttcher et al. [4], Dumas et al. [5], and Wittenberg, Grove [6] in this temperature range, seem to be significantly too high. Secrest et al. [3] and Crane, Gordon [7] find, contrary to all the other authors, that the thermal conductivity rises again strongly above 400 °C. At high temperatures, above 1 000 °C, most authors indicate that the thermal conductivity of uranium and plutonium carbides does rise slowly with increasing temperatures. Only the data of Hayes, DeCrescente [8], and Sobon et al. [9] show constant

Fig. 1-102

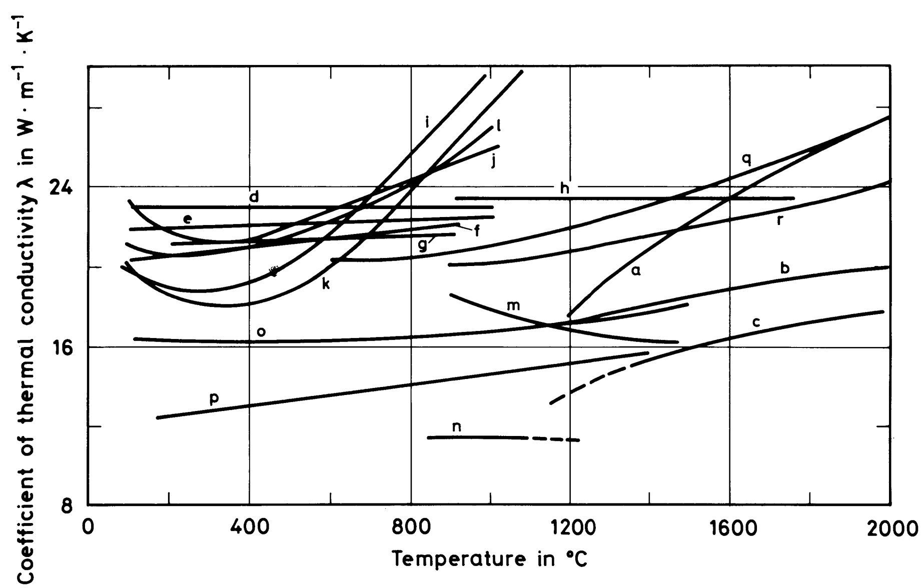


Thermal conductivity of uranium carbide obtained by various authors (according to [14]).

values, or even a slightly negative temperature coefficient of λ. The hatched area in Fig. 1-102 shows the probable values, within limits of error, of the thermal conductivity of monocarbide samples having densities ≈95% of the theoretical.

Thermal conductivity data of various authors [7, 9 to 13] obtained with samples of various carbon contents show no agreement, even not with respect to the tendencies of the curves (**Fig. 1-103**). Schmidt [14] supposed that it was difficult to produce samples having different carbon contents but otherwise identical properties. Carniglia [10], Russel [15], and Sobon et al. [9] found at temperatures below 1 000 °C that the λ values of hypostoichiometric uranium carbide* samples increased with increasing carbon contents. Crane, Gordon [7], on the contrary, found a decrease, but their samples, that had different carbon contents, also had

Fig. 1-103



Thermal conductivity of uranium carbides having various carbon contents.

code	a	b	c	d	e	f	g	h	i
Ref.	[12]	[12]	[12]	[10]	[10]	[10]	[10]	[11]	[7]
wt% C	4.70	5.00	5.20	4.58	4.33	4.24	4.04	5.30	4.40

code	j	k	l	m	n	o	p	q	r
Ref.	[7]	[7]	[7]	[9]	[9]	[13]	[13]	[24]	[24]
wt% C	4.35	4.80	5.20	4.75	4.63	5.20	3.60	4.30	4.85

---

*) hypo- and hyperstoichiometric uranium carbides are materials with <4.80 and >4.80 wt% carbon content, respectively, and consist of two phases, i.e., U-UC and UC-U_2C_3 or UC-UC_2, respectively.

different densities. In the hyperstoichiometric region below 1000 °C, an increase in the thermal conductivity with increasing carbon contents was found by Russel [15], Crane, Gordon [7], Noe et al. [16], and Bates [17]. Above 1400 °C, however, at least for hyperstoichiometric compositions, an increase in the carbon content caused a decrease in the thermal conductivity [12]. No quantitative estimates of the magnitudes of these effect could be made with the available data.

Washington [25] has reviewed the work of the authors cited in [1, 7 to 18, 26] and has recommended for 100% dense stoichiometric UC values given by eq. (2)

$$\lambda = 20 + 1.3\times10^{-3}\,(t - 500) \quad \mathrm{W\cdot m^{-1}\cdot K^{-1}} \quad (t \text{ in °C}) \tag{2}$$

between 500 and 2000 K. For hypostoichiometric UC the values are lower; for a carbide having 4.0 wt% C, Washington [25] has expressed the conductivity as:

$$\lambda = 17 + 1.9\times10^{-3}\,(t - 500) \quad \mathrm{W\cdot m^{-1}\cdot K^{-1}} \quad (t \text{ in °C}) \tag{3}$$

between 500 and 2000 K. The λ values of carbides having C contents between 4.0 and 4.8 wt% may be obtained by interpolation.

Lewis, Kerrisk [29] proposed, on the basis of the data of Kubota et al. [21], DeConick et al. [24], and Grossmann [11], the following expression for the coefficient of thermal conductivity of 100% dense UC_2 between 300 and 2000 °C:

$$\lambda = 3.24 + 6.92\times10^{-3}t \quad \mathrm{W\cdot m^{-1}\cdot K^{-1}} \quad (t \text{ in °C}) \tag{4}$$

and for 100% dense U_2C_3 having 15 vol% UC, between 27 and 1750°C:

$$\lambda = 6.58 + 5.63\times10^{-3}t \quad \mathrm{W\cdot m^{-1}\cdot K^{-1}} \quad (t \text{ in °C}) \tag{5}$$

The porosity effect may be corrected for by the simple eq. (6) [29]:

$$\lambda_M = (1 - P)\lambda_{TD} \tag{6}$$

where λ_M is the measured thermal conductivity of samples of porosity P, and λ_{TD} is that of a sample having the theoretical density. Alternatively, the somewhat more complicated eq. (7)

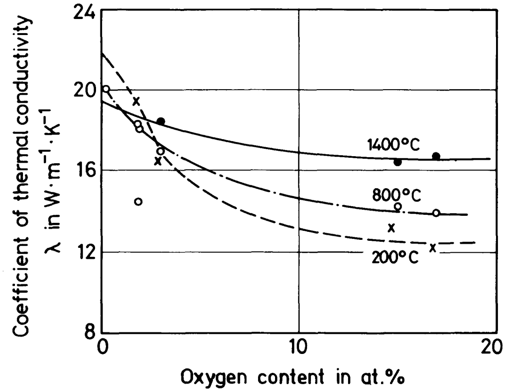
$$\lambda_M = [(1 - P)/(1 + P)]\lambda_{TD} \tag{7}$$

proposed by Washington [27], may be used.

Hayes, DeCrescente [8], Bates [17], and Wheeler et al. [30] have studied the effect of oxygen on the thermal conductivity of uranium carbide. Measurements made on samples having the composition $UC_{1-x}O_x$ agreed in finding decreasing thermal conductivities with increasing oxygen concentrations. A change of the oxygen content from 0.1 to 1.0 wt% reduced the λ value of uranium carbide by 40% at 200 °C, but by 15% only above 1 000 °C [8]. The thermal conductivity of uranium carbide diminished with incremental amounts of oxygen in the manner shown in **Fig. 1-104**.

Whereas oxygen and nitrogen reduced the thermal conductivity of uranium carbides, nickel raised it.

Fig. 1-104



Effect of the oxygen content on the thermal conductivity of UC at several temperatures (data from [8, 17, 30]).

Washington [27] recommended eq. (8) for UC having 5.0 at.% oxygen:

$$\lambda = 16 + 3.4\times10^{-3}\ (t - 500) \quad W \cdot m^{-1} \cdot K^{-1}\ (t \text{ in } ^\circ C) \tag{8}$$

and eq. (9) for UC having 7.5 at.% oxygen:

$$\lambda = 14 + 4.5\times10^{-3}\ (t - 500) \quad W \cdot m^{-1} \cdot K^{-1}\ (t \text{ in } ^\circ C) \tag{9}$$

between 500 and 2400 K. Lewis, Kerrisk [29] propose for dense UC having 0.3 wt% ($\approx$2 at.%) oxygen

$$\lambda = 21.3 - 4.66\times10^{-3}t + 2.40\times10^{-6}t^2 \quad W \cdot m^{-1} \cdot K^{-1}\ (t \text{ in } ^\circ C) \tag{10}$$

and for dense UC having 2 wt% ($\approx$17 at.%) oxygen

$$\lambda = 12.4 + 2.73\times10^{-3}\ t \pm 6.55\times10^{-7}t^2 \quad W \cdot m^{-1} \cdot K^{-1}\ (t \text{ in } ^\circ C) \tag{11}$$

between 100 and 2300 K.

The thermal conductivities of PuC and of (U,Pu)C samples have been measured by numerous authors [1, 6, 13, 15, 16, 18, 19, 30, 34, 35]. They generally agreed that the addition of plutonium reduced the thermal conductivity of uranium carbide. This effect was more significant below 1 000 °C than at higher temperatures. Leary et al. [16] and Wheeler et al. [30], in particular, have studied systematically the effect of the Pu:U ratio on the thermal conductivity. Washington's [27] preferred values for the thermal conductivity λ of 100% densified $(U_{0.8}Pu_{0.2})C$ were expressed by the eq. (12):

$$\lambda = 16 + 3.4\times10^{-3}\ (t - 500) \quad W \cdot m^{-1} \cdot K^{-1}\ (t \text{ in } ^\circ C) \tag{12}$$

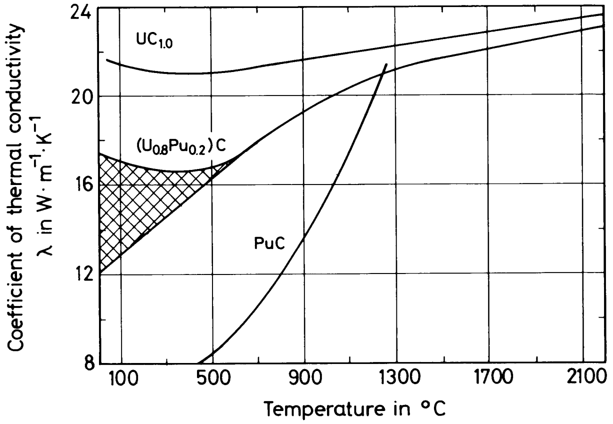
between 500 and 1 900 °C, whereas Lewis, Kerrisk [29] proposed eq. (13) between 500 and 2300 °C:

$$\lambda = 12.76 + 8.71\times10^{-3}t - 1.88\times10^{-6}t^2 \quad W \cdot m^{-1} \cdot K^{-1}\ (t \text{ in } ^\circ C) \tag{13}$$

The thermal conductivity data for mixed carbides having lower plutonium contents could be obtained by interpolation between the values for UC and $(U_{0.8}Pu_{0.2})C$.

A summary of all the values that have been proposed by Lewis, Kerrisk [29] is presented in **Fig. 1-105**.

Fig. 1-105



Proposed [29] values of the thermal conductivity of UC, PuC, and (U,Pu)C. UC: $\lambda = 21.7 - 3.01\times10^{-3}t + 3.61\times10^{-6}t^2$; $50 < t < 700$; $\lambda = 20.2 + 1.48\times10^{-3}t$; $700 < t \leq 2300$. $(U_{0.8}Pu_{0.2})C$: $\lambda = 17.5 - 5.65\times10^{-3}t + 8.14\times10^{-6}t^2$; $50 < t < 500$; $\lambda = 12.76 + 8.71\times10^{-3}t - 1.88\times10^{-6}t^2$; $500 < t \leq 2300$. PuC: $\lambda = 7.45 - 4.04\times10^{-3}t + 1.20\times10^{-5}t^2$ $100 < t \leq 1300$ (t in °C).

1.2.2.2.2.2 Nitrides

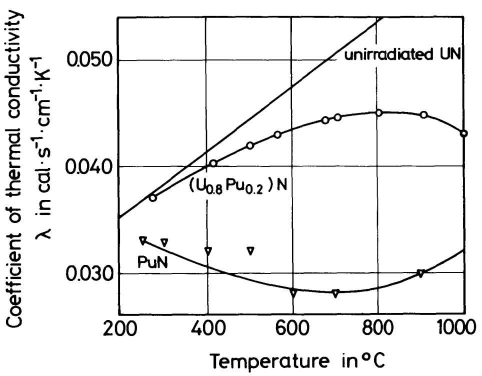
The earliest reported values of the thermal conductivity of UN, 46 to 63 $W\cdot m^{-1}\cdot K^{-1}$ between 310 and 1 000 °C (Taylor, McMurtry [36]), were higher than those of UC. Several authors have since tried to measure this value for UN [18, 37 to 48]. The values covered a wide temperature range (2 K [45] to over 1 900 K [41]), but they deviated mutually appreciably more than did those of UC, as may be seen from the presentation due to Takahashi et al. [47], shown in "Uranium" Suppl. Vol. C7, 1981, p. 32. From room temperature up to about 1 000 °C the dependencies of λ on t are linear [41, 46], and reach values between 20 and 26 $W\cdot m^{-1}\cdot K^{-1}$ at 1 000 °C. Beyond this temperatures the curves flatten and λ remains practically temperature independent. These data were evaluated critically by Moser et al. (1968) [13], Fulkerson et al. (1970) [26], Bauer (1972) [35], Washington (1973) [27], and Sheth, Leibowitz (1974) [28]. Fulkerson et al. [26] found agreement within ±13% for the λ values given by various authors [38 to 41, 43, 46, 47] at 1 000 °C, but the values of Taylor, McMurtry [36] were too high and those of Nasu and Kikushi [44] were too low. Furthermore, the temperature dependence of λ reported by Pascard [18] did not agree with the results of the other authors. Sheth, Leibowitz [28] reported the following temperature dependence of the coefficient of thermal conductivity for UN of theoretical density

$$\lambda_{UN} = 10.55 + 2.00\times10^{-2}t - 5.96\times10^{-6}t^2 \quad W\cdot m^{-1}\cdot K^{-1} \text{ (t in °C)} \qquad (14)$$

The thermal conductivity of PuN has been repeatedly measured at the Battelle Institute (BMI) in Ohio. The ascertained data are summarized in **Fig. 1-106**, due to Pardue et al. [49]. The results from the BMI can be expressed by eq. (15), due to Sheth, Leibowitz [28]:

$$\lambda_{PuN} = 7.74 + 1.337\times10^{-2}t - 9.49\times10^{-6}t^2 \quad W\cdot m^{-1}\cdot K^{-1} \text{ (t in °C).} \qquad (15)$$

Fig. 1-106



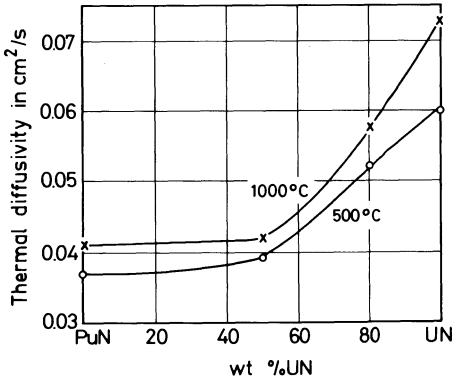
Thermal conductivity of UN, PuN, and $(U_{0.8}Pu_{0.2})N$ [49].

The low thermal conductivity of PuN affects also the thermal conductivity of mixed nitrides in a negative sense. The λ curve for $(U_{0.8}Pu_{0.2})N$ shown in Fig. 1-106 was corrected in subsequent publications from BMI [52]. Sheth, Leibowitz [28] expressed the temperature dependence by

$$\lambda_{(U_{0.8}Pu_{0.2})N} = 11.35 + 6.74\times10^{-3}t - 1.02\times10^{-6}t^2 \quad W \cdot m^{-1} \cdot K^{-1} \ (t \text{ in } ^\circ C) \quad (16)$$

This expression describes also the data of Van Craeynest et al. [19] for $U_{0.85}Pu_{0.15}N$ very well, so that it can be taken to be generally valid. **Fig. 1-107** shows the variation of the thermal conductivity with the PuN content in the mixed nitride in terms of the thermal diffusivity. The

Fig. 1-107



The effect of the composition of a U-Pu mixed nitride on the thermal diffusivity, corrected to zero porosity in the material [53].

coefficient of thermal conductivity λ and the thermal diffusivity α (in cm^2/s) are coupled by means of the specific heat at constant pressure, c_p (in $J \cdot K^{-1} \cdot g^{-1}$), and the density, ρ (in g/cm^3), according to

$$\lambda = \alpha \cdot c_p \cdot \rho \tag{17}$$

Hence λ and α vary in a similar manner.

The λ values of UC and UN show the largest differences at low temperatures, approaching each other closely at 1 000 °C. Pascard [18], Kamimoto [48], and Neumann [53] reported data on the thermal conductivity of uranium carbide nitrides. The thermal conductivity has an anomaly at low temperatures and intermediate compositions of the solid solutions, which may be attributed to a contribution from phonon conductivity [48]. Above 500 °C a minimum in λ was found at the composition $U(C_{0.6}N_{0.4})$ [18].

The thermal conductivity of (U,Pu) (C,N) solid solutions was measured by Pascard [18] and Van Craeynest et al. [19]. The latter authors reported the λ values in Table 1/27 for the various compositions.

Table 1/27
The Thermal Conductivity of (U,Pu) (C,N) Solid Solutions Having a U : Pu Ratio of 85:15 [19].

UN:UC ratio . . .	100:0	80:20	65:35	50:50	35:65	20:80	0:100
λ in $W \cdot m^{-1} \cdot K^{-1}$	22.2	30.8	34.1	28.5	26.9	33.6	38.9

References for 1.2.2.2.2:

[1] J. A. Leary, K. W. R. Johnson (Plutonium Fuel Technol. Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1968] 309/21); J. A. Leary, R. L. Thomas, A. E. Ogard, G. C. Wonn (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 365/72); J. A. Leary, A. E. Ogard (LAMS-2949 [1963] 13); J. A. Leary, A. E. Ogard (LAMS-3023 [1963] 6); J. A. Leary, A. E. Ogard (LAMS-3054 [1964] 6/10). – [2] F. A. Rough, W. Chubb (BMI-1554 [1961] 24/5). – [3] A. C. Secrest, E. L. Forster, R. E. Dickerson (BMI-1309 [1959] 1/17; N.S.A. **13** [1959] No. 4692). – [4] A. Böttcher, G. Schneider (Proc. 2nd U.N. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 6, pp. 561/3). – [5] J. P. Dumas, B. Mansard (EURAEC-1173 [1963] 1/42; N.S.A. **19** [1965] No. 7853).

[6] L. J. Wittenberg, G. R. Grove (MLM-1244 [1964] 52/5). – [7] J. Crane, E. Gordon (UNC-5080 [1964] 1/80; N.S.A. **18** [1964] No. 39828); J. Crane, E. Gordon (Trans. Am. Ceram. Soc. **7** [1964] 100/1). – [8] B. A. Hayes, M. A. DeCrescente (PWAC-480 [1965] 1/24; N.S.A. **20** [1966] No. 5893). – [9] J. T. Sobon, A. D. Miller, M. A. DeCrescente (CNLM-5621 [1964] 1/22; CONF-553-7 [1964]; N.S.A. **18** [1964] No. 34120; Bull. Am. Ceram. Soc. **43** [1964] 329). – [10] S. C. Carniglia (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 403/6).

[11] L. N. Grossman (J. Am. Ceram. Soc. Bull. **46** [1963] 264/7); L. N. Grossman (GEST-2015 [1963] 1/31; N.S.A. **17** [1963] No. 30970). – [12] M. J. Wheeler (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 358/64). – [13] J. B. Moser, O. L. Kruger, J. H. Handwerk (Proc. Brit. Ceram. Soc. **10** [1968] 129/39); J. B. Moser, O. L. Kruger (J. Nucl. Mater. **17** [1965] 153/8); J. B. Moser, O. L. Kruger (Carbides Nucl. Energy Proc. Symp., Harwell, U. K., 1963 [1964], Vol. 1, pp. 461/8); J. B. Moser, O. L. Kruger (J. Appl. Phys. **38** [1967] 3215/22); J. B. Moser, O. L. Kruger (ANL-7299 [1967] 130/3). – [14] H. E. Schmidt (KFK-1111-Pt. 7 [1969]). – [15] L. E. Russell (Conf. New Nucl. Mater. Technol. Incl. Non-Metal. Fuel Elem., Prague 1963, pp. 409/23; AERE-R-4330 [1963]).

[16] A. Noe, E. A. Elridge, H. W. Deem (BMI-1377 [1959]). – [17] J. L. Bates (BNWL-989 [1969] 1/45; N.S.A. **23** [1969] No. 27162); J. L. Bates (Therm. Conduct. Proc. 7th Conf., Gaithersburg 1967, pp. 477/89; NBS-SPEC-PUBL.-302 [1968] 477/89). – [18] R. Pascard (Plutonium Fuel Technol. Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1968] 345/68); R. Pascard (Plansee Proc. 4th Seminar, Reutte/Tyrol, Austria, 1961 [1962], pp. 387/416). – [19] J. C. VanCraeynest, J. C. Weilbacher, J. C. Salbreux (Therm. Conduct. Proc. 8th Conf., West Lafayette 1968 [1969], pp. 587/601). – [20] A. Accary, R. Caillat (in: H. H. Hausner, J. F. Schumar, Nuclear Fuel Elements, New York 1959, pp. 257/66).

[21] T. Kubota, Y. Seki, S. Takahashi (J. Nucl. Sci. Technol. **1** [1964] 93/100). – [22] M. A. DeCrescente, A. D. Miller (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 342/57). – [23] C. Mustacchi, S. Giuliani (EUR-337.e [1963] 1/27; N.S.A. **17** [1963] No. 36294). – [24] R. DeConick, W. Van Lierde, A. Gijs (J. Nucl. Mater. **57** [1975] 69/76). – [25] M. C. Regan, H. J. Hedger (Plansee Proc. 4th Seminar, Reutte/Tyrol, Austria, 1961 [1962], pp. 420/30).

[26] W. Fulkerson, T. G. Kollie, S. C. Weaver, J. P. Moore, R. K. Williams (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970, Pt. 1, pp. 374/84). – [27] A. B. G. Washington (TGR-Report 2236 [1973] 1/95; N.S.A. **29** [1974] No. 9370). – [28] A. Sheth, L. Leibowitz (ANL-APF-2 [1974] 1/21; N.S.A. **31** [1975] No. 17015). – [29] H. D. Lewis, J. F. Kerrisk (LA-6096 [1976] 1/33; INIS Atomindex **7** [1976] No. 272756). – [30] W. J. Wheeler, E. King, C. Manford, H. J. Hedger (J. Brit. Nucl. Energy Soc. **10** [1971] 55/64; AERE-R-6499 [1970]).

[31] G. A. Meerson, R. B. Kotel'nikov, S. N. Bashlykov (J. Nucl. Energy Reactor Sci. Technol. **16** [1962] 485/8). – [32] K. W. R. Johnson, J. A. Leary (Trans. Am. Nucl. Soc. **12** [1969] 591/2). – [33] S. Bocker, R. Boucher, R. Lorenzelli, C. Millet (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970, Pt. 1, pp. 113/9). – [34] J. M. Horspool, N. Parkinson, J. R. Findlay, P. E. Potter, M. H. Rand, L. E. Russell, W. Batey (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 3/16; STI-PUB-346-Vol. 1 [1974] 3/16). – [35] A. A. Bauer (Reactor Technol. **15** [1972] 87/104).

[36] K. M. Taylor, C. H. McMurtry (ORO-400 [1961] 1/94; N.S.A. **15** [1961] No. 27510). – [37] E. O. Speidel, D. L. Keller (BMI-1633 [1963] 1/67; EURAEC-706 [1963]; N.S.A. **17** [1963] No. 30906). – [38] T. G. Kollie, D. L. McElroy, R. S. Graves, W. Fulkerson (Compounds Interest Nucl. Reactor Technol. Proc. Symp., Boulder, Colo., 1964; Inst. Mining Met. Petrol Eng. Inst. Metals Div. Spec. Rept. Ser. Nr. 13 [1964] 651/76). – [39] R. W. Endebrock, E. L. Foster, D. L. Keller (BMI-1690 [1964] 1/24; N.S.A. **19** [1965] No. 6242). – [40] I. H. Waren, C. E. Price (Can. Met. Quart. **3** [1964] 183).

[41] B. A. Hayes, M. A. DeCrescente (PWAC-481 [1965] 1/21; N.S.A. **20** [1966] No. 7575). – [42] D. L. Keller (BMI-1784 [1966] 1/56; N.S.A. **21** [1967] No. 18308). – [43] J. Fauxinstier, J. C. VanCraeynest (Compt. Rend. Essai No. 475 [1967]). – [44] S. Nasu, T. Kikuchi (J. Nucl. Sci. Technol. **5** [1968] 318/9). – [45] L. G. Radosevich, W. S. Williams (J. Am. Ceram. Soc. **52** [1969] 514).

[46] J. P. Moore, W. Fulkerson, D. L. McElroy (J. Am. Ceram. Soc. **53** [1970] 76/82). – [47] Y. Takahashi, M. Murabayashi, Y. Akimoto, T. Mukaibo (J. Nucl. Mater. **38** [1971] 303/8). – [48] M. Kamimoto, Y. Takahashi, T. Mukaibo (J. Phys. Solids **35** [1974] 393/9). – [49] W. M. Pardue, F. A. Rough, R. A. Smith (Plutonium Fuel Technol. Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1968] 369/80). – [50] R. W. Dayton, S. J. Paprocki (BMI-1738-B [1965] 1/39; N.S.A. **20** [1966] No. 29616.

[51] D. L. Keller (BMI-1845-A [1968] 1/106, 60; N.S.A. **23** [1969] No. 1019, No. 1034). – [52] C. A. Alexander, J. S. Ogden, W. M. Pardue (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970, Pt. 1, pp. 95/103). – [53] D. L. Keller (BMI-1837 [1968] 1/85; N.S.A. **22** [1968] No. 28777). – [54] M. Neumann (JUEL-1079-RB-RW [1974] 1/122; N.S.A. **31** [1975] No. 11762).

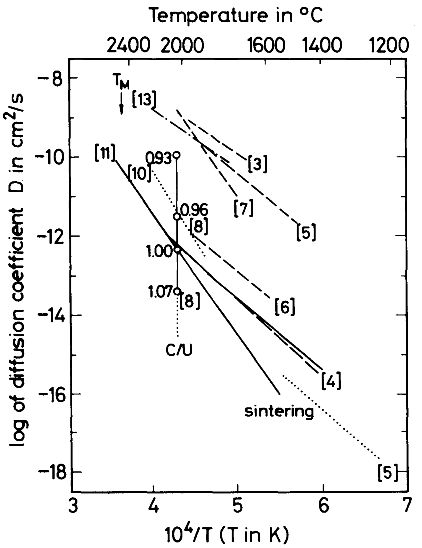
1.2.2.3 Diffusion

Self-diffusion and the diffusion of fission products in the crystal lattice of a nuclear fuel may lead to changes in the local composition and to processes such as creep, grain growth, densification and swelling, as well as to fission gas release, by means of material transport, and thereby to a direct effect on the behavior during irradiation. It is necessary to study the effects of the most important factors, such as the fuel composition, the amounts of foreign elements (impurities, fission products), the microstructure, and the temperature, because of the complexity of the diffusional behavior of the various species. Two reviews, those of Routbort, Singh [1] and of Matzke, Bradbury [2], deal very extensively with all the aspects of the problem.

1.2.2.3.1 Self-Diffusion in Uranium Carbides

Extensive results, due to intensive study [3 to 13], exist concerning the self-diffusion of uranium in UC, but only few measurements were made on UC_2 [14] and U_2C_3 [15]. Most of the data, obtained on nearly stoichiometric monocarbide samples, are shown as an Arrhenius plot in **Fig. 1-108**. In view of the large scatter noted in the diffusion data, it is necessary to indicate the possible sources of error. Mainly the following three facts are responsible for the lack of agreement among the results of the various authors: 1) the large effect of the C:U ratio influences the mobility of the uranium atoms; 2) impurities also can increase or decrease this mobility, in particular at low temperatures; 3) poor experimental techniques have sometimes

Fig. 1-108



The diffusion coefficient of uranium in nearly stoichiometric UC as a function of the temperature. The effect of the composition is indicated at 2150 °C. The numbers on the curves give the literature sources (see References on p. 174/5). T_m = melting point.

been the source of serious errors. The data obtained by Matzke et al. [11] (see Fig. 1-108) on arc-cast UC having <120 ppm metallic impurities cannot be described by a simple Arrhenius plot, but require for their description an expression of the form

$$D_u = D_{0\,1}\exp(-\Delta H_1^{\ddagger}/RT) + D_{0,2}\exp(-\Delta H_2^{\ddagger}/RT) \quad \text{(with T in K)} \qquad (1)$$

where $D_{0,i}$ are frequency factors and $\Delta H_i^{\ddagger}$ activation enthalpies. Routbort, Singh [1] considered eq. (1), proposed by Matzke et al. [11] for the description of the diffusion of uranium in UC, to be realistic. Matzke, Bradbury [2] gave the following values for the parameters of eq. (1):

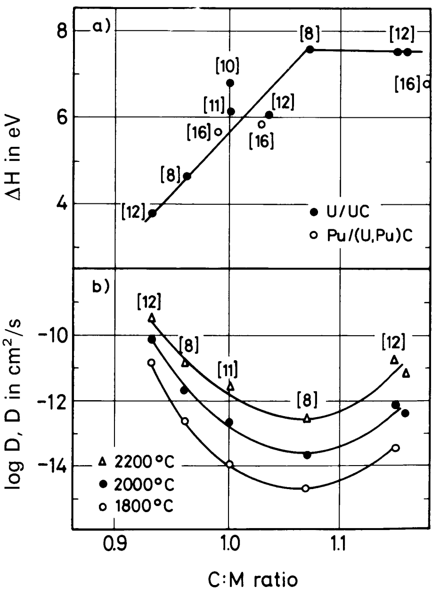
$$\begin{aligned} D_{0\,1} &= 6.9,\ \Delta H_1^{\ddagger} = 141 \pm 10\,\text{kcal/mol}; \\ D_{0\,2} &= 3.6\times10^{-5},\ \Delta H_2^{\ddagger} = 84.5 \pm 5\,\text{kcal/mol} \end{aligned} \qquad (2)$$

for D_U in $UC_{1.00}$ expressed in cm²/s. The second term expresses the effect of the impurities.

Effect of the Composition on the Diffusion of Uranium

Fig. 1-109 shows clearly that the diffusion coefficient of uranium in UC decreases by three orders of magnitudes, as the C:U ratio is increased from 0.93 to 1.07, but increases again for higher C contents. The latter increase in the diffusion coefficient could be due to the presence of the di- or sesquicarbide, since the mobility of uranium in these phases is larger than in the monocarbide [14, 15]. If this were the case, the ΔH values should have decreased again.

Fig. 109



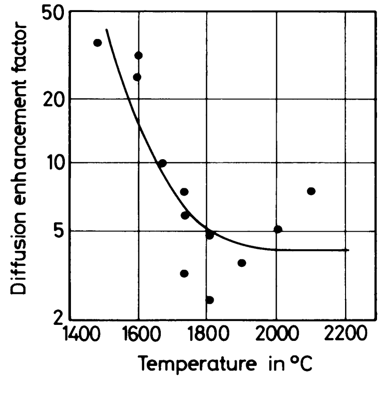
The effect of the C:U ratio on the self-diffusion of uranium (diffusion of Pu, see [16]) in UC. a) the activation enthalpy, and b) the diffusion coefficient (logarithmic, D in cm²/s). The numbers on the curves refer to the literature sources (see References on p. 174/5).

In order to determine the composition dependence of the uranium self-diffusion in UC, measurements were made over a wide C:U range. The results are shown in Fig. 1-109a. Beside the diffusion coefficients of uranium in UC_x and their activation enthalpies as functions of the C:U ratio, also the corresponding values for Pu in (U,Pu)C mixed crystals, obtained by Nitzki, Matzke [16], are shown. The activation enthalpy increases linearly from 3.8 eV/atom (1 eV/atom = 23038 cal/mol), at a C:U ratio of 0.93, to 7.6 eV/atom, at C:U = 1.07, and thereafter it remains constant.

Effect of Impurities on the Diffusion of Uranium

Some authors [17, 18] showed that the diffusion of uranium in UC was appreciably increased by doping with elements such as W, Fe, Ni, Ta, and V at above 120 ppm. The enhancement factor increased with diminishing temperatures; it was insignificant at high temperatures. **Fig. 1-110** shows, as an example, the variation of the enhancement factor with the temperature for (U + 0.15 wt% Ta)$C_{1.035}$. The enhancement factor is the ratio of the diffusion coefficients in samples with and without the Ta.

Fig. 1-110



The enhancement effect of 0.15 wt% Ta in $UC_{1.035}$ on the uranium diffusion as a function of the temperature.

Hitherto the dependence of the uranium mobility on the concentration of the impurity elements could not be determined exactly, but at low concentrations of these it could be expressed as

$$D(c) = D(0) \cdot (1 + bc) \tag{3}$$

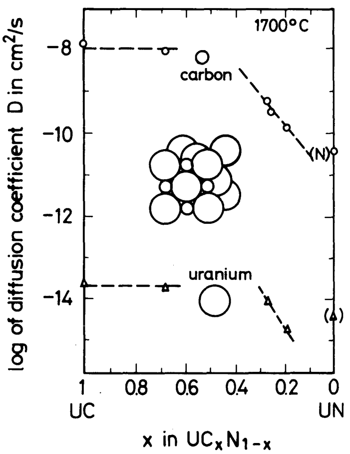
where c is the concentration and b the enhancement factor for a given impurity.

It is noteworthy that the foreign elements always cause an enhancement of the uranium diffusivity, even though they have different atomic radii and electronic structures. However, all the impurity elements studied have ionic radii which are smaller than that of the uranium [1].

Effect of Nitrogen on the Diffusion of Uranium

Matsui et al. [19] found a decrease in the self-diffusion of uranium in UC_xN_{1-x} as the nitrogen content increased. **Fig. 1-111** shows that the effect of the nitrogen becomes noticeable only when more than 50% of the carbon atoms have been substituted by nitrogen ones.

Fig. 1-111



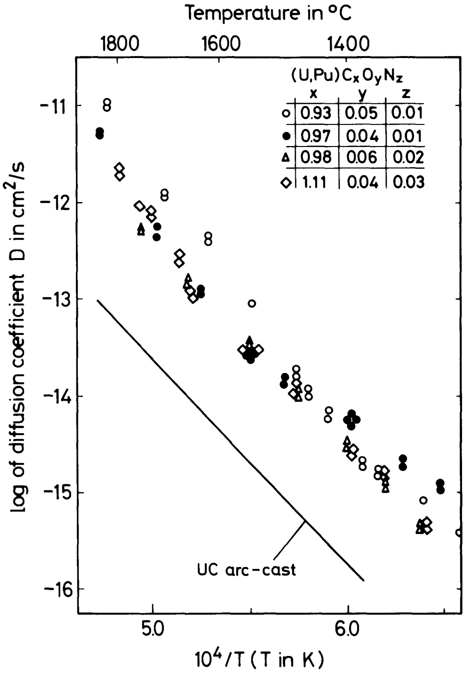
Diffusion of ^{233}U and of ^{14}C in UC_xN_{1-x} at 1700 °C as a function of x.

Diffusion of Other Actinides in Carbides

Nitzki, Matzke [16, 57] studied the diffusion of Pu in sintered (90 to 95% of theoretical density) $(U_{0.85}Pu_{0.15})C_xO_yN_z$. Although the quantitative aspects of the data are doubtful, in view of the presence of high concentrations of impurities, certain trends may still be derived from the results. The substitution of 5% of the C atoms by O or N atoms does not affect the mobility of the Pu. At higher temperatures the self-diffusion of Pu depends, as does that of the U, on the C: (U + Pu) ratio. Although the experiments on the U,Pu carbide mixed crystals were conducted only up to 1800 °C, the authors expressed their opinion, that the plutonium diffusion, like the uranium diffusion in UC, could be accounted for only if two different processes were considered jointly. Results of experiments on Pu diffusion in (U,Pu)C and of U diffusion in UC are summarized in **Fig. 1-112**, p. 168.

Hirsch, Scherff [8] observed, that Am and Pu ions diffused in $UC_{1.07}$ faster than U did, but Pa ions did so more slowly. This phenomenon may be explained by the different sizes of the ionic radii: that of Pa is somewhat larger, those of Pu and Am somewhat smaller than the ionic radius of U.

Fig. 1-112



The temperature dependence of the diffusion of Pu in $(U_{0.85}Pu_{0.15})$(C,N,O), compared with that of U in arc-cast UC.

The Contribution of Grain-Boundary Diffusion

Transport processes in nuclear fuels are characterized by a superposition of several diffusion processes. Besides the volume diffusion, such processes as diffusion along grain boundaries or dislocations, surface diffusion, transport via the gaseous phase and via chemical interdiffusion, and diffusion in a thermal gradient, should be noted. Grain-boundary diffusion in UC_x was first studied by Villaine [20]. Routbort, Matzke [21], using the so-called α-degradation technique, studied the grain-boundary diffusion in pure and in doped UC having various C:U ratios. Matzke, Bradbury [2] summarized the published results as follows:

– grain-boundary diffusion of uranium in carbides is 3 to 5 orders of magnitude faster than volume diffusion,

– grain-boundary diffusion is more pronounced and faster in hypostoichiometric UC than it is in stoichiometric and hyperstoichiometric uranium monocarbide,

– this type of diffusion is inhibited by impurities,

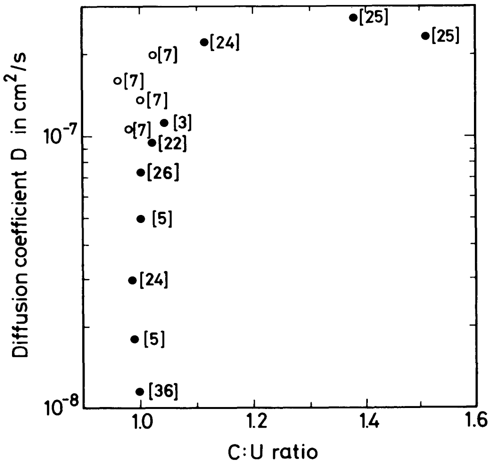
– the activation enthalpy for grain-boundary diffusion in stoichiometric UC is comparable with that for self-diffusion of carbon, but is only about 55% of that for the volume diffusion of uranium.

1.2.2.3.2 Diffusion of Carbon in Carbides

Also the diffusion of carbon in UC has been studied intensively by numerous authors [2, 3, 5, 7, 22 to 28]. The chemical diffusion coefficient of C in UC was also determined [26]. The results (to be shown in "Uranium" Suppl. Vol. C12) demonstrate that it is necessary to differentiate between low and high temperature processes for the diffusion of C in UC, as it was for the self-diffusion of U. It is seen that the $UC_{1.04}$ sample measured by Chubb et al. [3] and the $UC_{1.02}$ sample studied by Makino et al. [23] contained traces of U_2C_3 at low temperatures, the $UC_{1.07}$ and $UC_{1.18}$ samples studied by Lee, Barrett [5] contained appreciable quantities of U_2C_3, whereas the $UC_{0.96}$ sample of Bentle, Ervin [7] contained some free uranium. The deviations from a simple Arrhenius process are understandable in view of the presence of second phases like these. Furthermore, the impurities present in the UC, mainly oxygen and nitrogen, have a large effect not only on the diffusion of uranium, but also on that of carbon. Only the results for the high temperature range are therefore trustworthy. It should be noted, also, that the composition of strongly hyperstoichiometric UC changes during high temperature measurements, because of the incongruent vaporization (e.g. for 0.8 h in vacuum at 2130 °C a $UC_{1.38}$ sample changes its composition to $UC_{1.05}$).

The activation enthalpy seems to be a direct function of the carbon concentration: the $\Delta H^{\ddagger}$ values decrease with increasing C:U ratios from ≈94 kcal/mol at C:U = 0.96 to ≈55 kcal/mol at C:U = 1.1. Beyond this the $\Delta H^{\ddagger}$ value remains constant, if it is assumed that the C:U ratio does not vary during the diffusion process. The diffusion coefficient D_c (in UC) reported by various authors as a function of the C:U ratio is shown in **Fig. 1-113**.

Fig. 1-113



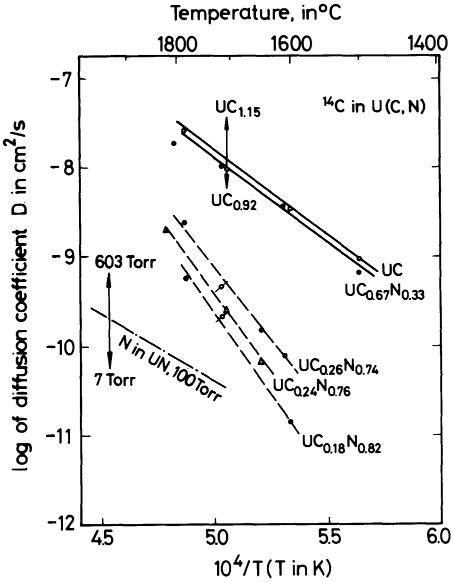
The variation of D_c in UC_x with the ratio C:U at 2100 K. The numbers are references to the literature sources.

References for 1.2.2.3 on pp. 174/5

The Effect of Nitrogen on the Mobility of the Carbon

Matsui et al. [19] studied the diffusion of carbon in four uranium carbide nitride samples, UC_xN_{1-x} with $x = 0.67, 0.26, 0.24$, and 0.18, using ^{14}C. The diffusion coefficients are shown as an Arrhenius plot in **Fig. 1-114**. A strong decrease of the diffusion coefficient of carbon with increasing nitrogen contents is noted. This behavior is similar to that of uranium, seen in Fig. 1-111, p. 167.

Fig. 1-114



Diffusion of carbon in UC_xN_{1-x} [19].

1.2.2.3.3 Self-Diffusion of Metal Atoms in Nitrides

The diffusion measurements of metal atoms in nitrides are limited because of experimental difficulties. Only Reimann et al. [38] have studied the self-diffusion of uranium in polycrystalline UN at partial pressures of nitrogen between 0.1 and 200 Torr and in the temperature range 1 600 to 1 850 °C. A linear relationship between D_U (in UN) and p_{N_2} was found, but at a given partial pressure the mobility of uranium was said to be independent of the temperature. This may possibly be explained by a compensation of the temperature effect by a shift of the N:U ratio at a constant N_2 pressure in these experiments. Routbort, Singh [1], too, have found in preliminary experiments a linear relationship between D_U (in UN) and p_{N_2}. A temperature dependency of D_U was, however, found at constant p_{N_2} (280 Torr, higher than the range studied by Reimann et al. [38]) in the temperature range 1 700 to 1 900 °C.

Bradbury, Matzke [39] reported the self-diffusion of plutonium, which they determined in two samples of (U,Pu)N having different compositions, different oxygen contents, and different densities. The results, shown in Table 1/28, are valid for the temperature range 1 500 to 1 800 °C. According to these data, the activation enthalpy for the diffusion of plutonium decreases when the N:(U + Pu) ratio increases. Since at high temperatures this ratio N:(U + Pu) varies with p_{N_2} (in Torr), the authors determined the following relationship for the diffusion coefficient D_{Pu} (in cm²/s) in (U,Pu)N mixed crystals at 1 720 °C:

$$\log D_{Pu} = -14.2 + 0.146 \log p_{N_2} \qquad (4)$$

Table 1/28
Diffusion of Plutonium in (U,Pu)N Mixed Chrystals.

composition	ΔH in kJ/mol	D_0 in cm²/s
$U_{0.81}Pu_{0.19}N_{0.98}C_{0.01}O_{0.09}$	496.5 ± 18.8	0.25
$U_{0.81}Pu_{0.19}N_{1.01}C_{0.01}O_{0.04}$	450.5 ± 14.2	0.019

1.2.2.3.4 Diffusion of Nitrogen in Nitrides

Several experiments [40 to 43] were made regarding the diffusion of nitrogen in UN, but only one result [43] is known, concerning D_N in (U,Pu)N mixed crystals. The data are summarized in Table 1/29. See also "Uranium" Suppl. Vol. C7, 1981, pp. 29/30. The D_N values of Benz, Hutchison [42] deviate considerably from those of the other authors. These deviations are due mainly to the use of different methods of measurements. Sturiale, DeCrescente [40] used the gaseous exchange method for determining D_N (in UN). They also reported the existence of a low temperature diffusion process involving grain boundary diffusion (at p_{N_2} = 100 Torr and T < 1 500 °C) with an activation enthalpy of 29 kcal/mol (120 kJ/mol). The gas exchange method led to values which were about five times higher than those obtained by Holt, Almassy [41], using $^{15}N(\alpha,n)^{18}F$ activation, and those obtained by Droege, Alexander [43], using isotope tracer techniques.

Table 1/29
Self-Diffusion of Nitrogen in Uranium Nitride.

temperature in °C	p_{N_2} in Torr	n in $D^N_{UN} \sim (p_{N_2})^n$	D_0 in cm²/s	ΔH in kJ/mol	Ref.
1 200 to 1 900	100	–	2.6×10^{-4} [a]	230[a]	[40]
1 700 to 2 000	7 to 603	0.36 (1 946 °C)	5×10^{-5} [a]	235[a]	[41]
1 800 to 2 400	15 to 1 500	nonsystematic	12	503 ± 105	[42]
1 370 to 1 810	0.8 to 76	0.5 (1 800 °C)	–	260[a]	[43]

[a] At a constant partial pressure of N_2 of 0.133 bar.

1.2.2.3.5 Diffusion of Fission Gases in Carbides and Nitrides

Diffusion of the noble gases – in particular Kr and Xe – plays a decisive role in the release of these fission products on the one hand, and in the swelling of the fuel during irradiation on the other. Only a few results concerning the diffusion of xenon [30 to 34, 44, 45] and of krypton [34, 46] have been obtained. The data for uranium monocarbide, summarized in Table 1/30, show a large scatter, which may be ascribed to several reasons. These include: a) the varying stoichiometry, b) the method of the sample preparation, since the diffusion is strongly dependent on impurities and crystal defects, c) the surface area relevant to gas release, which is not necessarily the same as that measured by the gas adsorption method, and d) when atoms or molecules are released by means of grain-boundary diffusion, the apparent diffusion coefficient naturally depends strongly on the grain-boundary distribution [32, 45]. Matzke, Springer [33] presume that as a consequence of variations in the neutron irradiation a diverse concentration of so-called "gas traps" is formed, and an apparently low diffusion is observed. The experiments of these authors showed, that up to an integrated neutron flux of 10^{16} cm^{-2} and a gas concentration of 10^{-5} at.% the mobility of the fission-produced noble gases was independent of the dose, whereas it diminished at higher integrated fluxes. Matsui et al. [44] determined the activation energy of the diffusion mechanism, on the one hand during an ascending heat treatment (AHT), i.e., the heating-up of irradiated samples, and on the other hand after a temperature of 1400 to 1500°C had been attained, during the cooling of the samples, i.e., a descending heat treatment (DHT). For various samples and at integrated neutron fluxes in the range 1.6×10^{15} to 1.0×10^{17} cm^{-2} these authors found for the AHT step a rather constant activation energy of 48 ± 5 kcal/mol. For an integrated neutron flux of 5.8×10^{17} cm^{-2} this rose to 76 ± 5 kcal/mol. After the DHT step an activation energy of 83 ± 5 kcal/mol was found for the diffusion of Xe in UC. This value was in good agreement with that determined by Matzke, Springer [33] for a UC single crystal, 84 ± 5 kcal/mol. Matzke [35] found that the rate of diffusion of Xe did not depend on the C content of monocarbides. The mobility of Kr in UC was, as expected, considerably larger than that of Xe [34, 36]. Several authors [47 to 50] determined diffusion coefficients in UC samples from measurements of the fission gas release at low temperatures or at low fluences, taking into consideration the geometry and the BET surface area. On the basis of measurements made on U, UO_2, and UC samples after irradiation (5×10^{15} n · cm^{-2} at about 100°C), Osawa [49] expressed the relationship between the percentage released F and the BET surface area S (in cm^2/cm^3) as $\log F = 4.36 + 0.88 \log S$, independent of the material. Samsonow et al. [51] found a dependence of the diffusion of Xe in UC on the integrated neutron flux, in agreement with Matsui et al. [44].

Table 1/30
Diffusion of Fission Product Noble Gases in UC

temperature in °C	D_0 in cm^2/s	ΔH^{+} in kcal/mol (kJ/mol)	neutron dose in n · cm^{-2}	Ref.
diffusion of Xe in UC				
1000 to 1400	2.1×10^{-5}	85.1 (356)	1.8×10^{-16}	[30]
800 to 1300	10^{-7} to 10^{-3}	45 (188)	10^{17}	[31]
1000 to 2000	$(1.17\pm0.16)\times10^{-6}$	54.9 ± 1.2 (230)	3.0×10^{15}	[32]
1000 to 1600	0.3	84.0 ± 5 (352)	6.0×10^{15}	[33]
1500	$(1.5\pm0.4)\times10^{-1}$	83.0 ± 5 (348)	5.0×10^{16}	[44]
950 to 1830	1.6×10^{-4}	62.7 ± 0.9 (263)	1.2×10^{18}	[45]
diffusion of Kr in UC				
1000 to 2500	1.4×10^{-2}	80 (335)	–	[46]

Table 1/31
The Diffusion Coefficient of ^{133}Xe in $UC_{1-x}N_x$, Calculated from the Rate of Release after Irradiation [52].

sample No.		UN	UN	$UC_{1-x}N_x$				
		A	B	C	D	E	F	G
x in $UC_{1-x}N_x$		1.00	1.00	0.93	0.61	0.48	0.26	0.10
specific surface area in cm^2/g		1850	1000	2100	2010	3550	210	780
mean diffusion coefficient in cm^2/s, at	800 °C	1.1×10^{-19}	3.8×10^{-19}	3.4×10^{-20}	4.2×10^{-20}	9.0×10^{-21}	3.7×10^{-18}	6.7×10^{-18}
	1000 °C	1.8×10^{-16}	4.4×10^{-17}	3.7×10^{-20}	1.6×10^{-18}	3.0×10^{-19}	9.9×10^{-18}	3.1×10^{-18}
	1200 °C	1.5×10^{-16}	1.8×10^{-16}	1.2×10^{-16}	4.4×10^{-17}	2.4×10^{-17}	7.6×10^{-17}	8.8×10^{-17}
	1400 °C	2.1×10^{-15}	4.1×10^{-15}	1.2×10^{-16}	9.9×10^{-16}	3.1×10^{-16}	9.9×10^{-16}	3.6×10^{-14}
	1600 °C	7.7×10^{-15}	4.1×10^{-14}	5.7×10^{-15}	1.4×10^{-15}	1.4×10^{-14}	1.4×10^{-15}	3.8×10^{-14}
activation enthalpy in kJ/mol		240	395	250	218	272	134	327

References for 1.2.2.3 on pp. 174/5

Biddle [52] determined the true diffusion coefficient of ^{133}Xe from the fission gas release rate in powdered U(C,N) solid solutions, using the Booth [53] model. These had compositions between UC and UN, and had been subjected to irradiation by 2×10^{17} n · cm^{-2} and to heating at temperatures between 800 and 1600 °C. The results are shown in Table 1/31, p. 173. With the exception of sample F, the activation energy for the diffusion of ^{133}Xe in these phases is in the same range as in UO_2 [54]. Whereas the diffusion coefficient in uranium mononitride, UN, is comparable to that in UO_2, there exists a close similarity of the values in U(C,N) and in UC. A minimum in the diffusion coefficient was noted at the composition $UC_{0.2}N_{0.8}$, contrary to the data of Iseki et al. [55], who found the minimum at the equimolar composition, $UC_{0.5}N_{0.5}$. These latter authors pointed out, that after an integrated neutron flux of 1.7×10^{16} cm^{-2}, the irradiation induced microcrack formation prevented a conclusion about the diffusion mechanism to be reached from the release rates determined by them.

References for 1.2.2.3:

[1] J. L. Routbort, R. N. Singh (J. Nucl. Mater. **58** [1975] 78/114). – [2] H. Matzke, M. H. Bradburg (EUR-5906 [1978] 1/111; INIS Atomindex **10** [1979] No. 423257). – [3] W. Chubb, R. W. Getz, C. W. Townley (J. Nucl. Mater. **13** [1964] 63/74). – [4] R. Lindner, G. Riemer, H. L. Scherff (J. Nucl. Mater. **23** [1967] 222/30). – [5] H. M. Lee, L. R. Barrett (J. Nucl. Mater. **27** [1968] 275/84).

[6] P. Villaine, J. F. Marin (Compt. Rend. C **264** [1967] 2015/8). – [7] G. G. Bentle, G. Ervin (AI-AEC-12726 [1968] 1/21; N.S.A. **22** [1968] No. 47701). – [8] H. J. Hirsch, H. L. Scherff (J. Nucl. Mater. **45** [1972/73] 123/30). – [9] H. J. Hirsch (Diss. Braunschweig T.U. 1970). – [10] S. Sarian, J. T. Dalton (J. Nucl. Mater. **48** [1973] 351/9).

[11] H. Matzke, J. L. Routbort, H. A. Tasman (J. Appl. Phys. **45** [1974] 5187/95). – [12] H. Matzke, J. L. Routbort (Thermodyn. Nucl. Mat. Proc. Symp., Vienna 1974, IAEA [1975] Vol. 1, pp. 397/407). – [13] P. S. Maiya, J. L. Routbort (J. Mater. Sci. **7** [1972] 609/14). – [14] H. Matzke, C. Politis (Solid State Commun. **12** [1973] 401/4). – [15] H. Matzke, C. Politis (Reaktortagung, Berlin 1974, pp. 269/72).

[16] V. Nitzki (Diss. Karlsruhe 1975). – [17] H. Matzke (J. Nucl. Mater. **52** [1974] 85/8). – [18] J. L. Routbort, H. Matzke (J. Nucl. Mater. **54** [1974] 1/8). – [19] H. Matsui, M. H. Bradburg, H. Matzke (Nucl. Sci. Eng. **66** [1978] 406/14). – [20] P. Villaine (Diss. Univ. Grenoble 1967).

[21] J. L. Routbort, H. Matzke (J. Am. Ceram. Soc. **58** [1975] 81/4). – [22] R. A. Krakowski (J. Nucl. Mater. **32** [1969] 120/5). – [23] Y. Makino, K. Asahi, P. Son, M. Miyake, T. Sano (J. Nucl. Sci. Technol. **9** [1972] 569/73). – [24] Y. Makino, K. Asahi, P. Son, M. Miyake, T. Sano (J. Nucl. Sci. Technol. **10** [1973] 493/500). – [25] Y. Makino, P. Son, M. Miyake, T. Sano (J. Nucl. Mater. **49** [1973/74] 225/31).

[26] T. C. Wallace, W. G. Witteman, C. L. Radosevich, M. G. Bowman (Plansee Proc. 6th Seminar, Reutte/Tyrol, Austria, 1968 [1969], pp. 676/702; LA-DC-8840 [1968] 1/45; CONF-680603 [1968]; N.S.A. **22** [1968] No. 38623). – [27] S. Sarian (J. Nucl. Mater. **49** [1973/74] 291/8). – [28] G. E. Murch (J. Nucl. Mater. **55** [1975] 355/6). – [29] W. Schüle, P. Spindler (J. Nucl. Mater. **32** [1969] 20/9). – [30] A. Auskern, Y. Osawa (J. Nucl. Mater **6** [1962] 334/5).

[31] R. Lindner, H. Matzke (Z. Naturforsch. **14a** [1959] 1074/7). – [32] H. Shaked, D. R. Olander, T. H. Pigford (Nucl. Sci. Eng. **29** [1967] 122/30). – [33] H. Matzke, F. S. Springer (Radiat. Eff. **2** [1969] 11/8). – [34] F. W. Felix, H. Seelig (Nukleonik **9** [1967] 389/92). – [35] H. Matzke (J. Nucl. Mater. **30** [1969] 110/21).

[36] Y. Bertaud (CEA-R-4227 [1971] 1/61; N.S.A. **26** [1972] No. 20678). – [37] M. Tetenbaum, P. D. Hunt (J. Nucl. Mater. **40** [1971] 104/12). – [38] D. K. Reimann, D. M.

Kroeger, T. S. Lundy (J. Nucl. Mater. **38** [1971] 191/6). – [39] M. H. Bradburg, H. Matzke (J. Nucl. Mater. **75** [1978] 68/76). – [40] T. J. Sturiale, M. A. DeCrescente (PWAC-477 [1965] 1/25; N.S.A. **20** [1966] No. 4394).

[41] J. B. Holt, M. Y. Almassy (J. Am. Ceram. Soc. **52** [1969] 631/5). – [42] R. Benz, W. B. Hutchinson (J. Nucl. Mater. **36** [1970] 135/46). – [43] J. W. Droege, C. A. Alexander (in: D. L. Keller, Progress on Development of Fuel and Technology for Advanced Reactors During July 1970 Through June 1971, BMI-1918 [1971] A5; N.S.A. **26** [1972] No. 8561). – [44] H. Matsui, K. Sakanishi, T. Kirihara (J. Nucl. Sci. Technol. **12** [1975] 436/41). – [45] K. Papathanasopulos (Diss. Braunschweig T.H. 1964).

[46] J. J. Weinstock, A. P. Pinkerton, K. D. Ziegel (NYO-9047 [1961] 1/22; C.A. **62** [1965] 2460). – [47] A. Accary, R. Darras, R. Caillat (Radiat. Damage Reactor Mater. Part Proc. Symp., Venice 1962 [1963], pp. 275/86). – [48] A. Auskern (J. Am. Ceram. Soc. **47** [1964] 390/4). – [49] Y. Osawa (J. Nucl. Sci. Technol. **2** [1965] 296/303). – [50] P. Schmeling (EUR-1752.e [1964] 1/46; N.S.A. **19** [1965] No. 14082).

[51] B. V. Samsonov, A. K. Frei (At. Energ. [USSR] **30** [1971] 358/62). – [52] P. Biddle (AERE-R-4700 [1964] 1/11; N.S.A. **19** [1965] No. 2715). – [53] A. H. Booth, G. T. Rymer (AECL-692 [1958]; CRDC-720 [1958] 1/30; N.S.A. **13** [1959] No. 573). – [54] D. Davies, G. Long (AERE-R-4347 [1963] 1/43; N.S.A. **17** [1963] No. 32563). – [55] T. Iseki, T. Hase, H. Suzuki, S. Kimura, T. Tamai (Bull. Tokyo Inst. Technol. No. 116 [1973] 91/5).

[56] P. Schmeling (EUR-1752.e [1964] 1/46; N.S.A. **19** [1965] No. 14082). – [57] V. Nitzki, H. Matzke (Reaktortagung, Nürnberg 1975, pp. 399/402).

1.2.2.4 Electrical Resistivity

1.2.2.4.1 Carbides

Like the thermal conductance, also the electrical conductance is evidence for the fundamental metallic character of UC. The electrical resistivity of carbidic fuels has been measured by Dayton, Tipton [1, 2] up to 1000 °C already in 1959. Since then, several authors [3 to 6] summarized and compared the series of measurements that have been reported.

Fig. 1-115, p. 176, shows a series of measurements of the electrical resistivity of UC of nearly stoichiometric composition.

Except for the data of Costa, Lallement [9], all the other data agree within ±8% [6]. If the data of Hayes, DeCrescente [11] are corrected by means of the expression

$$\rho_0 = \rho(1-P)^{1.38} \qquad (1)$$

which was suggested by Bates [4, 18], then the deviations are reduced to ±5%. In this expression ρ_0 is the electrical resistivity of UC having 100% of the theoretical density, ρ is that of porous UC, and P is the volume fraction of the pores in the sample.

The data of Griffiths [16], obtained up to 1000 °C, and those of Norreys, Wheeler [17], obtained for the range 800 to 2000 °C, which are not included in Fig. 1-115 also lie within the above mentioned limits.

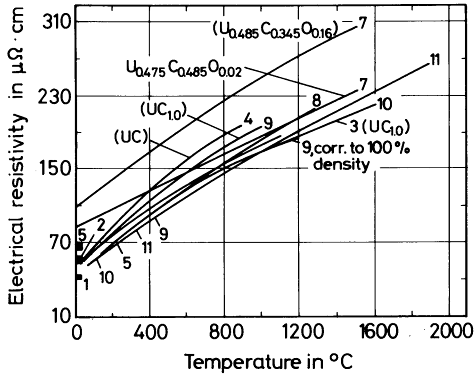
The electrical resistivity of dense UC between 25 and 1600 °C may therefore be expressed by means of eq. (2) [6]:

$$\rho = 32.9 + 0.159\,t - 2.688\times10^{-5}\,t^2\ \mu\Omega\cdot\mathrm{cm}\quad (t\ \mathrm{in}\ ^\circ\mathrm{C}). \qquad (2)$$

Whereas the effect of the stoichiometry on the electrical resistance cannot be described clearly, because of the lack of sufficient data [12 to 14], the effect of oxygen impurities seems to be

References for 1.2.2.4 on pp. 179/80

Fig. 1-115



The electrical resistivity of UC as a function of the temperature, according to the following authors:

curve	Ref.	first author	curve	Ref.	first author
1	[7]	Pascard	8	[11]	Hayes (91.4% theoretical density)
2	[8]	Kamimoto	9	[12]	Crane
3	[5]	Fulkerson	10	[13]	Rough
4	[9]	Costa	11	[14]	Grossmann
5	[10]	Leary	12	[15]	Carniglia
7	[4]	Bates			

significant, as shown by the results of Bates [4, 18], contrary to the statements of Hayes, DeCrescente [11]. From the data for $U_{0.495}C_{0.485}O_{0.02}$ ($= UC_{0.98}O_{0.04}$) having a density of 94% of the theoretical, the electrical resistivity is calculated [6] to be:

$$\rho = 86.20 + 0.1031\,t - 2.515 \times 10^{-6} t^2 \ \mu\Omega \cdot \text{cm} \quad (t \text{ in } ^\circ\text{C}) \tag{3}$$

and for $U_{0.495}C_{0.345}O_{0.16}$ ($= UC_{0.636}O_{0.323}$), having a density 92% of the theoretical

$$\rho = 104.18 + 0.1741\,t - 2.615 \times 10^{-5} t \ \mu\Omega \cdot \text{cm} \quad (t \text{ in } ^\circ\text{C}) \tag{4}$$

between 25 and 1570 °C.

The electrical resistivity data for PuC were summarized by Lewis, Kerrisk [6], Moser et al. [3], and Fulkerson et al. [5]. Generally they are significantly higher than for UC, but their temperature dependence is appreciably smaller [9, 10, 19 to 21]. For the monophasic PuC_{1-x} the temperature dependence may be described by eq. (5) [6], obtained from the data of Kruger [20]:

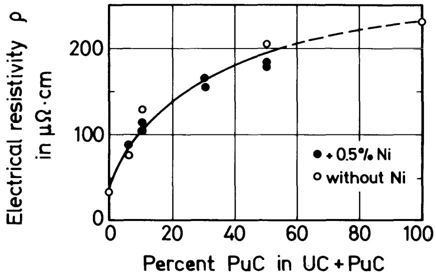
$$\rho = 258.0 - 0.0287\,t + 3.232 \times 10^{-5} t^2 \ \mu\Omega \cdot \text{cm} \quad (t \text{ in } ^\circ\text{C}) \tag{5}$$

between 25 and 750 °C, whereas for stoichiometric $PuC_{1.0}$, a mixture of PuC_{1-x} and Pu_2C_3 [22], the data of Leary et al. [10] are described [6] by eq. (6):

$$\rho = 278.5 - 1.661 \times 10^{-2} t + 3.867 \times 10^{-5} t^2 \ \mu\Omega \cdot \text{cm} \quad (t \text{ in } ^\circ\text{C}) \tag{6}$$

between 100 and 200 °C. The mixed carbide (U,Pu)C was subjected to more intensive study than was PuC. Pascard [7] determined the electrical resistivity at room temperature of UC-PuC mixed carbides with PuC contents up to 50% (**Fig. 1-116**).

Fig. 1-116



Electrical resistivity at 298 K of UC-PuC mixed carbides sintered with 0.5% Ni and without sintering aid.

It is difficult to describe the temperature dependence of the mixed carbides, since not only the density and the amount of oxygen impurity varied, but also the content of PuC in the samples.

The data of VanCraeynest et al. [23] up to 1 300 °C for a sample, having the composition $U_{0.85}Pu_{0.15}C$ and a density 91.5% of the theoretical, are approximated [6] by eq. (7)

$$\rho = 92.7 + 0.173t - 4.018\times10^{-5}t^2 \ \mu\Omega\cdot\text{cm (t in °C)} \qquad (7)$$

between 100 and 1300 °C. However, a linear temperature dependence of ρ is reported by Leary et al. [10] up to 800 °C and by Milet [25] up to 1 000 °C.

On the whole, the data of all these authors, when corrected according to Pascard [7] with respect of the composition and according to Bates [4] with respect of the density, are in good mutual agreement (±10%). Only the values given by Johnson et al. [24] are significantly higher and increase with the temperature more rapidly than those of the other authors, presumably because of oxygen and nitrogen impurities ($U_{0.80}Pu_{0.19}C_{0.97}O_{0.028}N_{0.013}$) in the samples studied by the former authors.

1.2.2.4.2 Nitrides

The electrical resistivity, ρ, of UN between room temperature and 800 °C was determined by Speidel, Keller [26], who found a linear temperature dependence of ρ in this range. Differences between the values found for various samples were explained by different microstructures and oxygen impurity contents. Generally, at room temperature, the electrical resistivity of UN is appreciably higher than that of UC, but its temperature dependence is much smaller, so that above 1 200 °C UN conducts the electrical current better than does UC [27].

Single crystal UN has a better electrical conductivity than has the polycrystalline material [28].

Moore et al. [29] analyzed the effect of the porosity on the electrical resistance of the nitrides. They found that for porosities in the range from 1.5 to 11 % this effect may be expressed by Eucken's equation [30]:

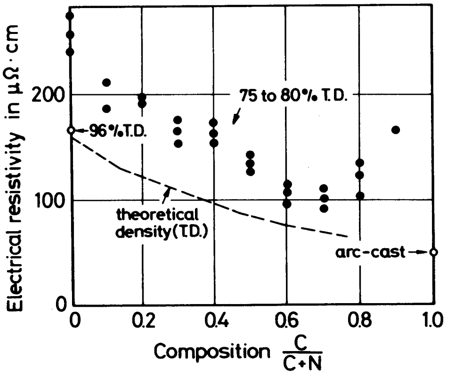
$$\rho_{TD} = \rho_{meas}(1-P)/(1+\beta P) \qquad (8)$$

where ρ_{TD} and ρ_{meas} are the corrected and measured resistivities, respectively, P the volume fraction of the pores, and β a correction factor, found to equal 0.5. A UO_2 phase, precipitated within the UN matrix by the oxygen impurity, has the same effect on the electrical conductivity of UN as the porosity has, because of the high resistivity of UO_2 [29]. Moore et al. [29] corrected in this way the data of all the other authors [26, 28, 31 to 33] and summarized the results in a figure [29].

The ρ values of UC-UN solid solutions were found [8, 34] to lie at room temperatures between those of UN (ρ = 144 μΩ · cm) and of UC (ρ = 53 μΩ · cm), **Fig. 1-117**.

The measurements of Neumann [35] on UC-UN solid solutions having various densities and stoichiometries up to 1600 °C show the strong influence of the porosity and of the stoichiometry. Absolutely, however, these data lie significantly higher than those for UN which are well established.

Fig. 1-117



The electrical resistivity of UC-UN solid solutions at room temperature [34].

The electrical conductivity of PuN was measured by Costa et al. [33] on a sample having a density of 10.85 g/cm^3 (76% of the theoretical) at temperatures between 5 and 300 K. The temperature dependence is similar to that of UN. The resistivity attains a value near 600 μΩ · cm at room temperature. Keller [36] found ρ values for PuN which are smaller than 400 μΩ · cm at 400 °C. The values for the mixed nitride $U_{0.8}Pu_{0.2}N$ are near 300 μΩ · cm between room temperature and 900 °C. The following values (Table 1/32) were found for a mixed nitride having the composition $U_{0.85}Pu_{0.15}N$ [23]:

Table 1/32
The Electrical Resistivity of $U_{0.85}Pu_{0.15}N$ in the Range 100 to 1300 °C [23].

t in °C	100	300	500	700	900	1100	1300
ρ in μΩ · cm	260	268	272	280	285	292	300

The electrical resistivity for compositions between $U_{0.85}Pu_{0.15}C$ and $U_{0.85}Pu_{0.15}N$ at 100 °C was determined by VanCraeynest et al. [23] as presented in Table 1/33

Table 1/33
The Electrical Resistivity of Various U,Pu Carbide Nitrides at 100 °C [23].

$U_{0.85}Pu_{0.15}C/U_{0.85}Pu_{0.15}N$	0/100	10/80	35/65	50/50	65/35	85/15	100/0
ρ in μΩ · cm	260	214	178	176	146	130	110

References for 1.2.2.4:

[1] R. W. Dayton, C. R. Tipton (BMI-1357 [1959] 1/109; N.S.A. **13** [1959] No. 21170). – [2] R. W. Dayton, C. R. Tipton (BMI-1524-Del. [1961] 1/104; N.S.A. **15** [1961] No. 32921). – [3] J. B. Moser, O. L. Kruger, J. H. Handwerk (Proc. Brit. Ceram. Soc. **10** [1968] 129/39). – [4] J. L. Bates (BNWL-989 [1969] 1/45; N.S.A. **23** [1969] No. 27162). – [5] W. Fulkerson, T. G. Kollie, S. C. Weaver, J. P. Moore, R. K. Williams (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970, Pt. 1; Nucl. Met. Met. Soc. AIME **17** [1970] 374/84).

[6] H. D. Lewis, J. F. Kerrisk (LA-6096 [1975] 1/33; INIS Atomindex **7** [1976] No. 272756). – [7] R. Pascard (Plansee Proc. 4th Semin., Reutte/Tyrol, Austria, 1961 [1962], pp. 387/416). – [8] M. Kamimoto, Y. Takahashi, T. Mukaibo (J. Phys. Chem. Solids **35** [1974] 393/9). – [9] P. Costa, R. Lallement (Phys. Letters **7** [1963] 21/2). – [10] J. A. Leary, R. L. Thomas, A. E. Ogard, G. C. Wonn (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 365/72).

[11] B. A. Hayes, M. A. DeCrescente (PWAC-480 [1965] 1/24; N.S.A. **20** [1966] No. 5893). – [12] J. Crane, E. Gordon (UNC-5080 [1964] 1/80; N.S.A. **18** [1964] No. 39828). – [13] F. A. Rough, W. Chubb (BMI-1554 [1961] 1/58; N.S.A. **16** [1962] No. 4961). – [14] L. N. Grossmann (GEST-2017 [1963]; J. Am. Ceram. Soc. **46** [1963] 264/7). – [15] S. C. Carniglia (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 403/26).

[16] L. B. Griffiths (Research [London] **15** [1962] 207/13). – [17] J. J. Norreys, M. J. Wheller (Trans. Brit. Ceram. Soc. **62** [1963] 183/7). – [18] J. L. Bates (Therm. Conduct. Proc. 7th Conf., Gaithersburg 1967, pp. 477/89; NBS-SPEC-PUBL.-302 [1968]). – [19] J. A. Leary, A. E. Ogard (LAMS-2949 [1963] 13); J. A. Leary, A. E. Ogard (LAMS-3023 [1963] 6); J. A. Leary, A. E. Ogard (LAMS-3054 [1964] 6/10). – [20] O. L. Kruger, J. B. Moser (ANL-7155 [1965] 105/9).

[21] O. L. Kruger, J. B. Moser (J. Chem. Phys. **46** [1967] 891/900). – [22] O. L. Kruger (J. Am. Ceram. Soc. **46** [1963] 80/5). – [23] J. C. VanCraeynest, J. C. Weilbacher, J. C. Salbreux (Therm. Conduct. Proc. 8th Conf., West Lafayette 1968 [1969], pp. 587/601). – [24] K. W. R. Johnson, J. F. Kerrisk (LA-4494-MS [1970] 45/8). – [25] C. Milet (CEA-R-3201 [1967] 1/44; N.S.A. **21** [1967] No. 28826).

[26] E. O. Speidel, D. L. Keller (BMI-1633 [1963] 1/67; N.S.A. **17** [1963] No. 30906). – [27] B. A. Hayes, M. A. DeCrescente (PWAC-481 [1965] 1/21; N.S.A. **20** [1966] No. 7575). – [28] R. W. Endebrock, E. L. Forster, D. L. Keller (BMI-1690 [1964] 1/24; N.S.A. **19** [1965] No. 6242). – [29] J. P. Moore, W. Fulkerson, D. L. McElroy (J. Am. Ceram. Soc. **53** [1970] 76/82). – [30] A. Eucken (Forsch. Gebiete Ingenieurwesens B **3** No. 353 [1932] 16).

[31] I. H. Warren, C. E. Price (Can. Met. Quart. **3** [1964] 183/96). – [32] T. G. Kollie, D. L. McElroy, R. S. Graves, W. Fulkerson (Compounds Interest Nucl. Reactor Technol. Proc. Symp., Boulder, Colo., 1964; Inst. Mining Met. Petrol Eng. Inst. Metals Div. Spec. Rept. Ser. No. 13 [1964] 651/76). – [33] B. Costa, R. Lallement, F. Anselin, D. Rossignol (Compounds Interest Nucl. Reactor Technol, Boulder, Colo., 1964; Inst. Mining Met. Petrol. Eng. Inst. Metals Div. Spec. Rept. Ser. No. 13 [1964], pp. 83/91). – [34] T. Ohmichi, T. Kikuchi (J. Nucl. Sci. Technol. **6** [1969] 101/2). – [35] M. Neumann (JUEL-1079-RB-RW [1974] 1/122; N.S.A. **31** [1975] No. 11762).

[36] D. L. Keller (BMI-1809 [1967] 1/206; N.S.A. **22** [1968] No. 602).

1.2.2.5 Compatibility with Metallic Materials

For the chemical reactions of uranium nitride with metals and metal compounds see "Uranium" Suppl. Vol. C7, 1981, pp. 50/6. Reactions of uranium carbide will be described in "Uranium" Suppl. Vol. 12.

The carbide and nitride nuclear fuels come into contact with metallic and ceramic material during both their various stages of fabrication and their employment in the reactor. Interactions between these materials, that depend on the temperature, cannot be avoided. To be noted in particular is the problem of the compatibility of the fuel with the normally used cladding materials. This compatibility provides an important criterion for the design of the fuel elements, not only with regard to limit the lifetime in the reactor, which is connected with the economic efficiency, but also with regard to safety aspects. The more complex in-pile compatibility problems have to be taken into account; these are dealt with in Section 1.2.3.2, from p. 196.

1.2.2.5.1 Compatibility of Carbide Fuels and Breeding Materials with Austenitic Steels

Table 1/34, due to Frost [1], summarizes the reactions between metallic materials and uranium monocarbide that had been known by 1963. The qualification of sodium as a coolant in fast breeder reactors using the monocarbide fuel, and its suitability as a medium for heat exchange between the fuel and the rod cladding (Na-bonding), becomes evident from these results.

Because of the negligible homogeneity range of single-phase U-C alloys deviating from the stoichiometric composition, these contain uranium metal carbides such as U_2C_3 or UC_2.

The free U and Pu of hypostoichiometric compositions mainly react with the cladding to form intermetallic compounds such as $(U,Pu)Fe_2$ and $(U,Pu)Ni_5$ [2 to 8], which have much lower melting points than stainless steel.

The higher carbon potential in hyperstoichiometric compositions leads to carburization of the cladding [8 to 10] with precipitation of carbides such as $Cr_{23}C_6$ and Cr_7C_3, which cause severe embrittlement of the cladding materials.

Table 1/34
Reactions Between UC and Various Metals and Alloys [1] (alphabetical order).

metal	reaction
Al	formation of UAl_3 and UAl_4 after 24 h at 620 °C
Be	UC dissolves 20 mol% Be_2C at 1700 °C
Bi	no reaction at 950 °C
Co	possibly pseudobinary, little solubility
Cr	UC-Cr euteric at ≈1100 °C; no solubility between UC and Cr
Cu	UC-Cu pseudobinary
Fe	UC-Fe eutectic at 1100 °C
Hf	complete solubility of HfC in UC; probably increase in the melting point (that of HfC is 3900 °C)
Mo	$UC + Mo \rightarrow Mo_2C$ at 1000 °C
Na	no reaction at 871 °C
Nb	complete solubility of NbC in UC; Nb is compatible with UC
Ni	UC-U_6Ni pseudobinary
Pb	no reaction
Pu	large range of solubility of Pu in UC and probably also in U_2C_3
Re	eutectic at 1850 °C
Si	$UC + 3Si \rightarrow USi_3 + C$ at 1000°C
Sn	no reaction
Ta	1. decarbonization: $UC + Ta \rightarrow TaC + U$; 2. complete solubility of TaC in UC
Th	continuous solid solution ThC–UC
Ti	UC dissolves < 2 mol% TiC
V	UC dissolves 4 to 9 mol% VC; VC does not dissolve UC
W	UC dissolves ≈10 mol% W; W does not dissolve UC
Zr	continuous solid solution between UC and ZrC; increase in the ZrC melting point of 3500 °C.
stainless steel (18 Cr, 8 to 12 Ni)	no reaction at 800 °C during 6 months; a 0.10 mm deep reaction zone in 6 days at 1100 °C; liquid phase at 1200 °C
Zircaloy-2	reacts in 1 h at 1200 °C, but not at 800 °C; possible formation of a ZrC diffusional barrier
Nb, at 40% Ti	a molton phase at 1200 °C
Inconel	0.008 mm corrosion in 100 h at 800 °C

The transfer of carbon from fuel to cladding occurs at high temperatures according to the general reaction (1):

$$UC + (Fe, Ni, Cr) \rightleftharpoons UFe_2 + (Fe, Cr)_{23}C_6 \qquad (1)$$

These reactions have unfavorable effects on the compatibility of both hypo- and hyperstoichiometric uranium monocarbide with the metallic cladding material, because of the narrow phase boundaries of UC at the operational temperatures in the reactor (<1000 °C). Although PuC has somewhat larger phase boundaries, the low Pu content of maximally 20 wt% in the mixed carbide results in a negligible effect of this positive aspect on the compatibility.

Two approaches to the improvement of the compatibility have been investigated. The one uses an interior coating of the cladding with, e.g., TiC, ZrC, or Cr [19], which acts as a diffusion barrier to carbon transport [11]. The other involves stabilization of the carbon potential in the monocarbide by the addition of one of the following additives: W-UWC_2 [11 to 13], V-UVC_2 [6, 14, 15, 108], Mo-$UMoC_2$ [6, 14 to 17, 108], Fe-UFe_2 [16, 17], Ti-TiC [9, 18, 19], and cerium [108]. Additionally, the structure of the cladding material may be stabilized against carbonation, at least partly by means of cold working structure [20].

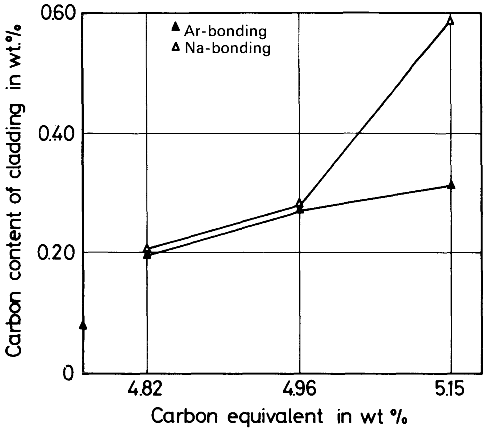
Cladding materials of fuel rods for Na-cooled fast breeder reactors consist almost exclusively of highly alloyed austenites [21] (Table 1/35). As is well known, carburization of these stainless steels leads to a decrease of ductility. Götzmann et al. [22 to 24, 109], in particular, studied the changes of the properties of cladding materials on contact with UC and (U,Pu)C. Already after 200 h contact at 750 °C with hyperstoichiometric UC (C $\approx$4.95 wt%) the alloy has lost some of its room temperature ductility.

Table 1/35
Alloys Discussed as Cladding Materials [21].

alloy	composition in wt%											
	Fe	Ni	Cr	C	Al	Ti	Mn	Si	Nb	Mo	W	other elements
AISI 316	65	12	17	0.08			2.0	1.0		2 to 3		
AISI 330	43	35	19	0.05			1.5	1.25				
A286	53	26	15	0.05	0.2	2.1	1.4	0.4		1 to 1.75		
M813	39	35	18	0.08	1.4	2.25				4.0		
PE16	43	35.5	16	0.1	1.2	1.2				3.0		
INCONEL706	40	41.5	16	0.03	0.2	1.75	0.18	0.18	2.9			
INCOLOY901	45	42.5	12.5	0.05	0.2	2.8	0.45	0.4		5.7		
INCONEL718	18.5	52.5	19	0.04	0.5	0.9	0.18	0.18	5.0	3.0		
HT9	85.5	0.5	12	0.20						1.0	0.5	0.3 (V)

Price et al. [25] and also Elkins [37] did not find appreciable differences in the compatibility of various austenitic steels towards UC. They expect, on the basis of these findings, that UC should be compatible with these steels at 900 °C for several years. Hayes [26] reached a similar conclusion. This is, however, contrary to the results of other authors [11, 19, 27 to 29, 108], who asserted, that although at t $\leq$800 °C, without Na-bonding, only a slight interaction between the fuel and the cladding took place, changes of up to several hundred µm become evident in the metallic structure above 800 °C already after a short while. The discrepancy between the conclusions of different authors should be due to the fact that the experimental conditions, e.g., the immediate contact between fuel and cladding, were not always comparable. Consequently, different transport of carbon from the UC to the metal took place. Furthermore, even small analytical errors in the composition of the fuels may lead to appreciable differences in the compatibility. Another source for favorable C-transport can be the composition of the gas in the gap between the fuel and the cladding, e.g., CO/CO_2 [22, 28, 30, 109] or H_2/CH_4 [30, 31]. Finally, Na-bonding enhances the rate of carburization significantly [4, 22, 23, 32 to 37] (**Fig. 1-118**). Because of the rapid transport of the carbon by the sodium,

Fig. 118



Comparison between carbon contents of stainless steel (DIN 1.4988) after 1000 h at 600 °C heat treatments in contact with uranium carbides over Ar- and Na-bonding.

the rate of carburization is determined by the rate of diffusion of C in the austenitic steel [38]. The compatibility of hypostoichiometric UC, however, is clearly improved by Na-bonding, since the free uranium is not transported by the sodium [35].

Under certain circumstances the rate of carburization may be determined by the removal of carbon from the carbide. Watanabe et al. [39] found a decarburization rate of 2×10^{-4} mm/h for arc-cast hyperstoichiometric UC, and 1×10^{-4} mm/h for the sintered material. It is mainly the kind and the form of the hyperstoichiometric carbide, that play an important role. For instance, whereas the excess carbon present as UC_2 platelets was depleted from a layer 410 μm deep during 2000 h at 700 °C, excess carbon in a sample of the same composition, but with U_2C_3 as the second phase, was depleted from a zone only 3 μm deep under the same conditions. Nishio, Shimokawa [40] spoke of a leaching of the carbon from the UC_2 phase of hyperstoichiometric UC. The carbon activity of the UC influences the carburization directly (Fig. 1-118). The depth and the concentration of the carburization zone depends also on the carbon activity of the cladding material at the area of contact with the uranium carbide [38].

The oxygen that is dissolved in the UC crystal lattice has also an appreciable effect. According to measurements of Tetenbaum, Hunt [41, 42], the carbon activity was reduced by two orders of magnitude, when the oxygen concentration in the UC lattice increased from 150 to 2000 ppm. Venter, Stumpf [30], however, pointed out that the uptake of oxygen by the UC during the contact of the fuel with the cladding had a negative effect on the compatibility of steels, such as 316 SS, 321 SS, and 347 SS. The reason was that free carbon was thereby formed, which caused carburization of the cladding material at 700 °C already after 1 000 h, for both Na- and He-bonding. Although the experiments had been conducted with UC powder, which naturally can be oxidized faster than the compact carbide, no effect of the surface area on the compatibility could be found by the authors up to a specific area of 200 m^2/kg. Only when the specific surface was 1 000 m^2/kg, was a clear effect noticeable: already after only 1 000 h could carburization be observed at 600 and 700 °C.

Furthermore, oxygen impurity of the sodium bonding oxidized the uranium carbide and released carbon, causing enhanced carburization [39, 44]. At 700 °C, an oxygen content of 5 to 10 ppm in the Na oxidized the UC and the carbon was transported five times faster to the 304 SS cladding than it was in oxygen-free sodium. If the UC was stabilized by the addition of vanadium, it could no longer be oxidized at the low oxygen contents of the sodium [30].

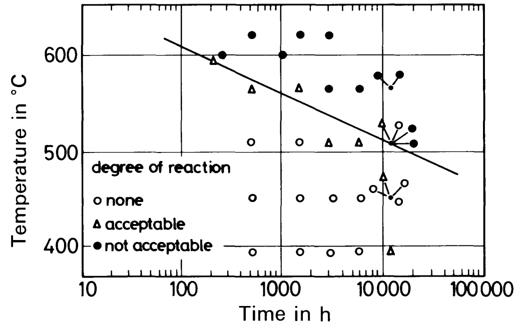
1.2.2.5.2 Compatibility of UC with Other Metallic Materials

Götzmann et al. [45, 109], Ihara et al. [46], and Whitlow et al. [47] compared the compatibility of UC with stainless steels on the one hand with that with vanadium alloys on the other. It was seen clearly, that compared with the steels, the vanadium alloys reacted more slowly, and were compatible even at 800 and 900 °C. Whitlow et al. [47] observed after contact at 800 °C for 3500 h a small reaction zone in the vanadium alloys, due to carburization. However, they attributed this to the carbon released by oxidation of the UC by oxygen present in the Na-bonding. The Ti content had a significant effect on the carburization of the vanadium alloys [80, 111]. Alloys containing 15 to 20 wt% Ti reduced the U_2C_3 to UC at 800 °C. However, alloys containing less than 5% Ti, or other metals that form stable carbides, interacted only slightly with hyperstoichiometric UC during 4000 h.

Hahn [35] pointed out niobium as a highly promising material for the cladding of hyperstoichiometric UC up to temperatures of 1600 °F (870 °C). Unfortunately, he dealt insufficiently with the radiation stability of this material.

The fuel-cladding system UC-SAP (sintered aluminium product) was forseen for the heavy water moderated organic cooled reactor. Numerous studies had as their aim the determination of the compatibility between UC and SAP [27, 29, 49 to 58]. The results have been summarized by Venard [48] in **Fig. 1-119**, which shows the limits of the compatibility between UC and SAP. Also Bremer [59] studied the compatibility in this system extensively, and identified in the reaction zone UAl_3, graphite, and various U-Al-Si phases. Impurities, such as N, O, Si, V, and Cd play a significant role in the reaction between uranium carbide and SAP. Bremer developed a numeric description of the reaction between the fuel UC and the cladding SAP, using a mathematical model [59].

Fig. 1-119



Temperature-time limits of the compatibility of SAP with UC (4.8 wt% C) [48].

Lensi, Schleicher [60] studied the application of liquid metals, such as Na, NaK, Bi, and Pb, as heat transfer media between UC and SAP. Of these four bonding metals only lead remained, because of the too large reactivity of SAP with Na, NaK, and Bi. Especially if the aluminium had been anodically oxidized, no reaction could be observed with liquid lead at 500 °C even after 8000 h. At higher temperatures, however, the system UC-Pb-SAP becomes unstable, independent of the stoichiometry of the carbide.

The development of fuel elements for thermionic reactors led to the employment of UC or (U,Zr)C with a tungsten cladding, because of the required high emission temperatures [61]. The chemical vapor deposition (CVD) process permitted the deposition of the tungsten directly on the fuel rod [62]. Tungsten claddings with ThO_2 additives were also used for this purpose [63]. Yang et al. [64] and Philipps [65] reported the results of their compatibility studies. They found that mainly UWC_2, but also some W_2C, was formed between the fuel UC and the cladding W. The UWC_2 layer grew very slowly (7 μm in 10^4 h at 1 650 °C) [64]. The growth of W_2C was at first rapid, due to the high diffusion coefficient of the carbon, but was slowed down drastically after the formation of the UWC_2 phase, because of the slow transport of C through this layer [65]. The same behavior was found by Philips [65] also for temperature gradients. The ZrC added for the stabilization of UC as a solid solution did not have as favorable an effect regarding the compatibility with tungsten. Phase broadening at temperatures above 1 500 °C caused by the ZrC provided more carbon for carbide formation with the tungsten than was provided by pure uranium monocarbide [66]. A tungsten additive was proposed for the stabilization of UC to be employed in thermionic fuel elements, in order to bind any excess carbon atoms [65]. The activities of carbon and uranium were strongly reduced by the equilibrium between the three phases UC, or (U,Zr)C + UWC_2 + W that had set in.

The addition of ThO_2 to the tungsten proved to be an effective barrier against the diffusion of carbon [63]. The compatibility between the fuel and the cladding has been influenced strongly, when highly enriched uranium was irradiated, because of recoil damage to the cladding. However, at a temperature of 1 470 °C this effect is unefficient, according to Yang [64].

The compatibility of UC with tantalum was studied by Nomura et al. [67, 68] in the temperature range from 1 200 to 2 350 °C. They found that the carbon diffuses significantly faster than the uranium did, in the interaction between UC and Ta. The reaction zone consisted of Ta_2C and TaC, and its thickness grew as the square root of the time. The diffusion coefficients of C, D_c in cm^2/s, calculated from the experimental data could be expressed by eqs. (1) to (3):

$$D_C\ (\text{in } Ta_2C \text{ at } 1\,400 \text{ to } 1\,800\,°C) = 1.7\times10^{-3}\exp(-26.0/RT) \qquad (1)$$

$$D_C\ (\text{in } Ta_2C \text{ at } 1\,800 \text{ to } 2\,350\,°C) = 6.2\times10^{2}\exp(-146.0/RT) \qquad (2)$$

$$D_C\ (\text{in } TaC \text{ at } 1\,800 \text{ to } 2\,350\,°C) = 4.5\exp(-103.0/RT) \qquad (3)$$

The activation energies in these equations are given in kcal/mol.

1.2.2.5.3 Compatibility of (U,Pu)C with Various Cladding Materials

The compatibility between (U,Pu)C mixed carbides and various cladding materials is similar to that found for uranium monocarbide, as is expected. Parameters, such as the temperature, the composition of the carbide or its C-potential, impurities, and the bonding between the fuel and the cladding (Na or He), are of importance for the compatibility [33, 69 to 81, 109]. A further important role plays the composition of the metallic cladding material [80].

