RADIOACTIVE WASTE SOLIDIFICATION

ASME Short Course

RADIOACTIVE WASTE MANAGEMENT FOR NUCLEAR POWER REACTORS AND OTHER FACILITIES

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INTRODUCTION

The processes whereby a given batch of low-level radioactive or mixed radioactive and hazardous waste is converted to a single, solid piece are referred to as solidification. Prior to being solidified, the waste could be in a variety of forms, e.g., liquid, slurry (liquid plus suspended solids), sludge (wet solids), or dry solid particles.

Solidification is accomplished by mixing the waste with a solidification agent or binder. The binder forms a monolithic solid by reacting chemically with the waste, by forming microscopic cells that encapsulate the waste, or by coating and binding the individual particles of waste together or by encapsulation of the waste. The primary reason for solidifying waste in the U.S. has been to satisfy regulatory requirements.

Regulatory requirements in the U.S., such as plant technical specifications, Department of Transportation requirements, and disposal site licensing requirements encourage solidification with stringent conditions placed upon waste packages containing liquids. The regulations have their roots in concern for public health and safety. Solidification of waste for transportation and burial is regarded as being part of the public protection which underlies most regulations; that is, the burial site (by its location, design, and management) provides barriers inhibiting the release of radioactivity to the environment. The waste package provides another barrier and solidification provides still another barrier to the release of radioactive material from the burial site.

Each of the regulatory requirements in the U.S. addresses a different phase of the radioactive waste disposal cycle, i.e., in-plant processing, transport from plant to disposal site, and disposal. These regulations may differ in detail and not be in full agreement, e.g., the use of sorbent materials may be allowed for waste processing and transportation, but not be acceptable for burial; certain types of waste packages may meet transportation requirements, but not those of a particular burial site; the limitations on allowable total radioactivity in a package may be different for transportation than for burial. It is the responsibility of the generator of radioactive waste to assure compliance with all of the applicable regulations.

SOME BASIC DEFINITIONS

ABSORPTION - Liquid enters the volume of the absorbing medium by either physical or chemical means, such as capillary or hydration.

ADSORPTION - Liquid adheres to the surface of the adsorbing medium.

BINDER - See Solidification Agent.

CONTAINER - The primary containment receptacle in which the wastes are contained.

DEWATERED - Liquid or slurry wastes that have had excess water removed.

ENCAPSULATION - To cover and surround an object with solidification agent.

FREE LIQUID - Uncombined liquid not bound by the solid matrix of the solid waste mass.

HOMOGENEOUS - Of uniform composition; the waste is uniformly distributed throughout the package.

IMMOBILIZE - To treat the radioactive wastes in such a manner as to eliminate the characteristics of fluidity, dispersability, or freedom of movement within the packaging.

PACKAGING - Container plus waste combined to assure compliance with applicable requirements.

RENDER NON-HAZARDOUS – To immobilize by a method that ensures hazardous constituents are not leachable beyond acceptable limits and consistent with the US EPA requirements.

SLURRY WASTES - Liquid radioactive wastes of high insoluble content (greater than 0.1% solid by weight).

SOLIDIFICATION AGENT - Material which when mixed in prescribed proportions with waste can form a freestanding monolith with no free liquid.

SOLIDIFY - To immobilize by a method, which converts the liquid, slurry, or powder to a solid. The immobilized substance shall be monolithic with a definite volume and shape, bounded by a stable surface of distinct outline on all sides (free standing).

STABILIZE – To immobilize by a method that ensures the waste form will pass the test requirements stated in the U.S. NRC Branch Technical Position on Waste Form.

GENERAL WASTE TYPES

A. SPENT ION EXCHANGE MEDIA
- Powdered resin
- Bead resin
- Zeolites

B. FILTER SLUDGES
- Carbon and cellulose media
- Diatomaceous Earth (DE)

C. EVAPORATOR CONCENTRATES
- Sodium sulfate
- Boric acid

D. OTHER WASTE

- Calcine
- Reverse osmosis concentrate
- Incinerator ash
- Decontamination waste
- Miscellaneous waste

EXPANDED LIST OF WASTE TYPES

Liquids (Including Slurries)

Evaporator Concentrates (Viscous Slurries)
- Borates (5% to 50% by wt.)
- Sulfates (8% to 50% by wt.)
- Mixed Borates and Sulfates (5% to 50% by wt.)

Reverse Osmosis Concentrates (3% to 10% by wt.)
Miscellaneous Decontamination Liquids
Contaminated Oils

Wet Solids
Ion Exchange Resins (Bead)
Ion Exchange Resins (Powdered)

Sludges
Diatomaceous Earth
Cellulose Fibers
Mixed Cellulose Fibers and Powdered Resins
Carbon

Dry Solids (Contaminated Trash Excluded)

Incinerator Ash (By Type of Feed) (DAW only)
Ion Exchange Resins, Dried Filter Sludges Dryer Residues and Mixtures
- Sodium Sulfate
- Sodium Borate/Boric Acid
- Sodium Sulfate/Sodium Borates

Sodium salts are typical; other metal salts may be produced by different processing methods.

