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# A SURVEY OF AGENTS AND TECHNIQUES APPLICABLE TO THE SOLIDIFICATION OF LOW-LEVEL RADIOACTIVE WASTES

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## SUMMARY

This report presents a review of the various solidification agents and techniques that are currently available or potentially applicable for the solidification of low-level radioactive wastes. An overview of the types and quantities of low-level wastes produced is presented. Descriptions of waste form matrix materials, the wastes types for which they have been or may be applied and available information concerning relevant waste form properties and characteristics follow. Also included are descriptions of the processing techniques themselves with an emphasis on those operating parameters which impact upon waste form properties. The solidification agents considered in this survey include: hydraulic cements, thermoplastic materials, thermosetting polymers, glasses, synthetic minerals and composite materials.

This survey is part of a program supported by the United States Department of Energy's Low-Level Waste Management Program (LLWMP). This work provides input into LLWMP efforts to develop and compile information relevant to the treatment and processing of low-level wastes and their disposal by shallow land burial.

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## 1. INTRODUCTION

It is the purpose of this report to identify and review those agents and processes that can be employed for the solidification of low-level radioactive wastes. The scope of this survey includes not only those agents and processes that are currently used for low-level waste solidification, but also others that are either under development or proposed. In addition, agents and processes utilized for the solidification of other types of wastes, such as chemical toxic wastes and high-level radioactive wastes, were also considered. Information concerning the characteristics of solidification agents, solidification agent chemistry and applicability to specific waste streams, processing techniques, and waste form properties is summarized.

Solidification agents and processes applicable to low-level waste solidification must be capable of meeting existing requirements for waste forms; those that do not are excluded from further consideration. These requirements are considered in a subsequent section of this report. Some agents and processes are not included because associated costs and process complexity are so great as to preclude their general applicability to low-level wastes under existing conditions. In particular, some processes proposed for high-level waste fall into this category.

This survey is part of a program supported by the United States Department of Energy's Low-Level Waste Management Program (LLWMP). This work provides input into LLWMP efforts to develop and compile information relevant to the treatment and processing of low-level wastes and their disposal by shallow land burial.

## 2. BACKGROUND

While a number of agents and processes have been used for the solidification of low-level wastes, operational difficulties have been observed for each of the systems under some conditions. Such difficulties include incompatibility with waste constituents inhibiting solidification, free standing liquids, fires and premature setting. Some specific waste types have proven difficult to solidify with one or more of the contemporary agents. Modifications of agents and processes can improve solidification of such "problem" wastes. In addition, similar difficulties are anticipated for the solidification of "new" low-level waste streams which are generated using advanced volume reduction technologies. A review of existing information on the operation of solidification agents and processes as well as past experience with specific waste types promotes improved solidification practices.

### 2.1 Purpose of Solidification

The purpose of solidification is to convert liquid and wet solid wastes into a solid monolithic waste form. The licensing conditions of commercial shallow land burial disposal sites prohibit the disposal of liquids. Wastes containing liquids must be solidified or at least dewatered. In addition, Federal (49 CFR 173) and various state regulations which govern the transportation of liquid radioactive materials encourage solidification of liquid and wet solid wastes. The Nuclear Regulatory Commission (NRC) has proposed licensing requirements for land disposal of radioactive waste (draft 10 CFR 61) which require that "liquid wastes, or wastes containing liquids, must be converted into a form that contains as little free standing

noncorrosive liquid as is reasonably achievable, but in no case shall the liquid exceed 1% of the volume of the waste." This draft regulation also requires that the waste be structurally stable under expected disposal conditions where such stability may be achieved either by processing (solidifying) the waste to produce a stable form, or by placing the waste into a container or structure that provides stability after disposal. These requirements are an extension of those included in the NRC Solid Waste Management Systems Standard Review Plan (NUREG-75/087, Section 11.4) and Branch Technical Position ETSB 11-3, "Design Guidance for Solid Radioactive Waste Management Systems Installed in Light-Water-Cooled Nuclear Power Reactor Plants."

The conversion of liquid and wet solid wastes into a stable monolithic form by solidification minimizes the potential for radionuclide release to the environment during interim storage, transportation and disposal. The solidified waste form should be of such chemical, mechanical, radiolytic and thermal stability that its integrity can be assured over appropriate time intervals. Low leachability is desirable where leachability refers to the removal of radionuclides from the waste form by fluids. In fact, leachability is perhaps the most important waste form property. Good mechanical properties are of significance especially during transportation, in order to reduce the probability of waste form fracture and breakage which may increase the rate of radionuclide release due to the increased surface area exposed to the environment. High thermal and radiolytic stability ensure that the waste form will retain its original properties over time and not pressurize the waste container. The waste form should also be chemically compatible with its container, although corrosion from the outside normally dictates container lifetime. Thermal stability refers primarily to waste form flammability and

the effects of external fires occurring under accident conditions. In addition, economics dictate that process costs as well as the volume of the solidified waste forms produced should be as low as practicable.

## 2.2 Low-Level Radioactive Wastes

### 2.2.1 Sources and Types of Low-Level Wastes

The traditional definition of low-level radioactive waste (LLW) in the United States as set forth in the Low-Level Radioactive Waste Policy Act (PL 96-573) is that LLW is radioactive waste not classified as either high-level radioactive waste, transuranic waste, spent nuclear fuel or uranium mill tailings. High-level radioactive waste (HLW) is defined in 10 CFR 50, Appendix F as those aqueous wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuels. Transuranic waste (TRU) is material, excluding high-level waste, which contains more than 10 nanocuries per gram of alpha emitting transuranic nuclides. As defined by the AEC (currently DOE) on the basis of half-life and specific radiotoxicity, the TRU waste classification includes all transuranic nuclides except Pu-238 and Pu-241 and, in addition, includes U-233 and its daughter products (AEC Manual, Chapter 0511, 1973).

LLW is produced as a consequence of both federal government and commercial operations. The federal government generates LLW from defense related activities (fuel fabrication, reactor operation, spent fuel storage, fuel reprocessing and associated chemical processing operations), facility decontamination and decommissioning, and research and development activities. Commercial generation of LLW results from both fuel cycle and non-fuel operations. Commercial fuel-cycle operations include uranium mining, uranium milling, UF<sub>6</sub> production, uranium enrichment, fuel fabrication, reactor operations,

spent fuel storage and facility decontamination and decommissioning. (There is currently no fuel reprocessing conducted by the commercial sector.) These commercial fuel cycle activities are similar in nature to federal government activities and hence, many of the wastes produced are analogous. Non-fuel operations, both institutional (including medical institutions and universities) and industrial (pharmaceutical and other industries) also produce LLW.

The types of LLW produced by the various sources are summarized in Table 2.1. These wastes may be classified as either dry wastes or wet wastes. Dry wastes are solids and include items such as paper, glass, metal, wood, plastic, rubber and rags. Dry wastes may further be broken down into two classes: combustible or non-combustible and compactible or non-compactible. Combustible dry wastes may be incinerated to reduce volume. The resultant incinerator ash residue is highly dispersible and may require solidification prior to disposal. The majority of wet wastes are produced from the cleanup of aqueous process streams and waste streams prior to recycle or discharge. The type of waste resultant from these cleanup operations depends upon the process employed (filtration, ion exchange, evaporation, centrifugation, reverse osmosis, ultrafiltration, flocculation and sedimentation). Filtration produces filter cartridge and filter sludge wastes. Spent resin, powdered resin sludges, and regenerant solution wastes result from ion exchange operations. Evaporation, centrifugation, reverse osmosis, ultrafiltration, flocculation and sedimentation processes concentrate waste products from aqueous streams to provide volume reduction and in so doing generate slurry, sludge and aqueous concentrate wastes. Reverse osmosis and ultrafiltration also produce membrane wastes. In addition, wastes resulting from cleanup operations are often subjected to additional treatment to reduce their volume for disposal. For spent resins and sludges this may include a dewatering operation (settling, centrifugation, or filtration) while volume reduction of aqueous

Table 2.1 Sources and Types of Low-Level Radioactive Wastes (1)

SOURCES	DRY WASTES				WET WASTES								
	COMBUSTIBLE		NONCOMBUSTIBLE		FILTER CAR- TRIDGES	SPENT RESINS	SLURRIES AND SLUDGES	AQUEOUS CONCEN- TRATES	SPECIAL AQUEOUS SOLUTIONS <sup>a</sup>	OILS	OTHER ORGANIC LIQUIDS	MEMBRANES <sup>b</sup>	BIOLOGICAL
	COMPAC- TIBLE	NONCOM- PACTIBLE	COMPAC- TIBLE	NONCOM- PACTIBLE									
GOVERNMENT DEFENSE	•	•	•	•	•	•	•	•	•	•	•	•	
D & D <sup>c</sup>	•	•	•	•		•			•				
RD & D <sup>d</sup>	•	•	•	•		•	•	•	•	•	•	•	•
COMMERCIAL FUEL CYCLE MINING	•	•	•	•			•	•					
MILLING	•	•	•	•			•	•					
UF <sub>6</sub> PRODUCTION	•	•	•	•			•						
ENRICHMENT	•	•	•	•			•			•	•		
FUEL FABRICATION	•	•	•	•			•			•			
POWER PLANTS	•	•	•	•	•	•	•	•	•	•		•	
SPENT FUEL STORAGE	•	•	•	•		•	•						
D & D	•	•	•	•		•			•				
NONFUEL CYCLE MEDICAL	•		•	•							•		•
PHARMACEUTICAL <sup>e</sup>	•			•							•		•
UNIVERSITIES	•		•	•		•					•		•
OTHER INDUSTRIES <sup>e</sup>	•			•		•							

a Decontamination, pickling, etching, electropolishing, etc. solutions.

b Membranes from processes such as ultrafiltration (UF) and reverse osmosis (RO).

c Decontamination and decommissioning (D & D) operations.

d Research, development, and demonstration (RD & D) programs.

e Data on these wastes are incomplete and difficult to obtain.

wastes is generally accomplished through some form of evaporation. Some wet wastes are combustible (resins, oils and organic liquids) and as such an incineration process could be employed to reduce waste volume. More detailed descriptions of these wastes and their origins can be found in the literature [2.1-2.4].

Because of the rapidly increasing cost of disposal by shallow land burial, there exists a strong incentive to decrease the volume of wastes produced. A number of advanced volume reduction systems are rapidly gaining acceptance which convert liquid and wet solid wastes to dry solids and high solids content aqueous concentrates (e.g. calciners, thin film evaporators, and crystallizers) and convert solid and wet solid wastes to volume reduced solid wastes (e.g. incinerators). These volume reduced wastes will generally require solidification to either convert remaining liquids to solid forms or to minimize waste dispersibility by converting particulate solid wastes into monolithic waste forms.

### 2.2.2 Generation Rates of Low-Level Wastes

A perspective of the major types of waste that require or may require solidification can be achieved by considering the generation rates of low-level wastes from their various sources and the projected increase in generation rates with time. The estimated annual generation rates of low-level wastes in the United States for 1980 are shown in Table 2.2 [2.5]. The majority of this waste (57% by volume) originates from commercial sources. LLW produced by the Federal government is not further broken down in Table 2.2 since this information is generally not available. Some 53% of commercial LLW is generated by fuel cycle operations. Reactor (power plant) operations produce 82% of the volume of fuel cycle LLW. Non-fuel cycle wastes constitute 47% of commercial LLW volume. The quantities of LLW produced by institutional

TABLE 2.2

ESTIMATED 1980 ANNUAL LOW-LEVEL WASTE GENERATION RATES BY SOURCE [2.5]

<u>Source</u>	<u>Generation Rate, m<sup>3</sup>/yr</u>
GOVERNMENT	$6.9 \times 10^4$
COMMERCIAL (Fuel Cycle + Non-Fuel Cycle)	$9.3 \times 10^4$
<u>Fuel Cycle (Total)</u>	$4.9 \times 10^4$
UF <sub>6</sub> Production	$1.6 \times 10^3$
Enrichment	$1.2 \times 10^2$
Fuel Fabrication	$7.0 \times 10^3$
Reactor Operations	$4.0 \times 10^4$
<u>Non-Fuel Cycle (Total)</u>	$4.4 \times 10^4$
Institutional <sup>(a)</sup>	$2.2 \times 10^4$
Industrial	$2.2 \times 10^4$

(a) Hospitals, medical schools, colleges and universities.

(hospitals, medical schools, colleges and universities) and industrial sources are estimated to be approximately equal [2.5]. Estimates of LLW generation through the year 2000 are listed by source in Table 2.3 [2.5]. Projections of the volume of fuel cycle LLW are based upon a proposed reference growth scenario projecting 180 GW(e) of installed nuclear capacity by the year 2000. While the generation rate of government LLW is expected to remain approximately constant over the period from 1980 to 2000, the volume of commercial LLW produced annually is projected to increase more than 150%. (These projections do not consider governmental LLW resulting from the decontamination and decommissioning of formerly utilized or surplus sites under the Formerly Utilized Sites Remedial Action Program (FUSRAP) or the Surplus Facilities Management Program (SFMP). They also do not consider LLW resulting from a possible resumption of commercial spent fuel reprocessing.) Most of this increase is due to increased quantities of fuel cycle wastes resulting from the expansion of installed power reactor capacity. The volume of fuel cycle LLW is anticipated to increase by a factor of 3.5 between 1980 and 2000 while non-fuel cycle waste will increase less than 60%. The mix of fuel cycle wastes over this period may remain similar to that shown in Table 2.2 for 1980, however, reactor operations in particular have significant incentive to reduce waste volume.

TABLE 2.3

PROJECTED LOW-LEVEL WASTE GENERATION RATES, 1980-2000 [2.5]

Year	Government, m <sup>3</sup> /yr		Commercial, m <sup>3</sup> /yr	
	Total	Fuel Cycle	Non-Fuel Cycle	Total
1980	6.9x10 <sup>4</sup>	4.9x10 <sup>4</sup>	4.4x10 <sup>4</sup>	9.3x10 <sup>4</sup>
1985	6.9x10 <sup>4</sup>	1.1x10 <sup>5</sup>	5.1x10 <sup>4</sup>	1.6x10 <sup>5</sup>
1990	6.9x10 <sup>4</sup>	1.6x10 <sup>5</sup>	5.7x10 <sup>4</sup>	2.2x10 <sup>5</sup>
1995	6.9x10 <sup>4</sup>	1.7x10 <sup>5</sup>	6.3x10 <sup>4</sup>	2.3x10 <sup>5</sup>
2000	6.9x10 <sup>4</sup>	1.7x10 <sup>5</sup>	7.0x10 <sup>4</sup>	2.4x10 <sup>5</sup>

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### 3.0 HYDRAULIC CEMENTS AS AGENTS FOR LOW-LEVEL WASTE

#### SOLIDIFICATION

Hydraulic cement was the original agent used for the solidification of low-level radioactive waste and it has remained in common use. The materials incorporated in cement waste forms generally consist of aqueous liquid wastes, and sludges. Recent developments in the use of hydraulic cements for waste disposal have evolved along three major lines. These are:

- (1) The use of additives to adjust the properties of the cement for specific wastes.
- (2) Pressurized emplacement of a cementitious grout, bearing radioactive waste, into underground fracture zones.
- (3) Pressing and sintering of cement containing waste to form a particularly stable monolithic waste form.

#### 3.1 Description of Hydraulic Cements

Hydraulic cement is a generic term for a group of inorganic materials which, when mixed with water, form a "rigid interlocking matrix of hydration products which gradually replace the water between the cement grains and finally bind the composite cement mass together" [3.1].

Hydraulic cements incorporate waste in two manners. Water in the waste combines chemically with cement constituents to form hydrated cement compounds although some water is also contained in the cement pore structure. Similarly, certain ionic species in the waste may be incorporated into or adsorbed by cement hydration products. Other liquid wastes are held in the porosity of the cement matrix and some may actually interfere with the hydration process. Solids contained in wet wastes are mechanically held by

the cement matrix. Large monolithic waste materials such as pipes, gloves, and failed equipment can be incorporated in cement not only to retain their associated activity but also to reduce dispersion and to provide shielding.

### 3.2 Types of Hydraulic Cements

Portland cement is produced by heating clay minerals at high temperatures (1480°C) with lime. Typically the clay is derived from crushed slate or shale while the lime (CaO) is the product of heating limestone (CaCO<sub>3</sub>). In the proper proportions these minerals form a "clinker" which when cooled, mixed with gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and pulverized is termed portland cement. By adjusting the proportions of raw materials, the quantities of major compounds comprising the cement are made to vary. This in turn affects such properties as strength, time of setting, generation of heat and resistance to shrinkage. Examples of specific cement formulations with well defined properties are portland cement types I-V. Type I portland cement is general purpose cement. Type II produces less heat, is slow setting and is sulphate resistant. Type III is a fast setting, high early strength cement which generates significant heat during hydration. Type IV is slow setting with little heat generation. Type V cement is highly resistant to sulphate attack and suggested for marine use. Table 3.1 indicates the chemical analysis and compound composition of portland cements. The characteristics of the major cement compounds are listed in Table 3.2

The product of portland cement is largely an amorphous colloidal gel of calcium silicate hydrates resulting from the hydration of the major components of the cement. In portland cements these major components are dicalcium silicate (2CaO·SiO<sub>2</sub>), tricalcium silicate (3CaO·SiO<sub>2</sub>), tricalcium aluminate (3CaO·Al<sub>2</sub>O<sub>3</sub>), tetracalcium aluminoferrite (4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>) and gypsum,

TABLE 3.1  
COMPOSITION OF PORTLAND CEMENTS [3.5]

Oxide Analysis, %	Type I Standard		Type II Moderate Heat		Type III H.E.S. <sup>a)</sup>		Type IV Low Heat		Type V Sulfate Res. <sup>a)</sup>
	Range	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Ave.
Lime (CaO)	66-62	64	65-62	63	67-63	65	65-58	60.5	64
Silica (SiO <sub>2</sub> )	23-19	21	24-20	22	22-18	20	26-22	24	26
Alumina (Al <sub>2</sub> O <sub>3</sub> )	8-5	6.5	6-4	5	7-4	5.5	6-3	5	2.5
Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	4-2	2.5	6-3	4	4-2	3	6-2	4.5	1.5
Magnesia (MgO)	4-1	2.5	4-2	3	4-0.6	2.3	4-1	3	2.5
Sulfuric Anhydride (SO <sub>3</sub> )	2.5-1	2.1	2-1	1.5	3-2	2.5	2-1	1.7	2
Ignition loss	2-0.6	1.3	2-1	1.1	2-0.8	1.5	2-1	1.1	1.3
Insoluble residue	0.08-0.01	0.02	0.05-0.01	0.02	0.07-0.01	0.02	0.03-0.01	0.02	0.02
<u>Compound Composition <sup>b)</sup></u>									
C <sub>3</sub> S	48		43		57		20		39
C <sub>2</sub> S	27		30		20		52		33
C <sub>3</sub> A	12		7.5		11		6		4.5
C <sub>4</sub> AF	8		12		7		14		16

(a) H.E.S. = High Early Strength; Res. = resistant.

(b) In cement terminology C<sub>3</sub>S stands for tricalcium silicate, C<sub>2</sub>S for dicalcium silicate, C<sub>3</sub>A for tricalcium aluminate, and C<sub>4</sub>AF for tetracalcium alumina ferrite.

TABLE 3.2  
THE BEHAVIOR OF PRINCIPAL COMPOUNDS WHICH OCCUR IN PORTLAND CEMENTS [3.6]

PROPERTY	RELATIVE BEHAVIOR OF EACH COMPOUND <sup>(a)</sup>			
	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
Rate of reaction	Medium	Slow	Fast	Slow
Heat liberated, per unit of compound	Medium	Small	Large	Small
Cementing value per unit of compound:				
Early	Good	Poor	Good	Poor
Ultimate	Good	Good	Poor	Poor

( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The cement-water reaction is exothermic and occurs as a three step process. As setting and curing proceed, the hydrated minerals first form a colloidal "sol." This then forms a tobermorite "gel". The final curing process is characterized by the formation of a network of interconnected radiating, tubular fibrils which impart strength to the concrete [3.1-3.4].

Another major type of hydraulic cement with potential for use as a solidification agent is high-alumina cement (HAC). This material is primarily composed of monocalcium aluminate ( $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ) and obtains the bulk of its strength within twenty-four hours. This cement is highly resistant to attack by sulphate and sea water, however, under conditions of high temperature and humidity the strength of this material can decrease rapidly [3.2]. High-alumina cement is made by heating bauxite and limestone together and grinding the resultant clinker.

Pozzolanic cement (I-P) is an interground mixture of pozzolana and portland cement clinker. Pozzolans are any of a number of materials such as some volcanic tuff, fly ash, and burnt clay which when mixed with lime and water produce a cementitious material. Pozzolans are typically used to improve workability, reduce the heat of hydration, prevent calcium hydroxide bleeding and reduce attack from salts and sulfates. In radioactive waste forms, pozzolans may also reduce leachability. Pozzolana lime mortars used by the Romans in their constructions are still in place after 2000 years. Pozzolanic cement typically has a specific gravity of 2.3-2.6 compared to 3.1 for portland cement, and as such is 15-25% lighter per unit volume [3.7].

Masonry cements consist of a mixture of portland cement, finely ground limestone or slaked lime and an additive to entrain air. These materials are designed for plasticity, improved water retention and reduced shrinkage

[3.2, 3.7]. It also is a more rapidly setting and curing cement which can be useful for the solidification of wastes containing chemicals which tend to retard or inhibit hydration.

### 3.3 Additives

A variety of materials have been used as additives in cement in order to better incorporate certain waste types or improve waste form properties. Many are specific clay minerals or materials which contain relatively large amounts of clay. The large absorptive and ion exchange capacities of these materials often suit them for use as fixatives for radionuclides. Other additive materials alter the characteristics of the wastes or the behavior of the cement itself in order to allow incorporation of wastes which normally would hinder cement solidification. Several additives are discussed below.

Crushed rock (bentonites) bearing clay minerals of the smectite group, particularly the mineral montmorillonite, have been used as additives in cement systems. These minerals have relatively high cation exchange capacities making them potentially useful as ion sorbers. Smectites also tend to swell significantly when wet, taking up large volumes of water.

Research at Oak Ridge National Laboratory (ORNL) has lead to the use of various materials as additives in their hydrofracture grout [3.8]. Among these are grundite (a trade name of a commercial clay product of the illite group), Attapulgate-150 (a drilling clay product of the polygorskite group which reduces phase separation of the grout mixture), crushed Conasauga shale and brick dust. These materials are primarily intended to reduce cesium leachability [3.9]. Experiments conducted by Delaware Custom Material Inc. suggest that Conasauga shale added to cement waste forms provides better cesium retention (by a factor of 100) than do either Na-bentonite or Ca-bentonite

[3.10]. Among the additives tested at Savannah River Laboratory are the clay mineral vermiculite, the natural zeolite clinoptilolite and synthetic zeolites [3.11].

Sodium silicate is an additive employed by some manufacturers of solidification systems. This material is reported to increase the waste packing efficiency in cement by as much as 75%, increase the liquid tolerance of cement and improve the characteristics of the solid in the presence of wastes bearing borate solutions [3.2]. The process involves the immobilization of multi-valent metal ions in a precipitated gel. Unhindered by the gel, the ions would normally tend to interact with the hydration products and potentially inhibit the development of cement.

Sulfonated naphthalene and melamine formaldehyde condensates have been added to cement as plasticizers. These materials reduce the volume of water necessary to produce a solid waste form of high density [3.12].

Some substances when added to cement mixtures act to inhibit setting. While normally this effect is detrimental, in some cases this action can be beneficial. For instance sugar, specifically in the form of delta gluconolactone, has been used to prolong setting times in the ORNL hydrofracture grout until after the grout has been placed [3.8]. Excess water may also be used to slow the setting process, but this method also tends to significantly weaken the end product [3.7]. Certain types of waste, specifically those bearing nitrates and borate are known to inhibit setting and can, if present in sufficient quantities, prevent cement from adequately solidifying [3.3]. Temperature and humidity have significant influences on set time and the strength of the product and must be controlled to optimize strength.

Certain other substances are known to promote the setting of cement. Calcium chloride (2-3 wt%) is commonly used as an accelerator as are aqueous

solutions of alkali salts such as hydroxides, carbonates, aluminates and silicates [3.7]. In cases where acidic wastes are incorporated in cements, NaOH or lime is often added in order to maintain the necessary high pH (10-12) required for the cement-waste mixture to set and produce optimum waste form properties.