Batey et al. [69] could not find any effect on the compatibility with Ni-based alloys of any of the following: the carbon content of the mixed carbide, the temperature (up to 800 °C), and the presence of an oxygen impurity (up to 3700 ppm). The observed carburization to a maximal depth of 75 μm was attributed by the authors to the enhancement of the C-potential during the experiment, caused by oxidation of the carbide by impurities in the He.

Other authors [70 to 72] found no difference between the behavior of UC and that of (U,Pu)C towards Ni-based alloys and Zircaloy-2. French, Hodkin [33], on the other hand, indicated less carburization with (U,Pu)C than with UC, at a given C equivalent (C equivalent = wt% C + (12/14) wt% N + (12/16) wt% O). The investigations by these authors showed also, that the phase M_2C_3 (M = U,Pu) was significantly more stable (about 3 months at 800 °C) than the MC_2 phase, since the latter was dissolved by giving up some of the carbon. Powers, Strasser [77] confirmed these observations with their experiments. They found, after calcination at 800 °C for 4000 h, no carburization of the cladding materials 304 SS, 316 SS, and Incoloy 800, if the (U,Pu)C contained the M_2C_3 phase. Similar results were obtained by Latimer et al. [78 to 80], who, in a more recent investigation [81] concerning the alloys in Table 1/36, differentiated after 1000 h experiments between the following:

a) For He-bonding, in the temperature range 600 to 775 °C, (U,Pu)C caused the same amount of carburization in alloys with Ni content $\leqq$35 wt% as in steels of the type 316 SS. Use of alloys having Ni contents >41 wt%, on the other hand, led to a slight formation of an intermetallic phase containing U,Pu, and Ni and to a deposition of carbide, that was more characteristic than for alloys having lower Ni contents.

b) If Na-bonding was employed in (U,Pu)C fuel rods at an annealing temperature of 600 °C, no evident carburization was observed for any of the metallic cladding materials studied. Only at a temperature of 725 °C could carburization be found for some cladding materials. Some super-alloys (such as M 813, PE 16, and HT 9) showed less carburization than did austenitic steel AISI 316 SS, whereas other super-alloys (e.g., A 286 and Inconel 706 and 718) showed larger amounts of carbide precipitation along the grain boundaries and in the matrix.

Batey et al. [110] were concerned with the compatibility of (U,Pu)C with the alloys Nimonic 80 and PE 16. At 800 °C a local interaction between the fuel and the cladding was observed. They therefore recommend a maximal operational temperature of 750 °C for these alloys. Similar conclusions were arrived at by Hodkin et al. [82] and Jacoby et al. [83], although the former group of authors found only slight carburization even at 900 °C and with He-bonding. They attributed the carburization in the case of He-bonding to hydrolytic oxidation of the mixed carbide, and in the case of Na-bonding to the MC_2 phase in the fuel. Thermodynamic calculations of Götzmann, Ohse [22] showed, that the chemical potential of the carbon in the carbide, which was contaminated with oxygen, led to the

Table 1/36
The Carbon Activities of Various Materials [84].

material	carbon activity at 800 °C
$(U_{0.85}Pu_{0.15})C$, single phase	2.3×10^{-2}
304 SS, having 0.7 wt% C	3.5×10^{-2}
MC, having 14 vol% M_2C_3[a]	1.1×10^{-1}
$(U_{0.85}Pu_{0.15})_2C_3$, single phase	3.3×10^{-1}

[a] M = $U_{0.85}Pu_{0.15}$ in the sample as a whole, but the U:Pu ratio is not the same in the two phases.

formation of a M_2C_3 phase in the region near the surface of the fuel, provided that a temperature gradient was present. Carburization of the cladding was then effected via the sodium. Holden, Führmann [84] determined the carbon activities given in Table 1/36 for various systems. According to these data, only the single phase mixed carbides should be compatible with austenitic steels at 800 °C from the thermodynamic standpoint. Presence of a M_2C_3 phase in the fuel, however, led to carburization.

1.2.2.5.4 Compatibility of Nitride Fuels with the Cladding

Mononitrides of uranium and plutonium have, like the carbides, only a narrow range of stoichiometries [85]. The preparation of the stoichiometric mononitrides, (see "Uranium" Suppl. Vol. C7, 1981, pp. 6/10) even on a technical scale, is much simpler than that of the corresponding carbides, since the higher nitrides decompose already at 1300 °C [86, 87]. Investigations on a hypostoichiometric nitride [88 to 94] showed, that such a material reacted with the cladding material, forming intermetallic compounds such as $(U,Pu)Fe_2$ or $(U,Pu)Ni_5$. Hyperstoichiometric nitride had U_2N_3 as a second phase, which caused nitriding of the metallic cladding.

In the temperature range from 600 to 1100 °C a good compatibility was found between UN or PuN and Ni-based alloys [95]. Katz [96] found the products in the reaction zone to be UNi_5 and U_2N_3. Of the austenitic steels, 304 SS behaved better than 316 SS [95]. Both steels did not show any interaction with the nitride fuel at 1000 °C up to 1000 h, and 304 SS was not attacked even after 5000 h [95 to 98]. At temperatures above 1000 °C the rate of the reaction increased rapidly, and at 1200 °C a melt was formed [100]. This was attributed to the fact that the $\Delta G°$ value for the reaction $3\ UN + 5\ Ni \rightleftarrows U_2N_3 + UNi_5$ becomes negative in this temperature range. Although Na-bonding should have had some effect on the nitriding of steels [93], a series of authors [90 to 92, 94] could observe no difference between He- and Na-bonding.

Oxygen may influence the interaction of a nitride fuel with the metallic cladding. As a result of oxidation of the nitride during storage, a higher nitrogen potential arises, accompanied by the formation of higher nitrides [91 to 93, 101]. On the other hand, the oxygen impurity of the fuel stabilizes the nitrogen potential of the higher nitrides, by means of the formation of UO_2-U_2N_3 solid solutions [93, 102, 103].

Pure vanadium was better compatible with UN than are V-Ti alloys [104]. The Ti content of the vanadium alloy gettered the oxygen that was present in the UN, leading to the formation of free uranium in the nitride, and to the observation of a high rate of migration of uranium in the cladding material. Ihara et al. [105], however, could not find after 1000 h exposure at 900 °C any reaction between UN and the alloy V-15% Ti-7.5% Cr. A temperature of 1200 °C was specified for the use of UN in the SNAP-50 reactor. Various high-melting metals were therefore tested as cladding materials for this reactor [106]. Niobium reacted with UN, forming Nb_2N and U-Nb alloys. After 5000 h a reaction zone of 350 μm was formed at 1190 °C (2200 °F). On the contrary, a UN fuel, which had been coated with tungsten by the chemical vapor deposition method, behaved well, since at the same exposure conditions complete compatibility could still be observed after 10^4 h. The metals tantalum and molybdenum were incompatible with UN at 1200 °C. A U-containing phase was formed at the grain boundaries of molybdenum, containing 44 wt% uranium. The W-26% Re alloy was also suitable; however it becomes brittle after long use (above 5000 h).

References for 1.2.2.5 on pp. 188/90

1.2.2.5.5 Compatibility of Uranium Carbide Nitrides ("carbonitrides")

Kuroda et al. [87] examined in short-time tests at 600 and 1 000 °C the compatibility of UC, UN, and U(C,N) with austenitic steels and Ni-based alloys. All the combinations tested, with the exception of the pair $U(C_{0.4}N_{0.6})$-Hastelloy B, showed no or only very slight interaction. Titanium-containing vanadium alloys led to depositions of TiC. Tantalum was well behaved in short-time tests (66 h) up to 1 400 °C.

When (U,Ce)(C,N) was used with 20% Ti-V and with 15% Ti-7.5% Cr-V at temperatures near 900 °C, diffusion of carbon into the alloy and of vanadium into the fuel occurred [105].

When U(C,N) solid solutions of various compositions were tested at 900 °C for 500 h they were very well compatible with both nonstabilized and Nb- or Ti-stabilized Cr-Ni steels [97]. Pure UC, under the same conditions, yielded a wide reaction zone, forming an intermetallic phase (51% Fe, 24% U, 25%Ni) in the steel, and a zone containing the cladding components that had formed in the UC matrix.

References for 1.2.2.5:

[1] B. R. T. Frost (J. Nucl. Mater. **10** [1963] 265/300). – [2] M. Hanson (Constitution of Binary Alloys, McGraw-Hill, New York 1958). – [3] B. R. Hayard (NAA-SR-11 450 [1965] 1/436; N.S.A. **20** [1966] No. 8392). – [4] F. B. Litton (LA-3799 [1968] 1/22; N.S.A. **22** [1968] No. 21 759). – [5] F. A. Schunk (Constitution of Binary Alloys, Suppl. No. 2, McGraw-Hill, New York 1969).

[6] O. Götzmann, D. D. Scherbl (KFK-1 213 [1970] 1/28; EURFNR-820 [1970]; N.S.A. **25** [1971] No. 29 940). – [7] K. Natesan, T. F. Kassner (J. Nucl. Mater. **37** [1970] 223/35). – [8] T. W. Latimer, W. R. Jacoby (Plutonium Fuel Technol. Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1967] 322/34), T. W. Latimer (ANL-7 827 [1971] 1/42; N.S.A. **26** [1972] No. 20675). – [9] M. Mouchnino (CEA-R-3 353 [1967] 1/35; N.S.A. **22** [1968] No. 23852). – [10] S. K. Dutta, J. White (Proc. Brit. Ceram. Soc. **7** [1967] 177/203).

[11] R. Pascard (Bull. Inform. Sci. Technol. **100** [1966] 41/56). – [12] W. Chubb (Nucl. Sci. Eng. **29** [1967] 176/9). – [13] M. Ugajin, I. Takahashi, Y. Suzuki, J. Abe, M. Kurihara (J. Nucl. Mater. **49** [1973/74] 151/60). – [14] F. Gorle, W. Timmermanns, F. Casteels, J. Van Geel, M. Brabers (Thermodyn. Nucl. Mater. Proc. Symp., Vienna 1967, pp. 481/96). – [15] A. Delbrassine, M. Coquerelle (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 247/60).

[16] K. R. Jordan, R. J. Herbst, R. G. Palm (ANL-7 120 [1965] 301). – [17] R. J. Herbst (Trans. Am. Nucl. Soc. **9** [1966] 17). – [18] C. A. Milet (CEA-R-3 656 [1968] 1/77; N.S.A. **23** [1969] No. 17392). – [19] T. S. Menshikova, F. G. Reshetnikov, G. A. Rymansheskij, I. G. Lebedev (Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Paper 454; A-CONF-49-P454 [1971]). – [20] W. E. Stumpf, S. Venter (PEL-242 [1975]; J. Nucl. Mater. **60** [1976] 195/202; C.A. **85** [1976] No. 69760).

[21] S. D. Harkness, R. Carlander, P. R. Okamoto (ANL/MSD-06 [1973]). – [22] O. Götzmann, R. W. Ohse (EUR-4892.e [1972]). – [23] O. Götzmann, P. Hofmann, Y. Sarikaya (KFK-1 942 [1973]; EURFNR-1 173 [1973] 1/30; N.S.A. **30** [1974] No. 176689). – [24] Y. Sarikaya, O. Götzmann (KFK-1 993 [1974] 1/58; N.S.A. **30** [1974] No. 32767; KEK-1 993 [1974] 1/66; N.S.A. **30** [1974] No. 27381). – [25] D. E. Price, J. M. Fackelmann, J. C. Hebeisen, R. D. Koester, M. D. Houston (BMI-1 900-VI [1958] 1/12).

[26] W. C. Hayes (TID-7676 [1967] 25/37). – [27] S. Katz (J. Nucl. Mater. **6** [1962] 172/81). – [28] P. Hofmann (EURFNR-1 139 [1973] 1/62). – [29] W. Chubb, R. F. Dickerson (J. Am. Ceram. Soc. **41** [1962] 564/9). – [30] S. Venter, W. E. Stumpf (J. Nucl. Mater. **59** [1976] 221/8).

[31] D. J. Hodkin, J. P. Evans, P. G. Mardon (AERE-R-5173 [1966] 1/26; N.S.A. **25** [1971] No. 11475). – [32] O. Götzmann, P. Hofmann (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 233/44). – [33] P. M. French, D. J. Hodkin (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 697/720). – [34] G. Nishio, H. Watanabe, J. Shimokawa (Nucl. Eng. Design **22** [1972] 326/33). – [35] R. D. Hahn (NAA-SR-7696 [1963] 1/32; N.S.A. **17** [1963] No. 16650).

[36] A. W. Hare, S. Alfant, F. A. Rough (Nucl. Sci. Energy **10** [1961] 24/30). – [37] P. E. Elkins (NAA-SR-7502 [1964] 1/59; N.S.A. **18** [1964] No. 35957). – [38] R. B. Snyder, K. Natesan, T. F. Kassner (J. Nucl. Mater. **50** [1974] 259/74). – [39] H. Watanabe, T. Kurusawa, T. Kikuchi, K. Furukawa, I. Nihei (J. Nucl. Mater. **40** [1971] 213/20). – [40] G. Nishio, J. Shimokawa (J. Nucl. Mater. **47** [1973] 87/94).

[41] M. Tetenbaum, P. D. Hunt (J. Nucl. Mater. **40** [1971] 104/12; C.A. **75** [1971] No. 83053). – [42] M. Tetenbaum, P. D. Hunt (Colloq. Intern. Centre Natl. Rech. Sci. Odeillo, France, No. 205 [1972] 255/8; C.A. **79** [1973] No. 70674). – [43] W. E. Stumpf, S. Venter (PEL-243 [1975]). – [44] H. Watanabe, T. Kurasawa, T. Kikuchi, H. Katsuta, K. Furukawa (J. Nucl. Mater. **40** [1971] 236/8). – [45] O. Götzmann, P. Hofmann (KFK-1546 [1972]; EURFNR-996 [1972] 1/20; CONF-711215 [1971]; N.S.A. **26** [1972] No. 31398).

[46] S. Ihara, K. Tanaka, S. Tojo, M. Kojima, Y. Akimoto (J. Nucl. Sci. Technol. **10** [1973] 106/10). – [47] G. A. Whitlow, J. Y. Chang, R. C. Deklever, P. M. French, M. H. Hodge (TID-25599 [1970] 1/23; N.S.A. **25** [1971] No. 6833). – [48] J. T. Venard (ORNL-TM-1705 [1967] 1/22; N.S.A. **21** [1967] No. 11300). – [49] W. C. Thurber, R. J. Beaver (J. Nucl. Mater. **3** [1959] 226/32; ORNL-2618 [1959] 1/49; N.S.A. **14** [1960] No. 3208). – [50] D. I. Sinizer (TID-7614 [1961] 1/156, 4/31; N.S.A. **15** [1961] No. 29718).

[51] European Atomic Energy Community (EURATOM's Scientific Activities, Orgel Program, Experimental Studies, EUR-1830.e-Pt. II [1964] 1/705, Chapter 5; N.S.A. **18** [1964] No. 40827). – [52] Danish Atomic Energy Commission (RISO-110 [1965] 1/53, 32; N.S.A. **20** [1966] No. 5838). – [53] J. E. Frank, R. D. Hahn, P. S. Olson (NAA-SR-Memo-11135 [1965] 1/33, 17; N.S.A. **19** [1965] No. 33607). – [54] N. Hansen, P. Knudsen, A. C. Winther, E. Adolph (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964 [1965], Vol. 9, pp. 122/37). – [55] T. Lauritzen, P. Knudsen (J. Nucl. Mater. **16** [1965] 173/83).

[56] J. L. Ballif (NAA-SR-Memo-8934 [1963]). – [57] P. E. Elkins, W. R. Kerr (AI-64-103 [1964]). – [58] W. R. Kerr (AI-64-103-Add. [1964]). – [59] A. B. Bremer (AI-CE-77 [1968] 1/64; N.S.A. **22** [1968] No. 46857). – [60] P. L. Lensi, H. W. Schleicher (J. Nucl. Mater. **33** [1969] 77/89).

[61] A. F. Weinberg, L. Yang (Advan. Energy Convers. **3** [1963] 101/11). – [62] L. Yang, R. G. Hudson (in: A. C. Schaffhauser, Chemical Vapor Deposition of Refractory Metals Alloys and Compounds, Interstate Printer, Danville, Ill., 1967, pp. 329/48). – [63] A. Schock, B. Reab (FHR-3641-A [1971]). – [64] L. Yang, R. G. Hudson, H. Johnson, H. Horner, D. T. Allen (Proc. Intern. Conf. Thermionic Elect. Power Generation, Jülich, Germany, 1972; CONF-720613-P2 [1972] 873/93). – [65] W. M. Phillips (Proc. Intern. Conf. Thermionic Elect. Power Generation, Jülich, Germany, 1972; CONF-720613-P2 [1972] 911/25).

[66] W. M. Phillips (IEEE Thermionic Conversion Spec. Conf., San Diego, Cal., 1971; CONF-711038 [1971] 334/43). – [67] S. Nomura, S. Muraoka, H. Itami (J. Nucl. Technol. **7** [1970] 380/1). – [68] S. Muraoka, H. Itami, S. Nomura (Nippon Genshiryoku Gakkaishi **14** [1972] 580/8). – [69] W. Batey, D. M. Donaldson, W. B. Finlayson (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 1063/86). – [70] A. Strasser, L. A. Neimark (Fast Reactor Technol. Proc. Natl. Meeting, Detroit, Mich., 1965; ANS-100 [1965] 126/56).

[71] L. A. Neimark, J. H. Kittel, C. C. Clothers (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 864/78). – [72] A. Strasser, D. Stahl (UNC-5134-Vol. 1 [1965] 1/117; N.S.A. **20** [1966] No. 27416). – [73] B. T. Bradbury, L. E. Russell, M. B. Waldron (ANL-7120 [1965] 328/54). – [74] R. Lorenzelli, P. DeLaroche, M. Housseau, D. Petit

(Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970; Nucl. Met. **17** [1970] 818/28). – [75] D. Stahl, A. Strasser, K. Taylor, J. Anderson (UNC-5074 [1963] 1/68; EURAEC-918 [1962]; N.S.A. **18** [1964] No. 8729).

[76] D. Stahl, A. Strasser (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 1, pp. 373/91). – [77] R. Powers, A. Strasser (UNC-5229 [1968] 1/66; N.S.A. **24** [1970] No. 7116). – [78] T. W. Latimer, W. R. Jacoby (Plutonium Fuel Technol. Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1968] 322/34). – [79] T. W. Latimer, L. A. Neimark, C. E. Johnson, C. E. Crouthameel (Trans. Am. Nucl. Soc. **12** [1969] 594/5). – [80] T. W. Latimer (ANL-7827 [1971] 1/42; N.S.A. **26** [1972] No. 20675).

[81] T. W. Latimer, J. F. Andrew (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 205/17). – [82] D. J. Hodkin, J. P. Evans, P. G. Mardon (AERE-R-5173 [1966] 1/26; N.S.A. **25** [1971] No. 11475). – [83] W. R. Jacoby, R. G. Palm, T. W. Latimer (Trans. Am. Nucl. Soc. **10** [1967] 108/9). – [84] R. B. Holden, N. Fuhrmann (Trans. Am. Nucl. Soc. **11** [1968] 511). – [85] H. Holleck (Thermodyn. Nucl. Mater. Proc. Symp., Vienna 1974, pp. 213/64).

[86] J. Bugl, A. A. Bauer (J. Am. Ceram. Soc. **47** [1964] 425/9). – [87] A. Naoumidis (JUL-472-RW [1967] 1/111; N.S.A. **21** [1967] No. 45980). – [88] B. J. Thamer (LA-3646 [1967] 1/12; N.S.A. **21** [1967] No. 22910). – [89] W. M. Pardue, V. W. Storhok, R. A. Smith (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 721/38). – [90] D. L. Keller (BMI-1837 [1968] 1/85; N.S.A. **22** [1968] No. 28777).

[91] D. L. Keller (BMI-1845 [1968] 1/69; N.S.A. **23** [1969] No. 1019). – [92] W. M. Pardue, A. A. Bauer, D. L. Keller (Ceram. Nucl. Fuels Proc. Intern. Symp., Washington, D.C., 1969, pp. 166/78; C.A. **72** [1970] No. 37975). – [93] J. C. Hebeisen, D. P. Moak, W. H. Pfeifer (BMI-1895 [1971] 1/32; N.S.A. **25** [1971] No. 22149). – [94] A. A. Bauer (Reactor Technol. **15** [1972] 87/104). – [95] D. L. Keller (BMI-1774 [1966] 1/26; N.S.A. **20** [1966] No. 37169; BMI-1778 [1966] 1/23; N.S.A. **21** [1967] No. 447; BMI-1784 [1966] 1/56; N.S.A. **21** [1967] No. 18308; BMI-1791 [1967] 1/96; N.S.A. **21** [1967] No. 20550; BMI-1798 [1967] 1/98; N.S.A. **21** [1967] No. 32951; BMI-1819 [1967] 1/51; N.S.A. **22** [1968] No. 15261).

[96] S. Katz (J. Nucl. Mater. **6** [1962] 172/81). – [97] J. Alikhan, A. Naoumidis, G. Pott (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 454/70). – [98] M. Allbutt, A. R. Junkison (AERE-R-5466 [1967] 1/36; N.S.A. **25** [1971] No. 32791). – [99] F. M. Smith (BNWL-1101 [1969] 1/18; N.S.A. **23** [1969] No. 41726). – [100] D. E. Price, D. P. Moak, W. Chubb, D. L. Keller (BMI-1760 [1966] 1/43; EURAEC-1591 [1966]; N.S.A. **20** [1966] No. 19187).

[101] D. L. Keller (BMI-1868 [1969] 1/242; N.S.A. **24** [1970] No. 1060). – [102] J. M. Leitnaker, R. L. Beatty, K. E. Spear (Trans. Am. Nucl. Soc. **12** [1969] 86/9). – [103] A. Naoumidis, H. Nickel (Reaktortagung, Berlin 1974, pp. 249/52). – [104] O. Götzmann (KFK-985 [1969] 135/59; N.S.A. **24** [1970] No. 9987). – [105] S. Ihara, K. Tanaka, S. Tojo, M. Kojima, Y. Akimoto (J. Nucl. Sci. Technol. **10** [1973] 106/10).

[106] M. A. DeCrescente, M. S. Freed, S. D. Caplow (PWAC-488 [1965]). – [107] Y. Kuroda, K. Tanaka, M. Suzuki, Y. Akimoto (J. Nucl. Mater. **34** [1970] 174/81). – [108] F. Casteels, A. Cools, J. Dresselaers (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 541/61). – [109] O. Götzmann, P. Hofmann, W. Stumpf (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 562/88). – [110] W. Batey, D. M. Donaldson, H. W. Irons, G. Yates (TRG-Report-1835 [1969] 1/17; N.S.A. **23** [1969] No. 38924).

[111] T. W. Latimer (Trans. Am. Nucl. Soc. **11** [1968] 511/2).

1.2.3 Irradiation Behavior

1.2.3.1 Changes in the Physical Properties

1.2.3.1.1 Irradiation-Induced Creep Processes in UC and UN

It has been emphasized in Section 1.2.2.1 (p. 143), that the plasticity and therefore the creep of the fuels are very important factors for the dimensional stability and integrity of the fuel rods under irradiation. The irradiation-induced creep in a ceramic nuclear fuel governs the low-temperature deformation under a mechanical stress and it therefore must be quantitatively known as well. It must be determined as a function of the neutron flux, the fission rate, and the burnup, for realistic values of the stresses and the temperatures. Solomon [1] has indicated, that for ceramic fuels below 1200 °C the irradiation-induced creep dominated the creep mechanism, whereas thermal creep could be neglected in this temperature range. The available data indicate that the creep rate of uranium carbides and nitrides under irradiation is smaller than that of the oxides (see Section 1.1.2.3, p. 14). This is in agreement with the concept of Brucklacher, Dienst [2], that the irradiation-induced creep of a fuel with a high thermal conductivity is determined by the thermal spikes.

Results for the steady-state creep of UC and UN obtained from irradiation experiments are summarized in Table 1/37. These data were obtained at different fission rates. They were normalized to the same fission rate, $F = 4.8 \times 10^{13}$ fissions $\cdot$ $cm^{-3} \cdot s^{-1}$, and to the same stress, $\sigma = 64$ MPa, for comparison in **Fig. 1-120**, under the assumption that the creep rate was proportional to these two quantities.

Matthews [8] analyzed these data and proposed for the dependence of the irradiation-induced creep rate of UC and (U,Pu)C, $\dot{\varepsilon}_R$ (in h^{-1}), on the fission rate F (in fissions $\cdot$ $cm^{-3} \cdot s^{-1}$) and the mechanical stress σ (in MPa) eq. (1):

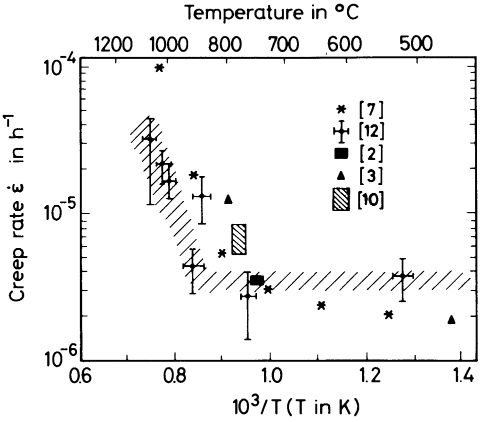
$$\dot{\varepsilon}_R = 3.6 \times 10^{-22} F \cdot \sigma \qquad (1)$$

Table 1/37
Irradiation-Induced Creep of UC and UN.

authors	material	$\dot{\varepsilon}_R$, in h^{-1}	experimental conditions
Clough [3]	UC	5×10^{-6}	4.85 wt% C, 95.5% theoretical density (= TD), 800 °C, 6×10^{12} fissions $\cdot cm^{-3} \cdot s^{-1}$, σ = 25.5 MPa
Clough [4]	UC	1×10^{-7} to 3×10^{-6}	4.85 wt% C, 97% TD, 450 °C, 1.2×10^{13} fissions $\cdot cm^{-3} \cdot s^{-1}$, σ = 13 to 53 MPa
Brucklacher et al. [5]	UC	2.5×10^{-7} to 1.3×10^{-6}	4.9 wt% C, 85% TD, 700 °C, 3.4×10^{14} fissions $\cdot cm^{-3} \cdot s^{-1}$, σ = 24 MPa
Brucklacher et al. [5]	UN	2.5×10^{-7} to 1.3×10^{-6}	stoichiometric UN, 95% TD, 700 °C, (6 to 9) $\times 10^{13}$ fissions $\cdot cm^{-3} \cdot s^{-1}$, σ = 24 MPa
Brucklacher, Dienst [2]	UN	1.5 to 2×10^{-6}	89% TD, 6 vol% UO_2, 750 °C, (6 to 9) $\times 10^{13}$ fissions $\cdot cm^{-3} \cdot s^{-1}$, σ = 40 MPa
Brucklacher [6]	UN	2×10^{-6}	93% TD, 4.8×10^{13} fissions $\cdot cm^{-3} \cdot s^{-1}$ σ = 63 MPa, for T < 900 °C enhancement, for T > 900 °C slight enhancement

References for 1.2.3.1.1 on p. 194

Fig. 120



Irradiation-induced creep rates of UC, (U,Pu)C, and UN [7]. EUR hypothesis [7], EUR data, UN [12], KFK, UN [2], Clough, UC [3], Dienst, (U,Pu)C [10].

Singh [9] considered the constant in eq. (1) to be temperature-dependent and described the irradiation-induced steady-state creep, $\dot{\varepsilon}$ in h^{-1}, at T ≤1 000 °C by means of eq. (2) for UC and of eq. (3) for UN:

$$\dot{\varepsilon}_R = 58\times10^{-9}\Omega^2(kT)^{-1}\ F\cdot\sigma \quad \text{for UC} \qquad (2)$$

$$\dot{\varepsilon}_R = 68\times10^{-9}\Omega^2(kT)^{-1}\ F\cdot\sigma \quad \text{for UN} \qquad (3)$$

where Ω is the atomic volume in cm^3 and k, Boltzmann's constant, is in J/K, the units of the other quantities being the same as in eq. (1).

No relationship between the irradiation-induced creep and the porosity of the fuel could be established because of the lack of data [10], unlike the case of the oxide (see p. 14) [2].

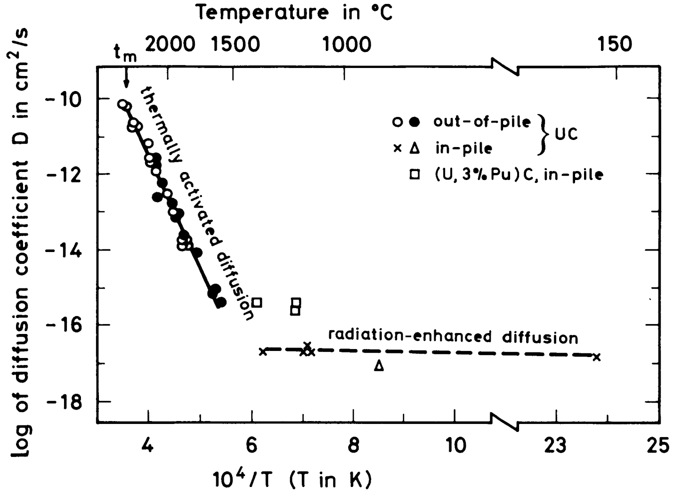
Recent measurements of Clough [11] on UO_2 and UC up to high burnup values (1×10^{21} fissions/cm^3, 2.4×10^4 MWd/t) showed for both 450 and 800 °C, that after a high initial creep rate a nominally steady-state creep rate of UC was attained at 6×10^{19} fissions/cm^3 (1.4×10^4 MWd/t), which was, however, eight times lower than the corresponding value for UO_2.

1.2.3.1.2 Irradiation Effects on Diffusional Processes

Diffusion in a solid is generally accelerated by neutron irradiation, because of the significant increase in the concentration of lattice defects [13]. This effect is enhanced appreciably in nuclear fuels because of additional changes, such as the thermal spikes caused by the fission products.

Höh, Matzke [14] measured the self-diffusion of uranium in stoichiometric arc-cast UC samples, at 900 °C. Recent measurements in the European Institute for Transuranium Elements

Fig. 1-121



Summary of the results of the RADIFI-5 irradiation experiments [15], normalized to a fission rate of $F = 3.5 \times 10^{12}$ fissions $\cdot$ cm$^{-3} \cdot$ s^{-1}. The data for $(U_{0.97}Pu_{0.03})C$ are normalized to $F = 1.9 \times 10^{13}$ fissions $\cdot$ cm$^{-3} \cdot$ s^{-1}.

in Karlsruhe [15, 16] confirmed that the diffusion coefficient of U in UC, irradiated at $t < 1000\,°C$, is between 1.3 and 4.5×10^{-17} cm$^2 \cdot$ s^{-1}, independent of the temperature (**Fig. 1-121**). It was shown thereby, that irradiation in this temperature region caused a significant enhancement of the mobility of the uranium. At $t > 1500\,°C$ it was thermal diffusion, that governs the mobility of the uranium.

These more recent irradiation experiments led also to a dependence of the altered rate of diffusion on the fission rate, F. The authors could not quantify this dependence clearly, however, and supposed that it must lie between $D^* = \text{const.} \times F$ and $D^* = \text{const.} \times F^{1/2}$, where D^* is the irradiation-induced diffusion coefficient.

1.2.3.1.3 Change of the Hardness on Irradiation

Kleykamp [17] measured the microhardness of a UC sample containing 4.96 wt% C, that had been irradiated to a burnup of 6170 MWd/t (2.47×10^{20} fissions/cm^3) only. He reported a value between 1000 and 1200 kp/mm^2 (9.8 to 11.8 GPa), independent of the radial position of the measurement. Compared with the literature value of 650 kp/mm^2 [18], this implied an irradiation-induced increase of this property.

The hardness of a sample of uranium nitride was measured after irradiation at BMI. Bugl, Keller [19] reported a clear increase in hardness of about 30%. The absolute values reported were, however, very low, so that this effect could not be considered as firmly established.

References for 1.2.3.1.2 and 1.2.3.1.3 on p. 194

References for 1.2.3.1.1, 1.2.3.1.2, and 1.2.3.1.3:

[1] A. A. Solomon (J. Am. Ceram. Soc. **56** [1973] 164/71). – [2] D. Brucklacher, W. Dienst (J. Nucl. Mater. **42** [1972] 285/96). – [3] D. J. Clough (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 321/42). – [4] D. J. Clough (AERE-R-7772 [1974]; J. Nucl. Mater. **56** [1975] 279/86). – [5] D. Brucklacher, W. Dienst, F. Thümmler (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 344/68).

[6] D. Brucklacher (Phys. Met. Reactor Fuel Elem. Proc. Intern. Conf., Berkeley, Calif., 1973, pp. 118/22). – [7] P. Zeisser, G. Maraniello, C. Merlini (J. Nucl. Mater. **65** [1977] 48/60). – [8] J. R. Matthews (AERE-M-2643 [1974] 1/28; C.A. **82** [1975] No. 91466). – [9] R. N. Singh (ANL-AFP-15 [1976] 1/13; INIS Atomindex **8** [1977] No. 305954). – [10] W. Dienst (J. Nucl. Mater. **65** [1977] 1/8).

[11] D. J. Clough (J. Nucl. Mater. **65** [1977] 24/36). – [12] A. Caridi, F. de Vita, C. Merlini, P. Zeisser (Energia Nucl. [Milan] **21** [1974] 267/75). – [13] A. C. Damask (in: G. J. Diennes, Studies in Radiation Effects in Solids, Gordon and Breach, New York 1967, pp. 1/102). – [14] A. Höh, H. Matzke (J. Nucl. Mater. **48** [1973] 157/64). – [15] H. Matzke, M. H. Bradbury (EUR-5906 [1978] 1/111; INIS Atomindex **10** [1979] No. 423257).

[16] H. Blank, R. Lindner, H. Matzke (Nuclear Power Its Fuel Cycle Proc. Intern. Conf., Salzburg 1977 [1978], Vol. 3, pp. 511/26). – [17] H. Kleykamp (J. Nucl. Mater. **47** [1973] 271/7). – [18] E. K. Storms (The Refractory Carbides, Academic, New York-London 1967). – [19] J. Bugl, D. L. Keller (Nucleonics **22** [1964] 66/70).

1.2.3.1.4 Changes of Thermal Conductivity

Little is known concerning the change of the thermal conductivity of ceramic uranium compounds by irradiation. Rough, Chubb [8] observed in irradiation experiments on uranium carbides at 300 to 800 °C, in which the samples were provided with thermocouples, that the in-pile thermal conductivity lay only marginally lower than those of nonirradiated UC. The authors admitted, however, that due to experimental uncertainties, any differences in the data up to a maximal fluence of 5.5×10^{20} fissions/cm^3 may not have been significant.

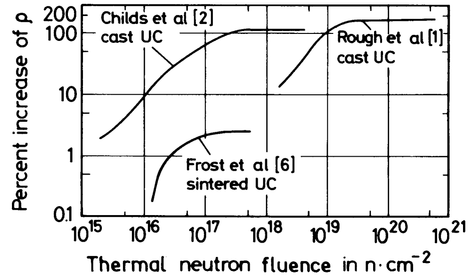
Since nonirradiated uranium carbide obeys the Wiedemann-Franz rule, it was assumed by Robertson [9], that the irradiation damage of UC influences the thermal conductivity in the same manner as it does the electrical conductivity. According to his opinion, the temperatures employed by Rough, Chubb [8] in their irradiation of real fuel samples were too high. The heat treatments of UC, for the annealing of lattice defects that affect the electrical conductivity, showed clearly (Fig. 1-123, p. 196) that irradiation temperatures below and above 150 °C led to quite different results. A similar effect was seen around 500 °C (see Fig. 1-123). Because of the annealing mechanism of the irradiation damage, the effect of the irradiation-induced changes of both the thermal and the electrical conductivity of UC increased with diminishing temperatures. Tachis et al. [10] determined the thermal conductivity during irradiation, using an extensive instrumentation. No effect of the irradiation on the thermal conductivity of UC was found in the range 300 to 800 °C up to a maximal burnup of 0.02% FIMA (0.16 MWd/kg, 6.6×10^{19} fissions/cm^3). Bradbury et al. [11], too, arrived at this conclusion, from the agreement of the calculated with the measured central temperature of a fuel having the composition $U_{0.85}Pu_{0.15}C$. Strasser et al. [12] concluded from the temperature course of the central thermocouples during the irradiation of (U,Pu)C, that the temperature change in the fuel was given by the change of the thermal conductivity of the He gap, rather than by any irradiation-induced changes in the thermal conductivity of the fuel itself.

Lagedrost, Storhok [13] studied the thermal conductivity of two UN samples, that had been irradiated up to 2.1×10^{21} fissions/cm^3 (5.0×10^4 MWd/t). The strong decline of the λ values that was observed was attributed to the formation of gas bubble pores on the one hand and to the formation of cracks on the other.

1.2.3.1.5 Changes of the Electrical Resistivity

The electrical resistivity of solids may change appreciably on irradiation with neutrons. As yet, only results for uranium carbide are available; those obtained by numerous authors [1 to 3, 6] for arc-cast UC are presented in **Fig. 1-122.** The temperature of the irradiation was generally $<100\,°C$, only in the experiments of Rough, Chubb [1] it was 600 to 800 °C. It is clearly seen in Fig. 1-122 that in all the experiments the electrical resistivity ρ first increases with the irradiation, as a result of the formation of lattice defects, and eventually reaches a saturation value. Griffiths [5, 7] pointed out, that the kind of sample material which had been used played a decisive role in the irradiation-induced enhancement of ρ. When sintered UC, having a mean grain size of 10 to 20 µm was used, the electrical resistivity changed by less than 3%, whereas for calcined samples, having grain sizes of 40 to 50 µm, the change was 60% [7]. The grain boundaries seemed to act as sinks for lattice defects.

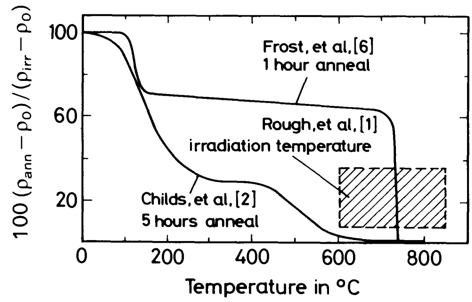
Fig. 1-122



Comparison of the results of various authors for the irradiation-induced change of the electrical resistivity of UC.

The lattice defects formed by irradiation may be annealed, at least partly, by a heat treatment. **Fig. 1-123** shows the annealing effect on the irradiation-induced electrical resistivity. In the case dealt with, a stepwise but complete annealing of the UC is achieved between 600 and 800 °C. It must be emphasized, however, that the annealing process by means of a high temperature treatment is very complex, and that it depends strongly on the primary radiation damage [14].

Fig. 1-123



Annealing of irradiation-induced electrical resistivity.

References for 1.2.3.1.4 and 1.2.3.1.5:

[1] F. A. Rough, W. Chubb (BMI-1554 [1961] 1/58; N.S.A. **16** [1962] No. 4961). – [2] B. G. Childs, A. Ogilvie, J. C. Ruckman, J. L. Whitton (Radiat. Damage Reactor Mater. Part Proc. Symp., Venice 1962 [1963], pp. 241/74). – [3] B. G. Childs, J. C. Ruckman (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 849/63). – [4] D. G. Freas, A. E. Austin, F. A. Rough (Am. Soc. Testing Mater. Spec. Tech. Publ. No. 306 [1961] 131/45). – [5] L. B. Griffiths (J. Nucl. Mater. **4** [1961] 336).

[6] B. R. T. Frost, B. T. Bradbury, L. B. Griffiths (Radiat. Damage Reactor Mater. Part Proc. Symp., Venice 1962 [1963], pp. 219/39). – [7] L. B. Griffiths (Trans. Brit. Ceram. Soc. **62** [1963] 189/95; AERE-R-4207 [1963]). – [8] F. A. Rough, W. Chubb (BMI-1441 [1960] 1/102; N.S.A. **14** [1960] No. 18107). – [9] J. A. L. Robertson (Irradiation Effects in Nuclear Fuels, Gordon and Breach, London-Paris 1969, pp. 214/303). – [10] A. M. Tachis, W. G. Mathers, J. E. May (AECL-2521 [1966] 1/30; N.S.A. **21** [1967] No. 6891).

[11] B. T. Bradbury, B. R. T. Frost, J. R. Findlay (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 963/75). – [12] A. Strasser, D. Stahl, K. Taylor, J. Andersen (UNC-5081 [1964]), D. Stahl, A. Strasser (Carbides Nucl. Energy Proc. Symp., Harwell, U.K. 1963 [1964], Vol. 2, pp. 373/91). – [13] F. G. Lagedrost, V. M. Storhok (BMI-1784 [1966] A10/A14). – [14] H. Matsui (J. Nucl. Mater. **56** [1975] 161/8).

1.2.3.2 In-Pile Compatibility

1.2.3.2.1 Carbide Fuels

Carburization of the metallic cladding is the main compatibility problem of fuel elements having carbide fuels. The carburization rate has been determined as a function of the carbon content in out-of-pile experiments [1]. Also the in-pile interaction of the carbidic fuel with the metallic cladding depends on the C activity at the surface of the fuel [2], hence on the C:U ratio in the starting material of the sample [3]. The initial potential of the carbon changes during the irradiation because of the formation of carbides of the fission products. Lorenzelli [4] concluded, on the basis of phase studies of the systems UC-RE (RE = rare earth element), UC-Mo, UC-Ru, and UC-Pd, and of simulation experiments involving burnup of 5, 10, and 15

$\times 10^4$ MWd/t(U + Pu), that the burnup had an influence on the carburization of the cladding. Haines, Potter [5] calculated from the composition of the phases that had been confirmed by them, that for 10% burnup the C potential remained constant only if an appreciable amount of the M_2C_3 (M = U + Pu) phase was present. For a starting composition $U_{0.8}Pu_{0.2}C_{1.09}$, on the other hand, the C potential decreased continuously with the burnup.

In order to simulate burnups of 10 or 20% (8 or 16 $\times 10^4$ MWd/t), Hofmann, Götzmann [6] mixed fission products with stoichiometric and hyperstoichiometric UC. The heat treatments led to no measurable interaction between the various cladding materials used and the simulated fission products at 600 to 800 °C. Even the added CsI did not react with the investigated steels. On the contrary, the addition of the fission products led to a reduction of the carburization of the cladding material.

As is well known, the heat flux plays an important role in the transport of carbon, and it is therefore taken into account in some out-of-pile experiments. Nishio et al. [7] found in experiments, where a simulated heat flux was applied, that the dissolution of the carbon and its transport in the Na-bonding limited the lifetime and the maximum burnup of a rod having an AISI 304 SS steel cladding. For linear rod power rates of 1 000 W/cm, respectively 500 W/cm, maximal burnups of 3.7, respectively 5.5, $\times 10^4$ MWd/t, were calculated by the authors for the lifetime of the cladding.

Vanadium alloys (e.g., V-Ti3-Si1 or V-Zr2-Cr15) were treated at various temperatures together with uranium carbides having various compositions and with a series of simulated fission products [8]. An increase of the hardness of the V alloys was observed, but this embrittlement effect was smaller in the experiments where fission products were present. This confirmed the behavior expected by Dorner, Schumacher [9] for this type of cladding material.

1.2.3.2.1.1 Results of Irradiation of UC with Cr-Ni-Steels

He-Bonding

The simulation results were confirmed to a large extent by irradiation experiments. Bradbury et al. [10] reported good compatibility between UC and stainless steels at temperatures around 550 °C for a burnup of $<1 \times 10^4$ MWd/t. Arnold [11] could not observe any migration of uranium and of carbon in hypostoichiometric or stoichiometric UC at burnups $<1 \times 10^4$ MWd/t, and cladding temperatures of 940 to 1 100 °F (500 to 600 °C). At higher temperatures, however, a slight carburization of the 304 SS steel occurred. Also Watanabe et al. [12] found no carburization at temperatures <800 °C up to a burnup of 2.4×10^4 MWd/t. Russian authors, on the contrary, reported a slight reaction of carbon with the metallic cladding (about 150 μm) after a burnup of 10.4% FIMA (8.55×10^4 MWd/t) at a maximal temperature of 680 °C. Carbon contents in the range from 4.7 to 4.95 wt% in the fuel did not cause significant differences in the carburization effect. The amount of UC_2, initially present in hyperstoichiometric UC, decreased on increasing burnup, possibly causing an embrittlement of the cladding material [14].

Na-Bonding

Irradiation experiment in the BR-5 research reactor in Moscow led to a satisfactory compatibility of fuel rods having UC (4.8 wt% C) fuel in a steel (16 Cr-15 Ni-Mo-Nb) cladding with Na-bonding [15]. When hyperstoichiometric carbides were employed, the authors proposed a chromium coating of the pellets in order to reduce the carbon transport. When fuel rods having Na-K-bonding were irradiated up to 7.1% FIMA (5.84×10^4 MWd/t), reaction zones in the steel cladding of $<50\,\mu m$ (or 100 to 150 μm) were observed for starting materials having <5.0 (or 5.1) wt% C. When these were coated with Cr- or Nb-based coatings, the depth of carburization did not exceed 30 μm [13]. Hypostoichiometric UC (≈4.6 wt% C) showed, after burnup of up to 1.92×10^4 MWd/t and at temperatures of 1 480 to 1 640 °F (800 to 900 °C, calculated from the power rate), a reaction between the fuel and the cladding in all the fuel rods, which was described as a decarburization [16]. No carbon transport was observed at 1 200 °F (650 °C) in the system UC_{1-x}-Na-304 SS [17]. Under the same conditions, hyperstoichiometric uranium carbides showed strong carburization, dependent on the C content. Irradiation, however, had no accelerating effect on the carburization.

1.2.3.2.1.2 UC with Tungsten

At temperatures between 1 400 and 1 800 °C and a burnup of 4×10^{19} fissions/cm^3 (0.1 MWd/t) no reaction was observed between UC and vapor-deposited tungsten during 1 200 h [18]. A UC-ZrC solid solution behaved similarly. Since first signs of a reaction between UC and W at 1 670 °C and 5×10^{19} fissions/cm^3 (0.125 MWd/t) burnup were obtained after 5445 h at a C:U ratio of 1.05, the authors recommended to limit the ratio to C:U = 1.03.

1.2.3.2.1.3 UC with Nb-1% Zr

Uranium carbide ($UC_{1.08}$) with Li-bonding in a cladding of Nb-1 % Zr (Nb is designated in the original [20] as columbium (Cb)) was irradiated up to about 1 % FIMA (0.82×10^4 MWd/t) at a temperature of 2 200 to 2 400 °F (1 200 to 1 315 °C) at the contacts between the fuel and the cladding [20]. Catastrophic failure of the rod resulted, due to large carburization of the niobium alloy and the formation of a U-Nb melt. A carbide having the composition $UC_{1.45}$ behaved better under these conditions. Although the niobium cladding was again weakly carburized, the formation of a U-Nb melt could be avoided when the surface temperature was kept below 2150 °F (1 177 °C). At temperatures between 2150 and 2370 °F (1 177 to 1 300 °C) a liquid phase was observed between the fuel and the cladding for $UC_{1.45}$ too, which led to a failure of the rod above 2350 °F (1 288 °C). DeCrescente [21] observed decarburization of the fuel and C transport to the Nb-1% Zr cladding in in-pile experiments, independent of the use of a tantalum barrier. A carbon content between 6.6 and 7.3 wt% was specified for in-pile operation at 2200 °F (1 200 °C) for 10000 h, based on extensive out-of-pile data. Fuel decarburization influenced the fuel design indirectly, since the transformation of UC_2 or U_2C_3 to UC is accompanied by a volume decrease.

Crane, Gordon [22] irradiated UC rods having Nb-1% Zr claddings and stoichiometries varying between $UC_{0.90}$ and $UC_{1.09}$ at surface temperatures between 660 and 800 °C up to burnups of 1.7 to 3.5×10^4 MWd/t. Whereas for Na-bonding the carburization extended to 125 μm for $UC_{1.09}$ and to 25 μm for $UC_{0.90}$, no reaction between the fuel and the cladding could be observed for He-bonding.

1.2.3.2.1.4 (U,Pu)C with Stainless Steel

The results of studies of the in-pile compatibility of (U,Pu)C with austenitic steels that had been conducted in the earlier sixties were described by Strasser et al. [23]. According to these, a satisfactory compatibility existed between the (U,Pu) mixed carbides and austenitic steels, such as 304 SS and 316 SS, at temperatures 520 or 850 °C and irradiation times of 2640 or 8730 h. Neimark et al. [24, 25] reported that some carbon was transported from the fuel $(U_{0.8}Pu_{0.2})C$ to the cladding (304 SS) during irradiation at 625 °C and 2.08×10^4 MWd/t burnup. Even in a hyperstoichiometric carbide some free plutonium could be detected after the irradiation experiment. It was noteworthy, that the interaction between the carbide and the metallic cladding was described by the authors as "slight" even in these cases.

The United Nuclear Corporation (UNC) carried out an irradiation program involving stoichiometric and hyperstoichiometric (10 vol% M_2C_3) (U,Pu) mixed carbides and claddings made of 316 SS and Incoloy 800 [26 to 28]. At a temperature of 520 °C and burnups up to 7.7 $\times 10^4$ MWd/t no reaction of the fission products and the cladding material could be observed. However, the interaction of the fuel with 316 SS led to a 50 μm thick layer in the cladding that included carbides and σ-precipitations, but had no hardening effect on the steel cladding. In Incoloy 800 an only 1 μm thick reaction zone formed, which consisted according to a microprobe analysis of reaction products of Cr, Ti, and Si from the cladding material with carbon from the fuel.

Latimer et al. [29] reported on a large-scale test involving 74 fuel elements and He-bonding. After burnups of 2 to 11% FIMA (1.6 to 9.0×10^4 MWt/d) reaction zones of 25 to 250 μm were found in 316 SS and of 40 to 110 μm in Incoloy 800. In the reaction zone Fe and Ni were depleted to a depth of 10 μm. Furthermore, on the inner surface of the cladding deposits of Am, U,Pu, and Ba were found, which did not, however, migrate into the cladding material.

Fuel pins with a 316 SS steel cladding and filled with MC (M = U,Pu) having an M_2C_3 fraction larger than 5%, showed at temperatures above 600 °C and rod power rates of 800 W/cm a carburization depth of 250 μm. Under similar conditions (1 000 W/cm, 5.7% FIMA, 650 °C) a UC fuel having <5% U_2C_3 showed a significantly lower carburization depth (<50 μm) [30].

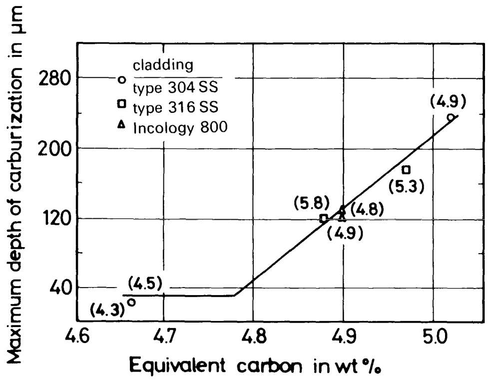
Na-Bonding

Na-bonding has been applied successfully since the 70's to carbide fuels. Barner [32] examined fuel rods having stoichiometric (U,Pu)C fuel and 316 SS cladding after burnup of 8% FIMA (6.6×10^4 MWd/t) at a maximal irradiation temperature of 690°C. At a few places only the author could find slight depletion of Fe and Ni and enrichment of Cr in the cladding, and this to a depth of only 4 μm using microanalysis. According to the observations of Barner, the carbon released from mixed carbides was less disadvantageous than prolonged out-of-pile heat treatments, which could lead to precipitation of a sigma-phase and enrichment of Ni in alloy resulting in the possible formation of a eutectic with the heavy metal. The author, therefore, considered a slight carburization to have favorable effects on the long-time behavior of steel claddings. Even continuation of the irradiation up to 11.5% FIMA (9.5×10^4 MWd/t) burnup at a linear power density of 30 kW/ft (≈1 000 W/cm) did not cause significant changes in the Na-bonded 316 SS cladding material [33, 33a].

(U,Pu)(C,O) fuel having oxygen contents up to 1 wt% showed after burnups up to 10.1% FIMA (8.30×10^4 MWd/t), but at a relatively low linear power density (300 to 400 W/cm), no interaction with the 316 SS cladding [34]. However, it was observed [35] that the two-phase fuel (MC + M_2C_3) had poorer compatibility than the single-phase mixed carbide fuel. A team work in Los Alamos showed that as the M_2C_3 content increased, so did the depth of the carburization zone in the cladding (**Fig. 1-124**).

A Ni-Pu rich phase, which contained also some fission products, could form in stoichiometric or hypostoichiometric mixed carbides, just as in out-of-pile experiments.

Fig. 1-124



Maximal depth of carburization of various austenitic steels during the irradiation of mixed carbides with Na-bonding, as a function of the equivalent carbon content of the fuel [35]. (The burnup in % FIMA in parentheses).

Mikailoff, Clottes [36] found a satisfactory compatibility of (U,Pu)C with austenitic steel after irradiation to a burnup of 2.70 × 10^4 MWd/t. Local carburization down to a depth of 30 to 130 µm was attributed by them to hot spots (up to 640 °C). A slightly hyperstoichiometric carbide having $\leq 2\%$ U_2C_3 caused a carburization zone of up to 120 µm in the 316 SS cladding after burnup of 2.70 × 10^4 MWd/t at a temperature of 850 °C. Combette [37] calculated on the basis of experimental data, that the increased carbon diffusion was induced by the irradiation, and he therefore expected higher carburization rates compared with out-of-pile data [38].

Barner et al. [39] observed for Na-bonding 2 to 3 times higher carburization rates than for He-bonding. Bagley et al. [40] summarized the in-pile experiments, carried out at the UKAEA, concerning the compatibility between MC and austenitic steels, as follows:

a) The penetration of carbon into the steel was nonlinear, contrary to the case in out-of-pile experiments.

b) At low linear power rates ($\approx$400 W/cm) no noticeable carburization, hence no significant changes of the properties of the steel cladding occurred.

c) At high linear power densities oxygen impurities contributed to the carbon transport as a result of the formation of CO.

Geithoff [41] observed for carbide samples, having a 15% M_2C_3 content, carburization as deep as half the cladding wall thickness after 5% FIMA (4.1 × 10^4 MWd/t) burnup. He confirmed thereby the literature data about enhanced carburization rates for carbide-containing fuel rods with Na-bonding. It was attempted to modify the fuel by the addition of Cr and Fe in order to achieve a stabilization of the carbon potential in the fuel and thereby a reduction of the carburization of the cladding. An irradiation experiment with unmodified and with Cr- and Fe-modified carbide led, however, to the result that the depth of carburization was greater for the Cr-modified than for the unmodified fuel [42]. It could be generally concluded, that additives were not able to reduce the C transport from the carbide fuel to the metallic cladding [43].

1.2.3.2.1.5 (U,Pu)C with Nb-1% Zr

Nb-1% Zr claddings showed better compatibility with (U,Pu) mixed carbides in in-pile experiments than did 316 SS. After a burnup of 2.62×10^4 MWd/t at temperatures not exceeding 625 °C no damage could be detected in the fuel rods [24]. In another series of irradiations, at surface temperatures between 570 and 650 °C, corresponding to an interior contact temperature of 700 °C, only local reaction regions could be seen in a few places after a burnup of 6.9% FIMA (5.7×10^4 MWd/t) [25]. Fuel rods made of $U_{0.8}Pu_{0.2}C$ pellets with Nb-1% Zr or alloyed steel claddings were irradiated at power levels (265 to 490 W/g) up to 11.3×10^4 MWd/t [31]. It was found that the rods that had been clad by Nb-1% Zr were in an excellent condition, whereas the stainless steel cladding showed noticeable cracks, because of carburization and a resulting drastic decrease of the ductility.

1.2.3.2.2 Nitride Fuels

The good compatibility between UN and metallic cladding materials, which is known from out-of-pile experiments, is not significantly affected by irradiation [44 to 47]. In irradiation experiments at the BMI [44], a nitrided zone of only 6 μm thickness was observed in austenitic steel after burnup of 3.8% FIMA (3.12×10^4 MWd/t) at a maximal temperature of 615 °C. The U_2N_3 second phase formed on the surface of the fuel does not react with the steel cladding. The material AISI 316 SS showed some embrittlement after higher burnups (4.6 to 6.3% FIMA, 3.78 to 5.18×10^4 MWd/t) at maximal temperatures of 630 °C, the reason for which could, however, not be understood [45].

No nitriding nor carburization of 316 SS was obtained with either UN or U(C,N) solid solutions after burnup to 2.40×10^4 MWd/t at maximal linear power densities of 880 W/cm and temperatures of 780 °C [47]. At higher power levels (1000 to 1600 W/cm), however, interaction between $U(C_{1-x}N_x)$ fuel (with $0.15 \leqq x \leqq 0.40$) and the steel cladding was repeatedly observed, even for relatively small burnups or irradiation times [48]. The authors found by means of various etching processes and microhardness determinations, that carburization occurred at hot spots. The decrease in the ductility of 304 SS, caused by this effect, coupled with a simultaneous swelling of the fuel, led after a burnup of 6.00×10^4 MWd/t to a failure of the fuel rods [49].

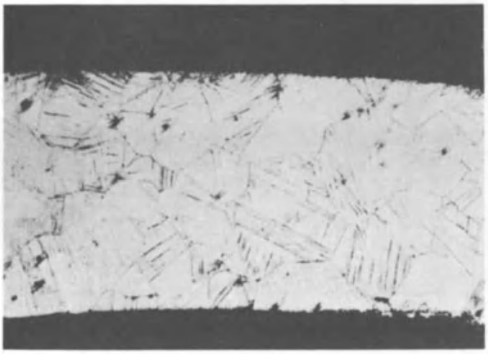
Uranium nitride rods, clad with a W-25.5% Re alloy were tested for the "Space Electric Power Program" in the USA. No reaction between the fuel and the cladding could be found after an irradiation for 3558 h at temperatures between 1350 and 1800 °C [50]. However, the interior swelling pressure caused the test rods to fail.

(U,Pu)N rods with [36, 51] and without [51, 52] Na-bonding showed excellent compatibility with austenitic steels in in-pile experiments. Only Mikailoff, Clottes [36] reported a slight nitriding, which did not lead to any negative effect on the mechanical properties of the steel cladding, however. Bauer et al. [51] irradiated (U,Pu)N fuel with and without Na-bonding to 304 SS up to top burnups of 15.3×10^4 MWd/t and maximal temperatures of 795 °C without being able to note any measurable reaction between the fuel and the cladding, as represented in **Fig. 1-125**, p. 202.

Microanalytical examination confirmed that the cladding did not contain any fuel, fission products, or nitrogen as traces. Also the fuel remained unchanged at the contact points. Only in one sample, which was exposed to a temperature above 1000 °C, metallic depositions, consisting of Fe, Cr, Ni, Ru, Rh, and Mo, were found in the cracks of the fuel and on the interior surface of the cladding.

References for 1.2.3.2 on pp. 202/4

Fig. 1-125



AISI 304 SS cladding (150× enlargement) after irradiation of Na-bonded (U,Pu)N fuel to a burnup of 15.3×10^4 MWd/t [51].

When (U,Pu)(C,N) fuels are irradiated, the following parameters affect the carburization of the cladding: the mean temperature of the cladding, the local power density, the carbon potential of the fuel, the type of bonding (Na or He), the type of fuel (pellet or Vipac, i.e., vibrationally compacted), and the burnup [53]. Blank [50] concluded from measurements of the distribution of the metal carbides formed on the cladding, that for He-bonded rods the carburization depended primarily on their linear power density, whereas for Na-bonded rods the temperature of the cladding played the major role.

References for 1.2.3.2:

[1] O. Götzmann, P. Hofmann, Y. Sarikaya (EURFNR-1173 [1973] 1/30; N.S.A. **30** [1974] No. 17689). – [2] B. Snyder, K. Natesan, T. F. Kassner (J. Nucl. Mater. **50** [1974] 259/74). – [3] M. Tetenbaum, P. D. Hunt (J. Nucl. Mater. **40** [1971] 104/12). – [4] N. Lorenzelli (CEA-R-4465 [1973] 1/126; ANL-Trans-979 [1973]; Diss. Univ. Paris 1973; N.S.A. **28** [1973] No. 24932). – [5] H. R. Haines, P. E. Potter (Thermodyn. Nucl. Mater. Proc. Symp., Vienna 1974, Vol. 2, pp. 145/73).

[6] P. Hofmann (KFK-1832 [1973] 1/62; N.S.A. **29** [1974] No. 21573), P. Hofmann (EURFNR-1177 [1974]), O. Götzmann, P. Hofmann (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 233/45). – [7] G. Nishio, H. Watanabe, J.

Shimokawa (Nucl. Eng. Design **22** [1972] 326/33). – [8] P. Hofmann, O. Götzmann (KFK-1718 [1973] 1/77; N.S.A. **28** [1973] No. 3132). – [9] S. Dorner, G. Schumacher (KFK-1410 [1971]; EURFNR-934 [1971] 1/17; CONF-710326-1 [1971]; N.S.A. **25** [1971] No. 49567). – [10] B. T. Bradbury, J. E. Cole, B. R. T. Frost, J. D. B. Lambert (TID-7676 [1963] 170/82), B. T. Bradbury, J. E. Cole, B. R. T. Frost, J. D. B. Lambert (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 879/95), B. T. Bradbury, J. E. Cole, B. R. T. Frost, J. D. B. Lambert (AERE-R-4323 [1963]; C.A. **60** [1964] 15390).

[11] J. L. Arnold (NAA-SR-11140 [1966] 1/53; N.S.A. **20** [1966] No. 23773). – [12] H. Watanabe, M. Kurihara, J. Shimokawa, M. Ichikawa, M. Uchida (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 361/74). – [13] V. A. Tsykanov, V. M. Gryazev, E. F. Davydov, V. I. Kuzmin, A. A. Maiershin, V. N. Syuzev, I. S. Golovnin, T. S. Men'shikova, Yu. K. Bibilashvili, R. B. Kotel'nikov (At. Energ. [USSR] **42** [1977] 378/82; KFK-tr-536 [1977] 1/17; At. Energ. [USSR] **42** [1977] 378/82; INIS Atomindex **9** [1978] No. 355481). – [14] A. Ya. Ladygin, I. A. Efimov, Yu. L. Likhatchev, Yu. I. Aleksandrov et al. (Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Paper 707; A/CONF-49/P707 [1971] 1/34; N.S.A. **25** [1971] No. 52471). – [15] I. S. Golovnin, T. S. Menshikova, F. G. Reshetnikov, Yu. K. Bibilashvili, V. M. Rodin, B. D. Rogozkin, V. S. Mukhin (TRG-Report-1911 [1969] 253/65; CONF-690427 [1969] 253/65; N.S.A. **24** [1970] No. 40892).

[16] R. D. Hahn (NAA-SR-11134 [1965]). – [17] D. I. Sinizer, B. A. Webb, S. Berger (Radiat. Damage Solids Reactor Mater. Part Proc. Symp., Venice 1962 [1963], pp. 287/318; NAA-SR-7248 [1962] 1/47; N.S.A. **16** [1962] No. 29440). – [18] General Atomic Div. General Dynamics Corporation (Present Status of Thermionic Fuel Element Materials GA-5622 [1964]). – [19] L. Yang, M. H. Horner, F. L. Cochran (GA-11004 [1970]). – [20] D. G. Freas, P. B. Shumaker, J. H. Stang, J. E. Gates (BMI-1622 [1963/73]).

[21] A. M. DeCrescente, M. S. Freed, S. D. Caplow (PWAC-489 [1965/73]). – [22] J. Crane, E. Gordon (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 896/918). – [23] A. Strasser, C. Wheelock, L. A. Neimark (Fast Reactor Technol. Proc. ANS Top. Meeting, Detroit 1965, pp. 126/56; CONF-650417 [1965]; N.S.A. **19** [1965] 35725; ANS-100 [1965]; N.S.A. **20** [1966] No. 12328). – [24] L. A. Neimark, J. H. Kittel, C. C. Crothers (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 864/78). – [25] L. A. Neimark (Trans. Am. Nucl. Soc. **9** [1966] 415).

[26] A. Strasser, M. Montgomery, R. Powers (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 849/67; Trans. Am. Nucl. Soc. **14** Suppl. No. 1 [1971] 40/1). – [27] M. Montgomery, A. Strasser (Trans. Am. Nucl. Soc. **15** [1972] 754/5). – [28] A. Strasser, M. Montgomery, R. Powers (GU-5286 [1972]). – [29] T. W. Latimer, J. O. Barner, J. F. Kerrisk, J. L. Green (LA-6249-MS [1976] 1/27; INIS Atomindex **7** [1976] No. 273709), T. W. Latimer, J. O. Barner, J. F. Kerrisk, J. L. Green (Trans. Am. Nucl. Soc. **19** [1974] 91). – [30] R. W. Stratton, L. Smith (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting Tucson, Ariz., 1977, pp. 348/60).

[31] A. Strasser, J. Cihi, S. Hurwitz, R. Martin (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 979/1003), A. Strasser, J. Cihi, W. Sheridan, V. Storhok (Inst. Mining Met. Petrol. Eng. Inst. Metals Div. Spec. Rept. Ser. No. 13 [1964] 729/52). – [32] J. O. Barner (LA-4669 [1971] 1/29; N.S.A. **25** [1971] No. 34358), J. O. Barner (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 819/47). – [33] J. C. Clifford, J. O. Barner, R. L. Cubitt, D. C. Kirkpatrick (Trans. Am. Nucl. Soc. **14** Suppl. No. 1 [1971] 39/40). – [33a] J. C. Clifford (LA-4951 [1973] 1/34; N.S.A. **28** [1973] No. 4544). – [34] K. Q. Bagley, E. Edmonds, H. J. Powell, R. G. Bellamy, R. Paris, J. M. Horspool (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 87/100). – [35] T. W. Latimer, D. S. Bost, J. F. Kerrisk, J. O. Barner, J. L. Green (LA-6077 [1975]).

[36] G. Clottes, M. Dieumegard, J. P. Dufayet, A. Groff, B. Kryger, H. Mikailoff, J. L. Ratier (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], pp. 113/27), H. Mikailoff, G.

Clottes (Bull. Inform. Sci. Tech. Comm. Energ. At. [France] No. 196 [1974] 41/8; ANL-trans-977 [1974]; C.A. **82** [1975] No. 146721), H. Mikailoff, M. Housseau, J. Erler (CEA-CONF-2920 [1974] 1/4; ANL-trans-965 [1974]; N.S.A. **32** [1975] No. 9326). – [37] P. Combette (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 343/7). – [38] H. Mikailoff, M. Housseau, J. Erler (Eur. Conf. Irrad. Behav. Fuel Cladding Core Component Mater. Compacts Contrib. Papers, Karlsruhe 1974, pp. 177/80; AED-Conf.-74-587-043 [1974]). – [39] O. J. Barner, T. W. Latimer, J. F. Kerrisk, R. L. Petty, J. L. Green (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 268/98). – [40] K. Q. Bagley, W. Batey, R. Paris, W. M. Sloss, G. P. Snape (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 313/28).

[41] D. Geithoff (Reaktortagung, Hannover 1978, pp. 656/9). – [42] P. J. Levine, B. L. Harbourne, B. Biancheria, T. W. Latimer, L. A. Neimark (Trans. Am. Nucl. Soc. **13** [1970] 606/7). – [43] B. L. Harbourne, P. J. Levine, T. W. Latimer, L. A. Neimark (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 869/94). – [44] R. A. Wullaert, J. F. Lagedrost, J. Bugl, J. E. Gates (BMI-1638 [1963] 1/35; EURAEC-760 [1963]; N.S.A. **17** [1963] No. 32660), R. A. Wullaert, J. E. Gates, J. Bugl (Am. Ceram. Soc. Bull. **43** [1964] 834/41). – [45] R. L. Martin, W. J. Zielenbach, V. M. Storhok, D. L. Keller, J. E. Gates (BMI-1731 [1965] 1/31; N.S.A. **20** [1966] No. 888).

[46] B. J. Thamer (LA-3646 [1967] 1/12; N.S.A. **21** [1967] No. 22910). – [47] H. Watanabe, M. Kurihara, J. Shimokawa, M. Ichikawa, M. Uchida (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting Tucson, Ariz., 1977, pp. 361/73). – [48] J. Alikhan, A. Naoumidis, G. Pott (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 454/73). – [49] G. Pott, M. Herren, A. Naoumidis (Results Five Years BR2 React. Util. Proc. Symp., Mol, Belg., 1973 [1974], pp. 227/32). – [50] H. Blank (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz. 1977, pp. 482/501).

[51] F. D. Albrecht, A. J. Rothman, J. D. Lee, J. M. Johnson, W. N. Hayes (Develop. Irradiat. Testing Technol. Proc. Natl. Symp., Sandusky, Ohio, 1969, pp. 595/628; Conf-690910 [1969]). – [52] A. A. Bauer, V. W. Storhok (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970; Nucl. Met. **17** Pt. II [1970] 532/44), A. A. Bauer, J. B. Brown, E. O. Fromm, V. W. Storhok (Fast Reactor Fuel Elem. Technol. 1971 Proc. Conf., New Orleans 1971, pp. 785/817), A. A. Bauer (Reactor Technol. **15** [1972] 87/104); A. A. Bauer, P. Cybulskis (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 299/311). – [53] K. Richter, M. Coquerelle, J. Gabolde, P. Werner (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 1, pp. 71/83).

1.2.3.3 Irradiation-Induced Swelling

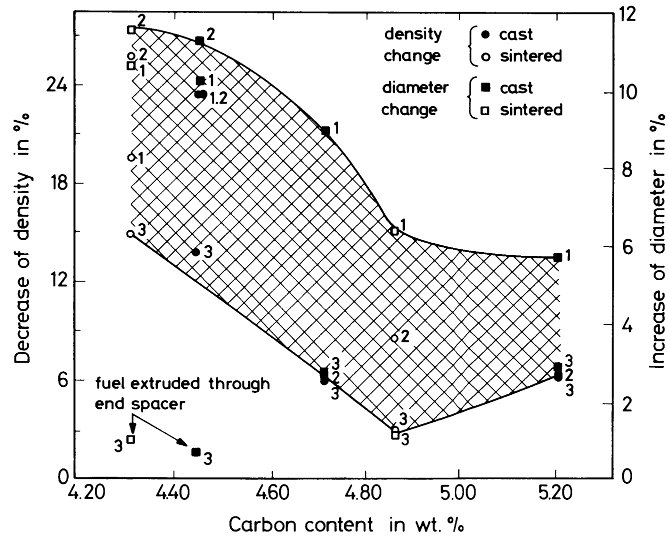
One of the most important changes up on irradiating fuel, is the decrease of its density, i.e., its swelling. This effect is due to the formation of solid fission products that have a lower density on the one hand, and to the formation of fission-gas bubbles on the other. The decrease of the density is of special interest, since the swelling behavior of the fuel may lead to its mechanical interaction with the cladding and eventually to a failure of the fuel rod.

1.2.3.3.1 Uranium Carbide

The first measurements of the changes in the dimensions and in the density of a slightly hyperstoichiometric UC having a density of 98% of the theoretical, after a burnup of only 0.14 $\times 10^4$ MWd/t at a fuel temperature of 730 °C, led to widely varying values of the swelling (a relative volume increase $\Delta V/V = 0.6$ to 2.5%) [1]. These irradiation experiments were continued at Atomic International [2], using monocarbides of various stoichiometries (between 4.6 and 5.2 wt % C), up to a burnup of 1.40×10^4 MWd/t. Hyperstoichiometric UC showed a swelling rate of $1.3\%/(10^4$ MWd/t) at 843 °C, whereas hypostoichiometric carbide showed a significantly higher swelling rate, $4.0\%/(10^4$ MWd/t), in spite of the lower temperature, 760 °C. These data were obtained from pycnometric density measurements. Since the cladding did not undergo any dimensional changes, it was concluded that the results were falsified because of microcracks. Rough et al. [3] found for hyperstoichiometric UC irradiated at 980°C swelling rates between 0.75 and 3.1% per % FIMA (0.91 to $3.77\%/(10^4$ MWd/t)). Hare, Rough, et al. [4 to 6] could find no effect of the stoichiometry of the UC (4.6, 4.8, and 5.0 wt% C), for irradiations at <750 °C up to burnups of 1.50 to 2.50×10^4 MWd/t, on the swelling rates between 1.4 and $1.8\%/(10^4$ MWd/t). Hahn [7] summarized the results obtained at the Battelle Memorial Institute (BMI) and at Atomic International (AI) up to the early sixties. He attributed the observed changes in the diameters of the rods to cracks in the fuel caused by thermal stress. Although within a given capsula there was a clear relationship between the change in the density and the burnup and the temperature, not all the data could be correlated.

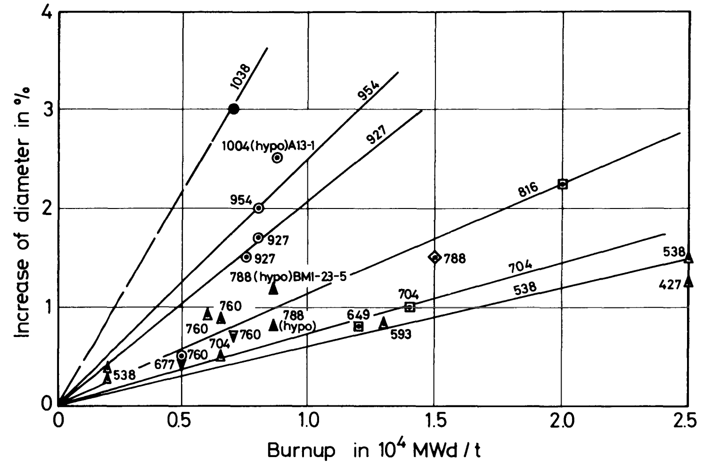
A similar summary by Melehan et al. [8], on the contrary, led to the statement, that the temperature of the irradiation played a major role in determining the rate of swelling. Strasser, Taylor [9, 10] reported for sintered stoichiometric UC a swelling rate of $0.87\%/(10^4$ MWd/t) (a swelling of 1.4% after burnup of 1.61×10^4 MWd/t) at 760°C. On the other hand, Burian et al. [11] reported for stoichiometric UC at an irradiation temperature of 1250 °F (677 °C) values of 3.2% for He-bonded and 9.4% for Na-bonded uranium monocarbide in a Nb–1 % Zr cladding after a burnup of 1.5×10^4 MWd/t. Variation of the composition of the fuel also showed that at 1250 °F (677 °C) the swelling rate depended strongly on the stoichiometry. Crane, Gordon [12] summarized these results in the representation shown in **Fig. 1-126**. The cross hatched area

Fig. 1-126



Percent change in the density and in the diameter of various irradiated UC samples having various compositions [12]. Numbers of capsules are indicated.

Fig. 1-127



Irradiation-induced swelling of arc-cast uranium carbides [13].

corresponds to a temperature of 1250°C and burnup values of 1.50×10^4 MWd/t (capsule 1) and 4.00×10^4 MWd/t (capsule 3). Capsule 2, irradiated to 2.30×10^4 MWd/t, showed the highest sensitivity of the density or the dimensional changes to the composition of the carbide. Sinizer et al. [13] analyzed the results of irradiations reported in various sources. Taking into account the stoichiometry at the various temperatures of irradiation, they found a linear dependence of the diameter of the rod on the burnup, shown in **Fig. 1-127**. Also other experiments at Atomic International [14] confirmed the dependence of the rate of swelling on the composition. For the temperature range studied, up to 1095°C, Sinizer et al. [13] determined the following empirical correlation:

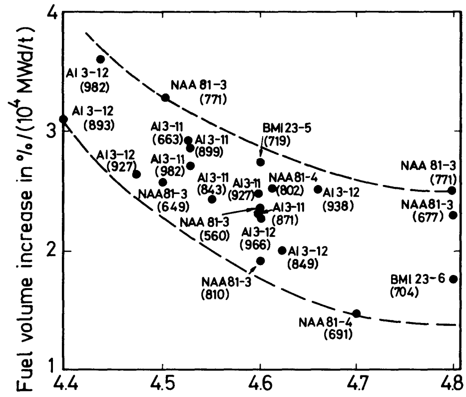
$$R_D = 0.60 + 0.77 \times (10^{-3}\, T_R - 1)^5 \qquad (1)$$

where R_D is the percent increase in the diameter per % FIMA, and T_R is the absolute temperature in degrees Fahrenheit. It changes to $R_D/(10^4\,\text{MWd/t}) = 0.73 + 0.937\ (0.0018\,t - 0.508)^5$, when using °C and referring to a burnup of 10^4 MWd/t. On this basis the swelling rate attains very high values only above 1000°C.

Frank et al. [15] could not find any temperature dependence of the volume increase. All the measured swelling rates were, in agreement with theoretical calculations of Brinkmann [16], in the range 1.5 to $3.5\%/(10^4\,\text{MWd/t})$, independent of the temperature. Supplementary to the results of Crane, Gordon [12], Frank et al. [15] observed a dependence of the swelling rate on the stoichiometry of the uranium carbide even at temperatures below 1000 °C, **Fig. 1-128**. For hypostoichiometric UC an appreciable increase of the swelling rate was found only above 1000°C.

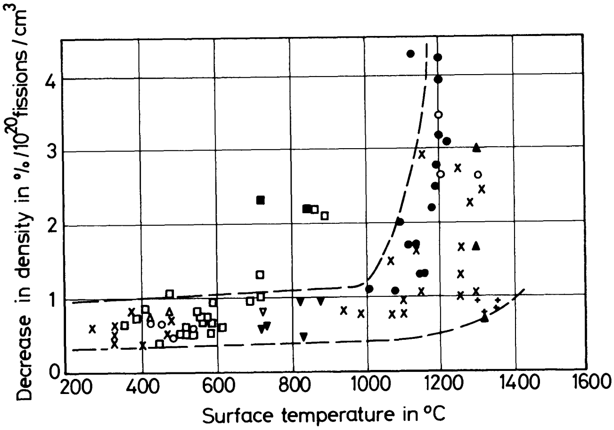
The numerous results of irradiation experiments conducted at various laboratories [12, 15, 17 to 21] were summarized by Melehan at al. [22] and by Wullaert et al. [23], as shown in **Fig. 1-129**.

Fig. 1-128



The swelling of arc-cast UC fuel samples having various carbon contents at <980 °C [15]. The points are identified by capsule code and temperature in °C (in parentheses).

Fig. 1-129



Swelling rate as a function of the temperature at the surface of the fuel [22]. ● P+W sintered UC; ○ BMI UC, 92% of theoretical density; × BMI arc-cast UC; △ BMI arc-cast hypostoichiometric UC; ▲ BMI UC, 87% theoretical density; □ UNC arc-cast hypostoichiometric UC; ■ UNC sintered hypostoichiometric UC; ▽ UNC sintered hypostoichiometric UC; ▼ UNC arc-cast hypostoichiometric UC; + BMI arc-cast UC with 1.0 or 1.5 mm thick cladding, all other cladding 0.5 mm thick; ⊡ AI arc-cast hypostoichiometric UC; ⊙ AI arc-cast hypostoichiometric UC

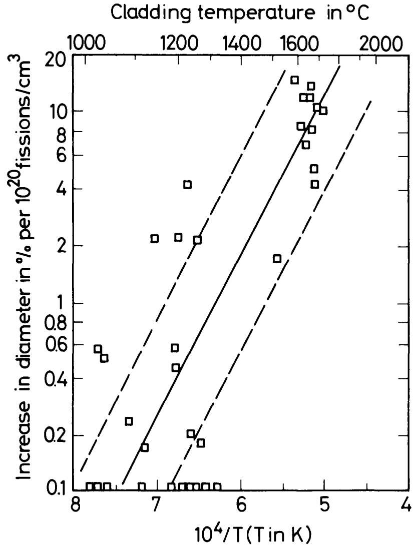
References for 1.2.3.3 on pp. 224/7

The temperature dependence of the data could be described by the empirical eq. (1) of Sinizer et al. [13]. A series of further results obtained in the seventies [24 to 29] conformed well with Fig. 1-129 within the uncertainty limits shown, and lended thereby even greater weight to the dependence displayed. A dependence of the swelling rate on the initial density, as was observed by Carlson, Felber [19] for the density range 90 to 100% of the theoretical, could not be confirmed, however. The plasticity of the fuel seemed to be the cause for its rapid creep into its own pores. Melehan et al. [22] supplemented the discussion of the dependence of the swelling rate on the density by the proposition that it might depend on the final, rather than on the initial density. A slight decrease of the swelling rate with increasing burnup, which occurred at temperatures between 1100 and 1300°C, was considered by Melehan et al. [22] as not typical for UC, and due to a more or less well developed gap between the fuel and the cladding. On the other hand, the cladding might restrain the swelling somewhat, by setting up external stresses. An indirect confirmation of these considerations was given by the authors [22], by comparing the growth of the diameters of two fuel rods having different claddings (W-26% Re and Nb−1% Zr) with different wall thickness. This effect of the cladding can be exploited, however, only at the expense of using extremely thick cladding walls.

A homogeneously distributed porosity of the fuel influenced only slightly the swelling rate of fuel rods having 0.5 mm thick claddings made of W-26% Re, at up to 1800 °C. **Fig. 1-130** shows the dependence of the swelling rate on the temperature (up to 1900 °C) as an Arrhenius plot [25].

Hausner et al. [26] considered the question of whether a central void in the UC fuel rod could compensate the volume change caused by the swelling. For a linear power density of 1950 W/cm and a central temperature of 1400°C they conducted their experiment up to a

Fig. 1-130



Dependence of the swelling rate of carbidic fuels having W-Re claddings on the cladding temperature [25].

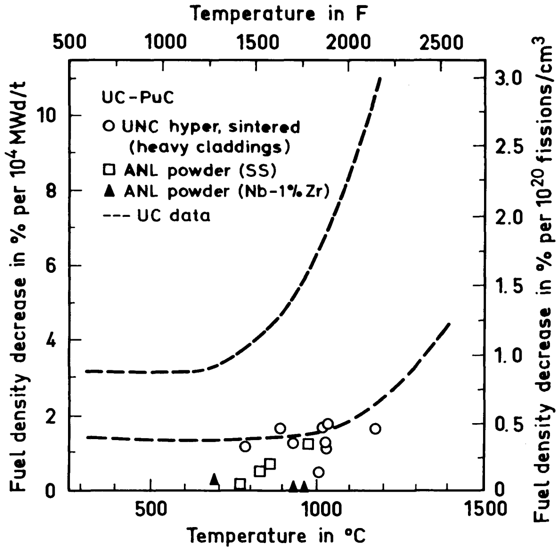
burnup of 1.876×10^4 MWd/t. The decrease of the density of 8.5%/(10^4 MWd/t), that was determined, was in good agreement with other data from the literature [23] valid for this temperature range. The central void closed-up completely during the irradiation. This result proved, that this method could reduce considerably the increase of the diameter and the stress of the cladding material caused thereby.

A different possibility of reducing the swelling rate was attained by the addition of tungsten to the UC. A homogeneous fine dispersion or a solid solution of the tungsten in the UC brought about a significant reduction of the swelling rate [30]. When tungsten was added to hypostoichiometric uranium monocarbide, it caused, on the contrary, an increase of the swelling rate [31].

1.2.3.3.2 Irradiation-Induced Swelling of (U,Pu)C Mixed Carbides

Wullaert et al. [23] reviewed the data [32 to 35] concerning the swelling of (U,Pu) mixed carbides with Pu contents up to 20% as a function of the temperature, that had been available by 1967, **Fig. 1-131**. It is seen that the swelling rates of the mixed carbide lie below the limits of the data for UC. The measurements of Kittel, Neimark et al. [34] led to negligibly small changes in the density, presumably because of the low temperature employed, 650 °C. Contrary to this, a previous report from ANL [36] gave $\Delta V/V = 1.57\%$ for very low burnup (not above 0.081×10^4 MWd/t) and temperature (380°C). Irradiation experiments at UNC [32, 33] extended to burnup values up to 11.4×10^4 MWd/t and covered the temperature range from 1100 to 1400°C, various carbide compositions, and variations of the cladding, in thermal and fast neutron fluxes. The results indicated that niobium cladding offered greater resistance to the swelling than did 316 SS cladding. Strasser et al. [33] pointed out, however, that despite of the relatively small increase in the diameter, $\Delta D/D = 0.6\%$ per % FIMA (0.5% per 10^4 MWd/t), the final burnup was limited to 10% because of the fuel swelling.

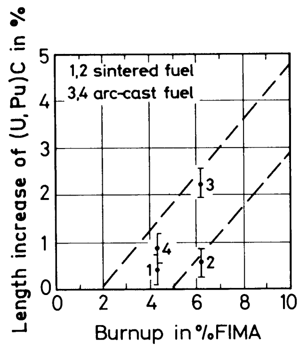
Fig. 1-131



Swelling of (U,Pu)C as a function of the mean central temperature of the fuel pellets [23].

Bradbury et al. [35] used metallography to analyze the swelling, and found that at a center temperature of 1 500 °C it reached about 2.0% per % FIMA (2.43% per 10^4 MWd/T) and about 0.5% per % FIMA (0.61 % per 10^4 MWd/t) at the periphery. Different stresses could thus arise in the fuel pellets. In an experiment of Bradbury, Frost [27], who employed a strong exterior stress at 850 °C, they could not observe either radial or axial swelling up to a burnup of 10.5% FIMA (8.63×10^4 MWd/t). On the other hand, Frost et al. [38] reported that for a burnup of 6.2% FIMA (5.18×10^4 MWd/t) the radial swelling was indeed small, but the increase of the length of the rod permitted a definite evaluation of the swelling rate, **Fig. 1-132**. This began for vibrationally compacted UC, having PuC grains of 120/240 mesh size, only after an incubation period of 2% FIMA (1.64×10^4 MWd/t). Metallographic studies indicated the higher plasticity of PuC compared with UC. Whereas fuel rods having 304 SS claddings showed changes in the diameter, that corresponded to a volume increase of 1.3%, only negligibly small changes could be observed in rods clad by Nb-1% Zr [39]. Since the PuC swelled right into the pores between the UC grains, values of $\Delta V/V$ of 1.2 to 2.8% per % FIMA burnup (1.46 to 3.41 % per 10^4 MWd/t) were calculated by Michels, Neimark [40], taking into consideration the free volume present. This result was in good agreement with the data of Wullaert et al. [23].

Fig. 1-132

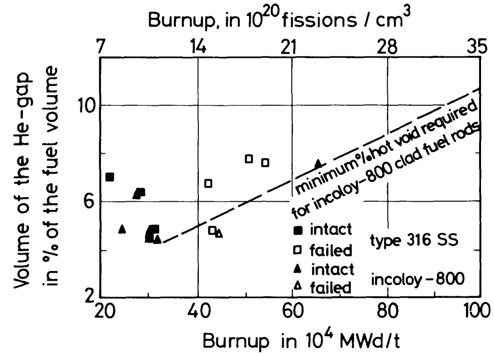


Length increase against burnup for niobium-clad (U,Pu)C [38].

(U,Pu)C sphere-pac fuel rods were produced and irradiated at EIR-Würenlingen [41 to 43]. After burnup of maximally 6.5% FIMA (5.3×10^4 MWd/t) the rods that remained intact suffered a maximal clad diametral strain of 0.5% per % FIMA (0.61 % per 10^4 MWd/t). Higher swelling rates led to failure of the cladding. Various values were found, as expected, for 316 SS claddings of different wall thicknesses and cold-forming histories.

In a further series of irradiation experiments at UNC [44 to 46] the optimal parameters for achieving a minimal rate of swelling were sought. This was done by varying the stoichiometry of the mixed carbide between (U,Pu)C and (U,Pu)C + 5 to 10 vol% $(U,Pu)_2C_3$, the density between 75 and 98% of the theoretical, the bonding in the cladding, and the cladding material (316 SS and Incoloy 800). Up to a maximal burnup of 6.5×10^4 MWd/t and for linear power densities between 420 and 720 W/cm, the rate of swelling was between 2.1 and 3.1% per

Fig. 1-133

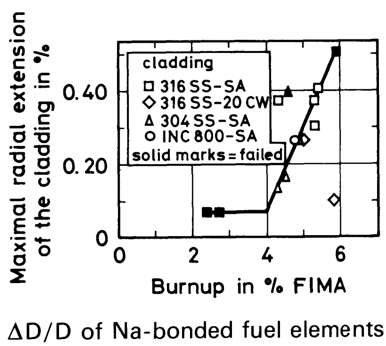


Percent hot void required for performance of He-bonded, high density carbide pellets rods [46].

10^4 MWd/t. A free volume was required for the swelling of the fuel in He-bonded rods. The minimal volume required, which was made up of the fuel porosity and the gap, is shown for Incoloy 800 cladding as a function of the burnup in **Fig. 1-133**. Extension of the irradiation experiment up to 7.7×10^4 MWd/t burnup confirmed the course of the curve in Fig. 1-133. At higher values of the burnup the stoichiometry, too, played an important role. Whereas a single-phase mixed carbide, having 84% of the theoretical density, behaved excellently under irradiation, fuel rods with a 10 vol% addition of $(U,Pu)_2C_3$ and a density 97% of the theoretical failed.

Latimer et al. [48] also reported about the swelling behavior of He-bonded fuels as a function of the fuel density, the gap, and the stoichiometry. For high dense fuel, the kind and size of the gap had a special significance. The gap was less significant for a steel cladding of $\geqq 0.5$ mm wall thickness or for a material of high strength, such as Incoloy 800. The behavior was similar for Na-bonded rods [49, 50]. The measured change of the diameter as a function of the burnup is shown in **Fig. 1-134**. It is seen that after an incubation period, the diameter of the

Fig. 1-134



Maximum cladding percent ΔD/D of Na-bonded fuel elements as a function of the burnup [49] cladding increased rapidly with the amount of burnup (but showed dependence on the cladding material), leading to eventual rod failure. This result was confirmed qualitatively by Dienst, Müller [51]. These authors found different incubation periods and swelling rates for mixed carbides of different densities or claddings of different strengths. Contrary to Montgomery, Strasser [47], who attributed the failure of the rods to the presence of 10 vol% $(U,Pu)_2C_3$, Dienst, Müller [51] maintained, that in addition to the composition, the density of the pellets affected the behavior under irradiation.