BENEFITS OF SOLIDIFICATION

- Prevent dispersion of fines and liquids during handling
- Minimize releases of radionuclides and hazardous constituents after disposal
- Reduce potential exposure to intruders, long term solution

DESIRABLE PROPERTIES OF A SOLIDIFICATION AGENT

- Availability
- Low Cost
- Volumetric Efficiency
- Simplicity Of Use
- Good Waste Form Properties

IMPORTANT PROPERTIES OF SOLIDIFIED WASTE FORMS

- Leachability
- Chemical Stability
- Compressive Strength
- Radiation Resistance
- Biodegradation
- Thermal Stability
- Solubility

SOLIDIFICATION AGENTS

Contemporary and non-traditional encapsulation materials, which may be applicable to low-and intermediate-level radioactive wastes

CEMENTS

Portland
Masonry cement
Cement-sodium silicate
Pozzolanic
High alumina
Blast furnace slag
Polymer modified gypsum
Polymer impregnated concrete

THERMOSETTING

Vinyl-ester styrene
Polyester styrene

THERMOPLASTIC

Bitumen
Polystyrene
Polymethylmethacrylate
Polyethylene

GLASS

Soda-lime
Phosphate
Slag

COMMON SOLIDIFICATION AGENTS

- Portland Cements
- Blended Cements (I.E., Flyash, Slags, Etc.)
- Bitumen
- Polymers
- Glass

CEMENT SOLIDIFICATION MECHANISM

- During absorption of water, hydrated mineral compounds form a colloidal disperse substance called "sol"
- The "sol" coagulates into a gel (setting begins) and precipitates (setting ends)
- The gel begins to crystallize (curing)

PRINCIPLE COMPOUNDS IN PORTLAND CEMENT

NAME OF COMPOUND	OXIDE COMPOSITION	ABBREVIATION
TRICALCIUM SILICATE	$3CaO \bullet SiO_2$	C_3S
DICALCIUM SILICATE	$2CaO \bullet SiO_2$	C_2S
TRICALCIUM ALUMINATE	$3CaO \bullet Al_2O_3$	C_3A
TETRACALCIUM ALUMINOFERRITE	$4CaO \bullet Al_2O_3 \bullet Fe_2O_3$	C_4AF

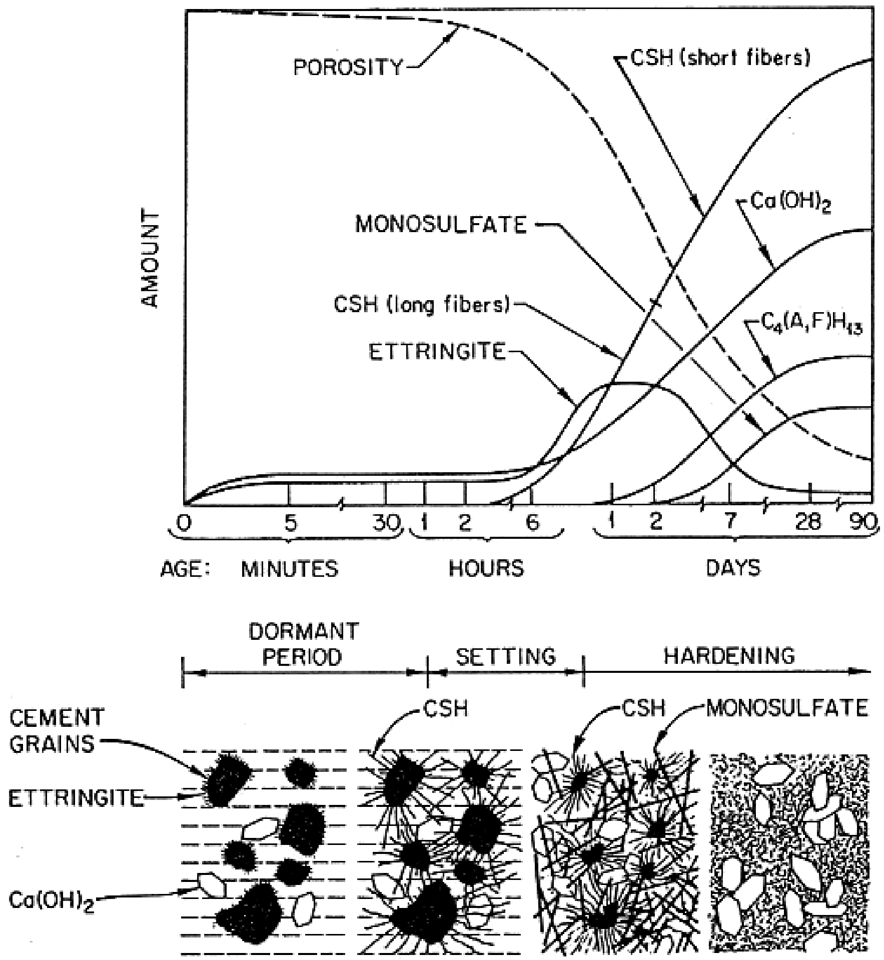


FIG. 1 COURSE OF CEMENT PASTE REACTIONS
(Courtesy of Chemical Publishing Company) [4]

