



ADVANCES IN SONOCHEMISTRY

Volume 6

Timothy J. Mason &
Andreas Tiehm

ADVANCES IN
SONOCHEMISTRY

Volume 6 • 2001

ADVANCES IN SONOCHEMISTRY

Series editor: TIMOTHY J. MASON

Volumes 1–5 were published by:

JAI PRESS INC.

100 Prospect Street

Stamford, Connecticut 06904-0811

USA

ADVANCES IN SONOCHEMISTRY

VOLUME 6

ULTRASOUND IN ENVIRONMENTAL PROTECTION

Edited by:

TIMOTHY J. MASON
*School of Natural and
Environmental Sciences
Coventry University
Coventry, UK*

ANDREAS TIEHM
*Water Technology Center
Karlsruhe, Germany*

2001



JAI

An Imprint of Elsevier Science
Amsterdam – London – New York – Oxford – Paris – Shannon – Tokyo

ELSEVIER SCIENCE B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

© 2001 Elsevier Science B.V. All rights reserved.

This work is protected under copyright by Elsevier Science, and the following terms and conditions apply to its use:

Photocopying

Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier Science Global Rights Department, PO Box 800, Oxford OX5 1DX, UK; phone: (+44) 1865 843830, fax: (+44) 1865 853333, e-mail: permissions@elsevier.co.uk. You may also contact Global Rights directly through Elsevier's home page (<http://www.elsevier.nl>), by selecting 'Obtaining Permissions'.

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 207 631 5555; fax: (+44) 207 631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works

Tables of contents may be reproduced for internal circulation, but permission of Elsevier Science is required for external resale or distribution of such material.

Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic Storage or Usage

Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.

Address permissions requests to: Elsevier Science Global Rights Department, at the mail, fax and e-mail addresses noted above.

Notice

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

First edition 2001

Library of Congress Cataloging in Publication Data

A catalog record from the Library of Congress has been applied for.

ISBN: 0-444-50705-1

© The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper). Printed in The Netherlands.

CONTENTS

LIST OF CONTRIBUTORS	vii
PREFACE	
<i>Timothy J. Mason and Andreas Tiehm</i>	ix
THE USES OF ULTRASOUND FOR BIOLOGICAL DECONTAMINATION	
<i>Sukhvinder S. Phull and Timothy J. Mason</i>	1
COMBINATION OF ULTRASONIC AND BIOLOGICAL POLLUTANT DEGRADATION	
<i>Andreas Tiehm</i>	25
ULTRASONIC DISINTEGRATION OF SEWAGE SLUDGE FOR ENHANCED ANAEROBIC BIODEGRADATION	
<i>Uwe Neis, Klaus Nickel and Andreas Tiehm</i>	59
THE SONOCHEMICAL DEGRADATION OF AROMATIC AND CHLOROAROMATIC CONTAMINANTS	
<i>Christian Petrier and Dominick Casadonte</i>	91
SONOLYTIC OZONATION FOR THE REMEDIATION OF HAZARDOUS POLLUTANTS	
<i>Linda K. Weavers</i>	111
ULTRASONICALLY ASSISTED LEACHING	
<i>Kodavanti M. Swamy and Kallepalli L. Narayana</i>	141
ULTRASONIC PHASE SEPARATION	
<i>Johannes F. Spengler, Martin Jekel and W. Terence Coakley</i>	181

ULTRASOUND IN FILTRATION AND SLUDGE DEWATERING <i>Pentti Pirkonen</i>	221
THE DESIGN OF ULTRASONIC REACTORS FOR ENVIRONMENTAL REMEDIATION <i>Timothy J. Mason</i>	247
INDEX	269

LIST OF CONTRIBUTORS

- Dominick Casadonte* Texas Tech. University
Department of Chemistry and Biochemistry
Lubbock
TX 79409, USA
- W. Terence Coakley* Cardiff University
School of Biosciences
P.O. Box 915
Cardiff CF10 3 TL
UK
- Martin Jekel* Technical University Berlin
Department of Water Quality Control
KF 4, Strasse des 17. Juni 135
D-10623 Berlin
Germany
- Timothy J. Mason* School of Natural and
Environmental Sciences
Coventry University
Coventry CV1 5FB
United Kingdom
- Kallepalli L. Narayana* Regional Research Laboratory
Bhubaneswar 751 013
India
- Uwe Neis* Department of Sanitary and
Environmental Engineering
Technical University of Hamburg-Harburg
D-21071 Hamburg
Germany

- Klaus Nickel* Department of Sanitary and
Environmental Engineering
Technical University of Hamburg-Harburg
D-21071 Hamburg
Germany
- Christian Petrier* Laboratoire de Chimie Moléculaire et
Environnement
ESIGEC, Université de Savoie
73376 le Bourget du Lac
France
- Sukhvinder S. Phull* School of Natural and
Environmental Sciences
Coventry University
Coventry CV1 5FB
United Kingdom
- Pentti Pirkonen* VTT Energy
Energy Use
Dewatering Research Group
P.O. Box 1603
Jyväskylä
FIN 40101, Finland
- Johannes F. Spengler* Cardiff University
School of Biosciences
P.O. Box 915
Cardiff CF10 3 TL
UK
- Kodavanti M. Swamy* Regional Research Laboratory
Bhubaneswar 751 013
India
- Andreas Tiehm* Water Technology Center
Karlsruher Strasse 84
D-76139 Karlsruhe
Germany
- Linda K. Weavers* Department of Civil and Environmental
Engineering and Geodetic Science
The Ohio State University
470 Hitchcock Hall
2070 Neil Ave
Columbus
OH 43210, USA

PREFACE

Previous volumes of *Advances in Sonochemistry* have contained individual chapters that relate to different areas of Sonochemistry. This has given readers of the series to date in-depth information over a range of applications. This new volume is different in approach in that it is a theme issue devoted to one of the more significant developments in the subject—environmental remediation. The book provides an overview on both the fundamentals and applications of ultrasound in environmental protection. Recent research and state-of-the-art information on the scientific basis, modes of use, and engineering developments are presented. A broad range of topics is covered: reactor design, sonochemical pollutant degradation, integrated ultrasonic/biological treatment, ultrasound in disinfection, leaching by ultrasound, and ultrasonically enhanced removal of suspended solids.

Ultrasound is generated and applied at frequencies from 20 kHz to several MHz. The physico-chemical parameters of the sonicated media, reactor design, applied intensity, and duration of sonication, dramatically influence the effects which can be achieved. We sincerely hope that this compilation will contribute to a better understanding and further development of sonochemistry as a clean technology not only for environmental remediation but also more generally.

The foundation of this compilation was formed during a workshop that was held at the Technical University of Hamburg-Harburg, Germany, in March 1999.

This was the very first workshop to be devoted to “Ultrasound in Environmental Engineering” and brought together experience and knowledge from a broad spectrum of disciplines including chemistry, biology, engineering, equipment manufacturing, and plant design. The success of the meeting encouraged us to produce this extended compilation.

This publication would not have been possible without the co-operation of all authors. We would like to thank all of them very much for their excellent contributions. Andreas Tiehm wishes to express his sincere thanks to Uwe Neis for giving him the opportunity to organise the 1999 workshop. We also wish to express our thanks to Elsevier Science for including this compilation in the *Advances in Sonochemistry* series.

Timothy J. Mason and Andreas Tiehm

THE USES OF ULTRASOUND FOR BIOLOGICAL DECONTAMINATION

Sukhvinder S. Phull and Timothy J. Mason

OUTLINE

1. Introduction	1
1.1 Some Definitions in Microbiology	4
2. Ultrasound and Biological Decontamination	8
2.1 Mechanisms of Ultrasonic Action	8
2.2 Decontamination of Surfaces	11
2.3 Decontamination of Solutions	14
3. Conclusion	21
References	21

1. INTRODUCTION

Water covers nearly 70% of the Earth's surface and is used to support all organic life forms. It is the most important resource in the world since no life can exist without it. We drink it, wash in it and most parts of the economy could not operate without it. During use man pollutes water and once

contaminated it is often no longer useable. It can carry and transmit diseases and it can disrupt the ecology in rivers and lakes. In most people's mind the term environmental pollution is associated with chemical contamination and removal of such pollution is dealt with in other chapters. In this chapter we will concentrate on the use of ultrasound for the removal and/or control of the other major environmental problem—biological contamination. Biological contaminants or pollutants fall mainly in the categories bacteria, viruses, algae and protozoa.

Biological contamination can transmit a wide variety of diseases and illnesses to man; some of these are listed in Table 1. Disease causing micro-organisms, known as pathogens, can be present in air, water and even in food. It has been estimated that approximately 30 000 people die every day from water-related diseases [1] and, significantly, not all of these deaths occur in “developing” countries. Therefore, it is of utmost importance to produce, through treatment processes, a final potable water which is both microbiologically and chemically safe and, at the same time is aesthetically acceptable to the population.

Water treatment can be broadly divided into two types: (a) sewage, and (b) potable (drinking) water. Sewage treatment plants deal with the treatment of wastewater which consists of sewage, road and agricultural surface run-offs as well as industrial effluent, whereas potable water treatment produces the final product for human consumption.

Whilst treatment processes are able to reduce the number of micro-organisms in water they can never ensure complete removal and so final

Table 1. Some Common Water-related Diseases

<i>Disease</i>	<i>Type of water relationship</i>
Cholera	Waterborne
Infectious hepatitis	
Typhoid	
Amoebic dysentery	Water-washed or Waterborne
Gastro-enteritis	
Conjunctivitis	Water-washed
Diarrhoeal diseases	
Leprosy	
Scabies	
Skin sepsis and ulcers	
Guinea worm	Water related
Malaria	
Sleeping sickness	
Yellow fever	

disinfection is perhaps the most important stage of water treatment being the final safeguard against water-borne microbial disease. In Europe and USA chlorination is widely used [2] and, despite the fact that micro-organisms differ in their susceptibility to chlorine, a judicious combination of disinfectant concentration and contact time provides effective destruction of pathogenic bacteria and viruses. Since 1978 most incidents of water-borne diseases in the UK have occurred due to inefficient disinfection [3].

Although chlorine disinfection has proved to be successful in eradicating water-borne diseases there are problems associated with using this method, these include:

1. Micro-organisms (especially bacteria) are capable of producing strains that are tolerant to normal chlorine treatment levels. This can be overcome by employing higher chlorine levels than those normally used; however, this can lead to the formation of unpleasant flavours and odours due to the formation of chlorophenols and other halocarbons.
2. Certain species of micro-organisms produce colonies and spores that agglomerate in spherical or large clusters. Chlorination of such clusters may destroy micro-organisms on the surface leaving the innermost organisms intact.
3. Fine particles such as clays are normally removed by flocculation using chemicals such as aluminium sulphate. The flocs can entrap bacteria and their spores protecting them from chlorination. The vast majority of floc particles are removed but one or two may pass through the system unaffected by the final disinfection stage.

Due to these problems alternative disinfection techniques are being evaluated and the benefits of the use of ultrasound in the water industry are now of considerable interest. This is, however, only one of several important research interests in the possibility of using ultrasound in the “biological sciences.” As a result there are several research groups that are actively investigating the use of ultrasound in several areas of microbiology and biotechnology (Table 2) [4].

Table 2. General Uses of Ultrasound in Biotechnology

Microbiological decontamination.

The control or enhancement of microbiological action, e.g. fermentation and bioreactors.

The control or enhancement of enzymatic processes.

The use of ultrasound for the processing of biological material, e.g. dewatering and cell separation.

In this chapter we will concentrate on the use of ultrasound in the field of biological decontamination. The influence of the physical effects of ultrasound upon microbiological agents will be described, as will some recent applications of ultrasound to biological decontamination.

1.1 Some Definitions in Microbiology

This chapter is devoted to the biological decontamination of water. This section is introduced for the benefit of those readers not conversant with microbiological terminology so that related articles and the remainder of the chapter will be more understandable.

1.1.1 *Micro-organisms*

Micro-organisms are those organisms which are too small to be seen by the naked eye and encompasses a large number of different types. With higher organisms it is convenient and easy to identify them as either plants or animals. Plants have rigid cell walls, are photosynthetic and do not move independently. Animals, on the other hand, have flexible cell walls, require organic food and are capable of independent movement. This simple method of differentiation cannot be applied to micro-organisms because of the simple structures of their cells and it has become a convention to term all micro-organisms “protists.” These can themselves be broadly divided into three types (Table 3). The comparative sizes of various micro-organisms are given in Table 4.

1.1.2 *Bacteria*

Bacteria (singular bacterium) are simple, colourless, single-celled plants that use soluble food and may operate either as autotrophes or as heterotrophes and are capable of self-reproduction without sunlight. As species, which are involved in the decomposition of matter, they fill an indispensable ecological role in the destruction of organic material in the natural environment and also, harnessed by man, in the handling of organic wastes in treatment plants.

Bacteria range in size from approximately 0.5 to 5 μm and are, therefore, only visible through a microscope. Individual cells may be spheres, rods, or spiral-shaped and may appear singly, in pairs, packets, or chains. Bacteria are broadly classified into two major groups: heterotrophic and autotrophic, depending on their source of nutrients.

Table 3. Broad Classification of Micro-organisms

Prokaryotes	These are small (< 5 μm) simple cell structures with rudimentary nucleus and one chromosome. Reproduction is normally by binary fission. Bacteria, actinomycetes and the blue-green algae are included in this group.
Eucaryotes	These are larger (> 20 μm) cells with a more complex structure and containing many chromosomes. Reproduction may be asexual or sexual and quite complex life cycles may be found. This class of micro-organisms includes fungi, most algae and the protozoa.
Viruses	Are a further group of micro-organisms, which do not readily fit into either of the above classes and which are thus considered separately.

Table 4. The Size Ranges for Various Types of Micro-organism

<i>Organism</i>	<i>Size range (μm)</i>
Bacterium:	
rod	0.5–1.0 (diameter) 1.0–10 (length)
sphere	0.1–1.0
Fungus: yeast cell	8–15 \times 4–8
Alga: Chlamydomonas	28–32 \times 8–12
Virus: tobacco mosaic virus	300 \times 15 nm

1.1.3 Endospores and Cysts

Some bacteria have the ability to prolong their existence by forming endospores that are resistant to high temperatures and toxic chemicals. This is characteristic of certain species of rod-shaped bacteria of the genera *Bacillus* and *Clostridium*. These (endo)spores are not reproductive units like the spores of fungi or higher plants since one cell produces only one endospore which germinates to produce only one new cell.

The bacterial endospore is a form of suspended animation, and can germinate when conditions for growth return to ideal. Some of these spores have a very long life and a well-known example of this is the Anthrax spore that can survive for over 50 years in soil. This longevity is due to an extremely resistant coating of the spore which may consist of several layers. In addition, the abnormally low water content of the spore cytoplasm (15% of vegetative cytoplasm) reduces the enzyme activity of the cell.

Some soil-dwelling bacteria such as *Azotobacter*, unable to form an endospore, round off and produce a cyst. The cell shortens and the cell wall

becomes thickened. Cysts have limited powers of resistance to unfavourable conditions. On germinating they give rise to new vegetative cells.

1.1.4 Fungi

Fungi are aerobic multicellular plants which do not rely on photosynthesis for energy. They include yeasts and moulds that are more tolerant of both acid conditions and a drier environment than bacteria. They utilise much the same food sources as the bacteria but their nitrogen requirement is less because their protein content is somewhat lower than the bacteria. Fungi form rather less cellular matter than bacteria from the same amount of food. They are capable of degrading highly complex organic compounds and some are pathogenic in man.

Yeasts are used industrially in fermentation in baking, wine making, brewing and from this the production of ethanol (by distillation). Fermentation processes, wherein yeast metabolises sugar to produce alcohol, are carried out under anaerobic conditions because such conditions incur a minimum generation of new yeast cells. Under aerobic conditions, however, alcohol is not produced and the yield of new cells is much greater. For this reason the growth of yeast as animal feed using waste sugar or molasses employs aerobic fermentation.

Over 100 000 species of fungi exist and they usually have a complex structure formed of a branched mass of thread-like hyphae. They have four or five distinct life phases with reproduction by asexual spores or seeds. Fungi occur in polluted water and in biological treatment plants, particularly in conditions with high carbon to nitrogen ratios.

1.1.5 Algae

Algae are plants, all of which use photosynthesis and most are multicellular although some types are unicellular. The majority of fresh-water forms are the main producers of organic matter in an aquatic environment. Inorganic compounds such as carbon dioxide, ammonia, nitrates and phosphate provide the food source to synthesise new algal cells and to produce oxygen.

Algae may be green, blue-green, brown or yellow depending upon the proportions of particular pigments within them. They occur as single cells, which may be motile with the aid of flagella, non-motile, or multicellular filamentous forms. Algae and bacteria growing in the same solution do not compete for food but have a symbiotic relationship in which the algae utilise the end products of bacterial decomposition of organic matter and produce oxygen to maintain an aerobic system. Algae of this

type release toxins that can be fatal to farm and domestic animals particularly if the animals drink water containing a significant amount of such algae. Toxins produced by blue-green algae can cause skin irritation to humans and may produce gastro-intestinal illness; this problem has been particularly highlighted with the increasing popularity of water-contact recreation.

1.1.6 Viruses

Viruses are the simplest forms of organism ranging in size from about 0.01 to 0.3 μm consisting essentially of nucleic acid and protein. They are all parasitic and cannot grow outside another living organism. All are highly specific both as regards the host organism and the disease which they produce. Human viral diseases include smallpox, infectious hepatitis, yellow fever, poliomyelitis and a variety of gastro-intestinal diseases. Identification and enumeration of viruses requires special apparatus and techniques.

1.1.7 Protozoa

Protozoa are unicellular organisms 1100 μm in length which reproduce by binary fission. Most are aerobic heterotrophes and often utilise bacterial cells as their main food source. They cannot synthesise all the necessary growth factors and rely on bacteria to provide these items. Protozoa are widespread in soil and water and may sometimes play an important role in biological waste-treatment processes. There are four main types of protozoa (Table 5).

Most pathogenic protozoa, especially those found in water, are capable of forming spores or cysts, (see Table 5) which are highly resistant to common

Table 5. Main Types of Protozoa

Sarcodina	Amoeboid flexible cell structure with movement by means of extruded pseudopod (false foot).
Mastigophora	Which utilise flagella for motility.
Ciliata	Motility and food gathering by means of cilia (hair-like feelers). This type may be free swimming or attached to surfaces by stalks.
Sporozoa	Non-motile spore-forming parasites which are not found in water.

disinfectants and can thus be a source of water-borne infection even in developed countries with temperate climates.

2. ULTRASOUND AND BIOLOGICAL DECONTAMINATION

2.1 Mechanisms of Ultrasonic Action

The biological effects of power ultrasound can be traced back to the early days of SONAR when it was being investigated for use in anti-submarine warfare and it was noticed that the sound waves used were killing fish. Thereafter, research into ultrasound as a method for destroying or inactivating cells flourished. In the 1960s research concentrated on understanding the mechanism of ultrasound interaction with microbial cells [5]. Cavitation phenomenon and associated shear disruption, localised heating and free radical formation were found to be primary causes. By 1975, it was shown that brief exposure to ultrasound caused a thinning of cell walls attributed to the freeing of the cytoplasm membrane from the cell wall [6]. The types of apparatus used for this purpose were acoustic horn (probe) systems operating at 20 kHz. These were the forerunners of the modern acoustic horns used for high power sonochemical operations in the laboratory. When the ultrasonic power is correctly adjusted it is possible to disrupt the cell wall and release its cellular contents, at the same time, without destroying or denaturing them. This is not such a simple operation as it might appear because most simple one-cell organisms have an exceedingly tough cell wall that is only a few microns in diameter, and similar in density to the medium that surrounds it. The protein and nucleic acid components contained within the cell are large macromolecules, easily denatured by extreme conditions of temperature or oxidation both of which may arise from cavitation. A delicate balance must therefore be struck between the power of the probe and the disruption rate, since, power ultrasound, with its associated cavitation collapse energy and bulk heating effect, can denature the contents of the cell once released. Indeed for this type of usage it is important to keep the cell sample cool during sonication.

Several theories have been proposed to describe the mechanism of cell damage through exposure to ultrasound.

2.1.1 Cavitation

The mechanical effects of power ultrasound on chemical systems in a liquid medium are mainly attributed to cavitation and these same forces have a dramatic effect on biological systems [7]. Acoustic cavitation

can be broadly divided into two types, transient and stable. The former occurs when the cavitation bubbles, filled with gas or vapour, undergo irregular oscillations and finally implode. This produces high local temperatures and pressures which would disintegrate biological cells and/or denature any enzymes present. The imploding bubble also produces high shear forces and liquid jets in the solvent that may also have sufficient energy to physically damage the cell wall or cell membrane. Mechanical effects of this type have been used on a small scale for the disinfection of water contaminated with microbial spores, e.g. *Cryptosporidium*, although, the acoustic energy required is high [8,9]. Stable cavitation, on the other hand, refers to bubbles that oscillate in a regular fashion for many acoustic cycles. The bubbles induce microstreaming in the surrounding liquid which can also induce stress in any microbiological species present. The microstreaming effect therefore provides a large force, without the bubbles having to burst [10]. This type of cavitation may well be important in a range of applications of ultrasound to biotechnology [11].

Before we look in detail at some of the applications of ultrasound in biological decontamination it is important to understand how ultrasound interacts with biological contaminants [12,13]. Possible applications of ultrasound to biotechnology have also been reviewed [14]. The cavitation bio-effects of continuous ultrasound at 1.5 MHz on three different classes of biosystems have also been reported [15]. The important topic of the possible damage to DNA through the effects of ultrasound has also been addressed [16]. It would appear that an acoustic field (via cavitation) plays a very important role in the activity of DNA replication that occurs prior to cell division [17]. If sonication leads to cavitation within the cell then this may cause the cytoplasmic proteins and/or the DNA/RNA of micro-organisms to become denatured and lead to mutation or death.

Ultrasound can affect micro-organisms through a variety of mechanisms some physical or mechanical and others more chemical in nature—some of the more important processes or modes of action are listed below.

2.1.2 Temperature

Most ultrasonic experiments are carried out in temperature-controlled systems to ensure that isothermal conditions are maintained. In this way bulk temperature effects will not influence any microbiological process. However, even a small general increase in microbial temperature can also influence both the active and passive transport systems of the cell membrane or cell wall [18] and this in turn may lead to an increased uptake of compounds. However, if the temperature is not controlled then sonication

could result in a large temperature increase ($> 60^{\circ}\text{C}$). This in turn will lead to the denaturation (deactivation) of enzymes, proteins and other cellular components present within the micro-organism [19].

The heating effect of ultrasound has, however, been utilised in a different situation for many years in physiotherapy, where it is used as an aid to massage for the treatment of various types of muscular strains. It can also be used to enhance the absorption of medicines through the skin although this is more related to the streaming effect of cavitation rather than heating (see Section 2.1.3). In one particular case the uptake of hydrocortisone, applied externally to swine, increased by 300% using ultrasound [20]. Ultrasound is also capable of increasing the permeability coefficient of hydrocortisone in cellulose by 23% in an aqueous solution at 25°C [21].

2.1.3 Mass Transport and Mass Transfer through Cell Walls

An important consequence of the fluid micro-convection induced by bubble collapse is a sharp increase in the mass transfer at liquid–solid interfaces. This has been demonstrated in the field of sonoelectrochemistry that ultrasound enhances mass transport to the electrode [22,23]. In microbiology there are two zones where this ultrasonic enhancement of mass transfer will be important [4]. The first is at the membrane and/or cellular wall and the second is in the cytosol, i.e. the liquid present inside the cell.

For many years it has been known that ultrasound is able to enhance mass transfer through both artificial and biological membranes. Thus the rate of NaCl transfer from 5% saline solution through a cellophane membrane into distilled water can be doubled when ultrasound is applied in the direction of diffusion [24]. The change in the rate of diffusion was shown to be due to ultrasound and not the result of either membrane damage or temperature variations in the medium. Similar effects have been reported in the case of the diffusion of potassium oxalate and other solutes [20,21,25].

The effects of ultrasound upon the permeability of the cell walls of the Gram-negative bacteria *Pseudomonas aeruginosa* toward hydrophobic compounds particularly antibiotics have been examined [26]. The penetration and distribution of 16-dosylstearic acid (16-DS) in the cell membranes of the bacteria was quantified by a spin-labelling EPR method. The results indicated that the intracellular concentration of 16-DS was higher in insonated cells and increased linearly with the sonication power. EPR spectra indicated that ultrasound enhanced the penetration of 16-DS into the structurally stronger sites of the inner and outer cell membranes. The effect of ultrasound on the cell membranes was transient in that the initial membrane permeability was restored upon termination of the

ultrasound treatment. These results suggested that the resistance of Gram-negative bacteria to the action of hydrophobic antibiotics was caused by a low permeability of the outer cell membranes and that this resistance may be reduced by the simultaneous application of antibiotic and ultrasound.

At an appropriate intensity level of ultrasound, intracellular microstreaming has been observed inside animal and plant cells with rotation of organelles and eddying motions in vacuoles of plant cells [27]. These effects can produce an increase in the metabolic functions of the cell that could be of use in both biotechnology and microbiology, especially, in the areas of biodegradation and fermentation.

2.1.4 Free Radical Production

Cavitation induced in any liquid system will result in the formation of radicals [28]. In the case of water sonication this generates highly reactive radicals which can undergo a range of subsequent reactions. An important product from the sonolysis of water is hydrogen peroxide, which, together with the radical species, provides a powerful bactericide and chemical oxidant [29].

The majority of references to the uses of ultrasound in biological decontamination are within two fields, i.e. separation processes and decontamination. In this chapter we will concentrate on decontamination.

2.2 Decontamination of Surfaces

One of the major long-established industrial applications of power ultrasound is in surface cleaning and it has proved to be an extremely efficient technology. Ultrasound is particularly useful in surface decontamination where the inrush of fluid which accompanies cavitation collapse near a surface is non-symmetric (Figure 1). The surface itself restricts the inrush of fluid from that side and so a jet of liquid is formed from the resultant major flow from the other side of the bubble. This powerful jet will dislodge dirt and bacteria from surfaces. The particular advantage of ultrasonic cleaning in this context is that it can reach crevices that are not easily reached by conventional cleaning methods. Objects that can be in cleaning range are from large crates used for food packaging and transportation to delicate surgical implements such as endoscopes. This was recognised some years ago, see for example, a general patent that relates to the use of ultrasound as a method of pasteurisation, sterilisation and decontamination of instruments and surfaces used within the medical, surgical, dental and food processing industries [30]. The use of ultrasound

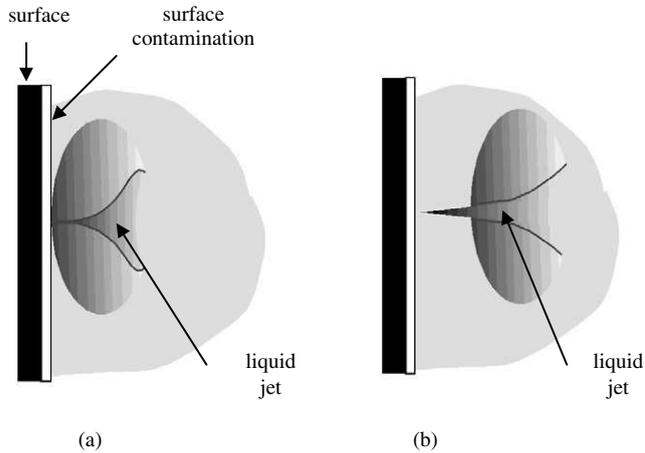


Figure 1. Liquid jet produced on collapse of an acoustic cavitation bubble: (a) on a surface, (b) close to a surface.

allows the destruction of a variety of fungi, bacteria and viruses in a much reduced processing time when compared to thermal treatment at similar temperatures.

The removal of bacteria from various surfaces is of great importance to the food industry and can be efficiently accomplished with the combined use of sonicated hot water containing biocidal detergents [31].

The core of an ultrasonic cleaning system is a heated stainless steel tank which contains a number of ultrasonic transducers and a dilute detergent/sterilising solution. The items to be cleaned are passed through the tank and subjected to the ultrasound as they pass in front of the transducers. In the case of a poultry processing factory the cleaning is expected to remove fat, blood, skin, meat and lime scale and sterilise the surface of the item. There has to be a balance struck between the tank temperature and the effectiveness of the ultrasound since maximum cavitation occurs at about 65–70°C falling to about half when the temperature is either lowered to 40°C or raised to 85°C.

In all food processing factories, cleanliness is obviously extremely important and inspection is part of day-to-day operation. Tests on surfaces of equipment used in poultry processing are made on an ongoing basis. Typical examples of the ultrasonic cleaning efficiency on items such as plastic baskets, shackles (the hooks used for hanging poultry on a production line) and conveyer belts are given (Table 6). The measurements are in terms of Total Viable Count (TVC) and ATP bioluminescence [32].

Table 6. Typical Analyses of Ultrasonic Cleaning Efficiencies

Method used	Type of sample	Before cleaning	After cleaning
TVC analysis	Plastic tray	2310	220
	Plastic tray	1420	100
	Steel basket	7280	80
	Steel basket	6240	10
	Steel shackle	300	0
	Steel shackle	320	0
Biotrace analysis (Relative Light Units)	Plastic tray	725	160
	Plastic tray	681	59
	Plastic tray (badly worn)	>500 000	717
	Plastic link belt	2485	52
	Plastic link belt	3087	32

It should be noted, however, that a full 100% kill rate on plastic surfaces is extremely difficult to obtain under routine cleaning conditions.

Chemicals such as chlorine are often used to clean and decontaminate food products and food processing surfaces. The increased effectiveness of ultrasound in combination with chlorine in decontaminating broiler breast skin inoculated with *Salmonella* has been investigated [33]. The *Salmonella* cells were released from the skin by bombardment with ultrasound and it was suggested that chlorine was able to penetrate the cells more easily, causing enhanced inactivation.

A synergistic effect has been reported in biocidal action between ultrasound and various antibiotics at levels and concentrations which individually did not themselves reduce bacteria viability [34]. This synergy reduced the viability by several orders of magnitude for cultures of *Pseudomonas aeruginosa*, *Escherichia coli*, *Staphylococcus epidermidis* and *Staphylococcus aureus*. Measurements of the bactericidal activity of gentamicin against *P. aeruginosa* and *E. coli* demonstrated that simultaneous application of 67-kHz ultrasound enhanced the effectiveness of the antibiotic. As the age of these cultures increased, the bacteria became more resistant to the effect of the antibiotic alone and the application of ultrasound appeared to reverse this resistance. The ultrasonic treatment-enhanced activity was not observed with cultures of Gram-positive *S. epidermidis* and *S. aureus*. These results may have application in the treatment of bacterial biofilm infections on implant devices, where sequestered bacteria are usually more resistant to antibiotic therapy. Synergistic killing was observed to be a function of ultrasonic intensity [35]. Greatest killing (approximately 5 log reduction in viable population) was realised at full intensity (4.5 W cm^{-2}), and decreased with reductions

in power density. At the lowest intensity used (10 mW cm^{-2}) there was no significant evidence of acoustically enhanced killing.

The effect of ultrasound frequency upon enhanced killing of *P. aeruginosa* biofilms by an antibiotic on polyethylene substrate has also been reported [36]. Biofilm viability was measured after exposure to $12 \mu\text{g ml}^{-1}$ gentamicin sulphate and at an ultrasonic intensity of 10 W cm^{-2} at frequencies of 70 kHz, 500 kHz, 2.25 MHz, and 10 MHz. The results indicated that a significantly greater fraction of the bacteria within the biofilm was killed by gentamicin when they were subjected to lower frequency rather than higher frequency ultrasound. Experiments have been carried out to determine whether this bio-acoustic effect was caused by ultrasonically induced changes in the morphology of the biofilm (biofilm break-up or disruption). Such disruption would be undesirable in the possible ultrasonic treatment of implant infections. A frequency of 500 kHz and a intensity of 10 mW cm^{-2} were used on biofilms of *P. aeruginosa* aged for 24 h and these were then examined by confocal scanning laser microscopy (CSLM). The CSLM results showed that the biofilm is a partial monolayer of cells with occasional aggregates of cells, non-cellular materials and extracellular spaces. The structure of biofilm was not changed when the biofilm was exposed to continuous ultrasound, which, under the same irradiation parameters, increased cell killing by nearly two orders of magnitude.

An *in vitro* investigation into the bactericidal effects of a dental ultrasonic scaler on bacterial biofilms using *Actinobacillus actinomycetemcomitans* and *Porphyromonas gingivalis* [37]. Suspensions of the bacteria were subjected to the vibrations of a Cavitron P1 insert for 2.5 and 5.0 min in an acoustically simulated model substrate. A 60% kill rate was achieved at a temperature of around 50°C which constituted an alternative treatment for bacterial biofilms.

A similar approach could be used to clean-up a range of biofilms which can be the cause for a number of environmental hazards.

2.3 Decontamination of Solutions

2.3.1 Ultrasonic Destruction of Biological Contaminants in Aqueous Solution

Although this chapter is primarily devoted to the decontamination of water it is important to recognise that investigations have also been carried out in aqueous solutions and other media. One of the areas which has attracted attention is the use of ultrasound in conjunction with heat to assist in sterilisation/pasteurisation. Heat treatment is one of the most frequently

used methods for stabilising foods because of its ability to inactivate enzymes and destroy micro-organisms. However, since heat can also alter many organoleptic properties and diminish the content or availability of some nutrients, there is a growing interest in searching for methods that are able to stabilise foods with little or no heat added. The first report on the synergy between ultrasound and heat as a mechanism for killing the vegetative bacterium *S. aureus* was published by a Spanish group [38]. They found that the use of power ultrasound allowed a reduction in the effective temperatures at which sterilisation could be achieved. “Thermosonication” is the term now given to the combined application of heat and ultrasound and it was found to reduce the concentration of *Bacillus subtilis* spores by up to 99.9% in the 70–90°C range in a small scale ultrasonic reactor using a 20 kHz, 150 W ultrasound source [39]. Work carried out at Coventry University has addressed the issues of the effect of the food substrate (orange juice, milk and rice pudding) on the thermosonication phenomenon using a range of organisms (*Zygosaccharomyces bailii*, *Listeria monocytogenes* and *Bacillus polymyxa*) [40]. The studies confirmed the synergistic effect of ultrasound and heat thus in milk, the heat resistance (*D* value) of *L. monocytogenes* was approximately 6-fold lower at 60°C when sonicated at 20 kHz and the *D* value of *Z. bailii* in orange juice was approximately 10-fold at 55°C lower when sonicated at 38 kHz.

Similar results were obtained in a study of the combined effect of ultrasound (20 kHz) and heat treatment on the survival of two strains of *B. subtilis* in distilled water, glycerol and milk [41]. When spores, suspended in water or milk, were subjected to ultrasonic waves before heat treatment, little or no decrease of the heat resistance was observed. However, when heat and ultrasound were applied simultaneously the heat treatment times in milk were reduced by 74% for *B. subtilis* var, niger-40 and by 63% for *B. subtilis* var, ATCC 6051 and similar results were obtained in glycerol. In water, however, thermosonication in water was more marked reducing the heat resistance of the spores by up to 99.9% in the 70–95°C range, this effect of thermosonication was slightly diminished to 75% as the temperature reached the boiling point of water.

Cutting fluids are emulsions used in metalworking. These fluids are recycled and suffer from a gradual accumulation of biological contamination. Destruction of typical contaminants in 3% v/v Clearcut 52 emulsions has been achieved using high power ultrasound [42]. One hundred litres of virgin emulsion was prepared and stored overnight in a new, steam-cleaned oil drum. A pump was used to drive liquid from the drum into the dormant ultrasonic cell from which it was recirculated back into the body of the stored emulsion via an injector pipe. Bacterial cultures of *E. coli* and *Fusarium* were introduced into the sample by injection into the circulatory stream and left for 30 min to ensure complete mixing and equilibration.

The bulk emulsion was then exposed to ultrasound for 180 min during which time samples were removed at 20 min intervals. Simple estimations of the bacteria or yeast or fungal populations were made using dip slides that were immersed in various samples, shaken to remove excess liquid and then incubated at 40°C for 48 h prior to analysis of the results. These were backed up by withdrawing several millilitres of emulsion from each sample and incubating on agar culture. These results are shown in Figure 2.

The bacterial population profiles in Figure 2 show that the use of ultrasound leads to a sharp increase in the kill rates of the biological contaminants present in the emulsion. In addition, it has been reported that the re-emergence of bacteria is minimal after one week of standing exposed to the atmosphere.

2.3.2 Ultrasonic Destruction of Biological Contaminants in Water

Several authors have shown that ultrasound on its own has a disinfecting effect upon micro-organisms [6,7,29]. The germicidal efficacy of ultrasound at a frequency of 26 kHz has been assessed by exposing aqueous suspensions of bacteria (*E. coli*, *S. aureus*, *B. subtilis*, and *P. aeruginosa*), fungus (*Trichophyton mentagrophytes*), and viruses (feline herpesvirus type 1 and feline calicivirus) to ultrasound. There was a significant effect of time for all four bacteria, with percent killed increasing with increased duration of exposure, and a significant effect of increased kill with intensity for all bacteria (except *E. coli*). Positive results were also recorded for the reduction

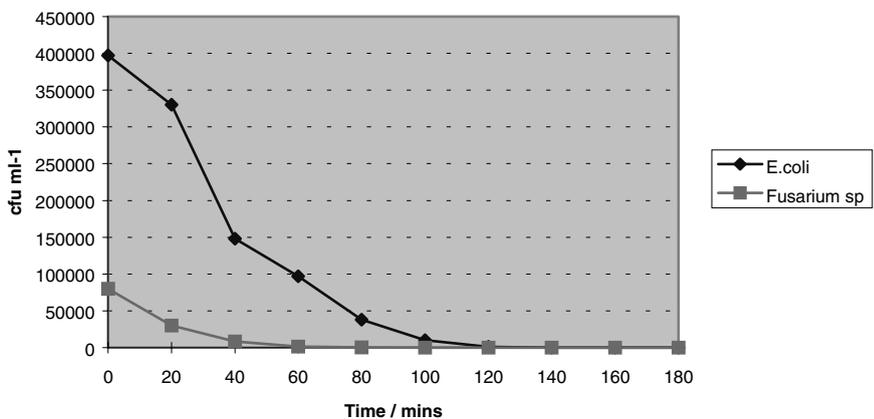


Figure 2. *E. coli* and *Fusarium* population profiles for ultrasonically treated cutting fluid.

in fungal growth and reduction in feline herpesvirus with increased ultrasound intensity but there was no apparent effect on feline calicivirus. The results suggest that ultrasound in the low kilohertz frequency range is capable to some degree of inactivating certain disease agents that may reside in water.

From these studies and others it has been established that sonication can provide powerful disinfection, however, to achieve 100% kill rates using only ultrasound it is necessary to use very high ultrasonic intensities. Unfortunately, this makes the technique expensive to use for general microbiological decontamination. However, over the last two decades scientists have found that micro-organisms are becoming resistant to the disinfection techniques involving chemicals, ultraviolet light and heat treatment and have once again started investigating ultrasound, but this time as an adjunct to other techniques [43,44].

Current trends are towards the reduction in use of chlorine as a disinfectant either by replacement with other biocides or by a reduction in the concentration required for treatment. Low power ultrasound offers the latter possibility since it is capable of enhancing the effects of chemical biocides. The effect is thought to be due, in part, to the break-up and dispersion of bacterial clumps and flocs which renders the individual bacteria more susceptible to chemical attack. In addition, cavitation-induced damage to bacterial cell walls will allow easier penetration of the biocide.

The results of a study of the combined effect of low power ultrasound and chlorination on the bacterial population of raw stream water are shown in Table 7. Neither chlorination alone nor sonication alone was able to completely destroy the bacteria present. It is significant, however, that extending the time of chlorination or sonication from 5 to 20 min seems to double the biocidal effect of the individual techniques. When sonication, however, is combined with chlorination, the biocidal action is significantly

Table 7. The Effect of Ultrasound and Chlorination on Bacterial Growth

<i>Treatment</i>	<i>% Bacteria kill after</i>	
	<i>5 min</i>	<i>20 min</i>
No treatment	0	0
Chlorine 1 ppm	43	86
Ultrasound alone	19	49
Ultrasound + chlorine	86	100

Conditions: 1:10 dilution of raw stream water, using ultrasonic bath (power input to system = 0.6 W cm^{-2}), temperature = 20°C .

improved. These results suggest that ultrasound could be used in conjunction with chemical treatments to achieve a reduction in the quantity of bactericide required for water treatment [29].

Zooplankton often accidentally pass through the purification cycle of a water-treatment plant, leading to regrowth and a clogging of filters located in the water-distribution system. It is therefore important to eliminate the plankton before the water reaches the flocculation process. Such inactivation can be achieved using power ultrasound through purely mechanical effects of acoustic cavitation which have been discussed above [45]. In order to inactivate plankton a sound intensity of approximately 1 W cm^{-2} and a high air content in the water is especially effective. The economic viability of a system for plankton treatment has been tested using a flow through system with a capacity of $300 \text{ m}^3 \text{ h}^{-1}$. The actual volume of treatment in the system was 2 m^3 with an active acoustic area of 2 m^2 . To inactivate a large number of real types of plankton such as Nauplii, Copopods and Rotifers a specific power of 0.05 kWh m^{-3} proved to be satisfactory.

A continuing problem in water treatment is the occurrence of algal blooms. Algae may be killed relatively easily on exposure to ultrasound and a lightly "polluted" system provides very little attenuation to sound transmission there is the possibility of using high frequency ultrasound (low power emission and consumption). Such high frequencies have been shown to give maximum activity, as shown through sonoluminescence, at the interface between liquids and gases. Logically, then, if a large number of small bubbles were introduced into a field of high frequency ultrasound there would be a very large gas-liquid surface area for cavitation activity and the bubbles themselves should also provide "seeds" for cavitation events. This is the basis of an approach to algae removal and control proposed by the Belgian company UNDATIM. In a trial involving the monocellular algae species *Scenedesmus capricornutum* some spectacular results were obtained. A cell was constructed to treat water at a rate of $2 \text{ m}^3 \text{ h}^{-1}$ using an acoustic power of 450 W. At a temperature of 25°C a deep green, highly concentrated, solution of the algae containing some 4×10^6 algal cells per cm^3 a single pass through the cell reduced the recovery threshold of the micro-organism by some 60%. This indicates that the SONOXIDE treatment even operating at algal concentrations that are far higher than might be encountered in normal treatments offers the potential not only to kill the micro-organism but also to severely restrict its reproductive ability.

This ultrasonic anti-algae methodology has been combined with an electromagnetic anti-scaling treatment to provide a new global water remediation technology for half-closed circuits, e.g. cooling towers, known as SONOXIDE [46]. This process tackles two major problems of cooling

circuits, namely the build up of scale and algae. These are solved with a minimal energy requirement, without the need to use soft water and without the addition of chemicals.

Over the last decade there has been considerable interest shown in the use of ultrasound for water. The so-called “Sonozone” process was developed in Denmark in the early 80s for the disinfection of water [47]. Inactivation of 3–4 decades of bacteria was obtained using 10–95% lower ozone concentration and 57–96% lower gaseous ozone dosage by the sonozonation process compared to ozonation alone. This synergy was obtained by the simple fact that a gas, like ozone, can be diffused in minute micro-bubbles creating a high gas–liquid surface contact area allowing a more efficient yield of the treatment compared to ordinary aerators or ozonizers. Ultrasound also disaggregates the viable microbial units *vide supra*.

Physical factors like electrical fields, UV radiation, laser excitation or ultrasound seems to increase the cytoplasmic membrane permeability, thereby, contributing to a better removal of bacteria by disinfectants such as Ag^+ and ClO^- [48]. Another advantage of the use of ultrasound is the enhancement of flocculation rates together with a lower flocculent consumption [49].

High power ultrasound in conjunction with disinfectants such as chlorine and hydrogen peroxide have been successfully applied in the destruction of faecal coliforms and protozoa such as cryptosporidium [50].

The inactivation of *E. coli* and *Hansenula polymorpha* has been achieved through the irradiation of TiO_2 suspensions in water [44]. Two types of batch reactors employing static and recirculating solutions were used in the study. Sonolysis, using a 20 kHz ultrasonic unit, was found to enhance the micro-organism inactivation in all instances, although the enhancement was more modest for the batch recirculation reactor. The mechanism based on sonolytic creation of $\cdot\text{OH}$ radicals appeared to provide the most satisfactory explanation of the data trends observed. The data also implicated $\cdot\text{OH}$ as the dominant bactericidal agent in irradiated TiO_2 suspensions.

Many micro-organisms have the ability to form resistant and dormant structures when subjected to a stress which are known as either spores or cysts. Spore production is a phenomenon amongst some species of micro-organisms. Spores have two functions: (1) Agent of dispersal, and (2) Survival during adverse conditions. The formation of spores is a significant factor in the distribution of the producer organism. Spores are abundant in the foam of rivers and streams, most of which are fungal spores which have adapted well to the production of dispersal spores than other organisms. To ensure spore survival they must be more resistant to adverse conditions than their parent cell to ensure dormancy occurs after its formation. Some spores have a very long life. Anthrax spores in the soil can

live for over 50 years. The longevity is due to an extremely resistant spore coat, which may be of several layers. In addition, the abnormally low water content of the spore cytoplasm (15% of vegetative cytoplasm) reduces the enzyme activity of the cell. The bacterial endospore literally represents suspended animation, and can germinate when conditions for growth are ideal.

The endospores of *Bacillus* and *Clostridium* species are of extreme importance to man; for example *Bacillus thermophilus* spores are only destroyed by heating at 100°C for 4 h. Spores possess a great resistance to desiccation (removal of water from cell), ultraviolet light, chemical and enzymatic attack. It is obvious therefore that any water treatment techniques should not only be able to destroy micro-organisms but also be able to destroy or remove any spores present—but spores are hard to kill.

The protozoa, *Cryptosporidium parvum*, has become recognised as a cause of the water-borne disease Cryptosporidiosis in humans and many cases have been reported in the news over the last decade. These outbreaks have occurred throughout Europe as well as the USA and are not just associated with the developing countries. The main concern of water suppliers is that conventional treatment methods are inadequate and are not a sufficient barrier in preventing the water-borne transmission of cryptosporidiosis. *Cryptosporidium parvum* forms spores known as oocysts which have a very thick outer wall. This prevents or makes it very difficult for normal disinfectants to penetrate the oocyst wall. The most commonly used disinfectant techniques used in water treatment, i.e. chlorination and ultraviolet light is ineffective but ozone seems to be able to destroy some of these oocysts. The Coventry group has been evaluating the use of ultrasound as an aid for the disinfection of water contaminated with cryptosporidium oocysts [50]. It was found that sonication reduced the number of oocysts by 25% in 2 min. And, more importantly, the proportion of oocysts rendered non-viable increases with duration of sonication.

Similar work has been carried out by Leeds University in conjunction with Biwater and their findings have been released as part of a patent [9]. In batch tests, it has been found that by subjecting to sonication a sample of water containing 25 000 cryptosporidia oocysts per 100 ml (series 1) or 78 000 oocysts per 100 ml (series 2) batch treatment with power ultrasound is capable of reducing the viable count of oocysts (Figure 3). In flow tests (19 l h⁻¹) with samples of tap water at 7°C, previously spiked with purified oocysts and with a contact time of approximately 3.6 s within a flow cell (20 kHz, 140 W), only 2.5×10^2 oocysts per litre were recovered from an initial concentration of around 2.4×10^5 . It is however clear that the power required for the complete removal of oocysts in mains water treatment will be extremely high.

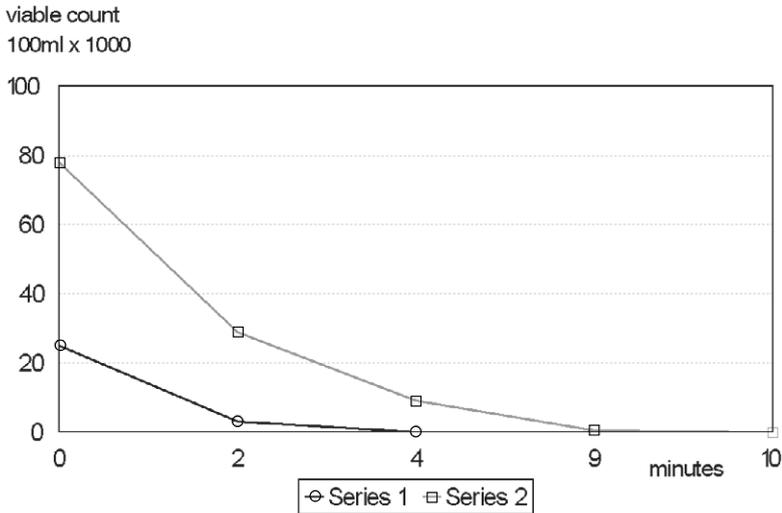


Figure 3. Effect of ultrasound (20 kHz) on water inoculated with *Cryptosporidium* oocysts.

3. CONCLUSION

The potential uses of power ultrasound continue to expand. From the foregoing it is proving to be a powerful tool for Integrated Pollution Control it can be used successfully for the total destruction of the biological pollutants. However, the use of ultrasound in biological decontamination is still in its infancy but as more researchers make use of sonication the subject of sonobiological decontamination will expand. It certainly offers great hope for the future of pollution control.

REFERENCES

- [1] Community Water Supply, WHO Technical Report No. 420.
- [2] Cheremisinoff, N., and Cheremisinoff, P. *Water Treatment and Waste Recovery—Advanced Technology, Chapter 2*, Prentice-Hall International, UK, 1993.
- [3] Galbraith, N. S., Barrett, N. J., and Stanwell-Smith, R. *J. Inst. Water, Environmental Management*, 1 (1987) 7.
- [4] Phull, S. S., and Mason, T. J. In Mason, T. J. (ed.), *Advances in Sonochemistry*, Vol. 5, JAI Press, 1999, pp. 175–208.
- [5] Hughes, D. E., and Nyborg, W. L. *Science*, 138 (1962) 108.
- [6] Alliger, H. *American Laboratory*, 10 (1975) 75.
- [7] Scherba, G., Weigel, R. M., and O'Brien, J. R. *Applied and Environmental Microbiology*, 573 (1991) 2079.

- [8] Phull, S. S., and Mason, T. J. Research report for Yorkshire Water, 1995.
- [9] European Patent 0 567 225 A1 Biwater Treatment Ltd., 1993.
- [10] Williams, A. R., Stafford, D. A., Callely, A. G., and Hughes, D. E. *Journal of Applied Bacteriology*, 33 (1970) 656.
- [11] Reynolds, C., and Wills, C. D. *Int. J. Radiat. Biol.*, 25 (1974) 113.
- [12] Beier, W., and Dorner, E. *Der Ultraschall in Biologie und Medizin*, Leipzig: Geogr. Theime, 1954.
- [13] Reid, I. M., and Sikov, M. R. *Interaction of Ultrasound and Biological Tissues*, Proceedings of Workshop, Washington 1972.
- [14] Sinistera, J. V. *Ultrasonics*, 30 (1992) 180.
- [15] Graham, E., Hedges, M., Leeman, S., and Vaughan, P. *Ultrasonics*, 18 (1980) 224.
- [16] Leeman, S., Khokhar, M. T., and Oliver, R. *Brit. J. Radiobiology*, 48 (1975) 954.
- [17] Glazunova, A. V., and Efimova, S. A. *Acoustical Physics*, 43 (1997) 45.
- [18] Lehninger, A. In *Biochemistry*, Worth Publishers, New York, 1975.
- [19] DeRobertis, E. D. P., and DeRobertis, E. M. F. *Cell and Molecular Biology*, Holt-Saunders, Tokyo, 1980.
- [20] Griffin, J. E., and Touchstone, J. C. *Am. J. Phys. Med.*, 42 (1963) 77.
- [21] Julian, T. N., and Zentner, G. M. *J. Pharm. Pharmacol.*, 38 (1986) 871.
- [22] Kowalska, E., and Mizera, J. *Ultrasonics*, 9 (1971) 81.
- [23] Lorimer, J. P., Mason, T. J., Phull, S. S., and Pollet, B. *Electrochem. Acta.*, 41 (1996) 2737.
- [24] Baumgarte, F. *Arztliche Forsch*, 3 (1949) 525.
- [25] Mendez, J., Franklin, B., and Kollias, J. *Biomedica*, (1976) 121.
- [26] Rapoport, N., Smirnov, A. I., Timoshin, A., Pratt, A. M., and Pitt, W. G. *Archives of Biochem. Biophys.*, 334 (1997) 114.
- [27] Nyborg, W. L. *J. Cancer*, 45 (1982) 156.
- [28] Reisz, P. In Mason, T. J. (ed.), *Advances in Sonochemistry*, Vol. 2, JAI Press, 1991, pp. 23–64.
- [29] Phull, S. S., Mason, T. J., Lorimer, J. P., Newman, A. P., and Pollet, B. *Ultrasonics*, 4 (1997) 157.
- [30] Boucher, R. M. G. US Patent 4 211 744 (1980).
- [31] Quartly-Watson, T. In Povey, M., and Mason, T.J. (eds), *Ultrasound in Food Processing*, Blackie Academic and Professional, 1998.
- [32] Information supplied by Production Line Cleaning Ltd., High Road, Bressingham, Diss, Norfolk, IP22 2AT, UK.
- [33] Lillard, H. S. *Journal of Food Protection*, 56 (1993) 716.
- [34] Pitt, W. G., Qian, Z., and Sagers, R. D. *Annals of Biomedical Engineering*, 25 (1997) 69.
- [35] Pitt, W. G., and Williams, R. G. *J. Biomaterial Applications*, 12 (1997) 20.
- [36] Pitt, W. G., Qian, Z., and Sagers, R. D. *Colloids and Surface Biointerfaces*, 9 (1997) 239.
- [37] O'Leary, R., Sved, A. M., Davies, E. H., Leighton, T. G., Wilson, M., and Kiesser, J. B. *Journal of Clinical Periodontology*, (1997) 24.
- [38] Ordonez, J. A. *Journal of Dairy Research*, 54 (1987) 61.
- [39] Ordonez, J. A., Sanz, B., Burgos, J., and Garcia, M.L. *J. Appl. Bacteriology*, 67 (1989) 619.
- [40] Mason, T. J., Phull, S. S., Betts, G., and Earnshaw, R. Internal Report, Campden and Chorleywood Food Research Association, 1995.
- [41] Garcia, M.L., Burgos, J., Sanz, B., and Ordonez, J. A. *J. Appl. Bacteriology*, 67 (1989) 619.
- [42] Information supplied by Sonic Process Technologies (SPT) Ltd.
- [43] FWR—Research Report, Applications of Ultrasonics in the Water Industry, 1995.
- [44] Stevenson, M., Bullock, K., Lin, W. Y., and Rajeshwar, K. *Res. Chem. Intermed.*, 23 (1997) 311.

- [45] Mues, A., Proc of 6th Meeting of European Society of Sonochemistry, (1998) 53.
- [46] Cordemans, E., and Hannecart, B. World Patent, WO 98/01394.
- [47] Dahi, E., and Lund, E. *Ozone Sci. Eng.*, 2 (1980) 13.
- [48] Kulsly, L. A., Savluck, O. S., Teselkin, V. V., and Deynega, O. Yu. *Visn. Akad Nauk Ukr RSR*, 11 (1983) 65.
- [49] *Khim Tekhnol Vody*, 11 (1989) 539.
- [50] Phull, S. S., Mason, T. J., and Cope, B. C. CERC Report No. 162, Coventry University, 1996.

This Page Intentionally Left Blank

COMBINATION OF ULTRASONIC AND BIOLOGICAL POLLUTANT DEGRADATION

Andreas Tiehm

OUTLINE

1. Introduction	26
1.1 Biological Pollutant Degradation	26
1.2 Ultrasonic Pollutant Degradation	27
1.3 Integrated Ultrasonic–Biological Degradation	28
2. Effect of Ultrasound on Micro-organisms	29
2.1 Ultrasound Frequency, Intensity, and Sonication Time	30
2.2 Susceptibility of Microbial Species to Ultrasound Damage	32
3. Enhanced Biodegradation by Ultrasonically Enhanced Mass Transfer	32
3.1 Sonochemical Pre-treatment of Phenanthrene	33
3.2 Simultaneous Sonication and Biodegradation	35
4. Ultrasonic Pre-treatment of Dissolved Low Molecular Weight Pollutants	40
4.1 Mixtures of Chlorobenzene and Easily Biodegradable Compounds	40
4.2 Reduction of Dichlorophenol Toxicity	44

Advances in Sonochemistry

Volume 6, pages 25–58.

© 2001 Elsevier Science B.V. All rights reserved.

4.3	Humic Acids and Pure Terephthalic Acid (PTA) Industrial Wastewater	46
5.	Ultrasonic Pre-treatment of Polymers and Sewage Sludge	48
5.1	Fragmentation of Polymers	48
5.2	Disintegration of Sewage Sludge	49
6.	Sonochemical Side Reactions	50
6.1	Formation of Hydrogen Peroxide	50
6.2	Formation of Nitrite and Nitrate	52
7.	Conclusion	54
	Abbreviations	55
	References	56

1. INTRODUCTION

1.1 Biological Pollutant Degradation

Biological degradation is generally considered the most environmentally friendly and cheapest method of pollutant elimination. Many standard techniques for environmental protection are based on biological activity, e.g. wastewater treatment, treatment of solid wastes, and the remediation of contaminated soil. Nevertheless, there are situations where biological treatment alone does not result in a successful elimination of the target pollutants. The following conditions hinder the biological degradation of pollutants:

- The lack of enzymes catalysing the degradation of a particular pollutant. For example, xenobiotics that occur only for short periods in wastewater will not be degraded, because the microbial community is not adapted to this type of contaminant.
- A low bio-availability of the pollutant. Since microbial uptake and degradation of most pollutants takes place in the aqueous phase, the degradation rate of many hydrophobic compounds is limited by a slow mass transfer.
- The presence of competing substrates. Small amounts of a poorly degradable pollutant will not be degraded in the presence of high concentrations of an easily degradable compound that is preferred as growth substrate.
- The presence of toxic compounds inhibiting any biological activity.
- A high molecular weight and/or branched structure of the pollutant. The degradation rates of biopolymers as well as synthetic polymers decrease with increasing polymerisation and branching.

Physico-chemical techniques provide an alternative to eliminate pollutants that are poorly biodegradable. These techniques on their own are rather expensive. Integrated bio- or physico-chemical processes are expected to be more efficient in many cases [1]. In this chapter it is the combination of ultrasonic and biological treatment for pollutant elimination, which will be discussed.

1.2 Ultrasonic Pollutant Degradation

Application of ultrasound causes the periodical compression and rarefaction of a liquid. Above a certain intensity threshold, gas bubbles are created that grow in size before they collapse within a few microseconds. This process is termed as “cavitation” [2]. Larger cavitation bubbles are generated at low frequency [3,4], resulting in most powerful hydromechanical shear forces. Additionally, sonochemical processes are induced by cavitation. Temperature and pressure inside the cavitation bubbles rise dramatically during adiabatic bubble collapse [5]. Therefore, collapsing bubbles function as “micro reactors” within the bulk liquid. Sonochemical processes resulting from high temperature and pressure in the bubbles comprise pyrolytic and radical reactions [6]. Degradation of environmental pollutants by ultrasound has been observed in the frequency range from 20 kHz up to about 1000 kHz.

It has been demonstrated that a variety of environmental pollutants can be degraded by ultrasound. Different types of pollutants have been investigated, e.g. chlorinated solvents, hydrocarbons, pesticides, phenols, and polymers (Table 1).

Reaction mechanisms vary according to the different physico-chemical properties of particular pollutants [6,11,24,31]:

- *Volatile pollutants* are degraded preferentially by pyrolytic reactions occurring in the vapour phase of the cavitation bubble.
- *Hydrophobic pollutants* accumulate and react in the hydrophobic boundary layer of the cavitation bubble. The concentration of OH radicals and H₂O₂ in the boundary layer is significantly higher than in the surrounding liquid. Pyrolysis and radical reactions contribute to the degradation.
- *Hydrophilic pollutants* in the bulk liquid, are degraded by reaction with free radicals or H₂O₂, produced by the sonolysis of water.
- *Macromolecules and particles* are also degraded by hydromechanical forces that are triggered by the collapse of the cavitation bubbles.

Most sonochemical degradation studies focus on the disappearance of the target pollutant. Less information is available concerning the reaction products. Recently published studies revealed that complete mineralisation

Table 1. Pollutants Degraded by Ultrasound

<i>Substrate</i>	<i>Reference</i>
<i>Azo dye:</i>	
Remazol Black B	[7]
<i>Chlorinated pollutants:</i>	
Carbon tetrachloride	[8]
Chlorobenzene	[9]
Chlorobenzene, Dichlorobenzene, Chlorophenol, ...	[6]
Chlorofluorocarbons	[10]
Chlorophenol	[11]
Methylene chloride, Chloroform, Dichloroethane, ...	[12]
Trichloroethylene	[13]
<i>Hydrocarbons:</i>	
Benzene, Ethylbenzene, Styrene, ...	[14]
Benzo[a]pyrene	[15]
Methane, Ethane, Propane, Butane, ...	[16]
Phenanthrene, Biphenyl	[17]
<i>Pesticides:</i>	
Atrazine, Pentachlorophenol	[18]
Chlorpropham	[19]
Parathion	[20]
<i>Phenols (non-halogenated):</i>	
Nitrophenol	[21]
Phenol	[22]
<i>Polymers:</i>	
Cellulose	[23]
Dextrane	[24]
Polystyrene	[25]
Pullulan, Poly(ethylene oxide), ...	[26]
Rice starch	[27]
<i>Others:</i>	
Humic acid	[28]
Hydrogen sulphide	[29]
Methyl <i>tert</i> -butyl ether (MTBE)	[30]

by ultrasound requires long irradiation periods, resulting in large energy consumption [7,11,32].

1.3 Integrated Ultrasonic–Biological Degradation

With respect to poorly biodegradable (recalcitrant) pollutants, combinations of physical–chemical techniques with biodegradation are considered

to be economically more favourable than complete mineralisation by physical–chemical methods alone. In such processes it is important to recognise both their potential and the limitations, in the design of more effective and economical integrated processes.

In the past, advanced oxidation processes (AOPs) have been frequently used to transform recalcitrant chemicals into better biodegradable products [1,33]. The AOPs result in the formation of the very reactive OH radical, e.g. by addition of ozone [34] or Fenton's Reagent [35], by UV-irradiation [36] or γ -irradiation [37], or by wet oxidation [38].

Ultrasound irradiation exhibits some similarity to AOPs in that OH radicals are produced. In contrast to the AOPs listed, ultrasonic cavitation additionally generates pyrolytic reactions and hydromechanical forces. Therefore, different types of ultrasonic reactions might be used to improve the biodegradability of recalcitrant pollutants. It is the aim of this chapter to discuss the potential of integrated ultrasound–biodegradation processes in the light of the underlying mechanisms. Successful combinations of ultrasonic and biological degradation of different environmental pollutants are presented as well as the side reactions that should be taken into consideration.

2. EFFECT OF ULTRASOUND ON MICRO-ORGANISMS

Two different strategies might be applied in an integrated ultrasound–biodegradation process: simultaneous ultrasonic and biological treatment, or ultrasonic pre-treatment followed by biodegradation. In case of simultaneous ultrasonic treatment and biodegradation, damage of the micro-organisms by ultrasound has to be avoided or, at least, the microbial growth rate has to equal the rate of ultrasonic inactivation. Therefore, knowledge of the most important parameters affecting microbial damage by ultrasound, is a prerequisite for the design of integrated processes in a combined sono–bioreactor.

The damaging effects of ultrasound on micro-organisms were recognised as early as 1929, when Harvey and Loomis [39] studied the destruction of luminous bacteria by high frequency sound waves at 375 kHz. In the following decades, the effect of ultrasound on micro-organisms has been studied predominantly in the context of inactivation of micro-organisms [39–49] or extraction of intracellular material [50–55]. Inactivation of micro-organisms has been studied focussing on ultrasound alone [39–43,45,46,49] and on ultrasound in combination with ozone [44] or high pressure and temperature [47,48]. In succeeding sections, the susceptibility of different micro-organisms to ultrasound will be discussed with regard to the ultrasound parameters employed.

2.1 Ultrasound Frequency, Intensity, and Sonication Time

In a recent study, the effect of ultrasonic frequency on the activity of micro-organisms was examined by sonicating activated sludge, constituting a mixture of different micro-organisms [56]. For sonication, identically shaped ultrasonic reactors were used operating at frequencies between 41 and 3217 kHz. The microbial activity was determined by measuring the oxygen utilisation rate (OUR) in the presence of the easily biodegradable substrate acetate. After ultrasonic irradiation, the lowest OUR was obtained at the lowest frequency of 41 kHz. The OUR was least reduced at the highest frequency of 3217 kHz (Figure 1). The results clearly indicate that damaging effects of sonication decrease with increasing frequency. Decreasing damage of micro-organisms at increasing ultrasound frequencies has also been observed in the context of zooplankton inactivation [42,43] and sewage sludge disintegration [57].

It is well known that the resonant cavitation bubble radius is larger at low frequencies than at high frequencies [3,4,57]. Therefore bubble collapse at low frequency, e.g. 20 kHz, results in the most powerful hydromechanical shear forces. In contrast, it has been reported that sonochemical effects are more pronounced at higher frequencies between 200 and 1000 kHz [4,58]. This demonstrates that damage of microbial cells is due to hydromechanical shear forces rather than sonochemical processes. The hydromechanical shear stress decreases with decreasing size of the collapsing cavitation

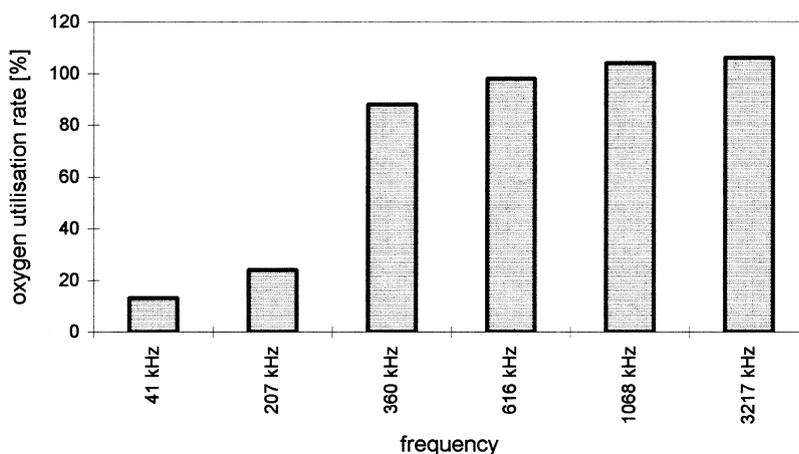


Figure 1. Effect of ultrasound frequency on the oxygen utilisation rate of activated sludge (intensity: 2 W/cm²; power: 50 W; volume: 250 ml; sonication period: 90 min). Damage of micro-organisms decreases with increasing frequency.

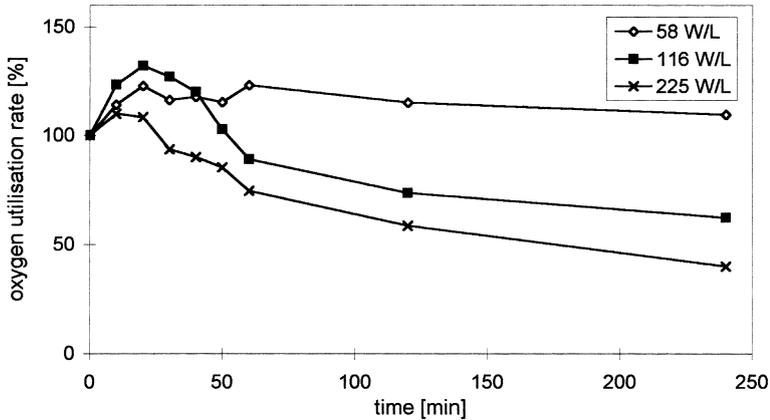


Figure 2. Effect of ultrasound density and sonication time on the oxygen utilisation rate (OUR) of activated sludge (frequency: 351 kHz). The increase of OUR at low ultrasound doses indicates the deagglomeration of microbial flocs. The following decrease is due to lysis of the single cells.

bubbles, and results in less pronounced cell rupture as ultrasound frequency increases.

The first action of ultrasound on microbial flocs is deagglomeration and dispersion of the single cells. Figure 2 illustrates this effect for the sonication of activated sludge. Again, microbial activity was determined as OUR in the presence of the easily biodegradable substrate acetate. The OUR first shows a rise due to a better availability of the substrates oxygen and acetate to the dispersed single cells. Afterwards, the biological activity decreases due to cell lysis. Similar observations have been made in pure cultures with respect to the number of viable cells [45]. After sonication, the number of viable cells first increased followed by a sharp decrease. This pattern also was attributed to the dispersion of previously clumped cells of the pure culture.

Figure 2 also demonstrates that the damage of micro-organisms increases with increasing ultrasound intensity or increasing treatment time. The same results have been reported for pure cultures of bacteria [41,45,47–49, 52,55,59], yeasts [52,55,59], other fungi and viruses [49], and zooplankton organisms [42,43,60].

The literature survey has shown that at low frequency, ultrasonic irradiation of micro-organisms without damaging effects, is possible only if ultrasound doses are low, i.e. periods are short or intensity is low. With increasing frequency or decreasing intensity, a longer irradiation of active micro-organisms is possible.

Simultaneous sonication has already been applied in the context of the extraction of intracellular material. Wang and Sakakibara [53] sonicated

Lactobacillus strains at 200 kHz to stimulate enzyme release and lactose hydrolysis during milk fermentation. Kilby and Hunter [51] applied 1.02 MHz irradiation to extract intracellular pigments of *Beta vulgaris* L. (red beetroot) cells without damaging the cells. Simultaneous sonication is discussed in more detail in Section 3.2 of this chapter.

2.2 Susceptibility of Microbial Species to Ultrasound Damage

The nature of a particular micro-organism affects its sensitivity to ultrasound. Studies with pure microbial cultures have revealed that the following factors determine the susceptibility of micro-organisms to ultrasonic disintegration:

- *Cell size*: damage of micro-organisms increases with increasing size. Wase and Patel [55] found a linear relationship between the mean cell volume and the disintegration rate of *Bacillus cereus*, *Escherichia coli*, and *Saccharomyces cerevisiae*. Furthermore, it has been shown that the inactivation of zooplankton, which is significantly larger than bacteria, is achieved with low ultrasonic energy input [42,43,60].
- *Shape of micro-organisms*: cylindrical rods are more easily disrupted than spherical cocci [45,47].
- *Cell wall composition*: there are several reports that a thick cell wall with numerous chemical cross-links yields the utmost protection against ultrasonically induced mechanical stress. Therefore, Gram-negative cells with a thin cell wall, e.g. *E. coli*, are more easily disrupted compared to Gram-positive cells that are characterised by a thick cell wall, e.g. Mycobacteria [41,47,50,55]. In contrast to most other reports, a recently published study did not find a higher susceptibility for Gram-negative bacteria leading to the hypothesis that the intracellular membrane structure might also be important [49].
- *Physiological state*: active, vegetative cells are more easily destroyed than their inactive spores. The higher resistance of spores to the ultrasonically induced shear stress is attributed to their reduced volume and thicker cell walls [40,41].

3. ENHANCED BIODEGRADATION BY ULTRASONICALLY ENHANCED MASS TRANSFER

The biodegradation of hydrophobic pollutants is often limited by a low bio-availability. The low bio-availability of hydrophobic, nonpolar compounds is due to their low water solubility, high adsorption tendency, and low

dissolution rate. The biodegradation rate of hydrophobic pollutants is a function of the mass transfer rate into the aqueous phase, where microbial uptake and degradation takes place [61–63]. Low bio-availability is the limiting factor in the bioremediation of soil contaminated with e.g. polycyclic aromatic hydrocarbons [64]. Also in wastewater treatment, sorption of hydrophobic pollutants to biomass has been shown to affect the biodegradation rate [65].

The bio-availability of hydrophobic pollutants can be improved by measures accelerating mass transfer into the aqueous phase. An enhanced mass transfer can be achieved by, for example, a high stirring rate [66] or addition of surfactants [64,67,68]. Enhanced mass transfer can also be achieved by adding polar substituents to the hydrophobic pollutants, thus modifying the chemical structure and increasing their water-solubility. Ozonation is a technique suitable for the production of reaction products with increased polarity [1].

Sonication is another suitable method for increasing the mass transfer of hydrophobic compounds into the aqueous phase. Improved mass transfer can be achieved by the hydromechanical and/or the sonochemical effects of ultrasound. A schematic illustration of the two mechanisms resulting in an enhanced bio-availability of hydrophobic pollutants is shown in Figure 3. If the mechanism is based on hydromechanical effects only (Figure 3B), immediate biodegradation of the dissolved pollutants is necessary to maintain the driving force of the process. Therefore, simultaneous sonication and biodegradation is favourable. If the mechanism is based on sonochemical transformation of the pollutants into better water-soluble reaction products (Figure 3C), then the overall water-solubility of the pollutants will no longer be a limiting factor. Therefore, a sequential technique can be applied: ultrasonic pre-treatment followed by subsequent biodegradation. Experimental results and a more detailed discussion are given in the following sections.

3.1 Sonochemical Pre-treatment of Phenanthrene

The effect of ultrasonic irradiation on bio-availability has been studied with phenanthrene—a poorly water-soluble pollutant. Phenanthrene is a nontoxic polycyclic aromatic hydrocarbon (PAH) frequently used in laboratory studies. Many other PAHs exhibit toxic, carcinogenic, and mutagenic potential. The effect of ultrasound frequency on mass transfer has been studied between 41 and 3217 kHz. After sonication of 250 mg of phenanthrene crystals suspended in 250 ml mineral buffer, the supernatants were analysed for the chemical oxygen demand (COD), the UV-absorption (254 nm), and the concentration of dissolved phenanthrene [69].

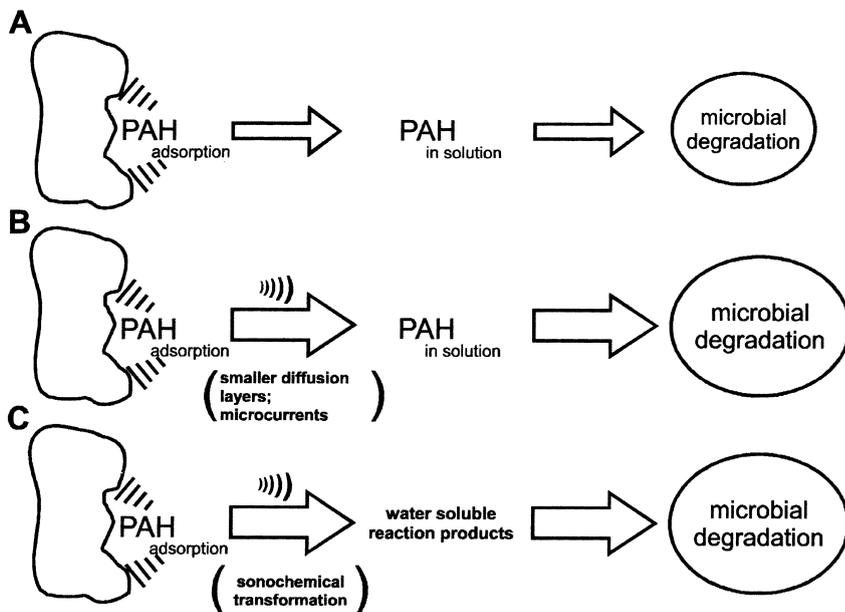


Figure 3. Schematic presentation of the enhanced bio-availability of polycyclic aromatic hydrocarbons (PAH) by ultrasound: (A) The mass transfer rate of adsorbed PAHs into the aqueous phase limits the rate of microbial degradation. (B) Mass transfer and biodegradation are enhanced by microcurrents produced by ultrasound. (C) Mass transfer and biodegradation are enhanced by sonochemical effects.

The maximum solubility of phenanthrene in water is 1.2 mg/l corresponding to a maximum aqueous phase COD of about 3.6 mg/l. The COD increased to >20 mg/l in the samples sonicated at 41, 207, or 616 kHz. The COD of the control sample and the sample sonicated at 3.2 MHz were below the detection limit of 2 mg/l (Figure 4). In the silent control sample, 0.3 mg/l phenanthrene were dissolved. This corresponds to about 0.9 mg/l COD.

Also the increase in UV-absorption was most pronounced in the frequency range between 41 and 616 kHz. The UV-absorption of the samples sonicated at 1068 kHz and 3217 kHz was almost the same as in the unsonicated control. The correlation of both parameters, COD and UV-absorption, indicated that mainly aromatic compounds were produced by the sonochemical treatment of phenanthrene [69].

Subsequent incubation of the sonicated supernatants showed that the sonochemical reaction products were biodegradable. A decrease in aqueous-phase COD and formation of biomass was observed (Table 2). No inhibiting or toxic products were produced by the sonochemical pre-treatment.

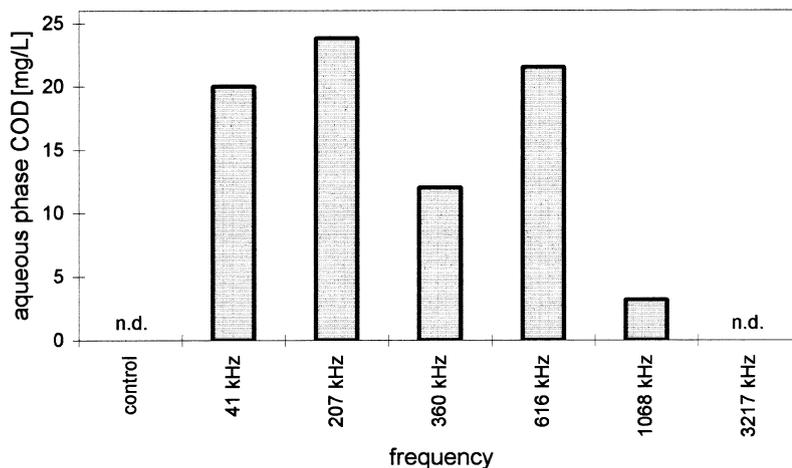


Figure 4. Effect of ultrasound frequency on the formation of water-soluble reaction products of phenanthrene (COD: Chemical Oxygen Demand; n.d.: not detectable) (intensity: 2 W/cm²; power: 50 W; volume: 250 ml; sonication period: 60 min).

Table 2. Effect of Ultrasound Frequency on the Formation and Biodegradation of Sonochemical Reaction Products of Phenanthrene

Frequency (kHz)	After sonication	After biological degradation	
	COD dissolved (mg/l)	COD dissolved (mg/l)	Protein (mg/l)
control (no ultrasound)	n.d.*	n.d.	n.d.
41	20.0	2.5	0.85
207	23.8	6.7	0.81
360	12.0	3.2	0.46
616	21.5	3.6	0.93
1068	3.2	n.d.	n.d.
3217	n.d.	n.d.	n.d.

* n.d., not detectable.

3.2 Simultaneous Sonication and Biodegradation

The application of ultrasound at the same time as biodegradation is only possible if the micro-organisms are not damaged by sonication. As has already been discussed in Section 2.1, damage of micro-organisms by ultrasound decreases with increasing frequency. At a frequency of 3.2 MHz and an ultrasound dose of 300 Wh/l, the oxygen utilisation rate of activated sludge was not affected (Figure 1). Therefore, this frequency was chosen [69]

to study the effect of simultaneous sonication on the biodegradation of solid naphthalene and phenanthrene, representing model polycyclic aromatic hydrocarbons (PAHs).

In order to obtain defined and reproducible experimental conditions, the solid PAHs were fixed by a method published by Mulder et al. [66]. Aluminium covers of Erlenmeyer flasks were cut at approximately 0.5 cm height. Phenanthrene or naphthalene crystals were put into the covers and melted on a hot plate at about 130°C. The melts were cooled at room temperature and smooth surfaces were obtained. The surface area of the PAH melts was about 12 cm². The covers containing solid naphthalene or phenanthrene were fixed in the ultrasonic reactor and the silent control reactor, as shown in Figure 5.

The mass transfer rate of solid naphthalene was increased by sonication at 3.2 MHz. An increased ultrasonic power input resulted in faster naphthalene dissolution (Figure 6). The initial rates of dissolution were 0.4 $\mu\text{mol}/(\text{min} \times \text{l})$ in the unsonicated control and 4.9 $\mu\text{mol}/(\text{min} \times \text{l})$ when sonicating with 58 W power input. Irradiation at 3.2 MHz also increased the dissolution rate of phenanthrene significantly. In case of phenanthrene, the initial rates of dissolution were 0.01 $\mu\text{mol}/(\text{min} \times \text{l})$ in the unsonicated control and 0.09 $\mu\text{mol}/(\text{min} \times \text{l})$ at 58 W power input. The higher dissolution rate of naphthalene was attributed to its better solubility compared to phenanthrene (water solubilities: naphthalene 30 mg/l, and

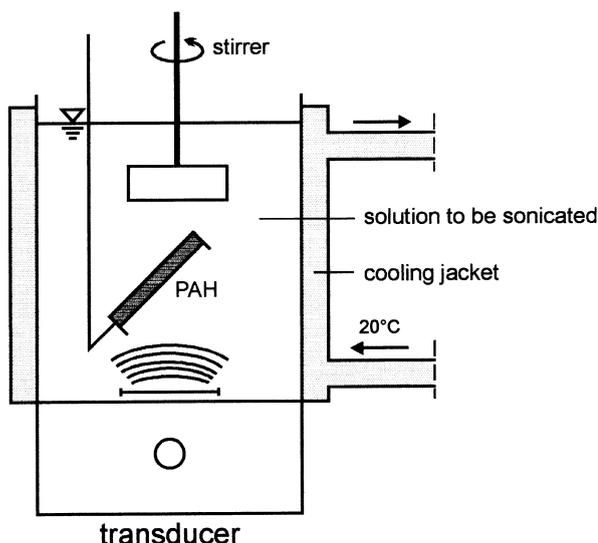


Figure 5. Experimental set-up to study the effect of sonication (frequency: 3217 kHz) on the dissolution of solid polycyclic aromatic hydrocarbons (PAH).