Montgomery et al. [52] determined for a Na-bonded mixed carbide at the temperature range from 710 to 790 °C a swelling rate of 2.5% per 10^4 MWd/t for single phase (U,Pu)C, and 1.4% per 10^4 MWd/t for a fuel having 10 vol% $(U,Pu)_2C_3$ admixture. Steiner et al. [53], on the contrary, did not find at 1 050 °C any significant differences between the swelling rates of the single phase monocarbide and mixed carbides having 10 or 75 vol% $(U,Pu)_2C_3$. French authors [54 to 56], too, found in irradiation experiments at 720 to 970 °C and burnup values of 1.5 to 2.7×10^4 MWd/t, an incubation period for the swelling of Na-bonded fuel. They attributed this effect to the restructuring of the initial porosity. The volume increase of the fuel could be expressed according to their results as

$$\Delta V/V = (1.62\times10^{-4}\tau-1.25) \qquad (2)$$

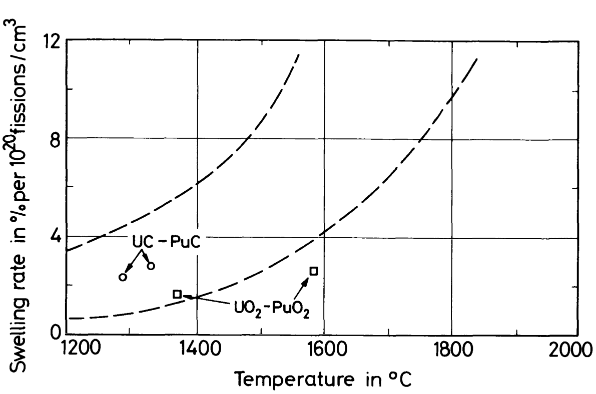
where τ is the burnup in MWd/t. The slope of the resulting curve could be confirmed also in experiments at temperatures between 1 000 and 1 100 °C, linear power densities of 900 W/cm, and burnup values up to 12.5% FIMA (10.3×10^4 MWd/t) [55, 57]. These data were also in good agreement with values obtained at UNC [52].

The rate of increase of the diameter is definitely a function of the irradiation temperature for Na-bonded rods. However, only above 1 000 °C does the percentage increase of the diameter, as does that of the volume, start to be significant, as shown by the following results [58, 59]:

temperature in °C	730 to 900	1 290	1 600
% per 1% FIMA	0.40 ± 0.09	0.57 ± 0.02	1.3
% per 10^4 MWd/t	0.48 ± 0.11	0.69 ± 0.02	1.6

A swelling rate between 1.5 and 2.5% per % FIMA (between 1.83 and 3.04% per 10^4 MWd/t) was determined by Barner [60] for the temperature range 1 150 to 1 400 °C, a linear rod power density of about 1 000 W/cm, and burnup values between 3.7 and 5.0% FIMA (3.0 and 4.1×10^4 MWd/t). Coquerelle [61] determined the volume change of (U,Pu)C pellets at a linear rod power density of about 1 350 W/cm up to 1.5% FIMA (1.23×10^4 MWd/t), and found it to be 2.48% per % FIMA (3.02% per 10^4 MWd/t). The author interpreted this swelling rate as free swelling, since at higher burnup values the resistance of the cladding reduced the swelling rate to 1.3% per % FIMA (1.57% per 10^4 MWd/t). This result was in good agreement with those of previous irradiations of pellets up to burnup values of 13% FIMA (10.7×10^4 MWd/t). It can be seen in **Fig. 1-135**, that the free swelling of mixed carbides is higher than that of mixed oxides [63]. The swelling rates of the carbide samples shown in Fig. 1-135 lie definitely higher than the data of other authors. The differences cannot be explained away as due to different stoichiometries, since one of the two samples contained 10 vol% $(U,Pu)_2C_3$. The statement that pure $(U,Pu)_2C_3$ and $(U,Pu)(C_{0.7}O_{0.3})$ have the unusually low swelling rate of 0.1 and 0.6% per 10^{20} fissions · cm^{-3} (0.4 to 2.4% per 10^4 MWd/t) is also not readily understood.

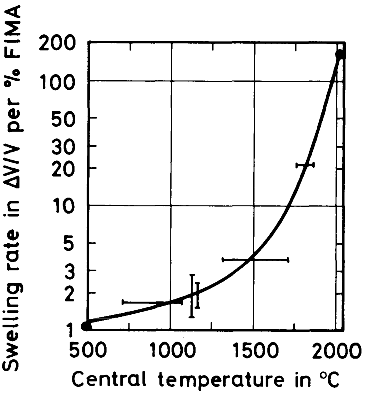
Fig. 1-135



Unrestrained swelling rate of mixed oxides and mixed carbides [63]. Between the two dashed lines: data for external volumetric swelling rate of UO_2 and UO_2-PuO_2 by BMI.

More recent data for the free swelling rate, that were reported by Mikailoff [64], and that covered temperatures up to 2000 °C (**Fig. 1-136**) were in better agreement with the results of Wullaert et al. [23] (see Fig. 1-131, p. 209).

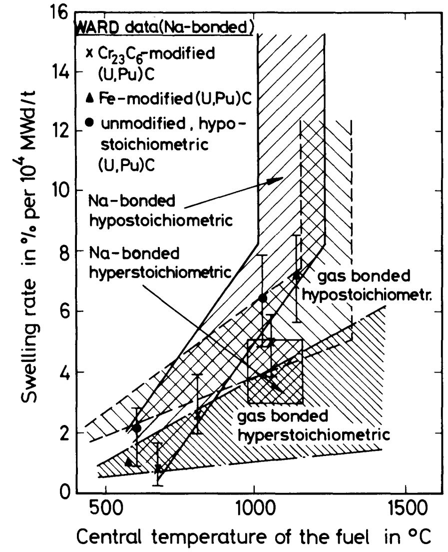
Fig. 1-136



Unrestrained swelling of carbide fuels [64].

The figure shows clearly, that because of the exponential rising of the swelling with the temperature, high irradiation temperatures should be avoided. In order to reduce this effect, it was attempted to modify by Cr or Fe additions especially the hypostoichiometric mixed carbides. The results of irradiation experiments with these modified fuels, for burnup values up to 5.0×10^4 MWd/t, are compared in **Fig. 1-137**, p. 214, with those for unmodified fuels taken

Fig. 1-137



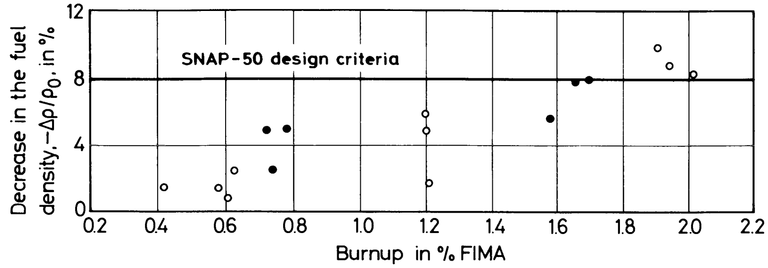
Comparison of the swelling rate of WARD modified carbide fuel [66] with other data from the literature.

from the literature. According to these results, the fuel modified by the addition of $Cr_{23}C_6$ swelled less than that with Fe addition or the unmodified, slightly hypostoichiometric mixed carbide. The differences in the swelling rates, however, were slight. Furthermore, irregular changes in the diameters were found for the modified fuels, more with the Cr- than with the Fe- modified ones. These oval changes of the cladding and other effects that led to irregular expansion of the cladding, such as the so-called bambus effect [69] are attributed to dislocated fuel fragments [49, 50, 70]. In order to overcome this problem, the pellets were first placed in a thin perforated tube (a "shroud tube") that was then placed in the actual cladding. The high swelling of the mixed carbides was counteracted by providing a sufficiently wide gap. This gap, if too wide, presents the danger of cladding failure caused fragmentation of ceramic fuel by heat stress. At a screening test with burnup up to 8.8% FIMA (7.23 × 10^4 MWd/t) no damage to the cladding occurred, and the fuel pellets held together even in the high power density sections of the fuel rod, in spite of a few local defects of the perforated inner cladding.

1.2.3.3.3 Nitride and Nitrogen-Containing Carbide Fuels: UN, U(C,N), (U,Pu)N, and (U,Pu)(C,N)

The use of nitride fuels was considered in the initial phase of the planning of nuclear power sources for interplanetary rockets, e.g., in the SNAP-50 reactor project [72], because of their high density compared with that of oxide or even carbide fuels. The decisive parameter for the specifications for rod power density and burnup was the swelling behavior, in view of the high fuel temperatures (up to 1 580 °C) [73]. Claddings of Nb-1 % Zr were used in irradiation tests

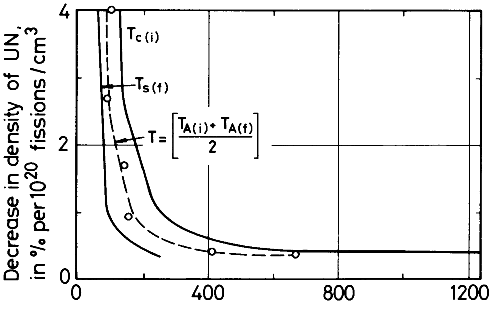
Fig. 1-138



Fuel density decrease as a function of burnup at high power density UN [74]. T(cladding) = 1025 to 1220 °C; T(fuel) = 1228 to 1565 °C; ○ 0.89 mm; ● 0.64 mm cladding thickness.

for the SNAP project [74]. The results for the swelling behavior, measured under stress, are shown in **Fig. 1-138** as a function of the burnup. The dispersion of the data cannot be explained by variations of the temperature alone. At temperatures below 250 °C the swelling rate increases rapidly, as shown by the BMI irradiation results [75], which are presented in **Fig. 1-139**. This effect was attributed to irradiation-induced changes in the lattice parameters of UN by lattice defects and their annealing [76]. In other irradiation tests at BMI [77] in the temperature range 900 to 1100 °C and at burnup values up to 6.3% FIMA (5.17×10^4 MWd/t), where the mode of production of the nitride fuel (isostatically pressed and arc-cast pellets) was varied, no dependence of the swelling rate on this parameter was found. The values lay between 1.3 and 2.9% per % FIMA (1.57 to 3.53% per 10^4 MWd/t, 0.35 to 0.80% per 10^{20} fissions/cm^3). A relationship between the swelling of UN and the microstructure of the fuel was found by Albrecht et al. [78], who irradiated in the temperature range from 1307 to 1414 °C uranium nitride samples of varying density (78 and 96 to 100% of the theoretical) and grain size (30 to 105 μm) as well as two single-crystal samples. The lowest swelling occurred in the single crystals: $\Delta V/V$ of 2.7 and 3.7% at a burnup of 2.4×10^{20} fissions/cm^3 (1.23% FIMA, 1.0×10^4 MWd/t). The largest volume change, $\Delta V/V = 12\%$, was found for the high density

Fig. 1-139



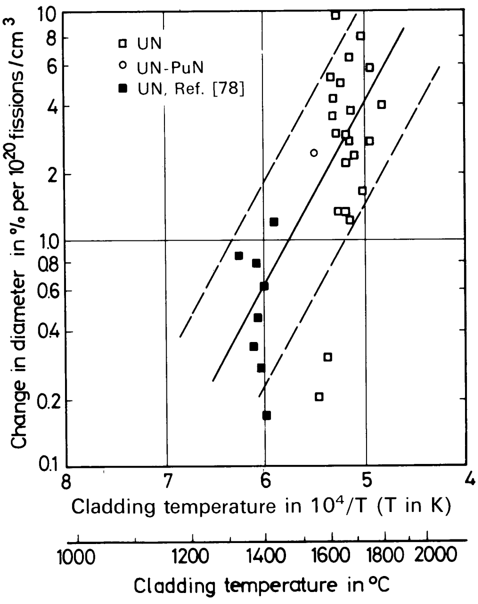
Swelling of UN at low irradiation temperatures [75].

fine-grained samples. A lowering of the density or a coarsening of the grain size improved the swelling behavior considerably. The temperature, too, played an important role in the range studied.

Hilbert et al. [79] succeeded in lowering the swelling rates appreciably by the introduction of well defined porosity into the pellets during their production. The results of these authors [80] concerning the swelling behavior of nitridic fuels at high temperatures are shown in **Fig. 1-140**, as are some data of Albrecht et al. [78]. **Fig. 1-141** shows, according to Hilbert et al. [24], a comparison of the swelling rates of slightly hyperstoichiometric UC and UN. The width of the uncertainty limits was attributed by the authors to differences in the initial structures of the fuels. It is clear that UN undergoes less swelling than does UC in the entire temperature range considered. Hypostoichiometric UN has a characteristic high swelling rate, as has the corresponding monocarbide [81].

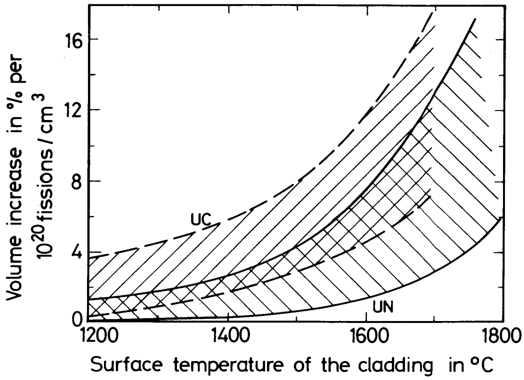
UC-UN solid solutions, too, undergo smaller volume changes than does UC during irradiation. For the temperature range 1 200 to 1 400 °C, irradiation of UC_xN_{1-x} having $0.5 \leq x \leq 0.9$ led to a decrease in density of 3 to 4% per % FIMA (3.65 to 4.87% per 10^4 MWd/t) [82]. These values were at the lower limit of the uncertainty range for UC in Fig. 1-129, p. 207. Watanabe et al. [27] irradiated together UC, UN, and U(C,N), with results that again fitted into the uncertainty range in Fig. 1-129, p. 207. Some of the swelling rates of the carbonitrides were higher than those of UN and UC. The differences were interpreted by the authors as being due to different fuel temperatures and power densities, which arose from the axial neutron flux profile.

Fig. 1-140



Swelling of UN in W-Re cladding as a function of the temperature [80].

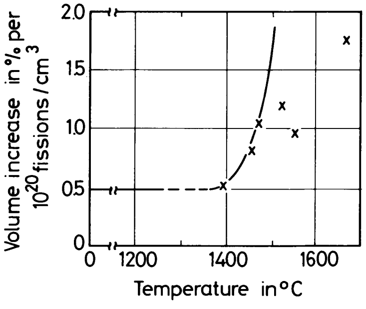
Fig. 1-141



Comparison of the volumetric swelling rate of UC and UN as a function of surface temperature of the W-25wt% Re cladding [24].

Mixed (U,Pu) nitrides and carbides were irradiated by Mikailoff et al. [83] at high linear rod power densities (up to 2400 W/cm) at a maximal central temperature of 1200 °C and using Na-bonding up to burnup values between 1.25 and 16.0 × 10^4 MWd/t. The swelling rate of the mixed nitride was relatively low for the high temperature: 4.25% per 10^4 MWd/t. Irradiation tests of Bauer et al. at BMI [84 to 86], using Na- and He-bonding, showed satisfactory irradiation behavior of the mixed nitrides. A series of irradiations with a thermal neutron flux, using again Na- and He-bonding, led at 1260 °C and burnup values between 8.6 and 15.2 × 10^4 MWd/t to swelling rates of 0.48% per 10^{20} fissions · cm^{-3} (1.54% per % FIMA, 2.01% per 10^4 MWd/t) [84, 85]. As is seen in **Fig. 1-142**, the swelling rate starts only at 1400 °C to rise rapidly with the temperature. This fact indicates a higher linear power loading possibility for the mixed nitride than for the corresponding carbides. In order to design the dimensions of

Fig. 1-142



The temperature dependence of the swelling rate of (U,Pu)N [85].

the gap, that should take up the fuel swelling, it is necessary to know the rate of swelling of the fuel, the difference in thermal expansion of the fuel and the cladding, the permissible stress on the cladding, and the rate of swelling of the cladding material. The design permits a burnup up to 15.0 × 10^4 MWd/t for a fuel having 95% of the theoretical density, a pellet column of 7 mm diameter, 0.38 mm thick stainless steel cladding, a Na-filled gap of 0.254 mm, a nominal linear rod power density of 1 060 W/cm (taking into account a possible 10% excess power) and a central temperature of 1 250 °C [85].

A considerable improvement of the irradiation behavior in a fast neutron flux could be achieved by the use of a shroud-tube for Na-bonded mixed nitrides as was the case for the mixed carbides [86]. No damage was observed in eight rods, which were irradiated at a power density of 900 W/cm to a burnup of 5.6% FIMA (4.56 × 10^4 MWd/t). The swelling rate found was between 0.8 and 1.26% per % FIMA (0.98 and 1.55% per 10^4 MWd/t). Coquerelle [61] reported irradiation results that were obtained with (U,Pu)N and (U,Pu)(C,N) in the fast neutron flux of the Dounreay Fast Reactor. At a linear rod power of 1 345 W/cm the following values were noted up to a burnup of about 1.5% FIMA (1.2 × 10^4 MWd/t):

composition of the fuel	(U,Pu)N	(U,Pu)(C,N)	(U,Pu)C
$\Delta V/V$ in % per % FIMA	1.55	1.86 to 2.00	2.48
$\Delta V/V$ in % per 10^4 MWd/t	1.90	2.28 to 2.45	3.04

After the fuel got into contact with the cladding the swelling rate was reduced to values between 0.9 and 1.3% per % FIMA (1.10 and 1.60% per 10^4 MWd/t), because of the restraining pressure of the cladding. Na-bonding provided no advantage at high rod power levels, since after a burnup of about 4% FIMA (3.3 × 10^4 MWd/t) the initially 400 µm wide gap had practically disappeared. Blank [87] analyzed these irradiation experiments more closely, and found that the relative increase in the diameter of the rod, $\Delta D/D_0$, showed two maxima along the rod (in the direction of increasing cladding temperatures). The change in the diameter had an incubation period b_i, that depended on the burnup, and a slope M, so that the change could be described by eq. (3):

$$(\Delta \bar{D}/D)_i = M_i\,(b-b_i) \qquad (3)$$

Whereas the carbon content of the (U,Pu)N, (U,Pu)(C,N), and (U,Pu)C samples affected mainly the second maximum, the first maximum depended primarily on the type of the fuel and on its production. Vibrationally compacted fuels behaved better than pelletized fuels. The results of Ronchi et al. [88] and Matzke et al. [89] confirmed the statement made above, namely that an acceptable swelling occurred for carbides only below a so-called critical temperature and at defined temperature gradients, whereas for nitrides more regular swelling and smaller swelling rates occurred over a broad temperature range. The in-pile change of the structure was better defined in nitrogen-rich carbide nitrides than in those poor in nitrogen, which showed more favorable carbide-like restructuring.

1.2.3.3.4 Mechanism of the Swelling of Carbide and Nitride Fuels

The swelling behavior of non-oxide nuclear fuels MX limits the lifetime of the fuel elements. The mechanism of the swelling has therefore been the subject of intensive study since the start of the irradiation experiments. This effect is naturally caused by the formation of solid and gaseous fission products, which leads to an increase of the volume of the fuel. Rough, Chubb [90] calculated the maximal swelling rate of UC as 1.6% per % FIMA (1.95% per

10^4 MWd/t), using the simple assumption, that the fission products occupied interstitial positions in the lattice. This swelling rate could be reduced to 1% per % FIMA (1.22% per 10^4 MWd/t), if the fission product atoms occupied those empty lattice positions, which had been occupied by the fissioned uranium atoms. The effect of the solid fission products on the swelling rate was proportional to the burnup. The neutron flux had some, but only slight, effect on the swelling behavior. Harrison, Davies [91] calculated the effect of the solid fission products on the swelling rate as a function of the burnup and the neutron flux, and found $S = \Delta V/V = 1.54\%$ per % FIMA (1.87% per 10^4 MWd/t) at a flux of 10^{12} n · cm^{-2} · s^{-1} and 1.30% per % FIMA (1.57% per 10^4 MWd/t) at 10^{15} n · cm^{-2} · s^{-1}.

Gaseous fission products were introduced into the lattice of MX as recoil atoms, and contributed as such only little to the swelling, similarly to the solid fission products. Swelling rates calculated by Harrison [92] agreed well with the experimental data, obtained from low-temperature irradiations of UC. When the surface energy of the fuel and the pressure of the gaseous fission products were taken into account, the swelling behavior could be estimated by calculation also for high temperatures [92, 93]. Calculations by Watanabe [94], who dealt with the formation of solid solutions between the solid fission products and the carbide fuel (UC or PuC) and their effects on the swelling, agreed relatively well with experimental swelling rates obtained at 1 000 °C [23]. Huegel [95] modified already in 1965 the Foreman equation [96], which had been used successfully for metallic uranium, and employed it for the determination of the swelling rates of UC and UN. It was assumed thereby, that the swelling process was caused by the creep of the fuel and remained unchanged during the irradiation. The fission gases, behaving as ideal gases, agglomerate to gas bubbles having diameters of more than 0.5 μm. The swelling behavior of UC could be described well with this model. The irradiation experiments on UN, however, led to smaller swelling rates than were calculated according to this assumption.

Huegel [95] explains the more desirable behavior of UN over UC by factors like:

a) A slower rate of bubble migration to, and agglomeration at, grain boundaries in UN than UC. This inhibition is apparently a result of the presence of an initially finely dispersed UO_2 precipitate in UN.

b) A higher thermal conductivity of UN over UC. In-pile, the influence of this effect is increased since migration of U_2C_3 to the outer periphery is anticipated to further reduce the thermal conductivity by imposing an additional barrier to heat transfer.

c) Freedom from gross structural instabilities in UN compared to that in hyperstoichiometric UC. The breakaway swelling effect in UC is thought to be closely related to decomposition of segregated U_2C_3 at the outer periphery because of reaction with barriers and cladding. This accelerates fission gas agglomeration in this zone.

d) The gas bubbles which migrate to grain boundaries in UC interconnect easier than in UC. This is thought to be a result of more rapid spheroidization of grain boundary bubbles in the case of UC than in UN. As a result, the grain boundary accumulation of gas in UC is trapped and promotes internal retention and consequently greater swelling.

According to Leach et al. [97], the irradiation-induced swelling could be satisfactorily described by eq. (4):

$$\Delta V/V = B \cdot K(T) \cdot t_{m(T)} \qquad (4)$$

where B is the burnup, t the time, and K(T) and m(T) are temperature dependent constants, determined analytically.

Agreement with the results of irradiation experiments was obtained in particular for UC fuel rods with Nb-1% Zr claddings. Also when W-26% Re was used as the cladding the authors found good agreement, though the constants were different, because of the hindered swelling.

Levine et al. [66] modified the Greenwood-Speight equation [98], in order to take into account the composition of hypostoichiometric carbides, and introduced the term $\ln(4.8-C)$, where C = wt% carbon. For Na-, respectively He-bonded carbide fuel they obtained eqs. (5), respectively (6):

$$\ln(\Delta V/V) = 1.494 \ln T + 1.227 \ln B + 0.366 \ln(4.8-C) - 19.863 \tag{5}$$

$$\ln(\Delta V/V) = 1.612 \ln T + 0.683 \ln B + 0.227 \ln(4.8-C) - 16.006. \tag{6}$$

For hyperstoichiometric carbide with He bonding they obtained eq. (7):

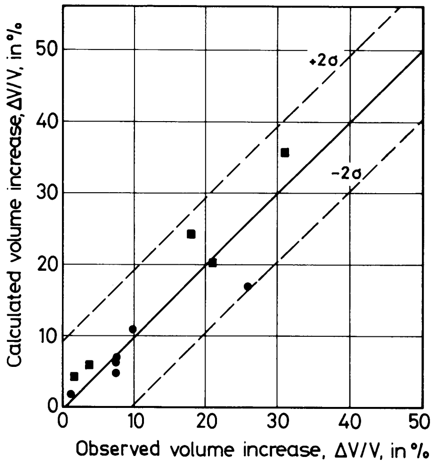
$$\ln(\Delta V/V) = 0.304 \ln T + 0.537 \ln B - 6.109 \tag{7}$$

where T and B are the
temperature (in K) and the burnup (in MWd/t) respectively.

The good agreement of the swelling rates calculated by means of these equations with the experimental results obtained at Westinghouse is shown **Fig. 1-143**.

A model for the diffusion-controlled growth of gas bubbles was developed by Markworth [99], who used it for the description of the temperature-dependent swelling of UC. The temperature limit, above which the swelling rates increased with the temperature, was'about one half of the absolute melting point of the fuel. In all the models developed and employed hitherto for the description of the swelling behavior of ceramic fuels, the diffusion of the gaseous fission products was assumed to be the decisive factor for the increase of the volume. Prajoto et al. [100] took into account in their model the so-called redissolution of the fission

Fig. 1-143



Comparison of the calculated and observed volume increase of hypostoichiometric or modified (U,Pu)C (with Cr (●), with Fe (■)) [66].

gases, that had been observed in oxide fuels. They found that the swelling was more sensitive to this effect than to the gaseous diffusion, to the surface tension, or to the temperature. They considered, that a reduction of the grain size of the fuel alone might, by means of the increased fission gas release coupled to it, lead to a reduction in the swelling.

Matzke, Ronchi [101] confirmed the "redissolution effect" for fission gases in the MX-type fuel, but assumed that this effect was 10 to 100 times smaller than for MO_2 fuels.

The relationship between fission gas release and swelling behavior, assumed to hold in all the models, was confirmed in irradiation experiments on UC, UN [74], and Pu-containing fuels [55]. At a given volume increase, nitride fuels released double the amount of fission gas than was released by carbide fuels [74]. DeCrescente et al. observed already after the short irradiation period of 890 h at 1230 °C, that in UN there existed pores filled with fission gas, having diameters below 1 μm, whereas in UC this form of porosity was missing [74]. In the latter, as already described, the fission gas had already been released in the form of bubbles at the grain boundaries. This confirmed the higher mobility of the gaseous fission products in UC. On the basis of these facts, the authors described the fission gas release, which affected the swelling, as occurring in three stages:

1) Agglomeration of fission gas atoms, that migrate under temperature gradients to the grain boundaries, where microbubbles (less then 100 Å) are formed.

2) Joining of these bubbles to long voids as they coalesce.

3) The long voids tend to spheroidize to lower the total surface energy. The porosity becomes disconnected and release of fission gas is delayed.

The formation of long voids and their migration in existing temperature gradients seemed to be a phenomenon, that was specific to UO_2 and UN. Such a movement of fission gas bubbles was not observed in UC, because of its low vapor pressure [102]. This moving process of the long voids was equivalent to a sublimation process that resembled zone melting in purifying the fuel from the fission gas, without a contribution of the latter to the swelling. Hilbert et al. [24] present in Table 1/38 the diffusion data of Xe and U, the sizes of the fission gas bubbles formed at 1600 to 1700 °C, and the swelling rates, for UC and UN. These different data for UC and UN are included in the model of DeCrescente et al. [74].

Table 1/38
Comparison of the Diffusion Coefficients, the Measured Bubble Sizes, and the Swelling Rates of UC and UN at 1600 to 1700 °C [24].

fuel	diffusion coefficient, in 10^{-13} cm²/s D_{Xe}	 D_U	bubble size, in μm after 2×10^{20} fissions/cm³	fuel swelling in %
UN	20	0.25	1 to 5	4 to 12
UC	3000	170	2 to 30	10 to 25

Chubb et al. [25] concluded that the swelling of nuclear fuels was generally determined by the formation of fission gas bubbles, their fundamental diffusion process, and the diffusional creep of the fuel. This explained the swelling rates which were at 1700 °C larger by a factor of ten than those at 1200 °C. Matzke, Ronchi [101] and Ross, Rose [103] could document by means of electron microscope pictures the joining together of bubbles to form larger pores, **Fig. 1-144**, p. 222. Above a critical temperature, ≈1200 °C, large bubbles at low densities are

Fig. 1-144

Electron micrograph (replica) of the hot zone of a pure carbide fuel showing coalescence between a gas bubble and a pore [101].

observed as well as essential swelling. The joining-up of the bubbles was caused by the mobility of the atoms in the fuel [101], that is by the high rate of diffusion of the nonmetal through the MX matrix on the one hand, and by the transport of the metal atoms through the gas phase on the other. The latter was due to the high vapor pressure above this matrix, in particular for the plutonium.

Albrecht et al. [78] achieved a significant dependence of the dimensional stability of uranium carbide on the microstructure. The low-density, fine-grained UN showed less swelling than the high-density materials. This can reasonably be interpreted as accomodation of volume increase with the self-contained voids of the fuel. On the other hand the larger the grain size in high-density UN or the fewer the grain boundaries, the better the resistance to swelling. The observed collection of fission gases in the grain boundaries is strikingly absent from the irradiated single crystal UN [78].

Ervin [31] demonstrates that the mobility of the microbubbles (0.05 to 0.2 µm) can be reduced by means of a finely dispersed precipitate of tungsten in stoichiometric and hyperstoichiometric uranium carbide. These findings are consistent with the premise that a dispersion of fine particles helps to reduce swelling of carbide fuels as a result in retaining the fission gases.

Leach et al. pointed out the important effect of exterior stress on the swelling, when they estimated the swelling rate [97]. From the studies of Matzke, Ronchi follows that the exterior stress needed to be taken into account only when the fuel was above a critical temperature T_C, since then the small bubbles joined to form large units [101]. Assuming a surface tension of 2000 dyn/cm (0.2 N/mm) for uranium nitride, and excluding creep processes, DeCrescente et al. calculated for fission gas bubbles having a diameter of about 100 Å pressures of up to 30000 lb/in^2 ($\approx$210 N/mm^2) [74]. The process of swelling by means of the coalescence of gas bubbles, and the increase in diameter caused thereby, could be reduced only by means of restraining cladding and the high pressures which built up [22, 26]. The swelling was not affected by claddings having small wall thickness [78, 79]. Albrecht et al. based this statement on the fact that they observed no changes in length, due to some kind of tooth-paste-like extrusion, for fuel rods with thin cladding [78]. Matzke, Ronchi, on the contrary, pointed out that an exterior stress would in any case affect the growth of the micropores, hence effect a raise in the critical temperature [89].

Mikailoff et al. [83] reported on the effect of the restructuring of carbidic and nitridic fuel during the irradiation on the swelling rate. They did not make their individual measurements in a systematic manner, however, so that an unambiguous statement of the effect was impossible. Bauer, Storhok [84] found for (U,Pu)N, even at a high burnup, only minimal changes in the microstructure of the mixed nitride. In sections of Na- and He-bonded (U,Pu)C and (U,Pu)(C,N) rods Coquerelle [61] observed different pore distributions. He found, that various zones having various porosities were formed in the radial direction, which depended both on the absolute temperature and on the temperature gradient in the fuel, and affected its swelling rate.

The restructuring of (U,Pu)C, (U,Pu)(C,N), and (U,Pu)N and its effect on the swelling process in these fuels were studied by Ronchi, Sari [88] by means of various heat treatments of the samples. The authors differentiated between the following four zones in the cross-section of the pellet:

Zone I: in the hottest part of the fuel (small thermal gradient), large rounded pores of sizes up to several 10 µm are observed causing a porosity of up to 30%. In addition, nitrides often show the formation of a central hole.

Zone II: in the part of the fuel having a large temperature gradient, densification occurs and pores and grains are stretched along grad T.

Zone III: next to Zone II, equiaxed grain growth with intergranular pores of a wide size range is observed.

Zone IV: at the cold edge, the initial structure of the fuel remains unchanged.

The authors attempted to explain the different swelling behavior of (U,Pu)C and (U,Pu)N by means of this zone model. A certain similarity in the swelling behaviors of (U,Pu)N and of UO_2 was attributed to the similar vapor pressures of these fuels and to comparable migration mechanisms.

As yet unanswered is the question whether acceptable swelling rates may be achieved much above the critical temperature, where high fission gas release and thermal creep occur, by means of the pressure exerted by the cladding tube. Matzke, Ronchi [89] set the following two conditions:

a) The restructuring of the fuel and the gas release must be so rapid, that the formation of large gas bubbles is prevented.

b) The released fission gas must find suitable channels in the fuel for it to escape.

Since these two conditions are not met simultaneously in carbide and nitride fuels, the swelling is the limiting quantity for the burnup in these fuels above the critical temperature.

References for 1.2.3.3:

[1] C. A. Smith, F. Rough (NAA-SR-3626 [1959]). – [2] H. Pearlman (NAA-SR-Memo 4631 [1959] 1/16; N.S.A. **14** [1960] No. 9818). – [3] F. A. Rough, A. W. Hare, R. B. Price, S. Alfant (Nucl. Sci. Eng. **7** [1960] 111/21). – [4] A. W. Hare, F. A. Rough (BMI-1452 [1960] 1/31; N.S.A. **14** [1960] No. 22108). – [5] A. W. Hare, S. Alfant, F. A. Rough, D. I. Sinizer (Nucl. Sci. Eng. **10** [1961] 24/30).

[6] A. W. Hare, F. A. Rough (BMI-1491 [1961] 1/27; N.S.A. **15** [1961] No. 7847). – [7] R. D. Hahn (NAA-SR-7696 [1963] 1/32; N.S.A. **17** [1963] No. 16650). – [8] J. B. Melehan, V. W. Storhok, R. J. Burian, M. Kangilaski, R. A. Wullaert (REIC-27 [1963] 1/80; N.S.A. **17** [1963] No. 34491). – [9] A. Strasser, K. Taylor (UNC-5003 [1961] 1/35; N.S.A. **16** [1962] No. 27565). – [10] A. Strasser, K. Taylor (UNC-5013 [1962] 1/28; N.S.A. **16** [1962] No. 27566).

[11] R. J. Burian, E. O. Fromm, J. F. Langedrost, J. H. Stang, J. E. Gates (in: R. W. Dayton, R. F. Dickerson, BMI-1624-Del. [1963] B6/B8; N.S.A. **17** [1963] No. 25685). – [12] J. Crane, E. Gordon (UNC-5080 [1964] 1/80; N.S.A. **18** [1964] No. 39828), J. Crane, E. Gordon (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 896/918). – [13] D. I. Sinizer, B. A. Webb, S. Berger (Radiat. Damage Solids Reactor Mater. Part Proc. Symp., Venice 1962 [1963], pp. 287/318; NAA-SR-7248 [1962] 1/47; N.S.A. **16** [1962] No. 29440). – [14] J. L. Arnold (NAA-SR-11140 [1966] 1/53; N.S.A. **20** [1966] No. 23773). – [15] J. E. Frank, R. E. Forrester, J. S. Buck (NAA-SR-11440 [1966] 1/49; N.S.A. **20** [1966] No. 45113).

[16] J. A. Brinkmann (NAA-SR-4164 [1959] 1/34; Trans. Am. Inst. Mining Met. Petrol. Eng. **6** [1959] 1/11; N.S.A. **14** [1960] No. 902). – [17] D. G. Freas, P. B. Shumaker, J. H. Stang, J. E. Gates (BMI-1622 [1963] 1/60). – [18] H. Pearlman, R. F. Dickerson (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 438/49). – [19] C. E. Carlson, F. F. Felber (TIM-770-Suppl. 4 [1964]), C. E. Carlson, F. F. Felber (TIM-885-Suppl. 5 [1965]), C. E. Carlson, F. F. Felber (TIM-885-Suppl. 6 [1965]). – [20] M. A. DeCrescente, K. J. Kelly, P. V. Treciokas (TIM-870 [1964]).

[21] R. D. MacDonald, W. G. Mathers, A. M. Tachis, J. E. May (AECL-2571 [1966] 1/82; N.S.A. **20** [1966] No. 46220). – [22] J. B. Melehan, A. J. Markworth, J. S. Perrin, R. A. Wullaert, W. Chubb, J. E. Gates (BMI-1806 [1967] 1/40). – [23] R. A. Wullaert, J. M. Fackelmann, W. Chubb (BMI-1799 [1967] 1/30; N.S.A. **21** [1967] No. 26925). – [24] R. F. Hilbert, V. W. Storhok, W. Chubb, D. L. Keller (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 753/69). – [25] W. Chubb, R. F. Hilbert, V. W. Storhok, D. L. Keller (Mater. Sci. Eng. **9** [1972] 293/300).

[26] H. Hausner, R. Klersy, A. M. Tachis (Reaktortagung, Berlin 1970, pp. 594/7). – [27] H. Watanabe, M. Kurihara, J. Shimokawa, M. Ichikawa, M. Uchida (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 361/74). – [28] A. Ya. Ladygin, I. A. Efimov, Yu. I. Likhatchev, Yu. I. Aleksandrov (Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Paper 707, pp. 199/215; A/CONF-49-P-707 [1971] 1/34; CONF-710901-417 [1971]; N.S.A. **25** [1971] No. 52471). – [29] V. A. Tsykanov, V. M. Gryazev, E. F. Davydov, V. I. Kuz'min, A. A. Maiershin, V. N. Syuzev, I. S. Golovnin, T. S. Men'shikova, Yu. K. Bibilashvili, R. B. Kotel'nikov (At. Energ. [USSR] **42** [1977] 378/82; KFK-TR-536 [1977] 1/17; INIS Atomindex **9** [1978] No. 355481). – [30] G. Ervin (AI-AEC-12928 [1970] 1/61; N.S.A. **24** [1970] No. 25803).

[31] G. Ervin (J. Am. Ceram. Soc. **54** [1971] 46/50). – [32] A. Strasser (Proc. Conf. Breed. Econ. Safety Large Fast Power Reactors, Argonne, Ill., 1963, pp. 297/313; ANL-6792 [1963] 297/313), A. Strasser, J. Cihi, W. Sheridan, V. W. Storhok (Compounds Interest Nucl. Reactor Technol. Proc. Symp., Boulder, Colo., 1963 [1964], pp. 729/52; Inst. Mining Met. Petrol. Eng. Inst. Metals Div. Spec. Rept. Ser. No. 13 [1964] 729/52; Nucl. Met. **10** [1964] 729/52), A. Strasser, D. Stahl, K. Taylor, J. Andersen (UNC-5081 [1964] 1/97; N.S.A. **19** [1965] No. 24923). – [33] A. Strasser, J. Cihi, S. Hurwitz, R. Martin (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 979/1003). – [34] H. J. Kittel, L. A. Neimark, R. Carlander, O. L. Kruger, R. C. Lied (ANL-6678 [1963] 1/15; N.S.A. **18** [1964] No. 5813), L. A. Neimark, H. J. Kittel, C. C. Crothers (Carbides Nucl. Energy Proc. Symp., Harwell, U. K., 1963 [1964], Vol. 2, pp. 864/78). – [35] B. T. Bradbury, J. E. Cole, B. R. T. Frost, J. D. B. Lambert (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 879/95), B. T. Bradbury, B. R. T. Frost, J. R. Findlay (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 949/78), B. T. Bradbury, B. R. T. Frost (AIME Nucl. Met. Symp. High Temp. Nucl. Fuels, Delavan, Wisc., 1966, pp. 329/52; CONF-661003 [1966] 329/52), B. T. Bradbury, L. E. Russel, M. B. Waldon (ANL-7120 [1965] 328/54).

[36] J. H. Kittel, R. Carlander, L. A. Neimark, O. L. Kruger, R. C. Lied (ANL-FGF-399 [1962] 1/6; N.S.A. **17** [1963] No. 12711). – [37] B. T. Bradbury, B. R. T. Frost (in: G. J. Dienes, Studies in Radiation Effects on Solids, Vol. 2, Gordon and Breach, New York 1967, pp. 159/297). – [38] B. R. T. Frost, J. M. Horspool, R. G. Bellamy (Plutonium Fuel Technol. Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1968] 490/506). – [39] L. A. Neimark (Trans. Am. Nucl. Soc. **9** [1966] 415). – [40] L. C. Michels, L. A. Neimark (Trans. Am. Nucl. Soc. **12** [1969] 88/9).

[41] L. Smith, K. L. Peddicords, P. Buetzer, P. Rickenbacher, B. Buergisser (EIR-265 [1974] 1/99; N.S.A. **31** [1975] No. 10380). – [42] R. W. Stratton (Trans. Am. Nucl. Soc. **23** [1976] 142/4). – [43] R. W. Stratton, L. Smith (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 348/60). – [44] D. Stahl, A. Strasser (UNC-5198 [1968] 1/53; N.S.A. **22** [1968] No. 39789). – [45] A. Strasser, M. H. Montgomery (Trans. Am. Nucl. Soc. **12** [1969] 597/8).

[46] A. Strasser, M. H. Montgomery, R. Powers (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 849/67; GU-5286 [1972]; C.A. **77** [1972] No. 108272). – [47] M. H. Montgomery, A. Strasser (Trans. Am. Nucl. Soc. **15** [1972] 754/5). – [48] T. W. Latimer, J. O. Barner, J. F. Kerrisk, J. L. Green (LA-6249-MS [1976] 1/27; INIS Atomindex **7** [1976] No. 273709), T. W. Latimer, J. O. Barner, J. F. Kerrisk, J. L. Green (Trans. Am. Nucl. Soc. **19** [1974] 91). – [49] T. W. Latimer, D. S. Bost, J. F. Kerrisk, J. O. Barner, J. L. Green (LA-6077 MS [1975] 1/23), J. O. Barner, T. W. Latimer, J. F. Kerrisk, D. Bost, J. L. Green (Trans. Am. Nucl. Soc. **19** [1974] 91/2). – [50] J. O. Barner, T. W. Latimer, J. F. Kerrisk, R. L. Petty, J. L. Green (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 268/98).

[51] W. Dienst, I. Mueller (Reaktortagung, Düsseldorf 1976, pp. 470/3). – [52] M. H. Montgomery, A. Strasser, J. C. Andersen, C. Grando (GU-5306 [1973] 1/67), M. H. Montgomery, C. Grando, A. Strasser (Trans. Am. Nucl. Soc. **14** [1971] 595/6). – [53] H. Steiner, D. Freund, O. Jacobi, P. Weimar (KFK-2451 [1977] 1/80; INIS Atomindex **8** [1977] No. 334682). – [54] G. Clottes, M. Dieumegard, J. P. Dufayet, A. Groff, B. Kryger, H. Mikailoff, J. L. Ratier (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973 [1974], Vol. 2, pp. 113/27). – [55] H. Mikailoff (Bull. Inform. Sci. Tech. Comm. Energ. At. [France] No. **196** [1974] 41/8; ANL-Trans-977 [1974]).

[56] A. Groff (CEA-R-4742 [1976] 1/101; INIS Atomindex **7** [1976] No. 268115). – [57] P. Combette (Advanced LMFBR-Fuels Proc. ANS Meeting, Tucson, Ariz., 1977, pp. 343/7). – [58] K. Q. Bagley, E. Edmonds, H. J. Powell, R. G. Bellamy, R. Paris, J. M. Hoorspool (Fuel Fuel Elem. Fast React. Proc. Symp., Brussels 1973, Vol. 1, pp. 87/100). –

[59] K. Q. Bagley, W. Batey, R. Paris, W. M. Sloss, G. P. Snape (Advanced LMFBR-Fuels Proc. ANS Meeting, Tucson, Ariz., 1977, pp. 313/25). – [60] J. O. Barner (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 819/47).

[61] M. Coquerelle (Reaktortagung, Düsseldorf 1976, pp. 538/41). – [62] M. Coquerelle, J. Gabolde, P. Werner (Reaktortagung, Hamburg 1972, pp. 423/6). – [63] C. Grando, M. H. Montgomery, A. Strasser (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 771/84), Gulf United Nucl. Fuels Corp. (GU-5288 [1972] 1/17). – [64] H. Mikailoff (Bull. Inform. Sci. Tech. Comm. Energ. At. [France] No. **196** [1974] 49/54; ANL-Trans-964 [1974]). – [65] B. L. Harbourne, P. J. Levine, A. Biancheria (Trans. Am. Nucl. Soc. **12** [1969] 89).

[66] P. J. Levine, B. L. Harbourne, A. Biancheria, A. Boltax (Ceram. Nucl. Fuels Proc. ACS Annual Meeting, Washington, D.C., 1969, pp. 156/65). – [67] P. J. Levine, B. L. Harbourne, A. Biancheria, T. W. Latimer, L. A. Neimark (Trans. Am. Nucl. Soc. **13** [1970] 606/7). – [68] B. L. Harbourne, P. J. Levine, A. Biancheria, T. W. Latimer, L. A. Neimark (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 869/94). – [69] D. Geithoff (Reaktortagung, Hannover 1978, pp. 656/9). – [70] J. F. Kerrisk, J. O. Barner, R. L. Petty (Nucl. Technol. **30** [1976] 361/75).

[71] J. F. Kerrisk, J. O. Barner, R. L. Petty (Advanced LMFBR-Fuels Proc. ANS Meeting, Tucson, Ariz., 1977, pp. 648/59). – [72] H. B. Banach, H. J. Richings (PWAC-431 [1964]). – [73] M. A. DeCrescente, K. J. Kelly, P. V. Treciokas (TIM-870 [1964]). – [74] M. A. DeCrescente, M. S. Freed, S. D. Caplow (PWAC-488 [1965]). – [75] R. A. Wullaert, J. F. Lagedrost, J. Bugl, J. F. Gates (BMI-1638 [1963] 1/35; N.S.A. **17** [1963] No. 32660), R. A. Wullaert, J. F. Gates, J. Bugl (Am. Ceram. Soc. Bull. **43** [1964] 834/41).

[76] M. D. Rogers, J. Adam (AERE-R-4046 [1962]). – [77] R. L. Martin, W. J. Zielenbach, V. W. Storhok, D. L. Keller, J. E. Gates (BMI-1731 [1965] 1/31; EURAEC-1431 [1965]; N.S.A. **20** [1966] No. 888). – [78] E. D. Albrecht, A. J. Rothman, J. D. Lee, J. M. Johnson, W. H. Hayes (Develop. Irradiat. Testing Technol. Proc. Natl. Symp., Sandusky, Ohio, 1969, pp. 595/628; CONF-690910 [1969]). – [79] R. F. Hilbert, V. W. Storhok, W. Chubb, D. L. Keller (Thermionic Conversion Specialist Conf., Miami Beach, Fla., 1970; CONF-701039 [1970] 18/25). – [80] W. Chubb, R. F. Hilbert, V. W. Storhok, D. L. Keller (Mater. Sci. Eng. **9** [1972] 293/300).

[81] R. F. Hilbert, V. W. Storhok, W. Chubb (Trans. Am. Nucl. Soc. **12** [1969] 547/8). – [82] G. Pott, M. Herren, A. Naoumidis (Results Five Years BR2 React. Util. Proc. Symp., Mol, Belg., 1973 [1974], pp. 227/32). – [83] H. Mikailoff, J. Leclere, B. Kryger, J. Bloch, M. Conte (CEA-N-1186 [1969]; EUR.f-4347 [1969] 1/92; N.S.A. **25** [1971] No. 52472); EURFNR-688 [1969] 1/103; N.S.A. **24** [1970] No. 14964). – [84] A. A. Bauer, V. W. Storhok (Plutonium 1970 Other Actinides Proc. 4th Intern. Conf., Santa Fe, 1970; Nucl. Met. **17** [1970] 532/44). – [85] A. A. Bauer, J. B. Brown, E. D. Fromm, V. W. Storhok (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 785/817).

[86] A. A. Bauer, P. Cybulskis, J. L. Green (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 299/311). – [87] H. Blank (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 482/501). – [88] C. Ronchi, C. Sari (J. Nucl. Mater. **58** [1975] 140/52). – [89] H. Matzke, C. Ronchi (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 218/44). – [90] F. A. Rough, W. Chubb (BMI-1441 [1960] 1/102; N.S.A. **14** [1960] No. 18107).

[91] J. W. Harrison, L. M. Davies (J. Nucl. Mater. **27** [1968] 239/40). – [92] J. W. Harrison (J. Nucl. Mater. **30** [1969] 319/23). – [93] J. W. Harrison (J. Nucl. Mater. **31** [1969] 99/106). – [94] H. Watanabe (Phys. Prop. Fast Reactor Fuels Proc. 2nd Seminar, Tokyo 1968; JAERI-1172 [1969] 1/62, 13/9; WAPD-Trans-125 [1969]; CONF-680326-2 [1968]; N.S.A. **23** [1969] No. 24855, **24** [1970] No. 10196). – [95] F. J. Huegel (PWAC-482-Pt. 2 [1965] 1/20; N.S.A. **26** [1972] No. 20696).

[96] A. J. E. Foreman (AERE-T/M 134 [1956] 1/18; N.S.A. **11** [1957] No. 10047). – [97] E. R. Leach, J. W. Ray, D. A. Dingee (BMI-1743 [1965]). – [98] G. W. Greenwood, M. V. Speight (J. Nucl. Mater. **10** [1963] 140/4). – [99] A. J. Markworth (Nucl. Sci. Eng. **49** [1972] 506/7). – [100] Prajoto, A. R. Wazzan, D. Okrent (Trans. Am. Nucl. Soc. **23** [1976] 170).

[101] H. Matzke, C. Ronchi (Phys. Met. React. Fuel Elem. Proc. Conf., Berkeley, U.K., 1973 [1975], pp. 259/65). – [102] R. L. Ritzman, A. J. Markworth, W. Olsfield (Nucl. Appl. Technol. **9** [1970] 167/87). – [103] A. M. Ross, D. H. Rose (AECL-2701 [1967] 1/59; N.S.A. **22** [1968] No. 765).

1.2.3.4 The Release of Gaseous Fission Products

The total release and the release rate of gaseous fission products from ceramic fuels are important quantities for characterizing the irradiation behavior of fuel elements containing carbide and nitride fuels. The release is determined according to standard methods in the post-irradiation examination of the fuel elements or rods. The primary interest in this determination rests upon the fact that after a burnup of, e.g., 10% FIMA, the fission gases formed (Kr and Xe) may fill at standard conditions (273 K, 0.1 MPa) a volume about 75 times that of the fuel.

The comparison between the increase of the volume of the fuel (its swelling) and the fraction of the fission gas that has been released, shows a definite relationship between the two. It indicates that the mechanisms of the swelling and of the gas release are closely related (see Section 1.2.3.3., p. 204). The aims of the present chapter are the description of this release mechanism from carbide and nitride fuels and the subsequent discussion of the measured data.

1.2.3.4.1 Mechanisms of the Fission Gas Release

Already since the early sixties attempts have been made to propose mechanisms, that describe the swelling behavior and the related fission gas release, on the basis of data on the fuels and the conditions of the irradiations [1]. More recent publications [2 to 4, 7] supplement these early concepts in a meaningful way.

Recoil atoms [1] contributed to the fission gas release, as found by several authors experimentally [5 to 16, 119]. Sinizer et al. [1] calculated, that Kr, for example, was released from a depth of 5.5×10^{-3} mm by recoil atoms, independently from the temperature and half-lives of the precursor nuclides. The contribution of these atoms to the fission gas release was considerable at temperatures up to ca. 1 000 °C and for fuels having large specific surfaces. A fraction of the released fission gas could redissolve in the lattice of the fuel, because of the external pressure generated [17 to 23, 129]. The xenon solubility in the UC lattice could be measured at 1 600 and 1 700 °C, and the ratio Xe:U was found to be 1×10^{-12} and 3.4×10^{-12}, respectively [17, 18].

Gautsch et al. [19, 20] reported for the Kr solubility in UC a value of 2×10^{-13} atoms/cm^3 at 1 bar pressure of Kr at 600 K. The experiments of Ronchi, Matzke [22] indicated, that the resolution of fission gases was considerably smaller in carbide fuels than in (U,Pu)O_2. Blank, Matzke [23] concluded in another study, that there was no appreciable resolution of the fission gases in (U,Pu)C or (U,Pu)N.

Another mechanism, that controls the fission gas release, is the diffusion of these fragments [1, 2, 13, 24 to 26, 129]. Groff [24] found that between 1 000 and 1 200 °C the fission gas release was controlled by both the thermal and the irradiation-induced diffusion, but above

1 200 °C only by the thermal diffusion. Hahn [25] explained in this manner also the differences between the release rates for hypo- and hyperstoichiometric UC, since the diffusion of Xe in uranium was 4 to 5 orders of magnitude faster than in UC at a temperature of 1 060 °C. Theoretical calculations of Iwamoto, Oishi [2], on the other hand, led to the conclusion that the diffusion of the fission gases had only a slight influence on their release, which was dictated primarily by the trapping sites. Furuya et al. [26] presumed that at temperatures between 1 650 and 2030 °C the only mechanism possible was diffusion. They calculated the diffusion coefficient from the measured release rate:

$$D_{Kr} = 1.6\times10^{-7}\exp(-56.400/RT) \qquad \mathrm{cm^2/s} \qquad (1)$$

with the activation energy given in kcal/mol. Freas et al. [27] found significant differences between the release rates for Kr and Xe at 1 230 °C. The release to birth ratio (R/B) was larger for Xe than for Kr. The authors attributed this effect to the considerably faster diffusion of the precursor of the xenon, i.e., the iodine.

As already described in Section 1.2.3.3, p. 204, the fission gases form bubbles in the fuel. The generation, growth, and mobility of the bubbles play an essential role in the release [19 to 21, 28 to 33]. The mobility of the bubbles in UC was controlled by the bulk diffusion [28]. The diameter of the bubble was an important quantity, that determined its mobility [30]. The coalescence of small bubbles to form pores had been proven qualitatively [22] and described quantitatively [23, 29].

These mechanisms gave rise to the hypothesis, that the following conditions of the irradiation should affect the fission gas release:

1. the temperature of the fuel,
2. the stoichiometry of the fuel,
3. the microstructure and the porosity,
4. the burnup and the fission rate.

In the following, therefore, the in-pile measured gas release is discussed with consideration of these parameters.

1.2.3.4.2 Fission Gas Release from UC

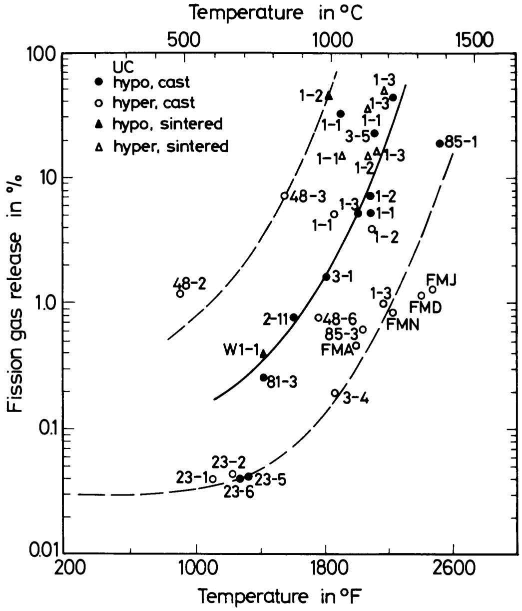
Measurements of the fission gas release from UC were reported in numerous studies [1, 5 to 15, 26, 35 to 51, 130 to 132]. Several reviews were also published [52 to 59], in which the release data were correlated with the various irradiation parameters.

1.2.3.4.2.1 The Temperature Dependence of the Fission Gas Release from UC

The data from the following sources [6, 13, 36, 39, 43, 44, 131, 132] have been summarized by Wullaert et al. [56] in the form of a diagram, **Fig. 1-145**. The corresponding Arrhenius plot indicates, that above ca. 1 000 °C it is the diffusion that controls the release rate.

McDonald et al. [39] found a linear dependence between the fuel temperature and the release. It must be pointed out, however, that these authors dealt with a narrow temperature range only, 1 100 to 1 350 °C. Measurements made at Atomic International [13, 45] between 760 and 1 650 °C showed clearly the exponential dependence.

Fig. 1-145

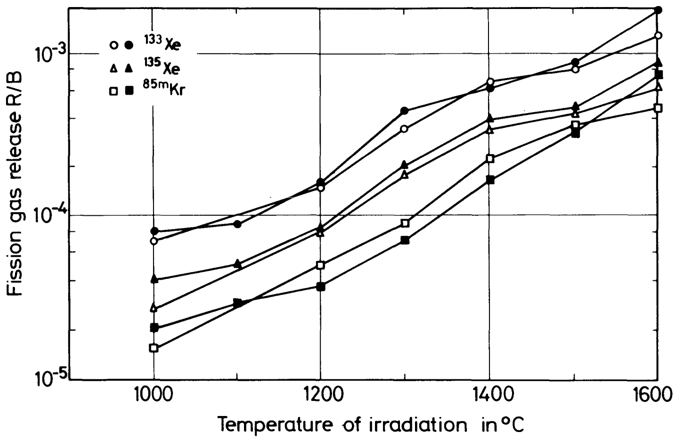


Effect of the temperature on the fission gas release of UC [56].
23-1, 23-2, 23-3, 23-4, 23-5, 23-6 [6, 36]; 3-1, 3-3, 3-5 [13, 44]; 48-1, 48-2, 48-3, 48-6 [44]; 85-1 [13]. W1-1 [73]; 1-1, 1-2, 1-3 [43]; FMA, FMD, FMN, FMJ [39].

A basic study in this area was conducted by Melehan et al. [7]. The released fission gases were measured continuously in a specially constructed capsula, while the temperature of the sample was increased stepwise from 1 000 to 1 600 °C and decreased again. The result was, that after about 40 to 70 h equilibrium was attained between the rate of formation of the fission gas (B = birth) and the rate of its release (R), leading to a constant value of R/B. **Fig. 1-146**, p. 230, shows a typical diagram of such measurements, made on a melted and homogenized sample of the composition $UC_{1.4}$.

The measurements of Russian authors [48, 49] indicated a temperature dependence of the fission gas release of 2% (or 6.3%) at 1 030 (or 1 650 °C) for a slightly hyperstoichiometric sintered UC sample. The data were insufficient, however, to establish a quantitative relation. DeCrescente et al. [42] found, that a temperature correction could not reduce the wide scatter obtained for the gas release in a series of irradiation experiments. This result, which was not in agreement with those of other studies, was understandable, however, in view of the wide variability of the properties of the UC samples irradiated by these authors at 1 000 to 1 700 °C.

Fig. 1-146



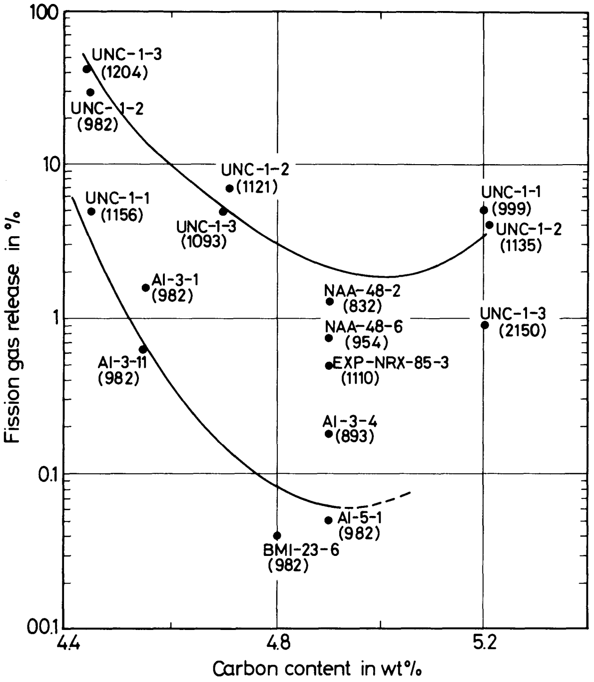
In-pile measured fission gas release of arc-cast and homogenized $UC_{1.4}$ at various irradiation temperatures [7].

1.2.3.4.2.2 Effect of the Stoichiometry on the Fission Gas Release from UC

Crane, Gordon [131, 132] were the first to find, that the composition of the uranium carbide influenced the fission gas release during the irradiation. This effect of the stoichiometry could not be confirmed, however, by MacDonald et al. [39]. The results of these authors [39, 43, 131, 132] and those from the BMI [6] were summarized by Wullaert et al. [56]. Their representation by Frank et al. [129] is shown in **Fig. 1-147**, but his representation does not include the data of MacDonald et al. [39], obtained in the range 4.6 to 4.75 wt% C at 600 to 1 000 °C, showing composition-independent gas release between 0.3 and 1.37%. Frank et al. [13] supposed, that above 760 °C there occurred a composition-dependent release, provided that diffusion contributed appreciably to the release process. There was no confirmation of this assumption by experimental data. Hahn [25] observed a composition-dependence in the hypostoichiometric range, provided that the uranium phase was continuous throughout the sample volume. According to Rothman et al. [60], the diffusion coefficient of Xe in U at 1 060 °C, 6×10^{-8} cm^2/s, was from 4 to 7 orders of magnitude higher than the value in UC. composition $UC_{1.01}$ had an R/B value ten times larger than $UC_{1.4}$ had at 1 000 °C, but the

The work of Melehan, Gates [7] also made a basic contribution to the understanding of the effect of the stoichiometry on the R/B values, by separating the various parameters from each other. When the temperature of $UC_{0.9}$ in the reactor was raised from 640 to 1 100 °C, the authors found that R/B increased from 1×10^{-4} to 1×10^{-2}, but that it remained nearly constant above that temperature. Only at the melting point of uranium, 1 128 °C, a sudden strong release of fission gases occurred, and the R/B values increased by one order of magnitude within 5 h. A smaller burst of released fission gas occurred during the $\beta \rightarrow \gamma$ transformation of uranium, whereas no such burst was observed during the $\alpha \rightarrow \beta$ transformation. Samples of the composition $UC_{1.01}$ had an R/B value ten times larger than $UC_{1.4}$ had at 1 000 °C, but the values were nearly the same at 1 600 °C. At the latter temperature, however, the R/B values of the hyperstoichiometric samples were an order of magnetitude lower than for $UC_{0.9}$.

Fig. 1-147



Fission gas release from high density (99% of the theoretical) uranium carbides of various compositions at 1 100 °C [129].
For capsule codes compare Fig. 1-145, p. 229, for codes of the research establishments see Section 1.2.1 (Introduction), on p. 141.

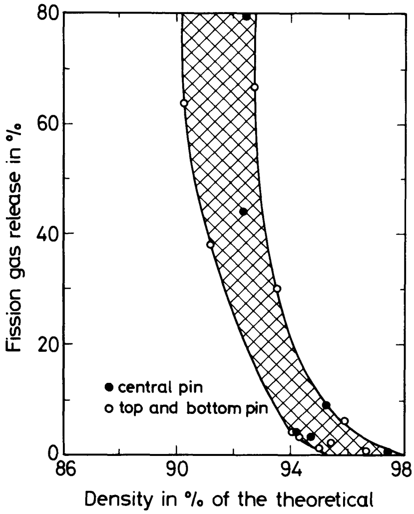
1.2.3.4.2.3 Effect of the Porosity and the Microstructure

Crane, Gordon [43, 131, 132] irradiated under the same conditions samples of sintered and arc-cast UC of different compositions. After a burnup of 1.43 and 2.23×10^4 MWd/t, the authors found that sintered UC (4.86 wt% C) released about double the amount of fission gas that arc-cast UC (4.70 wt% C) did, but this ratio reversed after a burnup of 4.0×10^4 MWd/t.

Frank et al. [13, 129] supposed that the porosity and the structure affected the fission gas release from UC, but could not demonstrate this effect experimentally. This assumption was based on a statement of Shaked [61], that in experiments, conducted in order to measure the diffusion coefficient of Xe in UC, an influence of the grain boundaries on the rate of fission gas release existed. However, Wullaert et al. [56] could not find in a cross-evaluation any effect of the initial density (in the range from 90 to 100% of the theoretical) on the fission gas release.

The systematic studies of Melehan, Gates [7], on the other hand, showed that at 1 000 °C the R/B value of a sintered $UC_{1.04}$ sample (density 93% of the theoretical) was five times as large as that of arc-cast $UC_{1.04}$. This ratio even rose to 30 at temperatures above 1 200 °C. The authors also observed that for sintered UC above 1 500 °C, the R/B value decreased slightly with increasing irradiation times, because of some small irradiation-induced sintering (the density after the irradiation was 95% of the theoretical). Extensive studies at Pratt & Whitney [41, 42] indicated that upon the use of hyperstoichiometric UC having an initial density higher than 94% of the theoretical, the goal set for the SNAP-50 project, of having $<20\%$ release at temperatures up to 1 200 °C (2200 °F) could be achieved. When a UC fuel having a lower density was used at the same temperature range, 1 000 to 1 200 °C, up to 80% release could be measured (**Fig. 1-148**).

Fig. 1-148

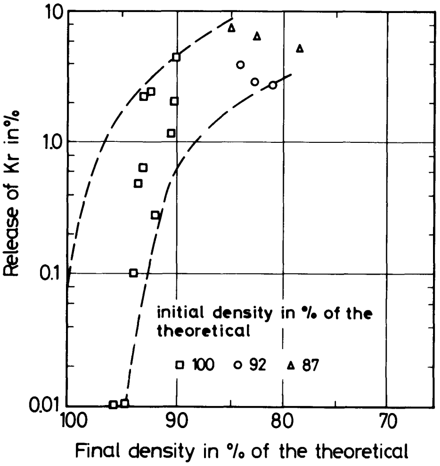


Fission gas release from sintered UC (4.8 to 5.3 wt% C) as a function of the initial density.

Melehan et al. [37] analyzed the extensive results obtained at the BMI for slightly hyperstoichiometric UC. They pointed out, that the fission gas release could be correlated better with the final density than with the initial density of the fuel (**Fig. 1-149**).

In this connection, and on the basis of photographs of the microstructure of the samples after the irradiation, DeCrescente et al. [42] indicated that it was not the density of the starting material alone, that controlled the release, but that the morphology of the porosity had an essential effect.

Fig. 1-149



Fission gas release as a function of the final density of UC [37].

Vibrationally compacted carbide fuel released a considerable fraction of the yielded fission gases [34]. This fraction R was related to the porosity P by the expression:

$$R = \text{const.}/(1-2\,P) \tag{2}$$

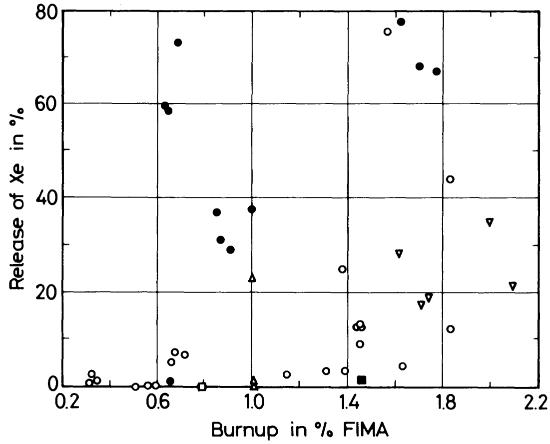
Bagley et al. [34] also mentioned, that at about 1 200 °C the morphology of the pores and in particular the growth of the fission gas bubbles and of their coalescence at the grain boundaries, were closely related to the fission gas release.

Melehan, Gates [7] reported, that also the microstructure, i.e., the presence of deposits such as UC_2 and U_2C_3 in hyperstoichiometric UC, could influence the release rate of fission gases. They observed during the heating-up of a sample between 1 400 and 1 500 °C an anomalous behavior (in particular of ^{133}Xe). They assumed, that the transformation of UC_2, present in hyperstoichiometric UC, at this temperature to U_2C_3, and the structural changes associated there with (UC_2 needles $\rightarrow$ U_2C_3 agglomerates) were responsible for this effect. The authors also supposed [7], that an eventual decarburization of the fuel by the cladding material (tungsten in the present case) had an effect. However, they did not find a confirmation of this in post-irradiation examinations of the microstructure of the samples. Recent metallographic studies of Melehan et al. [37] showed no significant differences among specimens in carbon depletion, which could be interpreted as contributing to the wide scatter in the gas release. However, the use of stabilizing additives, such as 1 wt% W or 10 wt% Zr, could change the fission gas release considerably [42].

1.2.3.4.2.4 Effect of the Burnup and of the Power Density

In the statements made up to this point, concerning the release of the fission gases, it was assumed implicitly that the gases were released linearly during the entire irradiation, i.e., that the

Fig. 1-150



Fission gas release at various amounts of burnup of hyperstoichiometric, sintered UC at fuel center temperatures between 1 340 and 1 580 °C [42]. ● Initial density $< 94\%$; ○ initial density $> 94\%$; △ fuel with W-additive; fuel with Zr-additive; □ long pin with center hole; ■ long pin with solid pellets.

burnup had no effect on the release rate. Melehan et al. [37] tried without success to find in their data a functional relationship between the fission gas release and the burnup. Also DeCrescente et al. [42] stated that a normalization of the data based on this aspect did not reduce their large scatter. The measurements of these authors [41, 42] (**Fig. 1-150**) show that no significant correlation exists between Xe release and burnup. This figure again indicates the relationship between the porosity and an enhanced fission gas release. For a given porosity (samples having above 94% of the theoretical density), values of both below and much above 20% release are obtained at higher burnups than 1.3% FIMA ($> 1.1 \times 10^4$ MWd/t).

Crane, Gordon [43, 131, 132] found some dependence of the fission gas release on the burnup, but only in samples with a carbon content of 4.8 wt%, and only after a burnup of 2.29×10^4 MWd/t.

The power level of the fuel rod, too, might have some effect on the fission gas release. According to Bagley et al. [34] there existed for vibrationally compacted carbide fuel rods a clear linear relationship between the release R and the power Q or the integrated heat power $\int \lambda_p d\vartheta$:

$$R = 0.2\,Q/(1-2P) = 2.5 \int \lambda_p d\vartheta \qquad (3)$$

where $\lambda_p = \lambda_0/(1-2P)$, λ_0 is the heat conductivity at zero porosity, λ_p that at porosity P.

1.2.3.4.3 Fission Gas Release from (U,Pu)C

The irradiation behavior of UC-PuC solid solutions, (U,Pu)C, has been studied since the early sixties, and has been also reported on the release of fission gases [14, 15, 44, 62 to 111, 133]. The mechanism and the various factors that affect this release have been discussed at the beginning of this chapter. Like other properties, also the fission gas release of UC and (U,Pu)C are similar but not identical, so that only qualitative predictions for the mixed carbides can be made from the numerous irradiation results obtained for UC [75].

The Argonne National Laboratory (ANL) reported [62 to 68] the irradiation behavior of arc-cast, sintered, and vibrationally compacted (U,Pu)C, with compositions varying from hypo- to hyperstoichiometric. Kittel et al. [62, 63] found that even for the low burnup of 0.1 $\times 10^4$ MWd/t and at a temperature of 650 °C, arc-cast (U,Pu)C released only 0.24% of the fission gas but high porosity samples ($P > 40\%$) released more than 12%. The authors attribute this result to the large fraction of open porosity in the latter. By means of mass spectrometric gas analysis they found that (U,Pu)C released considerably more Kr ($\approx 19\%$) than Xe ($\approx 11.3\%$). For the study of vibrationally compacted fuel, rods containing powdered PuC or physical mixtures of UC-20% Pu of different carbon contents as starting material were irradiated at burnups from 1.8 to 7.0×10^4 MWd/t. Fission gas release ranged from $< 1\%$ for the hyperstoichiometric to $> 40\%$ for the hypostoichiometric carbide [64 to 66]. At fuel center temperatures between 900 and 1100 °C the stoichiometry effect covered-up any temperature effect that might be present. In hypostoichiometric fuel, because of its plastic behavior, large pores were formed, whereas in hyperstoichiometric fuel only small bubbles were found. The results of these tests are summarized in Table 1/39.

Table 1/39
Fission Gas Release from Vibrationally Compacted UC-PuC Fuel Rods [65].

sample	fuel	wt% C in PuC or in (U,Pu)C	burnup, in % FIMA (in 10^4 MWd/t)	average fuel center temperature in °C	fission gas release in %
F-7	PuC	4.24	1.95 (1.60)	1000	35.2
F-6	PuC	6.22	5.43 (4.46)	1305	–
F-8	PuC	4.24	6.00 (4.93)	980	–
C-44	PuC	3.40	2.18 (1.79)	1070	45.9
C-43	PuC	4.24	5.30 (4.36)	820	31.0
F-18	UC-20 PuC	6.42	1.35 (1.11)	820	8.8
F-21	UC-20 PuC	3.40	1.40 (1.15)	770	25.7
F-19	UC-20 PuC	6.22	5.80 (4.77)	855	< 1.0
F-20	UC-20 PuC	4.24	6.80 (5.59)	975	40.0
C-69	UC-20 PuC	6.42	1.21 (0.99)	690	5.7
C-74	UC-20 PuC	3.40	1.57 (1.29)	820	21.5
C-72	UC-20 PuC	6.22	6.80 (5.59)	1000	< 1.0
C-70	UC-20 PuC	4.24	6.80 (5.59)	1025	20.0

The results of more recent irradiations at ANL have been reported since 1967 [67, 68], but only hyperstoichiometric carbides were employed. After a mean burnup of 3% FIMA (2.5 $\times 10^4$ MWd/t) pellets having a density of 81.4% of the theoretical released 4.1 %, a vibrationally compacted (U,Pu)C having a density of 85.9% of the theoretical released 8.6% of the total fission gas. A physical mixture of UC and PuC released a larger fraction, 13% [67]. After further burnup (about 7% FIMA, 5.8×10^4 MWd/t), this value is increased to about 17% for the vibrationally compacted carbide mixture, but remained near the low value, about 2.5%, for the (U,Pu)C.

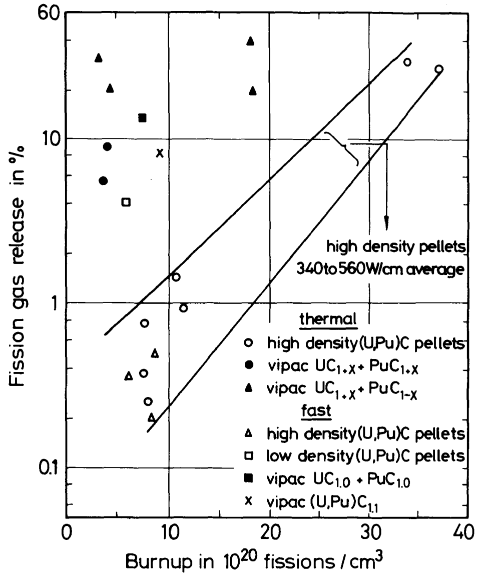
The United Nuclear Corporation (UNC) was concerned with the irradiation behavior of sintered mixed carbides. The aim of the first irradiation tests was, among others, to establish the effect of Ni ($\approx$0.1 wt%), used as a sintering aid [71 to 76]. Burnup values of from 2.1 to 11.4 $\times 10^4$ MWd/t were attained, see Table 1/40. According to Strasser et al. [75], the Ni-doped samples released slightly more gas than the undoped (U,Pu)C at temperatures around 1 000 °C and burnup up to 4.0×10^4 MWd/t. At higher burnup values, it is necessary to take into account a rather high gas release ($\approx$50%). The relatively favorable results could be attributed partly to the differing burnup across the pellets [76]. For example, the burnup at the center and at the periphery of the pellets of samples 63 and 66 (Table 1/40) was determined: at the relatively cold surface it reached 18.0 to 20.0×10^4 MWd/t, at the hot center only 3.5 to 4.0×10^4 MWd/t, because of strong self-shielding.

The results from ANL [62 to 68] and UNC [71 to 76] were reviewed by Strasser, Kittel [78], who considered also the first results from a new series of irradiations using high density pellets [77]. The authors concluded that a fuel, that consisted of a physical mixture of UC and PuC, released considerably more fission gas than fuels consisting of mixed carbides, because of the appreciably higher burnup of the PuC particles (about 110×10^{20} fissions/cm^3). This relatively high burnup of the PuC phase led to a coalescence of the gas bubbles and therefore to high rates of swelling. The results shown in **Fig. 1-151** confirm, that Vipac-$(U,Pu)C_{1+x}$ mixed carbides release less fission gases than the Vipac-mixed UC and PuC fuel rods, in spite of the higher linear rod power density in the former (850 W/cm) than in the latter (690 W/cm). The high density pellets release, as expected, less fission gases. In this type of fuel, however, the effect of the burnup is very significant.

Table 1/40
Summary of the Irradiation Results at UNC Obtained for Sintered (U,Pu)C Fuel [75].

sample	composition	average center fuel temperature in °C	mean burn-up in $10^4 \times$ MWd/t	fission gas release in %
UNC-61T	$(U_{0.8}Pu_{0.2})C$ + 0.1% Ni	1 030	2.17	0.37
61B	$(U_{0.8}Pu_{0.2})C$	1 015	2.42	0.25
UNC-62T	$(U_{0.8}Pu_{0.2})C$ 0.1% Ni	1 005	3.13	1.45
62B	$(U_{0.8}Pu_{0.2})C$	935	3.51	0.94
UNC-63T	$(U_{0.8}Pu_{0.2})C$ + 0.1% Ni	925	11.27	47.30
63B	$(U_{0.8}Pu_{0.2})C$	790	11.4	no measurement
UNC-64T	$(U_{0.8}Pu_{0.2})C$	1 125	2.34	0.75
64B	$(U_{0.8}Pu_{0.2})C$ + 0.1% Ni	1 175	2.28	12.70
UNC-66T	$(U_{0.8}Pu_{0.2})C$ + 0.1% Ni	1 030	10.1	51.30
66B	$(U_{0.8}Pu_{0.2})C$	885	10.05	51.30

Fig. 1-151



Effect of the burnup on the fission gas release of Pu-containing carbide fuels during thermal and fast neutron irradiation [78].

A series of irradiations at United Nuclear Corporation (UNC) [79], using He-bonded mixed carbides of high density (97 ± 3% of the theoretical) and hyperstoichiometric composition ((U,Pu)C + 10% $(U,Pu)_2C_3$), resulted in comparatively low gas release values (0.1 to 2.7%) at a burnup of 9 to 11 × 10^{20} fissions/cm^3 (2.2 to 2.8 × 10^4 MWd/t). No measurements could be made at higher burnup values because of rod failure. Also in further irradiation experiments it was confirmed, that a hyperstoichiometric high density mixed carbide fuel fails at burnup values of 7.7 × 10^4 MWd/t [80]. On the other hand, fuel rods with single-phase mixed carbides and densities $< 85\%$ of the theoretical survived this burnup value, but released a large fraction of the fission gas (15 to 42%).

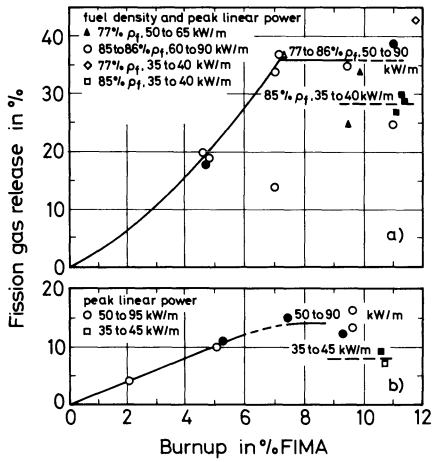
Grando et al. [81] compared for relatively low burnup values (4.9 and 7.0 × 10^{20} fissions/cm^3, 1.22 and 1.75 × 10^4 MWd/t) the fission gas release from (U,Pu)C, (U,Pu)C + 10% $(U,Pu)_2C_3$, and $(U,Pu)_2C_3$ at temperatures between 1275 and 1400 °C. It was established evidently, that in spite of the lower density, 94% of the theoretical, the fuel having the composition $(U,Pu)_2C_3$ released less fission gas (2.1%) than the one with the composition (U,Pu)C + $(U,Pu)_2C_3$ (10.6%), although the latter had an initial density 98% of the theoretical. A further comparison, due to Montgomery et al. [82, 133], was based on an irradiation experiment on (U,Pu)C (93% of the theoretical density) and (U,Pu)C + 10% $(U,Pu)_2C_3$ (97% of the theoretical density) in Na-bonded fuel rods, after burnup of 15 to 16 × 10^{20} fissions/cm^3 (3.32 to 3.55 × 10^4 MWd/t) at a fuel temperature of 770 °C. It was found that (U,Pu)C released from 12 to 35%, and (U,Pu)C + 10% $(U,Pu)_2C_3$ only 3 to 5% of the fission gas. The gas release was higher than for the He-bonded rods, and this was attributed to the formation of cracks in the fuel, that increased its surface area. It was also pointed out, that the sample that released 35% of the gas partly melted during the irradiation.

Another series of irradiation experiments was conducted at the Los Alamos Scientific Laboratory (LASL), using mixed carbides as fuel [83 to 89]. In some of the experiments Na-bonding was used for heat transfer between the fuel and the cladding [83 to 85, 88], in others He-bonding [86, 88]. Latimer et al. [85] summarized the results for the Na-bonded rods. The gas release ranged between 9 and 21% for those rods, that did not fail, but it could not be correlated with either the burnup or the power density. Neither did the composition nor the density show any clear effect on the gas release from the sintered mixed carbide. The Kr:Xe ratio in the released gas deviated from the well known ratio of their fission yields. This anomaly was attributed to the different solubilities of the precursors of these two fission gases [84].

In irradiation experiments with He-bonded fuel rods at intermediate fuel temperatures ($t_{surface}$ ≈550°C, linear rod power density ≈350 W/cm), no clear effect of the composition ((U,Pu)C or (U,Pu)C + 20% $(U,Pu)_2C_3$) on the fission gas release was found at LASL, but the effects of the burnup [86] and of the density [86 to 88] were evident. Fuels of densities <89% of the theoretical [86], or having a free volume (pores + gap) >19% [88] released a large fraction of the fission gas even at the intermediate temperature.

Barner et al. [89] showed these relationships in **Fig. 1-152**a and b. The fission gas release from dense fuel remained small. The burnup affected this quantity linearly, and was given as 0.5% per % FIMA (0.61% per 10^4 MWd/t) for the high density fuel. In the fuel design, however, the good retention of the fission gas was less important than the lower swelling rate of the lower density fuel, which, however, released a considerable fraction of its fission gas.

Fig. 1-152



Fission gas release up to high burnup values for He-bonded mixed carbide fuel rods. a) Fuel density 77 to 86% of the theoretical, free volume 19%; b) fuel density 91 to 95% of the theoretical, free volume 18% [89]. Solid marks indicate failed elements.

The first results of the irradiation experiments at the Atomic Energy Research Establishment (AERE) at Harwell indicated low fission gas release from arc-cast (U,Pu)C at temperatures of 780 and 1 010 °C after burnup of 1.65 and 0.65 × 10^4 MWd/t, respectively [14, 15, 90]. In some cases the volumes of the fission gases were lower than the values expected from the recoils in the miniature fuel rods. The authors attributed this result to the effect of the implantation of the recoils into the cladding. The prolongation of the irradiation program [91] with thermal neutrons confirmed the low gas release ($\leqq$2.5%) at fuel temperatures below 900 °C even for burnup values up to 9.0 × 10^4 MWd/t (10.6% FIMA), for high density fuel of the composition (U,Pu)C or (U,Pu)C + $(U,Pu)_2C_3$. Powdered fuel (ρ = 60% of the theoretical) of the same material, irradiated at the same temperature, released 6.2% of the gas, however. Even after irradiation in a flux of fast neutrons (experiment DFR-26), sintered $(U_{0.85}Pu_{0.15})C_{1+x}$ having a carbon content of 5.32 wt% and a density of 60% of the theoretical showed the unexpectedly low gas release (<2.5%) in spite of the high irradiation temperature (1 270 °C) and burnup, 5.2 to 5.4% FIMA (4.3 to 4.4 × 10^4 MWd/t).

Frost et al. [93] reported, that the first experiments with long rods (28 inches, 71.1 cm), too, were very positive with respect to low fission gas release. After a burnup of 5.4% FIMA (4.4 × 10^4 MWd/t) at a fuel temperature of 890 °C, a mixed carbide having 83.6% of the theoretical density released only 0.11% of the fission gas. Lambert et al. [94] could show clearly the influence of the temperature on the gas release. No effect was found for the fabrication method of the fuel (arc-cast or sintered mixed carbide), however. Lambert et al. [94] determined from microstructure analysis of fuel cross sections that fraction of the fuel, which was exposed to temperatures above 1 050 °C during the irradiation, under the assumption, that below 1 000 °C less than 2% of the gas was released from the fuel. It was calculated that this fuel fraction released some 26 to 56% of the fission gas at temperatures >1 050 °C.

Bagley et al. [95] reported that below 1 000 °C and up to a burnup of 8% FIMA (6.6 × 10^4 MWd/t) one had to reckon with 0.5% gas release, whereas this value rose to 1.5% release at 1 290 °C, for a burnup below 5% FIMA (4.1 × 10^4 MWd/t). The authors supposed, that there should be some critical value of burnup, dependent on the temperature, above which the gas bubbles at the grain boundaries and the gas release increased rapidly. However, Lambert et al. [94] could not confirm this assumption up to the burnup values attained in their experiments. Paris [96, 97] determined later, on the basis of numerous irradiation experiments, the critical burnup at various temperatures:

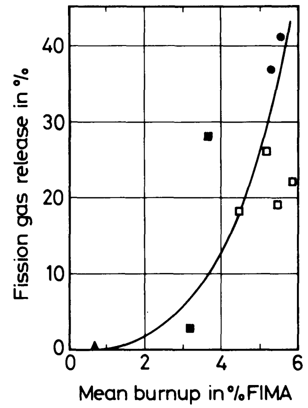
8.8% FIMA (7.23 × 10^4 MWd/t) at 900 °C,
7.1% FIMA (5.84 × 10^4 MWd/t) at 1 000 °C, and
4.4% FIMA (3.62 × 10^4 MWd/t) at 1 200 °C.

Vibrationally compacted rods expectedly released more gas than the sintered pellets at a similar free gas volume, as described by Parkinson after a burnup of 4.6 or 5.4% FIMA (3.78 or 4.44 × 10^4 MWd/t) [98].

A vibrationally compacted fuel was developed at the Eidgenoessisches Institut für Reaktorforschung (EIR) in Würenlingen, consisting of slightly hyperstoichiometric spherical particles of the mixed carbide, which were produced according to the sol-gel process [99 to 101], and had a density of more than 90% of the theoretical. Stratton, Smith [100, 101] reported a clear relationship between the burnup and the fission gas release from these fuel rods, as seen in **Fig. 1-153**, p. 240.

The first reports on the irradiation program of the Commissariat a l'Energie Atomique (CEA) appeared in 1965. The gas release from Na-bonded (U,Pu)C fuel rods irradiated in a thermal neutron flux after a burnup of about 2% FIMA (1.6 × 10^4 MWd/t) at a fuel temperature between 1 075 and 1 190 °C was 0.13% [102, 103]. In an epithermal flux, even at a fuel temperature of

Fig. 1-153



Effect of the burnup on the fission gas release from vibrationally compacted (U,Pu)C fuel rods [101]. ▲, ■, □ thermal neutron flux; ● epithermal neutron flux. Open symbols indicate failed pins.

1 357 °C, not more than 0.2% of the gas was released. These values lay in the range of the recoil release. Therefore, as Mustelier supposed [102], some of the fission products were trapped in the sodium and could not be measured. In much later experiments, Mikailoff, Clottes [107] could prove that the sodium indeed retained some 10 to 20% of the released gas. Sintered (U,Pu)C, with a density >90% of the theoretical and <5% $(U,Pu)_2C_3$ content, released after a burnup of 2.73×10^4 MWd/t at a linear power density of about 800 W/cm on the average 4.3% of the fission gas [105, 107]. This value was interpreted in terms of irradiation-induced diffusion of the fission gases [105, 106]. The instantaneous release rate (R/B) of a fission gas from mixed carbides could be described according to Mikailoff [106] after a burnup of 6.0 $\times 10^4$ MWd/t by means of eq. (4)

$$\log (R/B)_i = K + \alpha \log \lambda_i \qquad (4)$$

where K and α are constants ($0.5 < \alpha < 1$) and λ_i is the decay constant of the i-th nuclide. Mikailoff [106] did not see, however, an effect of the burnup on the release of ^{133}Xe (the value of R/B was 3×10^{-2} at a linear power density of 400 to 1 250 W/cm). The same R/B ratio was found in these experiments also for stable fission gases.

Combette [108] found that the release R of the fission gases at T $\leq$1 100 °C increased linearly with the square root of the time t, according to eq. (5)

$$R = A + B\,t^{1/2} \qquad (5)$$

where A and B are constants. This law is in accordance with the irradiation results. At higher temperatures the release was strongly temperature dependent.

Two studies at the EURATOM Transurane Institute (TUI) reported data on fission gas release from mixed carbides [109, 110]. Coquerelle et al. [109] attained burnup values of 13% FIMA (10.7×10^4 MWd/t) of mixed carbide samples having 75, 82, and 85% of the theoretical density placed in special capsules after 3 months irradiation in a thermal flux at about 1 200 °C They found, on the whole, a considerable amount of gas release (about 50%). Richter et al.

[110] conducted an irradiation experiment at the Dounreay Fast Reactor on (U,Pu)C having 88.2% of the theoretical density, up to a burnup of 1.3% FIMA (1.07×10^4 MWd/t). Since the temperature rose at the beginning of the experiment to 2000 °C, a large fraction of the total fission gas was released (64%), as expected.

An elaborated post-irradiative examination method was developed at the Kernforschungszentrum Karlsruhe (KfK) for the determination of the various fission gases in the Mol-11 [111] and Mol-15 [112] experiments. By means of this procedure, the amounts of fission gases residing in the free volume inside the cladding, in closed pores, and in the dissolved state in the fuel could be determined. In the Mol-11 experiment, between 27 and 37% of the gas was released after a burnup of 3.7 to 7.0% FIMA (3.04 to 5.75×10^4 MWd/t). An increase of the gas release with the burnup was clearly seen. These high values of the release were in good agreement with the results of other authors, considering the low initial density ($\approx$83% of the theoretical) and the high central temperature. The Mol-15 experiment showed similar results. After a burnup of 7.3 to 8.7×10^4 MWd/t, a release of 14 to 28% of the noble gases could be determined. It should be noted that the remainder resided mainly in pores of the fuel, and only 0.1 to 0.2 of it in the fuel lattice.

The effect of foreign elements on the irradiation behavior of mixed fuel carbides was determined in a series of studies. Additions of Fe [69, 70], Cr [69, 70], Ti [104], and Mo [107] should stabilize the mixed carbide, whereas Ni [73] and Ca [102, 103] were used as sintering aids. With regard to the fission gas release, only a small positive effect of Cr, was noted. The fission gas release at a burnup of 5 to 6% FIMA (4.1 to 4.9×10^4 MWd/t) from hypostoichiometric (U,Pu)C with or without Fe was about twice that found for the Cr-stabilized mixed carbide. Accurate measurements [70] gave a factor near 3 (60% to 18.7%). The effect of Ni (about 0.1 wt%) seemed to be considerably smaller, and was not commented on by the authors [75, 76]. No effect on the fission gas release appeared to be seen for Ca [102, 103], whereas Mo made this property of the mixed carbide even much worse.

Hoffmann, Johnson [113] developed a model for the description of the fission gas release, and examined it in the light of results from 19 (U,Pu)C fuel elements, which had been irradiated at ANL. The total release of the fission gas consisted, according to these authors, of three parts:

1. A part caused by recoil atoms, which was independent of the conditions of the irradiation, or depended on the geometry of the fuel.

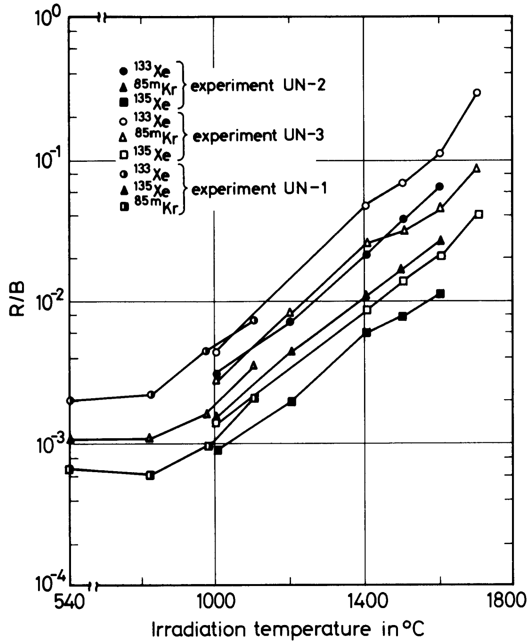
2. A part that was released from the outer regions of the fuel, and which was proportional to the square root of the time, to an exponential function of the "effective" activation energy divided by the temperature, and to the fraction of the fuel that was within this region.