COMPOUND COMPOSITION OF PORTLAND CEMENTS

TYPE OF CEMENT	COMPOUND COMPOSITION, wt%			
	C_3S	C_2S	C_3A	C_4AF
Normal	45	27	11	8
Modified	44	31	7	13
High Early Strength	53	19	10	7
Low Heat	20	52	6	14
Sulfate Resistant	38	43	4	8

HYDRATION REACTIONS OF MAJOR CEMENT COMPOUND

C_3S: $2(3CaO \bullet SiO_2) + 6H_2O \longrightarrow 3CaO \bullet SiO_2 \bullet 3H_2) + 3Ca(OH)_2$

(tricalcium silicate) (tobermorite) (calcium hydroxide)

C_2S: $2(2CaO \bullet SiO_2) + 4H_2O \longrightarrow 3CaO \bullet 2SiO_2 \bullet 3H_2O = Ca(OH)_2$

(dicalcium silicate) (tobermorite) (calcium hydroxide)

C_3A: $3CaO \bullet Al_2O_3 + 6H_2O \longrightarrow 3CaO \bullet Al_2O_3 \bullet 6H_2)$

(tricalcium aluminate) (tricalcium aluminate hydrate)

C_4A: $4CaO \bullet Al_2O_3 \bullet Fe_2O_3 + 10H_2O + 2Ca(OH)_2 \longrightarrow 6CaO \bullet Al_2O_3 \bullet Fe_2O_3 \bullet 12H_2O$

(tetracalcium aluminoferrite) (calcium hydroxide (calcium aluminoferrite hydrate)

MODIFIED OR BLENDED CEMENTS

TYPE	ADDITIVE	USE	FUNCTION
Masonry	Lime	Boric acid waste	Adjusts pH
Cement-sodium solidification	Sodium silicate	Boric acid waste Organic liquids	Accelerates set Reduces porosity
Pozzolanic	Reactive silica	Sulfate waste	Reacts with $Ca(OH)_2$ Reduces porosity
Grouts	Blast furnace slag Clay minerals Fly ash	Sulfate waste Wide range of waste types	Reacts with $Ca(OH)_2$ Ion exchangers
Modified Gypsum	Polymer emulsifier Oils, organics	Boric acid waste Reduces porosity	Accelerates set

ADVANTAGES AND DISADVANTAGES OF CEMENT

ADVANTAGES	**DISADVANTAGES**
Material and technology well known and available	Some wastes affect setting or otherwise produce poor waste forms
Compatible with many wastes	Swelling and cracking occurs with some products under exposure to water
Low cost	Volume increase and high density for shipping and disposal
Good impact and compressive strength	

THERMOSET SOLIDIFICATION MATERIALS

- Epoxies
  - Epichlorohydrin resins
  - Cycloaliphatic resins
- Polyester resins
  - Polyester styrene
  - Polyester toluidine
  - Water extendable polyester (WEP)
- Vinylester styrene (VES)

EPOXY POLYMERS

The most widely used epoxy resins are produced by the condensation reaction of epichlorhydrin and diphenylol propane using an alkaline catalyst such as sodium hydroxide. Epoxy resins are polymerized through condensation reactions, which can be induced by many different materials including polyamines, polyamides, polysulfides, and acids or acid derivatives. The properties of the polymer formed are highly dependent upon the molecular weight of the polymer. Epoxy resins have been used for the solidification of radioactive wastes, but is currently being used only on some specialized waste.

VINYL ESTER MONOMERS

The solidification of aqueous wastes with vinyl ester-styrene (VES) binder requires high shear mixing to promote the formation of a waste water-monomer emulsion. The water is dispersed within the emulsion as 2-5 µm droplets. The rate of waste addition and the mixing mode are important in forming a stable emulsion. An initiator / promoter system is used to permit the polymerization reaction to occur at room temperature. Some components in the waste may interact with the initiator or promoter, necessitating a change either in the order of addition or in the order of increased quantities of initiator and/or promoter. Vinyl ester monomers have also been used for the solidification of dry solid wastes. High shear mixing is not necessary with dry wastes since the process does not rely upon emulsion formation. Solid particulate is suspended in the waste-monomer mixture and remains dispersed as the monomer polymerizes. The ability to form a stable emulsion with aqueous wastes is a function of the specific vinyl ester monomer and is pH dependent. Routine solidification of wastes in the pH range of 2.5-12.5 can be accomplished.