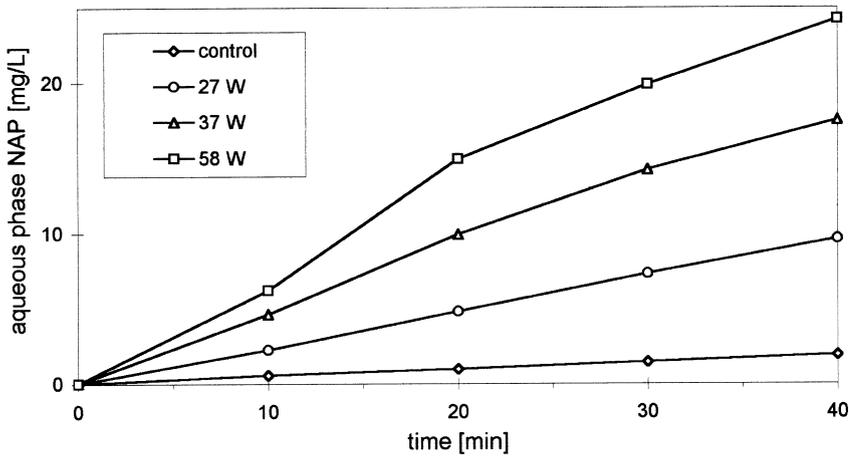


Figure 6. Increased dissolution of solid naphthalene in relation to sonication time and power input (frequency: 3217 kHz).

phenanthrene 1.2 mg/l). Neither high performance liquid chromatography (HPLC) analysis nor the absorption spectra of the supernatants indicated the occurrence of sonochemical reactions in these experiments [56].

The results presented so far have demonstrated that a faster dissolution of solid PAHs could be achieved under conditions that do not damage microorganisms. Consequently, a faster biodegradation of the PAHs could be expected when ultrasound and biodegradation are applied simultaneously. This hypothesis was confirmed experimentally. The simultaneous sonication and biodegradation was studied in a fermenter system equipped with a mass spectrometer for online offgas analysis (Figure 7). For inoculation, mixed cultures were used that had been pre-adapted to naphthalene or phenanthrene degradation, respectively.

Ultrasound-enhanced mass transfer of naphthalene resulted in an accelerated biodegradation as demonstrated by the CO_2 production in the fermenter (Figure 8). Immediately after the start of sonication, the concentration of CO_2 in the fermenter offgas increased. Corresponding to the higher CO_2 production, protein concentration and optical density in the fermenter increased. Similar effects were observed in the case of phenanthrene. Again, the production of CO_2 was increased by sonication. Due to the lower dissolution rate of phenanthrene, absolute mineralisation rates were smaller. However, for both model compounds, the increase of the biodegradation rate was not directly related to the increase of the dissolution rate. This was attributed to the formation of a biofilm on the surface of the PAHs [56] that also influences mass transfer processes [70].

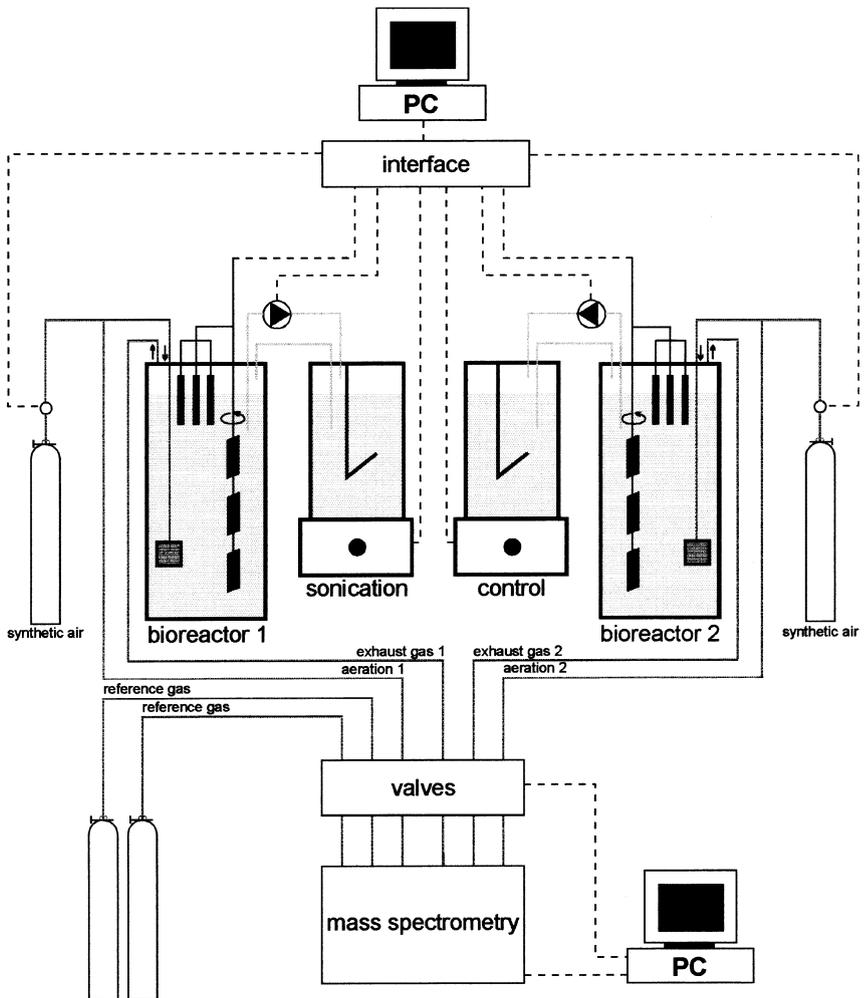


Figure 7. Experimental set-up of the fermenter system used for simultaneous sonication and biodegradation studies.

In the experiments presented so far, high frequency ultrasound was used in order to avoid damage of the active biomass. The results demonstrate that biodegradation processes limited by slow mass transfer can be significantly improved by ultrasound. This finding is consistent with previous biochemical studies with enzymes. Sonication at 7.6 MHz was shown to increase the activity of immobilised amylases [71]. The enzymes α -amylase and glucoamylase were bound to porous polystyrene

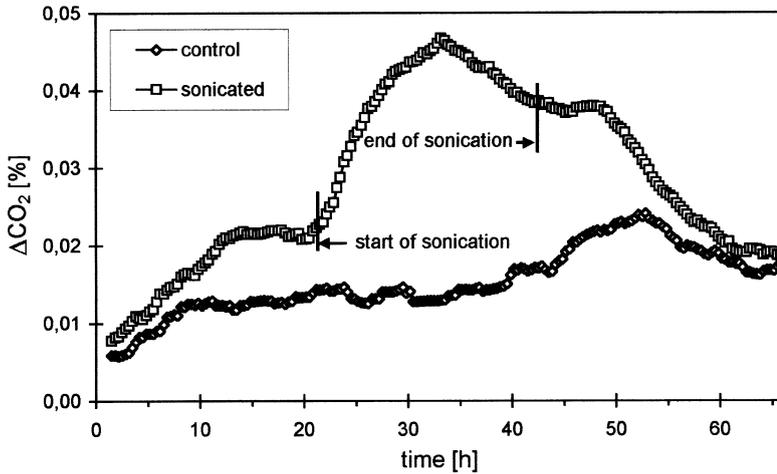


Figure 8. Effect of sonication on the formation of CO_2 during biodegradation of solid naphthalene (frequency: 3217 kHz; power: 50 W).

and the conversion rates of starch and maltose were determined, respectively. The maximum enzyme activity doubled in the presence of the ultrasonic field. No occurrence of cavitation was observed by hydrophone measurements. Schmidt et al. [71] set up a mathematical model for the interior and exterior substrate transport. From the theoretical considerations and the experiments, it was evident that the mechanism of the ultrasonic effect could be explained by a reduction of the diffusion layer around the matrix particles.

Increased enzyme activity also was achieved by sonication at 20 kHz [72]. The enzyme α -chymotrypsin was immobilised on agarose gel and the immobilised enzyme was employed for the proteolytic reaction under the influence of ultrasound. Casein was used as a substrate for α -chymotrypsin. The activity was 2.0–2.2 times that of the silent control. The acceleration of the enzyme activity by ultrasound was explained by improved mass transfer of casein into the agarose gel. In this study, some inactivation of the immobilised α -chymotrypsin was observed under ultrasound after repeated uses.

Bar [73] also applied 20 kHz ultrasound to increase cholesterol oxidation by *Rhodococcus erythropolis*. Sonication was applied using a sonication horn for 5–10 s every 10 min (ultrasound density: 2.8 W/50 ml). A significant ultrasonic breaking of cholesterol particles into finer ones was observed. Sonication had a beneficial effect on cholesterol oxidation at a cholesterol concentration of up to 2.5 g/l. The enhanced bioconversion of cholesterol in the presence of ultrasound was attributed to an increased dissolution

rate of the substrate crystals and enhanced mass transfer inside and outside a cell. At higher concentrations adverse effects were observed, possibly due to the increasing abrasive power of the crystals resulting in the break-up of the bacteria.

4. ULTRASONIC PRE-TREATMENT OF DISSOLVED LOW MOLECULAR WEIGHT POLLUTANTS

In the following, the removal of recalcitrant dissolved low molecular weight pollutants by integrated ultrasonic–biological processes is presented. The treatment of high molecular weight pollutants is discussed in Section 5 as it involves different ultrasonic reaction mechanisms.

In contrast to the solid or adsorbed hydrophobic pollutants described in Section 3, the biodegradation of dissolved pollutants is not limited by a low mass transfer rate into the aqueous phase. Reasons for a poor biodegradation of dissolved pollutants might be their toxicity, a chemical structure that resists biological degradation, or the presence of other compounds that are preferred as growth substrates. In case of dissolved low molecular weight pollutants, ultrasonically induced thermal and/or radical reactions are considered to be more important than hydromechanical forces. Therefore, ultrasonic pre-treatment should preferentially take place at frequencies between 200 and 1000 kHz, which have been shown to be more efficient in thermal conversion and radical production than frequencies below 200 kHz [4,58].

In the experiments presented in Sections 4.1 and 4.2, chlorinated compounds have been chosen as model pollutants. Chlorinated pollutants have attracted scientific and public attention because of their toxicity and persistence. Chlorinated aliphatic and aromatic hydrocarbons are used as solvents and degreasers. Chlorinated aromatic phenols are used as disinfectants and pesticides. They are released into the environment by point sources like industrial wastewater discharges, leaching of landfills, leaking tanks and by non-point sources like agricultural run-off. Both, chlorinated hydrocarbons and phenols, are mobile in contaminated soil [74] and have been detected in contaminated surface water and ground water [75,76].

4.1 Mixtures of Chlorobenzene and Easily Biodegradable Compounds

In wastewater, often low concentrations of a hazardous pollutant are mixed with high concentrations of easily biodegradable compounds. In

order to simulate such a situation, the sonochemical dehalogenation of chlorobenzene was investigated in the presence of acetate and glucose [77]. It has been shown previously that in mixtures there is a high selectivity for the dehalogenation of hydrophobic and volatile pollutants [58]. Therefore, selective ultrasonic degradation of chlorobenzene is expected even in the presence of high concentrations of hydrophilic compounds. Chlorobenzene is captured preferentially in the cavitation bubble where it is degraded primarily by pyrolytic reactions. A scheme of the proposed reactions is shown in Figure 9.

The influence of other organic compounds on the decomposition of chlorobenzene was studied by adding 2500 mg/l acetate or glucose to 80 mg/l chlorobenzene [77]. Ultrasonic degradation processes were monitored by analysing the concentration of chlorobenzene, the concentration of Adsorbable Organic Halogens (AOX), aqueous phase chloride, and the Chemical Oxygen Demand (COD).

The ultrasonic pre-treatment of chlorobenzene alone resulted in the complete decomposition of the substance and in reduction of AOX by approximately 90%. The increase of chloride corresponded to the AOX reduction (Figure 10). The addition of acetate or glucose did not influence

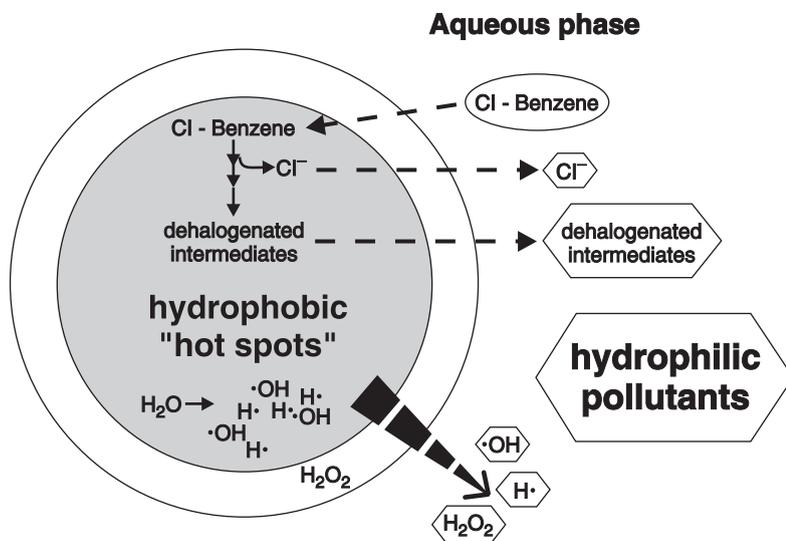


Figure 9. Schematic presentation of the processes involved in the selective sonochemical dehalogenation of hydrophobic and volatile pollutants like chlorobenzene. Hydrophobic compounds are symbolised by round frames, hydrophilic compounds by angular frames.

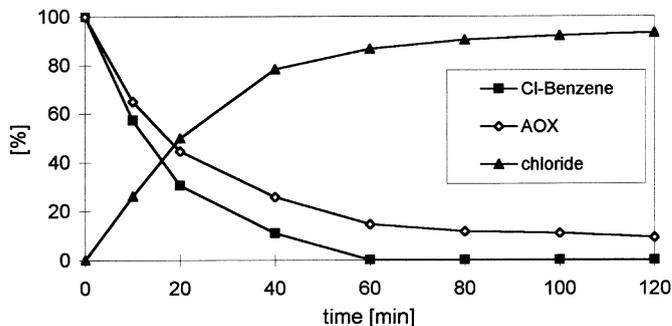


Figure 10. Decrease of chlorobenzene and AOX and increase of aqueous-phase Cl^- by ultrasonic treatment. The 100% value of chloride corresponds to the initial chlorine amount of chlorobenzene (frequency: 618 kHz; intensity: 4 W/cm²; power: 100 W; volume: 500 ml).

the sonochemical degradation rates of chlorobenzene and AOX (Figure 11). The degradation followed pseudo first-order kinetics. This is typical of many sonochemical degradation processes [8,12,14,30,78–81]. First-order rate constants were $k = 0.0555/\text{min}$ (correlation coefficient $r^2 = 1.00$) for chlorobenzene and $k = 0.0197/\text{min}$ ($r^2 = 0.91$) for AOX. The COD remained almost unchanged in the sonicated samples which indicated that overall oxidation of the organic compounds was low. Neither the dehalogenated intermediates of chlorobenzene nor acetate or glucose were oxidised significantly (Table 3). The sonochemical process was highly selective in favour of the degradation of chlorobenzene.

The results of the experiments done with chlorobenzene alone were consistent with previous findings that the sonication of chlorobenzene leads to the formation of chloride and dehalogenated intermediates [6,9,82]. Tiehm et al. [77] additionally studied the biodegradation of the intermediates after ultrasonic pre-treatment of chlorobenzene alone and of the mixtures with acetate and glucose. The COD remaining after sonochemical dehalogenation was significantly reduced by subsequent biodegradation (Table 3). Obviously, residual organic pollutants after sonochemical dechlorination were biodegradable. No production of inhibiting or toxic compounds during the ultrasound pre-treatment process was observed. In case of the model compounds used in this study, biological treatment as a single process technology would not result in chlorobenzene but in acetate or glucose degradation, respectively. Ultrasonic pre-treatment followed by biodegradation is suitable for the elimination of both the chlorinated compound of low concentration and the highly concentrated easily biodegradable pollutants.

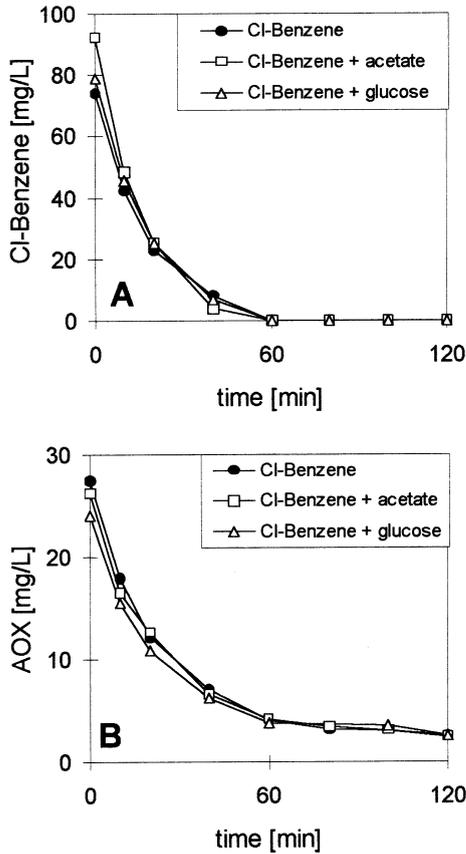


Figure 11. Ultrasonic degradation of (A) chlorobenzene and (B) AOX in the presence of 2500 mg/l acetate or glucose (frequency: 618 kHz; intensity: 4 W/cm²; power: 100 W; volume: 500 ml).

Table 3. Effect of Sonochemical Dechlorination of Chlorobenzene and subsequent Biodegradation on Aqueous Phase COD. Initial Concentrations of Chlorobenzene were between 74 and 92 mg/l

Substrate	COD (mg/l)		
	No treatment	After sonochemical dechlorination	After biological degradation
Chlorobenzene alone	101	98	23
Chlorobenzene + 2500 mg/l acetate	2566	2598	65
Chlorobenzene + 2500 mg/l glucose	2742	2724	46

4.2 Reduction of Dichlorophenol Toxicity

2,4-Dichlorophenol was selected as another chlorinated model pollutant to study the integrated ultrasonic–biological elimination process. Again, elimination of 2,4-dichlorophenol alone and of mixtures with acetate and glucose was examined. In contrast to chlorobenzene, the chlorophenol exhibited toxic effects. Therefore, sonochemical dehalogenation was a prerequisite to enable subsequent biodegradation [77].

The reaction rate of chlorophenols increases with decreasing pH, because the molecular chlorophenol species present at acidic pH diffuse more easily into the hydrophobic interfacial region of the cavitation bubbles, where the concentration of hydroxyl radicals is high. At alkaline pH the ionic species predominate and react only with the radicals that enter the bulk liquid [6,11,83].

Ultrasonic treatment at pH 4 resulted in the complete disappearance of 2,4-dichlorophenol [77]. In addition, the AOX were reduced to about 40%. Corresponding to AOX reduction, the chloride concentration increased from zero to 60% of the calculated maximum concentration possible (Figure 12). It is evident by a comparison of Figures 10 and 12 that after the disappearance of the initial pollutant (chlorobenzene: 60 min; 2,4-dichlorophenol: 120 min) the remaining AOX were significantly higher in the case of 2,4-dichlorophenol (chlorobenzene: 15%; 2,4-dichlorophenol: 38%). The formation of more chlorinated reaction products might be attributed to the more reactive structure of the phenolic molecule.

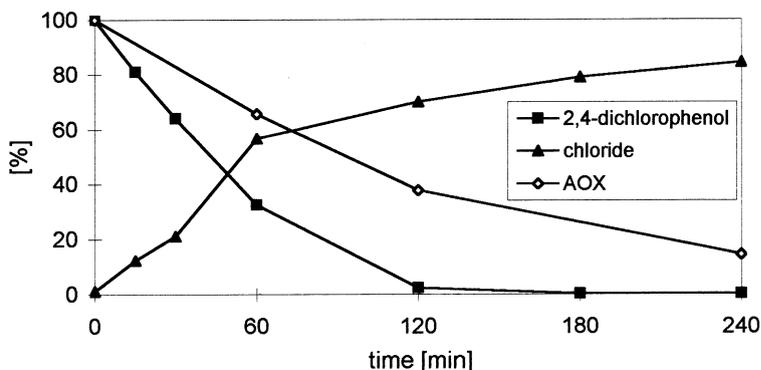


Figure 12. Decrease of 2,4-dichlorophenol and AOX and increase of aqueous phase Cl^- by ultrasonic treatment. The 100% value of chloride corresponds to the chlorine initially present in 2,4-dichlorophenol (frequency: 360 kHz; intensity: 4 W/cm^2 ; power: 100 W; volume: 500 ml).

The sonochemical degradation rates followed pseudo first-order kinetics (Figure 12). First-order rate constants were $k = 0.0189/\text{min}$ ($r^2 = 0.99$) for 2,4-dichlorophenol, and $k = 0.0082/\text{min}$ ($r^2 = 0.99$) for AOX. These values show that—under almost identical conditions—the sonochemical degradation of 2,4-dichlorophenol and the related AOX proceeds more slowly than that of chlorobenzene. Different decomposition rates are due to the different physico-chemical properties of both pollutants. It has been reported previously that the pyrolytic degradation of volatile compounds like chlorobenzene occurs faster than the degradation of more hydrophilic substances by radical reactions [6].

The addition of 900 mg/l of acetate or glucose did not significantly affect the decomposition rate of 2,4-dichlorophenol (Figure 13A) and the reduction of AOX was influenced only slightly (Figure 13B). Under the conditions of the study [77], ultrasonic irradiation was highly selective for the dehalogenation of 2,4-dichlorophenol. After 240 min of ultrasound treatment, 2,4-dichlorophenol had disappeared completely and the AOX had been reduced by 80%. In the same time, the COD was reduced only slightly in the solutions containing acetate or glucose (from 182 to 101 mg/l in pure 2,4-dichlorophenol, from 1202 to 1112 mg/l in 2,4-dichlorophenol + acetate, from 1257 to 1125 mg/l in dichlorophenol + glucose).

Biological treatment was not possible in the presence of 2,4-dichlorophenol. The purpose of the sonochemical pre-treatment was to decompose the toxic chlorinated compound. Subsequently microbial degradation was possible in order to eliminate the residual organic pollutants. Whereas no microbial activity was observed in untreated samples, the effect of ultrasound on biological oxygen consumption can be seen clearly in Figure 14. In a sonicated solution of pure 2,4-dichlorophenol, the Biological Oxygen Demand (BOD) was about 50 mg/l within 10 days of incubation (Figure 14A). The BOD₁₀ of sonochemically pretreated mixtures of 2,4-dichlorophenol and acetate or glucose reached 600 and 700 mg/l, respectively (Figure 14B,C). Ratios of COD/BOD₁₀ ranged from 1.6 to 2.0, indicating good biodegradability of the sonicated samples.

The positive effects of ultrasonic pre-treatment on the biodegradability of 2,4-dichlorophenol solutions were consistent with the results obtained in the bioluminescence test [83]. In Table 4 the effective concentrations resulting in a 50% reduction (EC50) of bioluminescence are shown before and after sonication. Increasing EC50 values correspond to decreasing toxicity. Before sonication, a concentration of 4.5% of 2,4-dichlorophenol solution in the bioluminescence medium reduced the bioluminescence intensity by half. After ultrasonic treatment, 11.7% of the solution could be added to the test medium before the 50% inhibition was reached. Reduced toxicities in the bioluminescence test were also observed when sonication took place in the presence of acetate or glucose (Table 4).

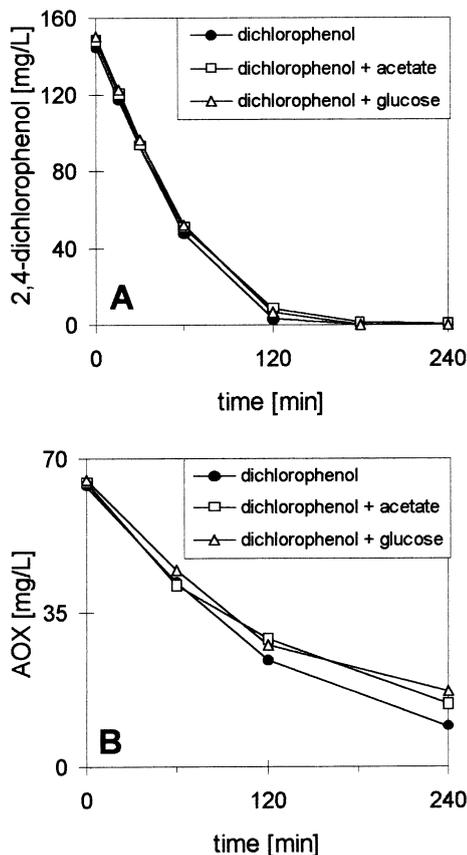


Figure 13. Ultrasonic degradation of (A) 2,4-dichlorophenol and (B) AOX in the presence of 900 mg/l acetate or glucose (frequency: 360 kHz; intensity: 4 W/cm²; power: 100 W; volume: 500 ml).

4.3 Humic Acids and Pure Terephthalic Acid (PTA) Industrial Wastewater

Ma and Lin [28] studied the effect of ultrasound pre-treatment on the biodegradability of 50 mg/l humic acids. The study was carried out in order to optimise the removal of organic matters and to reduce the formation of the by-products of disinfection. Ultrasonic pre-treatment at 20 kHz resulted in a decrease of TOC and in an increase of BOD. Biodegradability was improved with increasing sonication time. Both effects, the oxidation of humic acids by ultrasound and the enhanced biodegradation after sonication, resulted in a less pronounced chlorine demand for water disinfection.

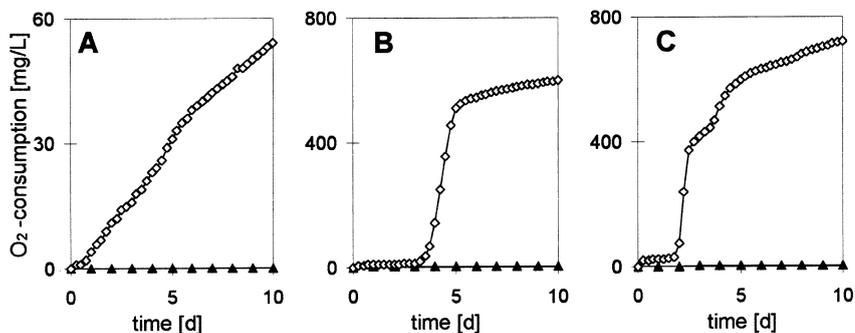


Figure 14. Biological oxygen consumption after sonication (\diamond) of (A) pure 2,4-dichlorophenol, (B) 2,4-dichlorophenol + 900 mg/l acetate, and (C) 2,4-dichlorophenol + 900 mg/l glucose. No microbial activity was observed without ultrasonic pre-treatment (\blacktriangle).

Table 4. Reduction of Toxicity in the Bioluminescence Test by Ultrasonic Treatment (Frequency: 360 kHz; Intensity: 4 W/cm²; Power: 100 W; Volume: 500 ml; Time: 240 min) of 2,4-Dichlorophenol Solutions. Toxicity is given as Effective Concentration Resulting in a 50% Inhibition (EC50). Initial Concentrations of 2,4-Dichlorophenol were between 145 and 150 mg/l

Substrate	EC50 [%]	
	before sonication	after sonication
2,4-Dichlorophenol alone	4.5	11.7
2,4-Dichlorophenol + 900 mg/l acetate	3.1	19.6
2,4-Dichlorophenol + 900 mg/l glucose	3.1	7.3

In another study [84], PTA industrial wastewater was treated with ultrasound-H₂O₂ to increase the biodegradability. PTA is one of the major raw materials of the polyester fibre and PET bottle manufacturing industry. The BOD and TOC of the wastewater were 13 200 mg/l and 6390 mg/l, respectively. The effect of ultrasound-H₂O₂ treatment on mineralisation and biodegradability was investigated with various concentrations of H₂O₂ and pH values. The rate of sonochemical mineralisation increased with decreasing pH values and increasing concentrations of H₂O₂. The biodegradability increased if the TOC was reduced by treatment with ultrasound-H₂O₂ but decreased if the TOC was reduced by ultrasound alone. The optimum conditions determined for the pre-treatment of PTA wastewater using the ultrasound-H₂O₂ process followed by biological treatment was found to be pH 3 and 200 mg/l H₂O₂.

5. ULTRASONIC PRE-TREATMENT OF POLYMERS AND SEWAGE SLUDGE

5.1 Fragmentation of Polymers

A general relationship exists between the average molecular weight of polymers and their amenability to biodegradation: the shorter the chains, the higher the likelihood of biodegradation. Not only does a lower degree of polymerisation yield a higher concentration of chain-end groups, but it also discourages the formation of crystalline domains that are generally difficult to biodegrade. High chain-end concentrations promote exo-type reactions, and, in synthetic polymers as well as in biopolymers, e.g. lignocellulose, noncrystalline regions are known to be preferentially biodegraded [85].

Ultrasonic treatment has been found to be a suitable method for changing the size of polymers [25]. Polymer fragmentation by ultrasound has been demonstrated, e.g. for dextran [86], pullulan, polyethylene oxide, and polyvinylpyrrolidone [87]. Portenlänger [86] stated that for low ultrasound frequencies in the range from 20 to 400 kHz the main effect correlates with the mechanical forces. With increasing frequency a decrease in the mechanical effects as compared to the radical effects has been observed. The mechanical effects increase for increasing molecular weight of the macromolecules. Below a defined molecular weight limit, no mechanical effects occur. For small molecules, only radical reactions lead to fragmentation [86].

The pre-treatment of polymers can significantly increase their susceptibility to the action of enzymes or micro-organisms. A frequently used synthetic model polymer is high molecular weight polyethylene glycol (PEG). Under both aerobic [88] and anaerobic [89] conditions, the rate of biodegradation was found to be inversely proportional to the number of ethylene glycol units present in the molecule. Pre-treatment of PEG polymers by wet air oxidation [90] or addition of ozone [91] resulted in the production of smaller PEG fragments. Both pre-treatment techniques were successfully applied to enhance subsequent biodegradation of PEG polymers. Because ultrasonic treatment is another method which causes scission of polymer chains, the sonication of macromolecules can be expected to result in better biodegradability. The proposed mechanisms are illustrated in Figure 15.

Tiehm et al. [92] studied the effect of ultrasound on polymer fragmentation and subsequent biodegradation of PEG. 1 g/l PEG with a molecular weight of 1 000 000 was ultrasonically treated for 30 min at 100 W/l. The sample was sonicated at 41 kHz producing predominantly mechanical effects and at 618 kHz producing predominantly radical effects. Viscosity

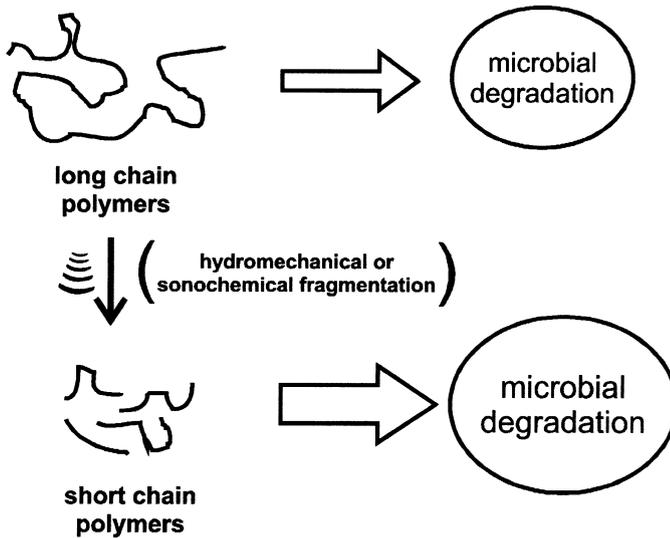


Figure 15. Schematic presentation of polymer fragmentation by ultrasound and subsequently improved biodegradability.

measurements revealed that fragmentation was achieved under both conditions. The molecular weight was reduced to about 75 000 and 100 000 by ultrasonic treatment at 41 and 618 kHz, respectively. The biodegradation of the polymer was stimulated by the ultrasonic pre-treatment with more pronounced effects at 41 kHz (Figure 16). Probably, the radical reactions predominating at high frequency not only lead to polymer fragmentation but also to a certain cross-linking of the fragments that might adversely influence biodegradation. The mechanical effects produced by low frequency ultrasound lead to a more specific chain scission in the middle of the molecule thus being more suitable for subsequent biodegradation.

5.2 Disintegration of Sewage Sludge

In the context of this chapter, reference also has to be made to the ultrasonic disintegration of sewage sludge. Pre-treatment of sewage sludge is another application of ultrasound making use of the mechanical effects of ultrasonically produced cavitation. The mechanical shear forces lead to the disintegration of sludge flocs and microbial cells. After disintegration, the quantity of bio-available organic material is significantly higher. Therefore, ultrasonic treatment accelerates the anaerobic digestion of sewage sludge.

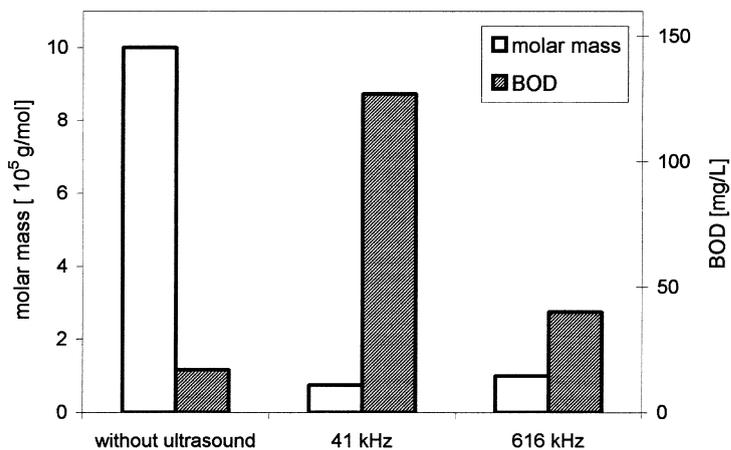


Figure 16. Effect of ultrasonic pre-treatment (intensity: 2 W/cm^2 ; power: 50 W ; volume: 400 ml) on the average molar mass of polyethylene glycol and subsequent biodegradability as represented by the Biological Oxygen Demand (BOD).

Digester through-put and biogas production can thus be increased. A comprehensive discussion of ultrasonic pre-treatment to enhance the anaerobic degradation of sewage sludge is given in Chapter 3 of this book.

6. SONOCHEMICAL SIDE REACTIONS

In the previous chapters, successful combinations of ultrasonic and biological pollutant degradation have been presented. Nevertheless, it has to be expected that the unspecific reactions triggered by acoustic cavitation might also have adverse effects on microbial activity under certain conditions. In the following, studies are presented that focus on sonochemical reactions producing inorganic by-products of biological significance.

6.1 Formation of Hydrogen Peroxide

Hydrogen peroxide is produced if an aqueous solution is sonicated. This is the result of several recombination reactions of the radicals produced by the sonolysis of water. One important mechanism resulting in the formation of hydrogen peroxide is the recombination of two hydroxyl radicals. Hydrogen peroxide formation was not only observed in pure water but also during sonochemical degradation of pollutants [58,93].

Gonze et al. [94] sonicated solutions of 0.1 mM sodium pentachlorophenate (NaPCP) in order to reduce the NaPCP toxicity. Concentrations of NaPCP and H_2O_2 , the toxicity in the bioluminescence test and the daphnids mobility test, and growth of activated sludge after ultrasonic pre-treatment were monitored. The study revealed that the toxic NaPCP was completely degraded by ultrasonic treatment (frequency: 500 kHz; density: 220 kW/m^3 ; sonication time: 120 min). Toxicity of the solution first decreased corresponding to NaPCP degradation. After 2 h of sonication, toxicity increased again. This effect could be explained by the formation of H_2O_2 that was a function of the specific energy dissipated during sonication of the reference solution and the NaPCP solution (Figure 17). The results showed that the increase in H_2O_2 was similar in both solutions and, consequently, that the production of H_2O_2 resulted from water sonication only. Both pure NaPCP and H_2O_2 solutions were toxic in the bioluminescence test. The total toxicity of the sonicated samples was a result of competition between the decrease in NaPCP toxicity and the increase in the toxicity of the products, mainly hydrogen peroxide (Figure 18). Similar effects were obtained in the daphnids mobility test.

In the same study [94] the toxicity became low enough to be harmless for activated sludge in spite of the residual toxicity due to hydrogen peroxide in the bioluminescence test. After a sonication period of 2 h or longer, development of the bacterial population was observed. For sonication times between 0–1.5 h, the toxicity of the solutions remained too high to keep

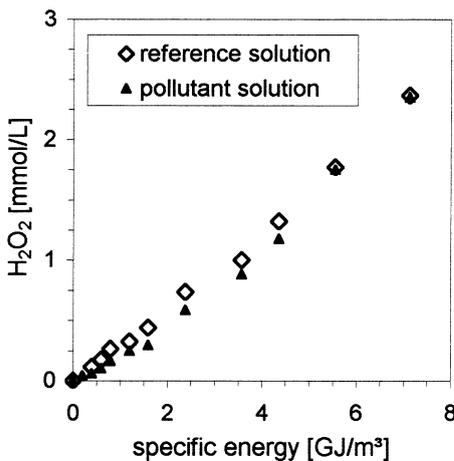


Figure 17. Production of hydrogen peroxide in reference and pentachlorophenate solutions in relation to the dissipated ultrasonic specific energy (reprinted from [94]; with permission of Elsevier Science S.A.).

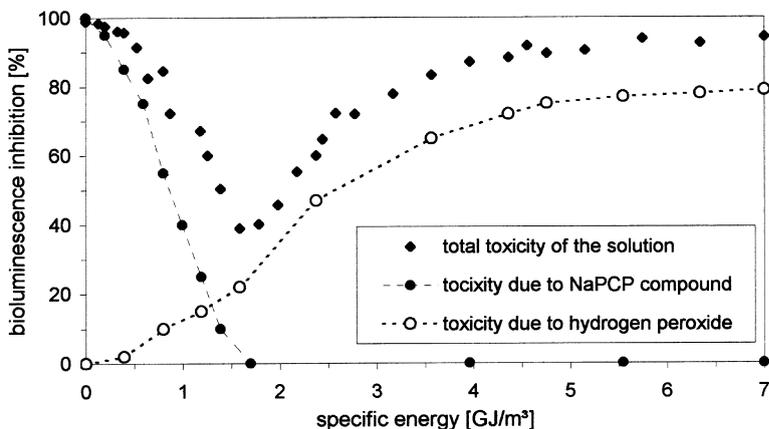


Figure 18. Evolution of total toxicity and parts of toxicity due to sodium pentachlorophenate (NaPCP) and hydrogen peroxide in relation to the dissipated specific energy. The increase in toxicity was attributed to hydrogen peroxide produced by water sonolysis (reprinted from [94]; with permission of Elsevier Science S.A.).

micro-organisms alive. Hence ultrasonic treatment was indispensable to activated sludge survival and microbiological pollutant degradation.

6.2 Formation of Nitrite and Nitrate

It is well known that nitrite and nitrate can be produced by the sonication of water [58,95]. Special attention has been paid to both compounds. First, nitrite is known to exhibit toxic effects to higher organisms in the aquatic environment. Second, the denitrifying bacteria can use nitrite and nitrate in place of oxygen as final electron acceptors under anaerobic conditions. Therefore, the sonochemical formation of nitrite and nitrate during ultrasonic sewage sludge disintegration would cause trouble in the anaerobic digester. It was evident that the formation of nitrite and nitrate had to be quantified under relevant conditions in water and sludge treatment.

Sonochemical nitrite and nitrate formation was studied in experiments dealing with the sonochemical transformation of phenanthrene into better water-soluble reaction products. The air-saturated solutions were sonicated at frequencies between 41 kHz and 3.2 MHz [56]. Formation of nitrate and nitrite occurred in the frequency range between 41 kHz and 1 MHz. Neither nitrite nor nitrate were produced in the control sample nor in the sample

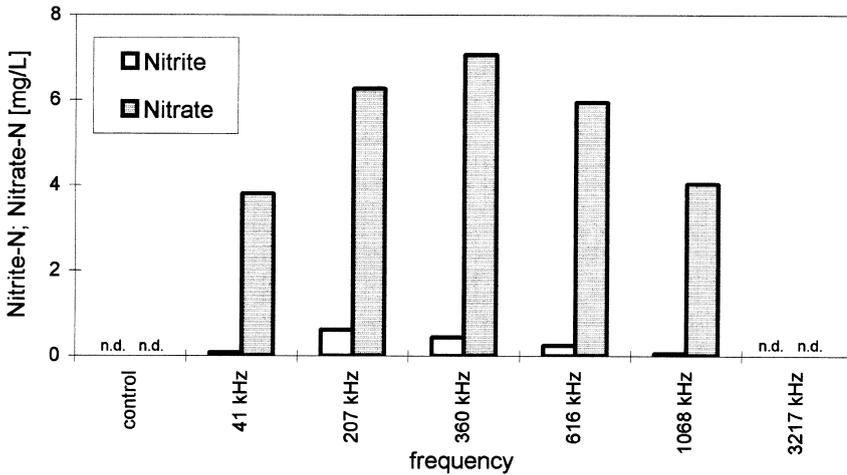


Figure 19. Effect of ultrasound frequency on the formation of nitrite and nitrate (n.d., not detectable) (intensity: 2 W/cm^2 ; power: 50 W; volume: 250 ml; sonication time: 60 min; air-saturated medium).

sonicated at 3.2 MHz. The concentration of nitrate was always significantly higher than the concentration of nitrite. Maximum values of nitrate and nitrite in terms of nitrate-N and nitrite-N were 7.1 mg/l and 0.6 mg/l, respectively (Figure 19). The small amount of nitrite produced did not inhibit the activity of a mixed microbial culture [55].

Supeno and Kruus [96] studied nitrite and nitrate production at varying ratios of N_2 to O_2 . Neither pure N_2 nor pure O_2 caused nitrite or nitrate formation whereas mixtures of N_2 and O_2 did. The study clearly indicated that OH radicals produced by the sonolysis of water are not taking part in the relevant reactions. The presence of molecular O_2 and molecular N_2 is a prerequisite for the production of nitrite or nitrate. Consequently, Neis and Tiehm [97] found that the formation of nitrite and nitrate was completely stopped if nitrogen and oxygen were stripped from the solution with argon. Ammonium was not converted to nitrite or nitrate. Also during ultrasonic disintegration of sewage sludge the formation of these compounds was never observed (Table 5). This was attributed to the fact that the sewage sludge was anaerobic.

In summary, nitrite or nitrate are not produced under anaerobic conditions and the nontoxic nitrate is the major product under aerobic conditions. Both findings are favourable with respect to integrated ultrasonic–biological treatments.

Table 5. Formation of Nitrite and Nitrate in Relation to Available Molecular Nitrogen and Oxygen (Frequency: 360 kHz; Intensity: 3.2 W/cm²; Power: 80 W; Volume: 350 ml)

Medium	Gases	Formation of	
		NO ₂ ⁻ -N (mg/l)	NO ₃ ⁻ -N (mg/l)
Mineral medium:			
+ 200 mg/l NH ₄ ⁺	air-saturated	0.2	2.8
+ 200 mg/l NH ₄ ⁺	Argon	< d.l. ^a	< d.l.
no NH ₄ ⁺	air-saturated	0.2	2.7
no NH ₄ ⁺	Argon	< d.l.	< d.l.
Sewage sludge ^b	anaerobic	< d.l.	< d.l.

^a d.l., detection limit.

^b sonicated at 41, 207, 360, 616, 1068, or 3217 kHz.

7. CONCLUSION

Combinations of ultrasonic and biological processes have the potential to eliminate environmental pollutants more thoroughly than biological treatment alone. The optimal design of a particular integrated ultrasonic–biological process depends on the physico-chemical properties of the pollutants to be treated. Figure 20 summarises the most favourable ultrasound applications in relation to the dominating primary effects occurring in particular frequency ranges.

Sonochemical effects, i.e. pyrolytic and radical processes, have been observed between 20 kHz and 1 MHz. Highest efficiencies were reported above 200 kHz. Biodegradation is stimulated if the sonochemical effects are used for an enhanced mass transfer of hydrophobic compounds, for selective dehalogenation and toxicity reduction of chlorinated pollutants, and for the fragmentation of polymers with a molar mass of up to about 40 000.

The hydromechanical effects produced by shear forces and jet-streams are most pronounced in the low frequency range between 20 and 100 kHz. Low frequency ultrasound is recommended for efficient deagglomeration of microbial flocs and sewage sludge disintegration as well as for the fragmentation of large polymers.

A selective use of the microcurrents produced by sonication is possible at high frequencies above 1 MHz. Since the micro-organisms are not damaged at such high frequencies, it is possible to use high frequency ultrasound at the same time as biodegradation. Under these conditions, sonophysically enhanced mass transfer of hydrophobic pollutants results in enhanced biodegradation.

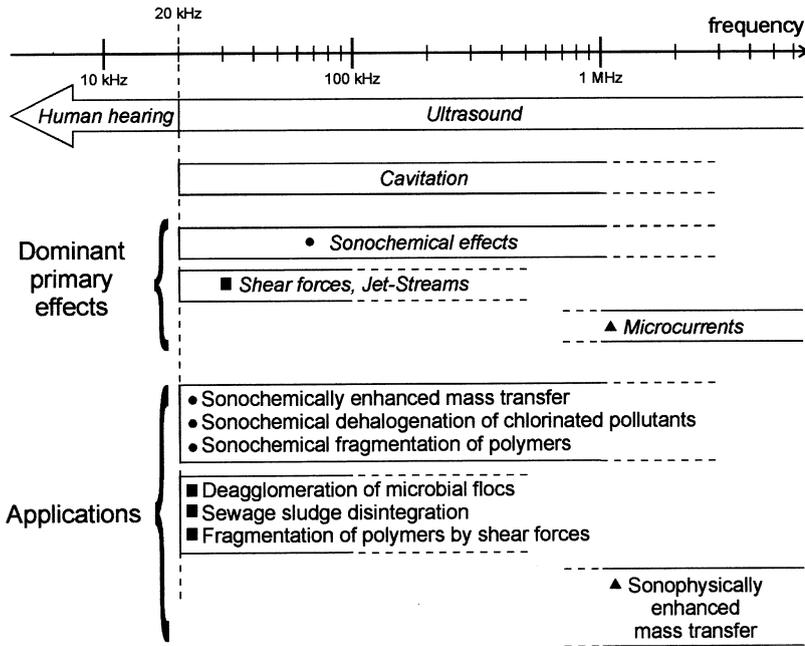


Figure 20. Primary effects dominating at specific ultrasound frequency ranges and applications taking advantage of the primary effects.

The combination of ultrasonic treatment and biodegradation represents a promising new technique in the field of environmental engineering. Firstly, different factors which restrict biodegradation can be ameliorated by ultrasound. Secondly, biodegradation of the pollutants remaining after ultrasonic treatment, is economically more favourable than complete removal by ultrasound alone. In this field the use of ultrasonic technology is in an early phase. Further studies are necessary to optimise the integrated process. More studies on real wastewater are encouraged in order to develop large scale applications.

ABBREVIATIONS

AOPs: Advanced Oxidation Processes; AOX: Adsorbable Organic Halogens; BOD: Biological Oxygen Demand; COD: Chemical Oxygen Demand; EC: Effective Concentration; *E. coli*: *Escherichia coli*; HPLC: High Performance Liquid Chromatography; NaPCP: sodium pentachlorophenate; OUR: Oxygen Utilisation Rate; PAH: Polycyclic Aromatic Hydrocarbon; PEG: Polyethylene Glycol; PTA: Pure Terephthalic Acid; TOC: Total Organic Carbon.

REFERENCES

- [1] Scott, J. P., and Ollis, D. F. *Environ. Progr.*, 14(2) (1995) 88.
- [2] Mason, T. *Practical Sonochemistry: User's Guide to Applications in Chemistry and Chemical Engineering*. Ellis Horwood Ltd., Chichester, UK, 1991.
- [3] Lorimer, J. P. In Mason, T. J. (ed.), *Sonochemistry: The uses of Ultrasound in Chemistry*. The Royal Society of Chemistry, Cambridge, 1990, pp. 9–26.
- [4] Hua, I., and Hoffmann, M. R. *Environ. Sci. Technol.*, 31 (1997) 2237.
- [5] Flint, E. B., and Suslick, K. S. *Science*, 252 (1991) 1397.
- [6] Pétrier, C., Jiang, Y., and Lamy, M.-F. *Environ. Sci. Technol.*, 32 (1998) 1316.
- [7] Vinodgopal, K., Peller, J., Makogon, O., and Kamat, P. V. *Wat. Res.*, 32(12) (1998) 3646.
- [8] Hua, I., and Hoffmann, M. R. *Environ. Sci. Technol.*, 30 (1996) 864.
- [9] Kruus, P., Burk, R. C., Entezari, M. H., and Otson, R. *Ultrasonics Sonochem.*, 4 (1997) 229.
- [10] Cheung, H. M., and Kurup, S. *Environ. Sci. Technol.*, 28 (1994) 1619.
- [11] Ku, Y., Chen, K.-Y., and Lee, K.-C. *Wat. Res.*, 31(4) (1997) 929.
- [12] Bhatnagar, A., and Cheung, H. M. *Environ. Sci. Technol.*, 28 (1994) 1481.
- [13] Drijvers, D., De Baets, R., De Visscher, A., and Van Langenhove, H. *Ultrasonics Sonochem.*, 3 (1996) 83.
- [14] De Visscher, A., Von Eenoo, P., Drijvers, D., and Van Langenhove, H. *J. Phys. Chem.*, 100 (1996) 11636.
- [15] Colarusso, P., and Serpone, N. *Res. Chem. Intermed.*, 22(1) (1996) 61.
- [16] Hart, E. J., Fischer, C.-H., and Henglein, A. *Radiat. Phys. Chem.*, 36(4) (1990) 511.
- [17] Wheat, P. E., and Tumeo, M. A. *Ultrasonics Sonochem.*, 4 (1997) 55.
- [18] Pétrier, C., David, B., and Laguian, S. *Chemosphere*, 32(9) (1996) 1709.
- [19] David, B., Lhote, M., Faure, V., and Boule, P. *Wat. Res.*, 32(8) (1998) 2451.
- [20] Kotronarou, A., Mills, G., and Hoffmann, M. R. *Environ. Sci. Technol.*, 26 (1992) 1460.
- [21] Hua, I., Höchemer, R. H., and Hoffmann, M. R. *Environ. Sci. Technol.*, 29 (1995) 2790.
- [22] Pétrier, C., Lamy, M.-F., Francony, A., Benahcene, A., David, B., Renaudin, V., and Gondrexon, N. *J. Phys. Chem.*, 98 (1994) 10514.
- [23] Marx-Figini, M. *Angew. Makromol. Chem.*, 250(4360) (1997) 85.
- [24] Portenlänger, G., and Heusinger, H. *Ultrasonics Sonochem.*, 4 (1997) 127.
- [25] Price, G. J. In Mason, T. (ed.), *Advances in Sonochemistry*, Vol. 1, JAI Press, 1990, pp. 231–287.
- [26] Koda, S., Mori, H., Matsumoto, K., and Nomura, H. *Polymer*, 35(1) (1994) 30.
- [27] Isono, Y., Kumagai, T., and Watanabe, T. *Biosci. Biotech. Biochem.*, 58(10) (1994) 1799.
- [28] Ma Y.-S., and Lin J.-G. *Wat. Sci. Tech.*, 38(6) (1998) 253.
- [29] Kotronarou, A., Mills, G., and Hoffmann, M.R. *Environ. Sci. Technol.*, 26 (1992) 2420.
- [30] Kang, J.-W., and Hoffmann, M. R. *Environ. Sci. Technol.*, 32 (1998) 3194.
- [31] Henglein, A. *Ultrasonics*, 25 (1987) 6.
- [32] Lin, J.-G., Chang, C.-N., Wu, J.-R., and Ma, Y.-S. *Wat. Sci. Tech.*, 34(9) (1996) 41.
- [33] Marco, A., Esplugas, S., and Saum, G. *Wat. Sci. Tech.*, 34(4) (1997) 321.
- [34] Camel, V., and Bermond, A. *Wat. Res.*, 32(11) (1998) 3208.
- [35] Prousek, J. *Chem. Lisy*, 89 (1995) 11.
- [36] Legrini, O., Oliveros, E., and Braun, A. M. *Chem. Rev.*, 93 (1993) 671.
- [37] von Sonntag, C. *The Chemical Basis of Radiation Biology*. Taylor and Francis, London, 1987.
- [38] Thomsen, A. B., and Kilen, H. H. *Wat. Res.*, 11 (1998) 3353.
- [39] Harvey, E. N., and Loomis, A. L. *J. Bacteriology*, 17 (1929) 373.
- [40] Ahmed, F. I. K., and Russell, C. J. *Bacteriology*, 39 (1975) 31.
- [41] Alliger, H. *American Laboratory*, October (1975) 75.

- [42] Clasen, J. (in German) *gwf Wasser Spezial*, 137(14) (1996) 163.
- [43] Clasen, J., and Sobotta, R. Proceedings of the IWSA Zurich regional conference, 1994, p. 251–259.
- [44] Dahi, E. *Wat. Res.* 10 (1976) 677.
- [45] Jacobs, S. E., and Thornly, M. J. *J. Bact.*, 17 (1954) 38.
- [46] Mues, A. (in German) *gwf Wasser Spezial*, 137(14) (1996) 167.
- [47] Pagán, R., Manas, P., Raso, J., and Condón, S. *Appl. Environ. Microbiol.*, 65 (1999) 297.
- [48] Raso, J., Pagán, R., Condón, S., and Sala, F. J. *Appl. Environ. Microbiol.*, 64 (1998) 465.
- [49] Scherba, G., Weigel, R. M., O'Brien, Jr., W. D. *Appl. Environ. Microbiol.*, 57 (1991) 2079.
- [50] Harrison, S. T. L. *Biotech. Adv.*, 9 (1991) 217.
- [51] Kilby, N. J., and Hunter, C. S. *Appl. Microbiol. Biotechnol.*, 33 (1990) 448.
- [52] Neppiras, E. A., and Hughes, D. E. *Biotechnol. Bioeng.*, 6 (1964) 247.
- [53] Wang, D., and Sakakibara, M. *Ultrasonics Sonochem.*, 4 (1997) 255.
- [54] Wang, D., Sakakibara, M., Kondoh, N., and Suzuki, K. *J. Chem. Tech. Biotechnol.*, 65 (1996) 86.
- [55] Wase D. A. J., and Patel Y. R. *J. Chem. Tech. Biotechnol.*, 35B (1985) 165.
- [56] Tiehm, A. In Tiehm, A., and Neis, U. (eds.), Technical University of Hamburg-Harburg Reports on Sanitary Engineering Vol. 25, (ISBN 3-930400-23-5), 1999, pp. 167–180.
- [57] Tiehm, A., Nickel, N., Zellhorn, M., and Neis, U. *Wat. Res.*, (2000) in press.
- [58] Pétrier, C., Jiang, Y., Francony, A., Lamy, M.-F. In Tiehm, A., and Neis, U. (eds.), Technical University of Hamburg-Harburg Reports on Sanitary Engineering Vol. 25, (ISBN 3-930400-23-5), 1999, pp. 23–37.
- [59] James, C. J., Coakley, W. T., and Hughes, D. E. *Biotechnol. Bioeng.*, 14 (1972) 33.
- [60] Bernhardt, H., Luesse, B. *Aqua*, 38(1) (1989) 23.
- [61] Thomas, J. M., Yordy, J. R., Amador, J. A., and Alexander, M. *Appl. Environ. Microbiol.*, 52 (1986) 290.
- [62] Mihelcic, J. R., Lueking, D. R., Mitzell, R. J., and Stapleton, M. *Biodegradation*, 4 (1993) 141.
- [63] Harms, H., and Zehnder, A. J. B. *Appl. Environ. Microbiol.*, 61 (1995) 27.
- [64] Tiehm, A., Stieber, M., Werner, P., and Frimmel, F. H. *Environ. Sci. Technol.*, 31 (1997) 2570.
- [65] Wang, L., and Grady, Jr., L. *Water Environ. Res.*, 67 (1995) 863.
- [66] Mulder, H., Breure, A. M., van Anandel, J. G., Grotenhuis, J. T. C., and Rulkens, W. H. *Biotech. Bioeng.*, 57(1998) 145.
- [67] Tiehm, A. *Appl. Environ. Microbiol.*, 60 (1994) 258.
- [68] Tiehm, A., and Fritzsche, C. *Appl. Microbiol. Biotechnol.*, 42 (1995) 964.
- [69] Tiehm, A., and Neis, U. In Wilhelm, A. M. (ed.), Proceedings of the 2nd conference on ultrasound in processing, PROGEP, Toulouse, 1999, pp. 165–170.
- [70] Mulder, H., Breure, A. M., van Honschooten, D., Grotenhuis, J. T. C., van Anandel, J. G., and Rulkens, W. H. *Appl. Microbiol. Biotechnol.*, 50 (1998) 277.
- [71] Schmidt, P., Rosenfeld, E., Millner, R., Czermer, R., and Schellenberger, A. *Biotechnol. Bioeng.*, 30 (1987) 928.
- [72] Ishimori, Y., Karube, I., and Suzuki, S. *J. Mol. Catal.*, 12 (1981) 253.
- [73] Bar, R. *Biotech. Bioeng.*, 32 (1988) 655.
- [74] Kitunen, V. H., and Salkinoja-Salonen, M. S. *Chemosphere* 20(10–12) (1990) 1671.
- [75] Beitz, H., Schmidt, H., and Herzel, F. In Börner, H. (ed.), *Pesticides in ground and surface water, Chemistry of plant protection* Vol. 9, Springer-Verlag, Berlin, 1994, pp. 1–56.
- [76] Canter, L.W., and Sabatini, D. A. *Intern. J. Environmental Studies*, 46 (1994) 35.
- [77] Tiehm, A., Kohnagel, I., and Neis, U. In 1st World Congress of the International Water Association (IWA), Paris, 3–7 July 2000, Book I, pp. 777–789.
- [78] Cost, M., Mills, G., Glisson, P., and Lakin, J. *Chemosphere* 27(9) (1993) 1737.

- [79] De Visscher, A., Van Langenhove, H., and Van Eenoo, P. *Ultrasonics Sonochem.*, 4 (1997) 145.
- [80] Drijvers, D., Van Langenhove, H., Nguyen Thi Kim, L., and Bray, L. *Ultrasonics Sonochem.*, 6 (1999) 115.
- [81] Hung, H.-M., and Hoffmann, M. R. *Environ. Sci. Technol.*, 32 (1998) 3011.
- [82] Ondruschka, B., and Hofmann, J. In Tiehm, A., and Neis, U. (eds.), Technical University of Hamburg-Harburg Reports on Sanitary Engineering Vol. 25, (ISBN 3-930400-23-5), 1999, pp. 139–151.
- [83] Tiehm, A., Kohnagel, I., and Neis, U. Unpublished results.
- [84] Liu, C.-H., Ma, Y.-S., and Lin, J.-G. In Rajar, R., and Brebbia, C. A. (eds.), *Water Pollution IV*, Computational Mechanics Publications, Southampton, UK, 1997.
- [85] Andrady, A. L. In Mark, J. E. (ed.), *Physical properties of polymer handbook*, American Institute of Physics, 1996, pp. 625–635.
- [86] Portenlänger, G. In Tiehm, A., and Neis, U. (eds.), Technical University of Hamburg-Harburg Reports on Sanitary Engineering Vol. 25, (ISBN 3-930400-23-5), 1999, pp. 11–22.
- [87] Koda, S., Mori, H., Matsumoto, K., and Nomura, H. *Polymer*, 35 (1994) 30.
- [88] Obradors, N., and Aguilar, J. *Appl. Environ. Microbiol.*, 57 (1991) 2383.
- [89] Dwyer, D. F., Tiedje, J. M. *Appl. Environ. Microbiol.*, 52 (1986) 852.
- [90] Mantzavinos, D., Livingston, A. G., Hellenbrand, R., and Metcalfé, I. S. *Chem. Engng. Sci.*, 51 (1996) 4219.
- [91] Suzuki, J., Hukushima, K., and Suzuki, S. *Environ. Sci. Technol.*, 12 (1978) 1180.
- [92] Tiehm, A., Alves, S., and Neis U. Unpublished results.
- [93] Keck, A., Bober, U., and Gilbert, E. In Tiehm, A., and Neis, U. (eds.), Technical University of Hamburg-Harburg Reports on Sanitary Engineering Vol. 25, (ISBN 3-930400-23-5), 1999, pp. 153–166.
- [94] Gonze, E., Fourel, L., Gonthier, Y., Boldo, P., and Bernis A. *Chemical Engineering Journal*, 73 (1999) 93.
- [95] Pétrier, C., Micolle, M., Merlin, G., Luche, J.-L., and Reverdy, G. *Environ. Sci. Technol.*, 26 (1992) 1639.
- [96] Supeno, and Kruus, P. Personal communication; Department of Chemistry, Carleton University, Ottawa, Canada, 1999.
- [97] Neis, U., and Tiehm, A. In Tiehm, A., and Neis, U. (eds.), Technical University of Hamburg-Harburg Reports on Sanitary Engineering Vol. 25, (ISBN 3-930400-23-5), 1999, pp. 39–61.

ULTRASONIC DISINTEGRATION OF SEWAGE SLUDGE FOR ENHANCED ANAEROBIC BIODEGRADATION

Uwe Neis, Klaus Nickel and Andreas Tiehm

OUTLINE

1. Introduction	60
2. Anaerobic Stabilisation of Sewage Sludge	61
2.1 Sources and Types of Sewage Sludge	61
2.2 Kinetics and Performance of Anaerobic Sludge Degradation	62
3. Ultrasonic Disintegration of Sewage Sludge	63
3.1 Fundamentals	63
3.2 Examination of Sludge Disintegration	64
3.3 Impact of Ultrasound Treatment Time, Intensity and Energy Input	67
3.4 Impact of Ultrasound Frequency	70
3.5 Sludge Solids Concentration and Sludge Type	71

Advances in Sonochemistry

Volume 6, pages 59–90.

© 2001 Elsevier Science B.V. All rights reserved.

4. Anaerobic Digestion After Ultrasonic Disintegration	74
4.1 Impact of Ultrasound Frequency and Sonication Time	74
4.2 Reduction of Anaerobic Digestion Times	79
4.3 Comparison of Sludge Types	81
5. Related Applications of Ultrasound	85
5.1 Improved Dewatering	85
5.2 Enhanced Sedimentation of Filamentous Sludge	86
6. Conclusions	88
Abbreviations	89
References	89

1. INTRODUCTION

In biological wastewater treatment large quantities of biomass (sludge) is produced. The sludge is highly putrescible. Therefore the sludge has to be stabilised before an environmentally safe utilisation and disposal can occur. Anaerobic digestion is the standard stabilisation technique. The end products are digested sludge with a reduced content of organic matter and biogas. In the European Union 50% of the municipal sewage sludges are stabilised anaerobically [1]. The slow biological sludge hydrolysis is the rate-limiting step of the anaerobic degradation. Large fermenters are necessary. Typical digestion times are 20 or more days. The degree of degradation of organic matter varies between 25 and 60%. Reduction of volatile solids (organic matter) is more pronounced in the digestion of primary sludge as compared to digestion of waste activated sludge (WAS).

The anaerobic digestion process has been extensively studied in the past 20 years and various methods for process improvement have been explored. The investigations concentrated on better sludge hydrolysis by, for example, thermal pre-treatment [2–4], chemical solubilisation by acid or base addition [5] and mechanical sludge disintegration [6,7]. Ultrasonic cell disintegration has been well known for many years in laboratory applications. Recent developments in high power transducers now allow the treatment of large amounts of sewage sludge [8,9]. The principal advantages of this no touch, no chemical and no moving mechanical parts technique were quickly recognised.

This chapter reviews current investigations on ultrasonic sewage sludge disintegration. The most important parameters for efficient sludge disintegration are discussed as well as the effects of ultrasonic sludge disintegration on subsequent digestion.

2. ANAEROBIC STABILISATION OF SEWAGE SLUDGE

2.1 Sources and Types of Sewage Sludge

The production of sewage sludge is a result of mechanical, biological and/or chemical wastewater treatment. In a mechanical–biological treatment plant (Figure 1) the wastewater influent first passes the primary clarifier resulting in the separation of settleable solids. These solids are removed as primary sludge. In the aeration tank aerobic micro-organisms oxidise fine-particulate and soluble organic substances. The aerobic metabolism yields a high amount of energy and thus triggers the growth of bacterial cells (biomass). In the secondary clarifier the surplus biomass is separated as waste activated sludge (WAS) from the main flow. Another part of the settled activated sludge is recycled into the aeration tank as inoculum for the biological aerobic wastewater degradation process. The term “raw sludge” defines the mixture of primary and WAS. Typically on a weight basis a municipal raw sludge contains equal amounts of primary and WAS. Because of its high content of putrescible organic material the raw sludge has to be stabilised. To this end the mesophilic anaerobic sludge

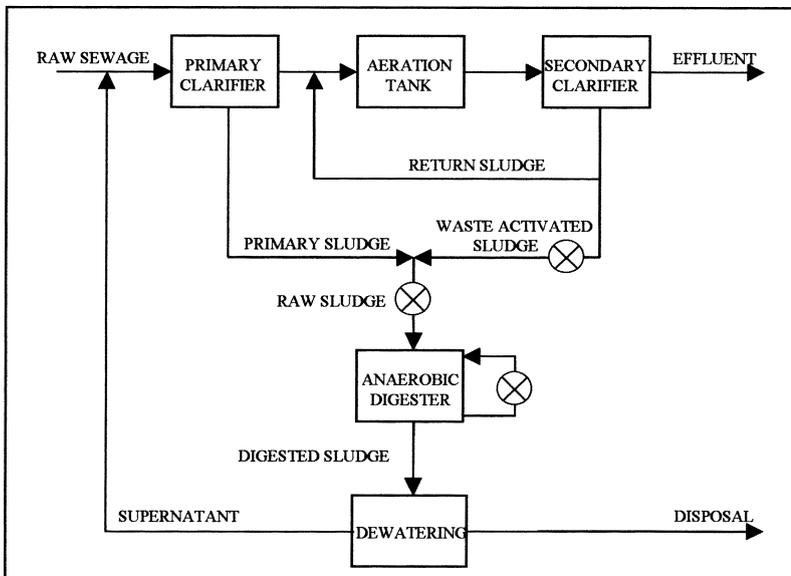


Figure 1. Typical flow chart of a municipal wastewater treatment plant (WWTP). The symbol ⊗ indicates most important locations where the application of sludge disintegration can be useful for enhanced anaerobic stabilisation.

stabilisation technique has been practised for about 100 years. In the process a net reduction of the sludge mass and volume is realised, a portion of the organic solids is microbiologically converted into methane and carbon dioxide. The final product is a stable, innocuous sludge that can be used as a soil conditioner or fertiliser [10].

As a result of the anaerobic sludge degradation, poorly biodegradable organic substances, ammonia and phosphorus are released into the sludge water phase. Because of the high concentrations of organic and inorganic compounds the digester supernatant in general is recirculated to the influent of the treatment plant. Usually the recirculated digester supernatant contributes to about 10% of the total nitrogen and phosphorus load of the wastewater treatment plant (WWTP).

2.2 Kinetics and Performance of Anaerobic Sludge Degradation

The anaerobic stabilisation of wastewater sludges is considered to be a sequential process. First, the solid organic material (volatile solids) is hydrolysed to soluble organic compounds. Second, the soluble organic compounds are fermented to volatile acids, carbon dioxide, and some hydrogen gas. The volatile acids are converted primarily to methane and carbon dioxide gas by anaerobic methane-forming bacteria. This mechanistic model of anaerobic sludge digestion is illustrated in Figure 2.

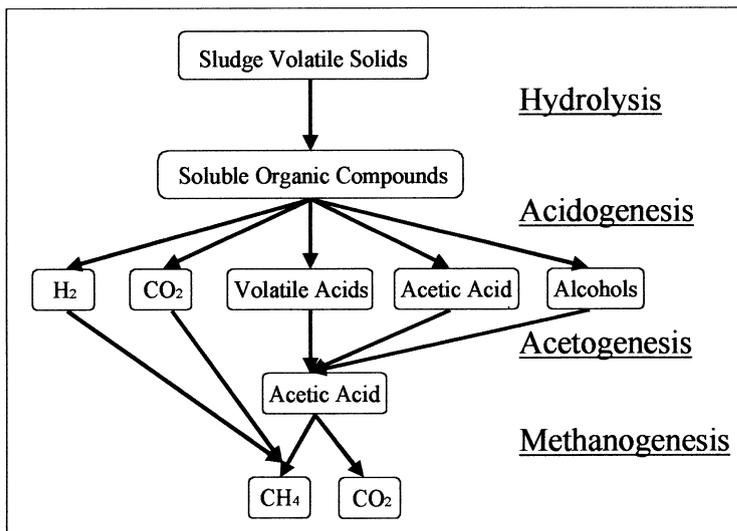


Figure 2. Mechanistic model of anaerobic sludge digestion [10].

The solid phase of sewage sludge is mainly composed of organic cell material. In order to pass the solid matter through the cell membranes of the fermentative organisms biological exoenzymes are produced, which eventually cause the necessary size reduction of the solids. The reaction rate of this sludge hydrolysis controls the overall rate of the sludge digestion [11]. Because of the complex molecular structures of the sludges they are not biodegradable to 100%.

The principal advantages of anaerobic sludge digestion compared to other stabilisation methods include [10]:

- Reduction in mass and volume of the sludge through the conversion of organic matter into methane, carbon dioxide and water. The total solids reduction of the feed sludge is usually 25–45%.
- Production of a solids residue that may be used as a soil conditioner. The anaerobically digested sludge contains nitrogen, phosphorus and other nutrients as well as organic material that can improve the fertility and texture of soils.
- Production of methane gas, which is a useable source of energy. The energy produced is in excess to that required to maintain the mesophilic temperature of the digesting sludge and to meet the energy requirements for mixing.
- The odour associated with the raw sludge is markedly reduced.
- Most pathogens associated with the feed sludge are deactivated during the anaerobic digestion process.

The principal disadvantages of anaerobic sludge digestion are:

- Long hydraulic retention times, more than 20 days, are required because of the slow biological sludge hydrolysis.
- The capital costs are high. Large, covered tanks along with pumps for feeding and circulating sludge, heat exchangers and compressors for gas mixing are required.

3. ULTRASONIC DISINTEGRATION OF SEWAGE SLUDGE

3.1 Fundamentals

The application of ultrasound in the fields of medical diagnosis, cleaning and flow detection has been a standard routine for many years, whereas for sewage sludge treatment it is a new application. Although the first ultrasound applications for sewage sludge treatment on a technical scale are operational, the acoustic-mechanical disintegration is still a young

technology. On the one hand, ultrasonic treatment has some advantages being a no chemical and no moving part technique compared to other disintegration methods. On the other hand, a number of scientific and technical questions still exist addressing, for example: the influence of the frequency and acoustic intensity, the influence of suspended solids concentration and dissolved gases on cavitation; the optimal reactor design; the economy, the reliability and the life expectation of ultrasound equipment [12].

Ultrasound can be generated at a broad range of frequencies beyond the human hearing between 20 kHz and 10 MHz. Ultrasonic reactors usually consist of electro-acoustical transducers, which are supplied by a high-frequency voltage. The acoustically induced cavitation creates shockwaves with high mechanical shear forces and/or sonochemical reactions resulting in the destruction of flocculent sludge structures and cell material. The effects that can be observed when cavitation is generated in an aqueous solution are summarised below.

Effects of Cavitation

- high mechanical shear stress
- radical reactions:
 1. creation of H and OH radicals, and
 2. subsequent chemical transformation of (organic) substances
- thermal breakdown of volatile hydrophobic substances

The ultrasonic power input is quantified by calorimetric [13] or electrical [9] measurements. The different ultrasonic parameters usually used are defined below:

- ultrasonic *intensity* relates to the power supplied per transducer area, unit: $[\text{W}/\text{cm}^2]$,
- ultrasonic *density* relates to the power supplied per sample volume, unit: $[\text{W}/\text{l}]$,
- ultrasonic *dose* relates to the energy supplied per sample volume, unit: $[\text{Wh}/\text{l}]$,
- ultrasonic *specific energy* is the energy input related to the sludge dry solids content, units: $[\text{Wh}/\text{kg}]$ or $[\text{kJ}/\text{kg}]$.

3.2 Examination of Sludge Disintegration

Sewage sludge consists of bacterial cells sticking together by extracellular polymer substances in a flocculent structure. If sewage sludge is exposed to

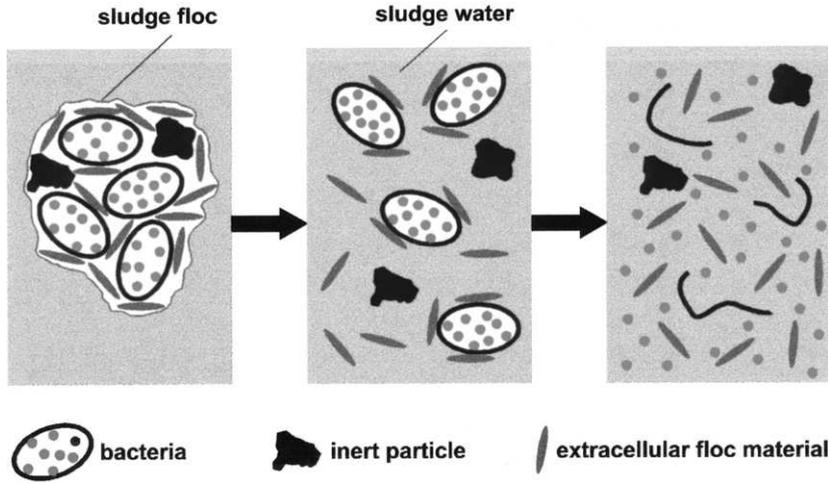


Figure 3. Schematic presentation of sludge floc decomposition and subsequent cell break-up as sonication time is increased.

ultrasonic energy the first effect is the deagglomeration of the sludge flocs. The flocs are separated and dispersed without disrupting the cells. After longer treatment time or higher ultrasonic energies, the micro-organism cell walls are broken and intracellular material is released into the liquid phase. Consequently, the amount of dissolved organic material is significantly increased [14]. This two-phase model of the ultrasonic disintegration process is illustrated in Figure 3.

The separation of the sludge flocs causes a decrease in the average particle size. Assessment of this deagglomeration process can be done by particle size distribution analysis [15–18]. If colony-forming units (cfu) are measured, first an increase in cfu counts would be observed when flocs are deagglomerated into single cells. Then after longer sonication times the number of cfu would be reduced because the cells are destroyed and the micro-organisms would be killed.

The extent of cell break-up can be described by several chemical and biological parameters:

1. The cell disruption leads to the release of intracellular organic compounds into the sludge water phase. Therefore, the extent of cell disintegration is determined by the increase in the Chemical Oxygen Demand (COD) of the sludge supernatant. A term often used is the ratio of soluble COD to total sludge COD (SCOD/TCOD) [5,19,20]. If the ultrasonic parameters are selected appropriately, up to 90% of the total sludge COD could be solubilised [20]. Other authors defined a

solubilisation ratio as concentration of Total Organic Carbon (TOC) in the supernatant after centrifuging of the sludge sample divided by the TOC concentration of the original [21].

2. Different sludges contain various types of micro-organisms with different strengths of their cell walls. For the purpose of comparison, a chemical hydrolysis process by incubation of sludge samples in 0.5 mol/l sodium hydroxide for 22 h at 20°C may be done [16,22]. By this method the effects of cell disruption becomes comparable for different sludges. A factor (DD_{COD}) “degree of disintegration” is defined as ratio of COD-increase in the supernatant by sonication or other disintegration techniques related to the COD-increase by the chemical hydrolysis method described above. The soluble COD fraction is obtained by high speed centrifugation (30 min at 40 000 *rcf*) followed by filtration through 0.45 μm pore size membrane filters [23]:

$$DD_{\text{COD}} = \frac{(\text{COD}_{\text{Ultrasound}} - \text{COD}_{\text{u}})}{(\text{COD}_{\text{NaOH}} - \text{COD}_{\text{u}})} \times 100 \quad [\%]$$

where $\text{COD}_{\text{Ultrasound}}$ is the chemical oxygen demand of the disintegrated sample (here by sonication), [mg/l];
 COD_{u} is the chemical oxygen demand of the untreated sample, [mg/l];
 COD_{NaOH} is the chemical oxygen demand of a reference sample hydrolysed chemically in a 0.5 M NaOH solution at 20°C for 22 h, [mg/l].

The impact of bacterial cell disruption can also be assessed by biological oxygen utilisation tests. Because a large fraction of sewage sludge is WAS and as such contains a considerable amount of aerobic bacteria, the oxygen utilisation rate (OUR) can be used to characterise the microbiological activity. If all bacteria of the sewage sludge are disrupted the OUR of the treated sludge is zero and the degree of disintegration (DD_{O}) reaches 100% [18]. The OUR is measured after addition of acetate as readily available substrate and aeration of the sludge samples. The oxygen utilisation rate of a disintegrated sludge sample $\text{OUR}_{\text{Ultrasound}}$ in relation to the oxygen utilisation rate of the untreated sludge OUR_{u} defines DD_{O} , the “degree of disintegration” in terms of oxygen utilisation:

$$DD_{\text{O}} = \left[1 - \left(\frac{\text{OUR}_{\text{Ultrasound}}}{\text{OUR}_{\text{u}}} \right) \right] \times 100 \quad [\%]$$

The methods outlined above to quantify cell disruption are based on different approaches. Hence if a sludge sample is disintegrated and subsequently analysed with these methods, different disintegration degree

values will be found. Therefore a comparison of values from literature does not make much sense. However, one might like to know the very few values that are available. In our investigations a DD_{COD} of 100% corresponded to average solubilisation ratios of $SCOD/TCOD = 47, 46$ and 40% for WAS, raw sludge and digested sludge respectively. Usually DD_O values are about twice as high as DD_{COD} values for the same sludge sample.

3.3 Impact of Ultrasound Treatment Time, Intensity and Energy Input

We investigated the effect of ultrasound intensity and treatment time on the disintegration of WAS and used a 20-kHz laboratory ultrasonic horn (Branson 450, Schwäbisch-Gmünd, Germany). Ultrasonic treatment at an intensity of 16 W/cm^2 and for a short period can result in a 60% increase in cfu (Figure 4A, left white column). The cfu increased because the microbial

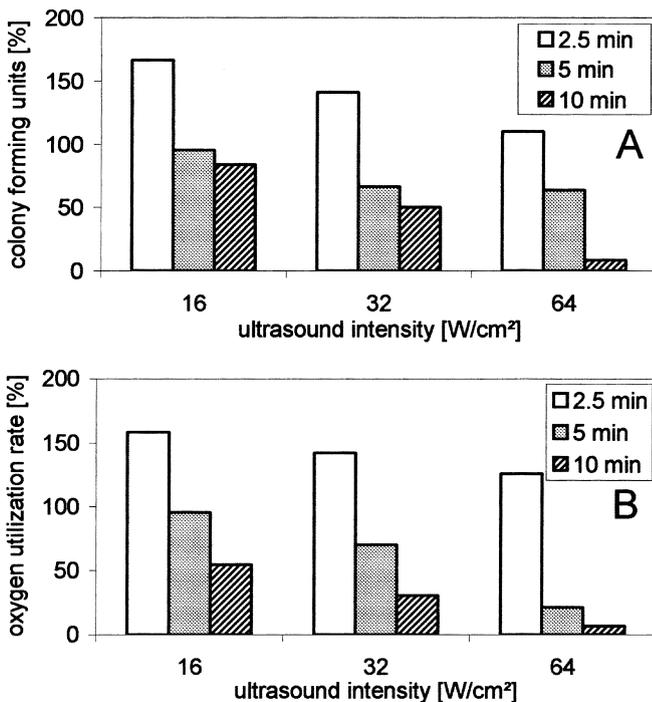


Figure 4. Effect of sonication time and ultrasound intensity on (A) the colony-forming units (cfu) and (B) the oxygen utilisation rate (OUR) of activated sludge. 500 ml sludge was sonicated at 20 kHz (transducer area: 1.2 cm^2). The non-sonicated control represented the 100% value.

flocs initially present were separated by the short ultrasound action. More single cells appeared. The cells were not damaged and remained viable. Due to the bacteria floc size reduction the availability of the substrates and oxygen increased and consequently the OUR also increased (Figure 4B, left white column). If the sonication time and the ultrasonic intensity were increased the damage of the bacteria cells was noticeable and the number of cfu as well as the OUR was reduced significantly.

King and Forster [15] tested the effects of sonication on activated sludge floc deagglomeration using a 20-kHz Dawe Soniprobe, Type 7530A (Dawe Instruments Ltd, London, UK). They increased the sonic power dose from 1.7 to 133 Wh/l and found a larger number of small particles when the higher power dose was applied. A clear relationship between the mean particle size and the sonic power was established and was used to characterise the floc strength of different activated and anaerobically stabilised sludges [24].

Lehne and Müller [18] investigated the impact of the ultrasonic treatment on WAS at 20 kHz. A laboratory scale sonoreactor Labsonic (B. Braun, Melsungen, Germany) operating at an intensity of 70 W/cm² was used. A rather low specific energy input of 3000 kJ/kg resulted in a considerable reduction of the median sludge particle size (Figure 5). This occurs when the sludge flocs are separated. Higher specific energies caused only minor changes of the median particle size. This part of the upper graph can be identified with the range where true cell disintegration takes place. The cell damage is also well reflected when the degree of disintegration DD_O is mapped accordingly (Figure 5 lower graph).

High degrees of disintegration can be obtained by applying longer sonication times or higher acoustic intensity. In other words, by increasing the energy dose. Figure 6 shows how the degree of disintegration (DD_{COD}) of WAS is increased with increasing specific energy input. Within the applied range the intensity did not influence the results when the frequency used is 41 kHz.