### 3.4 Solidification Processes Using Hydraulic Cements

Incorporation of radioactive waste in cement can be achieved in a variety of ways. Important considerations include: cement handling techniques, mixing methods, and equipment complexity and maintainability. Cement processing options are differentiated primarily by the method in which cement and waste are mixed. Recently developed and developing techniques impose specific pressure and temperature conditions. Cement waste solidification processes are discussed below.

#### 3.4.1 Drum Mixing

Figure 3.1 illustrates an in-drum mixing process developed by the Stock Equipment Company. Dry cement and a disposable mixing weight are placed in a 55-gallon drum outside of the shielded waste processing area. The drum is moved behind the shielding wall where the waste and any additional chemicals are added. The drum is then remotely capped and tumbled end-over-end in order to thoroughly mix the contents. An overview of the process indicating each of the individual process steps is shown in Figure 3.2.

Another form of in-drum mixing is employed by Delaware Custom Material, Inc. In their system, disposable rotor blades are turned within a 55 gallon drum by a pneumatic motor as the cement and waste are added (Figure 3.3). Hittman Nuclear and Development Corporation uses liners of between 70 and 170 cubic feet in volume for their in-container solidification systems.

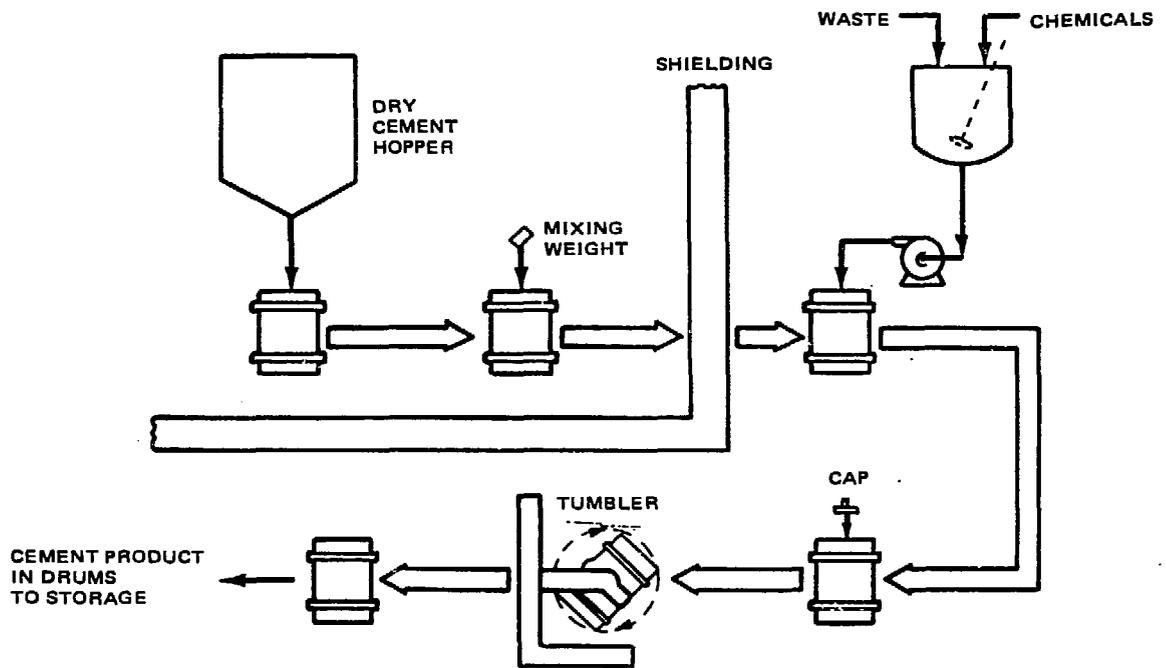


Figure 3.1. In-drum mixing processing for incorporating LLW in cement.

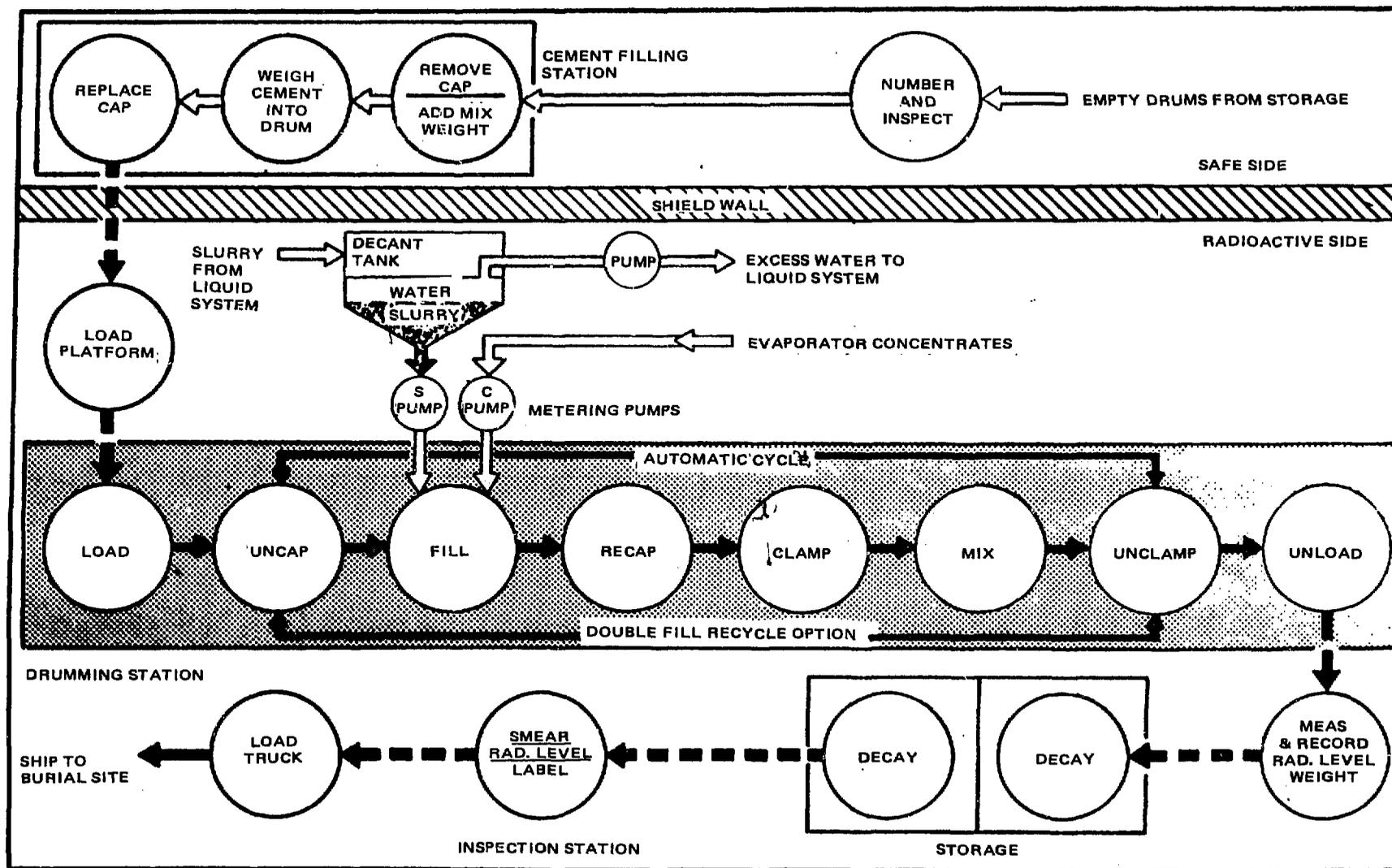


Figure 3.2. An overview of the Stock Equipment Company system, illustrating an in-drum mixing system.

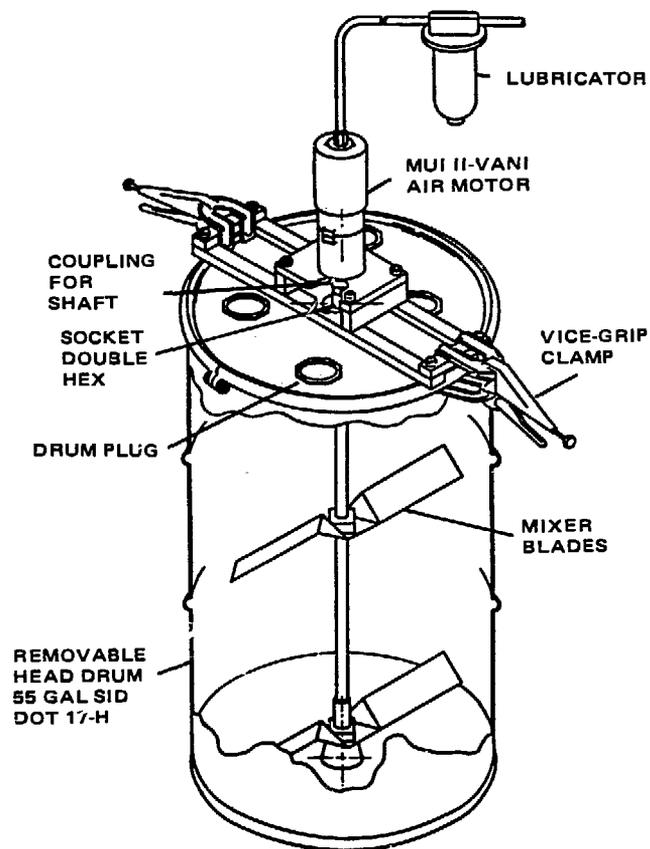


Figure 3.3. In-drum mixing assembly employing a dual bladed mixer of Delaware Custom Materials.

These liners are placed into shielded shipping casks after which waste and then cement are pumped into the liner through an assembly which contains the fill ports, the drive mechanism for the disposable rotor, and ultimately seals the liner.

The waste forms produced at Brookhaven National Laboratory incorporate low-level radioactive waste in a mixture of portland cement and vermiculite. Wastes solidified in this manner include liquid evaporator slurries, compacted trash and 55-gallon drums containing ion exchange resins. Cement and vermiculite (and large solid wastes, if any) are placed into the steel reinforced, precast concrete casks (15 cm thick walls, 4.5 m<sup>3</sup> capacity). Liquid waste is pumped into the cask through pipes embedded in the dry cement, with the vermiculite serving as a sorbent and water distribution agent. When the surface of the vermiculite and cement mixture appears moist, pumping is stopped. A steel reinforcing grid is placed on top of the cask and premixed uncontaminated concrete is poured as a seal. In a typical cask, 0.9 m<sup>3</sup> of concrete are used to solidify 1.25 m<sup>3</sup> liquid waste [3.13].

#### 3.4.2 In Line Mixing

In-line mixing processes combine the waste, any additives, water and cement before they are placed into the disposal container. Ribbon mixers and pug mills, among others, may be used to mix the waste and cement. Vendors of in-line cement solidification systems include: Atcor, Inc., Hittman Nuclear and Development Corporation and United Nuclear Industries, Inc. [3.14]. Figure 3.4 illustrates the United Nuclear Industries, Inc. in-line system which, in concept, is similar to most other in-line systems. Here pre-conditioned waste, adjusted for moisture content and pH, and the cement are blended at a mixing pump. Additives (if any) can be introduced at the fillport.

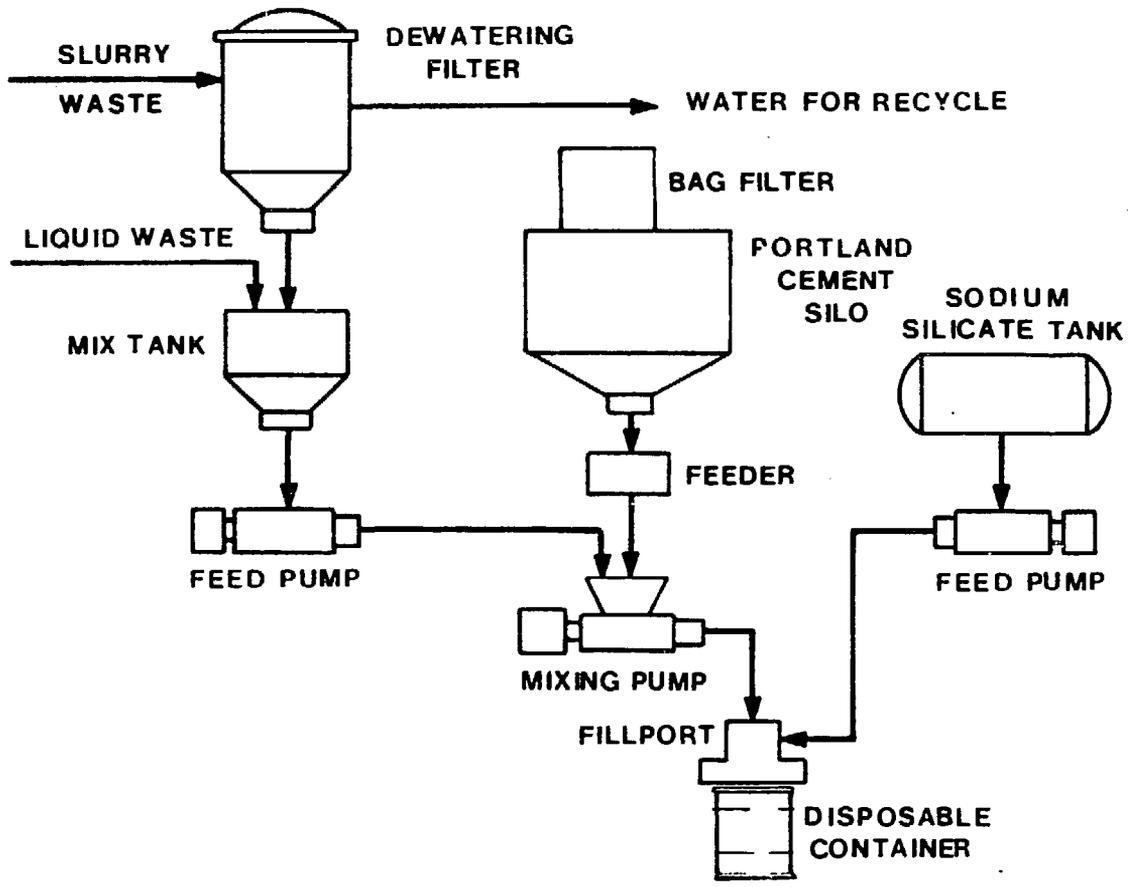


Figure 3.4. In-line mixing system with sodium silicate used as an additive (UNI Corporation).

### 3.4.3 Cementitious Grouts

Since 1966 Oak Ridge National Laboratory (ORNL) has been disposing of waste by the hydrofracture grout method developed there. This process, illustrated in Figure 3.5, involves pumping a premixed grout of cementitious material and waste into beds of Conasauga shale some 800-1000 feet underground. The pressure under which the fluid is pumped acts to fracture the shale allowing the grout to penetrate along the horizontal bedding planes of the shale in layers about 1/2" thick. More than two million gallons (by 1978) of waste solution have been injected containing a total activity of 600,000 curies [3.15].

The grout is composed of neutralized waste solution which is blended with predetermined weights of dry cement solids consisting of cement, fly ash, clay minerals (to increase adsorption and to reduce phase separation) and delta gluconolactane (a sugar) which retards the setting time of the grout. Similar mixtures of material can also be used to solidify low and intermediate-level wastes in drums [3.16].

### 3.4.4 Hot Pressed Cements

A process of hot pressing cement at elevated pressures and temperatures has been developed at Pennsylvania State University (PSU) [3.17]. Various types of portland cements (I, III and V) as well as other varieties of hydraulic cements have been shown to develop unusually high strength (ten times that of normal cements) and high density with very low porosity and permeability under hot pressing. This makes the product particularly well suited for the retention of radionuclides in the waste. Processing temperatures of 100°C to 300°C and pressures of 25,000 to 100,000 psi are used.

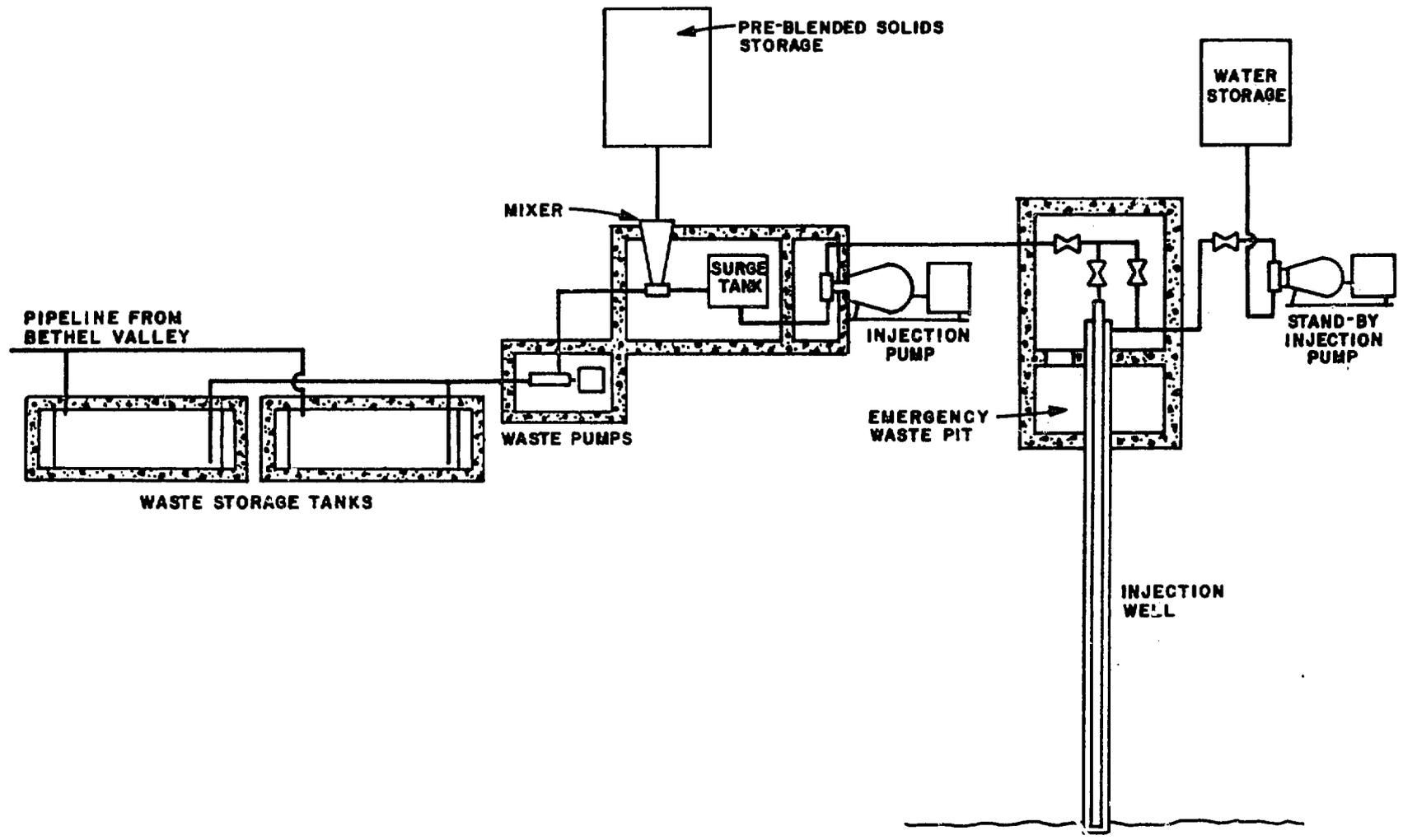


Figure 3.5. ORNL hydrofracture process [15].

In general, calcium aluminate cement was found to develop a better product than portland cement [3.17]. A flow chart for this process is provided as Figure 3.6. The addition of a hot-pressing step does introduce a significant process complexity.

Encapsulation of a hot-pressed waste pellet by an additional layer of hot-pressed calcium-aluminate cement was found to provide the best performances. Mixing of calcined waste with cement and hot-pressing the mixture was satisfactory while uncalcined waste mixed with cement extruded a paste containing  $\text{NaNO}_3$  and formed cracked samples. Leaching tests generally resulted in small weight gains and volume increases caused by additional hydration of the cement. Hot-pressed portland cement showed high resistance to leaching in 1:1 HCl. Hot pressed calcium aluminate cement mixed with waste showed resistance for several hours while standard calcium aluminate and portland cements disintegrated quickly [3.17].

#### 3.4.5 FUETAP

Following the lead of the Pennsylvania State University group and their own research with concrete waste forms, a group at ORNL developed the FUETAP (Formed Under Elevated Temperature and Pressure) process [3.18]. Cementitious materials, additives and calcined wastes, (Table 3.3) are mixed and poured into a sealed container. Heating to temperatures as low as  $100^\circ\text{C}$  with pressures of 0.1 MPa (15 psi) for 24 hours produce a good product. The process was developed for high-level waste, therefore, if there is sufficient activity in the waste the self-heating alone can provide an adequate temperature. Additional steps to vent unbound water are necessary to prevent subsequent container pressurization. Consequently, there is very little pressure or gas generated due to radiolysis of water in the concrete. Loading of waste is relatively low (12%). Figure 3.7 presents a flow chart of the FUETAP process [3.18].

Table 3.3

FUETAP Formulation [3.18]

Ingredient	wt %
Cement (Portland I)	22.
Fly Ash	11.
Clay	7.5
Simulated Waste Solids	15.0
Sand	27.75
NO <sub>3</sub>	0.75
Water	16.0

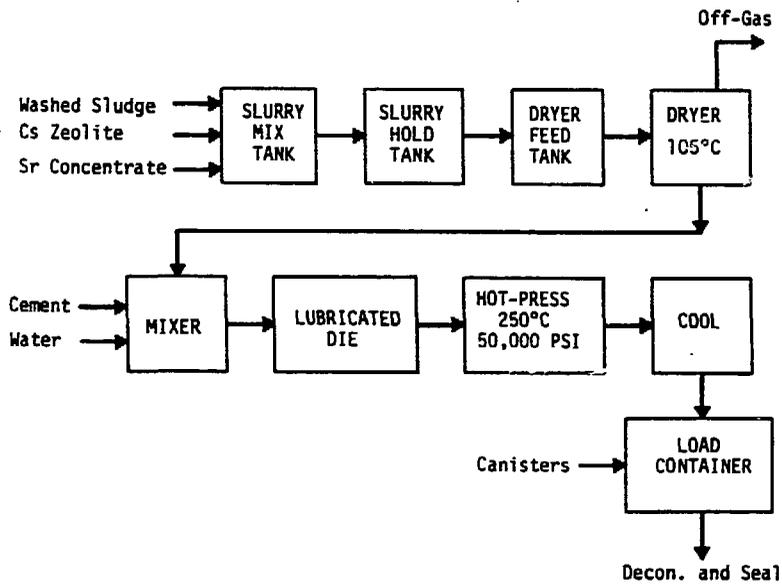


Figure 3.6. Schematic of the PSU hot-pressed cement process.

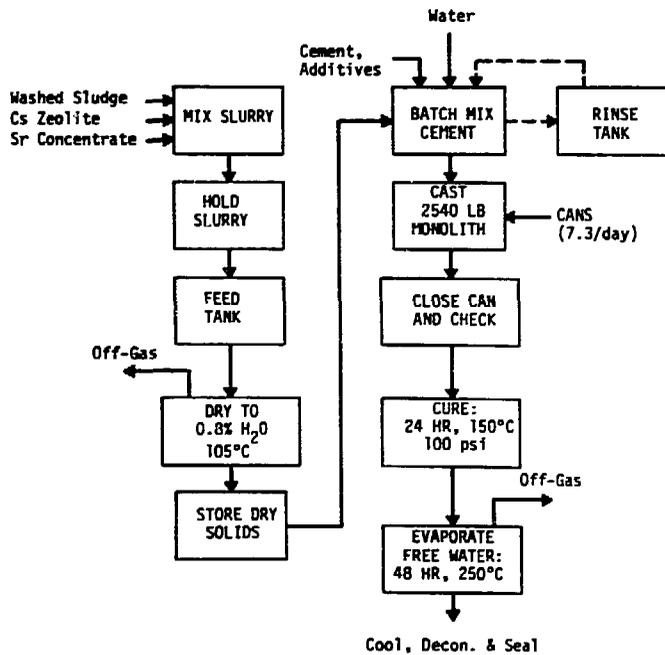


Figure 3.7. Schematic of the FUETAP process for the solidification of high-level waste.

### 3.4.6 Cold Pressed Cements

The cold pressing process developed at Mound Laboratory incorporates transuranic contaminated incinerator waste in either portland type I or high alumina cement. The ash and cement are formed into pellets at pressures of 25,000 psi. The low water content (3 wt%) and high loading ratio (65 wt%) do not adversely affect the waste form [3.19].