3. A part that was released from the inner region of the fuel, and which depended on various empirical factors, including the central temperature, the density, the grain size, and the stress on the fuel.

1.2.3.4.4 Fission Gas Release from Nitride Fuels

Extensive studies of the behavior of uranium mononitride, UN, on irradiation have been conducted at the Battelle Memorial Institute, BMI, in Ohio [7, 114 to 116, 130]. Melehan, Gates [7] measured the R/B values – as they did for UC – during the irradiation in the temperature range 540 to 1700 °C, **Fig. 1-154**, p. 242. They found that up to 800 °C the R/B values remained independent of the temperature, but started to increase exponentially above this temperature.

Fig. 1-154



Fission gas release from sintered uranium mononitride of various densities at various temperatures [7]. Experiment UN-1: $\rho = 96\%$ of the theoretical density (TD); experiment UN-2: $\rho = 95\%$ TD; experiment UN-3: $\rho = 92\%$ TD.

The density of sintered samples played a minor, but still recognizable role in the release of the fission gas, as Fig. 1-154 clearly indicates. A comparison of these data with those for uranium carbides, studied by the same authors, showed that at a given density, the nitrides released less fission gas than the carbides. This statement was supported also by other data in further publications [117, 127, 130].

Melehan, Gates [7] could not observe the decomposition of UN at $t \geq 1\,500\,^{\circ}C$, expected on thermodynamic data [128]. Neither was such a decomposition found in the post-irradiation examination. Wullaert et al. [114] and Bugl, Keller [115] reported less than 0.6% fission gas release from isostatically hot-pressed UN, having a density higher than 95% of the theoretical, that had been irradiated at an initial temperature of 1 260 °C and a final one of 576 °C to a burnup of 3.8% FIMA (3.10×10^4 MWd/t).

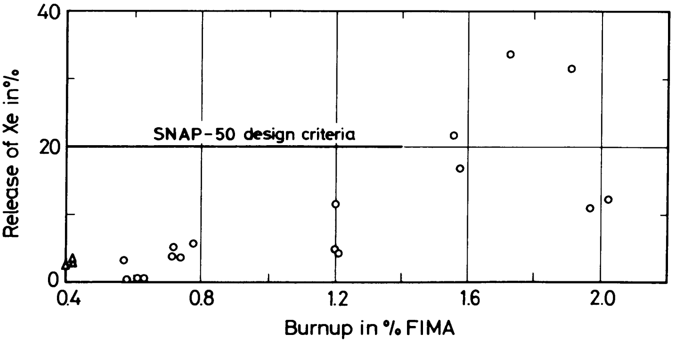
Martin et al. [116] irradiated sintered, isostatically hot-pressed and arc-cast UN up to burnup values of 5 to 6% FIMA (4.1 to 4.9×10^4 MWd/t). The best retention ability was obtained for sintered ($\rho = 87\%$ of the theoretical) and for arc-cast, partly monocrystalline ($\rho \approx 100\%$ of the theoretical) UN. This finding, unexpected at the first glance, was explained by the structure of the porosity of the samples. Metallographic examination showed that the pores of the sintered material were closed, so that gas released into them was retained. The uptake of the gas by the large grains of the arc-cast material also prevented its migration to the grain boundaries and release there. The grain boundaries of the isostatically pressure-sintered material were very numerous, because of the small grains that were present, and they let much fission gas through to the surface and to being released. Hilbert et al. [130] analyzed this effect in detail, in the present connection and in connection with the different swelling behavior of UC and UN, and established that UC (having both high or low density) released more fission gases than did UN (which released 1 to 5% for high, 20% for low density material), when irradiated at 1 700 °C up to 2×10^{20} fissions/cm^3 (0.5×10^4 MWd/t).

DeCrescente et al. [41, 117] could also establish that UN retains the fission gases better than did UC up to burnup values of 2% FIMA (1.6×10^4 MWd/t) at 2350 to 2850 °F (1 290 to 1 565 °C). **Fig. 1-155** shows the dependence of the fission gas release on the burnup. The UN fulfills the requirements for the SNAP-50 reactor designed at the Connecticut Advanced Nuclear Engineering Laboratory (CANEL), releasing less than 20% of the fission gas up to 1.4% FIMA (1.14×10^4 MWd/t) [117]. Like Hilpert et al. [130], also DeCrescente et al. [117] analyzed the microstructure of the fuel and found, that after a burnup of 0.19% FIMA (0.155×10^4 MWd/t, 400 h irradiation) at 2 025 °F (1 110 °C), fission gas bubbles having diameters of 0.1 μm formed in the UN, in the grains or at the grain boundaries.

The migration and agglomeration of the fission gases depended, according to DeCrescente [117], on the temperature, the temperature gradients, and the self-diffusion in the fuel. Since the latter quantity was about two orders of magnitude higher in UC than in UN, the differences in gas release between UC and UN become evident.

Albrecht et al. [118] attained burnup values of 2.3×10^{20} fissions/cm^3 (0.58×10^4 MWd/t) of UN at temperatures of 1307 to 1417 °C. The retention of the fission gas was better than 98% (the release less than 2%), independent of the density or the grain size of the material. Watanabe et al. [49] could, however, find hardly any differences between UC, UN, and U(C,N) solid solutions up to a maximal temperature of 1 360 °C and burnup of 1.20 to 2.10×10^4 MWd/t. All the release values were about 1%, independent of the composition. Irradiation of uranium carbide nitrides ("carbonitrides") at the Kernforschungsanlage (KFA) Jülich showed that at burnup values up to 1% FIMA (0.82×10^4 MWd/t) at temperatures from 1 300 to 1 600 °C the carbide nitride released only slightly more gas than did melted UC. At high burnup ($\approx 7.5 \times 10^4$ MWd/t), however, the gas release attained about 50% of the yielded.

Fig. 1-155

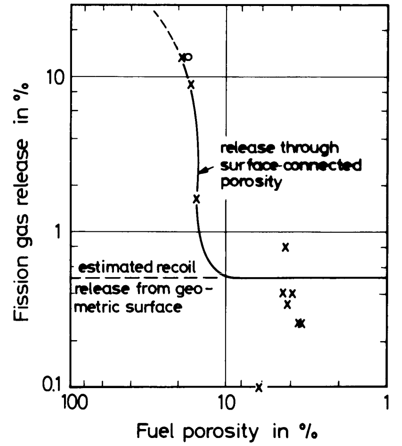


Fission gas release (Xe) from sintered UN at irradiation temperatures of 1 290 to 1 565 °C [117].

Biddle [121] studied the release of ^{133}Xe from powdered UN and UC_xN_{1-x}, and determined the diffusion coefficient of xenon in these materials. The author pointed out, that the ^{133}Xe release from the carbide nitride was comparable to that from UC, and the release from UN with that from UO_2.

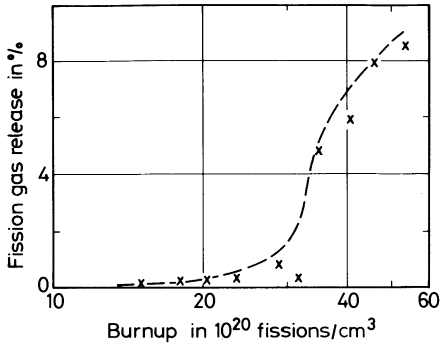
Bauer et al. [122 to 124] reported results on (U,Pu)N obtained at the BMI. The dependence of the fission gas release from the mixed nitride on the porosity of the fuel is shown in **Fig. 1-156**. The data are based on irradiation experiments, in which burnup values between 3.0 and 9.0×10^4 MWd/t were attained at a mean fuel temperature of 1100 °C ($t_{max} \leqq 1280$ °C). Fig. 1-156 shows the close connection between the fuel porosity and the fission gas release. It is seen that above 18% porosity a connection between the pores and the surface is established. The release of fission gas from samples of low porosity is consistent with the calculated release by fission recoil from the geometric surfaces. At higher values of the burnup (between 9.0 and 15.0×10^4 MWd/t) and at the same temperature the mixed nitrides of higher densities, too, start to release large quantities of fission gas (**Fig. 1-157**). The sharp increase of the release could not be interpreted by Bauer et al. [123], since no major structural changes or porosity development that could account for the increase are obvious. A further effect, that caused the enhanced fission gas release, according to the authors [123, 124], should be the content of a U_2N_3 phase, which, as was known, could be stabilized even above 1400 °C by oxygen impurities. An increase in the irradiation temperature (1550 to 1655 °C), finally, also increased considerably the fraction of the fission gas which was released (to about 17%) from the mixed nitrides, as was expected. There existed only a few results for irradiation experiments of (U,Pu)N in a fast neutron flux [125]. From these data some indication of increased gas release with increase in burnup is assumed, but the data are insufficient to permit a firm conclusion up to the burnup attained, 7.4% FIMA (6.03×10^4 MWd/t), and was falsified by the different power densities (hence central temperatures) of the fuel.

Fig. 1-156



Dependence of the fission gas release from (U,Pu)N on the porosity [123]. (×) Thermal irradiation data 16 to 40 kW/ft, $\leqq 32 \times 10^{20}$ fissions/cm^3, $t_{centerline} \leqq 1280$ °C. (○) Fast irradiation data 24.8 kW/ft, max., 10.1×10^{20} fissions/cm^3; $t_{centerline} \leqq 1760$ °C. 1 ft = 0.3048 m.

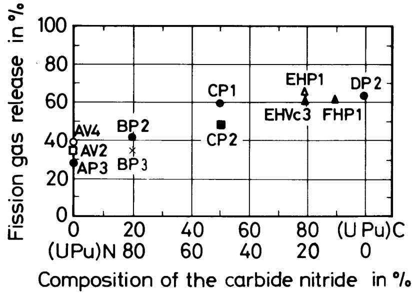
Fig. 1-157



Fission gas release from high density (>94% of the theoretical density) (U,Pu)N after high burnups.

Results from the CEA concerning irradiation experiments in the thermal and epithermal neutron flux, reported by Mikailoff et al. [103], also showed, that (U,Pu)N as also (U,Pu)(C,N) released only small amounts of fission gas (<1%) at temperatures up to 1 400 °C, however, after a small burnup of 0.155×10^4 MWd/t. Small differences were attributed to cracks, suffered mainly by the mixed nitride. A considerably higher release of gas was found by Mikailoff, Clottes [107] after a burnup of 2.70×10^4 MWd/t. These fuels released on the average 4.9 to 5.3% of the total gas, irrespective of the composition ((U,Pu)C,(U,Pu)N, or (U,Pu)(C,N)), with individual values varying between 2.2 and 9.1%.

Fig. 1-158



Fission gas release as a function of the carbon content in mixed carbide nitrides [127]. Application as pellets: ▲, ●, ■, ×; as Vipac-fuel: △, ○, □. Burnup: ▲, △: 1.05%; ●, ○ 1.30%; ×, □, 2.36%; □, ■ 3.79%.

References for 1.2.3.4 on pp. 246/9

Richter et al. [110] reported the release of fission products ^{131}Xe and ^{132}Xe gases from mixed nitrides, mixed carbides, and mixed carbide nitrides at very high temperatures (starting temperature 2000 °C) but low burnup values, less than 1.3% FIMA (1.06×10^4 MWd/t), in a fast neutron flux. They determined a relative release of 29 to 39% for the mixed nitrides, whereas the values for the mixed carbides and mixed carbide nitrides were 44 to 64%.

Coquerelle [127] summarized numerous irradiation experiments made at TUI (Transurane-Institut Karlsruhe). After a burnup of between 1 and 5% FIMA (0.82 to 4.10×10^4 MWd/t) he observed an increase of the fission gas released with an increase of the carbon content from (U,Pu)N to (U,Pu)($C_{0.5}N_{0.5}$), **Fig. 1-158**, p. 245. At such high gas release values, however, the effects of neither the burnup nor the fuel structure (sintered pellets or vibrationally compacted fuel rods) on the retention of the gaseous fission products could be recognized.

References for 1.2.3.4:

[1] D. I. Sinizer, B. A. Webb, S. Berger (Radiat. Damage Reactor Mater. Part Proc. Symp., Venice 1962 [1963], pp. 287/318; NAA-SR-7248 [1962] 1/47; N.S.A. **16** [1962] No. 29440). – [2] K. Iwamoto, J. Oishi (J. Nucl. Sci. Technol. **5** [1968] 387/96). – [3] H. Matsui (J. Nucl. Mater. **56** [1975] 161/8). – [4] H. Matsui, K. Sakanishi, T. Kirihara, T. Tamai (J. Nucl. Sci. Technol. **10** [1973] 512/5). – [5] F. A. Rough, A. W. Hare, R. B. Price, S. Alfant (Nucl. Sci. Eng. **7** [1960] 111/21).

[6] A. W. Hare, F. A. Rough (BMI-1452 [1960] 1/31; N.S.A. **14** [1960] No. 22108). – [7] J. B. Melehan, J. E. Gates (BMI-1701 [1964] 1/56; N.S.A. **19** [1965] No. 6358). – [8] C. A. Smith, F. A. Rough (NAA-SR-3625 [1959] 1/17; N.S.A. **13** [1959] No. 15356). – [9] H. Pearlman (NAA-SR-Memo-4631 [1959] 1/16; N.S.A. **14** [1960] No. 9818). – [10] B. A. Webb, R. D. Hahn (Trans. Am. Nucl. Soc. **5** [1962] 230).

[11] R. D. Hahn (NAA-SR-7696 [1963] 1/32; N.S.A. **17** [1963] No. 16650). – [12] C. W. Wheelock (NAA-SR-Memo-9757 [1965]; NAA-SR-10751 [1965] 1/81; C.A. **64** [1966] No. 6040). – [13] J. E. Frank, R. E. Forester, J. S. Buck (NAA-SR-11440 [1966] 1/49; N.S.A. **20** [1966] No. 45113; C.A. **66** [1967] No. 90698). – [14] B. T. Bradbury, J. E. Cole, B. R. T. Frost, J. D. B. Lamberts (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 879/95). – [15] B. T. Bradbury, J. E. Cole, B. R. T. Frost, J. D. B. Lamberts (Proc. 4th Uranium Carbides Conf., Hartford, Conn., 1963; TID-7676 [1964] 170/82; AERE-R-4323 [1963]; N.S.A. **18** [1964] No. 14377).

[16] M. Handa, S. Yamagishi, T. Fukuda, K. Shiba, Y. Takahashi (J. Nucl. Sci. Technol. **11** [1974] 387/94). – [17] R. L. Ritzman, R. B. Price, D. L. Morrison (Trans. Am. Nucl. Soc. **12** [1969] 79). – [18] R. L. Ritzman, A. J. Markworth, W. Oldfield, W. Chubb (Nucl. Appl. Technol. **9** [1970] 167/87). – [19] O. Gautsch, C. Mustacchi (EUR-2749.e [1966] 1/20; N.S.A. **20** [1966] No. 19255). – [20] A. Schürenkämper, O. Gautsch (EUR-3556.f [1967] 1/20; N.S.A. **22** [1968] No. 2708).

[21] H. Matzke, F. Springer (Radiat. Eff. **2** [1969] 11/8). – [22] H. Matzke, C. Ronchi (Phys. Met. React. Fuel. Elem. Proc. Intern. Conf., Berkeley, U.K., 1973 [1975], pp. 259/65). – [23] H. Blank, H. Matzke (Radiat. Eff. **17** [1973] 57/64). – [24] A. Groff (CEA-R-4742 [1976] 1/101; INIS Atomindex **7** [1976] No. 268115). – [25] R. D. Hahn (NAA-SR-11134 [1965] 1/54; N.S.A. **19** [1965] No. 42905).

[26] H. Furuya, J. Monatsu, T. Muto, A. Doi, K. Inoue (J. Nucl. Sci. Technol. **8** [1971] 256/61; PNC-N-831-70-02 [1970] 35/45; CONF-700345-3 [1970]; Ann. Meeting At. Energy Soc. Japan, Hiratsuka, Jap., 1970; N.S.A. **26** [1972] No. 33849). – [27] D. G. Freas, P. B. Shumaker, J. H. Stang, J. E. Gates (BMI-1622 [1963/73]). – [28] R. W. Weeks, R. O. Scattergood, S. R. Pati (J. Nucl. Mater. **36** [1970] 223/9). – [29] R. D. MacDonald (J. Nucl.

Mater. **22** [1967] 109/11). – [30] M. A. DeCrescente, E. G. Selleck (PWAC-476 [1965] 1/16; N.S.A. **20** [1966] No. 5892).

[31] R. S. Barnes, R. S. Nelson (Proc. Brit. Ceram. Soc. **7** [1967] 343/54). – [32] A. J. Markworth (J. Appl. Phys. **43** [1972] 2047/52). – [33] B. L. Eyre, R. Bullough (J. Nucl. Mater. **26** [1968] 249/66). – [34] K. Q. Bagley, W. Batey, P. Paris, W. M. Sloss, G. P. Snape (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 313/25). – [35] A. W. Hare, S. Alfant, F. A. Rough, D. I. Sinizer (Nucl. Sci. Eng. **10** [1961] 24/30).

[36] A. W. Hare, F. A. Rough (BMI-1491 [1961] 1/27; N.S.A. **15** [1961] No. 7847). – [37] J. B. Melehan, A. J. Markworth, J. S. Perrin, R. A. Wullaert, W. Chubb, J. E. Gates (BMI-1806 [1967] 1/40). – [38] R. F. Hilpert, V. W. Storhok, W. Chubb, D. L. Keller (Trans. Am. Nucl. Soc. **14** Suppl. No. 1 [1971] 35/6). – [39] R. D. MacDonald, W. G. Mathers, A. M. Tachis, J. E. May (High Temp. Nucl. Fuels Proc. Symp., Delavan, Wisc., 1966; Met. Soc. Conf. Proc. **42** [1966] 165/81; C.A. **71** [1971] No. 17894). – [40] C. E. Carlson, F. F. Felber (TIM-770-Suppl. 4 [1964/71]).

[41] M. A. DeCrescente, K. J. Kelly, P. V. Treciokas (TIM-870 [1964/73]). – [42] M. A. DeCrescente, M. S. Freed, S. D. Caplow (PWAC-489 [1965/73]). – [43] J. Crane, E. Gordon (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], pp. 896/918). – [44] H. Pearlman (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 438/48). – [45] R. D. Hahn (NAA-SR-9999 [1964] I-B-48/50; N.S.A. **19** [1965] No. 10675).

[46] H. Watanabe, M. Kurihara, J. Shimokawa, M. Ichikawa, M. Uchida (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 361/74). – [47] T. S. Men'shikova, F. G. Reshetnikov, G. A. Rymashevskii, I. G. Lebedev et al. (Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 10, pp. 217/38; A/CONF-49-P-454 [1971] 1/32; N.S.A. **25** [1971] No. 52468; CONF-710901-472 [1971]; C.A. **76** [1971] No. 134736). – [48] A. Ya. Ladygin, I. A. Efimov, Yu. L. Mikhatchev, Yu. I. Aleksandrov et al. (Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 10, pp. 199/215; A/CONF-49-P-707 [1971] 1/34; CONF-71901-417 [1971]; C.A. **76** [1972] No. 134738). – [49] E. F. Davydov, A. A. Maiershin, V. N. Syuvez et al. (At. Energ. [USSR] **39** [1975] 33/8; Soviet. At. Energy **39** [1975] 608/11; INIS Atomindex **7** [1976] No. 262751). – [50] V. A. Tsykanov, V. M. Gryazev, E. F. Davydov, V. I. Kuz'nin, A. A. Maiershin, V. N. Syuzev, I. S. Golovnin, T. S. Men'shikova, Yu. K. Bibliashvili, R. B. Kotel'nikov (At. Energ. [USSR] **42** [1977] 378/82; KFK-tr-536 [1977] 1/17; INIS Atomindex **9** [1978] No. 355481).

[51] A. Accary, R. Darras, R. Caillat (Radiat. Damage Reactor Mater. Part Proc. Symp., Venice 1962 [1963], pp. 275/86). – [52] B. R. T. Frost (J. Nucl. Mater. **10** [1963] 265/300). – [53] J. B. Melehan, V. W. Storhok, R. J. Burian, M. Kangilaski, R. A. Wullaert (REIC-27 [1963] 1/80; N.S.A. **17** [1963] No. 34491). – [54] M. D. Freshley (in: O. J. Wicke, Plutonium Handbook. A Guide to the Technology, Gordon and Breach, New York-London 1967, pp. 643/706). – [55] F. B. Litton (LA-3799 [1967] 1/22; N.S.A. **22** [1968] No. 21759).

[56] R. A. Wullaert, J. M. Fackelmann, W. Chubb (BMI-1799 [1967] 1/30; N.S.A. **21** [1967] No. 26925). – [57] W. Dienst (in: K. Kummerer, F. Thümler, KFK-1111 [1969] 1/399; EUR-4315.d-Chap. 9 [1969]; N.S.A. **24** [1970] No. 17226). – [58] J. A. L. Robertson (Irradiation Effects in Nuclear Fuel, Chap. 4, Gordon and Breach, New York-London 1969, pp. 200/28). – [59] B. D. Zope, V. K. Moorthy (BARC-I-61 [1970] 1/50; N.S.A. **25** [1971] No. 24625). – [60] S. J. Rothman, L. T. Lloyd, R. Weil, A. L. Harkness (ANL-5971 [1959] 1/39; Trans. Met. Soc. AIME **218** [1960] 605/7; N.S.A. **13** [1959] No. 21166).

[61] H. Shaked (UCRL-10462 [1962] 1/107; N.S.A. **17** [1963] No. 21670). – [62] J. H. Kittel, L. A. Neimark, R. Carlander, O. L. Kruger, R. C. Lied (ANL-FGF-399 [1962] 1/6; N.S.A. **17** [1963] No. 12711; ANL-6678 [1963] 1/15; UAC-7022 [1962]; N.S.A. **18** [1964] No. 5813). – [63] L. A. Neimark, J. H. Kittel, C. C. Crothers (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], Vol. 2, pp. 864/78). – [64] L. A. Neimark, R. Carlander (ANL-

6868 [1964] 53/7). – [65] L. A. Neimark, J. E. Ayer, O. L. Kruger, T. W. Latimer, C. M. Walter (Proc. Conf. Safety Fuels Core Des. Large Fast Power React., Argonne, Ill., 1965; ANL-7120 [1965] 314/27; CONF-651009 [1965] 314/27; N.S.A. **20** [1966] No. 38467).

[66] L. A. Neimark (Trans. Am. Nucl. Soc. **9** [1966] 415). – [67] F. L. Brown, L. A. Neimark, B. J. Koprowski, J. H. Kittel, J. E. Ayer, O. L. Kruger (Trans. Am. Nucl. Soc. **10** [1967] 473/5). – [68] T. W. Latimer, F. L. Brown, L. A. Neimark (Trans. Am. Nucl. Soc. **12** [1969] 87/8). – [69] P. J. Levine, B. L. Harbourne, A. Biancheria, T. W. Latimer, L. A. Neimark (Trans. Am. Nucl. Soc. **13** [1970] 606/7). – [70] B. L. Harbourne, P. J. Levine, A. Biancheria, T. W. Latimer, L. A. Neimark (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 869/94; Trans. Am. Nucl. Soc. **14** [1971] 41/2).

[71] A. Strasser (Proc. Conf. Breed. Econ. Safety Large Fast Power Reactors, Argonne, Ill., 1963; ANL-6793 [1963] 297/310). – [72] A. Strasser, J. Cihi, W. Sheridan, V. Storhok (Compounds Interest Nucl. Reactor Technol. Proc. Symp., Boulder, Colo., 1964; Inst. Mining Met. Petrol Eng. Inst. Metals Div. Spec. Rept. Ser. No. 13; Nucl. Met. **10** [1964] 729/52). – [73] A. Strasser, D. Stahl, K. Taylor, J. Andersen (UNC-5081 [1964] 1/97; N.S.A. **19** [1965] No. 24923). – [74] A. Strasser, J. Cihi (UNC-5134-Vol. 2 [1965] 1/196; N.S.A. **20** [1966] No. 27593). – [75] A. Strasser, C. Wheelock, L. Neimark (Fast Reactor Technol. Proc. ANS Top. Meeting, Detroit, Mich., 1965; ANS-100 [1965] 126/56).

[76] A. Strasser, J. Cihi, S. Hurwitz, R. Martin (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 979/1003). – [77] A. Strasser, D. Stahl, R. Martin (Trans. Am. Nucl. Soc. **10** [1967] 472/3). – [78] A. Strasser, J. H. Kittel (Plutonium Fuel Technol Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1968] 460/89). – [79] A. Strasser, M. Montgomery, R. Powers (Fast Reactor Fuel Elem. Technol. Proc. ANS Conf., New Orleans 1971, pp. 849/68; Trans. Am. Nucl. Soc. **14** Suppl. 1 [1971] 40/1; GU-5286 [1972] 1/19; C.A. **77** [1972] No. 108272). – [80] M. Montgomery, A. Strasser (Trans. Am. Nucl. Soc. **15** [1972] 754/5).

[81] C. Grando, M. Montgomery, A. Strasser (Fast Reactor Fuel Elem. Technol. Proc. ANS Conf., New Orleans 1971, pp. 771/9; Trans. Am. Nucl. Soc. **14** Suppl. 1 [1971] 36/47; GU-5288 [1972] 1/8). – [82] M. Montgomery, C. Grando, A. Strasser (Trans. Am. Nucl. Soc. **14** [1971] 595/6). – [83] J. O. Barner (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 819/47; LA-4669 [1971] 1/29; N.S.A. **25** [1971] No. 34358). – [84] J. O. Barner, T. W. Latimer, J. F. Kerrisk, D. Bost, J. L. Green (Trans. Am. Nucl. Soc. **19** [1974] 91/2). – [85] T. W. Latimer, D. S. Bost, J. F. Kerrisk, J. O. Barner, J. L. Green (LA-6077-MS [1975]).

[86] T. W. Latimer, J. O. Barner, J. F. Kerrisk, J. L. Green (Trans. Am. Nucl. Soc. **19** [1974] 91). – [87] T. W. Latimer, J. O. Barner, J. F. Kerrisk, J. L. Green (LA-6249-MS [1976] 1/27; INIS Atomindex **7** [1976] No. 273709). – [88] P. E. Rexroth, R. L. Petty (Trans. Am. Nucl. Soc. **24** [1976] 136). – [89] J. O. Barner, T. W. Latimer, J. F. Kerrisk, R. L. Petty, J. L. Green (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 268/98). – [90] B. R. T. Frost, B. T. Bradbury, L. B. Griffiths (Radiat. Damage Solids Reactor Mater. Part Proc. Symp., Venice 1962 [1963], pp. 219/39).

[91] B. T. Bradbury, B. R. T. Frost, J. R. Findlay (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 949/78). – [92] B. T. Bradbury, B. R. T. Frost (High Temp. Nucl. Fuels Proc. Symp., Delavan, Wisc., 1966; Met. Soc. Conf. Proc. **42** [1966] 329/52; C.A. **71** [1969] No. 17926). – [93] B. R. T. Frost, J. M. Horspool, R. G. Bellamy (Plutonium Fuel Technol. Proc. Intern. Symp., Scottsdale, Ariz., 1967; Nucl. Met. **13** [1967] 490/506). – [94] J. D. B. Lambert, R. Paris, J. E. Bainbridge (AERE-R-6740 [1971] 1/22). – [95] K. Q. Bagley, E. Edmonds, H. J. Powell, R. G. Bellamy, R. Paris, J. M. Horspool (Fuel Fuel Elem. Fast React. Proc. IAEA Symp., Brussels 1973 [1974], Vol. 1, pp. 87/100).

[96] R. Paris (AERE-R-7804 [1974] 1/15; N.S.A. **31** [1975] No. 23151). – [97] R. Paris (Microstruct. Sci. Proc. Int. Conf. 1974, Vol. 3, Pt. B, pp. 835/59; C.A. **85** [1976] No. 38410). – [98] N. Parkinson (High Temp. Nucl. Fuels Proc. Symp., Delavan, Wisc., 1966;

Met. Soc. Conf. Proc. **42** [1966] 297/309). – [99] L. Smith, K. L. Peddicord, P. Buetzer, P. Rickenbacher, B. Buergisser (EIR-265 [1974] 1/99; N.S.A. **31** [1975] No. 10380). – [100] R. W. Stratton (Trans. Am. Nucl. Soc. **24** [1976] 142/4).

[101] R. W. Stratton, L. Smith (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 348/60). – [102] J. P. Mustelier (Plutonium 1965 Proc. 3rd Intern. Conf., London 1965 [1967], pp. 1006/8). – [103] H. Mikailoff, J. P. Mustelier, J. Bloch, J. Leclere, L. Hayet (CEA-R-3223 [1967] 1/61; EURFNR-317 [1967]; EUR-3447.f [1967]; N.S.A. **21** [1967] No. 34973). – [104] H. Mikailoff, J. Leclere, B. Kryger, J. Bloch, M. Conte (CEA-N-1186 [1970] 1/92; N.S.A. **25** [1971] No. 52472; EURFNR-688 [1969] 1/103; N.S.A. **24** [1970] No. 14964). – [105] G. Clottes, M. Dieumegard, J. P. Dufayet, A. Groff, B. Kryger, H. Mikailoff, J. L. Ratier (Fuel Fuel Elem. Fast React. Proc. IAEA Symp., Brussels 1973 [1974], Vol. 1, pp. 113/27).

[106] H. Mikailoff (Trans. Am. Nucl. Soc. **19** [1974] 89/90). – [107] H. Mikailoff, G. Clottes (Bull. Inform. Sci. Tech. Comm. At. [France] No. 196 [1974] 41/8; ANL-Trans-977 [1974]; C.A. **82** [1975] No. 146721). – [108] P. Combette (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 343/7). – [109] M. Coquerelle, J. Gabolde, P. Werner (Reaktortagung, Hamburg 1972, pp. 423/6). – [110] K. Richter, M. Coquerelle, J. Gabolde, P. Werner (Fuel Fuel Elem. Fast React. Proc. IAEA Symp., Brussels 1973 [1974], Vol. 1, pp. 71/84).

[111] D. Freund, H. Elbel, H. Steiner (KFK-2268 [1976] 1/44; INIS Atomindex **7** [1976] No. 275252). – [112] H. Steiner, D. Freund, O. Jakobi, P. Weimer (KFK-2451 [1977] 1/80; INIS Atomindex **8** [1977] 334682). – [113] G. L. Hoffmann, D. L. Johnson (Trans. Am. Nucl. Soc. **21** [1975] 179/80). – [114] R. A. Wullaert, J. E. Gates, J. Bugl (Am. Ceram. Soc. Bull. **43** [1964] 834/41; BMI-1638 [1963] 1/35; EURAEC-760 [1963]; N.S.A. **17** [1963] No. 32668). – [115] J. Bugl, D. L. Keller (Nucleonics **22** [1964] 66/70).

[116] R. L. Martin, W. J. Zielenbach, V. W. Storhok, D. L. Keller, J. E. Gates (BMI-1731 [1965] 1/30; N.S.A. **20** [1966] No. 888). – [117] M. A. DeCrescente, M. S. Freed, S. D. Caplow (PWAC-488 [1965/73]). – [118] E. D. Albrecht, A. J. Rothman, J. D. Lee, J. M. Johnson, W. N. Hayes (Develop. Irradiat. Testing Technol. Proc. Natl. Symp., Sandusky, Ohio, 1969, pp. 595/629). – [119] J. Ali Khan, A. Naoumidis, G. Pott (Fast Reactor Fuel Fuel Elem. Proc. Intern. Meeting, Karlsruhe 1970, pp. 454/73; JUL-703-RW [1970] 1/17; CONF-700924-4 [1970]; N.S.A. **25** [1971] No. 24622). – [120] G. Pott, M. Herren, A. Naoumidis (Results Five Years BR2 React. Util. Proc. Symp., Mol, Belg., 1973 [1974], pp. 227/32).

[121] P. Biddle (AERE-R-4700 [1964] 1/11; N.S.A. **19** [1965] No. 2715). – [122] A. A. Bauer, V. W. Storhok (Plutonium 1970 Proc. 4th Intern. Conf. Plutonium Other Actinides, Santa Fe 1970; Nucl. Met. **17** [1970] 532/44). – [123] A. A. Bauer, J. B. Brown, E. O. Fromm, V. W. Storhok (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 785/817). – [124] A. A. Bauer (Reactor Technol. **15** [1972] 87/104). – [125] A. A. Bauer, P. Cybulskis (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 299/312).

[126] H. Matzke, C. Ronchi (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 218/44). – [127] M. Coquerelle (Reaktortagung, Düsseldorf 1976, pp. 538/41). – [128] J. Bugl, A. A. Bauer (J. Am. Ceram. Soc. **47** [1964] 425/9). – [129] J. E. Frank, R. E. Forester, J. S. Buck (AI-CE-Memo-9 [1966]). – [130] R. F. Hilpert, V. W. Storhok, W. Chubb, D. C. Keller (Fast Reactor Fuel Elem. Technol. Proc. Conf., New Orleans 1971, pp. 753/69).

[131] J. Crane, E. Gordon (UNC-5080 [1964] 1/80; N.S.A. **18** [1964] No. 39828). – [132] J. Crane, E. Gordon, J. E. Gates (Compounds Interest Nucl. Reactor Technol. Proc. Symp., Boulder, Colo., 1964; Nucl. Met. **10** [1964] 765/84; Inst. Mining Met. Petrol Eng. Inst. Metals Div. Spec. Rept. Ser. No. 13 [1964] 765/84). – [133] M. Montgomery, A. Strasser, J. C. Anderson, C. Grando (GU-5306 [1973]).

1.2.3.5 The Behavior of Solid Fission Products and of Plutonium in Carbide and Nitride Fuels during Irradiation

At the beginning of the development of carbide and nitride nuclear fuels the attention during the post-irradiation examination was concentrated on the determination of the behavior and the release of the gaseous fission products. The solid fission products, however, can also influence directly or indirectly the life of the fuel elements in a decisive manner. They can do it directly, by reacting, e.g., with the cladding material, and indirectly, by binding to a greater or lesser extent the carbon or the nitrogen that is released by the fission of fuel. They change thereby the stoichiometry, with consequences relating to the compatibility and the swelling behavior of the fuel [1 to 6]. Haines, Potter [6] present in Table 1/41 the calculated concentration of the fission-produced elements in two (U,Pu) mixed carbides having different carbon contents after a burnup of 10% FIMA (8.22×10^4 MWd/t).

The behavior of the plutonium during the irradiation is also of interest, since this element has the tendency to redistribute itself in the fuel rod, because of the radial temperature gradient in it and the different equilibrium vapor pressures of uranium and plutonium. This redistribution, which is known in particular from fuel rods consisting of the mixed oxides, may affect the compatibility of the fuel with the cladding on the one hand, and the swelling behavior and the fission gas release on the other.

Table 1/41
The Composition of Two Mixed Carbides, $(U_{0.80}Pu_{0.20})C$, After a Burnup of 10% FIMA in a Fast Neutron Flux and Subsequent Decay for 50 Days [6].

element	at.% in $U_{0.8}Pu_{0.2}C$	at.% in $U_{0.8}Pu_{0.2}C_{1.09}$	element	at.% in $U_{0.8}Pu_{0.2}C$	at.% in $U_{0.8}Pu_{0.2}C_{1.09}$
U	34.31	32.84	In	<0.01	<0.01
Pu	8.49	8.14	Sn	0.04	0.04
Am	0.02	0.02	Sb	0.02	0.02
Se	0.02	0.02	Te	0.15	0.14
Br	0.01	0.01	I	0.08	0.07
Kr	0.08	0.08	Xe	1.07	1.03
Rb	0.11	0.10	Cs	0.91	0.88
Sr	0.12	0.11	Ba	0.31	0.30
Y	0.10	0.10	La	0.28	0.27
Zr	0.97	0.94	Ce	0.59	0.57
Nb	0.02	0.02	Pr	0.23	0.23
Mo	1.02	0.99	Nd	0.69	0.67
Tc	0.29	0.28	Pm	0.09	0.08
Ru	1.01	0.97	Sm	0.16	0.16
Rh	0.27	0.26	Eu	0.03	0.03
Pd	0.65	0.63	Gd	0.02	0.02
Ag	0.07	0.07	C	47.73	49.87
Cd	0.04	0.04			

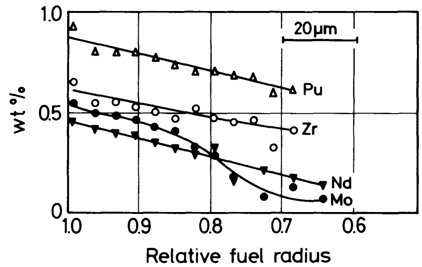
1.2.3.5.1 Solid Fission Products in the Fuel

The first information concerning the distribution of the fission products in the axial and radial directions in a fuel rod was obtained from the axial γ-scan of the rods and from β,γ-autoradiographic examination of sections. As far as the axial distribution was reported [7 to 9], no migration could be discerned. Parkinson [7] followed the axial distribution of the fission nuclides ^{95}Zr, ^{95}Nb, ^{103}Ru, ^{106}Ru, ^{140}Ba, and ^{140}La in the fuel rods on the basis of their specific γ-energies, without finding any distinct migration.

Strasser et al. [8, 10] found by means of β,γ-autoradiography a homogeneous distribution also in the radial direction. This homogeneity was disturbed, however, in fuels having a low density, in particular in vibrationally compacted fuel rods at a high linear power density [6, 11]. When an electron microprobe analyzer was used for the examination of the distribution of the individual fission products across the fuel rod cross section, Strasser et al. [12], along with all the other authors [13 to 18], found a more or less diverse distribution, dependent on the linear power density. They found an extensive migration of Cs, Ba, Xe, Nd, Pd, Rh, Pr, and Sm towards the cooler zones of the fuel rod, whereas the fission products Zr, Mo, Ce, and Ru remained homogeneously distributed throughout the cross section [12].

Kleykamp [14, 15] found a higher β,γ activity in an annular zone, and attributed this effect to the formation of intermetallic fission product-fuel phases. These have melting points between 1 100 and 1 300 °C, and therefore solidify and remain localized in this isothermal zone. He determined by means of a microprobe analysis the radial distribution of Zr, Nd, Mo, and Pu formed in a UC fuel after a burnup of 4% FIMA (3.3 × 10^4 MWd/t), **Fig. 1-159**. The concentration of these elements may be ten times as high at the surface of the rod as in the center of the fuel.

Fig. 1-159



Radial distribution of Zr, Nd, Mo, and Pu in a UC fuel rod after burnup of 4% FIMA [16].

Basic studies of the ternary systems fuel – fission product – carbon, as treated in certain studies [19 to 27], have been reviewed by Haines, Potter [6]. They concluded from the results, that in the irradiated carbide fuel the following types of compounds could be formed: U_2RuC_2, UPd_3, URu_3C, PuRu, Pu_5Rh_4, and $Ce_3Ru_2C_3$. The state of the fission products in an irradiated carbide fuel, could be described better by those authors [28 to 35], who admixed the fission product elements to a carbide fuel in such proportions as to simulate a burnup of, e.g., 10% FIMA (8.2 × 10^4 MWd/t). It could be concluded from the studies of Lorenzelli [3, 28, 30], that after burnup of a UC fuel of 7.0, 10.0, and 15.0 × 10^4 MWd/t, the following phases could be formed beside the UC matrix: U_2C_3, U_2RuC_2, $UMoC_2$, SrC_2, and CsI. Zr and Y were completely soluble in the UC matrix, whereas the solubility of Mo in UC was only 1% at 1 600 °C.

The solubility of the rare earth elements in the UC lattice depended on the carbon content of the fuel. On the whole, Lorenzelli [28, 29] divided the fission products into the following groups:

a) Fission products, that are completely soluble in the UC phase: Zr, Nb, Y.
b) Fission products, that are soluble to a limited extent in the UC phase: Mo, rare earth elements.
c) Fission products, that form ternary carbides: $(U,M)C_2$ (M = Mo, Re) and $(U_2M')C_2$ (M' = Ru, Rh, Pd, Mo, Te).
d) Fission products, that form separate dicarbides: M = Ba, Sr; M' = La, Ce, Nd, Pr, where MC_2 and $M'C_2$ are not mutually soluble.
e) Fission products, that form intermetallic phases UM_3 with uranium: M = Pd, Rh, Ru.
f) Nonmetallic fission products, such as I, Sb, and Se, that can form, e.g., CsI or USbSe.
g) Other metallic fission products, such as Cs and Rb, that combine neither with U nor with C.

Smailos, Holleck [4, 5, 31], who also simulated various burnups (10, 20, and 30% FIMA, i.e., 8.2, 16.5, and 24.7×10^4 MWd/t), distinguished between various initial compositions of the monocarbides.

For hypostoichiometric uranium carbide, UC_{1-x}, the following five phases have been formed in all mixtures simulating different burnups: (U, Zr, Mo, La, Ce, Pr, Nd)C, having about 0.5 wt% Mo and about 1.3 wt% rare earth elements; $UMoC_2$; $U_2(Ru, Rh)C_2$, having about 14 wt% Ru and 0.5 wt% Rh; $(U, La, Ce, Pr, Nd, Sm)_{x}(Ru, Rh)_{y_1}$ (having about 0.3 wt% dissolved C); $(U, La, Ce, Pr, Nd, Sm)_{x_2}(Ru, Rh, Pd)_{y}$ (having about 0.3 wt% dissolved C), where $x_1 > x_2$ and $y_1 > y_2$.

For hyperstoichiometric uranium carbide, UC_{1+x}, the following six phases were identified after heat treatments to equilibrium: (U, Zr, Mo, La, Ce, Pr, Nd)C, having about 0.5 wt% Mo and about 1.4 wt% rare earth elements; U_2C_3; $UMoC_2$; $U_2(Ru, Rh)C_2$, $(U, Zr)Pd_3$ $(La, Ce, Pr, Nd)C_{1.5\,\mathrm{to}\,2.0}$.

Benedict et al. [32] prepared (U,Pu)C, simulating a burnup of 17% FIMA (14.0×10^4 MWd/t), and homogenized it at 1 800 °C. Three phases were identified by means of X-ray structural analysis:

a) The (U,Pu)C phase, with a lattice parameter smaller by 0.02 Å than the starting material, as had been also found previously for irradiated carbide fuels [33].
b) A phase of the type $UMoC_2$ (orthorhombic phase).
c) A phase of the type U_2RuC_2 (body centered tetragonal phase).

The $UMoC_2$ and U_2RuC_2 phases had nearly the same lattice parameters as the pure compounds.

Oi [34] has first identified a second phase in irradiated carbide fuel. He heated in helium a UC sample that had been irradiated to 2.0×10^4 MWd/t at temperatures up to 1 800 °C, and isolated therefrom a phase, which was not dissolved by 8 M HNO_3 at room temperature. By means of microanalysis Oi determined the mass ratios of the Ru, Rh, and Pd he found in this phase to be 1.0:0.28:0.12. This was in good agreement with the fission yields, which related as 1.0:0.24:0.19. He concluded that the phase was a metallic alloy.

Bramman et al. [35] found in a fuel consisting of $U_{0.85}P_{0.15}C$, after a burnup of about 4.7% FIMA (3.86×10^4 MWd/t) at 1300 °C, small white deposits (<2 μm). After a special preparation of the sample, they could determine by means of a microprobe that the deposit was (U,Pu)(Pd, Ru, Rh)$_3$, with U:Pu = 1.4:1 and Pd:Ru:Rh = 6:1:1, in good agreement with the conclusion of Holleck, Kleykamp [36].

Kleykamp [14] was the first to report in detail results obtained with a microprobe on a carbide fuel irradiated to 0.7% FIMA (0.58×10^4 MWd/t). He could establish the presence of U_2(Tc, Ru, Rh)C_2 (with a small quantity of Pd), whereas the Zr and Mo remained distributed homogeneously, after low burnup. The Mo concentration, 0.06%, was considerably smaller than the solubility limit of "MoC" in UC, reported to be 1% [37].

Further studies on carbide fuels, UC and (U,Pu)C_{1+x}, after burnup values of 4 to 7.6% FIMA (3.3 to 6.2×10^4 MWd/t) confirmed these first results, and extended the knowledge about the formation of various phases and the distribution of the fission products between these precipitates and the mixed carbide matrix [15 to 17]. In a hyperstoichiometric mixed carbide two types of precipitates could be established:

1. A complex carbide, having a metallic appearance, the composition (U,Pu)$_2$(Tc, Ru, Rh)C_2, and a higher U:Pu ratio (80:20) than the starting ratio (85:15) in the fuel matrix.

2. Fission product carbides nearly free from fissile material with black appearance and nearly indistinguishable from pores. Their compositions were (La, Ce, Pr, Nd, Pm, Sm) carbide, (Cs, Sr, Ba, La, Ce, Tc) carbide, and at the cladding (Sr, Ba, Y, Ce, Zr, U, Pu) carbide.

In a stoichiometric fuel (a defective UC rod) also two types of precipitates were observed:

1. Intermetallic phases, having the overall compositions A_3B_4 and AB, where A = U, Pu, La, Ce, Pr, Nd, Pm, Sm (2% Pu) and B = Tc, Ru, Rh.

2. Mixed carbide deposits of U and the rare earth elements, with 18% U, which most likely existed as the sesquicarbide U_2C_3, and contained slight amounts of the coolant component, potassium.

The phases observed were generally in good agreement with the results obtained from simulation of the burnup of UC and (U,Pu)C_{1+x} [31]. The observed fission product-containing phases are summarized in Table 1/42.

Table 1/42
Identified Phases in UC and (U,Pu)C_{1+x} with Simulated Burnup.

stoichiometric UC	hyperstoichiometric (U,Pu)C_{1+x}
(U, Y, Zr, Mo, La ..., Sm)C	(U, Pu, Y, Zr, Mo, La ..., Sm)C
UMoC_x	(U,Pu)MoC_x
(U, La, ..., Sm)$_3$(Tc, Ru, Rh)$_4$	(U,Pu)$_2$(Tc, Ru, Rh)C_2
(U,La, ..., Sm)(Tc, Ru, Rh)	
(U, La, ..., Nd)$C_{1.5}$	(La, ..., Sm) carbide
(Sr, Ba, Ce)-carbide	(Cs, Sr, Ba, Ce) carbide
	(U, Pu, Sr, Y, Zr, Ba, Ce) carbide
	(Sr, Ba)Pd_x

Also Montgomery et al. [13] have observed, that in the vicinity of the enriched Pd, Ru, Rh, Tc, and Nd, also the Pu:U ratio was larger than elsewhere in the fuel matrix. Ewart et al. [18] arrived at similar conclusions, in the study of mixed carbides and mixed oxide carbides ("oxycarbides"), after burnup values of 3.6 to 10% FIMA (3.0 to 8.2×10^4 MWd/t). They summarized the results as follows:

– In the fuel region where the temperature was between 1 100 and 1 200 °C, a phase AB was precipitated from the mixed carbide, where A = U, Pu, lanthanides (Lan), and B = Ru, Rh, Pd. From the mixed oxide carbides the phase $(U,Pu)_x(Ru, Rh, Tc)C_y$, with x between 1.5 and 3 and y between 0.5 and 0.7, was deposited.

– A grey phase at the cracks of the oxide carbides contained Pu and lanthanides, and was taken to be the mixed oxide $(Pu, Lan)O_{2-x}$.

In an irradiated uranium carbide nitride having a 2000 ppm oxygen impurity also a lanthanide oxide phase has been identified [16]. The lanthanides form the most stable oxides and therefore gettered the oxygen impurities of the carbide fuel.

There are no reports, as yet, on the behavior of solid fission products in irradiated nitride fuels. Smailos [5], on the basis of his own experimental study of various quasibinary nitride systems and of thermodynamic data in the literature, arrived at the following conclusions concerning the behavior of various fission products in a nitride fuel:

– Zr should be dissolved in the fuel as the mononitride ZrN.

– Mo should be found in deposits as the metallic element or in an intermetallic phase with Pd.

– The platinum metals, Ru, Rh, and Pd, should be found in deposits of intermetallic phases containing U or Pu, as $(U,Pu)(Ru, Rh, Pd)_3$.

– The rare earth metals should be soluble in the fuel as the mononitrides.

– The alkaline earth metals Sr and Ba should be present as nitrides (probably as Sr_3N_2 or Ba_3N_2).

– The alkaline metals Rb and Cs should be separated in their elementary metallic form, or as compounds with iodine (RbI, CsI).

– Se and Te should be present in their elementary form or as caesium selenide or telluride.

1.2.3.5.2 The Distribution of Plutonium in Carbide and Nitride Fuels

Strasser, Kittel [8] supposed that uranium and plutonium undergo an axial redistribution in mixed carbides of low density and large open porosity (vibrationally compacted rods). Despite the very high burnup (up to 11.4×10^4 MWd/t), however, no change in the Pu concentration in the axial direction of the fuel rod could be found.

In the radial direction, too, no significant redistribution could be established, neither at low [38, 39] nor at high [10, 12] burnup values, at relatively low linear rod power densities (up to 730 W/cm).

A small increase of 3% in the Pu concentration in the direction from the surface of the pellet to its middle could generally be determined after irradiation in a thermal neutron flux. It was interpreted as due to the larger burnup in the outer zones of the pellets, because of the self-shielding of the fuel [8, 13, 15, 16].

A quantitative determination of the Pu:U ratio in micro-regions of the fuel rod cross-section showed, however, that local increases of the plutonium concentration could be observed. This occurred specifically in the hyperstoichiometric mixed carbide, $(U,Pu)C + (U,Pu)_2C_3$, in places where also a higher C concentration was observed [12, 13], and in the stoichiometric mixed carbide, (U,Pu)C, in places of lower C concentrations and of accumulation of fission products, such as Pd, Ru, Rh, Tc, and Nd [13]. The first effect could be explained by the different distribution of Pu in the phases (U,Pu)C and $(U,Pu)_2C_3$, when these phases were at equilibrium [40]. The second effect was related to the stabilization of the plutonium in intermetallic phases by fission products [15, 18].

During high linear power levels in the fuel rods, large radial temperature gradients were produced in the fuel, which could cause migration of the plutonium. Tetenbaum, Seth [41] examined the vapor phase in U-Pu-C systems and found that:

a) Pu was the predominant species in the vapor above a U-Pu-C sample.

b) The partial pressure of Pu increased with increasing ratios Pu:(U + Pu).

c) The calculation of Potter [40], that Pu was differently distributed in the two phases (U,Pu)C and $(U,Pu)_2C_3$, was valid.

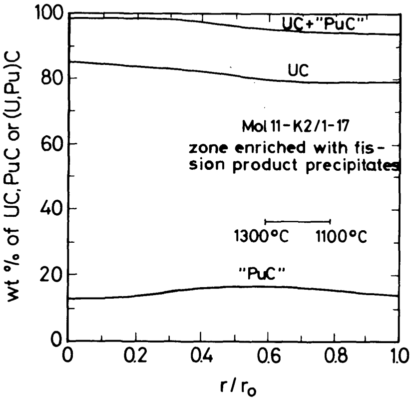
d) The presence of the $(U,Pu)_2C_3$ phase in a mixed carbide had a negligibly small effect on the vaporization behavior in the U-Pu-C system at 2000 to 2500 K.

Radial profile measurement by Kleykamp [15, 16] on irradiated mixed carbide fuel rods showed, that a demixing effect could, indeed, be established (**Fig. 1-160**), but that the mass flux was too small to produce as significant effects as were observed for the mixed oxides. The plutonium condensed "half-way" and was reincorporated into the carbide, before it reached the surface of the fuel. The decrease of the Pu concentration in the direction towards the surface was explained, as mentioned above, by the enhanced burnup at the surface caused by self-shielding.

Adamson [42] proposed a different transport mechanism for the plutonium in mixed carbides having relatively more oxygen impurities. Above these fuels a sufficiently high CO pressure could build up, that first of all caused a transport of oxygen from the center to the periphery of the fuel, which then caused there the formation of oxide phases, whereas a metallic phase, U + Pu, was simultaneously formed in the hotter regions of the fuel.

A light phase in the hot region of an irradiated (U,Pu) mixed carbide fuel has been found by Ewart et al. [18]. It contained a high proportion (32%) of Pu, but still contained some carbon. He assumed, that this (U,Pu) alloy molton during irradiation contained some carbon, when in contact with the mixed carbide at 1300 to 1600 °C.

Fig. 1-160



Radial UC and PuC profiles in a mixed carbide fuel rod after 4% burnup [15].

References for 1.2.3.5 on pp. 256/7

The presence of oxide precipitations at the periphery of a mixed carbide containing oxygen after a burnup of 5.3% FIMA (4.35×10^4 MWd/t) has been established by Kleykamp [43]. These deposits had a significantly higher Pu : U ratio than the carbide matrix, in agreement with Potter's [40] calculations for the U-Pu-C-O system.

1.2.3.5.3 Interaction of the Fuel and the Fission Products with the Cladding

Contrary to the case of the oxide fuels, the fission product elements simulating high burnups caused no compatibility problems [44]. In such experiments, only some carburization of the cladding was observed by Götzmann, Hofmann [44].

Montgomery et al. [13] analyzed by means of a microprobe the reaction products between the fuel (U,Pu)C, or (U,Pu)C + 10% $(U,Pu)_2C_3$, and the claddings AISI 304 SS or Incoloy 800, after a burnup of 3.5×10^4 MWd/t. Clear reaction zones were obtained for (U,Pu)C, where the product consisted mainly of Pu and Ni, with various small concentrations of U,Fe, and the fission products Ru, Rh, Mo, and Te. Around these reaction zones the cladding showed enrichment in Cr and a depletion of Fe and Ni.

The reaction zone of the cladding with (U,Pu)C + 10% $(U,Pu)_2C_3$ fuel could be less well related to the effect of the fission products. Although it contained small quantities of U and Pu, the main change was caused by carburization.

A reaction zone of about 10 μm thickness between stoichiometric (U,Pu)C and AISI 316 SS after a burnup of 3.7% FIMA (3.04×10^4 MWd/t) at a high power level (1300 W/cm) has been found by Latimer et al. [45]. In this limited reaction zone, the presence of mainly Ni and Pu could be established, as also found by Montgomery et al. [13], accompanied by small quantities of U, Fe, and Cr. Solid fission products, which have been observed in various sections, were not the same in all cases. In one case, for instance, Te, Ba, La, Rh, Mo, and Tc, in two others Nd and Ce, and in three further ones Pd, Pr, Sr, and Ru were determined. Latimer et al. [45] did not find penetration of the fission products through the cladding, with the exception of one case, where they found some lanthanides at a depth of 25 μm in the cladding.

Ewart et al. [18] have also found some interaction between the fuel and the cladding, when oxide carbides of U and Pu containing 1 wt% oxygen were exposed to 5.1% burnup, at points where the linear rod power density was high. Two phases could be established at fuel cracks and on the fuel surface:

1. metallic ingots in mayor cracks containing U, Pu, Ni, Pd and
2. a grey phase consisting of Pu and lanthanides likely to be mixed (Pu, Ln) oxides (Ln = Lanthanides).

In the absence of confirmatory observations with other compatibility studies [47, 48] the conclusion is that the severe clad interactions found in some of these fuel pins are atypical.

References for 1.2.3.5:

[1] H. Holleck (KFK-1111-pt. 3 [1969] 1/399; EURFNR-722 [1970] 1/402; N.S.A. **24** [1970] No. 38542). – [2] H. Holleck (KFK-1260 [1970] 1/31; N.S.A. **25** [1971] No. 13764). – [3] N. Lorenzelli, J. P. Marcon (J. Nucl. Mater. **44** [1972] 57/63). – [4] H. Holleck, E. Smailos (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 361/78). – [5] E. Smailos (KFK-1953 [1974]; EURFNR-1179 [1974]).

[6] H. R. Haines, P. E. Potter (Thermodyn. Nucl. Mater. Proc. 4th Symp., Vienna 1974 [1975], Vol. 2, pp. 145/173). – [7] N. Parkinson (in: A. N. Holden, High Temperature Nuclear Fuels Proc. Int. Symp., Delavan, 1966, Gordon and Breach, New York 1968; Met. Soc. Conf. **42** [1966] 297/309). – [8] A. Strasser, H. J. Kittel (in: K. E. Horton et al., Plutonium Fuels Technology Proc. Intern. Symp., Phoenix, Ariz., 1967; Nucl. Met. **13** [1968] 460/89). – [9] A. Ya. Ladygin, I. A. Efimov, Yu. L. Mikhatchev, Yu. I. Aleksandrov et al. (Proc. 4th U.N. Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 10, pp. 199/215). – [10] A. Strasser, M. Montgomery, P. Powers (Proc. Conf. Fast Reactor Fuel Elem. Technol., New Orleans 1971, pp. 849/67; Trans. Am. Nucl. Soc. **14** Suppl. No. 1 [1971] 40/1).

[11] R. W. Stratton, L. Smith (Advanced LMFBR-Fuels Proc. ANS Intern. Meeting, Tucson, Ariz., 1977, pp. 348/60). – [12] A. Strasser, M. Montgomery, R. Powers (GU-5286 [1972]). – [13] M. Montgomery, A. Strasser, J. Anderson, C. Grando (GU-5306 [1973]). – [14] H. Kleykamp (J. Nucl. Mater. **47** [1973] 271/7). – [15] H. Kleykamp (Reaktortagung, Düsseldorf 1976, pp. 542/5).

[16] H. Kleykamp (Advanced LMFBR-Fuels Proc. ANS Meeting, Tucson, Ariz., 1977, pp. 166/78). – [17] W. Dienst, H. Kleykamp, G. Mühling, H. Reiser, H. Steiner, F. Thümmler, H. Wedemeyer, P. Weimar (Nucl. Power Its Fuel Cycle Proc. IAEA Conf., Salzburg 1977 [1978], pp. 493/510). – [18] F. T. Ewart, B. M. Sharpe, R. G. Taylor (AERE-R-7962 [1975] 1/15; C.A. **84** [1976] No. 81268). – [19] P. Stecher, A. Neckel, F. Benesowsky, H. Novotny (Planseeber. Pulvermet. **12** [1964] 181/95). – [20] Ö. Inanc (JUEL-516-RW [1968] 1/46; N.S.A. **24** [1970] No. 34958).

[21] H. Holleck, W. Wagner (Thermodyn. Nucl. Mater. Proc. IAEA Symp., Vienna 1967 [1968], pp. 667/81). – [22] H. R. Haines, P. E. Potter (AERE-R-5613 [1970]). – [23] N. Lorenzelli, J. P. Markon (J. Less-Common Metals **26** [1972] 71/9). – [24] I. J. McColm, I. Colquhoun, N. J. Clark (J. Inorg. Nucl. Chem. **34** [1972] 3809/19). – [25] H. R. Haines, P. E. Potter (AERE-R-6512 [1970]).

[26] H. Holleck, H. Kleykamp (J. Nucl. Mater. **45** [1972/73] 47/56). – [27] Z. M. Alekseeva, O. S. Ivanow (Thermodyn. Nucl. Mater. Proc. IAEA Symp., Vienna 1974 [1975], Vol. 2, pp. 175/84). – [28] N. Lorenzelli, J. P. Marcon (Behav. Chem. State Irradiat. Ceram. Fuels Proc. Panel, Vienna 1972 [1974], pp. 99/113). – [29] N. Lorenzelli (CEA-R-4465 [1973] 1/126; C.A. **80** [1974] No. 65839). – [30] H. Mikailoff (Trans. Am. Nucl. Soc. **19** [1974] 89/90).

[31] H. Holleck, E. Smailos (Reaktortagung, Berlin 1974, pp. 384/7). – [32] U. Benedict, G. Giacchetti, H. Matzke, K. Richter, C. Sari, H. E. Schmidt (Nucl. Technol. **35** [1977] 154/61). – [33] U. Benedict (EUR-5766 [1977] 1/16; C.A. **89** [1978] No. 32771). – [34] N. Oi (J. Nucl. Mater. **34** [1970] 227/9). – [35] J. J. Bramman, R. M. Sharpe, R. Dixon (J. Nucl. Mater. **38** [1971] 226/9).

[36] H. Holleck, H. Kleykamp (J. Nucl. Mater. **35** [1970] 158/66). – [37] W. Chubb (J. Nucl. Mater. **23** [1967] 336/40). – [38] A. Strasser, D. Stahl (UNC-5054, Vol. II [1965] 1/102; N.S.A. **18** [1964] No. 6494). – [39] D. Stahl, A. Strasser (UNC-5198 [1968] 1/53; N.S.A. **22** [1968] No. 39789). – [40] P. E. Potter, W. G. Roberts (AERE-R-5661 [1968]).

[41] M. Tetenbaum, S. Sheth (Trans. Am. Nucl. Soc. **23** [1976] 129/30). – [42] M. G. Adamson (AERE-R-6897 [1972] 1/18; N.S.A. **28** [1973] No. 3015). – [43] H. Kleykamp (Reaktortagung, Hannover 1978, pp. 660/3). – [44] O. Götzmann, P. Hofmann (Fuel Fuel Elem. Fast React. Proc. IAEA Symp., Brussels 1973 [1974], Vol. 1, pp. 233/45). – [45] T. W. Latimer, D. S. Bost, J. F. Kerrisk, J. O. Barner, J. L. Green (LA-6077-MS [1975]).

[46] P. E. Potter, W. G. Roberts (Nucl. Met. **17** [1970] 859/73). – [47] H. Lawton, K. Q. Bagley, R. G. Bellamy, N. Parkinson, J. O. Pounder, A. E. Williams, E. Wilson (Proc. 4th UN Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 10, pp. 39/51). – [48) J. M. Horspool, N. Parkinson, J. R. Findlay, P. E. Potter, M. H. Rand, L. E. Russell, N. Batey (Fuel Fuel Elem. Fast React. Proc. IAEA Symp., Brussels 1973 [1974], Vol. 1, pp. 3/16).

2 Reprocessing of Spent Nuclear Fuels

2.1 Introduction

Owing to the accumulation of fission products, the depletion of fissile nuclides, and/or changes in the mechanical behavior of the cladding, a nuclear reactor fuel element must be removed from the reactor after a certain period of service, e.g., about 3 years in the case of a LWR. To separate the non-fissioned uranium and the built-up fissile materials such as plutonium and ^{233}U, the irradiated fuel element must be reprocessed after an intermediate "cooling" time to allow for the decay of short-lived radionuclides. Reprocessing of spent fuels strongly depends on the nature of the fuel and on the type of nuclear reactor. We may distinguish the following:

a) Fuels from research reactors. In such reactors a high neutron flux, but no great thermal power, is desired. To this end, the fuel elements of research reactors consist principally of highly enriched uranium, for example, up to 90% ^{235}U in Material Testing Reactors (MTR). The fuel elements are in most cases metallic (e.g., a U-Al alloy) or cermets (e.g., a dispersion of U oxides in Al).

Because excessive accumulation of fission products adversely affects the behavior of the metal (for example by causing swelling), only a moderate burnup of less than 0.5% is normally feasible. This facilitates reprocessing, but special precautions must be taken to avoid criticality (see "Uranium" Suppl. Vol. A6).

b) Fuels from power reactors. Here are two characteristically different fuel cycles:

- the U-Pu fuel cycle and
- the Th-U fuel cycle.

Characteristic for these fuel cycles is the high burnup ($\geqq 3\%$) of the fissile materials. The fuel consists of ceramic compounds, mostly oxides in a metallic cladding (Zircaloy for LWRs and stainless steel for the Fast Breeder Reactor FBR) or is dispersed in a graphite matrix (Thorium High Temperature Reactor THTR). The enrichment of fissile materials is normally lower than in research reactors, e.g., 3% ^{235}U in LWR or 15% Pu in FBR.

Reprocessing of spent fuels of the different reactor types will be treated here according to the composition of the fuel:

- high ^{235}U enriched fuels from research reactors
- fuels from the U-Pu nuclear fuel cycles (LWR, FBR)
- fuels from the U-Th nuclear fuel cycle (THTR).

2.2 Reprocessing of Spent Fuel of the U-Pu Nuclear Fuel Cycles

Two different types of fuel elements have to be distinguished here.

- Fuel elements from FBR with about 15% fissile material, and
- Fuel elements from:
  heavy water reactors with natural uranium
  LWR with enriched uranium containing about 3% ^{235}U
  LWR with about 3 to 5% recycled Pu.

The chemical process for reprocessing of these nuclear fuels is the PUREX process in its original or slightly modified version. It has been described extensively in "Transurane" A1, II, 1974, which includes data up to the end of 1971. Newer results of this process will be mentioned in a forthcoming supplement to this "Transuranium Elements" series. Therefore, the reprocessing of Pu-containing spent fuels will not be discussed in this volume.

However, the following newer comprehensive and/or review references [1 to 5] are given:

[1] G. Koch (Chemische Aufarbeitung der bestrahlten Kernbrennstoffe in: C. Keller, H. Möllinger, Kernbrennstoffkreislauf, Vol. 2, Hüthig, Heidelberg 1978, pp. 9/56; Chemiker-Ztg. **101** [1977] 64). – [2] F. Baumgärtner (Chemie der Nuklearen Entsorgung, Vol. 66 TB, Thiemig, Munich 1978, pp. 1/372). – [3] R. G. Wymer (Chemical Aspects of the Nuclear Fuel Cycle, Radiochim. Acta **25** [1978] No. 3/4). – [4] UKAEA (Fast Reactor Fuel Reprocessing Proceedings of a Symposium, Dounreay, U.K., 1979 [1980], pp. 1/220). – [5] G. Koch (Existing and Projected Reprocessing Plants: A General Review, Atomkernenerg.-Kerntech. **33** [1979] 241/50).

2.3 The Reprocessing of Enriched ^{235}U Fuels

G. N. Walton
Department of Chemical Engineering and Chemical Technology
Imperial College, London University,
London, U.K.

2.3.1 Introduction

General References:

F. S. Patton, J. M. Googin, W. L. Griffith, Enriched Uranium Processing, Pergamon, Oxford 1963.

J F. Flagg, Chemical Processing of Reactor Fuels, New York 1961.

United Nations, Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9.
Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17.
Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10.
Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 8.

P. L. Robertson, W. G. Stockdale, A Cost Analysis of the Idaho Chemical Processing Plant, ORNL-1792 [1959] 1/160; N.S.A. **14** [1960] No. 16728.

H. T. Williams, J. W. McWhirter, A. H. Chura, E. H. Wissler, R. E. Fields, M. C. Lawrence, Safety Analysis of Enriched Uranium Processing, NYO-2980 [1960] 1/199; N.S.A. **14** [1960] No. 11834.

J. D. Navratil, W. W. Schulz, Actinide Separations, 177th Natl. Meeting, Am. Chem. Soc., Honolulu, HI., 1979, pp. 1/569.

J. D. Navratil, Present Status and Future Role of Actinide Separation in Reactor Fuel Processing, Fast React. Fuel Reprocess. Proc. Symp. Dounreay, U.K., 1979 [1980], pp. 37/49.

J. M. Cerles, Choice and Utilization of Slightly Enriched Uranium Fuel for High Performance Research Reactors, Res. Advis. Group Meeting, Vienna 1978; IAEA-214 [1978] 291/9; INIS Atomindex **10** [1979] No. 484994.

L. Geller, Uranium in 1985, Resources and Supply, Trans. Am. Nucl. Soc. **28** [1978] 314.

M. Skrivankova, Nondestructive Determination of Nuclear Fuel Enrichment by Ge[Li] Spectrometer, Jaderna Energie **22** [1976] 441/3; INIS Atomindex **9** [1978] No. 379946.

T. S. Zaritskaya, A. K. Kruglov, A. P. Rudik, Effect of Nuclear Enrichment on Transuranium Isotope Production in Power Reactors, At. Energ. [USSR] **41** [1976] 321/5; Soviet At. Energy **41** [1976] 321/5; INIS Atomindex **8** [1977] No. 335228.

R. C. Dahlberg, Effects of U-236 and Other Uranium Isotopes in HTGR Fuel Cycle, Uranium Isot. Separ. Proc. Intern. Conf., London 1975, Paper No. 23; INIS Atomindex **8** [1977] No. 284172.

M. L. Hyder, W. C. Perkins, M. C. Thompson, G. A. Burney, E. R. Russell, H. P. Holcomb, L. F. Landon, Processing of Irradiated Enriched Uranium Fuels at the Savannah River Plant, DP-1500 [1979] 1/237; INIS Atomindex **11** [1980] No. 527445.

The reprocessing of nuclear fuels with highly enriched uranium is very different, from the point of view of the nuclear industry, from the reprocessing of natural uranium fuels and those with low degrees of enrichment. There are two fundamental reasons for this. First, the amount of power required for enriching uranium with the fissile isotope ^{235}U on an industrial scale, as currently practised, is comparable to the amount of power generated in consuming it so that the economic incentive in using highly enriched uranium fuel in nuclear power reactors is low. Secondly, during irradiation the isotope ^{235}U generates ^{236}U which itself has a high cross section for neutron capture (see "Uran" Erg.-Bd. A 2, 1980, pp. 149/53). This isotope, in effect, poisons ^{235}U in reactors and there is no feasible economic process for separating ^{235}U and ^{236}U on an industrial scale. The economic advantages that might otherwise be gained in recovering residual ^{235}U from irradiated fuel are thereby greatly reduced. The effect of ^{236}U on the economics of enriched uranium processing is discussed by Patton et al., p. 261, and by Dahlberg (see "General References", pp. 259, 260).

Nevertheless there are some very important advantages, other than economic ones in using highly enriched fuels in certain types of reactors and the recovery of the fuel after irradiation in these reactors is a continuing requirement. Extensive research and development has been pursued and a number of projects, on a laboratory, pilot plant, and plant scale, have been carried out.

Table 2/1 shows the reactors and reactor types which have been designed to operate with highly enriched uranium, together with the composition of the fuels and the countries in which the reactors operate. Many of the reactors shown in Table 2/1 have not proved economically viable and, as shown, the projects have been foreclosed, while others continue to operate and require replenishment with fuel. Much of the development work for enriched uranium processing has been directed at the requirements for recovering enriched fuel from the cores of reactors which have not proved viable and require dismantling.

The Research Reactors and Materials Testing Reactors (MTR's) in many cases operate at low power levels of a few megawatts, or less. In these cases the rates of consumption of fuel are sufficiently low so that a regular commitment to fuel processing is not required (i.e., fuel replenishment occurs over 5 to 10 year periods).

Table 2/1
Representative Reactors Using Highly Enriched Uranium.

reactor	fuel type	country
Research Reactors		
"LIDO"	Al-U alloy clad in aluminium	UK*
"Silwood"	UO_2 dispersed in aluminium	UK
Materials Testing Reactors		
"DIDO" "PLUTO"	UO_2 dispersed in aluminium, aluminium clad	UK
Army Package Power Reactor "APPR"	iron-uranium cermet clad in stainless steel	USA
Ship propulsion		
"Otto Hahn" BWR	Zr-U eutectoid, clad in zirconium alloys	Fed. Rep. Germany*
Submarines PWR	Zr-based fuel	USA*
Aircraft Carriers PWR	Zr-based fuel	USA*
Ice Breaker "Lenin" PWR	Zr-based fuel	USSR
Fast Reactors		
Dounreay Fast Reactor DFR	UO_2, PuO_2, clad in steel	UK*
Prototype Fast Reactor PFR	uranium carbides, $^{238}U + ^{239}Pu$	UK
"Phoenix" PFR		France
EBR 1, EBR 2		USA*
High Temperature Reactors		
"Dragon" HTR	UO_2 spheres	UK*
Peach Bottom HTR	silicon carbides	USA*
Fort St. Vrain HTR	and graphite	USA
AVR	UO_2 spheres in graphite	Fed. Rep. Germany
Other Reactors		
Aircraft Propulsion Reactor APR	uranium fluorides	USA*
Homogeneous Aqueous Reactor HAR	uranyl sulfate in sulfuric acid	USA*
Organic Moderated Breeding Reactor OMBR	UO_2, ThO_2, clad in steel	Canada*
Molten Salt Reactors MSR	uranium fluoride dissolved in lithium beryllium fluoride	USA*

* Reactor now closed down and development ceased.

2.3.2 Storage of Irradiated Fuel

As a consequence of the low priority afforded to reprocessing of highly enriched fuel after reactor irradiation, importance is attached to long term storage.

Short term storage after discharge from the reactor allows for the decay of such isotopes as ^{133}Xe (5.27 days half-life), ^{131}I (8.06 days), ^{234}Np (4.40 days), and ^{237}U (6.75 days) the last being particularly prevalent in enriched uranium fuel.

For long term storage fuel is normally kept in sealed steel containers, under water which furnishes shielding and cooling. The water is normally conditioned to maintain clarity and to avoid corrosive attack by circulating through replenishable exchange columns. See "Transurane" A1, II, 1974, p.179.

2.3.3 Disassembly of Fuel

In practice the initial treatment of fuel in the so-called "head-end" of a processing plant is a sensitive operation. This is particularly true of enriched fuel from which few losses can be tolerated. The fuel is massive and prone to damage and the remotely controlled procedures require to be designed so that all eventualities can be met without involving the dispersion of radioactive contamination. Methods may be mechanical or chemical [1, 2].

2.3.3.1 Mechanical Operations

Mechanical de-jacketing involving extrusion, milling, or cutting, as used in natural uranium and slightly enriched fuel, is rarely suitable for highly enriched material and chemical methods are preferred. However for "once off" operations mechanical processes have been used.

Rolling was operated at Oak Ridge on steel jacketed sodium-potassium (NaK) bonded fuel rods of UO_2 using a standard rotary steel roller. The rolling was repeated until the jackets split and released the fuel cores. The process appeared more suitable for metal assemblies, where metallic bonding could be loosened and split, rather than for canned UO_2 assemblies where the fuel is crushed and powdered [3].

Milling was practised for the fuel core of the Experimental Breeder Reactor EBR I when this was dismantled in the USA. The NaK bonding was removed by treatment with isopropyl alcohol and the uranium alloy rods were pushed mechanically from the steel tubes. The equipment was blanketed with CO_2 as a fire precaution [4].

Extrusion of each cylindrical fuel rod through a die has been used extensively on natural uranium fuel and has been adapted for enriched fuel [5]. However the method is sensitive to fuel distortion and prone to jamming failure.

Mechanical cutting by shearing the fuel with a guillotine is a more favored method for enriched fuel. The sheared pieces are dropped directly into dissolving tanks and the process does not involve losses. Abrasive cutting is also used as standard practice in remote handling caves where fuel is to be dismantled for experimental purposes. Lathe equipment is used so that rods or fuel slugs of any size can be cut in any position with an abrasive disc. Kerosene is used as a coolant by which particulate matter can be collected, and argon gas in the sealed caves can be used for fire prevention [6 to 8].

For processing Fast Reactor fuel cutting by means of a laser beam has been developed at Dounreay. This has the great advantage that the cutting is very clean and does not give rise to the swarf which mechanical methods produce [9].

References for 2.3.3.1:

[1] W. H. Reas (KR-126 [1967] 31/52; N.S.A. **22** [1968] No. 40163). – [2] F. H. Hammad, H. R. Higgy, A. A. Abdel Rassoul (J. Brit. Nucl. Energy Soc. **10** [1971] 21). – [3] F. L. Culler, R. E. Blanco (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 259/90; A-CONF-15-P-1930 [1958] 1/85; N.S.A. **12** [1958] No. 14712). – [4] H. V. Lichtenberger, M. Novick, B. C. Cerutti, R. A. Cameron, D. F. McGinnis, E. N. Pettitt, G. K. Whitham, R. A. Haroldsen, L. J. Koch (ANL-5023 [1953/57] 1/46; N.S.A. **11** [1957] No. 11743). – [5] H. W. Alter, C. J. Beck, B. V. Coplan (KAPL-1139-Del. [1954/57] 1/9; N.S.A. **12** [1958] No. 856).

[6] G. I. Torgeson (Hot Laboratory Operation and Maintenance, Vol. 3, Pergamon 1957). – [7] E. M. Van der Wall, E. M. Whitener, D. L. Bauer (IDO-14497 [1960] 1/29). – [8] R. E. Blanco (IDO-7534-Bk. 1 [1957] 251/61). – [9] P. R. Higginson, D. A. Campbell (Post-Irradiation Examination, British Nuclear Energy Society, London 1981, pp. 135/41).

2.3.3.2 Chemical Methods of Decladding and Dissolution

In some cases chemical methods can be used to dissolve away the cladding or canning leaving the fuel for subsequent treatment. In other cases the cladding and fuel are both dissolved together. In this section both processes are considered.

2.3.3.2.1 Aluminium Based Fuel

In enriched fuel from research and material testing reactors the aluminium content may well amount to 90% by weight. These fuels may be treated with boiling nitric acid with mercury(II) nitrate as catalyst. As discussed by Wymer and Foster [1] the net reaction for dissolution in 4 M nitric acid is $Al + 3.75\,HNO_3 \rightarrow Al(NO_3)_3 + 0.225\,NO + 0.15\,N_2O + 0.113\,N_2 + 1.87\,H_2O$. The rate of the reaction is dependent on the nitric acid and mercury(II) nitrate concentrations and on the fuel surface area. The rate is also dependent on the temperature and inversely on the concentration of dissolved aluminium. The rate is faster for more highly irradiated fuel where the burnup and fission product concentration is greater.

The mechanism of the reaction is proposed as initial depolarisation of the passive layer of Al_2O_3 by mercury(II) ion reduction, the formation of a Hg-Al alloy film, transfer of charged species through cationic vacancies, and finally oxidation of the mercury alloy layer by nitric acid which re-cycles the mercury(II) ion. The process has become a standard method for treatment of aluminium alloy and aluminium cermet fuels and has been studied by many workers [1, 2, 15]. Analytical methods for the process have been described by Shank, Rein [3]. The method has also been adapted for continuous processing [4] and pilot plant development [5].

The part played by mercury has been extensively studied [6]. More recently the process has been applied to highly irradiated fuel which gives rise to undissolved particles in the nitric acid solvent. Methods removing these have been derived [7, 8] and studied with respect to the composition of the fuel [14].

The mercury catalysed nitric acid method has been investigated in countries other than USA, e.g., France [9], the United Kingdom [10], Italy [11, 12], and other countries in Europe [13, 16].

References for 2.3.3.2.1:

[1] R. G. Wymer, D. C. Foster (Progr. Nucl. Energy III **2** [1958] 86/91). – [2] R. C. Andelin, F. H. Tingey, C. M. Slansky (IDO-14407 [1957] 1/45; N.S.A. **11** [1957] No. 10470). – [3] R. C. Shank, J. E. Rein (IDO-14412 [1957] 1/18; N.S.A. **12** [1958] No. 1292). – [4] A.

F. Boeglin, J. A. Buckham, L. Chajson, R. B. Lemon, D. M. Paige, C. E. Stoops (IDO-14341 [1955] 1/4; AICHE [Am. Inst. Chem. Eng.] J. **2** [1956] 190/4; N.S.A. **10** [1956] No. 6601). – [5] D. M. Paige, A. F. Boeglin, J. A. Buckham, L. Chajson, R. B. Lemon, C. E. Stoops (IDO-14304 [1954] 1/28; N.S.A. **16** [1962] No. 31674), A. F. Boeglin, J. A. Buckham, L. Chajron, R. B. Lemon, D. M. Paige, C. E. Stoops (IDO-14321 [1954] 1/93; N.S.A. **15** [1961] No. 23566), M. D. Martin, J. A. Buckham (IDO-14361 [1955] 1/31; N.S.A. **14** [1960] No. 16720).

[6] A. E. Erhard, R. H. Perkins (IDO-14242 [1953/60] 1/13; N.S.A. **14** [1960] No. 15691). – [7] B. E. Paige, M. E. Jacobson, T. L. Evans, V. H. Barnes (IN-1364 [1970] 1/47; N.S.A. **24** [1970] No. 27188; C.A. **74** [1971] No. 37388). – [8] W. P. Palica, M. D. Gold (IN-1153 [1966] 1/20; N.S.A. **23** [1969] No. 35257). – [9] C. E. A. Fontenay-aux-Roses (CEA-N-1148 [1969] 1/424; N.S.A. **24** [1970] No. 11649). – [10] A. Delpech, Commissariat a l'Energie Atomique (Fr. 1539924 [1967/68]; Brit. 1170385 [1969]; N.S.A. **24** [1970] No. 5737).

[11] G. Beone, R. Lojacono, G. P. Mazzoleni, A. Mocia (RT-CHI-6-8 [1967] 1/24; N.S.A. **22** [1968] No. 4234). – [12] G. Beone, G. P. Mazzoleni (RT-CHI-66-17 [1966] 1/41; N.S.A. **21** [1967] No. 6000). – [13] S. Cao, H. Dworschak, A. Hall (Proc. Intern. Solvent Extr. Conf., Lyon 1974, Vol. 2, pp. 1453/80; C.A. **83** [1975] No. 105012). – [14] B. E. Paige, K. L. Rhode (Nucl. Appl. **5** [1968] 218/23; C.A. **70** [1969] No. 33606). – [15] W. C. Perkins, Savannah River (DP-1337 [1973] 1/23; N.S.A. **29** [1974] No. 9999).

[16] B. F. Warner (Panel Reprocess. High. Irradiat. Fuels, Vienna 1969).

2.3.3.2.2 Uranium Metal

Boiling HNO_3 is the standard solvent for uranium metal. The net reaction for batchwise dissolution in 11.7 M acid is $U + 4.5\,HNO_3 \rightarrow UO_2(NO_3)_2 + 1.57\,NO + 0.84\,NO_2 + 0.005\,N_2O + 0.043\,N_2 + 2.25\,H_2O$. The dissolver is fitted with a reflux condenser and by passing air or oxygen into the system, the oxides of nitrogen may be recovered in the gas stream, or in the reflux condenser, as reusable nitric acid. The uranium is, in effect, being dissolved by the oxygen and the net reaction is $U + 2\,HNO_3 + 3/2\,O_2 \rightarrow UO_2(NO_3)_2 + H_2O$. The process can be operated as a continuous dissolution in which the decanned, or stripped, fuel is loaded with a feed of nitric acid and oxygen, and the uranyl nitrate solution is extracted. The dissolution rate is controlled as a function of nitric acid concentration, R. G. Hurst, G. O. Morris (Progr. Nucl. Energy III **2** [1958] 544/5).

2.3.3.2.3 Zirconium Based Fuel

Dissolution of zirconium-uranium fuels presents difficulties, and processes on an industrial scale have not been fully described. On a pilot plant scale Zr metal dissolves readily in hydrofluoric acid according to $Zr + 4\,HF \rightarrow ZrF_4 + 2\,H_2$. The rate increases with increasing acid concentration and is found to operate steadily at a mole ratio $\bar{F}/Zr$ of 6 in an acid concentration of 9 M. However in this reagent uranium precipitates as UF_4 and tin, where this is present as an alloying element in zircaloy, also does not dissolve.

If oxidising agents are added to the hydrofluoric acid the uranium may be kept in solution in the form of the uranyl ion. Nitric acid, chromic acid, and hydrogen peroxide have been used as additives to the hydrofluoric acid and these have been used for U-Zr alloy fuel solvents [1].

A "Zirflex" process has been described [2, 3] in which the fuel is dissolved in boiling NH_4F and NH_4NO_3. The principal reaction is written $Zr + 4.5\,NH_4^+ + 6\,F^- + 0.5\,NO_3^- \rightarrow ZrF_6^{2-} + 5\,NH_3$

$+ 1.5\ H_2O$. Tin becomes negligible in undissolved solids and both uranium metal and uranium oxide dissolve in the reactants as fluorides.

Hot concentrated H_2SO_4 at 12 to 14 M has also been investigated as solvent for Zr fuel with some success, but the reagent does not appear attractive for large scale operations [4, 5].

The main problem with large scale operations for the processing of Zr-based fuel is that finely divided Zr metal is prone to violent and explosive reactions with HNO_3 and other strong oxidising agents. Zr and its alloys form a highly passive or protective film in water or in other aqueous reagents which prevents the release of the heat in the highly exothermic reaction of Zr with oxygen: $Zr + O_2 \rightarrow ZrO_2$ $-1\,081$ kJ/mol. If the oxide film is broken, or otherwise loses its dielectric properties, the reaction can occur. If the Zr is finely divided, or becomes finely divided as a result of the reaction, the process can become rapidly self-propagating. This may lead to rapid superheating of the liquid and violent explosions can occur. The problem can clearly be overcome by introducing the aqueous reagent slowly to the Zr, or vice versa, so that no bulk materials are in contact simultaneously [6] (see Section 2.3.4, p. 266).

2.3.3.2.4 Stainless Steel Canned Fuel

Stainless steel can be dissolved at a rate suitable for an industrial process in hot H_2SO_4 at 4 to 6 M concentration. Uranium and uranium oxide are only partially dissolved in sulfuric acid unless oxidising agents, such as HNO_3, are introduced. Under these conditions stainless steel tends to remain passive, but this can be prevented by the addition of mild steel wool at the start of the dissolution. These processes have been used for the cermet type fuels where enriched uranium oxide is dispersed in steel as a cermet and clad in steel [5, 7].

The steel-clad uranium oxide fuel of the Advanced Gas Reactors (AGR) and the Fast Reactor, in the U.K., is cut into short lengths by laser beam cutting and then treated in stainless steel baskets in tanks with HNO_3. This dissolves out the uranium oxide and leaves the stainless steel cladding undissolved, which can be removed in the steel basket from the tank. This is a preferred procedure for enriched fuel.

2.3.3.2.5 Other Types of Fuel

Other types of Fast Reactor fuels, which have been developed, have consisted of enriched uranium in Mo alloys and in Nb alloys. The Mo alloy was mixed with Mg to give the composition 12% Mg, 8.1% Mo, 79.9% U. This was dissolved in 5 M nitric acid and the Mo was kept in solution by adding phosphoric acid. The Nb alloy required HF addition [5].

The coated particles of UO_2 or UC fuel in a graphite matrix are used in the cores of High Temperature Reactors. Experimental work has been carried out on burning the carbon off in oxygen, as CO_2, leaving the oxide particles for dissolution by the methods used for UO_2 fuel. For details of the reprocessing, especially with respect to HTR fuels, see Chapter 2.4, p. 276.

References for 2.3.3.2.3 to 2.3.3.2.5:

[1] E. M. Van der Wall, E. M. Whitener (Ind. Eng. Chem. **51** [1959] 51/4). – [2] E. M. Van der Wall, D. L. Bauer (IDO-14497 [1960] 1/29). – [3] J. L. Swanson (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Paper No. 2429; A-CONF-15-2429 [1958] 1/20; N.S.A. **12** [1958] No. 14715). – [4] R. H. Perkins (IDO-14042 [1952]). – [5] R. E. Blanco (TID-7534-Bk. 1 [1957] 251/61).

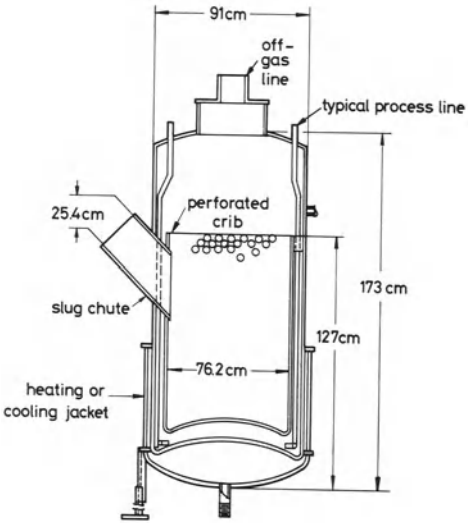
[6] J. R. Bower, K. L. Rohde (Progr. Nucl. Energy III **4** [1970] 171/211). – [7] E. C. Pitzer (KAPL-653 [1951]).

2.3.4 Dissolvers

The main difficulty in all fuel dissolution is to find containers which are not attacked by the vigorous reagents required to dissolve the fuel and cladding.

Al-based fuel is dissolved in stainless steel equipment without difficully. A typical batch dissolver is shown in **Fig. 2-1** for MTR-type fuel, where the dimensions are carefully determined to avoid criticality with the fuel and concentrations of dissolved material incurred. The vessel is fabricated of 309 niobium stainless steel and is suitable for 13 M nitric acid with both mercury(II) and fluoride ions as catalysts [1, 2].

Fig. 2-1



Batch dissolver for MTR fuel elements.

Continuous dissolvers for Al-based fuel have been designed as vertical pipes in which long fuel assemblies are allowed to sink slowly into the dissolving fluid as the lower end of the assembly reacts. Typical arrangements are shown in **Fig. 2-2** and 2-**3** where the vertical dissolver is about 16 feet ($\approx$4.9 m) in height and $7\frac{1}{2}$ inches ($\approx$19 cm) in diameter [3, 4]. An alternative is to dissolve the fuel in flat tanks of large area and thin depth [5].

For Zr-based fuel, requiring treatment with HF, stainless steel cannot be used. Ni-based alloys are used for solvents with HF or other fluoride reagents. **Fig. 2-4** shows a Monel pot for batchwise dissolution of Zr alloy highly-enriched uranium fuel. However in view of the explosion risks with Zr the arrangements of Fig. 2-2 and 2-3 are preferable.

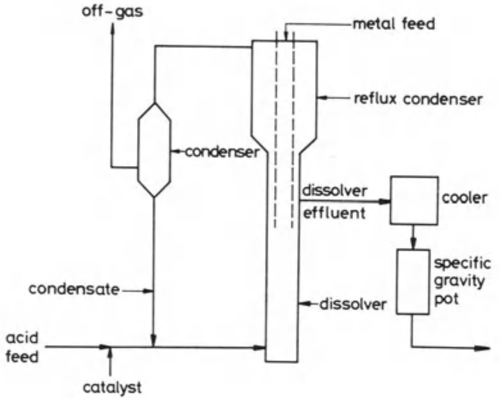


Fig. 2-2

Flooded dissolver.

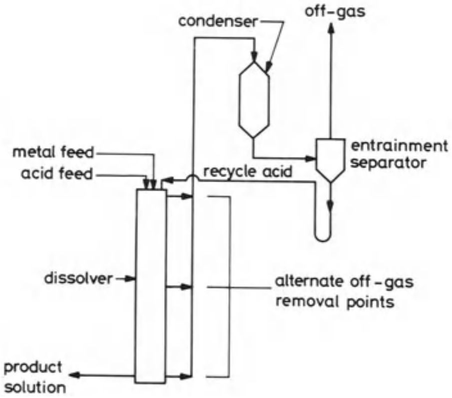


Fig. 2-3

Trickle dissolver.

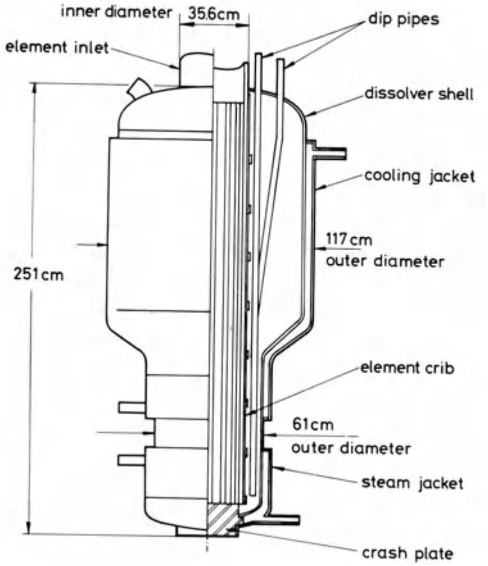


Fig. 2-4

Dissolver for zirconium fuel assemblies.