In this graph disintegration is already observed at a rather low intensity of 0.1 W/cm². This is well below the cavitation threshold for water which is reported to be about 0.4 W/cm² [25]. Due to the presence of a large number of solid particulate matter and gas bubbles, which act as cavitation nuclei in a sludge sample, a lower cavitation threshold seems reasonable. However, raising the intensity must not necessarily produce more intense cavitation. Under certain circumstances the contact between the radiating transducer surface and the liquid can get lost. The motion of the transducer and the liquid get out of phase, an effect which is called decoupling. Furthermore, higher intensities create more bubbles that may coalesce and lead to less pronounced effects. Therefore the energy transfer efficiency can sometimes be smaller at higher intensities [26]. We did not observe such effects in the

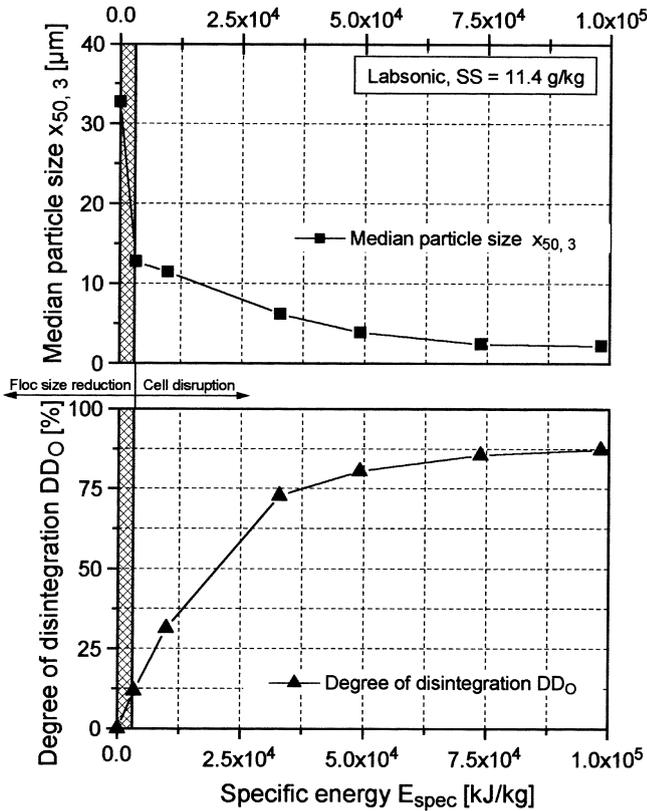


Figure 5. Degree of disintegration DD_O and median particle size of waste activated sludge (WAS) after ultrasonic disintegration (SS = sludge solids) [18].

reported range between 0.1 and 2 W/cm². However, Lehne and Müller [18] observed a decrease of the sludge cell disintegration after the ultrasound intensity of a sonotrode was increased from 130 to 520 W/cm².

Chiu et al. [5] disintegrated WAS with a combination of ultrasound (20 kHz) and alkali. Compared to the alkaline treatment alone the combined process was significantly more effective for sludge solubilisation. Alkaline treatment is capable of converting small flocs into soluble substances, while ultrasonic treatment was used for the break down of larger sludge floc structures. Combining this treatment, more than 80% of the total waste activated sludge COD was dissolved and the average molecular weight was significantly reduced from 31 000 amu (atomic mass unit) to 8500 amu. After a combined treatment the WAS can still maintain

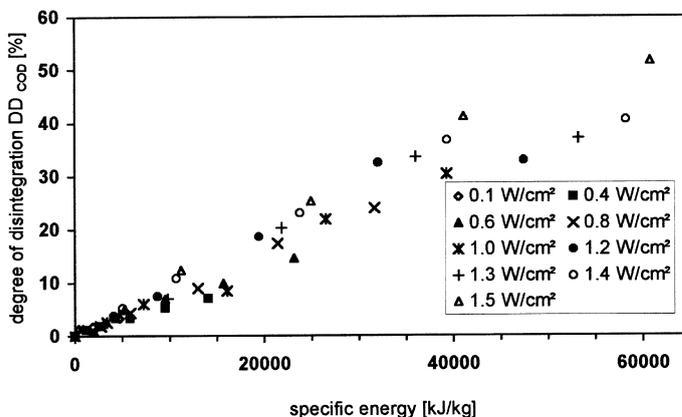


Figure 6. Effect of intensity and energy dose at 41 kHz on the degree of disintegration (lab reactor URS 1000, L-3 Communications ELAC Nautik, Kiel, Germany; sonication time: max. 2 h; WAS dry solids concentration: 25.9 g/kg).

satisfactory dewaterability characteristics [19] which is not the case in the alkaline process.

Shimizu et al. [21] reported an enhanced lysis of micro-organisms of WAS during ultrasonic treatment when surfactants were added. The authors applied 20 kHz with 200 W ultrasound in a 1-litre-reactor for 30–40 min. Adding 50 mg/l of Tween-80 (polyoxyethylene sorbitan monooleate) doubled the solubilisation rate of WAS and had no inhibiting effect on the sludge digestibility in the following anaerobic fermentation process.

3.4 Impact of Ultrasound Frequency

Ultrasound with varying frequencies in a range from 41 kHz to 3217 kHz was applied and its impact on the sludge disintegration in the lab reactor URS 1000 (Figure 8) was studied. As can be seen in Figure 7, the degree of WAS disintegration (DD_{COD}) decreased with increasing ultrasound frequency. The highest degree of disintegration was 80% obtained at the lowest frequency 41 kHz. It is well known that the resonant cavitation bubble radius increases with decreasing ultrasonic frequency [27]. Upon bubble collapse, hard shockwaves are induced by jet streams responsible for the mechanical break-up of the microbiological cell walls. We assume that the energy released by a jet stream is a function of the bubble size at the moment of collapse [14]. This is consistent with investigations published by Portenlänger [28] which show that especially at low ultrasound frequencies

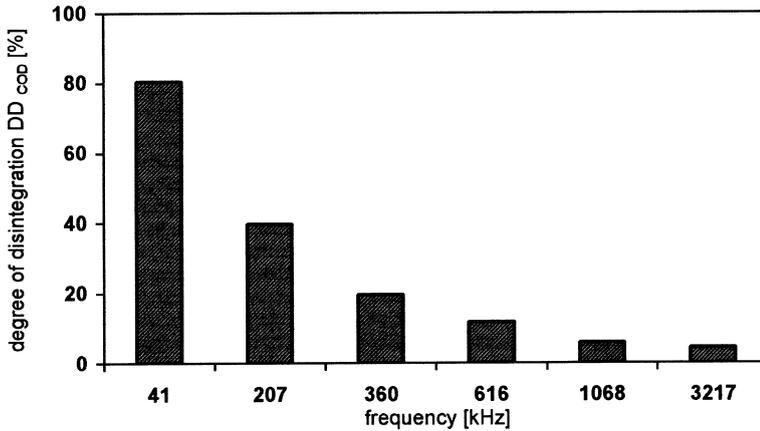


Figure 7. Effect of ultrasonic frequency on the degree of cell disintegration (intensity: 1.8 W/cm^2 , sonication time: 4 h).

strong mechanical forces are splitting high molecular macromolecules. Eventually our recommendation is to apply only low ultrasound frequencies (less than $\sim 40 \text{ kHz}$) for efficient sludge disintegration.

3.5 Sludge Solids Concentration and Sludge Type

Sludge suspensions are very different to pure water systems for which the theoretical calculations for cavitation and related phenomena are valid. First of all we might assume that there is a significant effect from the solids concentration in the medium on the extent of cavitation because inhomogeneities in the water body can be considered as potential cavitation sites. Furthermore the statistical probability that a solid is affected by mechanical jet streams during bubble implosion increases with higher solids concentration. In order to evaluate the influence of the sludge dry solids content we sonicated WAS in two different reactor types. A normal WAS has a dry solids content of about $5\text{--}10 \text{ g/kg}$. The solids concentration can be increased by thickening of the sludge up to $40\text{--}60 \text{ g/kg}$.

In the laboratory we used the system URS 1000 (L-3 Communications ELAC Nautik, Kiel, Germany; maximum power consumption: 200 W). A 41-kHz disk transducer (area 25 cm^2) was fixed at the bottom of a cylindrical tube equipped with a stirrer (Figure 8). Sonication was done batchwise while the maximum acoustic intensity applied was 2 W/cm^2 .

A new high-power pilot-scale reactor (maximum power consumption: 3.6 kW) was designed especially for sewage sludge treatment (system

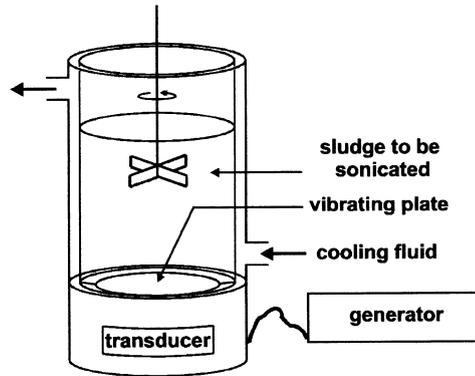


Figure 8. The laboratory ultrasonic reactor URS 1000 (L-3 Communications ELAC Nautik, Kiel, Germany; volume: 500 ml, max. power: 200 W).

SORA 3, STN ATLAS Elektronik, Bremen, Germany). This sonoreactor was developed to operate at a low frequency of 31 kHz and high acoustic intensities between 5 and 18 W/cm². The sonoreactor is a vessel with 12 piezoceramic transducers fixed at each of the four side-walls (Figure 9A). The reactor volume is 1.28 litre. Sonication was performed in a continuous mode while the sludge was pumped in an upward flow through the square channel (45 × 45 mm) of the reactor (Figure 9B).

In terms of specific energy demand, no influence of the sludge solids concentration on the cell disintegration was observed in the laboratory sonoreactor URS 1000. In contrast to this observation an augmentation of the WAS solids concentration had a positive effect on the disintegration when the pilot reactor SORA 3 was used (Figure 10). Obviously the design of the reactor plays a role. In the case of the URS 1000 with a single transducer at the bottom of the vessel it may be that the hydromechanical pressure field is damped with increasing solids content in the medium so that only a limited sludge volume above the bottom of the reaction tube is effected by cavitation forces. In the case of the pilot-scale device the transducers are mounted around the reactor on each of the four sides. Thus there will be a more homogenous pressure field and cavitation forces will be better distributed throughout the complete volume of the reactor even at high solid contents of the sludge. From Figure 10 we can conclude that at the same level of energy input, thicker sludge can be disintegrated much more efficiently.

Clark and Nujjoo [20] used a 9-kW processor comprising 3 × 3-kW radial horns for disintegrating different sewage sludges with varying dry solids content at maximum sonication times of 60 s. In this publication no detailed information about the ultrasound reactor and its mode of operation

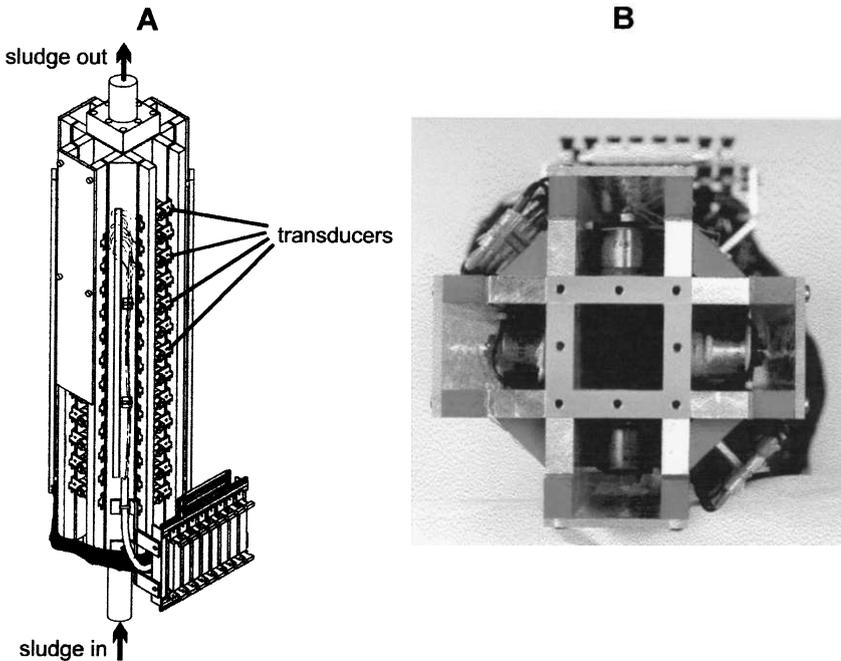


Figure 9. Scheme (A) and top-view (B) of the pilot ultrasonic reactor SORA 3 (STN ATLAS Elektronik, Bremen, Germany; volume: 1.28 l, max. power: 3.6 kW).

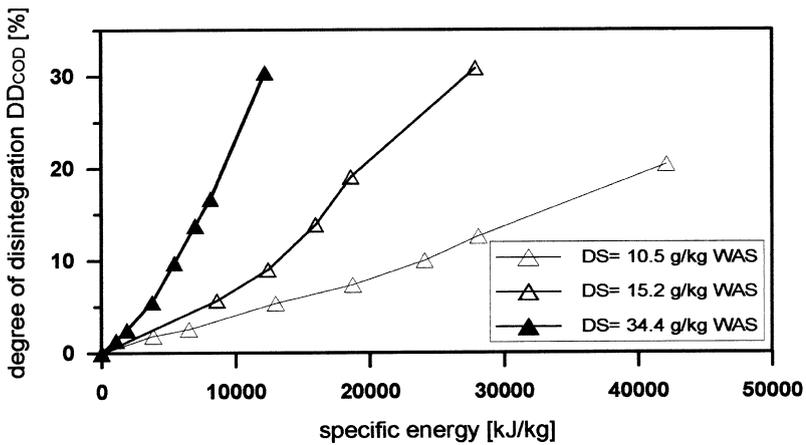


Figure 10. Effect of sludge dry solids content (DS) on specific energy demand for disintegration in the pilot sonoreactor SORA 3 (frequency: 31 kHz, intensity: 10.0–10.5 W/cm², sonication time: max. 96 s).

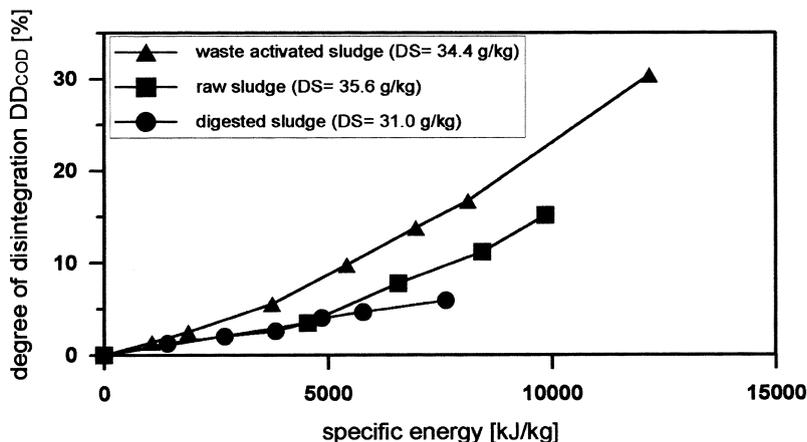


Figure 11. Effect of specific energy on degree of disintegration with regard to different sludge types (frequency: 31 kHz, intensity: 6.3–12.5 W/cm², sonication time: max. 96 s).

was given. Sludges with a solid content up to 6% were processed without attenuation effects by possible scattering or internal absorption. In thicker sludges that contain proportionally more organic material the increase of SCOD was considerably more pronounced. By increasing the sonication time to 60 s a solubilisation degree of COD up to 90% was observed.

We sonicated different sludge types using the pilot-scale device SORA 3: waste activated, raw and digested sludge. In WAS the ultrasonic treatment caused higher degrees of disintegration compared to the treatment of raw and digested sewage sludge (Figure 11). This is due to a higher concentration of micro-organisms in that sludge type. The most effective cell disruption in terms of specific energy input is obtained by treating thickened WAS in homogenous low frequency cavitation fields.

Similar results were reported by Clark and Nujjoo [20]. They also noted more solubilisation of activated sludge compared to primary sludge.

4. ANAEROBIC DIGESTION AFTER ULTRASONIC DISINTEGRATION

4.1 Impact of Ultrasound Frequency and Sonication Time

In the laboratory we investigated the impact of the ultrasound frequency applied for sludge disintegration on the subsequent anaerobic biodegradation. Sonication was performed in the URS 1000 reactor (Figure 8) filled

with 0.3 l WAS. The power input was 39 W for 60 min at 41, 207, 360 and 1068 kHz. One control fermenter was operated with untreated WAS. Five fermenters were used for the anaerobic digestion with a total volume of 1 litre each. Digested sludge was replaced by appropriate volumes of WAS three times a week over a period of 1 month. The resulting Sludge Retention Time (SRT) was 8 days.

Compared to the control conventional stabilisation, the anaerobic sludge degradation was best improved when the disintegration pre-treatment was done at the lowest frequency possible (Figure 12). Putting together the results of our fermentation studies it can be said that low frequency ultrasound is well suited for the disintegration of sewage sludge. As a result the anaerobic degradation of sludge is improved because significantly more dissolved organic matter will be available and degraded in the same period of time. An increased anaerobic degradation means that the sludge mass for final disposal is significantly reduced.

A second set of fermentation experiments was done with WAS using ultrasound of 41 kHz. Now, the sonication time was varied from 7.5 to 150 min [14]. All other parameters remained unchanged. At the shortest treatment time of 7.5 min no increase in soluble COD (DD_{COD}) was observed. However, sludge flocs were deagglomerated, which could be assessed by an increase of the OUR. Genuine cell disintegration was observed when the sonication lasted longer: 30, 60 or 150 min. The relevant degrees of disintegration DD_{COD} were 4.7, 13.1, and 23.7%, respectively. Eventually a better degradability of the disintegrated WAS was the result (Figure 13). The variation of volatile solids concentration and biogas

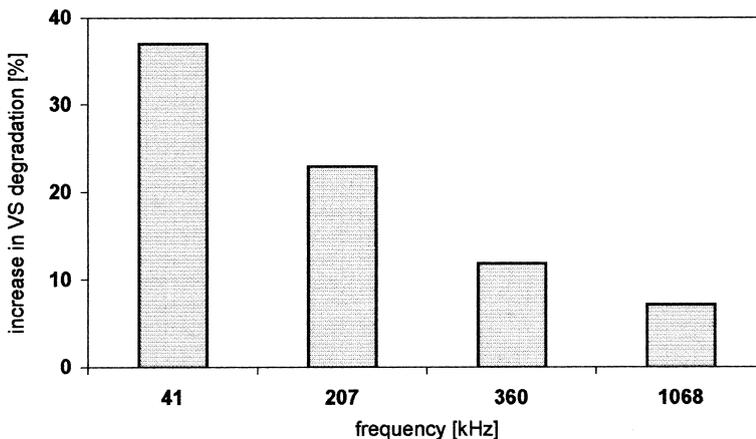


Figure 12. Effect of ultrasonic frequency applied for sludge disintegration on the anaerobic degradation of waste activated sludge (WAS) (SRT = 8 d).

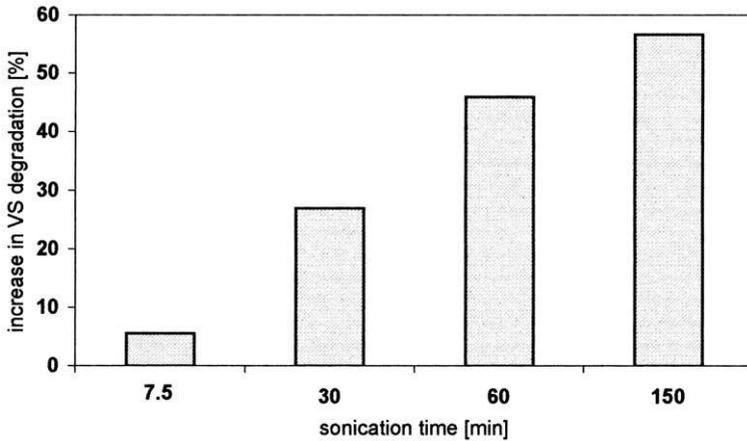


Figure 13. The effect of waste activated sludge (WAS) pre-treatment time with ultrasound of 41 kHz on the anaerobic degradation (SRT = 8 d).

production rate with test-run time are shown in Figure 14A and B for the control fermenter and one fermenter fed with disintegrated WAS. The anaerobic degradation of organic matter (volatile solids (VS)) increased up to 33.7% in the digester operated with disintegrated sludge (sonication 150 min) compared with the control. Accumulation of intermediate products like volatile fatty acids was not observed in any of the fermenters indicating a stable digestion process. The total biogas production was slightly reduced in the case of the WAS treated for only 7.5 min. In the other fermenters fed with disintegrated WAS the biogas production increased with increasing degree of disintegration. The percentage of energy-rich methane in the biogas increased with increasing degree of disintegration. This is consistent with fermentation experiments by Clark and Nujoo [20], who observed in the biogas composition a 2% increase of methane for sonicated WAS.

Figure 15 presents a summary of our experiences from these laboratory experiments and a pilot-scale study. The graph shows that anaerobic sludge stabilisation is intensified with increasing degrees of disintegration. A regression analysis of the data proves that the function is linear. The slope of the linear function is 1.9, which indicates that by increasing the degree of disintegration to, say 10%, the anaerobic VS degradation can be improved by 19%.

What may seem amazing at first glance is how could an increase in anaerobic VS degradation of 10.4% occur at zero cell disintegration. As we have shown earlier short sonication times cause floc deagglomeration but

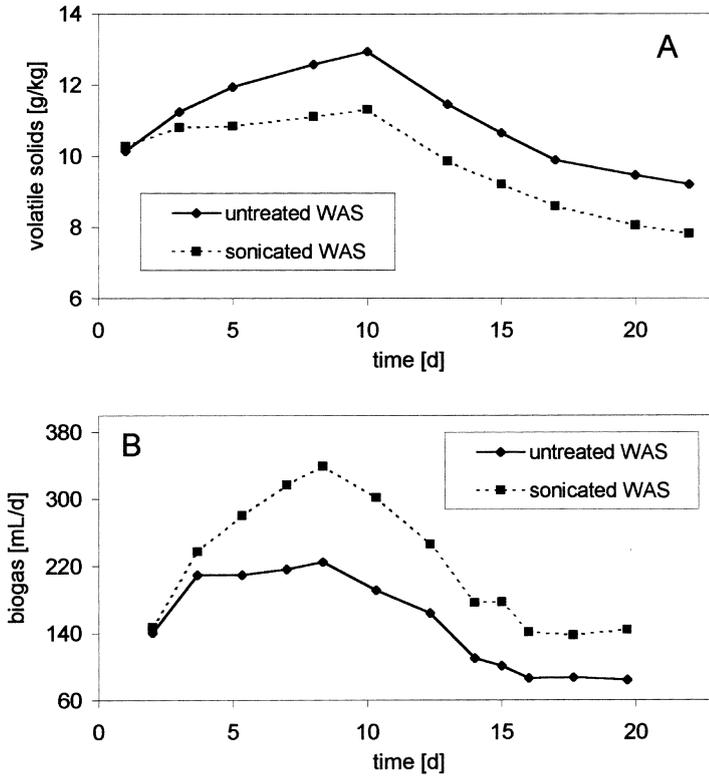


Figure 14. (A) Volatile solids (VS) concentration and (B) biogas production rate in the fermenters operated with untreated and disintegrated waste activated sludge (WAS) (150 min sonication at 41 kHz).

no cell destruction (Figure 3), even though the subsequent anaerobic VS degradation is slightly improved. The positive effect on the digestion process of the floc separation can be explained by better availability of single bacteria cells to enzymatic hydrolysis compared to cells which are embedded and protected in sludge floc agglomerates. The effect of floc deagglomeration on the VS degradation might change with respect to the floc strength and structure [24].

Chiu et al. [5] analysed the digestibility of disintegrated WAS in 125 ml anaerobic batch-tests over a period of 24 days. Different disintegration methods were used: 20 kHz ultrasonic treatment, addition of alkaline and a combination of both. Figure 16 summarises these results. At the highest solubilisation ratio achieved with the combined ultrasound–alkaline treatment a maximum improvement in anaerobic degradation was obtained.

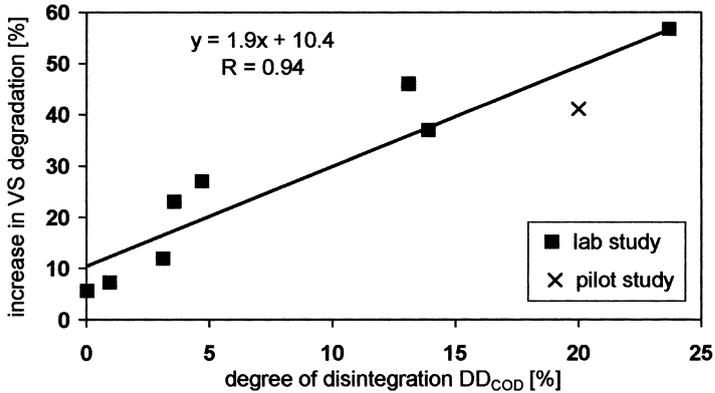


Figure 15. Enhanced volatile solids (VS) degradation of waste activated sludge (WAS) as function of the degree of sludge disintegration. The sludge retention time in the fermenters was 8 days.

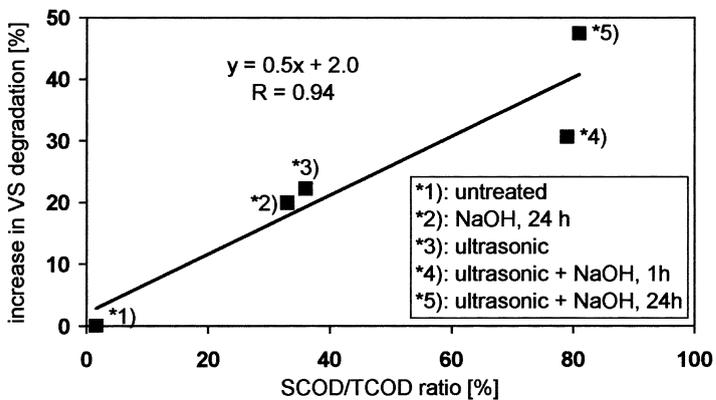


Figure 16. Enhanced volatile solids (VS) degradation of waste activated sludge (WAS) as function of the solubilisation ratio. The sludge retention time (SRT) in the batch-fermentation was 24 days. Ultrasonic treatment was done at 480 Wh/l and alkaline treatment with 40 mg/l NaOH [5].

A regression analysis of these data also allows a linear relation between the increase in VS degradation and the sludge disintegration to be derived. However, compared to our results (see Figure 15) the slope of the linear function is much lower. This might be due to the longer sludge retention time of 24 days in the batch tests of Chiu et al. [5]. A large VS degradation is probably already obtained by the conventional stabilisation of the untreated WAS.

4.2 Reduction of Anaerobic Digestion Times

Anaerobic stabilisation in the digesters operated with different sludge retention times (SRT) was studied to evaluate the acceleration of the WAS degradation after ultrasonic cell disintegration [29]. The pilot scale experimental set-up consisted of five stirred tank fermenters (each of 200 l volume) and the high-power sonoreactor SORA 3 (Figure 9). Ultrasonic sludge pre-treatment was done at a constant irradiation time of 90 s and with 8 W/cm² intensity. This ultrasound configuration resulted in an average degree of sludge disintegration DD_{COD} of 20%. According to the selected SRT, once a day certain volumes of digested sludge were replaced by fresh WAS. As a control, two fermenters were operated with untreated sludge at SRTs of 16 and 8 days. Three fermenters were fed with disintegrated WAS at SRTs of 16, 8, and 4 days (Figure 17).

The sludge VS degradation during four months of operation is shown in Figure 18. Table 1 presents the corresponding average degradation rates and degrees of degradation. The degradation rate of the sonicated WAS of 16 days SRT increased by more than 30% (335:257) compared to the conventional stabilisation. The highest rate was obtained from the shortest 4-day SRT. Compared to the 16-day SRT control fermenter the specific volumetric degradation rate increased by a factor of 3.9 (1011:257).

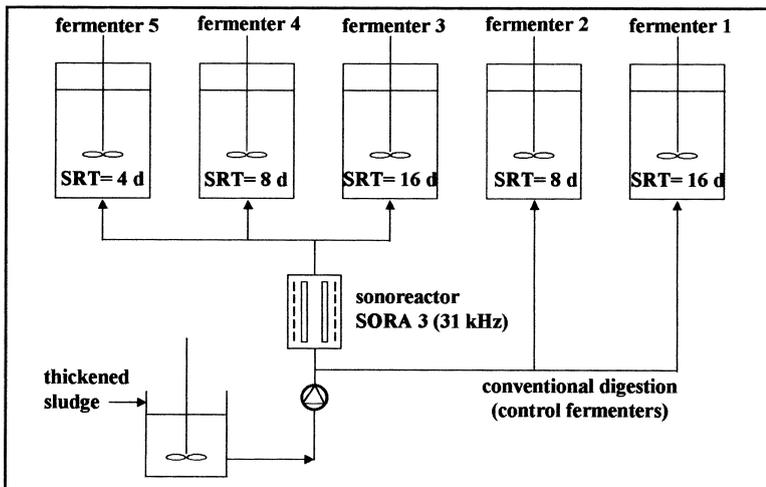


Figure 17. Pilot plant for the anaerobic stabilisation of waste activated sludge (WAS) allowing the operation of fermenters in parallel with different sludge retention times (SRT). This arrangement was also used for the secondary anaerobic fermentation of digested sludge.

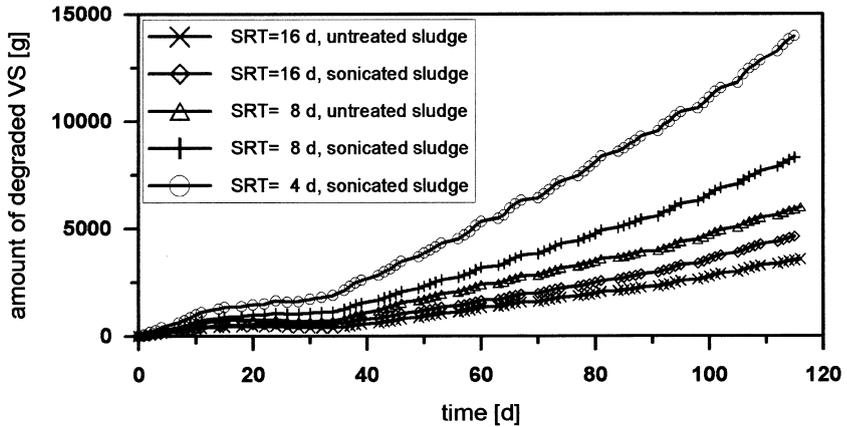


Figure 18. Degradation of volatile solids (VS) during the anaerobic fermentation of untreated and sonicated waste activated sludge (WAS).

Table 1. Effect of Ultrasound Pre-treatment and Digestion Time on rate and degree of Volatile Solids Degradation (VS_{deg}) of Waste Activated Sludge (WAS)

WAS	SRT [d]	degradation rate [g $VS_{deg}/m^3_{fermenter} \times d$]	degree of degradation [%]
Untreated	16	257	32.3
Sonicated	16	335	42.4
Untreated	8	430	27.0
Sonicated	8	603	38.1
Sonicated	4	1011	32.0

However, slightly higher concentrations of volatile fatty acids indicated that the fermentation on the 4-day SRT approaches limitation. The data demonstrate that the anaerobic degradation process is considerably accelerated by ultrasonic sludge pre-treatment and still yields about the same concentration of residual VS in the digested sludge. Therefore ultrasonic disintegration is a promising method to reduce the volume of new sludge digesters or to enable undisturbed sludge digestion of overloaded systems.

The enhanced degradation rates resulted in a significant increase of biogas production (Figure 19). Compared to the control systems more biogas was produced in the fermenters fed with ultrasonically disintegrated sludge. The highest biogas production was observed in the fermenter operated on the 4-day SRT with disintegrated sludge due to the high through-put rates and stable sludge degradation.

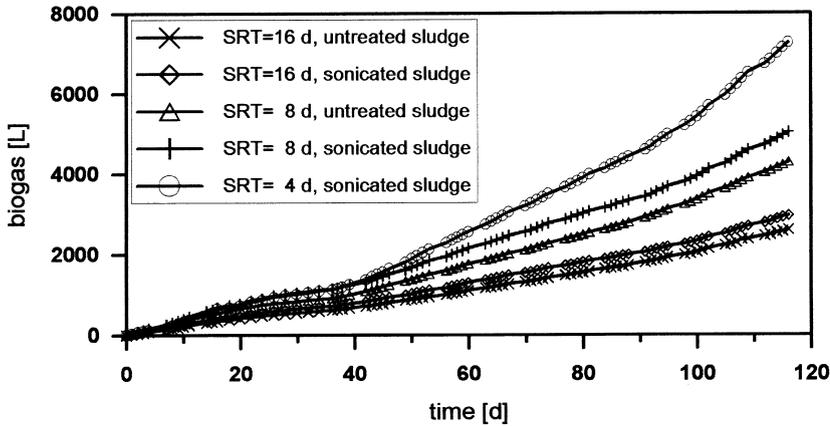


Figure 19. Biogas production during the anaerobic fermentation of untreated and sonicated waste activated sludge (WAS).

In another study [21], untreated WAS and supernatants obtained from sonicated sludge were continuously added to an anaerobic digester in order to clarify the effect of sludge solubilisation. The hydrolysis rates of solubilised intracellular organic substances and of the untreated WAS were examined and compared. The results showed that both hydrolytic processes followed a first-order kinetic. The calculated rate constants were 0.16 per day for the untreated WAS and 1.2 per day for the released organic substance (Table 2). The maximum anaerobic hydrolysis efficiency of the untreated WAS was about 65%, and of the released cell components was about 90%. Evaluating the effect of ultrasonic sludge disintegration, both the hydrolysis rate and the efficiency were well improved. Furthermore, the anaerobic hydrolysis of the main WAS organic components, protein, lipid, carbohydrate, and nucleic acid, was examined [21]. The hydrolysis rates also followed first-order kinetics, and were about 10 times higher than the hydrolysis rate of the untreated WAS (Table 2).

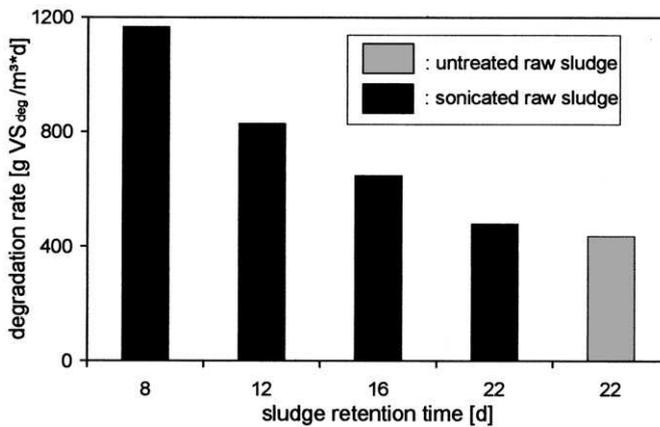
4.3 Comparison of Sludge Types

Since WAS mainly consists of bacterial cell material, most of the current disintegration studies focus on this sludge type. On the other hand it had already been shown in Section 3.5, that the treatment of primary, raw and digested sludge also resulted in an increase of solubilised organics.

Clark and Nujjoo [20] investigated the anaerobic degradation of sonicated primary sludges in laboratory scale chemostats at SRTs between 15 and 25 days. The results were given in terms of specific methane yield, the

Table 2. Hydrolysis of Waste Activated Sludge (WAS), Solubilised WAS, and most important Biopolymers [21].

Substrate	Hydrolysis rate constant [per day]	Maximum percent of hydrolysis [%]
WAS	0.16	65
Solubilised WAS	1.2	90
Protein	1.3	95
Nucleic acid	1.8	95
Lipid	0.76	88
Carbohydrate	1.2	90

**Figure 20.** Effect of the ultrasonic pre-treatment and anaerobic sludge retention time (SRT) on the specific degradation rate of raw sludge.

amount of methane produced per kg of VS degraded. At 15 days SRT an increase in the methane yield of more than 60% compared to the conventional primary sludge digestion was observed. At longer SRTs the percentage increase in specific methane production was reduced down to 41% on the 25-day SRT.

In our pilot experimental set-up we tested the effect of raw sludge disintegration on subsequent anaerobic stabilisation. Therefore, the raw sludge was sonicated for 64 s at 11.5 W/cm² intensity resulting in an average degree of disintegration DD_{COD} of 12%. The digestion time of the sonicated raw sludge was reduced from the conventional 22 days to 8 days (factor of 2.8 = 22/8) without negative impacts. The specific volumetric degradation rate increased from 437 to 1166 [g VS_{deg}/m³ × d] or by a factor of 2.7 (Figure 20). Parallel to that the biogas production also increased. This demonstrates again that a rapid sludge digestion is achieved because the sonicated sludge represents a much better degradable substrate [12,16].

Sludge stabilised by a common single-stage anaerobic process still consists of a high organic content. A further reduction of organics and thus maximum sludge stabilisation can be achieved by disintegration of the digested sludge and treatment in a second digestion process. Grüning and Orth [30] investigated the ultrasonic disintegration and second stabilisation of different anaerobically digested sludges. One litre of digested sludge was disintegrated and inoculated with 0.25 l of non-disintegrated digested sludge in batch tests. Ultrasonic treatment (VIBRA CELL VC 600, SONICS and MATERIALS, Danbury) was applied for 15 min, resulting in a degree of disintegration DD_{COD} of about 50%. The sonicated sludge showed a considerably increased degradation in the second fermentation as indicated by the additional biogas production (Figure 21). For the disintegrated sample, the gas yield after 8 days was already at the same level as the gas yield of the untreated sample after 60 days. However, it has to be considered that disintegrating digested sludge also results in the disruption of active anaerobic micro-organisms. For practical application the degree of disintegration has to be adjusted in a way that an optimum balance between the disintegrated and the still active micro-organisms results.

We investigated the anaerobic degradation of sonicated digested sludge in our pilot experimental set-up. The fermenters were operated in a semi-continuous mode with SRTs between 4 and 16 days (Figure 17). Disintegration was done for 96 s at 7.1 W/cm^2 acoustic intensity and the average degree of disintegration DD_{COD} was 8%. Although the digested

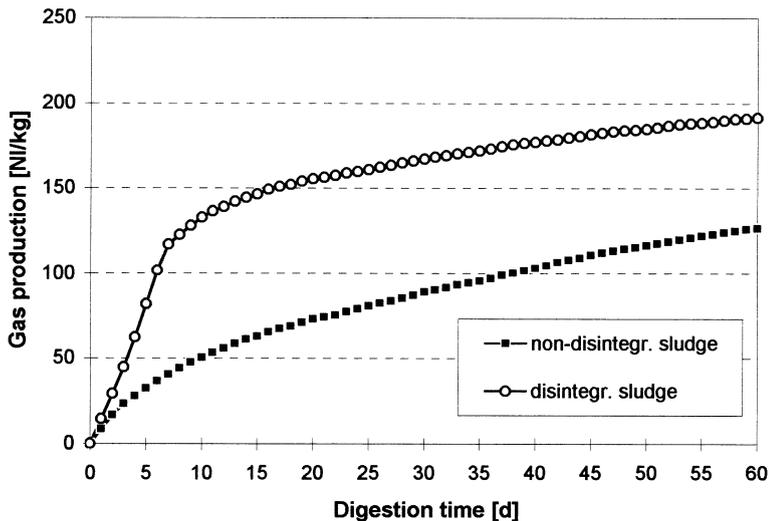


Figure 21. Specific gas production of a non-disintegrated and ultrasonically disintegrated digested sludge [30].

sludge had already been stabilised with a retention time of 30 days in a full-scale fermenter, it still contained sufficient quantities of digestible organics (Figure 22). This might be due to short-circuit flows in the digester, so that a certain quantity of only partly stabilised sludge leaves the digester after a very short residence time. Compared to the second stabilisation without ultrasonic pre-treatment for 16 days SRT ultrasonic disintegration increased the VS degradation more than 20% (22.4:18.2). After 8 days SRT the degradation was increased up to 45% (17.4:12.0). The VS degradation was still higher after 4 days SRT in case of sonicated sludge compared to the 8-day SRT second stabilisation without pre-treatment.

In Figure 23 the results of our pilot fermentation studies are summarised. The VS degradation is a function of the digestion time and the sludge type. While the biological hydrolysis takes days, the ultrasonic disintegration and break-up of cells occurs in seconds. The intracellular compounds are set free and are immediately available for biological degradation. The results (Figure 23) indicate that it is possible to increase the operating performance of the anaerobic digestion process and greatly improve the decomposition rate using sludge with destroyed cell walls. Therefore, the greatest benefits of the ultrasonic sludge pre-treatment are obtained, if the organic sludge part is mainly composed of biological cells and the hydraulic sludge retention times in the anaerobic digester are short. Thus, anaerobic stabilisation is more improved in the case of sonicated WAS compared to the raw sludge disintegration. The retention time of WAS was reduced from 16 to 4 days without losses in the degradation efficiency. This means that digester volumes could be reduced to one-fourth the conventional size.

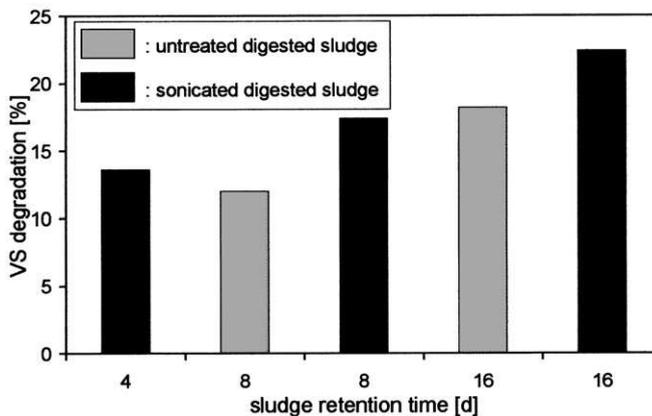


Figure 22. Effect of ultrasonic pre-treatment and retention time on the anaerobic volatile solids (VS) degradation of digested sludge in a second stabilisation.

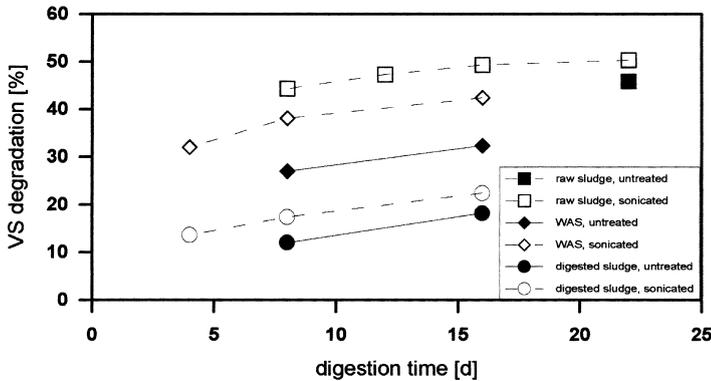


Figure 23. Anaerobic volatile solids (VS) degradation as a function of digestion time and sludge type (degrees of disintegration DD_{COD} were 12% for sonicated raw sludge, 20% for sonicated waste activated sludge (WAS), and 8% for sonicated digested sludge, respectively).

A considerable increase of VS reduction is also obtained by disintegrating anaerobically digested sludge and further short-time fermentation. This option is advantageous in aiming to minimise the sludge VS content in order to achieve a highly stabilised end product.

Our pilot ultrasound reactor was operated over a period of almost two years in a wastewater treatment plant. The average daily time of operation was 15 h. Over the whole period no clogging was observed. Although sewage sludges are a most difficult material to treat (sometimes containing, for example, gloves), there was never an operating problem with the sonoreactor. The risk of blocking an ultrasound reactor with sludge solids is very low compared to other mechanical disintegration devices [18]. In this respect it is a great advantage that the reactor vessel has a large diameter so that even coarse stuff can easily pass through. Reactor examination at the end of the study showed only slight wear of the transducers. The maintenance requirements for the reactor were low.

5. RELATED APPLICATIONS OF ULTRASOUND

5.1 Improved Dewatering

Ultrasonic disintegration also has been suggested for the improvement of the sludge dewatering process [15,17,24]. For example, Friedrich et al. [17] discussed two ways of improving the dewaterability: (1) in the case of

low energy input the primary particles in the sludge aggregates are redistributed forming new stable aggregates better suitable for flocculation and dewatering. (2) The dewaterability depends crucially on the particle size distribution. If the distribution is broadened by partial disintegration of sludge aggregates, the dewaterability is enhanced. A comprehensive presentation of the application of ultrasound for improved dewatering is given in another chapter of this book.

5.2 Enhanced Sedimentation of Filamentous Sludge

Poor settling of activated sludge has always been recognised as a problem of major concern in relation to the operation of the (WWTP) and sludge handling. Recent introductions of biological nutrient removal processes seem to have increased the problem. The settling properties of activated sludge are influenced by several factors. One such factor leading to poor compaction capability and deterioration of the wastewater effluent quality is the excessive growth of filamentous organisms. Furthermore, this bulking sludge causes foaming because gas bubbles are trapped within the hydrophobic filaments. Therefore floating sludge in the aeration tank, scum running off from the WWTP and the impossibility of anaerobic bulking sludge stabilisation are often evident.

The objective of bulking sludge sonication is the decomposition of the filamentous sludge structures in order to allow sedimentation and to reduce the floating potential. We carried out batchwise experiments using the laboratory sonoreactor URS 1000 (Figure 8) operating at a frequency of 41 kHz and a low acoustic power density of 0.14 W/cm^3 [23]. Irradiation was done at doses between 5.8 and 34.8 Wh/l. Related sonication times ranged between 2.5 and 15 min. The effects of sonication were evaluated by microscopic examination and settling experiments. The parameter, which was determined, is the sludge volume index (SVI). It represents the sludge level of the sample after a settling period of 30 min in relation to its dry solids concentration. Good sedimentation of the sludge is indicated by SVI values below 150 ml/g.

The effect of sonication on the activated sludge morphology is evident from the photos shown in Figure 24. In the control sample a high number of filaments is present causing the bulking floc structure. Even the low energy inputs applied caused a reduction in number and length of the filaments. More compact flocs are formed (Figure 24B) which then allow a much better settling of the sludge. Figure 25 presents the results of the sedimentation tests. The best results were observed at an applied dose of 11.6 Wh/l. The SVI was reduced down to 128 ml/g compared to 233 ml/g for the untreated sample. At higher power inputs the SVI increases again.

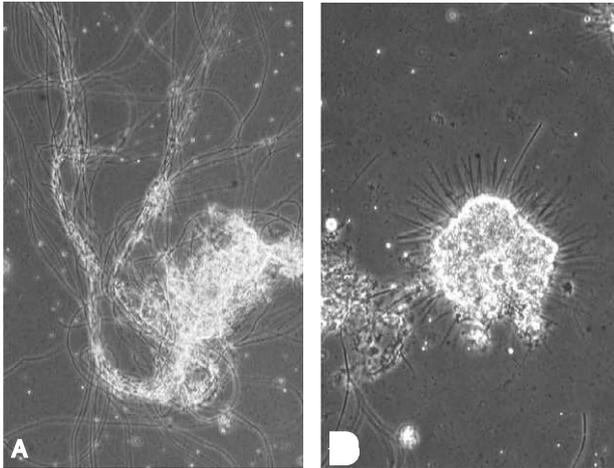


Figure 24. Light-microscopical images of (A) untreated and (B) sonicated filamentous sludge (power input: 5.8 Wh/l).

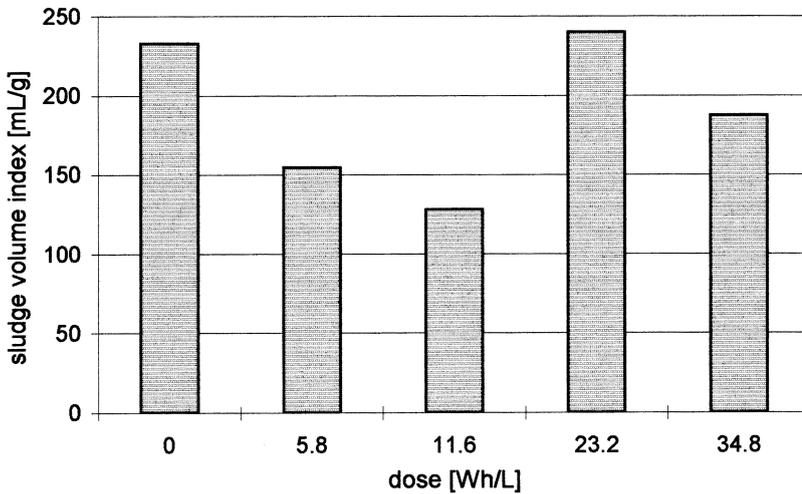


Figure 25. Effect of sonication on settleability of filamentous sludge as a function of energy input.

One reason for that is the appearance of an increased number of fine particles resulting from floc deagglomeration and cell disruption.

Similar results were found by King and Forster [15] investigating the effect of activated sludge sonication (20 kHz Dawe Soniprobe 7530A, Dawe Instruments Ltd., London, UK) on the particular characteristics.

The sludge SVI values dropped steadily with increasing ultrasonic power input up to 25 Wh/l. However, the improvement of sludge settleability was achieved at the expense of the supernatant clarity. The SVI was reduced to about 40% of the initial value at a dose of 15 Wh/l. At further increases in sonication dose the SVI began to stabilise and a large number of single micro-organisms could be observed by light-microscopy analysis.

Jorgensen and Kristensen [31] suggested that sonication might have a potential as a new method to control growth of filamentous bacteria in activated sludge. According to microscopic analysis, the laboratory sonication (RESON SYSTEMS AS, frequency 25–30 kHz) for 2 s at a dose of 0.5 Wh/l reduced the number and length of the filamentous micro-organism *Microthrix parvicella* significantly. However, the morphological and mechanical characteristics of the filamentous bacteria must be considered and ultrasonic treatment adjusted. Thus sonication of the thicker and more robust filament type 021N took a much longer time and higher power levels compared to the disintegration of activated sludge with a dominating growth of *M. parvicella*.

Friedrich et al. [17] postulated higher energy inputs for the ultrasonic treatment of bulking sludges compared to floating sludges without having identified the dominant micro-organisms in these different filamentous sludge types. In the case of the floating sludge the partial destruction of the thread bacteria was sufficient for subsequent complete settlement. Contrary to that the treatment of bulking sludge required the entire destruction of the thread bacteria.

By destruction of the sludge filaments the subsequent anaerobic stabilisation becomes possible as was shown for mechanical and thermal treatment. The operating problems are considerably reduced due to the prevention of foaming during biogas production [32,33]. Further work is necessary to substantiate these findings in the case of ultrasonic treatment.

6. CONCLUSIONS

Hydrolysis is the rate-limiting step of anaerobic sludge stabilisation. Low frequency ultrasound generates cavitation with high shear forces resulting in sludge disintegration. At short ultrasound application times, sludge floc agglomerates are separated and dispersed, while no cell destruction occurs. At longer treatment times or higher ultrasound intensity, the micro-organism cell walls are broken and intracellular material is released to the liquid phase.

The dissolved organic compounds are readily bio-available in the anaerobic digestion process. The fermentation rate is greatly improved by

using disintegrated sludge. Consequently the sludge retention time in the fermenter could be significantly reduced. The VS degradation is quantitatively enhanced in a linear function of the degree of cell disintegration. An increased production of energy-rich biogas is also observed.

Low ultrasound energy input causes the destruction of filamentous sludge flocs. As a result sludge sedimentation is made possible.

ABBREVIATIONS

CFU: Colony-forming units; COD: Chemical oxygen demand; DD_{COD} : Degree of disintegration_{Chemical oxygen demand}; DD_{O} : Degree of disintegration_{Oxygen}; DS: Dry solids; OUR: Oxygen utilisation rate; SCOD: Soluble chemical oxygen demand; SRT: Sludge retention time; SVI: Sludge volume index; TCOD: Total chemical oxygen demand; TOC: Total organic carbon; VS: Volatile solids; WAS: Waste activated sludge; WWTP: Wastewater treatment plant.

REFERENCES

- [1] Davis, R. D., and Hall, J. E. *Water Pollution Control*, 7 (1997) 9.
- [2] Haug, R. T., LeBrun, T. J., and Tortorici, L. D. *J. WPCF*, 55(1) (1983) 23.
- [3] Stuckey, D. C., and McCarty P. L. *Wat. Res.*, 18(11) (1984) 1343.
- [4] Kepp, U., Machenbach, I., Weisz, N., and Solheim, O. E. IAWQ Specialised Conference on Disposal and Utilisation of Sewage Sludge: Treatment and Application Modalities, Athens, Greece, 1999, pp. 161–168.
- [5] Chiu, Y.-C., Chang, C.-N., Huang, W.-S., and Chao, A. C. *J. of the Chinese Institute of Environmental Engineering*, 7(1) (1997) 25.
- [6] Kopp, J., Müller, J., Dichtl, N., and Schwedes, J. *Wat. Sci. Tech.*, 36(11) (1997) 129.
- [7] Dohányos, M., Zabránská, J., and Jeníček, P. *Wat. Sci. Tech.*, 36(11) (1997) 145.
- [8] Mues, A., and Peiffer, A. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 91–99.
- [9] Schneider, D. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 101–121.
- [10] Malina, J. F., Pohland, F. G. *Water Quality Management Library vol. 7: design of anaerobic processes for the treatment of industrial and municipal wastes*. Technomic Publishing Company, Lancaster, USA, 1999.
- [11] Eastman, J. A., and Ferguson, J. F. *J. WPCF*, 53 (1981) 352.
- [12] Neis, U., and Tiehm, A. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 39–61.
- [13] Mason, T. J. *Sonochemistry: The uses of Ultrasound in Chemistry*. The Royal Society of Chemistry, Cambridge, UK, 1990.
- [14] Tiehm, A., Nickel, K., Zellhorn, M., and Neis, U. *Wat. Res.*, (2001), in press.
- [15] King, R. O., and Forster, C. F. *Enzyme Microb. Tech.*, 12 (1990) 109.
- [16] Tiehm, A., Nickel, K., and Neis, U. *Wat. Sci. Tech.*, 36(11) (1997) 121.
- [17] Friedrich, H., Potthoff, A., Friedrich, E., and Hielscher, H. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 245–255.

- [18] Lehne, G., and Müller, J. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 205–215.
- [19] Chang, C.-N., Chiu, Y.-C., Huang, S.-J. (1997). 6th IAWQ Asia-Pacific Regional Conference Asian Waterqual, Vol. (1) Seoul, Korea, 1997, pp. 517–524.
- [20] Clark, P. B., and Nujjoo, I. CIWEM Presidential Conference: Treatment innovation for the next century, Cambridge, UK, 1998.
- [21] Shimizu, T., Kudo, K., and Nasu, Y. *Biotech. Bioeng.*, 41 (1993) 1082.
- [22] Müller, J., Lehne, G., Schwedes, J., Battenberg, S., Näveke, R., Kopp, J., Dichtl, N., Scheminski, A., Krull, R., and Hempel, D. C. *Wat. Sci. Tech.* 38 (1998) 425.
- [23] Nickel, K. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 217–232.
- [24] Morgan, J. W., and Forster, C. F. *J. Chem. Tech. Biotech.*, 55 (1992), 53.
- [25] Lorimer, J. P. In Mason, T. J. (ed.), *Sonochemistry: the Uses of Ultrasound in Chemistry*, The Royal Society of Chemistry, Cambridge, UK, 1990, pp. 9–26.
- [26] Horst, C., and Hoffmann, U. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 77–90.
- [27] Hua, I., Hoffmann, M. R. *Environ. Sci. Tech.*, 31 (1997) 2237.
- [28] Portenlänger, G. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 11–22.
- [29] Neis, U., Nickel, K., and Tiehm, A. *Wat. Sci. Tech.*, 42(9) (2000) 73.
- [30] Grüning, H., and Orth, H. In Tiehm, A., and Neis, U. (ed.), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Reports on Sanitary Engineering, Vol. 25, 1999, pp. 233–244.
- [31] Jorgensen, P. E., and Kristensen, G. H. IAWQ 18th Biennial International Conference: Water Quality International '96, Singapore, Conference Preprint Book 2, 1996, pp. 70–77.
- [32] Barjenbruch, M., Hoffmann, H., and Tranckner, J. IAWQ Specialised Conference on Disposal and Utilisation of Sewage Sludge: Treatment and Application Modalities, Athens, Greece, 1999, pp. 496–502.
- [33] Müller, J. IAWQ Conference on Sludge Management for the 21st Century, Perth, Australia, Preprints Session 4, 1999.

THE SONOCHEMICAL DEGRADATION OF AROMATIC AND CHLOROAROMATIC CONTAMINANTS

Christian Petrier and Dominick Casadonte

OUTLINE

Abstract	92
1. Introduction	92
2. Sonochemical Equipment	93
2.1 Devices	93
2.2 Ultrasonic Power Measurement	94
3. Ultrasonic Treatment of Water for an Air-equilibrated Solution	95
4. Phenol and 4-Chlorophenol Degradation	96
5. Benzene and Chlorobenzene Degradation	100
6. Degradation of Chloroaromatics	104
7. Sonochemical Yields	106
8. Conclusions	107
References	108

Advances in Sonochemistry

Volume 6, pages 91–109.

© 2001 Elsevier Science B.V. All rights reserved.

ABSTRACT

In the field of water treatment, the destruction of organic compounds that cannot be degraded by conventional means is a target of fundamental and applied investigations. The process based on the phenomena induced by ultrasonic cavitation has shown some potential in this regard, as demonstrated by the remediation of chloroalkanes and aromatic derivatives. In water the implosion and fragmentation of cavitation bubbles are high-energy processes that lead to thermal reactions and to the homolysis of water and dioxygen. The scission of H_2O , O_2 in water leads to the production of radical species (H^\bullet , OH^\bullet , HOO^\bullet) which are capable of decomposing organic matter. The rate of disappearance of starting materials as well as the nature of the products depends upon the physico-chemical properties of the target molecules. In the case of aromatics molecules it can be clearly demonstrated that volatile compounds (benzene, chlorobenzene, 4-chlorobiphenyl etc.) undergo thermal destruction inside the bubble of cavitation. Aromatics with hydrophilic characteristics (e.g. phenol, chlorophenol), with lower values of Henry's law constant, are eliminated stepwise through reaction with OH^\bullet . The aim of this chapter on the degradation of aromatics and chloroaromatics is two-fold: to point out the chemical fate of several by-products observed during sonochemical treatment, and to describe investigations conducted to improve sonochemical rates.

1. INTRODUCTION

The internal portion of a cavitation bubble is an enclosed space where matter is brought to either a thermally or an electrically excited state [1–4]. It behaves, then, as a microreactor which discharges radical species (H^\bullet , OH^\bullet , HOO^\bullet , O) and free electrons to the surrounding solution [5–8]. The reactions produced are currently under evaluation for the decomposition of water pollutants, allowing for the potential use of sonication for water treatment [9,10].

In initial studies, the process was found especially efficient for the elimination of aromatics and haloalkanes [11–14]. Generally, experimental results have reported the disappearance of starting materials, some primary intermediates, and changes in general environmental indices (chemical oxygen demand (COD), total organic carbon (TOC)).

In the case of pentachlorophenol (PCP), it was shown that ultrasonic processing produces PCP destruction with a quantitative recovery of chlorine atoms (Cl^-), together with a decrease in toxicity. It has also been noted that PCP disappears with the concomitant formation of CO and CO_2 , along with H_2O_2 , HNO_2 , HNO_3 production [15]. Another set of investigations has indicated that PCP sonochemical destruction is highly affected by the ultrasonic frequency employed (Figure 1 [16]).

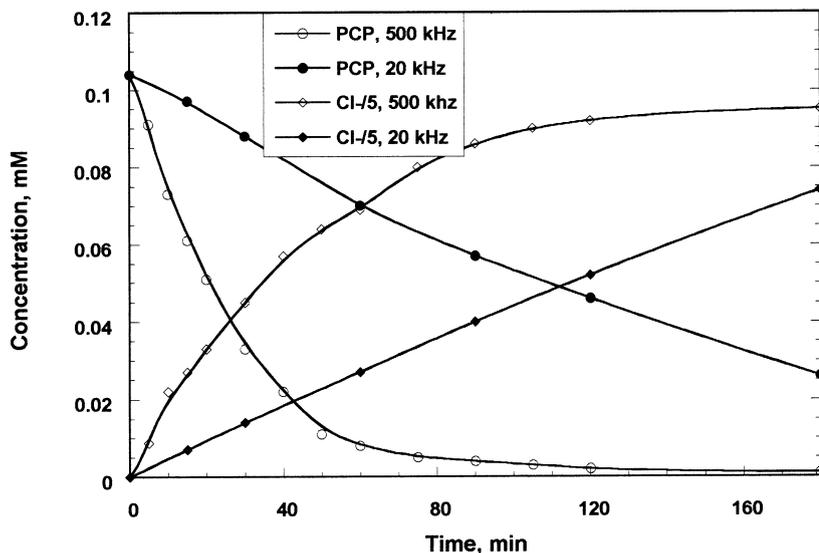


Figure 1. Kinetics of PCP disappearance and Cl^- formation during the sonochemical treatment (20 kHz or 500 kHz) of a continuously aerated solution. Ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

These results illustrate typical studies on the sonochemical degradation of aromatic compounds. Aromatic derivatives can exhibit different behavior which can be related to their physico-chemical properties. It is therefore important to understand the characteristics of such reactions in order to evaluate potential yields from the use of ultrasound for water treatment.

2. SONOCHEMICAL EQUIPMENT

2.1 Devices

Since 1980, most of the sonochemical reactions have been generally conducted in a cleaning bath or with the help of an ultrasonic probe. Such sonochemical devices designed for cleaning or disrupting applications [17,18] were found useful in the field of organic synthesis but rather inefficient for the elimination of organic contaminants of water [19].

Currently, whatever the frequency tested, most of the results are obtained with reactors having similar shapes [14,20,21]. Such design allows the control of essential sonochemical parameters: transducer size, temperature, inlet and exhaust gas.

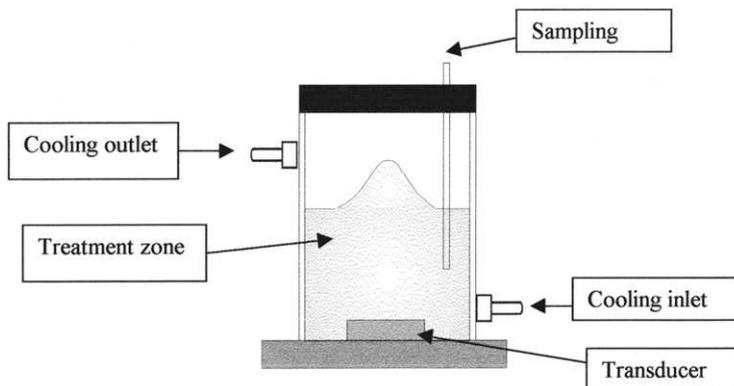


Figure 2. Scheme of a classical ultrasonic cell used for water treatment.

2.2 Ultrasonic Power Measurement

Evaluation of the energy needed to realize a given sonochemical transformation which is of crucial importance for water treatment, appears to be a difficult task. It can be done in different ways, each of them being correlated with a specific measurement [8,22,23].

- (a) The determination of the electrical energy (electrical Watt) dissipated to actuate the ultrasonic transducer.
- (b) The evaluation of the acoustical energy absorbed by the insonicated medium (transformation of mechanical energy into heat, Watt).
- (c) Chemical dosimetry, based on the formation or the elimination of chemical species. Examples include hydrogen peroxide formation and the Weissler reaction.

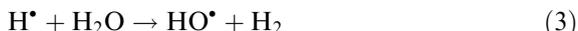
From a practical point of view, the ultrasonic power is generally evaluated through the calorimetric method (b), which can be easily performed and allows for an evaluation of the amount of energy input in the reactor, whatever the chemical system considered.

The calorimetric method is simple and requires only a thermal sensor (thermocouple) immersed in the reactor filled with water to determine the temperature rise generated by the sound absorption.

Power (P_w) is then estimated using the relationship: $P_w = m C_p (\Delta T / \Delta t)$, where P_w = power (Watt); m = mass of water (kg); C_p = heat capacity of water ($4.18 \text{ J kg}^{-1} \text{ K}^{-1}$); ΔT = temperature rise ($^{\circ}\text{C}$); Δt = interval of time (s).

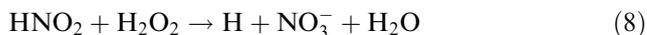
3. ULTRASONIC TREATMENT OF WATER FOR AN AIR-EQUILIBRATED SOLUTION

If an aqueous solution saturated with oxygen is sonicated, only hydrogen peroxide formation occurs. This is due to hydroxyl and hydroperoxyl recombination outside the cavitation bubble. $\cdot\text{OH}$ and $\cdot\text{OOH}$ radicals which were observed by spin trapping experiments [24] result from H_2O and O_2 homolytic cleavage inside the bubble, as shown in reactions (1)–(7) [6–25].



When sonication is conducted in an air-equilibrated medium, nitrous and nitrite ions accompany H_2O_2 evolution (Figure 3). During the first stages of the treatment, only H_2O_2 and NO_2^- build up simultaneously. As the reaction progresses, the rate of H_2O_2 production decreases and nitrite ions appear with a concentration that increases at the expense of that of nitrous ions.

This simple observation indicates clearly that H_2O_2 and NO_2^- are the primary products in air-equilibrated water. NO_3^- results from the oxidation of NO_2^- by hydrogen peroxide (reaction (8)). The rate of this reaction is dependent on the pH, which decreases rapidly with time [26].



The first steps involve molecular nitrogen that is oxidized to nitrogen oxide and nitrous oxide by reaction with $\cdot\text{OH}$ and O inside the bubble [27]. Further NO and N_2O oxidation with $\cdot\text{OH}$ and molecular oxygen leads to nitrous acid (reactions (9)–(13)) [28].



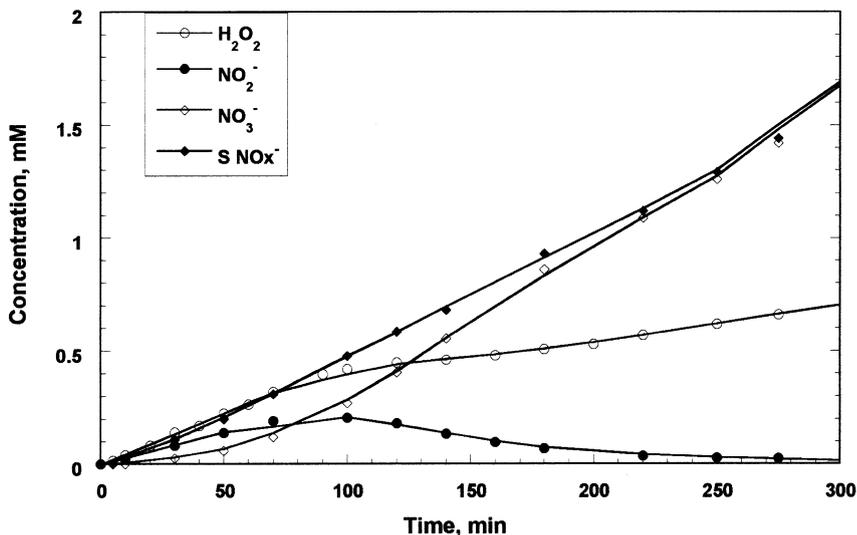


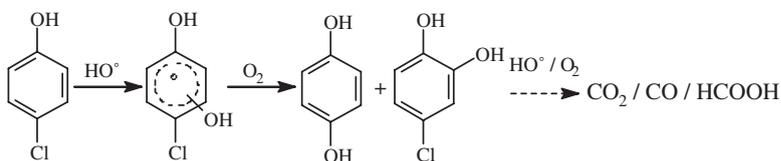
Figure 3. Concentration of H_2O_2 , NO_2^- , NO_3^- vs time during the ultrasonic treatment of water equilibrated with air. Frequency: 500 kHz, ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

The formation of H_2O_2 , NO_2^- , NO_3^- which occurs in air-equilibrated water is a common phenomenon that can also be observed during the treatment of water containing organic compounds.

4. PHENOL AND 4-CHLOROPHENOL DEGRADATION

The transformations of phenol (PH) and 4-chlorophenol (4-CP) in water submitted to an ultrasonic field continues to be of intense interest [14,29–31]. The comparison between their degradation kinetics shows great similarities. Only the curves concerning 4-chlorophenol are presented here.

The primary products resulting from the sonochemical treatment in air-equilibrated medium are mainly compounds characteristic of oxidation by $\cdot\text{OH}$ radical: hydroquinone (HQ) and catechol for phenol, and HQ and 4-chlorocatechol (4-CC) for 4-chlorophenol (Figure 4). These intermediates disappear as the reaction progresses.



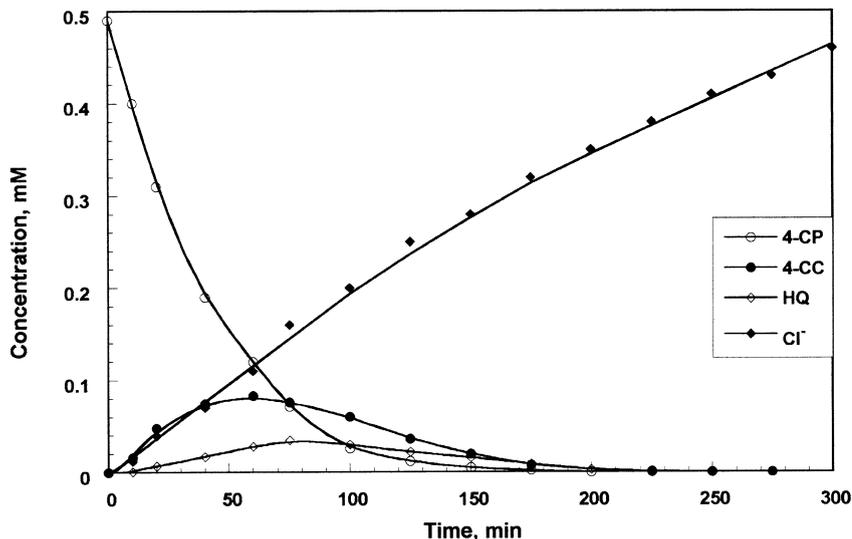


Figure 4. 4-CP (0.49 mM) decay and time course of reaction intermediates produced during ultrasonic treatment at 500 kHz. Ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

After an irradiation time of 300 min, the hydroxylated intermediates have completely vanished and the chlorine atoms are mineralized as chloride ions. The concentration of the final products (CO and CO₂) rises slowly (Figure 5). After 400 min they represent 21% of the starting 4-CP and 18% of the starting PH. In comparison with phenol, the faster degradation of 4-CP appears also in the initial rate (Table 1). These results are in agreement with previous studies [32,33], in which it was demonstrated that “the sonochemical reactivity” of an organic compound is related to its vapor pressure and hydrophobicity.

A compound with a high vapor pressure or hydrophobic character should trap hydroxyl radicals escaping from the cavitation bubble more efficiently than one with a greater solubility. It seems that the “liquid” surrounding the bubble constitutes a critical phase that concentrates organic compounds more or less depending on their solubility [34].

The evidence that 4-CP and PH degradation occurs outside the bubble is corroborated by the fact that the rate of NO₂⁻ formation is only weakly affected by the presence of these compounds. Conversely, the rate of hydrogen peroxide formation decreases notably because of the competition between reaction (6) and the reaction of [•]HO with the aromatic.

Whether or not the degradation of PH or 4-CP occurs at the bubble-liquid interface or in the bulk solution depends upon the frequency of

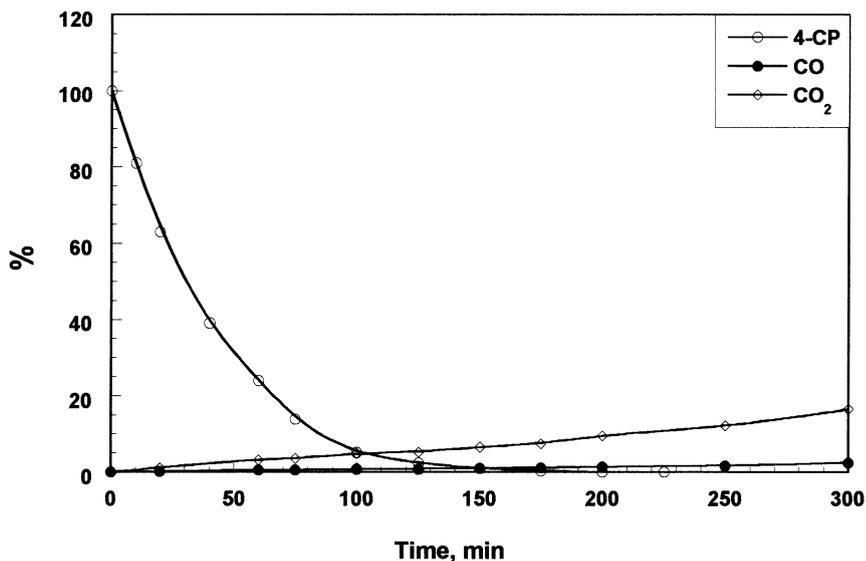


Figure 5. 4-CP degradation and percentage of carbon recovered as CO or CO₂ during sonochemical treatment at 500 kHz. Ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

Table 1. Initial Rate for Organic Compound Disappearance (V_{init}) and the Formation of H₂O₂, and NO₂⁻ + NO₃⁻ 10⁻⁶ l mol⁻¹ min⁻¹

	H ₂ O	Phenol	Chlorophenol	Benzene	Chlorobenzene
H ₂ O ₂	4.9	2.8	2.4	1.4	1.5
NO ₂ ⁻ + NO ₃ ⁻	4.7	4.4	4.2	0	0
V_{init}		5.1	6.6	17	20

insonication [14] and the initial concentration of the substrate [31]. When $(k_{\text{obs}})^{-1}$ for the degradation of 4-CP is plotted as a function of 4-CP concentration, the kinetics display a biphasic behavior. At low concentration ($< 75 \mu\text{M}$), degradation primarily occurs with $\cdot\text{OH}$ radicals in the bulk, and $(k_{\text{obs}})^{-1} = A[4\text{-CP}]$, where $A = 4.00 \pm 0.27 \mu\text{M}^{-1} \text{min}$ [31]. At high concentration ($> 75 \mu\text{M}$), much of the sonochemical reactivity occurs at the bubble-liquid interface, and $(k_{\text{obs}})^{-1} = B + C[4\text{-CP}]$, where $B = 202 \pm 14 \text{min}$ and $C = 1.45 \pm 0.05 \mu\text{M}^{-1} \text{min}$. The overall rate for the degradation of 4-CP is given as a combination of the two regimes, and is shown in Eq. (1) [31]:

$$\text{rate} = \frac{k_0 + kK[4\text{-CP}]_i}{(1 + K[4\text{-CP}]_i)} \quad (1)$$

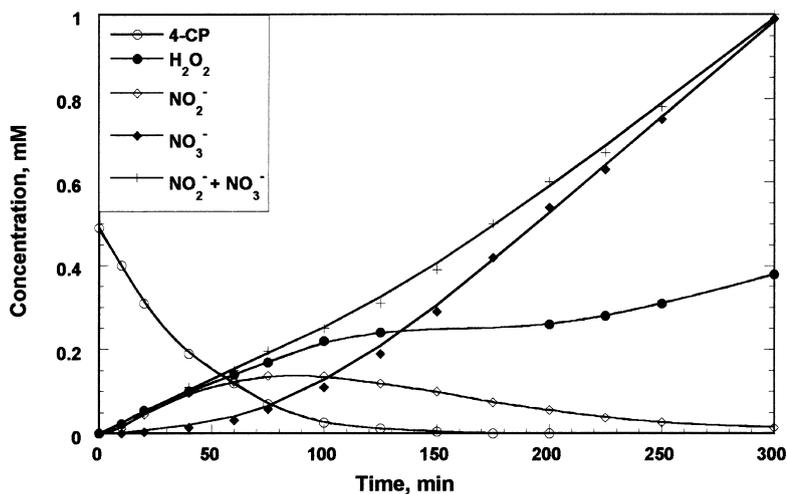


Figure 6. Time course concentration of H_2O_2 , NO_2^- , NO_3^- during the ultrasonic treatment of 4-CP in water solution equilibrated with air. Frequency: 500 kHz ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

where $k_0 = 0.25 \pm 0.03 \mu\text{M min}^{-1}$, $k = 0.69 \pm 0.03 \mu\text{M min}^{-1}$, and $K = 7.2 \pm 0.5 \mu\text{M}^{-1}$.

The first term in Eq. (1), k_0 represents a pathway which is independent of the concentration of 4-CP for low initial concentrations of 4-CP. At high concentrations the sonoactivity shows characteristics given by the second term in Eq. (1), which are similar to Langmuirian adsorption processes involving a gas–liquid interface [35]. This suggests that under conditions of high concentration reactivity occurs both in the bubble–liquid zone as well as in the bulk solution.

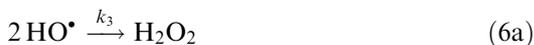
In treating the mechanism of the degradation of 4-CP, it has been assumed that the principal oxidant is hydroxyl radicals [31], as these are capable of escape from the bubble to emerge at the bubble–liquid interface or at the bulk solution, unlike other oxidants [30]. Sonolysis of water produces hydrogen and hydroxyl radicals according to reaction (1a).



where P represents the ultrasonic power.

These radicals can recombine at the interface according to reaction (14) or in the bulk according to reaction (6a).





Once hydroxyl radicals are present at the interface, oxidation of the 4-CP, whether in the bulk due to migration of the radicals, or at the interface, proceeds according to reaction (15).



Invoking rates k_1 through k_4 for the rate constants for the generation and subsequent recombination or reaction of $^\bullet\text{OH}$ as well as a steady-state approximation for the concentration of hydroxyl radicals under constant acoustic power P and a pseudo-first order approximation for water yields [31]:

$$\text{rate} = \frac{k_1 k_4 [4\text{-CP}]_i [P]}{(k_2 [^\bullet\text{H}] + k_3 [^\bullet\text{OH}] + k_4 [4\text{-CP}]_i)} \quad (2)$$

If the reactions were at the bubble–liquid interface under low concentrations of 4-CP (both in the bulk and at the interface), then a first-order dependence on 4-CP would be expected from Eq. (2). However, from Eq. (1), under these conditions the rate is zero order in 4-CP (i.e. only rate constant k_0 is operative). Accordingly, under low concentrations of 4-CP, the reaction leading to product must occur in the solution bulk.

At higher concentrations of 4-CP ($> 75 \mu\text{M}$, and certainly at the 0.49 mM concentration at which the experiments indicated in Figure 4 were conducted), 4-CP can accumulate at the interfacial region as well as in the bulk. There is a preequilibrium which can then exist for adsorption–desorption of 4-CP at the bubble–liquid interface, followed by subsequent reaction with $^\bullet\text{OH}$ either at the interface or in the bulk. The total expression in Eq. (1) is consequently followed for the rate of degradation, with the condition that $kK[4\text{-CP}]_i / (1 + K[4\text{-CP}]_i) \gg k_0$. That is, more reaction occurs at the bubble–liquid interface than in the bulk under conditions of high loading concentration of 4-CP.

5. BENZENE AND CHLOROBENZENE DEGRADATION

Benzene (Bz) and chlorobenzene (ClBz) sonochemical degradation display very different features in comparison with those of PH and 4-CP:

- A higher destruction yield ($\times 3$).
- The intermediates which would result from a $^\bullet\text{OH}$ radical attack (PH in the case of Bz or chlorophenols in the case of ClBz) are detected in very low yield (less than 0.5% of the starting material).

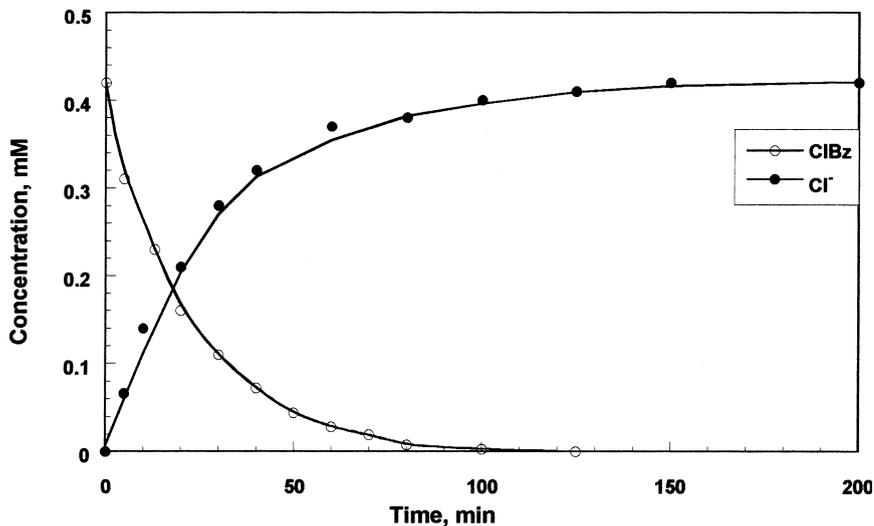


Figure 7. ClBz (0.42 mM) decay and time course of chloride evolution during ultrasonic treatment at 500 kHz. Ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

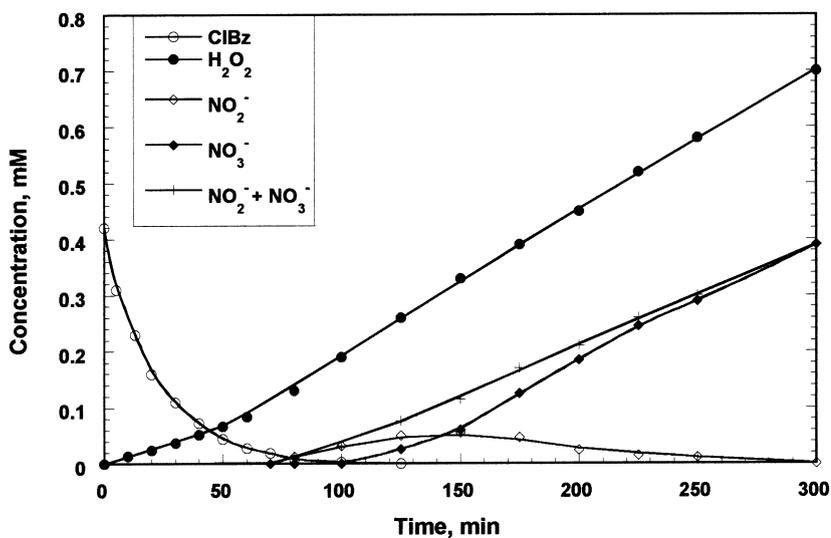


Figure 8. Time course concentration of H₂O₂, NO₂⁻, NO₃⁻ during the ultrasonic treatment of ClBz (0.42 mM) water solution equilibrated with air. Frequency: 500 kHz, ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

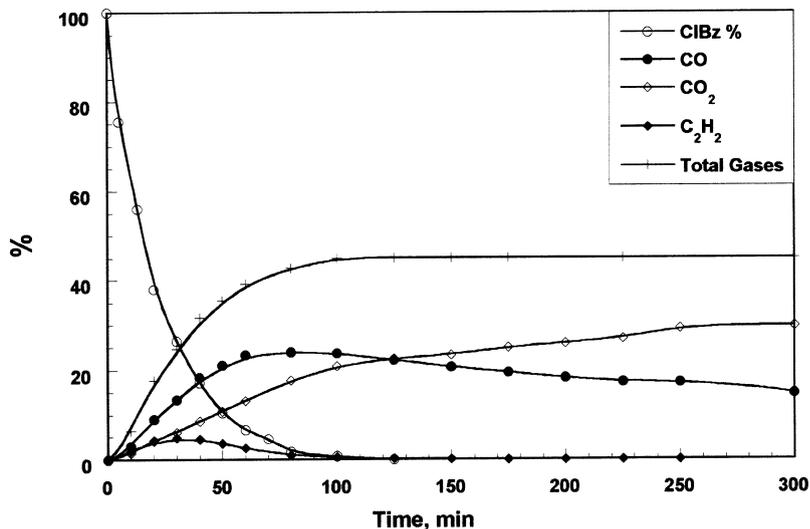
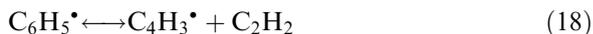
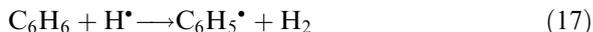


Figure 9. CIBz degradation and percentage of Carbon recovered as CO, CO₂, C₂H₂, during sonochemical treatment at 500 kHz. Ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

- A quantitative chloride release accompanies the concentration decrease of CIBz.
- At the end of the treatment, 70% of the carbon present initially is recovered essentially as carbon monoxide and carbon dioxide.