### 3.4.7 Surface Treatments

There are a wide variety of surface treatments for cement that can be used to provide a waterproof coating or a surface which is resistant to chemical attack. A brief list is given here while a more complete general discussion can be found in the literature [3.7]. Some of these materials are:

- (1) Sodium silicate, magnesium silico-fluoride, zinc silico-fluoride (surface hardeners)
- (2) Linseed, tung or mineral oil
- (3) Various paints & lacquers (e.g. bituminous or coal tar paints)
- (4) Epoxy-ester paints
- (5) Bituminous pastes and emulsions
- (6) Hot coal tar
- (7) Coal tar epoxy
- (8) Various two part resins
- (9)  $\text{SiF}_4$  gas treatment of precast concrete

The last two processes have received some attention relative to radioactive waste disposal. The silicon fluoride treatment is known as the Ocrate process and produces a coating of hydrated silica, alumina and calcium fluoride which is resistant to many agents [3.7]. This process has been mentioned as a possible means of decreasing permeability and porosity in

FUETAP concretes [3.18]. Impregnating cement with monomer resins has been explored at Brookhaven National Laboratory. This process is discussed in a later section.

### 3.5 Waste Form Characteristics

Hydraulic cements, as illustrated in the previous sections, are available in a wide range of compositions and can be implemented using several processes. By manipulating the mixture of cement, waste and additives and controlling the environment in which the waste forms are produced and cured, the characteristics of the solidified waste form may be significantly altered. Of all waste form materials, cement has perhaps the greatest adaptability in the sense that it can easily be "tailored" for specific uses.

#### 3.5.1 Chemical Compatibility of Wastes

The properties of the waste form are often highly dependent upon the nature and amount of the waste incorporated in the cement waste form. Consideration of the chemical compatibility of the waste with the solidification agent usually refers to the ability to produce a product meeting existing regulatory criteria which require the waste form to be a free-standing monolithic solid with no free-standing water. Table 3.4 generally indicates the chemical compatibility of typical wastes with hydraulic cements. Some wastes for which poor compatibility is indicated can readily be incorporated in small quantities in cement waste forms. Specific wastes within each typical waste type can be difficult to solidify even if good compatibility is indicated, dependent upon the chemical composition of the specific waste, and the quantity of waste one attempts to incorporate in the waste forms.

Table 3.4

Chemical Compatibility of Wastes with Hydraulic Cements

<u>Waste Type</u>	<u>Waste Compatibility</u>
Ion exchange	poor - good <sup>(a)</sup>
Sludges	good
Boric acid wastes	poor - good <sup>(b)</sup>
Sulfate wastes	fair
Nitrate wastes	good
Phosphate wastes	good
Carbonate wastes	good
Detergent solutions	poor
Complexing agent wastes	poor
Oils	poor
Organic liquids	poor
Acidic wastes	poor - good <sup>(c)</sup>
Alkaline wastes	good
Filter cartridges	good
Large items	good

(a) dependent upon resin type and form, waste loading and water/cement ratio.

(b) good with additives

(c) poor for highly acidic wastes, good with additives

While ion exchange resins can be successfully solidified with cement, instances have been observed in which waste form swelling occurs which produces a waste form with extremely low integrity [3.3, 3.4, 3.20]. This behavior has been shown to be dependent upon the resin type, resin loading, the waste loading in the cement and the water/cement ratio. It is postulated to result from resin swelling and shrinking in the waste form because of competition between the cement and resin for water during solidification, adsorption of soluble cement constituents by the resin and/or subsequent resin sorption of water from the environment.

Boric acid acts as a retarder for cement setting and curing. When present in sufficient quantities and concentrations, it can prevent the cement from solidifying. Additives, such as lime, can modify the chemical form of the boric acid and the pH of the waste sufficiently to promote satisfactory incorporation in cement. The problem is also minimized by selection of an optimal cement type for solidification.

Detergent wastes, oils and organic liquids are difficult to solidify with cement, primarily because they tend to prevent the interaction of the dry cement powder with the water required for hydration. When present in low concentrations in the waste, these materials can be solidified with cement. Some success has been achieved for the solidification of organic solvents which are immiscible with water by mixing with cement under high shear conditions [3.3].

Acidic wastes can be difficult to solidify if the pH of the waste is low. Cement is a highly alkaline medium and solidification requires a waste-cement mixture to have an alkaline pH. While cement is quite effective in raising the pH of most wastes, its ability to do so is limited, particularly with highly acidic wastes. In addition, the reaction between highly acidic

wastes and cement tends to be violent. Acidic wastes are typically solidified after pretreatment to neutralize the waste. Some cement types and/or cements with additives are better suited than others for the solidification of acidic wastes.

### 3.5.2 Leachability

The leachability of cementitious waste forms varies significantly depending on waste loading, waste type, cement type and the additives (if any) employed. The transport process is often dependent in part on the radionuclides in question, their ionic characteristics and their interactions with the waste form. Therefore, there are significant differences in the rates of leaching among the various radionuclides from the same waste form. For example, the plutonium leach rate from a cement waste form for a time interval of 1008 hours was  $0.97 \times 10^{-7} \text{ g}/(\text{cm}^2)(\text{d})$ . A similar test for strontium, over 1008 hours, gave a total leachability of  $0.20 \times 10^{-3} \text{ g}/(\text{cm}^2)(\text{d})$  [3.21]. Figure 3.8 illustrates the differences in the leachability of  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$  and alpha emitters from a cement waste form [3.21]. While the waste used here is a low heat generating sludge from a reprocessing operation which is not representative of commercially generated waste, it does indicate that varying the waste content can significantly affect leachability. Similarly, in Table 3.5 three types of waste from the Savannah River Plant are shown to cause significant differences in strontium leachability [3.21].

Incorporation of various additive materials, such as cesium sorbants, has significant effect on the leachability of that element. The use of local materials such as crushed shale, pottery clay and grundite was investigated at Oak Ridge National Laboratory in their hydrofracture grout [3.8]. Results as shown in Figure 3.9 indicate significant differences in the relative abilities of these materials to retain cesium. Investigations of the effects of other

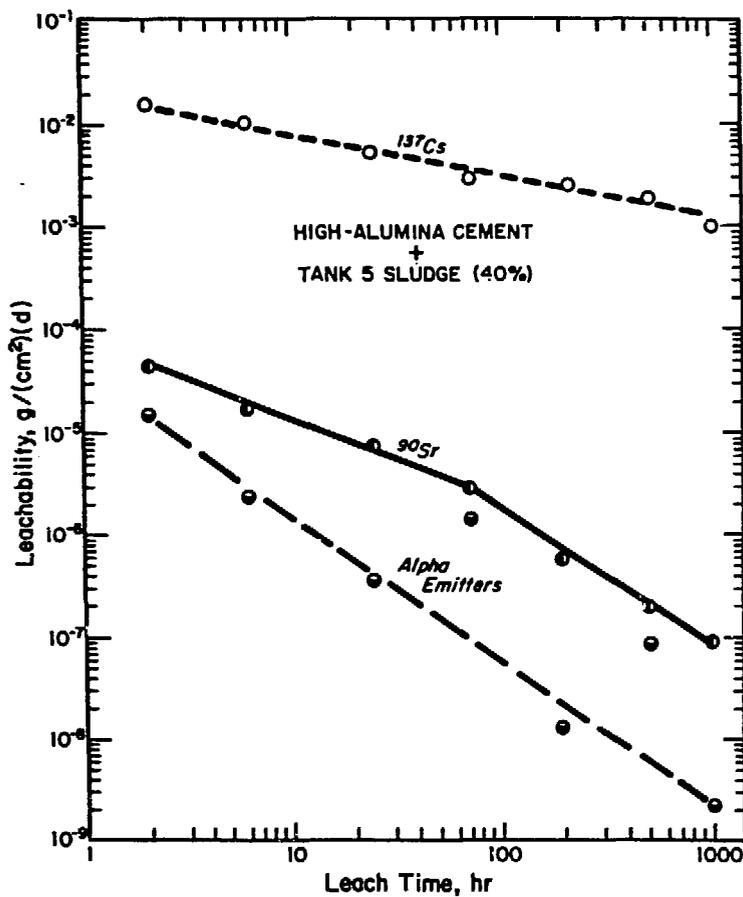


Figure 3.8. Differences in leachability, from the same waste form, of <sup>90</sup>Sr, <sup>137</sup>Cs and alpha emitters.

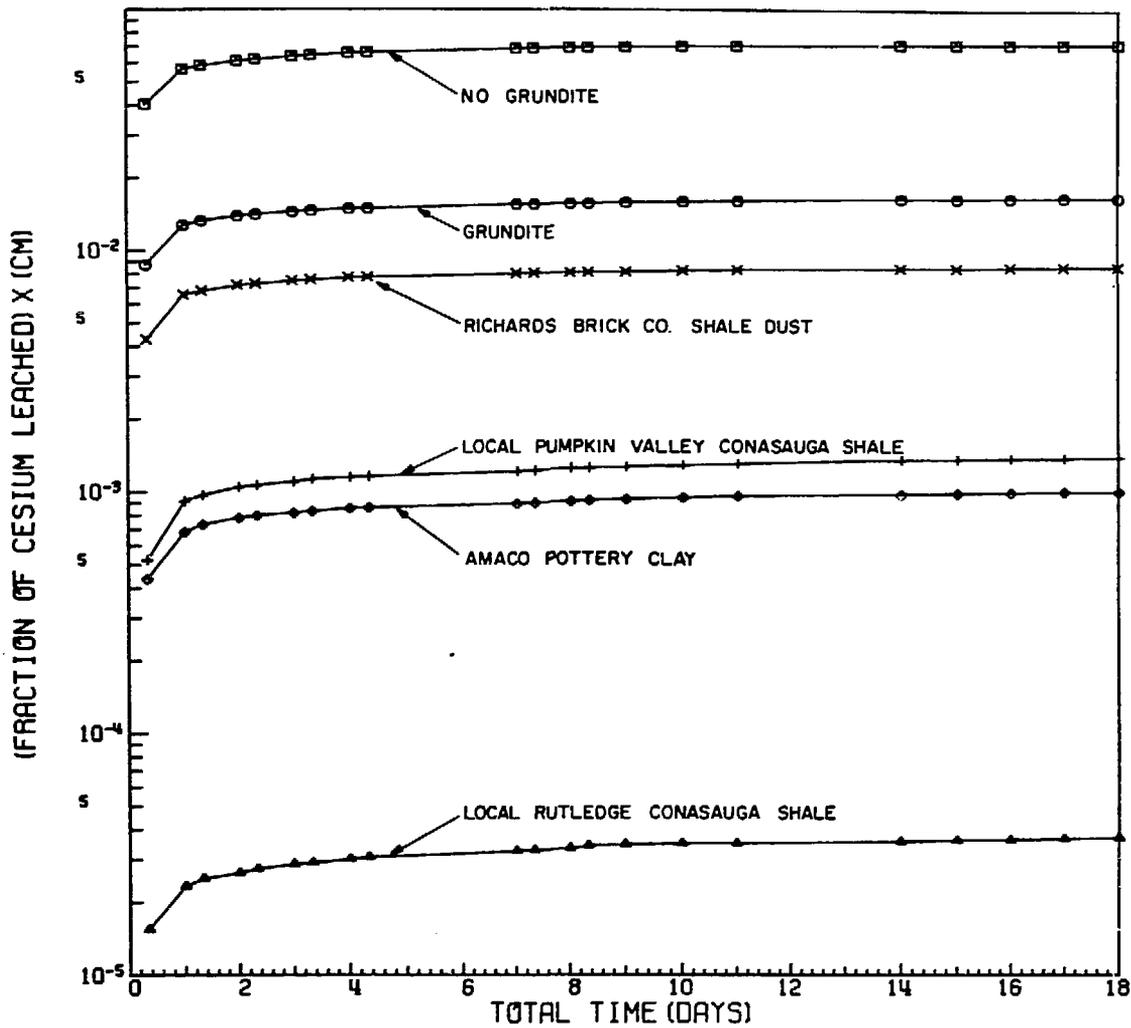


Figure 3.9. Effect of additives on cesium leachability [3.8].

Table 3.5

## Typical Strontium Leachabilities for Concrete Waste Forms [3.21]

Time, hr	Sludge <sup>a</sup>	Sr Leachability, $10^{-2}$ g/(cm <sup>2</sup> ) (d), for Cement Types					
	Content, %	I	II	III	V	I-P	HAC
2 <sup>c</sup>	0	2.7	12.0	5.0	3.4	3.6	9.1
	10	2.5	7.6	4.7	2.4	2.7	6.6
	25	3.3	4.6	2.5	2.7	2.1	5.8
	40	2.2	2.8	2.7	1.6	2.5	5.3
72 <sup>c</sup>	0	1.5	1.2	1.4	1.4	1.5	1.5
	10	0.73	1.1	1.2	1.2	0.79	1.0
	25	0.63	0.83	0.72	1.1	0.53	0.48
	40	0.37	0.82	0.56	0.52	0.24	0.22
1008 <sup>c</sup>	0	0.25	0.24	0.14	0.18	0.16	0.23
	10	0.16	0.22	0.13	0.17	0.13	0.13
	25	0.13	0.11	0.15	0.11	0.093	0.041
	40	0.079	0.098	0.11	0.13	0.054	0.024

a. Sludge III: 50% Fe(OH)<sub>3</sub>, 50% MnO<sub>2</sub> in mole %

b. Each entry is the average of six measurements

c. Error factor E (95% confidence): at 2 hr, E = 1.24; at 72 hr, E = 1.49; at 1008 hr, E = 1.40.

additives such as synthetic zeolites on cesium retention have been conducted at Savannah River Laboratory with high-alumina cement and pozzolanic cement [3.11]. These results as shown in Table 3.6 indicate differences in retention abilities for these additives.

A significant factor in leachability studies is the type of leachant used. Experiments at Brookhaven National Laboratory were designed to observe the differences in leach rates of plutonium from identical cement samples [22]. Results shown in Figure 3.10 show significant differences between demineralized water, brine, sodium dominated groundwater, calcium dominated groundwater and bicarbonate dominated groundwater leachants. The leachate

LEACHANT KEY FOR LEACH TEST CURVES

<u>CURVE NO</u>	<u>SYMBOL</u>	<u>LEACHANT</u>
1	—○—	DEMINERALIZED WATER
2	-□-	WIPP BRINE "B"
3	-◇-	SODIUM DOMINATED GROUNDWATER
4	-◇-	CALCIUM DOMINATED GROUNDWATER
5	-●-	BICARBONATE DOMINATED GROUNDWATER

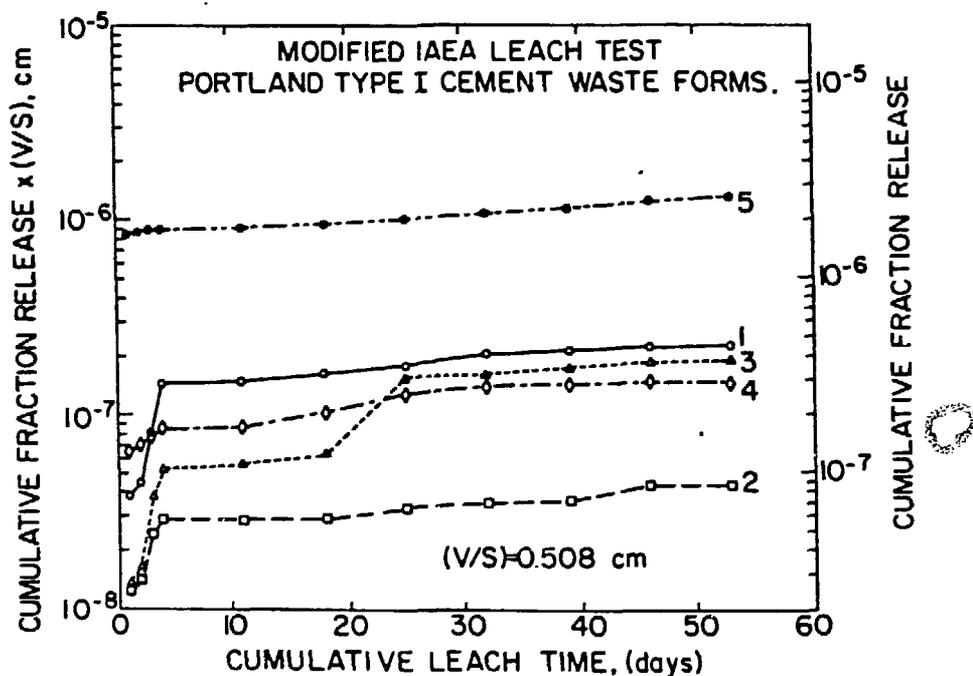


Figure 3.10. Differences in leachability from identical cement waste forms in various leachants.

Table 3.6

## Effect of Additives on Cesium Leachability [3.11]

<u>Additive</u>	<u>% cesium leached after 28 days</u>	
	<u>HAC</u> <sup>a</sup>	<u>I-P</u> <sup>b</sup>
AW-500	5.7	4.6
Z-900	6.0	3.9
Vermiculite	6.3	3.8
Z-500	6.5	4.5
Z-200	9.1	6.5
Clinoptilolite	13.1	9.2
AW-300	17.9	9.3

a. High Alumina Cement

b. Portland Type I, Pozzalanic Cement

with the greatest fraction release was bicarbonate, that with the least release was brine [22]. In FUETAP cement leachability for  $^{137}\text{Cs}$  in distilled water is  $10^{-6}$  g/(cm<sup>2</sup>)(day), for  $^{90}\text{Sr}$  it is  $10^{-4}$  g/(cm<sup>2</sup>)(day) and for  $^{239}\text{Pu}$  it is  $<10^{-8}$  g/(cm<sup>2</sup>)(day). Clay additives significantly reduce the  $^{137}\text{Cs}$  leaching [23].

### 3.5.3 Mechanical Strength

Mechanical strength is most important during the transportation of the waste form. Good compressive strength and impact resistance are significant properties particularly in the event of transportation accidents. During storage the principal interest rests in the waste forms ability to support itself without crumbling and thereby increasing its effective surface area and, subsequently, leachability. The strength of cement results from

cement curing and hydration. This in turn is a factor of age, cure temperature and amount of water in the mix. Amount and type of radioactive waste also significantly affect the strength of concrete. While high compressive strengths are desirable, primary significance should be directed towards avoiding very low compressive strengths.

Compressive strengths for four types of portland cements, pozzolanic cement (I-P) and high-alumina cement (HAC) mixed with each of three sludge types are given in Table 3.7 [3.21]. High-alumina cement achieves the highest compressive strengths as high waste loadings are increased. Compressive strengths for cement waste forms containing evaporator concentrate wastes are also available [3.3].

Compressive strengths for FUEIAP concrete consistently are about 2000 psi for types I and III portland cements [3.18]. Hot pressed cements have been reported to have a maximum tensile strength (5000 psi) with a waste loading of 10%. Strength steadily declined with increased percentages of waste. At 50% waste content the tensile strength was 2000 psi [3.17]. The tensile (splitting) strength is about 10% of the compressive strength.

Limited impact testing of cement waste forms has been conducted. While compressive strength indicates loading required to fracture the waste form in compression, the most important aspect of waste form performance in impact loading is its tendency to produce particulates. For brittle materials such as cement which have generally high compressive strengths but are weak in tension, impact strength is closely related to the waste forms tensile strength. Figure 3.11 indicates the amount and size of particulates produced in impact loading of cement-diatomaceous earth waste forms as a function of waste loading [3.24].

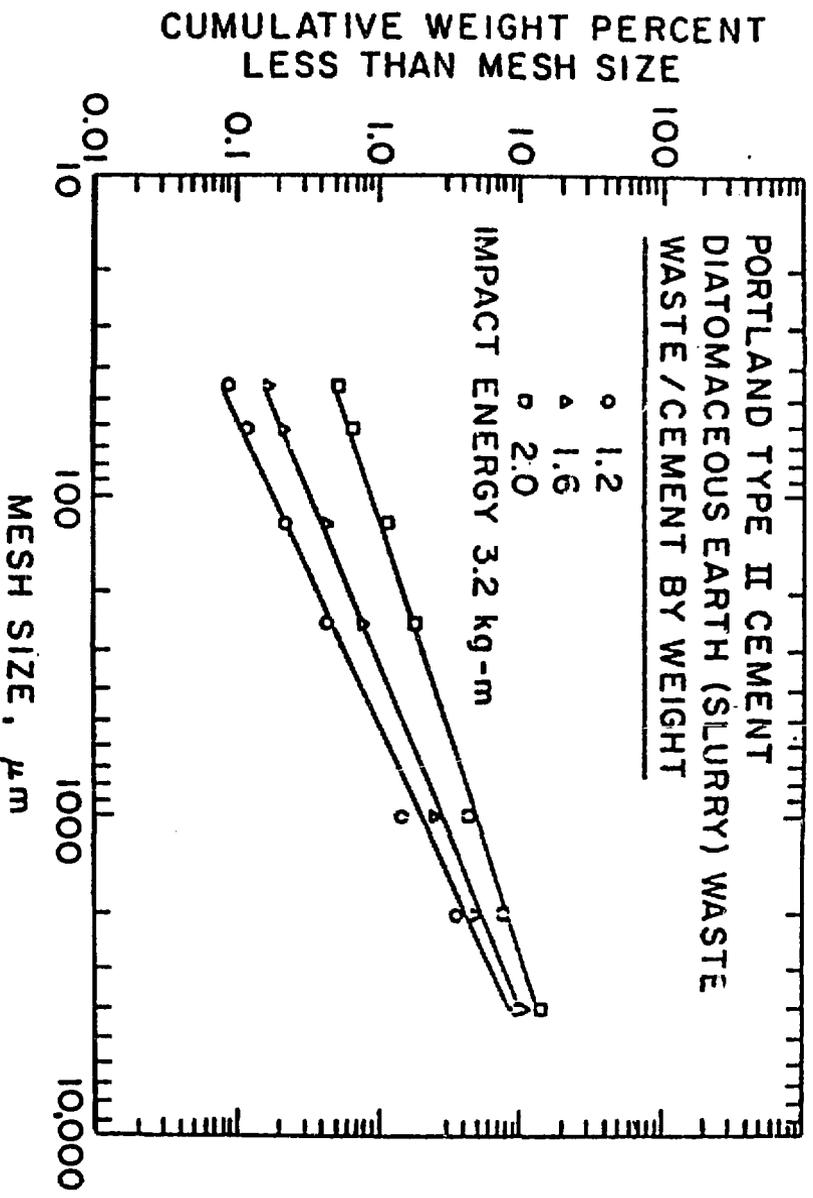


Figure 3.11. Cumulative weight percent less than mesh size versus mesh size (microns) for impact testing of diatomaceous earth (slurry) waste/portland type II cement specimens as a function of W/C ratio.

Table 3.7

## Compressive Strength of Concrete Waste Forms [3.21]

Sludge Type	Content, %	Compressive Strength, psi, for Cement Types <sup>a</sup>					
		I	II	III	V	I-P	HAC
None <sup>b</sup>	0	10,824	11,281	13,478	11,898	11,916	9,311
Ib	10	8,402	8,243	8,694	8,829	8,296	9,574
	25	4,588	4,630	6,180	5,620	4,472	5,792
	40	464	1,259	1,456	3,054	2,380	4,364
IIb	10	8,973	9,045	9,321	11,159	7,692	9,624
	25	5,779	6,412	7,230	7,158	5,855	7,158
	40	3,932	3,352	4,736	4,234	3,311	5,884
IIIb	10	9,313	7,557	7,603	8,490	7,761	8,465
	25	5,171	4,627	5,817	4,732	4,930	6,658
	40	2,388	2,884	3,317	2,700	3,088	3,371

a. Each entry is the average of six measurements.

b. Error factor E (95% confidence), where upper limit is  $\times E$  and lower limit is  $/E$ : No sludge,  $E = 1.15$ ; Sludge I,  $E = 1.12$ ; Sludge II,  $E = 1.15$ ; Sludge III,  $E = 1.08$ .