References for 2.3.4:

[1] E. E. Erikson (IDO-14450 [1958] 1/27; N.S.A. **13** [1959] No. 3680; IDO-14451 [1959] 1/51; N.S.A. **13** [1959] No. 5334; IDO-14452 [1959] 1/34; N.S.A. **13** [1959] No. 11689). – [2] Anonymous (Reactor Fuel Processing **1** [1958] No. 4, 4/8). – [3] A. F. Boeglin, Z. A. Buckham, L. Chajson, R. B. Lemon, D. M. Paige, C. E. Stoops (IDO-14321 [1954/61] 1/93; N.S.A. **15** [1961] No. 23566). – [4] K. L. Rohde, J. A. Buckham (Panel Reprocess. High Irradiat. Fuels, Vienna 1969, p. 257). – [5] H. Vietzke, B. Bernhardt (Ger. 2721183 [1978]; INIS Atomindex **10** [1979] No. 466504).

2.3.5 Solvent Extraction

The above procedures aim to obtain the enriched uranium as uranyl nitrate with the fission products and transuranium elements as nitrates, in strong nitric acid solution. The material is then suitable for solvent extraction by techniques similar to those described for low-enrichment uranium fuels (see "Transurane" A1, II, 1974, p. 193ff.). However, the techniques differ in that the residual ^{235}U is the only major fraction of fissionable material to be recovered and the separation and retention of Pu is not a major objective. Furthermore the degree of enrichment makes the total mass of material to be processed smaller than that for the unenriched fuel for equivalent power rating. Also to avoid criticality hazards the dimensions of the equipment must be small. Consequently in the reprocessing of enriched fuel the installations used are never the same as those used for the reprocessing of unenriched, or slightly enriched, fuel although the procedures can be very similar.

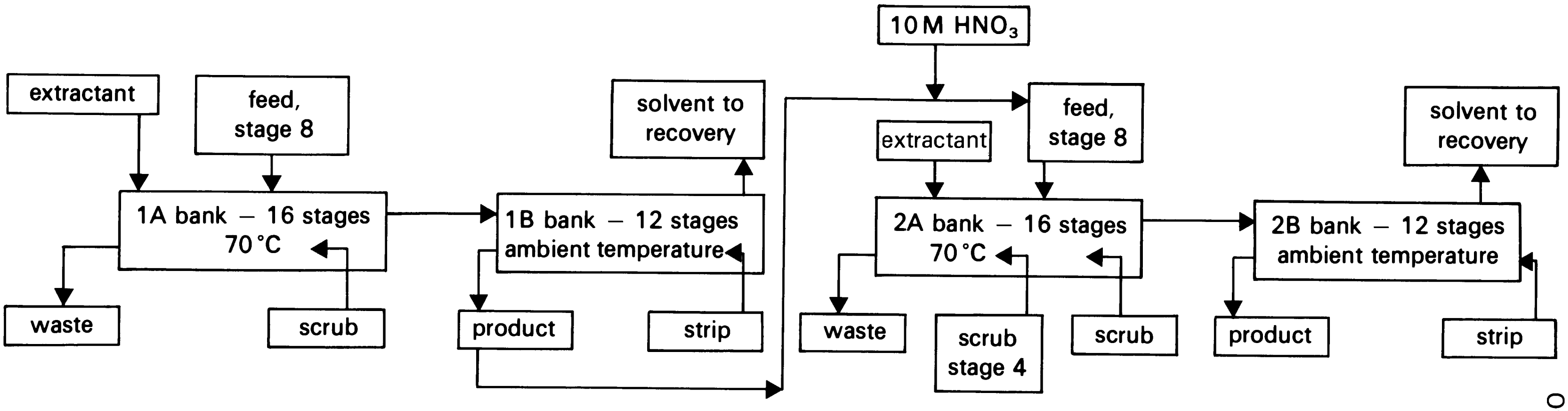
The feed solutions will be expected to contain larger fractions of the cladding and alloying elements such as aluminium, steel, or zirconium at concentrations greater than those met in the processing of natural, or low-enriched, uranium. As a result processes, that have been developed and operated, consist mainly of repetitive cycles in which salting out agents are used to promote the extraction of uranium into hexone (= methyl isobutyl ketone) or tributyl phosphate with suitable diluents.

Fig. 2-5 shows solvent extraction cycles for separating 90% enriched uranium from Al-based fuels employing aluminium nitrate as a salting out agent as described by Stephenson [1]. The table in the figure shows the reagent concentration and relative flow details. Further details of the process were given by Cooper, Welling at the 2nd Geneva Conference [2] and described again by Bruce et al. [3]. Studies on the effect of temperature, particularly on the decontamination from Ru and Zr fission products in extraction processes of the type shown in Fig. 2-5 have been extensively carried out [4].

Fig. 2-6, p. 270, shows a process similar to that shown in Fig. 2-5 but applied to steel based fuels. This was used for the recovery and purification of enriched uranium from the Army Package Power Reactor fuel where the initial stages undergo the "DAREX" process [5, 13, 14]. Here the fuel is dissolved in a mixture of HNO_3 and HCl, and the chloride ion is removed by oxidative distillation. In this latter process Fe^{II} amidosulfate ("ferrous sulphamate") is used to reduce any Pu present to the trivalent condition so that it remains in the aqueous phase and does not extract with uranium. The amidosulfate is added to remove nitrous acid from the nitric acid so as to control the redox potential of the Fe^{II} ion.

A recent paper describes experiences with the type of flow sheet shown in Fig. 2-6 at the Savannah River Plant (SRP). Here fuel from the High Flux Isotope Reactor (HFIR) is processed to recover transuranium elements as well as fuel containing enriched uranium. Fission product activities were reported which gave doses of 3×10^5 rad/h to the feed solutions. Doses at this

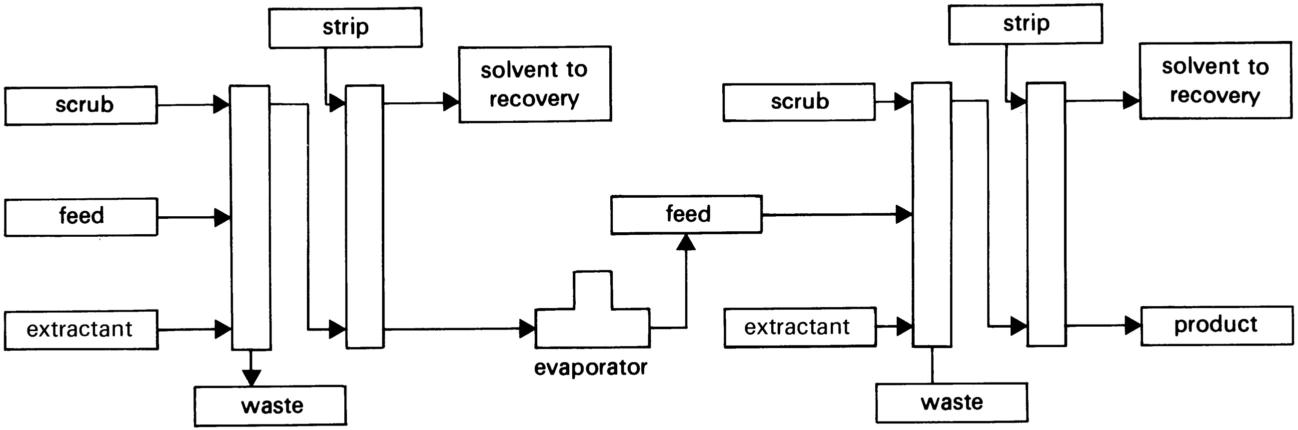
Fig. 2-5



High temperature flow sheet for highly-enriched uranium fuels alloyed with aluminium.

stream	relative flow	composition
	(first cycle)	
feed	100	3 g U/l, 1.2 M Al(NO$_3$)$_3$, 0.5 M HNO$_3$
scrub	15	1.2 M Al(NO$_3$)$_3$, pH 1.3
extractant	35	6 vol% TBP, 94 vol% n-dodecane
strip	5	0.01 M HNO$_3$
product	5	60 g U/l, βDF = 2.6×10^6, γDF = 4.3×10^5
	(second cycle)	
feed	7.1	42.3 g U/l, 3.0 M HNO$_3$
10 M HNO$_3$	2.1	
scrub, stage 4	3	3.0 M HNO$_3$
scrub, stage 1	3	0.01 M HNO$_3$
extractant	21	18 vol% TBP, 82 vol% n-dodecane
strip	14	0.01 M HNO$_3$
product	14	21.4 g U/l, βDF = 2.6×10^8, γDF = 4.3×10^8

Fig. 2-6



Flow sheet for highly-enriched uranium fuels clad in stainless steel.

stream	relative flow	composition
first cycle feed	100	5 g U/l, 3 M HNO_3, Fe, Cr, Ni, $\beta DF = 1$, $\gamma DF = 1$
first cycle scrub	20	3 M HNO_3, 0.75 M $Al(NO_3)_3$, 0.01 M $Fe(NH_2SO_3)_2$
first cycle extractant	83	5 vol% TBP, 95 vol% Amsco 125-82
first cycle strip	83	0.01 M HNO_3
first cycle product	83	6 g U/l, $\beta DF = 4.8 \times 10^5$, $\gamma DF = 6.0 \times 10^4$
second cycle product		$\beta DF = 1.6 \times 10^8$, $\gamma DF = 1.5 \times 10^8$

level were sufficient to oxidise the Fe^{II} ions in the feed solution to Fe^{III} ions in a few hours and this prevented the separation of Np and Pu from the uranium. The flow sheet was modified by delaying the addition of Fe^{II} amidosulfate until immediately before the relevant extraction stage [6, 7].

A further adaptation of the process shown in Fig. 2-6 has been associated with improvements in phase separations by the use of gelatin to control surface tension and MnO_2 to control flocculation [8].

Lewis, Rohde [9] have reported on fission product behavior in extraction systems for enriched uranium. Similar studies using the "EUREX" pilot plant have been reported from Italy [10], France [12], and Spain [11, 21]. Development of the solvent extraction process for enriched uranium has been reported from Australia [15]. More recent experiences on the "EUREX" pilot plant for enriched fuel have been reported by Cao, Hall [10], see [18], and on the "PUREX" process for fast reactor fuel by Bondry [17]. A new flow sheet has been used for moderately enriched uranium by General Atomics at San Diego [19]. This is based on new measurements of uranyl ion distribution coefficients between nitric acid and tributylphosphate [20].

Little work has been done using solvents other than tributylphosphate with diluents, but Siddall from Savannah River reports on other organophosphorous reagents [22]. Certain organic amines have also been studied as extraction agents [16].

References for 2.3.5:

[1] C. E. Stephenson (Papers Belg. Symp. Chem. Reprocess., Brussels 1957; TID-7534 Bk. 1/3 [1957] 1/481, 1/331, 1/364; N.S.A. **12** [1958] No. 154). – [2] V. R. Cooper, M. T. Walling (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Paper No. 2409; A-CONF-15-P-2409 [1958] 1/68; N.S.A. **12** [1958] No. 14714). – [3] F. R. Bruce, J. M. Fletcher, H. H. Hyman (Progr. Nucl. Energy III **3** [1961] 1/474). – [4] D. G. Karraker (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 333/8). – [5] F. L. Culler, R. E. Blanco (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 259/90).

[6] E. K. Dukes, R. M. Wallace (DP-871 [1964] 1/7; N.S.A. **18** [1964] No. 22004). – [7] M. C. Thompson, G. A. Burney, M. C. Hyder (DP-1396 [1976] 1/19; INIS Atomindex **7** [1976] No. 265173). – [8] H. D. Harmon (DP-1376 [1975] 1/14). – [9] L. C. Lewis, K. L. Rohde (Proc. Intern. Solvent Extract. Conf., Lyon 1974, Vol. 2, pp. 1534/50). – [10] S. Cao, H. Dworschak, A. Hall (Proc. Intern. Solvent Extract. Conf., Lyon 1974, Vol. 2, pp. 1543/80).

[11] L. S. Ramos, J. Ortega, A. Uriarte, P. Michel (Compt. Rend. 1st Colloq. Fr. Esp. Trait. Combust. Irradies, Fontenay-aux-Roses, France, 1967 [1968]), B. Lopez Perez, A. Uriarte-Nueda, L. Ramos Salvador, D. G. Folques (Compt. Rend. 1st Colloq. Fr. Esp. Trait. Combust. Irradies, Fontenay-aux-Roses, France, 1967 [1968], pp. 5/10; C.A. **73** [1970] No. 93910). – [12] P. Michel (Bull. Inform. Sci. Tech. [Paris] No. 127 [1968] 61/73; C.A. **69** [1968] No. 102195). – [13] J. R. Flanary, J. H. Goode (CF-57-11-77 [1957] 1/6; N.S.A. **13** [1959] No. 4554). – [14] F. G. Kitts, B. C. Finney, J. H. Goode (CF-58-11-82 [1958] 1/24; N.S.A. **13** [1959] No. 8783). – [15] M. G. Baillie, R. C. Cairns (AAEC-E-40 [1958] 1/24; N.S.A. **14** [1960] No. 3564; AAEC-E-56 [1960] 1/21; N.S.A. **15** [1961] No. 15694).

[16] S. Cao, H. Dworschak, A. Hall (RT-CHI-73-10 [1973]; C.A. **80** [1974] No. 151734). – [17] J. C. Bondry, P. Miquel (Proc. Intern. Solvent Extract. Conf., Lyon 1974, Vol. 2, pp. 1551/67). – [18] E. Detilleux, S. Cao, A. Capella (Neue Tech. B **11** [1969] 15/9). – [19] L. Abraham (GA-A-15145 [1978] 1/90; INIS Atomindex **10** [1979] No. 451603). – [20] M. C.

Thompson, B. E. Murphree, R. L. Shankle (DP-1384 [1975] 1/22; INIS Atomindex **7** [1976] No. 232695).

[21] R. De Witte, L. Greens, J. Van Bylen, J. Centeno (ETR-198 [1966] 1/34; NP-16598 [1966] 1/34; N.S.A. **21** [1967] No. 17706). – [22] T. H. Siddall (TID-18299 [1963] 1/39; N.S.A. **17** [1963] No. 18182).

2.3.6 Pyrometallurgical Processing

2.3.6.1 Introduction

The heat of solution of uranium metal as ions in water is, like with all heavy metals, very high and the processing procedures, by which the fuel as metal, or oxide is dissolved for solvent extraction and then recovered as metal again, have always seemed wasteful. There has been, in the past, very extensive research and development on methods by which the aqueous solution stage is by-passed and the processing effected by fused salts, liquid metals, or by gasification, acting directly on the fuel material at elevated temperatures. Enriched uranium fuels, in so far as they are small in bulk, compared to unenriched uranium fuels, would seem to lend themselves to these so-called pyrometallurgical techniques.

There are also great economic incentives in shortening the time between removing the fuel from a reactor, and returning the unburned fuel, or new fuel from the "breeding" process, after reprocessing, for further stages of irradiation. The "turn round" time in a fuel cycle determines the total inventory of fuel required for reactor operation. A long "turn round" time has great economic penalties for reactor operation, which are particularly high for enriched uranium, in so far as it increases the overall fissile material inventory required for continuing reactor operation. Pyrometallurgical processing offers possibilities of shortening the "turn round" time, as compared with aqueous processing and is consequently economically attractive.

However, in practice, the degree of purification, and the efficiency of recovery without loss, that can be effected in aqueous processing is not matched in dry processing and the pyrometallurgical methods have not, in general, achieved success sufficient to be adopted as standard industrial methods. In particular the dry methods give rise to slags and residues from processed fuel which contain appreciable fractions of the materials to be recovered or separated. These slags and residues can be treated by dissolution in acids followed by aqueous processing. However, if aqueous processing installations require to be operated for the slags and residues there is little economic incentive not to use aqueous methods for the whole fuel.

The dry methods for reprocessing uranium can be listed under:

1 Fluoride volatility
2 Melt refining
3 Melt extraction (fused salts or liquid metals)
4 Fractional crystallization from molten solvent
5 Electric refining.

"Pyrometallurgical methods" do not normally involve fluoride volatility.

The advantages of these methods include:

1 Reduction of fuel inventory by the ability to process material after short periods of radioactive decay.
2 Simplification of shielding requirements of small compact process equipment as compared to the extensive ducting of aqueous systems.
3 Reduction of the number of processing steps and chemical conversions.

4 Recovery of alloying reagents.
5 Reduction of critical mass problems and lessening of the criticality hazard involved in the introduction of water in aqueous solutions as a neutron moderator.
6 Reduction of the total volume of high level active waste.
7 Reduction of the hazard of polluting water supplies and the natural water table by the escape of aqueous solutions.

This last advantage may be crucial in making the reprocessing of nuclear fuel acceptable to the environment in highly populated areas. A general account of pyrometallurgical methods is given by Levenson [9].

2.3.6.2 Fluoride Volatility

This was originally developed in the recovery of uranium from uranium ore concentrates and was used by the Allied Chemical Corporation from 1959 to 1964 to supply UF_6 to the USAEC at the rate of some 5000 tons U_3O_8 per year [1 to 3]. The process has been adapted and developed for a variety of high-enriched alloy fuels and also for oxide or ceramic fuels such as fast reactor fuels. In France and Belgium the program has been directed specifically for Zr and Al alloy fuels where recovery of Pu is not required. The General Electric Corp. has developed the process called "Aquafluor" in which fluoride volatility is combined with aqueous steps [4]. The uranyl nitrate from the final stages of the aqueous processing plant is converted to solid UO_3 in a fluid bed calciner and converted to UF_6 by reaction with fluorine [5].

For Zr and Al alloy fuels aqueous processing in the initial stages can be eliminated by hydrochlorination. Here the fuel is granulated, by cutting or other mechanical methods. It is then mixed with silicaceous, or other inert material and fluidised with hydrogen chloride gas. Separation occurs through the formation of volatile $ZrCl_4$ or $AlCl_3$, and UCl_3 remains with the fluid bed material. The same bed is then fluidised with fluorine gas, and UF_6 is condensed from the gas stream. Subsequent fractional distillation of the condensate effects separation from the small amounts of the volatile fluorides of the fission products that accompany the uranium [6, 7, 11, 19, 25, 26].

At Oak Ridge the same type of process was developed for the separation of enriched uranium from the Molten Salt Reactor (MSR) fuel [8, 17].

In France the process was extended by carrying out fractional sublimation of the chlorides [10, 18, 20 to 22].

In the USA the fluoride volatility process was developed as a pilot plant to treat the Aircraft Reactor Experiment (ARE) fuel [13 to 15, 24] and also for the Liquid Metal Fast Breeder Reactor (LMFBR) [16]. Investigations on the fluoride volatility method have also been reported by workers in the USSR [23].

2.3.6.3 Melt Processing

The possibilities of melt refining for fuel recovery have been investigated and reported upon mainly for application to fast reactor fuels. The fuel is melted in an oxide crucible and maintained molten for several hours in the region of 1000 to 1300°C. During this time the fission products and other elements fractionate. Noble gases such as Xe and Kr and volatile elements, such as Cs, vaporise. The surface skin in the melt collects highly electropositive elements, such as the rare earths, and can be removed by mechanical skimming. Many of the other impurities remain as a crucible "skull" left after the main melt is poured off.

ZrO_2, mechanically stabilised by the addition of 5% CaO, has been found suitable for crucible material and melt refining operations have been carried out on a 10 kg scale as reported at the 1958 Geneva Conference [27]. Under these conditions no selective partition occurred with Te, Mo, Ru, Rh, or Pd. The rare earth elements La, Ce, and Nd, were removed virtually completely (99%) whereas Eu was less completely removed (90%). Ba and Sr were completely in the oxide slag. Cd and iodine both volatilise, but the latter tended to collect in the furnace environment.

The distribution of the fission products is altered by introducing an atmosphere of N_2 which causes nitriding of some of the elements reported on at the Argonne National Laboratory [28]. Further work has been reported from the Argonne Laboratory [29].

An "Airox" process for pyrometallurgical separations has also very recently been reported from the Argonne Laboratory [33]. Another development called the "Voloxidation" process has been reported from Japan [34].

Work has continued in fractional separation of fission products with varying success by extracting the molten irradiated fuel with a molten metal phase. Molten Zn and molten Mg have been used as solvents to extract fission products. However this pyrometallurgical method causes serious technical difficulties in filtration processes or in other solid-liquid separation processes, and to date there has been no industrial application of this method to the treatment of highly active fuels [30].

No recent references have been found that show work in the field of fractional crystallization from melts as distinct from the melt refining methods (see above).

Electrorefining using LiCl-KCl melts has been studied with a view toward possible application in the Molten Salt Reactor (MSR). In such a reactor, uranium chloride or fluoride dissolved in a molten salt becomes critical and develops heat as it circulates through vessels of suitable geometry. It might be feasible to electrolytically remove fission products from the melt as it passes through the coolant circuit.

With an Fe cathode it is possible to remove Zr, Mo, Ru, La, and Ce from irradiated enriched uranium alloys dissolved in a chloride melt [31, 32].

References for 2.3.6:

[1] W. C. Ruch, D. A. Peterson, E. A. Gaskill, H. G. Tepp (Chem. Eng. Progr. Symp. Ser. **56** No. 28 [1960] 35/41). – [2] A. H. Sutton, J. C. Bishop, M. H. Cohen, K. J. Stahman (Chem. Eng. Progr. Symp. Ser. **62** No. 65 [1966] 20/30). – [3] W. H. Mears, R. V. Townend, R. D. Broadley, A. D. Turissin, R. F. Stahl (Ind. Eng. Chem. **50** [1958] 1771/3). – [4] General Electric Corp. (DOCKET-50-268 [1967] 1/328; N.S.A. **21** [1967] No. 30495). – [5] A. A. Jonke (At. Energy Rev. **3** No. 1 [1965] 3/60).

[6] M. Burgeois, G. Lefort, G. Manevy, Y. Rochedeveux (Proc. Conf. Remote Syst. Technol. **15** [1967] 68/74; C.A. **69** [1968] No. 48545). – [7] J. Schmets, G. Camozzo, A. Francesconi, R. Heremans, G. Pierini, P. Speeckaert (EUREAC-1479 [1966] 1/99; EUR-2399 [1966] 1/99; N.S.A. **20** [1966] No. 27034). – [8] G. I. Cathers, W. H. Carr, R. B. Lindauer, R. P. Milford, M. E. Whalley (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 473/9; A-CONF-15-P-535 [1958] 1/6). – [9] M. Levenson (Status of Pyrometallurgical Processing of Irradiated Reactor Fuels, Preprint Paper No. 52, Engineers Joint Council, New York 1962, pp. 1/14; N.S.A. **16** [1962] No. 29053). – [10] P. Speeckaert (R-1915 [1966]; AEC-tr-4553 [1960]; N.S.A. **15** [1961] No. 17007).

[11] P. Faugeras (AEC-tr-5811 [1963] 1/41; N.S.A. **17** [1963] No. 25359). – [12] N. Levitz, J. Barghusen, E. Carls, A. A. Jonke (ANL-6342 [1961] 1/105; N.S.A. **16** [1962] No.

4215). – [13] G. I. Cathers, R. L. Jolley, E. C. Moncrief (CF-60-3-11 [1960] 1/21; N.S.A. **14** [1960] No. 19018). – [14] W. H. Carr (Chem. Eng. Progr. Symp. Ser. **56** No. 28 [1960] 57/61). – [15] C. L. Whitmarsh (CF-59-4-9 [1959] 1/9; N.S.A. **14** [1960] No. 4380), J. B. Ruch (CF-59-5-89 [1959] 1/14; N.S.A. **15** [1961] No. 7396), C. L. Whitmarsh (CF-59-5-108 [1959] 1/42; N.S.A. **15** [1961] No. 7397), C. L. Whitmarsh (CF-59-8-73 [1959] 1/39; N.S.A. **13** [1959] No. 19982), R. A. Cross, C. L. Whitmarsh (CF-59-8-98 [1959] 1/7; N.S.A. **15** [1961] No. 8868), C. L. Whitmarsh (CF-59-9-2 [1959] 1/75; N.S.A. **14** [1960] No. 2454), R. A. Cross, C. L. Whitmarsh (CF-59-9-5 [1959] 1/8; N.S.A. **15** [1961] No. 8869), G. I. Cathers (CF-59-11-110 [1959] 1/8; N.S.A. **15** [1961] No. 8871).

[16] P. Heylen, W. Claes, H. Le Cerf, J. van Impi, R. De Beukelaer (Trans. Am. Nucl. Sci. **20** [1975] 629). – [17] J. J. Barghusen (Reactor Fuel Process. Technol. **10** [1966/67] 226/33). – [18] M. Bourgeois, M. Perrot (Panel Reprocess. High Irradiat. Fuels, Vienna 1969; CEA-CONF-1360 [1969] 1/17; CONF-690535-2 [1969] 1/17; N.S.A. **23** [1969] No. 49883). – [19] J. Sauteron, P. Faugeras (Panel Reprocess. High Irradiat. Fuels, Vienna 1969; CEA-CONF-1363 [1969] 1/13; CONF-690535-6 [1969] 1/13; N.S.A. **23** [1969] No. 49886). – [20] G. Manevy, Y. Rochedereux (Symp. Reprocess. Nucl. Fuels, Ames, Iowa, 1969; CEA-CONF-1379 [1969] 1/23; CONF-69801-1 [1969] 1/23; N.S.A. **23** [1969] No. 49887).

[21] Y. Rochedereux, M. Perrot, M. Manteja, G. Manevy, M. Burgeois (Symp. Non-Aqueous Reprocess., Mol, Belgium, 1968, Paper 28; CEA-CONF-1194 [1968] 1/36; CONF-681040-11 [1968] 1/36; N.S.A. **23** [1969] No. 13817; C.A. **71** [1969] No. 35260). – [22] M. Burgeois, P. Faugeras (Symp. Non-Aqueous Reprocess., Mol, Belgium, 1968, Paper 7; CEA-CONF-1195 [1968] 1/7; CONF-681040-9 [1968] 1/7; N.S.A. **23** [1969] No. 13818). – [23] V. N. Prusakov, V. K. Ezhov, O. G. Lebedev, V. K. Popov (Ind. Chim. Belge **32** [1967] Spec. No., pp. 787/92; 36th Intern. Congr. Ind. Chem., Brussels 1967, Group IV, Sect. 11, Paper 753). – [24] W. H. Carr, L. J. King, F. G. Kitts, W. T. McDuffee, F. W. Miles (ORNL-4574 [1971] 1/78; N.S.A. **25** [1971] No. 34693). – [25] J. J. Barghusen, A. A. Jonke, N. Levitz, M. Steindler, R. C. Vogel (Progr. Nucl. Energy III **4** [1970] 347/98).

[26] G. Strickland, F. L. Horn (Progr. Nucl. Energy III **4** [1970] 399/425). – [27] L. Burris, N. R. Chellew, S. Lawroski, G. A. Bennett, A. A. Chilenskas, M. Ader, H. M. Feder, J. B. Knighton, I. O. Winsch, J. Wolkoff, W. A. Rodger (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 401/6; A-CONF-15-P-538 [1958] 1/20; N.S.A. **12** [1958] No. 14812). – [28] T. R. Johnson, G. F. Brunzie, R. K. Steunenberg (ANL-6211 [1960] 1/23; N.S.A. **15** [1961] No. 6043). – [29] N. R. Chellew (Nucl. Sci. Eng. **9** [1961] 59/90). – [30] F. S. Martin, I. L. Jenkins, N. J. Keen (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Paper 32; A-CONF-15-P-32 [1960] 1/8; N.S.A. **13** [1959] No. 6499).

[31] L. W. Niedrach, A. C. Glamm, G. R. Fountain (KAPL-1692 [1957] 1/36; N.S.A. **11** [1957] No. 10472). – [32] J. A. Leary, R. Benz, D. F. Bowersox, C. R. Bjorklund, K. W. R. Johnson, W. J. Maraman, L. J. Mullins, J. G. Reavis (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Paper 529; A-CONF-15-P-529 [1958] 1/14; N.S.A. **12** [1958] No. 14811). – [33] L. F. Grantham, R. C. Clark, R. C. Hoyt, J. R. Miller (117th Natl. Meeting Am. Chem. Soc., Honolulu 1980, pp. 219/32; INIS Atomindex **11** [1980] No. 569262). – [34] H. Takeda, T. Hoshino, T. Segawa (Fast Reactor Fuel Process. Proc. Symp., Dounreay, U.K., 1979, pp. 123/32; INIS Atomindex **11** [1980] No. 569285).

2.4 Reprocessing of Spent ^{232}Th-^{233}U Fuels

E. Merz
Institut für Chemische Technologie, Kernforschungsanlage Jülich
Jülich, Bundesrepublik Deutschland

2.4.1 Application of the Thorium Cycle for Energy Production

Two fuel cycles form the basis for the utilization of nuclear energy: the uranium/plutonium and the thorium/uranium cycles [1, 2]. Breeding reactions are possible for the two isotopes ^{238}U and ^{232}Th, producing ^{239}Pu and ^{233}U, respectively. Without them, the world reserves of the naturally occurring and economically producible nuclear fuel ^{235}U would be relatively soon exhausted [3 to 6]. In this manner, however, the naturally available amount of fissile material can be increased manyfold in a relatively simple way. The enormous investments, that are required for building-up a nuclear industry, are thereby justified macro-economically.

The present-day utilization of nuclear energy is based practically exclusively on the uranium/plutonium cycle. It employs mainly light water reactors with slightly enriched uranium. In a few countries also heavy water reactors with natural uranium are being employed. Thorium is no nuclear fuel properly speaking, only a breeding material, since neutron capture in ^{232}Th does not initiate any fission. An optimal utilization of the ^{232}Th-^{233}U cycle requires the availability of a recycling technology, i.e., a separation of the ^{233}U that is bred, and its reintroduction into the reactor as new fuel elements [7, 8].

A decisive argument for the utilization of the thorium cycle is the long range availability of the raw material. A series of calculations of reactor operation strategies has reached an almost unanimous conclusion, that a meaningful application of thorium in various reactor systems leads to considerable medium- and long-range savings of uranium ores. A combined use of both the uranium and the thorium cycles guarantees a long-range supply of nuclear fuel at tolerable and more or less stable prices [9 to 16].

2.4.1.1 Nuclear Reactions and the Buildup of Actinides in the Thorium Cycle

The three fissile nuclides, which are the most important for the utilization of nuclear energy, ^{235}U, ^{239}Pu, and ^{233}U, have different neutron yields as a function of the neutron energy. For thermal neutrons, ^{233}U has the largest neutron yield, followed by ^{235}U. Because of the larger values of α, i.e., the more favorable ratio of neutron capture to fission for ^{233}U, larger conversion factors are attained in the thorium cycle than in the U-Pu one. For fast neutrons, on the other hand, ^{239}Pu delivers the most fission neutrons, and ^{233}U occupies only the second place. The differences though not very large, are still of practical significance. Therefore, the ^{232}Th-^{233}U cycle should be advantageous for thermal neutron operation, the ^{238}U-^{239}Pu cycle for fast neutron operation [17 to 21].

In the neutron field of a nuclear reactor there occur not only nuclear fission reactions, but simultaneously and in a competitive manner also a whole series of neutron capture reactions. To these belongs the above mentioned breeding process. They lead partly to the desired product ^{233}U, but partly also to other nuclides, which affect unfavorably the overall nuclear fuel cycle. The two fuel cycles differ appreciably with regard to the buildup of long-lived transuranium or actinide isotopes [22, 23]. The thorium cycle is more favorable in this regard, since the buildup of the transuranium elements Pu, Am, and Cm is manyfold lower in this than in the uranium cycle [24, 25]. This reduces the dangers of long-range storage of the radioactive waste containing these actinides, that is produced in the reprocessing of "burned-up" fuel elements. On the assumption that the separation factors for the two cycles are the same, this danger would be smaller by two orders of magnitude for the thorium cycle [26 to 31]. The undesired nuclide ^{237}Np is formed in both cycles by double neutron capture in ^{235}U and subsequent β^- decay. Further neutron capture, forming ^{238}Np, and β^- decay leads to ^{238}Pu, which is also undesired, on account of its relatively short half-life and high radiotoxicity. Particularly undesired is ^{232}U, that is formed from ^{232}Th by (n,2n) reactions, or from traces of ^{230}Th present, by double neutron capture, (n,γ), reactions. The absolute quantities formed are quite small, being 50 to 500 ppm relative to ^{233}U, but some of the members of the decay chain of ^{232}U emit highly energetic γ quanta, so that special radiation protection arrangements have to be made in handling this ^{233}U (see Section 2.4.9.1, p. 349). The following Table 2/2 summarizes the half-life and specific activity values of the most important actinide isotopes relevant to this discussion.

Table 2/2
Long-Lived Alpha Emitters in the Nuclear Fuel Cycle.

isotope	half-life in a	specific alpha activity in Ci/g	isotope	half-life in a	specific alpha activity in Ci/g
^{230}Th	7.5×10^{4}	2.1×10^{-2}	^{237}Np	2.1×10^{6}	7.6×10^{-4}
^{232}Th	1.4×10^{10}	1.1×10^{-7}	^{238}Pu	8.8×10^{1}	1.8×10^{1}
^{232}U	7.2×10^{1}	2.2×10^{1}	^{239}Pu	2.4×10^{4}	6.4×10^{-2}
^{233}U	1.6×10^{5}	9.6×10^{-3}	^{240}Pu	6.5×10^{3}	2.4×10^{-1}
^{234}U	2.4×10^{5}	6.2×10^{-3}	^{242}Pu	3.9×10^{5}	4.0×10^{-3}
^{235}U	7.0×10^{8}	2.2×10^{-6}	^{241}Am	4.3×10^{2}	3.5×10^{0}
^{236}U	2.3×10^{7}	6.7×10^{-5}	^{243}Am	7.5×10^{3}	2.1×10^{-1}
^{238}U	4.5×10^{9}	3.5×10^{-7}	^{244}Cm	1.8×10^{1}	8.7×10^{1}

2.4.1.2 The Use of Thorium in Various Reactor Systems

It is useful to consider in this respect the light- and heavy water and high temperature reactors (HTR), operated with a thermal neutron flux on the one hand, and the breeder reactors operated with fast neutrons (fast breeder reactors, FBR) on the other [32 to 34]. The latter are either gas- or Na-cooled. There exist no significant differences regarding the application of Th in the fuel cycles in these two reactor concepts, so that they may be treated here uniformly. This is valid also for cooling concepts for fast breeders, that have been abandoned, such as cooling with water vapor. Thermal reactors, for which a ^{232}Th-^{233}U cycle was a viable prospect, have not been realized. Much effort went in the USA into the so-called molten salt reactor [35]. It has reached a rather advanced stage of technological development: experiments have been conducted for numerous years in a prototype facility, although only with the reactor part, without the heat exchanges required for the production of useful energy. The reactor core consisted of the eutectic salt melts UF_4-Li_2BeF_4 or UF_4-ThF_4-Li_2BeF_4 [36 to 39]. Reprocessing, i.e., the direct and continuous separation of the ^{233}U that was bred by the fluoride volatility process in a side stream, was to be provided for [40, 41]. A net breeding gain under attractive economical operating conditions was calculated theoretically for this system. However, in attempts to realize this concept practically, many obstacles crept up.

A second unsuccessful concept, that provided for the use of Th as a fertile material, was the heavy-water moderated organic cooled reactor [42, 43]. The best known project bore the name ORGEL, and was financed by EURATOM [44, 45].

An analysis of the possibility of the use of thorium for breeding in thermal reactors of present-day construction shows, that in all cases a saving of uranium is achieved, provided, that an effective ^{233}U-recycling technology is available [46, 47]. Under certain circumstances, in particular if the prices of uranium rise, slight cost advantages may even be achieved by applying the thorium cycle. The best prospects for success seem to exist for high temperature reactors [48 to 58]. This type of reactor promises to provide a particularly economical manner of operation, when the Th-^{233}U fuel cycle is applied. When graphite is used as the moderator, a good converter is obtained, but not a true breeder [59 to 62]. It was therefore proposed, that the use of beryllium oxide as an additional moderator and as a neutron multiplier will lead to conversion factors near unity [63, 64]. No technical break-through of this idea has as yet taken place, however.

Beside the gas cooled high temperature reactors, also heavy water moderated reactors of the CANDU type promise economic advantages, when operated with a Th-^{233}U cycle strategy. The first considerations thereof originated in the early sixties [65 to 70]. Both systems show about as good fuel utilization, with significantly higher capital costs of the heavy water reactor, however, the main reason being the extra costs of the heavy water, D_2O [71 to 77]. Somewhat technically modified heavy water reactor concepts were examined in Sweden and in India [78, 79].

Also in light water reactors of present day construction, i.e., both boiling water and pressurized water reactors, may Th and ^{233}U be introduced successfully, with appreciable savings of uranium. The fuel cycle costs are, however, considerable higher than for the other reactor types. Most of the calculations were carried out for pressurized water reactors. Application of Th in light water reactors will, therefore, be of interest only if the introduction of fast breeders into commercial operation suffers a long delay, or if the prices of uranium show a strong upward tendency [80 to 84]. As yet, a Th-containing fuel element for light water reactors has been realized in the West only in the Elk River Reactor in the USA [85]. A demonstration attempt of an advanced light water breeding project, using ^{233}U fuel elements, has proceeded at the rebuilt Shippingport Reactor since the beginning of 1978 [86, 87].

Fast breeder reactors, too, are suitable for operation with Th, in several alternative manners. Considerations and calculations have been initiated for using Th exclusively in the breeding mantle and chemically separated ^{233}U as fissile fuel in the core [88]. It may, however, be even possible to use Th in the core itself. Finally, proposals have been made to follow a mixed utilization strategy [89 to 99]. Other considerations deal with the gas cooled fast breeders [100].

2.4.1.3 Types of Fuel Elements

The form and the chemical composition of nuclear fuel elements differ sometimes considerably, dependent on their use in light water, heavy water, high temperature, or fast breeder reactors. Also the production of fuels and of fuel elements depends on the reactor type, for which they are to be provided. There is, in principle, no basic difference in either form or constitution between the U and U/Pu fuel elements, which are being used at present, and those envisaged for Th. Although metallic fuels and breeding materials are discussed for light water and fast breeder reactors, their practical use is improbable, for the same reasons valid also for the U/Pu elements. Although metals or metallic alloys yield higher rates of conversion to fissile isotopes, they are at a disadvantage relative to the ceramic fuels preferred nowadays, because of their inferior mechanical properties and their higher liability to corrosion. Th metal, though, behaves somewhat better than does U metal. Small U contents in the thorium do not have any measurable negative effect [81, 84, 101 to 105].

The preferred fuel for Th reactors is the oxide, and in certain cases the carbide. For water reactors, till now, only oxidic fuels and breeding materials have been considered, in particular for the CANDU D_2O reactor [106, 107]. The oxides are either pressed into pellets, or vibrated-in as small particles into stainless steel or Zircaloy cladding tubes. The initially preferred vibrational compacting technique was later displaced by the use of the oxide pellets [108 to 114], but recently the former method has been revived [115]. Because of the evidently less troublesome production method for highly radioactive materials, the wet chemical production of the particles and their subsequent introduction into the fuel rods by vibration or form pressing by remote control have certain advantages. The behavior of these fuel elements under irradiation was tested and found to be very satisfactory [116, 117]. No appreciable differences are expected for fast breeder elements with Th relative to the conventional U/Pu ones.

The fuel element conception for high temperature reactors, however, is quite different. Two basically different fuel element types are now recognized: the American prismatic fuel element blocks [118 to 120], and the German spherical fuel elements [121 to 124]. A third type was the tubular fuel element of the DRAGON reactor [125 to 127]. The construction and mode of operation of these three reactor types are quite different, but they have the common feature of the use of helium as the cooling gas. Also the composition of the fuel shows similarities. The fuel and the breeding material are introduced in all cases as small spherulets (diameter of 0.2 to 1.0 mm), which are coated with one or several layers of pyrolitic carbon or SiC in order to improve the retention of the fission products. The choice exists of the introduction of the two elements either as pure oxides or carbides separately, or as the mixed compounds. The coated fuel particles are embedded in a graphite matrix, either homogeneously, for the spherical fuel elements, or heterogeneously, for the prismatic and tubular fuel elements, as dictated by reactor-physical considerations. The mass fraction of graphite and of carbon are nearly equal, being 90 to 95% [128 to 131]. Extensive results provide evidence for the good behavior upon irradiation [132 to 142]. A Pu/Th/Be mixed oxide fuel element concept of the Australians has not been pursued [143, 144].

References for 2.4.1:

[1] M. Benedict, T. H. Pigford (Nuclear Chemical Engineering, McGraw-Hill, New York-Toronto-London 1957, pp. 65/128). – [2] A. M. Weinberg (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 3, pp. 19/25). – [3] P. Engelmann, U. Hansen, G. Kolb, D. Leushacke, E. Teuchert, H. Werner (JUEL-1612 [1979] 91). – [4] P. R. Kasten (At. Energy Rev. **8** [1970] 473/534). – [5] E. R. Merz (IAEA-CN-36-96 [1977] 37/53; Nucl. Power Its Fuel Cycle Proc. Intern. Conf., Salzburg 1977, Vol. 2, pp. 37/52; INIS Atomindex **9** [1978] No. 368451).

[6] P. R. Kasten, F. J. Homan, E. J. Allen, D. E. Bartine, W. L. Carter, E. H. Gift, J. D. Jenkins, A. L. Lotts, K. J. Notz, R. Olsen, R. H. Rainey, J. E. Rushton, M. L. Tobias (ORNL-TM-5565 [1977] 253; INIS Atomindex **8** [1977] No. 316134). – [7] E. L. Nicholson, L. M. Ferris, J. R. Flanary, J. H. Goode, B. A. Hannaford, J. W. Landry, J. G. Moore, R. H. Rainey, C. D. Watson, H. O. Witte (CONF-660524-6 [1966] 1/42; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 589/615; N.S.A. **20** [1966] No. 33414). – [8] E. Merz, M. Laser, E. Zimmer (Kerntechnik **15** [1973] 249/56). – [9] M. W. Rosenthal, H. F. Baumann, L. L. Bennett, R. S. Carlsmith, D. R. Vondy (ORNL-TM-1145 [1965] 1/29; CONF-650615-4

[1965] 1/28; Proc. Panel Util. Thorium Power Reactors, Vienna 1966; N.S.A. **19** [1965] No. 38186). – [10] M. F. Duret, M. J. Halsall (STI-DOC-10-52 [1965] 55/76; N.S.A. **20** [1966] No. 32822).

[11] P. U. Fischer, S. Jaye, H. B. Stewart (SM-111-70 [1968]; Advan. High Temp. Gas Cooled Reactors Proc. Symp., Vienna 1968 [1969], pp. 745/60; C.A. **71** [1969] No. 55839). – [12] H. Gutman, H. Larsen, U. Hansen, H. J. Neef, R. H. Brogli (GA-A-13055 [1974]; ANS Transactions **20** [1975] 416/8). – [13] J. Schlösser (IAEA-SM-105-24 [1968]; Symp. Econ. Nucl. Fuels, Vienna 1968, pp. 399/412; C.A. **73** [1970] No. 115568). – [14] E. A. Eschbach, D. E. Deonigi (CONF-660524-14 [1968] 1/26; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 13/27). – [15] E. Teuchert, H. J. Rütten, H. Werner, K. A. Haas, R. Schulten (JUEL-1569 [1979] 1/43).

[16] Oak Ridge National Laboratories (WASH-1099 [1971] 1/260; N.S.A. **26** [1973] No. 16913). – [17] G. C. Hanna, C. H. Westcott, H. D. Lemmel, B. R. Leonard, J. S. Story, P. M. Attree (At. Energy Rev. **7** [1969] 3/92). – [18] D. Okrent (Power Reactor Technol. **7** [1964] 107/37). – [19] D. R. Vondry, B. A. Worley (ORNL-5484 [1979] 1/174). – [20] A. M. Perry, A. M. Weinberg (Ann. Rev. Nucl. Sci. **22** [1972] 317/54).

[21] P. R. Kasten, M. L. Tobias (Trans. Am. Nucl. Soc. **22** [1975] 334/9). – [22] R. H. Clarke, H. F. McDonald, J. Fitzpatrick, A. J. H. Goddard (Ann. Nucl. Energy **2** [1975] 451/66). – [23] H. O. Haug (KFK-2020 [1975] 1/203). – [24] R. Schulten (JUEL-1243 [1975] 1/27; INIS Atomindex **7** [1976] No. 249533). – [25] R. D. Baybarz (At. Energy Rev. **8** [1970] 327/60).

[26] M. J. Bell, R. S. Dillon (ORNL-TM-3548 [1971] 1/23; N.S.A. **26** [1972] No. 9543). – [27] A. S. Kubo, D. J. Rose (Science **182** [1973] 1205/11). – [28] U. Wenzel, M. Laser, E. Merz (Trans. Am. Nucl. Soc. **22** [1975] 350/2). – [29] M. Rückert, R. Hecker, J. Migenda, N. Mirza (JUEL-1285 [1976] 1/37; INIS Atomindex **7** [1976] No. 271226). – [30] F. Gera, D. G. Jacobs (ORNL-4762 [1972] 1/151; N.S.A. **26** [1972] No. 31620).

[31] J. Hamstra (Nucl. Safety **16** [1975] 180/9). – [32] P. Wenzel (Kernenergie **8** [1965] 625/35). – [33] P. R. Kasten, F. J. Homan (IAEA-CN-36-402 [1977] 1/11; Intern. Conf. Nucl. Power Its Fuel Cycle, Salzburg 1977, pp. 2.4.-T.1/06; INIS Atomindex **8** [1977] No. 303902). – [34] H. B. Stewart (AED-CONF-76-090-005 [1976]). – [35] P. R. Kasten (CONF-660524-5 [1968] 1/20; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1960, pp. 185/99; N.S.A. **20** [1966] No. 35026).

[36] M. W. Rosenthal, R. E. Adams, L. L. Bennett, W. L. Carter, D. A. Douglas, R. E. Hoskins, C. G. Lawson, A. L. Lotts, R. C. Olson, A. M. Perry, J. T. Roberts, R. Salmon, D. R. Vondy (ORNL-3686 [1965] 1/257; N.S.A. **19** [1965] No. 10552). – [37] P. R. Kasten et al. (ORNL-TM-1467 [1967]). – [38] P. R. Kasten, E. S. Bettis, H. F. Bauman, W. L. Carter, W. B. McDonald, R. C. Robertson, J. H. Westsik (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 41/63). – [39] P. N. Haubenreich (CONF-660524-18 [1965] 1/11; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 671/9; N.S.A. **20** [1966] No. 47015). – [40] C. D. Scott, W. L. Carter (ORNL-3791 [1966] 1/128; N.S.A. **20** [1966] No. 43422).

[41] W. R. Grimes (ORNL-TM-1853 [1967] 1/138; N.S.A. **21** [1967] No. 30163). – [42] F. Lafontaine, J. Noailly, B. Haytink (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 119/28). – [43] W. B. Lewis (Ann. Nucl. Energy **2** [1975] 779/86). – [44] European Atomic Energy Community (EUR-1830.e-Pt. I [1964] 1/434, Pt. II [1964] 1/705, Pt. III [1964] 1/360; N.S.A. **18** [1964] No. 40826/8). – [45] G. Blässer (CONF-660524 [1968] 1/27; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 201/6; N.S.A. **21** [1967] No. 21728).

[46] L. W. Lang (Nucl. Appl. Technol. **9** [1970] 242/9). – [47] W. V. McNabb, J. C. Scarborough (Trans. Am. Nucl. Soc. **13** [1970] 470/1). – [48] S. Brandes (EUR-2780.e [1965] 371/88; N.S.A. **20** [1966] No. 40469). – [49] L. R. Shepherd, H. de Bruijn, K. O.

Hintermann, R. A. U. Huddle (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 1, pp. 326/34). – [50] R. S. Carlsmith, C. M. Podeweltz, W. E. Thomas (ORNL-TM-1112 [1965] 1/19; N.S.A. **19** [1965] No. 25729).

[51] P. R. Kasten, I. Spiewak, M. L. Tobias (IAEA-SM-200-85 [1975] 1/28; INIS Atomindex **7** [1976] No. 240953). – [52] L. E. Eckart, B. J. Rumble (Trans. Am. Nucl. Soc. **24** [1976] 223/4). – [53] E. Teuchert, H. J. Rütten (IAEA-SM-200-84 [1975] 1/12; INIS Atomindex **7** [1976] No. 245034). – [54] H. B. Stewart, R. C. Dahlberg, W. V. Goddel, D. B. Trauger, P. R. Kasten, A. L. Lotts (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 4, pp. 433/47). – [55] F. J. Homan (Trans. Am. Nucl. Soc. **17** [1973] 314/7).

[56] R. C. Dahlberg, K. Asmussen, D. Lee, L. Brooks, R. K. Lane (Nucl. Eng. Design **26** [1974] 58/77). – [57] L. L. Bennett, R. K. Lane (CONF-740501 [1974] 128/45; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 128/45; C.A. **82** [1975] No. 91468). – [58] H. Oehme (CONF-740501 [1974] 72/91; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 72/91; C.A. **82** [1975] Nr. 91434). – [59] V. Maly, R. Schulten, E. Teuchert (Atomwirtsch. Atomtech. **19** [1974] 601/3). – [60] P. Fortescue (Ann. Nucl. Energy **4** [1977] 59/63).

[61] R. K. Lane, R. Brogli, R. F. Turner, N. Koo (GA-A-14029 [1976] 1/67; INIS Atomindex **8** [1977] No. 318782). – [62] H. Werner (JUEL-1365 [1976] 1/96; INIS Atomindex **8** [1977] No. 332987). – [63] W. Gemmell, J. P. Pollard, J. C. Symonds (CONF-660524-7 [1968] 1/14; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 107/18; N.S.A. **20** [1966] No. 45176). – [64] A. Bicevskis, E. W. Hesse, D. J. Mercer (CONF-660524-20 [1968] 1/31; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 129/55; N.S.A. **21** [1967] No. 1195). – [65] D. F. Babcock, R. R. Hood, D. S. St. John (Ger. 864 [1963] 1/40; N.S.A. **18** [1964] No. 9643).

[66] D. S. St. John, J. W. Wade (Nucleonics **22** [1964] 54/7). – [67] J. W. Boswell (DPST-64-416 [1964] 1/77; N.S.A. **18** [1964] No. 45015). – [68] P. R. Kasten (JUEL-276-RG [1965] 1/163; N.S.A. **20** [1966] No. 14126). – [69] C. A. Rennie (CONF-670437 [1967] 39/44; 3rd Foratom Congr. Ind. Aspect Fast Breeder Reactor Programme, London 1967, pp. 39/44; N.S.A. **22** [1968] No. 35497). – [70] G. Cardoni, P. Venditti (RT-FI-66-42 [1968] 1/118; N.S.A. **22** [1968] No. 44835).

[71] W. B. Lewis, M. F. Duret, D. S. Graig, J. I. Veeder, A. S. Bain (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 9, pp. 239/53). – [72] C. Steinert (AED-CONF-71-100-32 [1971] 1/15; CONF-710901-528 [1971] 1/15; N.S.A. **26** [1972] No. 30211). – [73] S. Banerjee, E. Critoph, R. G. Hart (Can. J. Chem. Eng. **53** [1975] 291/6). – [74] J. S. Foster, E. Critoph (Ann. Nucl. Energy **2** [1975] 689/703). – [75] E. Critoph, M. S. Milgram, J. I. Veeder, S. Banerjee, F. W. Barclay, D. Hamel (AECL-5501 [1976] 1/20; ANS Winter Meeting, San Francisco 1975; INIS Atomindex **7** [1976] No. 258022).

[76] S. R. Hatcher, S. Banerjee, A. D. Lane, H. Tamm, J. I. Veeder (AECL-5398 [1976] 1/28; ANS Winter Meeting, San Francisco 1975; INIS Atomindex **8** [1977] No. 284196). – [77] E. Critoph (IAEA-CN-36-177 [1977] 1/11; Intern. Conf. Nucl. Power Its Fuel Cycles, Salzburg 1977, pp. 2.A.1.P.1/01; INIS Atomindex **8** [1977] No. 303895). – [78] B. Almgren (CONF-660524-11 [1968] 1/24; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 65/79; N.S.A. **20** [1966] No. 47009). – [79] B. P. Rastogi, H. K. Bhatia, A. N. Nakra, K. R. Srinivasan, T. A. Subramanian (CONF-660524-17 [1968] 1/31; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 359/76; N.S.A. **20** [1966] No. 45105). – [80] S. Baldetti, F. Doria, M. Gabaglio, S. Grifoni (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 9, pp. 255/69).

[81] G. B. Zorzoli (Energia Nucl. [Milan] **19** [1972] 151/61). – [82] G. B. Zorzoli (Reaktortagung, Karlsruhe 1973, pp. 745/8). – [83] C. C. Lin, B. A. Zolotar (Trans. Am. Nucl. Soc. **21** [1975] 261/2). – [84] R. L. Hellens, R. A. Matzie, J. R. Rec, P. R. Sehgal (Trans. Am.

Nucl. Soc. **23** [1976] 272/3; INIS Atomindex **8** [1977] No. 120673). – [85] J. R. Fisher, E. D. Kendrick (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 681/94).

[86] C. S. Bohanan, D. H. Jones, H. F. Raab, A. Radkowsky (U.S. 3988692 [1976]; U.S. 3960655 [1976]; C.A. **85** [1976] No. 84524). – [87] W. M. Pardue (Ann. Nucl. Energy **2** [1975] 835/46). – [88] P. J. Wood, M. J. Driscoll (Trans. Am. Nucl. Soc. **17** [1973] 314/7). – [89] T. Oikawa (Genshiryoka Kogyo **9** [1963] 20/5). – [90] A. I. Leipunskii, O. D. Kozachkovskii, S. B. Shikhov, V. M. Murogow (At. Energ. [USSR] **18** [1965] 342/50).

[91] R. S. Singh, H. H. Hummel (ANL-6930 [1966] 1/28; N.S.A. **20** [1966] No. 32790). – [92] C. B. Mills (Nucl. Appl. **3** [1967] 589/90). – [93] W. O. Allen, D. J. Stoker, A. V. Campise (CONF-660524-16 [1966] 1/18; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 81/90; N.S.A. **20** [1966] No. 47047). – [94] V. K. Shukla, S. B. Garg (BARC-550 [1971] 1/16; N.S.A. **26** [1972] No. 11336). – [95] A. I. Leipunskii, L. N. Yurova, S. B. Bobrov, V. M. Murogov, L. V. Tochenyi, M. F. Troyanov, A. N. Shmelev (At. Energ. [USSR] **30** [1971] 491/8; C.A. **75** [1971] No. 93542).

[96] R. H. Broglie, K. R. Schultz (Proc. Am. Power Conf. **36** [1974] 247/58; C.A. **82** [1975] No. 176813). – [97] R. Broglie, G. Schlueter (GA-A-13110 [1974] 1/9). – [98] B. R. Seghal, C. Lin, J. Naser, W. B. Loewenstein (Trans. Am. Nucl. Soc. **21** [1975] 422/3). – [99] B. R. Seghal, J. Naser, C. Lin, W. B. Loewenstein (Trans. Am. Nucl. Soc. **22** [1975] 704/5; INIS Atomindex **7** [1976] No. 252516). – [100] R. J. Cerbone, N. Tsaulfanidis (Trans. Am. Nucl. Soc. **22** [1975] 703/4; INIS Atomindex **7** [1976] No. 252410).

[101] B. R. Hayward, L. E. Wilkinson (NAA-SR-3411 [1959] 1/35; N.S.A. **13** [1959] No. 20165). – [102] J. E. Gates, G. E. Lamale, R. F. Dickerson (BMI-1334 [1959] 1/51; N.S.A. **13** [1959] No. 13516). – [103] J. H. Kittel, J. A. Horak, W. F. Murphy, S. H. Paine (ANL-5674 [1963] 1/36; N.S.A. **17** [1963] No. 27887). – [104] C. Lin, B. Zolotar (EPRI-NP-2 [1975] 1/19). – [105] A. Boettcher (Ger. 2034549 [1974]; C.A. **81** [1974] No. 144554).

[106] L. R. Haywood, J. A. L. Robertson, J. Pawliw, J. Howieson, L. L. Bodie (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 8, pp. 185/99). – [107] S. V. K. Rao (CRFD-1154 [1963] 1/45; AECL-1785 [1963] 1/45; N.S.A. **18** [1964] No. 2217). – [108] N. M. Griesenauer, M. S. Farkas, F. A. Rough (BMI-1680 [1964] 1/33; N.S.A. **18** [1964] No. 35925). – [109] E. Sokolowski, A. J. W. Andersson, R. Persson, C. E. Wikdahl (CONF-660524-23 [1966] 1/17; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 29/39; N.S.A. **21** [1967] No. 2884). – [110] W. J. Robertson, W. J. S. Smith, T. H. Sublett (CONF-660524-15 [1966] 1/14; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 735/44; N.S.A. **20** [1966] No. 43850).

[111] J. M. Kerr, L. D. Barnes, J. W. Ryon (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 537/46). – [112] J. B. Fisher, E. D. Kendrick (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 681/94). – [113] M. E. A. Hermans, H. S. G. Slooten (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 450/7). – [114] F. W. Hamburg, N. van der Kley, E. B. M. Majoor, T. van der Plas, P. F. Sens, J. H. N. Verheugen, F. W. van der Bruggen, M. E. A. Hermans, J. B. W. Kanij, A. J. Noothout, C. Hubers (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 8, pp. 263/79). – [115] Westinghouse Electric Comp. (WAPD-TM-1242-43 [1975]; WAPD-TM-1262-63 [1975]).

[116] A. R. Olsen, D. B. Trauger, W. O. Harms, R. E. Adams, D. A. Douglas (ORNL-TM-1142 [1965] 1/63; N.S.A. **19** [1965] No. 37175). – [117] E. Balthesen, K. Ehlers, K. G. Hackstein, H. Nickel (CONF-740501 [1974] 201/17; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 201/17; C.A. **82** [1975] No. 104571). – [118] T. D. Gulden, J. L. Scott, C. Moreau (CONF-740501 [1974] 176/200; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 176/200; C.A. **82** [1975] No. 104467). – [119] J. H. Coobs, P. R. Kasten (ORNL-5108 [1976] 1/513; INIS Atomindex **8** [1977] No. 315839). – [120] J. W. Landis, E. W. O'Rokke, C. L. Rickard, P.

Fortescue, J. V. Everett, R. F. Walker, D. B. Trauger (Proc. 4th Internat. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 5, pp. 345/65).

[121] M. Herren, K. H. Neeb, M. Peehs, K. Reichardt, B. Thiele (Atomkernenergie **17** [1971] 33/8). – [122] E. Balthesen, K. Ehlers, K. G. Hackstein, H. Nickel (CONF-740501 [1974] 201/17; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 201/17; C.A. **82** [1975] No. 104467). – [123] M. Hrovat, G. Spener (Ber. Deut. Keram. Ges. **43** [1966] 220/3). – [124] M. Hrovat, H. Huschka, G. Spener, P. Venet (Energie Nucl. **9** [1967] 373/85). – [125] R. A. U. Huddle (Trans. Am. Nucl. Soc. **6** [1963] 382/3).

[126] R. A. U. Huddle, M. S. T. Price, M. Houdaille, W. G. Popp (EUR-2780.e [1965] 1/26; N.S.A. **20** [1966] No. 40466). – [127] L. W. Graham, M. S. T. Price, R. A. Saunders, E. Smith (CONF-740501 [1974] 218/56; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 218/56; C.A. **82** [1975] No. 104468). – [128] Y. Yamazaki, K. Yohida, M. Komori (Nippon Genshiryoku Gakkaishi **9** [1967] 326/8; C.A. **67** [1967] No. 121682). – [129] P. Koss, H. Bildstein (CONF-660524-12 [1968] 1/31; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 253/72; N.S.A. **20** [1966] No. 43860). – [130] H. Stöcker (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 293/8).

[131] M. S. Farkas (CONF-660524-8 [1966] 1/25; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 445/62; N.S.A. **20** [1966] No. 47010). – [132] C. B. Scott, D. P. Harmon (Nucl. Technol. **35** [1977] 442/54). – [133] D. P. Harmon, C. B. Scott (Nucl. Technol. **35** [1977] 343/52). – [134] T. B. Lindemer, H. J. de Nordwall (ORNL-4926 [1974] 1/85; N.S.A. **29** [1974] No. 17563). – [135] R. A. Olstad, A. R. Olsen, R. B. Fitts, E. L. Long, T. B. Lindemer (ORNL-TM-4397 [1974] 1/62; N.S.A. **30** [1974] No. 20361).

[136] J. Baier (JUEL-1038-HT [1973] 1/141; C.A. **81** [1974] No. 57199). – [137] E. Balthesen, H. Ragoß (CEGB-BNL [1973] 231/4). – [138] H. Nickel, E. Balthesen (JUEL-1159-RW [1975] 1/39; C.A. **83** [1975] No. 105073). – [139] L. A. Neimark (Trans. Am. Nucl. Soc. **5** [1962] 226/8). – [140] S. A Rabin, J. W. Ullmann, E. L. Long, M. F. Osborne, A. E. Goldman (ORNL-3837 [1965] 1/66; N.S.A. **20** [1966] No. 2429).

[141] A. R. Olsen, J. H. Coobs, J. W. Ullmann (CONF-660524-10 [1966] 1/30; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 475/94; N.S.A. **20** [1966] No. 40385). – [142] C. S. Luby, A. S. Schwartz (CONF-660524-26 [1966] 1/24; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 495/508; N.S.A. **21** [1967] No. 11323). – [143] A. Bicevskis (AAEC-TM-350 [1966] 1/21; N.S.A. **21** [1967] No. 25612). – [144] R. C. Cairns, M. G. Baillie, M. S. Farrell, J. R. May (CONF-660524-21 [1966] 1/40; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 217/52; N.S.A. **21** [1967] No. 1192).

2.4.2 Classification of Reprocessing Methods

The aims of the chemical reprocessing of the spent nuclear fuel are twofold: the removal of the radioactive fission products from the unconsumed nuclear fuel, and the separation of the ^{233}U produced by the breeding from the Th. The mass of the fission products and of the bred isotopes constitute normally only a small fraction of the material that has to be processed. Very large decontamination of the fissile material from the fission products (decontamination factors of 10^6 to 10^8) is nowadays demanded from a reprocessing method. The reason is the desire to refabricate from the recovered fissile material new fuel elements without the need of special radiation protective shielding. The question has, however, often been raised, whether this method is necessarily simpler and more economical than a remote-controlled refabrication behind shielding, after less strict decontamination. This question is still undecided, and a compromise will probably be struck at the end: High yields of the fissile material are required on economical grounds, with decontamination factors of at least 10^4. Refabrication without radiation shielding is then hardly possible.

Another question that has been debated, is whether a reprocessing plant integrated with the power plant offers any advantages [1 to 3]. The decision was clearly in favor of a centralized reprocessing facility, on both technical and economical grounds.

The need for reprocessing of spent fuel elements altogether has been recently questioned for various reasons. The main argument arose from the political camp: it was feared that fissile material might be diverted to military uses. Another fraction doubted the economical basis for reprocessing, and the opponents of nuclear power, finally, reject a nuclear fuel recycling industry in principle.

There are two good arguments why reprocessing and recycling of the recovered fissile material cannot be dispensed with in the long run:

1. In order to ensure a longer-range provision of raw materials for fuel fabrication it is necessary to reuse the fissile material (both the unused and the bred-in materials) contained in the spent fuel. The limited supply of uranium in the earth's crust does not permit the throwing away of bred-in fissile material.

2. A low-risk disposal of the large amounts of radioactive fission products, necessarily containing long-lived α-decaying actinide elements (including plutonium) can only be made by reprocessing and recycling. This is the prerequisite to low-risk waste disposal. The dangerous radioactive materials are thereby cleanly separated, so that they can be transferred to final storage after suitable further preparation.

These statements, however, must not be misconstrued, as meaning that immediate reprocessing must be provided for. According to the situation, an interim storage of the fuel elements removed from the reactor for up to 20 years before submitting them to reprocessing may be justified, without endangering the environment. These temporarily stored fuel elements may, of course, be sent to final disposition without reprocessing, if certain disadvantages incurred are accepted.

2.4.2.1 Listing of the Processes

Several separation methods, that are different in principle, are known in chemistry. They may be classified as follows:

1. Wet (aqueous) processes, subdivided into:

a) precipitation processes,
b) ion exchange processes, and
c) solvent extraction processes.

2. Dry processes, which again may be subdivided into:

a) halide volatilization processes, and
b) pyrochemical or pyrometallurgical processes.

Each reprocessing method is subdivided for practical purposes into four individual stages:

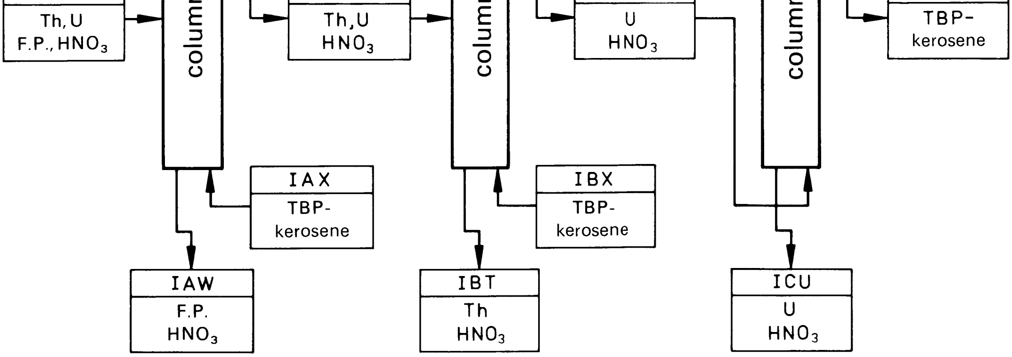
- head-end treatment,
- chemical separation,
- tail-end treatment or final purification, and
- reconversion, as a preliminary stage to refabrication.

If some other methods, that could conceivably be used for the separation, are not included in the above list, it is not because they have not undergone minute examination (e.g., wet processes such as electrolysis or electrophoresis), though not in connection with the Th-^{233}U cycle. The few studies, that have been conducted with them for the U/Pu cycle, however, yielded such bad results, that they were not examined further [4 to 6]. Whereas the aqueous processes have already shown their usefulness and dependability for industrial application, this is not the case for the other processes. During the last 20 years, a whole series of considerations was pursued, of how could Th-containing fuel elements be reprocessed and the ^{233}U recovered in pure form in the most effective manner. The few older studies are concerned with the recovery of ^{233}U from the fuel elements of water-cooled reactors [7 to 12]. Besides the Americans, it was the Italians who made extensive efforts to demonstrate the reprocessing technology of Th-containing nuclear fuels [13 to 16]. Several engineering studies were devoted to the conversion of existing LWR reprocessing facilities to the processing of Th-containing nuclear fuels [17 to 19].

The development was advanced to a great extent, however, only with the advent of the advanced high temperature reactor line. Numerous theoretical and experimental studies were concerned with the general aspects of the Th cycle [20 to 33], with the problems of the process technology [34 to 56] as well as with the economical aspects [57 to 71]. First considerations were given also to the fuel cycles of a gas-cooled Th breeder [72] and the molten salt thorium breeder, by now abandoned [73, 74].

Almost all these studies reached the unanimous conclusion, that an extractive reprocessing, according to the so-called THOREX principle, should be the best choice. Counter-current extraction processes for the recovery and decontamination of fissile and fertile materials were always multi-stage processes. The following simplified presentation of the THOREX process in **Fig. 2-7** shows, that Th and U are first separated together from the fission products (the

Fig. 2-7



Simplified flow diagram of the THOREX process. F.P. = fission products.

References for 2.4.2 on pp. 290/3

columns, or mixer-settlers, IA). This coextraction is followed by a division into separate product streams in subsequent units of the extraction equipment (IB and IC). If the purity of the recovered materials falls below the specifications, further purification cycles follow the first one.

The development of a flow scheme for a counter-current extraction process always starts with the determination of the optimal flux ratios of the aqueous and organic phases (A:O ratio) in the extraction and scrubbing parts of column IA. This ratio is determined first of all for the major component A of the feed solution IAF (for the THOREX process: Th). Important criteria, which serve for the plant design, are:

– maximal saturation of the organic phase, in order to attain high decontamination factors,
– high yields of the valuable materials (>99.9% in the theoretical planning stage),
– not too many theoretical stages, in order to minimize the height of the columns or the sizes of the mixer-settlers.

Methodologically, it is possible to make use for this purpose either of numerical methods, with the aid of computers, or of graphical methods, according to McCabe-Thiele. A prerequisite for carrying out these calculations is a knowledge of the distribution data for the system HNO_3-A-TBP/kerosene (TBP = tri-n-butyl phosphate). Once the ratio A:O and the number of stages required for the extraction of the component A (= Th) are known, the second component, B (= U) can be taken into consideration by a second iterative process. At very low concentrations of B ($\leq$1%) it will not affect the extraction behavior, but at higher concentrations a mutual influence of A and B must be reckoned with.

It is necessary to distinguish for the development of the head-end process between the metal-clad fuel elements of water-cooled and fast breeder reactors on the one hand, and the graphite containing coated particles in the fuel elements of high temperature gas-cooled reactors on the other. In all the cases, however, it is necessary to remove the metallic cladding or the matrix material before the chemical dissolution of the fuel proper. Nitric acid serves almost exclusively as a dissolution reagent.

2.4.2.2 The History of the Development of ^{232}Th-^{233}U Reprocessing

The recovery of ^{233}U from reactor-irradiated Th or the reprocessing of Th-containing nuclear fuels has not yet taken place on an industrial scale, in contrast to the recovery of Pu in the U fuel cycle (see Section 2.2., pp. 258/9 and "Transurane" A1, II, 1974, from p. 177). The start of the development of suitable processes, however, followed with but a few years of delay. The interest centered from the beginning on wet-chemical processes of solvent extraction [75 to 77], after the PUREX process had been invented near the end of the World War II at the Clinton Works (later the Oak Ridge National Laboratory), for the recovery of weapon-grade Pu from irradiated U fuel elements [78 to 81].

A chemically and technologically very similar process, the THOREX process, was proposed for Th-containing fuel elements. It constitutes till today the unchallenged most favored reprocessing method. In both cases, counter-current extraction with tri-n-butyl phosphate (TBP), dissolved in an inert diluent (kerosene, dodecane), is the nucleus of the process [4, 82 to 84]. The nuclear fuels must have been previously dissolved in nitric acid, i.e., the nitrate system is being used. The ability of TBP to extract tetra- and hexavalent metal nitrates was recognized first by Warf [85, 86].

The essential developmental work for the recovery of ^{233}U from irradiated Th, took place at the Oak Ridge National Laboratory (ORNL) in the USA. A total of four different processes was developed and tested there during the fifties:

1. the HEXONE-^{233}U process [87],
2. the INTERIM-^{233}U process [88],
3. THOREX No. 1 process [89], and
4. THOREX No. 2 process [90].

Only the THOREX No. 2 process was finally used for demonstration with irradiated materials. The "Kilorod" pilot plant, which was commissioned in Oak Ridge in 1955, worked according to this flow scheme [91, 92]. A total of 1.3 t irradiated ThO_2 was reprocessed in it during an 8 months campaign. A demonstration plant, that should have worked according to the same principles, called TRIP (Thorium Recycle Integrated Plant), was planned by the U.S. company Babcock & Wilcox [93, 94]. A pilot plant for the refabrication of ^{233}U-containing fuels of the same company was operated in 1965 for a few months for the production of about 100 kg (Th, $^{233}U)O_2$ fuel [95].

The hot-cell building, that had been made ready at ORNL for the uptake of the HTR (High Temperature Reactor) fuel elements of the so-called TURF plant (Thorium Uranium Recycle Facility) [96] many years ago stands still unused. The demonstration plant at Rotondella, built by the Italian governmental nuclear energy authority, has not yet started its hot operation. Originally, it was forseen, that the Th-containing fuel elements of the Elk River Reactor would be reprocessed there [15]. A semiworks plant is being built in the F. R. Germany for the reprocessing of HTR fuel elements. The so-called JUPITER plant (Juelich Pilotanlage für Thorium Element Reprocessing) has a throughput of 2 kg/day of heavy metal. It was supposed to start its hot operation with spent fuel elements of the Jülich experimental power plant AVR during 1980 [97, 98].

In the past, considerable quantities of Th-containing nuclear fuels from military programs have been reprocessed in PUREX plants in special campaigns, but no details have become available publicly. On the other hand, the literature contains some pieces of information concerning the recovery of ^{233}U from reactor-irradiated Th. The two US governmental plants at Hanford and at Savannah River have been used for this purpose [99 to 101]. Most recently, the possible use of the Barnwell Nuclear Fuel Plant in the USA for the reprocessing of Th-containing nuclear fuels has been considered, within the framework of the so-called International Nuclear Fuel Cycle Evaluation Program [102]. This plant had originally been built for the reprocessing of fuel from light water reactors, but has not yet been commissioned for hot operation [103]. This procedure, i.e., the use of a LWR reprocessing plant for Th-containing nuclear fuel, cannot be satisfactory for commercial purposes. Firstly, difficult to remove, contamination by ^{233}U and Th may occur, but more decisive are the unfavorable process procedure and the use of corrosive fluoride-containing solutions. In the PUREX process, U is the primary and Pu the secondary component. In the THOREX process Th is the primary component, but is found in the Pu part of the PUREX process. For U, the secondary component in the THOREX flow scheme, however, the PUREX plant is highly overdimensioned. A THOREX flow scheme may, therefore, be realized in a PUREX plant only by making a series of disadvantageous technological compromises. Criticality saftey poses a particularly difficult problem [104]. In any case, for commercial purposes specifically designed plants are necessary.

The THOREX No. 2 process, which today forms the basis for all further developments, was originally designed for the reprocessing of solutions of irradiated Th that contained 1 kg ^{233}U/t Th. This corresponded to a feed solution of 350 g Th/L and a U content of about

0.3 g/L. The extraction agent was 42.5 vol% TBP in dodecane; the salting-out agent in both the extraction and scrubbing parts of column IA was $Al(NO_3)_3$.

A revision of this scheme by the Knolls Atomic Power Laboratory led in 1956 to the KAPL acid THOREX process [77]. Two changes relative to the ORNL process were introduced:

a) The $Al(NO_3)_3$ in the scrubbing part of column IA was given up, thereby reducing the salt content of the IAW waste stream.
b) The concentration of the extracting agent was reduced from 42.5 to 30 vol% TBP.

U was treated as a trace component.

The problem of recovering larger quantities of U together with the Th arose only in 1962, when Consolidated Edison thorium reactor fuel elements (96% ThO_2, 4% UO_2) came to be reprocessed. For these the ORNL-acid THOREX process was developed, which abandoned completely the use of $Al(NO_3)_3$ as a salting-out agent on the one hand, but permitted the reprocessing of Th solutions having U contents up to 10% on the other with 30 vol% TBP (feed: 267 g Th/L, $\leq$ 20 g U/L, -0.15 mol HNO_3/L, i.e., a nitric acid deficiency) [105]. Since no higher U contents were expected in fuel solutions, even for later HTR programs, conditioned by the dependence on the burnup/breeding cycle, no need arose in the USA to conduct further flow scheme studies. The development was therefore practically stopped, and only in recent years was it taken up again to a limited extent. It involved the writing of computer programs for the calculation of the simultaneous distribution of U, Th, and HNO_3 and the simulation of THOREX runs. The aim even now is not the further development of the THOREX process, in view of the processing of solutions having larger U contents, but rather the exact theoretical mastery and the technological optimization of the ORNL flow sheet of the year 1962.

Experiments, dealing with the reprocessing of Th solutions containing up to 20% U under THOREX conditions, were carried out in the early 70's in the F. R. Germany, in the framework of the project "Reprocessing of Thorium-Containing Nuclear Fuels" [106]. It was shown by experiments, that if the flow rate ratio of the organic extractant to the aqueous feed was raised from 7:1 to (8 to 9.5):1 (with adjustment of the flow rates in columns IB and IC), up to 55 g U/L could be extracted with the Th and subsequently separated from it. It was also shown, however, that thereby the upper limit for U in the ORNL flow scheme was reached, since no smaller A:O ratio (aqueous to organic) could be achieved under practical processing conditions in the column IA [107].

In the case that the reprocessing of fuel elements having an even higher U content became necessary in a so-called alternative fuel cycle [108 to 110], advanced flow schemes would have to be developed [111]. A practically new process would then have to be set up, the conditions of which would still require both theoretical development and experimental testing. A further difficulty which would arise, is that Pu could then no longer be considered as a trace component, but would have to be taken into account as a fourth component beside Th, U, and HNO_3.

The forced development of the gas-cooled high temperature reactor, in which the use of the Th fuel cycle was economically particularly attractive, gave a new impetus in the mid-60's to the developmental work, which has slipped somewhat to the background. Since then extensive research and development programs have been conducted, mainly in the USA and in the F. R. Germany. According to the results that have been attained to date, there exist justified hopes that the reprocessing of Th-containing nuclear fuels and breeding materials and the recovery of ^{233}U can be realized as well technologically as is the case in the competing U/Pu cycle.

A special case presents the separation of the intermediate link in the breeding chain: ^{233}Pa, when fuel elements have to be reprocessed after a short cooling only. The relatively long half-life of 27 days (compared with 2.35 days for ^{239}Np in the U/Pu cycle) dictates the choice between either a cooling period of about one year, or the giving-up of a part of the potentially bred fissile material, in the form of ^{233}Pa that has not yet converted to ^{233}U. Normally, in the THOREX process, Pa reaches the fission product waste stream, and is thus lost. A way out is the application of a preliminary separation step, in which the Pa is selectively adsorbed on a suitable sorbent, and then eluted. The nitric acid-containing dissolution liquor coming from the dissolver is led to an adsorption column, filled with Vycor glass particles (a special silica glass with a large surface) or with silica gel. The Pa, which exists in the solution almost exclusively as polymeric species, is retained selectively, whereas all the other ions pass through the column [112 to 119]. The Pa is subsequently eluted with oxalic acid, or else the U, which is eventually formed as ^{233}U from beta decay of the ^{233}Pa, is dissolved off after waiting for the necessary period [120 to 122].

A broad gamut of methods has been considered in the recent studies, consisting of both "classical" aqueous as well as all kinds of nonaqueous processes (see Sections 2.4.7 and 2.4.8). It was found, however, quite rapidly that the THOREX processing scheme is preferable to all the alternatives [123, 124].

2.4.2.3 Composition of the Irradiated Fuel Elements

The chemical reprocessing becomes simpler, the less radioactive the material to be processed is. The interim storage in large water- or also air-cooled stores is taken today as a necessary measure for bridging any bottlenecks occurring in the reprocessing.

The calculation of the composition of the irradiated fuel elements is considered nowadays as a more or less routine problem. Basic expressions for this calculation may be found in [125]. The calculation program, that is most widely used today is called ORIGEN [126]. Various publications about the composition of AVR and HTR fuel elements made use of this program [127]. Other programs were also published [128 to 130].

Nuclear fuel elements are retained for 2 to 4 years in the reactor, according to their composition and the operational strategy. After they have left the reactor, their composition has changed significantly. Table 2/3 shows, as an example, that from the originally present 3 component system (graphite, fuel, and fertile material) a multicomponent system has been formed. It contains beside the unused fertile material, ^{232}Th, and the primary fissile material, ^{235}U, the newly formed fissile material ^{233}U, transuranium elements, Pu and Np, and fission products. The latter are constituted by practically all the elements with atomic numbers between 34 and 64.

A high temperature reactor of 1160 MW (electrical) contains a total of 38 t heavy metal, of which 36 t are Th and about 2 t U, containing $\approx$1.6 t ^{235}U and ^{233}U. Almost 9 t fuel elements must be exchanged per year, so that their mean residence time in the reactor is 4 years. The ratio of carbon to heavy metal is between 150 and 250.

Similar, but by no means identical, compositions of heavy metals and fission products occur in Th-containing fuel elements of other reactor systems. Table 2/4 summarizes the compositions of various types of fuel elements.

Table 2/3
Composition of New and of Partly Burned-up Fuel Elements of the THTR-300 (simplified). FIMA = Fission of initial heavy metal atoms.

component	new fuel element in g	burned-up fuel element after 12% FIMA, in g
graphite	ca. 190	ca. 190
^{232}Th	10.20	9.25
^{233}U	–	0.237
^{235}U	1.000	0.028
^{236}U	–	0.179
^{238}U	0.075	0.056
^{237}Np	–	0.026
Pu isotopes (238 to 242)	–	0.013
fission products	–	1.20

Table 2/4
Composition of Feed Solutions from Various Th-Containing Nuclear Fuels, and from an LWR Fuel Element for Comparison.

fuel element	HNO_3 in mol/L	Th in g/L	U in g/L	Pu in g/L	Th:U
HTR-MEU-Th 10.5 GWd/t	−0.15 to 1.0	267	286	7.5	0.93
AVR-HEU-Th 5 GWd/t	−0.15 to 1.0	267	45	0.04	6
AVR-HEU-Th 10 GWd/t	−0.15 to 1.0	267	33.6	0.1	8
HTR-HEU-Th 10 GWd/t	−0.15 to 1.0	267	13.9	0.2	19.2
LWR-MEU-Th 3.3 GWd/t	−0.15 to 1.0	267	67	13	4
LWR-LEU 3.5 GWd/t	−1.0 to 3.0	–	226	2	–

AVR = Arbeitsgemeinschaft Versuchreaktor; HTR = high temperature reactor; LWR = light water reactor; HEU = highly enriched uranium (ca. 93% ^{235}U + ^{233}U); MEU = medium enriched uranium (ca. 20% ^{235}U + ^{233}U); LEU = low enriched uranium ($\leq$8% ^{235}U + ^{233}U).

References for 2.4.2:

[1] W. E. Unger, F. E. Harrington, J. R. May, S. F. Scott, T. N. Washburn (ORNL-3959 [1967] 1/108; N.S.A. **21** [1967] No. 23611). – [2] F. L. Culler (ORNL-TM-678 [1963] 1/45; N.S.A. **17** [1963] No. 36876). – [3] J. R. May, J. M. Devine (AAEC-E-175 [1967] 1/47; N.S.A. **21** [1967] No. 45188). – [4] J. F. Flagg, I. Wells, D. Pepper (in: J. F. Flagg, Chemical Processing of Reactor Fuels, Academic, New York 1961, pp. 305/47). – [5] S. Lawrowski (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 575/82).

[6] M. Benedict, T. H. Pigford (Nuclear Chemical Engineering, McGraw Hill, New York 1957, pp. 304/58). – [7] A. R. Irvine, A. L. Lotts (TID-7650 [1962] 333/50; N.S.A. **17** [1963] No. 28462). – [8] A. R. Irvine, A. L. Lotts (ORNL-TM-149 [1962] 1/80; N.S.A. **16** [1962] No. 10103). – [9] D. A. Orth (Nucl. Technol. **43** [1979] 63/74). – [10] R. H. Rainey (Nucl. Sci. Eng. **18** [1964] 530/1).

[11] J. K. Davidson, R. S. Miller (CONF-193-Vol. 1 [1967] 242/58; 8th Nucl. Congr., Rome 1963, Vol. 1, pp. 242/58). – [12] J. L. Gray (Can. Mining Met. Bull. **66** [1973] 60/4). – [13] J. K. Davidson, G. Orsenigo, A. Pedretti, A. C. Schafer (TID-7650 [1962] 285/332; N.S.A. **17** [1963] No. 28461). – [14] G. Orsenigo (Tech. Rept. Ser. Intern. At. Energy Agency No. 52 [1966] 127/37). – [15] G. Calleri, S. Cao, M. Fiorelli, G. Orsenigo, U. Piotti, C. Vallone (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 8, pp. 375/94).

[16] A. C. Schafer (Reactor Fuel Process. Technol. **12** [1969] 243/63). – [17] S. L. Reese, P. Burn, S. E. Donelson, K. G. Steyer (GAMD-6360 [1964] 1/67; N.S.A. **21** [1967] No. 43016). – [18] J. J. Shefcik (GAMD-7657 [1967] 1/62; N.S.A. **23** [1969] No. 6197). – [19] N. Srinivasan, M. N. Nadkarni, G. R. Balasubramanian, R. T. Chitnis, H. R. Siddiqui (BARC-643 [1972] 1/38; C.A. **79** [1973] No. 48322). – [20] W. L. Carter (ORNL-TM-241 [1962] 1/57; N.S.A. **16** [1962] No. 23789).

[21] W. Giesser (EUR-2780.e [1965] 389/99; N.S.A. **20** [1966] No. 40470). – [22] G. W. Horsley, L. A. Podo, F. C. Wood (DP-Report-338 [1965] 1/30; N.S.A. **24** [1970] No. 46302). – [23] J. T. Roberts (KR-126 [1967] 279/323; N.S.A. **22** [1968] No. 42387). – [24] G. Orsenigo, U. Piatti Forni, C. Vallone (RT-ING-71-18 [1971] 54 pp.; N.S.A. **26** [1972] No. 20192). – [25] J. J. Shefcik (GAMD-8382 [1967] 1/131; N.S.A. **23** [1969] No. 2369).

[26] J. Wharton, G. D. C. Short (DP-Report-540 [1968] 1/25). – [27] B. F. Roth (Atom Strom **17** [1971] 30/40). – [28] G. D. C. Short, G. Orsenigo, E. Römberg (CONF-660524 [1966] 617/46; AEC Symp. Ser. No. 12 [1968] 617/45; N.S.A. **22** [1968] No. 23092). – [29] J. J. Shefcik (GAMD-8615 [1968] 1/22; N.S.A. **23** [1969] No. 2370). – [30] R. G. Wymer (CONF-720928-1 [1972] 1/25; N.S.A. **26** [1972] No. 58672).

[31] K. G. Hackstein (Atomwirtsch. Atomtech. **18** [1973] 294/7). – [32] E. Fischer, G. Kaiser, M. Laser, E. Merz, H. J. Riedel, H. Witte (Tech. Rept. Ser. Intern. At. Energy Agency 115 [1970] 201/22). – [33] R. C. Dahlberg, K. Assmussen, D. Lee, L. H. Brooks, R. K. Lane (Nucl. Eng. Design **26** [1974] 58/77). – [34] B. Almgren (Tech. Rept. Ser. Intern. At. Energy Agency No. 52 [1966] 169/71). – [35] E. L. Nicholson, L. M. Ferris, J. R. Flanary, J. H. Goode, B. A. Hannaford, J. W. Landry, J. G. Moore, R. H. Rainey, C. D. Watson, H. O. Witte (ORNL-P-2192 [1966] 1/42; CONF-660524-6 [1966] 1/42; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966; N.S.A. **20** [1966] No. 33414).

[36] R. G. Wymer, A. L. Lotts (ORNL-4275 [1969] 181; N.S.A. **23** [1969] No. 16509). – [37] L. H. Brooks, C. R. Davis, D. D. Peterman, M. E. Spaeth (CONF-730918-2 [1975] 1/8; GA-A-12272 [1973] 1/8; Joint Power Generat. Conf., New Orleans 1973; N.S.A. **29** [1974] No. 3147). – [38] H. Jauer, M. Laser, E. Merz, S. Storch, U. Tillessen (JUL-943-CT [1973] 1/77; C.A. **79** [1973] No. 142065). – [39] E. R. Merz, E. Zimmer (AED-CONF-75-241-001 [1975] 1/8). – [40] L. H. Brooks (GA-A-12853 [1974] 1/79).

[41] L. H. Brooks, A. L. Lotts, R. G. Wymer (CONF-740501 [1974] 257/67; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 257/67; C.A. **82** [1975] No. 104469). – [42] E. R. Merz, G. Kaiser, E. Zimmer (CONF-740501 [1974] 268/87; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 268/87; C.A. **82** [1975] No. 128951). – [43] C. A. Heath, M. E. Spaeth (CONF-750424-2 [1975] 1/38; GA-A-13279 [1975] 1/38). – [44] A. P. Roeh, B. R. Wheeler (Trans. Am. Nucl. Soc. **22** [1975] 336/7). – [45] R. C. Dahlberg, R. F. Turner, R. K. Lane, D. M. Jackson, R. Finkbeiner (Trans. Am. Nucl. Soc. **20** [1975] 413/4).

[46] U. Tillessen, E. Merz, G. Kaiser (Trans. Am. Nucl. Soc. **20** [1975] 636/9). – [47] J. Brisbois, P. Couture, X. Roudier, R. Sartorius (Trans. Am. Nucl. Soc. **20** [1975] 414/6). – [48]

J. N. Sharmahd (GA-A-15662 [1979] 1/25). – [49] E. Merz, G. Kaiser, M. Laser, E. Zimmer (AED-CONF-76-337-002 [1976] 1/15). – [50] L. H. Brooks, C. A. Heath, J. J. Shefcik (CONF-760823-3 [1976] 1/25; GA-A-13807 [1976] 1/23; INIS Atomindex **8** [1977] No. 283229).

[51] E. Merz, G. Kaiser (Reaktortagung Düsseldorf 1976, Sect. 2, pp. 331/4; INIS Atomindex **7** [1976] No. 239759). – [52] K. J. Notz (ORNL-TM-5328 [1976] 1/73). – [53] D. F. Leushacke, G. G. Kaiser (Trans. Am. Nucl. Soc. **31** [1979] 190/3). – [54] A. L. Lotts, J. H. Coobs (ORNL-TM-5501 [1976] 1/48) – [55] W. D. Burch, A. L. Lotts (Intern. Conf. Nucl. Power Its Fuel Cycle, Salzburg 1977, pp. 2.7.-T.1/12; IAEA-CN-36-14 [1977] 1/19; INIS Atomindex **8** [1977] No. 302950).

[56] G. Kaiser, E. Merz, E. Zimmer, H. Pirk, P. Vygen (Intern. Conf. Nucl. Power Its Fuel Cycle, Salzburg 1977, pp. 2.7.-T.1/11; IAEA-CN-36-112 [1977] 1/9; INIS Atomindex **8** [1977] No. 302965). – [57] A. L. Lotts, R. G. Wymer (ORNL-TM-2377 [1968] 1/55; N.S.A. **23** [1969] No. 2034). – [58] M. C. Edlund (TID-7650 [1962] 721/35; N.S.A. **17** [1963] No. 28479). – [59] M. C. Edlund (Proc. Am. Power Conf. **26** [1963] 128/35). – [60] M. Zifferero (EUR-2780.e [1965] 289/97; N.S.A. **20** [1966] No. 40392).

[61] E. C. Moncrief (BAW-288 [1966] 1/10). – [62] E. C. Moncrief, G. Schileo (BAW-393-3 [1966] 1/47; N.S.A. **24** [1970] No. 50004). – [63] J. T. Roberts, L. M. Ferris, E. L. Nicholson, R. H. Rainey, C. D. Watson (Tech. Rept. Ser. Intern. At. Energy Agency No. 52 [1966] 313/52). – [64] G. B. Scuricini, D. Lavrencic, A. Lummetti, P. Venditti (EUR-2537.i [1966] 1/118; N.S.A. **20** [1966] No. 35019). – [65] J. J. Shefcik, K. G. Steyer (GAMD-8458 [1967] 1/27; N.S.A. **22** [1968] No. 42812).