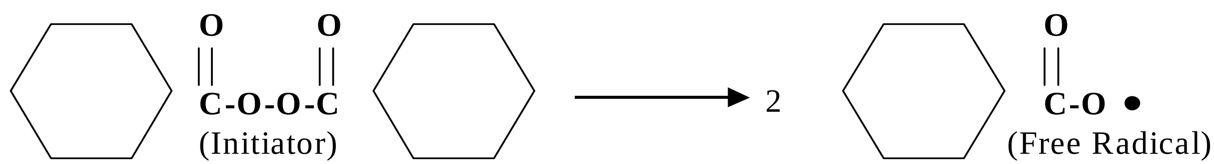
Waste-to-binder ratios recommended are typically 1.5-2.0 by volume for aqueous wastes and up to 2.5 for dry wastes. While vinyl ester styrene is compatible with most wastes, wastes, such as boric acid concentrates, require pretreatment to provide acceptable waste forms.

TYPICAL PROMOTER-CATALYST SYSTEMS FOR "ROOM TEMPERATURE" CURE

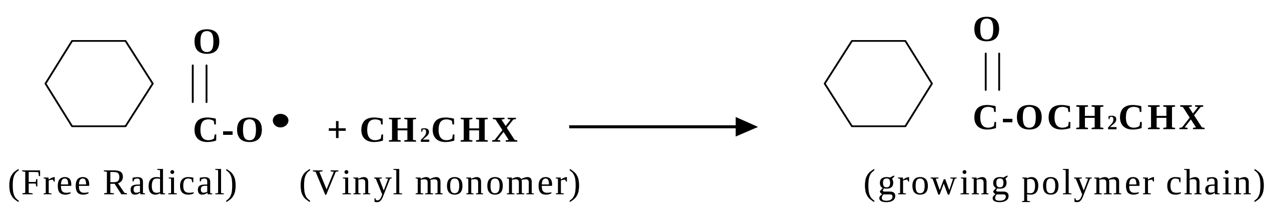
MONOMERS	CATALYST	PROMOTER
Vinylester styrene	Benzoyl peroxide	Dimethyl toluidine
Polyester styrene	MEKP (a)	Cobalt naphthenate
Methyl methacrylate	Benzoyl peroxide	Dimethyl aniline
Styrene + Divinyl benzene	Benzoyl peroxide	Dimethyl aniline