Comparison of the results obtained for PH and 4-CP shows a tremendous difference and seems to indicate degradation having a thermal origin. This hypothesis is reinforced by the results of the sonochemical degradation of CIBz in argon-saturated water. In this case, carbon monoxide is evolved as the main compound with methane and acetylene as gaseous intermediates (Figure 10).

According to Smith and Johnson [36], Bz pyrolysis leads first to acetylene (reactions (16)–(20)) which by reaction with $\cdot\text{OH}$ generates CO and CH₄. These two compounds are then oxidized in further stages [37,38]; reactions (21)–(23). The amount of carbon recovered does not correspond to the amount of carbon in the starting material because of the formation of filterable soot particles (reaction (20)).





In contrast to the kinetics of degradation of 4-CP, the kinetics for the sonodegradation of ClBz are dominated by pyrolysis reactions which occur within the cavitation site, followed by subsequent reaction of the intermediate pyrolytic species formed. De Visscher et al. [39] have developed an extensive kinetic scheme which can be modeled as shown in Eq. (3):

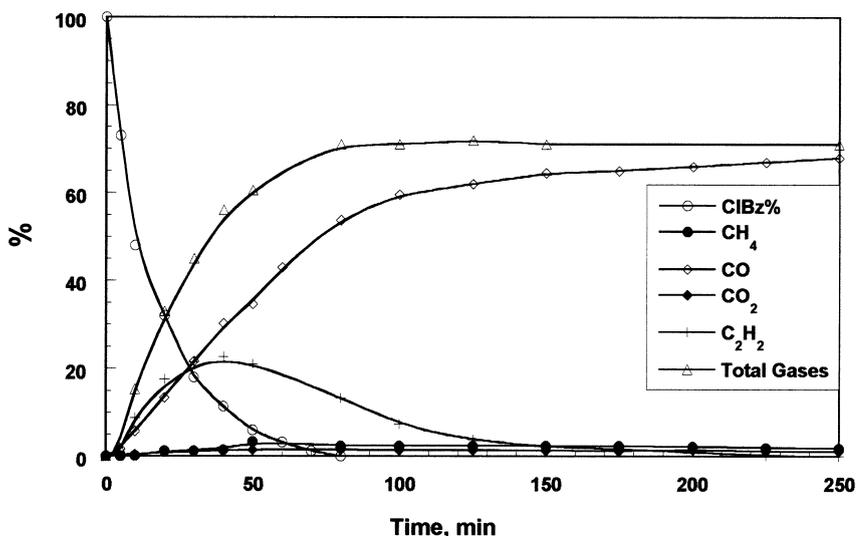
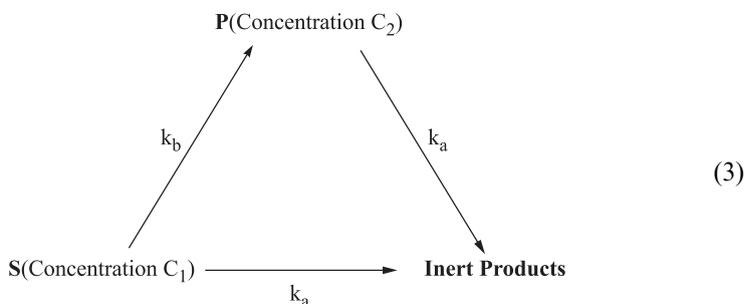


Figure 10. ClBz degradation and percentage of carbon recovered as CO, CO₂, CH₄, C₂H₂ during sonochemical treatment at 500 kHz in medium saturated with Argon. Ultrasonic power: 30 W, volume treated: 200 ml, temperature: 20°C.

Where **S** signifies the chlorinated aromatic reactant, and **P** the set of reactive intermediate products.

With the assumptions that the rates of degradation of **S** and **P** are the same, and that **S** and **P** can consequently be lumped together as a single pseudo-species of concentration $C_{1,2}$ with a common activation energy, two reaction rates emerge. r_1 is the rate for the reaction of **S** and r_2 is the reaction rate for the combined pseudo-species **S** + **P**:

$$r_1 = k_{1,0} \exp(-a C_{1,2}) C_{1,1} \quad (4)$$

$$r_2 = f k_{1,0} \exp(-a C_{1,2}) C_{1,1} \quad (5)$$

The term f here represents the fraction of **S** which is directly converted to inert product. The value of f is very nearly zero for chloroaromatics, indicating that pyrolysis within the bubble does indeed occur first (reactions (16)–(20)), followed by oxidation (reactions (21)–(23)). Equilibrium time for the diffusion of substrate between the liquid and gas phase components (i.e. the time it takes to partition the gas phase reactants into the bubble) is expected to be faster for smaller bubbles at higher frequencies [40].

The fact that a significant concentration of chloroaromatics occurs in the cavitation site prior to collapse is further supported by calculating aqueous cavitation temperatures with and without the presence of aromatics [39]. For water alone the collapse temperature is calculated to be 2521 K, while for water with 3.38 mM Bz the cavitation temperature is estimated to be 2335 K. The lowering of the cavitation collapse temperature is presumably due to the introduction of a species such as the chloroaromatic with a higher polytropic ratio $\gamma(=c_p/c_v)$ into the bubble.

6. DEGRADATION OF CHLOROAROMATICS

Recourse to ultrasound as a remediation agent appears particularly efficient in the case of volatile chloroaromatic compounds. Extensions of the process were checked and found applicable to the destruction of several xenobiotic derivatives (Table 2).

Chloroaromatic hydrocarbons decompose faster than more hydrophilic compounds like phenols. The destruction of these two kinds of pollutants occurs at different sites in or around the cavitation bubble and follows different pathways. The consequences are of importance for the treatment of wastewater containing chemicals with very different volatilities. Figure 11 presents the sequence for the degradation of 4-CP and ClBz in water. During the first stage, chlorobenzene decomposes. 4-CP transformation

Table 2. Initial Concentration and Chloride Yield after 150 min Irradiation for the Degradation of Chloroaromatics. Volume Treated: 250 ml, Ultrasonic Power: 30 W, Electric Power: 50 W, Frequency 500 kHz

Chloroaromatic	Concentration (mM)	Yield of Cl ⁻ (%)
1,2-Dichlorobenzene	0.4	90
1,3-Dichlorobenzene	0.05	89
1,4-Dichlorobenzene	0.2	95
1,3,5-Trichlorobenzene	0.02	95
1-Chloronaphthalene	0.04	98

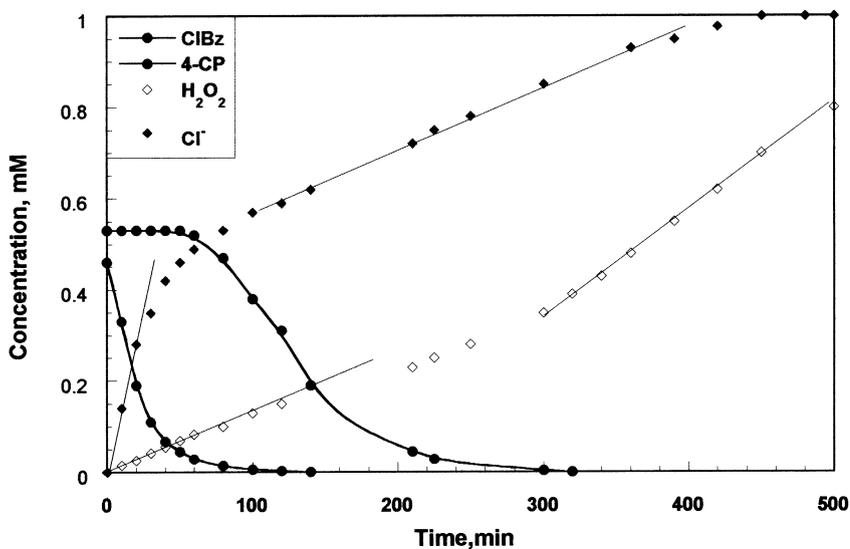


Figure 11. Simultaneous treatment of ClBz (0.5 mM) and 4-CP (0.55 mM) at 500 kHz.

starts only when the chlorinated hydrocarbon concentration is less than 0.02 M. This result shows clearly that the presence of a compound with a high vapor pressure (Henry's law constant for ClBz = 3.77×10^3 atm. $\text{m}^3 \text{mol}^{-1}$) efficiently hinders the degradation of a compound having a lower vapor pressure (Henry's law constant for 4-CP = 2.4×10^3 atm. $\text{m}^3 \text{mol}^{-1}$). The inhibition must not be considered as an inhibition of cavitation [41].

7. SONOCHEMICAL YIELDS

From a review of experiments found in the literature, it can be stated that the sonochemical method can be a ubiquitous way to destroy organic pollutants, but currently the development of the technique is crucially dependent upon an increase in the reaction rates, especially for hydrophilic compounds. Increasing the rates is a difficult task because of the lack of information concerning the basic parameters that produce sonochemical reactions. If, for example, in order to increase the rate of reaction a new sonicator design is required, little is known that would be useful to guide proper design parameters [42–45]. Nevertheless, several experiments indicate that a study of the effect of ultrasonic frequency on sonochemical reactivity may provide a key area for yield improvement.

Starting with the work of Busnel and Picard [46], frequency effects have recently received great attention and have led to numerous observations [47–50]

In an investigation conducted at 20, 200, 500, 800 kHz with transducers having similar diameters (4 cm) and operating with the same power, it was previously shown that the rate of sonochemical destruction for an organic compound is frequency dependent. In addition, there is an optimum frequency that is dependent upon the physical and the chemical properties of the organic compound [49]. In the same frequency range, similar work with 4-CP and ClBz as substrates shows comparable results. 4-CP degrades faster at 200 kHz, while the best rate for sonochemical destruction of ClBz is observed at higher frequency (Figure 12).

As previously displayed for PH and carbon tetrachloride, the comparison between 4-CP and ClBz clearly demonstrates the frequency effect. Reactions which involves $\cdot\text{OH}$ radical (hydrogen peroxide formation and 4-CP degradation) take place at the interface of the cavitation bubble with a yield that reaches a maximum value at an optimal frequency of 200 kHz. This optimum can be explained by a two-step reaction. In the first step, H_2O and O_2 are sonolysed inside the cavitation bubble. In the second step, $\cdot\text{OH}$ and $\cdot\text{OOH}$ radicals move to the bubble interface to react with the organic substrate or to form H_2O_2 . In this case the reaction rate depends on the amount of radical formed inside the bubble *and* on the release of radicals into the liquid. It can be postulated that the cavitation event occurring at low frequency more efficiently decomposes molecules inside the bubble, but that most of the radicals combine inside the cavity during the lifetime of the collapse (12.5 μs). With an increase in frequency, collapse occurs more rapidly (1.25 μs at 200 kHz; 0.5 μs at 500 kHz; 0.3 μs at 800 kHz) and more radicals escape from the bubble before recombination can occur. However, as the frequency increases the cavitation threshold also increases,

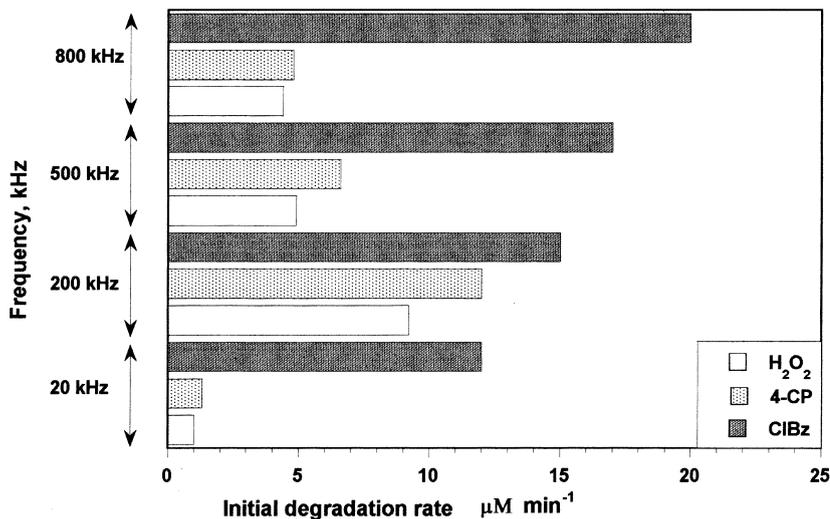


Figure 12. Rate of hydrogen peroxide formation and initial rate of degradation for 4-CP and ClBz. Acoustic power: 30 W.

with a decrease in the energy released by the cavity (smaller pulsating bubble). This will reduce the yield of sonolysis (step 1) and hence the amount of radicals ejected.

If ClBz destruction occurs in the bubble, the rate of degradation should be connected to the number of bubbles produced if each bubble releases enough energy to “burn” the volatile pollutant. Above the cavitation threshold, as frequency increases, the number of acoustic cycles increases, and consequently the rate of ClBz degradation is higher than at low frequency.

8. CONCLUSIONS

This chapter provides an understanding of the behavior of aromatic and chloroaromatic compounds when they are submitted to ultrasonic irradiation. It appears that sonochemical action is particularly efficient with compounds possessing high vapor pressure. Sonochemical treatment generates some drawbacks through nitrite and nitrate ion formation, but in any case, the fact that hydrogen peroxide is formed upon aqueous sonolysis provides an effective mechanism for water treatment through the application of high-intensity ultrasound.

REFERENCES

- [1] Flynn, G. In Mason, W. P. (ed.), *Physical Acoustics*. Vol. 1, Academic Press. New York, 1964, p. 58.
- [2] Walton, A. J., and Reynolds, G. T. *Adv. Phys.*, 33 (1984) 595.
- [3] Lepoint, T., and Mullie, F. *Ultrasonic Sonochemistry*, 1 (1994) S13.
- [4] Lepoint, T., and Lepoint-Mullie, F. In Mason, T. J. (ed.), *Advances in Sonochemistry*, Vol. 5, JAI Press Inc, 1999, pp. 1–108.
- [5] Riesz, P., Berdhal, D., and Christman, C. L. *Environm. Health Perspect.*, 64 (1985) 233.
- [6] Hart, E. J., and Henglein, A. *J. Phys. Chem.*, 89 (1985) 4342.
- [7] Kondo, T., Misik, V., and Riesz, P. *Ultrasonic Sonochemistry*, 3 (1996) S193.
- [8] von Sonntag, C., Mark, G., Tauber, A., and Schumann, H.-P. In Mason, T.J. (ed.), *Advances in Sonochemistry*, Vol. 5, JAI Press Inc; 1999, pp. 109–146.
- [9] Hoffmann, M. R., Hua I., and Hochemer, R. *Ultrasonic Sonochemistry*, 3 (1996) S163.
- [10] Colarusso, P., and Serpone, N. *Res. Chem. Intermed.*, 22 (1996) 61.
- [11] Cheung, H. M., Bhatnagar, A., and Jansen, G. *Environ. Sci. Technol.*, 25 (1991) 1510.
- [12] Nazu, K., Noyara, Y., and Maeda, Y. *Chem. Lett.*, (1993) 57.
- [13] Kotronarou, A., Mills, G., and Hoffmann, M. R. *J. Phys. Chem.*, 95 (1991) 3630.
- [14] Pétrier C., Lamy, M.-F., Francony, A., Benhcene, A., and David, B. *J. Phys. Chem.*, 98 (1994) 10514.
- [15] Pétrier, C., Micolle, M., Merlin, G., Luche, J.-L., and Reverdy, G. *Environ. Sci. Technol.* 26 (1992) 1639.
- [16] Pétrier, C., David, B., and Laguian, S. *Chemosphere*, 32 (1996) 1709.
- [17] Goodwin, T. J. In Mason, T. J. (ed.), *Chemistry with ultrasound*, Vol. 28, Elsevier Applied Science, London, 1990, p. 159.
- [18] Keil, F. J., and Swamy, K. M. *Reviews in Chemical Engineering*, 15 (1999) 85.
- [19] Pétrier, C., Jeunet, A., Luche, J.-L., and Reverdy G. *J. Am. Chem. Soc.*, 114 (1992) 3148.
- [20] Hua, I., and Hoffmann, M. R. *Environ. Sci. Technol.*, 31 (1997) 2237.
- [21] Renaudin, V., Gondrexon, N., Boldo, P., Pétrier, C., Bernis, A., and Gonthier, Y. *Ultrasonics Sonochemistry*, 1 (1994) S81.
- [22] Mason, T. J., Lorimer, J. P., and Bates, D. M. *Ultrasonics*, 30 (1992) 40.
- [23] Kimira, T., Sakamoto, T., Lévêque, J.-M., Sohmiya, H., Fujita, M., Ikeda, S., and Ando, T. *Ultrasonics Sonochemistry*, 3 (1996) S157.
- [24] Riesz, P., and Kondo, T. *Free Rad. Biol. Med.* 13 (1992) 247.
- [25] Fischer, C. H., Hart, E. J., and Henglein, A. *J. Phys. Chem.*, 90 (1986) 1954.
- [26] Lee, Y. N., and Lind, J. A. *J. Geophys. Res.*, 91 (1986) 2793.
- [27] Hart, E. J., Fischer, C. H., and Henglein, A. *J. Chem. Phys.*, 90 (1986) 5989.
- [28] Hart, E. J., and Henglein, A. *J. Chem. Phys.*, 90 (1986) 5992.
- [29] Berlan, J., Trabelsi, F., Delmas, H., Wilhelm, A.M., and Pettrignani, J. F. *Sonochemistry*, 1 (1994) S97.
- [30] Serpone, N., Terzian, R., Colarusso, P., Minero, C., Pelizzetti, E., and Hidaka, H. *Res. Chem. Intermed.*, 18 (1992) 183.
- [31] Serpone, N., Terzian, R., Hidaka, H., and Pelizzetti, E. *J. Phys. Chem.*, 98 (1994) 2634.
- [32] Henglein, A., and Kormann, C. *Int. J. Radiat. Biol.*, 48 (1985) 251.
- [33] Von Sonntag, C., Mark, G., Schuchmann, H. P., Von Sonntag, J., and Tauber, A. Cost meeting : chemical processes and reactions under extreme or non-classical conditions. COST action D6, ISBN 92-828-1986-8. 1998, pp. 11–18.
- [34] Hua, I., Hochemer, R. H., and Hoffmann M. R. *J. Phys. Chem.*, 99 (1995) 2335.
- [35] Mathews, R. W. In Pelizzetti, E., and Schiavello, M. (eds), *Photochemical Conversion and Storage of Solar Energy (IPSS)*, Kluwer Academic Publ, Inc., Dordrecht, The Netherlands, 1991, pp. 427–449.

- [36] Smith, R. D., and Johnson, A. L. *Comb. Flame*, 51 (1983) 1.
- [37] Hart, E. J., Fischer, C. H., and Henglein, A. *J. Phys. Chem.*, 94 (1990) 284.
- [38] Gehring, M., Hoyermann, K., Wagner, H. G., and Wolfrum, O. *J. Z. Naturforsch.*, 25a (1970) 675.
- [39] De Visscher, A. E., Eenoo, P. V., Drijvers, D., and Langenhove, H. V. *J. Phys. Chem.*, 100 (1996) 11636.
- [40] Crank, J. *The Mathematics of Diffusion*, Oxford University Press, 1967.
- [41] Pétrier, C., Jiang, Y., and Lamy, M.-F., *Environ. Sci. Technol.*, 32 (1998) 1316.
- [42] Henglein, A., Ulrich, R., and Lillie, J. *J. Am. Chem. Soc.*, 111 (1989) 1974.
- [43] Henglein, A., and Gutierrez, M. *J. Phys. Chem.*, 97 (1993) 158.
- [44] Gondrexon, N., Renaudin, V., Bernis, A., Gonthier, Y., and Boldo, P. *Environ. Technol.*, 14 (1993) 587.
- [45] Gondrexon, N., Renaudin, V., Pétrier, C., Clément, M., and Boldo, P. *Ultrasonics Sonochemistry*, 5 (1998) 1.
- [46] Busnel, R.-G., and Picard, D. *Comptes rendus*, 234 (1952) 1217.
- [47] Entezari, M. H., and Kruus, P. *Ultrasonics Sonochemistry*, 3 (1996) 19.
- [48] Laborde, J.-L., Bouyer, C., Caltagorone, J.-P., and Gerard, A., *Ultrasonics*, 36 (1998) 581.
- [49] Pétrier, C., and Francony, A. *Wat. Sci. Tech.* 35 (1997) 175.
- [50] Portenlanger, G., and Heusinger, H. *Ultrasonics Sonochemistry*, 4 (1997) 127.

This Page Intentionally Left Blank

SONOLYTIC OZONATION FOR THE REMEDIATION OF HAZARDOUS POLLUTANTS

Linda K. Weavers

OUTLINE

1. Introduction	112
1.1 Sonochemistry	112
1.2 Ozone	115
1.3 Sonolytic Ozonation	116
2. Kinetics and Mechanism of Sonolytic Ozonation	116
3. Modeling of Ozone Decomposition in a Collapsing Cavitation Bubble . .	122
3.1 Description of the Model	122
3.2 Results	124
3.3 Discussion	130
4. Conclusions	137
Acknowledgments	137
References	137

Advances in Sonochemistry
Volume 6, pages 111–139.
© 2001 Elsevier Science B.V. All rights reserved.

1. INTRODUCTION

Advanced oxidation processes (AOPs) such as ultrasonic and ultraviolet irradiation have been shown to be effective for the elimination of organic and inorganic pollutants from water [1–44]. AOPs are generally grouped together because they all result in the *in situ* formation of radicals or more specifically, hydroxyl radicals, in sufficient quantity to affect water treatment [22,45]. These processes are often needed when conventional approaches to water and wastewater treatment are ineffective. However, AOPs are often costly and sometimes ineffective for the degradation of contaminants in water or wastewater that contains a mixture of organic and inorganic compounds.

To overcome some of the deficiencies of traditional AOPs, chemical oxidants can add additional oxidizing power to reach target levels of water quality. Oxidants such as ozone have high oxidation potentials but are either selective, have large activation energies, or both. Combining these oxidants with ultrasound or ultraviolet irradiation broadens the range of compounds that can be degraded by the creation of reactive free radicals. Activation energies of free radical reactions with compounds are typically less than those of multi-electron oxidants. Depending on the cost of the oxidants, the overall cost of using AOPs may be decreased by reducing the time required for oxidation reactions to occur.

1.1 Sonochemistry

The collapse of cavitation bubbles in water generates a variety of chemical processes and reaction sites [12–14,16–18,20,25–30,32–38,40,41,43,46–51]. Cavitating water is considered to have four main reactive regions. First is the vapor bubble which pyrolyzes vaporous water molecules into hydroxyl radical and hydrogen atoms during collapse:



Gases such as O₂ and high Henry's law solutes also exist in the vapor region and undergo direct pyrolysis reactions [17,18,20,25–28,30,52]. Next is the interfacial sheath around the vapor. Here supercritical water is thought to exist [49] along with dissolved radicals from the bubble. This is the reaction site for nonvolatile solutes and also the site for liquid phase pyrolysis. Also, it is believed to be possible for liquid to be injected into the center of a cavitation bubble as it collapses asymmetrically, referred to as a spume [53]. Similar to the interfacial sheath, it is where liquid phase pyrolysis is expected to occur. Finally, in the bulk phase there is an increase in

metastable oxidants such as hydrogen peroxide which are formed from radical recombination reactions [25,52].

The physical properties of a solute are important in identifying its capability to be decomposed by sonication. The Henry's Law constant of a compound, which is its equilibrium air-water distribution, is defined by:

$$H = \frac{P_i}{C_w} \quad (2)$$

where H ($\text{Pa m}^3 \text{ mol}^{-1}$) is the Henry's Law constant, P_i is the partial pressure of the chemical species i in the gas phase, and C_w is the aqueous phase concentration of the solute. This parameter characterizes relative amounts of a solute that will enter the vapor bubble. For a variety of compounds studied (experimental details in references [54–56]) with parameters as shown in Table 1 [57–60], Figure 1 demonstrates the effect of H on the degradation rate of a variety of compounds in a sonicating aqueous solution [61]. For comparison purposes, the first-order degradation rate constants were normalized to the power density (W l^{-1}) in each system. Clearly, as H increases the degradation rate increases at both 20 and 500 kHz. In fact, at very high H , the normalized degradation rates increase more rapidly with H at 20 kHz than at 500 kHz, until the degradation rates are similar at both frequencies.

The octanol-water partitioning coefficient, K_{ow} , is another key parameter. It approximates the hydrophobicity of a compound. It is defined by:

$$K_{ow} = \frac{C_o}{C_w} \quad (3)$$

where C_o is the concentration of the compound in the octanol phase. This constant gives insight into the amount of surface excess at the cavitation bubble interface. Figure 2 demonstrates the effect of K_{ow} on the degradation rate. Again, as K_{ow} increases the degradation rate is observed to increase

Table 1. Selected Properties and Rate Constants of Compounds [57–60]

Compound	pK_a	H ($\text{Pa m}^3 \text{ mol}^{-1}$)	$\log K_{ow}$	k_{O_3} ($\text{M}^{-1} \text{ s}^{-1}$)	k_{OH} ($\text{M}^{-1} \text{ s}^{-1}$)
Ozone	–	1.08×10^4	–	–	1.1×10^8
Nitrobenzene	–	1.3	1.83	0.09	3.9×10^9
4-Nitrophenol	7.14	4.21×10^{-5}	1.2	<50	3.8×10^9
4-Chlorophenol	9.38	0.0567	2.16	600	7.6×10^9
Pentachlorophenol	4.71	0.079	2.68*	$> 3 \times 10^5$	3.7×10^9
Cyclohexene	–	4.57×10^3	2.86	3.9×10^6	8.8×10^9

* Reported as $\log K_{ip}$ (ion-pair partition coefficient).

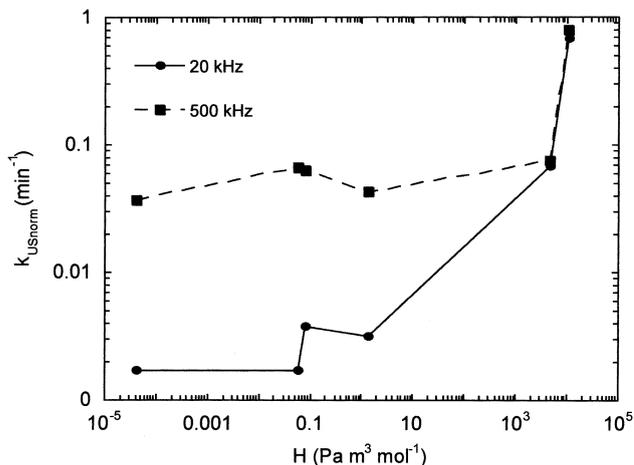


Figure 1. Normalized degradation rate constant for sonication versus the Henry's Law constant of the compound at both 20 and 500 kHz ultrasonic frequency.

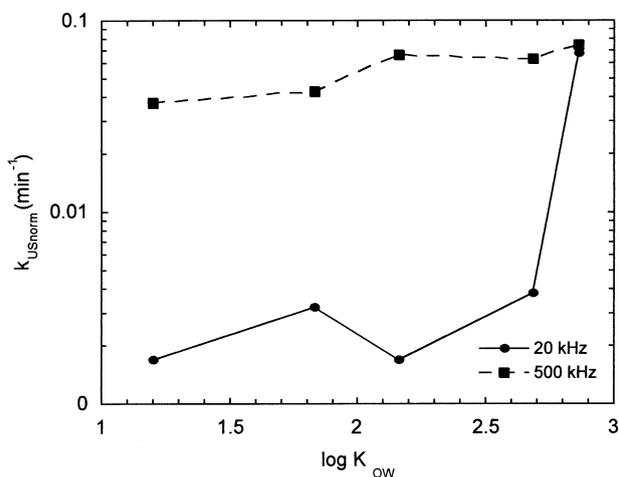


Figure 2. The normalized degradation rate constant for sonication at both 20 and 500 kHz ultrasonic frequency versus the octanol–water partition coefficient.

at both frequencies. Obviously H and K_{ow} are interrelated. In addition, other physical–chemical parameters of the contaminant such as the reaction rate with OH^\bullet and the specific heat of the compound are important in determining degradation rates. Therefore, it is difficult to determine the relative importance of K_{ow} , H , and other parameters in the

degradation of particular compounds although both parameters appear to be important.

1.2 Ozone

Ozone (O₃) is a very strong oxidant that can oxidize organic compounds to carbon dioxide and water. However, the kinetics of oxidation of many organic compounds with ozone is slow. Standard reduction potentials for half reactions of the reduction of various oxidizing radicals and ozone are shown in Table 2 [62].

Ozone has been widely studied for the degradation of aqueous contaminants. Ozone is being implemented at water and wastewater treatment plants in a variety of applications including the reduction of trihalomethane formation resulting from chlorination [63]. Ozone has resonance structures that allows it to act as an electrophile or a nucleophile. Although the molecule has a very high oxidation potential, ozone reactions are very selective, and limited to molecular sites with high electron density such as alkenes or sites where the carbon contains an electron-withdrawing group. Ozone, however, is unstable and undergoes chain decomposition in alkaline systems to liberate hydroxyl radicals [63]. Hydroxyl radical is non-selective in its reactions allowing it to react with organic compounds either by H-atom abstraction, direct electron transfer, or insertion.

Another method of generating free radicals from ozone is the use of ultraviolet irradiation (O₃-UV). Peyton and Glaze [10] found that hydrogen peroxide produced initially by irradiation of O₃, formed hydroxyl radicals by O₃ reactions with hydroperoxide anions resulting in enhanced destruction rates of contaminants [4,5,9,10,23,24]. Another AOP which combines hydrogen peroxide and ozone directly (H₂O₂-O₃), bypasses the need for UV light [21]. H₂O₂-O₃ does not depend on the transmissivity of the solution in the UV region where O₃ absorbs; therefore, it has wider applicability. However, O₃-UV systems are attractive in some situations, especially if the pollutant absorbs UV light. Although less studied, the combination of cavitation with ozone, also has potential. The generation of free radicals, particularly OH•, by these

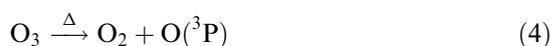
Table 2. Reduction Potentials of Selected Oxidants [62]

<i>Redox half-reaction</i>	<i>E° (volts)</i>
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$	+ 1.77
$\text{OH}^\bullet + \text{H}^+ + \text{e}^- = \text{H}_2\text{O}$	+ 2.80
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- = \text{O}_2 + \text{H}_2\text{O}$	+ 2.07
$\text{HO}_2^\bullet + \text{H}^+ + \text{e}^- = \text{H}_2\text{O}_2$	+ 1.50

processes can significantly reduce times required for destruction of organic contaminants.

1.3 Sonolytic Ozonation

The coupling of ultrasonic irradiation with ozonation provides another possible AOP. In this case, OH^\bullet is generated from the decomposition of ozone. However, ozone is decomposed thermolytically in the vapor phase of a cavitation bubble as follows [25,26,55].



The initiation reaction yields atomic oxygen that reacts with water to form hydroxyl radical:



The reaction sequence of Eqs. (4) and (5) occurs in the vapor phase of cavitation bubbles. The products then migrate to the interfacial sheath of the bubble where they are transferred into the aqueous phase. The combination of O_3 and ultrasound should be an effective oxidation system since two OH^\bullet molecules are formed per O_3 molecule consumed. However, the reaction of ozone with atomic oxygen results in the loss of OH^\bullet production:



Hydrogen peroxide accumulation in the aqueous phase provides an indirect measure of OH^\bullet production in the vapor phase and in the interfacial region. Previous studies have measured increased H_2O_2 production by sonolytic ozonation over sonolysis of oxygen [12,26].

2. KINETICS AND MECHANISM OF SONOLYTIC OZONATION

Studies of the combined process involving ultrasound and ozone have shown faster degradation rates for humic and fulvic acids, 4-nitrophenol, trinitrotoluene, phenol, and methyl *tert*-butyl ether (MTBE) than either system alone. Additionally, very rapid decomposition of ozone due to an ultrasonic field has been observed [11,12,15,25,26,30,46,47,54,55,64–68]. Sonolytic ozonation has also been investigated for the disinfection of water

[64,69,70]. In this case, ultrasound was thought to act on the bacteria and viruses directly by breaking up clusters and particulate organic matter as well as decomposing O_3 .

Furthermore, researchers have reported increased mass transfer coefficients, $k_L a$ (s^{-1}), of ozone diffusing into solution in the presence of ultrasound [47,55,64,65]. k_L is the mass transfer velocity ($cm\ s^{-1}$) and a is the specific interfacial area for mass transfer ($cm^2\ cm^{-3}$). Many hypotheses for enhanced mass transfer have been developed. Olson and Barbier [47] hypothesized that the apparent enhancement was due to mechanical effects such as greater mixing and break up of gas bubbles as they enter an ultrasonic reactor. Increased mass transfer may also be the result of an ozone diffusing bubble oscillating or cavitating in the applied ultrasonic field. In this case, higher pressures in the ozone bubble force more ozone into solution. On the other hand, the apparent mass transfer effects may be due to the sonication of ozone reducing the aqueous ozone concentration below saturation allowing more ozone to be absorbed from the gas-phase into solution per unit time. Finally, degassing may be a factor in sonolytic ozonation due to the high Henry's Law constant of ozone ($H = 1.08 \times 10^4\ Pa\ m^3\ mol^{-1}$) [71], specially at low frequency. Weavers and Hoffmann [55] performed a detailed study to investigate the various mass transfer processes occurring and attributed enhanced mass transfer to the rapid degradation rates of ozone in a sonicating solution reducing the ozone concentrations, resulting in a larger driving force of ozone to solution. In addition, degassing of ozone was determined to be minimal in a 20 kHz probe system and non-existent in the high frequency system studied. Figure 3 shows the various processes occurring upon the addition of ozone to an ultrasonic field.

In order to anticipate the applicability of sonolytic ozonation to a variety of aqueous systems, the effect of the second-order reaction rate constant with ozone was explored. Compounds were selected with varying second-order reaction rate constants with ozone as shown in Table 1 to observe compound destruction by ozone, sonication, and sonolytic ozonation simultaneously. The overall rate of contaminant (C) disappearance in the sonolytic ozonation process can be represented by a linear combination of contributing terms similar to that proposed by Peyton et al. [9].

$$-\frac{dC}{dt} = k_{US}[C] + k_{O_3}[C] + k_{US-O_3}[C] \quad (7)$$

where k_{US} , k_{O_3} , and k_{US-O_3} , are the first-order degradation rate constants for sonolysis, ozonolysis, and the residual kinetic effect upon combining the two systems, respectively. If gas stripping was determined to be significant, k_{US} , k_{O_3} , and k_{US-O_3} were corrected to reflect this additional loss mechanism. Figure 4 shows the degradation of nitrobenzene by sonication,

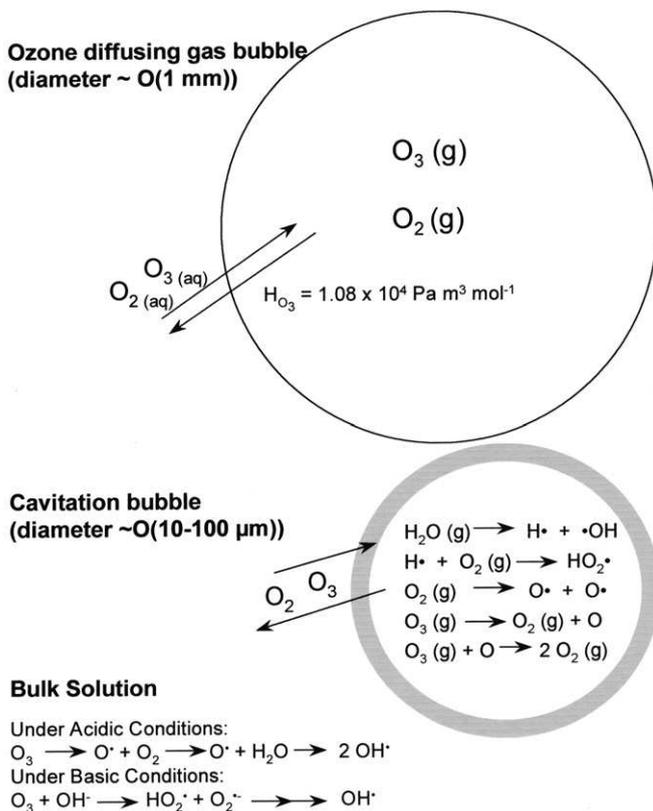


Figure 3. Processes occurring with ozone bubbling through an ultrasonic reactor.

ozonation, and sonolytic ozonation in a 20 kHz probe reactor. The “model” in this figure represents the addition of the first-order degradation rates by sonication and ozonation. This essentially is the degradation line beyond which sonolytic ozonation has enhanced degradation compared to performing sonication and ozonation separately (i.e. $k_{US} + k_{O_3}$). In other terms, it is the point at which the residual kinetic effect is zero (i.e. $k_{US-O_3} = 0$).

To compare the enhancement of the combined system an enhancement factor was defined as:

$$\text{enhancement} = \frac{k_{US-O_3}}{k_{US} + k_{O_3}} \times 100 \quad (8)$$

For 20 and 500 kHz frequencies, the enhancement factor for 5 compounds with varying reaction rate constants with O_3 was plotted as a function of the reported second-order reaction rate constants for reaction with O_3 , k_{C-O_3} , as

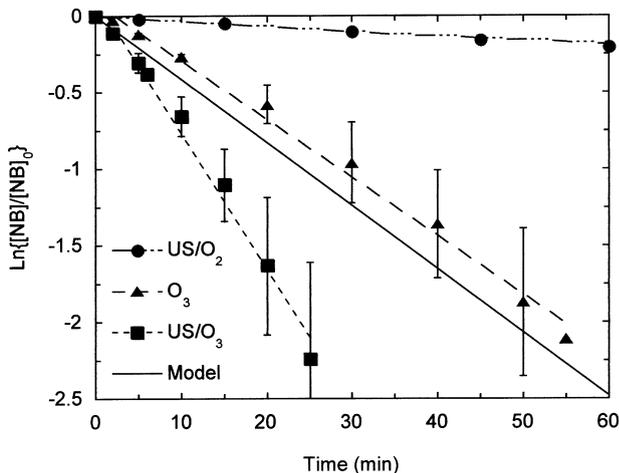


Figure 4. First-order degradation of NB, 4-NP, and 4-CP due to sonication with O₂ ozonation, and sonolytic ozonation in the 20 kHz reactor. O₃ gas flowrate = 10 ml min⁻¹ pH = 2.4 ± 0.2, T = 293 K, initial concentration of substrate = 100 μM, power = 56.1 W. Reprinted with permission from Weavers et al., *Environ. Sci. Technol.*, 32 (1998) 2727. Copyright 1998 American Chemical Society.

shown in Figure 5. For the reaction rate constants shown, the 20 kHz frequency consistently shows enhancement whereas sonolytic ozonation in the 500 kHz frequency resulted in antagonism for the compounds studied. With the 500 kHz frequency, a maximum antagonism was observed at a moderately high reported second-order reaction rate constant with O₃. Regardless of observed antagonism or synergism for the degradation of the parent compound in the combined sonolytic ozonolysis system, the loss of total organic carbon (TOC) was consistently accelerated compared to the individual sonolysis and ozonolysis experiments.

For compounds with large k_{C-O_3} , O₃ reacts at the gas-liquid interface of a diffusing gas bubble resulting in little to no O₃ in aqueous solution. As a result, the sonication and ozonation processes, although occurring simultaneously, are acting independently due to the rapid reaction rate of ozone with the contaminant. A detailed mass transfer study of ozone in the presence of ultrasound demonstrated marginal increased mass transfer with the 20-kHz probe reactor due to physical processes such as turbulence and acoustic streaming. At 500 kHz, increased mass transfer was not observed. In addition, a diffusing gas bubble (in the size ranges studied, ~1 mm) was not influenced by ultrasound. Therefore, ozone diffuses into solution before it is available to enter a cavitating gas bubble where

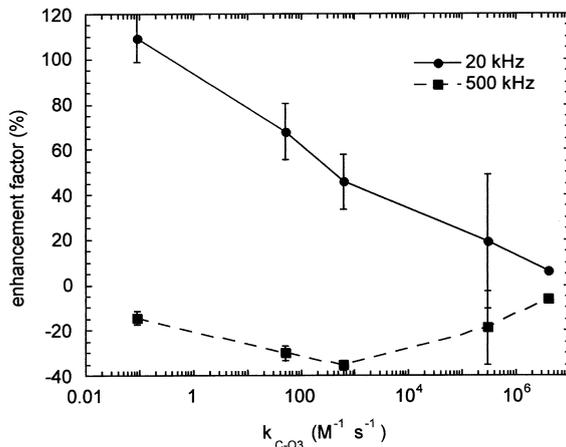


Figure 5. Enhancement of the combined system compared to the linear combination of separate sonolysis and ozonolysis experiments at 20 and 500 kHz versus reported second-order rate constants of compound reaction with ozone.

it undergoes thermal decomposition [55]. As a consequence, sonolytic ozonolysis at high k_{C-O_3} results in $k_{US-O_3} = 0$ (i.e., the process is neither enhancing nor detrimental).

At the other extreme where $k_{C-O_3} = 0$, no reactions will occur between the contaminant and O_3 . In this situation, any O_3 that is converted to OH^\bullet is beneficial to increasing the reaction rate of the system. Although not shown, the degradation of trinitrotoluene and MTBE resulted in enhanced degradation rates upon combining sonolysis and ozonolysis [46,67]. Both of these compounds have slow to negligible reaction rates with O_3 . As k_{C-O_3} increases, benefits of the combined system are reduced.

In between these extremes, the separate sonolysis and ozonolysis processes are interactive. A conceptual diagram of possible pathways of compound degradation and interactions of sonolysis and ozonolysis is shown in Figure 6. Pathways 1 and 2 indicate ozonolysis processes occurring in the absence of sonication including mass transfer of ozone from the gas phase to solution (pathway 1) and solution reactions of the compound with ozone or radicals from O_3 autodecomposition occurring in the absence of sonolysis (pathway 2). Pathways 6 and 7 are sonolysis reactions that occur in the absence of ozonolysis. Upon combining the processes, additional processes occur by pathways 3, 4, 5, and 8. In addition, pathways 2, 6, and 7 may be altered by the direct interaction of sonolysis and ozonolysis. For example, ozone decomposes in a cavitation bubble to form OH^\bullet that is available to react with C (pathway 3). Additionally, O_3 may react with $O(^3P)$ generated from the thermal decomposition of O_3 in the cavitation bubble

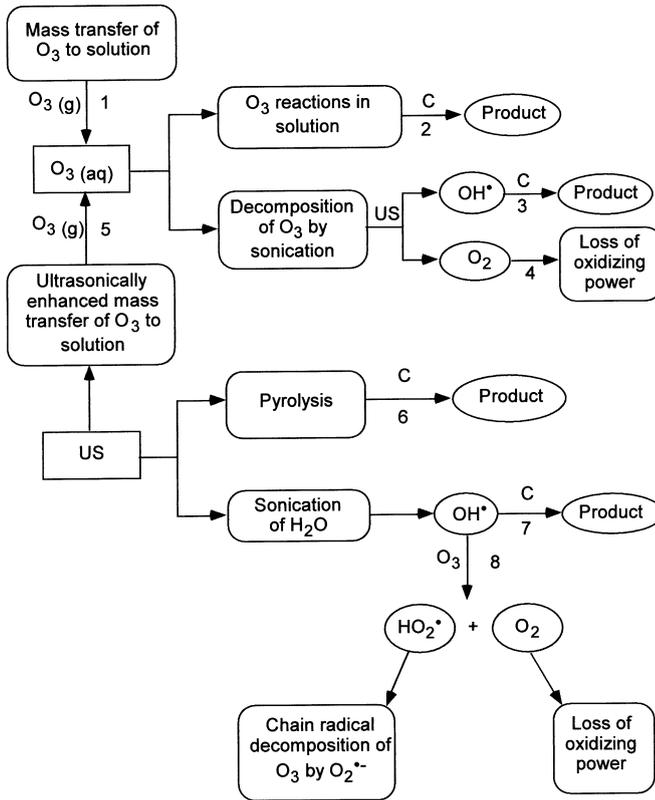
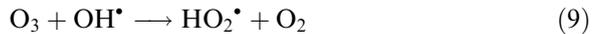


Figure 6. Conceptual diagram of possible pathways of contaminant (C) degradation and interactions of sonolysis and ozonolysis. Reprinted with permission from Weavers et al., *Environ. Sci. Technol.*, 32 (1998) 2727. Copyright 1998 American Chemical Society.

resulting in O₂ (pathway 4). Both of these pathways reduce the O₃ available to react via pathway 2. Furthermore, O₃ may scavenge OH[•] formed from sonication via pathway 8



reducing both the OH[•] available to react with C and [O₃]. Depending on the reaction rate of O₃ with C and the selectivity of pathway 3 versus 4 and pathway 3 versus 8, sonolytic ozonation may be beneficial or detrimental to enhancing the reaction rate.

Recognizing that the pathways of the separate processes are altered in the combined system and referring back to Eq. (7) and Figure 5, it is apparent

that under antagonistic conditions a contaminant (C) is not formed (i.e., a negative enhancement, $k_{US-O_3} < 0$). Rather, the rates of the separate processes are altered in the combined system. A modified version of Eq. (7) that describes the system more accurately is:

$$-\frac{dC}{dt} = k'_{US}[C] + k'_{O_3}[C] + k_{US-O_3}[C] \quad (10)$$

where k'_{US} and k'_{O_3} are the altered rate constants for sonolysis and ozonolysis, respectively. Under conditions of antagonism in the combined system (i.e., at the 500 kHz frequency), k'_{US} and/or k'_{O_3} are smaller than k_{US} and k_{O_3} from the separate sonolysis and ozonolysis experiments. The addition of pathways 3 and/or 5 does not compensate for reductions in pathways 2 and/or 7 in the combined system compared to the individual systems. Furthermore, the selectivity of pathway 4 over pathway 3 may be dominant in antagonistic situations. When sonolytic ozonation is synergistic (i.e. $k_{US-O_3} > 0$) pathways 3 and/or 5 more than compensate for reductions in pathways 2 and 7. In addition, the sonication of ozone (pathways 3 and 4) may select pathway 3 versus 4. However, from the experiments performed, it is impossible to determine the values of k'_{US} , k'_{O_3} , and k_{US-O_3} .

3. MODELING OF OZONE DECOMPOSITION IN A COLLAPSING CAVITATION BUBBLE

The objective of this section is to determine if the bubble collapses at 20 and 500 kHz in the presence of O_3 are different, resulting in synergism in one case and antagonism in the other. It is also interesting to recall that the loss of TOC is accelerated in all cases. The pathway of destruction of a substrate to CO_2 will most likely include compounds that do not react with O_3 . Therefore, the enhanced loss of TOC indicates that substrates which do not react with O_3 will be accelerated in any case. By investigating, the formation of oxidizing species from the bubble collapse, we will gain insight into the mechanism of synergism or antagonism. This is important in determining optimum reaction conditions for adding O_3 to ultrasound.

3.1 Description of the Model

A full model of sonochemical action would deal with cavitation cloud collapse, asymmetric collapse, and bubble-bubble interactions. However, in this study a single bubble was modeled. This study was part of a larger bubble collapse modeling study (see Colussi et al. 1998 for details) [72].

Although many differences exist between the behavior of a single bubble and bubble clouds, the analysis of a single bubble will provide the basis of bubble cloud characteristics. In order to determine the collapse of the bubble, its energy balance was assumed to be given by:

$$\Delta KE + \Delta UE + Q = \Delta PE + \Delta SE \quad (11)$$

where KE is the kinetic energy of the collapsing bubble, UE is the internal energy of gas in the bubble, Q is the energy consumed by gas-phase chemical reactions, PE is the potential energy of the collapsing bubble, and SE is the surface energy of the bubble. Expressing the energy equation in terms of the bubble radius, R , and assuming the gas in the bubble is ideal, it becomes:

$$\begin{aligned} 2\pi\rho R^3 \left(\frac{dR}{dt}\right)^2 + (T - T_0) \sum_i n_i C_{V_i} + \sum_i \Delta H_{\text{form}_i} (n_i - n_{i0}) \\ = \frac{4}{3} \pi P_m (R_{\text{max}}^3 - R^3) + 4\pi\sigma (R_{\text{max}}^2 - R^2) \end{aligned} \quad (12)$$

where ρ is the density of the liquid, T is the temperature in the bubble, T_0 is the initial bubble temperature, n_i is the number of molecules of species i , n_{i0} is the initial number of molecules of species i , C_{V_i} is the molecular specific heat of species i , ΔH_{form_i} is the heat of formation of species i , P_m is the external pressure on the bubble (assumed constant), R_{max} is the maximum radius obtained at the end of the expansion cycle, and σ is the surface tension of water.

The time dependent gaseous bubble temperature was assumed to be completely mixed and uniform. It was determined by equating the thermal energy of the gas and energy consumed by reactions to the work done compressing the bubble:

$$(T - T_0) \sum_i n_i C_{V_i} + \sum_i \Delta H_{\text{form}_i} (n_i - n_{i0}) = \int_0^t \frac{3}{R} n k_B T \frac{dR}{dt} dt' \quad (13)$$

where k_B is the Boltzman constant, and n is the total number of molecules in the bubble. Therefore, the polytropic approximation is no longer needed nor is it applicable. The changing numbers of gas species are followed during collapse rather than assuming a polytropic constant throughout collapse.

Bubbles were assumed to grow during the expansion cycle isothermally [73], and reach R_{max} . The subsequent vaporous collapse is dependent on the density of the liquid, the applied frequency ($\omega = 2\pi f$), and the hydrostatic (p_0) and acoustic (P_A) pressure but is independent of the initial radius [74].

$$R_{\text{max}} = \frac{4}{3\omega} (P_A - p_0) \left[\frac{2}{\rho P_A} \right]^{1/2} \left[1 + \frac{2}{3p_0} (P_A - p_0) \right]^{1/3} \quad (14)$$

A series of 40 equations of the species O_3 , O_2 , H_2O , OH , O , H , H_2 , HO_2 , and H_2O_2 were considered as shown in Table 3 [75–81]. Organic species were omitted from the reaction mechanism since even a simple compound such as CH_3OH along with all of the intermediates produced would complicate the mechanism considerably. However, in most cases organic contaminants will be present in small concentrations compared to other species. Rate constants as a function of temperature were determined from Arrhenius parameters as follows:

$$k = AT^\beta \exp\left(-\frac{E_a}{\mathfrak{R}T}\right) \quad (15)$$

where E_a is the activation energy, and \mathfrak{R} is the universal gas constant. Table 3 lists reduced activation energies (E_a/\mathfrak{R}) in units of Kelvin. Rate equations and Arrhenius parameters were taken from the latest NIST compilation of combustion studies and were validated over a range from 300 to at least 2500 K.

A chemical kinetics program using a Gear method to solve the system of differential equations was implemented [82]. Differential equations for R , chemical species, and mass transfer were solved numerically.

3.2 Results

The addition of 1% O_3 to an O_2 bubble with chemical reactions is shown in Figure 7. Although the shape of the bubble collapse is identical in both cases, the temperature during the collapse of the bubble with O_3 is slightly lower due to the additional chemical reactions occurring with O_3 .

Figure 8 shows the major chemical species produced from the collapse of an O_2 bubble influenced by a frequency of 20 kHz. OH is produced in the largest quantity followed by O , HO_2 , H , and H_2 . Radical species are produced only in the last 30 ns when the temperature increases rapidly. The collapse of a bubble with the same initial radius and 1% O_3 is shown in Figure 9. Since O_3 has a lower activation energy as shown in Table 3, it pyrolyzes at a lower temperature, and hence earlier in the collapse than H_2O vapor or O_2 . $O(^3P)$ from O_3 decomposition forms and decays before the end of the collapse and before significant OH is formed. OH formation is increased slightly in the presence of O_3 .

Starting with the same initial bubble radius, $R_0 = 41 \mu\text{m}$ but with a higher pressure amplitude, $P_A = 11 \text{ atm}$, the bubble collapses more violently and results in a different ratio of species. Figure 10 shows that H_2 is the major product in this bubble. The collapse time is much longer than with a smaller pressure amplitude but the chemical reactions occur only in the last 10 ns.

Table 3. Chemical Equations and Arrhenius Parameters

Reaction	A^* ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$)	β	E_a (K)	Ref.
$\text{O}_3 + \text{M} \rightarrow \text{O}_2 + \text{O} + \text{M}$	7.15e-10		11172	75
$\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$	8.0e-12		2060	77
$\text{O}_3 + \text{H} \rightarrow \text{OH} + \text{O}_2$	1.4e-10		480	77
$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	1.9e-12		1000	77
$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2$	1.4e-14		600	77
$\text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M}$	3.01e-6	-1	59429	80
$\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$	4.0e-32	-1		76
$\text{O}_2 + \text{H} + \text{M} \rightarrow \text{HO}_2 + \text{M}$	1.77e-29	-1		80
$\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$	5.85e-8	-0.7	8589	78
$\text{O}_2 + \text{OH} \rightarrow \text{O} + \text{HO}_2$	3.7e-11		26500	80
$\text{O}_2 + \text{H}_2 \rightarrow \text{H} + \text{HO}_2$	2.4e-10		28500	80
$\text{O}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{HO}_2$	9.0e-11		20000	80
$\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}$	5.8e-9		52900	80
$\text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{OH}$	7.60e-15	1.30	8605	80
$\text{H}_2\text{O} + \text{H} \rightarrow \text{OH} + \text{H}_2$	1.03e-16	1.9	9265	80
$\text{OH} + \text{M} \rightarrow \text{O} + \text{H} + \text{M}$	4.0e-9		50000	80
$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	1.6e-23	-3		80
$\text{OH} + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	3.5e-16	1.4	-200	80
$\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}$	7.49e-10	-0.5	30	80
$\text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	6.11e-26	-2		80
$\text{OH} + \text{H} \rightarrow \text{O} + \text{H}_2$	8.1e-21	2.8	1950	80
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	2.4e-8	-1		80
$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	2.9e-12		160	80
$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	1.06e-17	2	1490	80
$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	5.21e-35		-900	80
$\text{O} + \text{H} + \text{M} \rightarrow \text{OH} + \text{M}$	1.3e-29	-1		80
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	2.9e-11		-200	80
$\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$	1.6e-17	2	2000	80
$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	2.49e-17	2	3801	81
$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	1.5e-29	-1.3		80
$\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}$	2.8e-10		440	80
$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	1.1e-10		1070	80
$\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}$	9.12e-11		914	79
$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$	4.11e-11		2000	80
$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2$	8e-11		4000	80
$\text{HO}_2 + \text{M} \rightarrow \text{H} + \text{O}_2 + \text{M}$	2e-5	-1.18	24363	80
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	3e-12			80
$\text{HO}_2 + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}_2$	5e-11		13100	80
$\text{H}_2\text{O}_2 + \text{M} \rightarrow \text{OH} + \text{OH} + \text{M}$	2.14e-9	-4.86	26795	80
$\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$	7.59e-5	-1.4	52530	80

* Thermolecular reactions have units ($\text{cm}^6 \text{molec}^{-2} \text{s}^{-1}$).

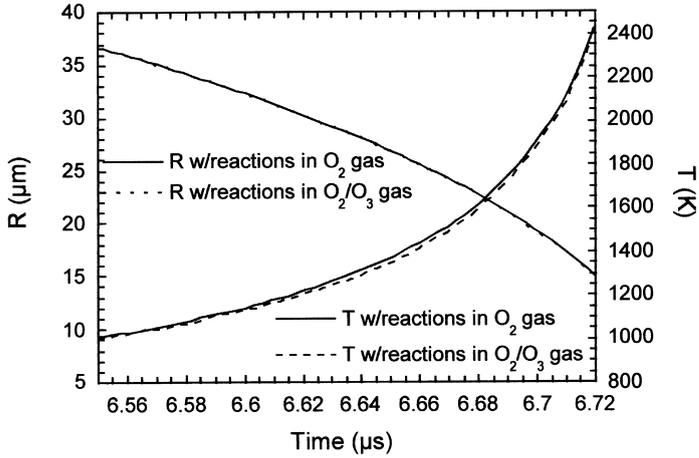


Figure 7. The collapse of an oxygen and oxygen–ozone bubble and temperature produced initially at $R_0 = 41 \mu\text{m}$ influenced at 20 kHz and $P_A = 2 \text{ atm}$ and considering chemical reactions.

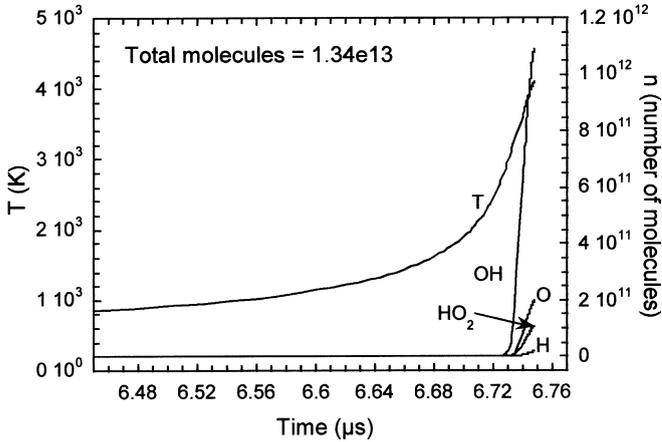


Figure 8. The temperature and chemical species produced from the collapse of an oxygen bubble initially at $R_0 = 41 \mu\text{m}$, influenced by $P_A = 2 \text{ atm}$ and 20 kHz.

With the addition of O_3 , it appears that OH and H_2 formation is less, than without O_3 as shown in Figure 11. Also, in this bubble, H_2O is more than an order of magnitude larger than O_2 , whereas at $P_A = 2 \text{ atm}$, O_2 was larger than H_2O . Oxygen is produced in the final stages of collapse rather than consumed and 27% of the water is consumed.

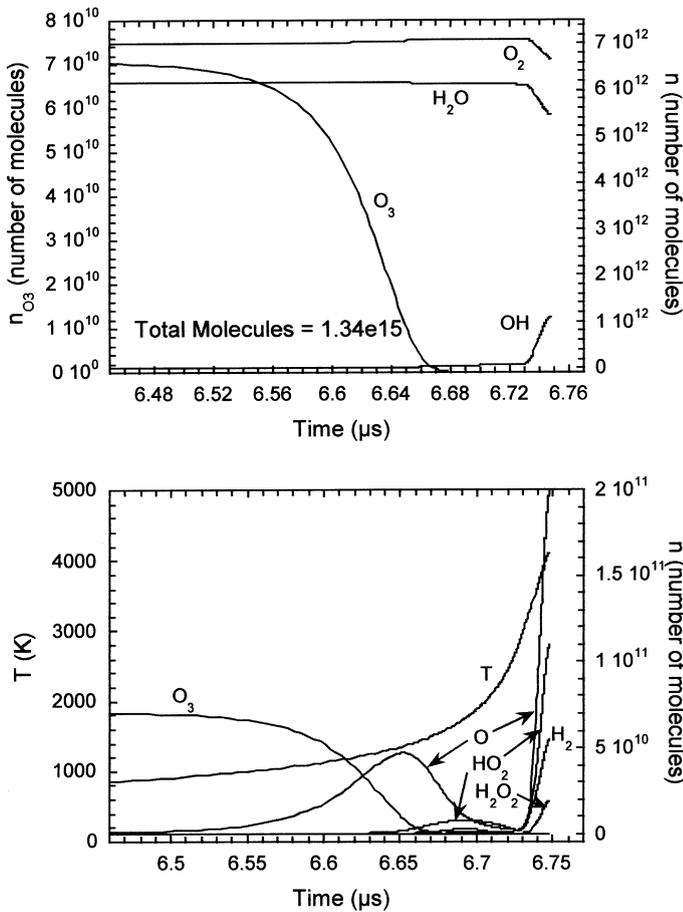


Figure 9. The temperature and chemical species produced from the collapse of an oxygen bubble with 1% O_3 , initially at $R_0 = 41 \mu\text{m}$, influenced by $P_A = 2 \text{ atm}$ and 20 kHz.

In Figure 12, the collapse of a larger bubble at 20 kHz and $P_A = 11 \text{ atm}$, results in similar species to Figure 8. The time scale of formation of the species, $\sim 50 \text{ ns}$, is longer than in Figure 10. Upon the addition of O_3 Figure (13), significant improvement in the amount of OH is observed, $n_{OH} = 5 \times 10^{14}$ without O_3 to $n_{OH} = 1.5 \times 10^{15}$ with O_3 . Approximately 50% of the H_2O is consumed and about 20% of the O_2 .

At 500 kHz, the bubble collapse is very rapid. The generation of radicals occurs in less than 1 ns as seen in Figure 14. Again, OH is formed in the largest amount followed by O. In Figure 15, OH^* production is slightly

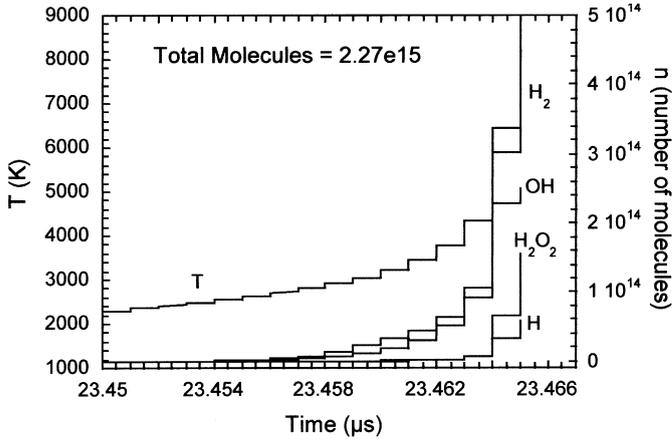


Figure 10. The temperature and chemical species produced from the collapse of an oxygen bubble initially at $R_0 = 41 \mu\text{m}$, influenced by $P_A = 11 \text{ atm}$ and 20 kHz .

improved upon addition of O_3 compared to with only O_2 . Comparing 500 to 20 kHz frequency, pyrolysis of O_3 occurs much closer to the end of the collapse. The n_{O} peak occurs 3 ns from the end of collapse compared to 500 ns from the end at 20 kHz with $P_A = 11 \text{ atm}$.

A range of initial bubble radii were investigated to determine the effect of the ratio R_{max}/R_0 on the formation of the major oxidizing species, OH and O. Figure 16 shows that an R_{max}/R_0 ratio of 5–8 is optimal for the production of oxidizing radicals without O_3 . Below $R_{\text{max}}/R_0 = 5$, the percentage of OH and O in the bubble rapidly decreases and at $R_{\text{max}}/R_0 = 2$, $\chi_{\text{OH}} + \chi_{\text{O}}$ reaches zero. At high R_{max}/R_0 , the percent of OH and O asymptotically levels off to $\sim 10\%$.

The addition of varying amounts O_3 to the bubble was examined at both 20 and 500 kHz as shown in Figures 17 and 18. At 20 kHz, the $\chi_{\text{OH}} + \chi_{\text{O}}$ peaks grow, decay, and then grow again dramatically at the end of the collapse. A larger fraction of O_3 results in a larger $\chi_{\text{OH}} + \chi_{\text{O}}$ at the end of the collapse, however, a smaller χ_{O_3} does not have as dramatic a decay in $\chi_{\text{OH}} + \chi_{\text{O}}$ as a larger χ_{O_3} . At 500 kHz the oxidizing species increase due to O_3 pyrolysis and continue to increase as water vapor is pyrolyzed due to the shorter time scale of collapse.

Tables 4 and 5 show $\chi_{\text{OH}} + \chi_{\text{O}}$ at the end of bubble collapse for a variety of bubble sizes and χ_{O_3} . $R_0 = 41 \mu\text{m}$ stimulated by 20 kHz and $P_A = 2 \text{ atm}$ results in an increase of oxidizing species whereas at $P_A = 11 \text{ atm}$ the oxidizing species are decreased. At the higher pressure amplitude, Mach 1 is broken, so it may not be practical to reach this condition at $P_A = 11 \text{ atm}$. Although shockwaves will form even earlier than Mach 1 for a bubbly

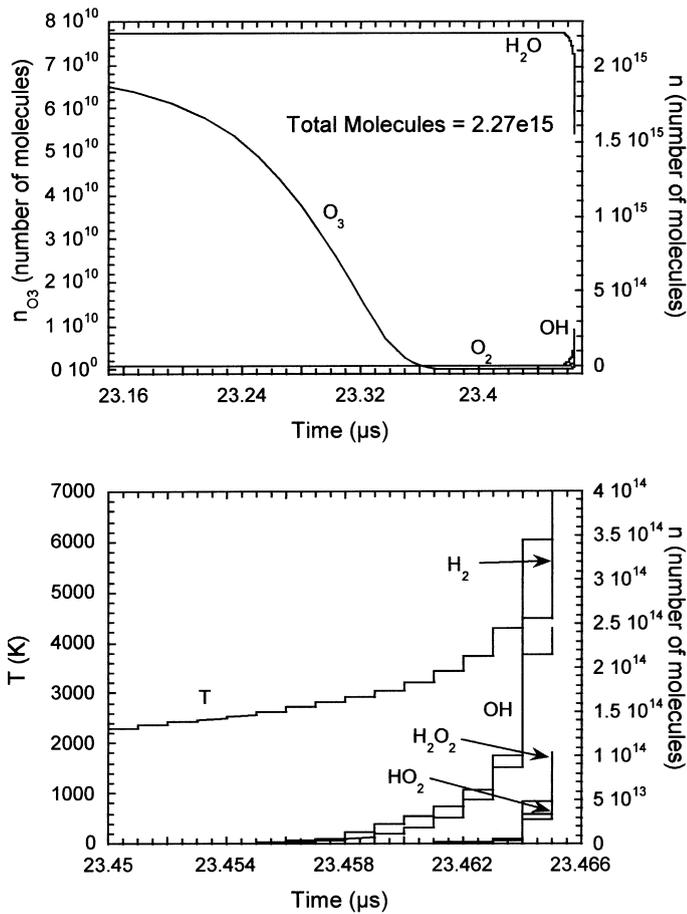


Figure 11. The temperature and chemical species produced from the collapse of an oxygen bubble containing 1% O_3 , initially at $R_0 = 41 \mu\text{m}$, influenced by $P_A = 11 \text{ atm}$ and 20 kHz.

mixture, Mach 1 will give an indication of the conditions before the end of the collapse. In addition, Mach 1 was used as the stopping point in Prasad Naidu et al. [83] calculations. At Mach 1, nearly an order of magnitude enhancement is observed in oxidizing species production. At $R_{\text{max}}/R_0 = 2.3$ the largest enhancement in $\chi_{\text{OH}} + \chi_{\text{O}}$ production is observed at both pressure amplitudes and both frequencies. The addition of O_3 to the bubble results in a 1.3-fold increase at 20 kHz and $P_A = 2 \text{ atm}$, a 3.7-fold increase at 20 kHz and $P_A = 11 \text{ atm}$, and a 2880-fold increase at 500 kHz and $P_A = 2 \text{ atm}$. At R_{max}/R_0 above 3.4 the addition of O_3 appears to be detrimental to the production of oxidizing species.

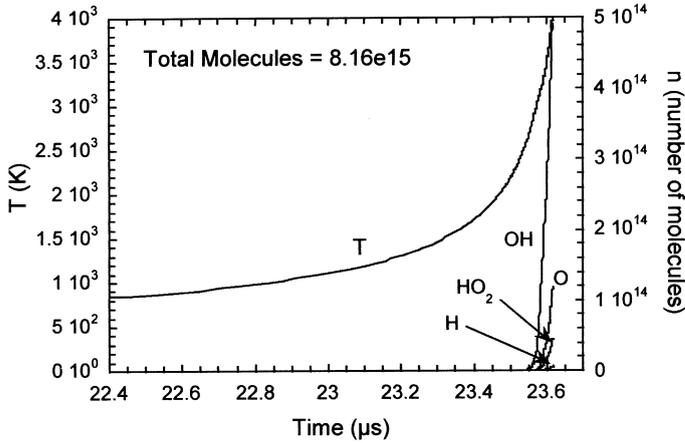


Figure 12. The temperature and chemical species produced from the collapse of an oxygen bubble initially at $R_0 = 390 \mu\text{m}$, influenced by $P_A = 11 \text{ atm}$ and 20 kHz .

3.3 Discussion

Flynn examined the energy dissipation and maximum temperature of the collapse as a function of R_{max}/R_0 [84]. In the region $2 R_0 < R_{\text{max}} < 3 R_0$ a transition was observed which has been considered to be the transition from stable to transient (inertial) cavitation. For R_{max}/R_0 of 2–3, the bubble undergoes explosive growth and violent collapse. The collapse occurs in such a manner as to concentrate the kinetic energy of implosion significantly. Below R_{max}/R_0 of 2 the energy dissipation dominates the collapse. The lower threshold for transient cavitation is dependent on P_A and bound by the Blake threshold [74].

$$P_B = p_0 + \frac{8\sigma}{9} \sqrt{\frac{3\sigma}{2R_B^2 \left(p_0 + \frac{2\sigma}{R_B} \right)}} \quad (17)$$

where P_B is the acoustic pressure required to generate transient cavitation of a bubble with radius R_B . However, the reason the bubble does not cavitate is a result of the growth phase rather than the collapse. From Eq. (17) we see that at very small bubble sizes, surface tension inhibits growth. Due to the nature of our model we could not observe the effects of reaching the Blake threshold. However, the Blake radius will be approximately $0.3 \mu\text{m}$ at 20 and 500 kHz with $P_A = 2$ and at 20 kHz and $P_A = 11$ the Blake radius will be $0.05 \mu\text{m}$. R_{max} is a function of the frequency, resulting in a larger expansion at a lower frequency. Therefore, the size range of bubbles

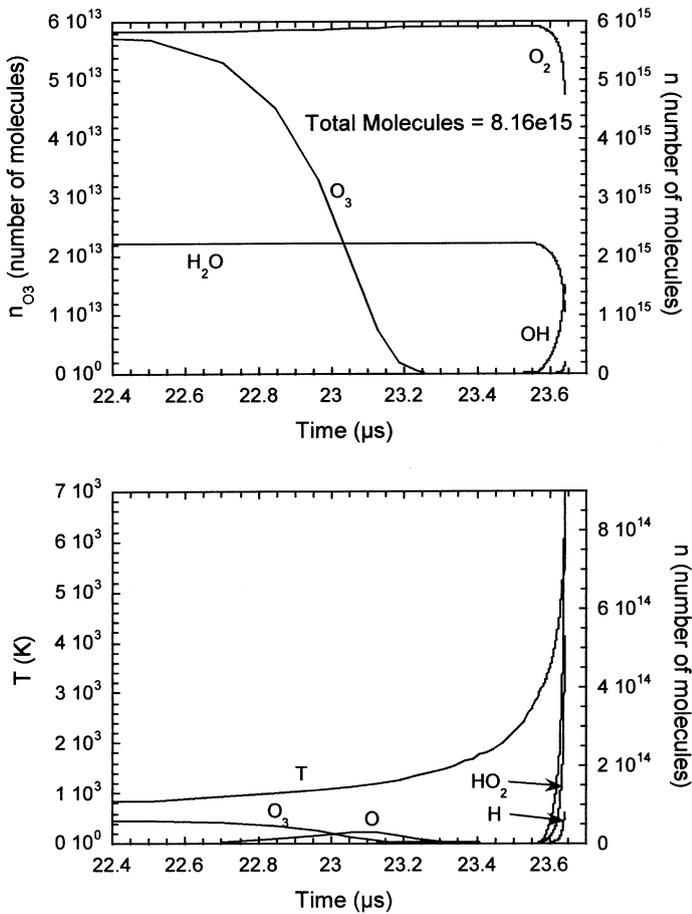


Figure 13. The temperature and chemical species produced from the collapse of an oxygen bubble containing 1% O_3 , initially at $R_0 = 390 \mu\text{m}$, influenced by $P_A = 11 \text{ atm}$ and 20 kHz .

available for growth is much smaller at 500 kHz than at 20 kHz, although the number density and size distribution of bubbles in the presence of ultrasound is not well understood but expected to be biased to the smaller sizes.

Previous investigations of bubble dynamics observed the “best” bubbles to be those which had the largest expansion ratio due to the violent nature of the collapse, and hence higher temperatures were observed [74,85]. In this study, although higher temperatures were observed with the largest R_{max}/R_0 ratio, these were not the “best” bubbles in producing OH and O radicals.

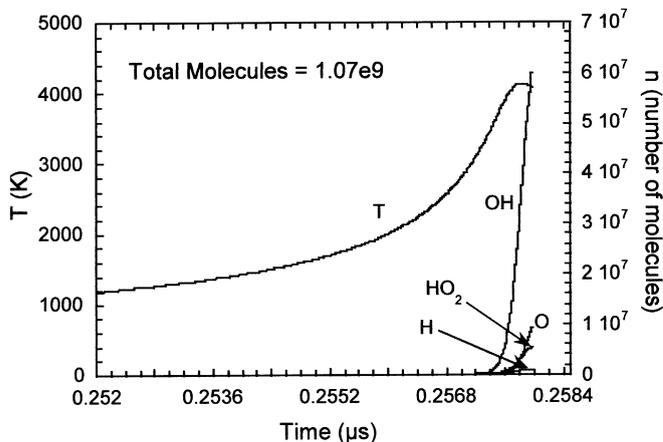


Figure 14. The temperature and chemical species produced from the collapse of an oxygen bubble initially at $R_0 = 1.5 \mu\text{m}$, influenced by $P_A = 2 \text{ atm}$ and 500 kHz .

Without O_3 , the optimal bubble size ranged from 6 to 8, however, at this size range the effect of O_3 was detrimental to the additional formation of oxidizing species at $R_{\text{max}}/R_0 = 6$ to 8. The maximum increase in oxidizing species with O_3 in the bubble occurred with a smaller expansion ratio.

The cavitation growth cycle was assumed to be relatively slow allowing the H_2O vapor pressure to remain equilibrated with liquid H_2O . Therefore, changing R_{max}/R_0 also resulted in different ratios of H_2O to gas. The bubble, $R_0 = 41 \mu\text{m}$, in Figures 8–11 show dramatically different ratios of H_2O to O_2 and O_3 . In Figure 9, the concentration of gas is slightly larger than H_2O , however, in Figure 11 n_{O_2} is 50-fold smaller than $n_{\text{H}_2\text{O}}$. It is apparent that 1% O_3 in O_2 gas will have negligible impact with a large R_{max}/R_0 .

The initiation of O_3 decomposition with temperature results in atomic oxygen and O_2 gas formation as shown in Eq. (4). Since this initiation occurs at a lower temperature than H_2O and O_2 decomposition, radical concentrations before the very end of collapse are the result of O_3 pyrolysis only. Therefore, the major sinks of $\text{O}(^3\text{P})$ are Eqs. (5) and (6). As discussed in Section 2, to have the largest benefit from O_3 addition, reaction (5) should be maximized. It is also important to maximize this pathway if O_3 reacts with the substrate directly in the liquid-phase, since cavitation bubbles could reduce that pathway which would result in observed antagonism in the combined system. At larger R_{max}/R_0 the fraction of H_2O overwhelms the gas concentration, increasing the reaction rate of Eq. (5), but also minimizing the effect of O_3 at the end of collapse. Similarly, as the concentration of O_3 is increased in the bubble, the reaction rate of Eq. (6) is increased. Bubbles which are not optimal without O_2 appear to show more enhancement with

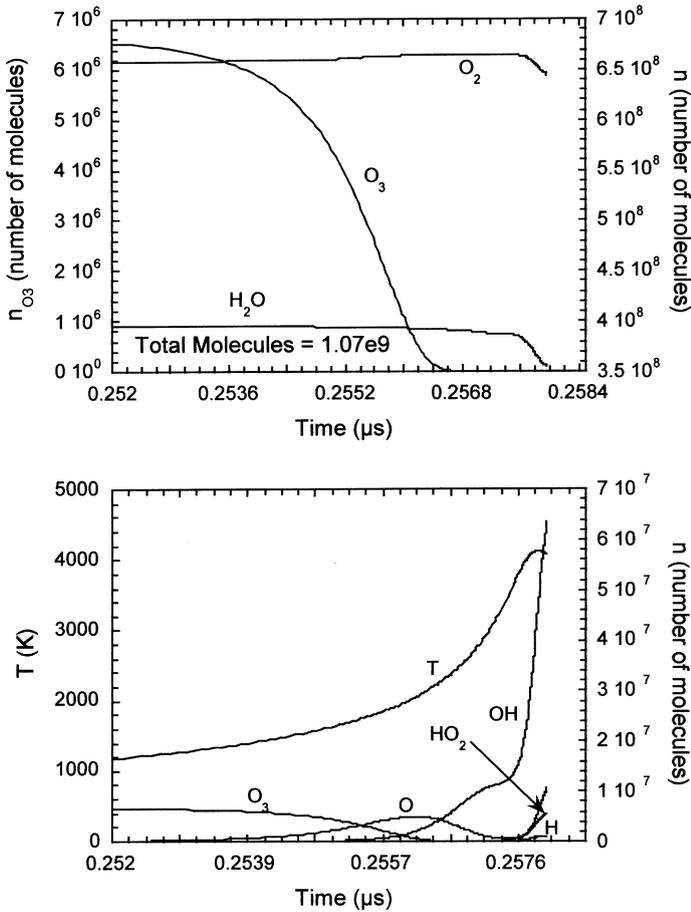


Figure 15. The temperature and chemical species produced from the collapse of an oxygen bubble containing 1% O_3 , initially at $R_0 = 1.5 \mu\text{m}$, influenced by $P_A = 2 \text{ atm}$ and 500 kHz .

O_3 than the optimal bubbles. In some cases this is clearly due to very little OH and O produced with O_2 alone, however, in other bubbles, O_3 must be altering the temperature in the bubble and chemical reactions so that production is increased or decreased more than if O_3 were efficiently producing OH and O .

In Section 2, more enhancement was observed at 20 kHz than at 500 kHz . At 20 kHz , the P_A applied was approximately 11 atm while $P_A = 2 \text{ atm}$ was used at 500 kHz and for the degradation of pentachlorophenol at both frequencies. In the absence of O_3 , 20 kHz required considerably more energy

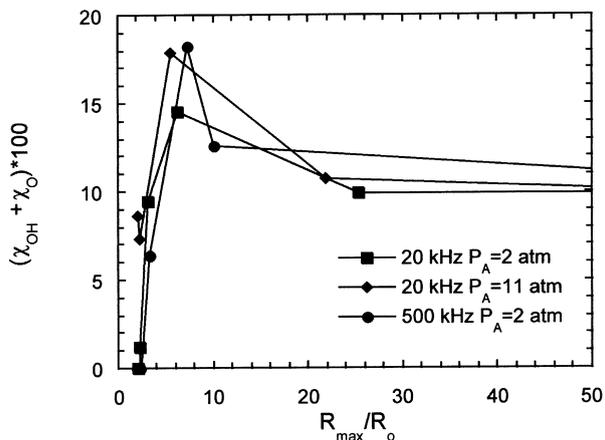


Figure 16. The mole fraction of OH and O produced as a function of the expansion ratio at 20 kHz and $P_A = 11$ atm, 20 kHz and $P_A = 2$ atm and 500 kHz and $P_A = 2$ atm.

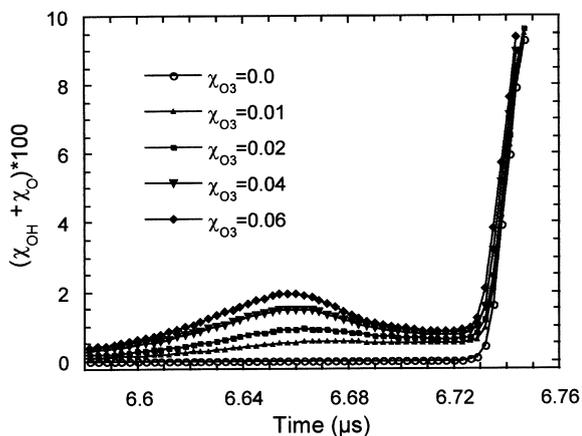


Figure 17. The mole fraction of OH and O produced in a collapsing bubble initially at $R_0 = 41$ μm and influenced by $P_A = 2$ atm at 20 kHz for various mole fractions of O_3 .

to degrade the same amount of substrate although n_{OH} produced in a bubble was approximately 10^{12} and 10^{14} molecules at $P_A = 2$ and 11 atm, respectively, whereas $n_{\text{OH}} < 10^8$ molecules at 500 kHz. There are 25 compression and rarefaction cycles at 500 kHz for every cycle at 20 kHz so the 500 kHz bubble could produce $n_{\text{OH}} < 10^9$ molecules per 20 kHz

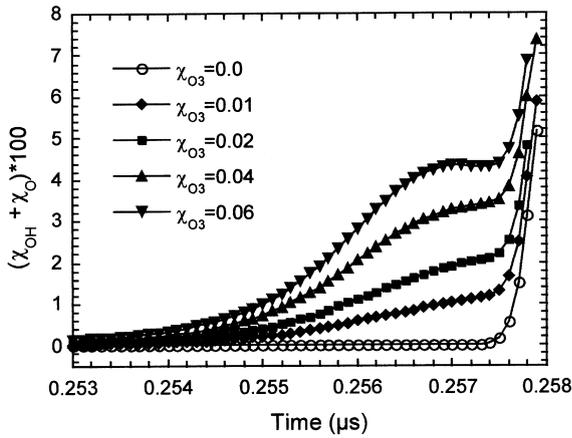


Figure 18. The mole fraction of OH and O produced in a collapsing bubble initially at $R_0 = 1.5 \mu\text{m}$ and influenced by $P_A = 2 \text{ atm}$ at 500 kHz for various mole fractions of O_3 .