[66] K. G. Steyer, H. E. Stelling (GA-7107 [1966] 1/19; C.A. **66** [1967] No. 90746). – [67] H. E. Stelling, K. G. Steyer (GAMD-7294 [1966] 1/114; N.S.A. **23** [1969] No. 4711). – [68] G. D. Short, J. Wharton (DP-470 [1967] 1/28). – [69] J. J. Shefcik (GAMD-9089 [1968] 1/12; N.S.A. **23** [1969] No. 17513). – [70] L. L. Bennet, W. E. Thomas (ORNL-TM-3852 [1972] 1/20).

[71] E. J. Detilleux (Tech. Rept. Ser. Intern. At. Energy Agency No. 158 [1973] 447/58). – [72] L. Meyer (JUEL-CONF-14 [1975] 295/311; C.A. **84** [1976] No. 23464). – [73] C. D. Scott, W. L. Carter (ORNL-3791 [1966] 1/128; N.S.A. **20** [1966] No. 43422). – [74] W. L. Carter, M. W. Whatley (ORNL-TM-1852 [1967] 1/50; N.S.A. **21** [1967] No. 30505). – [75] B. J. Fontana (TID-5223-Pt. 1 [1952] 134/42; N.S.A. **11** [1957] No. 11493).

[76] A. T. Gresky (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 505/10). – [77] W. O. Haas, D. J. Smith (KAPL-1306 [1956] 1/96; N.S.A. **11** [1957] No. 2224). – [78] D. E. Ferguson, T. C. Runion (ORNL-260 [1949] 1/47). – [79] W. B. Lanham, T. C. Runion (ORNL-479-Del. [1960] 1/11; N.S.A. **14** [1970] No. 22950). – [80] F. L. Culler (Progr. Nucl. Energy III **1** [1956] 172/94).

[81] B. Goldschmidt, P. Regnaut, J. Prevot (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 492/7). – [82] F. L. Culler (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 464/83). – [83] S. M. Stoller, R. B. Richards, A. T. Gresky, D. E. Ferguson, P. E. Smith (in: S. M. Stoller, R. B. Richards, Reactor Handbook, Vol. 2, Interscience, New York 1961, pp. 208/25). – [84] J. T. Long (Engineering for Nuclear Fuel Reprocessing, Gordon and Breach, New York 1967, pp. 162/96). – [85] J. C. Warf (CC-2402 [1945]; ISC-8 [1947]).

[86] J. C. Warf (J. Am. Chem. Soc. **71** [1949] 3257/8). – [87] J. F. Flagg (in: J. F. Flagg, Chemical Processing of Reactor Fuels, Academic Press, New York 1961, pp. 249/70). – [88] C. D. Hylton (ORNL-1425-Del. [1952] 1/36; N.S.A. **13** [1959] No. 1204). – [89] A. T. Gresky, M. R. Bennett, S. S. Brandt, W. I. McDuffee, J. E. Savolainen (ORNL-1367-Rev. [1953] 1/157; N.S.A. **11** [1957] No. 8395). – [90] R. H. Rainey, A. B. Merservey, R. G. Mansfield (ORNL-2591 [1959] 1/55; N.S.A. **13** [1959] No. 7596).

[91] F. R. Bruce, E. M. Shank, R. E. Brooksbank, J. R. Parrott, G. S. Sadowski (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 49/72). – [92] R. E. Brooksbank, J. P. Nichols, A. L. Lotts (CONF-660524-3 [1966] 1/34; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 321/40). – [93] E. C. Moncrief, G. Schileo (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 157/84). – [94] E. C. Moncrief, C. A. Burkart, D. A. Nitti (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 509/36). – [95] J. M. Kerr, L. D. Barnes, J. W. Ryon (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 537/46).

[96] J. D. Sease, R. B. Pratt, A. L. Lotts (CONF-660524-2 [1966] 1/23; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 341/57; N.S.A. **20** [1966] No. 25525). – [97] G. Kaiser, E. Merz, H. J. Riedel (Nucl. Met. **15** [1969] 25/36). – [98] G. Kaiser, E. Merz, P. Sckuhr (Trans. Am. Nucl. Soc. **14** [1971] 79/81). – [99] R. L. Walser, R. R. Jackson (ARH-2127 [1977] 1/194, 82; INIS Atomindex **9** [1978] No. 351694). – [100] J. M. Boswell, R. D. McCrosky, J. T. Stringer, W. K. Woods (CONF-660524-1 [1966] 1/22; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 745/63; N.S.A. **20** [1966] No. 25466).

[101] H. C. Rathvon, A. G. Blasewitz, R. Maher, J. C. Eargle, A. E. Wibble (CONF-660524-19 [1966] 1/75; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 765/824; N.S.A. **20** [1966] No. 43415). – [102] A. Giambusso (Fuel Cycle Conf. '78, New York 1978, 9 pp.). – [103] J. A. Buckham (Fuel Cycle Conf. '78, New York 1978, 20 pp.). – [104] S. R. Bierman, E. D. Clayton (BNWL-2115 [1976] 1/25; INIS Atomindex **8** [1977] No. 317879). – [105] R. H. Rainey, J. G. Moore (ORNL-3155 [1962] 1/29; N.S.A. **16** [1962] No. 17762).

[106] L. Küchler, L. Schäfer, B. Wojtech (Kerntechnik **13** [1971] 319/22). – [107] G. Kaiser, J. Wolf (Kerntechnik **20** [1978] 550/5). – [108] R. A. Matzie, J. R. Rec, A. N. Terney (Trans. Am. Nucl. Soc. **26** [1977] 306/7). – [109] E. Teuchert (JUEL-1470 [1977] 1/54; INIS Atomindex **9** [1978] No. 395857). – [110] I. Spiewak (Fuel Cycle Conf. '78, New York 1978, 23 pp.).

[111] E. Merz (Naturwissenschaften **65** [1978] 424/31). – [112] L. I. Ilmenkova, L. D. Sheidina, I. J. Starik (Radiokhimiya **2** [1959] 168/70). – [113] L. I. Ilmenkova, L. D. Sheidina, I. J. Starik (Radiokhimiya **4** [1962] 44/9). – [114] J. G. Moore, R. H. Rainey (ORNL-TM-543 [1963] 1/27; N.S.A. **17** [1963] No. 20101). – [115] J. G. Moore, J. H. Goode, J. W. Ullmann, R. H. Rainey, J. R. Flanary (ORNL-3773 [1965] 1/19; N.S.A. **19** [1965] No. 20051).

[116] R. C. Thompson (TID-5222 [1951] 131/43; N.S.A. **12** [1958] No. 4778). – [117] A. V. Davydov, E. S. Palschin (At. Energ. [USSR] **22** [1967] 389/92). – [118] J. G. Moore (ORNL-3599 [1964] 1/15; N.S.A. **18** [1964] No. 22020). – [119] J. H. Goode, J. G. Moore (ORNL-3950 [1967] 1/33; N.S.A. **21** [1967] No. 30502). – [120] O. Coenegracht (JUEL-822-CT [1972] 1/67).

[121] O. Coenegracht, G. Kaiser, E. Merz (Kerntechnik **14** [1972] 526/32). – [122] E. Zimmer, H. Ringel (Chem. Ing. Tech. **47** [1975] 710/2). – [123] G. Kaiser, E. Merz (Kerntechnik **16** [1974] 388/92). – [124] E. Merz (Chemiker-Ztg. **101** [1977] 81/91). – [125] S. A. Reynolds (Progr. Nucl. Energy III **2** [1958] 562/72).

[126] M. J. Bell (ORNL-4628 [1973] 1/148). – [127] V. Maly, R. Wagemann (AVR-Bericht, Abbranddaten, Pt. I/II, Jülich 1977, pp. 126, 127). – [128] Y. Liu (JUL-678-RG [1970] 1/191; N.S.A. **25** [1971] No. 12776). – [129] U. Hansen (JUL-904-RG [1972] 1/41). – [130] E. Teuchert, J. J. Rütten, H. Werner (Nucl. Technol. **38** [1978] 374/83).

2.4.3 Head-End Processing of Irradiated Thorium-Containing Fuel Elements

The first step in the reprocessing, for which the term "head-end" treatment has gained acceptance, consists of the mechanical or chemical pretreatment of the reactor-irradiated fuel element in preparation for the actual chemical separation and purification processes. The head-end treatment starts with the mechanical dissection or diminution of the fuel element, in order to make the fuel or fertile material amenable to attack by the dissolution reagent.

Wet (i.e., aqueous) processes are preferable for the chemical separation, nonaqueous (i.e., halide volatilization, pyrometallurgy) processes are less advantageous. Liquid-liquid extraction is nowadays the only process employed on a technical scale. Thorium, uranium, and the fission products must be fed into the solvent extraction unit in the form of a nitrate solution. It is, therefore, the aim of the head-end treatment to transfer the heavy metals and the fission products into a solution in nitric acid, preferably while separating off structural material and the moderator. The head-end step is completed when the feed solution has been adjusted suitably for the following separation process. Similar considerations are valid for the dry processes, where the fuel and fissile material must again be freed for their subsequent processing.

Practically all nuclear fuel and fertile materials are provided with a cladding for the retention of the fission products and the prevention of the contamination of the coolant. Depending mainly on the reactor concept, this cladding may consist of:

1. aluminium (only in obsolescent systems),
2. stainless steel,
3. Zircaloy (a Zr alloy with about 96% Zr),
4. pyrolytic carbon ("PyC"),
5. silicon carbide (SiC),
6. steel alloys with Nb/V additives.

Fuel elements for water-moderated reactors take claddings from groups 1 to 3, but Al-clad fuel elements are hardly in use any more. Fuel elements for high temperature reactors are clad with pyrolytic carbon or SiC, whereas fast breeder reactors are provided with claddings from group 6.

General considerations for the head-end treatment can be found in references [1 to 6].

2.4.3.1 Removal of the Metallic Cladding of the Fuel

The freeing of the fuel or fertile material in preparation to its dissolution may, in principle, proceed according to various methods:

1 a. mechanical removal of the cladding by cutting open, shearing off, grinding and crushing (shear-leach, grind-leach),
1 b. chopping-up of the fuel element in single- or bundlerod choppers (chop-leach),
2. chemical removal of the cladding,
3. joint dissolution of the cladding with the fuel.

It is attempted to introduce as little of the inert cladding material as possible into the feed solution for the subsequent separations. Therefore methods 1 a and 1 b are the preferred ones.

At one time it was attempted to chemically dissolve the cladding selectively:

aluminium with caustic alkalies [11 to 15] (5 to 10% NaOH + 1.2 M $NaNO_3$),
stainless steel [16 to 19] with 8 M H_2SO_4 (SULFEX decladding) [20 to 22], or with 5 M HNO_3 + 2 M HCl (DAREX decladding) [23 to 25],
Zircaloy [26] with H_2SO_4 + HF or by dry chlorination.

After the selective dissolution of the cladding the remaining fuel is washed and then dissolved in HNO_3 or in THOREX reagent (see 2.4.3.3, p. 298). This processing method was used only occasionally. It has the disadvantage, that only in few cases the cladding is dissolved alone, since the fuel is partially co-dissolved and fuel losses result. Furthermore, large volumes of waste solution are produced. It is better to declad mechanically and to dispose the cladding as solid waste. Chemical decladding by means of "dry" chlorination of Zircaloy claddings promises theoretically good chances for success. Zr reacts with gaseous HCl, forming volatile $ZrCl_4$, that has a sublimation point of 321 °C. The boiling points of UCl_3 or UCl_4 are, on the other hand, 835 or 787 °C, respectively, so that a clean separation should be possible. Practically, however, this has not been successfully accomplished [27, 28].

In the case of pyrolytic carbon coated fuel particles from HTR fuel elements, a chemically selective removal of the structural and coating materials is nowaday practiced: the graphite and pyrolytic carbon are burned-off with oxygen (see Section 2.4.3.2).

The joint dissolution of the cladding and of the fuel was practiced in the older processes. For example Al claddings were co-dissolved with Th-containing fuels. The dissolution medium was a mixture of 13 M HNO_3 + 0.0025 M $Hg(NO_3)_2$ + 0.04 M HF [29 to 31]. The Hg^{2+} ions acted as a catalyst for the dissolution of the Al. A joint dissolution of the Zircaloy cladding and the heavy metal could be effected by the ZIRFLEX process [32 to 34]. The dissolution medium was a mixture of NH_4F + NH_4NO_3. The SULFEX solution with added small amounts of fluoride, as a catalyst, could serve for the joint dissolution of cladding and heavy metal too [35]. The decisive disadvantage of these procedures is the production of large quantities of radioactive wastes, and the overloading of the chemical separation processes with the inert materials.

When mechanically decladded, the head and tail ends of the fuel element were first sawed off, and then it was chopped with a single- or a bundle rod chopper into 1 to 5 cm long pieces. Subsequently the fuel is dissolved out of the pieces, when necessary with an added catalyst, by means of boiling HNO_3. This process was first developed in the USA, and is designated as the "chop and leach" process. It represents today the standard procedure for all kinds of fuel elements for water cooled reactors. It can be expected that with some modifications it will be used also for fuel elements from fast breeder reactors. The shear-leach process has not proved to be as useful, although it was used preferentially in the few reprocessing campaigns for Th-containing fuel elements, that have been conducted so far [36 to 42].

The remaining cladding sections are scrubbed, and enclosed in storage cans, which are then sealed with concrete.

Attempts to remove the cladding electrolytically have met only little success. The fuel elements are dipped as anodes in an acid bath, the cathode being PbO_2, Ni, or Pt, depending on the electrolyte: H_2SO_4, HCl, or HNO_3. The corrosion and the hydrogen production, which entails the danger of the formation of detonating gas, are problematic. Since a selective electrolytic dissolution of the cladding is very difficult, the joint dissolution of the cladding and of the heavy metal has been considered also in this case [43 to 48].

In conclusion it is necessary to mention some pyrochemical processes, that aim at a decladding of the fuel. Stainless steel dissolves readily in molten Zn at 800 °C [49, 50]. Other proposals concern the use of a molten Sb-23 wt% Cu alloy as a solvent for stainless steel at a reaction temperature of 800 to 950 °C [51].

2.4.3.2 Removal of the Pyrolytic Carbon Coating and of the Graphite Matrix of HTR Fuel Elements

The fuel encased in metallic claddings may be readily dissolved out by boiling HNO_3 after the fuel element has been chopped up to short sections. Graphite-containing fuel elements of high temperature reactors, on the contrary, require a special pretreatment. The fuel or fertile material, is present as small spheres, coated with several layers of pyrolytic carbon, in some cases including an intermediate layer of SiC, and embedded in a graphite matrix. It must be freed from the carbon before it can be dissolved. According to extensive studies, this may be effected most readily by burning-off all the pyrolytic carbon and the graphite in a fluidized bed burner between 750 and 850 °C. In the case of pure "PyC" coatings, the resulting oxide residue can be dissolved directly in the THOREX reagent for feeding-in to the subsequent THOREX separation process. If a SiC layer had been added for even better retention of the fission products, the burning ceases at the SiC layer. A mechanical breaking-up step, and a combustion of the liberated interior "PyC" buffer layer must then precede the acid dissolution of the fuel. The SiC shells, which are insoluble in HNO_3, must be filtered off before the solution can be fed to the THOREX process [52 to 71].

Two processes have been proposed for the combustion of the graphite matrix of the fuel element:

1. the stationary bed (heap) process, and
2. the fluidized bed process.

The latter has decisive advantages relative to the former process, in particular when exothermic processes are involved. Technologically and operationally simpler, however, is the shaft-oven, into which either pre-crushed [58, 72, 73] or even whole fuel elements [74, 75] are fed. In the fluidized bed, the heat exchange between the particles and the reactive gases, as also that between the particles and the heat exchange surfaces, is excellent, because of the effective mixing of the solids. The temperature is practically uniform in the entire layer, with the exception of the region near the walls and the bottom (about 10% of the volume), and may be readily regulated within narrow limits. Local overheating is practically absent, in contrast to stationary bed processes. High specific throughputs are attained in the fluidized bed process at continuous operation [76 to 82]. In the earlier experiments in the USA, inert alumina granules were added in order to stabilize the fluidized bed [83 to 92]. This disadvantageous mode of operation could later be substituted by an inert fluidized layer [93 to 96]. With a relatively low burning temperature the technically possible least contamination of the off gases by volatile radionuclides is achieved. The occurrence of very large quantities of off gases causes problems. Special provisions must be made for the removal of the heat of combustion [97 to 102]. Because of the requirements of reliable nuclear criticality safety, only gas cooling can be employed. Water cooled ovens present too high a risk, since incidents such as entry of water into the oven cannot be absolutely excluded, or else only small oven diameters are permissible. Without water moderation, the permissible diameter is about 60 cm for highly enriched fissile material [103 to 107]. At a given diameter, the throughput may be increased by overpressure combustion. An overpressure of 5 bar permits a 3-fold throughput at a given geometry. This requires, however, additional provisions for effective heat removal, since the ratio of the volume to the surface area of the combustion chamber becomes less favorable. These provisions built into the chamber for better cooling, affect, in turn, the streaming behavior in the fluidized bed [108, 109].

A further technical problem is the satisfactory recovery of the dust [110].

The combustion of the carbon may also be effected indirectly, in an oxidizing melt consisting of potassium persulfate, nitrates, peroxides, or hydroxides while an oxidizing gas is being led in. The carbon is then oxidized to the carbonate ion, which forms CO_2 that escapes from the solution, when the melt is dissolved and acidified. It is also conceivable to co-dissolve the SiC coating in a suitable melt. U and Th are dissolved during this treatment in some of the molten salts, whereas they precipitate as oxides or uranate in others. These processes, however, cannot be used for technical purposes, because of the formation of large quantities of waste [111 to 114].

The residue from the combustion process is in any case an oxidic heavy metal "ash", independent from whether oxidic or carbidic fuel has originally been used. Under favorable reaction conditions, a carbon-free oxide ash is directly obtained. Otherwise a recombustion is necessary [115 to 117]. The ash may be dissolved in a suitable dissolution reagent for subsequent processing.

Alternative head-end processes for uncovering the heavy metal content of the graphite fuel element are the so-called high temperature attack, the chlorination attack, and the chemical disintegration process.

The high temperature attack consists of heating the entire fuel element in an inert gas to 2500 to 3000 °C, causing the destruction of the "PyC" and SiC coatings. The heavy metals form carbides, that may be further processed by wet or dry methods. This method did not prove itself [118, 119].

Most successful to date was the chlorination attack. The so-called CHLORINEX process provides for a two-stage grinding with a closed air-stream oversize particle recirculation device of the fuel elements, in which all the particles are broken up. Subsequently, a high temperature chlorination causes the volatilization of the U and Th chlorides, separating them from the graphite. Many of the fission products, however, accompany the heavy metals in this step. Therefore a further purification step was proposed, involving amine extraction from aqueous solutions. The main problem with this process is the corrosion in the chlorination reactor at temperatures >900 °C [120 to 125].

The chemical disintegration of the graphite fuel elements appeared at first to be highly promising, but could not compete with the combustion process in view of technical and economical disadvantages. Effective chemical disintegration of the graphite can be caused by the action of Cs metal, bromine, or iron chloride at room temperature to 500 °C. So-called intercalation compounds are thereby formed with the graphite (see "Kohlenstoff" B 3, 1968, pp. 890/2, 856/63, 900/2, resp.), which is destroyed due to strong swelling [126 to 129]. The chemical decomposition of the graphite depends on the kind of graphite used. For example, $FeCl_3$ destroys the porous matrix graphite, but not the dense pyrolytic carbon of the coated particles. Caesium, on the other hand, decomposes both kinds of carbon. It was hoped that selective attack and separation could be achieved by proper combinations [130 to 134]. The disintegration of graphite fuel elements may also be achieved by partial electrochemical oxidation of the carbon in aqueous electrolytes. The major part of the graphite matrix crumbles thereby and forms a flaky scum that floats on the electrolyte [135 to 144].

The head-end method, that is simplest in principle, is the mechanical destruction of the graphite by the grind-leach process [145 to 150]. Good results were obtained for non-irradiated material, but irradiated samples suffered intolerable losses of uranium, caused by recoil and adsorption at the graphite [151 to 154]. When the ground material is leached with conc. HNO_3, humic acids are formed, which interfere with the subsequent extraction process by foaming. Filtration problems are also encountered. Further problems arise from the storage of the waste slime. A grind-leach process was proposed also for the reprocessing of BeO-containing mixed oxide fuels [155]. Direct attack of graphite-containing fuel elements with conc. HNO_3 in an autoclave led to unsatisfactory results [156, 157].

The combustion-leach process, that is favored nowadays, is non-problematic, as long as the reprocessing of pure "PyC" coated mixed oxide fuels are considered. The grinding of the block-shaped or spherical fuel elements proceeds satisfactorily [158 to 164]. The reprocessing of separate fissile and bred fertile material particles is more difficult. The combustion process of TRISO-coated fuel particles is stopped at the SiC layer. For further processing, it is necessary to break up the SiC shells mechanically. Two processes which could in principle be used are:

a) mechanical destruction by grinding of the particles,

b) the breaking-up of the layer by the collision of the particles, that have been highly accelerated in an air stream, with a wall.

The mechanical grinding process has the disadvantage of the high wear, that the grinding parts suffer, because of the abrasive character of SiC. The nozzle stream process is therefore more advantageous, there being no mechanical moving parts, few fines, and since it is also possible to combine the disintegration and the removal of the SiC shells into one step, as it is possible to integrate a cycloning separation into the process [165 to 173].

2.4.3.3 Dissolution of Thorium-Containing Fuels and Fertile Materials

Nowadays only nitric acid is being used as a dissolution reagent for nuclear fuels. Th-containing mixed oxides require a catalyst, and hydrofluoric acid is commonly used. In older processes, where simultaneous dissolution of the metallic cladding and of the carbidic or oxidic fuel was sought after, H_2SO_4 + HF (SULFEX process), NH_4F + NH_4NO_3 (ZIRFLEX process) or a mixture of HNO_3 and HCl (DAREX process) were used [174]. Dissolution in 11 M HCl + 0.01 M SiF_6^{2-} was attempted in France, in order to make an anion exchange separation process possible. In no case satisfactory results could be achieved, since a complete dissolution of a metallic or oxidic Th fuel element can be accomplished only in the so-called THOREX reagent (13 M HNO_3, 0.05 M HF, 0.1 M $Al(NO_3)_3$). The $Al(NO_3)_3$ is added to the mixture of concentrated nitric acid and hydrofluoric acid in order to complex the fluoride ions, and suppress their corrosive effect. The mechanism of the catalytic action of the fluoride ions has not received unanimous interpretation. It is assumed, that in the dissolution of metallic fuels in HNO_3 a protective oxide layer is formed, which is dissolved away from the surface by the F^- ions. The mechanism of the catalytic action on the dissolution of oxidic fuels is less clear [176 to 192].

The earlier practiced procedure of adding dissolution catalysts such as SO_4^{2-} or PO_4^{3-} ions for complexation purposes has been completely discontinued, since more disadvantages than advantages have been brought forth. Electrolytic dissolution was also examined, and abandoned [193, 194].

Nitric acid dissolves uranium and thorium metals and oxides, forming the nitrates, in an oxidizing manner, i.e., nitrogen oxides are formed as reaction products, besides water, but no hydrogen:

$$Th + 6\,HNO_3 \xrightarrow{F^-} Th(NO_3)_4 + NO + NO_2 + 3\,H_2O$$

$$ThO_2 + 4\,HNO_3 \xrightarrow{F^-} Th(NO_3)_4 + 2\,H_2O$$

$$2\,UO_2 + 6\,HNO_3 \xrightarrow{F^-} 2\,UO_2(NO_3)_2 + NO + NO_2 + 3\,H_2O.$$

Thorium dioxide reacts considerably more slowly than thorium metal. A simultaneous dissolution of metallic Th with the Al cladding succeeds in the presence of F^- and Hg^{2+} ions [195]. The $Al(NO_3)_3$ formed acts subsequently as a salting-out agent in the solvent extraction. Concentrations of HNO_3 lower than 13 M are unable to dissolve ceramic ThO_2 [196]. The influence of eventually dissolved Si has also been examined. It may arise from alloy components of metallic fuels or from the SiC shells of HTR fuels. The solubility of the latter was found to be negligibly small [197]. Larger quantities of dissolved Si, as silicic acid, may be either dehydrated and filtered-off, or kept in solution by the addition of gelatine [198].

The reaction of the carbides with HNO_3 is considerably more complicated [199 to 206]:

$$ThC_2 + 4\ HNO_3 \rightarrow Th(NO_3)_4 + C_nH_{2n}$$
$$ThC_2 + 4\ HNO_3 \rightarrow ThO_2 \cdot x\ H_2O + 4\ NO_2 + 2\ C$$
$$ThO_2 \cdot x\ H_2O + 4\ HNO_3 \rightarrow Th(NO_3)_4 + (4 + x)\ H_2O.$$

The carbides of U and Th are stable in dilute HNO_3, up to 0.5 M. At higher concentrations of this acid, a conversion into nitrates, soluble organic acids, NO_2, NO, CO, and traces of H_2O occurs. The fraction of NO_2 increases at increasing concentrations of nitric acid. Between 50 and 80% of the carbidic carbon turn up as CO_2, the rest forms oxalic and mellitic acids and some unidentified aromatic compounds [207 to 211]. Contrary to the hydrolysis of carbides in water, however, no H_2, CO, or aliphatic hydrocarbons were reported [211]. The organic components cause difficulties in the further processing of the solutions [207 to 211]. It is therefore of advantage to convert the carbides to oxides in the head-end pretreatment, as necessarily occurs in the combustion head-end process.

The rate of dissolution is a function of numerous parameters:

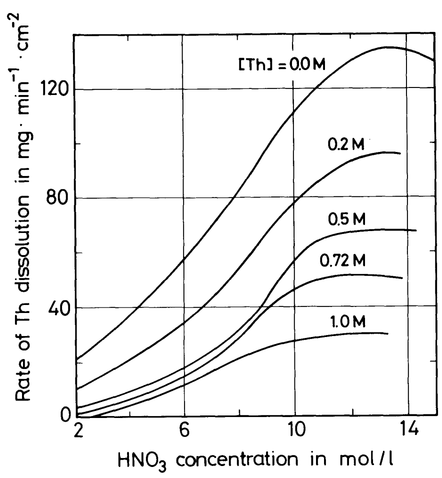
1. Time
2. Temperature
3. Concentration of the acid
4. Additives, catalysts
5. Pressure.

Medium to highly concentrated boiling HNO_3 is generally employed, since the rate increases with the temperature and the acid concentration. Although increased pressure accelerates the dissolution, the use of this measure is not favored, since the technological difficulties it entails are considerable. On the contrary, reduced pressure is commonly applied in the dissolution vessel. A whole series of different designs of dissolvers exists, for both continuous and discontinuous (batch) operation [212 to 216].

The kinetics of the dissolution is affected also by the concentration of the Th ions in the solution, in addition to the above mentioned parameters [127], see **Fig. 2-8**, p. 300.

The rate decreases strongly with the Th concentration already present in the solution. An initially rapid dissolution is therefore observed, which subsequently becomes more and more sluggish. The various effects were studied in a series of publications [216 to 226]. A special case is the dissolution of Th/U mixed oxides, imbedded homogeneously in a BeO matrix. This fuel element concept has been proposed by Australians [227, 228].

Fig. 2-8



The rate of Th dissolution as a function of the nitric acid concentration and that of the Th already present in the solution [127].

2.4.3.4 Treatment of the Off-Gases

Two sources for the formation of off-gases must be considered:

1. Off-gases formed in the head-end combustion process of graphite-containing fuel elements.
2. Off-gases formed in the dissolution of the nuclear fuels in HNO_3.

These two problems may be technologically solved only separately [229 to 231].

The off-gas formed in the combustion of graphite-containing HTR fuel elements contains as the main components dust, aerosols, and true gases. The fluidized bed, in particular, provides a large fraction of gas, that is separated in a cyclone or filter and reintroduced into the oven. Aerosols of the high-boiling fission products, mainly the oxides, may enter the off-gas, up to 1% of their total amount. Higher fractions of certain fission products are possible under particular circumstances. They have diverse degrees of dispersion. The formation of the colloidal dispersion in the off-gas is favored by the pre-existence of fission product accumulations in the nuclear fuel in fluid-disperse form. The large ratio of surface area to volume in the aerosols causes a transfer of the aerosols to the off-gas even at low flow velocities of the gas. The following fission products are of importance in the aerosols: ^{75}Se, ^{79}Se, ^{95}Nb, ^{95}Zr, ^{103}Ru, ^{106}Ru, ^{110}Ag, ^{125}Sb, ^{137}Cs, ^{140}Ba, ^{140}La, ^{141}Ce, ^{144}Ce, and ^{144}Pr. After leaving the processing stage and the dust cyclone, the aerosol-containing off-gas passes a multistage filtering arrangement, in which the particles are removed from the gas stream. The choice of the filter depends, as conventional in filter technology, on the extent of loading of the off-gas by solids and on the state of the gas, the temperature being also an important parameter. A combination of a sintered-metal filter, a fiber, cloth or electrical filter, and a filter for suspended material proved to be particularly effective [232 to 248].

The molecularly dispersed systems in the off-gases, formed by vaporization, may be caused to aggregate to larger particles by condensation. Depending on the temperature, a dynamic transition between filtration of aerosols and condensation of vaporized fission products occurs on the filters or on the surfaces of the tubes. The construction of the gas purification line consists necessarily of consecutive processing stages, that start with the cooling of the gas.

The transformation of the graphite of the HTR fuel elements into CO_2 during the head-end stage has as a consequence, that the radiocarbon, ^{14}C, formed by various processes in the reactor, enters the off-gas, and must be removed from it by expensive physico-chemical separation methods. The most reasonable one should be the conversion to $CaCO_3$ with $Ca(OH)_2$ [249 to 252]. After this pretreatment only the noble gases remain in the off-gas. Of importance from the radiation-ecological standpoint is ^{85}Kr. Four processes are, in principle, suitable for the removal of the noble gases [253 to 259]:

a) Passage through permselective membranes.
b) Selective absorption in solvents.
c) Adsorption on solids.
d) Cryogenic distillation.

These processes are partly suitable for the removal of the noble gases from both the combustion and the dissolution stages. They utilize various physical phenomena, and are often specific for certain off-gases, on the basis of cost evaluation. The processes generally remove Kr and Xe jointly. Subsequent liquefaction of the mixture and fractional distillation can be used to separate the Kr and Xe, if so desired.

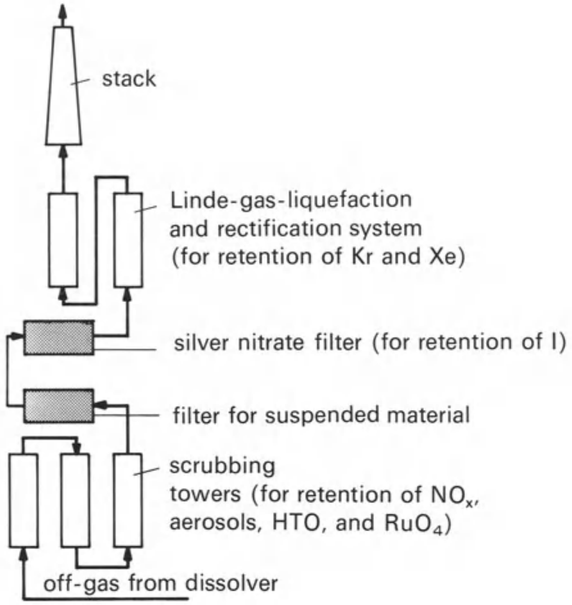
Absorption in CO_2 and subsequent rectification (the AKUT or KALC process) [260 to 273] has proved to be best for the removal of the noble gases from the off-gases of the combustion. Low temperature distillation (the KRYOSEP process) [274, 275] is best for the dissolution off-gases. The different boiling points of the off-gases are utilized for this purpose. The decontamination factors attainable are between 10 and 500, depending on the lay-out of the plant.

A further radiological problem may arise from the emission of ^{220}Rn, a natural decay product of Th. Proposals have been made to overcome this problem [276, 277].

When fuels and fertile materials are dissolved in acid, gaseous fission products, in particular, are liberated into the off-gases. However, also aerosols in the form of droplets are formed to an appreciable extent. Important constituents of the off-gas are: radioactive aerosols, iodine, ruthenium, krypton, xenon, and possibly also radon and tritium. These volatile or gaseous contaminants are liberated into the off-gas partly during the cutting open of the fuel elements and partly during the dissolution. Besides these, the off-gases contain also flushing air, nitrous oxides, and other components. **Fig.** 2-**9**, p. 302, shows schematically the off-gas filtering system, placed after the dissolver.

The off-gas, that leaves the dissolver, is first passed through a multistage scrubbing system. In the first scrubber the nitric oxides are retransformed into HNO_3 and led back into the dissolver. Thereby also a part of the radioactive aerosols, the volatile ruthenium, the tritiated water, and the iodine are simultaneously removed from the off-gas. The scrubbing towers are followed by a wet-precipitator, an electrofilter, and a filter for suspended material, then an iodine filter (impregnated with $AgNO_3$), and then the low temperature noble gas removing system, that has already been mentioned [278, 279]. In the plants, that are in operation today,

Fig. 2-9



Schematics of an off-gas treatment system.

the iodine, ruthenium, and aerosols are removed by scrubbers, whereas Kr and T are released to the environment, without exceeding the permissible emission limits. For future large scale plants, an improved iodine removal and a considerable retention of the Kr and T are regarded as necessary, in order to avoid exceeding local permissible doses and long term risks of accumulation [280 to 287].

2.4.3.5 Adjustment of the Feed Solution

The solutions taken from the dissolver are next freed from eventually present solids by filtration or centrifugation. The clear solutions still require further treatment, before they can be fed into the chemical separation process proper. This step is called feed-adjustment, and consists of:

a) Adjustment of the desired or required concentration of the ions of the main elements.

b) Adjustment of the required pH value (acid concentration).

c) Freeing of the solution from undesired constituents, such as hydrolysis products, colloids, etc.

During the concentration of the solution coming from the dissolver, a distillate concentrated in nitric acid is obtained. It is upgraded to the azeotropic point in an acid recovery plant, and returned to the dissolving stage. The preparation of the acid deficient feed solution for the THOREX process consists of three steps:

1. Evaporation of the acid, until the boiling point reaches 135 °C.
2. Blowing-in of somewhat overheated steam at a constant temperature, in order to drive away nitrate that is not bound to metal ions (steam stripping).
3. Filling-up with water to the predetermined volume, so that the desired concentration of the heavy metal ions is attained.

The last step must follow its predecessor immediately, without letting the solution cool down, in order to avoid the crystallization of thorium and uranyl nitrates from the cooled, supersaturated solution [288 to 291].

References for 2.4.3:

[1] R. W. Stoughton (TID-5222 [1951] 51/83; N.S.A. **12** [1958] No. 4778). – [2] F. W. Schuler, F. L. Steahly, R. W. Stoughton (TID-5223 [1952] 307/17; N.S.A. **11** [1957] No. 11493). – [3] G. R. Howells, T. G. Hughes, D. R. Mackey, K. Saddington (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1959, Vol. 17, pp. 3/24). – [4] F. L. Culler, R. E. Blanco (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 259/90). – [5] R. E. Blanco (Progr. Nucl. Energy III **2** [1958] 223/45).

[6] S. M. Stoller, R. B. Richards (Reactor Handbook, Vol. 2, Interscience, New York 1961, pp. 68/72). – [7] C. M. Slansky (in: J. F. Flagg, Chemical Processing of Reactor Fuels, Academic, New York 1961, pp. 75/124). – [8] J. T. Long (Engineering for Nuclear Fuel Reprocessing, Gordon and Breach, New York 1967, pp. 273/325). – [9] J. T. Roberts, L. M. Ferris, E. L. Nicholson, R. H. Rainey, C. D. Watson (Tech. Rept. Ser. Intern. At. Energy Agency No. 52 [1966] 313/52). – [10] L. M. Ferris (ORNL-3952 [1966] 1/33; N.S.A. **20** [1966] No. 27041).

[11] A. T. Gresky (ORNL-1208-Del. [1952] 1/82; N.S.A. **15** [1961] No. 4048). – [12] M. G. Baillie, R. C. Cairns, J. R. May (Mech. Chem. Eng. Trans. **4** [1968] 113/5). – [13] R. D. Fletcher, M. E. Jacobson, H. R. Beard (IDO-14606 [1963] 1/27; N.S.A. **17** [1963] No. 23431). – [14] W. W. Schulz (BNWL-204-Pt. 2 [1966] 1/17; N.S.A. **21** [1967] No. 5987). – [15] J. F. Phillips, H. D. Huber (BNWL-240 [1968] 1/36; N.S.A. **22** [1968] No. 40151).

[16] L. M. Ferris, A. H. Kibbey (ORNL-2934 [1960] 1/27; N.S.A. **15** [1961] No. 2700). – [17] R. A. Ewing, H. B. Brugger, D. N. Sundermann (BMI-1427 [1960] 1/22; N.S.A. **14** [1960] No. 11679). – [18] L. M. Ferris, A. H. Kibbey (ORNL-3143 [1961] 1/17; N.S.A. **15** [1961] No. 27699). – [19] R. A. Ewing, H. B. Brugger, D. N. Sundermann (BMI-1560 [1961] 1/42; N.S.A. **16** [1962] No. 7286). – [20] J. E. Savoleinen, R. E. Blanco (Chem. Eng. Progr. **53** [1957] 78/81).

[21] F. G. Kitts, J. J. Perona (CF-57-6-125-Rev. [1957] 1/23; N.S.A. **12** [1958] No. 16297). – [22] B. C. Finney, B. A. Hannaford (ORNL-3072 [1961] 1/32; N.S.A. **15** [1961] No. 15658). – [23] F. G. Kitts, W. E. Clark (ORNL-2712 [1962] 1/99). – [24] L. M. Ferris, A. H. Kibbey (ORNL-2714 [1959] 1/25; N.S.A. **14** [1960] No. 258). – [25] T. A. Gens (ORNL-2785 [1961] 1/14; N.S.A. **14** [1960] No. 2464).

[26] R. E. Blanco (TID-7583 [1959] 235/45). – [27] J. J. Perona, J. B. Adams, J. E. Savoleinen, T. A. Gens (ORNL-2631-Del. [1959] 1/62; N.S.A. **13** [1959] No. 21805). – [28] T. A. Gens, R. L. Jolley (ORNL-2992 [1961] 1/21; N.S.A. **15** [1961] No. 19459). – [29] A. T. Gresky (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 505/10). – [30] F. R. Bruce (TID-7534 [1957] 180/8; N.S.A. **12** [1958] No. 154).

[31] W. D. Bond (ORNL-2519 [1958] 1/22; N.S.A. **13** [1959] No. 2059). – [32] J. L. Swanson (HW-49633-Del. [1957] 1/24; **13** [1959] No. 17952). – [33] J. L. Swanson

(Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 154/61). – [34] P. W. Smith (HW-65979 [1960] 1/51; N.S.A. **15** [1961] No. 12994). – [35] L. P. Hatch, W. H. Regan, J. J. Reilly (Am. Nucl. Soc. Meeting, Pittsburgh, Pa., 1957).

[36] H. W. Alter, C. J. Beck, B. V. Coplan (KAPL-1139-Del. [1954] 1/10; N.S.A. **12** [1958] No. 856). – [37] E. J. Bernett, R. W. Powell, A. D. Rand (TID-5280 [1955] 1/389, 46/55; N.S.A. **4** [1955] No. 7306; Nucleonics **12** No. 12 [1954] 36/100). – [38] C. D. Watson, J. B. Adams, G. K. Ellis, G. A. West, F. L. Hannon, W. F. Schaffer (TID-7583 [1960] 306/99; N.S.A. **14** [1960] No. 6323). – [39] F. L. Culler, R. E. Blanco, H. E. Goeller, C. D. Watson (ORNL-2265-Del. [1957] 1/133; N.S.A. **12** [1958] No. 804). – [40] V. P. Kelly (HW-69667 [1961] 1/26).

[41] J. B. Adams, A. M. Benis, C. D. Watson (ORNL-3227 [1962] 1/58; N.S.A. **16** [1962] No. 16457). – [42] B. C. Finney, B. A. Hannaford, G. A. West, C. D. Watson (ORNL-3984 [1969] 1/68). – [43] J. A. McLaren, W. D. Cline, H. S. Clinton, J. J. Finley, J. H. Goode, J. A. Westbrook (K-587 [1950] 1/10; N.S.A. **11** [1957] No. 13696). – [44] E. Détilleux (Energ. Nucl. [Paris] **11** [1969] 292/7). – [45] A. T. Clark, L. H. Meyer, J. H. Owen, F. G. Rust (DP-647 [1961] 1/24; N.S.A. **16** [1962] No. 17759).

[46] J. R. Aylward, E. M. Whitener (IDO-14584 [1962] 1/23; N.S.A. **16** [1962] No. 23783). – [47] C. M. Slansky (J. Metals **16** [1964] 25/32). – [48] D. M. Paige (Reactor Fuel Process. **9** [1966] 75/83). – [49] R. G. Wymer (ORNL-2182-Del. [1956] 1/15; N.S.A. **13** [1959] No. 7595). – [50] R. D. Pierce (ANL-7675 [1970] 20/4; N.S.A. **24** [1970] No. 50439).

[51] J. G. Wurm, M. Payrisset (IAEA-115 [1970] 167/200; N.S.A. **26** [1972] No. 20178). – [52] K. R. Hyde, D. J. O'Connor (AERE-R-4107 [1962] 1/27). – [53] L. M. Ferris, A. H. Kibbey, M. J. Bradley (ORNL-3186 [1961] 1/36; N.S.A. **16** [1962] No. 3067). – [54] L. M. Ferris (ORNL-TM-193 [1962] 1/9; N.S.A. **16** [1962] No. 17763). – [55] C. D. Scott, L. E. McNeese, J. C. Suddath (ORNL-TM-185 [1962] 1/9).

[56] L. M. Ferris, K. S. Warren, J. W. Ullmann, L. A. Byrd, C. T. Thompson (ORNL-TM-688 [1963] 1/14; N.S.A. **18** [1964] No. 3882). – [57] C. D. Scott (ORNL-3456 [1964/71] 1/76; N.S.A. **25** [1971] No. 46276). – [58] R. E. Blanco, G. I. Cathers, L. M. Ferris, T. A. Gens, R. W. Horton, E. L. Nicholson (Nucl. Sci. Eng. **20** [1964] 13/22). – [59] H. Zuest, H. R. von Gunten, P. Baertschi (EUR-2780.e [1965] 245/58; N.S.A. **20** [1966] No. 40390). – [60] J. T. Roberts, L. M. Ferris, E. L. Nicholson, R. H. Rainey, C. D. Watson (ORNL-TM-1139 [1965] 1/51; N.S.A. **19** [1965] No. 30324).

[61] C. B. Bartlett, E. Wirsing, S. J. Wachtel, R. Johnson, J. J. Reilly, L. P. Hatch (BNL-9348 [1964] 1/23). – [62] G. W. Horsley, L. A. Podo, F. C. Wood (DP-338 [1965] 1/31; N.S.A. **24** [1970] No. 46302). – [63] H. O. Witte (ORNL-TM-1411 [1966] 1/15; N.S.A. **20** [1966] No. 14640). – [64] J. J. Reilly, S. J. Wachtel, R. Johnson, E. Wirsing, L. P. Hatch (Ind. Eng. Chem. Process Design Develop. **5** [1966] 51/9; C.A. **64** [1966] 4537). – [65] L. A. Decker, R. A. Hammer (IN-1018 [1967] 1/19; N.S.A. **21** [1967] No. 12497).

[66] K. G. Steyer, H. E. Stelling (CONF-660524-22 [1966] 1/19; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 575/88; N.S.A. **21** [1967] No. 144). – [67] E. L. Nicholson, L. M. Ferris, J. R. Flanary, J. H. Goode, B. A. Hannaford, J. W. Landry, J. G. Moore, R. H. Rainey, C. D. Watson, H. O. Witte (CONF-660524-6 [1966] 1/42; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 589/615; N.S.A. **20** [1966] No. 33414). – [68] L. M. Ferris (Progr. Nucl. Energy III **4** [1970] 121/70). – [69] U. Tillessen, E. Merz (JUEL-CONF-14 [1975] 271/9; INIS Atomindex **7** [1976] No. 233971). – [70] H. Barnert-Wiemer, R. Böhnert (JUEL-1320 [1976] 1/57; INIS Atomindex **8** [1977] No. 283227).

[71] N. Holder, L. Abraham (GA-A-14320 [1977] 1/109; INIS Atomindex **9** [1978] No. 365104). – [72] U. Tillessen (Reaktortagung, Berlin 1970, pp. 541/4). – [73] H. Pirk, U. Tillessen (Kerntechnik **14** [1972] 158/61). – [74] H. Barnert-Wiemer, J. W. Snider, D. C.

Watkin (ORNL-TM-4520 [1974] 1/158). – [75] P. A. Haas (ORNL-TM-4519 [1974] 1/41; N.S.A. **30** [1974] No. 31720).

[76] M. Leva, M. Grummer, M. Weintraut, M. Pollchick (Chem. Eng. Progr. **44** [1948] 511/20). – [77] S. Ergun (Chem. Eng. Progr. **48** [1952] 89/94). – [78] F. Schytil (Wirbelschichttechnik, Springer, Berlin 1961, pp. 1/120). – [79] J. Beranek, D. Sokol (Wirbelschichttechnik, VEB-Verlag für Grundstoffindustrie, Leipzig 1964). – [80] C. D. Scott (Ind. Eng. Chem. Process Design Develop. **5** [1966] 223/33).

[81] H. O. Witte (Ind. Eng. Chem. Process Design Develop. **8** [1969] 145/9). – [82] S. J. Wright, R. Hickman, H. C. Ketley (Brit. Chem. Eng. **15** [1970] 1551/4). – [83] R. E. Blanco, G. I. Cathers, L. M. Ferris, T. A. Gens, E. L. Nicholson (ORNL-TM-667 [1963] 1/29). – [84] E. L. Nicholson, L. M. Ferris, J. T. Roberts (ORNL-TM-1096 [1965] 1/28; N.S.A. **19** [1965] No. 22406). – [85] J. J. Reilly, S. J. Wachtel, R. Johnson, E. Wirsing, L. P. Hatch (Ind. Eng. Chem. Process Design Develop. **5** [1966] 51/9).

[86] D. T. Young (GA-A-14816 [1978] 1/156; INIS Atomindex **10** [1979] No. 423039). – [87] J. R. Johnson, W. E. Rowe (U.S. 3087779 [1963]; C.A. **59** [1963] 1252). – [88] L. M. Ferris (ORNL-3763 [1965] 1/34; N.S.A. **26** [1972] No. 28582). – [89] L. A. Decker (IDO-14659 [1965] 1/12). – [90] D. W. Rhodes, L. A. Decker (IDO-14661 [1966] 38/40; N.S.A. **20** [1966] No. 27036).

[91] S. J. Wachtel, J. J. Reilly, C. B. Bartlett, R. Johnson, E. Wirsing (BNL-973 [1966] 1/10; N.S.A. **20** [1966] No. 35584). – [92] R. E. Blanco, L. M. Ferris, C. D. Watson, R. H. Rainey (TID-7650 [1963] 384/435; N.S.A. **17** [1963] No. 28464). – [93] R. Böhnert, G. Kaiser, E. Merz (Advan. Chem. Ser. **133** [1974] 25/33). – [94] R. Böhnert (JUEL-1041-CT [1974] 1/118; C.A. **81** [1974] No. 57187). – [95] R. Böhnert, G. Kaiser (Reaktortagung, Nürnberg 1975, pp. 475/8).

[96] R. Böhnert, G. Kaiser, H. Pirk, U. Tillessen (JUEL-1152 [1975] 1/47; C.A. **83** [1975] No. 117681). – [97] B. J. Baxter, L. H. Brooks, A. E. Hutton, M. E. Spaeth, R. D. Zimmerman (GA-A-12285 [1972] 1/17; N.S.A. **27** [1973] No. 11887). – [98] W. B. Palmer (ICP-1068 [1975] 1/36). – [99] G. W. Hogg, J. A. Rindfleisch, W. B. Palmer, D. L. Anderson, J. S. Varuska (ICP-1074 [1975] 1/107). – [100] D. T. Young (GA-A-13748 [1975] 1/15).

[101] R. T. Stula, D. T. Young, H. H. Yip (GA-A-13546 [1976] 1/113; INIS Atomindex **7** [1976] No. 270369). – [102] R. T. Stula, D. T. Young, J. S. Rode (GA-A-14643 [1977] 1/173; INIS Atomindex **9** [1978] No. 388785). – [103] H. Werner (Dipl.-Arbeit, Aachen T.H. 1972, pp. 1/69; KFA-ICT [1972] 1/69). – [104] O. Schaffer (JUEL-922-SB [1973] 1/30; C.A. **79** [1973] No. 99538). – [105] R. Böhnert, M. Münster (Reaktortagung, Düsseldorf 1976, pp. 514/7).

[106] M. Münster, H. Bonka, R. Böhnert (JUEL-1350 [1976] 1/77; INIS Atomindex **8** [1977] No. 315844). – [107] H. Kronschnabel (KFA-ICT-IB-421 [1978] 1/57). – [108] H. Tischer (JUEL-1574 [1979] 1/137). – [109] N. Hoogen (KFA-ICT-IB-417 [1977] 1/50). – [110] N. Hoogen (Dipl.-Arbeit, Aachen T.H. 1972, pp. 1/65; KFA-ICT-IB-423 [1978] 1/65).

[111] E. Lopez-Menchero, G. Vermeulen, E. Détilleux (EUR-2780.e [1965] 199/238; N.S.A. **20** [1966] No. 40383). – [112] J. G. Wurm, A. A. Avogadro (Ger. 1228595 [1966]; C.A. **66** [1967] 25284). – [113] H. J. Riedel, E. Merz (Nukleonik **11** [1968] 32/8). – [114] O. Knacke, M. Laser, E. Merz, H. J. Riedel (Ger. 1592440 [1965/71]; Fr. 1483117 [1968]; Brit. 1099331; C.A. **68** [1968] No. 45435). – [115] W. S. Rickmann (GA-A-13540 [1975] 1/150; INIS Atomindex **7** [1976] No. 267903).

[116] J. S. Rode (GA-A-14452 [1977] 1/156; INIS Atomindex **9** [1978] No. 362343). – [117] J. S. Rode (GA-A-14510 [1977] 1/161; INIS Atomindex **9** [1978] No. 365109). – [118] J. Hartwig, K. H. Ulrich (Tech. Mitt. Krupp Forschber. **27** [1969] 27/36; C.A. **71** [1969] No. 97400). – [119] J. Hartwig (Ger. 1533052 [1966/70]; Brit. 1185098 [1969]; C.A. **72** [1970] No. 138831). – [120] T. A. Gens (ORNL-3376 [1963] 1/36).

[121] J. L. Cook, R. L. Hamner (ORNL-3586 [1964] 1/27; C.A. **61** [1964] 1468). – [122] E. Fischer, M. Laser, E. Merz (Kerntechnik **12** [1970] 321/6). – [123] K. Knotik, H. Bildstein (Kerntechnik **13** [1971] 323/9). – [124] E. Merz, M. Laser, E. Fischer, R. Thomas, J. Krabe (Ger. Offen. 1806077 [1970]; Brit. 1226718 [1970]; C.A. **73** [1970] No. 82992). – [125] J. Bohnenstingl, H. Gebhardt, M. Laser, G. Loßmann (JUEL-1129-CT [1974] 1/51; C.A. **83** [1975] No. 17385).

[126] G. R. Hennig (Progr. Inorg. Chem. **1** [1959] 125/205). – [127] W. Rüdorff (Advan. Inorg. Chem. Radiochem. **1** [1959] 223/66). – [128] F. J. Salzano, S. Aronson (J. Chem. Phys. **42** [1965] 1323/30). – [129] E. Merz, H. Scharf (Atomkernenergie **17** [1971] 287/92). – [130] F. J. Salzano, S. Aronson (Nucl. Sci. Eng. **28** [1967] 51/4).

[131] W. Rüdorff, E. Stumpp, W. Spriessler, F. W. Sieke (Angew. Chem. **75** [1963] 130/6). – [132] G. A. Saunders, A. R. Ubbelohde, F. R. S. Young (Proc. Roy. Soc. [London] A **271** [1963] 499/511). – [133] E. Merz (Nukleonik **11** [1968] 38/44). – [134] U. Gat, R. Hörbe (Atomkernenergie **14** [1969] 400/2). – [135] L. W. Fromm (ORNL-238 [1949] 1/25; N.S.A. **11** [1957] No. 12398).

[136] L. W. Fromm (U.S. 2903402 [1959]; C.A. **1960** 118). – [137] P. F. Wace, T. Hayes (AERE-C-R-232 [1957] 1/12). – [138] R. A. Ewing, T. S. Elleman, R. B. Price (Trans. Am. Nucl. Soc. **4** [1961] 152/3). – [139] M. J. Bradley, L. M. Ferris (ORNL-2761 [1960] 1/36; N.S.A. **14** [1960] No. 10530). – [140] J. Shimokawa, M. Mishima (J. At. Energy Soc. Japan **5** [1963] 841/6).

[141] A. H. Kibbey, L. M. Ferris (ORNL-TM-384 [1962] 1/7; N.S.A. **16** [1962] No. 31677). – [142] H. Bildstein, K. Knotik (Kerntechnik **8** [1966] 110/5). – [143] E. Merz (Kerntechnik **12** [1970] 341/6). – [144] G. Beone, G. Lazzaretto, A. Moccia (Kerntechnik **15** [1973] 270/4). – [145] M. J. Bradley, L. M. Ferris (Nucl. Sci. Eng. **8** [1960] 432/6).

[146] M. J. Bradley, L. M. Ferris (Ind. Eng. Chem. **53** [1961] 279/81). – [147] C. D. McKinney, W. B. Tarpley, R. S. Wichester (NYO-2581 [1961] 1/42; N.S.A. **15** [1961] No. 23571). – [148] K. Iwamoto, F. Kobayashi, J. Shimokawa (J. At. Energy Soc. Japan **5** [1963] 461/5). – [149] K. Iwamoto (Nucl. Sci. Eng. **18** [1964] 189/94). – [150] L. M. Ferris (ORNL-4110 [1967] 1/50; N.S.A. **21** [1967] No. 30504).

[151] F. S. Lapteva, B. V. Ershler (At. Energ. [USSR] **1** [1956] 63/6; Soviet At. Energy **1** [1965] 513/6). – [152] G. Nilsson (J. Nucl. Mater. **20** [1966] 215/30). – [153] M. O. Rogers (J. Nucl. Mater. **15** [1965] 65/72). – [154] H. J. Riedel, E. Merz (Kerntechnik **10** [1968] 260/3). – [155] M. G. Baillie, R. W. Hubery (AAEC-E-162 [1966] 1/14; N.S.A. **21** [1967] No. 24823).

[156] P. E. Ferguson, R. G. Wymer, R. E. Blanco, K. B. Brown, M. E. Whatley, H. E. Goeller, R. E. Brooksbank (ORNL-3830 [1965] 1/317; N.S.A. **20** [1966] No. 8812). – [157] P. A. Haas, L. M. Ferris (Ind. Eng. Chem. Process Design Develop. **5** [1966] 234/8). – [158] H. O. Witte, L. M. Ferris (ORNL-TM-1412 [1966] 1/10; N.S.A. **20** [1966] No. 13218). – [159] B. J. Baxter, E. Cook, C. M. Miller, J. B. Strand (GA-A-13275 [1975] 1/139; INIS Atomindex **7** [1976] No. 227716). – [160] B. J. Baxter, A. Gasparovic, A. H. Bond (GA-A-12939 [1976] 1/38; INIS Atomindex **7** [1976] No. 274972).

[161] H. Tischer, K. Hartmann (Atomwirtsch. Atomtech. **24** [1979] 331/3). – [162] B. J. Baxter, G. E. Benedict, R. D. Zimmermann (GA-A-13808 [1976] 1/28; INIS Atomindex **8** [1977] No. 283228). – [163] H. Tischer, K. Hartmann, N. Hoogen, P. C. Schmidt (JUEL-CONF-30 [1979] 13/27). – [164] J. B. Strand, J. W. Baer, E. J. Cook (GA-A-14645 [1978] 1/232; INIS Atomindex **9** [1978] No. 394571). – [165] J. J. Shefcik (GAMD-8615 [1968] 1/22).

[166] J. J. Shefcik (GAMD-8661 [1968] 1/16; N.S.A. **23** [1969] No. 2371). – [167] S. Langer, H. R. Phillips (GA-9888 [1970] 1/21; N.S.A. **24** [1970] No. 46304). – [168] S. Langer, N. L. Baldwin, H. R. Phillips (GA-9258 [1970] 1/12; N.S.A. **24** [1970] No. 46303). –

[169] S. Langer, N. L. Baldwin, H. R. Phillips (Nucl. Technol. **12** [1971] 26/30). – [170] D. de Lesdernier (GA-A-13135 [1975] 1/207).

[171] C. Walter, J. Wehmeier, R. Böhnert (Reaktortagung, Mannheim 1977, Sect. 3, pp. 377/80; INIS Atomindex **8** [1977] No. 302985). – [172] W. S. Rickmann (GA-A-14542 [1977] 1/129; INIS Atomindex **9** [1978] No. 373125). – [173] K. Hartmann (JUEL-1592 [1979] 1/151). – [174] D. L. Foster, J. E. Savoleinen, R. G. Wymer (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 546/50). – [175] A. Chesne, P. Regnaut (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 583/5).

[176] D. L. Foster, E. O. Nurmi (CF-52-2-95 [1952] 1/21). – [177] F. W. Schuler, F. L. Steahly, R. W. Stoughton (CC-3576 [1946] 1/16; N.S.A. **11** [1957] No. 8271). – [178] R. E. Blanco (TID-7534-Bk. 1 [1957] 22/44). – [179] R. L. Moore, C. A. Goodall, J. L. Hepworth, R. A. Watts (Ind. Eng. Chem. **49** [1957] 885/7). – [180] L. M. Ferris (ORNL-2822 [1960] 1/12; N.S.A. **14** [1960] No. 9549).

[181] T. A. Gens (ORNL-3023 [1961] 1/16; N.S.A. **15** [1961] No. 22365). – [182] W. L. Marshall, R. Slusher (J. Inorg. Nucl. Chem. **25** [1963] 283/90). – [183] L. M. Ferris, J. W. Ullmann (ORNL-TM-867 [1964] 1/18; N.S.A. **18** [1964] No. 25608). – [184] J. R. Flanary, J. H. Goode, M. J. Bradley, J. W. Ullmann, L. M. Ferris, G. C. Wall (ORNL-3660 [1964] 1/33; N.S.A. **18** [1964] No. 39380). – [185] M. S. Farrell (AAEC-E-42 [1959] 1/21; N.S.A. **15** [1961] No. 7311).

[186] J. H. Goode, J. R. Flanary (ORNL-3725 [1965] 1/25; N.S.A. **19** [1965] No. 9251). – [187] W. W. Wallace, W. Pease, A. Richard (Trans. Am. Nucl. Soc. **14** [1971] 487/8). – [188] J. F. Phillips, H. D. Huber (BNWL-240 [1968] 1/36; N.S.A. **22** [1968] No. 40151). – [189] L. M. Ferris (ORNL-3876 [1965] 1/31; N.S.A. **20** [1966] No. 5500). – [190] J. H. Goode, J. R. Flanary (ORNL-4213 [1968] 1/14; N.S.A. **22** [1968] No. 18866).

[191] R. E. Lerch, C. R. Cooley (Trans. Am. Nucl. Soc. **15** [1972] 86/7). – [192] R. F. Maness (BNWL-CC-449 [1966] 1/10; N.S.A. **26** [1972] No. 53604). – [193] H. Katz, J. Wagner (BNL-7352 [1963] 1/15; N.S.A. **18** [1964] No. 3875). – [194] M. R. Bomar (IDO-14563 [1961] 1/20; N.S.A. **16** [1962] No. 4220). – [195] I. Wells, C. M. Nicholls (Progr. Nucl. Energy III **1** [1956] 223/41).

[196] A. T. Gresky (Progr. Nucl. Energy III **1** [1956] 212/22). – [197] E. Zimmer, G. Schröder, H. J. v. Wachtendonk (JUEL-CONF-30 [1979] 28/41). – [198] B. J. Newby, B. E. Paige (IDO-14468 [1959] 1/49; N.S.A. **14** [1960] No. 5257). – [199] L. M. Ferris, M. J. Bradley (J. Am. Chem. Soc. **87** [1965] 1710/4). – [200] F. Mannone, C. Stoppa, G. Sanso (EUR-1913.i [1964] 1/15; N.S.A. **19** [1965] No. 4241).

[201] G. Baudin, J. Besson, P. Blum, J. Spitz (Compt. Rend. **254** [1962] 4179/81). – [202] M. B. Sears, L. M. Ferris (J. Inorg. Nucl. Chem. **29** [1967] 1548/52). – [203] E. W. Murbach (NAA-SR-11235 [1965] 1/19; N.S.A. **19** [1965] No. 36337). – [204] L. M. Ferris, M. J. Bradley (ORNL-3719 [1964] 1/204; N.S.A. **19** [1965] No. 5994). – [205] Y. Sasaki, F. Ichikawa, H. Imai, S. Uruno (Nature **195** [1962] 267/8).

[206] M. J. Bradley, J. H. Goode, L. M. Ferris, J. R. Flanary, J. W. Ullmann (Inorg. Chem. **3** [1964] 454/5). – [207] P. L. Pauson, J. McLean, W. J. Clelland (Nature **197** [1963] 1200/1). – [208] H. Imai, S. Uruno (Nature **206** [1965] 691/3). – [209] F. H. Pollard, G. Nickless, S. Evered (J. Chromatog. **15** [1964] 223/7). – [210] J. L. Drummond, B. J. McDonald, H. M. Ockenden, S. A. Welch (J. Chem. Soc. **1957** 4785/9).

[211] L. M. Ferris, M. J. Bradley (J. Am. Chem. Soc. **87** [1965] 1710/4). – [212] H. Wathley, P. A. Haas, R. W. Horton, A. D. Ryon, J. C. Suddath, C. D. Watson (ORNL-3868 [1965] 1/104; N.S.A. **20** [1966] No. 12928). – [213] W. S. Groenier (ORNL-TM-3194 [1971] 1/64; N.S.A. **25** [1971] No. 26327). – [214] E. L. Nicholson, L. M. Ferris, J. T. Roberts (ORNL-TM-1096 [1965] 1/27; N.S.A. **19** [1965] No. 22406). – [215] A. E. Sands (U.S. 3195984 [1965]; N.S.A. **19** [1965] No. 32186).

[216] P. Sckuhr (JUEL-976-CT [1973] 1/93; N.S.A. **18** [1973] No. 29775). – [217] C. A. Goodall, J. L. Hepworth, R. L. Moore, R. A. Watts (HW-40250 [1955] 1/34; N.S.A. **11** [1957] No. 12372). – [218] M. S. Farrell, S. R. Isaacs (AAEC-E-143 [1965] 1/17). – [219] M. S. Farrell, S. R. Isaacs, M. E. Shying (AAEC-E-154 [1966] 1/24; N.S.A. **21** [1967] No. 8324). – [220] M. E. Shying, E. J. Lee, M. S. Farrell (AAEC-E-180 [1967] 1/31; N.S.A. **21** [1967] No. 45189).

[221] F. G. Bodewig, W. Johannisbauer, G. Kaiser, P. Sckuhr (Reaktortagung, Karlsruhe 1973, pp. 421/4). – [222] F. G. Bodewig, G. Kaiser (JUEL-733-CT [1971] 1/23; N.S.A. **25** [1971] No. 39564). – [223] G. Beone, G. Caropreso, F. Ferri, G. Galuppi (RT-CHI-70-20 [1970] 1/109; N.S.A. **25** [1971] No. 23648). – [224] R. G. Wilbourn (GA-A-13552 [1975] 1/21; INIS Atomindex **7** [1976] No. 241956). – [225] A. E. Hutton (GA-A-13278 [1975] 1/406; INIS Atomindex **7** [1976] No. 239754).

[226] R. W. Dyck, R. Taylor, D. G. Boase (AECL-5957 [1977] 1/47; INIS Atomindex **9** [1978] No. 397695). – [227] R. C. Cairns, M. G. Baillie, M. S. Farrell, J. R. May (CONF-660524-21 [1966] 1/40; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 217/52; N.S.A. **21** [1967] No. 1192). – [228] S. L. Bennett, W. J. Biermann (Can. J. Chem. **40** [1962] 73/7). – [229] J. T. Roberts, L. M. Ferris, E. L. Nicholson, R. H. Rainey, C. D. Watson (ORNL-TM-1139 [1965] 1/51; N.S.A. **19** [1965] No. 30324). – [230] H. Beaujean, J. Bohnenstingl, M. Laser, E. Merz, H. Schnez (IAEA-SM-172/17 [1973] 1/17; Environ. Behav. Radionuclides Released Nucl. Ind. Proc. Symp., Aix-en-Provence, France, 1973, pp. 63/78; C.A. **81** [1974] No. 110836).

[231] R. Böhnert (JUEL-1089-CT [1974] 1/19; C.A. **82** [1975] No. 115471). – [232] L. J. Colby (NAA-SR-6107 [1961] 1/12; C.A. **59** [1963] 9542). – [233] L. T. Lackey, J. R. Bower (IDO-14620 [1963] 1/427; N.S.A. **18** [1964] No. 26977). – [234] H. O. Witte (ORNL-TM-1506 [1966] 1/15; N.S.A. **20** [1966] No. 35591). – [235] J. W. Snider, R. E. Leuze (CONF-720823-14 [1972] 1/26; N.S.A. **26** [1972] No. 53060).

[236] V. C. A. Vaughen, J. R. Flanary, J. H. Goode, H. O. Witte (ORNL-4120 [1970] 1/63; N.S.A. **24** [1970] No. 13997). – [237] R. S. Lowrie, C. L. Fitzgerald, V. C. A. Vaughen (CONF-720823-11 [1972] 1/15; N.S.A. **26** [1972] No. 53078). – [238] H. Beaujean, P. Filß, S. Halaszovich, M. Laser, E. Merz, D. Thiele (Reaktortagung, Hamburg 1972, pp. 267/70). – [239] R. W. Glass, P. A. Haas, R. S. Lowrie, M. E. Whatley (ORNL-TM-3527 [1972] 1/53; N.S.A. **26** [1972] No. 47936). – [240] H. Beaujean, P. Filß, U. Grahmann, M. Laser, E. Merz, U. Tillessen (JUEL-925-CT [1973] 1/98; C.A. **79** [1973] No. 86385).

[241] H. Bonka, R. Bieselt, D. Brenk, K. Brüssermann, J. Darvas, M. Laser, H. Schnez, G. Schwarz, K. J. Vogt, P. Winske (JUEL-1220 [1975] 1/229; C.A. **85** [1976] No. 9934). – [242] R. W. Glass, H. D. Cochran, D. M. Levins, J. W. Snider, D. C. Watkin, W. M. Woods, M. E. Whatley (ORNL-TM-4596 [1975] 1/144; N.S.A. **31** [1975] No. 19369). – [243] C. L. Fitzgerald, V. C. A. Vaughen, K. J. Notz, R. S. Lowrie (ORNL-TM-5090 [1975] 54; N.S.A. **33** [1976] No. 9001). – [244] J. A. Rindfleisch, V. H. Barnes (ICP-1093 [1976] 1/30; INIS Atomindex **7** [1976] No. 26904). – [245] H. S. Meyer (GA-A-13929 [1976] 1/23).

[246] W. Davis, R. E. Blanco, B. C. Finney, G. S. Hill, R. E. Moore, J. P. Witherspoon (ORNL/NUREG/TM-4 [1976] 1/193; INIS Atomindex **8** [1977] No. 293444). – [247] H. Beaujean, J. Bohnenstingl, M. Laser, E. Merz (Reaktortagung, Düsseldorf 1976, pp. 335/8). – [248] U. Griemert (KFA-ICT-414-IB-77 [1977] 1/130). – [249] H. Bonka, G. Schwarz, H. B. Wibbe, R. Böhnert (Kerntechnik **15** [1973] 297/300). – [250] A. G. Croff (ORNL-TM-5171 [1976] 1/62; INIS Atomindex **7** [1976] No. 269339).

[251] C. W. Forsberg (ORNL-TM-5825 [1977] 1/58; INIS Atomindex **9** [1978] No. 374410). – [252] P. Schmidt (JUEL-1567 [1979] 1/108). – [253] R. v. Ammon, H. W. Beaujean (in: F. Baumgärtner, Chemie der nuklearen Entsorgung, Thiemig, München 1978, pp. 142/61). – [254] G. W. Keilholz (Nucl. Safety **8** [1966] 155/60). – [255] R. H. Rainey, W. L. Carter, S. Blumkin (ORNL-4522 [1971] 1/58; N.S.A. **25** [1971] No. 29317).

[256] W. Guber, G. Rudolph, J. Saidl (KFK-1789 [1973] 1/56; N.S.A. **28** [1973] No. 8834). – [257] G. F. Offutt, C. L. Bendixsen (IN-1221 [1969] 1/47; N.S.A. **23** [1969] No. 24343). – [258] R. D. Penzhorn (KFK-2482 [1977] 1/67; INIS Atomindex **9** [1978] No. 396106). – [259] M. Laser, H. Beaujean, J. Bohnenstingl, P. Filß, M. Heidendael, S. Mastera, E. Merz, H. Vygen (Symp. Manage. Radioactive Wastes Fuel Reprocess. Proc., Paris 1972 [1973], pp. 77/98; C.A. **81** [1974] No. 162480). – [260] H. Barnert-Wiemer, H. Beaujean, M. Laser, E. Merz, H. Vygen (Ger. Offen. 2437810 [1976]).

[261] M. Laser, H. Barnert-Wiemer, H. Beaujean, E. Merz, H. Vygen (CONF-740807-Vol. 1 [1975] 246/62; Proc. 13th DOE Nucl. Air Cleaning Conf., Springfield, Va., 1974 [1975], Vol. 1, pp. 246/62; C.A. **85** [1976] No. 67443). – [262] S. Mastera (JUEL-1380 [1976] 1/120; INIS Atomindex **9** [1978] No. 351527). – [263] S. Mastera, J. Bohnenstingl, M. Laser, E. Merz (Brennstoff-Wärme-Kraft **29** [1977] 214/7). – [264] S. Mastera, M. Laser, E. Merz (Environ. Sci. Technol. **12** [1978] 85/8). – [265] H. Barnert-Wiemer, R. Böhnert (JUEL-1320 [1976] 1/57; INIS Atomindex **8** [1977] No. 283227).

[266] C. W. Forsberg (ORNL-TM-5826 [1977] 1/75; INIS Atomindex **9** [1978] No. 366076). – [267] L. M. Toth, J. T. Bell, D. W. Fuller, S. R. Buxton, H. A. Friedman, M. R. Billings (ORNL-TM-5656 [1976] 1/26; INIS Atomindex **8** [1977] No. 307539). – [268] R. W. Glass, T. M. Gilliam, V. L. Fowler (ORNL-TM-4947 [1976] 1/181; INIS Atomindex **7** [1976] No. 244038). – [269] J. C. Mullins, R. W. Glass (ORNL-TM-5099 [1976] 1/105; INIS Atomindex **8** [1977] No. 293984). – [270] R. D. Ackley, K. J. Notz (ORNL-5122 [1976] 1/37; INIS Atomindex **8** [1977] No. 297025).

[271] A. D. Ryon (ORNL-TM-5298 [1976] 1/46). – [272] K. J. Notz, A. B. Meservey (ORNL-5121 [1976] 1/65). – [273] R. W. Glass, H. W. R. Beaujean, V. L. Fowler, T. M. Gilliam, D. J. Inman, D. M. Levins (ORNL-TM-5095 [1976] 1/55; INIS Atomindex **7** [1976] No. 263683). – [274] J. Bohnenstingl, M. Heidendael, M. Laser, S. Mastera, E. Merz (IAEA/SM-207/20 [1976] 1/9; Manage. Radioact. Wastes Nucl. Fuel Cycle Proc. Symp., Vienna 1976, Vol. 4, pp. 129/38; INIS Atomindex **9** [1978] No. 358471). – [275] S. H. Böll-Djoa (Kerntechnik **19** [1977] 165/70).

[276] R. D. Ackley (ORNL-TM-4883 [1975] 1/30; N.S.A. **32** [1975] No. 3151). – [277] F. A. Hohorst (ICP-1114 [1977] 1/56; INIS Atomindex **8** [1977] No. 348321). – [278] D. T. Pence, T. R. Thomas (WASH-1332-74-V-1 [1974] 427/44). – [279] H. Barnert-Wiemer, M. Heidendael, H. Kirchner, E. Merz, G. Schröder, H. Vygen (Proc. 15th DOE Nucl. Air Cleaning Conf., Boston, Mass., 1978 [1979], pp. 1/17). – [280] I. J. Perona, J. D. Blomeke, W. C. T. Stoddart (Trans. Am. Nucl. Soc. [1969] 449/50).

[281] J. H. Goode (ORNL-3956 [1966] 1/20; N.S.A. **20** [1966] No. 31447). – [282] R. Böhnert, H. Bonka (JUEL-763-RG [1971] 1/95; N.S.A. **26** [1972] No. 4427). – [283] T. R. Thomas, B. A. Staples, L. P. Murphy, J. T. Nichols (ICP-1119 [1977] 1/42; INIS Atomindex **9** [1978] No. 366084). – [284] H. Barnert-Wiemer, H. Hackfort, M. Heidendael, J. Patay, H. Vygen (JUEL-CONF-30 [1979] 85/103). – [285] H. Bonka, K. Brüssermann (Reaktortagung, Karlsruhe 1973, pp. 590/3).

[286] H. Schnez, M. Laser, E. Merz (JUEL-1099-CT [1974] 1/82; C.A. **83** [1975] No. 17375). – [287] H. Schnez (JUEL-1223 [1975] 1/124; C.A. **84** [1976] No. 23478). – [288] R. H. Rainey, J. G. Moore (ORNL-3155 [1961] 1/29; N.S.A. **16** [1962] No. 17762). – [289] F. G. Bodewig, W. Johannisbauer, G. Kaiser, P. Sckuhr (Reaktortagung, Karlsruhe 1973, pp. 421/4). – [209] H. Schnez (Dipl.-Arbeit, Aachen T.H., 1972, pp. 1/76).

[291] C. A. Brown (GA-A-13858 [1976] 1/51; INIS Atomindex **7** [1976] No. 274973).

2.4.4 Chemical Separation by Means of Solvent Extraction

2.4.4.1 Chemistry of the Aqueous Process Solution

In aqueous solutions mainly U^{IV} and U^{VI} compounds exist, and in the latter case, the uranium is present as the uranyl ion, UO_2^{2+}. When uranium compounds are dissolved in HNO_3, this ionic form is obtained quantitatively. Uranyl nitrate is readily soluble in water. Tetravalent uranium compounds are obtained only under strongly reducing conditions. Thorium, on the other hand, is preferably tetravalent in its compounds. The solutions commonly undergoing processing, therefore, contain Th in its tetravalent form and U in its hexavalent form. No special problems of valency adjustment is met with for these two elements. The tendency to form polymeric ions, that is observed with Pu [1] is unknown for Th and U. Large fractions of the U, Th and many fission products form anionic complexes in the process solutions. If pure HNO_3 solutions are dealt with, these are nitrato complexes. If stronger complexing anions are present, such as fluoride, acetate, sulfate, or phosphate, these displace the nitrate anions. The complex species formed may then be cationic, neutral or anionic, e.g., UO_2F^+, UO_2F_2, or $UO_2F_3^-$. The neutral and anionic nitrato complexes play an important role in the solvent extraction process. They form the extractable species, whereas many other anionic complexes exist as non-extractable species, and thus permit an effective separation of mixtures of the elements [2].

2.4.4.2 Choice of the Extraction System

The chemical separation of the nuclear fuels, that have been dissolved in acid, into different fractions is effected nowadays almost exclusively by means of solvent extraction [3 to 7]. This consists of the selective distribution of the constituents of the burned-up fuel between two immiscible liquids: the aqueous process solution and an organic extractant. The latter is generally applied not in its neat form, but diluted with a suitable diluent (kerosene, etc). The aqueous nitrate system has proved to be the most useful, since HNO_3 is a suitable reagent for the dissolution, the corrosion problems have been brought under control (stainless steel and Zr metal are resistant against HNO_3), and good distribution equilibria exist for the nitrates. Many requirements must be met by the extractant: e.g., selectivity, radiation stability, solubility, safety, viscosity, and high distribution constants. These are fulfilled for technical processes by only few solvents [8]. The extraction of the actinides and of fission products is described in detail in "Transurane" A1, II, 1974, Chapter 5, from p. 177.

2.4.4.3 Characteristics of the Processes and the Plants

Two special requirements are set before the reprocessing, on ecological, radiation protection, and economic grounds:

1. High chemical purity of the separated uranium (decontamination factor $>10^6$).
2. High chemical yield ($>99.5\%$).

Both requirements must be met simultaneously, and this increases the technical complexity of the system. The reprocessing itself and the construction of the processing plant and buildings differ appreciably from the conventional technology. This is caused by the high radiation of the materials to be treated, which make mandatory remote controlled automatic operation on the one hand, and various radiation protection measures on the other.

Liquid-liquid extraction processes meet best these difficult and complicated requirements. They may be operated continuously, act in a multiplicative purifying manner, and lead to minimal loss of product by application of the counter-current principle [9]. Practical multistage extraction can be conducted in three different kinds of equipment [10 to 13]:

1. packed or pulsed perforated plate columns,
2. mixer-settlers, or
3. centrifugal extractors.

The following aspects must be considered in the choice of the most suitable type:

1. The rate and completeness of the material transfer. The rate controlling step in extractive material transport is the diffusion through the interfaces, in most cases relevant to nuclear technology.

2. Dispersion into small drops for the attainment of a large total surface area and a good mixing of the phases.

3. Clean phase separation, no emulsion formation and no back-mixing of the phases, due to local build-up of pressure in the extraction apparatus.

4. Least possible contact times, in order to avoid decomposition of the organic phase by the radiation.

5. Continuous operation with an acceptable specific material throughput.

6. Small volume (especially height), because of the costs of radiation shielding.

7. Insensitivity to the presence of solids in the solution, due to so-called crud formation, and good hydraulic behavior.

8. Simple construction and long maintenance-free operation.

9. Criticality safety, by maintaining certain geometrical measurements.

The decision for the one or the other process is not so simple, and often the subjective operative experience plays a role in the judgement [14 to 17].

2.4.4.4 Extraction with Ketones

The first process for the extractive separation of ^{233}U utilized methyl isobutyl ketone, $CH_3COCH_2CH(CH_3)_2$, designated commercially as hexone, and used as a diluent for lacquers. It must be pointed out that this choice of hexone fell on the basis of existing laboratory experience, but not on that of extensive testing [18, 19]. The process received the code-name hexone-23 in the military usage, where it served in the early days of nuclear energy development for the production of the first sizable amounts of ^{233}U.

Uranium is extracted by hexone selectively from an acid deficient solution containing $Al(NO_3)_3$ as a salting-out agent. Thorium is poorly extracted under these conditions. The decontamination factor achieved for the majority of the fission products was 10^5 [20 to 23]. The ability of hexone to extract also plutonium led to its use in the so-called REDOX process, that was developed for reprocessing in the U-Pu cycle [24, 25]. Certain serious disadvantages were found when this process was carried out on a technical scale, that led to its eventual abandonment. For one, strong nitration and oxidation of the hexone by concentrated nitric acid occur [26], then, a high concentration of the salting-out agent must be present, and finally, increasing extraction of the fission-produced Ru, Zr and Ce occurs at increasing nitrate or HNO_3 concentrations. Another ketone that has been proposed for the extraction is methyl cyclohexanone [27]. The disadvantages are characteristic not only for hexone, but for all ketones.

2.4.4.5 Extraction with Ethers

Ethers received during the early stages of reprocessing technology special consideration as extraction reagents, since they generally show good selectivity and distribution properties. Two processes were even applied temporarily on an industrial scale in the U-Pu fuel cycle. The TRIGLY process, that had been developed in Canada, utilized triglycol dichloride, $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$, as a plutonium extractant. Uranium can be extracted only under very special conditions [28]. The BUTEX process, applied for many years in the Windscale plant in England, permits a good extraction of both uranium and plutonium. The solvent used is dibutoxydiethyl ether, $C_4H_9OC_2H_4OC_2H_4OC_4H_9$ (= DBC, dibutylcarbitol) [29]. A comparative study of the separation of ^{233}U from reactor-irradiated thorium by DBC and TBP is described in [30]. A process was developed in the USSR, that used 15% dibutyl ether, $C_4H_9OC_4H_9$, in CCl_4 as diluent [31]. A comparison of the extraction ability of various ethers for the separation of ^{233}U was conducted also in the USA [32].

Polyethers are superior to monoethers at the same extraction ability, because of their lower volatility and lower aqueous solubility. Diisopropyl ether, $C_3H_7OC_3H_7$, diisobutyl ether, $C_4H_9OC_4H_9$, di-n-butyl ether [34], several dialkyl diethers [35], and dibutyleneglycolmonoethyl ether have been examined [33]. All the extractants yielded, in principle, satisfactory separation or decontamination factors. Only fission-produced ruthenium caused appreciable troubles. Other disadvantageous properties of the ethers are the formation of peroxides, induced by radiation or in the presence of higher HNO_3 concentrations. These constitute a safety hazard, in view of their instability.

2.4.4.6 Extraction as Chelates

The extractive separation of metal ions as chelates has not proved itself technically. A certain β-diketone, thenoyltrifluoroacetone (= $CF_3COCH_2COC_4H_4S$ = HTTA), has selective extraction properties relative to numerous elements, including U and Pu. The extraction proceeds over the enol form, with the replacement of the enol-hydrogen by the metal ion, i.e., by chelate formation, rather than by adduct formation as with the ketones, as which HTTA may be classified. The uranium HTTA chelate is highly soluble in diluents such as C_6H_6, $CHCl_3$, or CCl_4. Under certain processing conditions its satisfactory separation from accompanying elements like Th or fission products may be achieved. However, the theoretically expected separations could not be achieved in practice [37]. Disadvantageous is the slow extraction kinetics, since the slow rate of enolization is the rate controlling step for the extraction. Problems arising from radiative decomposition of the reagent have also not yet been satisfactorily eliminated [35 to 38].

The distribution of U and Th chelates between HNO_3 or $HClO_4$ solutions and four cycloethers is described in [39]. A review of radiochemical separation methods for the actinide elements, preferably by solvent extraction is given in [40].

2.4.4.7 Extraction with Alkylphosphorus Compounds

On the whole, the neutral, and partly also acid, alkylphosphorus esters are the most important class of extractants in nuclear technology. By far the most important representative of these is TBP, tri-n-butyl phosphate, $(C_4H_9O)_3PO$. It fulfills all the essential requirements from a good extractant: chemical stability, high extracting ability, selectivity for the actinides, good radiation stability, and low production costs. The search did not cease, however, for even better extractants. The neutral alkylphosphorus esters may be classified into four groups:

phosphates (RO)(R′O)(R″O)P=O, phosphonates (R″O)(R′O)RP=O
phosphinates (RO)R′R″P=O, phosphine oxides RR′R″P=O

(where usually, but not always R = R′ = R″).

The extracting ability of these alkylphosphorus esters is a function of the basicity of the P=O group [41]. The substitution of hydrogen atoms in the alkyl groups by electronegative atoms like Cl destroys the extracting ability.

The extractive properties of acid dialkyl phosphates were studied in both the sulfate and the nitrate systems [42]. TBP has been compared with dialkyl phosphonates in a series of extensive studies. Better distribution properties and a higher radiation resistance were said to characterize di-n-butylphosphate $HO(C_4H_9O)_2PO$ and di-sec-butyl phenyl phosphonate $(s\text{-}C_4H_9O)_2\text{-}C_6H_5PO$ relative to the U/Th separation [43 to 50]. Other studies were concerned with a comparison of aliphatic sulfoxides with TBP [51].

Still, there exists no doubt that TBP will remain the favored extractant for the technical scale reprocessing of Th-containing nuclear fuels. It is the basis of the THOREX process. The extraction depends on the formation of a stoichiometric metal-TBP complex. TBP is always used in a diluted form (4 to 40%), being too viscous in the neat form. Aliphatic saturated hydrocarbons, such as kerosene or pure dodecane, serve as the diluents, which form together with the TBP the organic phase. TBP has approximately the same density as water, but the solutions in the less dense diluents have the required difference in density. TBP dissolves up to 0.6 vol% in water and takes up 7 vol% dissolved water. The aliphatic diluent should be free from aromatics, since these may be nitrated by the concentrated HNO_3, forming derivatives that may extract some of the fission products. The fundamental aspects of the extraction with TBP have been studied intensively [52 to 58].

2.4.4.8 Extraction with Amines

The application of amines as extractants for reprocessing is based on their use for the recovery of U and Th from ores [59 to 65]. Tertiary amines have proved themselves best. Dissolved in hydrocarbons, they form trialkyl ammonium salts with inorganic acids. They act as liquid anion exchangers, binding metal salts present in neutral or anionic species as follows [66 to 72]:

$$MX_n(aq) + m\ R_3NHX(org) \rightleftarrows (R_3NH)_mMX_{n+m}\ (org)$$
$$MX_{n+m}^{m-}(aq) + m\ R_3NHX(org) \rightleftarrows (R_3NH)_mMX_{n+m}(org) + m\ X^-(aq).$$

A comprehensive description of the extraction mechanism of actinides with amines is found in [73].

Many amines exhibit high selectivity towards U and Th. The decontamination factors obtained in the laboratory are good [74 to 80]. It was further expected that the amines will be more radiation resistant than TBP, since the radiolysis products (secondary and primary amines) do not perturb the extraction behavior of the U. The expectations were fulfilled only partly, however [81 to 89]. Furthermore, for satisfactory extraction a salting-out agent is required, HNO_3 alone being insufficient. This leads to the formation of additional radioactive waste. The extraction ability increases with decreasing molecular weight of the amine, but the aqueous solubility increases in the same direction. The courses of the extraction of U, the fission products, and some corrosion products (Fe, Cr) are parallel, as the process variables (the temperature and the concentrations of the amine, the acid, and the salting agent) vary. The problem of the formation of three phases is enhanced in the case of amines, and as a countermeasure, the use of an aromatic diluent (e.g., trimethylbenzene) has been recommended. This, in turn, has been troublesome on account of the nitration that occurs at higher HNO_3 concentrations.

Various systems have been examined. The nitrate system has been of interest for laboratory studies, but nothing has been published about its practical application for the reprocessing of Th-containing nuclear fuel [90 to 96]. More extensive studies exist for the sulfate system, in particular in the range 0.01 to 0.1 M H_2SO_4 [97 to 101]. Secondary amines extract preferentially the thorium, whereas tertiary amines are more advantageous for the extraction of the uranium. As secondary amines, di-n-octylamine and bis(tridecyl)amine found application, as tertiary amines, mainly trioctylamine, tridecylamine (tricaprylamine), and tridodecylamine (trilaurylamine).

A process flow sheet for the amine extraction from sulfate solutions was proposed, but it has never been realized practically [98]. A similar fate befell a process for the extractive reprocessing of Th-containing nuclear fuels from chloride solutions by means of long chain tertiary aliphatic amines [102]. A process utilizing a quaternary amine in chloride solutions is described in [103]. The quaternary amines have particularly high distribution coefficients for the uranium [104, 105]. They are, however, not advantageous, since they have extraordinarily high distribution coefficients also for Ru and Mo [78 to 80]. The extractive behavior of an amine depends not only on its structure and on the aqueous electrolyte, but it depends also strongly on the nature of the diluent used [106].

References for 2.4.4:

[1] K. A. Kraus (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 7, pp. 245/57). – [2] A. Naylor (KR-126 [1967] 101/14, 120/42; N.S.A. **22** [1968] No. 40160, No. 40169). – [3] V. I. Kuznetsov (Usp. Khim. **23** [1954] 654/96; AERE-LIB-TRANS-532 [1955] 1/58; N.S.A. **10** [1956] No. 6596). – [4] H. Irving (Quart. Rev. London **5** [1951] 200/26). – [5] G. H. Morrison, H. Freiser (Solvent Extraction in Analytical Chemistry, Wiley, New York 1957).

[6] Y. Marcus, A. S. Kertes (Ion Exchange and Solvent Extraction of Metal Complexes, Wiley-Interscience, London 1969, from p. 429). – [7] J. F. Flagg (Chemical Processing of Reactor Fuels, Academic, New York 1961, pp. 125/98). – [8] C. M. Nicholls (Progr. Nucl. Energy III **1** [1956] 54/8). – [9] R. E. Treybal (Liquid Extraction, McGraw-Hill, New York 1963). – [10] C. Hanson (Brit. Chem. Eng. **10** [1965] 34/7).

[11] R. B. Akell (Chem. Eng. Progr. **62** No. 9 [1966] 50/5). – [12] G. H. Reman (Chem. Eng. Progr. **62** No. 9 [1966] 56/61). – [13] R. E. Treybal (Chem. Eng. Progr. **62** No. 9 [1966] 67/75). – [14] W. D. Jamrack (Rare Metal Extraction by Chemical Engineering Techniques, Pergamon, Oxford 1963). – [15] J. T. Long (Engineering for Nuclear Fuel Reprocessing, Gordon and Breach, New York 1967, pp. 161/272).

[16] H. Goldacker (Chem. Tech. [Heidelberg] **4** [1975] 83, 135/42). – [17] G. Koch, W. Ochsenfeld, H. Schmieder (Atomwirtsch. Atomtech. **20** [1975] 123/7). – [18] F. L. Steahly (MonN-125 [1946] 1/62; N.S.A. **11** [1957] No. 7539). – [19] I. Perlman (CN-3627 [1946] 1/75; N.S.A. **14** [1960] No. 21567). – [20] J. F. Flagg (in: J. F. Flagg, Chemical Processing of Reactor Fuels, Academic, New York 1961, pp. 249/70).

[21] F. L. Culler (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 464/83). – [22] F. L. Fuller, F. R. Bruce (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 484/91). – [23] F. R. Bruce (Proc. 1st Intern. Conf. Peaceful Uses At.

Energy, Geneva 1955, Vol. 7, pp 100/12). – [24] S. Lawrowski, M. Levenson (TID-7534-Bk. 1 [1957] 45/68; N.S.A. **12** [1958] No. 154). – [25] S. Lawrowski, M. Levenson (Progr. Nucl. Energy III **2** [1958] 258/78; C.A. **1959** 8835).

