# 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 (wetsolids), 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 producedby 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 | $3CaO \cdot SiO_2$ | $C_3S$ |
| DICALCIUM SILICATE | $2CaO \cdot SiO_2$ | $C_2S$ |
| TRICALCIUM ALUMINATE | $3CaO \cdot Al_2O_3$ | $C_3A$ |
| TETRACALCIUM ALUMINOFERRITE | $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ | $C_4AF$ |

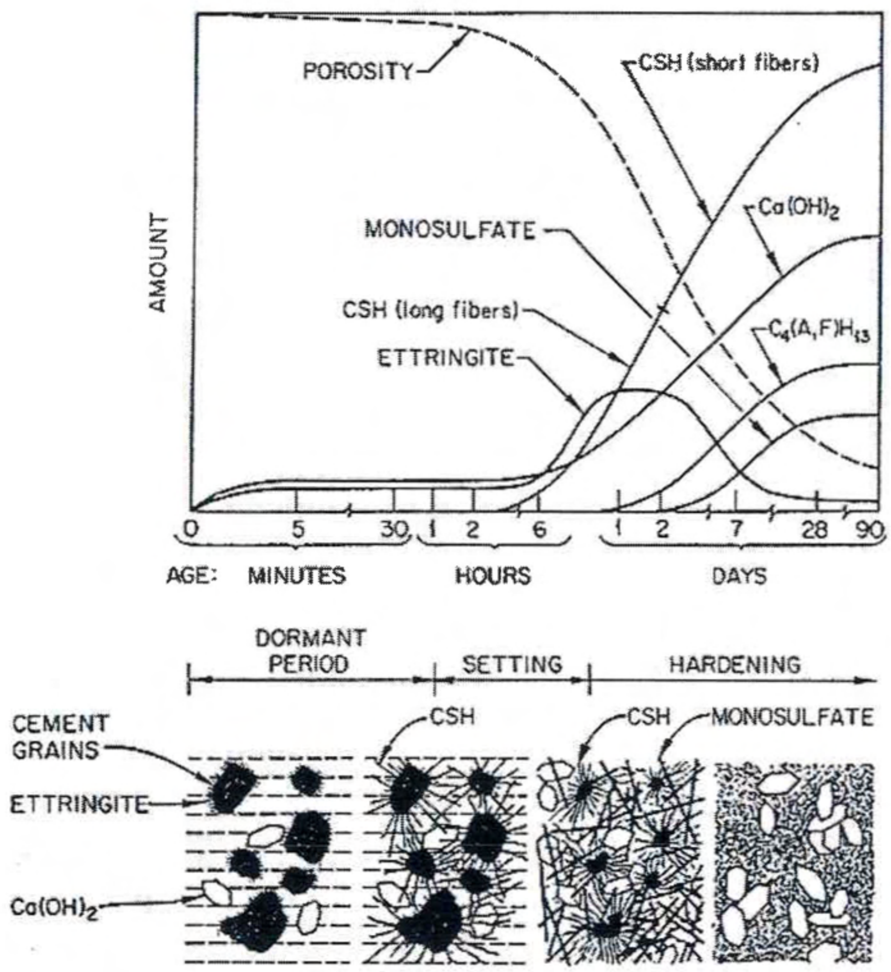



**FIG. 1 COURSE OF CEMENT PASTE REACTIONS**
**(Courtesy of Chemical Publishing Company) [4]**

## 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<br>Organic liquids | Accelerates set<br>Reduces porosity |
| Pozzolanic | Reactive silica | Sulfate waste | Reacts with $Ca(OH)_2$<br>Reduces porosity |
| Grouts | Blast furnace slag<br>Clay minerals<br>Fly ash | Sulfate waste<br>Wide range of waste types | Reacts with $Ca(OH)_2$<br>Ion exchangers |
| Modified Gypsum | Polymer emulsifier<br>Oils, organics | Boric acid waste<br>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

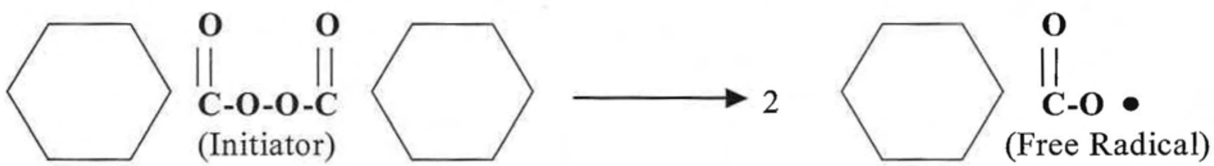
The solidification of aqueous wastes with vinyl ester-styrene (VES) binder requires high shear mixing to promote the formation of a waste water-monomer emulsion. The water is dispersed within the emulsion as 2-5 μm droplets. The rate of waste addition and the mixing mode are important in forming a stable 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**