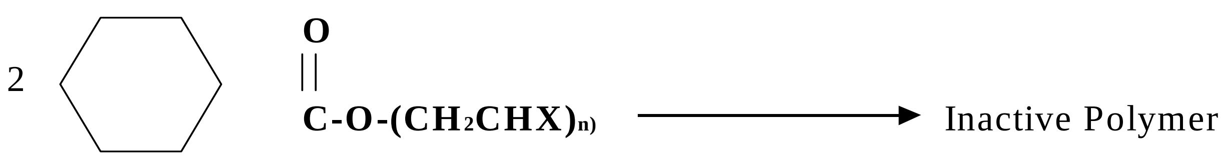
FREE RADICAL (ADDITION) POLYMERIZATION

Free radicals are formed by the decomposition of an initiator

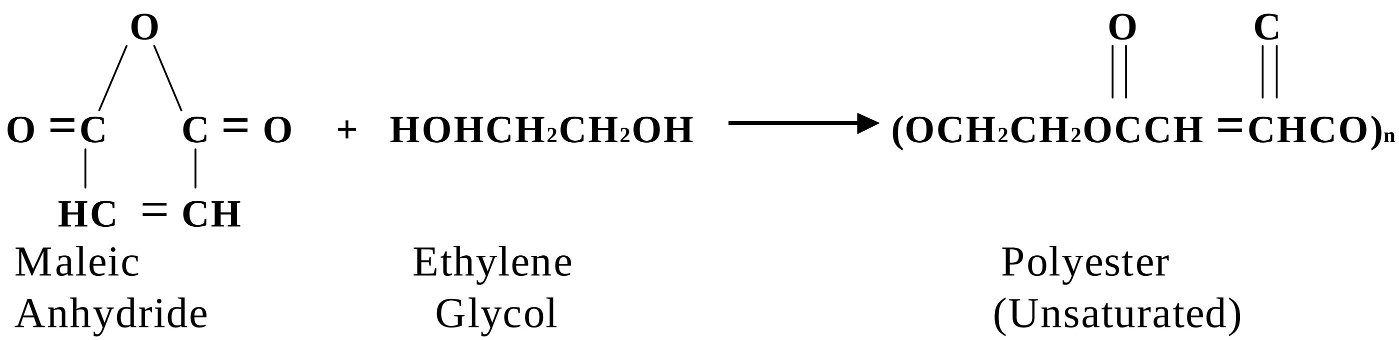


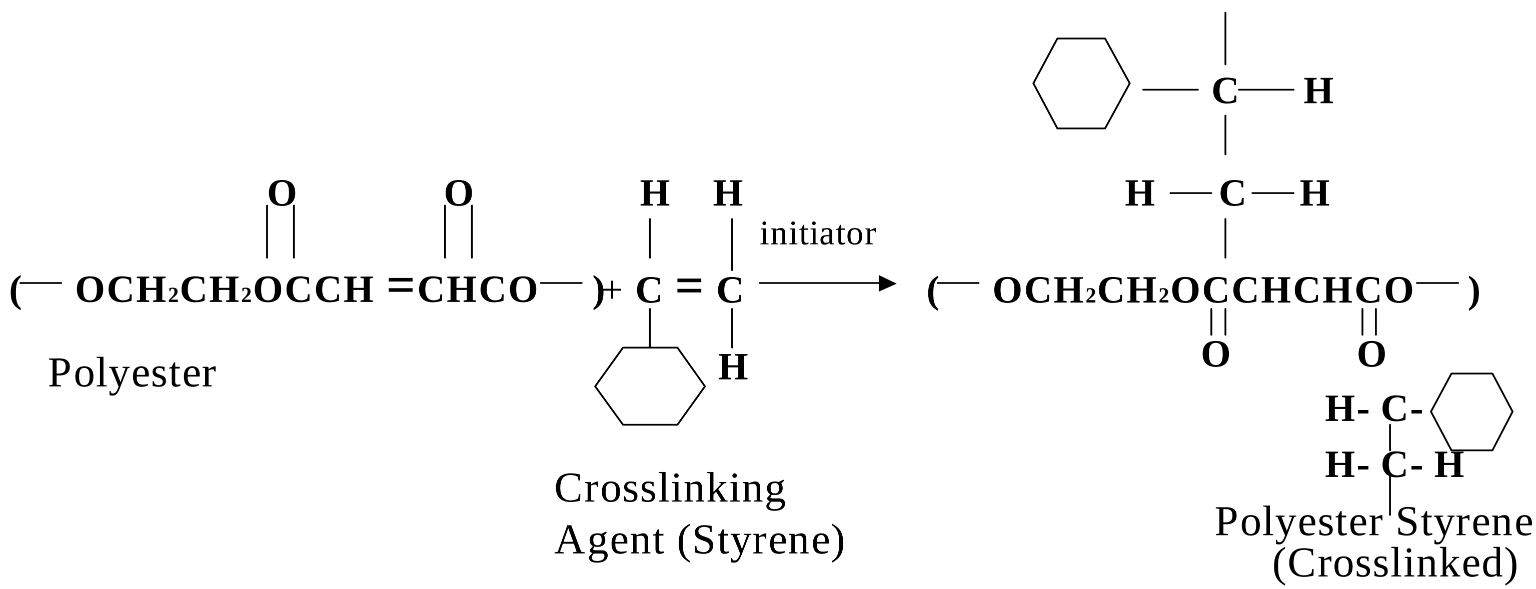
The free radical reacts to open the double bond of a monomer, regenerating the unpaired electron