[26] B. R. Jones, L. L. Burger (HW-19096 [1957] 1/22; N.S.A. **11** [1957] No. 8278). – [27] V. Veselý, H. Beranová, J. Malý (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 162/7). – [28] M. W. Campbell (Nucleonics **14** [1956] 92/6). – [29] G. R. Howells, T. G. Hughes, D. R. Mackey, K. Saddington (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 3/24). – [30] H. A. C. McKay, J. M. Fletcher (Progr. Nucl. Energy III **1** [1956] 147/60).

[31] V. M. Vdovenko, M. P. Kovalskaia (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 329/32). – [32] D. E. Ferguson, R. E. Leuze (ORNL-374 [1957] 1/13; N.S.A. **11** [1957] No. 8392). – [33] H. W. Alter, W. O. Haas, E. J. Zebroski (KAPL-442 [1950] 1/38). – [34] H. J. Born, S. Krawszynski, W. Ochsenfeld, H. Scholz (Chem. Ing. Tech. **34** [1962] 537/41). – [35] L. L. Burger (J. Chem. Eng. Data **9** [1964] 112/4).

[36] R. L. Stevenson, P. E. Smith (in: S. M. Stoller, B. B. Richards, Reactor Handbook, Vol. 2, New York 1961, pp. 107/234). – [37] F. L. Culler (Progr. Nucl. Energy III **1** [1956] 172/94). – [38] A. T. Kandil, H. F. Aly, M. Raich, G. R. Choppin (J. Inorg. Nucl. Chem. **37** [1975] 229/32). – [39] M. Branica, E. Bona (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 172/4). – [40] E. K. Hyde (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1956, Vol. 7, pp. 281/303).

[41] L. L. Burger (HW-44888 [1957] 1/25; N.S.A. **11** [1957] No. 5762). – [42] C. A. Blake, K. B. Brown, C. F. Coleman (ORNL-1903 [1955] 1/130; N.S.A. **11** [1957] No. 2357). – [43] A. T. Gresky, R. G. Mansfield (ORNL-CF-59-6-15 [1959] 1/87; N.S.A. **15** [1961] No. 7398). – [44] C. A. Blake, K. P. Brown, C. F. Coleman (ORNL-1964 [1955] 1/11; N.S.A. **10** [1956] No. 7573). – [45] T. H. Sidall (DP-219 [1960] 1/20; N.S.A. **15** [1961] No. 8875).

[46] J. C. White, W. J. Ross (NAS-NS-3102 [1961] 1/60; N.S.A. **15** [1961] No. 23567). – [47] L. E. Marc de Chazal, A. R. Lister (AERE-M-698 [1960] 1/4; N.S.A. **14** [1960] No. 25535). – [48] C. A. Blake, A. T. Gresky, J. M. Schmitt, R. G. Mansfield (ORNL-3374 [1963] 1/33; N.S.A. **17** [1963] No. 10738). – [49] A. Apelblat (Proc. Intern. Solvent Extract. Conf., The Hague 1971, pp. 1208/15). – [50] M. F. Pushlenkov, V. G. Shumkov, V. I. Zemlyanukhin, B. Ya. Zilberman, O. N. Shuvalov, V. G. Voden, N. N. Shchepetilnikov (Progr. Nucl. Energy III **4** [1970] 215/31).

[51] G. J. Laurence, M. T. Chaieb, J. Talbot (Proc. Intern. Solvent Extract. Conf., The Hague 1971, pp. 1150/9). – [52] C. V. Ellison, D. E. Ferguson, T. C. Runion (ORNL-258 [1949] 1/5; N.S.A. **11** [1957] No. 12399). – [53] D. E. Ferguson, T. C. Runion (ORNL-260-Del. [1949] 1/47; N.S.A. **11** [1957] No. 9655). – [54] H. A. C. McKay (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 7, pp. 314/7). – [55] H. A. C. McKay (Progr. Nucl. Energy III **1** [1956] 122/9).

[56] D. F. Peppard, G. W. Mason, J. L. Maier (J. Inorg. Nucl. Chem. **3** [1956] 215/28). – [57] E. Hesford, H. A. C. McKay, D. Scargill (J. Inorg. Nucl. Chem. **4** [1957] 321/32). – [58] E. Hesford, H. A. C. McKay (Trans. Faraday Soc. **54** [1958] 573/86). – [59] K. B. Brown, C. F. Coleman, D. J. Crouse, J. O. Denis, J. G. Moore (AECD-4142 [1954] 1/118; N.S.A. **10** [1956] No. 9740). – [60] J. G. Moore, K. B. Brown, C. F. Coleman (AECD-4145 [1955] 1/96; N.S.A. **11** [1957] No. 975).

[61] W. D. Arnold, D. J. Crouse (ORNL-3030 [1961] 1/43; N.S.A. **15** [1961] No. 6051). – [62] C. F. Coleman, K. B. Brown, J. G. Moore, D. J. Crouse (Ind. Eng. Chem. **50** [1958] 1756/61). – [63] K. B. Brown, C. F. Coleman, D. J. Crouse, C. A. Blake, A. D. Ryon (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 3, pp. 472/87; C.A. **1959** 7525). – [64] D. D. Crouse, K. B. Brown (Ind. Eng. Chem. **51** [1959] 1461/5). – [65] J. B. Rosenbaum, S. R. Borrowman, J. B. Clemmer (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 3, pp. 505/9).

[66] C. F. Coleman (Nucl. Sci. Eng. **17** [1963] 274/7). – [67] D. J. Carswell, J. J. Lawrence (J. Inorg. Nucl. Chem. **11** [1959] 69/75). – [68] C. F. Coleman, K. B. Brown, J. G. Moore, K. A. Allen (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 28, pp. 278/88). – [69] V. M. Vdovenko, A. A. Lipovskii, M. G. Kuzina (Radiokhimiya **3** [1961] 555/66; Radiochemistry [USSR] **3** [1962] 197/209). – [70] A. M. Wilson, L. Churchill, K. Liluk, P. Hovsepian (Anal. Chem. **34** [1962] 203/7).

[71] C. F. Coleman, C. A. Blake, K. B. Brown (Talanta **9** [1962] 297/323). – [72] W. E. Keder, A. S. Wilson (Nucl. Sci. Eng. **17** [1963] 287/92). – [73] W. Müller (Actinides Rev. **1** [1971] 71/120). – [74] F. L. Moore (Anal. Chem. **30** [1958] 908/11). – [75] F. L. Moore (NAS-NS-3101 [1960] 1/114; **15** [1961] No. 22362).

[76] W. E. Keder (J. Inorg. Nucl. Chem. **24** [1962] 561/70). – [77] T. Kojima, H. Fukutomi, H. Kakihana (J. Nucl. Sci. Technol. [Tokyo] **6** [1969] 81/9). – [78] T. Ishimoni (J. At. Energy Soc. Japan **3** [1961] 698/704). – [79] T. Murase (J. At. Energy Soc. Japan **5** [1963] 971/9). – [80] C. F. Coleman (At. Energy Rev. **2** [1964] 3/54).

[81] T. U. Ishihara (J. At. Energy Soc. Japan **4** [1962] 307/12). – [82] M. Zifferero (Aqueous Reprocess. Chem. Irradiat. Fuels Symp., Brussels 1963, pp. 107/15). – [83] T. U. Ishihara, Y. Komaki (J. Nucl. Sci. Technol. [Tokyo] **2** [1965] 463/7). – [84] R. B. Neel, I. D. Eubanks, M. C. Thompson, G. A. Burney (DP-1066-Vol. 2 [1966] 57/64; CONF-660305-7 [1966] 1/9; ANS [Am. Nucl. Soc.] Top. Meeting, Augusta, Ga., 1966; N.S.A. **20** [1966] No. 14636). – [85] G. Caspari (Z. Naturforsch. **22b** [1967] 574/9).

[86] I. D. Eubanks (At. Energy Rev. **7** [1969] 49/90). – [87] R. M. Wagner, L. H. Towle (AECU-4054 [1958] 45 pp.; N.S.A. **13** [1959] No. 11419). – [88] R. M. Wagner, L. H. Towle (AECU-4053 [1958] 40 pp.; N.S.A. **13** [1959] No. 11418). – [89] G. A. Swan (J. Chem. Soc. **1958** 4669/72). – [90] W. E. Keder, J. L. Ryan, A. S. Wilson (J. Inorg. Nucl. Chem. **20** [1961] 131/9).

[91] V. M. Vdovenko, M. P. Kovalskaya, Y. V. Shirvinskii (Radiokhimiya **3** [1961] 3/6; Radiochemistry [USSR] **3** [1961/62] 1/5). – [92] J. M. P. J. Verstegen (J. Inorg. Nucl. Chem. **26** [1964] 1589/93). – [93] J. C. Sheppard (HW-51958 [1957] 1/13; N.S.A. **12** [1958] No. 2267). – [94] A. S. Kertes, I. T. Platzner (J. Inorg. Nucl. Chem. **24** [1962] 1417/28). – [95] P. R. Danesi, F. Orlandini, G. Scibona (J. Inorg. Nucl. Chem. **27** [1965] 449/56).

[96] A. Chesné, G. Koehly, A. Bathelliar (Nucl. Sci. Eng. **17** [1963] 557/62). – [97] K. A. Allen, W. J. McDowell (J. Phys. Chem. **67** [1963] 1138/40). – [98] M. A. Awwal (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1965, Vol. 10, pp. 443/8). – [99] W. J. McDowell, K. A. Allen (J. Phys. Chem. **65** [1961] 1358/61). – [100] M. A. Awwal (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 8, pp. 559/74).

[101] F. Mannone, C. Stoppa (EUR-1911.i [1964] 1/41; N.S.A. **18** [1964] No. 43708). – [102] R. Thomas (Proc. Intern. Solvent Extract. Conf., The Hague 1971, pp. 1188/96). – [103] C. Jacobelli-Turi, S. Terenzi, M. Palerma (Ind. Eng. Chem. Process Design Develop. **6** [1967] 162/70). – [104] E. Lopez-Menchero, L. Gehem (Aqueous Reprocess. Chem. Irradiat. Fuels Symp., Brussels 1963, pp. 147/64; C.A. **60** [1964] 14086). – [105] G. Koch (in: H. A. C. McKay, T. V. Healy, I. L. Jenkins, A. Naylor, Solvent Extraction Chemistry of Metals, London 1966, pp. 247/66).

[106] G. Yu. Frolov, A. V. Ochkin, V. V. Sergievsky (At. Energy Rev. **7** [1969] 71/138).

2.4.5 Extractive Reprocessing of Thorium-Containing Nuclear Fuels and Breeding Materials with the HNO_3-TBP-Kerosene System

2.4.5.1 General Aspects

Tri-n-butyl phosphate turned out to be the best extracting agent. It formed the basis of the world-wide accepted PUREX and THOREX processes [1 to 3]. The first proposal to use this compound, that is manufactured on a large industrial scale as an antifoaming agent and as a plasticizer, for the extractive separation of the actinides and the fission products was made in 1945 [4]. At first it was considered for the recovery of uranium from the residues of the coprecipitation of Pu with the $BiPO_4$ process. An extractant was sought, that was stable to oxidation and could withstand even concentrated HNO_3 [5 to 7]. Its chemical properties are described in [8] in detail, see also in Section 2.4.4.7, p. 312. In solvent extraction, the diluent together with the TBP constitute the organic phase. Since HNO_3 is preferentially used for the dissolution of the nuclear fuel, it constitutes the aqueous phase.

2.4.5.2 The Chemistry of the Separation

Th^{IV}, U^{VI}, Np^{IV}, Np^{VI}, Pu^{IV}, and Pu^{VI} are all well extracted by TBP. The extraction process depends on the formation of a stoichiometric complex, in which two or three TBP molecules are bound via the polar phosphoryl group to the central metal atom. The butyl groups are responsible for the solubility of the complex in organic media. It transfers into the organic phase as the neutral nitrate. The tetravalent actinide nitrates have a particular tendency to form such complexes.

$$UO_2^{2+}(aq) + 2\,NO_3^-(aq) + 2\,TBP(org) \rightleftharpoons UO_2(NO_3)_2(TBP)_2(org)$$
$$Pu^{4+}(aq) + 4\,NO_3^-(aq) + 2\,TBP(org) \rightleftharpoons Pu(NO_3)_4(TBP)_2(org)$$
$$Th^{4+}(aq) + 4\,NO_3^-(aq) + 2\,TBP(org) \rightleftharpoons Th(NO_3)_4(TBP)_2(org).$$

Contrary to the tetra- and hexavalent elements, which bind two TBP molecules per metal nitrate, the much less extractable tervalent elements bind 3 TBP molecules per metal nitrate. **Fig. 2-10** shows some typical distribution curves.

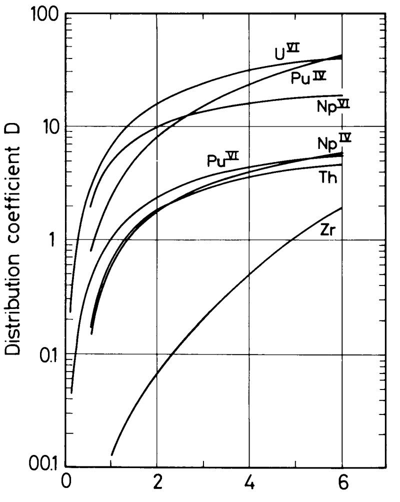


Fig. 2-10

The distribution ratios of U^{VI}, Pu^{IV}, Pu^{VI}, Np^{IV}, Np^{VI}, Th, and Zr between 30% TBP in n-dodecane and aqueous nitric acid solutions [1].

The extraction process may be described by reaction equations, because of the formation of stoichiometric compounds, and the mass-action law may be applied to obtain information on the effect of the participating components on the extraction process. The basic studies on the extraction of U and Th by TBP from nitric acid solutions have already been made in the 50's [9 to 24].

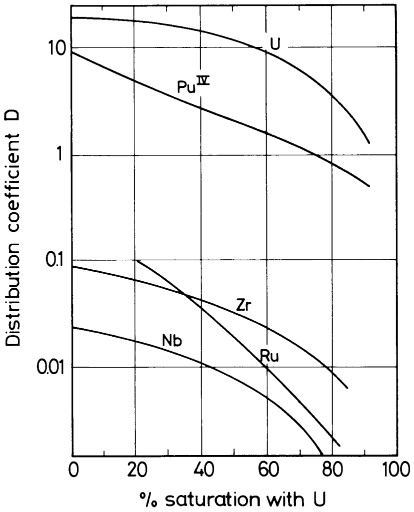
Among the fission products, Zr, Nb, and Ru are bound and extracted to some extent by TBP. It is bound in the first ligand coordination sphere of Zr and Nb, as it is in that of U and Pu [25 to 27]. On account of the formation of various nitrato complexes, Ru is particularly troublesome in the purification. The major fraction of the Ru exists as nitrato and nitrito complexes of the nitrosylruthenium(III) cation. The equilibria among the various species shift as a function of the nitric acid concentration [28 to 35]. See also in "Ruthenium", Erg. Bd., 1970, pp. 261, 339ff, 136ff.

Under realistic process conditions, it is not a single component that is extracted, but a multicomponent system is present, where U, Th, Pu, and Zr, Nb and Ru from among the fission products, compete for the ligand, TBP, as does the acid, if present in excess. Some other fission products also compete, but much less effectively. See **Fig. 2-11**.

The decrease of the distribution ratios with increasing saturation with U shows the displacing action of U with respect to the other elements. This saturation effect is an important factor in the conduction of the extraction, affecting strongly the yield of the U, and controls the decontamination factor [36 to 39]. The acid concentration, too, affects the distribution ratios strongly [40, 41].

In the design of flow schemes for the reprocessing of Th-containing nuclear fuels, the prevention of the formation of a third phase is one of the main problems. The presence of two

Fig. 2-11



Effect of the saturation of the solvent (30 vol% = 1.1 M TBP) by uranium (100% saturation = 0.55 M) on the distribution of carrier-free Pu^{IV}, Zr, Nb, and Ru [1].

organic phases causes operative difficulties in the countercurrent extraction. The separation of a TBP phase, that is highly loaded with Th, into two phases, of which the heavier one contains most of the extractable Th, is a phenomenon known already for a long time. However, the compositions of the two phases have not yet been ascertained completely [42 to 46]. Several studies yielded the limiting conditions for the avoidance of third phase formation [47 to 51].

2.4.5.3 Chemical and Radiation-Chemical Stability of the Extractant

It is necessary to differentiate between the actual extractant, TBP, and the solvent or diluent. Of greatest importance is the stability of the TBP against hydrolysis and radiolysis, as also against oxidative reactions [52]. TBP has considerable thermal stability, and it hardly reacts at all, or only very slowly, with most oxidants at room temperature. An important exception is the sudden reaction in the aqueous TBP-$UO_2(NO_3)_2$-HNO_3 system above 135 °C, the boiling point of uranyl nitrate dissolved in its water of crystallization. This circumstance requires special precautions to be taken when the corresponding solution is evaporated [53].

The decomposition of TBP to dibutyl phosphate (= HDBP), monobutyl phosphate (= H_2MBP), and finally to phosphoric acid H_3PO_4 and butanol may proceed both under the influence of radiation but also on account of chemical hydrolysis. The acidic phosphate esters, HDBP and H_2MBP are strong complexing agents for actinide ions, and may lead to losses of the product, because of appreciable aqueous solubility. Additionally, they may extract some of the fission products better than TBP, causing contamination of the organic phase, and H_2MBP and H_3PO_4 form with Zr insoluble precipitates, that accumulate at the interface. The muddy precipitates are designated as crud, and may cause operational disturbances.

The extent of the hydrolysis depends on many factors, for instance, an acid-catalyzed effect was observed [54 to 56]. Hydrolysis proceeds in both acid and alkaline media.

The radiolysis of TBP produces various gaseous products, mainly hydrogen, alkanes, and alkenes, from C_1 to C_4. Besides HDBP and H_2MBP also many polymeric products are formed. The kind and quantity of the decomposition products depend, of course, on the radiation dose, the temperature, and the chemical composition of the organic phase, e.g., on the presence or absence of HNO_3 or diluent [57 to 67]. Oxygen, too, has a strong effect on the formation of HDBP, explaining the effect of air stirring on the process of radiolysis [68]. This subject was covered till 1966 in a bibliography [69]. The predominant decomposition product is HDBP. Since the complexation of U^{VI} and tetravalent metal ions by HDBP and H_2MBP leads to unsatisfactory decontamination and product yields, these acidic esters must be removed from the solvent after each cycle by an alkaline wash (solvent purification step). Radiolysis products of the diluent, that have complexing properties, are not removable by the alkaline wash and may also accumulate. These include long-chain acidic phosphate esters [70 to 75]. Analytical procedures for the determination of the important radiolysis products are described in [76 to 83].

A clear gradation of the thermal and radiolytic stability exists among the diluents. Normal paraffins are more stable than the corresponding iso compounds, which are more stable, in turn, than naphthenes and olefins [84, 87]. The decomposition of the TBP was said to increase with the stability of the diluent. The radiolysis of the diluent worsens the attainable decontamination factors and product yields. The primary radiolytic products are nitro and carbonyl compounds, carboxylic acids, nitrite esters, etc. The secondary products and the reactions leading to metal ion complexation have not yet been clarified [84 to 88]. The nitrogen- and oxygen-containing radiolysis products of the diluent are not removable by the alkaline wash, and build up in the organic phase.

2.4.5.4 The THOREX Process

The THOREX (thorium recovery by extraction) process for the reprocessing of Th-containing fuel elements has proved to be superior to all its alternatives. It is similar in principle to the PUREX process, that has for many years been applied on an industrial scale for the reprocessing of the fuels of light water reactors [89]. The core of the process, in both cases, is the countercurrent extraction with diluted TBP from aqueous nitrate solutions.

In spite of the many similarities of the chemical separation step, the THOREX process requires its specific facilities. Large quantities of Th-containing material have been reprocessed in the past in PUREX plants in special campaigns, but in no case has this been a good solution. On the one hand, contamination of the plant by ^{233}U and Th occurs, on the other, and more decisive, the process operation is unfavorable. In the PUREX process, U is the main- and Pu the by-product. In the THOREX process, Th is the main product, but is found in the Pu part of the PUREX process. For the by-product U in the THOREX flow scheme, the PUREX plant is considerably overdimensioned. Since Th is less well extractable with TBP than U, a larger number of moles of TBP per mole of metal is required for its extraction. The flow of the solvent is therefore higher. The end effect is that the capacity for Th is only about a half of that for U, in plants of the same size. The THOREX flow scheme may thus be realized in a PUREX plant only by making many technologically disadvantageous compromises [90].

The present-day THOREX flow scheme was preceded by the so-called THOREX No. 1 process. It was developed at the Oak Ridge National Laboratory, and employed three different extractants. The ^{233}Pa was extracted selectively in the first battery with dibutyl carbitol (diethylene glycol dibutyl ether, $C_4H_9OC_2H_4OC_2H_4OC_4H_9$). Selective separation of U with 5% TBP followed in the second extraction cycle. Finally, Th was extracted with 45% TBP in the last cycle [91]. This process attained only academic interest, since it was too complicated. It was replaced in 1952 by the THOREX No. 2 process, which is taken today to represent the THOREX principle. Its characteristic feature is the use of relatively concentrated TBP solutions (30 to 45% in dodecane) for the joint extraction of U + Th from aqueous nitrate solutions of various acidities. It does not extract Pa at all, and requires $Al(NO_3)_3$ as a salting agent. The process was designed for a solution of irradiated Th (1.5 kg ^{233}U per ton Th) with a Th content of 350 g/l [92 to 98]. The ^{233}U content was later increased to 3 to 4 kg/ton Th, and modifications of the original flow scheme became necessary. The two-cycle, acid and acid-deficient, THOREX processes were then developed [97, 99 to 110]. The acid flow scheme developed at Knolls Atomic Power Laboratory included two essential changes: the use of the salting agent $Al(NO_3)_3$ was given up, and the TBP concentration was reduced from 42.5 to 30 vol%. The first measure was of great importance for the reduction of the amount of the radioactive waste [111, 112]. The developments in the field of the THOREX process that took place in England were described in [113, 114].

A simplified process scheme, the so-called INTERIM-23 process, does'nt involve the separation of the Th, which reached, together with the fission products, the waste stream. The ^{233}U was extracted selectively with dilute, 1.5 to 5%, TBP. Relatively high decontamination factors were attained [95, 114 to 118].

The problem of recovering larger quantities of U together with Th arose only in 1962, when Consolidated Edison Reactor fuel elements (96% ThO_2, 4% UO_2) were presented for reprocessing in the USA. The acid THOREX process was developed for this purpose at Oak Ridge National Laboratory, that dispensed with the $Al(NO_3)_3$ salting agent on the one hand, and permitted the reprocessing of Th solutions with U contents up to 10% on the other. A typical feed solution contained 267 g Th/L, 20 g U/L, and 0.15 mol HNO_3/L, the solvent was 30% TBP [119 to 127]. A smaller plant was built in Rotondella in Italy in the 60's, for the reprocessing of Th-containing fuel elements from the Elk River Reactor in the USA, but it has never been commissioned [128 to 130].

The THOREX process was planned to provide the reprocessing of Th-containing fuel elements having a BeO matrix from reactor systems mainly in Australia [131 to 133].

Attempts have been made since the end of the 60's, both in the F. R. of Germany and in the USA, to reprocess Th solutions with up to 20% U under THOREX conditions, in order to close the fuel cycle of high temperature reactors. It appeared to be possible to co-extract up to 55 g U/L with the Th, and to separate it subsequently [134 to 154].

A special problem in the Th fuel cycle is provided by ^{233}Pa, the intermediate member of the breeding chain, when fuel elements that have been cooled for only short periods must be reprocessed. Because of the relatively long half-life of 27 days, either cooling periods of up to one year must be taken into account, or a part of the potentially bred fissile material must be given up. Normally, the ^{233}Pa reaches the fission product waste stream in the THOREX process, and is thereby lost. Attempts to make the Pa extractable by the addition of phosphate ions have not been very successful, but a pre-separation by coprecipitation with MnO_2 was recommended [155 to 158]. A better alternative is the institution of an initial Pa separation step, before the usual extraction step, in which the Pa is first adsorbed selectively on a suitable sorbent, and then eluted. Pa is present in acidic solutions almost exclusively in the form of polymers, which may be readily sorbed selectively by silica gel or similar adsorbents (e.g., Vycor glass), whereas all the other ions flow on. The Pa may then be eluted by oxalic acid, or, after waiting for the ^{233}Pa to decay into ^{233}U, the U is removed [159 to 163].

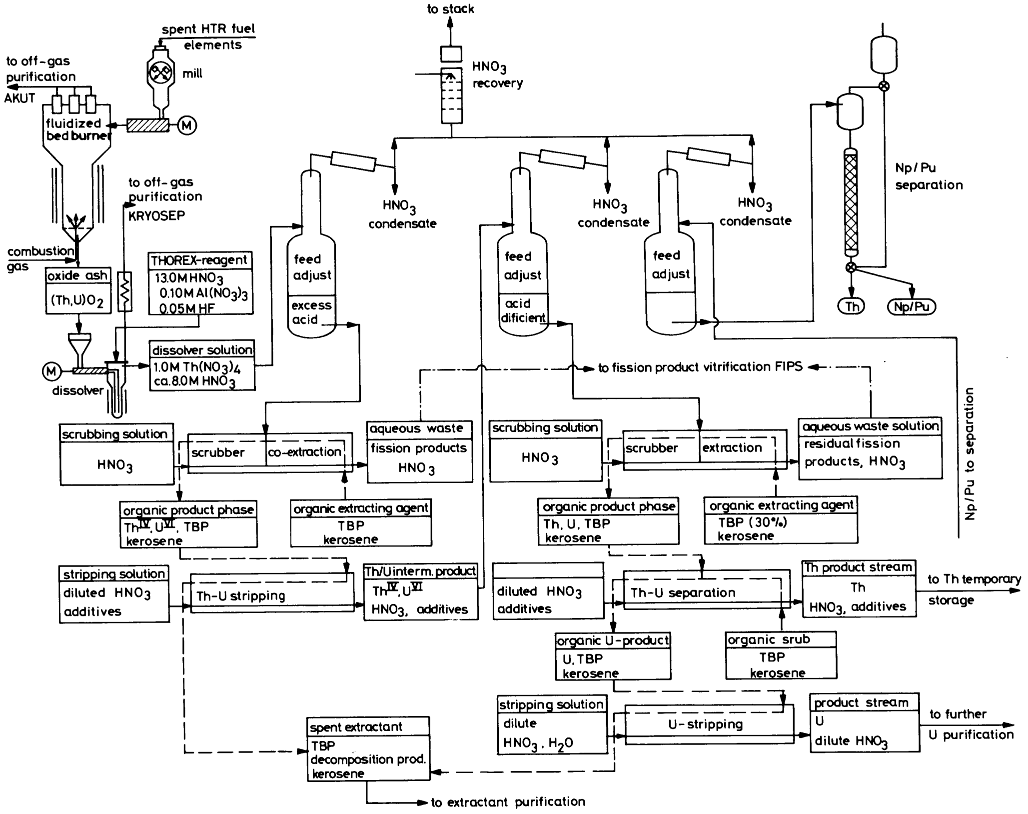
The fundamental problems in the THOREX process are similar to those in the PUREX process. The tendency to form a second organic phase is enhanced in the former relative to the latter process [155]. It turned out that dispensing with the use of $Al(NO_3)_3$ or an alkali nitrate as a salting agent acts favorably on the avoidance of the formation of a second organic phase. It was shown that the HNO_3 and $Th(NO_3)_4$ present suffice as salting agents. The charging of the waste stream with nitrate salts is thus avoided, and better decontamination factors are obtained than with $Al(NO_3)_3$.

A two-cycle THOREX process has to date proved itself best in laboratory scale experiments. It consists of a co-decontamination cycle with an acid feed, for preventing the precipitation of hydrolysis products, and a separation cycle with an acid-deficient feed. The following **Fig. 2-12**, p. 322, clarifies the flow scheme. It is to be set up at the JUPITER (Juelich Pilot Plant for Thorium Element Reprocessing) facility in the F. R. of Germany [146, 147, 167].

In order to achieve high decontamination factors for the separated uranium (eventually also thorium), it is necessary to employ a second or even a third extraction cycle. A Np/Pu separation is provided for in the tail end, using extraction chromatography. The stationary phase is a polymer having functional groups based on TBP or trioctylamine. The mobile phase is dilute HNO_3, alone or with suitable additives [168].

Operational experience in reprocessing thorium-containing fuels in a PUREX plant is described in [86, 93, 151, 169 to 171]. Criticality safety provides a particularly difficult problem [172].

Fig. 2-12



Schematic flow diagram of the JUPITER facility.

References for 2.4.5:

[1] T. H. Siddall (in: J. F. Flagg, Chemical Processing of Reactor Fuels, Academic, New York 1961, pp. 199/248). – [2] F. Baumgärtner, H. Philipp (Fortschr. Chem. Forsch. **12** [1969] 712/74). – [3] E. Merz (in: C. Keller, H. Möllinger, Kernbrennstoffkreislauf, Vol. 1, Hüthig, Heidelberg 1978, pp. 219/43). – [4] J. C. Warf (J. Am. Chem. Soc. **71** [1949] 3257/8). – [5] C. V. Ellison, D. E. Ferguson, T. C. Runion (ORNL-258 [1949] 1/5; N.S.A. **11** [1957] No. 12399).

[6] D. E. Ferguson, T. C. Runion (ORNL-260-Del. [1949] 1/47; N.S.A. **11** [1957] No. 9655). – [7] F. L. Culler (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 9, pp. 464/83). – [8] H. A. C. McKay, T. V. Healy (Progr. Nucl. Energy III **2** [1958] 546/56). – [9] R. M. Diamond, D. G. Tuck (Progr. Inorg. Chem. **2** [1960] 109/92). – [10] H. A. C. McKay, J. M. Fletcher (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 7, pp. 314/7).

[11] H. A. C. McKay (Progr. Nucl. Energy III **1** [1956] 122/9). – [12] E. Hesford, H. A. C. McKay, D. Scargill (J. Inorg. Nucl. Chem. **4** [1957] 321/5). – [13] E. Hesford, H. A. C. McKay (Trans. Faraday Soc. **54** [1958] 573/86). – [14] D. F. Peppard, G. W. Mason, J. L. Maier (J.

Inorg. Nucl. Chem. **3** [1956] 215/28). – [15] D. F. Peppard, W. J. Driscoll, W. J. Sironen, S. McCarthy (J. Inorg. Nucl. Chem. **4** [1957] 326/33).

[16] K. Alcock, F. C. Bedford, W. H. Hardwide, H. A. C. McKay (J. Inorg. Nucl. Chem. **4** [1957] 100/5). – [17] K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedey, H. A. C. McKay (Trans. Faraday Soc. **52** [1956] 39/47). – [18] T. V. Healy, H. A. C. McKay (Trans. Faraday Soc. **52** [1956] 633/42). – [19] T. V. Healy, H. A. C. McKay (Rec. Trav. Chim. **75** [1956] 730/6). – [20] R. A. Ewing, S. J. Kiehl, A. E. Bearse (BMI-955 [1954] 1/70).

[21] D. Scargill, K. Alcock, J. H. Fletcher, E. Hesford, H. A. K. McKay (J. Inorg. Nucl. Chem. **4** [1957] 304/14). – [22] A. D. Ryon (ORNL-3045 [1961] 1/14; N.S.A. **15** [1961] No. 7411). – [23] W. W. Wendlandt, J. Bryant (J. Phys. Chem. **60** [1956] 1145/6). – [24] R. H. Rainey, J. G. Moore (U.S. 3049400 [1961]). – [25] A. Naylor (KR-126 [1967] 101/19).

[26] R. E. Connick, W. H. McVey (J. Am. Chem. Soc. **71** [1949] 3182/91). – [27] R. E. Connick, W. H. Reas (J. Am. Chem. Soc. **73** [1951] 1171/6). – [28] P. G. M. Brown, J. M. Fletcher, A. G. Wain (AERE-C-R 2260 [1957] 1/61; N.S.A. **11** [1957] No. 13289). – [29] P. G. M. Brown, J. M. Fletcher, C. J. Hardy, J. Kennedy, D. Scargill, A. G. Wain, J. L. Woodhead (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 118/29). – [30] D. Scargill, C. E. Lyon, N. R. Large, J. M. Fletcher (J. Inorg. Nucl. Chem. **27** [1965] 161/71).

[31] J. Klaas (Proc. 11th Intern. Conf. Coord. Chem., Haifa and Jerusalem 1968, Abstr. I-21; Progress in Coordination Chemistry, Amsterdam-London-New York 1968, pp. 706/8). – [32] R. M. Wallace (J. Inorg. Nucl. Chem. **20** [1961] 283/9). – [33] J. M. Fletcher, C. E. Lyon, A. G. Wain (J. Inorg. Nucl. Chem. **27** [1965] 1841/51). – [34] P. G. M. Brown (J. Inorg. Nucl. Chem. **13** [1960] 73/83). – [35] M. Takigishi (J. Nucl. Energy A/B **18** [1964] 67/79, 261/77; C.A. **60** [1964] 15392, **61** [1964] 3883).

[36] J. G. Moore (ORNL-4348 [1969] 1/35; N.S.A. **23** [1969] No. 13827). – [37] F. Baumgärtner (KFK-709 [1969] 1/23; N.S.A. **22** [1968] No. 48897). – [38] F. R. Bruce (Progr. Nucl. Energy III **1** [1956] 130/46). – [39] R. L. Stevenson, P. E. Smith (in: S. M. Stoller, R. B. Richards, Reactor Handbook, Vol. 2, New York 1961, pp. 107/234). – [40] G. F. Best, H. A. C. McKay, P. R. Woodgate (J. Inorg. Nucl. Chem. **4** [1957] 315/20).

[41] K. Alcock, G. F. Best, E. Hesford, H. A. C. McKay (J. Inorg. Nucl. Chem. **6** [1958] 328/33). – [42] A. T. Gresky, M. R. Bennett, S. S. Brandt, W. T. McDuffee, J. E. Savoleinen (ORNL-1367-Del. [1952] 1/157; N.S.A. **11** [1957] No. 8395). – [43] L. J. Katzin (J. Inorg. Nucl. Chem. **4** [1957] 187/204). – [44] H. A. C. McKay, G. N. Naish, D. Scargill (AERE-C-R-1168 [1953] 1/13). – [45] M. S. Farell, J. D. Goldrick (AAEC-E-26 [1958] 1/19; N.S.A. **13** [1959] No. 16740).

[46] W. W. Schulz, E. E. Voiland (HW-32417 [1954] 1/24; N.S.A. **11** [1957] No. 12967). – [47] D. P. Granquist, E. T. Merrill (HW-17747 [1951] 1/41; N.S.A. **12** [1958] No. 774). – [48] D. E. Horner (ORNL-4724 [1971] 1/32). – [49] J. R. May (AAEC-E-61 [1961] 1/35; N.S.A. **16** [1962] No. 2666). – [50] A. L. Mills, W. R. Logan (CONF-660805 [1967] 322/6; Solvent Extract. Chem. Proc. Intern. Symp., Goteborg, Sweden, 1966 [1967], pp. 322/6; C.A. **69** [1968] No. 70364).

[51] H. J. v. Wachtendonk (Atomwirtsch. Atomtech. **23** [1978] 288/9). – [52] L. L. Burger (Progr. Nucl. Energy III **2** [1958] 307/19). – [53] A. T. Gresky (TID-7534 [1957] 1037/79; C.A. **1958** 908). – [54] L. L. Burger (HW-40910 [1955] 1/75; N.S.A. **12** [1958] No. 5214). – [55] E. Blumenthal, J. B. M. Herbert (Trans. Faraday Soc. **41** [1945] 611/7).

[56] B. G. Brodda, D. Heinen (Nucl. Technol. **34** [1977] 428/37). – [57] L. L. Burger, E. D. McClanahan (Ind. Eng. Chem. **50** [1958] 153/6). – [58] G. L. Richardson (HEDL-TME-73-51 [1973] 1/134; N.S.A. **29** [1974] No. 2583). – [59] C. A. Blake, W. Davis, J. M. Schmitt (ORNL-3524 [1963] 1/37; N.S.A. **18** [1964] No. 20100). – [60] E. S. Lane (Nucl. Sci. Eng. **17** [1963] 620/5).

[61] A. J. Huggard, B. F. Warner (Nucl. Sci. Eng. **17** [1963] 638/43). – [62] W. Davis, A. H. Kibbey (ORNL-TM-3062 [1970] 1/24; N.S.A. **24** [1970] No. 43995). – [63] C. J. Hardy,

D. Scargill (J. Inorg. Nucl. Chem. **11** [1959] 128/31). – [64] R. E. Blanco, C. A. Blake, W. Davis, R. H. Rainey (ORNL-TM-527 [1963] 1/39; N.S.A. **17** [1963] No. 16146). – [65] R. W. Wagner, E. M. Kindermann, L. H. Towle (Ind. Eng. Chem. **51** [1959] 45/50).

[66] C. A. Blake, A. T. Gresky, J. M. Schmitt, R. G. Mansfield (ORNL-3374 [1963] 1/33; N.S.A. **17** [1963] No. 10738). – [67] E. V. Barelko, I. P. Solyania (At. Energ. [USSR] **35** [1973] 239/45). – [68] L. W. Stieglitz, W. Ochsenfeld, H. Schmieder (KFK-691 [1969] 1/31; EURFNR-663 [1969] 1/31; N.S.A. **23** [1969] No. 43384, **24** [1970] No. 262). – [69] L. Salomon, E. Lopez-Menchero (ETR-203 [1966] 1/50; ORNL-tr-1901 [1966] 1/50; N.S.A. **22** [1968] No. 18873). – [70] J. Carva, M. Pagès (Radiochim. Acta **4** [1965] 88/91).

[71] C. J. Hardy, D. Scargill (J. Inorg. Nucl. Chem. **17** [1961] 337/49). – [72] P. Faugeras, X. Talmont (CEA-CONF-1265 [1968] 1/25; N.S.A. **23** [1969] No. 31397). – [73] T. Rigg, W. Wild (Progr. Nucl. Energy III **2** [1958] 320/31). – [74] R. H. Moore (HW-34502-Rev. [1955] 1/19; N.S.A. **11** [1957] No. 13667). – [75] T. H. Siddall, R. M. Wallace (DP-286-Del. [1958] 1/23; N.S.A. **15** [1961] No. 17003).

[76] D. W. Brite (HW-30643-Rev. [1954] 1/18; N.S.A. **10** [1956] No. 61). – [77] L. L. Burger (HW-44888 [1957] 1/25; N.S.A. **11** [1957] No. 5762). – [78] L. Stieglitz (Proc. Intern. Solvent Extract. Conf., The Hague 1971, pp. 155/62). – [79] R. Becker, L. Stieglitz (KFK-1373 [1973] 1/43; N.S.A. **29** [1974] No. 26770). – [80] J. G. Burr (Radiation Res. **8** [1958] 214/22).

[81] R. W. Wilkinson, T. F. Williams (AERE-R-3528 [1960] 1/20). – [82] J. G. Moore, D. J. Crouse (ORNL-4618 [1970] 1/24; N.S.A. **25** [1971] No. 6400). – [83] B. G. Brodda, E. Merz (Z. Anal. Chem. **273** [1975] 113/6). – [84] A. L. Marston, D. L. West, R. N. Wilhite (Solvent Extract. Chem. Metals Proc. Intern. Conf., Harwell, Engl., 1965 [1967], pp. 213/32; C.A. **69** [1968] No. 92192). – [85] C.A. Blake, W. Davis, J. M. Schmitt (Nucl. Sci. Eng. **17** [1963] 626/37).

[86] D. A. Orth, T. W. Olcott (Nucl. Sci. Eng. **17** [1963] 593/8). – [87] F. Barconelli, G. Grossi (Solvent Extract. Chem. Metals Proc. Intern. Conf., Harwell, U.K., 1965 [1967], pp. 197/212). – [88] E. S. Lane (AERE-M-809 [1961] 1/9; N.S.A. **15** [1961] No. 17001). – [89] G. Koch ("Transurane" A1 II, 1974, pp. 177/326). – [90] A. T. Gresky, D. E. Ferguson, P. E. Smith (in: S. M. Stoller, R. B. Richards, Reactor Handbook, Vol. 2, Interscience, New York 1961, pp. 208/25).

[91] A. T. Gresky (Reactor Sci. Technol. **4** [1954] 43/57). – [92] A. T. Gresky (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 505/10). – [93] G. F. Smith (ARH-1748 [1970] 1/56). – [94] A. T. Gresky (Progr. Nucl. Energy III **1** [1956] 212/22). – [95] F. L. Culler (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 464/83).

[96] T. H. Siddall (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 339/47). – [97] V. R. Cooper, M. T. Walling (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 291/323). – [98] T. H. Siddall (BNL-483 [1958] 149/53; N.S.A. **13** [1959] No. 9456). – [99] W. W. Morgan (AECL-508 [1958] 1/30; CRDC-674 [1958] 1/30; N.S.A. **14** [1960] No. 5250). – [100] R. P. Wischow, R. G. Mansfield (ORNL-1994-Del. [1956] 1/60; N.S.A. **12** [1958] No. 802).

[101] R. E. Blanco, L. M. Ferris, D. E. Ferguson (ORNL-3219 [1962] 1/35; N.S.A. **16** [1962] No. 11786). – [102] F. R. Bruce, E. M. Shank, R. E. Brooksbank, J. R. Parrott, G. S. Sadowski (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 49/72). – [103] A. D. Ryon (ORNL-3153 [1961] 19/22; N.S.A. **15** [1961] No. 30770). – [104] V. R. Cooper, M. T. Walling (Progr. Nucl. Energy III **3** [1961] 229/88). – [105] E. M. Shank (Progr. Nucl. Energy III **2** [1958] 279/301).

[106] F. R. Bruce, T. H. Siddall, E. M. Shank (BNL-483 [1958] 145/56; N.S.A. **13** [1959] No. 9455/7). – [107] R. H. Rainey, A. B. Meservey, R. G. Mansfield (ORNL-2591 [1959] 1/55; N.S.A. **13** [1959] No. 7596). – [108] R. E. Blanco, L. M. Ferris, C. D. Watson, R. H.

Rainey (ORNL-3418 [1962] 1/56; ORNL-TM-420 [1962] 1/56; N.S.A. **17** [1963] No. 6186). – [109] R. H. Rainey (ORNL-TM-177 [1962] 1/92, 32/8; N.S.A. **16** [1962] No. 20537). – [110] F. R. Bruce (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 7, pp. 100/12).

[111] W. O. Haas, D. J. Smith (KAPL-1306-Del. [1956] 1/67; N.S.A. **17** [1963] No. 40929). – [112] R. H. Rainey, J. G. Moore (Nucl. Sci. Eng. **10** [1961] 367/71). – [113] H. A. C. McKay, J. M. Fletcher (Progr. Nucl. Energy III **1** [1956] 147/60). – [114] I. Wells, C. M. Nicholls (Progr. Nucl. Energy III **1** [1956] 223/41). – [115] D. E. Ferguson, H. K. Jackson, E. L. Nicholson (ORNL-651 [1950] 1/39; N.S.A. **11** [1957] No. 7554).

[116] C. D. Hylton (ORNL-1425-Del. [1958] 1/36; N.S.A. **13** [1959] No. 1204). – [117] A. T. Gresky, M. R. Bennett, S. S. Brandt, W. T. McDuffee, J. E. Savolainen (ORNL-1367-Rev. [1952] 1/157; N.S.A. **11** [1957] No. 8395). – [118] J. R. Flanary (ORNL-1993 [1964] 1/61; C.A. **62** [1965] 4868). – [119] L. M. Ferris, A. H. Kibbey (ORNL-2934 [1960] 1/27; N.S.A. **15** [1961] No. 2700). – [120] W. H. Farrow (DP-566 [1961] 1/239; N.S.A. **15** [1961] No. 22389).

[121] R. H. Rainey, J. G. Moore (ORNL-3155 [1962] 1/29; N.S.A. **16** [1962] No. 17762). – [122] D. A. Orth (Nucl. Technol. **43** [1979] 63/74). – [123] W. E. Prout, A. E. Symonds (DP-1036 [1967] 1/16). – [124] C. A. Burkart, E. C. Moncrief, T. L. Sweeney (BAW-279 [1965] 1/116; N.S.A. **20** [1966] No. 35582). – [125] E. C. Moncrief, G. Schileo (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 157/84; UCRL-16108 [1966] 1/174; C.A. **66** [1967] No. 25035; BAW-393-3 [1966] 1/147; N.S.A. **20** [1966] No. 31317).

[126] C. E. Moncrief, C. A. Burkart, D. A. Nitti (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 509/35; AEC Symp. Ser. No. 12 [1968] 509/35; C.A. **70** [1969] No. 83282). – [127] H. C. Rathvon, A. G. Blasewitz, R. Maher, J. C. Eargle, A. E. Wibble (CONF-660524-19 [1966] 1/75; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 765/824; N.S.A. **20** [1966] No. 43415). – [128] G. D. C. Short, G. Orsenigo, E. Römberg (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 617/45; AEC Symp. Ser. No. 12 [1968] 617/45; C.A. **70** [1969] No. 63199). – [129] J. R. Fisher, E. D. Kendrick (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 681/94). – [130] G. Calleri, S. Cao, M. Fiorelli, G. Orsenigo, U. Piatti, C. Vallone (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1972, Vol. 8, pp. 375/94.

[131] D. E. Horner, C. F. Coleman (ORNL-2830 [1959] 1/46; N.S.A. **14** [1960] No. 2466). – [132] R. C. Cairns (J. Nucl. Mater. **14** [1964] 55/68). – [133] R. C. Cairns, M. G. Baillie, M. S. Farrell, J. R. May (CONF-660524-21 [1968] 1/40; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 217/52; N.S.A. **21** [1967] No. 1192). – [134] L. Schäfer, B. Wojtech, G. Kaiser, E. Merz, P. Sckuhr (AED-CONF-71-100-22 [1971] 1/16; N.S.A. **26** [1972] No. 17632). – [135] W. L. Carter (ORNL-TM-241 [1962] 1/57; N.S.A. **16** [1962] No. 23789).

[136] R. E. Blanco, L. M. Ferris, C. D. Watson, R. H. Rainey (TID-7650 [1963] 384/435; N.S.A. **17** [1963] No. 28464). – [137] A. V. Nikolaev, A. I. Ryabinin, Yu. A. Afanas'ev (Izv. Sibirsk. Otd. Akad. Nauk SSSR Ser. Khim. Nauk **1964** No. 3, pp. 60/2; C.A. **63** [1965] 1257). – [138] A. V. Nikolaev, A. I. Ryabinin, Yu. A. Afanas'ev (Radiokhimiya **8** [1966] 421/4; Soviet Radiochem. **8** [1966] 455/8). – [139] G. Kaiser, E. Merz, H. Witte (Reaktortagung, Bonn 1971, pp. 686/9). – [140] G. Kaiser, E. Merz, H. J. Riedel (Nucl. Met. **15** [1969] 25/36).

[141] G. Kaiser, E. Merz (Z. Anal. Chem. **229** [1967] 81/9). – [142] L. Küchler, L. Schäfer, B. Wojtech (Kerntechnik **12** [1970] 327/33). – [143] L. Küchler, L. Schäfer, B. Wojtech (Kerntechnik **13** [1971] 319/22). – [144] B. G. Brodda, H. Kirchner, H. J. Riedel (6th Intern. Symp. Mikrotech., Graz 1970, pp. 41/7). – [145] E. Merz, M. Laser, E. Zimmer (Kerntechnik **15** [1973] 249/56).

[146] G. Kaiser, E. Merz (Kerntechnik **16** [1974] 388/92). – [147] E. Merz, G. Kaiser, E. Zimmer (CONF-740501 [1974] 268/86; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 268/86; C.A. **82** [1975] No. 128951). – [148] H. D. Gerold (JUEL-741-RW [1971] 1/102; C.A. **75** [1971] No. 104185). – [149] R. M. Burgoyne (GA-A-14125 [1976] 1/266; INIS Atomindex **8** [1977] No. 317880). – [150] N. Srinivasan, G. R. Balasubramanian, R. T. Chitnis, S. Venkateswaran, R. T. Kulkarni (BARC-681 [1973] 1/18; C.A. **81** [1974] No. 144507).

[151] R. R. Jackson, R. L. Walser (ARH-2127 [1977] 1/194; INIS Atomindex **9** [1978] No. 351694). – [152] B. Baxter, G. E. Benedict, R. D. Zimmerman (GA-A-13808 [1976] 1/28; INIS Atomindex **8** [1977] No. 283228). – [153] G. W. Reddick (GA-A-13835 [1976] 1/69; INIS Atomindex **7** [1976] No. 267902). – [154] G. Kaiser, E. Merz, E. Zimmer, H. Pirk, P. Vygen (IAEA-CN-36/112 [1977] 1/7; Intern. Conf. Nucl. Power Its Fuel Cycles, Salzburg 1977, pp. 2.7.-T.1/11; INIS Atomindex **8** [1977] No. 302965). – [155] W. O. Haas, D. J. Smith (KAPL-1306 [1956] 1/67; N.S.A. **17** [1963] No. 40929).

[156] R. E. Blanco, L. M. Ferris, C. D. Watson, R. H. Rainey (ORNL-TM-420 [1962] 1/56; N.S.A. **17** [1963] No. 6186). – [157] R. E. Blanco (ORNL-TM-177 [1962] 1/92; N.S.A. **16** [1962] No. 20537). – [158] W. W. Schulz (ARH-2420 [1972] 1/30; N.S.A. **27** [1973] No. 2463). – [159] J. G. Moore (ORNL-3599 [1964] 1/19; N.S.A. **18** [1964] No. 22020). – [160] J. G. Moore, R. H. Rainey (ORNL-TM-543 [1963] 1/27; N.S.A. **17** [1963] No. 20101).

[161] J. G. Moore (ORNL-3945 [1966] 42/3; N.S.A. **20** [1966] No. 45787). – [162] O. Coenegracht (JUEL-822-CT [1972] 1/67; C.A. **78** [1973] No. 10728). – [163] E. Zimmer, H. Ringel (Chem. Ing. Tech. **47** [1975] 710/2). – [164] A. T. Gresky (CF-56-2-157 [1956] 1/201; N.S.A. **11** [1957] No. 8357). – [165] R. G. Wilbourn (GA-A-15030 [1978] 1/87; INIS Atomindex **10** [1979] No. 444337).

[166] J. R. Oliver (ORNL-2473 [1958] 1/16; N.S.A. **12** [1958] No. 7761). – [167] E. Merz (Chemiker-Ztg. **101** [1977] 81/91). – [168] R. Kankura (JUEL-1372 [1977] 1/135; INIS Atomindex **8** [1977] No. 334488). – [169] R. E. v. d. Cook, G. L. Ritter (ARH-1757 [1970] 1/31). – [170] G. A. Nicholson (ARH-1774 [1970]).

[171] R. R. Jackson (ARH-1775 [1970] 1/63). – [172] W. E. Matheison, G. C. Oberg, G. L. Ritter (ARH-1514 [1970] 1/51).

2.4.6 Chemical Separation by Means of Sorption and Ion Exchange

The possibilities for the selective separation of ^{233}U from reactor-irradiated Th have received special attention since the beginnings of nuclear technology. From the fundamental standpoint, ion exchange and sorption methods were evaluated favorably in a comparison of the different methods [1 to 4]. Yet, these methods never came near to the expectations.

Anion and cation exchangers have always been widely applied as effective and selective materials for radiochemical separations. Their application in the chemistry of the transuranium elements merits particular mention. The discovery and isolation in pure form of these elements would not have come about so rapidly, if effective synthetic ion exchangers were not available [5 to 9].

A second widespread application of ion exchangers is made for the concentration of ions from dilute solutions, generally combined with a purification of the element considered. This circumstance provides for the widespread application of ion exchangers in the recovery of U from ores and in its purification [10 to 15], see e.g., "Uran" Erg.-Bd. A3, 1981, from p. 42.

A reprocessing method, that is based exclusively on the application of ion exchangers or solid sorbents, has never been introduced successfully into nuclear technology. The requirements for the purpose of reprocessing from the large variety of effective cation and anion exchangers, existing beside the natural zeolites, have been described in [16]. Furthermore, besides the classical stationary bed exchangers there exist today numerous techniques for continuous operation, e.g., pulsed countercurrent systems, Higgins contactors, and fluidized bed contactors [17 to 24].

U is separated from acidic solutions most advantageously on anion exchangers, which exhibit a much higher selectivity for this purpose than do cation exchangers. The reasons why anion exchangers were unacceptable for large scale technological reprocessing were the following:

1. Organic ion exchange resins have only a limited radiation resistance. The exchange capacity and the selectivity decrease rapidly above a received radiation dose of 10^7 to 10^8 rad, so that the resins become useless [25 to 31]. Regeneration is impossible. Because of operational and economic reasons the resins must withstand many cycles of loading and elution. Inorganic exchangers, such as phosphates, titanates, stanates, etc., which are more stable to radiation, have not proved themselves, since they have too low capacities and often are prone to irreversible sorption [32 to 36]. However, surface active inorganic materials, such as silica gel, are favored as selective adsorbents for the quantitative separation of several fission products, such as Zr, Nb, and Ru. In this case, recovery is dispensed with knowingly, and the adsorbents, loaded with the fission products, are directed to the radioactive waste disposal. The adsorber bed generally acts also as a filter.

2. The two elements of interest, U and Th, behave rather similarly towards ion exchangers. Effective separations are not simple, requiring the use of large quantities of chemicals, increasing thereby the amount of radioactive waste [37 to 40].

3. At high radiation levels, the radiolytically produced gas becomes seriously disturbing because of the formation of bubbles and voids in ion exchange columns.

2.4.6.1 Primary Separation by Ion Exchange

Already at the beginning of the development of nuclear technology the suitability of ion exchange processes for reprocessing has been studied intensively. A review of the early results may be found in [41]. The interest was limited exclusively to the U/Pu cycle [42 to 44]. The experiments, however, did not extend beyond the laboratory scale. The Canadians have later tried unsuccessfully to apply such a process on a large technical scale. They tried to replace thereby the not very successful TRIGLY process (see p. 312) [45 to 48].

The first proposals to separate ^{233}U from irradiated Th by means of cation exchangers and silica gel were described in [49 to 53]. These methods had no technical significance. An attempt was made in France to develop this principle into an industrially useful process, but, again, no progress was made beyond the laboratory scale. The process set out from concentrated (8 mol/l) hydrochloric acid as the feed solution. A synthetic resin with amino and oxyamino functional groups was used as an anion exchanger. $(NH_4)_2SiF_6$ was added to the feed solution as a complexant. U and Pa were first sorbed jointly on the exchanger, and then separated by selective elution. The distribution of U, Pa, and Th yields very good results, but no details on the decontamination from the fission products and on the effects of high radiation doses were given [54]. Later, a combined cation and anion exchange process was reported from the same laboratory [55].

A U-Th separation was conducted successfully in India on an exchanger made of ammonium phosphotungstate, using HNO_3 media. Here, too, no demonstration with "hot" materials was made [56]. Other unsuccessful efforts, mainly in Italy, were concerned with the reprocessing of nuclear fuels by ion exchange in salt melts [57]. An electrophoretic Th-U-Pa separation, useable only for analytical purposes, was also reported [58, 59].

An ion exchange process, among others, was proposed for the reprocessing of the fuel of a heavy water moderated breeding reactor developed at the time in the USA. The use of a ^{233}U-Th fuel cycle in this reactor type promised special advantages. A two-zone breeding reactor was under consideration: the core consisting of a uranyl sulfate solution and the mantle of a ThO_2 suspension [60, 61]. Ferguson [62, 63] proposed a flow scheme for the quasi-continuous reprocessing of the core. After 5 days cooling in a side stream, the fission products were separated with a cation exchanger from ^{233}U, which is returned to the cycle. A solvent extraction process was provided for the reprocessing of the breeding mantle. The ThO_2 suspension was to be separated in a cyclone, dried, and dissolved in acid. The eluates from the ion exchangers should have been treated together with this solution, in order to recover any residual ^{233}U.

A variant of this idea is the single-zone suspension reactor proposed by the Dutch. Minute oxide particles are used, both as fuel and as breeding material. The fission products largely leave the mixed oxide particles on account of the recoil effect, and reach the aqueous medium. They were supposed to be removed by adsorption in a side stream cycle [64, 65]. The system has not proved feasible and was given up.

A special problem in the Th-^{233}U cycle is the separation of the ^{233}Pa, formed in the breeding chain, in so far as fuel elements cooled for short periods are to be reprocessed. The relatively long half-life of 27 days necessitates either cooling for a long period, or the giving up of some of the potentially bred fissile material, i.e., the ^{233}Pa that had not yet decayed into ^{233}U [66]. Normally, Pa reaches the waste stream in the THOREX process, and is lost. As an expedient, separation by adsorption on a surface active material, such as silica gel or Vycor glass, prior to the solvent extraction step, holds back the Pa, present as polymeric species, whereas all other ions pass on. Subsequently, the Pa may be eluted with oxalic acid, or, after waiting for decay into ^{233}U, the latter is eluted [67 to 69].

An alternative Pa separation proceeds by means of sorption on an anion exchanger from 6 to 8 M HCl, to which fluoride has been added for complexation of the Pa [70 to 74]. A further proposal provides for coprecipitation of the Pa from the feed solution by means of MnO_2 [75].

2.4.6.2 Purification of the Uranium Product by Sorption and Ion Exchange

Ion exchange and sorption processes are of great significance at the so-called tail-end of the reprocessing. In the purification of the U and Th that have been separated by solvent extraction, ion exchange processes serve very well. They are unsurpassed in their ability to remove the last traces of difficult to remove fission products. The required theoretical data are well known [76]. The radiation level at this stage is so much reduced, that a multi-cycle process operation can be realized without serious losses of capacity or selectivity. The valuable materials are also concentrated in the sorption-desorption process, besides being purified [77]. The main purpose of the use of the ion exchanger may be either the concentration or the purification.

The separation may proceed by a single sorption-desorption stage, provided the difference in the binding strength is sufficiently large. Generally, however, the breakthrough technique must be used. In certain cases the separation may be simplified, namely when the U is present as an anionic species whereas the impurities, i.e., the fission products, exclusively as cationic ones. The U is then bound quantitatively to an anion exchanger, and the impurities pass through the column unhindered. The elution of the U ions is made by displacement with concentrated nitrate or chloride solutions.

A significant decontamination effect may arise from the mere filtration of the solution by the exchanger bed. Impurities present in the solution as suspended solids or as colloids may be retained either purely mechanically or by adsorptive forces [78]. Silica gel is often used for this double purpose, and it may be regenerated with oxalic acid, if necessary [79, 80].

In the common THOREX flow schemes, the U stream leaving the stripping column is passed over a column of silica gel, in order to remove trace impurities of Pa, Zr, Nb, and eventually also Ru. Then follows a small cation exchanging column, in which a sulfonated resin (e.g., Dowex 50) retains residual Th ions and corrosion products. Finally, a large cation exchange column is used to concentrate the dilute aqueous U stream. Loading proceeds upwards with a feed containing 0.4 g U/L and 0.02 M H^+/L. The U concentration found in the raffinate was <0.01 mg/L. The uranium that has been taken up by the resin from the solution is periodically eluted in concentrated form by 6 M HNO_3 or 2 M CH_3COONH_4 and 0.4 M CH_3COOH. Two columns are operated alternately. It is advantageous to operate at elevated temperatures (about 70 °C) in order to achieve good separations. The eluate has a concentration of 90 g ^{233}U/L [81 to 85]. The additional decontamination factors attained at the tail-end were between 100 and 1 000 [86]. Purification of Th with an anion exchanger has also been tried [87].

2.4.6.3 Extraction Chromatography

Extraction chromatography, which is a combination of solvent extraction and adsorption chromatography, may be regarded as a special form of ion exchange. Regularities similar to those of solvent extraction are therefore valid for the distribution [88]. The stationary phase is generally an inert carrier in the form of grains, covered by a film of the organic phase. Attempts have also been made to anchor the organic solvent molecules to the polymeric skeleton by chemical bonding [89]. The mobile phase is generally an aqueous medium. Advantages of chromatography relative to extraction are better material transport through to enlargement of the phase boundary area and the shortening of the diffusion paths in the phases, a higher specific capacity, simple operation, and small amounts only of secondary radioactive waste. On the other hand, it is necessary to register also the disadvantages, which are partly serious: the small total capacity, discontinuous operation, and sensitivity of the carrier material to radiation. As yet, extraction chromatography has been used only at the laboratory scale [90]. It has special significance for the isolation in purified form of some of the transuranium elements [91 to 94].

The first proposal for the utilization of extraction chromatography in nuclear technology came from Sweden. The material distribution occurs therein between a stationary aqueous phase bound to silica gel and a mobile organic phase. It was even planned to build a pilot plant according to this principle, called SILEX, in Kjeller in Norway [95 to 98].

Extraction chromatography was proposed anew, and tested on a laboratory scale, for the reprocessing in the Th-^{233}U fuel cycle [99 to 104]. The main point was the minimization of long-term storage risks of radioactive waste by as good a separation of the long-lived actinides as possible [105 to 108]. The process proposed was based on the fact that the tetravalent actinides form nitrato complexes in nitric acid, that are well extractable by tri-n-octyl amine (TOA). The process streams are led through a column, in which TOA has been loaded on a polymeric carrier. The hexanitrato complexes of the tetravalent actinides are bound to the TOA

References for 2.4.6 on pp. 330/2

and are sorbed on the column. A shorter or longer retention by the column occurs, depending on the strength of the binding and the resulting distribution ratios. The materials may be separated by collecting suitable fractions.

References for 2.4.6:

[1] S. Lawrowski (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 575/82). – [2] L. M. Ferris (ORNL-3952 [1966] 1/34; N.S.A. **20** [1966] 1/34; N.S.A. **20** [1966] No. 27041). – [3] R. L. Stevenson, K. M. Black (in: S. M. Stoller, R. B. Richards, Reactor Handbook, Vol. 2, Interscience, New York 1961, pp. 226/7). – [4] M. A. Awwal, D. J. Carswell (Chem. Rev. **66** [1966] 279/95). – [5] G. T. Seaborg (Actinides Rev. **1** [1967] 3/38).

[6] K. A. Kraus, F. Nelson (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 7, pp. 113/25). – [7] D. C. Stewart (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 7, pp. 321/30). – [8] E. K. Hyde (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 7, pp. 281/303). – [9] V. M. Vdovenko, M. P. Kovalskaia (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 329/32). – [10] A. M. Gaudin, R. Schuhmann, J. Dasher (J. Metals **8** [1956] 1065/1384).

[11] M. Urgell, J. A. Perez Bustamente, T. Batuecas Rodriguez, F. de la Cruz, R. Fernandez Cellini (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 3, pp. 444/64; C.A. **1959** 7898). – [12] R. E. Robinson, R. G. Velthuis, E. T. Pinkney (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 3, pp. 415/26). – [13] L. A. Painter, T. F. Izzo (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 3, pp. 383/6). – [14] B. Lopez Perez, A. Uriarte, M. Perarnau, L. Gutierrez Jodra (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 3, pp. 427/43). – [15] T. V. Arden, J. B. Davis, G. L. Herwig, R. M. Stewart, E. A. Swinton, D. E. Weiss (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 3, pp. 396/414).

[16] S. Ahrland (Aqueous Reprocess. Chem. Irradiat. Fuels Symp., Brussels 1963, pp. 331/40; C.A. **60** [1964] 14086). – [17] E. A. Swinton, D. E. Weiss (Australian J. Appl. Sci. **4** [1953] 316/20). – [18] E. S. Grimmett, B. P. Brown (IDO-14541 [1961] 1/17; N.S.A. **17** [1963] No. 3085). – [19] V. P. Caracciolo (DP-624 [1961] 1/28; N.S.A. **16** [1962] No. 4217). – [20] A. M. Platt (TID-7607 [1961] 33/44; N.S.A. **15** [1961] No. 14344).

[21] J. T. Roberts (ORNL-2504 [1958] 1/45; N.S.A. **12** [1958] No. 9726). – [22] I. R. Higgins (U.S. 2815322 [1957]). – [23] R. Kunin, F. McGarvey (Ind. Eng. Chem. **47** [1955] 565/75). – [24] T. A. Arehart, J. C. Bresce, C. W. Hancher, S. H. Jung (Chem. Eng. Progr. **52** [1956] 353/9). – [25] I. R. Higgins (ORNL-1325 [1953] 1/14; N.S.A. **10** [1956] No. 4157).

[26] L. L. Smith, H. J. Groh (DP-549 [1961] 1/14). – [27] G. I. Cathers (Progr. Nucl. Energy III **1** [1956] 68/78). – [28] G. R. Hall, M. Streat (J. Chem. Soc. **1963** 5205/11). – [29] K. A. Nater (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 29, pp. 238/45). – [30] W. D. Burch, W. C. Yee, W. Davis (ORNL-3965 [1966] 1/93; N.S.A. **21** [1967] No. 1421).

[31] M. T. Ahmed, P. G. Clay, G. R. Hall (J. Chem. Soc. B **1966** 1155/9). – [32] E. R. Russel, A. W. Adamson, J. Schubert, G. E. Boyd (U.S. 2859093 [1958]). – [33] E. Merz (Z. Elektrochem. **63** [1959] 288/92). – [34] J. Gal, O. S. Gal (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 28, pp. 24/30). – [35] C. B. Amphlett (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 28, pp. 17/23).

[36] S. Ahrland, J. Albertsson (Acta Chem. Scand. **18** [1964] 1861/78). – [37] G. R. Hall, F. L. D. Cloete, G. C. Coggan, S. Hartland, G. H. Nancollas, L. V. C. Rees, J. E. Salmon, M. Streat, D. G. Tuck, J. C. R. Turner (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 382/91; A-CONF-28-P-562 [1964] 1/15; N.S.A. **18** [1964] No. 37271).

– [38] J. L. Ryan (J. Phys. Chem. **64** [1960] 1375/85). – [39] J. L. Ryan (Inorg. Chem. **2** [1963] 348/58). – [40] J. L. Ryan (Inorg. Chem. **3** [1963] 211/4).

[41] G. E. Boyd, J. Schubert (Progr. Nucl. Eng. III **4** [1970] 319/43). – [42] W. H. Swift (TID-7607 [1961] 21/33). – [43] J. A. Swartout, D. N. Hume (CN-1839 [1944] 1/15; N.S.A. **11** [1957] No. 7521). – [44] A. Ayres (ISC-49 [1949] 1/124; N.S.A. **11** [1957] No. 8402). – [45] G. M. Allison, R. G. Hart (AECL-1372 [1953] 1/38).

[46] W. M. Campbell (Nucleonics **14** [1956] 92/7). – [47] A. M. Aikin (Chem. Eng. Progr. **53** [1957] 82/5). – [48] T. I. Jones, R. G. Hart, J. A. Brothers, I. W. Allam (AECL-735 [1958] 1/24; CRFD-810 [1958] 1/24; N.S.A. **13** [1960] No. 8916). – [49] D. C. Overholt (ORNL-1364 [1952] 1/22; N.S.A. **11** [1957] No. 8394). – [50] R. E. Leuze, V. C. A. Vaughen (CF-55-12-88 [1955] 1/17; N.S.A. **13** [1960] No. 582).

[51] F. R. Bruce, T. H. Sidall, E. M. Shank, G. E. Brand, E. W. Murbach, A. G. Buyers, J. A. Kircher, O. E. Dwyer, D. E. Ferguson (BNL-483 [1958] 145/71; N.S.A. **13** [1960] No. 9455/61). – [52] A. I. Zkukov, E. I. Kazantsev, V. A. Vakulenko (Zh. Prikl. Khim. **38** [1965] 43/7; J. Appl. Chem. [USSR] **38** [1965] 38/42). – [53] D. J. Pietrzyk, D. L. Kiser (Anal. Chem. **37** [1965] 1578/80). – [54] A. Chesné, P. Regnaut (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 583/5). – [55] A. Chesné, F. Mannonne (Proc. 11th Ciclo Combust. Uranium Thorium, CNEN-Rome 1961, pp. 319/25; 6th Congr. Nucl., Rome 1961 [1962], Pt. 1, pp. 321/39; C.A. **61** [1964] 15623).

[56] N. Srinivasan, M. N. Nadkarni, S. V. Kumar, P. K. S. Kartha, R. R. Sonavane, M. V. Ramaniah, S. K. Patil (BARC-734 [1974] 1/12; BARC-735 [1974] 1/12; C.A. **82** [1975] No. 104568/9). – [57] G. Alberti, A. Conte, S. Allulli (J. Chromatog. **18** [1965] 564/71). – [58] H. P. Raaen, P. F. Thomason (TID-2505-Del. [1958] 211/8; N.S.A. **12** [1958] No. 17414). – [59] E. Merz (Z. Anal. Chem. **211** [1965] 331/4). – [60] R. Hurst, I. Wells, D. Newby (J. Brit. Nucl. Energy Conf. **2** [1957] 395/407).

[61] I. Wells, E. Lofthouse (Trans. Inst. Chem. Eng. [London] **36** [1958] 373/81). – [62] D. E. Ferguson (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 514/9). – [63] D. E. Ferguson (Progr. Nucl. Energy III **1** [1956] 249/58). – [64] H. de Bruyn (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 3, pp. 116/20). – [65] M. E. A. Hermans, T. v. d. Plas (Nucl. Sci. Eng. **2** [1957] 224/6).

[66] A. T. Gresky (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 505/10). – [67] J. G. Moore, R. H. Rainey (ORNL-TM-543 [1963] 1/27; N.S.A. **17** [1963] No. 20101). – [68] O. Coenegracht (JUEL-822-CT [1972] 1/67; C.A. **78** [1973] No. 10728). – [69] E. Zimmer, H. Ringel (Chem. Ing. Tech. **47** [1975] 710/2). – [70] K. A. Kraus, G. E. Moore (J. Am. Chem. Soc. **72** [1950] 4293/4).

[71] M. K. Barnett (J. Inorg. Nucl. Chem. **4** [1957] 358/66). – [72] K. A. Kraus, G. E. Moore (J. Am. Chem. Soc. **77** [1955] 1383/4). – [73] A. G. Maddock, W. Pugh (J. Inorg. Nucl. Chem. **2** [1956] 114/7). – [74] J. S. Nairn (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 216/35). – [75] W. O. Haas, D. J. Smith (KAPL-1306-Del. [1956] 1/67; N.S.A. **17** [1963] No. 40929).

[76] C. J. Hardy (Progr. Nucl. Energy III **2** [1958] 357/62). – [77] D. J. Smith (KAPL-M-DJS-1 [1955] 1/17; N.S.A. **11** [1957] No. 11628). – [78] J. L. Ryan, E. L. Wheelwright (HW-55893-Del. [1959] 1/104; N.S.A. **13** [1959] No. 22147). – [79] R. D. B. Brooks (EuroNuclear **1** [1964] 212/5). – [80] S. Ahrland, I. Grenthe, B. Noren (Acta Chem. Scand. **14** [1960] 1059/76).

[81] F. R. Bruce (TID-7534-Bk. 1 [1957] 1/481, 303/10; N.S.A. **12** [1958] No. 154). – [82] F. R. Bruce (Progr. Nucl. Energy III **2** [1958] 363/76). – [83] F. W. Tober (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 574/84). – [84] F. R. Bruce, E. M. Shenck, R. E. Brooksbank, J. R. Parrett (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 49/72). – [85] I. Wells, C. M. Nicholls (Progr. Nucl. Energy III **1** [1956] 223/41).

[86] F. L. Culler (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 464/83). – [87] K. A. Kraus, F. Nelson (Am. Soc. Testing Mater. Spec. Tech. Publ. No. 195 [1958] 27/57, 52/5; Am. Soc. Testing Mater. Proc. **56** [1956] 1454; C.A. **1958** 15321). – [88] E. Glückauf (Trans. Faraday Soc. **54** [1958] 1203/5). – [89] G. Ritter (KFA-ICT-IB-412 [1977] 1/42). – [90] P. Markl (Extraktion und Extraktionschromatographie in der Anorganischen Analytik, Akademische Verlagsgesellschaft, Frankfurt a. M. 1972).

[91] E. Hesford, H. A. C. McKay (AERE-C-R-1893 [1958] 1/20; N.S.A. **12** [1958] No. 16998). – [92] M. D. Snyder (DP-768 [1962] 1/16; N.S.A. **26** [1972] No. 33226). – [93] J. A. Kelley (DP-1308 [1972] 1/40; N.S.A. **27** [1973] No. 24506). – [94] G. Koch, Z. Kolarik, H. Haug, W. Hild, S. Drobnik (KFK-1651 [1972] 1/31; N.S.A. **27** [1973] No. 22307). – [95] A. Hultgren, E. Haeffner (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 324/8).

[96] A. Hultgren (Progr. Nucl. Energy III **4** [1970] 287/318). – [97] E. Haeffner, A. Hultgren, A. Larsson (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 370/81). – [98] K. Jönsson (AE-183 [1965] 1/25; N.S.A. **19** [1965] No. 28435). – [99] D. Gourisse, A. Chesne (Anal. Chim. Acta **45** [1969] 321/5). – [100] D. Gourisse, A. Chesne (Anal. Chim. Acta **45** [1969] 311/9).

[101] D. Herz, R. Kankura, U. Wenzel (Ger. 2365114 [1973/75] 1/3; C.A. **83** [1975] No. 138737). – [102] D. Herz, R. Kankura, U. Wenzel (JUEL-1212 [1975] 1/35; INIS Atomindex **7** [1976] No. 239752). – [103] R. Kankura (JUEL-1372 [1976] 1/135; INIS Atomindex **8** [1977] No. 334488). – [104] H. H. Remagen (JUEL-1505 [1978] 1/83). – [105] H. J. Riedel, U. Wenzel (6th Intern. Symp. Mikrotech., Graz 1970, pp. 271/5).

[106] U. Wenzel, H. J. Riedel (IAEA-SM-149-59 [1971] 1/10; Anal. Methods Nucl. Fuel Cycle Proc. Symp., Vienna 1971 [1972], pp. 549/62; C.A. **78** [1973] No. 91569). – [107] C. L. Da Silveira Branquinho, U. Wenzel (JUEL-1536 [1978] 1/34; INIS Atomindex **10** [1979] No. 449611). – [108] A. M. dos Santos (JUEL-1284 [1976] 1/73; INIS Atomindex **7** [1976] No. 270367).

2.4.7 Reprocessing by Means of Halide Volatilization Processes

Efforts have been made to replace the aqueous extraction process for the recovery of ^{233}U from reactor irradiated Th by nonaqueous reprocessing methods. These have concentrated in two directions: halide vaporization and pyrochemical methods. A theoretical consideration of the various possibilities points out clearly the advantages of fractional distillation for the separation of the halogen compounds that have different volatilities. Of the four elements to be considered: fluorine, chlorine, bromine, and iodine, fluorine is the most suitable, since U forms a readily volatile fluoride in its highest valency form, UF_6 (sublimation point 56 °C), whereas Th forms the nonvolatile ThF_4 (m.p. $\approx$1100 °C). Chlorine is the next best and only alternative for technical use, but the volatility of the compounds obtained by chlorination is rather similar (UCl_4, b.p. = 792 °C, $ThCl_4$, sublimation point $\approx$750 °C). The special advantage of the fluorination process is that only few fission products can be volatilized as the fluorides, namely As, Sb, Te, Mo, Tc, Nb, and possibly Ru, whereas Th and most of the fission products remain in concentrated form as a solid residue.

The expected advantages of the halide volatilization process are the compact construction of the plant, the exclusion of water, which acts as a moderator, and the direct yield of solid form of the radioactive waste. A further advantage is the fact, that the uranium is obtained directly in the chemical form, which, after further suitable purification, may be fed back into the isotope enrichment plant. Relatively high decontamination factors are attained for the uranium, after additional purification by sorption/desorption on beds of NaF-MgF_2 or by fractional distillation. Values of 10^6 to 10^7 were obtained on the laboratory scale. The case for chloride volatilization appears to be much less favorable.

Good chances for success were originally ascribed to the fluoride volatility process in particular for the reprocessing of fuel elements from fast breeder reactors. The high specific radioactivity (due to short cooling periods and high Pu contents) causes considerable operational difficulties in the PUREX process, because of the strong radiolytic decomposition of the organic phase. "Dry" fluoride processes are more stable in this respect. Fluoride volatilization was developed as the reprocessing method for these fuel elements in several countries. Interest centered almost exclusively on the U/Pu fuel cycle. The principle is applicable for both heterogeneous and homogeneous reactor, for metal, carbide, or oxide fuels. For a long period good chances for success were ascribed to a homogeneous molten salt breeder reactor, with either ^{238}U or ^{232}Th in the mantle. The fissile and fertile materials were distributed homogeneously in a fluoride melt in this case.

Besides the advantages mentioned above, the fluoride volatility process has also serious disadvantages. The main ones are the unsolved materials problem, due to the high incidence of corrosion, and the poor yields of uranium. The completely unsatisfactory UF_6-PuF_6 separation, which in the final count was responsible for abandoning this process in the U/Pu cycle, does not play any role in the Th/^{233}U cycle, since ThF_4 is extremely nonvolatile. This circumstance allows, in principle, a simple Th-U separation. The nonvolatility of ThF_4, unfortunately, causes poor U yields from a Th matrix, due to the formation of covering layers. It was attempted to counter this difficulty by operating at a higher reaction temperature, up to about 700 °C, but the U yields remained poor, whereas the extent of the corrosion became unacceptable [1 to 8].

In the long run, the application of the Th/^{233}U fuel cycle in light water, heavy water, and graphite moderated thermal reactors and in salt melt and fast breeder reactors, requires that the cycle be closed. The process development for the isolation of pure bred ^{233}U by fluoride volatilization concentrated to date of fuels on the basis of Zr-U or of Al-U [9 to 11], and on graphite containing Th/U elements of high temperature reactors [12 to 17]. Successfully demonstrated was also the fused salt fluoride volatility process, FSFVP, during the reprocessing of the fuels of the Aircraft Reactor Experiment (ARE), the submarine thermal reactor [10, 18 to 22], and of molten salt reactors (MSRE, Molten Salt Reactor Experiment) [23 to 41].

2.4.7.1 Fluorination of Solids

Thorium-containing fuels and fertile materials may be fluorinated for the purpose of separating the ^{233}U bred in them by two methods: the metal or oxide may be treated with either gaseous or liquid fluorinating agents. The first method has proved itself.

Fluorination reactions using liquid mixtures of interhalogen compounds, such as ClF_3, BrF_3, or BrF_5, or hydrogen fluoride mixed with nitrogen oxides, are dangerous in their technical application. The removal of the evolved heat of reaction is often uncontrolled, and may lead to an explosive course of the reaction [42]. In the so-called Nitrofluor process, the nuclear fuels are decomposed or dissolved in a liquefied mixture of anhydrous HF and nitrogen oxides. The ternary azeotropic mixture of NOF, N_2O_3, and HF boils at 95 °C at atmospheric pressure. After the fuel is dissolved in this very reactive mixture, the excess of the solvent is evaporated off, leaving a solid residue, which contains the uranium. This is then treated with BrF_3 at 150 °C, and the UF_6 is distilled off. The metallic claddings of Zircaloy, Al, or stainless steel are hardly attacked [43].

Much more advantageous is the fluorination of the solids with gaseous reactants in a stationary bed, in a turning tube oven, or most usefully in a fluidized bed. The most often used fluorinating agent is HF combined with elementary fluorine, which yielded to date the best results. Less successful was a series of other gaseous fluorinating agents, such as ClF_3, BrF_3, BrF_5, SF_4, and SF_6 [44 to 48]. Special advantages are expected from using a fluidized bed. The evolved heat of the reaction may be removed in a readily controlled manner, and the reaction temperature may be readily regulated. A fluidized bed oven is simple in its construction, and may be relatively easily set up in a hot cell. On the other hand, the fluidized bed technique requires a powder of as uniform grain size as possible, a requirement which cannot always be met. Local overheating may result, leading to sintering of the reacting material. These difficulties may be made less troublesome by the admixture of an inert fluidizing agent, such as granular Al_2O_3. This, however, causes poorer yields of the U and higher quantities of radioactive waste. Pure Ni or Ni-containing alloys are suitable as the materials of construction.

Reprocessing by fluorination may, in principle, take different reaction courses:

1. The fuel element is pretreated in the head-end step, either by removing the cladding completely, or by freeing the fuel mechanically. A conversion in a single step to UF_6, using elementary fluorine at 500 °C, follows [49 to 51]: $(U,Th)O_2 + F_2 \rightarrow UF_6 + ThF_4 + O_2$. Direct fluorinations with other reagents, halogen fluorides, or sulfur hexafluoride, proceed similarly. The latter reagent provides a particularly simple reaction path: $UO_2 + SF_6 \rightarrow UF_6 + SO_2$. The handling of this reagent is relatively safe, but the reaction temperature required is high, about 800 °C [48]. Metallic materials of construction cannot be used, and ceramic materials, such as alumina must be employed, introducing appreciable technological problems.

In order to reduce the amount of U remaining in the residues from the fluorination, it is possible to subject them to steam pyrohydrolysis, and subsequently to refluorinate. Still, the U losses remain relatively high.

2. A different method employs a stepwise fluorination. The fuel elements that have been pretreated in the head-end step are first subjected to a treatment with gaseous HF (hydrofluorination). Independently of whether oxidic or carbidic fuels were employed, a mixture of the nonvolatile UF_4 and UO_2F_2 is always formed: $UO_2 + ThO_2 + 8\,HF \rightarrow UF_4 + ThF_4 + 4\,H_2O$; $ThC_2 + 4\,HF + 2\,O_2 \rightarrow ThF_4 + 2\,CO + 2\,H_2O$; $3\,UC_2 + 8\,HF + 10\,O_2 \rightarrow 2\,UO_2F_2 + UF_4 + 6\,CO_2 + H_2O$. The reaction products of the hydrofluorination are then treated with elementary fluorine (fluorination) [52 to 56]: $UF_4 + UO_2F_2 + 3\,F_2 \rightarrow 2\,UF_6 + O_2$. Both process steps may be carried out in the usual reactors for solids. This method has the advantages, relative to the direct fluorination, that the appreciable heat of the reaction is distributed between two process streams, and that theoretically only $\approx 30\%$ of the amount of fluorine must be added in the form of the expensive elementary fluorine. This method, too, may be improved by steam pyrohydrolysis, in order to reduce the U content of the matrix.

Many publications about the kinetics of the fluorination reactions have appeared [57 to 66]. The transformation of UF_4 with oxygen to UF_6, in order to dispense with the use of elementary fluorine has also been studied [67, 68]. Extensive laboratory experiments dealt with the hydrofluorination of SiC-coated fuel particles of high temperature reactor fuel elements [14].

2.4.7.2 Fluorination of Molten Salts

It is known that U may be volatilized as UF_6 by fluorination of fluoride salt melts, in which the U is contained as UF_4, by fluorine. Other molten salts, besides the fluorides, are not suitable for this purpose, since they are not stable with respect to fluorine. Although fluorination of molten salts leads most readily to quantitative yields of U, the corrosion of the materials of construction is most severe in this method. Most liable to attack is the wall of the container at the boundary between the melt and the gas space [69 to 72]. A further disadvantage of this method is the enlargement of the volume of the high activity waste by the large quantities of the molten salt.

It is required from the molten salt systems, that they provide at as low a temperature as possible (leading to acceptable rates of corrosion) a sufficient rate of dissolution and as large a solubility of the tetrafluorides that have been formed as possible. The oxide mixture coming from the head-end stage is transformed in ZrF_4-containing melts at 500 to 600°C to oxide fluorides or fluorides, dispersed inhomogeneously in the melt: $(U,Th)O_2 + ZrF_4 \rightarrow (U,Th)OF_2 + ZrOF_2$; $(U,Th)O_2 + 2\,ZrF_4 \rightarrow (U,Th)F_4 + 2\,ZrOF_2$. When hydrogen fluoride gas is led into this melt, a homogeneous melt is formed, containing the tetrafluorides: $(U,Th,Zr)OF_2 + 2\,HF \rightarrow (U,Th,Zr)F_4 + H_2O$. Uranium may be volatilized from this melt as UF_6 by leading fluorine into it.

This process variant is limited to ZrF_4-containing melts, since only these can dissolve appreciable quantities of U/Th oxides. Compared with other fluoride melts, however, their ability to dissolve the U and Th tetrafluorides is relatively small, limited below 600°C to 10 to 20 wt%. This causes the accumulation of large quantities of waste during technical operation of this process. Furthermore, hydrofluorination in this melt at temperatures near 600°C is very unfavorable from the standpoint of corrosion. Volatilization takes place most readily from melts rich in uranium, e.g., 31.5 wt% UF_4, 25.7 wt% NaF, 25.7 wt% LiF, and 17.1 wt% ZrF_4 [73 to 90].

A process variant that has been proposed avoids these disadvantages, by carrying out the hydrofluorination in a reactor for solids. The mixture of UF_4, UO_2F_2, and ThF_4 that is obtained is then melted in the presence of additional metal fluorides, and U is volatilized from the melt with elementary fluorine as UF_6. One no longer depends on ZrF_4-containing melts, and one may choose fluorides or their mixtures, which form with UF_4 and ThF_4 systems that have melting points below 600°C at high U and Th contents [91].

Large quantities of salt are required, because of the relatively low solubility of Th in the fluoride melts. There exists no possibility for the recovery of the Th. Neither can the salt be reused, because of the accumulation of Th up to the solubility limit.

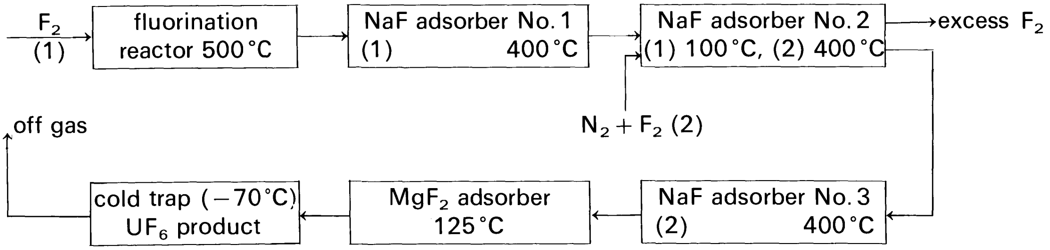
2.4.7.3 Purification of UF_6

The UF_6, which is the primary product of the fluoride volatilization process, is still more or less contaminated by volatile fission products. It requires further purification, in order to facilitate its subsequent handling. Two methods are available for this step:

1. fractional adsorption-desorption on and from $NaF\text{-}MgF_2$ beds, and
2. fractional distillation.

NaF reacts with UF_6 to form the double salt Na_2UF_8. Under certain circumstances this reaction may be reversed: $Na_2UF_8 \rightleftharpoons UF_6 + 2\,NaF$. The dissociation pressure of the double salt obeys the Arrhenius expression log p (p in Torr) $= 10.88 - 5090/T$ (T in K) in the range 80 to 400°C. The temperature dependent reversibility of the reaction permits the rather complete liberation of the UF_6 from contaminating fluorides, i.e., its purification.

Normally, three NaF and one MgF_2 adsorption beds are used:



1st step: The UF_6 passes the first NaF adsorber and is held by the second. The first one acts as a filter, holding back ZrF_4, CrF_5 (corrosion product), NbF_5 and others. The third adsorber is not needed in this step.

2nd step: The temperature of the second NaF adsorber is raised to 400 °C, letting the UF_6 desorb. It is necessary, however, to scrub with $F_2 + N_2$ in order to achieve complete desorption and to prevent the interfering reaction $Na_2UF_8 \rightleftarrows Na_2UF_6 + F_2$ from proceeding to the right, since in Na_2UF_6 the UF_4 is bound irreversibly to NaF. The third NaF adsorber is held at 400 °C, in order to retain a few fission product fluorides (including CrF_5). The MgF_2 adsorber, maintained at 125 °C, holds back the fluorides of Tc and Np that accompany the UF_6. The UF_6 is finally condensed in a cold trap.

The entire adsorption-desorption technique is still plagued by three difficulties:

1. It is difficult to achieve the stoichiometric capacity that corresponds to the formula $UF_6 \cdot 2\,NaF$, even approximately.

2. The NaF pellets fall appart to a fine powder after numerous cycles. The process proceeds, furthermore, partly irreversibly.

3. Too little is as yet known about the behavior of the other fluorides on the NaF columns. A separation of the ternary mixture UF_6-MoF_6-TcF_6 on NaF and MgF_2 beds is only partly successful, so that either small Mo contents in the UF_6 must be tolerated or lower UF_6 yields must be accepted [92 to 105].

Besides the purification of UF_6 at alkali and alkaline earth metal fluoride beds, its fractional distillation has been considered [106]. A column may be calculated theoretically only with great reservations, since the impurities are in the ppm range. UF_6 may be distilled or rectified in packed columns at a slightly elevated pressure, e.g., 2 to 3 bar. The unit contains usually two columns, one for low and the other for high boiling components. However, TcF_6 and NpF_6 may not be satisfactorily separated by distillation, because of the similarity in the vapor pressures. The de-sublimation of UF_6 from a fluorine-inert gas mixture is a known technology.

2.4.7.4 Chlorination of Solids

Interest in the "dry" chlorination of nuclear fuels for the purpose of reprocessing had started in the USA within the framework of the Manhattan Project already in the years 1943 to 1946. The main purpose at that time was to reprocess Pu-containing nuclear fuels. Many of the experiences were, however, of great significance for the isolation of ^{233}U from irradiated Th

[107 to 131]. Many attempts were subsequently made to apply the chloride volatilization method for the separation of U in the Th cycle. The results achieved were only partly satisfactory. The reasons therefore were unsatisfactory U yields, due to incomplete volatilization, poor decontamination factors for the separated U, and serious corrosive attack on the materials of construction. The difficulty is compounded by the impossibility of vaporizing the U exclusively in the highest valency state, i.e., as UCl_6. Depending on the actual reaction conditions, various amounts of UCl_4 and UCl_5 are obtained. The vapor pressures of several chlorides lie closely together in the temperature range necessary for the volatilization of the uranium. This causes strong mutual effects, both in the volatilization and in attempts at fractional condensation or desublimation. The theoretical basis for the evaluation of the process has been worked out in a series of studies [132 to 138].

The chlorination of the heavy metal oxides, that have been set free in a chemical or mechanical head-end treatment, succeeds with various chlorinating agents, such as chlorine, CCl_4 or $COCl_2$. It proceeds according to the general equation $MO_2 + 2\,Cl_2 + 2\,C \rightarrow MCl_4 + 2\,CO$. ThO_2 cannot be chlorinated at 800 °C with chlorine alone, and an oxygen acceptor is required.

The number of studies published about the chlorination of ThO_2 is small relative to that about U and Pu oxides. The studies carried out for the determination of the chlorination parameters, both in a fluidized bed and in a stationary bed, show, that the chlorination temperature must be above 800 °C, in order to achieve sufficiently high rates of volatilization. At 1 000 °C, even with relatively short chlorination periods of 30 min, it is possible to attain $>99\%$ yield of the U. A separation of Th and U by means of fractional condensation is only partly successful. A large fraction of the U adheres to the Th chloride in the form of U chloride. Even a repeated fractional resublimation does not lead to completely satisfactory results. Desublimation to form the solid phase must be caused to occur in the gas phase, in order to prevent the formation of a crust on the wall of the desublimation vessel. If formed, this crust reduces strongly the heat transfer and the desublimator might be stopped-up [139 to 154]. The treatment of the off-gas from the chlorination is rather expensive and complicated [155].