Table 4. Comparison of O_3 Addition to Oxidizing Mole Fraction at 20 kHz

R_0 (μm)	P_A (atm)	R_{max}/R_0	χ_{O_3}	$\chi_{\text{OH}} + \chi_{\text{O}}^*$
41	2	3.1	0.0	9.48
41	2	3.1	0.01	9.55
41	2	3.1	0.02	9.72
41	2	3.1	0.04	9.98
41	2	3.1	0.06	10.32
55	2	2.3	0.0	1.198
55	2	2.3	0.01	1.54
5	2	25.3	0.0	9.92 (1.74)
5	2	25.3	0.01	4.33 (1.74)
0.7	2	181	0.0	9.789 (1.69)
0.7	2	181	0.01	4.06 (1.69)
390	11	2.3	0.0	7.36
390	11	2.3	0.01	27.02 (13.9)
41	11	21.9	0.0	10.77 (0.0008)
41	11	21.9	0.01	10.6 (0.007)

* values in parenthesis are mole fractions at Mach = 1.

bubble. Also, $P_A = 11 \text{ atm}$ was less effective than $P_A = 2 \text{ atm}$ at 20 kHz. In comparing the observed enhancement from Section 2, this requires at least one of the following to occur: (1) more of the optimal cavitation bubbles are formed at a lower pressure amplitude and higher frequency since smaller

Table 5. Comparison of O₃ Addition to Oxidizing Mole Fraction at 500 kHz

R_0 (μm)	P_A (atm)	R_{max}/R_0	χ_{O_3}	$\chi_{\text{OH}} + \chi_{\text{O}}^*$
1.5	2	3.4	0.0	6.43
1.5	2	3.4	0.01	6.84
1.5	2	3.4	0.02	7.09
1.5	2	3.4	0.04	7.15
1.5	2	3.4	0.06	7.94
2.2	2	2.3	0.0	0.0004
2.2	2	2.3	0.01	1.15
0.7	2	7.24	0.0	18.2 (7.76)
0.7	2	7.24	0.01	18.27 (7.75)

* values in parenthesis are mole fractions at Mach = 1.

bubbles are needed to reach the optimal R_{max}/R_0 , or (2) due to the more violent collapse at $P_A = 11$ atm a shockwave results from reaching Mach 1 of the bubble wall, hence, the 20 kHz bubbles collapse asymmetrically before attaining high mole fractions of OH that the single bubble model produced without O₃ present. Also, this would account for the significant increase in substrate destruction upon the addition of O₃. As shown for the bubble $R_0 = 41$ μm excited at $P_A = 11$ atm, no enhancement is seen if the bubble is collapsed to the theoretical end. However, at Mach 1 an order of magnitude increase in $\chi_{\text{OH}} + \chi_{\text{O}}$ is observed comparing an oxygen bubble with 1% O₃ to an O₂ bubble. It is also possible that bubbles growing by rectified diffusion may compress enough in the compression phase of the ultrasonic wave to increase the bubble temperature so that O₃ is decomposed. At 20 kHz, a larger fraction of bubbles is growing by rectified diffusion per unit time than at 500 kHz due to the larger resonant radius at 20 kHz.

Although this model is for a single bubble, whereas in an ultrasonic reactor a bubble cloud exists, the model reveals that at high amplitude the bubble collapses much harder and most likely does not maintain its spherical shape. At low amplitude a spherical collapse is possible and may be the reason for the observed accelerated rates in degradation reactions at 500 kHz over 20 kHz with O₂. However, the addition of shockwaves to the model and modeling a bubble through many cycles would give more insight into the transfer of chemical species out of the bubble. Heat and mass transfer are other variables that may control the temperature and oxidants produced from bubble collapses. More research is also needed on the bubble size distribution in an ultrasonic reactor. The size of the bubble plays a key role in the mole fractions of species produced and the effectiveness of O₃ in the bubble.

4. CONCLUSIONS

The degradation of organic contaminants with a variety of reaction rate constants resulted in enhanced degradation at 20 kHz and reduced degradation at 500 kHz for the contaminants discussed. At low k_{C-O_3} , any O_3 converted to OH^* enhances the degradation reaction and at very high k_{C-O_3} , sonolysis and ozonolysis reactions, although occurring simultaneously, act independently. In between these extremes, ozonolysis and sonolysis are interactive.

Modeling of ozone decomposition in a collapsing cavitation bubble demonstrates the importance of understanding bubble size and distributions during sonication under various conditions. The maximum increase in oxidizing species with O_3 compared with only O_2 occurred with smaller expansion ratios. This is due in part to the fraction of water vapor and O_2 and O_3 gases in the bubble. At higher expansion ratios, O_3 contributes a smaller fraction of the bubble composition, resulting in a smaller impact.

Overall it is important to maximize the formation of OH^* (Eq. (5)) versus the formation of O_2 (Eq. (6)). From experimental results, it appears that the lower frequency is more effective at optimizing the conversion of O_3 to OH^* . This may be due to the sub-optimal conditions of bubbles at this lower frequency or due to the asymmetric collapse of 20 kHz bubbles before a large amount of OH^* radical is produced. Additional studies need to be performed to test these hypotheses.

ACKNOWLEDGMENTS

The experiments were performed and model was developed at the California Institute of Technology in the laboratory of M. R. Hoffmann. A. J. Colussi contributed substantially to the model development.

REFERENCES

- [1] Hoffmann, M. R., Martin, S. T., Choi, W., and Bahneman, D. W. *Chem. Rev.*, 95 (1995) 69.
- [2] Barbeni, M., Pramauro, E., and Pelizzetti, E. *Chemosphere*, 14 (1985) 195.
- [3] Jardim, W. F., Moraes, S. G., and Takiyama, M. M. K. *Wat. Res.*, 31 (1997) 1728.
- [4] Legrini, O., Oliveros, E., and Braun, A. M. *Chem. Rev.*, 93 (1993) 671.
- [5] Masten, S. J., and Davies, S. H. R. In Nriagu J. O., and Simmons, M. S. (eds), *Environmental Oxidants*, John Wiley & Sons: New York, 1994, pp. 517–547.
- [6] Mills, G., and Hoffmann, M. R. *Environ. Sci. Technol.*, 27 (1993) 1681.
- [7] Minero, C., Pelizzetti, E., Malato, S., and Blanco, J. *Chemosphere*, 26 (1993) 2103.
- [8] Peill, N. J., and Hoffmann, M. R. *Environ. Sci. Technol.*, 30 (1996) 2806.
- [9] Peyton, G. R., Huang, F. Y., Burleson, J. L., and Glaze, W. H. *Environ. Sci. Technol.*, 16 (1982) 448.

- [10] Peyton, G. R., and Glaze, W. H. *Environ. Sci. Technol.*, 22 (1988) 761.
- [11] Sierka, R. A., and Amy, G. L. *Ozone Sci. Engng.*, 7 (1985), 47.
- [12] Barbier, P. F., and Pétrier, C. *J. Adv. Oxid. Technol.*, 1 (1996) 154.
- [13] Berlan, J., Trabelsi, F., Delmas, H., Wilhelm, A. M., and Petrigani, J. F. *Ultrasonics Sonochemistry*, 1 (1994) S97.
- [14] Bhatnagar, A., and Cheung, H. M. *Environ. Sci. Technol.*, 28 (1994) 1481.
- [15] Chen, J. W. *Water*, 69 (1972) 61.
- [16] Cost, M., Mills, G., Glisson, P., and Lakin, J. *Chemosphere*, 27 (1993) 1737.
- [17] Drijvers, D., De Baets, R., De Visscher, A., and Van Langenhove, H. *Ultrasonics Sonochemistry*, 3 (1996) S83.
- [18] De Visscher, A., Van Eenoo, P., Drijvers, D., and Van Langenhove, H. *J. Phys. Chem.*, 100 (1996) 11636.
- [19] De Visscher, A., Van Langenhove, H., and Van Eenoo, P. *Ultrasonics Sonochemistry*, 4 (1997) 145.
- [20] Francony, A., and Pétrier, C. *Ultrasonics Sonochemistry*, 3 (1996) S77.
- [21] Glaze, W. H., Kang, J. W., and Chapin, D. H. *Ozone Sci. & Engng.*, 9 (1987) 335.
- [22] Glaze, W. H. *Environ. Sci. Technol.*, 21 (1987) 224.
- [23] Glaze, W. H., and Peyton, G. R. *Environ. Sci. Technol.*, 16 (1982) 454.
- [24] Gurol, M. D., and Vastistas, R. *Wat. Res.*, 21 (1987) 895.
- [25] Hart, E. J., and Henglein, A. *J. Phys. Chem.*, 89 (1985) 4342.
- [26] Hart, E. J., and Henglein, A. *J. Phys. Chem.*, 90 (1986) 3061.
- [27] Hart, E. J., and Henglein, A. *J. Phys. Chem.*, 91 (1987) 3654.
- [28] Hart, E. J., Fischer, C. H., and Henglein, A. *J. Phys. Chem.*, 94 (1990) 284.
- [29] Hua, I., Höchemer, R. H., and Hoffmann, M. R. *Environ. Sci. Technol.* 29 (1995) 2790.
- [30] Hua, I., and Hoffmann, M. R. *Environ. Sci. Technol.*, 30 (1996) 864.
- [31] Hua, I. PhD Thesis, California Institute of Technology, 1996.
- [32] Kontronarou, A., Mills, G., and Hoffmann, M. R. *J. Phys. Chem.*, 95 (1991) 3630.
- [33] Kontronarou, A., Mills, G., and Hoffmann, M. R. *Environ. Sci. Technol.*, 26 (1992) 2420.
- [34] Kontronarou, A., Mills, G., and Hoffmann, M. R. *Environ. Sci. Technol.*, 26 (1992) 1460.
- [35] Makino, K., Mossoba, M. M., and Riesz, P. *J. Phys. Chem.*, 87 (1983) 1369.
- [36] Nagata, Y., Hirai, K., Bandow, H., and Maeda, Y. *Environ. Sci. Technol.*, 30 (1996) 1133.
- [37] Okouchi, S., Nojima, O., and Arai, T. *Wat. Sci. Tech.*, 26 (1992) 2053.
- [38] Pétrier, C., Jeunet, A., Luche, J.-L., and Reverdy, G. *J. Am. Chem. Soc.*, 114 (1992) 3148.
- [39] Pétrier, C., Micolle, M., Merlin, G., Luche, J. L., and Reverdy, G. *Environ. Sci. Technol.*, 26 (1992) 1639.
- [40] Pétrier, C., Lamy, M.-F., Francony, A., Benahcene, A., and David, B. *J. Phys. Chem.*, 98 (1994) 10514.
- [41] Pétrier, C., David, B., and Laguian, S. *Chemosphere*, 32 (1996) 1709.
- [42] Riesz, P., Kondo, T., and Krishna, C.M. *Ultrasonics*, 28 (1990) 295.
- [43] Turai, L. L., and Rosario, F. D. *Appita*, 35 (1982) 407.
- [44] Pelizzetti, E., Carlin, V., and Minero, C. *New J. Chem.*, 15 (1991) 351.
- [45] Peyton, G. R. In *Emerging Technologies in Hazardous Waste Management 1990*, pp. 100–118.
- [46] Höchemer, R. H. PhD Thesis, California Institute of Technology, 1996.
- [47] Olson, T. M., and Barbier, P. F. *Wat. Res.*, 28 (1994) 1383.
- [48] Gonze, E., Gonthier, Y., Boldo, P., and Bernis, A. *Canadian J. Chem. Engng.*, 75 (1997) 245.
- [49] Hua, I., Höchemer, R. H., and Hoffmann, M. R. *J. Phys. Chem.*, 99 (1995) 2335.
- [50] Hua, I., and Hoffmann, M. R. *Environ. Sci. Technol.*, 31 (1997) 2237.
- [51] Serpone, N., Terzian, R., Hidaka, H., and Pelizzetti, E. *J. Phys. Chem.*, 98 (1994) 2634.

- [52] Mason, T. J., and Lorimer, J. P. *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry*, Ellis Horwood Ltd: Chichester, 1988.
- [53] Prosperetti, A. In *Proceedings of the NATO Advanced Study Institute on Sonochemistry and Sonophysics*, Leavenworth, WA, 1997, pp. 39–62.
- [54] Weavers, L. K., Ling, F. H., and Hoffmann, M. R. *Environ. Sci. Technol.*, 32 (1998), 2727.
- [55] Weavers, L. K., and Hoffmann, M. R. *Environ. Sci. Technol.*, 32 (1998) 3941.
- [56] Weavers, L. K., Malmstadt, N., and Hoffmann, M. R. *Environ. Sci. Technol.*, 34 (2000) 1280
- [57] Mackay, D., Shiu, W. Y., and Ma, K. C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*, Vol. IV, Lewis Publishers: Boca Raton, 1995.
- [58] Neta, P., Huie, R. E., and Ross, A. B. *J. Phys. Chem. Ref. Data*, 17 (1988) 1027.
- [59] Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B. *J. Phys. Chem. Ref. Data*, 17 (1988) 513.
- [60] Jafvert, C. T., Westall, J. C., Grieder, E., and Schwarzenbach, R. P. *Environ. Sci. Technol.*, 24 (1990) 1795.
- [61] Weavers, L. K. PhD Thesis, California Institute of Technology, 1997.
- [62] Latimer, W. M. *Oxidation Potentials*, 2nd ed., Prentice-Hall: Englewood Cliffs, 1952.
- [63] Langlais, B., Reckhow, D. A., and Brink, D. R. *Ozone in Water Treatment Application and Engineering*, AWWA Research Foundation and Lewis Publishers: Chelsea, 1991.
- [64] Dahi, E. *Wat. Res.*, 10 (1976) 677.
- [65] Sierka, R. A. "Mass Transfer and Reaction Rate Studies of Ozonated MUST Wastewaters in the Presence of Sound Waves," University of Arizona, 1976.
- [66] Sierka, R. A. *Ozone Sci. Engng.*, 6 (1985) 275.
- [67] Kang, J. W., and Hoffmann, M. R. *Environ. Sci. Technol.*, 32 (1998) 3194.
- [68] Kang, J. W., Hung, H. M., Lin, A., and Hoffmann, M. R. *Environ. Sci. Technol.*, 33 (1999) 3199.
- [69] Burlleson, G. R., Murray, T. M., and Pollard, M. *Appl. Microbiol.*, 29 (1975) 340.
- [70] Katzenelson, E., Kletter, B., and Shual, H. I. *Journal AWWA*, 66 (1974) 725.
- [71] Seinfeld, J. H. *Atmospheric Chemistry and Physics of Air Pollution*, Wiley-Interscience: New York, 1986.
- [72] Colussi, A. J., Weavers, L. K., and Hoffmann, M. R. *J. Phys. Chem. A*, 102 (1998) 6927.
- [73] Leighton, T. G. *Ultrasonics Sonochemistry*, 2 (1995) S123.
- [74] Leighton, T. G. *The Acoustic Bubble*, Academic Press: London, 1994.
- [75] Heimer, J. M., and Coffee, T. P. *Combust. Flame*, 35 (1979) 117.
- [76] Hippler, H., Rahn, R., and Troe, J. *J. Phys. Chem.*, 93 (1990) 6560.
- [77] Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F. J., Kerr, J. A., and Troe, J. *J. Phys. Chem. Ref. Data*, 18 (1989) 881.
- [78] Masten, D. A., Hanson, R. K., and Bowman, C. T. *J. Phys. Chem.*, 94 (1990) 7119.
- [79] Baldwin, R. F., and Walker, R. W. *J. Chem. Soc. Faraday Trans. 1*, 75 (1979) 140.
- [80] Tsang, W., and Hampson, R. F. *J. Phys. Chem. Ref. Data*, 15 (1986) 1087.
- [81] Warnatz, J. In Gardiner, W. C. (ed.), *Combustion Chemistry*, Springer-Verlag: New York, 1984, pp. 197–360.
- [82] Curtis, A. R., and Sweetenham, W. P. In United Kingdom Atomic Energy Authority Harwell: Oxfordshire, 1987.
- [83] Prasad Naidu, D. V., Rajan, R., Kumar, R., Gandhi, K. S., Arakeri, V. H., and Chandrasekaran, S. *Chem. Eng. Sci.*, 49 (1994) 877.
- [84] Flynn, H. G. *J. Acoust. Soc. Am.*, 58 (1975) 1160.
- [85] Roy, R. A. In Proceedings of the NATO Advanced Study Institute on Sonochemistry and Sonoluminescence, Leavenworth, WA, 1997, pp. 25–38.

This Page Intentionally Left Blank

ULTRASONICALLY ASSISTED LEACHING

Kodavanti M. Swamy and Kallepalli L. Narayana

OUTLINE

1. Introduction	142
2. Basics	144
2.1 What is Leaching?	144
2.2 What is Ultrasound?	144
3. Cavitation in Heterogeneous Ore Slurry	145
3.1 Cavitation in Liquids	145
3.2 Cavitation at Solid–Liquid Interfaces: Micro-jet Formation	145
4. Leaching in an Ultrasonic Field	148
5. Principles of Ultrasonic Leaching	150
5.1 Factors Influencing Leaching	150
5.2 Role of Ultrasound	150
5.3 Role of Ultrasonic Intensity and Energy Density	151
6. Limitations of Ultrasonic Leaching	153
7. Analysis of Experimental Results: Different Metals and Soil Decontamination	155
7.1 Copper	155
7.2 Zinc	159

Advances in Sonochemistry

Volume 6, pages 141–179.

© 2001 Elsevier Science B.V. All rights reserved.

7.3	Precious Metals	161
7.4	Tungsten	163
7.5	Titanium	164
7.6	Nickel	164
7.7	Rare, Other Metals and Oxides	165
7.8	Soil and Solid Waste Decontamination by Ultrasound	166
8.	Proposed Leaching Mechanism	168
9.	Benefits of Ultrasonic Leaching	171
10.	Sonication System for Leaching	171
10.1	Recommended Ultrasonic Parameters	171
10.2	Health and Safety Aspects	174
11.	Conclusions	174
	Acknowledgments	175
	References	176

1. INTRODUCTION

The recent advances in applications of high intensity ultrasound has been extensively studied for a wide variety of industrial applications, like cleaning, filtration, crystallisation, sieving, extraction etc. [1–5]. This emerging new technology is gaining worldwide recognition. Ultrasound can be advantageously used for leaching applications to increase both dissolution rates and yields of products (metal values). Dramatic increase in leaching rates by ultrasonic irradiation has been reported for many ores [6,7]. For example, ultrasonic irradiation of ores, such as galena, crocoite and arsenolite, resulted in 20, 30 and 50 times faster rates of dissolution respectively, when compared to those in the absence of an ultrasonic field. With the gradual depletion of high grade ores, the present global trend is directed towards utilisation of lean and complex mineral resources for extraction of metals. In the rapidly growing field of metal extraction from lean ores, selectivity in reactions [8,9], improved methods or novel techniques like ultrasound are expected to play an important role. Some new developments in this direction include, research related to hydrothermal enrichment of mineral concentrates and passivation of diffusion product layers during leaching. There is significant literature which establishes that ultrasonic vibrations can cause, amongst other effects, a decrease in the diffusion layer thickness and, thus, an increase in the leaching rate [10]. Even though, Sastri and Mackinnon [11] suggested the usefulness of ultrasound in the leaching of ores containing copper, zinc, lead, gold and silver etc. as early as in 1977, not much progress was attained in this area until the late eighties. Medvedev and Korshunov [12] have reviewed the modern methods for intensification of hydrometallurgical processes by gamma and

ultrasound irradiation, mechanical and thermal action giving some examples of industrial applications. A continuous solid–liquid extractor based on a vertical pulsed column was recently patented [13] for the use of ultrasound at an energy density of $10\text{--}10^6$ kW m⁻³. Zhao [14] reported the industrial application of ultrasonic wave-aided leaching of gold recovery from refractory ores. In view of the importance of ultrasound energy in extractive metallurgy the authors have recently reviewed the leaching of various metals from ores using ultrasound [15,16].

Modern achievements in ultrasonics have produced the rapid development of a new and advanced trend to revolutionise metal extraction from ores. Such useful investigations into ultrasonic leaching should not only be limited to this area, but, should be extended to applied aspects of research such as: metal removals from different types of soils like, hazardous wastes, surface soil, overburden in mines, mine filling soil, river sediments, crude, etc. The first and foremost step in this area would be to develop a rapid, reliable and clean analytical method of estimating on-site metal contents in soils by the use of ultrasound. Newman et al. [17] have investigated the ultrasonic treatment of polluted solids containing copper. Batch tests for accelerating leaching on five metal finishing residues of hazardous, radioactive and mixed wastes have been carried out [18] using ultrasonic agitation. Remedial technologies for soils and their application towards removing radio nuclides and heavy metals from soils have become a primary focus of many government agencies globally. Therefore, ultrasonically assisted soil decontamination technologies for such purposes are currently under development [19].

The use of ultrasound is drawing increasing attention due to its faster process kinetics and because of lower cost of generating ultrasonic power and availability of high intensity sound sources (transducers) for continuous use. Further, energy savings are possible in the processes by combination techniques. In view of these developments, there is a possibility that power ultrasound may be able to compete with other processes in the near future when the less expensive “ultrasonic watt” will be readily available. This brings in new techniques and new kind of reactors, viz., sonochemical reactors to the domain of extractive metallurgy, a topic, which needs to be thoroughly exploited. Some attempts have been made in chemical reaction engineering through mathematical modelling [20–22], which help in the design of the next generation of sonochemical reactors. The exact mechanism by which ultrasound effects leaching is still not fully clear, because sonication has both physical (hydrothermal) and chemical effects. These need to be discriminated for a better understanding of leaching by ultrasound. In this chapter the authors have attempted to give an overview of the current state of knowledge in this field of research.

2. BASICS

As the subject is inter-disciplinary in nature, the terminology, leaching and ultrasound are briefly described.

2.1 What is Leaching?

Leaching is the liberation of metals from ores by chemical dissolution, and it forms the basis of most hydrometallurgical extraction processes. The main aim of leaching is to liberate selectively the maximum amount of the valuable metal. This unit operation is an established and relatively successful method of metal extraction, especially when treating high-grade ores. In contrast, the treatment of low-grade ores is expensive, mainly because the resultant pregnant solution has a low level of valuable species relative to the contaminants. This implies that large volumes of the pregnant solution must be processed. Further, the leaching of valuable metal from ores is often concentration dependent. In other words, it is more difficult to leach valuable metal from the ore into solution with increasing concentration in the pregnant solution. Leaching is closely related to solvent extraction, in which a soluble substance is dissolved from one liquid by a second liquid immiscible with the first. Both leaching and solvent extraction are often called extraction. Leaching is also known as solid-liquid extraction, lixiviation, washing etc.

2.2 What is Ultrasound?

The theory concerning the propagation of ultrasound in liquids and the effects caused are described elsewhere in this volume and in other published work [2–5].

The range of human hearing is from about 16 Hz to 16 kHz. Ultrasound is the name given to sound waves having frequencies higher than those to which the human ear can respond, i.e. >16 kHz. The upper limit of ultrasonic frequency is approximately 5 MHz for gases and 500 MHz for liquids and solids. The uses of ultrasound within a large frequency range may be broadly divided into two areas: low power-high frequency (1–10 MHz) used for diagnostic purposes and high power-low frequency (20–100 kHz) normally used for cleaning, chemical reactions, leaching etc. The aim of high power ultrasound is to produce a permanent chemical or physical change in a material. To achieve this, a relatively high power intensity (from less than one W cm^{-3} to thousands of W cm^{-3}) is required. The energy output produces cavitation and microstreaming in liquids.

3. CAVITATION IN HETEROGENEOUS ORE SLURRY

The leaching of ores can be positively affected by acoustic cavitation induced by powerful ultrasound waves. The phenomenon of acoustic cavitation results in an enormous concentration of energy. If one considers the energy density in an acoustic field that produces cavitation and that in the collapsed cavitation bubble, there is an amplification factor of over eleven orders of magnitude. The cavitation occurring in homogeneous media and at solid–liquid interfaces, is briefly described in Section 3.2, this is responsible for creation of enormous local temperature and pressure.

3.1 Cavitation in Liquids

The chemical effects of ultrasound derive from the physical phenomenon of acoustic cavitation [23]. This is a three-step process: consisting of the formation, growth, and implosive collapse of bubbles in liquids irradiated with high intensity sound. Tiny bubbles, whose life time is only a few acoustic cycles long, during which they expand to four or five times their original size and are fed by vapour pumped into the bubble as its surface expands and contracts with the changing pressure in the liquid. These bubbles then move towards the pressure anti-nodes and collapse violently during the next compression half-cycle. Cavitation bubble collapse in a liquid is schematically shown in Figure 1. The local temperatures and pressures generated by the collapse are huge, of course, with very short life time. In clouds of cavitating bubbles, these hot spots [24,25] have equivalent temperatures of roughly 5000 K, pressures of about 100 M Pa and heating and cooling rates above 10^{10} K s^{-1} . The effects of physical parameters on cavitation are summarised and can be seen at a glance in Table 1.

3.2 Cavitation at Solid–Liquid Interfaces: Micro-jet Formation

A very different phenomenon arises when cavitation occurs near extended liquid–solid interfaces. There are two proposed mechanisms for the effect of cavitation near surfaces: micro-jet impact and shockwaves damage. Whenever a cavitation bubble is produced near a boundary, the asymmetry of the liquid particle motion during cavity collapse can induce a strong deformation in the cavity [26]. The potential energy of the expanded bubble is converted into kinetic energy with the formation of a liquid jet that extends through the bubble's interior and penetrates the opposite bubble wall. Because most of the available energy is transferred to the accelerating

Table 1. Physical Parameters Effecting Cavitation

<i>Particulars of parameter</i>	<i>Variable</i>	<i>Effects</i>
I. Reaction medium (lixiviant)	(1) Vapour pressure	<ul style="list-style-type: none"> • The higher the vapour pressure the less violent the collapse. • Cavitation is more difficult with low vapour pressure.
	(2) Viscosity	<ul style="list-style-type: none"> • Cavitation is easier in solvents with low viscosity.
	(3) Compressibility	<ul style="list-style-type: none"> • Improves gas bubble dynamics and cavitation is expected with ore slurries due to their relatively low compressibilities. • Enhanced cavitation is expected with ore slurries due to their relatively low compressibilities.
	(4) Bubbled gas	
	(a) solubility	<ul style="list-style-type: none"> • Dissolved gas acts as cavitation nuclei and leads to more facile cavitation. • More number of cavitation events. • The greater the amount of dissolved gas the smaller the intensity of shockwave.
	(b) specific heat ($\gamma = c_p/c_v$)	<ul style="list-style-type: none"> • γ should be high as the collapse temperature is proportional to $(\gamma-1)$.
	(c) thermal conductivity (k)	<ul style="list-style-type: none"> • The smaller the k of the gas the higher the local heating during collapse.
	(5) Presence of ore particles	<ul style="list-style-type: none"> • Any particles or motes present in the solvent will act as seeds for cavitation as they possess entrapped gases in their crevices and recesses which readily become the nuclei for newly forming cavitation bubbles.
II. Reaction conditions	(1) External temperature	<ul style="list-style-type: none"> • Temperature rise increases vapour pressure and collapse is less violent. • Further, less intensities are needed to induce cavitation.

III. Ultrasonic parameter	(2) External pressure	<ul style="list-style-type: none"> ● Temperature near the boiling point of the solvent dramatically increases the number of bubbles which can act as sound barrier. ● Pressure rise decreases vapour pressure and collapse is more violent. ● High intensity is necessary to induce cavitation. ● Enhances energy transfer efficiency.
	(1) Intensity	<ul style="list-style-type: none"> ● With intensity the probability of cavitation events per unit volume increases. ● Considerably higher intensity at high frequency is necessary to maintain the same leaching as at low frequency. ● Indefinite increase of cavitation is not possible with increased intensity, decoupling of the sound energy with the system due to large number of bubbles and is a sound transmission barrier.
	(2) Frequency	<ul style="list-style-type: none"> ● Long cycle, large bubble, low amplitude required to induce cavitation.
	(i) low	<ul style="list-style-type: none"> ● Short cycle, high amplitude necessary, increased attenuation, weak or no cavitation in the millihertz range as rarefaction cycle is too short to create bubbles.
	(ii) high	<ul style="list-style-type: none"> ● Reactivity enhances with time, but has an optimum value. ● Greater heat induction is possible with increased time of irradiation.
	(3) Time of irradiation	<ul style="list-style-type: none"> ● Reactivity enhances with time, but has an optimum value. ● Greater heat induction is possible with increased time of irradiation.

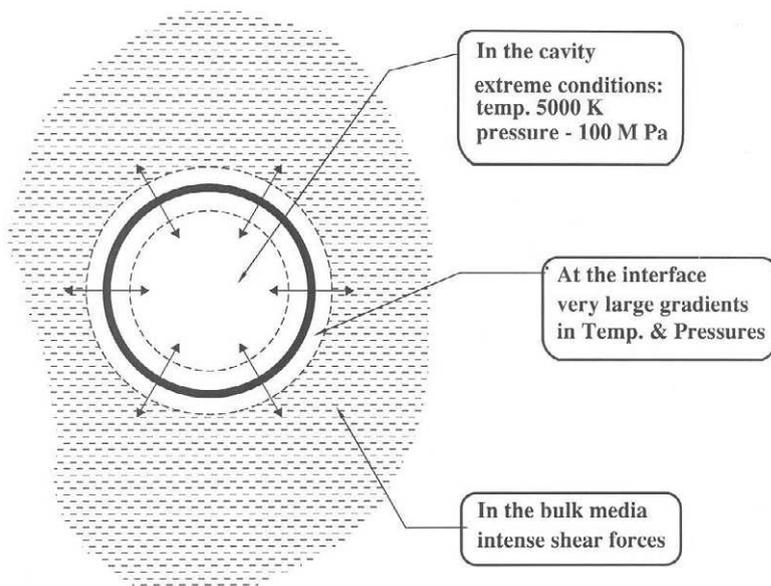


Figure 1. Cavitation in a homogeneous media.

jet, rather than the bubble wall itself, this jet can reach velocities of hundreds of metres per second. Because of the induced asymmetry, the jet often impacts the solid boundary and can deposit enormous energy densities at the site of impact. Such energy concentration can result in severe damage to the boundary surface. Figure 2 is a schematic view of a jet developed in a collapsing cavity. The second mechanism of cavitation induced surface damage invokes shockwaves created by cavity collapse in the liquid. The impingement of micro-jets and shockwaves on the surface is responsible for ultrasonic cleaning and changes solid surfaces profoundly creating fissures and cracks. For minerals, inter-particle collisions will cause breakage of particles.

4. LEACHING IN AN ULTRASONIC FIELD

This section briefly describes how ultrasound assists in leaching. The leaching effect of ultrasound does not arise from a direct interaction with molecular species. Consequently, no direct coupling of the acoustic field with ores on a molecular level can account for enhanced leaching. Their influence on the leaching of metals is mainly due to the effect on the cavitation process. However, ultrasound supplies enough vibrational energy

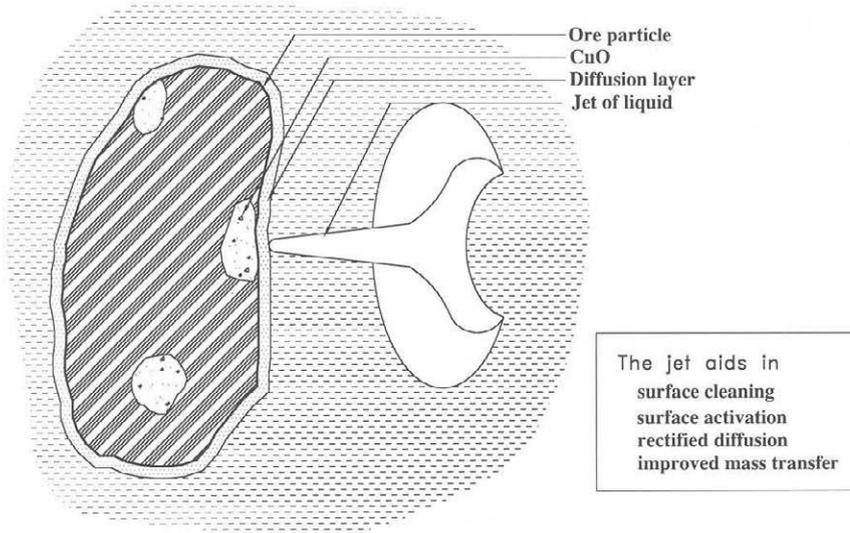


Figure 2. Cavitation bubble collapse near ore particle.

and also produces a radiation force, which can keep the ore grains partly suspended. This is one of the important aspect in leaching to take place. Ultrasound has a mechanical effect on particles, avoiding agglomeration during leaching. The additional source of energy that is provided by the cavitation process, aids further in increasing the leaching rate by many fold when compared to mechanical mixing. The collapse of a cavitation bubble near an ore particle, as already shown in Figure 2, produces rapid liquid motion and jetting which cleans the surface of ore grains and so improve the leaching. The diffusion layer surrounding the mineral surface gets passivated by the vigorous agitation. Similarly low frequency ultrasound causes microgrinding of ore particles through inter-particle collision, thereby increasing the total surface area. Due to the availability of fresh surface to the lixiviant and due to the presence of short lived high temperatures in the bubble as well as the large pressure gradients developed, mass transfer from the solid surface to the liquid occurs more rapidly than in conventional leaching. Both the rate of extraction and the recovery of metals are thus enhanced.

Ultrasonic leaching is attractive for two reasons. The first is that ultrasound allows the leaching to occur under less absolute conditions through cavitation bubble collapse. The second relates to the metal dissolution kinetic studies in which ultrasound agitation decreases the activation energy as compared to other types of agitation. Hence, ultrasound, aids in enhancing and improving leaching.

5. PRINCIPLES OF ULTRASONIC LEACHING

5.1 Factors Influencing Leaching

For a fixed temperature the following different factors influence the rate of leaching of metals from ores.

- (i) Area of contact between the material being leached and the lixiviant.
- (ii) Pre-treatment of the material to increase its activity during leaching.
- (iii) Selection of more effective reagents.
- (iv) Generation of favourable conditions, e.g. stirring and use of various catalysts.
- (v) External factors such as a dc field, ultrasonics etc.

5.2 Role of Ultrasound

When a liquid is irradiated with ultrasound, then small bubbles appear, grow, oscillate and collapse, as the acoustic pressure becomes sufficiently high. When these collapses occur near a solid surface in a slurry consisting of the ore particles, then, they cause cleaning, erosion and fragmentation of the solid. Sometimes the high local turbulence created can improve the solid-liquid mass transfer [27]. In the absence of any agitation the dissolution reaction proceeds very slowly and appears to be controlled by liquid diffusion. Such a process is controlled by mass transfer through a liquid boundary film for which the rate law is:

$$\text{Rate} = \frac{K_d A_p C_0}{\sigma} \quad (1)$$

where σ is the thickness of the liquid boundary film. A_p is the total surface area of the particles, C_0 is the initial concentration of the solvent and K_d is the mass transfer coefficient. It is known that σ decreases with increasing agitation (either by speed of stirring or by ultrasonic agitation) and the rate of dissolution increases as a consequence. During the ultrasonic treatment of ores, microgrinding occurs as well as inter-particle collision taking place, causing breakage of particles. Ultrasound promotes a decrease in particle size as a consequence of which the total surface area of the solid particles increases resulting in an improvement in the reaction rate as evident from Eq. (1). During ultrasound applications the mass transfer coefficient [27,28] is expressed by the following equation.

$$K_d = \frac{D}{d} \left[2 + 0.4 \left\{ E^{1/4} \frac{d}{D^{1/3}} \left(\frac{\rho_L}{\mu_L} \right)^{5/12} \right\} \right] S \quad (2)$$

where μ_L and ρ_L the viscosity and density of the solvent and E is the ultrasonic power dissipated per unit mass of the liquid and D diffusivity of the reagent in the solvent, d is average particle size and S is the shape factor.

Application of ultrasound reduces the effective viscosity of the solvent resulting in an increase in the mass transfer coefficient, K_d as per Eq. (2). In addition mass transfer is accelerated because of the decrease in boundary layer thickness, σ , thus increasing the mass transfer coefficient. As mentioned earlier sonication is likely to increase the reaction surface area because of changes in surface characteristics and morphology.

5.3 Role of Ultrasonic Intensity and Energy Density

Ultrasound leaching is potentially important. It is necessary to distinguish the cavitation effect at ultrasonic and sonic frequencies and to quantify the ultrasonic intensity. Understanding these helps in improving the reproducibility of results. Keeping the present developments in view the following is described.

5.3.1 Cavitation at Ultrasonic Frequencies

The maximum ultrasonic intensity applied to a reaction mixture is generally defined as the energy emitted per unit area per unit time by the ultrasonic transducer. The intensity, which is closely associated with the acoustic pressure is responsible for producing cavitation bubbles. But increasing the acoustic amplitude continuously, cannot increase the leaching rates without limit. Because as the vibrational amplitude increases, decoupling occurs between the vibrating plate and the liquid near the radiating surface due to a shroud of bubbles, which will diminish the penetration of the sound into the liquid. But, usage of low sonic frequencies can create strong cavitation effects in slurries as described in Section 5.3.2.

5.3.2 Cavitation at Low Sonic Frequencies

It is known that higher intensity cavitation generates higher temperatures, and shear forces. These are some of the mechanisms responsible for the acceleration of kinetic process in liquids and slurries. Equation (3) given below is a relation between acoustic energy intensity, I and the properties of the media; density, ρ , velocity of sound, c , frequency of vibration, f , and vibrational amplitude, A .

$$I = \frac{1}{2} \rho c f^2 A^2 \quad (3)$$

It is seen from Eq. (3) that acoustic intensity can be enhanced either by increasing the frequency or amplitude of the driving force. At 20 kHz frequency small amplitudes typically 25 μm are reported, while in the low frequency of around 100 Hz, in the sonic range, higher amplitudes of ~ 10 mm can be obtained [29]. Since $I \propto (fA)^2$, the respective values of sonic and ultrasonic ranges are $(20 \text{ kHz} \times 25 \mu\text{m})^2$ against $(100 \text{ Hz} \times 10 \text{ mm})^2$. Thus, four times greater intensities are possible with low sonic frequencies than at ultrasonic frequencies. This point needs consideration in future equipment development. However, due to their relatively high cost, transducers with heavy mass and practical feasibility have limited use.

5.3.3 Quantification of Ultrasound Intensity

There are several complications and difficulties reported in measuring ultrasonic intensity [30], as many workers use different methods. Some workers report the nominal output as stated by the equipment manufacturers, other estimate the transducer efficiency, and some actually measure the intensity in the liquid. To overcome these problems, it was suggested that a correlation of properties should be made in terms of the total energy input into the system (i.e. the product of intensity and time) one can use leaching of metal value, q where,

$$q = \frac{It}{VC} \quad (4)$$

I is the ultrasonic intensity, t is the irradiation time, V is the volume of ore slurry and C is the initial concentration. This generalised equation of q takes care of the effects of the shape and size of the container in addition to the other factors. Although parameter q is analogous to the photochemical quantum yield, this is sometimes difficult to measure.

Another important observation made was that the improvement in recovery decreased as the volume of the treated slurry increased. This suggests an alternate way for expressing units of ultrasonic intensity from the normally used energy per unit area to energy per unit volume, i.e., W cm^{-2} to kW m^{-3} (or J cm^{-3}) and this system expressing intensity is currently practised. Zhen et al. [31] reported that the peak power density plays an important role but not the average ultrasonic power, as is commonly used. In future the acoustic intensity should not only be expressed as W cm^{-3} as mentioned above, but in addition the peak power of acoustic intensity used, should also be mentioned, which helps in reproduction of results by different researchers. As already mentioned the commercial equipment manufacturers should provide a peak intensity indicator, in addition to the total ultrasonic power in future.

6. LIMITATIONS OF ULTRASONIC LEACHING

Ultrasound has the ability to enhance leaching, but it has not been integrated into many industrial leaching processes due to its inherent limitations, which are enumerated below.

A primary limitation of ultrasonic leaching is the utilisation of a small fraction of the acoustic power actually involved in the cavitation events. This might be significantly improved, however, if a more efficient means of coupling the sound field to generate cavitation can be found.

It must be remembered that the application of ultrasound over longer periods need not result in enhanced metal recovery. This observation has been supported by the recent report [32] that sonication enhances dissolution but, prolonged sonication may result in decrease of solubility affecting concentration. Some times ultrasound did not show significant influence on the rate of dissolution of metals, like, zinc in acids [33].

Another important aspect is that under some specific conditions, ultrasound may not influence leaching. The authors have introduced the concept of “critical grain size” which is elaborated in detail in Section 7.1 of this chapter. Greater benefits of using ultrasonic waves is realised at larger ore particle sizes. Even with the application of ultrasound, the benefits are lowered with smaller particle sizes. So there exists a critical particle size below which application of ultrasound is not effective in improving metal recovery any more than the conventional method. In the case of CuO ore it is found to be 45 μm . Hence, the ore grain size also limits ultrasound use in metal dissolution.

For ultrasonic sound waves to participate and improve any process there exists a threshold limit. For liquid atomisation by sound waves, there exists a critical sound pressure, below which sound waves do not have a disintegrating effect and affect the atomisation process [34,35]. For example, the sound pressure threshold levels for atomisation of water and glycerine respectively are 5.4×10^3 Pa and 1×10^4 Pa; whereas, the same are identical for molten tin and indium at $1.2\text{--}1.3 \times 10^4$ Pa. Similarly, using airborne sound, in another unit operation like drying of materials, a critical sound pressure level also exists. The value is expressed as 135 dB [36,37] below which, the drying process does not differ very much from the ordinary convective drying. In the present application, leaching of materials from ores in the presence of ultrasound is also not possible at all ultrasonic power levels. It should be pointed out that “no leaching occurs without cavitation” and several published examples contain parallel experiments showing that vigorous stirring or mechanical agitation will not produce such a marked increase in the leaching rate. It leads to the conclusion that this is not primarily a mixing effect. The interaction of sound with matter through the

process of cavitation offers a range of energies for the chemical dissolution of metals that are not available from other sources. Below the cavitation threshold value, the amplitude of the sound field is not large enough to induce nucleation or bubble growth. The typical behaviour of acoustic intensity in the generation of cavitation at different ultrasonic frequencies for air-free and aerated water [38] are illustrated in Figure 3. Recently Naito et al. [39] investigated the cavitation threshold as a function of the amount of dissolved air in water and the frequency of ultrasound in the megahertz range and obtained a relation between them. This study was conducted to know the limitation of ultrasonic cavitation, which is a significant cause of bio-effects in medicine. It is evident from Figure 3 that higher acoustic energy application is needed to produce a cavitation effect at megahertz range than at kilohertz frequency range. This fact can be understood from the first principles, that the attenuation of sonic energy, α in liquid medium is proportional to the square of the frequency, f . As a consequence one might expect similar ultrasound effects to occur at high frequencies and high intensities as those that happen at low frequencies at low intensities. The leaching experimental results for Platinum (Section 7.3) and Zinc (Section 7.2) establish this. Even though ultrasound is well established in accelerating leaching, the fundamental limitation for its large-scale use may be the result of the large attenuation of sonic energy during propagation in ore slurry. Hence, usage of frequencies lower than 20 kHz might be a possible alternative.

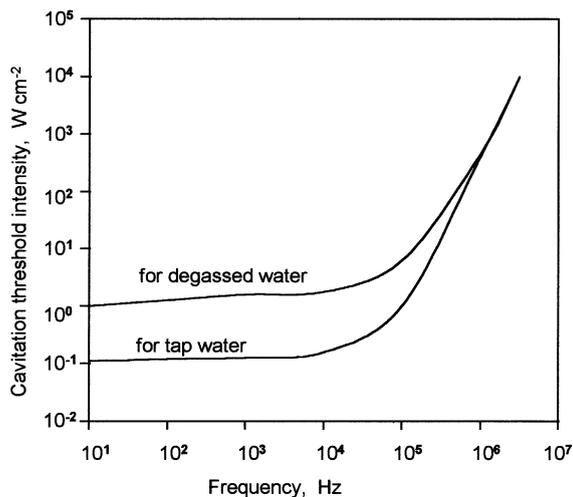


Figure 3. Relationship between ultrasonic intensity and frequency to produce cavitation and hence leaching.

7. ANALYSIS OF EXPERIMENTAL RESULTS: DIFFERENT METALS AND SOIL DECONTAMINATION

Ultrasound recently has been studied as a new and novel technique in the removal of metals from contaminated soils and hazardous wastes. Over the past few years there has been considerable interest shown in using ultrasound and sometimes by combining this technique with other methods like dc field etc., for leaching of metals from ores. Some of the important papers in this field are reviewed below.

7.1 Copper

The application of ultrasonic vibrations [40] resulted in enhancing the copper extraction rate of chalcocite powder (74 μm size), 10 times more than that obtained by only mechanical stirring during leaching by 5% H_2SO_4 and 2% $\text{Fe}_2(\text{SO}_4)_3$. The solid-liquid (S/L) ratio used was 1:140. When the leaching medium was 2% H_2SO_4 and 5% $\text{Fe}_2(\text{SO}_4)_3$ and S/L ratio 1:5, the recovery of copper increased from 46.9 to 71.2% for chalcocite with an ultrasonic field and from 0 to 3% for chalcopyrite. The leaching effect in an ultrasonic field increased parabolically with the reduction in the particle size from a range of 595–250 μm . Chrysocolla reacted better in 5% H_2SO_4 medium with ultrasonic irradiation for 30 min yielding 99.8% copper recovery [41]. The same authors [42] studied the copper dissolution under the effect of ultrasonic and dc fields. Chalcocite ore responded well to an ultrasonic field, whereas a dc field showed better effect on chalcopyrite ore. This study showed that the nature and composition of ore plays an important role in the dissolution of metal values under sonication.

Khavskii [43] has also reported on a laboratory scale, the use of ultrasound for increasing the rate of dissolution. The leaching rate of copper in ammoniacal solution increased 3–4 times in the presence of an ultrasonic field, whereas for copper dissolution in sulphuric acid containing Fe^{3+} ions, the effect was more pronounced. Copper ores were leached by sulphuric acid of 1.5 g l^{-1} concentration from three different deposits. It was demonstrated [44] that rotation mixing time could be brought down from 20–60 min to 5–10 min using ultrasound. The leaching efficiency also increased by 5–15%. Similarly, during ultrasonic vibration leaching of pyrite cake, about 90% of the copper was extracted in 4–8 min and leaching time of copper ores decreased by a factor of 3–12 when compared to leaching through mechanical agitation alone [45]. A comparative study on mixing has been carried out by Orlov [46] in both laboratory and industrial type reactors. As shown in the Figure 4, the study indicated that the time of

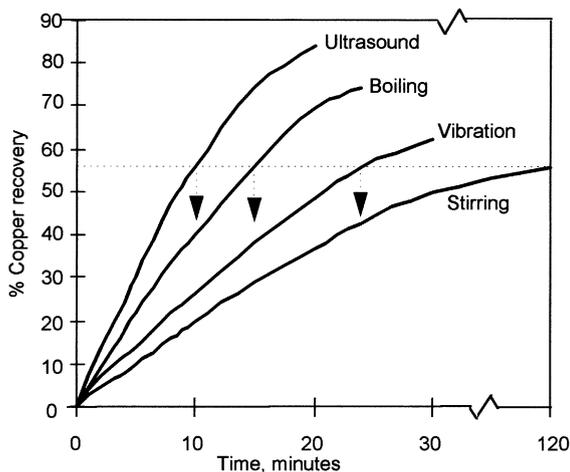


Figure 4. Leaching curves by different methods with time.

leaching of copper from CuO ore reduced ~ 5 times by vibration, ~ 8 times by boiling layer and ~ 12 times by the action of ultrasound, in comparison with a stirring effect, in which a maximum of copper recovery of 56% has been obtained in 120 min.

The authors studied ammonia leaching of a lean grade copper oxide ore containing 3.5% Cu [47]. The leaching studies indicate that the initial rate of copper extraction with mechanical agitation is faster, whereas under sonication condition, not only the initial extraction rate is higher than that obtained under mechanical agitation but a higher rate of extraction is also achieved as seen from Figure 5. A cup horn type transducer was used here and similar to the experimental set up by Suslick et al. [48]. From experiments over the same time interval of 20 min of leaching, 51% and 73% copper extractions were obtained with mechanical and ultrasonic agitation, respectively in a particular grain size of $-75 + 53 \mu\text{m}$. For other grain sizes also ultrasound improved leaching. Compared to this, even a longer leaching time of 120 min of mechanical agitation could give only 60% copper extraction. Thus, it is obvious that copper recovery is accelerated and enhanced by ultrasound. Further studies on laboratory scale investigation has clearly established [47] the positive influence of ultrasound on copper recovery from oxide ores containing 3.5% Cu in ammoniacal medium. A maximum recovery of copper of about 70% was obtained under the following leaching conditions: temperature 298 K; particle size, $-300 + 150 \mu\text{m}$; ammonia concentration, 2.0 mol l^{-1} ; and solids concentration 10 g l^{-1} of slurry with sonication. The recovery further increased up to 91% by the application of pulsed ultrasound [47]. These investigations show that,

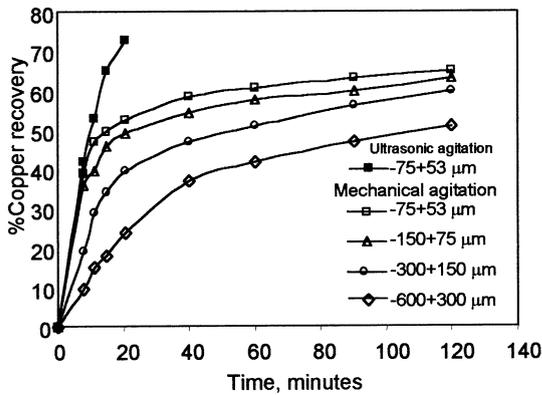


Figure 5. Effect of particle size on copper recovery with and without ultrasound.

ultrasound decreased the leaching time by a factor of ~ 6 times and also decreased the reagent consumption compared to that during leaching using mechanical agitation. For the same particle size, ultrasound not only enhanced the extraction rate but also improved the yield. Other conditions remaining the same, intermittent use of ultrasound (pulsed ultrasound) had a better effect over the continuous use of ultrasound. Ultrasound decreased the apparent activation energy from 20.8 to 18.5 kJ mol^{-1} .

Leaching of metals with different particle sizes of ore in the presence of ultrasound is of considerable importance. For example, the recovery of copper in percent obtained by sonication is always more than by mechanical agitation after 20 min duration for all grain sizes studied [47]. The effect of particle size was investigated using four size fractions. The results show, as expected that the leaching rate was effected by the particle size, being found to increase with a decrease in particle size. This can be attributed to the increase in the number of particles per unit weight of the solid, resulting in an increased unit surface area that results in greater exposure of ore particles to the lixiviant. Figure 6 shows the variation of the percentage increase in Cu recovery for different ore particle sizes [49]. As seen the larger the ore particle size the more ultrasound yields greater benefits. It is seen from Figure 6 that there is an inflation in grain size versus more percent metal recovery curve. There is a sudden drop in the increased recovery to less than 5%, a point that was considered as critical grain size. This shows an existence of a critical particle size of 45 μm (d_p), below which, application of ultrasound is not effective in improving metal recovery more than that obtained with the conventional method. This observation made from experimental results is very interesting, indicating that the ore grain size can also limit the effectiveness of ultrasound. The authors arrived at the critical

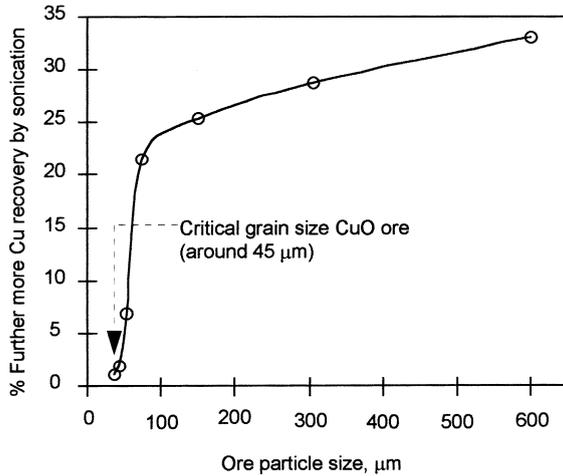


Figure 6. Additional metal recovery obtained by ultrasound for different grain sizes.

grain size by considering any improvement of less than 5% as no improvement. The most plausible explanation for this critical grain size concept is given in Section 3.2 of this chapter where micro-jet formation during cavitation at liquid–solid interfaces was described. It should be noted that a solid surface several times larger than the resonance bubble size is necessary to induce distortions during bubble collapse. For ultrasound of ≈ 20 kHz damage associated with jet formation cannot occur if the solid particles are smaller than ≈ 150 μm , an evident limit. But practically, from our investigation [49] the critical particle size was determined as 45 μm for leaching of CuO ore.

In order to enhance the leaching of metals the combined action of ultrasound and electric fields have also been attempted [50]. Thus, Chizhikov et al. [50] determined the degree of metal extraction in leaching of copper from chalcocite containing sulphide ore after one hour treatment. It was reported that the composite effect of both fields was more beneficial than individual effects of each energy field. Kinetic studies on copper leaching with mechanical mixing under an ultrasonic field also show improved leaching rates [51].

The effectiveness of ultrasound has been studied [52] for the dissolution of Cu, Ni, Pt and Pd contents from different ores. It appears that to obtain the same amount of dissolution and leaching of the metal values, one has to use either a low frequency ultrasound of 18 kHz at $4\text{--}5$ W cm^{-2} intensity or a high frequency ultrasound of 2 MHz at high intensity of $15\text{--}20$ W cm^{-2} .

Ultrasound is found to have a similar effect [15] during ammonia leaching of a Cu–Zn–Pb sulphide concentrate containing 3.6% Cu. The studies have

revealed that the amount of copper extracted with mechanical agitation was only 3.8% in 40 min at room temperature, whereas, with ultrasonic agitation, it increases to 11.5 % over the same leaching period.

7.2 Zinc

Gramtikov and Mekhandzhiev [53–55] studied the influence of ultrasonic intensity and frequency on leaching of Zn from zinc cake and ferrite zinc. Firstly, at a constant frequency of 22 kHz and at an intensity level of 4 W cm^{-2} the recoveries of zinc and iron were improved by 200–300%, whereas for copper a lesser degree of enhancement was reported [53]. This indicates that response to an ultrasonic field was not uniform in extraction of all metals equally. Another important observation made was that the improvement in recovery decreased as the volume of the treated slurry increased [54]. This suggests an alternate way for expressing units of ultrasonic intensity from the normally used energy per unit area to energy per unit volume, i.e. from W cm^{-2} to kW m^{-3} . Currently this is what is used, as mentioned in Section 5.3. Secondly, when the intensity was varied from 4 to 8 W cm^{-2} at any constant frequency between 22–36 kHz, there was an additional 50% enhancement in recoveries [53]. It was, however, shown that on increasing the frequency from 36 kHz to 1000 kHz, there was an adverse effect on recovery [53]. The beneficial effect of using the ultrasonic treatment was attributed to the intensification of mass transfer and dispersion of the cinder, which in turn increased the total contact area between solid and liquid phases. The negative result, reported at high frequencies, was attributed to the predominant role of acoustic cavitation rather than radiation pressure and acoustic streaming.

It is well known that with an increase of ultrasound intensity either at low frequencies (18–40 kHz) or at high frequencies (1–2 MHz), the relative cavitation effect increases. However, the order of magnitude differs. At higher frequencies, higher intensities are required to yield the same useful effect or cavitation effect on leaching. It can be deduced from Figure 3 that when a higher frequency is employed a greater amount of energy is required to produce cavitation in a liquid. It was shown [52] that for dissolution of metals like Cu, Ni, Pb and Pd, ultrasound at 18 kHz, $4\text{--}5 \text{ W cm}^{-2}$ had the same effect as that of ultrasound at 2 MHz, $15\text{--}20 \text{ W cm}^{-2}$. This may be the reason that even though improved leaching of zinc was reported [53–55] at 22–36 kHz frequency, higher frequency of 1 MHz, at identical ultrasound intensity of $4\text{--}8 \text{ W cm}^{-2}$ showed reduced effects.

The effect of ultrasonic vibrations on ammonia–ammonium chloride leaching of zinc from galmei ore [56] also indicated that the ultrasonic field decreased the leaching time considerably. The recovery of leachable

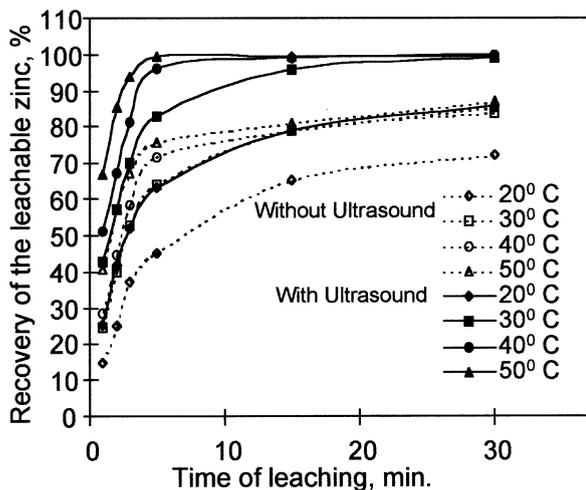


Figure 7. Zinc leaching at different temperatures as a function of time, for both sonicated and non-sonicated samples.

zinc as a function of leaching time at different temperatures in the range 20–50°C are shown in Figure 7. At a temperature of 30°C and within 15 min of ultrasound leaching, about 96% of the leachable zinc was solubilised. By increasing the temperature to 50°C it was possible to recover 99% of the leachable zinc after 5 min of leaching, while, without ultrasound only 87% of the leachable zinc was solubilised even after 30 min. The leaching effect in an ultrasonic field increased parabolically with increase in temperature. At any given leaching time and at all temperatures studied, ultrasound always released more yields. Subsequently the variation of more zinc recovery obtained with ultrasound exhibited maxima with a leaching time as is shown in Figure 8 for different temperatures. Interestingly the peak values were found to shift towards 2 min of leaching time from 4.5 min with increase in magnitude of recovery at temperatures from 20 to 50°C.

Ultrasound has been demonstrated [57] to be very beneficial in the selective acid leaching of zinc from electric arc furnace (EAF) dusts. With nitrogen bubbling in 1.8 M HCl and 1.2 M CaCl₂ medium at 50°C zinc dissolution was enhanced by ultrasound. The ratio of percentage of zinc extracted to that of iron extracted was 15.6 as compared to 3.6 obtained without ultrasound. With ultrasound there was little difference between data obtained by air bubbling and nitrogen bubbling suggesting that ultrasound produces an overriding effect. The presence of ultrasound enhances zinc dissolution but retards iron dissolution presumably due to localised adverse conditions and ferric hydroxide precipitation. It appears that some of zinc not recovered in the leach may well be in the form of ferrite.

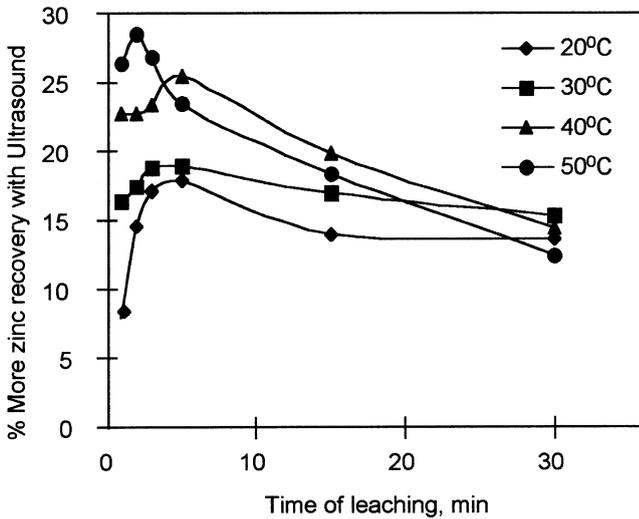


Figure 8. More recovery of leachable zinc by ultrasound with leaching time for different temperatures.

7.3 Precious Metals

Precious metals which include gold, silver and the platinum group of metals are present in ore bodies in very low concentration and any improvement in their yield will lead to substantial economic benefits and hence, several researchers have attempted to apply ultrasound for improvement in their recovery. Improved recoveries of precious metals are realised through the scrubbing action of crushed ore particles in slurry at a flow rate of 50 gallons min^{-1} by the use of 16 kW ultrasound energy [58]. Such a system requires a very high level of ultrasonic energy into a flowing stream, though for a brief period of time [59], and is known as reverberatory ultrasonic mixers.

In the cyanidation of Au and Ag ores mass transfer has been reported [60] to be enhanced by ultrasound. Ultrasonic pre-treatment aided precious metal recoveries from ore slurries in a vibratory trough due to deagglomeration and surface cleaning of the ore particles [61]. An apparatus has been devised for extraction by applying combination methods, which facilitate the applied radiation and the passage of current through the mass. Powdered complex silicate ores when subjected to high electrical discharge concurrently with ultrasonic irradiation resulted [62] in better extraction of Au and Ag.

Interestingly, ultrasound produces further breakage in a ground ore when placed in an aqueous medium as well. Ultrasound causes a widening of secondary fissures in the ore and allows exposure of new surfaces that

include microscopic gold particles resulting in enhanced rate and degree of dissolution of gold from the ore [63].

Pilot plant size ultrasonic reactors were reported to be used in two alternate methods in the extraction of noble metals [64]. In the first method, premixed slurry with 25% pulp density was allowed to pass over a sonically vibrated inclined metal trough, which cleans up the surface of the particles through scrubbing. It resulted in a beneficial effect on compaction of the treated material and improves the solid-liquid separation. It also makes tailing disposal more effective. In the second method, a newly developed tube version of magnetostrictive type transducer was used to produce highly intense ultrasonic vibrations. During the leaching of a variety of ore types not only the cleaning effect of ore surfaces and a substantial increase in metal recoveries were observed, but also a reduction in leach time [64,65].

For reducing the thiourea consumption in gold extraction, leaching studies under the influence of ultrasound were carried out with a gold bearing quartz sample (a pyrite ore) of 200-mesh particle size containing 1.1 oz Au per ton ore and some manganese. After 5 min of pre-leach in H_2SO_4 and 0.1% $\text{Fe}_2(\text{SO}_4)$ at pH of 1.5 various concentrations of thiourea were added. Gold recoveries up to 86%, in 52.5 min time was possible by the use of ultrasound with a decrease in thiourea consumption from 8 lb to 6 lb per ton of ore [64]. The results obtained may be explained due to a combination of effects like cleaning, increase in contact between ore and solvent, and generation of heat caused by ultrasound.

Clayish ore containing gold was leached with 0.1% NaCN, pH 10.5 w/NaOH under 1200 rpm agitation for 30 min. The gold extraction was about 90% in presence of sonic treatment whereas the extraction was reduced by about 30–40% when sonic treatment was terminated. It was noticed that up to a further 15% of gold was reprecipitated and probably readsorbed on the clay. Active carbon which has a higher affinity for gold than clay was used to avoid reprecipitation. The problem of readsorption was solved by maintaining the ultrasonic unit in operation until the carbon was separated from the pulp [64].

For the determination of mineralogical form of silver in a silver rich complex ore conventional acidic thiourea leaching [66] yielded 35% of Ag. In the same complex sulphide ore, under the effect of ultrasonic treatment 65% of Ag can be extracted. Further enhancement of Ag recovery up to 96.8% is achieved after leaching of Zn and Cu from the roasted ore. The leaching rate of silver was attributed to diffusion control and the activation energy obtained was $10.49 \text{ kJ mol}^{-1}$.

Zhao [67] has studied the process of ultrasonic leaching (PUL) of gold and silver from silver concentrates on both laboratory and pilot scale. Gold and silver recoveries up to 97–99% and 95–96% respectively, were obtained at the optimum conditions. The leaching time is only one-third of the

traditional cyanide leaching time. The specific consumption of sodium cyanide was reduced by 10 kg t^{-1} . Further, tube-type and tank-type autoclave reactors are suggested for industrial use. This PUL method has been claimed to have all the advantages like higher extraction of gold and silver, shorter leaching time and lower consumption of sodium cyanide. The same group also reported the industrial application of ultrasonic wave-aided leaching of gold recovery from ores [14] with 95% recovery and decrease in time from 22 to 0.5 h.

The dissolution of metals like Pt from ore was found [67] to have the same values under different ultrasonic conditions viz., at low ultrasound frequencies 18 kHz using $4\text{--}5 \text{ W cm}^{-2}$ and at high ultrasound frequencies 2 MHz using $15\text{--}20 \text{ W cm}^{-2}$.

7.4 Tungsten

Tungsten is a refractory metal having extensive use in metal working, mining and construction machinery and equipment etc. Its availability is very limited. Recently attempts have been made to improve its yield from ore bodies by applying ultrasound. The application of ultrasound for accelerating the autoclave sodium carbonate leaching [68–74] and acid leaching [75–77] of scheelite ore have been studied by different investigators. Autoclave soda leaching of scheelite ore with a particle size of $74 \mu\text{m}$ (about 70–80% passing through a 200-mesh) and ultrasonic field of 5–10 kHz frequency has reduced the autoclave pressure from 5 to 18 atm to ~ 7 atm and simultaneously increased [69] the degree of leaching by 3–6%. The influence of ultrasound on Na_2CO_3 leaching of scheelite at 4.5 atm pressure with different variables was studied. In 60 min time at 100°C maximum extraction of 42.9% WO_3 was obtained [70] with the solid–liquid ratio of 1:4 and with soda equivalent of 3. At the same soda equivalent of 3, when the pressure was raised to 7 atm for 95 min duration higher tungsten extraction up to 81.6% was achieved [71]. The synergetic effect of increased pressure with ultrasound resulted in 3–4-fold increase of WO_3 extraction as compared with the same treatment at atmospheric pressure [70]. The large improvement of the leaching in the field of acoustic vibrations and the simplicity of the process suggests the introduction of the method into industrial practice [71].

The autoclave soda leaching of scheelite concentrate by ultrasonic treatment at various pressure, temperatures, solid–liquid ratios and times were studied at atmospheric and at high hydrostatic pressure. Leaching of scheelite was accelerated in presence of ultrasound at all stages [72,73]. In another study the total consumption of reagents (soda, acid) was found to be decreased with simultaneous lowering of the autoclave temperature [78].

In presence of acoustic vibrations the decomposition of scheelite was found [75] to be nearly complete (99%) at 90.5°C in one hour using 150% excess of 30% HNO₃ due to a decrease in activation energy from 28.1 to 6.4 kJ g⁻¹ mol⁻¹. The kinetics of the primary leaching of scheelite was also carried out using rotation and pulsation hydrodynamic apparatus [74]. The enhanced leaching could be attributed to the rupture of the carbonate film on the surface of scheelite which acted as a diffusional barrier and also to additional disintegration of the mineral, with the exposure of a larger surface to the action of the leaching solution [69]. During HNO₃ leaching of scheelite, acoustic intensification causes a chemical transformation at the phase boundary by the turbulence impeding H₂WO₄ hydration and thus the process occurring in the kinetic region, which otherwise is diffusion controlled [76,77]. Microscopic studies were conducted on the effect of high power ultrasonic vibration on scheelite leaching [79].

7.5 Titanium

Titanium, a refractory metal, has many superior properties and finds applications in jet engines, air flames, space and missiles. Use of ultrasound during hydrometallurgical treatment of titanium alloy wastes was studied by Smirnov et al. [80]. The leaching of the Ti–Al–V alloy hydride using composite reagent under ultrasonic vibrations reduced the process duration as well as lowering the temperature compared with that of conventional vat leaching. Ultrasound is known to reduce particle size reduction during leaching. As a result over grinding of certain parts of the solid phase poses problems in further treatment of suspensions [80]. Srikanth et al. found [81] that even though acoustic waves stimulate the leaching process, in extracting potassium from mica remarkably, the particle size of mica being a significant parameter in enhancing the leaching rate; below a critical particle size acoustic waves do not affect the leaching process [81]. So, ultrasound has some limitations in leaching when the material cracks easily, or the method is ineffective below a critical particle size.

Ultrasound was used to reduce the chlorine content and simultaneously to decrease the leaching time of titanium powder [82]. During acid leaching of titanium salt, ultrasound effectively decreases the chlorine content [82,83].

7.6 Nickel

Nickel is one of the important alloying metals used in stainless steel production. However, its availability in ore bodies is in very low concentration. For improving the recovery researchers have tried the

influence of ultrasound. In an attempt to seek innovative and economic ways to exploit large US deposits of low-grade nickel laterites (oxide ores), Pesic and his co-workers [84] conducted laboratory tests using an ammonia leach with ultrasound. It was found that 70% nickel extraction was achieved in 15 min, compared with 1 h without ultrasound. The speeding up of leaching of nickel from oxide ore using ultrasound was attributed to the ultrasonic disruption of a hydroxide film that is believed to surround unleached nickel particles.

A 20 kHz, 20-W ultrasonic source applied to solution through a submerged titanium horn to the conventional method of reduction roast followed by an ammonia leach. Further, to prove the effectiveness, they also tested [84] ultrasound on solvent extraction of nickel from sulphuric acid leach solution, deliberately choosing slow acting solvents. In one case the time to reach equilibrium was reduced from about 120 to 6 min and in the other from about 240 to 20 min.

7.7 Rare, Other Metals and Oxides

Application of ultrasound in the recovery of rare and other metals has been pursued by many investigators throughout the world and encouraging results were reported. Ultrasound has intensified the rare metal dissolution process by depressing the effect of diffusion and the influence of capillarity [85]. With the application of ultrasound, during a chemical phase analysis of antimony and arsenic ores, the leaching of Sb_2O_3 from the ore in 1.5 N aqueous tartaric acid was complete within 1.5–2 h, whereas in 2 N aqueous HCl the dissolution was complete in 30 min. Without ultrasound, 75% Sb_2O_3 was dissolved in 14–16 h, and completely dissolved [86] in 24 h, about 2–4 min ultrasonic treatment of continuously flowing crude rare metal concentrates decreased [87] slime formation from 5 to ~1%. Gasgnier et al. have recently studied [88] selective leaching of rare earth oxide powders of Pr and Tb in acetic acid with ultrasonic irradiation. Surprisingly the dissolution of metals at ~325 K starts after 5 min of ultrasonic irradiation. The present authors are of the opinion that this observation needs thorough further investigation.

Exposure to ultrasound enhances, the diffusion leaching of bauxite and leaching of ores by speeding up the exchange of liquid in the pores and dissolution of the reactants, increasing the dispersion of the particles and thus the active surface, and boosting chemical reactions. The pores clogged by silica gel was freed by the ultrasonic vibrations thereby increasing the yield, and also facilitate automation of the process. The ultrasound emitters are situated under the ore suspension at regular intervals along the entire separation line [89].

Steven and Lawrence [29] used a Resonant Sonic reactor of 10 l capacity with 76 Hz frequency and amplitude of pressure wave intensity 190 dB for processing bauxite to conduct leach tests at 20°C. By the use of Resonant Sonic reactor they established in a 1000 ton-per-day plant, the annual savings would vary from \$1.5–4.0 million for steam alone. The beneficial effect was attributed to cavitation and micro-streaming processes caused by sound, which is an effective means to disperse steam through the solution and/or slurry on a molecular level to accelerate the leaching of trihydrate alumina from the bauxite ore.

Ultrasound replaces the acid leaching in the removal of iron and manganese oxides from tantalum-niobium ore concentrates [90]. Ultrasonic irradiation has also been found to enhance germanium extraction on only 11–23 µm particle size fraction from its concentrate [91]. Ultrasound was found to be effective in analysis of ores and their conversion products of Cu, Ni, Pt and Pd compounds [92]. Ultrasonic radiation has enhanced [93] the uranium extraction from alumino-silicate mineral in 5% Na₂CO₃ and from carnotite ore in H₂SO₄ medium [94].

7.8 Soil and Solid Waste Decontamination by Ultrasound

Remedial technologies for soils and their application toward removing heavy metals, radionuclides from soils have become a primary focus globally by many government agencies. Even though high extraction efficiency dissolution technologies were investigated, they have been found to be cost prohibitive mainly due to the large volume of the contaminated soil involved. So it is not likely that ultrasonic leaching will find an immediate large-scale use in the field of soil decontamination. But, it can offer a reliable, rapid sample leaching procedure for on-site analysis. It is a first and foremost step in attempting to decontaminate soil. Ultrasound can be used in the assessment of the hazardous potential of soil contaminated with waste, with regard to its leaching behaviour. This is applied to various categories of soils:

- on the surface
- in a land fill
- over burden mines
- industrial hazardous wastes, residues and refuse
- river sediments crude, etc.

Ultrasonic energy is found to have pronounced use in soil decontamination effected by chemicals which has been recently reported, for example, ultrasound solvent extraction of pesticides from soils [95,96]; DDT (toxic pesticides) extraction from soil ultrasonically [97]; ultrasonic disintegration

of biological sewage sludge of a paper industry [98], ultrasonically assisted chemical destruction was developed [19] in a pilot plant module to process 1 ton-per-hour, to remediate soils contaminated with Polychlorinated biphenyl (PCB) for reducing the PCB levels from 2000 ppm down to less than 2 ppm in 30 min contact time; which falls outside the scope of this review. However, this section will examine some of the leaching practices being used or considered for use at on-site metal bearing hazardous waste soils only.

Ultrasonic extraction (UE) of heavy metals in the industrial hygiene arena is increasing. Recently, Ashley [99] reviewed the applicability of UE method for a number of environmental and industrial hygiene samples. He showed that UE is an effective method in extracting heavy metals, and the same method can be used for sample preparation purposes in environmental analytical chemistry. Further, extraction by ultrasound will become more widespread, owing to its simplicity, ease of use, speed, and enhanced safety when compared with other more traditional preparation procedures.

The same group further studied [100] the Pb dissolution from environmental reference materials like soils and paints under ultrasonic agitation for 30 min in 5% (v/v) nitric acid. The solubilised lead was evaluated by inductively coupled Plasma-atomic emission spectrometry (ICP-AES) and it was found that acceptable recoveries ($100 \pm 10\%$) of lead are obtained by ultrasonic extraction. They suggested that the sample preparation method could be carried out for lead dissolution by ultrasound which may be used in lieu of more rigorous digestion procedures involving concentrated strong acids and elevated temperatures.

In the preparation of synthetic rutile from ilmenite sand rusting process has become prominent, as it is environment friendly. Experiments have shown that [101] through intermittent separation of iron oxides from the reaction system and by the use of ultrasound it is possible to bring down the process time from 12 to 8 h duration with a better quality. Sonication is beneficial for the oxidation of iron.

A Chinese group studied [102] ultrasound-assisted thiourea leaching of methyl-mercury from sediments for gas chromatograph/ion trap mass spectrometric analysis. They obtained the optimal conditions for MeHg extraction in an aqueous thiourea solution of 0.5% m/v, using a solid to liquid ratio 1:8, the leaching time was 50 min. The ultrasound-assisted leaching procedure is reported to be an attractive alternative to the HCl procedure because of its rapid speed, simple and selective, the capability of providing a cleaner extraction and the absence of degradation reactions.

An acid leaching process was developed [103] to achieve $\approx 100\%$ extraction of vanadium and nickel from Orinoco crude. The use of ultrasonics during acid leaching improves vanadium extraction from

a control of 73% recovery to 85%. The recovery is found to improve as a function of the ultrasonic energy applied.

The application of ultrasound was found to aid precious metal recovery from waste products including industrial, municipal and mine wastes [64]. The recovery of gold from resin was enhanced by ultrasonic waves and the resin elution process appears to be economical by using ultrasonic units [64]. Ultrasonic aided leaching was carried out on leach residues of electronic scrap to recover gold and silver [104]. During these attempts about 38% of copper was extracted in 20% H_2SO_4 during the first 30 min in the presence of ultrasound, but subsequent dissolution of copper was very slow, yielding only a value of 41% in 240 min, over the same period of 240 min silver extraction was less than 1%. However, when HNO_3 is added from 0 to 10 ml a gradual rise from 38 to 94% in recovery of Cu and a co-extraction of Ag from 1 to 7% was noticed in 240 min leach time. Whereas under the conventional pressure leaching optimum conditions like temperature 80–90°C, pressure 50–80 psig, in 3 leach cycles of 4 h total duration, the total Cu extracted [104] was 89.8% and <0.0006% of Ag. This study reveals, even though ultrasonically aided leaching is superior over conventional pressure leaching, it is not adequate for complete extraction of noble metals.

Newman et al. [17] formulated a model contaminated soil in the form of a granular pieces of brick impregnated with copper oxide. A comparative study using a tray shaken conventionally and with ultrasonic irradiation resulted in 40% and 6% of Cu removal respectively. The cleaning effect of ultrasound is responsible for the improvement. Caldwell et al. [18] studied using five highly concentrated contaminants of metal finishing residues and compared the performance of metal dissolution by several methods including an ultrasonically agitated version. They established ultrasonics as an accelerated test method because it can break the liquid boundary layer surrounding individual waste particles ensuring a maximum concentration gradient between solid and liquid phases.

8. PROPOSED LEACHING MECHANISM

From the above review it is obvious that ultrasound has definitely improved the yields in the extraction of various metals from their ore bodies, residues etc. However, the exact mechanism is not fully understood.

Laboratory studies of conventional leaching systems indicate that surface chemical reactions are often rate-controlling. The main factors of reaction rate in leaching indicate that:

- (i) the reaction rate is proportional to reactive mineral surface area, and
- (ii) the reaction rate is highly temperature dependent.

Further it has been shown that the reaction rate in leaching does not depend upon

- (i) agitation, provided there is enough to keep particles in suspension, and,
- (ii) on solution concentration of products.

The region of partially leached mineral particle, without sonication is illustrated in Figure 9a with an assumption that the rate of reaction of individual mineral particles is fast enough. In this model [105] the spherical ore matrix was divided into j concentric shells of thickness r , with $j = 1$ corresponding to the centre and $j = n$ to the outer edge of the spherical matrix particle. In this model during the course of reaction, a reaction zone of thickness moves topochemically inward. A steady state diffusion occurs through the reacted outer region and is equal to the rate of reaction within the reaction zone itself. It is assumed that the effective area of mineral particles within the moving reaction zone is constant. The effective area is also assumed to be independent of the mineral particle—size distribution, since new particles in each size fraction will begin to leach at the leading edge of the reaction zone.

While any leaching phenomenon follows the above route, ultrasound follows entirely a different path. The effect of ultrasound on the course of leaching is hypothesised by the authors in the following way. Ultrasound is mediated through cavitation bubbles, generated for leaching of metals from ore particles. Each cavitation bubble acts as a localised “hot spot” generating temperature [106,107] of more than 5000 K and pressures in excess of 100 MPa. The implosion happens with a collision density of 1.5 kg cm^{-2} and pressure gradients of 2 Tpa cm^{-1} with life times shorter than $0.1 \text{ }\mu\text{s}$ and cooling rates above 10^{10} K s^{-1} . Another study [108] on cavitation thermometry indicated temperatures of the order of 20 000 to 100 000 K would be generated instantaneously for a fraction of time. High temperatures and pressures are attained [109] inside the cavitating bubbles when they collapse. The cavitation bubbles collapse asymmetrically in the vicinity of solids. Asymmetric collapse leads to formation of high-speed micro-jets. The micro-jets can enhance transport rates, the increase of surface area through pitting as well as particle fragmentation through collisions. Also during the explosion of cavitation bubble, pressures of very large magnitude are generated and shockwaves occur in the narrow region on the surface of the particle. These micro-explosions cause particle cracking, through which the leaching agent enters into the interior of particle by capillary action and thereby improves the leaching phenomenon.

Figure 9b shows the particle undergoing reaction in the leaching medium under the influence of ultrasound or sonication. Ultrasound can be transmitted through any substance which possesses elastic properties. There is no

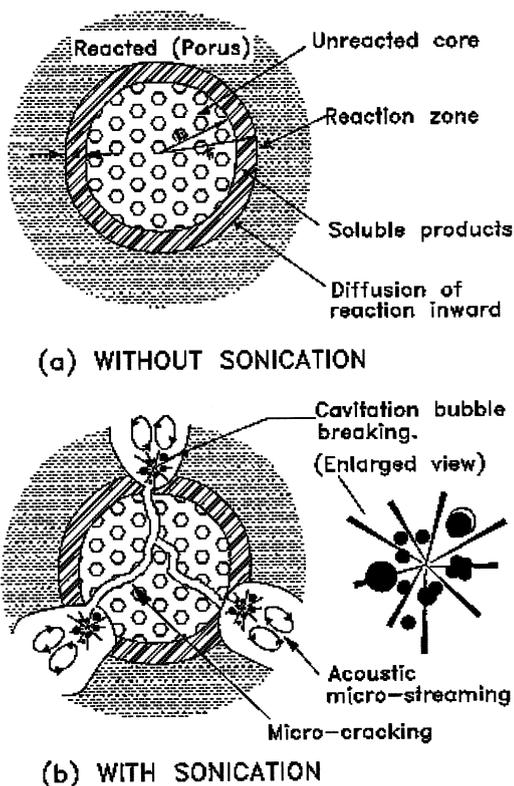


Figure 9. Illustration of metal leaching from mineral particles (a) without sonication (b) with sonication.

direct coupling of the acoustic field with ore particle or chemical species, as the wave-lengths are much greater than the molecular dimensions.

As shown in Figure 9b, during the breaking of the cavitation bubble, the reaction zone consisting of the layer of soluble metals, would also break, causing an acoustic streaming effect which disturbs the existing steady-state diffusion resulting in improvement in leaching. The dissolution rate would be further enhanced due to increased mineral surface area through pitting as well as ore particle fragmentation caused by acoustic cavitation.

As mentioned earlier the cavitation bubble generates very high temperatures and significant changes in pressure in the reaction vessel for a very short time of the order of $0.1 \mu\text{s}$. Due to the high temperature and pressure gradients caused, the leaching rate is therefore expected to be enhanced as the leaching process is highly temperature dependent. Even at these high temperatures and high pressures the reaction vessel does not melt or explode,

because cavitation is a localised phenomenon, occurring on the micro scale, and the energy released is swiftly dissipated in to the bulk mixture.

High intensity ultrasound can cause rectified diffusion. When ultrasonic energy is well coupled to the ore particles to be leached the material is subjected to a rapid series of contractions and expansions at a frequency of the ultrasonic wave. At each contraction the ore particle releases a minute quantity of leach solution that previously entered into micro-cracks of the ore particle. As the operation takes place several thousand times in a second an appreciable amount of leach solution is migrated. Thus, diffusion through pores to the reaction zone (in Fig. 9b) would be enhanced by an ultrasonic field resulting in larger values of rate of reaction. Thus, ultrasound can improve the leaching rate over the conventional method.