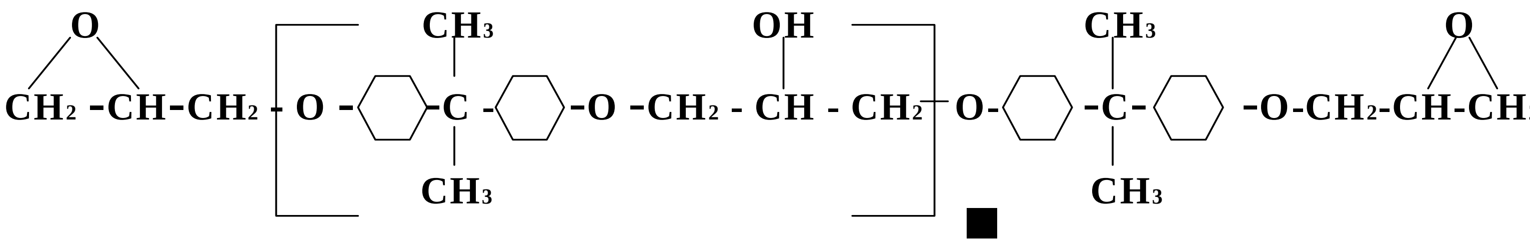


POLYESTER RESINS

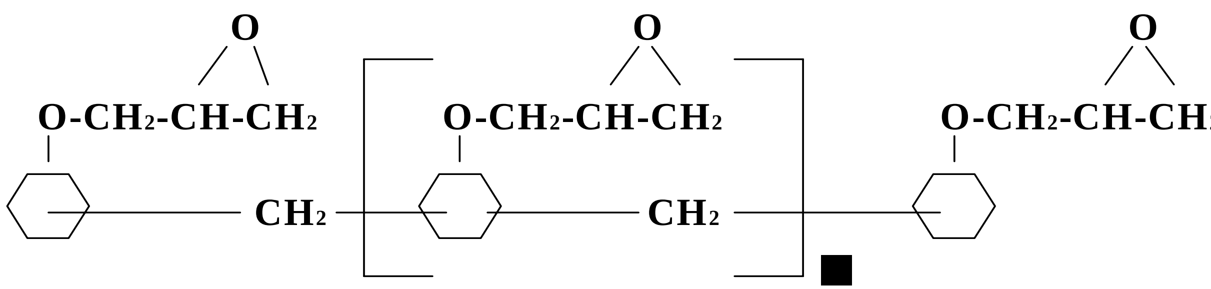




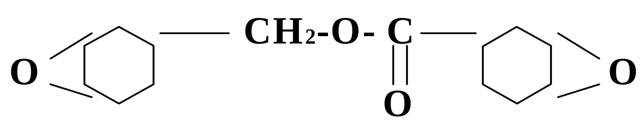
EPOXY RESINS



Bisphenol A-Epichlorohydrin Resins



Epoxy Novolak Resins



Cycloaliphatic Epoxy Carboxylate

POLYETHYLENE

Polyethylene is a lightweight thermoplastic material of the chemical formula $(CH_2CH_2)_x$. There are different types of polyethylene products whose properties depend upon the molecular weight and structure of the material. High-density polyethylenes (sp. gr. 0.945-0.965) are the products of a low-pressure process that produces a linear, more crystalline molecular structure. Low density polyethylenes (sp. gr. 0.915-0.925) are usually produced in a high pressure process which results in molecules that contain long and short branch chains which interfere with the close approach of the molecules and hence produce a product of lower crystallinity. Typical high-density polyethylene has a softening point of about 12?C, while low-density polyethylene softens at about 86°C. Polyethylene products are available that are mixtures of high density and low-density polyethylenes.

Since polyethylene is a thermoplastic material, its use for the solidification of LLW's is similar to asphalt. The polyethylene is heated, after which aqueous waste or waste solids are added. The water is evaporated from the waste and, after cooling, waste solids are mechanically held in a polyethylene matrix. Evaporator concentrates and ion-exchange resins have been solidified in polyethylene. However, because polyethylene is more expensive than asphalt, its use as a radioactive waste binder has been limited.

CHEMICAL RESISTANCE PROPERTIES OF POLYMERS

Properties	ASTM Test Method	Epoxy (Thermoset)	Polyester Styrene (Thermoset)	Vinylester Styrene (Thermoset)	LDPE* (Thermoplastic)
Burning rate (in./min.)	D635	Slow	Slow to self extinguishing	Burns	Very slow
Effect of weak acids	D543	None	None	Slight	Resistant
Effect of strong acids	D543	Attacked	Attacked	Slight	Attacked by oxidizing acids
Effect of weak alkalies	D543	None	Slight	Slight	Resistant
Effect of strong alkalies	D543	Slight	Attacked	Slight	Resistant
Effect of organic solvents	D543	Resistant	Slight to considerable	Slight to moderate	Resistant below 60°C

*Low-density polyethylene

GLASS

Glass melters use modern glass science to convert a liquid mixed waste into stable glass. The glass produced is leach resistant (typically passing the TCLP for nickel and other components), stable (glass maintains its mechanical integrity for thousands of years), and economical (large volume reduction). The hazards associated with this technology are minimal and the process has been demonstrated as a safe and reliable method of treating radioactive and hazardous wastes. The operation of vitrification has been performed safely for more than 20 years. Glasses of various compositions have received considerable attention for the solidification of high level wastes. The capital and operating costs of glass systems have largely precluded their application to LLW. However, glass systems applicable to LLW have been developed and used successfully for both low level and mixed waste solidification. Briefly, glasses are materials with a high melting point, generally inorganic oxides that, upon cooling, solidify, forming an (typically) amorphous structure with little long-range order. Waste solids are generally incorporated into the glass structure as oxides produced during the high temperature processing conditions (1200°C) of the process. The amount of waste oxides that can be incorporated in glass is limited, particularly if a single-phase glass is desired. However, because of the processing conditions, a large volume reduction is achieved, particularly for combustible wastes.

BITUMEN COMPOSITION

Mixture of high molecular weight hydrocarbons

Two major components:

- Asphaltene compounds - colloidal properties
- Malthene compounds - viscous liquid properties

Bitumen types:

- Straight run distillation asphalts
- Oxidized (blown) asphalts
- Cracked asphalts
- Emulsified asphalts

CHARACTERISTICS OF TYPICAL BITUMEN USED FOR SOLIDIFICATION

PROPERTY	VALUE
Softening point	200°F (93°C)
Flash point Cleveland Open cup method	550°F (288°C)
Percent Volatiles by volume	0.1%
Ignition point	600°F (316°C)
Density	1 g/cm
Vapor pressure	1 mm Hg (max)
Vapor density (air-1)	0.01 maximum