### 3.5.4 Radiation Stability

Stability of the waste form to radiation interactions is desirable to prevent the degradation of waste form properties and container pressurization resulting from gaseous radiolysis products. Waste form leachability, mechanical strength, dispersibility, and physical form may be affected by radiation. Gaseous radiolysis products may result in waste container pressurization (and possible failure), and the gaseous species produced may also be potentially explosive or radioactive themselves. Since it would typically take a long time to accumulate a substantial radiation dose from low-level waste forms because of their activity content, the immobility of their radioactive contents becomes of concern primarily in disposal. For example, cumulative radiation doses as a function of time are shown in Figures 3.12 and 3.13 as a

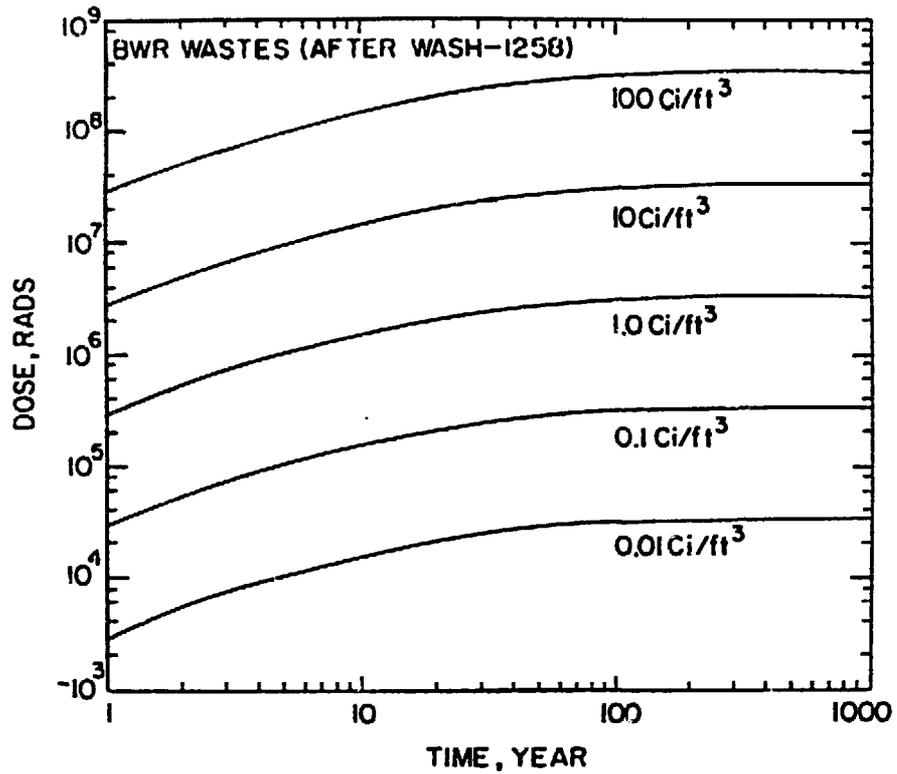


Figure 3.12. Cumulative radiation dose for BWR waste forms as a function of activity concentrations.

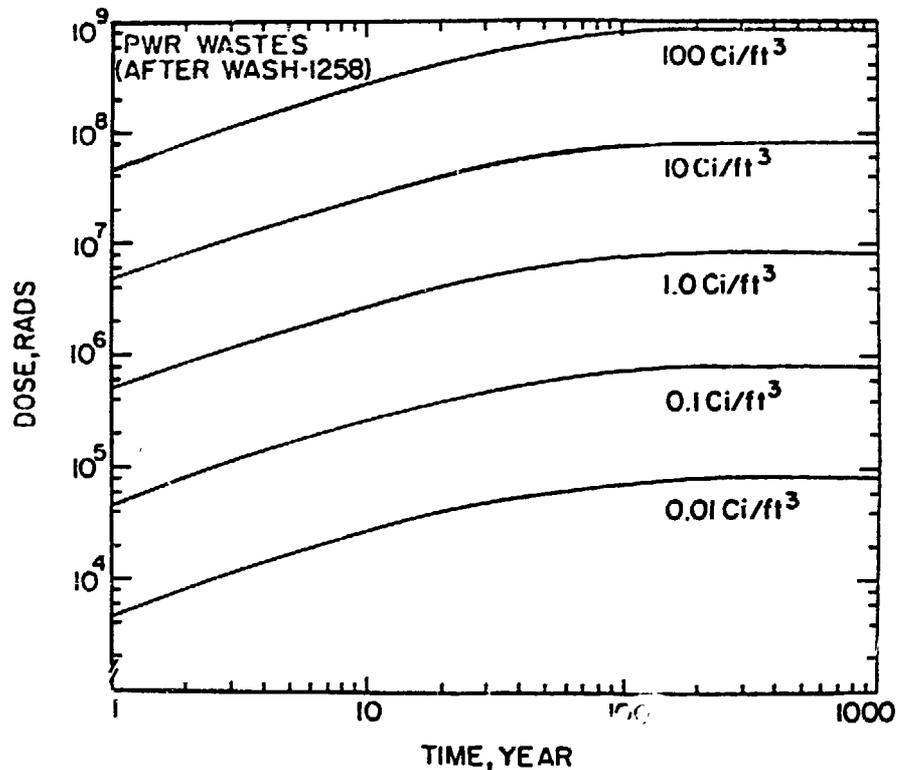


Figure 3.13. Cumulative radiation dose for PWR waste forms as a function of activity concentrations.

function of activity concentration for boiling water reactor (BWR) and pressurized water reactor (PWR) wastes respectively. Observed activity levels in light water reactor (LWR) solidified radwaste are listed in Table 3.8. The differences in shielding properties of the various solidification agents at typical waste/binder ratios must also be considered in relation to waste package handling and personnel exposure.

Table 3.8

Observed Activity Levels for LWR Solidified Radwaste [3.26]

		Evaporator bottoms	Filter/demineralized resins	Filter/demineralizer sludge
BWR	Generation rate (ft <sup>3</sup> /MWE)	25.5	4.0	19.5
	Activity content (Ci/ft <sup>3</sup> )			
	Range	0.0003-0.14	0.001-6.5	0.004-20.0
	Average	0.39	2.0	2.0
	Av. total activity (Ci/MWE)	1.0	8.0	3.9
PWR	Generation rate (ft <sup>3</sup> /MWE)	30.7	2.7	-
	Activity content (Ci/ft <sup>3</sup> )			-
	Range	0.002-0.4	0.03-37.0	-
	Activity	0.045	4.5	-
	Av. total activity (Ci/MWE)	1.4	12	-

Hydrogen is the predominant species produced by gamma radiolysis of concrete waste forms and results from the decomposition of water. Work using <sup>60</sup>Co gamma irradiation indicates that the initial rate of H<sub>2</sub> production is proportional to dose rate [3.25]. As the radiation dose increases, H<sub>2</sub> pressurization increased (and the rate of H<sub>2</sub> production decreased) until a steady state container pressurization was attained as shown in Figure 3.14. The steady state H<sub>2</sub> pressure decreased as the dose rate decreased, as shown in Figure 3.15. The G value for H<sub>2</sub> production, (G(H<sub>2</sub>), molecules/100eV absorbed

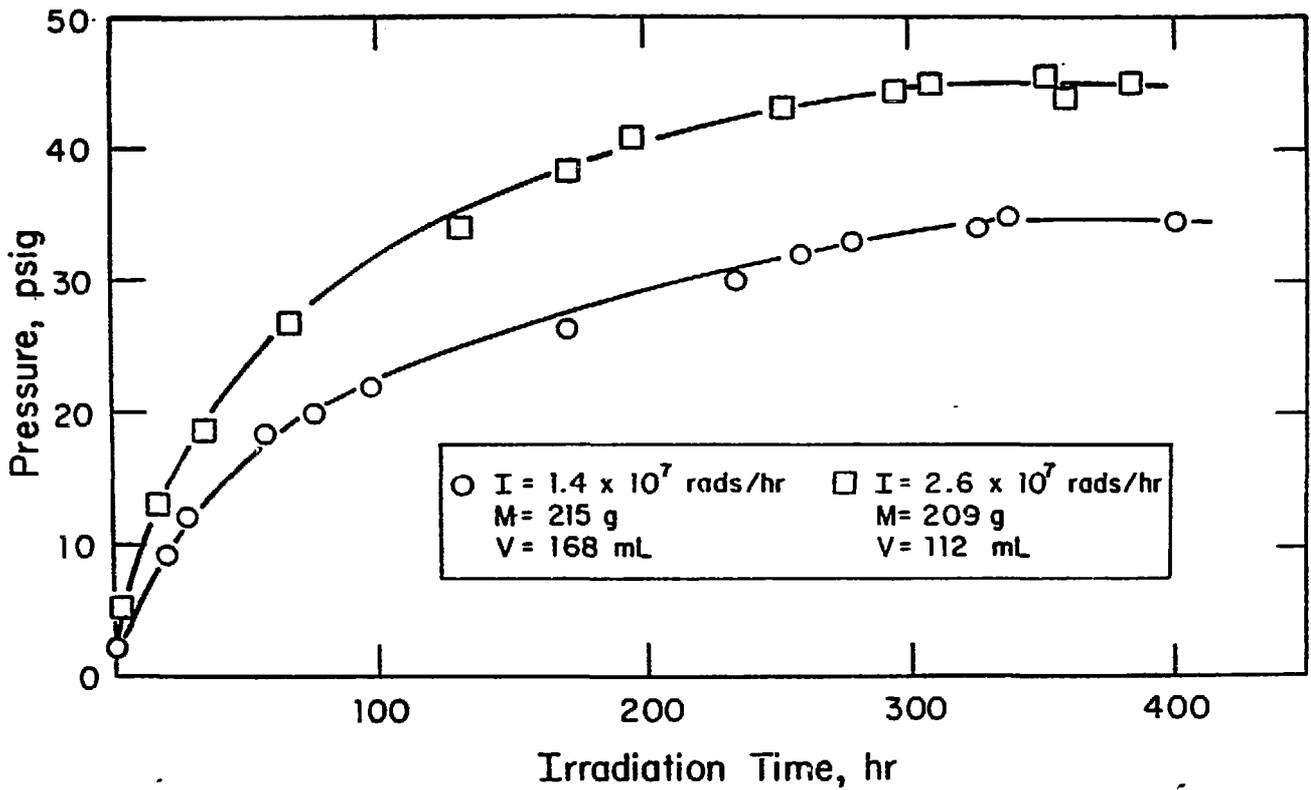


Figure 3.14. Pressurization from gamma radiolysis of concrete at 47°C.

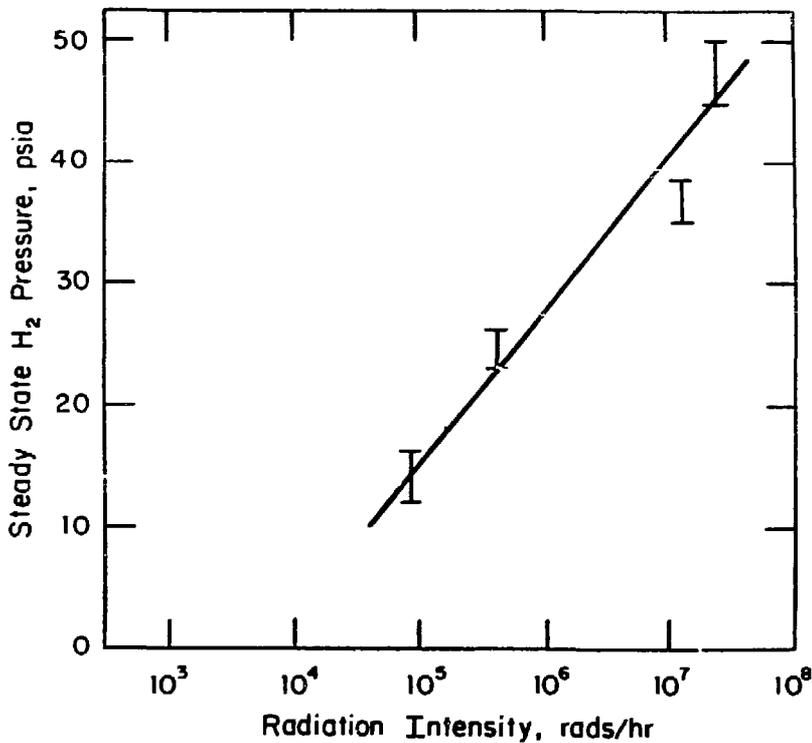


Figure 3.15. Effect of dose rate on steady state H<sub>2</sub> pressure from gamma radiolysis of concrete.

energy) was 0.03 molecules/100 eV and was independent of dose rate over the range studied. In these tests, oxygen in the air sealed in the container was partially consumed and nitrogen was unaffected. The steady state container pressurization extrapolated to the dose rate of typical low-level waste products is low (below 10 psi). This steady state pressurization may not in fact be realized since at low dose rates, the rate of hydrogen diffusion out of the container may be comparable to or greater than the rate of hydrogen production.

Gas generation may be reduced by the addition of nitrate and nitrite ions and by the reduction of free water content within the cement [3.22]. The latter may be accomplished by heating the cement waste form above 100°C or by employing one of the pressing techniques described earlier. An additional feature of the FUEAP product appears to be the catalytic recombination of radiolytic hydrogen and oxygen, thus reducing the gas problem [3.22].

#### 3.5.5. Thermal Properties

The thermal stability of a waste form may influence its ability to retain activity in certain environments. It is of concern during transportation and to a lesser extent during interim storage. The greatest potential for radionuclide release would result from accident conditions with external fires. Waste form temperature increases may cause melting, decomposition, combustion, degradation of mechanical properties, and dispersion of radionuclides in the form of gas, smoke, or aerosol. The waste form container, which serves as a barrier to release, may be breached by the accident conditions or by pressurization due to waste decomposition. Other less severe environments may also produce some thermal degradation of the waste form. Thermal stability is determined by synergistic interactions of the solidification agent and the incorporated waste.

Upon heating at 100°C, portland cement waste forms will slowly lose weight due to evaporation of uncombined but physically held (in the pore structure) water. Additional water can be removed at higher temperatures due to dehydration of the lower stability hydrated compounds. While this results in a decrease in mechanical strength properties the waste form will normally retain its integrity. Heating to 100°C for up to three months was shown to result in a 6-16% decrease in weight due to the loss of capillary water; this caused a 25% loss in compressive strength [3.21]. Heating at high temperatures (above 400°C) for long times leads to severe degradation of the cement waste form (although some cements, notably high alumina cement, are refractory cements and will retain their integrity).

Exposure to the thermal environment resultant from a petroleum fire after a transportation accident, will typically produce minimal effects with full-size cement waste forms (55 gallon drum size or larger). This is a consequence of the low thermal conductivity of cement waste forms, which has been measured as 0.0029 cal/cm-sec-degree C [3.4]. In effect, while the exterior of the waste form is heated to high temperatures, the interior of the waste form is not subjected to significant heat unless the time in the high temperature environment is very long. Flammability tests (ASTM D635-74) characterize portland cement waste forms as non-flammable [3.4].

### 3.6 Advantages and Disadvantages

Table 3.9 presents advantages and disadvantages of employing cement as a solidification matrix for low-level radioactive waste. Perhaps the greatest advantage to its use is that cement is a well known, common material which is particularly adaptable to a variety of conditions. Note that in this (and subsequent) comparison tables particular items are often of much greater importance than others. Hence, the number of advantages and/or disadvantages for a particular matrix is not in itself significant.

TABLE 3.9

Advantages and Disadvantages of Cement Solidification

Advantages	Disadvantages
1. Material and technology well known and available	1. Some wastes affect setting or otherwise produce poor waste forms
2. Compatible with many wastes	2. pH sensitive-pretreatment of waste may be necessary
3. Most aqueous wastes chemically bound to matrix	3. Swelling and cracking occurs with some products under exposure to water
4. Low cost of cement	4. Volume increase and high density in shipping and disposal
5. Good self-shielding	5. Excessive setting exotherms may develop with certain cement and waste combinations
6. No vapor problems	6. Dust problems with some systems
7. Long shelf life of cement powder	7. Equipment for powder feeding difficult to maintain
8. Good impact and compressive strengths	8. Potential maintenance problems resulting from premature cement setting, especially in-line mixers
9. Low leachability for some radionuclides	9. Requires heating and/or pressing equipment for some processes (hot pressed and FUEAP materials)
10. No free water if properly formulated	
11. Rapid, controllable setting-no differential settling	
12. In container and in-line mixing processes available	

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#### 4. BITUMEN AS AN AGENT FOR LOW-LEVEL WASTE SOLIDIFICATION

Bitumen has been used to solidify radioactive waste since a pilot plant at Mol, Belgium was commissioned in 1962. Much of the research in the methodology of bitumen solidification and the subsequent application to actual operations has occurred in Europe. A notable exception is the work at ORNL with emulsified asphalt. Among the plants utilizing bitumen as a solidification medium for low-level and intermediate-level waste are those operating at Mol, Belgium; Marcoule, France; Harwell, England and Karlsruhe, Federal Republic of Germany.

##### 4.1 Description of Bitumen

Bitumen or asphalt is a mixture of high molecular weight hydrocarbons which is obtained as a residue in petroleum or coal tar refining. It has two major components: asphaltene compounds, which give bitumen colloidal properties, and maltheane compounds, which impart viscous liquid properties. Bitumen is a thermoplastic material and can behave mechanically as either a viscous liquid or a solid depending on temperature [4.1].

The incorporation of waste in bitumen usually relies upon its thermoplastic properties. The bitumen is typically heated in the presence of waste, with the heat serving both to liquify the bitumen sufficiently for mixing and to evaporate water from the waste, thereby providing volume reduction of the waste. Waste solids are thus mixed and coated with bitumen in a liquid state. Upon cooling, waste solids are mechanically held in a solid bitumen matrix. Exceptions to employing the thermoplastic properties of bitumen are emulsified

bitumen processes where a solvent is used to liquify bitumen at room temperatures. The water in the waste is removed thermo-mechanically while mixing the waste with the bitumenous material. The mixture solidifies as the solvent is allowed to evaporate.

#### 4.2 Types of Bitumen

There are five generic types of bitumen available with differing properties which make them appropriate for a variety of uses. Bitumen, being a natural material, can vary significantly from batch to batch. Therefore, specific commercial products have been developed which are made to conform to a relatively narrow range of properties. Even these materials will vary somewhat in characteristics in different shipments of the same named product and grade. The five major types of bitumen are listed below [4.2]:

- (1) Straight-run distillation bitumen (the residue after distillation of heavy petroleum)

Softening point	from 34 to 65°C
Penetration	from 22 to 2 mm

- (2) Oxidized bitumens (Highly colloidal bitumen products formed by blowing air heated to 300°C through certain petroleum). Temperature fluctuations usually have little effect on oxidized bitumens.

Softening point	70 - 140°C
Penetration at 25°C ranges	0.7 to 4.5 mm

- (3) Cracked bitumens (obtained by pyrogenic breakdown of heavy molecules). Temperature fluctuations have a considerable effect on cracked bitumens. They are used mainly in cases where good flow at high temperatures and subsequent rapid hardening on cooling is required.

Softening point	77 - 85°C
Penetration at 25°C	<0.5 mm

- (4) Bitumen emulsions (formed by the emulsification of bitumen in soapy water). There are two types of bitumen emulsions: anionic (emulsifier: alkaline soap) and cationic (emulsifier: amine salt). Bitumen emulsions can be used without previous heating. On contact with a prepared surface, the emulsion spreads over it, the water evaporates and a rigid coating is left.
- (5) Pitches (bitumens liquified by addition of a solvent)

The two types most widely used for the solidification of radioactive wastes are straight run distillation bitumens and the oxidized bitumens. The Werner and Pfleiderer Corporation recommends the use of Pioneer 221 bitumen (Witco Chemical Corporation) in their domestic solidification system installations [4.1]. This material is a steep roofing type of asphalt which has the characteristics given in Table 4.1. Other named products that have been employed extensively in European applications include Mexphalt 10/20 and Shell pH 55-65.

#### 4.3 Additives

A variety of additives have been used with bitumen to either increase the ability of the waste form to retain radionuclides or to improve the physical characteristics of the form itself.

The addition of clay minerals, other natural earth materials and synthetic products has been used to reduce the leachability of specifications such as  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ . Similar materials have been incorporated in cement waste forms for the same purpose. Some of the products used are: Bentonel AF (calcic magnesium bentonite), Betsil RV (marine diatoms), calcium silicate, Argisil A (sepiolite), and activated alumina [4.3]. Addition of 2 wt% water glass ( $\text{Na}_2\text{SiO}_3$ ) resulted in 50-90% decreases in the observed leach rate for  $^{137}\text{Cs}$  from similar waste forms without the additives [4.3]. These same additives were also found to significantly reduce the flamability of samples containing 60 wt% nitrate salts [4.3].

Table 4.1

Characteristics of a Typical Bitumen Used for  
Radioactive Waste Solidification [4.1]

<u>Property</u>	<u>Specification</u>
Softening Point	200°F or 93°C
Flash Point of Volatiles (ASTM Test D-92)	500°F or 288°C minimum
Percent Volatiles by Volume	0.1%
Ignition Point (Minimum)	600°F or 315°C
Specific Gravity (g/cc)	1.05
Viscosity (250 - 400°F)	900-100 cp
Penetration	2.2-3 mm 77°F or 25°C
	4.0-6 mm 115°F or 46°C
	1.3-1.8 mm 32°F or 0°C
Vapor Pressure	1 mm Hg maximum
Vapor Density (Air=1)	0.01 maximum

Other materials, often clay products, are used to control the properties of the solidified waste form. Organic liquids can dissolve bitumen so that a solid waste form cannot be produced. Experiments at ORNL have used a variety of materials to act as fillers, allowing the bitumen mixture to flow at about 160° but solidify adequately at 25°C. The organic liquid used was tributyl phosphate (TBP) and the fillers used were: Attapulgite-150 (a drilling clay), Attaclay Filler, Neospectra Mark I Filler (carbon black) and Cab-0-Sil Filler (high surface area silica). Attapulgite-150 was the only material which provided an acceptable waste form; this in the proportions of 25 wt% TBP, 38 wt% bitumen and 37 wt% Attapulgite-150. Irradiation to 10<sup>8</sup> rads with <sup>60</sup>Co caused no change in the waste form [4.2, 4.4].

#### 4.4 Waste Form Preparation

There are five basic methods used to produce mixtures of bitumen and waste. In these methods, heat is required to soften the bitumen and/or is used to evaporate water. In all cases, the off-gases generated are treated for volatilized organic oils which are driven from the bitumen during heating.

##### 4.4.1 Stirred Bitumen Process (Mol Method)

The first process for encapsulation of radioactive waste in bitumen was developed at Mol, Belgium. In this process, liquid or solid wastes are mixed with molten bitumen at a temperature of 160° to 230°C with simultaneous evaporation of water and volatile constituents [4.2]. Figure 4.1 shows a schematic of the improved version of the "Mummy" installation at Mol. A similar plant was put into use at AERE, Harewell, UK in 1968 [4.5].

The method of fixing wastes in bitumen developed in Mol, Belgium, uses non-emulsified asphalts. Radioactive concentrates (sludges) obtained after filtration on a drum filter are fed by a screw conveyor into a mixer-evaporator. The evaporation of the remaining moisture and mixing of the solid waste residue with molten bitumen takes place at a temperature between 200 to 230°C and is accompanied by vigorous stirring. The maximum content of solid wastes incorporated in the final product does not exceed 45%, thus ensuring a uniform waste form on cooling [4.2].