9. BENEFITS OF ULTRASONIC LEACHING

- Enhances particle fragmentation and deagglomeration. Increased instantaneous particle velocity improves wetting and liquid–solid interface dynamics. Agglomerated particles are set apart for chemical activation on new clean surfaces. Particles are individually scrubbed into the micron domain.
- Significantly increases mass transfer rates and molecular diffusion.
- Reduces reagent consumption due to molecular mixing.
- Minimises other catalytic sources requirement.
- Application of ultrasound lowers the operating parameters like temperature, pressure and duration.
- Ultrasound significantly enhances the leaching rate, however, below a critical particle size acoustic waves do not effect the leaching process.

10. SONICATION SYSTEM FOR LEACHING

10.1 Recommended Ultrasonic Parameters

The use of ultrasonic waves in metallurgy was viewed as a convenient technique for dissolving materials. To carry out leaching applications in any sonication system two components are essential: (1) an ore slurry medium and (2) an ultrasonic device. In general, an ultrasonic device consists of a generator and a transducer with an emitter. While the generator is used to convert the electricity at line frequency to electrical energy at the

ultrasonic frequency, the transducer converts this energy into ultrasonic vibrating energy and this vibration is transmitted by an emitter into the reaction medium. Ultrasound can be introduced into a system either by immersing the ultrasonic source in the leaching medium directly (direct sonication) or by dipping the vessel containing the ore and leachant mixture into a tank containing sonicated liquid (indirect sonication) [16,110]. As the benefits of the use of ultrasound in leaching operations have become more apparent, equipment that can be operated continuously on a large scale are clearly needed. Some of the major question marks which were associated with industrial scale leaching can now be erased. Although some commercial equipment is available for leaching, there are drawbacks like reproducibility and control of experiments. To derive the full potential of the benefits of applying ultrasound for leaching of metals purpose-built sonochemical reactors are necessary. Therefore, to circumvent some of the issues the authors conceived and recommended the following four key features for leaching of metals ultrasonically. Other applications can be in soil decontamination etc.

10.1.1 Transducer Type

Piezoelectric transducer should be preferred over magnetostrictive and other types because

- of their high conversion efficiency of electrical to mechanical energy.
- they have been consistently tested for more than 10 000 h of continuous use which show no signs of deterioration.
- there is no separate water cooling of transducer is necessary.
- if one or many transducers used in an piezoelectric array fail during continuous process it is not necessary to shut down the system immediately. Replacements can be made during a periodical maintenance schedule. It is possible to replace any defective transducers individually.

The cavitation erosion caused under high energy and prolonged sonication can be minimised with appropriate reactor design and by using new materials for construction [111], which can be up to 500% more resistant to cavitation. These features practically contribute greatly in process economics, particularly in leaching unit operation.

10.1.2 Recommended Frequency

Even though wide frequencies, ranging from 18 kHz to 2 MHz have been used for metal leaching applications, the majority have used frequencies of

around 20 kHz, since the high frequency waves are more easily attenuated and dampened. Using a conventional single frequency the yields cannot be increased without limit, even when an acoustic intensity 10 times the threshold was applied. But by the use of bi-frequency ultrasound, yields were improved due to its ability to induce cavitation efficiently. So two frequencies are better than one, as further more metal recoveries are obtained with dual frequency [112]. Preferably when the two piezoelectric transducers with 16 and 20 kHz frequencies are mounted coaxially and located exactly in opposite direction on two parallel plates. Under these conditions any ore slurry flowing between the plates is subjected to an ultrasonic intensity greater than that expected from simple doubling of a single plate intensity. The ultrasound “reverberates” and is magnified in its effect. As a result, strong mechanical force has a propensity to break up ore particles at these micro fissure locations, exposing sorbed metals for dissolution that would otherwise remain encapsulated in the ore bodies. So the system suits well and applicable for leaching process.

10.1.3 Pulsed Ultrasound for Energy Saving

Using continuous wave ultrasound for leaching application the total energy consumed is high and may not be offset even by the substantially lower extraction time. However, it was found that continuous ultrasound was not required for the extraction of metals [47,113]. Improved extractions are reported [114] by the application of pulsed ultrasound. This phenomenon can be explained by the micro-droplets formed in the presence of ultrasound, which did not disappear immediately after the ultrasound was turned off. The interfacial area produced allowed extraction to continue even in the absence of ultrasound. When a significant number of droplets coalesced, ultrasound was again required to form a new batch of droplets and to continue extraction.

Pesic [115] has shown that whatever nickel could be extracted (in liquid–liquid extraction) with 61 W of continuous ultrasound, the same amount of nickel could be obtained by only with 2.66 W pulsed ultrasound. Similarly, for extracting the same amount (70%) of gallium (in solid–liquid extraction) 39 W of ultrasound could be replaced with 14 W of pulsed ultrasound. As seen, the energy savings could be attractive, but lower in solid–liquid extraction than in liquid–liquid extraction. Therefore, pulsed ultrasound is always preferable for leaching applications due to substantial energy savings. In the absence of pulsed ultrasound, the authors recommend that separation between the two neighbouring modular systems, operating with continuous ultrasound should be twice the length of each individual module.

10.1.4 Combination Method

The initial rate of leaching with conventional mechanical agitation is similar to ultrasonic agitation. But, the leaching rate was lowered significantly after a brief period (say 10 min) of time by mechanical agitation. As such, ultrasound is found to be effective in the leaching of metals during the last phase, in order to maintain the higher leaching rates as well as to extract more metal values than with conventional methods. Two advantages can be derived by this method. One is considerable energy savings in the process and the second is enhancement of transducer durability. As such, the pre-treatment of ore slurry with conventional agitators, i.e. the primary leaching followed by ultrasonic leaching is recommended. This combination technique is more promising. Similar recommendations have been given earlier for other ultrasonic applications like ore grinding [116], atomisation of liquid metals [117,118], etc.

10.2 Health and Safety Aspects

When a laboratory or industrial scale ultrasonic reactors are in operation they invariably generate [119] audible noise associated with harmonic, sub-harmonic and broadband noise of the fundamental frequency. Sometimes the noise levels are more than 100 dBA. Radiating noise of such high levels effect the health. The major harmful effect of noise is to impair hearing, sometimes causing lasting damage. It can cause many physiological and psychological effects; stress related ailments, nervous irritability, difficulty in falling asleep, blood circulation, digestive and metabolic activity etc. The health and safety aspects associated with the use of ultrasound is of paramount importance, since strict noise regulations are imposed by the Federal, State and other local agencies. So it is essential to reduce the implant noise. Three ways of guarding against radiated noise by which it is possible to reduce noise levels down to 75 dBA are

- (i) Suppressing the noise generated at the source by producing anti-noise at the same amplitude and frequency but with anti-phase.
- (ii) By means of an acoustic enclosure in the form of box around the apparatus.
- (iii) Using ear muffs and ear plugs.

11. CONCLUSIONS

It is now established that ultrasound can appreciably accelerate a leaching processes. The enhancement of reaction rate depends on a number

of factors like frequency, intensity, time of irradiation of ultrasound as well as physical properties of lixiviant used and the nature of ores. Response to the ultrasonic field is different for different minerals present in an ore, and thus ultrasound can aid selective leaching. For leaching applications the frequency and intensity of operation at 18 kHz and 4 W cm^{-2} similar metal recoveries as at 2 MHz and 15 W cm^{-2} , suggesting that lower frequency of operation is more effective for large scale applications. It is preferable to express the ultrasonic intensity with kW m^{-3} or J cm^{-3} .

Ultrasound accelerates leaching processes through the following effects.

- (a) Passivation of product layer.
- (b) Enhanced stirring and therefore, enhanced mass transfer.
- (c) Change in the characteristics of mineral surface, cracking.
- (d) Inter particle collisions etc.

The inherent and possible limitations of ultrasound on leaching were described in this review. Homogeneous sonochemistry typically is not a very energy efficient process compared to heterogeneous sonochemistry, which is several orders of magnitude better.

Use of ultrasonic extraction procedure in environmental analytical chemistry will become more widespread, owing to its simplicity, ease of use, speed, capable of providing more clean extraction and the absence of degradation reactions; and enhanced safety when compared with other more traditional sample preparation procedures involving concentrated strong acids and elevated temperatures for rigorous digestion. Therefore, the use of ultrasound in on-line leaching of metals from soils for the replacement of traditional analytical methods is of great practical interest.

At present the application of ultrasound for leaching of ores and minerals is at its laboratory and bench scale level. For processing the both lean and complex sulphide ores on an industrial scale, the technique would be increasingly used in future as more and more efficient equipment is available commercially.

Undoubtedly much remains to be done for industrial use of ultrasound for leaching applications and combined efforts are to be coherently made by Physicists, Chemists, Metallurgists and Engineers to achieve this. Power ultrasound will be considered as a viable option for metal extraction on a commercial scale in the near future.

ACKNOWLEDGMENTS

The authors are thankful to the Director, Regional Research Laboratory, Bhubaneswar for permission to publish this. They thankfully acknowledge Mr A. S. Rao for helping in preparation of graphics.

REFERENCES

- [1] Abramov, O. V. *High Intensity Ultrasound: Theory and Industrial Applications*, Gordon & Breach, London, 1998.
- [2] Mason, T. J. *Phil. Trans. R. Soc. Lond.*, A357 (1999) 355.
- [3] Suslick, K. S. (ed.), *Ultrasound: Its Chemical, Physical and Biological Effects*, VCH Weinheim, 1988.
- [4] Rosenberg, L. D. *High Intensity Ultrasonic Fields*, Plenum, New York, 1971.
- [5] Fredrick, J. R. *Ultrasonic Engineering*, Wiley, London, 1965.
- [6] Polyukhin, P. I. *The Use of Ultrasonics in Extractive Metallurgy*, Techni copy: Stonehouse, UK, pp. 157 (translated from Russian) 1978.
- [7] Diez-Barra, E., De la Hoz, A., Diaz-oritz, A., and Prieto, P. *Synlett*, November, (1992) 893.
- [8] Luche, J. L., Einhorn, C., and Einhorn, J. *Synthesis*, (1989) 787.
- [9] Suslick, K. S., and Doktyez, S. J. In Mason, T. J. (ed.), *Advances in Sonochemistry*, Vol. I. JAI press Ltd., London, 1990, pp. 197–230.
- [10] Vasil'ev, V. V., and Kovenya, A. V. *Chem. Abstr.*, 71 (1969) 119/325.
- [11] Sastri, V. S., and Mackinnon, D. J. *J. Scient. Ind. Res.*, 36 (1977) 379.
- [12] Medvedev, A. S., and Korshunov, B. G. *Modern methods for intensification of hydrometallurgical process*, Tsvetn. Met. (Moscow), 9, 10–19 (Russ.) *Chem. Abstr.*, 120 (1993) R 275964J.
- [13] Rivalier, P., Ros, P., Molina, I., and Duvoux, J. *Continuous solvent extraction combined with ultrasonic treatment*, Eur. Pat. Appl. EP 583,200. *Chem. Abstr.*, 120 (1994) P 302530g.
- [14] Zhao, W. *Kuangye* (Beijing) 5(4) (1996) 51.
- [15] Swamy, K. M., SarveswaraRao, K., Narayana, K. L., Murty, J. S., and Ray, H. S. *Min. Proc. Ext. Met. Rev.*, 14 (1995) 179.
- [16] Narayana, K. L., Swamy, K. M., Sarveswara Rao, K., and Murty, J. S. *Min. Proc. Ext. Met. Rev.*, 16 (1997) 239.
- [17] Newman, A. P., Lorimer, J. P., Mason, T. J., and Hutt, K. R. *Ultrason. Sonochem.*, 4 (1997) 153.
- [18] Caldwell, R. J., Stegemann, J. A., and Chao C. C. *Stabilization and Solidification of Hazardous, Radio Active and Mixed Wastes*, ASTM Spec. Tech. Publ., STP 1240, 413–425, 1996.
- [19] Misra, M., and Mehta, R. K. *J. O. M.*, 47 (1995) 45.
- [20] Keil, F. J., and Dahnke, S. *Hung. J. Ind. Chem.*, 25 (1997) 71. & *Ind. Eng. Chem. Res.*, 37 (1998) 848.
- [21] Dahnke, S., Swamy, K. M., and Keil, F. J. *Ultrason. Sonochem.* 6 (1999) 31 & 221.
- [22] Migeot, J. L. Y. In Kuhl, P. K., and Crum, L. A. (eds), *Proc. of the 16th Int. Congr. on Acoustics with the 135th meeting of the Acoustical Society of America 1998*, Vol. 3, pp. 1539–1540. Acoustical Society of America.
- [23] Suslick, K. S., Doktyez, S. J., and Flint, E. B. *Ultrasonics*, 28 (1990) 280.
- [24] Riesz, P., Kondo, T., and Murali Krishna, C. *Ultrasonics*, 28 (1990) 295.
- [25] Suslick, K. S. *Scientific American*, 260 (1989) 80.
- [26] Leighton, T. G. *The Acoustic Bubble*, Academic Press, London, pp. 531–551, 1994.
- [27] Wilhelm, A. M., Contamine, F., Berlin, U., and Delmas, H. *Measurement of liquid-solid mass transfer in ultrasonic reactor*. Ultrasonics International 93 Conference Proceedings 715, Butterworth, London, 1993.
- [28] Ratoarinoro, F., Contamine, Wilhelm, A. M., Berlin, J., and Delmas, H. *Chem. Engg. Sci.*, 50 (1995) 554.
- [29] Steven, F. M., Lawrence, C. F. *J. O. M* May (1998) 34–37.
- [30] Eltseton, B. S., and Berlin, A. A. *Poly. Sci. USSR*, 5 (1964) 668.

- [31] Zhen, Q., Richard, D. S., and William, G. P. *Colloids Surf. B* 9(5) (1997) 239.
- [32] Beck, M. T. *Pure Appl. Chem.*, 70(10) (1998) 1881.
- [33] Krstic, B., and Stanojevic, D. *Tehhnika (Belgrade)* 53(3) (1998) RGM1.
- [34] Abramov, O. V., Borisov, Yu. Ya., and Oganyan, R. A. *Sov. Phys. Acoust.*, 33(4) (1987) 339.
- [35] Swamy, K. M., Narayana, K. L., and Murty, J. S. *Fuel*, 68 (1989) 387.
- [36] Swamy, K. M., Narayana, K. L., and Murty, J. S. *Drying Technology.*, 6(3) (1988) 501.
- [37] Westervelt, P. J. *J. Acoust. Soc. Amer.*, 32(3) (1960) 337.
- [38] Boucher, R. M. G. *Brit. Chem. Engg.*, 15 (1970) 363.
- [39] Naito, T., Ohdaira, E., Masuzawa, N., and Ide, M. *Jpn. J. Appl. Phys. Part I.*, 37(5B) (1998) 2990.
- [40] Vasil'ev, T. D. Kan., Muratova, Fazovyi *Khim. Analiz Rudi Mineralalov*, Leningr. Gos. Univ. 50-5, *Chem. Abstr.*, 57 (1962) 14774a
- [41] Rusikhina, I. P., and Ozolin, L. T. *Chem. Abstr.*, 79 (1973) 339194r.
- [42] L. Ozolin, L., and Rusikhina, L. P. *Zh. Met., Abstr.*, no.8G248, *Chem. Abstr.*, 70 (1968) 89853w.
- [43] Khavskii, Neue Huette, 17(10) 577–580 (Ger). *Chem. Abstr.*, 78 (1972) 19129f.
- [44] Yu. D. Matyskin, *Tr. Irkutsk. Politekh. Inst.*, no.37 (Pt. 1) 90–98 (Russ). *Chem. Abstr.*, 72 (1967) 124125a.
- [45] Rudenko, K. *Sb. Probl. Fiz. Khim. Protessay Gorn. Proizvod.*, 1971, 68–72 (Russ). From Ref. *Zh. Met. Abstr.*, no. 3G222., *Chem. Abstr.*, 1972, no. 77, 142677q.
- [46] A. I. Orlov, *Improvement of the leaching process.*, *Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall.*, 185–189 (In Russian), *Chem. Abstr.*, 82 (1975) 143246p.
- [47] Rao, K. S., Narayana, K. L., Swamy, K. M., and Murty, J. S. *Metall. and Materials Trans.*, 28B (1997) 721.
- [48] Suslick, K. S., Schubert, P. F., and Goodal, J. W. *IEEE Ultrason. Symp. Proc.*, 1981, 612.
- [49] Swamy, K. M., and Narayana, K. L. To be communicated.
- [50] Chizhikov, M. N., Novitskii, B. G., Fridman, Y. M., Khavskii, N. N., and Smirnov, Yu. R. *Use of joint action of ultrasonic and electric field to improve leaching metals.*, *Sb. Mosk. Inst. Stali Splavov.*, no.77, 94 (In Russian). *Chem. Abstr.*, 82 (1975) 173957p.
- [51] Orlov, A. I., and Matyskin, Yu.d. *Kontr. Avtomat. intensifik Technol. Protessov*, (Met. Obogashch. Khim. Tech). 1972, No. 1,50–58 (Russ). From Ref. *Zh. Met.*, Abstr. no. 3G273., *Chem. Abstr.*, 80 (1974) 17782f.
- [52] Krasnozhen, S. V., Khavskh, N. N., and Zelikman, Yu. L. *Ref. Zh. Khim Abstr.*, no. 13G 186, *Chem. Abstr.*, 77 (1972) 42624b.
- [53] Gramatikov, M. V., and Mekhandzhiev, M. R. *Chem. Abstr.*, 71 (1969) 12748m.
- [54] Gramatikov, M. V., and Mekhandzhiev, M. R. *God. Nauchnoizsled. Inst. Tsvet. Met. Plovdiv.*, 8, pp. 91–103 (Bulg.) *Chem. Abstr.*, 79 (1973) 69043q.
- [55] Gramatikov, M. V., and Ivanovskii, M. D. *Sb. Mosk. Inst. Stali Splavov*, 77, 81, *Chem. Abstr.*, 82 (1974) 46564h.
- [56] Slaczka, A. ST. *Ultrasonics*, 24 (1986) 53.
- [57] Barrera-Godinez, J. A., Okeef, T. J., and Watson, J. L. *J. Minerals Engineering.*, 5 (1992) 1365.
- [58] Hunicke, R. L. *Ultrasonics*, 28 (1990) 291.
- [59] Holl, R. A. *Apparatus and processes for the treatment of materials by ultrasonic longitudinal pressure oscillation. US Patents*, 4,071,225, January 31, 1978.
- [60] Sipos, I. *Cyanidation of silver and gold bearing ores. Rom. Patent.*, 55,914 Sept. 5th, 1973.
- [61] Fairbanks, H., Morton, W., and Wallis, J. *Precious metal recovery aided with ultrasound. precious Met. Proc. Int. Precious Met Inst. Conf.*, 9th 1985, 305-7. Ed-Edward D. Zysk and John A. Bonucci., (Publ. 1986).

- [62] Compagnie Francaise Metallurgie Aurifere. Brit. 757,718 (Sept.26,1956). *Chem. Abstr.*, 1957, 51,7284c.
- [63] Yannopoulos, J. C. (ed.) *The extractive metallurgy of gold*, Van Nostrand Reinhold, New York, 63–164, 1991.
- [64] Steensma, R. S. In Torma, A. E., and Gundiler, I. H. (ed), *Precious and Rare Metal Technologies*, Elsevier, Oxford, 1989, pp. 175–182.
- [65] Steensma, R. S. *Application of ultrasonics in the extraction of gold and silver ores*, Randol Gold Forum 88, Lakewood, Colorado, 1988.
- [66] Jin Zuomei., Wang Lisheng., and Liao Wei. In Mishra Manoranjan (ed), *Extraction of Silver from Ag-rich Complex Sulphide Ore*, Sep. Processes proc. Symp., 1995, pp. 269–274.
- [67] Zhao, W. *Kuangye (Beijing)*., 1995, 4(3) 60(Ch.), CA. 124, 122650m.
- [68] Pugin, B. *Ultrasonics*, 25 (1987) 49.
- [69] Khavskii, N. N., and Bershitskii, A. A. *Chem. Abstr.*, 72 (1970) 69559e.
- [70] Bershitskh, A. A., Agranat, B. A., Vil'chik, S. S., Khavskh, N. N., and Shmalei, B. N. *Chem. Abstr.*, 74 (1971) 144810q.
- [71] Bershitskh, A. A., Khavskii, N. N., Shmalei, B. N., Yakubovich, I. A., Kal'kov, A. A., and Rumyantsev, V. K. *Sb. Mosk. Inst. Stali Splavov*, No. 60, 193–7 (Russ.) *Chem. Abstr.*, 75 (1971) 24116s.
- [72] Khavaskh, N. N., Bershitskh, A. A., Vilchik, S. S., and Shmalei, B. N. *Chem. Abstr.*, 78 (1973) 6713s.
- [73] Bershitskh, A. A., Khavskii, N. N., Shmalei, B. N., and Smirnov, Yu. R. *Chem. Abstr.*, 78 (1973) 60260e.
- [74] Bershitskii, A. A., Khavskii, N. N., Shmalei, B. N., and Grizatulina, R. A. *Priment Ultrazvka Met. Protgesska*, 69–72 (Russ). *Chem. Abstr.*, 80 (1974) 16992n.
- [75] Bershitskii, A. A. *Sb. Nauchn. Tr-Sredneaziatt Nauchno-Issled Proekt. Inst. Tsvetn. Metall.*, 11, 1314 (Russ). *Chem. Abstr.*, 85 (1976) 127861h.
- [76] Bershitskii, A. A., and Shmalei, B. N. *Sb. Nauchn. Tr-Sredneaziatt Nauchno-Issled Proekt. Inst. Tsvetn. Metall.*, 11, 126–31 (Russ). *Chem. Abstr.*, 85 (1976) 127680g.
- [77] Terenin, E. P., Zelikman, A. N., Khavskii, N. N., and Shmalei, B. N. *Action on elastic vibrations on films of the reaction products from the decomposition of scheelite with nitric acid*. *Sb. Moosk. Inst. Stali Splavov*. No.133,13 (Russ). *Chem. Abstr.*, 96 (1982) 107745f.
- [78] Bershitskii, A. A., Khavskii, N. N., Gural'nik, N. N., Shmalei, B. N., and Yakubovich, I. A. *Chem. Abstr.*, 80 (1974) 28905z.
- [79] Khavskii, N. N., Smirnov, Yu. R., Egorv, B. L., and Terenin, E. P. *Use of optical microscopy for studying the effect of high power ultrasonic vibrations on the solid phase during leaching of scheelite concentrate with sodium flouride.*, *Sb. Mosk. Inst. Stali Splavov*. No. 117, 22(Russ). *Chem. Abstr.*, 91 (1979) 178846x.
- [80] Smirnov, Yu. R., Liskovich, V. A., Khavskii, N. N., Meerson, G. A., and Boiko, A. I. *Primer. Ultrazvuka Met. Protesaka*, 1972, 98–102 (Russ). *From Ref. Zh. Met., Abstr.*, 5G267. *Chem. Abstr.*, 78 (1972) 60748.
- [81] Srikanth, V., Roy, R., and Komarneni, S. *Mater. Lett.*, 15(1–2) (1992) 127.
- [82] Kortnev, A. V., Vartanov, V. G., Serdenko, V. V., Antipin, L. N., and Drozdenko, V. A. *Akust. Ultrazvukovaya Tekhh.*, no. 7, 21–27(Russ). *Chem. Abstr.*, 79 (1972) 56322e.
- [83] Kortnev, A. V., Olesov, Yu. J., Serdenko, V. V., Vartanov, V. G., and Drozenko, V. A. *Akust. Ultrazvuk Tech.*, 10, 23–5 (Russ), *Chem. Abstr.*, 84 (1975) 77343f.
- [84] Pestic, B. *Chem. Engg.*, 94(3) (1987) 10.
- [85] Khavskii, N. N., Yakubovich, I. A., Agravat, B. A., Kirillov, O. D., and Tsvetn, Vasil'ev. *Met.*, 6(3) 106110, *Chem. Abstr.*, 60 (1963) 1365c.
- [86] Vasil'ev, V. V., and Kovenya, A. V., Shutova. *Chem. Abstr.*, 66 (1967) 21219f.
- [87] Mamina, A. V., Tyutynnik, N. D., Dokshira, I. D., and Akopova, K. S. *Tsvet. Metal.*, 44(11) 75–77 (Russ), *Chem. Abstr.*, 76 (1971) 48497.

- [88] Gasgnier, M., Albert, L., Derouet, J., Beaury, L., and Caro, P. *C. R. Acad. Sci., Ser 11, Mec., Phys., Chim., Astron.* 318(7) 915920, *Chem. Abstr.*, 121 (1994) 14374d.
- [89] Martinus, V., and Jankech, D. *Czech Patent* 133, 206, 15 July, 1969., *Chem. Abstr.*, 73 (1970) 68869c.
- [90] Tyutyunnik, N. D., Dokshina, I. D., and Akopova, K. S. *Izy. Vyssh. Ucheb. Zaved., Tsvet Metl.*, 16(2) 13–18 (Russ), *Chem. Abstr.*, 80 (1973) 5885d.
- [91] Zelikman, Yu. L., and Krasnozhen, S. V. *Tsvet .Metal., Mosk.*, 44(9) 57–9 (Russ). *Chem. Abstr.*, 76 (1971) 16812w.
- [92] Krasnozhen, S. V., Khavskh, N. N., and Zelikman, Yu.L. *Ref. Zh. Khim* 1971, Abstr. no. 13G 186, *Chem. Abstr.*, 77 (1972) 42624b.
- [93] Andreev, P. F., Rogozina, E. M., and Rogozin, Yu. M. *Zhur. Fiz. Khim.*, 34, 24292430, *Chem. Abstr.*, 55 (1960) 7963d.
- [94] Munoz Ribadeneira, F. J., and Munoz Candelario, R. *Politecnica*, 1(2) 15–39. *Chem. Abstr.*, 71, (1968) 52432c.
- [95] Dedek, W., Weil, L., and Niessner, R. *Fresenius Environ. Bull.*, 5(5/6) (1996) 241.
- [96] Babic, S., Petrovic, M., and Kastelan -Macan, M. *J. Chromatogr.*, A823 (1 + 2) (1998), 3.
- [97] Evans, J., Kaake, R. H., Orr, M., and Watwood, M. *J. Soil Contam.*, 7(5) (1998) 589.
- [98] Sporn, R. *PTS- Manuskr.*, (PTS-MS 61, Wasser - und Umwelttechnik: Grundlagen), 1997, 14/1–14/11.
- [99] Ashley, K. *Tr AC, Treuds Anal. Chem.*, 17(6) (1998) 366.
- [100] Millson, M., and Ashley, K. *Meas. Toxic Related. Air Pollut.*, Proc. Spec. Conf. 1, 1997, 304.
- [101] Swamy, K. M., Muralidhar, J., Narayana, K. L., and Murty, J. S. *J. Acoust. Soc. India*, 25 (1997) IV2.1.
- [102] Hu, G., Wang, X. *Anal. Lett.*, 31(8) (1998), 1445.
- [103] Hepworth, M. T., and Slimane, R. *J. Solid Waste Technol. Manage.*, 24(2) (1997) 104.
- [104] Hilliard, H. E., Dunning, B. W. Jr., Kramer, D. A., and Soboroff, D. M. *Hydrometallurgical treatment of electronic scrap to recover gold and silver*. Report of investigation 8940, Bureau of Mines United States Dept. of the interior.
- [105] Rousseau, R. W. (ed.) *Hand Book of Separation Process Technology*, John Wiley & Sons. New York, 1987.
- [106] Mason, T. J., and Cordemans, E. D. *Trans. Inst. Chem. Engrs. Part A Chem. Engg. Res and Design*, 74 (1966) A5, 551.
- [107] Lickiss, P. D., and McGrath, V. E. *Chemistry in Britain*, 32(3) (1966) 47.
- [108] Bernstein, L. S., Zakin, M. R., Flint, E. B., and Suslick, K. S. *J. Phys. Chem.*, 100 (1966) 6612.
- [109] Suslick, K. S., Doktycz, S. J., and Flint, E. B. *Ultrasonics*, 28 (1990) 280.
- [110] Mason, T. J. *Practical Sonochemistry. User's Guide to Applications in Chemistry and Chemical Engineering*, Ellis Horwood, London, 1991.
- [111] *Colin McCaul Chem. Engg.*, 103 (6) (1996) 23 & 25.
- [112] Swamy, K. M., and Narayana, K. L. *Intl. Conf. and Exhibition on Ultrasonics*, New Delhi, Dec. 2–4, 1999.
- [113] Pesic, B., and Zhou, T. *Metall and Materials Trans.*, 23B (1992) 13.
- [114] Swamy, K. M., and Narayana, K. L. *J. Acoust. Soc. India*, 27 (1999) 117.
- [115] Pesic, B., and Zhou, T. *J. O. M.*, 41(6) (1989) 42.
- [116] Mason, T. J. *Chem. & Industry*, 2nd Nov. (1998), 878.
- [117] Abramov, O. V., Borisov, Yu. Ya., Oganyon, R. A., and Podolskii, S. L. *Sov. Phys. Acoust.*, 27 (1981) 445.
- [118] Abramov, O. V. *Ultrasound in liquid and solid metals*, CRC Press, London, 1994. Mcqueen, D. H. *Ultrasonics*, 26 (1988) 286.

This Page Intentionally Left Blank

ULTRASONIC PHASE SEPARATION

Johannes F. Spengler, Martin Jekel
and W. Terence Coakley

OUTLINE

1. Introduction	182
1.1 General	182
1.2 Historic Overview of Research on Ultrasonic Standing Wave Effects in Dispersions	183
2. Phenomena and Theory of Suspension Behavior in Ultrasonic Standing Waves	186
2.1 Particle Aggregation by the Ultrasonic Radiation Force	187
2.2 Aggregation Disturbance by Acoustic and Convective Streaming	190
2.3 Particle–Particle Interaction Forces	194
3. Ultrasonically Assisted Sedimentation Processes	195
3.1 Ultrasonic Standing Waves in the Context of Phase Separation Technology	195
3.2 Separation Efficiency	195
3.3 Reactor Design and Operation	197
4. Results of Lab- and Pilot-scale Experiments	199
4.1 Separation of Particles from Aqueous Suspensions	199
4.2 Thickening of Pre-settled Sludge	213

Advances in Sonochemistry

Volume 6, pages 181–220.

© 2001 Elsevier Science B.V. All rights reserved.

5. Feasibility of Implementation on an Industrial Scale	215
6. Conclusions	216
Acknowledgments	218
References	218

1. INTRODUCTION

1.1 General

Phase separation processes are an important and vital issue in many fields of chemical and environmental engineering, biotechnology and analytical science. A large number of separation technologies are available (e.g. sedimentation, flotation, filtration, centrifugation). The decision to apply a particular process is influenced by: (i) the properties of the dispersion (e.g. dispersing and dispersed phase, concentration and the size distribution of the dispersed phase), (ii) the goal of the separation (clean dispersing phase or purified dispersed material), (iii) the separation efficiency required of the process, and (iv) the discharge–production quantity. Conditioning processes are often employed in order to improve the performance of a separation. The addition of chemicals, which facilitate or accelerate aggregation of the dispersed phase, is a common method. Thus, the aggregates formed can be separated more easily because of their larger size. Examples for this method are the addition of salt and polymers in flocculation processes and of surfactants in emulsion splitting. A combination of different conditioning and separation methods is often necessary in order to achieve the desired result (e.g. centrifugation after a combined flocculation–sedimentation separation). This brief outline indicates the general importance, the widespread application and also the complexity of phase separation technology. Despite the fact that a large variety of approved processes are available, there is still a great interest in further development of established methods as well as introduction of advantageous alternative approaches. The application of ultrasound counts in the latter context as a possible conditioning method, which enhances the performance of a subsequent separation process. The non-cavitating ultrasonic standing waves (USSW), which will be the main topic of this contribution, induce forces, which can bring particles together and aggregate them. In this sense USSW suspension conditioning might be referred to as “physical flocculation”. Advantages of the USSW technology are seen in: (i) the physical, i.e. non-chemical, way it works, (ii) the non-touch and no-moving mechanical parts design of the reactors and (iii) a simple process control. The main force exploited is the acoustic

radiation force, which concentrates the particles in clumps. The aggregation of particles in suspension is most pronounced at frequencies in the lower megahertz range (about 2–3 MHz). Particle aggregation is sometimes disturbed by large-scale acoustic streaming, which can be avoided by appropriate reactor design and operation. However, acoustic streaming can be beneficial for thickening of already settled sludge, when mechanical movement of the sludge volume builds drainage channels. Frequencies in the mid kilohertz range (40–350 kHz) have been found to work best for this purpose.

The present contribution concentrates on the application of USSW to the conditioning of solid–liquid dispersions in conjunction with sedimentation. A historic overview of the fundamental and application research in this field will be followed by the introduction of the basic phenomena of particle concentration and aggregation in the standing wave and of the effect of large-scale streaming. Theoretical descriptions of the underlying mechanisms will be presented (Section 2). Principle design and operation methods for USSW–sedimentation processes will be outlined in Chapter 3 and results from recent lab- and pilot-plant experiments will be presented in Section 4. Part of the experiments investigated the separation of particle-containing waters in a continuous process, which aimed at the clarification of the suspending phase. Thickening of already settled sludge by USSW, which sought maximum solids concentration in the sediment, was examined in a lab- and a pilot-scale batch system. The findings will be compared with data reported in the literature. The feasibility of USSW application on a large-scale in environmental technology will also be discussed (Chapter 5).

1.2 Historic Overview of Research on Ultrasonic Standing Wave Effects in Dispersions

Standing waves have been investigated since about 1935 as a manipulation method for disperse systems [1,2]. The principal effect exploited, however, has already been described by Kundt and Lehmann in the 19th century [3,4]. They reported a structuring effect on dispersions in a standing sound wave, established by the interference of an emitted and a reflected wave. Aerosols were placed in a closed cylinder and it was seen that the solid particles gathered at well-defined positions in the standing wave field. These positions were periodically located half a wavelength apart from each other [3]. Similar experiments with aqueous suspensions were proposed by the same authors [4]. Kundt and Lehmann also observed that particles could be brought in close contact by pushing them into the pressure nodal planes of the standing wave. Particle concentration in these “bands” is considerably increased in comparison to a homogeneous particle

distribution in an unsonicated dispersion. Increased particle concentration can accelerate aggregation considerably because of the higher likelihood for particle–particle contacts.

1.2.1 Early Work on Aerosol Aggregation and Separation

Brandt and colleagues investigated, experimentally and theoretically, the aggregation of aerosols in a Kundt tube [1,5,6]. They calculated the oscillation amplitudes and phase shifts between the aerosol particles oscillating in the sound field and identified the importance of these effects for the aggregation process. Optimal frequencies for effective aggregation were found experimentally to lie between 1 and 50 kHz and the aggregation efficiency increased significantly with sound intensity.

1.2.2 Early Work on Suspension Conditioning

Söllner and Bondy (1936), who sonicated suspensions of quartz and water, emulsions of oil and water as well as tri-phase dispersions of oil, quartz and water, also picked up Kundt's and Lehmann's findings [2]. Söllner and Bondy benefited from the recent availability at that time of a high frequency USSW system (about 250 kHz). They observed that the solid quartz particles (density higher than water) were driven into planes at half wavelength separation (pressure nodes). The oil droplets (density lower than water) also collected in planes, but these were shifted by a quarter wavelength from the bands formed by the solid particles. The oil droplets were driven into the pressure antinodes. These findings were in agreement with the theory of the direct acoustic radiation force (DRF), that had recently been presented 1935 by King [7]. Söllner and Bondy additionally postulated the importance of different compressibility for particle behavior in USSW (theoretically treated by Yosioka and Kawasima in 1955) [8]. Söllner and Bondy also investigated experimentally the influence of the particle diameter on USSW aggregation. Larger particles moved considerably faster into the banding planes than smaller ones. No banding and aggregation was observed for particles smaller than 1 μm .

1.2.3 Fundamental Studies of Acoustic Streaming

The major aggregation disturbing effects are large-scale acoustic and thermal convective streaming. The first type is often called Eckart streaming or “quartz wind.” Eckart published a theoretical paper in 1948, in which he predicted this container-scale acoustically driven flow [9]. His predictions were experimentally verified by Liebermann one year later [10]. Large-scale

streaming exerts drag on the particles. This drag acts against the DRF, responsible for the banding of particles, and may drive particles out of these bands. The major efforts recently made in order to control this effect will be reported below.

The role of acoustic micro-streaming, as investigated by Rayleigh (scale about one wavelength) [11] and boundary layer Schlichting streaming (scale much smaller than a wavelength) [12] on particle behavior has not yet been completely clarified.

1.2.4 Recent Fundamental Work on Particle Behavior in USSW

After the rather active research period around 1935, few authors published results from research in USSW technology throughout the following three decades [8,13]. This situation changed dramatically in 1971 with a paper by Dyson and colleagues, in which they reported sonically induced (3 MHz) aggregation and clotting of blood cells in chick embryos [14]. The authors were primarily concerned about safety issues of the diagnostic and therapeutic use of ultrasound and sparked a number of research activities on cell aggregation and biological effects on suspended cells in USSW [15–17]. Fundamental studies on aggregation and particle behavior in USSW were also stimulated at that time [18–20]. Theoretical contributions investigated the influence of the DRF on suspended particles and considered the influence of Brownian motion [21] and the DRF potential structure in USSW fields of different geometry [22]. Sonically induced particle–particle interaction mechanisms, which contribute to particle aggregation, have been of interest to a number of authors [18,23–25]. Also, a theoretical criterion for onset of ultrasonically induced particle aggregation was derived [26]. The role of acoustically induced streaming on particle manipulation in USSW was also addressed [24,27]. Many recent contributions have brought further insights into the complex field of USSW manipulation of disperse systems. A large number of publications have theoretically investigated the non-linear nature of USSW fields as well as viscous and thermal influences on the DRF for a variety of geometric and operational conditions [28–33]. Combined theoretical and experimental studies investigated particle concentration in stationary [27] and quasi-standing waves [34]. Measurements of the axial DRF [35] and the lateral DRF component have also been reported [36,37].

1.2.5 Work on Application of USSW for Phase Separation Purposes

An overview of fundamentals and applications of the DRF in USSW for phase separation was given by Apfel in 1990 [38]. At that time a

considerable number of patents for acoustically assisted separation methods had already been awarded [39]. These achievements were largely supported by design advances in the sonication systems available. Comprehensive reviews have been published recently on fundamentals of USSW phase separation technology [40], design of USSW reactors [41] and on analytical applications [42]. A main emphasis of USSW applications is seen in filtration of cells from fermentation tanks [43–46] and analytical biotechnology [47]. A commercial USSW cell filter is already on the market [48]. A considerable number of different designs of USSW devices for suspended particle filtration [47,49–56] and fractionation [57,58] have been described. Most of these methods have been developed at laboratory-scale or are specially designed for analytical purposes with lower throughput than that usually required in processing. Suspensions of interest have been a variety of aqueous model systems (e.g. latex, bentonite and calcite), suspended microorganisms [59] and blood [60,61].

Pioneer work in the application of USSW phase separation in processing and environmental technology has been carried out by two groups around Benes and Frischherz in Vienna [50,62]. The studies focused on the application in drinking water purification. Results obtained with a lab-scale USSW separation reactor, which combined particle aggregation and sedimentation, marked the proof of principle for the suitability of the process. The same authors presented the concept of a pilot-scale USSW device. Results from a differently designed proto-type pilot-plant, which operated with a similar aggregation–sedimentation combination to that of Benes and Frischherz, showed the possibility of a successful scale-up of the technology [63,64]. A summary of this work will be given below.

Most publications on USSW technology with potential environmental application considered solid–liquid and solid–air dispersions [65,66]. The aggregation of aerosols from combustion fumes up-stream of an electro-static filter has already been developed into pilot-plant scale [67]. Only a small number of authors have investigated the potential use of ultrasound for sonically induced droplet coalescence in emulsions [68,69]. Reasons for this include the small droplet size (often smaller than 1 μm), which results in a very weak radiation force, and the high stability of emulsions, i.e. high repulsive forces between the droplets.

2. PHENOMENA AND THEORY OF SUSPENSION BEHAVIOR IN ULTRASONIC STANDING WAVES

The high number of different and simultaneously acting forces on particles in non-cavitating USSW fields makes it difficult to fully describe

ultrasonic particle aggregation mathematically. In the following, the general phenomena will be illustrated and the most important mechanisms and forces will be introduced to the extent necessary for thorough discussion of the experimental results presented later.

2.1 Particle Aggregation by the Ultrasonic Radiation Force

2.1.1 Schematic of USSW Particle Aggregation

The principal phenomenon of particle aggregation in USSW is shown in Figure 1. Suspended particles are put in a container that is fabricated with an ultrasound transducer at one end and a reflector at the opposite in order to produce a standing wave. Only one wavelength is shown in Figure 1 for reasons of clarity. However, the following description of ultrasonic aggregation also applies to multi-wavelength systems. Particle movements are seen, shortly after the sound is switched on. Homogeneously distributed particles (Figure 1a) are first driven into the pressure nodes as indicated in Figure 1b within a time period of the order of 1 s, depending on the reactor and the operation conditions. After a longer period of time (of the order of some seconds up to a few minutes) the particles will have moved within the bands to favored positions, where they concentrate into clumps and where aggregation is accelerated because of the higher particle concentration

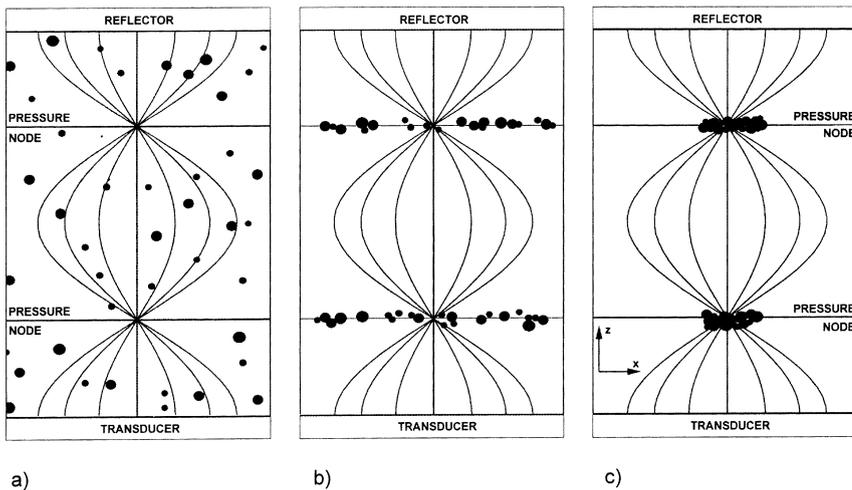


Figure 1. Schematic of aggregation of suspended particles in USSW.

and sonically induced interaction forces (Figure 1c). The aggregates formed settle considerably faster than the initial single particles, when the sound is switched off. The lateral concentration of the particles in clumps often gives the impression that the solid particles are concentrated in “columns”. This applies especially to systems with many wavelengths pathlength between transducer and reflector. However, these columns consist, to be precise, of single planar aggregates of particles, lying one on top of the other.

2.1.2 Theory of the Direct Acoustic Radiation Force

The axial (in the direction of the sound propagation) component of the direct acoustic radiation force (DRF), is the force responsible for the banding of particles in the pressure nodes (Figure 1b). It acts directly on single particles and particle aggregates. Lateral components, acting within the bands, contribute to the lateral concentration into clumps. Gor'kov (1962) formulated a potential equation for the DRF [13]. The actual force is derived from this potential (U) by determination of its negative gradient. The approach is valid for arbitrary acoustical fields, a non-viscous fluid and compressible spherical particles, which are smaller than the wavelength. For a plane harmonic standing wave the axial DRF component (z -direction) is found to be

$$F_z = \left| -\frac{\partial}{\partial z} U(\vec{x}) \right| = V_p \langle E_{ac}(x, y) \rangle k \left(f_1 + \frac{3}{2} f_2 \right) \sin 2kz \quad (1)$$

with

$$f_1 = 1 - \frac{c_0^2 \rho_0}{c_p^2 \rho_p}, \quad f_2 = 2 \frac{\rho_p - \rho_0}{2\rho_p + \rho_0}$$

The bracketed parameter E_{ac} is the mean acoustic energy density, which is proportional to the square of the sound pressure and may show lateral variations, k is the wave number (linearly proportional to the frequency, f), V_p is the volume of the particle and the term in round brackets is referred to as the acoustic contrast factor. It is a function of c_0 and c_p , the speed of sound, and ρ_0 and ρ_p , the density of the suspending medium (index 0) and the particle (index p), respectively. The contrast factor determines the type of plane towards which particles are driven. Particles are pushed into the pressure nodes, which is usually the case for solids suspended in water, if the contrast factor is positive. A negative value is often found for liquid dispersed particles, which are concentrated in the antinodes. The z -spatial distribution of the axial DRF shows a half-wavelength periodicity contributed by the sine term and corresponds to the half wavelength separation of the planes where particles gather.

A problem for the practical application of Eq. (1) is that the real distribution of the acoustic energy density is often not known. Even plane harmonic standing waves may show lateral pressure gradients due to non-ideal transducer radiation and reflection of the incident wave at a non-ideal reflector.

A numerical calculation of the DRF potential has been carried out by Jöhring [70]. He assumed a piston excitation in an unbounded water volume. An ideal reflector was simulated by a mirror source. The result of the solution of the Rayleigh integral is shown in Figure 2.

The contour plot of the DRF potential covers the region just underneath the reflector, which is located at $5A$ (A is the radius of the circular transducer). The calculation was carried out for 2 MHz and a solid particle ($c_p = 5000 \text{ m s}^{-1}$, $\rho_p = 2500 \text{ kg m}^{-3}$) with $10 \text{ }\mu\text{m}$ diameter. Regularly alternating potential maxima and minima are seen in axial (z -) direction. A maximum is located at the reflector, indicating a pressure antinode. Potential variations are indicated also in lateral (x -) direction. The actual force acting on a suspended particle is proportional to the gradient of the

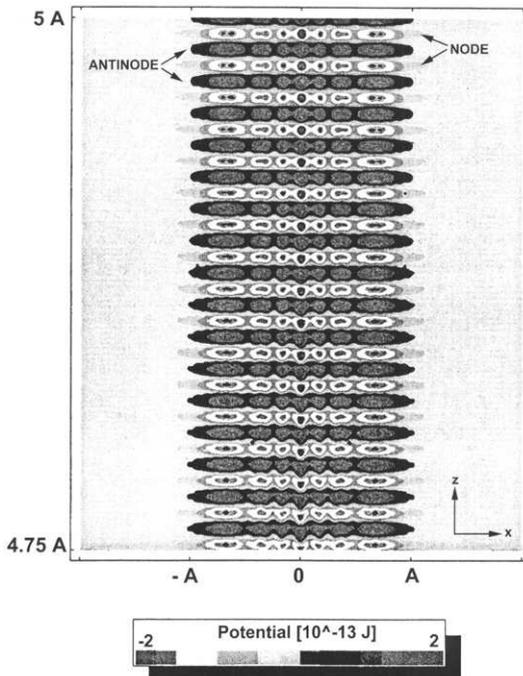


Figure 2. DRF potential for a $10 \text{ }\mu\text{m}$ solid sphere ($c_p = 5000 \text{ m s}^{-1}$, $\rho_p = 2500 \text{ kg m}^{-3}$) in a 2 MHz, 1 MPa standing wave [70].

DRF potential. The force is stronger the closer together different grey-scale values are located in Figure 2. It can be estimated from this that the force is considerably stronger in the axial direction than in the lateral (the z -axis is stretched by a factor 20 for reasons of clarity). This is in agreement with measurements of axial and lateral DRF force distributions [35–37]. It was shown experimentally that the force in the lateral direction is about 100 times weaker than the axial component of the DRF. The situation in Figure 2 is axially symmetric. This means that the potential minima, where particles gather, are concentric rings, an arrangement, which is different from most experimental results, when column formation is observed. This can be attributed to the assumption of a piston excitation with ideal reflection. Theoretical and experimental investigation of particle behavior in a narrow tube, excited in the lowest axial mode, showed the formation of a single column in the center of the waveguide [27]. Laser interferometric measurement of the displacement amplitude distribution on the transducer and reflector surface of a reactor, which was very similar to a commercial cell filter, were found to correlate with the observed column pattern, present in the sonicated volume [71]. The findings presented allow two conclusions: (i) the DRF is responsible for the banding effect and contributes significantly to the lateral concentration of particles in columns, (ii) the actual pattern of columns developed in USSW systems is dependent on the radiation characteristic of the transducer and on the quality of the reflector.

2.2 Aggregation Disturbance by Acoustic and Convective Streaming

The general review on acoustic and convective effects in USSW application given in the following is complemented by typical recent experimental results.

2.2.1 Observation of Large-scale Streaming in USSW

Figure 3 shows views inside a multi-wavelength ultrasonic reactor (details are given in Section 3). The transducer is located at the bottom of the glass cylinder employed, the reflector is seen on top of each image. Sonication of water, containing iron hydroxide particles, has been carried out at 2 MHz. The wavelength (λ) at that frequency in water (speed of sound almost 1500 m s^{-1}) is 0.75 mm. Thus, the spacing between two pressure node planes is about 0.38 mm, since one wavelength contains two nodes. The pathlength between transducer and reflector in Figure 3 is about 10 cm. Therefore over 260 pressure node planes are present in the sonicated volume.

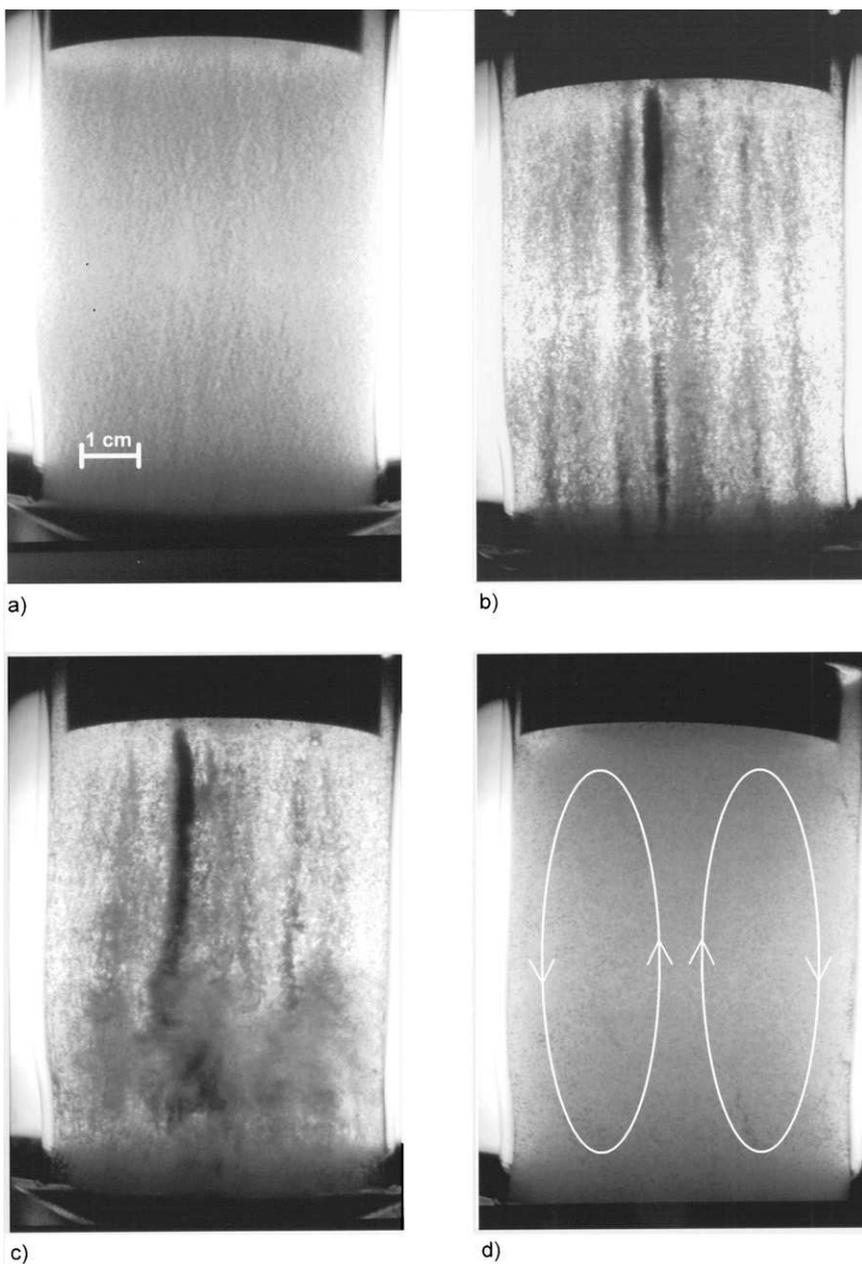


Figure 3. Sonication of an iron hydroxide suspension in a 2 MHz batch system; spacing between transducer (bottom) and reflector (top) was about 10 cm; picture (a) and (b) show the formation of the typical plane and column structure at 10 W power input, (c) and (d) container-scale streaming after power was increased to 25 W.

The image in Figure 3a was taken immediately after the sound was switched on. Figure 3b shows the situation after 3 min sonication with 10 W electrical power input. The distinct structure of planes is resolved best in the middle of the photograph, where the perspective is exactly perpendicular to the sound axis. Also the pronounced lateral concentration of particles in columns is clearly visible. The plane and column formation is the core phenomenon in USSW conditioning of suspensions, as already described in the last paragraph. However, when the power was increased to 25 W (Figure 3c), the situation changed spontaneously. Rapid and turbulent streaming was set up that destroyed the ordered plane and column structure. The first perturbances of the bottom plane and column structures are captured in Figure 3c. Within seconds the whole suspension in the container was moving around in a vortex ring, indicated by arrows in Figure 3d.

2.2.2 Acoustic and Thermal Convective Streaming

The streaming described in Section 2.2.1 was large-scale Eckart streaming in conjunction with thermal convective flow. Eckart and Liebermann treated the case of a plane traveling wave in a cylinder with an absorbing border opposite the transducer [9,10]. The authors calculated and observed the same pattern of streaming as indicated in Figure 3d. For an ideal standing wave, no such streaming was expected. However, the findings for a traveling wave can be adapted to standing waves, since a real standing wave always has a traveling wave component. Comprehensive reviews on acoustically driven flows have been published [72,73]. The authors not only treat the container-scale streaming phenomenon, which is of interest here, but also small-scale micro-streaming. An overview of the different types of streaming is given in Table 1.

Large-scale streaming acts against the aggregation of particles. It may drag particles out of the desired positions where clumps form and can even

Table 1. Types, Scale in Comparison to the Wavelength λ , Origin of Streaming in USSW and the Effect on USSW Suspension Conditioning

<i>Streaming Type</i>	<i>Scale</i>	<i>Origin</i>	<i>Effect</i>
Eckart–quartz wind [9,10,75]	$\gg \lambda$	Sound absorption in the bulk volume, heating of surfaces	Negative for aggregation by drag and aggregate disruption; positive for thickening by drainage
Thermal convective [77]	$\gg \lambda$		
Rayleigh [11] Schlichting [12]	$\approx \lambda$ $\ll \lambda$	Losses in viscous boundary layers, inhomogeneous acoustic velocity distribution	Not finally clarified, yet

disrupt aggregates by shear. A theoretical cut-size for particles, which are just held by the DRF in the banding planes against the streaming drag, has been found to be of the order of 1 μm for common sonication regimes [74]. Streaming can, on the other hand, support thickening of already settled sludges by mechanical conditioning of the sludge structure. The influences of micro-streaming on USSW suspension conditioning are not yet clearly resolved.

Acoustic streaming is in general a consequence of viscous sound energy absorption in the sonicated volume and the viscous boundary layers. The driving force for Eckart streaming is proportional to the coefficient of sound absorption and the acoustic energy density [73,75]. The latter dependence indicates that the acoustic streaming is faster with higher power input to the reactor (higher source amplitude). It has also been found that the streaming velocity increases with the free pathlength that is available for acceleration of the flow [64,75,76]. Thermal-convective streaming may also be present in addition to the acoustically driven flow. The influence of acoustic Eckart and thermal streaming have been clarified in experiments under micro-gravity conditions [77]. Thermal streaming has its origin in temperature gradients in the bulk volume and in energy losses in the transducer, the reflector and the container walls, which result in heating of these reactor parts. It is not possible to thoroughly distinguish between these types of container-scale streaming under the influence of gravity. Large-scale streaming is especially undesired, if the flow state becomes turbulent. It has been shown that the acoustically induced vortical disturbances of an acoustic flow, which act as “turbulent seeds” and cause the transition into large-scale turbulence, show a chaotic behavior [78].

2.2.3 Large-scale Streaming Control

A number of different methods have been reported to combat aggregation-disturbing streaming. Small container dimensions, especially in the axial direction, are advantageous, because they provide only a short pathlength for the build-up and acceleration of streaming. Sometimes, however, a large sonicated volume is required, e.g. for achievement of high flow rates. In this case the sonic chamber can be divided by acoustically transparent film (ATF) [63,64,76]. This restricts the free pathlength necessary for streaming development, but provides maximum volume with just one sonic chamber (see Chapter 3). Other possibilities for streaming control are the application of only low power input, the excitation of the transducer by tone bursts [79] and active cooling of the transducer and reflector [41].

2.3 Particle–Particle Interaction Forces

A number of different types of interaction forces, which can promote aggregation of particles in USSW, are described below.

2.3.1 *Bernoulli Interaction*

Hydrodynamic interaction forces between particles are induced by the oscillation of the fluid elements in the sound field. These forces can be deduced from Bernoulli's law. Particles with different density to that of the surrounding phase follow the oscillations of the fluid with a phase shift because of their inertia. A particle is therefore subjected to a fluid flow around it. If two particles are located side by side (e.g. in a pressure node plane), the oscillating fluid between them is forced to move faster than the surrounding bulk, because of the “nozzle” formed in the gap. This leads, according to Bernoulli's law, to a lower pressure between the particles than on the outside. The particles experience a mutually attractive force.

2.3.2 *Bjerknes Forces*

Particles present in the sound wave act as wave scattering obstacles, which cause additional radiation force fields in their proximity. These forces are known as Bjerknes forces [80,81]. Particles, which are aligned perpendicular to the sound propagation direction, are attracted to each other. Those aligned on an axis parallel to the sound propagation direction experience a repulsive force. Bjerknes and also Bernoulli interaction forces are in general short distance forces. They are, as a rule of thumb, only of significant influence, if the particle–particle separation is less than one particle diameter [82]. The Bjerknes interaction forces increase with particle diameter. Particle interaction forces are therefore larger between already formed aggregates and approaching single particles than between two single particles. It is therefore reasonable to assume that single particles are more and more effectively drawn into clumps as these grow. This proposed effect, which is essentially a consequence of the Bjerknes interaction, is called “concentration effect” and currently under experimental investigation. It might be another mechanism involved in the formation of columns.

2.3.3 *Differential Oscillation*

Differential oscillations of particles with different size or other distinguishing properties have been found to be important for the aggregation of aerosols [1]. The effect leads to an increased collision rate between

particles and is also known as ortho-kinetic aggregation. Another important aggregation mechanism for aerosols is the so-called acoustic wake effect [83,84]. It means the attractive force on a particle in the sound field, when it is located in the “wake”, while following another oscillating particle. The latter two mechanisms described are of high relevance in air, where the displacement amplitude of the suspending medium is high. They are not very pronounced in suspensions and emulsions, because of the very small acoustic displacement amplitudes in these systems (usually less than $0.1\ \mu\text{m}$ under common sonication conditions, i.e. 1 MPa at 1 MHz).

3. ULTRASONICALLY ASSISTED SEDIMENTATION PROCESSES

The ultrasonic methods presented here are suspension conditioning processes that enhance the efficiency of a separation or reduce the time required for a certain separation result.

3.1 Ultrasonic Standing Waves in the Context of Phase Separation Technology

The schematic shown in Figure 4 illustrates a simplified decision matrix for the choice of a suitable separation method. It has been adopted and modified from Svarovsky’s text book on solid–liquid separation [85]. Two selection criteria are considered in the matrix: particle size and suspended solids concentration of the suspension. Sedimentation is therefore suitable for separation of low concentrated suspensions, which contain particles larger than $10\ \mu\text{m}$. Ultrasound can be used to increase particle size by aggregation, which facilitates the separation of particles smaller than $10\ \mu\text{m}$ by sedimentation. This approach of USSW assisted separation of suspensions with a low concentration of solids will be discussed in Section 4.1. Figure 4 furthermore indicates that USSW technology is also suitable for increasing the concentration of suspended solids. A sedimentation based USSW thickening process for pre-settled sludge is presented in Section 4.2.

3.2 Separation Efficiency

The principal function of a continuous separation process is shown in Figure 5 [85], modified. Arrows indicate three flows, one going into the

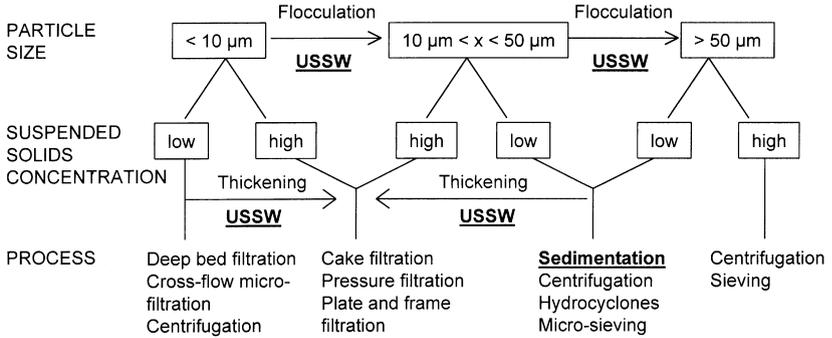


Figure 4. Simplified decision matrix for choice of solid-liquid separation methods ([85], modified).

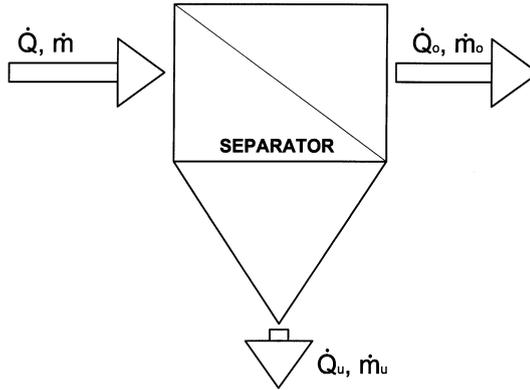


Figure 5. Principal continuous separation process ([85], modified).

separator and two leaving the process. The terms \dot{Q} and \dot{m} represent the volume flow of the suspension and the solids mass flow, respectively. No index is applied to the mixed suspension going into the process. This untreated suspension is called reactor feed. The separation process splits the feed into the overflow (index o), which contains fewer particles than the feed, and the underflow (index u), which is particle enriched. The volume flow of the overflow is usually much higher than that of the underflow. Mass conservation applies: $\dot{m} = \dot{m}_o + \dot{m}_u$. The efficiency of a separation is defined as the ratio between retained solids mass in the underflow and the feed mass flow (\dot{m}_u/\dot{m}). Mass flow detection is often not an easy task. Suspended solids concentration (SC) is a common parameter that is often measured routinely. SC can be expressed as the ratio of the mass flow over the volume flow.

With the assumption that the volume flow of feed and overflow are nearly identical, the total separation efficiency of a continuous separation process is finally given by

$$\eta = \left(1 - \frac{SC_o}{SC}\right) \times 100\% \quad (2)$$

The efficiency of separation processes is usually particle size sensitive. The definition of a grade efficiency takes this size dependent performance into account.

$$\eta_i = \left(1 - \frac{SC_o p_{o,i}}{SC p_i}\right) \times 100\% \quad (3)$$

The grade efficiency can be determined for each particle size category i , if the discrete size distribution of feed and overflow is known. The term p_i represents the amount of solids with size i in the feed, $p_{o,i}$ in the overflow. The explanations given above apply also for batch processes, if the flow terms are multiplied with the time required for one batch cycle. This multiplication turns the flow terms into absolute values of mass and volume per cycle. Equations 2 and 3 apply for continuous and batch processes.

3.3 Reactor Design and Operation

USSW assisted sedimentation processes can be categorized by: (i) the orientation of sound propagation, flow and settling direction to each other, and, (ii) batch or continuous operation mode. Figure 6 illustrates two principle orientations of the sound direction with respect to the gravity vector: parallel (Figure 6a) and perpendicular (Figure 6b). The first layout (Figure 6a) is only suitable for batch mode, since the particle aggregates formed settle on the surface of the ultrasonic transducer. This additional mass, contributed by the solids on the transducer, alters the radiation characteristics of the system. Therefore, a periodically complete drainage of the chamber is required in order to remove the settled solids. Such reactors are usually operated in sonic mode for a certain time, followed by a sedimentation phase when sound is turned off. The aggregates often start settling during sonication, if the gravity force is large enough to overcome the radiation force, which holds them in the pressure node planes. All aggregates formed are allowed to sediment, when the sound is switched off. However, aggregates might be disrupted during sedimentation by shear forces, which is often undesired. Sonication in a pulsed mode, when, e.g. 5 s sonication are followed by 2 s silence, can overcome this problem [34,59]. The aggregates only sediment through a small number of

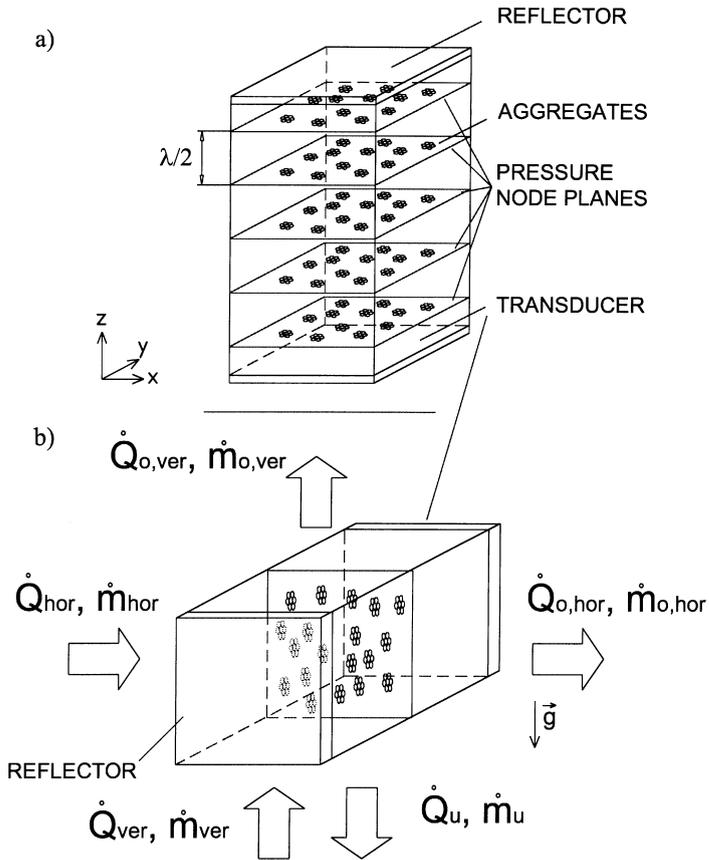


Figure 6. USSW reactor design and operation, possible lay-outs.

nodal planes during the unsonicated phase. They are captured and held in a lower node, when the sound is switched on again. A controlled sedimentation is possible in this manner, by maintaining the shape of the aggregates, until they reach the bottom of the ultrasonic container.

The problem of particles settling on the transducer is avoided with the reactor arrangement in Figure 6b. The particle sediment within the pressure node planes and therefore do not alter the transducer radiation by adding mass to it. Note that for reasons of clarity, only one pressure node plane is indicated in Figure 6b. The information given is also valid for multi-pressure node systems. The layout seen in Figure 6b is suitable for batch and flow through operation. It can be run in cross-flow mode (feed and overflow horizontal, index “hor”) or counter-flow mode (feed and overflow vertical,

index “ver”). The underflow orientation is in both cases determined by the gravity vector, \vec{g} .

4. RESULTS OF LAB- AND PILOT-SCALE EXPERIMENTS

The results presented below have been derived from lab- and pilot-scale experiments with model dispersions as well as sample suspensions of practical industrial interest. The results were obtained with a commercial lab sonication system (URS 1000) by ELAC Nautic Kiel, Germany. The transducers (about 25 cm² surface) were electrically matched in order to minimize reflected power to the electronics. The acoustic efficiency of this transducer type was found to lie between 55 and 85% [86]. The electronics had a “true power” control, which held the electrical power input constant over the sonication time, even when conditions in the sonicated volume changed due to e.g. changes of the temperature or the particle concentration. The standard batch reactor supplied with the sonication kit was a 6 cm diameter, 0.5 l glass cylinder with water cooling jacket and stainless steel reflector.

The influences of the most important processing parameters like sonication time, reactor geometry, power input etc. on the separation result will be presented and discussed. These data are strictly valid only for the reactor systems described. However, the general tendencies and dependence of the USSW separation efficiency from the process parameters discussed can be transferred to other systems, based on the aggregation–sedimentation approach.

4.1 Separation of Particles from Aqueous Suspensions

The continuous USSW assisted sedimentation process presented below was designed according to fundamental data obtained from batch experiments. The parameters measured and interpreted in the following are turbidity (Hach 2100 N), suspended solids concentration (filter method analogous German DIN38409) and particle size distribution (Malvern particle sizer 2600). Model suspensions used were iron hydroxide (Fe(OH)₃) suspended in water and bentonite suspension. Iron hydroxide suspension contained particles between 2 and about 50 μm with a maximum of the volume distribution at about 10 μm. Bentonite suspension had a bi-modal volume distribution (maxima at about 4 and 8 μm) with a minimum size of about 0.5 μm and a maximum size of about 30 μm. Industrial sample suspensions investigated were filter backwash water from drinking water

treatment, which contained precipitated iron and manganese hydroxide particles with a mono-modal size distribution from about 2 to 50 μm and a maximum at around 10 μm . Other investigated “real” suspensions included wastewater samples from a truck wash, the effluent of a glass grinding plant and the wash water from a garage air conditioning system.

4.1.1 Preliminary Batch Experiments [87]

The experimental procedure was as follows: suspension was put into the batch reactor (0.5 l) and sonicated for a period of time between 30 s and 15 min. The sample was left on the bench for another time period, after the sound was switched off, until a total treatment time of 30 min had elapsed and the supernatant was taken for analysis. The result of the sonicated sample was compared with an unsonicated reference batch, which was allowed to sediment for 30 min. Results from experiments with model $\text{Fe}(\text{OH})_3$ suspension and filter backwash water showed: (i) most effective tested (1, 2 and 3.3 MHz) frequency was 3.3 MHz, (ii) power input was restricted, due to large-scale streaming, to 10 W or less (true electrical power, measured at the transducer), depending on frequency and suspension, (iii) a sufficient sonication time of the order of some minutes was found. No further separation improvement was seen for longer sonication times (see Figure 7). The last result allows an estimate for the residence time required in the sound field of a continuous USSW reactor. As seen in Figure 7, no further improvement of separation efficiency in comparison to the unsonicated reference sample was achieved beyond about 4 min for the $\text{Fe}(\text{OH})_3$ model suspension investigated in these experiments. Maximum reduction of turbidity in comparison to the unsonicated reference was about 60%, SC reduction could be increased by about 85% through ultrasonic treatment. It was therefore reasonable to expect a minimum residence time in the sonicated volume of a flow through system to be of the order of some minutes.

4.1.2 Design and Operation of Lab- and Pilot-scale Flow Through Systems

The flow through reactors were specially designed and built at the Technical University, Berlin and combined with the URS 1000 (ELAC Nautik, Kiel) lab-scale transducers and electronics. The electronics were also employed for the pilot-scale experiments. The transducer in this case was a proto-type array with 16 ceramics and was developed and manufactured by ELAC Nautik (Kiel, Germany). The reactors were constructed as cross-flow devices (compare with Figure 6b). It was desired to reach high flow rates while simultaneously keeping separation efficiency high. Large sonication chambers were necessary for the realization of high

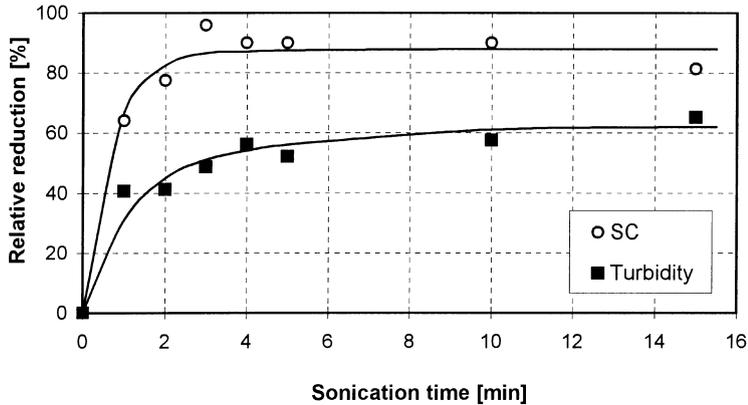


Figure 7. Relative SC and turbidity reduction versus sonication time (sonicated result related to silent reference); 3.3 MHz batch system, 250 ml, 10 W, model $\text{Fe}(\text{OH})_3$ suspension, initial SC, 3.8 g l^{-1} , initial turbidity, n/a.

flow rates, since it was estimated from the batch experiments that the residence time would be of the order of some minutes (Section 4.1.1). However, it was also known that large dimensions of the chamber intensify the development of large-scale streaming (Section 2.2). This can have undesired effects on particle aggregation. The chamber was, therefore, equipped with ATF dividers, which acted as barriers for the streaming and, therefore, prevented the built-up of the container-scale eddies. By this means, it was possible to control large-scale streaming and sonicate a large volume. The principal design of the reactors is shown in Figure 8.

The reactors consisted of an inlet module (part A in Figure 8), in which the suspension was distributed over the whole flow through cross-section of the reactor, the sonic chamber and a sedimentation module with an outlet for the clarified liquid (part B). Sludge hoppers were fitted underneath the sonication chamber and the outlet module in order to collect the settling particle aggregates. Figure 9 shows as an example the detailed cross-section through the pilot-plant sonication chamber.

The sonic chamber was formed by a transducer (16 ceramics proto-type array on the right) and a stainless steel reflector (left in Figure 9). The thickness of the reflector was chosen for optimal sound reflection. The chamber was divided by the ATF (15 μm PE film by Dupont), inserted perpendicular to the sound propagation direction in order to control streaming. Table 2 summarizes the characteristics of the reactors used.

Two versions of the lab-scale reactor were built. The first had a transducer-reflector spacing of 14 cm and a minimum ATF spacing of

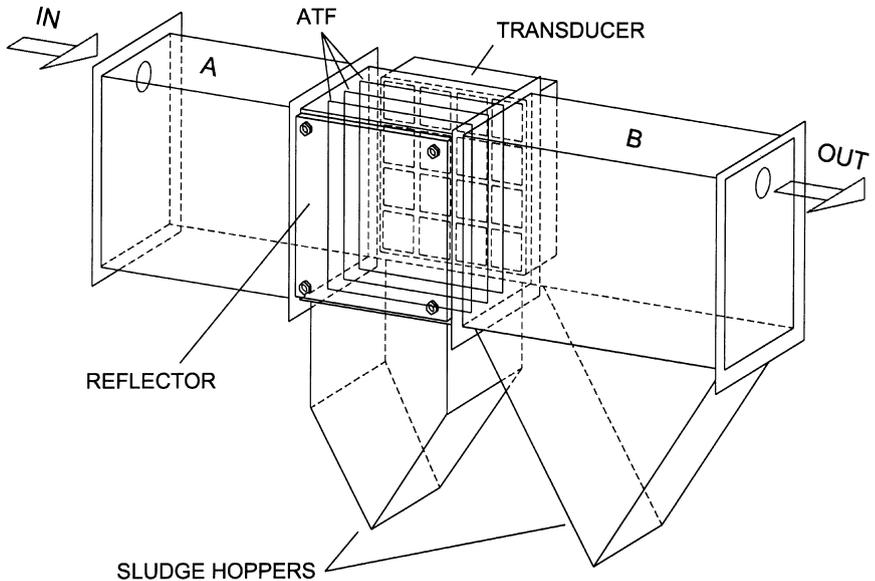


Figure 8. Continuous USSW-sedimentation reactor, principal design.

4 mm. The second version was designed similarly to the first lab-device with the difference of a longer transducer-reflector path (20 cm) and a minimum ATF spacing of 2 mm. The pilot-plant was designed according to the experiences gained with the lab reactors and scaled-up with a threshold trajectory sedimentation model. Details of the scale-up and comparative performance results of lab- and pilot-plant have been reported earlier [63].

Every continuous flow process requires a certain period of time until the operation conditions have stabilized. Figure 10 shows the typical performance behavior of a continuous USSW-sedimentation reactor before and after ultrasound was switched on.

Stable SC concentration and turbidity were measured at the outlet of the reactor after the first 15 min flow through without ultrasound at 8 l h^{-1} (14 cm lab-reactor). The efficiency, which can be calculated from these data and the initial values of the untreated suspension, is called the “silent (unsonicated) reference”. It describes the ability of the reactor to separate by means of gravity alone. It took another 15 min after the sound was switched on (after 25 min) to reach the stable state of the sonicated system. A considerable decrease of turbidity and SC concentration at the reactor outlet is seen in comparison with the unsonicated performance. The reactor operated continuously without performance variation for the remainder

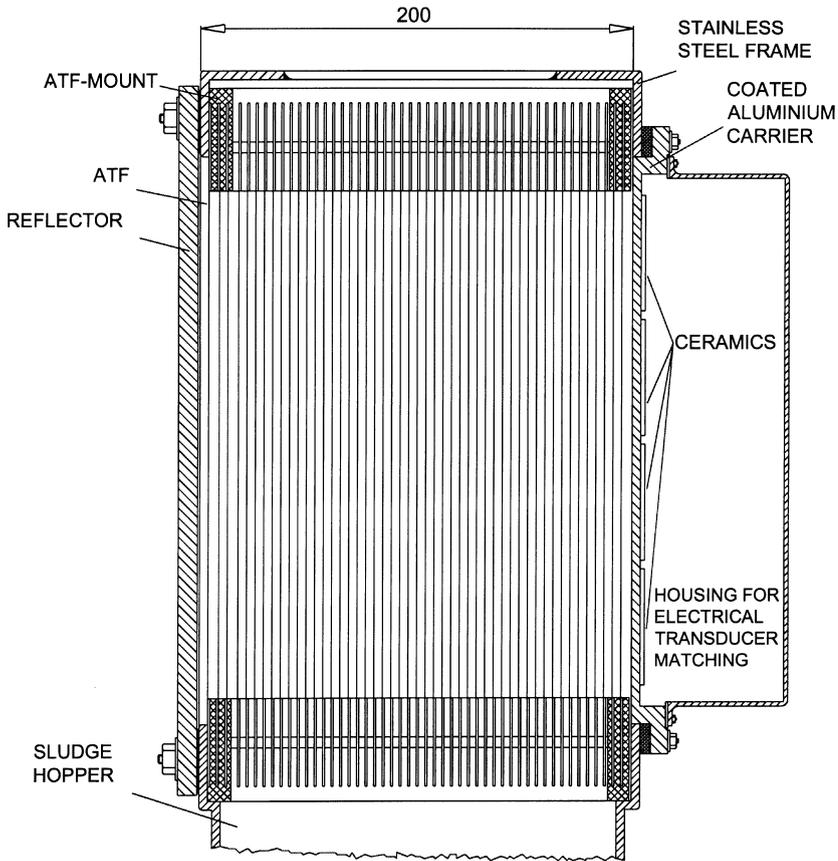


Figure 9. Cross-section through sonication chamber, pilot-scale.

Table 2. Characteristics of the Continuous Lab- and Pilot-scale Reactors for USSW Particle Aggregation

	<i>Lab-scale</i>	<i>Pilot-scale</i>
Frequency	1, 2, 2.4 and 3.3 MHz	3.3 MHz
Operation mode	Continuous flow	Continuous flow
Active transducer surface area	~ 20 cm ² , circular	~ 580 cm ² , square
Transducer-reflector distance (minimum ATF spacing)	14 cm (4 mm) and 20 cm (2 mm)	20 cm (4 mm)
Flow rate investigated	24 l h ⁻¹ maximum	150 l h ⁻¹ maximum
Maximum power	50 W (45 W continuous)	200 W

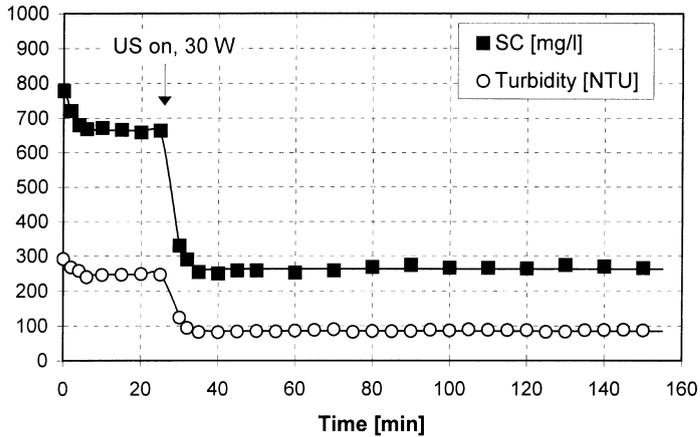


Figure 10. Separation performance without and with sonication; 3.3 MHz, 14 cm pathlength lab-scale reactor, 8 l h^{-1} , 30 W, ATF at 4 mm spacing, bentonite suspension; average residence time in the system was about 10 min, 2 min in the sonicated volume.

of the experiment. It is important that experimental samples are taken after the reactor has reached its stable operation.

The effect of the division of the sonic chamber on the separation efficiency is demonstrated in Figure 11, showing separation efficiency results on lab-scale (14 cm reactor) for different input power at an ATF spacing of 4 mm and without inserted ATF, respectively. With ATF, an increase in separation performance with power input is seen up to 95% total SC reduction at 45 W. The maximum power of the lab transducers used where 50 W for 4 min sonication. The value of 45 W for continuous sonication was chosen in order to prevent transducer damage. However, the monotonous increase of the efficiency values suggests that even better separation efficiency at power levels higher than 45 W might be achieved with ATF segmentation of the sonic chamber. Without ATF, a maximum separation efficiency of about 80% is seen at 5 W. The performance decreases significantly with higher power input. At 45 W, the separation efficiency is down to almost the same value as the unsonicated reference of 65% SC reduction.