CHEMICAL COMPATIBILITY OF WASTES WITH BITUMEN

WASTE TYPE	WASTE COMPATIBILITY
Ion exchange resin	Fair
Sludges	Good
Boric acid	Good-Poor
Sulfate	Poor
Nitrate	Poor
Carbonate	Good
Organic	Poor
Acidic	Fair
Alkaline	Fair
Incinerator ash	Fair

ADVANTAGES AND DISADVANTAGES OF BITUMEN

ADVANTAGES	DISADVANTAGES
Technology and materials are well known and available	Tendency to swell
Insoluble in water	Bitumen is combustible
High waste loading capacity	Process requires elevated temperatures
Low cost	Settling of particulates during cooling
Good mixability	Possibility of chemical reactions

PRESENT REGULATORY COMPLIANCE
PART 61 CEMENT WASTE FORM REQUIREMENTS
CLASS B & C WASTE

CRITERIA	OLD REQUIREMENTS	CURRENT REQUIREMENTS
Compressive strength	60 psi	500 psi
After thermal cycling	60 psi	500 psi
After irradiation	60 psi	500 psi
After biodegradation test	60 psi	500 psi
After immersion test	60 psi	500 psi* **
Free liquids	<0.5%, pH 4.0 to 11.0	<0.5%, pH >9
Leach testing	L > 6, 90 days	L > 6, 5 days
Full-scale correlation	Simulated waste	Simulated waste, then compressive test

* If post immersion is < 75 % of original strength, immersion test must be performed for longer immersion periods (120, 150, 180 days).

** For bead resin, chelates, filter sludge, and floor drain wastes, seven-day immersion is followed by seven days of drying, then examined and compressive strength test run.

DESIRABLE PROPERTIES OF SOLIDIFICATION AGENTS IN THE UNITED STATES

- Simplicity of use, forgiving of operator error
- Noncorrosive to containers, no free liquid
- Physical stability, ruggedness
- Good packaging efficiency
- Low cost
- Radiation resistance
- Low leachability of waste for radioactive and hazardous
- Long shelf life
- Resistance to biodegradation

SOLIDIFICATION AGENTS CURRENTLY IN USE

- Cement, with and without additives
- Glass or Ceramic
- Vinyl ester styrene
- Sodium silicate with Portland cement
- Epoxy
- Additives with or without cement
  (MagOx, Metal Plex, etc.)

INTERIM COMPRESSIVE STRENGTH SPECIFICATIONS AND RECOMMENDED TESTS

Solidification Agent	Typical Compressive Strength (psi)	Test Method	Failure Mode
Hydraulic Cement	500	ASTM C-39	Check Mode Stress-Strain Curve
Thermoplastic Organic Binders	750	ASTM D-695	Plastic Deformation
Thermosetting Organic Binders	1000	ASTM D-695 ASTM C-39	Check Mode Stress-Strain Curve
Sulfur Cement	1000	ASTM C-39	Brittle
Glass/Crystalline	5000	ASTM C-39	Brittle

TYPES OF MIXING PROCESSES

<u>In-Container Mixing Processes</u>

- ➢ Rolling
- ➢ Rotary Paddles
  - ▪ Insert and remove
  - ▪ Disposable

<u>In-Line Mixing Processes</u>

- ➢ Extruders
- ➢ High shear kneading and screw auger
- ➢ High speed, high shear, low pressure batch mixer
- ➢ Positive displacement pumps