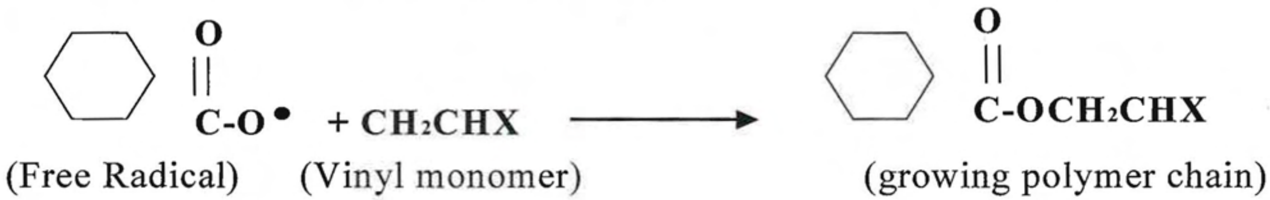
| MONOMERS | CATALYST | PROMOTER |
|---|---|---|
| Vinylester styrene | Benzoyl peroxide | Dimethyl toluidine |
| Polyester styrene | MEKP (a) | Cobalt naphthenate |
| Methyl methacrylate | Benzoyl peroxide | Dimethyl aniline |
| Styrene + Divinyl benzene | Benzoyl peroxide | Dimethyl aniline |

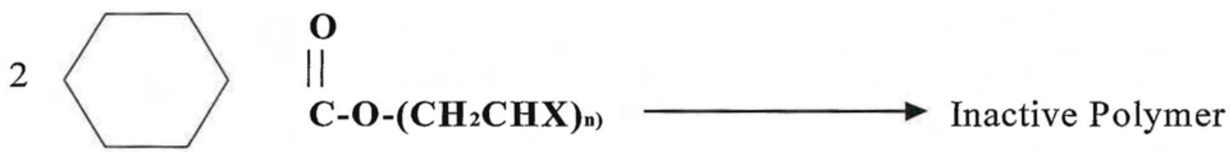
# FREE RADICAL (ADDITION) POLYMERIZATION

Free radicals are formed by the decomposition of an initiator

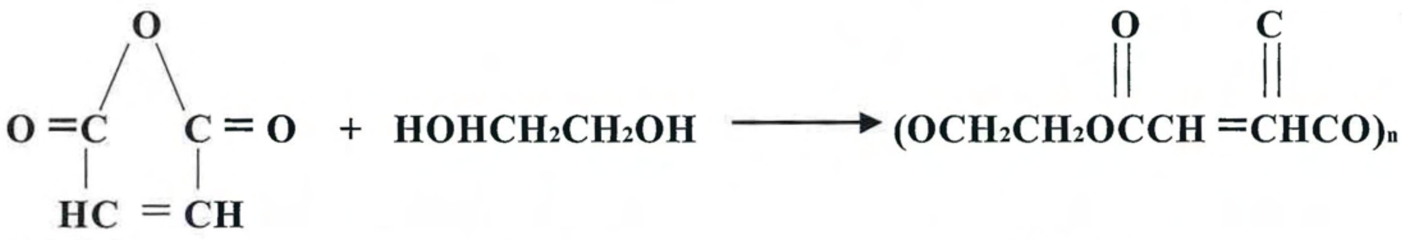



The free radical reacts to open the double bond of a monomer, regenerating the unpaired electron