The basic apparatus, a mixer-evaporator, is a cylindrical steel tank with a flat bottom divided internally into two sections, a lower one called the "mixing chamber" and an upper one called the "expansion chamber". The process of mixing sludge with molten bitumen takes place in the mixing chamber, while the expansion chamber serves for quenching of the foam which may be formed when sludges with a high water content are processed. At the

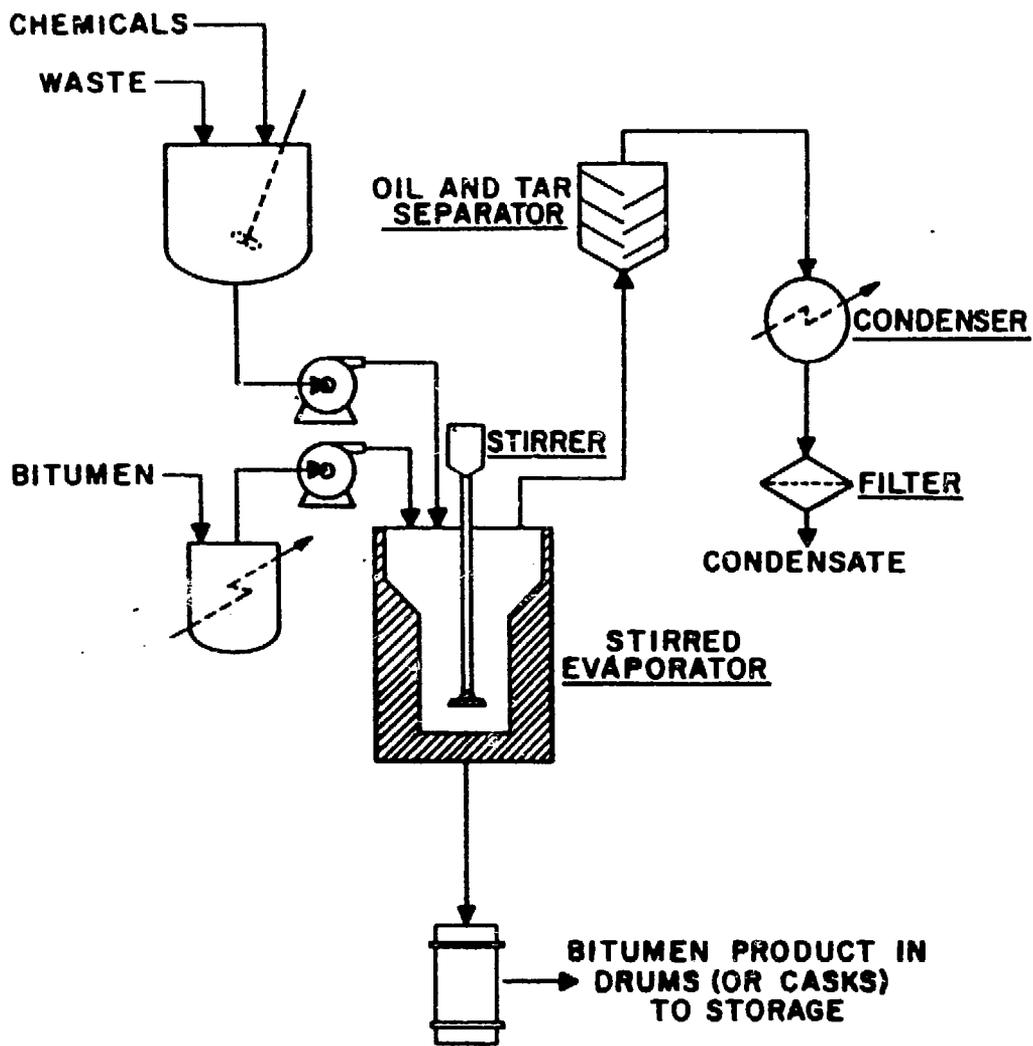


Figure 4.1. Schematic of the stirred bitumen process.

bottom of the mixer-evaporator there is an outlet valve equipped with a heating mantle. System throughput is determined by the water content of the waste. The Mol system can evaporate up to 100 liters of water per hour. When the waste solids content in the bitumen reaches about 40%, the mixture is discharged into 55 gallon drums. This is accomplished by pressing the barrels against the discharge outlet valves by means of a hydraulic lift so that a hermetic seal is produced. The mixture is allowed to cool and solidify, after which the drums are sealed with steel lids. Some drums can be heated keeping the bitumen fluid in order to allow incorporation of plastic wastes into the form [4.2]. Process off-gases are treated for volatilized bituminous oils.

At the Harwell installation a different type of sludge treatment was adopted for which vibratory feed equipment was unsatisfactory. The solution was to treat the sludge in a slowly rotating drum. At 50-60 wt% solid content, the sludge takes the form of spherical pellets. When dropped into hot bitumen the water remaining in these pellets is rapidly heated, causing the pellets to disintegrate, spreading the dehydrated waste throughout the bitumen. Drying in this way drastically reduces the mixing time necessary [4.5].

Fire suppression systems are normally incorporated in these installations since bitumen is flammable. In one instance, a fire was accidentally started at the Harwell plant when the mixing device stopped while the immersion heating elements were still energized. This resulted in extreme local heating and ignition of the asphalt near the heaters. The fire was extinguished by the CO<sub>2</sub> sprays which are built into the system [4.5].

#### 4.4.2 The "Temporary Emulsion" Process

The "Temporary Emulsion" process developed at Marcoule, France entails the mixing of sludges, emulsifying agents and bitumen together, separation of the water from the emulsion resulting in bitumen coated sludge

particles, and finally complete drying of the product [4.2]. Figure 4.2 is a schematic of this process [4.2].

The sludges are normally concentrated by using a rotary filter to remove water, and are then fed to the "coating" machine together with the bitumen and the surface-active agents. In the first coatings section of the process, mixing and coating of the solid particles takes place together with separation of approximately 80% of the water while the temperature is maintained at about 90°C. In the second coating section, the temperature is raised to 110°C facilitating further mixing of waste with the bitumen and separation of remaining water. Transport, mixing and water separation in the coating machine are achieved through the movement of the mixture, via screws of various pitches and velocities, thereby pressurizing and depressurizing the bitumen-waste mixture as it is processed. Final dehydration (to <0.5% water) of the product is achieved in a twin screw drying machine at temperatures of 130°C, from which the bituminous waste is discharged into drums. The plant described is capable of handling 600 kg of sludge per hour and started operation in 1966 following intensive trials [4.2].

#### 4.4.3 Sedimentation Process

Another type of process, developed in Austria, employs the greater density of dried salts compared to that of hot bitumen to incorporate the waste salts into the asphalt. A schematic of this process is shown in Figure 4.3 [4.6].

Thin film evaporator concentrate, which is powdery and contains a very small amount of moisture, falls by its own weight into the molten bitumen beneath it. The bitumen is kept at a suitable temperature (~200°C) to guarantee a low viscosity. As a result of the density difference, the waste solids settle in the mixture to a highly packed sediment of bitumen coated solids

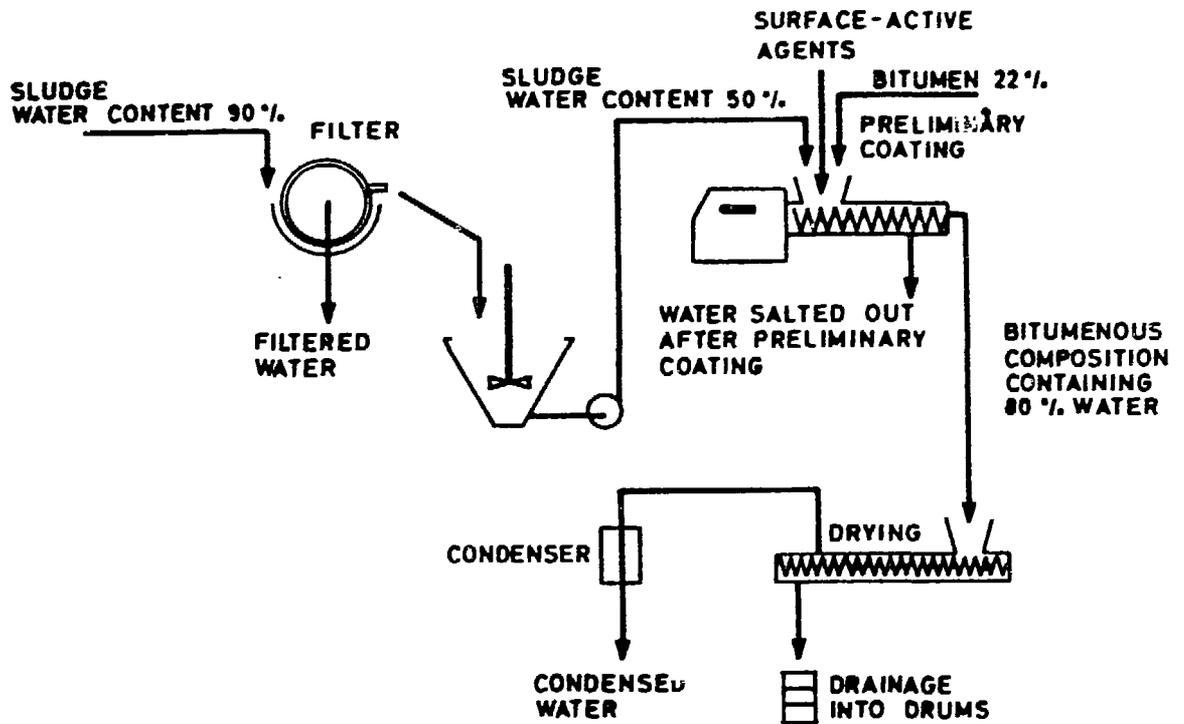
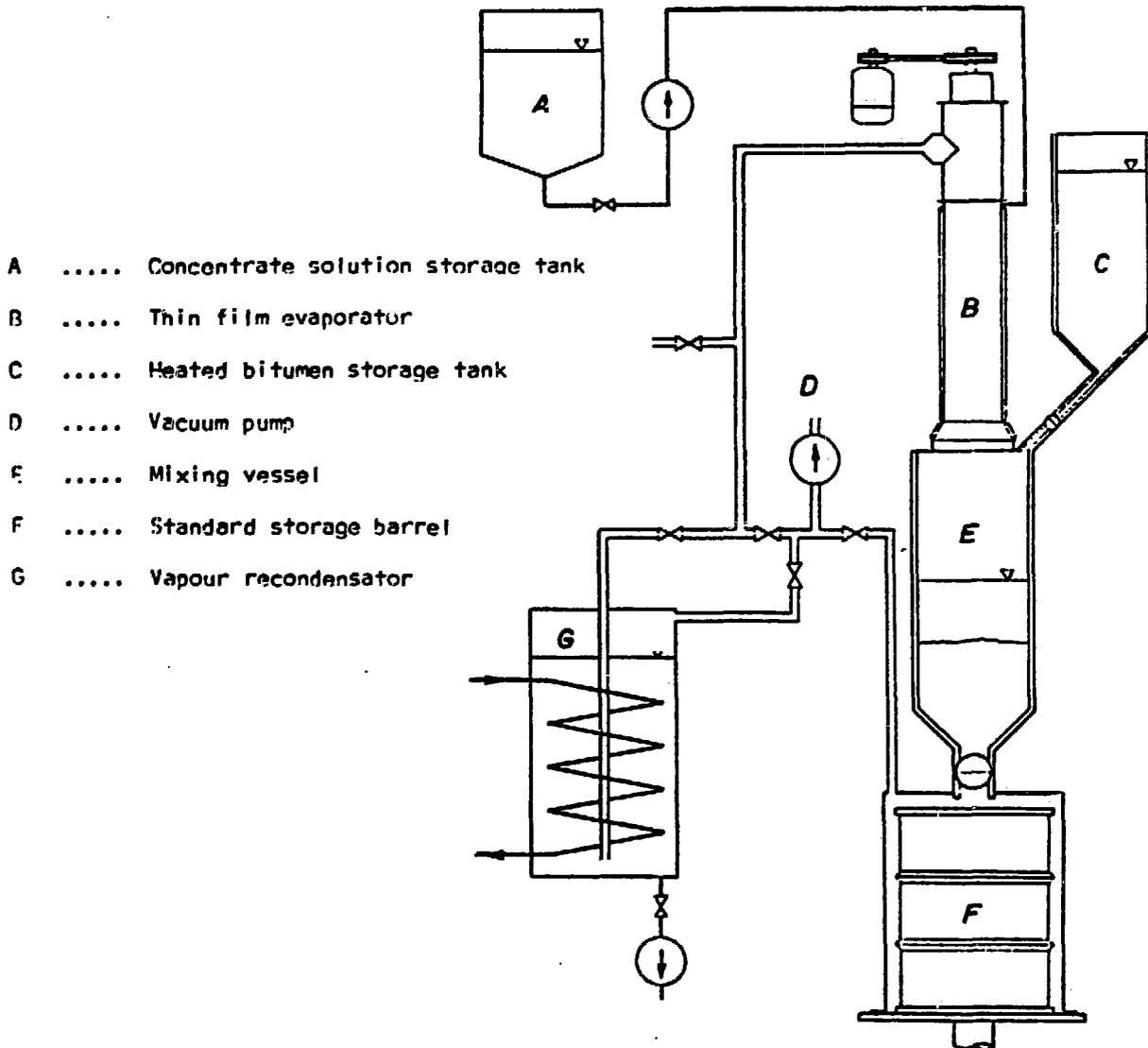


Figure 4.2. Schematic of the temporary emulsion process.



- A ..... Concentrate solution storage tank
- B ..... Thin film evaporator
- C ..... Heated bitumen storage tank
- D ..... Vacuum pump
- E ..... Mixing vessel
- F ..... Standard storage barrel
- G ..... Vapour recondensator

Figure 4.3. Schematic of the sedimentation process.

which gradually fill the mixing vessel. When the mixing vessel is filled, the product is emptied into a storage barrel. The entire system, from the thin film evaporator to the storage barrel, is closed and maintained at reduced pressure. It is thereby possible to operate without any contamination of the environment [4.6].

A pilot plant which started operation in 1973 is able to process 25 kg per hour of concentrate solutions and precipitation sludge. The final product reaches a packing density of 50-70 wt% salts in bitumen.

#### 4.4.4 Screw Extruder Process

This system, marketed in the United States by Werner & Pfleiderer Corporation, uses a twin-screw extruder of the type employed in the plastics industry. In this process, liquid bitumen (140°C) and wet solid wastes are continuously pumped at predetermined rates into one end of the extruder. They are spread by screws into a thin film on the heated surface of the extruder barrel. Steam is employed for barrel heating. This mechanical processing at an elevated temperature of 170°C effects essentially complete evaporation of the water in the waste and provides homogeneous mixing of waste solids with bitumen. The evaporated distillate water is vented through large disengaging sections called steam domes which are drained to a condensate system. The bitumen-waste mixture is discharged from the extruder directly into solidification containers, where it is allowed to cool and solidify. Because the mixture shrinks on cooling, each container is normally filled, allowed to cool and then topped off to provide more complete usage of its volume. A schematic of this process is shown in Figure 4.4 [4.7].

These screw extruders are available in various sizes, with barrel diameters typically 12 cm. The processing rate depends upon the water content of the waste and the temperature at which the individual heating sections are

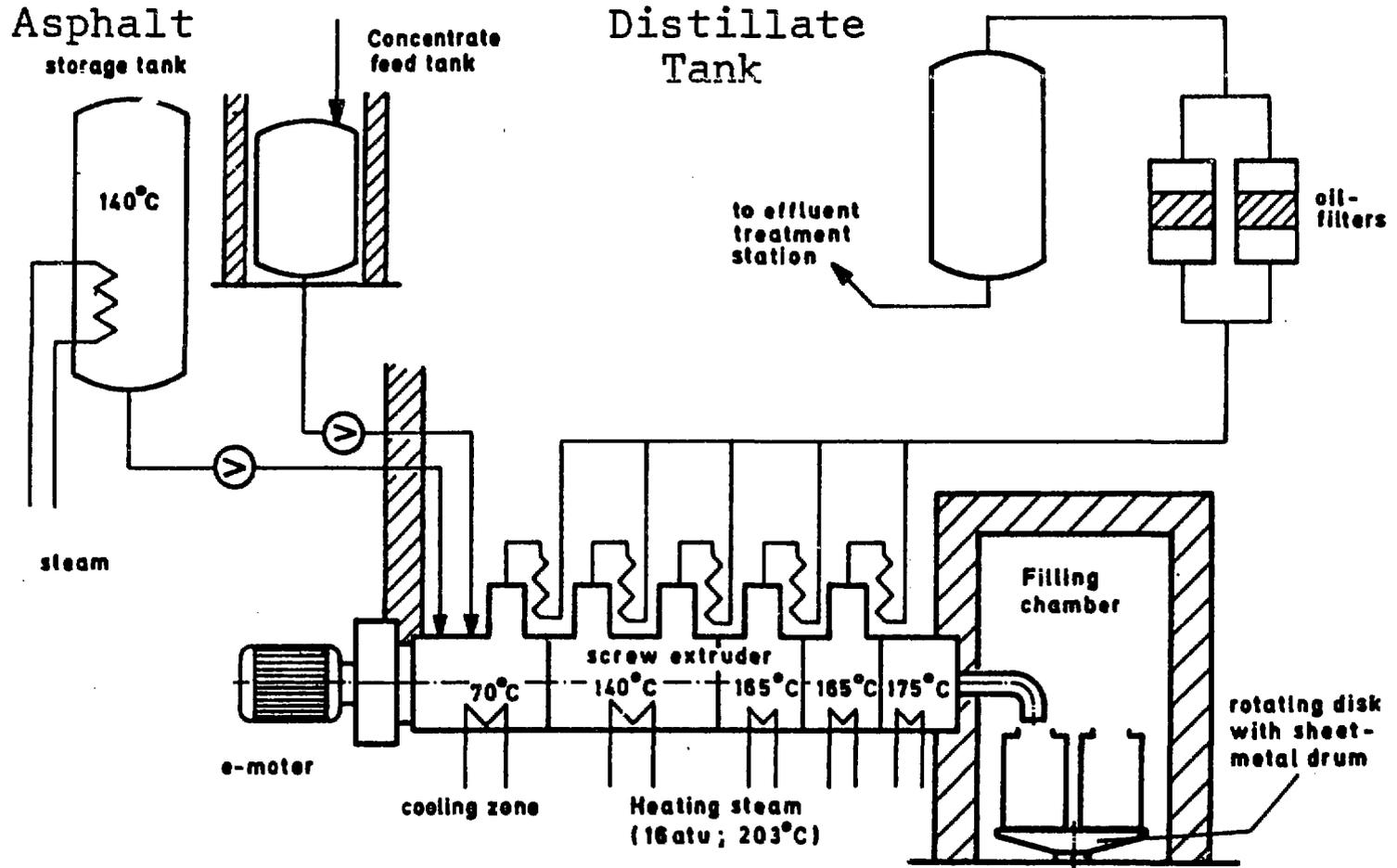


Figure 4.4. Schematic of the screw extruder system.

operated. The waste and bitumen feed rates are controlled to provide a product of approximately 50 wt% waste solids.

#### 4.4.5 Emulsified Bitumen Process

The emulsified bitumen process was developed at Oak Ridge National Laboratory to avoid a major criticism of other bitumen processes which is the heat required to melt the bitumen [4.4, 4.8, 4.9]. Heating presents two main difficulties: 1) the possibility of a fire, and 2) the high operating temperature may volatilize some constituents of the waste before they are solidified in the asphalt. In an effort to overcome these problems, emulsified asphalt, which is fluid at room temperatures, was used. Both a batch process and a continuous process were developed. A pilot plant was commissioned around 1965.

The batch process consists of 1) adding the waste directly to emulsified asphalt in an evaporator tank initially operating at a temperature of up to  $\sim 100^{\circ}\text{C}$ . The tank also contains a stirrer and a bottom outlet rotating at a rate of about 100 rpm, 2) evaporating the water in the mixture by raising the temperature to  $160^{\circ}\text{C}$ , and 3) draining the product into a disposal container. In the continuous process, the waste and asphalt are introduced at the top of a wiped film evaporator and the mixture flows down the walls of the evaporator operated at  $160^{\circ}\text{C}$ . Agitator paddles sweep the walls continuously at about 300 rpm and provide good mixing and heat transfer. The process was demonstrated on a laboratory scale with nonradioactive waste in a 4 inch diameter x 6 inch high evaporator and on a pilot plant scale with a 12 inch diameter x 16 inch high Pfaudler wiped film evaporator with a  $4\text{ ft}^2$  of heat transfer surface. The processing rate in the large unit was about 4 gal/hr of product containing 60 wt% solids [4.8].

Waste form products containing from 20 to 80 wt% waste solids have been prepared [4.8]. The bitumen was an emulsified asphalt used in the surface treatment of roads (type RS-2: a rapid setting, high viscosity, emulsified asphalt containing 63 wt% asphalt, 35 wt% water, and 2 wt% emulsifying agent). Products containing 20 to 60 wt% waste solids flowed freely from the evaporator at 130°C, whereas the product containing 80 wt% solids was removed with difficulty at 195°C. The product containing 60 wt% waste solids represented a good compromise of properties, volume reduction, viscosity, and ductility [4.11].

#### 4.5 Bitumen Waste Form Characteristics

The characteristics of bitumen waste forms which have received most attention are leachability and those related to the stability of the material under heat and radiation. Mechanical strength is a moot point since bitumen is thermoplastic. Viscosity, however, can be measured by penetrometer tests at defined temperatures. Most characteristics of bitumen are dependent on the type and amount of waste incorporated within the waste form, as well as the grade of bitumen utilized.

##### 4.5.1 Chemical Compatibility of Waste

Table 4.2 indicates the chemical compatibility of typical wastes with bitumen. The chemical compatibility of specific wastes within the general classes indicated is dependent upon the exact chemical nature of the waste.

Solidification of ion exchange resins can present difficulties since the temperatures at which they begin to decompose are within the operating temperatures of the processes. This decomposition can generate gaseous by-products which may be detrimental to the product. Decomposition may be avoided by minimizing the time during which resin wastes are exposed to high

TABLE 4.2

Chemical Compatibility of Wastes With Bitumen

<u>Waste Type</u>	<u>Waste Compatibility</u>
Ion exchange resins	fair
Sludges	good <sup>(a)</sup>
Boric acid wastes	good
Sulfate wastes	fair
Nitrate wastes	poor
Phosphate wastes	good
Carbonate wastes	good
Oils	poor-fair
Organic liquids	poor-fair
Acidic wastes	fair
Alkaline wastes	fair
Filter cartridges	(b)
Large items	(b)

---

(a) Caution required with oxidizing sludges

(b) Processes generally not applicable to these wastes

temperatures. Sulfate waste products have been observed to deteriorate rapidly upon immersion in water due to hydration of anhydrous sulfate salts. In addition, the incorporation of other salts, such as  $\text{NaNO}_2$ ,  $\text{MgCl}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{MgSO}_4$  and  $\text{NaAlO}_2$  can be detrimental to the bitumen itself. Nitrate and nitrite waste have been shown to accelerate burning of bitumen waste forms and to increase their hardness [4.2, 4.10]. Addition of most waste solids to the bitumen will tend to elevate the flash point, while oxidizing wastes, particularly those that are volatile below the flash point of the bitumen used ( $280^\circ\text{C}$ ), will tend to lower it. Some workers [4.2] have observed explosive ignition of bitumen waste forms loaded with 46 wt% nitrate salt, but more recent tests trying to detonate such waste forms suggests that they are not explosive [4.2, 4.10]. Addition of organic liquid wastes will soften and tend to liquify the bitumen as increasing quantities are added. Filter cartridges and other large items can be solidified with bitumen; however, most processes are not directly applicable to such wastes.

#### 4.5.2 Leachability

Leach rates of bitumen waste forms have been shown to depend upon a complex interplay of a variety of factors, as is the case with most other solidification media. Figure 4.5 is a plot of the leach rate of a variety of constituents from an actual asphalt waste form [4.11]. The general form of the curves is due to an initial high leach rate of surficial contamination from the waste form. The first minima is due to reduced leaching through a hard coating that typically forms on an asphalt waste form. The remainder of the curve is the leach rate as it approaches the steady state condition [4.2].