The empirically observed effect of the ATF on reactor performance in terms of separation efficiency can be explained in detail as follows: The efficiency of the ultrasonic aggregation–sedimentation process discussed here is in the first place dependent on a strong acoustic radiation force (see Section 2.1). This DRF increases linearly with the acoustic energy density in the sonicated volume (Eq. (1)). Therefore, a higher power input leads to an

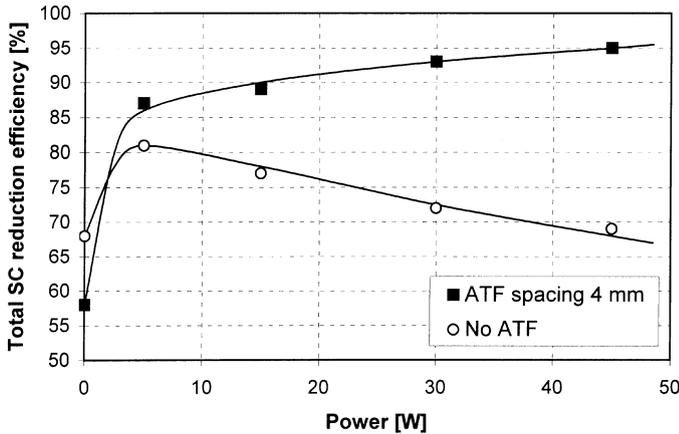


Figure 11. Total SC reduction versus power input with and without division of the sonic chamber by ATF; 3.3 MHz, 14 cm pathlength lab-scale reactor, 4 l h^{-1} , filter backwash water, initial SC 230 mg l^{-1} .

increased acoustic energy density and to a higher DRF, which is beneficial for good particle aggregation and subsequently high separation performance of the system. It was seen on the other hand that excessive power input causes aggregation-inhibiting streaming (Section 2.2). The insertion of ATF limits the free pathlength, which is available for the built-up of streaming. Therefore, higher power input is possible with ATF than without ATF, before the undesired streaming effect on particle aggregation outweighs the desired effect of the DRF. The hypothesis was that controlled streaming is responsible for the experimental result presented in Figure 11, which was confirmed recently by optical investigation of the particle banding structure and streaming patterns in different sonic chamber set-ups [64]. It was observed in these experiments that turbulent streaming destroyed the banding of particles, when only one ATF was centrally inserted into the pilot-plant chamber investigated, which corresponded to a free pathlength of 100 mm. Almost regular particle banding was seen under exactly the same conditions, but with two additional ATF, inserted symmetrically around the center ATF at a spacing of 24 mm. No turbulent streaming could be detected there.

4.1.3 Parameter Studies

The effect of the experimental variation of some selected process parameters on the reactor performance will be presented in the following.

The results will give insights into the possibilities and current limits of the technology presented. Most of the parameter studies have been carried out with the very stable bentonite model suspension. The aim of these experiments was high reproducibility and sensitivity to a parameter alteration. For the latter purpose, “mediocre” separation efficiencies were desired in order to minimize the measurement error, which increases towards the ends of any measurement scale (in this case, e.g. very low SC at the reactor outlet). Therefore, no high performance separation results will be seen for bentonite. However, the practically important performance will be demonstrated with results obtained with filter backwash water in this paragraph as well as with other industrial sample suspensions in the next section (4.1.4).

Figure 12 shows the effect of ATF spacing variation on the separation efficiency for different particle sizes of a bentonite suspension. It is seen that a significant increase in separation performance with narrower ATF spacing (more ATF inserted) could be achieved. A sharp performance increase with ATF number is seen especially for small particle sizes (about $< 15 \mu\text{m}$), which were not separated effectively by gravity alone (reference curve). This enhanced removal of small particles, which are commonly regarded as critical in separation technology [85], is a particular strength of the USSW process. Even 50% removal of the $2 \mu\text{m}$ particles, which were not separated without ultrasound, was achieved with 4 mm ATF spacing,

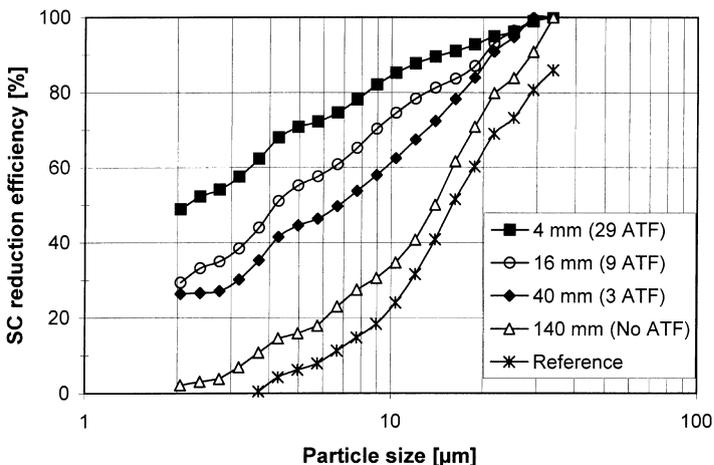


Figure 12. SC reduction versus particle size for varied ATF spacing; 3.3 MHz, 14 cm pathlength lab-scale reactor, 8 l h^{-1} , 30 W, bentonite suspension, initial SC 800 mg l^{-1} ; total efficiencies were 73% (ATF at 4 mm), 59% (16 mm), 48% (40 mm), 25% (200 mm), 15% (reference).

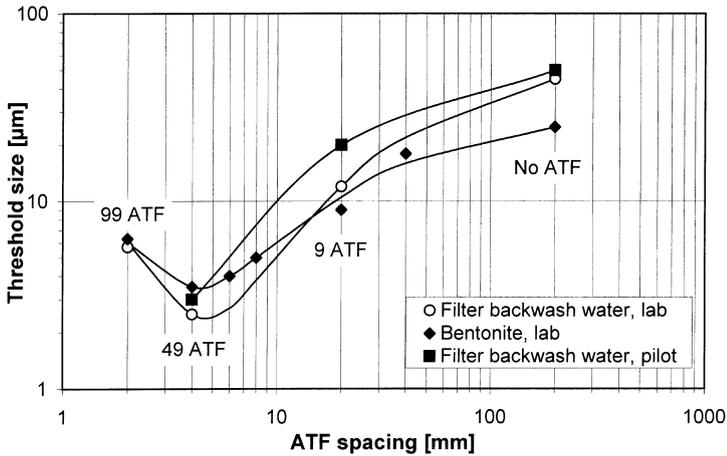


Figure 13. Separation threshold size versus ATF spacing; 3.3 MHz, 20 cm pathlength lab-scale reactor (12 l h^{-1} , 45 W) and pilot-scale reactor (150 l h^{-1} , 200 W), bentonite suspension (initial SC 1300 mg l^{-1} , 60% efficiency threshold), filter backwash water (initial SC 520 mg l^{-1} , 90% efficiency threshold) [64].

where large-scale streaming effects could be ruled out. However, larger particles are separated more effectively, which is in agreement with the much stronger radiation force on larger particles (see Section 2.1, Eq. (1)).

The question, whether the performance could be increased with an even narrower ATF spacing, arose from the results present above. Results from experiments with the 20 cm version of the lab-reactor (2 mm minimum ATF spacing) and the pilot-plant (20 cm transducer-reflector separation, 4 mm minimum ATF spacing) are summarized in Figure 13. A special parameter was defined in order to compare the results obtained for the different reactors and suspensions investigated. Every “threshold size” data point, plotted in Figure 13, represents the center particle size of that particle size category, which just exceeds a suspension dependent “separation threshold efficiency”. The latter value was chosen to be 60% for bentonite suspension and 90% for the less stable filter backwash water.

The “threshold size concept” holds, because all processed efficiency-particle size spectra increased monotonously with particle size. Therefore, an experimentally determined threshold size of e.g. $5 \mu\text{m}$ for backwash water means that all particles larger than $5 \mu\text{m}$ were separated from suspension with an efficiency higher than 90%. An optimum ATF spacing (ATF number), with the smallest threshold size, is seen at 4 mm for experiments with bentonite suspension and filter backwash water on the lab-scale. A narrower ATF spacing of 2 mm increased the threshold size significantly. This effect is attributed to sound energy absorption and reflection of the

ATF, which do not exactly match the acoustic properties of the suspension and which are therefore not completely transparent to the sound. This effect outweighs the beneficial streaming control by the ATF, if a certain number of them are exceeded, whereas the disturbance of the sound field can be neglected for a small number of ATF. The minimum ATF spacing in the pilot-plant was 4 mm. The pilot-scale results from experiments with backwash water, shown in Figure 13, are consistent with the high separation efficiency at 4 mm ATF spacing on the lab-scale. Corresponding results from lab- and pilot-scale experiments show larger threshold sizes for the pilot-plant. This is attributed to the low power–transducer surface ratio of the pilot-plant transducer (200 W maximum over 580 cm²) compared with the lab-scale transducers (45 W maximum over 20 cm²). Large surface pilot-scale transducers with higher power input are likely to increase separation performance on the pilot-scale significantly.

A question of high practical relevance, apart from the optimum design and operation of the USSW process, is the effect of the initial SC in the reactor feed on the separation performance. A huge variety of different suspensions with different concentrations may appear in processing and environmental engineering. Therefore, a flexible separation process with high dynamic capabilities in terms of concentrations and suspensions is desired. Figure 14 shows the separation efficiency for bentonite suspensions with varied initial SC and different power inputs.

An increase in separation performance with suspended solids concentration as well as with power input is seen. The general trend that separation efficiency increases with power input has also been reported for ultrasonic

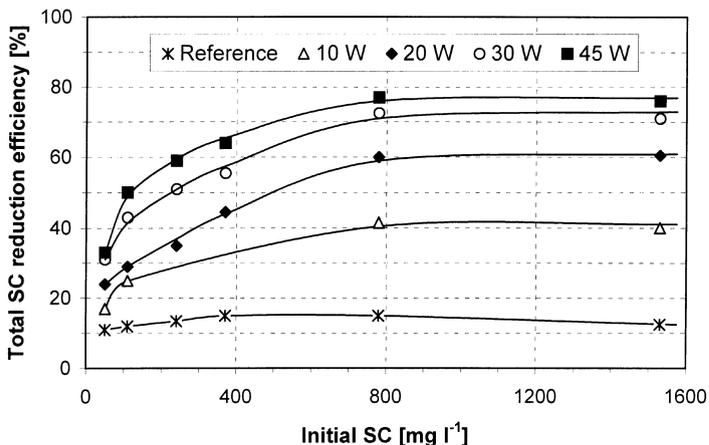


Figure 14. Total SC reduction versus initial SC for varied power input; 3.3 MHz, 14 cm pathlength lab-scale reactor, 8 l h⁻¹, ATF at 4 mm, bentonite suspension.

cell filter systems in biotechnology [88,89]. Separation efficiency enhancement by sonication, compared with the silent reference, increased significantly from 50 mg l⁻¹ initial SC up to about 800 mg l⁻¹ bentonite. About the same separation efficiencies as with 800 mg l⁻¹ were measured at the double concentration of particles (1530 mg l⁻¹). The USSW-sedimentation process is apparently not suitable for very low concentrated suspensions. This result, obtained with bentonite model suspension, is in agreement with data reported for bacteria and yeast cells, removed from suspension in a small volume batch system [59]. The low separation performance enhancement by sonication at low concentrations may be attributed to a lack of collision partners, since aggregation velocity in general increases with particle concentration [90]. The decreased separation efficiency at the lower end of the concentration range investigated might, therefore, be acknowledged as a kinetic effect.

4.1.4 Different Suspensions of Practical Interest

Results from experiments with different suspensions of practical interest will be presented in this paragraph. The data of the efficiency versus particle size spectra were obtained from non-optimized screening experiments. They provide some guidance to identify conditions for which an USSW-sedimentation separation is suitable.

Figure 15 shows results for filter backwash water, a wastewater stream from drinking water purification (see Section 4.1). The results presented in

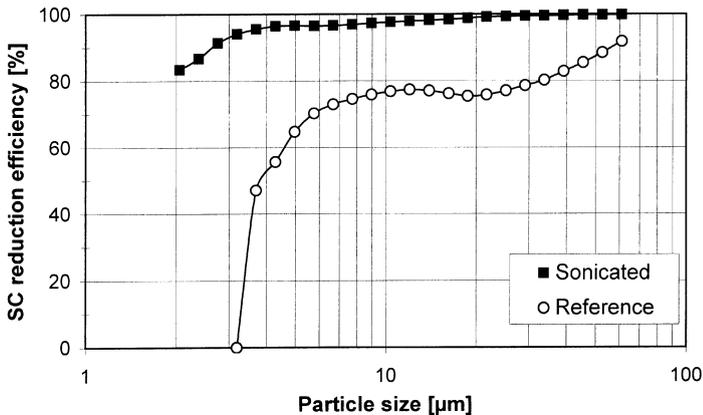


Figure 15. SC reduction versus particle size; 3.3 MHz, 14 cm pathlength lab-scale reactor, 4 l h⁻¹, 45 W, ATF at 4 mm, filter backwash water, initial SC 370 mg l⁻¹; total efficiency was 98% (sonicated) and 77% (reference) [63].

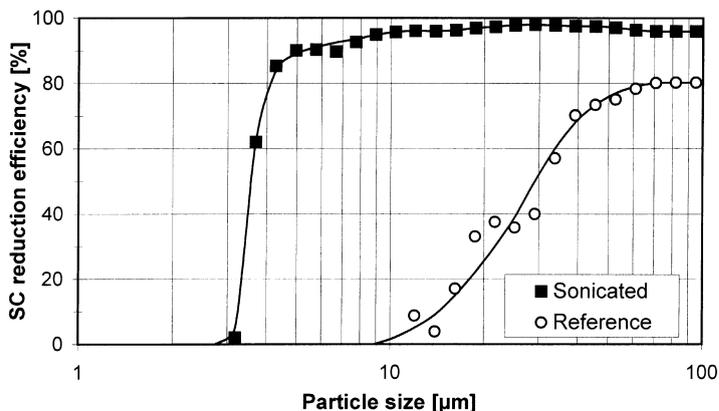


Figure 16. SC reduction versus particle size; 2 MHz, 20 cm pathlength lab-scale reactor, 24 l h^{-1} , 45 W, ATF at 4 mm, air scrubber wash water, initial SC 380 mg l^{-1} ; total efficiency was 97% (sonicated) and 57% (reference).

Figure 16 were measured with the wastewater from the air cleaning system of a public transport garage. It contained mainly diesel soot particles and aggregates, which were collected from the exhausts of the vehicles serviced and washed out from the gas phase in the scrubber system. The example in Figure 17 originated from the glass grinding plant of a TV screen factory. It contained mainly “rubbed off” glass particles in detergent rich washing liquid. Figure 18, finally, shows an experiment with the wastewater of an industrial truck wash. The vehicles were mainly employed in earth movement and the wash water therefore contained earth, clay and sand particles as main solid components.

Total separation efficiency but mainly the separation of small, critical particles could be significantly enhanced by sonication for each of the four suspension examples presented. The details of the experiments are given in the corresponding figure captions.

4.1.5 Cost Reflections

The costs involved make an important contribution to the assessment of the applicability of a particular processing method. The pilot transducer used in this work was a proto-type. Therefore, a comprehensive calculation of the overall costs in comparison with similar, already established technologies like flocculation, is not possible at the moment, due to lack of data on investment costs for USSW devices produced on a high number scale. However, the energy costs for the USSW separation method presented

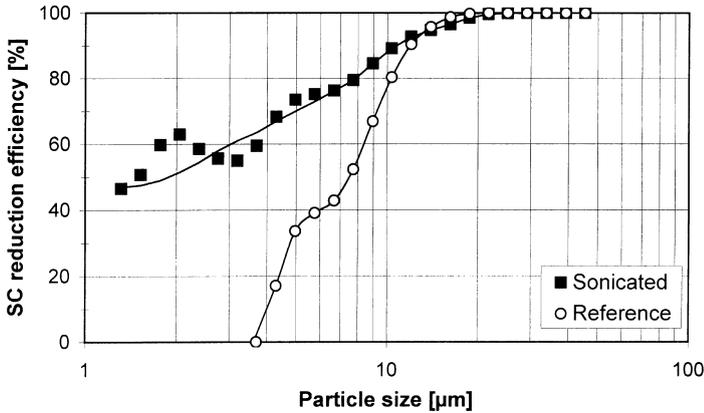


Figure 17. SC reduction versus particle size; 3.3 MHz, batch reactor, 400 ml, 5 W, 10 min sonication followed by 20 min sedimentation time, glass grinding wastewater, initial SC 520 mg l⁻¹; total efficiency was 81% (sonicated) and 32% (reference).

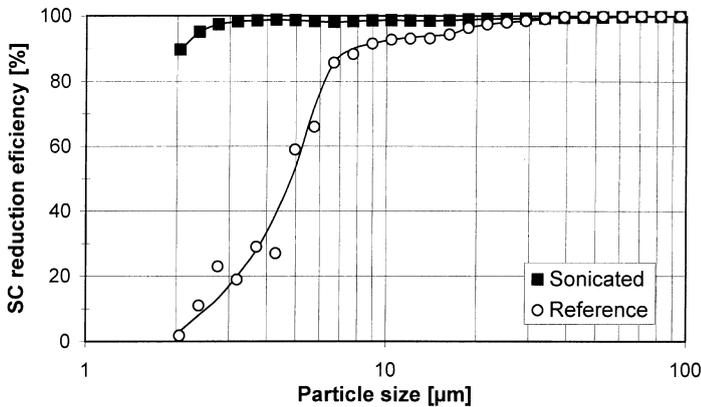


Figure 18. SC reduction versus particle size; 2 MHz, 20 cm pathlength lab-scale reactor, 12 l h⁻¹, 45 W, ATF at 4 mm, truck wash water, initial SC 8.1 g l⁻¹; total efficiency was 99.3% (sonicated) and 90% (reference).

above will be estimated, in order to provide some insight into the economics of USSW technology. Figure 19 shows the USSW separation efficiency for filter backwash water (initial SC about 500 mg l⁻¹), which could be achieved with a distinct volume specific energy input.

The specific volume demand for treatment of a certain amount of suspension in a continuous process is calculated by division of the power input

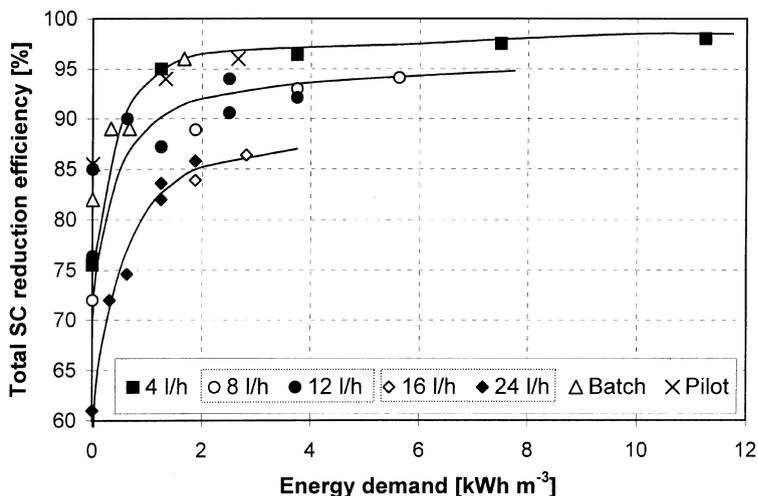


Figure 19. Total SC reduction efficiency versus specific energy demand; 3.3 MHz, 14 cm lab scale reactor (4, 8, 16 l h⁻¹), 20 cm lab-scale reactor (12, 24 l h⁻¹), pilot-scale reactor (80, 150 l h⁻¹), batch reactor (500 ml, 10 W), filter backwash water, different samples, initial SC about 500 mg l⁻¹.

by the flow rate. Power input times sonication time over the treated volume gives the energy needed for the treatment in case of a batch system. Most data shown in Figure 19 were measured with the continuous flow lab-scale reactors and are complemented by data from batch and continuous flow pilot-scale experiments. The flow rate of 8 l h⁻¹ was applied to the lab-reactor with 14 cm transducer-reflector spacing and corresponds with a flow of 12 l h⁻¹ (applied to the 20 cm reactor), since the average flow rate and residence time was identical in both cases due to the reactor geometry. The same situation is given for 16 l h⁻¹ (14 cm reactor) and 24 l h⁻¹ (20 cm reactor). The curves shown in Figure 19 indicate the tendency of the data. A higher specific energy input is associated with higher separation efficiency for a given flow rate. Also, an increase in performance is seen with longer residence time or lower flow rate, respectively, which is in agreement with results published for biotech ultrasonic separation reactors [88,89,91]. Best performance was measured at 4 l h⁻¹ and about 11 kWh m⁻³ (14 cm reactor) with 98 % SC separation efficiency. The maximum specific energy input was limited by the maximum power delivered by the ultrasonic transducers. The general trend of the plot suggests, however, that higher efficiency might be achieved with more powerful transducers. Especially the data given for the pilot-scale reactor shows good performance at very moderate energy consumption.

A significant potential for further separation efficiency enhancement with more powerful large-scale transducers can be predicted on the basis of this result. It can also be concluded from Figure 19 that the volume specific energy demand is of the order of some kWh m^{-3} , depending on the desired flow rate and efficiency. The energy costs have to be considered in the context of the overall costs of the whole process, in which the separation is one processing step. An energy demand of some kWh m^{-3} for a normal wastewater treatment process is in any case of an order of magnitude, which has to be considered carefully. It will depend on the particular situation, however, whether the energy demand is prohibitive. In case of the filter backwash water, discussed here, the energy used has to be related to the total amount of drinking water produced. On average, only 2% of the filtered raw water is used for backwashing of the filters and therefore, the energy demand has to be divided by a factor 50 in order to obtain the product related energy consumption of the filter backwash water separation in an USSW system. This is, then, of the order of one-tenth of a kWh m^{-3} , which is acceptable in the context of the overall costs of the drinking water purification process.

4.2 Thickening of Pre-settled Sludge

The separation of particle-containing water presented above was focused on the clarification of the suspending phase. But also, enrichment of the solids concentration of already settled sludges by thickening, could be achieved by application of USSW. Ultrasound in the range of 40–350 kHz has been found to be suitable for this purpose on the lab-scale (URS 1000 system by ELAC Nautik, up to 0.5 l sonicated volume). Flocculation sludge from a surface water treatment plant was sonicated for up to 10 min and then allowed to sediment. A considerable acceleration of the sedimentation process was achieved by sonication, compared with pure gravitational settling. The acceleration effect was seen up to a power-transducer surface area ratio of about 0.8 W cm^{-2} . This upper power limit of the acceleration effect coincided with the cavitation threshold, which could be detected by the erosion of aluminum foil. Disruption of the flocculation aggregates and resuspension of the solids was observed above this power limit. The sonic thickening effect was attributed partly to a change of the sludge structure, which was observed during the sonication, but also to a drainage effect by large-scale streaming, which was found to be beneficial for the thickening process. The thickening reactor was therefore not divided by ATF. Sonication leads to a mechanical opening of drainage channels, through which the water, bound in the gel structure of the sludge, can escape. A simple batch

process on the pilot-scale has been developed on the basis of the lab experiments. The pilot-scale batch reactor (70 l sonicated volume) was equipped with a 40 kHz “off the shelf” transducer, usually employed in industrial cleaning baths (ELAC Nautik, Kiel). Details of the lab and pilot plant reactors and the scale-up method have been described earlier [54]. USSW thickening was found to be effective for sludges with up to 1% initial solids concentration. Up to 50% volume reduction within 30 min could be achieved for such sludges, whereas, no sludge volume reduction by gravity alone was seen. The USSW thickening effect was considerably more pronounced for less concentrated sludges. An example for a 5 g l^{-1} initial SC sludge is shown in Figure 20.

A sludge volume reduction down to about 25% of the initial value after 30 min total treatment time is seen for 10 min sonication on the lab- and the pilot-scale. The sonic thickening process is also faster compared with stirring (conventional blade stirrer), which is a commonly used thickening method. The specific energy demand of the thickening process has been determined to be of the same order of magnitude as the MHz-frequency USSW process described above (some kWh m^{-3}). This value has to be related to the total amount of drinking water produced. About 1% of the treated surface water flow is obtained as flocculation sludge. The energy consumption of an USSW thickening process is, therefore, of an order of magnitude of tenth of a kWh m^{-3} .

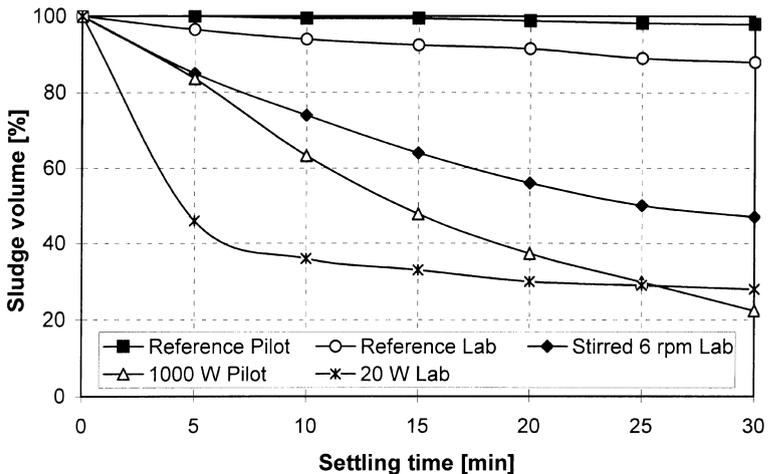


Figure 20. Sludge volume versus settling time, 40 kHz, batch lab-reactor (400 ml), pilot-scale reactor (70 l), first 10 min sonicated, flocculation sludge from surface water treatment, initial SC 5 g l^{-1} .

5. FEASIBILITY OF IMPLEMENTATION ON AN INDUSTRIAL SCALE

The two USSW–sedimentation processes described and discussed above have been successfully developed into pilot-plant scale. The possible further development to an industrial scale is mainly dependent on the availability of powerful large surface transducers. In the case of the kilohertz frequency application for thickening pre-settled sludge, current commercially available systems can be used. The higher frequency megahertz aggregation technology requires further transducer development. The currently realized through put is a maximum of 150 l h^{-1} for the continuous aggregation–sedimentation system. The process of aggregation takes time in the order of magnitude of a couple of minutes. Simultaneously, limits of enlargement of the sonic chamber have been found, due to large-scale acoustic and convective streaming and the available transducer size. These constraints suggest that a further increase of the capacity can rather be achieved by a “scale-out”, which means the parallel operation of multiple devices, than by a further scale-up. The same concept of this “scale-up by replication” is possible for the batch sludge thickening process. The reactor could be operated in a sequencing mode and be scaled-out easily by running many reactors in parallel. However, there might be situations, where the already realized through put is sufficient. This is the case for the latter three industrial sample suspensions, investigated in Section 4.1.4. The samples were all taken from processes, where essentially a washing liquid is used in a closed cycle. Currently, the whole suspension of washing liquid and washed out solids is periodically taken out of these processes, treated and the solids and the used washing liquid are finally disposed. An USSW–sedimentation device could be integrated into such processes in a side stream arrangement. A simplified schematic of such a continuous USSW separation is shown in Figure 21.

A relatively small flow would be by-passed and treated continuously in the sonic reactor. The solids, which are washed out in the primary wash cycle, would be separated continuously and a considerable amount of the treated washing liquid could be recycled into the washing process. However, a small wastewater bleed flow is inevitable in order to prevent too high concentrations of dissolved substances, (e.g. salts) and to substitute used detergent. This concept works not only for the example suspensions, which are of environmental relevance and have been investigated in this contribution. Continuous ultrasonic treatment of a harvest flow from perfusion bio-reactors has already been developed to a commercial stage [48]. Suspension is taken from the bio-reactor and the cells are retained in the ultrasonic chamber. The cells sediment back into the fermenter,

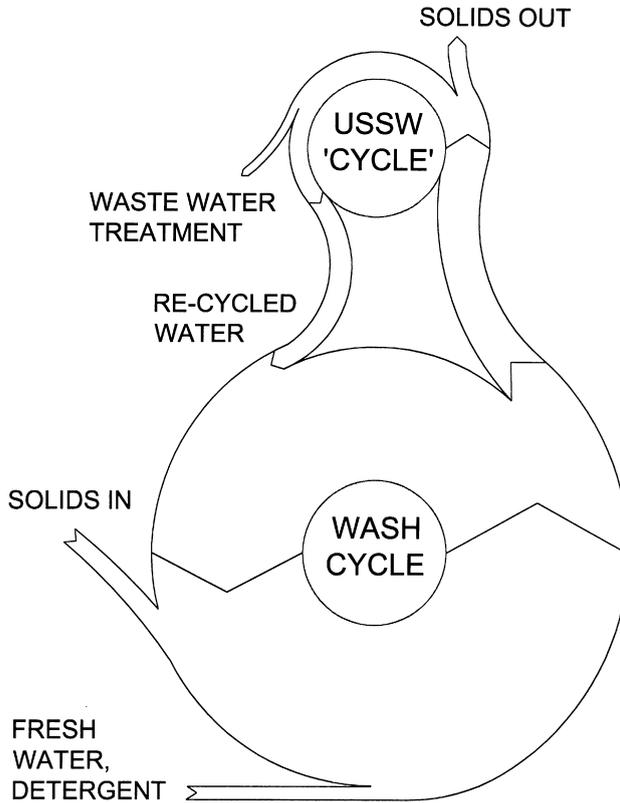


Figure 21. Schematic integration of a continuous USSW separation process.

whereas clarified liquid, containing the product of the bio-process, is extracted. Cell-liquid separation efficiency in excess of 99% has been reported [44,45,88]. Two versions of the system are currently available: (a) 10 l d^{-1} , and (b) 50 l d^{-1} ultrasonic filter. The method still has scale-up potential [48].

6. CONCLUSIONS

It has been shown that USSW conditioning of suspensions in separation technology is applicable for flow through treatment (150 l h^{-1}) of particle-containing suspensions as well as for batch thickening (70 l) of pre-settled sludges. Both methods have been successfully scaled-up and tested for separation purposes in environmental technology.

It has been seen that higher power input is beneficial for aggregation of particles in suspension at a frequency of 3.3 MHz, when large-scale streaming is controlled. Streaming was controlled here, by division of the sonicated volume with acoustically transparent PE film. An optimum geometry was found with the ATF inserted at 4 mm spacing in the sonicated volume. Separation performance has shown a strong dependence on the initial solids concentration of the suspension. The process works better with higher concentrations. The results obtained from lab- and pilot-scale experiments are consistent with each other and indicate considerable further separation efficiency increase on the pilot-scale with more powerful transducers. Such high power megahertz transducers still need to be developed.

The optimal power input per unit area of the transducer was comparable to the cavitation threshold determined for thickening of flocculation sludge from surface water treatment (0.8 W cm^{-2}). Streaming was found to assist the thickening process. The 40 kHz sonication system used for thickening was a standard device usually employed in industrial cleaning baths. The sludge volume could be decreased down to 25% of the initial value for sludges of about 5 g l^{-1} solids concentration, whereas sedimentation by gravity alone did not show a significant effect. The ultrasonic process was also more effective than conventional thickening by stirring of the sludge. The upper limits for USSW thickening in terms of solids concentration of this type of sludge was found to be 2%.

A specific advantage of the USSW technology is the avoidance of chemicals and of the dosage systems for their application. This leads to reduced waste volumes, an easy process control and therefore, to reduced costs. However, the specific energy demand for conditioning of a certain amount of suspension is of the order of some kWh m^{-3} . This is of a magnitude, which is relevant in terms of environmental technology, since environmental protection is commonly a cost sensitive area. Calculations of the overall costs of USSW processes in comparison to already established separation technologies still have to be carried out. The same applies to a life cycle and environmental impact assessment of the overall resources and energy demand of USSW processes. The cost issue is of minor importance in biotechnology, where already commercial USSW systems (current maximum capacity 50 l d^{-1}) [48] are available, due to the usually high value of biotech products.

A number of potential applications for treatment of waste suspensions from water industry and industrial washing processes have been presented here. The promising results encourage, to further improvement efforts of the technology. Parallel development of similar USSW–sedimentation approaches in biotechnology and alternative separation methods, based on the application of ultrasonic fields [49,50,52,55,56], are likely to further

stimulate and fertilize research on ultrasonic phase separation in environmental technology.

ACKNOWLEDGMENTS

The work has been supported by the German Ministry of Education and Science, Research and Technology (BMBF 02 WT 9428/8 and 02 WT 9678/9) and EU TMR Network *UltraSonoSep* (#ERBFMRXCT97-0156).

REFERENCES

- [1] Brandt, O., Freund, H., and Hiedemann, E. *Z. Phys.*, 104 (1937) 511.
- [2] Söllner, K. and Bondy, C. *Trans. Faraday Soc.*, 32 (1936) 616.
- [3] Kundt, A. *Ann. Phys. Chem.*, 135 (1868) 337.
- [4] Kundt, A. and Lehmann, O. *Ann. Phys. Chem.*, 153 (1874) 1.
- [5] Brandt, O. and Hiedemann, E. *Kolloid Z.*, 75 (1936) 129.
- [6] Brandt, O., Freund, H. and Hiedemann, E. *Kolloid Z.*, 77 (1936) 103.
- [7] King, L. V. *Proc. R. Soc. London*, A137 (1935) 212.
- [8] Yosioka, K. and Kawasima, Y. *Acustica*, 5 (1955) 167.
- [9] Eckart, C. *Physic. Rev.*, 73 (1948) 68.
- [10] Liebermann, L. N. *Physic. Rev.*, 75 (1949) 1415.
- [11] Raleigh, J. W. S. *The theory of sound*, Vol. 2, Dover Publications: New York USA, 1945 (reprint).
- [12] Schlichting, H. *Phys. Z.*, 33 (1932) 327.
- [13] Gor'kov, L. P. *Sov. Phys. Dokl.*, 6 (1962) 773.
- [14] Dyson, M., Woodward, B. and Pond, J. B. *Nature*, 232 (1971) 572.
- [15] Baker, N. V. *Nature*, 239 (1972) 398.
- [16] Miller, D. L., Nyborg, W. L. and Whitcomb, C. C. *Ultras. Med. Biol.*, 4 (1978) 545.
- [17] Miller, D. L., Nyborg, W. L. and Whitcomb, C. C. *Science*, 205 (1979) 505.
- [18] ter Haar, G. and Wyard, S. J. *Ultras. Med. Biol.*, 4 (1978) 111.
- [19] Gould, R. K. and Coakley, W. T. *Proc. of the 1973 Symposium on finite-amplitude wave effects in fluids*, Copenhagen, Denmark, 252.
- [20] Fittipaldi, F. *Acustica*, 41 (1979) 263.
- [21] Higashitani, K., Fukushima, M. and Matsuno, Y. *Chem. Eng. Sc.*, 12 (1981) 1877.
- [22] Barmatz, M. and Collas, P. *J. Acoust. Soc. Am.*, 77 (1985) 928.
- [23] Weiser, M. A., Apfel, R. E. and Neppiras, E. A. *Acustica*, 56 (1984) 114.
- [24] Coakley, W. T., Bardsley, D. W., Grundy, M. A., Zamani, F. and Clarke, D. J. *J. Chem. Tech. Biotechnol.*, 44 (1989) 43.
- [25] Danilov, S. D. and Mironov, M. A. *Sov. Phys. Acoust.*, 38(3), (1992) 250.
- [26] Nyborg, W. L. *Ultras. Med. Biol.*, 15 (1989) 93.
- [27] Whitworth, G. and Coakley, W. T. *J. Acoust. Soc. Am.*, 91 (1992) 79.
- [28] Beissner, K. and Makarov, S. N. *J. Acoust. Soc. Am.*, 97 (1995) 898.
- [29] Makarov, S. and Ochmann, M. *Acustica acta acustica*, 82 (1996) 579.
- [30] Makarov, S. and Ochmann, M. *Acustica acta acustica*, 83 (1997) 197.
- [31] Ochmann, M. and Makarov, S. *Acustica acta acustica*, 83 (1997) 827.
- [32] Doinikov, A. A. *Physic. Rev.*, 54(6), (1996) 6297.
- [33] Doinikov, A. A. *J. Acoust. Soc. Am.*, 101 (1997) 713.
- [34] Whitworth, G., Grundy, M. A. and Coakley, W. T. *Ultrasonics*, 29 (1991) 439.

- [35] Yasuda K. *Jpn. J. Appl. Phys.*, 38 (1999) 3316.
- [36] Tuziuti, T., Kozuka, T. and Mitome, H. *Jpn. J. Appl. Phys.*, 38 (1999) 3297.
- [37] Woodside, S. M., Bowen, B. D. and Piret, J. M. *AIChE J.*, 43(7), (1997) 1727.
- [38] Apfel, R. E. *Fortschritte der Akustik - DAGA*, 1990, 19.
- [39] Schram, C. J. In Mason, T. J., (ed.), *Advances in Sonochemistry*, JAI press: London England, 1991, Vol. 2, pp. 293-322.
- [40] Gröschl, M. *Acustica acta acustica*, 84 (1998) 432.
- [41] Gröschl, M. *Acustica acta acustica*, 84 (1998) 632.
- [42] Coakley, W. T., Hawkes, J. J., Sobanski, M. A., Cousins, C. M. and Spengler, J. *Ultrasonics*, 38 (2000) 638.
- [43] Benes, E., Burger, W., Gröschl, M., Schaffner, A., Trampler, F., Bolek, W., Gaida, T., Doblhoff, O. and Hager, F. *Proc. Ultrasonics International 1993, Conference Proc.*, 515.
- [44] Bierau, H., Perani, A., Al-Rubeai, M. and Emery, A. N. *J. Biotechnol.*, 62 (1998) 195.
- [45] Zhang, J., Collins, A., Chen, M., Knyazev, I. and Gentz, R. *Biotechnol. Bioeng.*, 59 (1998) 351.
- [46] Gröschl, M., Burger, W., Handl, B., Doblhoff-Dier, O., Gaida, T. and Schmatz, C. *Acustica acta acustica*, 84 (1998) 815.
- [47] Coakley, W. T. *Trends in Biotechn.*, 15 (1997) 506.
- [48] Oudshoorn, A., Trampler, F. and Benes E. *Biotech International*, 11 (1999) 27.
- [49] Benes, E., Hager, F., Bolek, W. and Frischherz, H. *Fortschritte der Akustik - DAGA*, 1990, 1143.
- [50] Frischherz, H., Ilmer, A., Stuckart, W., Benes, E., Hager, F., Gröschl, M. and Bolek, W. In Biffl, W., (ed.), *Trinkwasseraufbereitung mit Ultraschall II*, Wiener Mitteilungen Wasser-Abwasser-Gewässer, Universität für Bodenkultur: Vienna, 1991, Vol. 94.
- [51] Tolt, T. L. and Feke, D. L. *Chem. Eng. Sc.*, 48 (1993) 527.
- [52] Hawkes, J. J. and Coakley, W. T. *Enzyme Microbiol. Technol.*, 19 (1996) 57.
- [53] Gupta, S. and Feke, D. L. *AIChE J.*, 44 (1998) 1005.
- [54] Spengler, J. and Jekel, M. In Tiehni, A., and Neis, U., (eds), *Ultrasound in Environmental Engineering*, TU Hamburg-Harburg Rep. Sanit. Eng., GFUE: Hamburg-Harburg, 1999, Vol. 25, pp. 189-204.
- [55] Wakeman, R. J. and Bailey, A. J. L. *Trans IChemE*, 78A (2000) 651.
- [56] Hill, M., and Wood, R. J. K. *Ultrasonics*, 38 (2000) 662.
- [57] Mandralis, Z. I. and Feke, D. L. *AIChE J.*, 39 (1993) 197.
- [58] Gupta, S., Feke, D. L., and Manas-Zloczower, I. *Chem. Eng. Sc.*, 50 (1995) 3275.
- [59] Limaye, M. S. and Coakley, W. T. *J. Appl. Microbiol.*, 84 (1998) 1035.
- [60] Yasuda, K. *Jpn. J. Appl. Phys.*, 36 (1997) 3130.
- [61] Cousins, C. M., Holownia, P., Hawkes, J. J., Price C. P., Keay, P., and Coakley, W. T. *Ultrasonics*, 38 (2000) 654.
- [62] Frischherz, H., Benes, E., Ernst, J., Hager, F. and Stuckart, W. In Biffl, W. (ed.), *Trinkwasseraufbereitung mit Ultraschall I*, Vol. 85, Wiener Mitteilungen Wasser-Abwasser-Gewässer, Universität für Bodenkultur: Vienna, 1989.
- [63] Spengler, J. and Jekel, M. *Proc. Joint meeting 137th ASA meeting, 2nd convention EAA: Forum Acusticum, 25th DAGA conference, Berlin, Germany 1999, CD-ROM.*
- [64] Spengler, J. and Jekel, M. *Ultrasonics*, 38 (2000) 624.
- [65] Riera-Franco de Sarabia, E., Gallego-Juárez, J. A., Rodríguez-Corral, G., Elvira-Segura, L., and González-Gomez, I. *Ultrasonics*, 38 (2000) 642.
- [66] Holwill, I. L. J. *Ultrasonics*, 38 (2000) 650.
- [67] Gallego-Juárez, J. A., Riera-Franco de Sarabia, E., Rodríguez-Corral, G., Hoffmann, T. L., Gálvez-Moraleda, J. C., Rodríguez-Maroto, J. J., Gómez-Moreno, F. J.,

- Bahillo-Ruiz, A., Martín-Espigares, M., and Acha, M. *Environ. Sci. Technol.*, 33 (1999) 3843.
- [68] Gardner, E. A. and Apfel, R. E. *J. Coll. Interf. Sc.*, 159 (1993) 226.
- [69] Singh, B. P. *Acoustics Letters*, 19 (1995) 78.
- [70] Jöhring A. *Einsatz von Ultraschall zur Partikelagglomeration und fest-flüssig Separation*, PhD dissertation, Technical University Berlin, 1998.
- [71] Woodside, S. M., Piret, J. M., Gröschl, M., Benes, E., and Bowen, B. D. *AIChE J.*, 44(9) (1998) 1976.
- [72] Nyborg, W. L. In Mason, W. P., (ed.), *Physical acoustics*, Academic press: New York USA 1965, Vol. 2, pp. 265–331.
- [73] Zarembo, L. K. In Rozenberg, L. D., (ed.), *High-intensity ultrasonic fields*, Plenum press: New York, USA 1971, pp. 137–199.
- [74] Jöhring A. Proc. World Congress on Ultrasonics Berlin, Germany 1995, 769.
- [75] Mitome, H. *Electronics and Communications in Japan*, 81(10) (1998) 1.
- [76] Beissner, K. *Fortschritte der Akustik - DAGA*, 1982, 779.
- [77] Hawkes, J. J., Cefai, J. J., Barrow, D. A., Coakley, W. T. and Briarty, L. G. *J. Phys. D: Appl. Phys.*, 31 (1998) 1.
- [78] Thompson, C., Mulpur, A., Mehta, V. and Chandra, K. *J. Acoust. Soc. Am.*, 90 (1991) 2097.
- [79] Mitome, H., Kozuka, T., and Tuziuti, T. *J. Acoust. Soc. Am.*, 100 (1996) 2589
- [80] König, W. *Ann. Phys. Chem.*, 42 (1891) 353.
- [81] Bjerknes, V. *Hydrodynamische Fernkräfte*, Band 1, Leipzig Germany, 1902.
- [82] Nyborg W.L. In Fry, F.J. (ed.) *Ultrasound: Its Applications in Medicine and Biology*, part 1, Elsevier, Amsterdam. pp. 1–75.
- [83] Hoffmann, T. L. and Koopmann, G. H. J., *Acoust. Soc. Am.*, 99 (1996) 2130.
- [84] Hoffmann, T. L. and Koopmann, G. H. J., *Acoust. Soc. Am.*, 101 (1997) 3421.
- [85] Svarovsky, L. *Solid-liquid separation*, Butterworths Monographs in Chemistry and Chemical Engineering: London, England, 3rd ed., 1990.
- [86] Mark, G., Tauber, A., Laupert, R., Schuchmann, H.-P., Schulz, D., Mues, A., and von Sonntag, C. *Ultrasonics Sonochemistry*, 5 (1998) 41.
- [87] Pankau, J. and Jekel, M. Proc. World Congress on Ultrasonics Berlin, Germany (1995), 773.
- [88] Doblhoff-Dier, O., Gaida, T., Katinger, H., Burger, W., Gröschl, M., and Benes, E. *Biotechnol. Prog.*, 10 (1994) 428.
- [89] Gaida, T., Doblhoff, O., Strutzenberger, K., Katinger, H., Burger, W., Gröschl, M., Handl, B., and Benes, E. *Biotechnol. Prog.*, 12 (1996) 73.
- [90] Smoluchowski, M. *Z. Phys. Chem.*, 92 (1918) 129.
- [91] Trampler, F., Sonderhoff, S. A., Pui, P. W. S., Kilburn, D. G., and Piret, J. M. *Bio/Technol.*, 12 (1994) 281.

ULTRASOUND IN FILTRATION AND SLUDGE DEWATERING

Pentti Pirkonen

OUTLINE

1. Introduction	222
2. Origin of Ultrasonically Induced Effects	222
3. Pre-treatment Prior to Dewatering	223
4. Dewatering	227
4.1 Vacuum Filtration	227
4.2 Electro-acoustic Filtration	230
5. Ultrasonic Effects in Microfiltration (MF), Ultrafiltration (UF) and Nanofiltration (NF)	233
5.1 Ultrasonically Assisted Membrane Filtration	233
5.2 Electro-acoustically Assisted Membrane Filtration	236
5.3 Ultrasonically Aided Cake Filtration	238
6. Ultrasonical Effects in Reverse Osmosis (RO) and Dialysis	241
7. Summary	243
References	243

Advances in Sonochemistry
Volume 6, pages 221–246.

© 2001 Elsevier Science B.V. All rights reserved.

1. INTRODUCTION

The use of additional forces to aid filtration and dewatering has gained an increasing recognition in recent years. Magnetically assisted filters are now widely accepted as technical alternatives in the choice of solid–liquid separation equipment. Commercial electrically assisted filters exist but have not been widely adopted [1–3], and ultrasonically assisted filters are found almost exclusively in research laboratories. There is a general understanding of the role of magnetic and electric fields when used to enhance filtration [4]. Properties and small-scale uses of ultrasound (US) have been studied extensively by physicists, chemists, and others. The resulting macrosonic applications can be found in several areas of industrial process engineering, e.g. in extraction processes, cleaning, atomisation, emulsification and cell disruption, dispersion of solids, nucleation and growth of crystals, and degassing [5].

The present text is focussed on ultrasonically assisted filtration and sludge dewatering and especially on environmental applications and studies. The advantages expected from using US in filtration and dewatering include: more rapid liquid removal rate, higher dry solids (DS) content in the product, lower processing temperature, maintenance of product integrity and product recovery. The main reasons hindering the breakthrough of filtration technologies connected with ultrasonics are non-development of transducer technology and control of erosion caused by cavitation at high ultrasonic intensities.

2. ORIGIN OF ULTRASONICALLY INDUCED EFFECTS

In general, power US is characterised by an ability to transmit substantial amounts of mechanical power through small mechanical movements. The passing of ultrasonic waves of a suitably high intensity through liquid and gaseous media is accomplished by primary phenomena such as cavitation, radiation pressure, acoustic streaming, and secondary phenomena of a physico-chemical nature such as: dispersion, coagulation, and change in liquid properties [6–10]. In many cases the effect of US is due to a combination of many effects acting synergistically.

As with any sound wave, US is propagated via a series of compression and rarefaction waves induced in the molecules of the medium through which it passes. At sufficiently high power, the rarefaction cycle may exceed the attractive forces of the liquid molecules, and cavitation bubbles will form. Cavitation occurs at frequencies of roughly 20–1000 kHz. In aqueous systems, each cavitation bubble acts as a localised “hot spot,” generating

Table 1. Parameters Affecting the Cavitation Threshold [4,5,7,14]

<i>Parameter</i>	<i>Influence of increasing this parameter on the cavitation threshold</i>
Dissolved gas saturation	Decrease
Hydrostatic pressure	Increase
Surface tension	Increase
Temperature	Decrease
Solids concentration	Decrease
Particle size	Decrease

temperatures of about 4000–6000 K and pressures of 100–200 MPa. The implosion occurs with lifetimes of $<10 \mu\text{s}$ [11,12]. Bubble size can be as much as 100–200 μm prior to implosion [12], but the most effective bubble collapse occurs at a bubble size of several micrometres [13]. Atschley and Crum [14] compiled general observations from published results on the effects of liquid properties on the transient cavitation threshold, which are summarised in Table 1 [4,5,7,14].

In a heterogeneous solid–liquid situation, collapse of the cavitation bubble will have significant mechanical and chemical effects, e.g. on cell destruction and formation of free radicals. Collapse near a surface produces an unsymmetrical inrush of fluid to fill the void, with the result that a liquid jet with a speed of the order of 110 m/s is formed and targeted at the surface [7,11,15]. The liquid jet serves as a basis, e.g. for widely used commercial cleaning processes. The ultrasonic power used in cleaning varies between 0.5 and 6 W/cm^2 [5, 16].

Ultrasonic radiation without cavitation can cause particle agglomeration, due to particle collision (orthokinetic-, radiation-, Oseen-, and Stokes forces) and to the attraction of particles caused by Bernoulli's effect [6,7]. Ultrasonic agglomeration is also explained by disturbances in the symmetry of the electric double layer around the moving particles, creation of a dipole moment and its consequence, increased intermolecular influence, causing attraction and coagulation of particles [8].

3. PRE-TREATMENT PRIOR TO DEWATERING

Typical industrially-used pre-treatment methods for enhancing solid–liquid separation processes include: filter aids such as diatomaceous earth, inorganic coagulants, polyelectrolytes, grinding, freezing, heating e.g. wet carbonisation, and pH regulation.

The design of the properties of sludge flocs in connection with dewatering plays an important role in the overall optimisation of wastewater treatment

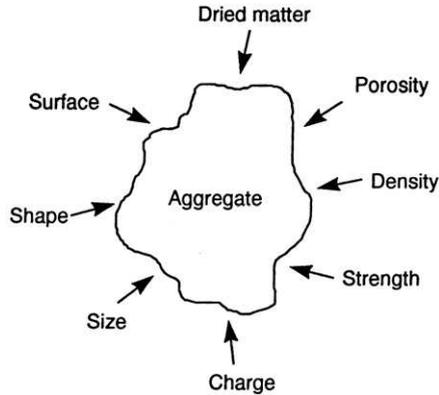


Figure 1. Characteristic parameters of aggregate structure in sewage sludges [17].

(see Figure 1). The use of a centrifuge requires flocs with high strength, and consequently sludge aggregates prior to flocculation should exhibit maximum stability and density. In contrast, the use of a belt filter press requires very loose aggregates that release their loose water very rapidly [17]. The effects of US in pre-treatment would be expected to include the following:

- Breaking down and formation of floc structures [6,17–24].
- Destruction of cell walls and deformation of polymer chains [8,23,26,27].
- Inactivation of micro-organisms [17,28].
- Cleaning and activation of particle surfaces [23,29,30].

Pre-treatment of different wastewater sludges by US with specific energy inputs between 20 and 100 W/l has led to a re-arrangement of sludge aggregates, forming more compact and stronger structures. DS content increased up to 5% units in lab-scale filtration while the quality of effluent water remained constant [17]. Even higher improvements in DS content have been obtained in other lab-scale vacuum filtration experiments (Table 2). The optimum time for sonication with a 20 kHz transducer prior to filtration has been 90–120 s, sonication even lowered the required polyelectrolyte dose [23]. On the other hand, in other cases ultrasonic disintegration of sludge has increased the dose of polyelectrolytes by as much as 200% [17].

The particle agglomeration phenomenon in ultrasonic standing-wave has long been known. A concept utilising a standing field is shown schematically in Figure 2 [20].

Due to the primary acoustic radiation force, the suspended particles are collected in planes perpendicular to the direction of sound propagation.

Table 2. Final Moisture Content of Dehydrated Organic Sludge (Initial Water Content 93.4%) Subjected to Vacuum Filtration [23]

Method of preparation		Final water content in vacuum filtration
Reagent	Dose	%
Unprepared	–	87.4
Ultrasound	–	78.2
Polyelectrolyte	1.4	75.4
Ultrasound + Polyelectrolyte	0.8	72.3

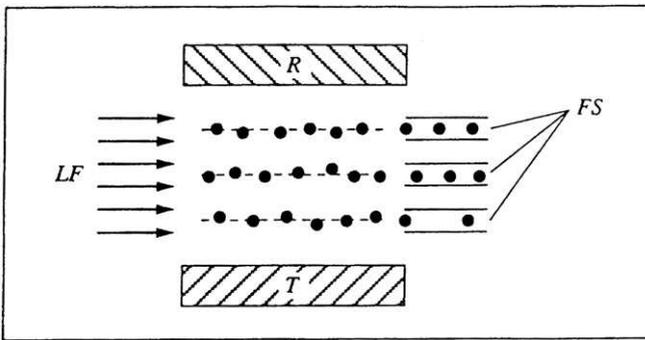


Figure 2. Principle of particle separation in a standing acoustic field by means of divided fluid flows. T: transducer, R: reflector, LF: laminar flow, FS: flow splitters [20].

Subsequently, agglomeration of collected particles occurs, aided by the acoustic interaction force. After switching off the sound field, the larger agglomerates sediment due to gravity. The method has been reported to be applicable only to particles having a tendency to form stable agglomerates, such as municipal sludge [6] and fibre particles [19] or generally those having very low solid contents and small particle sizes [24]. Acoustic separation systems can be designed to operate in batch mode or in continuous-flow mode. In the latter case nodal planes move slowly in pseudo-standing waves [20]. Typical frequencies used for agglomeration–filtering range from 2 to 3.3 MHz [18], but successful application of 20 and 40 kHz has also been reported [6,19]. Energy input must be lower than that needed for the creation of cavitation, because cavitation of the suspension creates gas bubbles that hinder the agglomeration process in the standing wave situation.

Although extensive research has been conducted on acoustic particle agglomeration–separation, most has been restricted to the demonstration of fundamentals and/or the development of lab-scale devices. A particularly

high potential for applications exists in the field of biotechnology, due to low flowthrough volumes and high product values [20]. Two commercial biotechnical applications utilising standing-wave technology have been developed. Sono flocc (Biotech Inc., Richmond, BC, Canada) is a device for retentate hybridoma [21], and Anton PAAR GmbH, Gratz, Austria has developed a device to separate mammalian cells in the fermentation process [25]. Spengler and Jekel compiled an extensive number of standing-wave applications in the environmental industry [18].

The active performance of the US does not only decrease particle size, but also causes partial breakage of hydrogen bonds, and fragmentation of 2-, 4- and 8-hydrogen bonded agglomerates, is said to occur [23]. Cell destruction requires an energy input that usually exceeds the economic resources of a sewage plant. Lower energy input only results in disintegration of particle aggregates [17]. Ultrasonic treatment of different polyelectrolytes for 5–15 s using a 20-kHz transducer prior to lab-scale vacuum filtration of digested sludge resulted in higher DS contents of cake with lower polyelectrolyte dosages in comparison to filtration with no ultrasonic treatment. The polyelectrolytes after ultrasonic treatment were stretched, less branched, and elongated. This effect is time- and polyelectrolyte-dependent [26,27].

Ultrasonic pre-treatment of zooplankton under the conditions of a 50 ml flowthrough reactor, ultrasonic input power of 200 W, and frequency of 20 kHz not only resulted in inactivation but also in the complete destruction of zooplankton within 10 s. After flocculation and sand filtration of drinking water, elimination of about 93% of these organisms was attained compared with about 20% without ultrasonic treatment (Figure 3). This result equals that of usual inactivation method using potassium permanganate [28].

Ultrasound (US) can be used to partially or totally destroy threaded bacteria in floating and bulking sludge, resulting in a dramatic increase in sedimentation rate [17]. Ultrasonic disintegration of sludge also releases intracellular water [22] and enhances anaerobic digestion processes resulting in better dewatering properties of sludges through mineralisation of organic matter [31].

Ultrasound (US) also may cause changes in the activity of particle surfaces, which jointly affect the increase in particle packing ability [8]. Ultrasonic treatment of iron ore tailings was effective only when it was done after dosing with starch. The explanation suggested did not involve a direct effect on starch structure; instead, the US was assumed to remove clay materials, which may have prevented starch adsorption from the surface of iron particles. A 22-kHz transducer with input power of 500 W/l was used in the ultrasonic laboratory treatment [29]. Fairbanks [30] observed that treatment of coal coated with sulphurous clay bloom in an ultrasonic tray

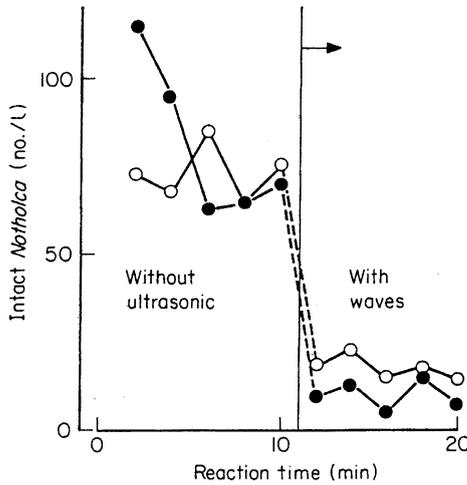


Figure 3. Amount of intact *Notholca caudata* in the raw water before and after initiation of ultrasonic treatment. Reaction time 12 s. Counts of parallel tests are shown [28].

literally exploded the bloom away from the surface of coal particles, due to the collapse of cavitation bubbles. Water content was also decreased in subsequent screening, and the screening rate improved significantly. Fairbanks [30] used the same ultrasonic tray to treat settling pond water and obtained as much as 10 times faster settling rates than without ultrasonic treatment and even with lower flocculent dosage. This is explained by the ultrasonic destruction of the gel layer around the particles, which makes the water layer around the particles thinner and thus enables particles to interlock more easily with adjacent particles.

4. DEWATERING

4.1 Vacuum Filtration

The ultrasonic radiation effect is mainly based on either the removal of particles from the filter surface or the cleaning of the filter pores. Reduction in viscosity due to local heating may cause an increase in flow rate [7,32]. Few studies dealing with environmental application of ultrasonics have been reported prior to the 1990s. Ultrasonic whistles have mainly been used to remove water from different materials based on phase change (atomisation and drying) [24]. In general, enhancements in filtration efficiencies of ten to

several hundred percent have been reported [32–39]. Without ultrasonic power the flow rate rapidly decreases; with ultrasonic power the decrease is much smaller and appears to approach a constant value after a few hours (Figure 4) [32,36,37]. This phenomenon has also been observed in other types of filtration presented in the Sections 8.4.2, 8.5.1, and 8.5.3.

The ultrasonic transducer(s) have either been coupled to the filter element [32,35,39], mounted on the slurry side [32,33,36,37,39,40] or filtrate side [38] of the filter element (Figure 5), or located on the side of the filtration chamber at the level of the filter element [34]. Pore size and material of the filter element vary widely among studies. Pore size ranges from about 5 to 10 μm . The typical type of filter employed uses metal wire. Placement of a transducer on the slurry side may easily increase the penetration of small particles through the filter [34]. In contrast, filtrate-side placement of a transducer can even lower particle concentration in the filtrate [38].

Typical frequencies of ultrasonic transducers ranged 19–20 kHz [32,33,36,40]. Transducers operating at frequencies of 20–100 kHz are still within the band of power US where cavitation is easily obtained with low power consumption and with the transducers easily commercially available. Björnö et al. [37] used frequencies of 15 and 45 kHz in oil filtration and recommended the use of pulsed ultrasonic radiation. Pulsation of US leads to lower energy consumption and lower erosion of the filter element. Tuori et al. [7,34] compared frequencies of 11, 39, and 61 kHz in gravity filtration and 16, 32, and 52 kHz in the vacuum filtration of bio-fibre sludge with 1% DS content originating from the wastewater plant of a paper mill.

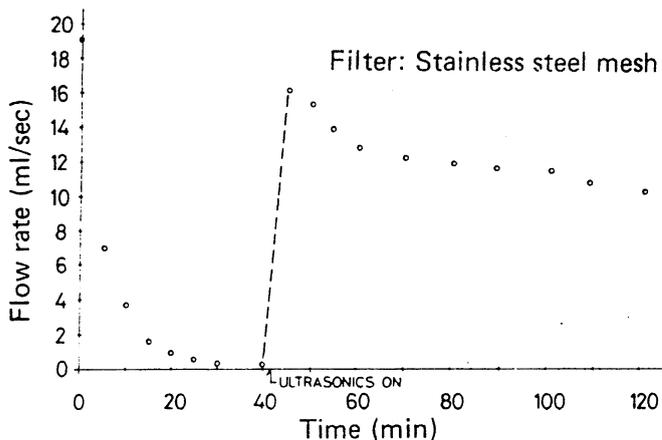


Figure 4. Flow rate of stainless steel wire cloth filter with ultrasonic enhancement and long off periods [32].

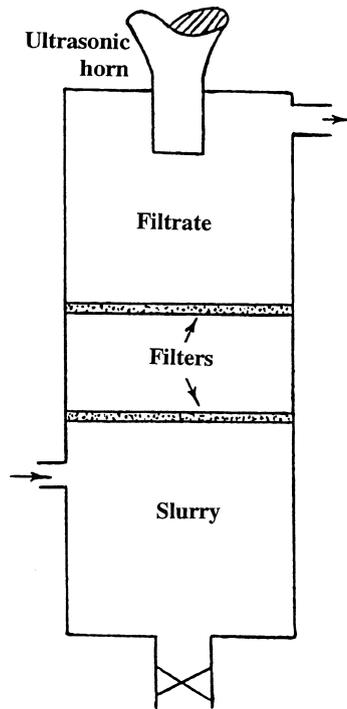


Figure 5. Schematic sketch of the closed ultrasonic filtration unit [33].

A filter with a surface area of 0.015 m^2 was placed on the bottom of a 7-l tube. The lowest frequency was the best in both filtration systems and the best filtration efficiencies were almost 20 times higher when compared with the reference. Ultrasonic radiation has kept the filter surface open but also increased the flow of dry matter through the filter to some extent, because the pore size of the filter element was 2 mm. Vacuum filtration tests were also carried out with a device also having stationary suspension but at double the filtration area. Filtration enhancement due to the use of US was 12-fold higher compared with the reference [34].

Fairbanks [33] filtered a slurry consisting of oil with 5–7% by weight of crushed coal washer waste with particle sizes ranging from 1–40 μm and obtained a 12 times increase in the filtration rate by using ultrasonic radiation of 20 kHz. A transducer with an input power of 150 W was placed 0.1 m above the filter element. The filter elements were stainless-steel plates with a pore size of 120 μm and a layer of sandstone with a pore size of 25 μm . Thus, filter aids were used to prevent small particles from penetrating through the filter.

Almost all the studies referred deal with lab-scale investigations. Bigger scale studies have been carried out in keeping the felt of a 5-cylinder paper machine open [40], and Semmelink [32] has reported a Russian filter of 1 m² filter surface for filtering slurries with greasy deposits. Fuji Filter Manufacturing Co. has launched an industrial filter (ultrasonic power of 1.2–2.4 kW) to realise precise classification or filtering of fine particles in slurry [36]. Thus, it is actually a particle classification device.

4.2 Electro-acoustic Filtration

Ultrasonic and electric fields have been suggested to have some synergistic effects in filtration based on the following mechanisms [10,41]:

- Greater compaction of the cake through the influence of ultrasonic stresses across the cake. This maintains electrical continuity longer and thus increases the water removal due to electro-osmosis.
- Material tending to coat electrodes can be removed ultrasonically promoting better electrical contact.
- Ultrasonic removal of liquid droplets from the bottom of the filter by inertial forces.
- Combined assistance in transferring liquid through the filter.

The most comprehensive ultrasonically enhanced electro-acoustic vacuum filtration studies were undertaken at the Battelle Memorial Institute which patented the electro-acoustic dewatering method (EAD) [42]. The basis of the EAD process is a synergistic effect of combining electric (dc) and ultrasonic fields in concert with a conventional driving force: vacuum or pressure. The relative effects of these 3 fields are dependent on the hydrodynamic, rheological, surface chemical, and electrokinetic properties of suspensions. Battelle Institute tested the applicability of over 50 different types of sludge for the EAD process. The key applications for the waste treatment are in sewage, wastewater treatment, process effluent (e.g. in the paper and pulp industry), and hazardous waste sludges. A lab-scale test device is presented in Figure 6.

A continuously operating vacuum filtration device was also designed to be operated along the lines of commercial vacuum filters with 2 endless belts serving as 2 electrodes. The unit is equipped for continuous feeding and filter cake discharge with a throughput of 5–10 kg/h [43]. Later, this technology was commercialised together with Ashbrook-Simon-Hartley Inc. The press (Figure 7) is utilised after conventional dewatering devices and can remove up to 50% of the water from filtered sludge cake at a fraction of the cost incurred by existing thermal drying devices. The dominant mechanism of sludge dewatering with the EAD press has

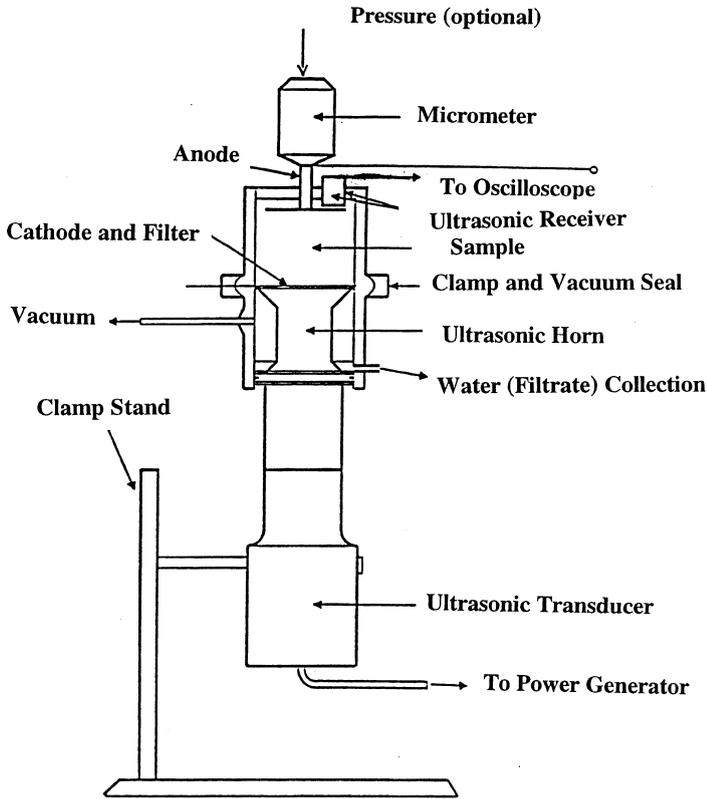


Figure 6. Schematic of vacuum electro-acoustic dewatering unit [43].

been shown to be electro-osmosis. The ultrasonic field aids electro-osmosis in consolidation of the filter cake and release of inaccessible liquid [43–45]. The EAD press has been tested successfully on a variety of materials, including sewage sludge, waste-activated sludge, and coal fines [45].

The electro-acoustic method has also been applied to the filtration of post-feculent phosphoric acid using either separate or combined fields [7]. Studies were undertaken with 3 different devices, but only the results of the final-stage studies are referred to here. The results of all phases have been promising. A filter of BEKIPOR ST3AL3SS steel membrane (3-micron pore size, acid-proof steel) with a surface area of 0.015 m² was used. The particle size of the suspension was about 25 μm. Two transmitters were used to keep the filter unclogged and to lower the liquid viscosity. One transmitter was placed on the back of the filter itself and the other directed

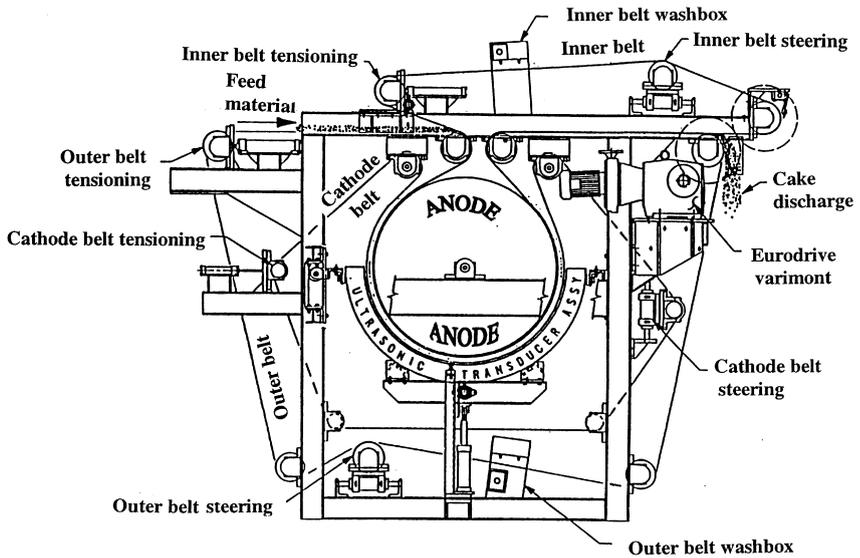


Figure 7. Electro-acoustic dewatering (EAD) general arrangement [44].

straight at the filter 1.8 cm away (half-wavelength of the pressure maximum). Both transmitters operated at 40 kHz and were used to transmit continuous US at 400 W input power. A lower frequency (16 kHz) transducer was not used due to the excessive noise produced. When the electric field was used (dc, 5.5 A, 5 V) the steel anode was positioned between the transmitters [7].

The best filtration results were obtained when ultrasonic and electric fields were applied simultaneously, in contrast to the results of Battelle Institute, where the electro-osmosis had been shown to have the dominant effect. Combined use of these fields increased the filtration capacity 15-fold, use of only the ultrasonic field to more than 10-fold, and of an electric field alone 2-fold (Figure 8). The purity of the filtrate was clearly below the target value (solid matter content <0.5 m-%) [7].

The viscosity of post-feculent acid was 0.13 Pa s, which is over 100 times higher than the viscosity of water. Tuori [7] concluded that mechanisms of the effect of electro-acoustic treatment consist of lowering the viscosity, electro-osmosis, electrophoresis, and prevention of filter clogging. Ultrasonic treatment also enhanced the filtration of magnetic ink by lowering the viscosity [46]. The same phenomenon has also been observed in the ultrasonically assisted crossflow filtration of glycerol–water mixtures [4].

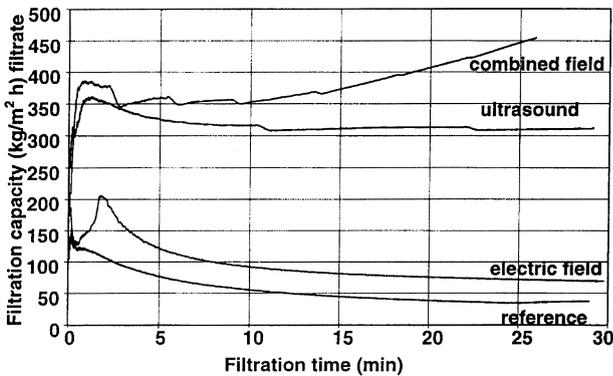


Figure 8. Effects of electric, ultrasonic and combined fields on the filtration of 3 m-% of phosphoric acid with post-deposit [7].

5. ULTRASONIC EFFECTS IN MICROFILTRATION (MF), ULTRAFILTRATION (UF) AND NANOFILTRATION (NF)

5.1 Ultrasonically Assisted Membrane Filtration

During the filtration process, the permeate flux can decrease significantly and rapidly with time until a final steady state is attained in which the flux no longer decreases. The decline in flux is commonly connected with two phenomena: concentration polarisation and fouling. The level of membrane fouling is dependent on the feed suspension properties (particle size, particle concentration, pH, ionic strength), membrane properties (hydrophobicity, charge, pore size), and hydrodynamics (crossflow velocity, transmembrane pressure) [47].

Sabri [48] studied several membrane types in ultrasonically assisted filtration of two different wastewater effluents from paper mills and brackish water. An experimental module (Figure 9) with a filtration area of about 0.02 m² was connected to a test rig. Four ultrasonic transducers of 27 or 40 kHz were installed on a vibrating plate placed in front of the filter element.

Transmembrane pressure, crossflow velocity, and the pulse mode for ultrasonic radiation were also among the variables studied. Flux and permeate quality were the parameters followed in the experiments. Energy consumption was estimated using the so-called NPF value, which is the ratio of total power consumption by the ultrasonically assisted filter to that consumed by the conventional filter (under the same conditions). The best net enhancement of the process is obtained when NPF is minimised and is

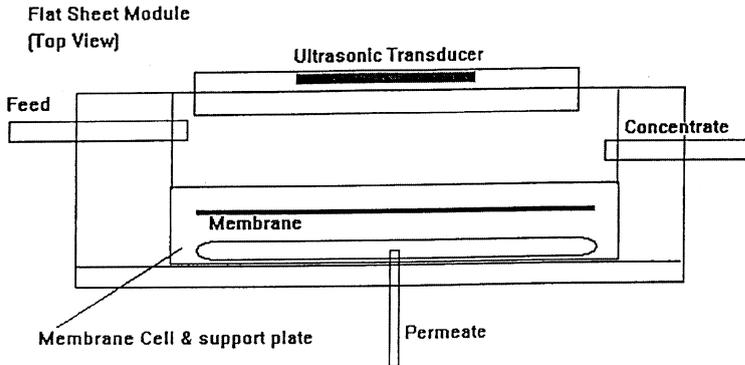


Figure 9. Flat sheet membrane filtration module (membrane area = 0.02 m², maximum operating pressure. Acoustic cavitation field is generated inside the module [48].

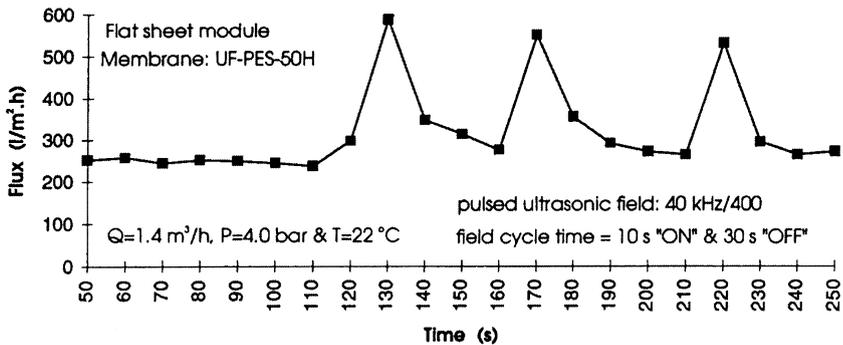


Figure 10. Ultrasonically enhanced ultrafiltration of “white water” effluent [49].

< 1 [48]. Flux enhancements were up to 400% higher than in the reference cases. One example of the results is presented in Figure 10 [48].

In most of the cases studied the NPF-value was clearly < 1. Severe wear problems were encountered when ultrasonic radiation was used for long periods under the cavitation conditions; polymeric membranes especially broke down quite rapidly. Cavitation was needed to obtain enhancements in the flux, thus much must be done to control and obtain even acoustic fields without excessively high peak intensities [48,49]. When using the same test rig with a ceramic UF filter in ultrasonically assisted filtration of bark press filtrate, enhancement of filtration was 100% compared with the reference [50]. The same test rig was also used for ultrasonically aided microfiltration of oily water. Enhancement of the flux was clear (Figure 11),

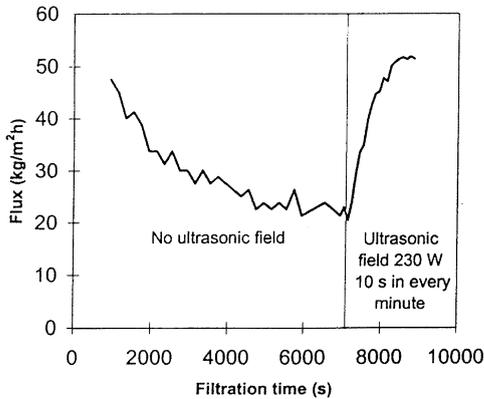


Figure 11. Enhancement of flux with ultrasonic force field during the filtration of electrically pre-treated emulsion. $V = 0.3$ m/s, $p = 2.5$ bar, $T = 25^\circ\text{C}$ and membrane pore size $0.1\ \mu\text{m}$ [51].

but membrane wear was also a problem even though the membrane was ceramic in nature [51].

High enhancements have also been obtained with suspensions other than waste. Chai et al. [52] used UF and MF membranes immersed in a cleaning bath to successfully filter peptone. An ultrasonic transducer was placed at the concentrate side of the membrane as also in references [4,48–51,53,54]. Matsumoto et al. [55] installed a transducer on the permeate side of the membrane and obtained 4–6-fold enhancements in crossflow microfiltration of baker's yeast and bovine serum albumin compared with the reference. This type of transducer placement could result in lower membrane wear. Wakeman and Tarleton obtained almost the same magnitude enhancement in ultrasonically assisted crossflow microfiltration of anatase and china clay suspensions [4]. Gavrilko et al. [56], Pirkonen and Sabri [53], and Nyfferel et al. [57] observed high enhancement in MF and UF filtration of potable water. Clogging of filters remained a problem and wear of filter surfaces was severe [53,57].

The effects of several parameters on the flux was studied by Matsumoto et al. [55] and Wakeman and Tarleton [4]. Both groups examined the effects of ultrasonic power. Matsumoto et al. also studied the effects of transmembrane pressure, pore size of the membrane, and crossflow velocity. Wakeman and Tarleton also examined the effects of ultrasonic frequency, feed concentration, and particle size and viscosity of the suspension. The transducer frequency ranged from 27–45 kHz in both studies. Increase in transmembrane pressure generally increased the flux except when the smallest pore size was used, in which case a decrease in flux was observed. Flux was highest with the smallest pore size of membrane. Crossflow velocity

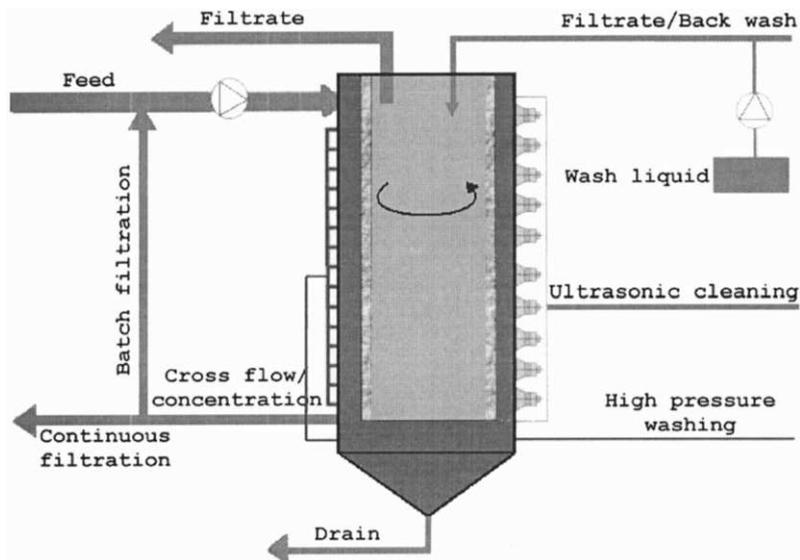


Figure 12. CERTUS-polishing ceramic MF [58].

had no effect on the flux. Increase of frequency, feed concentration, particle size, and viscosity of the suspension, lowered enhancement of the filtrate flux.

Filtermat Oy has developed a ceramic MF filter that has been tested in industrial pilot-scale runs. The pilot filter (Figure 12) consists of one ceramic microfilter tube with a filter area of 0.33 m^2 [58]. The industrial device will incorporate many of these tubes, which will rotate against the direction of suspension to increase the efficiency of crossflow velocity. Ultrasonic transducers are placed in front of the tube, and cleaning is carried out periodically together with back flushing to open the blocked pores. The pilot filter has been successfully tested with several paper and pulp mill waste and process waters. Filtration tests were carried out using membrane tubes with pore sizes of 0.25, 1, and $3 \mu\text{m}$. The capacities increased according to pore size from $1.9\text{--}6.8 \text{ m}^3/(\text{m}^2 \text{ h})$, e.g. in filtration of paper mill white water with DS content of $50\text{--}150 \text{ mg/l}$ [59,60].

5.2 Electro-acoustically Assisted Membrane Filtration

Wakeman and Tarleton [4] suggested that electrophoresis and electro-osmosis are the phenomena affecting the enhancement of filtration by an electric field. The main reason suggested for the enhancement by an

ultrasonic field was cavitation, and the synergistic effects of ultrasonic and electric fields. Wakeman and Tarleton [4] examined the combined effects of ultrasonic and electric fields on MF filtration; their test rig is presented in Figure 13.

The filter was specially designed to include mesh electrodes on both sides of the planar membrane and ultrasonic transducers in contact with the suspension on the upstream side of the MF membrane. Separate experiments were carried out to obtain the best conditions for combined field runs. A low crossflow velocity was chosen to keep the energy consumption small. An ultrasonic frequency of 23 kHz was preferred over 38 kHz and the highest possible field density was chosen. The suspension charge density was regulated to a level of -50 mV and an electric field of 50 V/cm served as an intermittent value chosen for further experiments. Other parameters affecting fouling included suspension concentration, particle shape, and surface properties of the particles in suspension. Some results are presented in Figure 14. The best fluxes recorded were an order of magnitude higher than corresponding tests with no imposed force fields. The effect of the electric field proved to be dominant compared with that of the ultrasonic field, as was also observed by Battelle researchers in the electroacoustic belt filter experiments [43, 44].

Electro-acoustic augmentation of MF-filtration has been suggested to be the most effective method for feeding suspensions containing small particles that are well dispersed in a liquid with a viscosity somewhat less than 10 cp.

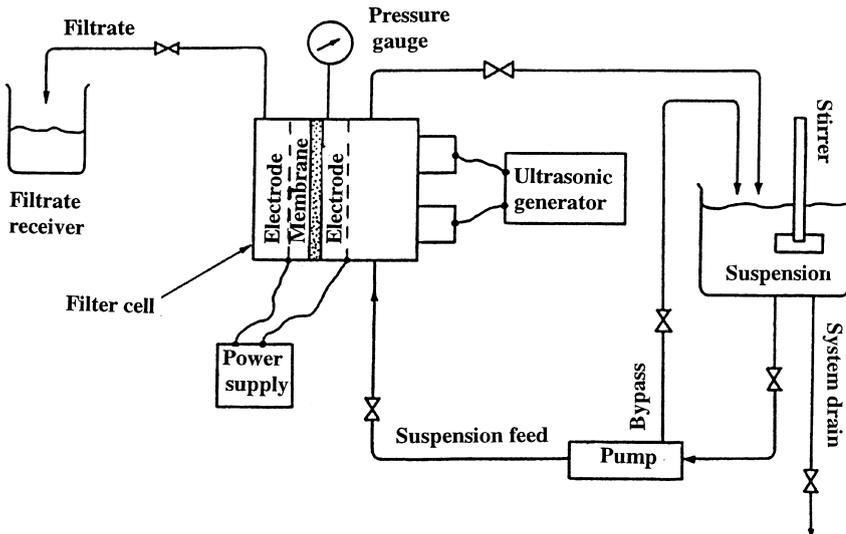


Figure 13. Schematic diagram of the electroacoustic filter [4].