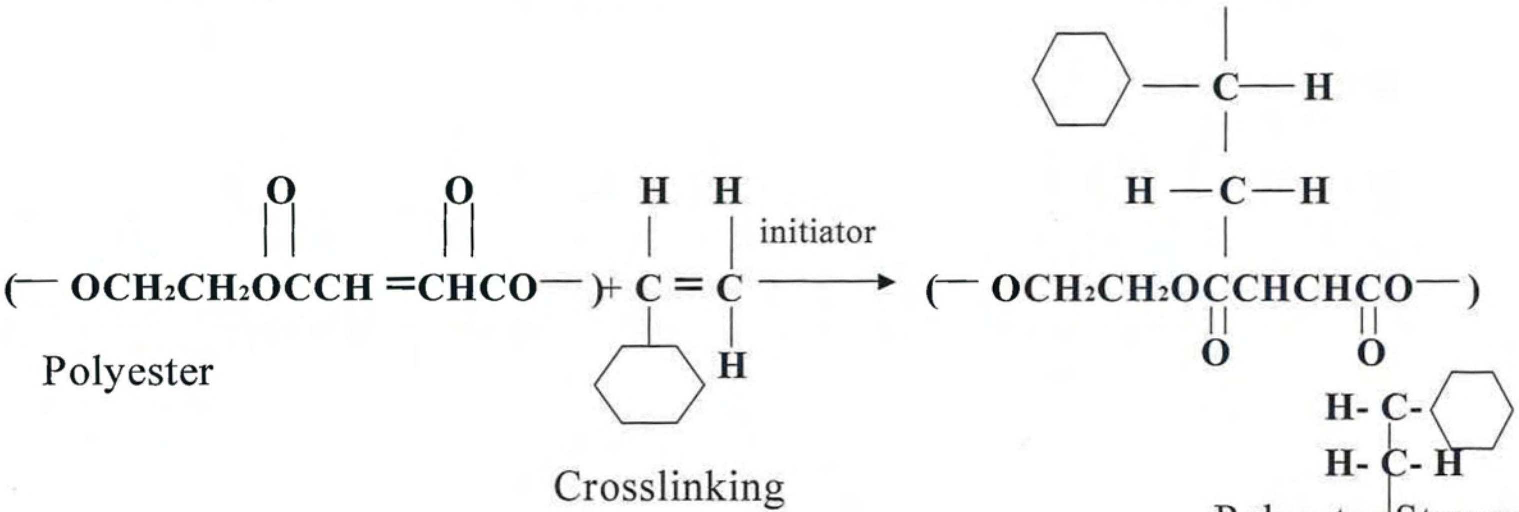
# POLYESTER RESINS




Maleic Anhydride

Ethylene Glycol

Polyester (Unsaturated)

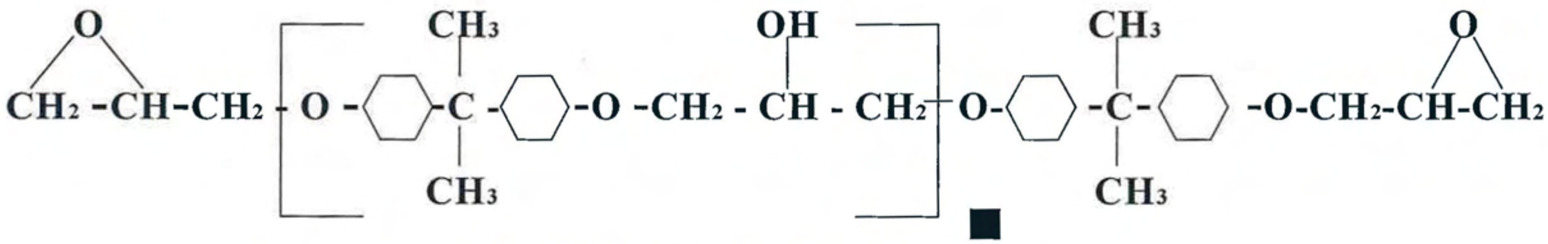



Polyester

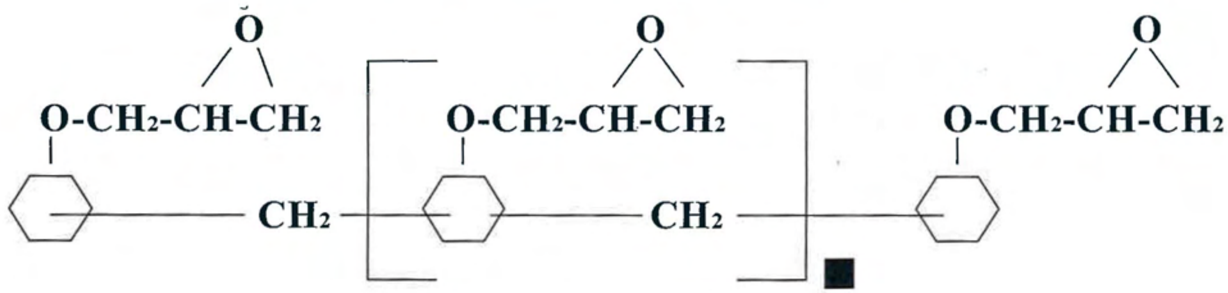
Crosslinking Agent (Styrene)