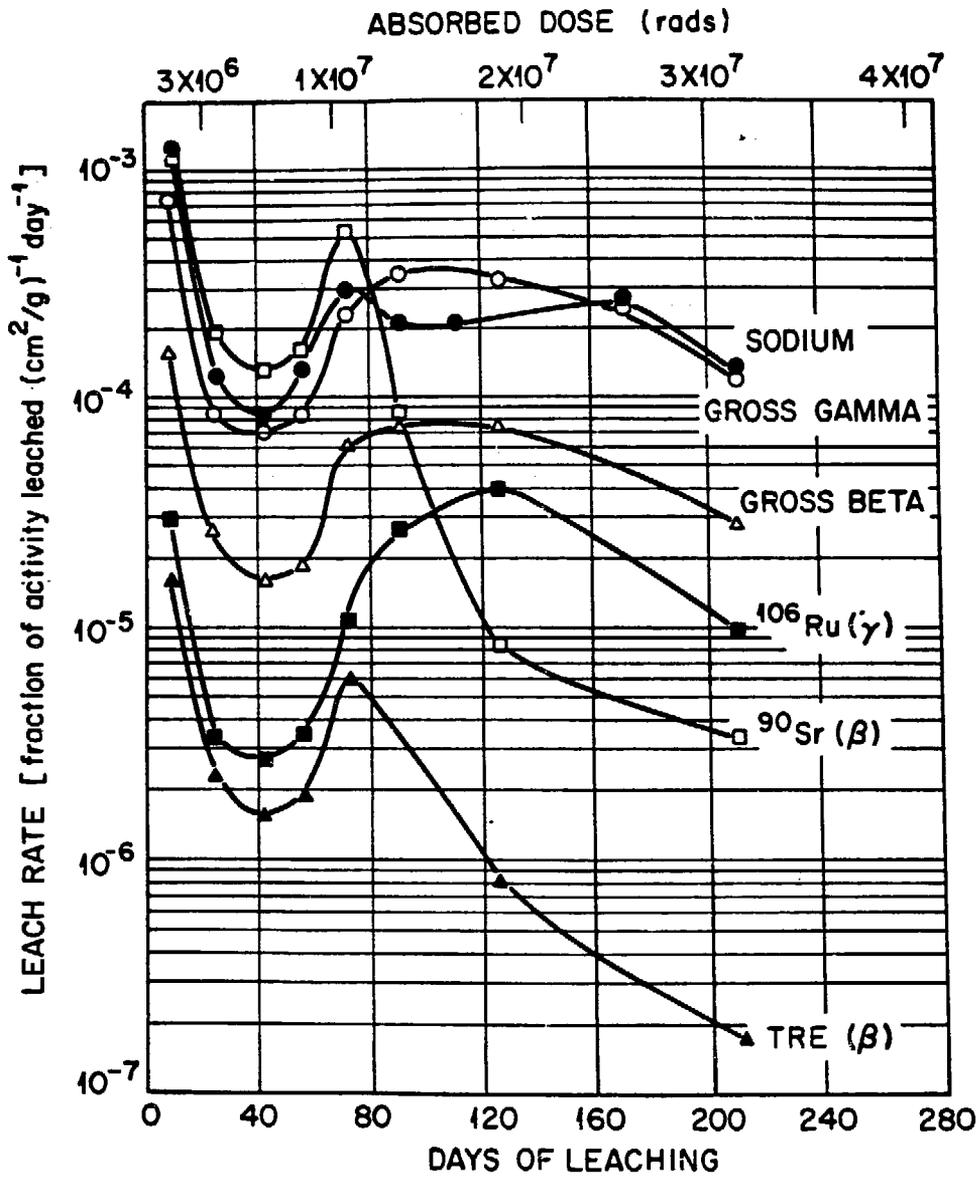


Figure 4.5. Leach rate curves for various constituents of a bitumen waste form.

The leach rates for the different radionuclides shown differ by several orders of magnitude. Absorbed dosage shown at the top of the figure refers to internal self-irradiation of the waste form.

Leaching tests with distilled water show that the rates at which strontium, ( $10^{-6}$  g/(cm<sup>2</sup>)(day), and ruthenium are leached from asphalt products containing nitrate wastes are low [4.2, 4.3]. The leach rate for cesium is 50-100 times higher than this, but addition of grundite to the waste form provided a leach rate of  $7 \times 10^{-5}$  g/(cm<sup>2</sup>)(day), half that of cesium without clay added.

Work in the Soviet Union has shown that the softer type (BN-III) asphalt is superior by 3 orders of magnitude, for preventing leaching of sodium nitrate wastes, than the harder BN-IV [4.2]. Other workers, however, report somewhat less significant difference between asphalt types. Figure 4.6 shows leach rates for two dissimilar types of asphalt: Mexphalt 40/50 (distillation products) and Mexphalt R 90/40 (oxidized bitumen) and for two types of leachants [4.2]. The leachant differences are slightly more important than asphalt type, although none are large compared to differences seen among various radionuclides leached.

The type of waste and the relative proportion of it incorporated in the waste form are strong influences on leachability. Figure 4.7 shows the leach rates of <sup>137</sup>Cs from three types of waste incorporated in similar waste forms.

Leach rates are also influenced by the amount of waste incorporated in the product. Experiments at Oak Ridge National Laboratory using intermediate level waste forms with two different waste loadings, 20 wt% waste solids and 60 wt%, gave steady state leach rates of  $1.5 \times 10^{-4}$  g/(cm<sup>2</sup>)(day) and  $3 \times 10^{-4}$  g/(cm<sup>2</sup>)(day), respectively [4.11].

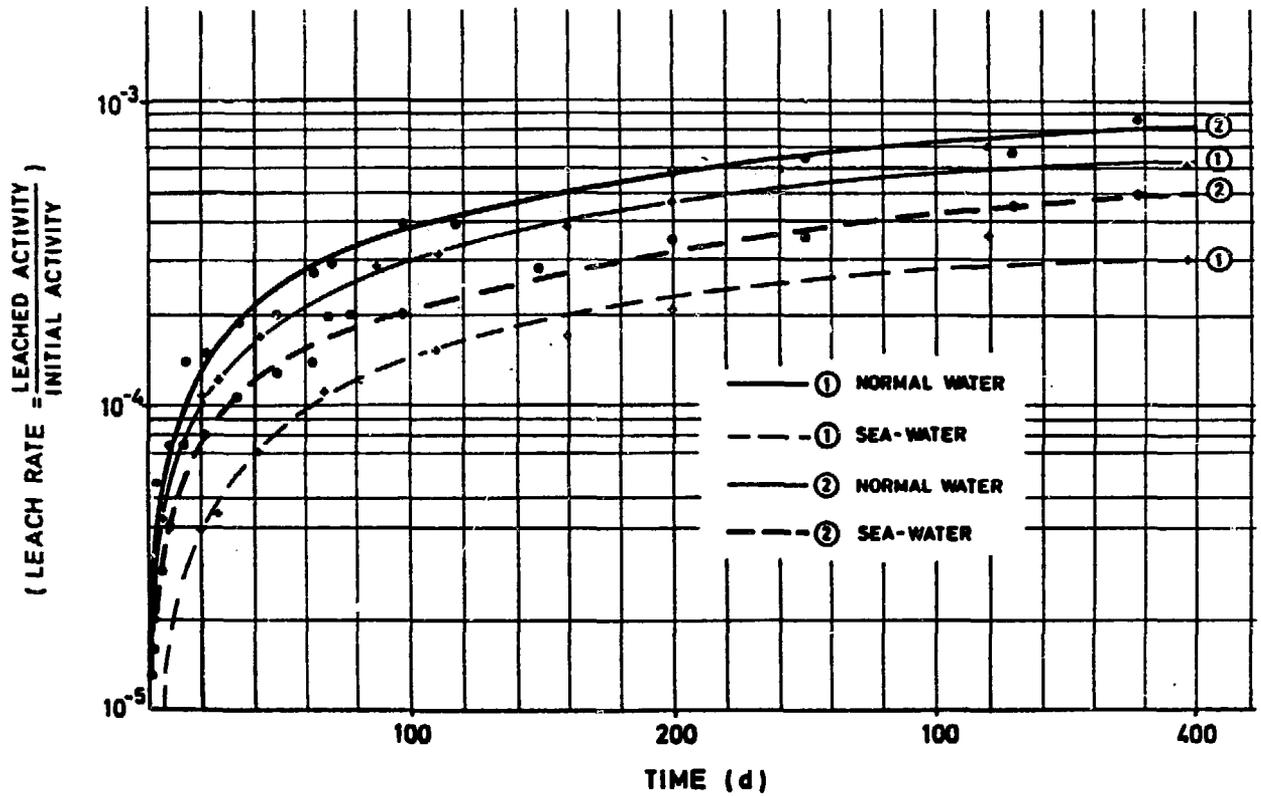


Figure 4.6. Leach rates from bitumen waste forms containing evaporator concentrates and 44% bitumen. 1 denotes mexphalt 40/30 and 2 denotes mexphalt R 90/40.

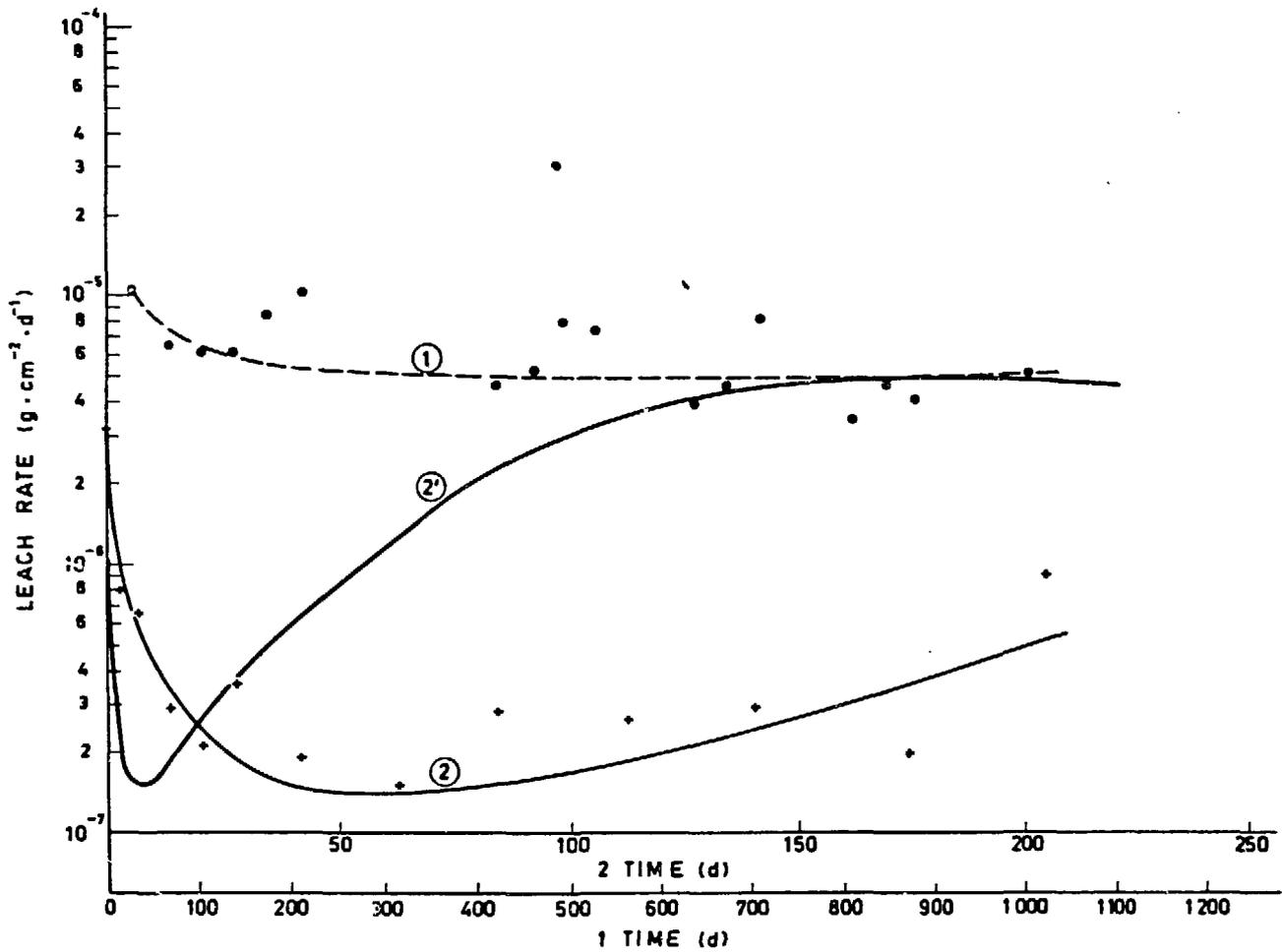


Figure 4.7. Leach Rate of  $^{137}\text{Cs}$  from Bitumen BN-III containing: 1) 40% sodium nitrate, 2) 40% calcium nitrate and 3) 40% calcium carbonate.

The temperature at which  $^{90}\text{Sr}$  bearing waste is mixed with asphalt can be important. With a  $120^{\circ}\text{C}$  processing temperature a steady state strontium leach rate of  $10^{-5}$  g/(cm<sup>2</sup>) (day) was measured while with a  $160^{\circ}\text{C}$  processing temperature the leach rate was significantly lower ( $<10^{-6}$  g/(cm<sup>2</sup>) (day) [4.2]. This was ascribed to reactions, at higher temperatures, of strontium with the bitumen. Another process factor which can affect leach rate is the percentage of water which remains in the waste form after solidification. An 8 wt% increase in initial water content (most bitumen samples will absorb some water during leaching) will result in more than an order of magnitude increase in the leach rate [4.2]. This may be related to the increased surface area exposed to leaching by pores filled with water in the waste form. As mentioned previously, leach rates from bitumen waste forms containing sulfate wastes can be very high due to the deterioration that results as the anhydrous sulfate waste solids absorb water and form hydrates.

#### 4.5.3 Mechanical Properties

Since bitumen flows under pressure at ambient temperatures, normal compression and impact testing techniques cannot be directly applied. However, while bitumen will flow under pressure, it does not fail by a fracture mechanism common to compression failures of non-thermoplastic materials. (Bitumen can be made to fail under compression at sub-ambient temperatures.) Similarly, bitumen does not tend to fracture and generate particulates under impact loadings at ambient temperatures. Tests are available to measure the resistance of bitumen to penetration.

#### 4.5.4 Radiation Stability

Products containing 60 wt% solids of Oak Ridge intermediate and low-level waste were prepared using a hard-base asphalt and  $^{60}\text{Co}$  irradiated to doses of  $10^6$  to  $10^8$  rads. At a dose of  $10^6$  rads, only negligible changes were observed. A dose of  $10^7$  rads caused slight swelling, while a dose of  $10^8$  rads caused a sample to swell about 36% in volume and a dose of  $10^9$  rads caused a sample to swell 70% in volume. In contrast, similar samples prepared from a soft-base asphalt and irradiated to a dose of  $10^8$  rads showed only a slight increase in volume. Presumably, gaseous products (if formed) were released by the softer material. The swelling observed in such studies may be dependent upon the dose rate. If gases are generated faster than they can diffuse from the bitumen product, swelling can result. However, in actual practice, dose rates and hence gas generation resulting from radiolysis may occur slowly. In addition to swelling, the samples became harder with increasing radiation dose. However, the samples that were irradiated to the highest doses were still pliable at room temperature [4.12]. The effects of internal irradiation, up to  $10^8$  rads, have been reported to be negligible [4.12]. External irradiation to the same dosage caused significant effects; however, the dose rate may be an important factor. Internal exposure required over 838 days to reach that level. In this time, the rate of gas generation was apparently close to the ability of the bitumen to recombine or to release the gas. Thus, few gas bubbles and no swelling were observed.

#### 4.5.5 Thermal Properties

A major concern with bitumen as a waste form matrix is the danger of fire both in the processing of the waste form and during subsequent interim

storage, transportation and disposal. Incorporation of inert solids into bitumen acts to elevate the flash point of the product [4.12]. However, solidification of wastes containing waste solids which are oxidants such as nitrate salts, may present a hazard. Tests have shown that EWR wastes in asphalt had a slightly higher flash point than did plain asphalt. The flame point and the softening point both increase with addition of nitrates. However, it was noted that the rate of combustion also increased [4.2]. Exposure of bitumen waste forms to heat and consequent bitumen softening can also result in the settling of waste solids within the waste form or cause the waste form to flow.

#### 4.6 Advantages and Disadvantages

Table 4.3 lists advantages and disadvantages of employing bitumen as a solidification agent for low-level radioactive waste. A major advantage associated with the use of bitumen is its potential for substantial volume reduction of aqueous wastes as a result of the evaporation of contained water occurring during the solidification process.

TABLE 4.3

## Advantages and Disadvantages of Bitumen Solidification

Advantages	Disadvantages
1. Technology and material are well known and available	1. Bitumen is flammable and burns spontaneously at temperatures as low as 390°C
2. Compatible with a wide range of wastes	2. Limited loading of salts due to hardening effects
3. Concurrent volume reduction of aqueous wastes	3. May swell in water leading to increased leachability and product degradation
4. No free standing water	4. Potential for radiolytic gas generation
5. Individual waste particles are coated	5. Exposure to heat may cause melting or phase separation of waste form
6. Low cost of bitumen	6. Process requires elevated temperatures
7. No difficulty with improper setting since it is not a chemical process	7. Heating must be well controlled and spread evenly
8. Typically low leachability	8. Storage of asphalt before use requires elevated temperatures to maintain fluidity of material
	9. Capital equipment costs are relatively high
	10. Generation of off-gas during processing oil evaporate may clog filters

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## 5. POLYETHYLENE AS AN AGENT FOR LOW-LEVEL WASTE SOLIDIFICATION

Use of the thermoplastic polymer polyethylene as a binder for low-level radioactive waste has been limited. Most experimental work was performed by Oak Ridge National Laboratory in conjunction with their bitumen studies.

### 5.1 Description of Polyethylene

Polyethylene is a lightweight thermoplastic of the chemical formula  $(\text{CH}_2\text{CH}_2)_x$ . While the properties of polyethylene vary significantly, dependent largely upon chain length and density, some chemical properties of polyethylene lend themselves to the solidification of low-level radioactive waste. Polyethylenes are highly resistant to degradation by many chemicals, with the exception of free halogens, oxidizing acids and some ketones [5.1]. Polyethylenes are highly resistant to attack by water. However, stress cracks may develop if polyethylene is subjected to multiaxial stresses in contact with some polar liquids, such as metallic soaps, organic esters, liquid hydrocarbons and silicone fluids.

### 5.2 Types of Polyethylenes

While polyethylenes are chemically all the polymerization products of ethylene, there are some differences in the properties of various types. High density polyethylenes (specific gravity 0.945-0.965) are the products of a low pressure process, producing a linear, more crystalline molecular structure, which is relatively strong and corrosion resistant. Low density polyethylenes (specific gravity 0.915-0.925) are the product of a high pressure polymerization process and have lower strengths and reduced resistance to chemical attack. Typical high density polyethylene has a softening point of about  $127^\circ\text{C}$ , while the low density material softens at about  $86^\circ\text{C}$ . A broad range of

polyethylene products are available which are mixtures of the two types or have other olefin type plastics added to adjust their properties [5.1].

### 5.3 Additives

Some additives are available which may be used to improve certain characteristics of polyethylene. Because the plastic is subject to attack by ultraviolet light, carbon black may be added to block these effects. Similarly, antioxidants may be used. This is not typically viewed as significant for waste disposal applications. Resistance to stress cracking may be improved by adding polyisobutylene. Additives for decreasing leachability can be incorporated as was described for bitumen. However, no significant efforts in this area have been identified.

### 5.4 Solidification Processes Using Polyethylene

The processes employed to solidify radioactive waste with polyethylene use either screw extruders or wiped film evaporators. These processes are virtually identical to those used for bitumen. Other bitumen type processes could potentially be employed for use with polyethylene.

#### 5.4.1 Wiped Film Evaporators

In experiments at Oak Ridge National Laboratory, [5.2] 100g batches of polyethylene were processed in a wiped film evaporator operated at temperatures of 100-170°C. The evaporator was revolved at 100-300 rpm and a waste feed rate of between 1 and 3 ml/min employed, depending on the solids concentration. Evaporation took place at about the same speed as the feed rate.

Evaporate concentrates and sodium borate wastes in concentrations of 20-40 wt% were satisfactorily prepared using polyethylene, although 40 wt% loading was the maximum (compared to about 60 wt% loading for asphalts). Organic tributyl-phosphate (TBP) wastes were incorporated in polyethylene at loadings of 20-50 wt% TBP. A good product was obtained with loads of 30 wt% TBP in DYLIT polyethylene (Eastman Kodak Company). At higher concentrations some bleeding of TBP occurred. No acceptable waste form could be produced in these studies using asphalt (with fillers) and TBP waste.

#### 5.4.2 Screw Extruder

A twin helical screw extruder has been used at the Japan Atomic Energy Research Institute to solidify spent ion exchange resins in polyethylene. Loadings of 50 wt% were achieved with good results [5.3]. Apparently one power plant in The Netherlands has used a screw extruder to produce polyethylene waste forms.

### 5.5 Polyethylene Waste Form Characteristics

#### 5.5.1 Chemical Compatibility of Wastes

Polyethylene is compatible with a variety of waste components, more so than many other solidification agents. Workers at Oak Ridge National Laboratory report that polyethylene was acceptable for all types of waste tested except oxidizing acids. Polyethylene accommodated 30-40 wt% organic solvents, while asphalt could incorporate only 25 wt%. Typical maximum loadings of inorganic solids was about 40 wt%. Actual practice using polyethylene for low-level waste solidification is limited.

### 5.5.2 Leachability

A few studies concerning the leachability of polyethylene waste forms have been conducted. Data are available for leach rates of sodium,  $^{106}\text{Ru}$  and  $^{137}\text{Cs}$ . Figure 5.1 shows fraction release curves for sodium from waste forms containing varying amounts of  $\text{NaBO}_2$  and two types of polyethylene products, DYDT and DYLT (Eastman Kodak Co.) (Bakelite polyethylene resins, Union Carbide Plastic Co) [5.2]. Significant differences are reported for the different types of polyethylene matrix materials. Polyethylene waste forms containing 30 wt% tributyl phosphate and  $0.1 \mu\text{Ci/ml } ^{106}\text{Ru}$  had a leach rate of  $1.5 \times 10^{-6} \text{ g}/(\text{cm}^2)(\text{day})$  [5.2]. The cumulative fraction release of  $^{137}\text{Cs}$  from ion exchange resin solidified in polyethylene was as low as 0.1% after one year [5.3].

### 5.5.3 Mechanical Strength

Because polyethylene is a thermoplastic material, its mechanical strength is best measured as a function of fluidity at a given temperature. However, a uniaxial compressive strength of approximately  $300 \text{ kg}/\text{cm}^2$  was reported for a waste form containing 50-60 wt% ion exchange resin [5.4]. After exposure to gamma irradiation to a dose of  $10^8 \text{ R}$ , a 33% drop in compressive strength was observed.

### 5.5.4 Radiation Stability

Radiation stability tests at Oak Ridge National Laboratory using a  $^{60}\text{Co}$  source indicated that an external dose of  $10^6 \text{ R}$  caused no damage. Doses of  $10^7$  to  $10^9 \text{ R}$  caused some slight shrinkage and discoloration. No significant gas generation was observed. Others [5.1] report that when polyethylene is irradiated, hydrogen and smaller volumes of methane, ethane and propane are produced [5.1]. Irradiation induces crosslinking within the polyethylene

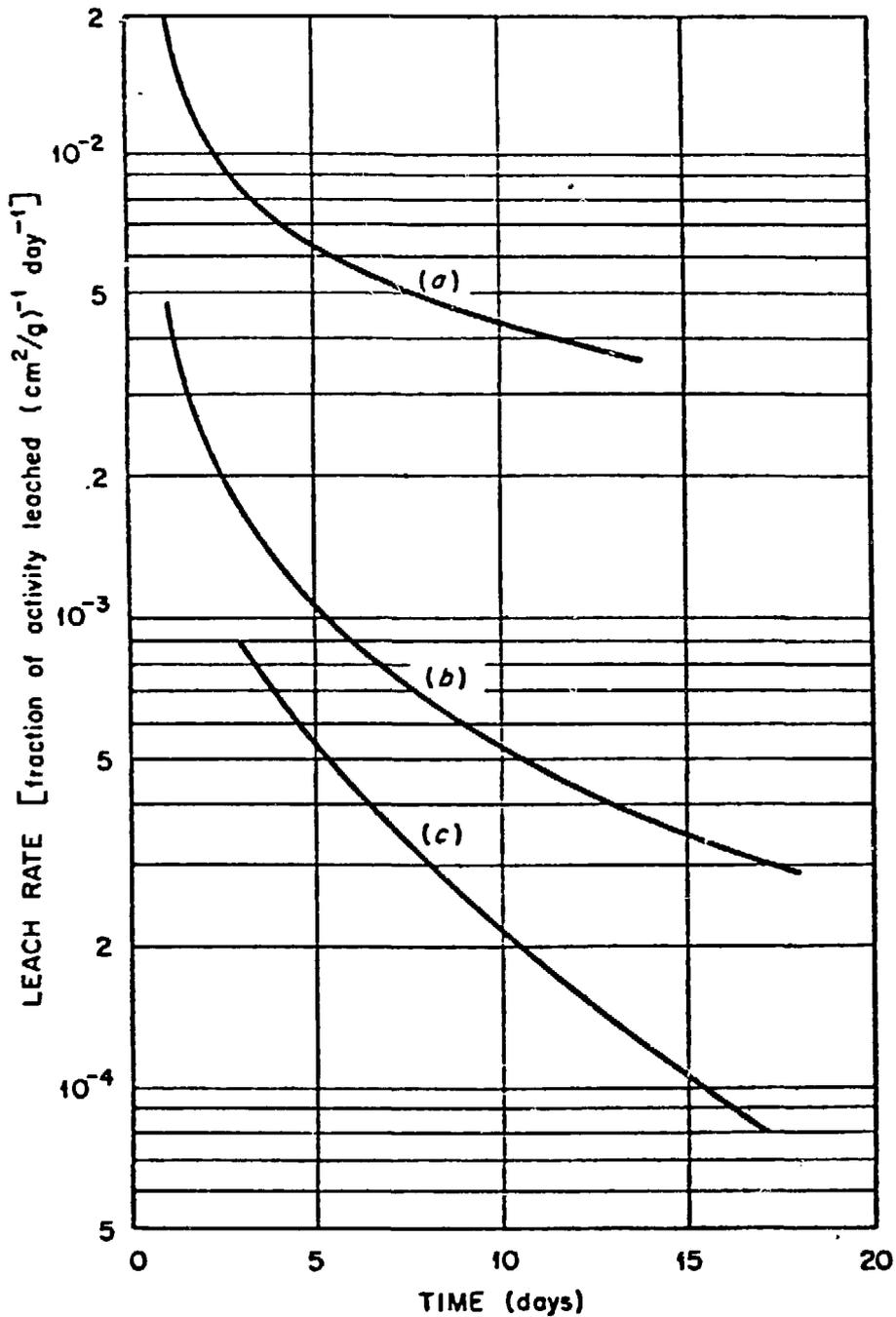


Figure 5.1. Results of leaching polyethelene waste forms in Water: a) Na from 40% NaBO<sub>2</sub> - 60% DYDT, b) Na from 40% NaBO<sub>2</sub> - 60% DYLT and c) Na from 20% NaBO<sub>2</sub> - 80% DYLT illustrating differences in leaching from two types of polyethelene.

which decreases its solubility, and induces brittleness. In essence, irradiation causes it to become also a thermosetting plastic. Irradiation also causes color changes in which the material first yellows and with additional exposure turns dark red.