The poor results obtained on the whole with the chlorinating reprocessing, led to two modified flow schemes. In these the chlorination is applied only as a head-end step, for the separation of the U and Th from the large excess of graphite component of the fuel elements of the gas-cooled high temperature reactors. The fuel elements are crushed in a suitable milling facility, an air stream taking care of the fines, so that a favorable grain size distribution for the subsequent chlorination results. The ground material is conveyed continuously into a stationary bed reactor, and treated with chlorine at 1 000 to 1 200 °C. The chlorides of U, Th, and some of the fission products are thereby volatilized, and are deposited in a snow-like form in the desublimator. The graphite and the majority of the fission products are held back as solid waste [156 to 161] thus avoiding the emission of ^{14}C, which otherwise occurs in the combustion of the graphite to CO_2 [162]. Chlorine, the reaction gas, is circulated, and only a fraction of it must be handled as off-gas. The trapped metal chlorides may be purified after a dissolution step by means of solvent extraction with amines directly in the chloride system [163], or, after conversion to the nitrate system, with tributyl phosphate according to the effective PUREX (THOREX) method [164, 165].

In another process variant, chlorination is again used only in the head-end treatment. The chloride mixture is subjected to hydrofluorination in a stationary bed reactor, and subsequently to a fluorination, whereby U is separated as UF_6. Since hydrofluorination occurs already at 100 °C, and since no water is formed as a reaction product, the corrosion of the materials of construction is significantly smaller than when the oxides are hydrofluorinated [166, 167].

References for 2.4.7:

[1] S. Lawrowski (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 575/82). – [2] H. H. Hyman, R. C. Vogel, J. J. Katz, (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 613/26). – [3] R. K. Steunenberg, R. C. Vogel (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 438/51). – [4] A. A. Jonke (At. Energy Rev. **3** [1965] 3/60). – [5] R. C. Vogel, W. H. Carr, G. I. Cathers, J. Fischer, L. P. Hatch, R. W. Horton, A. A. Jonke, R. P. Milford, J. J. Reilly, G. Strickland (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 491/8).

[6] J. Schmets, C. Lamozzo, A. Francesconi, P. Godrie, R. Heremans, G. Pierini, P. Speeckarts (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 520/9). – [7] M. Bourgeois, P. Faugeras (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 483/90). – [8] L. Burris, G. A. Bennett (Reactor Fuel Process. **9** [1965] 32/9). – [9] G. I. Cathers (Nucl. Sci. Eng. **2** [1957] 768/77). – [10] G. I. Cathers, W. H. Carr, R. B. Lindauer, R. P. Milford, M. E. Whatley (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 473/9).

[11] R. G. Wymer (ORNL-2183 [1957] 1/29; N.S.A. **14** [1960] No. 20256). – [12] E. Merz (Atomwirtschaft **13** [1968] 417/21). – [13] H. Friedrich, R. Kreutz, J. Massonne (Kerntechnik **12** [1970] 105/9). – [14] R. Kreutz, W. Kuhrt, J. Massonne (Kerntechnik **13** [1971] 21/3). – [15] W. H. Carr (Chem. Eng. Progr. Symp. Ser. **56** No. 28 [1960] 57/61).

[16] W. L. Carter (ORNL-TM-241 [1962] 1/57; N.S.A. **16** [1962] No. 23789). – [17] R. P. Milford (ORNL-TM-717 [1963] 1/22; N.S.A. **18** [1964] No. 3883). – [18] G. I. Cathers (CF-57-1-118 [1957] 1/19; N.S.A. **11** [1957] No. 4392). – [19] R. P. Milford, S. Mann, J. B. Ruch, W. H. Carr (Ind. Eng. Chem. **53** [1961] 357/62). – [20] E. C. Moncrief (ORNL-TM-398 [1962] 1/10).

[21] E. C. Moncrief (ORNL-TM-447 [1962] 1/21; N.S.A. **17** [1963] No. 10742). – [22] W. L. Carter, R. P. Milford, W. G. Stockdale (ORNL-TM-522 [1962] 1/88; N.S.A. **17** [1963] No. 21778). – [23] F. T. Miles, R. J. Heus, R. H. Wiswall (BNL-482 [1954] 1/28; N.S.A. **12** [1958] No. 13039). – [24] G. I. Cathers (ORNL-1709 [1954] 1/12). – [25] G. I. Cathers, M. R. Bennett (ORNL-1885 [1955] 1/24).

[26] R. E. Leuze, G. I. Cathers, C. E. Schilling (ORNL-1877-Rev. [1955] 1/15; N.S.A. **12** [1958] No. 2741). – [27] R. C. Briant, A. M. Weinberg (Nucl. Sci. Eng. **2** [1957] 797/803). – [28] G. I. Cathers, M. R. Bennett, R. L. Jolley (ORNL-2661 [1959] 1/33; N.S.A. **13** [1959] No. 10983). – [29] D. O. Campbell, G. I. Cathers (Ind. Eng. Chem. **52** [1960] 41/4). – [30] G. J. Nessle, W. R. Grimes (Chem. Eng. Progr. Symp. Ser. **56** No. 28 [1960] 51/8).

[31] W. D. Powers, S. I. Cohen, N. D. Greene (Nucl. Sci. Eng. **17** [1963] 200/11). – [32] J. H. Shaffer, W. R. Grimes, G. M. Watson, D. R. Cuneo, J. E. Strain, M. J. Kelly (Nucl. Sci. Eng. **18** [1964] 177/81). – [33] G. I. Cathers, M. R. Bennett, R. L. Jolley (Chem. Eng. Progr. Symp. Ser. **60** No. 47 [1964] 31/6; C.A. **62** [1965] 4865). – [34] W. R. Grimes (ORNL-3913 [1966] 1/51; N.S.A. **20** [1966] No. 22856). – [35] C. D. Scott, W. L. Carter (ORNL-3791 [1966] 1/128; N.S.A. **20** [1966] No. 43422).

[36] P. R. Kasten, E. S. Bettis, H. F. Bauman, W. L. Carter, W. B. McDonald, R. C. Robertson, J. H. Westsik (CONF-660524-5 [1966] 1/20; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 41/63; N.S.A. **20** [1966] No. 35026). – [37] P. N. Haubenreich (CONF-660524-18 [1968] 1/11; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 671/9; N.S.A. **20** [1966] No. 47015). – [38] M. E. Whatley, W. L. Carter, R. B. Lindauer, L. E. McNeese, C. D. Scott, J. R. Hightower (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 653/69). – [39] P. N. Haubenreich (Nucl. Eng. Intern. **14** [1969] 325/9). – [40] J. M. Chandler, R. B. Lindauer (Nucl. Met. **15** [1969] 97/120).

[41] J. R. Hightower (ORNL-TM-4870 [1976] 1/48). – [42] L. Stein, R. C. Vogel (ANL-5441 [1955] 1/20; N.S.A. **12** [1958] No. 7160). – [43] F. Maslan (BNL-571 [1959] 1/99; N.S.A. **14** [1960] No. 8325). – [44] R. C. Vogel, M. Levenson, J. H. Schraidt, J. Royal (ANL-7175 [1966] 42/103; N.S.A. **20** [1966] No. 31164). – [45] J. Schmets, G. Camozzo, A. Francesconi, R. Heremans, G. Pierini, P. Speeckhaert (EUR-2399.f [1966] 1/99; EURAEC-1479 [1966] 1/99; N.S.A. **20** [1966] No. 27034).

[46] V. Y. Labaton (J. Inorg. Nucl. Chem. **10** [1959] 86/93). – [47] O. Knacke, M. Laser, E. Merz, H. J. Riedel (EUR-2780.e [1965] 239/43; N.S.A. **20** [1966] No. 40389). – [48] M. Laser, E. Merz (Nukleonik **11** [1968] 57/60). – [49] G. T. Seaborg, J. W. Gofman, R. W. Stoughton (U.S. 2887357 [1959]). – [50] D. E. Ferguson, R. G. Wymer, R. E. Blanco, K. B. Brown, M. E. Whatley, H. E. Goeller, R. E. Brooksbank (ORNL-3830 [1965] 69/96; N.S.A. **20** [1966] No. 9045).

[51] M. Laser, E. Merz (J. Inorg. Nucl. Chem. **31** [1969] 349/60). – [52] J. L. Williams (AECD-3335 [1951] 1/14; Y-769 [1952] 1/14; N.S.A. **6** [1952] No. 2640). – [53] J. J. Barghusen, A. A. Jonke, N. M. Levitz, M. J. Steindler, R. C. Vogel (Progr. Nucl. Energy III **4** [1970] 347/98). – [54] J. J. Reilly, S. J. Wachtel, R. Johnson, E. Wirsna, P. Hatch (Ind. Eng. Chem. Process Design. Develop. **5** [1966] 51/9). – [55] J. Massonne, H. Friedrich, R. Kreutz (Ger. Offen. 1771401 [1968]; Fr. Demande 2003589 [1969]; C.A. **74** [1971] No. 27329).

[56] R. Kreutz, W. Kuhrt, J. Massonne (Kerntechnik **13** [1971] 21/3). – [57] V. Y. Labaton, K. D. B. Johnson (J. Inorg. Nucl. Chem. **10** [1959] 74/85). – [58] W. J. Mecham, A. A. Jonke, J. D. Gabor, J. Wehrle (ANL-6145 [1960] 1/191, 103/4; N.S.A. **14** [1960] No. 21559). – [59] G. Strickland, F. L. Horn (Progr. Nucl. Energy III **4** [1970] 399/425). – [60] M. J. Steindler, L. J. Anastasia, L. E. Trevorrow, A. A. Chilenskas (Nucl. Met. **15** [1969] 177/210).

[61] L. J. Anastasia, W. J. Mecham (Ind. Eng. Chem. Process Design Develop. **4** [1965] 338/44). – [62] C. E. Johnson, J. Fisher (J. Phys. Chem. **65** [1961] 1849/52). – [63] C. E. Johnson, J. Fisher (ANL-6117 [1960] 1/19; N.S.A. **14** [1960] No. 25536). – [64] W. P. Ellis, B. W. Roberts (J. Chem. Phys. **39** [1963] 1176/81). – [65] M. Iwasaki (J. Inorg. Nucl. Chem. **26** [1964] 1853/61).

[66] T. Yahata, M. Iwasaki (J. Inorg. Nucl. Chem. **26** [1964] 1863/7). – [67] L. B. Asprey, R. A. Penneman (J. Am. Chem. Soc. **89** [1967] 172/3). – [68] C. D. Scott, J. B. Adams, J. C. Breese (Ind. Eng. Chem. Process Design. Develop. **3** [1964] 266/70). – [69] L. R. Trotter, E. E. Hoffman (ORNL-2495 [1958] 1/41; N.S.A. **13** [1959] No. 211). – [70] A. P. Litman, A. E. Goldman (ORNL-2832 [1961] 1/188; N.S.A. **15** [1961] No. 21095).

[71] A. E. Goldman, A. P. Litman (ORNL-2833 [1961] 1/86; N.S.A. **16** [1962] No. 2136). – [72] A. P. Litman (ORNL-3253 [1962] 1/32; N.S.A. **16** [1962] No. 10455). – [73] G. I. Cathers (Nucl. Sci. Eng. **2** [1957] 768/77). – [74] R. P. Milford (Ind. Eng. Chem. **50** [1958] 187/91). – [75] C. J. Barton, W. R. Grimes, H. Insley, R. E. Moore, R. E. Thoma (J. Phys. Chem. **62** [1958] 665/76).

[76] J. T. Long (Ind. Eng. Chem. **51** [1959] 169/73). – [77] R. E. Thoma, H. Insley, B. S. Landau, H. A. Friedman, W. R. Grimes (J. Phys. Chem. **63** [1959] 1266/72). – [78] C. J. Barton, H. A. Friedman, H. Insley, J. D. Redman, R. A. Strehlow, R. E. Thoma, C. F. Weaver (ORNL-2931 [1960] 1/206, 3/27; N.S.A. **14** [1960] No. 17795). – [79] G. I. Cathers, R. L. Jolly, H. F. Soard (ORNL-3280 [1962] 1/29; N.S.A. **16** [1962] No. 31675). – [80] R. E. Thoma, H. Insley, A. A. Friedman, G. M. Hebert (J. Am. Ceram. Soc. **46** [1963] 37/42).

[81] R. E. Thoma (ORNL-2548 [1959] 1/206; N.S.A. **14** [1960] No. 2739). – [82] R. E. Blanco, G. I. Cathers, L. M. Ferris, T. A. Gens, R. W. Horton, E. L. Nicholson (Nucl. Sci. Eng. **20** [1964] 13/22). – [83] W. H. Carr (Chem. Eng. Progr. Sym. Ser. **56** No. 28 [1960] 57/61). – [84] R. E. Thoma, H. Insley, A. A. Friedman, G. M. Hebert (J. Chem. Eng. Data **10** [1965] 219/30). – [85] M. J. Kelly (ORNL-3919 [1966] 1/119, 35/7; N.S.A. **20** [1966] No. 21224).

[86] B. F. Frasier, C. F. Baes, H. H. Stone (ORNL-3913 [1966] 1/51, 38/40; N.S.A. **20** [1966] No.22856). – [87] A. L. Mathews, C. F. Baes, B. F. Hitch (ORNL-3789 [1965] 56/65). – [88] F. F. Blankenship (CONF-660524-26 [1966] 1/9; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 647/52; N.S.A. **21** [1967] No. 4594). – [89] W. Bannasch, H. Jonas, E. Podschus (Nucl. Met. **15** [1969] 279/94; Symp. Reprocess. Nucl. Fuels, Ames, Iowa, 1969, pp. 1/763, 279/94; CONF-690801 [1969] 1/15; N.S.A. **23** [1969] 38055). – [90] J. J. Schmets (KR-126 [1967] 1/532, 324/41; N.S.A. **22** [1968] No. 40174).

[91] R. Kreutz, J. Massonne, H. Friedrich (Kerntechnik **12** [1970] 109/11). – [92] G. I. Cathers, M. R. Bennett, R. L. Jolley (Ind. Eng. Chem. **50** [1958] 1709/10). – [93] J. H. Krause, J. D. Potts (TID-11398 [1960] 1/50; N.S.A. **15** [1961] No. 7412). – [94] I. Sheft, H. H. Hyman, R. M. Adams, J. J. Katz (J. Am. Chem. Soc. **83** [1961] 291/4). – [95] L. E. McNeese, S. H. Jury (ORNL-P-281 [1964] 1/17; CONF-571-10 [1964] 1/17; Abstr. Papers 148th Meeting Am. Chem. Soc., Chicago 1964, No. R-47; N.S.A. **18** [1964] No. 41372).

[96] L. E. McNeese (ORNL-3494 [1963] 1/135; N.S.A. **18** [1964] No. 1616). – [97] S. Katz (ORNL-3544 [1964] 1/11; N.S.A. **18** [1964] No. 12038). – [98] S. Katz (Inorg. Chem. **3** [1964] 1598/600). – [99] A. A. Chilenskas, K. S. Turner, J. E. Kincinas, G. L. Potts (ANL-6994 [1966] 1/43; N.S.A. **21** [1967] No. 24059). – [100] S. Katz (Inorg. Chem. **5** [1966] 666/8).

[101] S. H. Smiley, D. C. Brater, C. C. Littlefield, J. H. Pashley (Ind. Eng. Chem. **51** [1959] 196/206). – [102] S. H. Smiley (Progr. Nucl. Energy IV **4** [1961] 191/278). – [103] G. I. Cathers, R. L. Jolley, E. C. Moncrief (Nucl. Sci. Eng. **13** [1962] 391/7). – [104] W. Kuhrt, H. Friedrich, J. Massonne (Kerntechnik **12** [1970] 334/7). – [105] W. Kuhrt, R. Kreutz, J. Massonne (Kerntechnik **13** [1971] 17/20).

[106] J. M. Lenoir (CF-51-4-176 [1951] 1/22; N.S.A. **11** [1957] No. 7476). – [107] C. Williams (4th Inter-Am. Symp. Peaceful Appl. Nucl. Energy Papers, Mexico City 1962, Vol. 1, pp. 153/62). – [108] R. E. Blanco, W. K. Eister, D. E. Ferguson (ORNL-2210-Del. [1957] 1/20; N.S.A. **11** [1957] No. 13682). – [109] T. A. Gens (CF-59-4-9 [1959] 1/9; N.S.A. **14** [1960] No. 4380). – [110] A. R. Gibson (AERE-M-M-67 [1954] 1/9; N.S.A. **11** [1957] No. 10034).

[111] D. Bradley (AERE-CE-R-2215 [1956] 1/53; N.S.A. **12** [1958] No. 4685). – [112] E. R. Harrison (AERE-GP-R-2409 [1958] 1/12; N.S.A. **12** [1958] No. 5943). – [113] S. A. Rosenfeld (B.P. 841681 [1960]). – [114] S. Brown, G. T. Seaborg (U.S. 2875021 [1959]). – [115] P. Speeckaert (BLG-38 [1959] 1/24; N.S.A. **14** [1960] No. 6318).

[116] T. A. Gens (Chem. Eng. Progr. Symp. Ser. **60** No. 47 [1964] 37/47). – [117] T. A. Gens, T. B. Borne (ORNL-3435 [1963] 1/29). – [118] G. Jangg, W. Ochsenfeld, A. Burker (Atompraxis **7** [1961] 332/6). – [119] T. Ishihara, K. Hirano, T. Honda (Nippon Genshiryoku Gakkaishi **4** [1962] 231/9). – [120] T. Ishihara, K. Hirano (Nippon Genshiryoku Gakkaishi **5** [1963] 549/54).

[121] T. Ishihara, K. Hirano (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 530/7). – [122] K. Iwamoto, F. Kobayahi, J. Shimokawa (Nippon Genshiryoku Gakkaishi **5** [1963] 560/71). – [123] D. Naumann (Kernenergie **5** [1962] 118/9). – [124] D. Naumann (Kernenergie **6** [1963] 73/6). – [125] D. Naumann (Kernenergie **6** [1963] 243/51).

[126] J. H. Goode (ORNL-TM-828 [1964] 1/27; N.S.A. **18** [1964] No. 23704). – [127] J. Schmets, J. Broothaerts, G. Camozzo (EUR-2088.f [1965] 1/145; N.S.A. **20** [1966] No. 7188). – [128] T. A. Gens (ORNL-TM-1258 [1965] 1/20; N.S.A. **20** [1966] No. 1816). – [129] H. Parthey (Nukleonik **7** [1965] 473/7). – [130] K. S. Warren, L. M. Ferris (ORNL-3977 [1966] 1/29; N.S.A. **20** [1966] No. 35590).

[131] B. Kanellakopolus, H. Parthey (Nukleonik **12** [1968] 1/3). – [132] A. Glassner (ANL-5750 [1957] 1/70; N.S.A. **12** [1958] No. 2733). – [133] J. J. Katz, E. Rabinowitsch (The Chemistry of Uranium, McGraw-Hill, New York 1951). – [134] I. V. Budajew, A. N.

Volsky (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 28, pp. 316/30). – [135] M. H. Rand, O. Kubaschewski (The Thermochemical Properties of Uranium Compounds, Oliver and Boyd, Edinburgh-London 1963).

[136] U. Gat (Diss. Aachen T.H. 1968, pp. 1/57). – [137] J. Krahe, F. Müller (JUEL-565-CT [1968] 1/39; N.S.A. **23** [1969] No. 43383). – [138] E. Fischer, M. Laser, E. Merz (CONF-690801 [1969] 645/58; Symp. Reprocess. Nucl. Fuels, Ames, Iowa, 1969, pp. 645/58; Nucl. Met. **15** [1969] 645/58; N.S.A. **23** [1969] No. 38042). – [139] H. H. Hyman, R. C. Vogel, J. J. Katz (Progr. Nucl. Energy III **1** [1956] 261/73). – [140] K. Hirano, T. Ishihara (Nucl. Met. **15** [1969] 241/59).

[141] O. C. Dean, J. M. Chandler (Nucl. Sci. Eng. **2** [1957] 57/72). – [142] N. Levitz, J. Barghusen, E. Carls, A. A. Jonke (ANL-6342 [1961] 1/105; N.S.A. **16** [1962] No. 4215). – [143] J. H. Goode (ORNL-TM-828 [1964] 1/27; N.S.A. **18** [1964] No. 23704). – [144] R. E. Blanco, G. I. Cathers, L. M. Ferris, T. A. Gens, E. L. Nicholson (ORNL-TM-667 [1963] 1/29). – [145] Yeng Kung-Fan, Li Shao-Chung, G. I. Novikov, (Zh. Neorgan. Khim. **8** [1963] 89/92; Russ. J. Inorg. Chem. **8** [1963] 44/7).

[146] J. L. Cook, R. L. Hamner (ORNL-3586 [1964] 1/28; N.S.A. **18** [1964] No. 17934). – [147] J. L. Cook, R. L. Hamner (Trans. Am. Nucl. Soc. **7** [1964] 396/400). – [148] W. L. Lyon (U.S. 3030176 [1962]). – [149] T. G. Gens (Chem. Eng. Progr. Ser. **60** No. 47 [1964] 37/47). – [150] N. M. Levitz, J. J. Barghusen, J. T. Holmes, A. A. Jonke (Chem. Eng. Progr. Symp. Ser. **60** No. 47 [1961] 84/9).

[151] A. V. Hariharan, S. P. Sood, R. Prasad, D. D. Sood, K. Rengan, P. V. Balakrishnan, M. V. Ramaniah (Nucl. Met. **15** [1969] 261/77). – [152] H. Bildstein, K. Knotik (Kerntechnik **8** [1966] 110/5). – [153] K. Knotik, H. Bildstein, G. Falta, H. Wagner (SGAE-CH-71 [1970] 1/32). – [154] K. Knotik, H. Bildstein (Kerntechnik **13** [1971] 323/9). – [155] H. Barnert-Wiemer (JUEL-826-CT [1972] 1/91; N.S.A. **26** [1972] No. 42848).

[156] E. Fischer (Diss. Aachen T.H. 1970, pp. 1/73). – [157] E. Fischer, M. Laser, E. Merz (Kerntechnik **12** [1970] 321/6). – [158] M. Laser, J. Bohnenstingl, E. Fischer (Ger. Offen. 2040686 [1972]; C.A. **76** [1972] No. 142785). – [159] E. Fischer, M. Laser, E. Merz (Nucl. Met. **15** [1969] 645/58). – [160] J. Bohnenstingl, H. Gebhard, M. Laser, G. Loßmann (Ger. Offen. 2262881 [1975]; C.A. **82** [1975] No. 60698).

[161] J. Bohnenstingl, H. Gebhardt, M. Laser, G. Loßmann (JUEL-1129-CT [1974] 1/51; C.A. **83** [1975] No. 17385). – [162] P. C. Schmidt (JUEL-1567 [1979] 1/108). – [163] C. F. Coleman (Progr. Nucl. Energy III **4** [1970] 233/85). – [164] L. Küchler, L. Schäfer, B. Wojtech (Chem. Eng. Tech. **43** [1971] 601/4). – [165] L. Küchler, L. Schäfer, B. Wojtech (Kerntechnik **12** [1970] 327/33).

[166] R. Kreutz, W. Kuhrt, J. Massonne (Kerntechnik **14** [1972] 162/5). – [167] R. Kreutz, W. Kuhrt, J. Massonne (Ger. Offen. 2040426 [1972]).

2.4.8 Reprocessing by Application of Pyrochemical Processes

Pyrochemical processes are characterized by the use of high operating temperatures. The nuclear fuel either remains in the metallic state, or is transformed by "dry" conversion in a suitable chemical medium into the oxides or the halides. The first case is referred to as a pyrometallurgical, the second as a pyrochemical process, the reaction media being a metal and a molten salt, respectively.

The feasibility of a metallurgical process for the separation of fissile and fertile materials from one another was considered already at the beginning of the development of nuclear energy [1 to 3]. The separations obtained in this way were and have remained poor, and serious problems with the materials of construction had to be countered because of the high

References for 2.4.8 on pp. 346/8

temperatures involved. During the years 1952 to 1967, big efforts were made to explore systematically the effectiveness of such methods. A large number of thermodynamic measurements and calculations of the enthalpies of formation resulted at that time. Numerous phase diagrams and tabulated lists of data were prepared [4 to 15]. Presumably more money and efforts were expended on the development of this process than on the PUREX process. Several studies were concerned already at that time with cost estimates of the various processes. They proved all to be wrong, since the values were much too optimistic [16 to 19].

The methods that have been proposed may be classified into two main categories [20 to 23]:

a) Physical processes, involving fractional distillation or sublimation and crystallization, and liquid-liquid distribution processes involving immiscible metals and molten salts.

b) Chemical processes, such as oxidizing slag formation and cyclic oxidation and reduction, using chemical or electrochemical processes.

Because of the high operating temperatures, in all the variants, all of the gaseous fission products and a part of the readily volatile solid fission products are liberated into the off-gases. This fact necessitates an expensive off-gas treatment. In almost all the cases a recycling by fractional distillation or sublimation was provided for the molten metal or salt used as separating media. At the beginning it was thought that the nuclear fuels, of power reactors as of fast breeders, would preferably be metallic, and that metallurgical processes would be particularly suitable for them. But even the displacement of metallic by ceramic fuels let some advantages, due to the use of pyrochemical processes, to be expected. Most of the proposals were very soon abandoned, and only a few reached the pilot-plant testing stage. The advantages hoped for concentrated on the following:

– higher radiation stability of the chemicals employed, which is especially important for highly burned-up and short-term cooled breeder fuel elements;

– simple and compact construction of the separating plant;

– smaller criticality risks, due to the absence of materials acting as moderators, in particular water, and

– simplified radioactive waste problems, since almost all the materials occur in a compact solid form.

It was speculated, that a reprocessing plant might be built near every nuclear power station. No high decontamination factors were aimed at in the integrated plants, since from the start the concept involved remote controlled operation. These considerations proved to be a complete failure, from both the technical and the economical aspects. The EBR-II process for U-Pu-containing breeder elements was developed furthest, or at least became the best known [24, 25]. Much less effort was invested in the Th cycle [26 to 36].

2.4.8.1 Fractional Crystallization and Distillation

A partial purification may be achieved by simple distillation, due to the fact that many fission products are more volatile than metallic U and Th. No even half-way satisfactory U/Th separation can be achieved, however, because of the too small difference in their vapor pressures. Material problems cause difficulties, because of the high operating temperatures, 1600 to 1800 °C. In contrast to the purely single step distillation, melting experiments with irradiated Th in crucibles made of ZrO_2, ThO_2, or TiC, yielded better results. The volatile fission products evaporate at the high temperature almost completely, whereas the more reactive ones combine with the material of the crucible. However, this leads to an additional waste problem, afforded by the heavily contaminated melting crucibles. In any case, this method of reprocessing could not meet the targets set for it, and all the efforts were therefore soon stopped [37 to 41].

Another variant of distillative purification exploits the thermal decomposition of the iodides principle according to the van Arkel and de Boer growth process. The principle seems to work, but an industrial application fails, because of excessive costs [42, 43].

The method of fractional crystallization from molten metals achieved somewhat better success. The fuel elements are dissolved in molten Bi, Pb, Sn, Al, Mg, Zn, Cd, or Ag, the melts are left to cool down slowly, keeping certain concentration ratios. It is possible to obtain, at least partly, pure phases or intermetallic components, according to the prevailing phase diagram. After separation of the solid phase, the intermetallic component must, as the case may be, be treated further, in order to obtain the desired material in pure form. This is generally done by a distillative separation in an inert atmosphere. The metallic separation medium must be processed after each cycle and recycled, because of economic reasons. Distillative purification seems to be the most effective for this purpose. Detailed data about binary and ternary mixtures, that have been studied in this connection, are found in the literature [44 to 50].

Zone melting, which gives only poor yields of pure product is not suitable for the reprocessing of irradiated fuel elements [51 to 60].

2.4.8.2 Distribution between Immiscible Metal and Salt Melts

The well known principles of liquid-liquid distribution may be applied also to metallic systems. The difficulties with the extraction devices are understandably considerable, due to the high temperatures and the corrosion phenomena. Despite this, there was no lack of attempts to utilize the particular advantages that the higher radiation stability of molten metals afford. It is possible, for instance, to extract from molten uranium a part of the fission products, by contacting it with molten Cu or Ag. Experiments have been conducted also with Th-containing fuels, to separate out, or free from the fission products, the ^{233}U that had been bred in it, by means of pyrometallurgical processes. Systems containing Mg, Ag, or Bi have been the subject of most of the studies. The attainable distribution coefficients are, however, not very different for the materials to be separated, so that only small separation factors could be achieved.

Solid-liquid extraction was also tried, besides the liquid-liquid extraction. Certain molten metals may extract certain components out of finely divided solid fuel. The technological problems encountered in this process are, however, enormous. An example of the special problems is the filtration of suspensions of finely dispersed metals. Additional hydrogenation-dehydrogenation processes have been employed, in order to accelerate the diffusion processes that control the reaction rate.

Extraction with molten salts has also been studied intensively, generally as a mixed system, involving molten metals and molten salts. Multicomponent chloride melts were favored, because they have relatively low melting points and high thermal stability. The driving forces for the exchange and distribution reactions are the different Gibbs free energies of formation of the various compounds [61 to 63]. A kind of molten salt chromatography was also tried. The liquid Th/U melt was passed through a column packed with CaF_2, in order to separate out selectively the fission products [74].

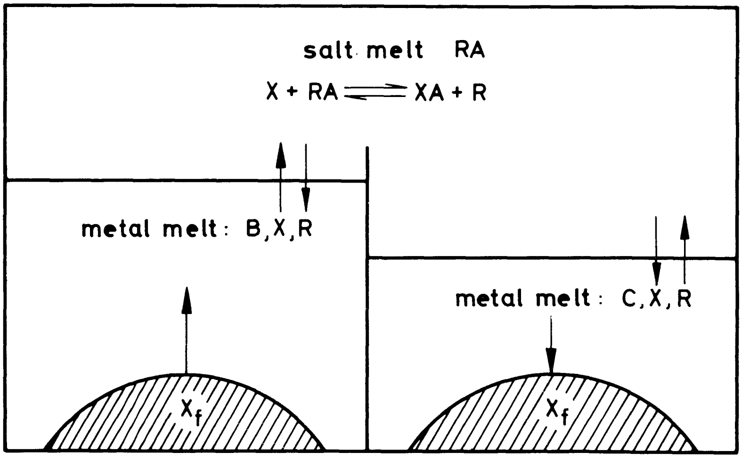
2.4.8.3 Oxidation-Reduction Reactions, Slag Formation

It should be possible to separate cleanly any desired chemical component from a mixture by using a suitable oxidation-reduction cycle. This suitability is judged on the basis of thermodynamic considerations about the relative stabilities of chemical compounds. The oxidation-reduction cycle may be carried out both chemically and electrochemically. Oxidative slag formation falls into this category. The reprocessing that became known as melt purification, applied to the American breeding reactor at Idaho Falls, is apparently the only pyrochemical process that has till now been developed through the technical scale, and been demonstrated "hot" at least for a short while. Despite the seemingly successful demonstration, the facility was shut down in 1968 and subsequently entirely demounted.

The fuel or fertile material is first removed from the cladding material by mechanical dismantling of the elements, and is then melted in the melt purification process in a crucible made of a ceramic material (ZrO_2, Al_2O_3). The oxides are formed successively, depending on the prevailing partial pressure of oxygen and on the values of the Gibbs free energies of their formation. Since, however, U oxides have smaller absolute ΔG_f° values than ThO_2, no effective separation of ^{233}U from irradiated Th may be achieved in this manner [20, 75 to 81].

More was expected from the so-called salt transport separation processes. The principle of this method is based on the fact, that a molten salt may extract selectively certain materials from a molten metal, and after transport in the molten salt, these may be stripped by a second, spatially separate, metallic melt. The extraction and stripping involve, respectively, oxidation and reduction reactions. The selectivity and the direction of the transport may be controlled by selecting the kinds and compositions of the salt and, above all, the metal. The molten salt acts as a solvent, as an oxidant, and as a transport medium. Material transport through the phase boundary, between immiscible phases in contact, occurs if its chemical potential in the two phases is different. The substance may be transported in one of the phases mechanically to a second phase boundary, and there transfer to a third phase. In the simplest case, two metal phases of different compositions, separated by a wall, are in contact with a common salt phase, see **Fig. 2-13**. The metallic phases may be constituted from a solvent B or C (a metal or an

Fig. 2-13



Schematic representation of the salt transport process.

alloy), a solute metal X, and a metal R, of which the salt RA (A is the anion) acts as an oxidant in the salt melt.

The redox reaction may be formulated as $X + RA \rightleftharpoons XA + R$ neglecting the stoichiometric coefficients. The activity of X and R must be selected in both metallic phases in such a manner, that the reaction proceeds at one metal/salt phase boundary from left to right and at the other from right to left. This causes a net transport of X in the one direction and of R in the other. If the solubility of X in the metallic phases is small, it will be present initially as a solid in the one phase, and dissolve during the transport process. At the same time it will precipitate in the second phase as the metal or as an intermetallic compound. The transport may proceed as long as the solid phase X has not vanished completely in the first phase or a stationary equilibrium has been established. The reducing agent R and its salt RA have a great significance, since the redox reactions should separate selectively certain components of the irradiated fuel from the molten metal. It turned out, on the basis of thermodynamic considerations and many individual experiments, that Mg is the most suitable metal for this purpose.

Processes according to this principle have been proposed by the Americans and the Germans for the reprocessing of Th-containing nuclear fuels, in particular from high temperature reactors, and for the recovery of ^{233}U. They have both failed when carried out practically [82 to 92].

Attempts with very simple pyrochemical reprocessing methods have also been reported. These involve the dissolution of the oxidic fuel or fertile material in alkali chloride, nitrate, or carbonate melts or in molten $K_2S_2O_7$, and subsequent precipitation of oxides or of uranate. Although some partially satisfactory separations were achieved, such processes were hardly suited for application on a technical scale, since the reaction media must be present at a large excess, leading to an enormous amount of radioactive waste [93 to 98].

2.4.8.4 Electrochemical Separation Processes

Electrochemical processes for the reprocessing of irradiated nuclear fuels have been discussed again and again in the past. The theoretical prospects for an effective separation of the U from the Th, as well as a satisfactory purification from the fission products, are not bad. Efforts were, therefore, not spared to develop electrochemical molten salt processes. Despite extensive efforts, these did not meet with success, except for the refining of U or Pu, which has achieved some technological significance. No data appear in the literature concerning the preparation of pure Th metal.

Only halide salt melts can be considered as electrolytes for carrying out oxidative or reductive depositions at electrodes. Mixtures of the fluorides and the chlorides of the alkali and alkaline earth metals are the most suitable for this purpose. U and Th are deposited almost exclusively cathodically from the liquid salt melt, either in a metallic or in oxidic form. The mechanically freed Th breeding material is set up as an anode in the molten salt electrolyte. Bath temperatures may be as high as 1 000 °C. There have always been difficulties with the production of reliable anodes. A graphite basket, with the Th-containing breeding material tamped solidly into it, has generally been used. If an anodic deposition is preferred, problems arise with the phase separations, since the oxides occur very finely dispersed [99 to 112].

A process flow scheme, analogous to the so-called Hanford Salt Cycle, was proposed for Th-containing breeder elements, which was never subjected to large scale testing, however. If the deposition is carried out in metallic form at the cathode, the problem of phase separation is avoided in a simple manner. The metal adheres strongly to the graphite cathode, which may be

References for 2.4.8 on pp. 346/8

removed periodically from the molten salt electrolyte for stripping. The metal deposits, however, exhibit extensive molten salt inclusions. An alternative is the deposition of Th, U, and also Pu at liquid metal cathodes. Experiments were made mainly with U deposition at a liquid Mn cathode, that forms a low-melting eutectic with U. The Mn can subsequently be recovered from the cathode by fractional distillation [113]. Zn and Bi cathodes were also tested [114, 115]. The relatively more noble fission products, such as Zr, Nb, Mo, Ru, and Rh, accumulate as anode mud, whereas the readily volatile ones, such as iodine, escape from the melt. The other fission products remain in the salt melt and are enriched there. The electrolyte must therefore be renewed periodically, since as the impurities exceed a certain concentration, they too deposit at the cathode and contaminate the deposited uranium.

The possibility of electrodepositing Th from a molten fluoride salt has also been demonstrated. The experiments were carried out at 950 to 1 250 °C at a liquid Ni cathode [116].

Disadvantages of the electrodeposition from salt melts are the corrosion problems arising from the high temperatures, low current efficiencies, long electrolysis periods, low material yield and generally poor decontamination. It should also be hardly possible to operate the processes continuously, a fact which pushes the already high operating costs even higher.

References for 2.4.8:

[1] H. M. Feder, I. G. Dillon (in: S. M. Stoller, R. B. Richards, Reactor Handbook, Vol. 2, Interscience, New York 1961, pp. 313/41). – [2] W. L. Carter (ORNL-TM-241 [1962] 1/57; N.S.A. **16** [1962] No. 23789). – [3] E. W. Murbach, W. N. Hansen (Ind. Eng. Chem. **51** [1959] 177/8). – [4] L. A. Hanson (NAA-SR-Memo-3954 [1959] 1/16; N.S.A. **14** [1960] No. 2463). – [5] K. K. Kelley (U.S. Bur. Mines Bull. No. 476 [1949] 1/241; C.A. **1950** 4768).

[6] L. L. Quill (Natl. Nucl. Energy Ser. Div. IV B **19** [1950] 1/329). – [7] J. P. Coughlin (U.S. Bur. Mines Bull. No. 542 [1954] 1/80; C.A. **1955** 48). – [8] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, I. Jaffe (NBS-Circ.-500 [1952] 1/1266; C.A. **1952** 5417). – [9] E. L. Anderson, K. L. Mattern, W. H. McVey, H. Schneider (LRL-107 [1954] 1/14; N.S.A. **11** [1957] No. 9835). – [10] A. Glassner (ANL-5750 [1957] 1/70; N.S.A. **12** [1958] No. 2733).

[11] R. J. Ackermann, R. J. Thorn (in: J. E. Burke, Progress in Ceramic Science, Vol. 1, Pergamon, New York 1961, pp. 39/88). – [12] A. G. Buyers, E. W. Murbach (NAA-SR-1793 [1957] 1/15; N.S.A. **11** [1957] No. 5260). – [13] A. S. Coffinberry, F. H. Ellinger (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 138/46). – [14] S. T. Konobeevskii (Sess. Akad. Nauk SSSR Mirnomu Ispol'z. At. Energ. Zased. Otd. Khim. Nauk, Moscow 1955, pp. 362/74; Conf. Acad. Sci. USSR Peaceful Uses At. Energy. Sess. Div. Chem. Sci., Moscow 1955, pp. 207/14; C.A. **1956** 14336). – [15] W. J. Hammer, M. S. Malmberg, B. Rubin (J. Electrochem. Soc. **103** [1956] 700/1).

[16] R. C. Reid, D. Duffey, J. E. Vivian (Nucleonics **14** [1956] 22/5). – [17] J. E. Vivian (LRL-88 [1954] 1/30; N.S.A. **10** [1956] No. 2074). – [18] M. Levenson, V. G. Trice, W. J. Meecham (ANL-7137 [1966] 1/168; N.S.A. **20** [1966] No. 43410). – [19] W. P. Barthold (Atomwirtschaft **11** [1966] 598/601). – [20] G. E. Brand, E. W. Murbach, A. G. Buyers (BNL-483 [1958] 157/63; N.S.A. **13** [1959] No. 9458).

[21] G. E. Brand, A. G. Buyers, W. J. Gardner, E. E. Motta (NAA-SR-1997 [1957] 1/25; N.S.A. **12** [1958] No. 147). – [22] G. E. Brand, A. G. Buyers, W. J. Gardner, E. E. Motta, E. W. Murbach (NAA-SR-2168 [1958] 1/37; N.S.A. **12** [1958] No. 6521). – [23] G. E. Brand, D. I. Sinizer, E. W. Murbach, W. N. Hansen, J. R. Foltz, K. L. Mattern (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 407/13). – [24] L. Burris, I. G. Dillon, R. K. Steunenberg (ANL-6818 [1964] 1/28; N.S.A. **18** [1964] No. 22165). – [25] P. Faugeras (Energie Nucl. **7** [1965] 214/27).

[26] J. J. Katz, E. Rabinowitch (The Chemistry of Uranium, Pt. I, McGraw-Hill, New York-Toronto-London 1951, pp. 1/609; Natl. Nucl. Energy Ser. Div. VIII **5** [1951] 1/609). – [27] S. Isserow (Nuclear Reactor Fuel Elements, Metallurgy and Fabrication, Interscience, New York 1962, pp. 622/37). – [28] S. Lawrowski (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 575/82). – [29] E. E. Motta (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 596/603). – [30] A. F. Voigt (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 591/5).

[31] O. E. Dwyer, R. J. Teitel, R. H. Wiswall (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp 604/12). – [32] H. M. Feder (Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva 1955, Vol. 9, pp. 586/90). – [33] F. S. Martin, G. L. Miles (Progr. Nucl. Energy III **1** [1956] 329/41). – [34] P. Chiotti, A. F. Voigt (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 368/75). – [35] P. Chiotti, H. E. Shoemaker (Ind. Eng. Chem. **50** [1958] 137/41).

[36] R. D. Pierce, L. Burris (TID-8540 [1964] 411/76; N.S.A. **18** [1964] No. 33683). – [37] T. A. Milne, C. T. Young (NAA-SR-1680 [1956] 1/19; N.S.A. **11** [1957] No. 12487). – [38] F. W. Dodge, E. W. Murbach, L. A. Hanson (NAA-SR-3219 [1958] 1/20; N.S.A. **13** [1959] No. 13364). – [39] F. J. Keneshea, A. G. Buyers, E. E. Motta (NAA-SR-1374 [1957] 1/18; N.S.A. **11** [1957] No. 9639). – [40] N. D. Potter (NAA-SR-1734 [1957] 1/16; N.S.A. **11** [1957] No. 6294).

[41] G. E. Brand, A. G. Buyers, W. J. Gardner, E. E. Motta, E. W. Murbach (NAA-SR-2168 [1958] 1/37; N.S.A. **12** [1958] No. 6521). – [42] A. G. Buyers (NAA-SR-1724 [1956] 1/29; N.S.A. **11** [1957] No. 7550). – [43] A. G. Buyers, E. E. Motta (NAA-SR-1710 [1957] 1/34; N.S.A. **11** [1957] No. 3756). – [44] S. Lawrowski, L. Burris (At. Energy Rev. **2** [1965] 3/69). – [45] A. A. Jonke (At. Energy Rev. **3** [1965] 3/60).

[46] H. M. Feder, R. J. Teitel (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 383/400). – [47] P. Chiotti, H. E. Shoemaker (ISC-841 [1957] 1/24; N.S.A. **11** [1957] No. 11978). – [48] R. J. Teitel, G. S. Layne (TID-11692 [1960] 1/180; N.S.A. **15** [1961] No. 26115). – [49] P. Chiotti, A. F. Voigt (Progr. Nucl. Energy III **3** [1961] 340/54). – [50] A. F. Messing, O. C. Dean (ORNL-2871 [1960] 1/20; N.S.A. **14** [1960] No. 17931).

[51] W. G. Pfann (J. Metals **4** [1952] 747/54). – [52] J. E. Antill, E. Barnes, M. Gardner (Progr. Nucl. Energy V **2** [1959] 9/18). – [53] R. D. Burch, G. T. Young (NAA-SR-1735 [1956] 1/23; N.S.A. **11** [1957] No. 6295). – [54] L. Burris, C. H. Stockman, I. Dillon (J. Metals **7** [1955] 1017/20). – [55] L. Burris, M. Levenson, J. H. Schraidt, R. K. Steunenberg (Trans. Am. Nucl. Soc. **4** [1961] 192/4).

[56] J. E. Antill (Nucl. Power **1** [1956] 155/61). – [57] R. D. Burch (NAA-SR-1688 [1956] 1/16; N.S.A. **11** [1957] No. 1128). – [58] E. W. Murbach, A. G. Buyers (NAA-SR-1989 [1957] 1/14; N.S.A. **11** [1957] No. 12309). – [59] R. E. Johnson, E. W. Murbach (NAA-SR-3590 [1959] 1/15; N.S.A. **13** [1959] No. 15179). – [60] T. E. Allibone (Brit. 831305 [1960]).

[61] O. E. Dwyer (AIChE [Am. Inst. Chem. Eng.] J **2** [1956] 163/8). – [62] M. D. Adams, J. Fischer, R. J. Meyer, N. D. Phillips (ANL-6017 [1959] 1/19; N.S.A. **13** [1959] No. 19980). – [63] L. A. Hanson (NAA-SR-3954 [1959] 1/16). – [64] A. M. Feder, R. J. Teitel (Progr. Nucl. Energy III **3** [1961] 355/90). – [65] R. E. Johnson, J. D. Chilton (NAA-SR-5506 [1960] 1/19; N.S.A. **15** [1961] No. 7410).

[66] P. Chiotti (U.S. 2990273 [1961]). – [67] P. Chiotti, P. F. Woerner, S. J. S. Parry (IS-302 [1961] 1/54; N.S.A. **15** [1961] No. 22360). – [68] F. W. Dodge, J. D. Chilton, L. A. Hanson (NAA-SR-4942 [1960] 1/24; N.S.A. **14** [1960] No. 14815). – [69] P. Chiotti (TID-7650 [1962] 436/53; N.S.A. **17** [1963] No. 28465). – [70] J. D. Chilton, L. A. Hanson, E. W. Murbach, F. W. Dodge (NAA-SR-6666 [1962] 1/21; N.S.A. **16** [1962] No. 8810).

[71] L. A. Hanson (NAA-SR-6405 [1962] 1/16; N.S.A. **16** [1962] No. 33068). – [72] L. A. Hanson (Trans. AIME **230** [1964] 2/6). – [73] P. Chiotti (U.S. 3120435 [1964]). – [74] A. G. Buyers, J. D. Chilton, W. E. McKee (NAA-SR-2047 [1957] 1/17; N.S.A. **11** [1957] No. 13292). – [75] A. G. Buyers, S. J. Yosim, E. E. Motta (NAA-SR-1529 [1956] 1/26; N.S.A. **11** [1957] No. 13680).

[76] P. F. Woerner, P. Chiotti (ISC-928 [1957] 1/45; N.S.A. **12** [1958] No. 15323). – [77] G. E. Benedict, K. M. Harmon, G. Jansen, L. K. Mudge, F. A. Scott (HW-SA-2915 [1963] 1/24; N.S.A. **17** [1963] No. 26760). – [78] P. Chiotti, S. J. S. Parry (IS-286 [1961] 1/67; N.S.A. **16** [1962] No. 10100). – [79] J. S. Klepfer (Diss. Iowa State Univ. 1964, pp. 1/141). – [80] C. E. Wicks, F. E. Block (U. S. Bur. Mines Bull. No. 605 [1963] 1/146; C.A. **59** [1963] 13406).

[81] R. H. Wiswall, J. J. Egan, W. S. Ginell, F. T. Miles, J. R. Powell (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 17, pp. 421/7). – [82] P. Chiotti, J. S. Klepfer (Ind. Eng. Chem. Process Design Develop. **4** [1965] 232/9). – [83] J. B. Knighton, W. Knoch, R. K. Steunenberg (U.S. 3326673 [1967]). – [84] D. Ramaswami, N. M. Levitz, A. A. Jonke (Nucl. Appl. **1** [1965] 293/300). – [85] A. V. Hariharan, J. B. Knighton, R. K. Steunenberg (ANL-7058 [1965] 1/17; N.S.A. **20** [1966] No. 742).

[86] R. C. Vogel, M. Levenson, J. H. Schraidt, J. Royal (ANL-7175 [1966] 1/242, 1/41; N.S.A. **20** [1966] No. 31164). – [87] W. Knoch (Habilitationsschr. Braunschweig T.H. 1967, pp. 1/132). – [88] L. Burris, K. M. Harmon, G. E. Brand, E. W. Murbach, R. K. Steunenberg (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 501/10). – [89] R. C. Vogel, M. Levenson, J. H. Schraidt, J. Royal (ANL-7225 [1967] 1/253, 23/63; N.S.A. **21** [1967] No. 25935). – [90] D. A. Wenz, R. D. Wolson, I. Johnson (ANL-7463 [1968] 1/13; N.S.A. **23** [1969] No. 19688).

[91] B. Amecke (Diss. Braunschweig T.U. 1971). – [92] R. Lindner (BMBW-FBK-71-18 [1971] 1/28; N.S.A. **26** [1972] No. 23210). – [93] W. L. Lyon, R. H. Moore, E. E. Voiland (HW-58068 [1958] 1/9; N.S.A. **16** [1962] No. 22266). – [94] R. H. Moore, W. L. Lyon (HW-59147 [1959] 1/36; N.S.A. **15** [1961] No. 32537). – [95] J. R. Morrey, R. H. Moore (HW-SA-2597 [1962] 1/15; N.S.A. **17** [1963] No. 10586).

[96] H. J. Riedel (Nukleonik **8** [1966] 425/8). – [97] E. Merz, G. Kaiser, H. J. Riedel, M. Laser (Ger. 1592129 [1972]). – [98] P. Chiotti (U.S. 3982928 [1976]). – [99] C. Marzano, R. A. Noland (ANL-5102 [1953] 1/40; N.S.A. **11** [1957] No. 7568). – [100] L. W. Niedrach, A. D. Glamm (KAPL-1154 [1954] 1/40; N.S.A. **10** [1956] No. 2683).

[101] L. W. Niedrach, A. D. Glamm (Ind. Eng. Chem. **48** [1956] 977/81). – [102] L. W. Niedrach, A. D. Glamm (J. Electrochem. Soc. **103** [1956] 521/8). – [103] E. E. Motta, G. E. Brand, A. G. Buyers, W. J. Gardner (NAA-SR-1872 [1957] 1/23; N.S.A. **11** [1957] No. 7144). – [104] W. Rafalski (CONF-207-9 [1963] 1/43; 2nd Yugosl.-Pol. Symp. Uranium Technol. Met., Zakopane, Pol., 1963, Paper No. 9; N.S.A. **17** [1963] No. 39209). – [105] G. Chauvin, H. Coriou, J. Hure (Metaux Corrosion Ind. **37** [1962] 112/26).

[106] G. A. Buyers, R. A. Barney, W. N. Hansen, W. E. McKee, E. W. Murbach, T. Smith (NAA-SR-1791 [1956] 1/14). – [107] T. Kuroda (Denki Kagaku **33** [1965] 116/21). – [108] K. Nakajima, M. Koizumi, M. Suzuki, T. Kuroda (Denki Kagaku **33** [1965] 122/6; J. Electrochem. Soc. Japan **33** [1965] 54/62). – [109] S. K. Kantan, N. Shreenivasan, G. S. Tendolkar (Chem. Eng. Progr. Symp. Ser. **50** No. 12 [1954] 63/7). – [110] W. N. Hansen (NAA-SR-4885 [1960] 1/20; N.S.A. **14** [1960] No. 17928).

[111] W. N. Hansen (U.S. 2951793 [1960]). – [112] W. N. Hansen, W. L. Long, E. W. Murbach (NAA-SR-4660 [1960] 1/18; N.S.A. **14** [1960] No. 7448). – [113] W. N. Hansen (NAA-SR-7660 [1963] 1/20; N.S.A. **17** [1963] No. 18177). – [114] M. E. Sibert, M. A. Steinberg, R. J. Teitel (J. Electrochem. Soc. **104** [1957] 374/8). – [115] R. E. Johnson (J. Electrochem. Soc. **109** [1962] 989/91).

[116] T. R. Johnson (Reactor Fuel Process. Technol. **10** [1967] 79/84).

2.4.9 Refabrication of New Nuclear Fuels from ^{233}U

2.4.9.1 Radiation Safety Provisions in the Handling of ^{233}U

The handling of ^{233}U, that has been recovered from reactor-irradiated Th for the production of new fuel elements, requires special precautions from the point of view of radiation safety. The radiological and radioecological effects of the risk potential of the ^{233}U, that is contaminated with ^{232}U, were studied and described [1 to 5]. Besides the so-called breeding reaction of ^{232}Th, which by neutron capture and double beta decay leads to ^{233}U, side reactions lead to the uranium isotope ^{232}U, in amounts ranging from 100 to above 1 000 ppm, depending on the circumstances of the irradiation and on the initial ^{230}Th content of the thorium [6, 7]. The nuclide ^{232}U may be formed by mainly two reaction chains:

$$^{230}\mathrm{Th(n,\gamma)}\ ^{231}\mathrm{Th} \xrightarrow{\beta^-} {}^{231}\mathrm{Pa(n,\gamma)}\ ^{232}\mathrm{Pa} \xrightarrow{\beta^-} {}^{232}\mathrm{U}$$

$$^{232}\mathrm{Th(n,2n)}\ ^{231}\mathrm{Th} \xrightarrow{\beta^-} {}^{231}\mathrm{Pa(n,\gamma)}\ ^{232}\mathrm{Pa} \xrightarrow{\beta^-} {}^{232}\mathrm{U}.$$

Both paths lead over the nuclide ^{231}Pa [8, 9]. It was originally assumed that the (n,2n) reaction yielded the major fraction, but more recent studies showed that it is the ^{230}Th content of the thorium that is responsible for the ^{232}U production [10]. For the preparation and properties of ^{232}U see "Uran" Erg.-Bd. A2, 1980, from p. 21. Th is commonly found associated with U; it contains therefore ^{230}Th, a member of the decay chain of ^{238}U. The content of ^{230}Th in natural uranium varies between 0.01 and 100 ppm, depending on the source. The rate of formation of ^{232}U is a function of the irradiation time, the neutron flux, and the neutron energy [6, 8, 11 to 13]. The α-emitter ^{232}U decays with a half-life of 71.7 a into ^{228}Th, which in turn has a half-life of 1.9 a, yielding through a chain of mainly very short-lived α-emitters the stable nuclide ^{208}Pb. Some very energetic γ-quanta are emitted in this decay chain, with energies up to 2.6 MeV. Beside the penetrating γ-rays, it is necessary to consider also neutron emission, arising from (α,n) reactions with light elements that accompany the U or Th as impurities [14, 15].

Six days after the purification, the level of radioactivity has reached back its natural level, that of Th in equilibrium with its daughters, namely about 1 μCi/g. After about 30 days waiting, this level has already reached a 20-fold excess and is still rising [12, 15 to 20]. The refabrication of the two elements, Th and U, must doubtless proceed under heavy radiation shielding. The thickness of this shielding depends on many factors and is approximately 1.0 to 1.5 m normal concrete or 18 to 25 cm lead [18].

The strong radioactivity of the recovered Th has decreased to an acceptable level after 10 half-lives of ^{228}Th, i.e., after about 20 a. On the contrary, the activity of the separated ^{233}U increases initially, by formation of ^{228}Th, for some 10 a, falling thereafter with the half-life of ^{232}U. It is advisable to store the Th, which is relatively inexpensive, for the period required to avoid its expensive refabrication in hot cells. This solution can hardly be realized for the highly valuable fissile material ^{233}U, and its refabrication to new fuel elements must be done as soon as possible after the separation [21, 22].

The ^{233}U, contaminated as it is with traces of ^{232}U, is, on the basis of its strong radioactivity, a "proliferation-resistent" fissile material. It guards itself against misuse by its penetrating γ radiation [23], and is suitable as starting material for so-called "denatured fuel cycles", which use mixed ^{233}U/Th and Pu/^{238}U cycle strategies. Mixed oxide U/Th fuel elements are thereby used, containing maximally 20% ^{235}U or 12% ^{233}U enriched uranium. Even with this high enrichment the material is no longer of weapon grade. The ^{233}U that has been bred from ^{232}Th may be separated from ^{238}U only by isotope separation [24 to 27].

References for 2.4.9 on pp. 353/7

2.4.9.2 Processes for the Refabrication of ^{233}U Fuels

The handling of ^{233}U requires special techniques, because of its radiotoxicity and its radiation emission. There are however no compelling technical difficulties to prevent refabrication, the ^{233}U behaving chemically as natural U. The processes nowadays commonly used for so-called cold fabrication require manual handling and the presence of personnel in the fabrication hall. The handling of the ^{233}U, even after purification from the fission products, must be made under remote control in hot-cells [28]. It has been proposed, in order to avoid this, to repurify the ^{233}U from the decay products of the ^{232}U immediately before the fabrication. The processes that have been recommended are: purification by solvent extraction with tri-n-butyl phosphate [29] or di-sec-butyl phosphonates [30, 31], and purification by cation exchange at normal pressure [32 to 35] or at high pressure [36].

Freshly purified ^{233}U may be handled without shielding against γ radiation for 4 to 6 days. In any case, it is necessary to handle it in air-tight glove boxes, because of its high α-radiotoxicity. After this period the γ radiation level has risen so much, that the radiation exposure of the personnel exceeds the permissible level. This mode of operation, involving the steps: chemical purification of ^{233}U from the decay products (of ^{232}U), processing, and meticulous cleaning of the equipment from residual U, is uneconomical and can serve only as an interim solution. This principle has, however, served till now for the production of test and prototype fuel charges. No commercial refabrication of ^{233}U has taken place anywhere in the world so far, although there exist examples for the production of ^{233}U-containing fuels as prototypes. Older reactor concepts provided for mixed oxides of UO_2 and ThO_2 of various compositions and isotope enrichments in the fissile ^{233}U and ^{235}U. The American Elk River Reactor, for example, was operated with sintered $(U,Th)O_2$ pellets, enclosed in stainless steel cladding. The U content was 5%, enriched to 90% in fissile material [37, 38].

On the use of $(U,Th)O_2$ as nuclear fuel see "Uran" Erg.-Bd. A3, 1981, from p. 180 on.

The required mixed oxides were to be produced either by powder metallurgy or by oxalate precipitation and calcination. Remote controlled refabrication in hot cells was studied by CNEN in Italy [39, 40]. The results achieved were not completely satisfactory [41, 42].

An alternative mixed oxide production method tried to use arc melting. The desired products were metallic or carbidic Th/U mixtures or also $(Th/U)Be_{13}$, containing 10 mol% U [43 to 46]. Melting processes for the fabrication of mixed oxide particles were also tried [47, 48].

It was thought at the beginning of the 60's, that the Th/^{233}U fuel cycle can be realized by employing either of the two fuel element concepts:

1. Th-U-Zr metal alloys or sintered pressed pellets of metallic Th/U in Al_2O_3 [51], or

2. $(Th,U)O_2$ spherulets, preferably produced by the sol-gel technique, and vibrated-in as compactly as possible into metallic claddings.

The considerations and efforts centered about the question, whether direct, semidirect or completely remote-controlled and radiation shielded handling of the ^{233}U is required. The first alternative fuel concept was soon abandoned on reactor technological grounds, and further interest concentrated only on ceramic fuels, i.e., carbides and oxides [52, 53].

Two experimental facilities were set up and operated in the USA for the production of mixed oxides. At the Babcock and Wilcox Company, the TRIP facility demonstrated successfully the production of $(U,Th)O_2$ mixed oxide particles, contaminated with 42 ppm ^{232}U, in unshielded glove boxes [54, 55]. The ^{233}U was first purified by cation exchange from the ^{228}Th and its decay products, and was then processed in a 5 day cycle to fuel elements. After one week's operation, the equipment in the glove boxes had to be completely emptied and cleaned, in order to be charged anew with freshly purified material having an acceptable radiation level. Altogether, nearly 100 kg mixed oxide containing 3% ^{233}U were treated in this manner [56].

At the Oak Ridge National Laboratory the KILOROD facility was used [11], commissioned in 1964. During an 8 month long campaign, Th/U mixed oxides containing 3 wt% ^{233}U were fabricated at a rate of 10 kg a day, the ^{232}U content being 38 ppm [57 to 59]. The plant was operated in a heavily shielded hot cell [60, 61]. It was shown definitely, that industrial refabrication of ^{233}U-containing fuels is possible only by a remote controlled technique behind shielding. The otherwise required repurification of the ^{233}U feed solution before the actual refabrication and the short working periods of only one week produce unacceptable difficulties [62, 63]. The radiation exposure of the personnel, while in the permitted range, reaches intolerable levels. The relationships between the throughput of a plant, the ^{232}U content in the ^{233}U, and various modes of operation have been analyzed in detail. The technological consequences and the resulting construction techniques have been worked out from the engineering aspects [64, 65].

The sol-gel technique was used in both plants for the production of the fuel particles [66 to 71], after it had been found that all the other possibilities, such as controlled crystallization from uranium solutions [72, 73], spray drying of uranium solutions [74], spray calcination of molten uranyl nitrate [75], and power metallurgical processes, yielded relatively unsatisfactory results [76, 77]. The dried and sintered mixed oxide particles were vibrated-in compactly into Zircaloy tubes [78]. Even the shielded KILOROD facility caused a relatively high radiation exposure of the personnel, since the not yet completely worked out refabrication process required frequent interventions for maintenance, repairs, and changes in the hot cells. Furthermore, the process operation was only semi-automatic, and required continuous manual interventions with manipulators. The use of Th- and ^{233}U-containing fuel in water-moderated power reactors lost subsequently its attractivity, but its use in advanced reactor types gained in significance.

2.4.9.3 Production of Fuel Particles for the Recycling of ^{233}U in Advanced Reactor Systems

Fuels and fertile materials are applied in high temperature reactors exclusively as spherical particles of diameters in the range from 200 to 800 μm. Either pure U oxide or carbide kernels are used, or mixed compounds of U with Th or with plutonium [79 to 84]. For an effective retention of the fission products and the prevention of a radioactive contamination of the coolant, each particle is coated with a sealed layer of pyrolytic carbon. In certain cases an intermediate layer of SiC is interposed to improve further the barrier effect of the coating [85 to 89]. For coated nuclear fuel particles see "Uran" Erg.-Bd. A3, 1981, from p. 182 on.

Only wet-chemical precipitation methods are applied nowadays for the production of the above mentioned fuel kernels, starting from the nitrate solutions obtained in the reprocessing. Powder-ceramic processes, that were used at the beginning, are hardly used any more technically [90 to 92]. Unsuitable for the remote operated handling of ^{233}U are also artificial resin polymerization processes [93], based on phenol (e.g., resorcinol)-aldehyde (e.g., formaldehyde) condensation reactions. The resin particles have been decomposed thermally to carbides or oxides.

The wet-chemical processes have all a common basis in principle. Both cold and hot fabrication require the following steps:

- production of the fuel kernels,
- coating of the kernels, and
- production of the fuel compacts, i.e., assembly of the fuel elements.

The first step is the preparation of a casting solution of exact specifications. This is divided through nozzles into individual drops, which solidify while sinking in the reaction chamber due to a gelation reaction. This reaction step may be carried out according to various methods. Following the casting step, a scrubbing step removes undesired components, in particular the nitrate, from the gel particles. In some processes this step is unnecessary, since the nitrate has been removed prior to the formation of the sol by extraction or by steam denitration [94 to 97]. After the scrubbing, the gel particles are transformed into heavy metal oxide or carbide particles by a high temperature process. Up to this step there are considerable differences between the various processes.

For instance, it is necessary to differentiate between external and internal gelation (hydrolysis) [97, 98]. The hydrolysis process depends on the spontaneous solidification of drops of a U-containing solution in hot oil, whereby a gel of colloidal $UO_2(OH)_2$ is formed through homogeneous hydrolysis [99, 100]. The solution is prepared from a uranyl nitrate-urea solution (containing $UO_2(NH_2CONH_2)_2(NO_3)_2$) by stirring-in solid hexamethylenetetramine. A sufficiently concentrated, metastable solution is produced thereby, which solidifies spontaneously above 30 °C. This process cannot be classified as a gel precipitation process, like, e.g., the KEMA process [101 to 103] or the SNAM process [98, 104].

The spherulets that have been obtained are first freed from oil, then from nitrate, by scrubbing, then they are dried and finally sintered in a reducing atmosphere.

The largest amount of experience has accumulated concerning the sol-gel processes, which are very versatile [105 to 110]. An emulsion process, developed by the NUKEM company in the F. R. of Germany, has been applied by it for cold production [97, 111 to 113]. A discontinuous mode of operation and a large amount of maintenance efforts characterise most processes. Therefore their applicability in hot cells is very limited. The following requirements are set:

a) a continuous operation, as a prerequisite for automation,
b) low liability of the equipment to repairs, and
c) design for easy maintenance and low maintenance requirements.

The special requirements from remotely-controlled refabrication processes are described in a series of publications [114 to 121]. Some of the processes that were proposed have already been tested for the production of Pu-containing fuel particles [122, 123].

A critical evaluation of the wet-chemical processes [124 to 126] for "hot" fabrication shows, that it is advantageous to start with a casting solution or a sol, which does not contain significant amounts of additives, such as polyvinyl alcohol. The scrubbing, drying, and calcination steps are facilitated thereby.

A resin grain process was developed in the USA as an alternative to the wet-chemical process, loading the uranyl ions on spherical ion exchange resin particles [127 to 130]. The wet cation exchanger resin grains, classified according to size and form, are loaded from a uranyl nitrate solution. They are then dried in air at 110 °C, and heated slowly in an inert atmosphere to 1 200 °C, causing the resin matrix to coke. Further heating to 1 800 °C causes partial or complete reduction of the uranium oxide by the carbon, kernels of the oxide carbide, UC_xO_y, being formed [131]. The pH of the solution must be controlled within close limits in order to achieve a high loading of the resin. The pH may be controlled by different methods, such as:

- addition of UO_3 powder to a uranyl nitrate solution [132 to 134],
- partial removal of HNO_3 by extraction with an amine [135, 136], or
- use of the NH_4^+ form of the cation exchange resin [137].

A modified process was developed at the KFA-Jülich, where the H^+ form of the resin is employed, and the pH is adjusted by the addition of aqueous NH_3 to the loading solution. A countercurrent loading battery was proposed for the technical application, using a four-stage cascade, which is particularly suitable for remote operation. The attainable resin loading from a 1.5 mol/L $UO_2(NO_3)_2$ solution was 1.15 gU/g dry resin [138].

In the final count, only the resin kernel process [138 to 143] and a gel precipitation process [119, 145 to 147] are suitable for automatizable and remote operation in hot cells, the former not completely satisfactorily [144]. Two variations must be applied, on account of the difference between Th and U.

Production of (Th, U)O_2 Kernels

A solution containing $Th(NO_3)_4$ and $UO_2(NO_3)_2$ (Th/U ≥ 3) is transformed into a sol by leading in gaseous NH_3 under stirring at 95 °C. In this manner 90% of the precipitation reaction $Th(NO_3)_4 + 4\,NH_4OH \rightarrow ThO_2 \cdot x\,H_2O + 4\,NH_4NO_3$, and the corresponding one for U, are accomplished. The 2 to 3 mol/L sol is divided into drops in a 1 wt% aqueous NH_3 solution to complete the reactions. The gel spheres hereby produced are washed free from NH_4NO_3 by water, dried in air, and sintered. Use of the possibilities that the sol-gel chemistry presents, and the choice and the construction of the equipment, makes it possible to do without any materials or chemicals other than NH_3, water, and air.

Production of UO_2 or UC_xO_y Kernels

Solutions of UO_2^{2+} cannot be converted into sols, and gel-like precipitates with NH_3 are produced only in the presence of complexing agents. Process development has involved here the use of a urea-containing casting solution, which is introduced dropwise into a 7 mol/L aqueous NH_3 solution. An appreciable concentration of NH_4NO_3 must be present in the drops during the precipitation, which may be recovered by recycling the wash water. The scrubbing removes all the additives, facilitating the subsequent treatment of the kernels. Drying is done with air, and the subsequent high temperature treatment depends on the end product desired. The carbon that is required for the carbo-thermic reduction to UC_xO_y or UC_2 must be introduced into the casting solution in a dispersed form.

Production methods for HTR fuels have gained recently some additional interest, in connection with the use of denatured Th fuel cycles for water moderated reactors.

References for 2.4.9:

[1] E. D. Arnold (Nucl. Safety **5** [1964] 382/9). – [2] F. E. Owen (HW-81933 [1964] 1/11; N.S.A. **19** [1965] No. 26575). – [3] J. E. Till (ORNL-5016 [1975] 9/10). – [4] J. E. Till (ORNL-TM-4768 [1975] 1/26; N.S.A. **31** [1975] No. 14406). – [5] J. E. Till (ORNL-TM-5049 [1976] 1/33).

[6] J. M. Boswell, R. D. McCrosky, S. C. Aiken, J. T. Stringer, W. K. Woods (CONF-660524-1 [1966] 1/22; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 745/63; N.S.A. **20** [1966] No. 25466). – [7] R. A. Kirchner, K. J. Freiberg (RFP-538 [1965] 1/19). – [8] U. Grahmann, U. Tillessen, E. Zimmer (Reaktortagung, Nürnberg 1975, pp. 387/90). – [9] A. G. Croff (CONF-760622-3 [1976] 1/20). – [10] A. M. dos Santos (JUEL-1284 [1976] 1/73).

[11] C. C. Haws, J. L. Matherne, F. W. Miles, J. E. Van Cleve (ORNL-3681 [1965] 1/168; N.S.A. **19** [1965] No. 44638). – [12] J. Fresco, E. Jelter, J. Harley (Nucleonics **10** [1952] 60/4). – [13] G. Schlosser, E. Behrens (Nukleonik **9** [1967] 36/42). – [14] E. D. Arnold (Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 13, pp. 137/50). – [15] R. H. Meichle (Trans. Am. Nucl. Soc. **8** [1965] 520/1).

[16] E. D. Arnold (ORNL-1869 [1955]; Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva 1958, Vol. 13, pp. 237/50). – [17] E. D. Arnold, R. P. Wischow (ORNL-2056 [1956] 1/41; N.S.A. **17** [1963] No. 6185). – [18] E. D. Arnold (TID-7650 [1962] 253/84; N.S.A. **17** [1963] No. 28460). – [19] M. J. Bell, J. P. Nichols (CONF-700502 [1970] 74/84; N.S.A. **24** [1970] No. 30003). – [20] T. Hashimoto, T. Imai (Radiochimica Acta **21** [1974] 69/72).

[21] A. L. Lotts, D. A. Douglas, R. L. Pilloton (ORNL-TM-1115 [1965] 1/49; N.S.A. **19** [1965] No. 25706). – [22] J. P. Nichols, R. E. Brooksbank, D. E. Ferguson (Nucl. Appl. **1** [1965] 176/8). – [23] E. Merz (Intern. Conf. Nucl. Power. Its Fuel Cycle, Salzburg 1977, Vol. 2, pp. 37/54). – [24] P. R. Kasten, F. J. Homan, E. J. Allen (ORNL-TM-5565 [1977] 1/253; INIS Atomindex **8** [1977] No. 316134). – [25] R. A. Matzie, J. R. Rec, A. N. Terney (TIS-5161 [1977]; Trans. Am. Nucl. Soc. **26** [1977] 306/7).

[26] E. Teuchert (JUEL-1470 [1977] 1/54; INIS Atomindex **9** [1978] No. 395857). – [27] E. Merz (Naturwissenschaften **65** [1978] 424/31). – [28] J. D. Sease, A. L. Lotts (ORNL-TM-5334 [1976] 1/25; INIS Atomindex **7** [1976] No. 274984). – [29] H. C. Rathvon, A. G. Blasewitz, R. Maher, J. C. Eargle, A. E. Wible (CONF-660524-19 [1966] 1/75; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 765/824; N.S.A. **20** [1966] No. 43415). – [30] R. H. Rainey (ORNL-TM-177 [1962] 25/47).

[31] J. G. Moore (ORNL-4095 [1967] 1/44; N.S.A. **22** [1968] No. 57). – [32] D. C. Overholt (ORNL-1364 [1952] 1/22; N.S.A. **11** [1957] No. 8394). – [33] T. Murase, E. L. Lind, F. Nelson (J. Chromatog. **14** [1964] 478/81). – [34] D. Dyrssen (Svensk. Kem. Tidskr. **7** [1950] 153/60). – [35] F. R. Bruce (Progr. Nucl. Energy III **2** [1958] 363/76).

[36] R. H. Rainey (ORNL-4731 [1972] 1/47). – [37] A. B. Shuck, J. E. Ayer (Nucl. Sci. Eng. **12** [1962] 398/404). – [38] J. R. Fisher, E. D. Kendrick (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 681/94). – [39] C. Cogliati, R. DeLeone, S. Ferrari, M. Gabaglio, A. Liscia (RT/CHI-62-19 [1962] 1/13; N.S.A. **17** [1963] No. 8253). – [40] R. S. Miller, A. Liscia (TID-7650 [1963] 553/84; N.S.A. **17** [1963] No. 28471).

[41] G. Orsenigo, S. Cambi (CONF-660524-9 [1968] 1/42; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 547/73; N.S.A. **20** [1966] No. 39006). – [42] J. K. Davidson, A. C. Shafer, G. Orsenigo, A. Pedretti (TID-7650 [1963] 285/332; N.S.A. **17** [1963] No. 28461). – [43] M. S. Farkas (CONF-660524-8 [1966] 1/25; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 445/62; N.S.A. **20** [1966] No. 47010). – [44] M. S. Farkas, A. A. Bauer, R. F. Dickerson (BMI-1568 [1962] 1/20; N.S.A. **16** [1962] No. 12651). – [45] M. M. Griesenauer, M. S. Farkas, F. A. Rough (BMI-1680 [1964] 1/33; N.S.A. **18** [1964] No. 35925).

[46] J. O. Gibson (Carbides Nucl. Energy Proc. Symp., Harwell, U.K., 1963 [1964], pp. 816/25; C.A. **63** [1965] 1436). – [47] H. Bildstein (Ber. Deut. Keram. Ges. **41** [1964] 108/11). – [48] K. Knotik, H. Bildstein, P. Koss (Kerntechnik **7** [1965] 361/65). – [49] E. C. Moncrief, G. Schileo (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 157/84; CONF-660524 [1968] 157/84). – [50] L. R. Weissert, G. Schileo (Fabrication of Thorium Fuel Elements, Am. Nucl. Soc., Hinsdale, Ill., 1968, pp. 52/125).

[51] J. P. Bertino, J. A. Kircher (LA-2245 [1958] 1/46; N.S.A. **13** [1959] No. 5319). – [52] G. Schileo, L. R. Weissert (TPCC-723 [1963] 1/10). – [53] E. J. Kosiancic, R. H. Dodd, C. J. Halva (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 417/43). – [54] G. Schileo (STI-DOC-10-52 [1965] 1/382; N.S.A. **20** [1966] No. 32807). – [55] J. M. Kerr, L. D. Barnes, J. W. Ryon (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 537/45; CONF-660524 [1968] 537/45).

[56] G. Schileo (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 299/319). – [57] A. R. Irvine, A. L. Lotts (TID-7650 [1962] 333/50; N.S.A. **17** [1963] No. 28462). – [58] D. E. Ferguson (Progr. Nucl. Energy, Vol. 4, Pergamon, New York [1970], pp. 37/78). – [59] S. Isserow, W. B. Nowak (NMI-1198 [1957] 1/9). – [60] A. L. Lotts, J. D. Sease, R. E. Brooksbank, A. R. Irvine, F. W. Davis (TID-7650 [1962] 351/83; N.S.A. **17** [1963] No. 28463).

[61] J. D. Sease, A. L. Lotts, F. C. Davis (ORNL-3539 [1964] 1/102; N.S.A. **18** [1964] No. 16455). – [62] A. L. Lotts, D. A. Douglas (ORNL-TM-1141 [1965] 1/52; N.S.A. **19** [1965] No. 31520). – [63] R. E. Brooksbank, J. P. Nichols, A. L. Lotts (CONF-660524-3 [1968] 1/34; N.S.A. **20** [1966] No. 31690). – [64] J. M. Chandler, F. E. Harrington (ORNL-TM-1109-Rev. [1966] 1/34; N.S.A. **20** [1966] No. 33846). – [65] C. C. Haws, J. W. Snider (Trans. Am. Nucl. Soc. **10** [1967] 95/6).

[66] O. C. Dean, C. C. Haws, A. T. Kleinsteuber, J. W. Snider (TID-7650 [1962] 519/42; N.S.A. **17** [1963] No. 28469). – [67] M. Kerr, T. N. Washburn (TID-7650 [1962] 606/13; N.S.A. **17** [1963] No. 28473). – [68] D. E. Ferguson, O. C. Dean, D. A. Douglas (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 10, pp. 307/15). – [69] G. Cogliati, R. DeLeone, G. R. Guidotti, R. Lanz, L. Lorenzini, E. Mezi, G. Scibona (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 552/8). – [70] G. Cogliati, R. Lanz, E. Mezi (RT-CHI-65-30 [1965] 1/9; N.S.A. **20** [1966] Nr. 2226).

[71] G. Cogliati, L. Lupparelli, E. Mezi, A. Recrosio (DP-Report-401 [1966] 1/33). – [72] Stichting Reactor Centrum Nederland (U.S. 3097062 [1963]; Brit. 919523 [1963]; Ger. 1147930 [1963]; C.A. **58** [1963] 13399). – [73] M. E. A. Hermans, T. van der Plas, Stichting Reactor Centrum Nederland (U.S. 3126250 [1964]; Brit. 968679 [1963]; Ger. 1171890 [1963]; C.A. **61** [1964] 2763). – [74] R. S. Hansen, R. E. Minturn, USAEC (U.S. 2824784 [1958]; N.S.A. **12** [1958] No. 10253). – [75] K. Knotik, H. Bildstein, P. Koss (Kerntechnik **7** [1965] 361/5).

[76] N. R. Williams (AERE-M-888 [1961] 1/22). – [77] J. J. Huet, F. Gorlé (Kerntechnik **7** [1965] 365/7). – [78] W. J. Robertson, W. J. S. Smith, T. H. Sublett (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 735/43; CONF-660524 [1968] 735/43; N.S.A. **20** [1966] No. 43850). – [79] R. E. Pahler (TID-7654 [1963] 1/9; N.S.A. **17** [1963] No. 25693). – [80] T. D. Gulden, J. L. Scott, C. Moreau (CONF-740501 [1974] 176/200; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 176/200; C.A. **82** [1975] No. 104467).

[81] R. C. Dahlberg, K. Asmusen, D. Lee, L. Brooks, R. K. Lane (Nucl. Eng. Design **26** No. 1 [1974] 58/77). – [82] E. Merz, M. Laser, E. Zimmer (Kerntechnik **15** [1973] 249/56). – [83] E. R. Merz, G. Kaiser, E. Zimmer (CONF-740501 [1974] 268/87; ANS Top. Meeting Gas-Cooled Reactors HTGR GCFBR, Gatlinburg, Tenn., 1974, pp. 268/87; C.A. **82** [1975] No. 128951). – [84] E. Merz (Chemiker-Ztg. **101** [1977] 81/91). – [85] K. G. Hackstein (Atomwirtsch. Atomtech. **16** [1971] 245/6).

[86] M. Kadner, J. Baier (Kerntechnik **18** [1976] 413/26). – [87] A. L. Lotts, T. N. Washburn, L. Geller, H. H. Klepfer, W. H. Layman (Proc. 4th Intern. Conf. Peaceful Uses At. Energy, Geneva 1971, Vol. 8, pp. 201/14). – [88] F. J. Homan, T. B. Lindemer, E. L. Long, T. N. Tiegs, R. L. Beatty (Nucl. Technol. **35** [1977] 428/41). – [89] H. Nickel (JUL-687-RW [1970] 1/44; N.S.A. **25** [1971] No. 24621). – [90] G. Fleischhauer, K. G. Hackstein, H. Huschka, P. Venet (Ber. Deut. Keram. Ges. **43** [1966] 231/8).

[91] G. W. Horsley, R. C. Burnett (DP-Report-542 [1968] 1/37). – [92] T. N. Washburn, R. C. Burnett (DP-Report-551 [1968] 1/52). – [93] H. Bildstein, K. Knotik (Kerntechnik **9** [1967] 57/62). – [94] P. A. Haas, F. G. Kitts, H. Beutler (Chem. Eng. Progr. Symp. Ser. **63** No. 80 [1967] 16/7; C.A. **68** [1968] No. 55708). – [95] P. A. Haas (ORNL-TM-3978 [1972] 1/38; N.S.A. **27** [1973] No. 12399).

[96] B. C. Finney, P. A. Haas (ORNL-4802 [1972] 1/44; N.S.A. **27** [1973] No. 15141). – [97] F. J. Herrmann, P. Vygen (Kerntechnik **12** [1970] 159/64). – [98] G. Brambilla, P. Gerontopolus, D. Neri (Energia Nucl. [Milan] **17** [1970] 217/24). – [99] R. Förthmann, A. Naoumidis, H. Nickel, W. Burck (JUL-655-RW [1970] 1/17; C.A. **73** [1970] No. 136392). – [100] R. Förthmann (JUL-950-RW [1973] 1/39; N.S.A. **28** [1973] No. 30425).

[101] M. E. A. Hermans, H. S. G. Slooten (Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva 1964, Vol. 11, pp. 450/7). – [102] F. W. van der Brugghen, M. E. A. Hermans, J. B. W. Kanij, A. J. Noothout, T. van der Plas, H. S. G. Slooten (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 377/90). – [103] F. W. van der Brugghen, J. B. W. Kanij, A. J. Noothout, M. E. A. Hermans, O. Votocek (CONF-700502 [1970] 253/63; N.S.A. **24** [1970] No. 30015). – [104] A. G. Facchini (Energia Nucl. [Milan] **17** [1970] 225/33). – [105] P. A. Haas, C. C. Haws, F. G. Kitts, A. D. Ryon (ORNL-TM-1978 [1968] 1/49; N.S.A. **22** [1968] No. 12476).

[106] R. G. Wymer (ORNL-TM-2205 [1968] 1/63; N.S.A. **22** [1968] No. 26073). – [107] H. Huschka, P. Vygen (Nucl. Technol. **35** [1977] 238/45). – [108] J. P. McBride, W. D. Bond, P. A. Haas, S. D. Clinton (ORNL-3874 [1966] 1/57; N.S.A. **20** [1966] No. 15008). – [109] P. A. Haas, M. H. Lloyd, W. D. Bond, J. P. McBride (CONF-660524-4 [1966] 1/42; 2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 391/415; N.S.A. **20** [1966] No. 31689). – [110] J. R. Parrott, F. L. Daley, J. T. Furman, J. W. Snider (Trans. Am. Nucl. Soc. **12** [1969] 27/8).

[111] H. Förster, K. G. Hackstein, M. Kadner (Ger. Offen. 2037232 [1970]). – [112] E. Zimmer, P. Naefe, H. Ringel (Reaktortagung, Karlsruhe 1973, pp. 361/4). – [113] P. Naefe (JUEL-1229 [1975] 1/78; C.A. **84** [1976] No. 66537). – [114] J. D. Sease, R. A. Bradley, E. Zimmer (Trans. Am. Nucl. Soc. **22** [1975] 336/7). – [115] A. B. Shuck, J. E. Ayer (Nucl. Sci. Eng. **12** [1962] 401/2).

[116] P. A. Haas, S. D. Clinton (Ind. Eng. Chem. Prod. Res. Develop. **5** [1966] 236/44). – [117] J. D. Sease, R. B. Pratt, A. L. Lotts (2nd Intern. Thorium Fuel Cycle Symp., Gatlinburg, Tenn., 1966, pp. 341/57; CONF-660524 [1968] 341/57; N.S.A. **20** [1966] No. 25525). – [118] P. Naefe, E. Zimmer (JUEL-1286 [1976] 1/34). – [119] E. Zimmer, P. Naefe, H. Ringel (Reaktortagung, Hannover 1978, pp. 502/5). – [120] P. Naefe, E. Zimmer (Nucl. Technol. **42** [1979] 163/8).

[121] S. R. McNeany, J. D. Jenkins (ORNL-TM-6136 [1978] 1/55; INIS Atomindex **9** [1978] No. 379328). – [122] M. H. Lloyd, W. T. McDuffee, O. K. Tallent, L. E. Morse, R. G. Haire (CONF-700502 [1970] 100/12; N.S.A. **24** [1970] No. 30004). – [123] M. E. A. Hermans, J. B. W. Kanij, F. W. van der Brugghen (CH-EIR-33 [1973] 1/24). – [124] E. Zimmer, P. Naefe, H. Ringel (Trans. Am. Nucl. Soc. **32** [1979] 234/5). – [125] H. Ringel (JUEL-1258 [1975] 1/143; C.A. **85** [1976] No. 100842).

[126] E. Zimmer, P. Naefe, H. Ringel (Radiochim. Acta **25** [1978] 161/9). – [127] W. D. Bond, B. C. Finney, P. A. Haas, C. C. Haws (CONF-700502 [1970] 123/36; N.S.A. **24** [1970] No. 30005). – [128] P. R. Kasten, C. B. Pollock (ORNL-4760 [1973] 96/101). – [129] K. J. Notz, P. A. Haas, J. H. Shaffer (Radiochim. Acta **25** [1978] 153/9). – [130] P. A. Haas (ORNL-5300 [1977] 1/86; INIS Atomindex **9** [1978] No. 365103).

[131] J. H. Coobs, J. L. Scott, W. P. Eatherly (ORNL-4760 [1973] 96/100). – [132] P. A. Haas (ORNL-TM-3817 [1972] 1/39; N.S.A. **26** [1972] No. 55901). – [133] K. J. Notz (ORNL-4911 [1973] 29/31). – [134] H. D. Ringel, P. A. Haas (ORNL-TM-6264 [1978] 1/32). – [135] P. A. Haas (ORNL-TM-4955 [1975] 1/48; N.S.A. **32** [1975] No. 27699).

[136] P. A. Haas (Trans. Am. Nucl. Soc. **22** [1975] 317/8). – [137] R. O. Whipple (GA-A-13359 [1975] 1/17). – [138] N. Abd el Monem (JUEL-1494 [1978] 1/93; INIS Atomindex **10** [1979] No. 421389). – [139] D. R. Johnson, W. J. Lackey, D. J. Sease (ORNL-TM-4989 [1975] 1/28; INIS Atomindex **7** [1976] No. 225023). – [140] J. C. Mullins, R. W. Glass (ORNL-TM-5099 [1976] 1/105; INIS Atomindex **8** [1977] No. 293984).

[141] K. J. Notz (U.S. 3995009 [1977]). – [142] R. D. Spence, P. A. Haas (ORNL-TM-5973 [1978] 1/57; INIS Atomindex **9** [1978] No. 382048). – [143] P. A. Haas, J. P. Drago, D. L. Million, R. D. Spence (ORNL-TM-6061 [1978] 1/63; INIS Atomindex **9** [1978] No. 378467). – [144] J. A. Carpenter (ORNL-TM-6067 [1977] 1/42; INIS Atomindex **9** [1978] No. 365018). – [145] P. Naefe, B. Müller (JUEL-CONF-30 [1979] 59/70).

[146] E. Zimmer, P. Naefe, H. Ringel (Reaktortagung, Hannover 1978, pp. 502/5). – [147] E. Zimmer (Ger. 2323072 [1976]).

Table of Conversion Factors

Following the notation in Landolt-Börnstein [7], values which have been fixed by convention are indicated by a bold-face last digit. The conversion factor between calorie and Joule that is given here is based on the thermochemical calorie, $cal_{th\,ch}$, and is defined as 4.184**0** J/cal. However, for the conversion of the ,,Internationale Tafelkalorie'', cal_{IT}, into Joule, the factor 4.1868 J/cal is to be used [1, p. 147]. For the conversion factor for the British thermal unit, the Steam Table Btu, BTU_{ST}, is used [1, p. 95].

Force	N	dyn	kp
1 N (Newton)	1	10^{5}	0.1019716
1 dyn	10^{-5}	1	1.019716 × 10^{-6}
1 kp	9.8066**5**	9.8066**5** × 10^{5}	1

Pressure	Pa	bar	kp/m^2	at	atm	Torr	lb/in^2
1 Pa (Pascal) = 1 N/m^2	1	10^{-5}	1.019716 × 10^{-1}	1.019716 × 10^{-5}	0.986923 × 10^{-5}	0.750062 × 10^{-2}	145.0378 × 10^{-6}
1 bar = 10^{6} dyn/cm^2	10^{5}	1	10.19716 × 10^{3}	1.019716	0.986923	750.062	14.50378
1 kp/m^2 = 1 mm H_2O	9.8066**5**	0.98066**5** × 10^{-4}	1	10^{-4}	0.967841 × 10^{-4}	0.735559 × 10^{-1}	1.422335 × 10^{-3}
1 at = 1 kp/cm^2	0.98066**5** × 10^{5}	0.98066**5**	10^{4}	1	0.967841	735.559	14.22335
1 atm = 76**0** Torr	1.0132**5** × 10^{5}	1.0132**5**	1.033227 × 10^{4}	1.033227	1	760	14.69595
1 Torr = 1 mm Hg	133.3224	1.333224 × 10^{-3}	13.59510	1.359510 × 10^{-3}	1.315789 × 10^{-3}	1	19.33678 × 10^{-3}
1 lb/in^2 = 1 psi	6.89476 × 10^{3}	68.9476 × 10^{-3}	703.069	70.3069 × 10^{-3}	68.0460 × 10^{-3}	51.7149	1

Work, Energy, Heat	J	kWh	kcal	Btu	MeV
1 J (Joule) = 1 Ws = 1 Nm = 10^7 erg	1	2.778×10^{-7}	2.39006×10^{-4}	9.4781×10^{-4}	6.242×10^{12}
1 kWh	$3.\mathbf{6} \times 10^{6}$	1	860.4	3412.14	2.247×10^{19}
1 kcal	4184.**0**	1.1622×10^{-3}	1	3.96566	2.6117×10^{16}
1 Btu (British thermal unit)	1055.06	2.93071×10^{-4}	0.25164	1	6.5858×10^{15}
1 MeV	1.602×10^{-13}	4.450×10^{-20}	3.8289×10^{-17}	1.51840×10^{-16}	1

Power	kW	h. p. (PS)	kp m/s	kcal/s
1 kW = 10^{10} erg/s	1	1.35962	101.972	0.239006
1 h. p. (PS)	0.73550	1	**75**	0.17579
1 kp m/s	$9.8066\mathbf{5} \times 10^{-3}$	0.01333	1	2.34384×10^{-3}
1 kcal/s	4.184**0**	5.6886	426.650	1

References:

[1] A. Sacklowski, Die neuen SI-Einheiten, Goldmann, München 1979. (Conversion tables in an appendix.)
[2] International Union of Pure and Applied Chemistry, Manual of Symbols and Terminology for Physicochemical Quantities and Units, Pergamon, London 1979; Pure Appl. Chem. **51** [1979] 1/41.
[3] The International System of Units (SI), National Bureau of Standards Specl. Publ. 330, [1972].
[4] H. Ebert, Physikalisches Taschenbuch, 5th Ed., Vieweg, Wiesbaden 1976.
[5] Kraftwerk Union Information, Technical and Economic Data on Power Engineering, Mülheim/Ruhr 1978.
[6] E. Padelt, H. Laporte, Einheiten und Größenarten der Naturwissenschaften, 3rd Ed., VEB Fachbuchverlag, Leipzig 1976.
[7] Landolt-Börnstein, 6. Aufl., II. Bd., 1. Tl., 1971, S. 1/14.