Polyester Styrene (Crosslinked)

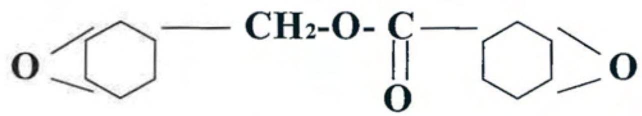
# EPOXY RESINS




**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<br>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
- Tumbling

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

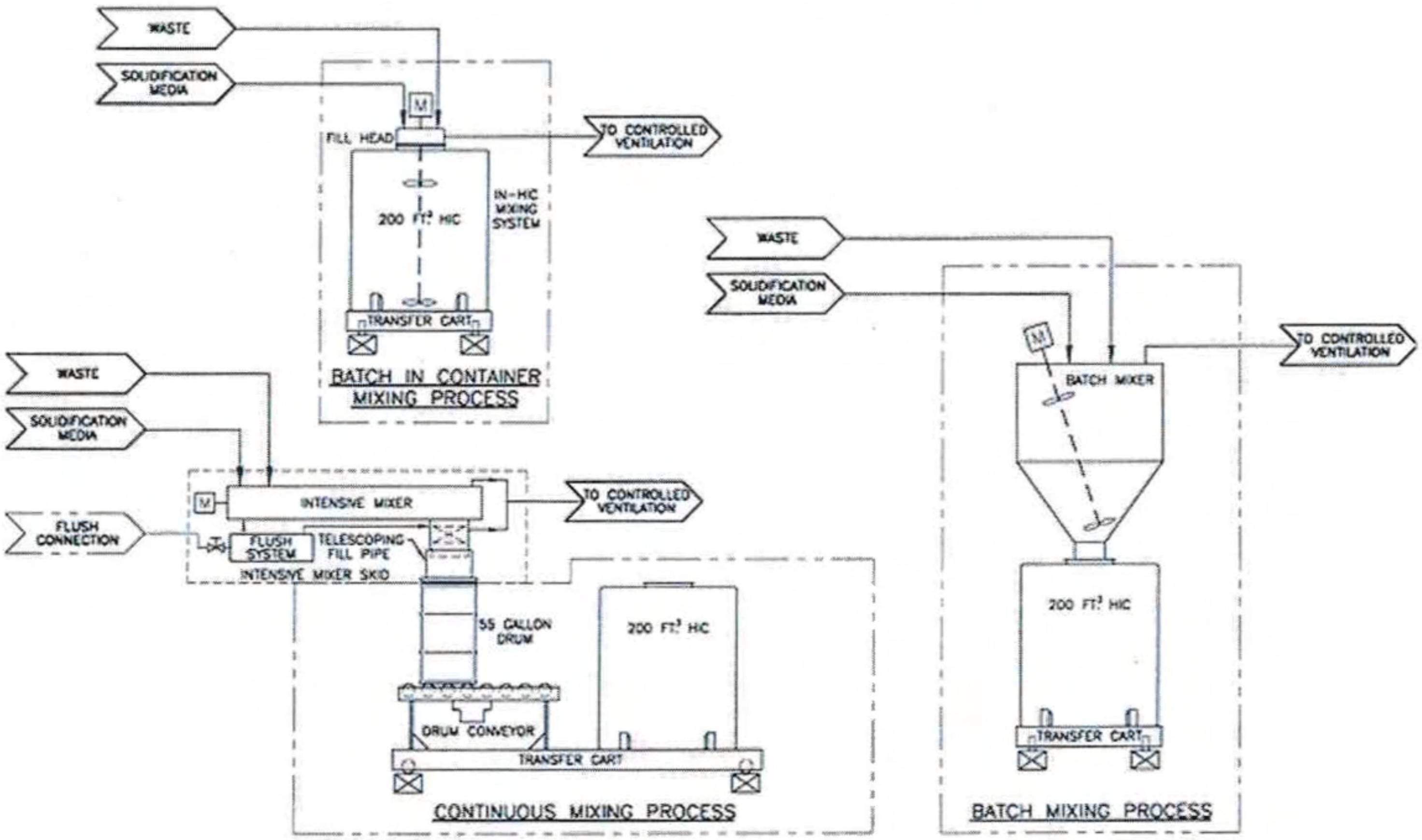
- Extruders
- High shear kneading and screw auger
- High speed, high shear, low pressure batch mixer
- Positive displacement pumps
- Screw augers
- Static mixers

**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 1 μCi/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, ad 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.