#### 5.5.5 Thermal Properties

Polyethylene waste forms are flammable. A waste form containing 40 wt% nitrate salts ignited spontaneously at 440°C burning with a steady, yellow flame [5.2, 5.3]. A similar test with bitumen resulted in vigorous burning. Polyethylene itself does not spontaneously ignite upon heating to a temperature of 550°C. However, exposure to temperatures of greater than 300°C oxidizes the material.

#### 5.6 Advantages and Disadvantages

No table is presented for the advantages and disadvantages of polyethylene because of the paucity of information available for the use of this material as a solidification agent. The advantages/disadvantages are expected to be generally similar to those identified for bitumen. However, the cost of polyethylene is considerably higher than bitumen.

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## 6. UREA-FORMALDEHYDE RESIN AS AN AGENT FOR LOW-LEVEL WASTE

### SOLIDIFICATION

Urea-formaldehyde (UF) is a thermosetting polymer which has been widely used in various industries as adhesives, molding compounds and grouts to seal loose soils [6.1, 6.2]. In 1972 Protective Packaging, Inc. (Louisville, KY), began marketing its urea-formaldehyde system for solidifying radioactive wastes [6.1]. A variety of vendors have since developed UF processes both as permanent installations and as mobile systems. Urea-formaldehyde systems have been used extensively in the nuclear electric power industry. Urea-formaldehyde gained rapid acceptance in the industry as a result of its process advantages over the cement systems in use at that time. For example, there is no dusting problem, mixing is easy and rapid, mixers are readily cleanable and the equipment is relatively simple, inexpensive and has a small space requirement. In recent years, free-standing water problems with the waste form product have limited the use of urea-formaldehyde and have, in fact, led to movement away from UF systems.

#### 6.1 Description of Urea-Formaldehyde

Urea-formaldehyde, in the form used for low-level radioactive waste solidification, is an aqueous emulsion of 65 wt% partially polymerized monomethylol urea ( $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH}$ ) and dimethylol urea ( $\text{CH}_2\text{OH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH}$ ) solids in water [6.3]. Crosslink polymerization occurs when 2-3 volume % of a weak acid catalyst such as ammonium sulphate, sodium bisulphate or phosphoric acid is added to the UF resin waste. Generally two parts of waste are added to one part UF resin by volume, giving a volume efficiency (ratio of input waste volume to solidified waste volume) of 0.75 [6.2]. The solidification reaction is both pH and temperature dependent, with a preferred pH of

1.5 ± 0.5 [6.3]. Gelling begins within a few minutes of the catalyst addition and a free-standing solid will generally be formed with 30 minutes. Complete polymerization requires several hours or days of curing [6.4]. The liquid waste mixed in the urea-formaldehyde is not chemically reacted with the solidification matrix; rather it is entrapped in the polymer as small, discrete parcels of water. This encapsulated water is weakly acidic, moderately corrosive, and may be subject to some evaporation from the waste form [6.1, 6.2]. Solids in the waste are mechanically held by the matrix. In order to prevent rapid corrosion of the canister, a protective coating or lining must be used. Urea-formaldehyde resin has a limited shelf life of several months to a year. Shelf life is strongly dependent on temperature. Aged resin may result in poor solidification, producing a "cottage cheese" like waste form. This condition may also be caused by low temperatures during the solidification reaction.

## 6.2 Additives

In other uses, wood flour and bleached wood pulp (cellulose) are added to urea-formaldehyde resins to improve the strength of the solid [6.1]. As with cement, various clay minerals can be used to aid in the retention of particular radionuclides, especially cesium and strontium. Portland cement is sometimes added to the waste container, after the urea-formaldehyde has solidified, in order to bind any free-standing water present after solidification [6.1]. Other materials, such as plasticizers, could be used to modify the characteristics of the solid.

## 6.3. Solidification Processes Using Urea-formaldehyde

Differences in urea-formaldehyde processes principally involve the manner of mixing the waste, UF resin, and finally the catalyst. Thorough mixing is

regarded as crucial for proper solidification of waste forms because the low viscosity of the UF resin would otherwise allow differential settling of solids. As with cement, both in-container and in-line mixing processes are available. The in-container processes are best suited to incorporate resin beads into the waste form, while in-lining mixing is better suited for liquid wastes [5.5].

### 6.3.1 In-container Mixing

In-container mixing is carried out in standard 55 gallon drums, or more commonly, in large carbon steel liners with volumes of 50-300 cubic feet. Mixing may be accomplished by a disposable paddle which is lowered into a drum, spun as the components are added (catalyst last), and then left in the solidifying mass. Another approach is to place a disposable air sparger at the bottom of the container and, as the components are added, to pump air through the sparger piping. Small holes in the pipe allow air to bubble up, mixing the liquid. The sparger is also left in the waste form.

In-container systems are provided industrially as both installed and portable units. Portable units are operated by Chem-Nuclear Systems, Inc. (CNSI) and by Hittman Nuclear and Development Corporation (HNDC) [6.6]. These systems are built into a housing that is easily transportable by truck and can couple to the waste storage system of the plant. Mobile systems of this type appear to have gained in popularity among the nuclear power industry for a variety of reasons. Among these are: production of waste either beyond the capacity of the installed system at the plant, lack of an installed system, or inoperative/unsuitable installed system [6.5].

### 6.3.2 In-line Mixing

In-line mixing of urea-formaldehyde is a process that is similar to that of cement, although the equipment requirements are considerably simpler because the UF is a low viscosity liquid [6.5]. The principal difference between the cement and UF system is the type of mixer used. UF can be blended with waste in a static mixer which contains no moving parts; the two fluids are mixed as they flow past stationary blades. Figure 6.1 shows a flow chart for an in-line continuous mixer system of United Nuclear Industries. Note that the catalyst is added last in order to allow time for complete mixing and prevent solidification in the process equipment. Once it is added, the waste form should start to gel within a few minutes.

## 6.4 Urea-Formaldehyde Waste Form Characterization

### 6.4.1 Chemical Compatibility of Wastes

The chemical compatibility of generic waste types with urea-formaldehyde is shown in Table 6.1. Sulfate wastes, such as those generated by regeneration of ion exchange resin wastes, can interfere with urea-formaldehyde polymerization. The incorporation of less than 10 wt% sulfate in the final product or the addition of calcium chloride to the waste has been reported to reduce this problem [6.4]. Difficulties have been encountered for the solidification of detergent solutions and complexing agent wastes, as well as with oils and organic liquids which are not miscible with water. Alkaline wastes can be solidified, but only after they have been pretreated to adjust pH (and hence at reduced efficiency).

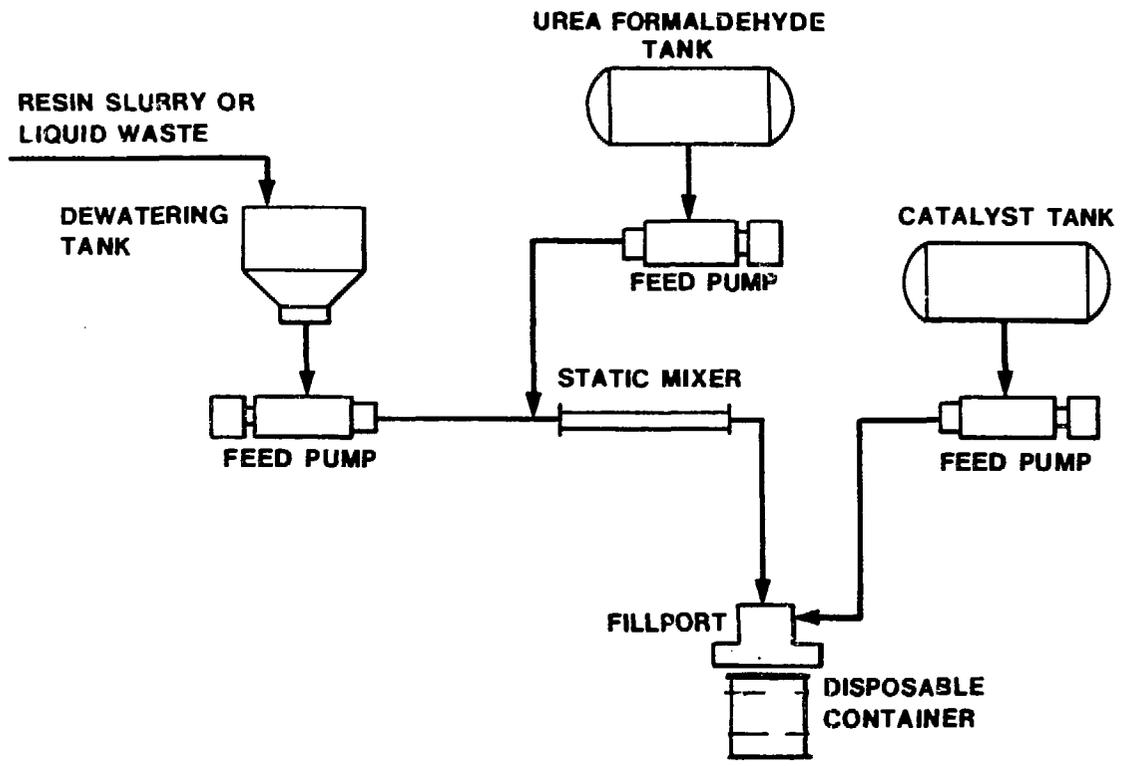


Figure 6.1. Schematic of an in-line urea-formaldehyde system by UNI.

#### 6.4.2 Free-Standing Water

As mentioned previously, urea formaldehyde gained rapid acceptance primarily as a result of the processing advantages it presented over competing cement systems. The resultant urea-formaldehyde waste form also met existing solidification requirements. However, problems have been encountered with unsolidified liquids, so-called free-standing water. Free-standing water in UF waste forms is typically acidic and corrosive toward the waste container.

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TABLE 6.1

#### Chemical Compatibility of Wastes with Urea-Formaldehyde

<u>Waste Type</u>	<u>Urea-Formaldehyde Waste Compatibility</u>
Ion exchange resins	good
Sludges	good(a)
Boric acid wastes	good
Sulfate wastes	poor-fair
Detergent solutions	poor
Complexing agent wastes	poor
Oils	poor
Organic liquids	poor
Acidic wastes	good
Alkaline wastes	poor-fair(b)
Large items	good

---

(a) good if pH is well controlled  
(b) require treatment to adjust pH

---

Urea-formaldehyde waste forms retain liquid wastes as small droplets physically held within the solidified matrix. However, after the waste form has solidified there is often a significant amount of drainable free-standing water. This is water and waste liquids that are not bound either chemically or physically in the solidification matrix. While the majority of this water typically comes from the waste itself, some additional water is produced as a result of the condensation polymerization reaction that occurs during solidification. Free-standing water may increase in volume with time. A complex relationship between the percentage of free-standing water and the  $H_2O/UF$  ratio was observed, as shown in Figure 6.2, which is also related to shrinkage of the waste form [6.4]. High percentages (as much as 26%) of free-standing water were observed for the solidification of some wastes in urea-formaldehyde. The quantity of free standing water is generally minimized by the addition of sufficient acid catalyst to produce a UF-waste mixture pH of  $1.5 \pm 0.5$  [6.4]. Among the factors affecting the generation of free-standing water are: the percentage of water in the waste and percentage of waste in the matrix, type of waste, and the amount of catalyst used.

The free-standing water is acidic with a pH approximately equal to that of the UF-waste mixture after acid catalyst addition (pH  $\sim 2$ ). The activity content and concentration in the free-standing water is typically the same as that in the input waste stream. General corrosion rates as high as 10 mil/year were observed for exposure of mild steel to free-standing water [6.4]. Both general and non-uniform (pitting) corrosion occurred. The rate was dependent upon the waste type. Corrosion in contact with a urea-formaldehyde waste form was typically lower.

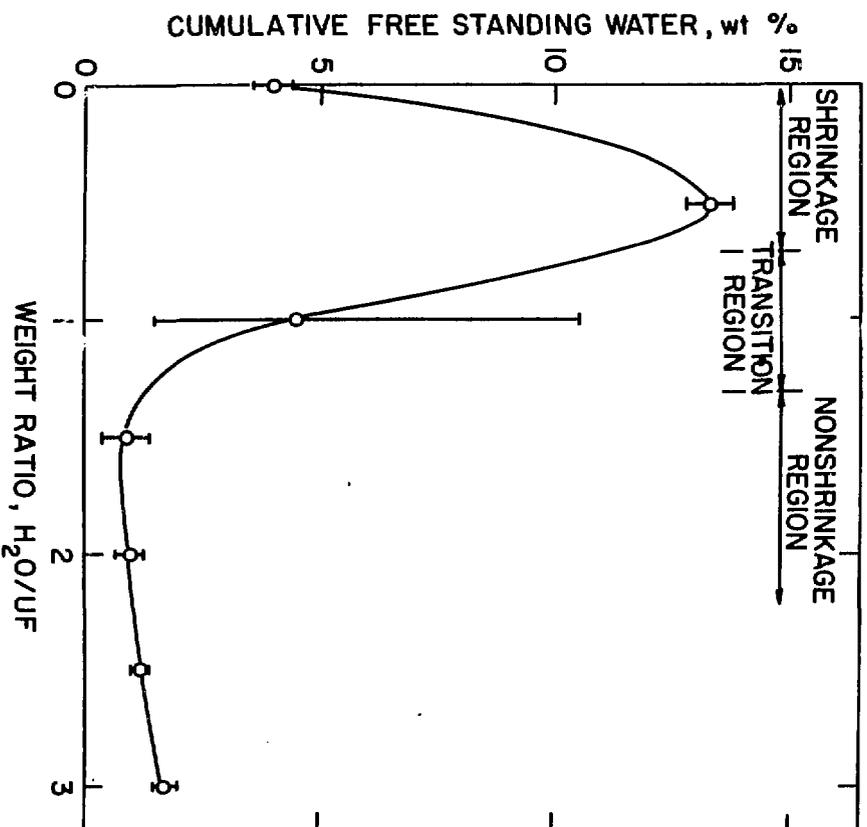


Figure 6.2. The % weight of free standing water is plotted against the ratio of water to UF.

### 6.4.3 Leachability

Cumulative fraction releases for leach tests performed on (2.5 cm diameter x 5.1 cm) urea-formaldehyde waste forms are shown in Figure 6.3 for  $^{60}\text{Co}$ ,  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$  [6.6].

The leach rates, are typically reported to vary from  $10^{-1}$  to  $10^{-2}$  g/(cm<sup>2</sup>)(day) [6.2, 6.4]. These rates are generally higher than those measured for other types of waste forms. As with other binders, the leach rate varies for different nuclides. The type of leachant also affects the leach rate. Figure 6.4 illustrates the differences in cumulative fraction release from a UF waste form using saltwater, distilled water and tapwater leachants. The differences here are similar to the differences observed among nuclides leached. The waste type and waste/UF ratio also affect the leach rates.

While proprietary additives have been reported as effective in decreasing leachability, this has not been confirmed. Such additives are not in routine use for LLW solidification. Leach rates were not influenced by the mechanical strength of the samples [6.7].

Gamma irradiation also increases waste form leachability as shown in Figures 6.5 and 6.6 for release of  $^{137}\text{Cs}$  and  $^{85}\text{Sr}$  respectively. The threshold of this effect appears to be about  $10^6$  rads.

### 6.4.4 Mechanical Strength

Compressive strengths of urea-formaldehyde waste forms are dependent on the type of waste incorporated and the waste/UF ratio. Density has little effect. Compressive strengths ranged from  $61 \pm 22$  psi to  $387 \pm 53$  psi for a range of reactor waste types [6.4]. The highest strengths were achieved with BWR precoat filter cakes. Typically, urea-formaldehyde resin alone has a strength of about 700 psi. Prolonged drying also reduces the strength of the waste form [6.7]. The impact strength of UF waste forms varies depending upon

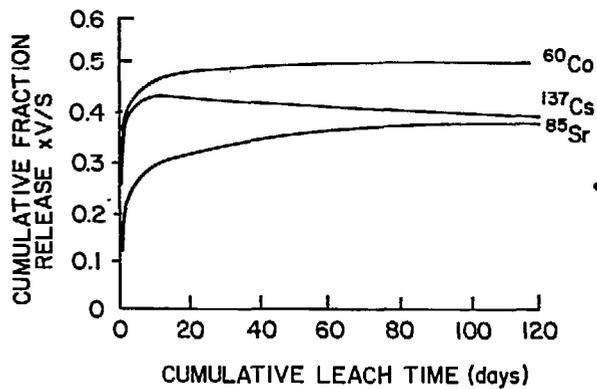


Figure 6.3. Cumulative fraction releases for <sup>60</sup>Co, <sup>85</sup>Sr and <sup>137</sup>Cs from UF waste forms.

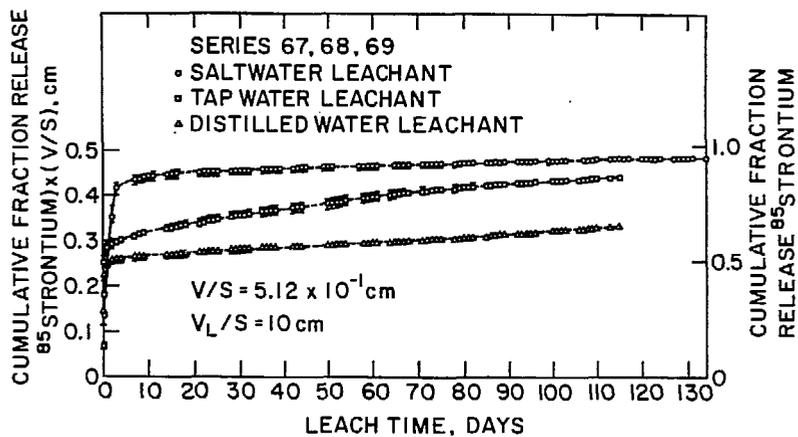


Figure 6.4. Cumulative fraction release for <sup>85</sup>Sr with varying leachants.

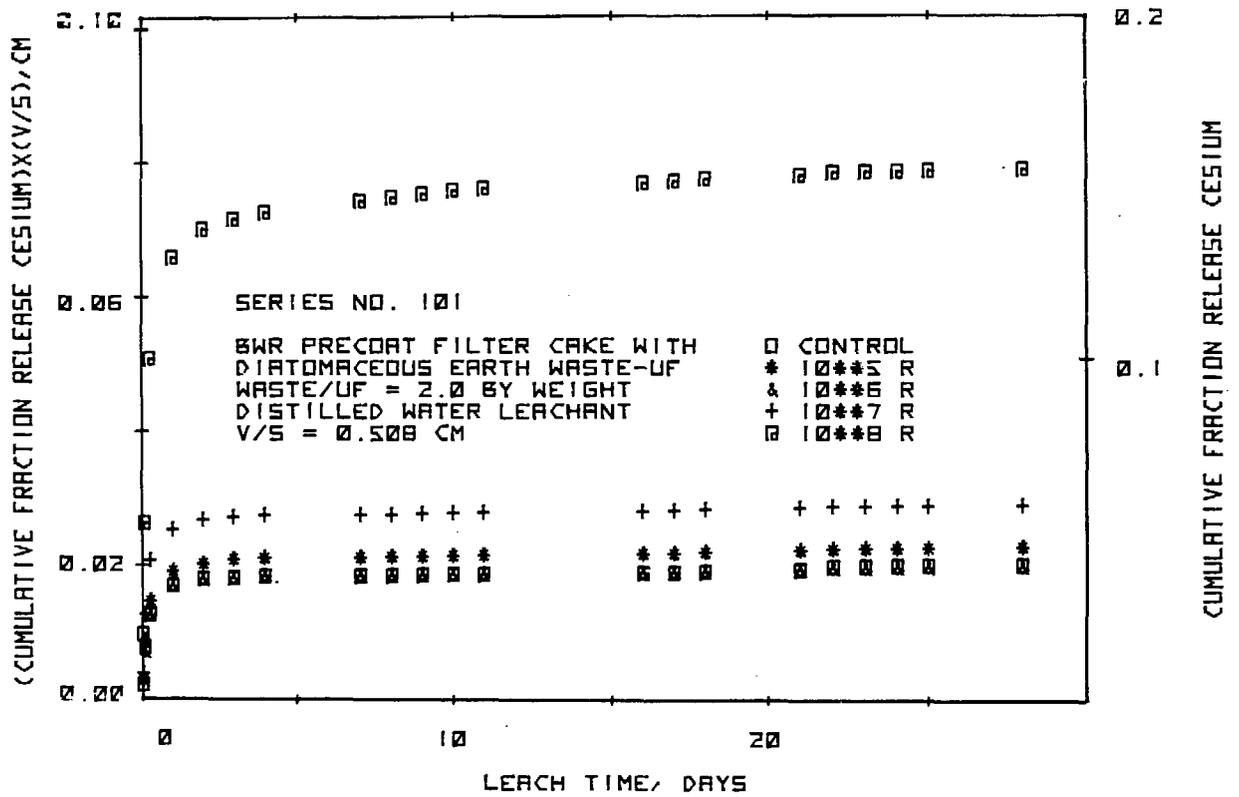


Figure 6.5. The effect of varying doses of <sup>60</sup>Co irradiation of the leachability of <sup>137</sup>Cs.

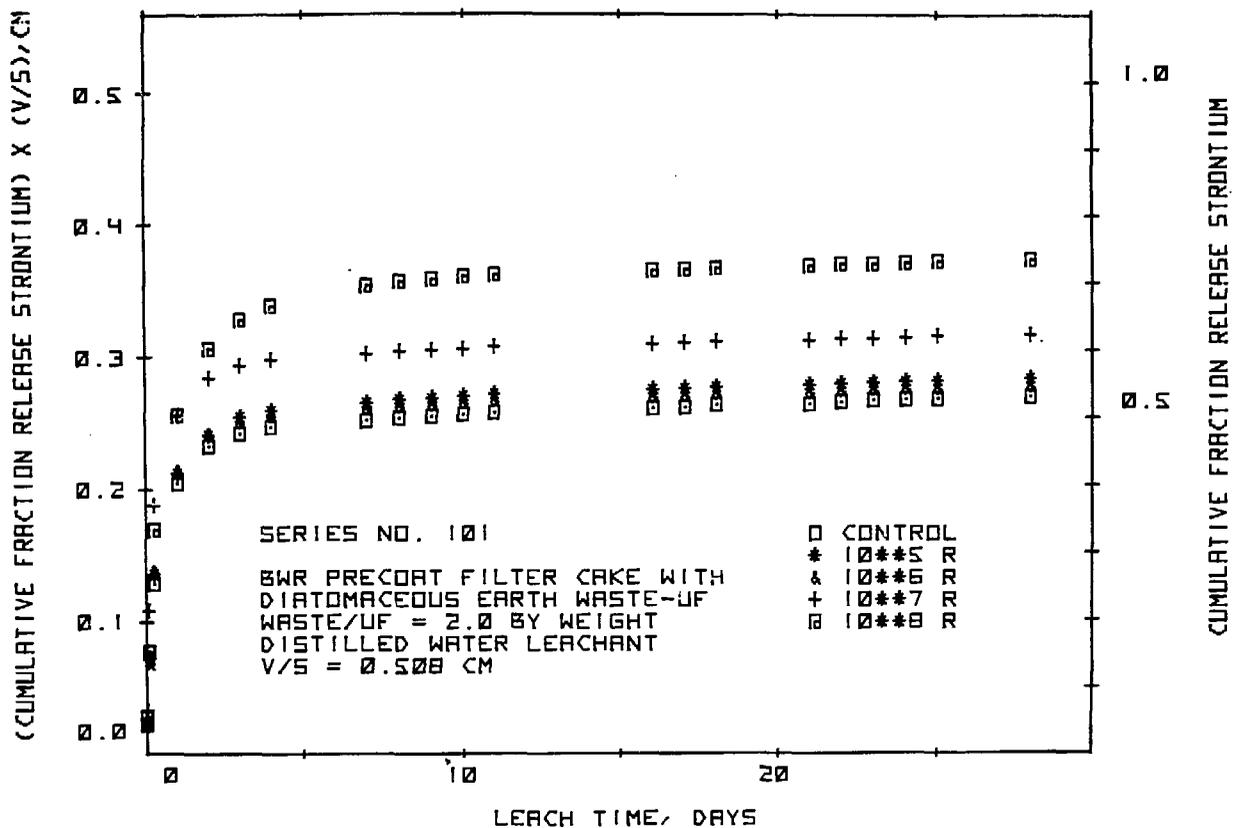


Figure 6.6. The effect of varying doses of  $^{60}\text{Co}$  irradiation on the leachability of  $^{85}\text{Sr}$ .