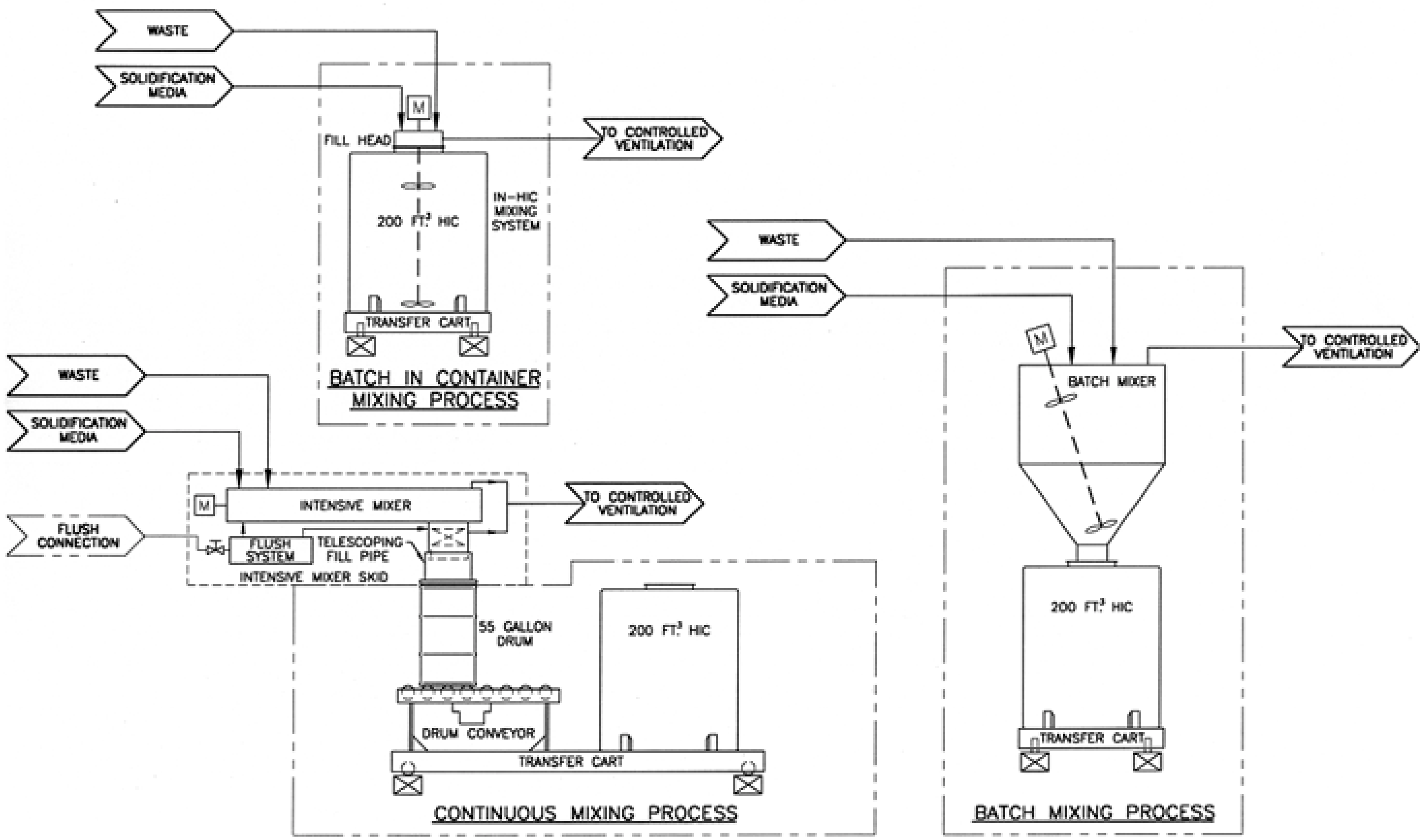
- Tumbling
- Screw augers
- Static mixers

WASTE FORM PROPERTIES

Property	Portland Cement	Asphalt	Unsaturated Polyester	Polyethylene	Glass
Product density, lb/ft^3	90-125	62-90	69-81	70-86	150-175
Water-binding strength	High	N/A	Moderate-High	High	N/A
Free-standing water	Occasionally	Never	Seldom	High	None
Compressive strength, psi	500	—	750	1000	5000
Mechanical stability	High	Moderate	Moderate-High	Moderate-High	High
Flammability	None	Moderate	Low-Moderate	Low	None
Leachability	Moderate	Low-Moderate	Moderate	Low	Low
Corrosivity to mild steel	Protective	Non-corrosive	Noncorrosive	Non-corrosive	Non-corrosive

*Due to material cost or undesirable characteristic, asphalt solidification is not currently used.

VARIOUS MIXING PROCESSES



ALTERNATIVES TO SOLIDIFICATION

In the past, some radioactive waste was shipped for burial in the form of liquids or liquids adsorbed or absorbed by a porous medium. This type of packaging is allowed today for only very small quantities of low activity waste. This practice is not allowed for normal nuclear power plant wastes. Some wet solid wastes, particularly ion exchange resins, have been shipped by first "dewatering" them (i.e., pumping away all drainable liquid) and then putting them into suitable containers. In the U.S., the burial of dewatered resins with radiological activity greater than 1µCi/cc is allowed only if they are packaged in a high integrity container (HIC).

For some special types of waste, such as filter cartridges, forms of encapsulation have been used to immobilize the filter and the radioactive material trapped in it. In one encapsulation method, a container is pre-lined with cement; the filter cartridge is placed in the interior cavity, and is then sealed in by cement. Multiple filters are also encapsulated with VES in large liners in excess of 60 ft^3 working volume to increase packaging efficiency as compared to a 55-gallon drum. In another encapsulation method, the filter is placed in a basket or rack within the container and the container is then filled with a mixture of waste and solidification agent. A similar technique has been used in Europe and Japan to encapsulate incinerator ash. In this case, a 55 gal (210 L) drum is lined with cement, and a 30 gal (110 L) drum filled with ash is placed inside its cavity, and sealed in place with cement.

REFERENCES

[1] American Society of Mechanical Engineers, “Radioactive Waste Technology,” Chapters 8 and 9, New York, 1986

[2] Brownstein, M., Columbo, P, and Dole, L, “Radwaste Solidification” presented

at the ASME Radwaste Short Course, 1981-1995.