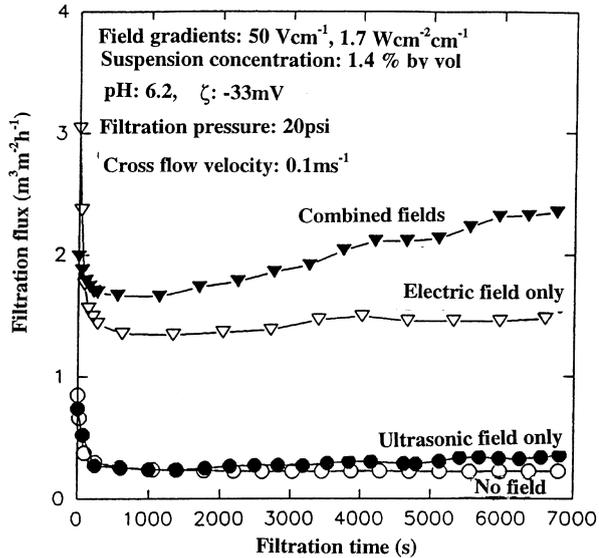


Figure 14. Synergy between electric and ultrasonic fields during the filtration of china clay suspensions [4].

In terms of the filtration parameters, the filter design should accommodate an US source with a frequency of 23 kHz, and both sonic and electric field strengths should be as high as possible. The latter point, especially from the standpoint of the ultrasonic field, is dangerous due to severe membrane wear in high-intensity ultrasonic fields [48,57,61]. The upper limit for viscosity was suggested to be 10 cp but electroacoustic filtration of post-ferculent phosphoric acid with viscosity of as much as 130 cp have succeeded well [7].

5.3 Ultrasonically Aided Cake Filtration

Ultrasonic cake filtration applications centering around microfiltration have not been published frequently. Tuori [7] and Heikkinen et al. [62] carried out comprehensive work with ultrasonically and electrically assisted microfiltration of mineral suspensions. Studies were undertaken with three different devices, but only the results of the final-stage studies are referred to here. The results were promising at all stages. Filtration of pyrite suspension (78 m-%) was carried out by a device with a filter area of 200 cm^2 . This device can be programmed to operate as an actual ceramic microfilter. The best location for the transmitter (22 kHz, input power 200 W) was observed to be behind the ceramic plate. Pulsed US produced the best results (Figures 15 and 16); continuous ultrasound clogged the filter.

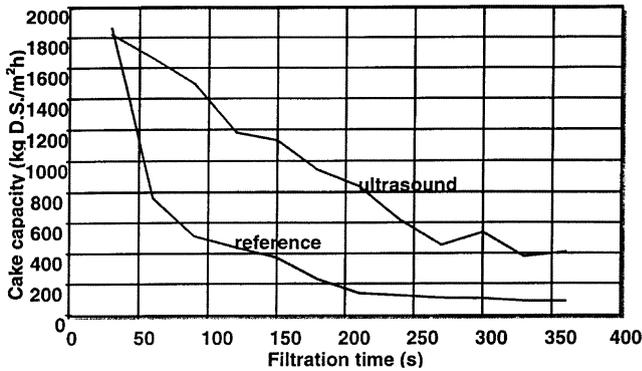


Figure 15. Effect of an ultrasonic field on the cake capacity of pyrite [7].

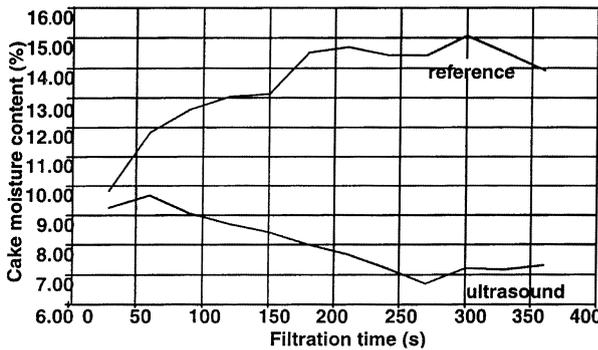


Figure 16. Effect of an ultrasonic field on the cake moisture of pyrite [7].

Energy consumption was much less than in the reference case [7]. Placement of the transducer behind the ceramic plate is the main technical hindrance to the utilisation of these favourable results.

Heikkinen et al. [62] has studied the ultrasonically aided filtration of TiO_2 concentrate suspension in the cake-dewatering phase; the experimental set-up is presented in Figure 17. A somewhat similar situation was observed in the Battelle Institute cake-filtration studies at Battelle Institute [43]. An ultrasonic field was combined with compression between the filter belts in Battelle's set-up and in Figure 17 it was combined with an under pressure in the ceramic microfilter.

An up to 6% decrease in cake moisture content (Figure 18) was obtained on filtration of the TiO_2 suspension. Later, the set-up presented in Figure 17 was installed on a pilot-scale continuously operating test filter manufactured by Outokumpu Mintec Oy. Pilot-scale experiments confirmed the results

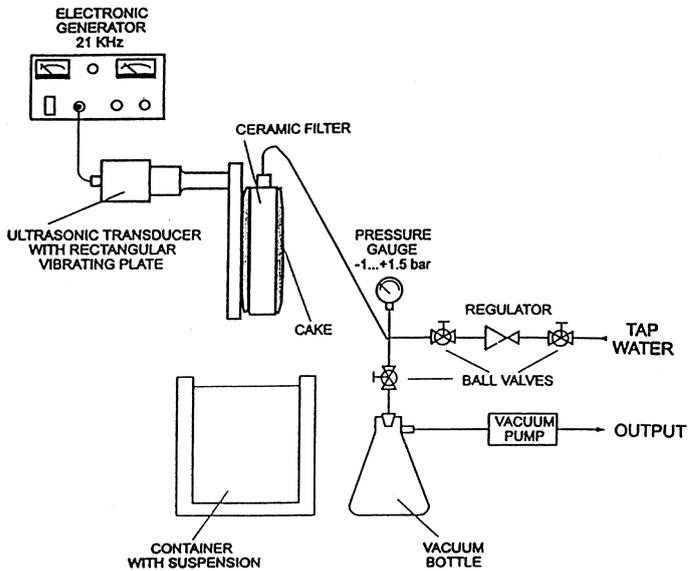


Figure 17. Ultrasonically assisted experimental set-up for cake dewatering [62].

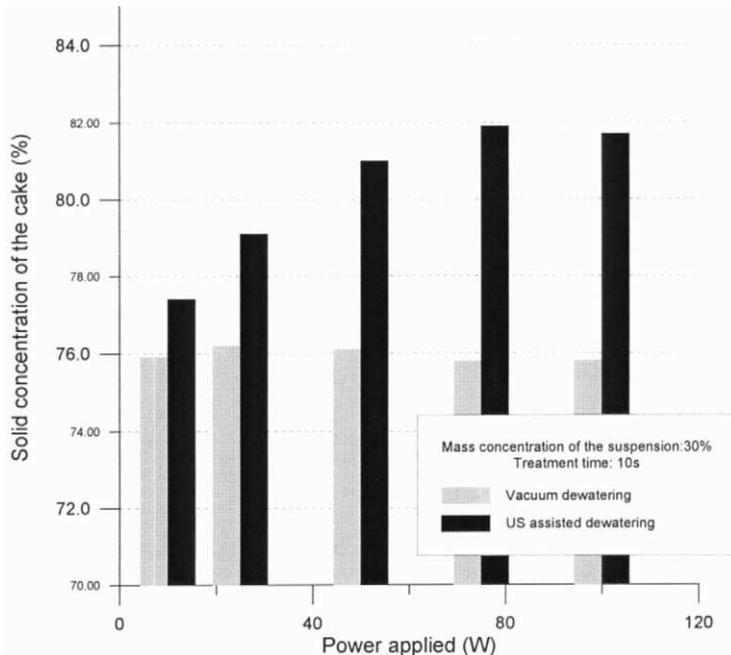


Figure 18. The effect of ultrasonic power on the cake moisture of TiO_2 [62].

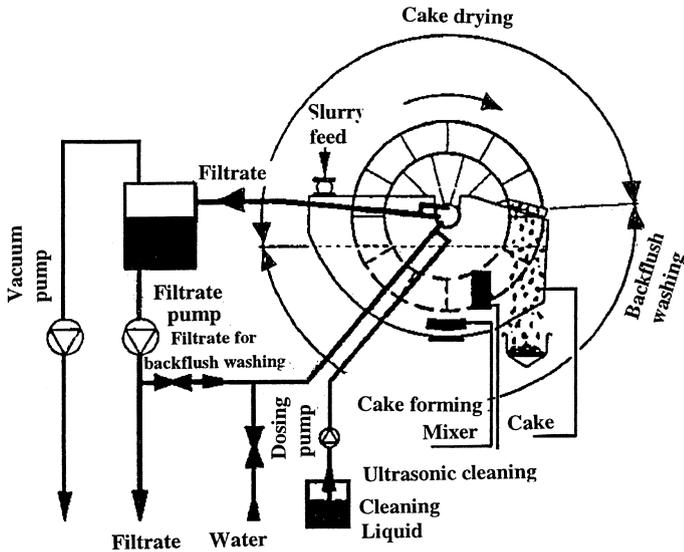


Figure 19. Scheme of a ceramic MF manufactured by Outokumpu Mintec Oy [63].

obtained with the smaller test rig. Commercialisation of ultrasonic assisted ceramic microfiltration technology based on the results of this study will be the next step [62].

Outokumpu Mintec Oy manufactures industrial ceramic microfilters (Figure 19) for cake filtration of suspensions in the mining industry. Very low energy consumption and clean effluent water are the best features of this technology from the standpoint of the environment. Ultrasonic cleaning of the filter elements is carried out periodically in a separate cleaning sequence [63,64].

6. ULTRASONICAL EFFECTS IN REVERSE OSMOSIS (RO) AND DIALYSIS

High-quality potable water can be produced with reverse osmosis (RO) technology from surface waters. The studies of Lozier and Sierka [65] conducted on the fouling deposits on RO membranes have shown the material to be colloidal in nature, and mainly comprised of organics with varying amounts of clay and silica. Attempts were made to solve this fouling by combining the US and ozone treatments. This idea is based on the ability of US to activate the O_3 and thus catalyse oxidation of organics in aqueous solutions. Ozonation increased the filterability of a low concentration of

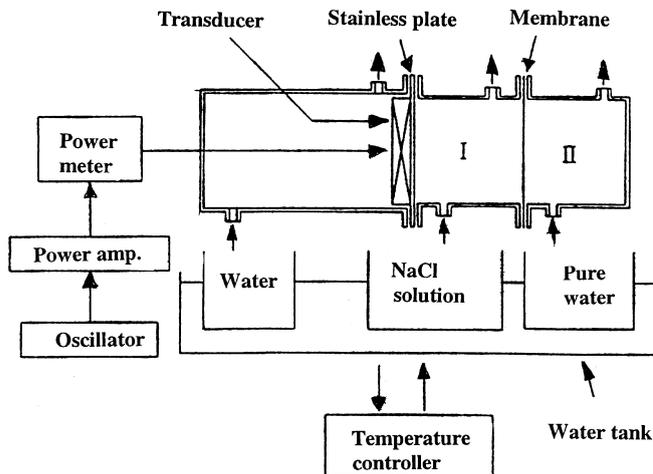


Figure 20. Experimental set-up for ultrasonic irradiation [61].

humic acids, but the application of US during ozonation was detrimental, probably because the sound waves may have reduced the average particle size of colloidal and suspended solids in suspension.

Japanese researchers have conducted a series of dialysis studies with KCl [66] and NaCl [61,67,68] solutions enhanced with US. All studies were carried out with an ultrasonic frequency of 28 kHz and using the benefits of standing-wave phenomena, i.e. placing the transducer just at the point where the acoustic pressure is lowest and particle movement the greatest. A typical set-up is presented in Figure 20 [61].

Permeate flux increased significantly and progressively at higher ultrasonic intensities. The effect of US frequency on NaCl filtration resulted in a maximum value at 400 kHz in the frequency range of 28–1000 kHz [61]. Cavitation was observed to cause membrane breakdown, and the cavitation threshold was 20 kPa at 28 kHz and 38 kPa at 400 kHz. Operation under the cavitation threshold was recommended [61]. A planar membrane was used in all studies except that in which the tubular membrane was used, and both planar and cylindrical transmitters were compared [68]. The cylindrical transmitter that was placed around the tubular membrane worked more favourably than the planar. Next Masuzawa et al. [68] plan to place a bundle of tubular membranes inside the cylindrical transmitter.

Ultrasound-assisted dialysis techniques can be used, e.g. seawater-salt dialysis and blood dialysis [68]. Band et al. [69] studied the influence of US on the water desalination process in a small ultrasonic bath by means of ion-exchange hollow fibres. Results have shown that $\text{Na}^+\text{-H}^+$ ion-exchange was enhanced by 40–60%.

A process including electrodialysis (ED) is available for producing pure NaOH from the waste ash of recovery boilers operating in the pulp industry. NaOH is one of the cooking chemicals used in pulp production. This process has been nonprofitable mainly because of ineffective ED process due to membrane fouling. US technology could aid in solving this problem, and a study centering around this problem has been initiated in the research group led by the present author.

7. SUMMARY

Research in the fields of filtration and dewatering connected with the use of US to enhance flux has been carried out, but still mainly with small lab-scale batch or continuously operating devices. A common consensus seems apparent on the basic phenomena regarding the possible effects that could be achieved by ultrasound. The main phenomena in the enhancement of waste material filtration and general filtration include cavitation, acoustic agglomeration, radiation pressure and acoustic drifting of particles. Depending on the application the effect of US is due to a combination of many phenomena acting synergistically.

Industrial applications exist in biotechnology for retentiate hybridoma and separating mammalian cells using standing-wave (Sono flocc, Biotech Inc. and Anton PAAR GmbH.) in classification or filtration of small particles with a mesh filter (Fuji Filter Inc.), in organic sludge dewatering using an EAD press (Ashbrook-Simon-Hartley Inc.), and cake filtration (MF) of slurries in the mining industry (Outokumpu Mintec Oy). A CERTUS clarification filter, e.g. used to purify waste and process waters in the pulp and paper industry (Filtermat Oy) and an acoustic dewatering method for the vacuum-dewatering phase of the ceramic MF (Outokumpu Mintec Oy) are close to the industrial stage.

The main reason hindering the breakthrough of filtration technologies connected with ultrasonics are the lack of development of transducer technology and the control of erosion caused by cavitation at high ultrasonic intensities.

REFERENCES

- [1] Pletcher, D., and Walsh, F. *Industrial Electrochemistry*, 2nd ed., Chapman and Hall, London, 1990.
- [2] Bowen, W. R. In Williams, R. A. (ed.), *Colloid and Surface Engineering*, 1992, pp. 215–247.
- [3] Shirato, M., Kobayashi, K., and Iwata, M. Recent developments in solid–liquid separation technology in Japan, in Proc. of 10th Anniversary International Symposium of Recent Advances in Papermaking Technology, 1998, pp. 141–150.

- [4] Wakeman, R., and Tarleton, E. *Trans IChemE*, 69A (September 1991) 387.
- [5] Tarleton, E., and Wakeman, R. In Povey, J., and Mason, T. (ed.), *Ultrasound in Food Processing*. Thomas Science, 1998, pp. 193–218.
- [6] Muralidhara, H. S., Beard, R. B., and Senapati, N. *Filtration & Separation*, Nov./Sep. (1987) 409.
- [7] Tuori, T. Enhancing Filtration by Electro-acoustic Methods. PhD. Thesis. Loughborough University, UK, 1998, p.162.
- [8] Kowalska, E., Bien, J., and Zielewicz-Madej, E. *Drying Technology*, 6(3) (1988) 447.
- [9] Muralidhara, H. S., Senapati, N., Ensminger, D., and Chauhan, S. P. *Filtration & Separation*, Nov./Dec. (1986) 351.
- [10] Ensminger, D. *Ultrasonic: Fundamentals, Technology and Applications*, 2nd ed. Marcel Dekker Inc. New York, 1988, p. 581.
- [11] Mason, T., and Cordemans, D. *Trans IChemE*, 74A (July 1996) 511.
- [12] Price, G. J. *Current Trends in Sonochemistry*. The Royal Society of Chemistry, 1992.
- [13] Mettin, R. Luther, S., and Lauterborn, W. Bubble size distributions and structures in acoustic cavitation. Proc. of 2nd Conference, Applications of Power Ultrasound in Physical and Chemical Processing. Toulouse 6–7 May 1999, pp. 125–129.
- [14] Atchley, A., and Crum, L. In Suslick, K. (ed.), *Ultrasound*, VCH Publishers Inc. 1988, pp. 1–63.
- [15] Abramov, O. V. *High-intensity Ultrasonics; Theory and Industrial Applications*. Gordon and Breach Science Publishers, 1998, p. 692.
- [16] Ensminger, D. *Ultrasonic: Fundamentals, Technology and Applications*, 2nd ed. Marcel Dekker Inc. New York, 1988, p. 580.
- [17] Friedrich, H., Potthoff, A., Friedrich, E., and Hielscher, H. *TU Hamburg-Harburg Reports on Sanitary Engineering* Vol. 25 (1999), pp. 245–255, ISBN 3-930-400-23-5.
- [18] Spengler, J., and Jekel, M. *TU Hamburg-Harburg Reports on Sanitary Engineering* Vol. 25 (1999), pp. 189–204, ISBN 3-930-400-23-5.
- [19] Moreno de Barrera, L., Gonza'les, I., Carbo'-Fite', R., and Gallego-Jua'rez, J. Effects of high-power ultrasound on suspensions. Proc. 1995 World Congress on Ultrasonics, pp. 749–752.
- [20] Gröschl, M. *ACUSTICA-Acta Acustica*, 84 (1998) 632.
- [21] Coakley, W. T., *Tibtech.*, 15 (Dec. 1997) 506.
- [22] Kopp, J., Dichtl, N. Konditierungs- und Entwässerungsverhalten von aufgeschlossenen und gefaulten schlamm. In: Klärschlammintegration-Forschung und Anwendung. Veröffentlichung des Instituts für Siedlungswasserwirtschaft der Tech. Univ. Braunschweig, Vol. 61, 1998, pp. 215–228.
- [23] Bien, J. *Filtration & Separation*, Nov./Dec. (1988) 425.
- [24] Ensminger, D. In Muralidhara, H. S. (ed.), *Advances in Solid-Liquid Separation*, Battelle Press, 1986.
- [25] Gröschl, M., Burger, W., and Handl, B. *ACUSTICA-Acta Acustica*, 84 (1998) 815.
- [26] Bien, J., Wolny, L. *Wat. Sci. Tech.*, 36 (11) (1997) 101.
- [27] Bien, J. B., Kempa, E., and Bien, J. D. *Wat. Sci. Tech.*, 36 (4) (1997) 287.
- [28] Bernhardt, H., Lusse, B. *Aqua*, 38 (1989) 23.
- [29] Singh, B. P., and Singh, R. *Separation Science and Technology*, 32 (5) (1997) 993.
- [30] Fairbanks, H. V., Morton, W., and Wallis, J. Separation process aided by ultrasound. Proc. of 4th World Filtration Congress 1986.
- [31] Tiehm, A., Nickel, K., and Neis, U. *Wat. Sci. Tech.*, 33 (11) (1997) 121.
- [32] Semmelink, A. Ultrasonically enhanced liquid filtration. Proc. of Ultrasonics International Conference, London 1973, pp. 7–10.
- [33] Fairbanks, H. V., Ultrasonically enhanced liquid filtration. Proc. of Ultrasonics International Conference, London 1973, pp. 11–15.

- [34] Tuori, T., Martikainen, P., and Järvelä, E. Enhancement of Bio/fiber sludge filtration by electro-acoustic method. Proc. of 6th World Filtration Congress 1993, pp. 206–210.
- [35] Sora, M., Jinescu, M., Sora, I. *F & S Separieren*, Jahrgang 6 (1992) heft 6, pp. 35.
- [36] Miyazaki, K., Takahashi, Y., and Shiomi, K. *Filtration & Separation*, Jan./Feb. (1990) 28.
- [37] Björnö, L., Gram, S., and Steenstrup, P. R. *Ultrasonics*, May (1978) 103.
- [38] Fairbanks, H. V., and Hackett, W. L. Influence of ultrasonics on filtration. Proc. of Ultrasonic Symposium 1975, IEE Cat. #75 CHO 994-4SU, pp. 585–587.
- [39] Otsuka, T., and Fairbanks, H. Ultrasonic assist in dewatering fine particles. Proc. of Ultrasonics Symposium, IEE cat. #76 Ch1120-5SU, pp. 119–120.
- [40] King, H. Ultrasonic felt cleaning: the wave of the future. *Tappi*/June, Vol. 62, No 6, 1979 pp. 23–24.
- [41] Muralidhara, H., Ensminger, D., and Putnam, A. *Drying Technology*, 384, 529.
- [42] United States Patent No. 4 561 953, 31.12.1985. Inventors: Muralidhara, H., Parekh, B., and Senapati, N.
- [43] Chauhan, S. P., Muralidhara, H. S., Kim, B. C., Senapati, N., Beard, R.E., and Jirjis, B. F. Electroacoustic dewatering (EAD)- A novel process. Proc. of Summer National AIChE Meeting. Minneapolis, August 16–19 1987, p. 15.
- [44] Golla, P., Johnson, H., and Senthilnathan, P. *Environmental Progress* 11 (1) (Feb. 1992) 74.
- [45] DOE/ID/13132-T1. Improved electroacoustic dewatering (EAD) belt press for food products, Phase III. Technical Progress Report. February 1994, p. 38.
- [46] IBM Technical Disclosure Bulletin, Vol. 27 No. 11, April 1985.
- [47] Huisman, I. Crossflow microfiltration of particle suspensions. PhD. Thesis. Department of Food Processing, Lund University, 1998.
- [48] Sabri, M. Effective utilization of energy by filter system: Introducing electric and ultrasonic methods to control fouling in membrane filtration. VTT Energy-European Union; Non-Nuclear Programme. Final Report; Contract No. JO-CT97-5002, p. 32.
- [49] Sabri, N., Pirkonen, P., and Sekki, H. Ultrasonically enhanced membrane filtration of paper mill effluent. Proc. of Applications of Power Ultrasound in Physical and Chemical Processing. Toulouse 1997, pp. 99–104.
- [50] Sabri, N., Tuori, T., and Huotari, H. Ultrasonically enhanced ultrafiltration of waste waters from pulp and paper industries. Poster presentation. Proc. of 3rd International Symposium EUROMEMBRANE '97; Progress in Membrane Science and Technology.
- [51] Huotari, H. Ultrasonically enhanced microfiltration of oily water. Proc. of 3rd Nordic Filtration Symposium. Copenhagen 1997, p. 3.
- [52] Chai, X., Kobayashi, T., and Fujii, N. *Separation and Purification Technology*, 15 (1999) 139.
- [53] Pirkonen, P., and Sabri, N. Ultrasonically assisted membrane filtration of lake water. To be published as Poster in Proc. of 8th World Filtration Congress. April 3–7, 2000.
- [54] Kogugan, T., Fujiwara, K., and Shimizu, M. *Membrane*, 20 (3) (1995) 213.
- [55] Matsumoto, Y., Miwa, T., Nakao, S., and Kimura, S. *Journal of Chemical Engineering of Japan*, 29 (4) (1996) 561.
- [56] Gavrilko, V. G., Nikolski, G. S., and Ruditsler, L. R. Intensifying ultrafiltration with ultrasound. *Khimiya i Tekhnologiya Vody*, 6 (6) (1984) 20.
- [57] Nyffeler, F., Ruch, P., and Beck, C. *Marine Geology*, 84 (1988) 119.
- [58] CERTUS-polishing filter. Filtermat Oy, proschure 1999.
- [59] Rantala, P., and Kuula-Väisänen, P. Filtration of paper mill process waters using a Certus-polishing filter with ceramic membrane. Proc. of 6th IAWQ Symposium on Forest Industry Wastewaters. June 6–10, 1999 Tampere, pp. 239–244.

- [60] Rantala, P. CERTUS-Kirkastussuodin-EKY-08. In Year Book '99 of the Technology Programme: Water Management in Papermaking, pp. 87–88. Abstract in English.
- [61] Yamaguchi, R., Ohdaira, E., Masuzawa, N., and Ide, M. *Jpn. J. Appl. Phys.*, 37 (1998) 2988.
- [62] Heikkinen, J., Tuori, T., Wakeman, R., Gallego-Juarez, J., Elvira, L., Rodriguez, G., Kaess, J., and Ekberg, B. Development of deliquoring method enhanced by electric and acoustic force fields. To be published In Proc. of 8th World Filtration Congress. April 3–7, 2000.
- [63] Mapes, C. Development and Application of Ceramic Media Disc Filter Technology at Phelps Dodge Morenci Inc. SME National Convention, February 1994 Albuquerque, New Mexico, p. 12.
- [64] History's Most Successful Story of Solid–Liquid Separation. Outokumpu Mintec Oy, Proschure 1996.
- [65] Lozier, J., and Sierka, R. *Journal AWWA*, 77 (8), (1985) 60.
- [66] Li, H., Ohdaira, E., and Ide, M. *Jpn. J. Appl. Phys.*, 34 (1995) 2725.
- [67] Li, H., Ohdaira, E., and Ide, M. *Jpn. J. Appl. Phys.*, 35 (1996) 3255.
- [68] Masuzawa, N., Yoshimura, T., Ohdaira, E., and Ide, M. *Jpn. J. Appl. Phys.*, 36 (1997) 3136.
- [69] Band, M., Gutman, M., Faerman, V., Korngold, E., Kost, J., Plath, P. J., and Gontar, V. *Desalination* 109 (1997) 303.

THE DESIGN OF ULTRASONIC REACTORS FOR ENVIRONMENTAL REMEDICATION

Timothy J. Mason

OUTLINE

1. Introduction	248
2. A Brief Overview of Laboratory Equipment	248
3. Ultrasonic Transducers	250
4. Preliminary Scale-up Considerations	254
5. The Design of Ultrasound Reactors	256
5.1 Low Intensity Systems	257
5.2 High Intensity Ultrasonic Systems	259
6. Conclusions	267
References	268

Advances in Sonochemistry

Volume 6, pages 247–268.

© 2001 Elsevier Science B.V. All rights reserved.

1. INTRODUCTION

It has been recognised for many years that power ultrasound has great potential for use in a wide variety of processes in the chemical and allied industries (Table 1). These uses have been reviewed periodically and for all of them one can find an impressive number of papers and patents.

In point of fact large scale processing using power ultrasound is not a new concept. In the 1960s the industrial uses of power ultrasound were recognised [1,2]. There are many examples in the literature, which also testify to this, for example, a series of papers appeared in the journal *Ultrasonics* back in 1970s entitled "Macrosonics in Industry" [3]. One of the more recent additions has been a text translated from the Russian [4]. Progress over the last few years in the field of large scale ultrasonic processing has accelerated for two reasons, firstly the greater general awareness of the possibilities for ultrasonic processing and secondly the ever-widening span of applications which has attracted the attention and investment of more companies.

Some techniques are already being used at an industrial scale, e.g. cleaning, homogenisation or emulsification, deagglomeration and plastic welding. Current laboratory research suggests that there will be a requirement for large-scale ultrasonic equipment in the treatment of environmental pollution, both chemical and biological. In connection with these studies, various types of ultrasonic apparatus have been devised for laboratory, pilot and in some cases industrial scale applications.

2. A BRIEF OVERVIEW OF LABORATORY EQUIPMENT

Most readers will be familiar with the three simple types of laboratory equipment generally used for sonochemistry—the whistle, bath and probe (or horn). Nevertheless, before embarking upon a discussion of scale-up it

Table 1. Uses of Ultrasound in Chemical Technology

Sonoprocessing	Degassification
	Extraction
	Crystallisation
	Emulsification or dispersion
	Cleaning and sterilisation
	Aggregate or particle size reduction
Sonochemistry	Electrochemistry
	Enzyme activation
	Chemical synthesis
	Polymer synthesis and degradation
	Heterogeneous and phase transfer catalysis

is advantageous to consider the relative advantages (and disadvantages) of each of these systems (Table 2) [5]. Several of the constraints will also apply on a larger scale. The whistle reactor (Figure 1) relies on mechanical generation of ultrasonic power whereas electromechanical transducers drive the other two—the bath (Figure 2) and probe (Figure 3) systems. The standard laboratory cleaning bath (35–40 kHz) continues to be of widespread use, but many sonochemistry groups are now working with purpose built baths affording different frequencies and more accurate sound fields (these are referred to elsewhere in this volume).

Table 2. A Comparison of the Types of Electromechanical Ultrasonic Apparatus

Liquid whistle (Figure 1)	<p><i>Advantages</i></p> <ul style="list-style-type: none"> (i) robust and durable (ii) ideal for homogenisation and mixing (iii) pump is only source of movement (iv) hydrodynamic cavitation does not generate large number of radicals (may be a disadvantage in some applications) <p><i>Disadvantages</i></p> <ul style="list-style-type: none"> (i) requires fast liquid flow to create cavitation and so is unsuitable for viscous fluids (ii) may be blocked by large particulate material
Cleaning bath (Figure 2)	<p><i>Advantages</i></p> <ul style="list-style-type: none"> (i) the most widely available laboratory source of ultrasonic irradiation (ii) reaction vessels can be immersed in bath liquid without special adaptation (iii) fairly even source of energy through reaction vessel walls—when correctly positioned in bath <p><i>Disadvantages</i></p> <ul style="list-style-type: none"> (i) reduced power compared with probe system (ii) fixed frequency (and different frequencies depending on type) (iii) temperature control required (iv) position of reaction vessel in bath will effect intensity of sonication
Probe system (Figure 3)	<p><i>Advantages</i></p> <ul style="list-style-type: none"> (i) high powers available (no losses due to acoustic energy transfer through vessel walls) (ii) probes can be tuned to give optimum performance at different powers <p><i>Disadvantages</i></p> <ul style="list-style-type: none"> (i) fixed frequency (ii) temperature control required (iii) radical species may be generated at the tip (iv) tip erosion may occur leading to contamination of medium with metallic particles

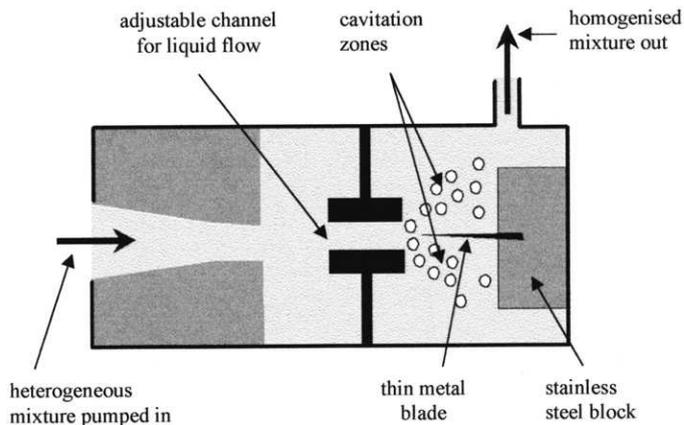


Figure 1. Liquid whistle for sonochemistry.

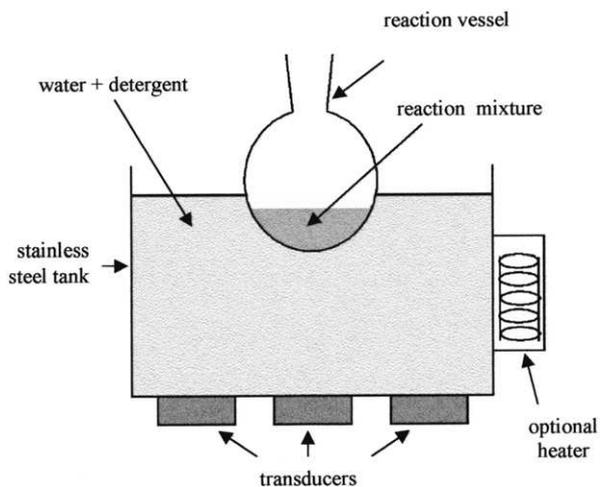


Figure 2. Ultrasonic cleaning bath for sonochemistry.

3. ULTRASONIC TRANSDUCERS

Whatever application of sonochemistry or ultrasonic processing is to be studied and developed one essential component of the system will be the transducer of which there are three main types. One is liquid driven and the other two are electromechanical, all of them have been in use for many years. A fourth type of transducer has been introduced; the magnetically driven vibrating bar which generates very high power vibrations in the

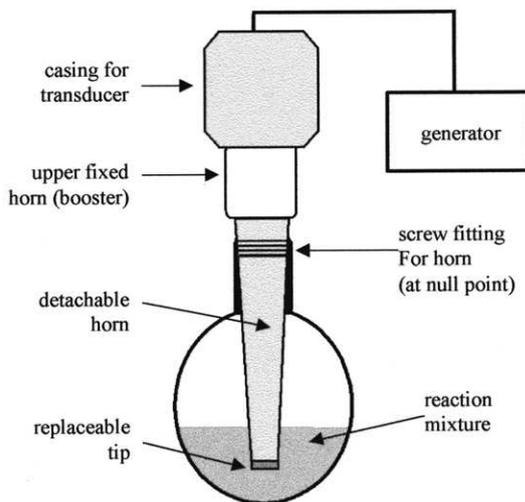


Figure 3. Probe (or horn) system for sonochemistry.

audible frequency range. This has some potential for heavy duty processing and has been described elsewhere [6].

Liquid whistles are particularly useful in applications where homogenisation and efficient mixing are important (Figure 1). Process material is forced under pressure generated by a powerful pump through an orifice from which it emerges, as a jet, into a mixing chamber. The jet impacts upon a thin steel blade which is caused to vibrate and thereby produce mixing of the process material flowing over it. Additional mixing is produced through the Venturi effect as the liquid rapidly expands into a larger volume on exiting the orifice. There have been no significant advances in the basic design of this type of device in recent years, but the range of applications is broad and new uses continue to emerge. Examples of existing commercial processes include the preparation of foods, cosmetics (skin cream), in textiles (to disperse pigments) and in the plastics industry (to disperse thickening agents and pigments).

Magnetostrictive transducers use a property of certain materials, e.g. nickel which reduce in size when placed in a magnetic field (magnetostriction) and then return to normal dimensions when the field is removed (Figure 4). Improvements in the operating efficiency of this type of transducer have been based on finding a more efficient magnetostrictive core. More electrically efficient cobalt-iron combinations and, more recently, aluminum-iron with a small amount of chromium have replaced the original nickel alloys. One of the latest developments in magnetostrictive technology has been the introduction of a new material called "Terfinol-D" [7].

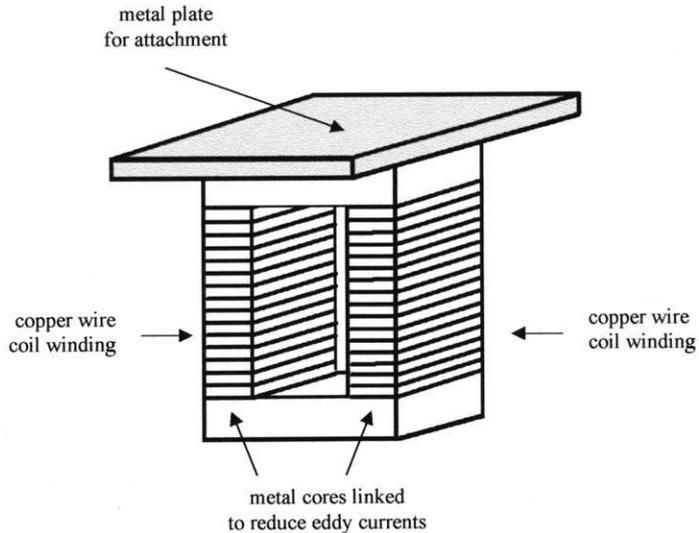


Figure 4. Construction of a magnetostrictive transducer.

This is an alloy of the rare earth elements terbium and dysprosium with iron which is zone refined to produce a material almost in the form of a single crystal. It can be produced in various forms, rods, laminates, tubes etc. and, several major advantages have been claimed for this material compared with the more conventional alloys used, e.g. it can generate more power, it is more compact (about 50% smaller) and also lighter than other magnetostrictives. Terfinol does suffer from the same disadvantage as other magnetostrictive materials, in that, it has an upper limit of frequency response (about 70 kHz in this case).

Piezoelectric transducers are the most widely used devices for the generation of ultrasound and can be used over the whole range of ultrasonic frequencies (Figure 5). Current developments using such transducers exploit their versatility in terms of both size and available frequency range. Piezoelectric systems have been used to drive large and powerful ultrasonic welders and cleaning baths, but are also finding more refined uses in a new field of medicine called “therapeutic ultrasound” [8].

New possibilities exist for the development of piezoelectric devices using so-called 1–3 composites. These consist of an array of piezoelectric pillars embedded in a pliable material providing a transducer in the form of a flexible sheet (Figure 6), which can be molded to fit the shape of a reactor. A particular advantage of such a system is that the emitting face is a combination of ceramic and plastic and can provide much better acoustic transmission into aqueous systems.

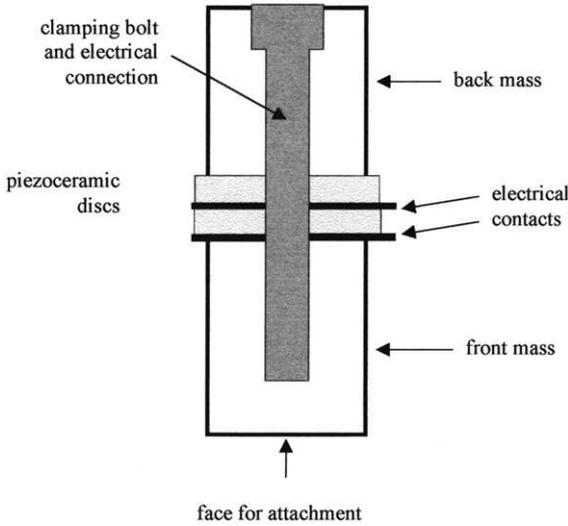


Figure 5. Construction of a piezoelectric sandwich transducer.

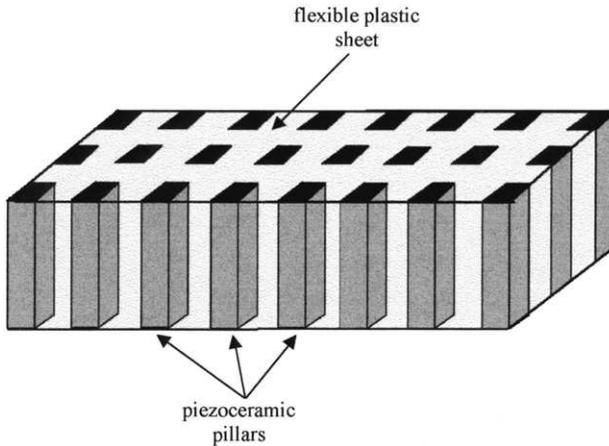


Figure 6. Construction of a 1-3 composite array.

There is also a great deal of interest in the production of single crystal piezo material from a mixture of lead, zirconium and niobium compounds (from which they get the name PZN). Such single crystal transducers would provide low loss, high strain, low modulus and have high coupling coefficients. At the time of writing, these materials are not yet commercially available, but are a key target in transducer manufacture.

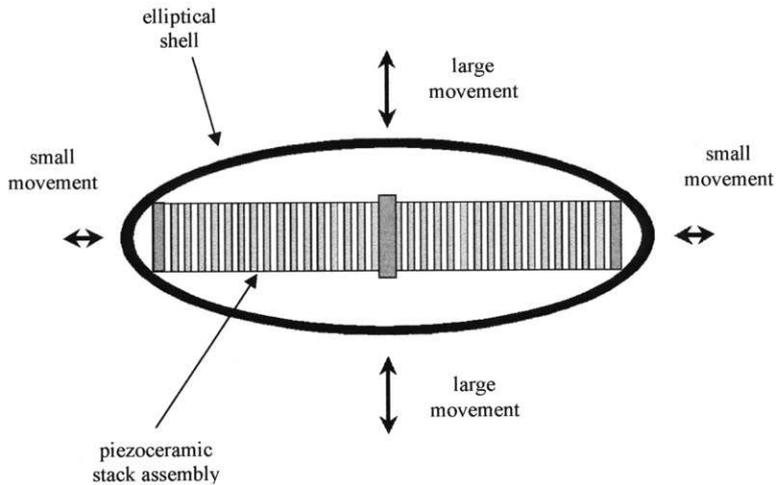


Figure 7. Construction of a flexensional transducer.

Historically, some of the drive to obtain higher-powered transducers came from naval acoustics. An obvious way to extend the range of long distance SONAR is to increase the vibrational amplitude of the source. A first step in this is to put together a stack of transducers to magnify the overall amplitude of the vibration as a sum of the individual transducers. Beyond this further magnification can be achieved using the so-called flexensional transducer (Figure 7). This device uses an oval shaped flexible steel construction in which stacks of conventional transducers drive across the long axis. As a result, the vibration is magnified through the resulting orthogonal movement across the shorter axis.

4. PRELIMINARY SCALE-UP CONSIDERATIONS

When deciding on the type of ultrasonic treatment required, the first question which must be addressed is whether the ultrasound is providing a predominantly mechanical or a truly sonochemical process. An example of the former is process for improving the removal of oil from oily water emulsions via oil-consuming bacteria [9]. Ultrasound is used to improve the mixing of oil and bacteria and thus to improve the efficiency of the oil degradation through the generation of a fine colloidal distribution of the oil. An example of the latter would be the destruction of biological contaminants in a water flow subjected to cavitation induced by ultrasound [10]. If it is mechanical rather than chemical action that is needed, then,

ultrasonic pre-treatment may be all that is required before subsequent conventional processing. However, if the ultrasonic effect is truly sonochemical, then, sonication must be provided during the overall processing. Whichever type of ultrasonic treatment is required, there are a limited number of ways in which ultrasound can be introduced into the system (Table 3).

One of the first steps will be to establish the optimum conditions for the introduction of ultrasound in terms of the variables which influence cavitation (Table 4). Thus, the physical properties of the medium itself will have a real influence, as will various external parameters. Such factors can be identified in general terms (Table 4), but several of these “variables” are fixed by the type of medium to be treated.

In almost all cases the medium treated will be water based and so any change in viscosity will be produced by dissolved material. Sewage will contain solids and particulate matter which will reduce the ability of sound to penetrate into the material. The presence of gases, such as methane will facilitate cavitation, but the initial effect of the acoustic energy input will be to cause degassing. The pressure for most remediation processes will be atmospheric and the temperature of operation will be ambient. The frequency will be important for oxidative processes because radical production during acoustic cavitation is generally better at higher frequencies. Mechanical effects are best achieved in the lower (20–40 kHz) range. In addition to these considerations, it is to be expected that the size and the geometry of the reactor employed will have a great bearing on the efficiency of ultrasonic action.

Table 3. Methods of Introducing Ultrasound into a Reactor

Immerse reactor in a tank of sonicated liquid. (e.g. flask in a cleaning bath).
Immerse an ultrasonic source directly into the reaction medium. (e.g. probe dipped into a reaction vessel).
Use a reactor constructed with ultrasonically vibrating walls. (e.g. using the tank of a cleaning bath as the reactor).

Table 4. Factors which Influence Cavitation

Viscosity and vapour pressure of the medium
Presence of gases or solid particles
Overpressure
Reaction temperature
Sonic power and frequency
Size and geometry of chemical reactor

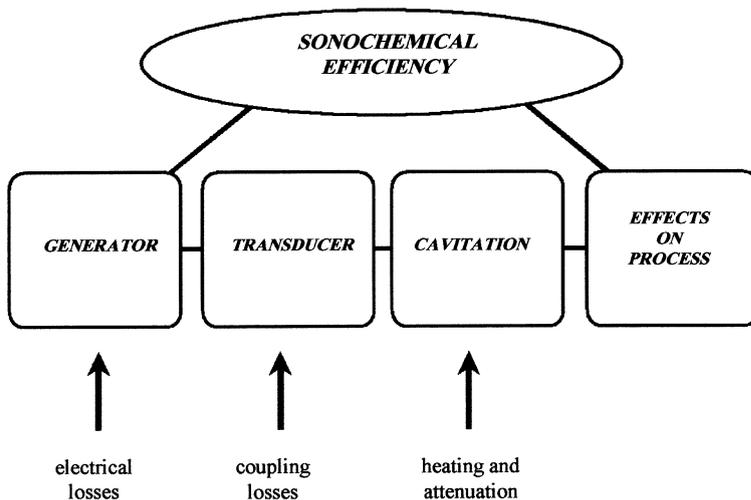


Figure 8. Energy losses in ultrasonic processing.

Since an ultrasonic reactor must in essence convert electrical energy into cavitation energy and then chemical reactivity, one might expect that there must be energy losses accrued in driving such a system (Figure 8). Initially there will be electrical and heating losses as electrical input drives the mechanical motion of the transducer through the generator. In turn, the transducer motion must be transferred to the liquid medium involving coupling losses. The sound energy, then produces cavitation bubbles, however, the generation of cavitation bubbles itself involves energy losses. Finally, there will be attenuation of sound energy through the medium by bubbles or suspensions. In the reactor itself, energy will be absorbed (and reflected) from stirrers, baffles, cooling coils or any other devices within it.

5. THE DESIGN OF ULTRASOUND REACTORS

There are a number of companies who offer water treatment systems incorporating ultrasound. In this chapter, some examples of different configurations have been chosen from various suppliers. The selection of a particular system in itself, is not intended as a recommendation, it is simply chosen as an example of that particular type of reactor.

Solutions to the problem of the scale-up of ultrasonic processing do exist, but they are not necessarily as straightforward as simply the use of bigger versions of laboratory equipment. In a production situation, the volumes

treated will be very much larger than those considered in the laboratory and the type of process will govern the choice of reactor design. It could well be that some processes would be more suited to low intensity sonication (cf. using a laboratory cleaning bath) whereas others may need higher intensity irradiation (cf. using a probe type system).

5.1 Low Intensity Systems

In cases, where low intensity irradiation is needed batch treatment could be as simple as using a large-scale ultrasonic cleaning bath as the reaction vessel. A useful variant to this and indeed one that offers greater flexibility in use is the sealed, submersible transducer assembly (Figure 9). Thus, one might envisage an existing vat treatment facility into which some submersibles are introduced. In order to ensure efficient sonication of the bulk of the material in the vat some form of additional (mechanical) stirring would almost certainly be needed.

A bath type reactor could also be used as part of a flow system. In this case, the liquid undergoing treatment could be continuously fed into an ultrasonic tank with outflow over a weir to the next process. Such treatment could be intensified by recycling or by connecting a number of such sonicated tanks in line. Alternatively, the submersible could be placed in the base of a flowing culvert so that liquid passing over it can be treated.

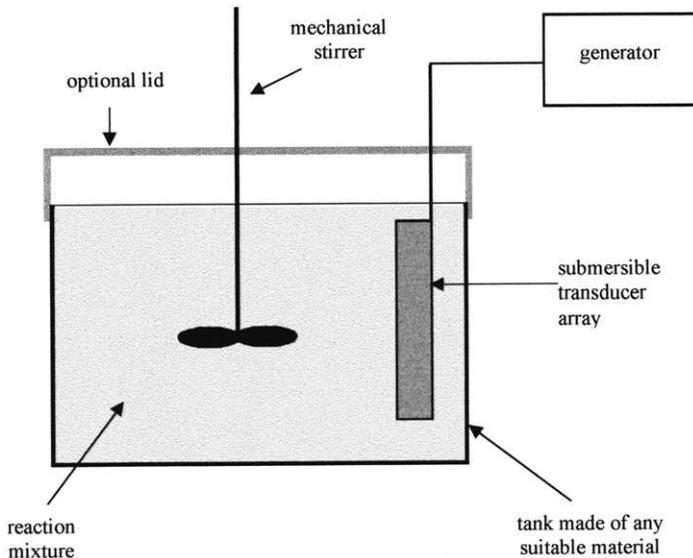


Figure 9. Low intensity (batch) reactor using submersible transducer.

This latter option is that used in a water treatment facility produced in Germany for the control of protozoa growth [11]. In order to be able to estimate the economic advantages of ultrasonic inactivation of plankton, a pilot flow reactor at 1/10 scale was developed. The module consisted of a transducer array with a resonance frequency of 40 kHz generating a homogeneous cavitation field in a water volume of around 2000 l. At a throughput of 300 m³/h and a specific energy of 54 Wh/m³, 90% of the test organisms (e.g. Nauplii, Copopods and Rotifers) were inactivated. At the then current electricity price of DM 0.20 per kilowatt-hour, energy costs averaged, DM 0.011/m³.

A further example of a low intensity flow reactor is the Sonoxide process [12] (Figure 10). The high frequency, low power ultrasound is applied through a tube containing the flowing coolant water at a rate of 20 m³/h. Combined with an alternating magnetic field, the system will remove algae build-up and stop pipe scaling without the need for added chemical biocides or descalers (see Chapter 1 by Phull and Mason in this volume).

In Russia, there has been some considerable success with the application of low power ultrasonic agitation generated by hydrodynamic converters in water treatment [13]. These systems can be used for a range of processes and operate with the following specifications:

- frequency range 0.5–20 kHz
- intensity up to 3 W/cm² at a power of up to several kilowatts
- capacity from 0.3 to 20 m³/h
- standard pumps can be used with pressures 0.3–0.5 Mpa

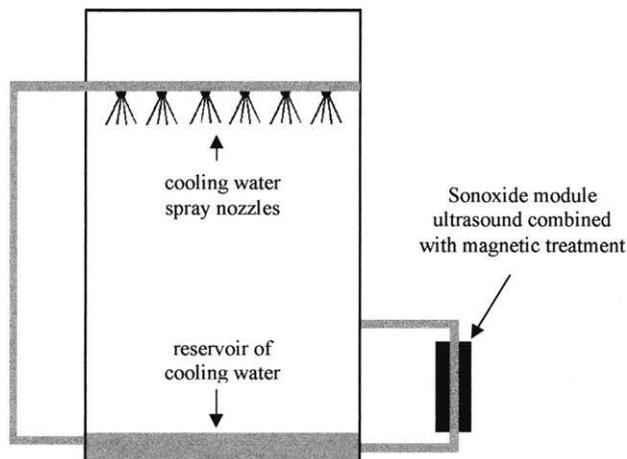


Figure 10. Low intensity (flow) reactor for cooling tower water.

Typical applications for such systems include:

- (i) The dispersion of coagulant chemicals. With ultrasonics, the amount of coagulant e.g. $\text{Al}_2(\text{SO}_4)_3$ can be reduced by 50% and its distribution in the system becomes more uniform.
- (ii) The regeneration of absorbents (e.g. sand, coal) at open pools and filters. This treatment increases their useful lifetime by 25–50%, and reduces the amount of absorbent and water needed for regeneration by 30%. The hydrodynamic converter is used in the water flow during the regeneration process.
- (iii) Ultrasonics can be used for process of chlorine and ozone treatment of drinking water. For water in a pipe with diameter about 1 m, the use of hydrodynamic oscillator with capacity $20 \text{ m}^3/\text{h}$ permits the reduction of the amount of chlorine by 50% and reduces the proportion of ozone needed to be mixed with air by a factor 7–10 without reducing the water standard.
- (iv) It is also possible to use the converters for the aeration of wastewater. This can increase the oxygen concentration in water by a factor 3 and consequently improve biological activity in subsequent treatment processes.

Hydrodynamic processors are not used widely in the West, but have some potential in large-scale water treatment.

5.2 High Intensity Ultrasonic Systems

Ultrasound has been known as a method for the removal of micro-organisms for many years. Current studies also suggest that it can also be used for the decomposition of chemical contaminants. However, the latter oxidative processes would require high power consumption for the high throughputs of today's water treatment systems which reach several cubic metres per second. It therefore seems likely that high intensity ultrasound is unlikely to be used in this domain. Nevertheless, in certain areas of specialist treatment, involving smaller volumes, high intensity ultrasound may be economically feasible.

For larger scale operations, where high intensity ultrasound is required, the sonic horn, or indeed any other source of high power ultrasound, is best utilised as part of a flow system. Such a flow treatment could be part of a loop outside of the main reactor or simply a one-pass treatment within a processing plant. This permits the processing of large volumes and provides several major advantages over a simple batch configuration:

- (i) High intensity sonication is provided for a continuously flowing liquid reaction at controllable exposure and power by the adjustment of

- either input power to the transducer or the flow rate through the cell.
- (ii) Temperature control can be provided through the general temperature of the large volume of circulating reaction mixture, in a flow loop, a heat exchanger downstream from the ultrasonic source or a pulse option for intermittent sonication.

Apart from the reduced heating effect compared with continuous ultrasound, the choice of a pulsed mode also seems to provide a more pronounced effect and a saving of energy. For these reasons, a pulse mode is a common choice in the scale-up of water or sewage treatment. A consideration to be made for all flow system is that pumping (or gravity feed) is required for circulation through the flow cell. This is not a problem for water processing but can become a consideration for sewage and sludge treatment.

In the laboratory an efficient high power, but low volume system is afforded by a probe system with flow cell attachment (Figure 11). When operating at high powers, tip erosion can be a problem.

An alternative arrangement would involve a number of probes inserted through the walls of a vessel allowing a much larger sonochemical treatment zone. Such a system will suffer from the same problems as the individual flow cell, except that it will continue to function, even if, one or two probe units fail (Figure 12).

Such an approach has been adopted for the high power treatment of wastewater or sewage sludge. A 30-kW unit used for sludge disintegration is shown (Figure 13). This uses a series of probes (each 1 kW and operating

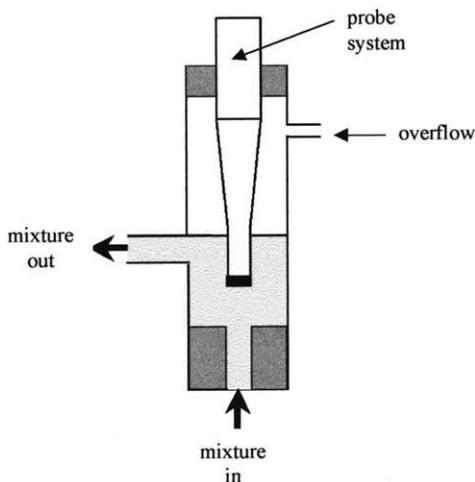


Figure 11. Laboratory flow cell.

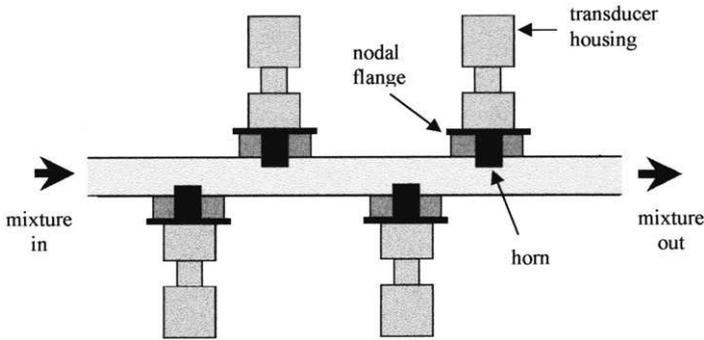


Figure 12. Flow processing with probe system inserts.



Figure 13. Sludge treatment plant using high power probe system inserts.

at 20 kHz) that are configured on one side of the flow system [14]. High-powered probes operating at 20 kHz with individual power ratings of up to 4 kW are available for this purpose. At this level of power input, the transducers require cooling to avoid the overheating and consequent depolarisation which can accompany such usage.

As an alternative to high power probe inserts, it is also possible to use an array of transducers slotted into a plastic tube. In such a system, the metal transducer face is emitting the energy and the plastic is simply providing the supporting tube. This is the approach used for the disintegration of sewage

sludges with dry solid contents between 0.5 and 4% [15]. A reactor module was built using PE-HD (high-density polyethylene) with a square channel (48×48 mm) with an overall length of 700 mm. This plastic has been chosen for its high resistance to chemicals, low water absorption and also, because it is highly impervious to water vapour and resistant to stress cracks. Some 60 transducers are used (15 transducers each 31 kHz on each face) affording an overall power of around 3.6 kW provided an acoustic intensity of about 7.5 W/cm^2 in flow-through mode with a reactor volume of 1.6 l. The emitting face of each transducer is titanium in order to minimise wear and reduce chemical reactions at the liquid interface. In order to achieve uniform sonication, the transducers are arranged in a spiral configuration. This is achieved by placing the transducers, in sequence on each face at a height difference of one quarter of the transducer diameter (Figure 14). Using eight modules in series, the treatment capacity lies between 0.2 and $2.5 \text{ m}^3/\text{h}$. The method of mounting transducers in different planes was first suggested as a means of producing focal ultrasound fields with spiral-shaped wave fronts [16].

If transducers are fixed to the external surface of a tube, then the tube itself becomes the source of ultrasonic energy. The liquid to be processed can then be passed through the tube and receive sonication directly from the ultrasonically vibrating walls. Two design engineering problems are associated with this type of sonicator: (i) the correct mounting of the transducers on the outer tube, and (ii) the length of the tube must be such

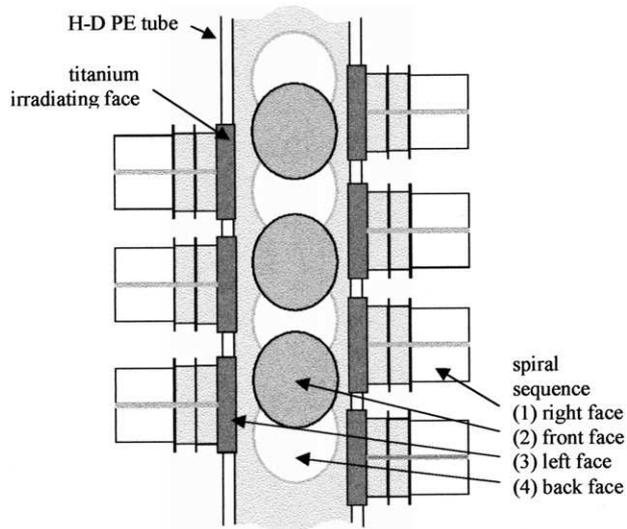


Figure 14. Flow processing with sandwich transducer inserts.

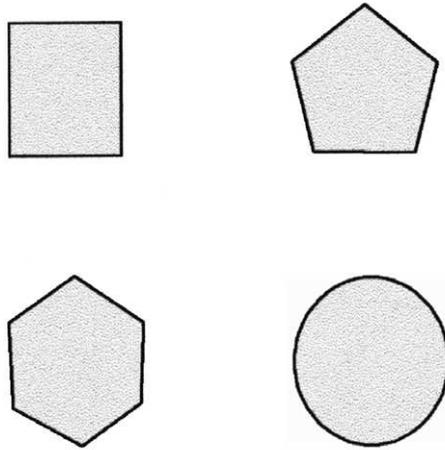


Figure 15. Cross-sectional geometry possibilities for flow processors.

that the ends are at a null point in the sound wavelength in the unit. This will eliminate vibrational problems associated with the coupling of the unit to existing pipework. The choices for pipe cross-section are generally one of four (Figure 15), but in practice, the current choices for environmental treatment are predominantly rectangular or circular.

The vibrating faces are opposite each other in the rectangular cross-section geometry and so, the possibility exists for the severe erosion of these faces. For this reason, the design of such apparently simple flow reactors must be handled with care. Unless the pipe is seamless, then, high-powered ultrasonic vibration is also likely to find any weaknesses in the welded construction, particularly at corner joints.

Another type of rectangular reactor employs opposite emitting faces with different ultrasonic frequencies is known as the Nearfield Acoustic Processor (NAP) (Figure 16). This system can be visualised as two sonicated metal plates—each similar to the base of a cleaning bath. These enclose a flow system, the plates are driven at different frequencies—normally 16 and 20 kHz, (these are magnetostrictive transducers in the Lewis Corporation device) [17]. Adjustable spacers permit different intensity conditions in the gap between the stainless steel plates. Under these conditions, any liquid flowing between the plates is subject to an ultrasonic intensity greater than that expected from a simple addition of the single plate intensities. The ultrasound “reverberates” and is magnified in its effect. An additional benefit is that the vibrating plates can be of large area (simply requiring the appropriate number of transducers to drive them). The processor is therefore, able to cope with very large throughputs.

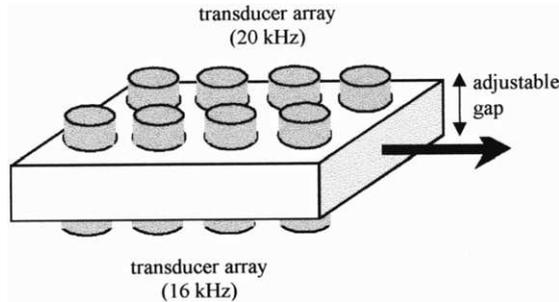


Figure 16. Nearfield Acoustic Processor (NAP).

To make a permanent bond for a high power transducer to the curved surface of a flow reactor of cylindrical cross-section is not as easy as to a flat surface, but several examples of this design exist. One important feature of the geometry of the tubular configuration is the intensification effect. When the walls are subjected to ultrasonic vibration, the inner surface focuses the ultrasonic energy towards the middle of the tube. A resonating pipe of 6-inch diameter operating at 25 kHz has been developed and installed on offshore oil drilling rigs for the deagglomeration of drilling mud (Figure 17) [18]. This process is required so that the jettisoned muds disperse with the movement of the sea and do not simply sink to the seabed under the platform. Accumulations of mud around the platform legs presenting a problem to sea life and eventually, rig maintenance. A similar, but smaller, tubular reactor was used for the biological clean up of cutting fluids (see Chapter 1 by Phull and Mason in this volume).

A neat method of introducing ultrasound into a medium flowing through a tube is via the coaxial insertion of a radially emitting bar into a pipe containing the flowing liquid. The vibrational energy is transferred from the longitudinal mode oscillations of a transducer at one end to vibrational motion directed perpendicular to the surface of the tube (radial). A number of systems are available for this purpose [19]. Two are illustrated, a hollow tube driven by a single transducer (Telsonic tubular resonator), and a solid tube driven by a transducer at each end (Martin Walter Push-Pull system) (Figure 18). In each case, the tube is the source of radial ultrasound at half-wavelength distances along its length.

A newer device, powered by a magnetostrictive transducer, is able to treat a large volume of liquid with high efficiency and a uniform ultrasonic (Figure 19). The distribution of cavitation fields produced by this system is claimed to be much more uniform in comparison with a classical rod waveguide system. The reactor is driven by a magnetostrictive transducer incorporating a newly developed (Tb, Dy)Fe₂ alloy. The properties of a

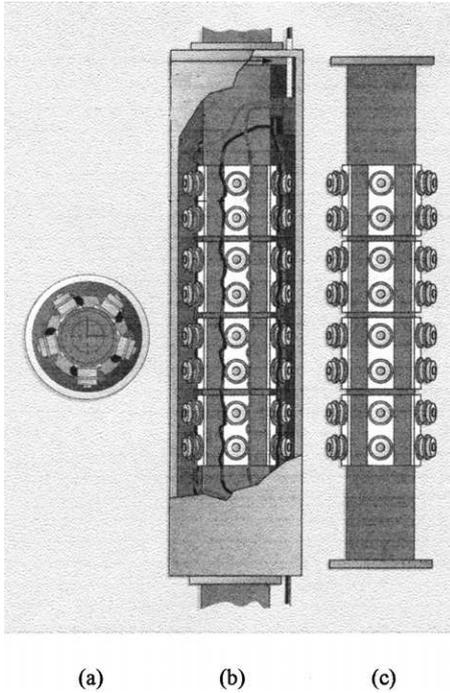


Figure 17. Cylindrical tube processor showing, from the left: (a) arrangement of transducers around outside of processing tube, (b) processing tube with outer protective casing, (c) inner processing tube with transducers attached.

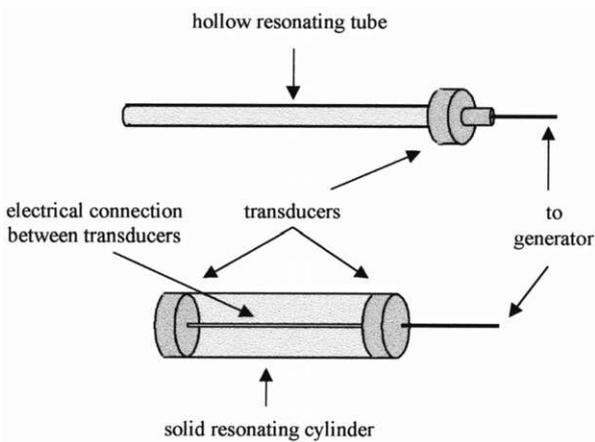


Figure 18. Cylindrical tube processors used as inserts into flow systems—axial mode.

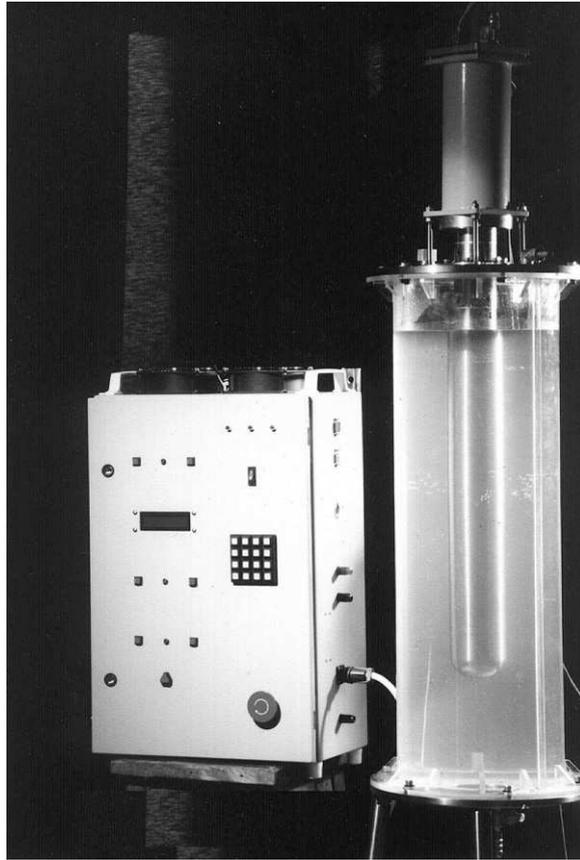


Figure 19. Radial processor with magnetostrictive transducer (25 kHz, 5 kW).

magnetostrictive (Tb, Dy)Fe₂ alloy are relatively good and can be produced simply and economically. Systems have been developed with powers of 6 kW and a resonance frequency of 25 kHz [20].

One device of this type is effectively a submersible transducer, which has been developed in the shape of a rod [21]. When placed inside a tube, the reactor produces steady and highly intense cavitation in a volume of 2.5 l at an intensity of 250 W/l at 40 kHz. The performance intensity in the cavitation field can be increased by the additional equipment with oscillating systems on the outside of the reactor housing (Figure 20). The unit has been used for the homogenisation and reduction of dry matter load of sewage sludge and the decomposition of heavy metal compounds of harbour sludge with antifouling substances.

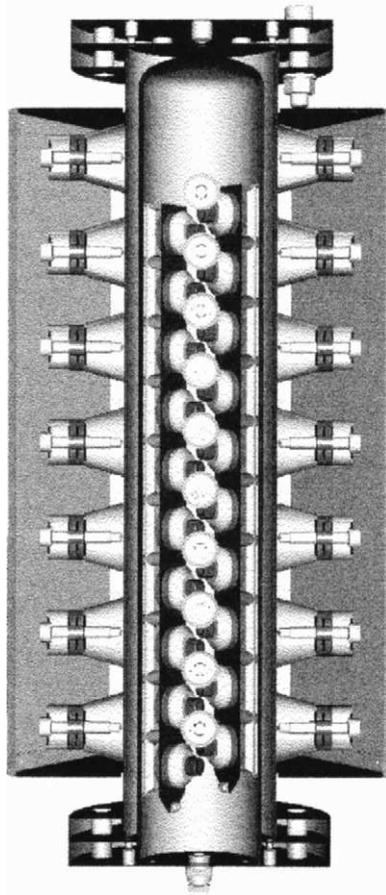


Figure 20. Radial processor inside reactor pipe with outer wall also sonicated.

6. CONCLUSIONS

Sonochemistry is an expanding field of study that continues to generate outstanding laboratory results. In the field of environmental protection, a number of trends are now evident including the combination of ultrasound with biocides for bacterial destruction and ozone in advanced oxidation methods. Future prospects are likely to encompass a much wider range of applications as the frequency effects are exploited and more studies of sonochemistry in conjunction with other technologies, such as photochemistry and electrochemistry are investigated. Equipment design is coming on apace both in the laboratory and in the development work necessary for

scale-up [22]. Many of these advances can be linked to the formation of various national groups involved in sonochemistry research and the more broadly based European Society of Sonochemistry (ESS). Greater efforts in sonochemical research are in prospect as co-operative ventures and technology exchanges are established both within Europe and between Europe and the rest of the world.

REFERENCES

- [1] Brown, B., and Goodman, J. E., *High Intensity Ultrasonics*, Iliffe Books Ltd, London, 1965.
- [2] Frederick, J. R., *Ultrasonic Engineering*, John Wiley, London, 1965.
- [3] The first in the series was *Macrosonics in Industry*:1. Introduction, E. A. Neppiras, *Ultrasonics*, 10 (1972) 9.
- [4] Abramov, O. V., *High-Intensity Ultrasound: Theory and Industrial Applications*, Gordon and Breach, London, 1998.
- [5] Mason, T. J., *Sonochemistry*, Oxford University Primer Series No. 70, Oxford Science Publications, 1999.
- [6] Russell, J. P., and Smith, M. In Mason, T. J (ed.), *Advances in Sonochemistry*, Vol. 5, JAI Press, 1999, pp. 175–208.
- [7] Information on Terfinol-D and applications of transducers utilizing this material may be obtained from Etrema Products Inc., 2500 North Loop Drive, Ames, Iowa 50010, U.S.A.
- [8] Crum, L., and Hynynen, K., *Physics World* (1996) 28.
- [9] STN ATLAS Elektronik GmbH, European Patent 94112879 (1994).
- [10] Masri, S. A., United States Patent 4,961,860 (1990).
- [11] Mues, A., Rodefeld, R., and Sobetta, R., *Proceedings of First World Congress in Ultrasonics*, 2 (1995) 765.
- [12] Information supplied by Undatim Ultrasonics, Zoning Industriel, rue de l'Industrie 3, B1400 Nivelles, Belgium.
- [13] Information supplied by Professor O. V. Abramov, Institute General & Inorganic Chemistry, 31 Leninski Prospect, Moscow.
- [14] Information supplied by Dr Hielscher GmbH, Warthestrass 21, D-14513 Teltow, Berlin, Germany.
- [15] Schneider, D. In Tiehm, A., and Neis, U. (eds), *TUHH Reports on Sanitary Engineering* Vol. 25 1999 p. 101.
- [16] Kawabata, K., and Umemura, S., *Ultrasonics*, 31 (1993) 457.
- [17] Hunicke, R. L., *Ultrasonics*, 28 (1990) 291.
- [18] Avern, N., and Copernici, P. A., *World Oil*, (1997) 75.
- [19] Mason, T. J. *Sonochemistry*, Oxford University Primer Series No. 70, Oxford Science Publications, 1999.
- [20] European Union INCO-COPERNICUS programme Contract number: IC15 CT98-0110. Project title: *Development of new generation of ultrasonic equipment and processes of physical and chemical action on water treatment.*
- [21] Information supplied by Bandelin Electronic, Heinrichstrasse 3-4, D-12207 Berlin, Germany.
- [22] Keil, F. J., and Swamy, K. M. *Reviews in Chemical Engineering*, 15 (1999) 85.

INDEX

- Acetate 43, 46
- Acetylene 102
- Acoustic contrast 188
- Acoustic efficiency 199
- Acoustic energy 94
- Acoustic streaming 183–185, 190–193
- Acoustic/ultrasonic intensity 152, 154, 159
- Acoustically transparent film 193, 201–205
- Adsorption 99, 100
- Advanced oxidation processes (AOPs) 29, 112, 115
- Agglomeration 149, 225
- Algae 6, 18
- Ammonium 54
- Anaerobic digestion 60–63, 74–85
- AOX 42, 46
- Aromatic 91–93, 97, 102, 104
- Autoclave 163
- Azo dye 28

- Bacteria 4–7, 31, 32, 117
- Batch operation 200, 214
- Benzene (Bz) 91, 92, 98, 100, 102, 104

- Bernoulli interaction 194
- Bi-frequency 173
- Bioavailability 32–40
- Biodegradation 26–29, 32–40, 40–47, 48–50, 51, 52, 54–55, 62, 63, 74–85
- Biofermenter 38
- Biofilm 14
- Biogas 60, 63, 75–77, 80–83, 88
- Bioluminescence test 45, 52
- Biomass 60, 61
- Bjerknes forces 194
- Bubble implosion 70, 71
- Bulking sludge 86–88

- Calorimetry 94
- Catechol 96
- Cavitation 64, 68, 71, 72, 74, 92, 95, 97, 103–107, 144–149, 151, 153, 158, 169–171, 223, 224, 235
 - bubble 41
 - bubble growth 131, 132
 - collapse 112, 122, 123, 124, 127, 130, 132, 136
 - expansion ratio 128, 129, 130, 131, 132, 137

- Cavitation (*cont.*)
 mechanism 8
 nuclei 68
 threshold 68
- Cell disruption 29–32, 49, 55, 65, 66, 74, 87
- Cell wall permeability 10
- Chemical degradation by oxidation 112, 113, 114, 115, 117, 133, 136, 137
- Chemical oxygen demand (COD) 34, 35, 43, 45, 65–67, 69, 74
- Chloride (Cl^-) 92, 93, 97, 101, 102, 105, 106
- Chlorinated pollutants 28, 40–47
- Chlorination 17
- Chlorine 92
- Chloroaromatic 91, 92, 104, 105, 107
- Chlorobenzene (ClBz) 40–43, 91, 92, 98, 100–104, 106, 107
- 4-chlorophenol 113, 119
- 4-chlorobiphenyl 92
- 4-chlorocatechol 96
- 4-chlorophenol (4-CP) 91, 92, 96–100, 102–107
- Cholesterol 39
- CO 96–98, 102, 103
- CO₂ 92, 96–98, 102, 103
- CO₂ production 37–39
- Collapse Lifetime 106
- Colony-forming units (cfu) 65, 67, 68
- Contaminants 93, 105
- Continuous flow 200–205, 215–216
- Convective streaming 192–193
- Costs of separation technology 210–213, 217
- Critical grain size 153, 157, 158
- Critical sound pressure 153
- Chlorohexene 113
- Deagglomeration 31, 55, 65, 68, 76, 77, 87
- Dechlorination 40–47, 50
- Decontamination 26–55, 142, 143, 155, 166
- Decontamination, biological 2, 8, 14
 solution 14–16
 surface 11–14
 water 16–21
- Degradation 91–93, 96–100, 102–107
- Degradation pathway 12–122, 132
- Degree of disintegration (DD) 66–71, 73–76, 78, 79, 82, 83, 85
- Dehalogenation 40–47, 55
- Deliquoring 240
- Dewatering 85, 86
- Dichlorophenol 44–46
- Differential oscillation 194
- Diffusion 142, 165, 16, 170
- Diffusivity 151
- Digested sludge 60–63, 67, 74, 75, 79, 80, 81, 83–85
- Disintegration 31, 49, 60, 61, 63, 64–74, 80, 83–85
- Dissolution 36, 37
- Dosimetry 94
- Dry solids 71–73, 86
- Eckart streaming 184, 192–193
- Effect of frequency 14
- Effect of temperature 9, 15
- Enhancement of oxidation process 118, 119, 122, 129, 132, 133, 135, 136
- Electrical energy 94
- Electro-acoustic 230, 232, 233, 236–238
- Energy demand 210–213, 214
- Enzyme activity 39
- Filamentous sludge 86–88
- Filtration 222, 227–233, 236–239
- Flocculation 86, 181, 196, 224, 226
- Fragmentation 48, 50, 55, 150

- Frequency 30, 35, 50, 53, 55, 64, 68,
70–72, 74, 75, 86, 92, 93, 96,
97, 99, 101, 105–107
- Glucose 43, 46
- H[•] 95, 99, 100, 102, 103
- H₂O₂ 92, 95, 96, 100, 106
- Haloalkanes 92
- Henry's Law 92, 105, 113–114
- High frequency ultrasound 35–40
- HNO₂ 92, 95
- HNO₃ 92
- Humic acids 28, 46
- Hydrocarbons 28
- Hydrogen peroxide 47, 50–52, 94,
95, 97, 106, 107
- Hydrogen sulphide 28
- Hydromechanical forces 48–50, 55
- Hydrophilic 92, 104
- Hydrophobic 97
- Hydroquinone (HQ) 96
- Hydroxyl radical 99, 100, 112, 115,
116, 120, 121, 124, 126, 127,
128, 131, 133, 137
- Impingement 148
- Inactivation 29–31, 226, 227
- Industrial scale 215–216
- Intensity 31, 64, 67–69, 71, 72, 79,
82, 83
- Interface 97–100, 106
- Jet stream 48–50, 55, 70, 71
- Kinetics 93, 96, 98, 103
- Leaching 142–151, 153–161,
163–168, 170–175
- Lixiviant 146, 149, 150, 157, 175
- Macromolecules 48, 50, 55
- Mass transfer 32–40, 55, 117, 119,
136
- Membranes (ED) 243
- Membranes (RO) 241, 242
- Membranes (UF, MF) 233–236, 241
- Methane 62, 63, 76, 81, 82
- Methyl *tert*-butyl ether (MTBE) 28
- Microcurrents 35–40
- Micro-explosions 169
- Micro-grinding 149, 150
- Micro-jet 145, 148, 149, 158, 169
- Micro-organisms 3–5, 15
- Microthrix parvicella* 88
- Naphthalene 35–40
- Nitrate 52, 53
- Nitrite 52, 53
- Nitrite ion 95, 107
- Nitrobenzene 113, 117, 119
- Nitrogen oxide 95
- 4-nitrophenol 113, 116, 119
- Nitrous acid 95
- Nitrous ion 95
- Nitrous oxide 95
- NO₂⁻ 95, 96, 98, 99, 101
- NO₃⁻ 95, 96, 98, 99, 101
- Nucleation 154
- O 95
- Octanol-water partition coefficient
113–114
- OH[•] 92, 95, 96, 98, 100, 102, 106
- OOH[•] 92, 95
- Oxidants 112, 113, 136
- Oxygen utilisation rate (OUR) 30,
31, 66–68
- Ozonation 116, 118
- Ozone 112, 113, 115–122, 124, 126,
127, 128, 132, 133, 136, 137
- Ozone decomposition model 118,
122–137
- Ozonolysis 119, 120
- Particle aggregation 182–185,
187–190

- Particle size distribution 65, 86
- Particle-particle interaction 194-195
- Pentachlorophenate 51
- Pentachlorophenol (PCP) 92, 93, 113, 133
- Pesticides 28
- PH 95, 97, 106
- Phenanthrene 32-40
- Phenol (PH) 91, 92, 96, 97, 100, 102, 104
- Phenols 28
- Pollutant mixtures 40-47
- Polycyclic aromatic hydrocarbons (PAH) 32-40
- Polyethylene glycol (PEG) 48-50
- Polymers 28, 48, 50, 55
- Polytropic ratio 104
- Power 91, 94, 96, 97, 99-103, 105, 106
- Power input 204-205, 208
- Pressure node 182, 187
- Primary sludge 60, 61, 74, 81
- Protozoa 7
- Pyrolysis 41, 102, 103, 104

- Radiation force 182-183, 188-190
- Radiation force potential 189-190
- Radicals 11, 92, 95-100, 106, 107
- Raw sludge 61, 63, 67, 81, 82, 84, 85
- Rayleigh streaming 185, 192-193
- Reactor design 197-199
- Reactors
 - efficiency 256
 - high intensity 259-267
 - low intensity 257-267
 - radial processors 265-267
- Remediation 92, 104
- Re-precipitation 162
- Reverberatory 161

- Scale-up 186, 215-216
- Schlichting streaming 185, 192-193

- Scrubbing 161, 162
- Sedimentation 183, 195-198
- Separation efficiency 195-197
- Sewage sludge 49, 54, 55, 60, 61, 64, 66, 71, 72, 74, 75, 85
- Shear forces 48-50, 55, 64
- Shockwaves 64, 70, 145, 146, 148
- Side reactions 50-54
- Sludge 224, 231
- Sludge disintegration 31, 49
 - hydrolysis 60, 62, 63, 81, 82, 84
 - solids concentration 71, 72
 - stabilisation 61, 62, 76, 83, 86
 - thickening 183, 193, 196, 213-214
 - volume index (SVI) 86-88
- Soil bioremediation 26-28, 33
- Sonic reactor 166
- Sonication 143, 155, 156, 160, 170, 171
- Sonochemical
 - effects 27, 32-35, 40-47, 49, 51, 55
 - pollutant degradation 27, 32-35, 40-47, 49, 51, 55
 - reactions 64
- Sonolysis 99, 107
- Sonolytic ozonation 116-122
- Sonophysical effects 35-40, 55
- Sonotrode 69
- Soot 102
- Spores 5, 15, 19
- Standing wave 182, 195-196, 225, 226
- Suspended solids content 208-209
- Suspension conditioning 181, 196

- Temperature 93, 94, 96-99, 101-104
- Terephthalic acid 46
- Total organic carbon (TOC) 119, 122
- Toxicity 34, 44-47, 52

- Transducer(s) 93, 94, 106
 - 1,3-composite 253
 - flextensional 254
 - liquid whistle 259
 - manetostrictive 252
 - piezoelectric 253
- Ultrasonic density 31, 64, 86
- Ultrasonic detoxification 45, 52
- Ultrasonic dose 64, 68, 86–88
- Ultrasonic intensity 31
- Ultrasonic pollutant degradation
 - 27, 32–35, 40–47, 49, 51, 55
- Ultrasonic specific energy 64, 68–70, 74
- Ultrasound 142–144, 148, 150–162, 164–168, 171–175
- Ultrasound equipment
 - laboratory 248–250
 - scale-up 254–256
- Ultrasound frequency 30, 35, 50, 53, 55
- Ultrasound Watt 143
- Vapor pressure 97, 105, 107
- Viruses 31, 117
- Volatile solids 60, 62, 75–78, 80, 82, 84, 85
- Waste activated sludge (WAS) 60, 61, 66, 67–82, 84, 85
- Wastewater treatment 26–28, 32–55, 60, 61, 86
- Xenobiotic 104
- Yeasts 31, 32
- Yields 93, 100, 105, 106, 107
- Zooplankton 31