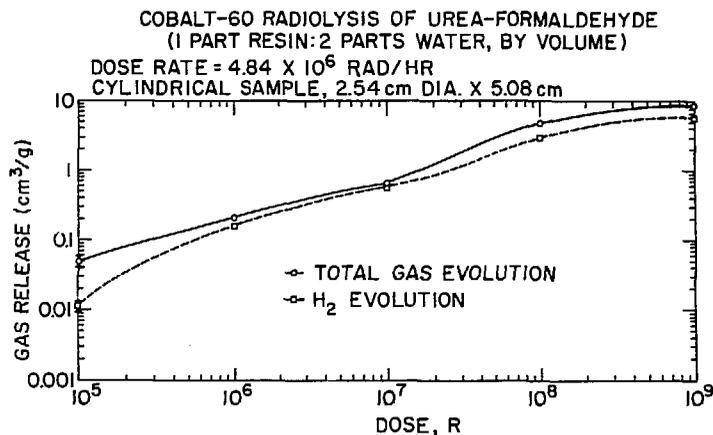


Figure 6.7. Radiolytic gas evolved from  $^{60}\text{Co}$  irradiation of a urea-formaldehyde waste form.

waste type and loading. Particle size distributions for particulate generated under impact have been reported for urea-formaldehyde waste forms [6.8].

#### 6.4.5 Radiation Stability

Doses of  $3 \times 10^6$  rads can cause mild to moderate radiation damage, while doses of  $2 \times 10^7$  rads can cause moderate to severe damage [6.6]. Inclusion of cellulose fillers in urea-formaldehyde waste forms increases the susceptibility of the material to radiation damage. Excessive exposure to gamma radiation will cause the form to become brittle, blister, swell and crumble [6.2]. Radiolytic evolution of gas can occur in urea-formaldehyde and is dependent on the amount and type of waste solidified. Figure 6.7 shows the volume of gas generated as a function of radiation exposure [6.4].

#### 6.4.6 Thermal Stability

Upon exposure to flame, urea-formaldehyde is a self-extinguishing material. The surface of the solid contains large proportions of water. When exposed to fire the water evaporates and the surface chars forming an insulating layer which produces carbon dioxide as the UF begins to decompose. Weight losses, upon burning, of less than 10% were attributed principally to loss of water [6.4].

Thermogravimetric analysis has demonstrated that rapid weight loss occurs first between  $100^{\circ}\text{C}$  and  $150^{\circ}\text{C}$  due to evaporation of water, and again at  $290^{\circ}\text{C}$  when the resin begins to decompose [6.4]. Water from urea-formaldehyde waste forms is also released by drying in air. Figure 6.8 shows the percentage of initial weight as a function of time for urea-formaldehyde samples exposed to air at  $20^{\circ}\text{C}$  and 50% relative humidity. These specimens were cylinders, one inch in diameter and two inches in length ( $V/S = 0.51 \text{ cm}$ ). During such drying, the waste form loses weight, decreases in density, becomes more brittle, and also has lower compressive strength.

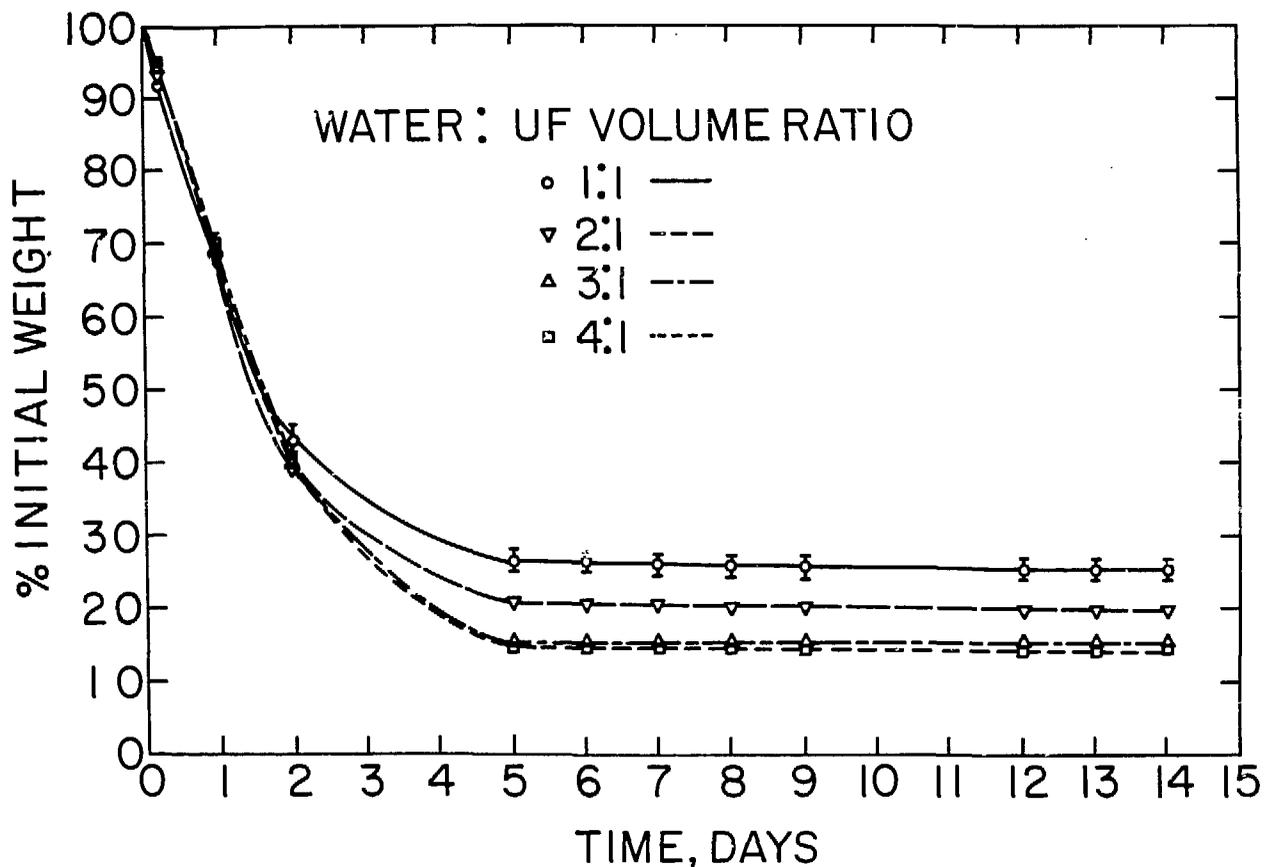


Figure 6.8. Percentage of initial weight plotted against time for UF samples exposed to air.

### 6.5 Advantages and Disadvantages

Table 6.2 presents the advantages and disadvantages associated with the solidification of waste with urea-formaldehyde. The major disadvantage to use of this material is the free-standing water which often occurs. This problem is leading to the disuse of urea-formaldehyde as a low-level waste form.

Table 6.2

Advantages and Disadvantages of Low-Level Waste Matrices  
Urea-Formaldehyde

Advantages	Disadvantages
1. Material and technology well known	1. Occurrence of free standing water
2. Additives may be used to fix certain nuclides or increase strength	2. Free standing water is acidic-can corrode container
3. Simple equipment requirements	3. Incompatible with some wastes, e.g.: organic liquids, detergents
4. Material cost is moderate	4. Limited shelf-life
5. Ease of working with liquid components	5. Mixing must be thorough in order to assure no differential settling
6. Relatively high waste loading	6. Vapor is a concern during storage and processing
	7. Water loss due to evaporation
	8. Relatively high leachability
	9. Relatively low compressive strength

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## 7. POLYESTER TYPE POLYMER SYSTEMS AS AGENTS FOR LOW-LEVEL WASTE SOLIDIFICATION

Polyester type resins have been investigated for low-level waste solidification. One such system is coming into use as a mobile unit at nuclear power plants.

### 7.1 Description of Polyester Type Resins

Polyester resins are thermosetting polymers and are part of a large group of materials that are the products of the condensation reaction between a polyhydric alcohol and a polybasic acid [7.1]. Polyester resins are liquids at room temperatures that, with the proper initiators, accelerators and conditions (e.g., temperature) will polymerize, forming a hard solid. These are thermosetting polymers and cannot again be liquified without destroying the material. Many of the liquid monomers present some handling problems prior to solidification due to vapor and fire hazards. Polyester resins can be made water extensible, that is, they can form an emulsion with water in the waste (solute) under high shear mixing. After addition of the appropriate catalyst/promoter the solvent (polyester resin) can solidify, physically immobilizing the water in a small closed cell structure within the solidified matrix. Waste solids are physically entrapped in the polymer matrix. Other polyester resins are appropriate only for the solidification of dry solid wastes. Vinyl esters are typically diluted with 40-50 wt% styrene in order to reduce the viscosity of the monomer. Aqueous wastes are introduced into water extensible vinyl ester-styrene under high shear mixing in order to form an emulsion with water in the waste. Polymerization is induced at room temperature by use of a catalyst-promoter addition. The promoter serves to cause the catalyst to decompose at room temperature and induce polymerization. Benzoyl peroxide

catalysts alone decompose and produce free radicals only at elevated temperatures ( $\sim 50^{\circ}\text{C}$ ). Some low temperature polymerization catalysts are available but then they tend to be unstable and are more difficult to use than the catalyst/promoter system. Some wastes may interact with the catalyst or promoter, necessitating increased additions of these materials. Wastes in the pH range of 2.5 to 10.5 can be solidified with the vinyl ester-styrene marketed by Dow Chemical Company, although some wastes, such as boric acid, may require pretreatment [7.1, 7.2]. Vinyl esters are relatively resistant to chemical attack because of the double carbon bonds at each end of the chain [7.1]. Crosslinking takes place only at the ends of the molecule, thereby producing a polymer which can elongate under stress [7.1].

Other polyester or polyester-styrene resins do not form an emulsion with water and are unsuitable for the solidification of aqueous wastes. They can however, be used to solidify solid wastes.

## 7.2 Additives

Additives such as those described in Section 3.1 could be incorporated into polyester waste forms to inhibit leaching of radionuclides. More typically, additives are used to precondition waste, for instance by adjusting the pH, before being mixed with the solidification agent.

## 7.3 Solidification Processes Using Polyester Resins

### 7.3.1 Vinyl Ester-Styrene (Dow Chemical Company)

Dow Industrial Services, a division of Dow Chemical Company, Midland, MI, has developed a system to solidify low-level radioactive waste using a vinyl ester-styrene which can form an emulsion with aqueous wastes. This material is the only thermosetting polymer, other than urea-formaldehyde,

that has been employed in industry. This system has recently (Sept., 1980) come into regular industrial use at the Quad-Cities (Cordova, Ill.) power plant where eight 50 ft<sup>3</sup> liners have been processed. Previous experience consisted of a variety of full-scale demonstration projects at power plants in the USA and Japan and some work at the Three Mile Island cleanup. Systems are currently being installed in other plants.

The waste form containers, either 55 gallon drums or 50 ft<sup>3</sup> liners, are first filled with a predetermined volume of binder. Each is then conveyed to the filling position where a measured volume of waste, which previously had been blended or pretreated if necessary to suit the process, is added at a predetermined rate to the binder. High shear mixing is performed in the container to form an emulsion of the liquid waste within the binder. Care must be taken to attain the proper waste/binder ratio in order to avoid "breaking" the emulsion. Appropriate catalyst and promoter additions are also made, in a specific sequence, to the binder or to the waste-binder emulsion. The waste form solidifies at room temperature in about an hour [7.3]. Progress of the solidification process is monitored at a station where the exothermic heat evolved (60-70°C) and resistance to penetration are measured by remote probes. The nominal solidification rate is 3 gallons per minute of radioactive waste, filling six 55 gallon drums in an hour. Figure 7.1 is a schematic of the process [7.3].

### 7.3.2 Water Extensible Polyester

A similar method for encapsulation of wastes in a polyester-waste emulsion was developed to the prototype stage at Washington State University

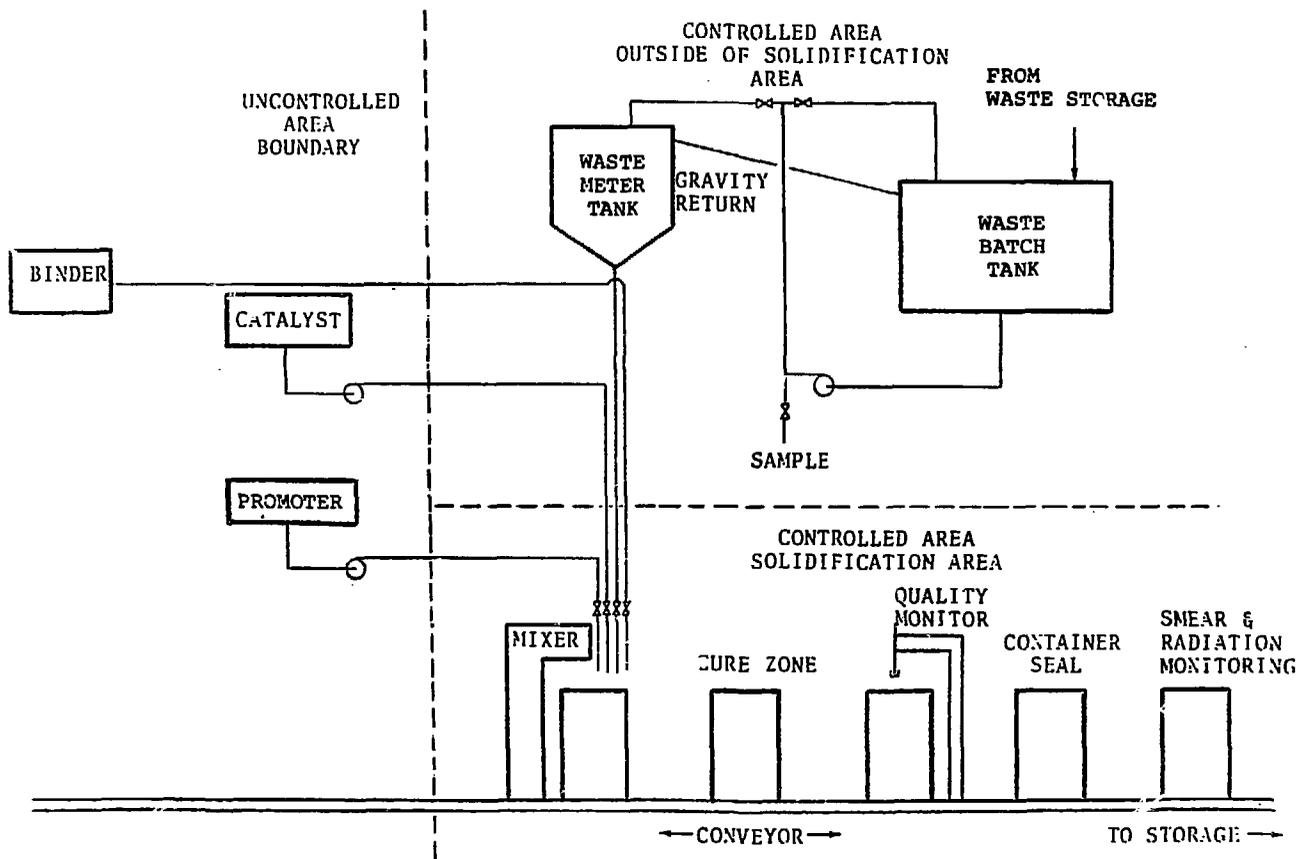


Figure 7.1. A schematic of the Dow process.

[7.4, 7.5, 7.6]. In essence, this method is similar to the Dow Chemical process and also employs the concept of high shear mixing of waste in a polyester resin in order to produce closed cells containing the waste within a matrix of the polymer. However, an in-line rather than in-container mixer is used. This process also employs a different polyester resin than the Dow process.

### 7.3.3 Polymer Concrete

Another system utilizing polyester type resins is the polymer-concrete (PC) system. Polymer-concrete was developed at Brookhaven National Laboratory as a means of solidifying dry wastes and liquid wastes absorbed on a solid substrate. Polymer concrete is a composite formed by mixing dry waste solids with a monomer and then polymerizing the monomer. The monomer systems typically used are a mixture of 70% styrene and 30% divinylbenzene, methylmethacrylate or polyester-styrene. Polymerization is generally achieved through addition of a catalyst but additional polymerization and crosslinking may be provided by heat or irradiation. Between 10 and 50 wt% of the total waste form is comprised of the monomer, with 20% being commonly used. Bulk volume increases after addition of the monomer are generally small or negligible and can be produced in two ways. The monomer, catalyst, promoter, additives and the waste can be blended in a mixer and then poured into the waste container. High shear mixing is not required, since the process does not rely on emulsion formation. Simulated Idaho Falls  $Al_2O_3$  and  $ZrO_2$  calcine wastes were solidified in polymer-concrete using a styrene monomer with 1 wt% benzoyl peroxide as a catalyst, and 2.5 wt% divinylbenzene to induce crosslinking between the polymer chains [7.7]. Extensive crosslinking forms a network which renders the polymer hard and inelastic [7.3].

Another method of producing polymer-concrete waste forms simply entails filling a waste container with the dry waste and then pouring the monomer-catalyst mixture into the container. This method works best if the dry waste is coarse grained, allowing the fluid to easily flow into the pore spaces. If the waste is very fine grained, the penetration of the fluid through the waste may be poor or an air bell may form inhibiting thorough penetration of the monomer. This problem can be overcome by introducing the fluid, through a fitting, into the container from the bottom. A gravity feed from an elevated tank provides more complete saturation of the waste with the monomer. Vacuum or pressure techniques could also be applied. Little increase in bulk volume results.

#### 7.4 Waste Form Characteristics

##### 7.4.1 Chemical Compatibility

Vinyl ester-styrene waste forms are compatible with most wastes. It is imperative, however, that the waste be of an acceptable pH, otherwise a stable emulsion may not be formed. Other wastes, such as boric acid concentrates, require pretreatment to provide an acceptable waste form. Some wastes may interact with the catalyst and/or promoter and thus require increased catalyst/promoter additions or modification of the order of addition. Waste to binder ratios from 1.5 to 2.0 are typically recommended for various waste types.

Data on the chemical compatibility of polymer concrete are limited. The chemical compatibility of wastes for the PC system should be similar to that for water-emulsion systems. However, solidification in PC does require that the waste be either dry or that it bear water as a stable solid containing absorbed water. This process cannot accommodate significant quantities of unbound water.

#### 7.4.2 Leachability

Leaching studies have been carried out by the Dow Chemical Company and by Brookhaven National Laboratory for vinyl ester-styrene waste forms. The latter samples were prepared to Dow Chemical specifications, and as such should simulate products of their system. Figure 7.2 presents the leachability for  $^{60}\text{Co}$  and  $^{137}\text{Cs}$ . As with most other waste forms, the leachability varies from nuclide to nuclide and with different types of waste [7.8]. The effect of prior heating at  $538^{\circ}\text{C}$  for ten minutes on the leachability of vinyl-ester styrene is shown in Figure 7.3 [7.9]. Heating resulted in an acceleration of initial leaching of  $^{137}\text{Cs}$ ; however, the overall cumulative fraction leached began to approach that of the control after 90 days [7.9].

Cumulative leachability of sodium from the Washington State University polyester waste forms has been reported to be approximately 0.2% (at 50 wt% loading) after 6 months. At loadings of 70 wt% the cumulative leaching was about 2% [7.4].

Experiments have been performed at BNL to observe the leachability of  $\text{NaNO}_3$  and cesium from polymer-concrete and to determine the effect of additives on these waste forms. The results are shown in Fig. 7.4 for  $\text{NaNO}_3$  leaching and in Figure 7.5 for cesium. These specimens were 2.5 cm diameter x 5.1 cm long. The polyester-styrene (PS) and the polymethyl methacrylate (PMMA) waste forms exhibited fraction releases of about 0.20 and 0.24  $\text{NaNO}_3$ , respectively, achieving an equilibrium leach rate very rapidly. The difference in leachability between the two waste forms is believed to have been the product of the packing of  $\text{NaNO}_3$  crystals during preparation of the samples. This high initial release was due to dissolution of  $\text{NaNO}_3$  exposed at the surface of the waste form which was not well encapsulated by the resin. Addition

LEACH TEST RESULTS FOR NUCLEAR POWER PLANT  
PWR WASTE AT 1.50/1.0 WASTE/BINDER RATIO

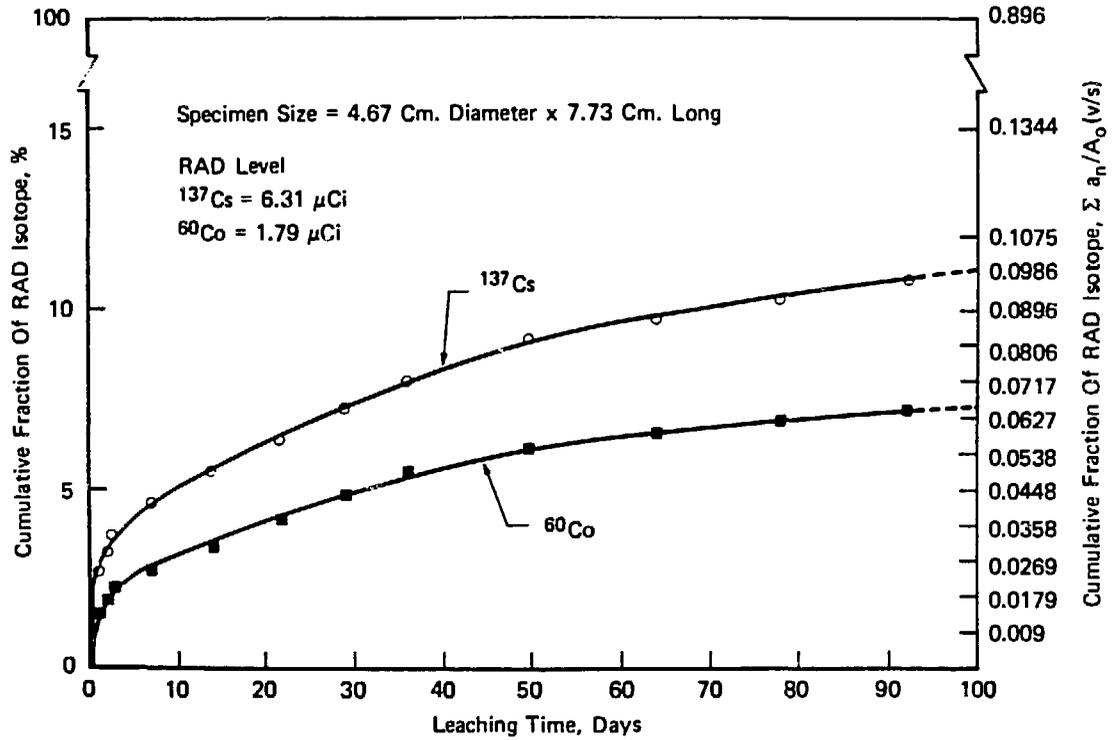


Figure 7.2. Fraction release of  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  from evaporator sludge solidified in vinyl ester-styrene.

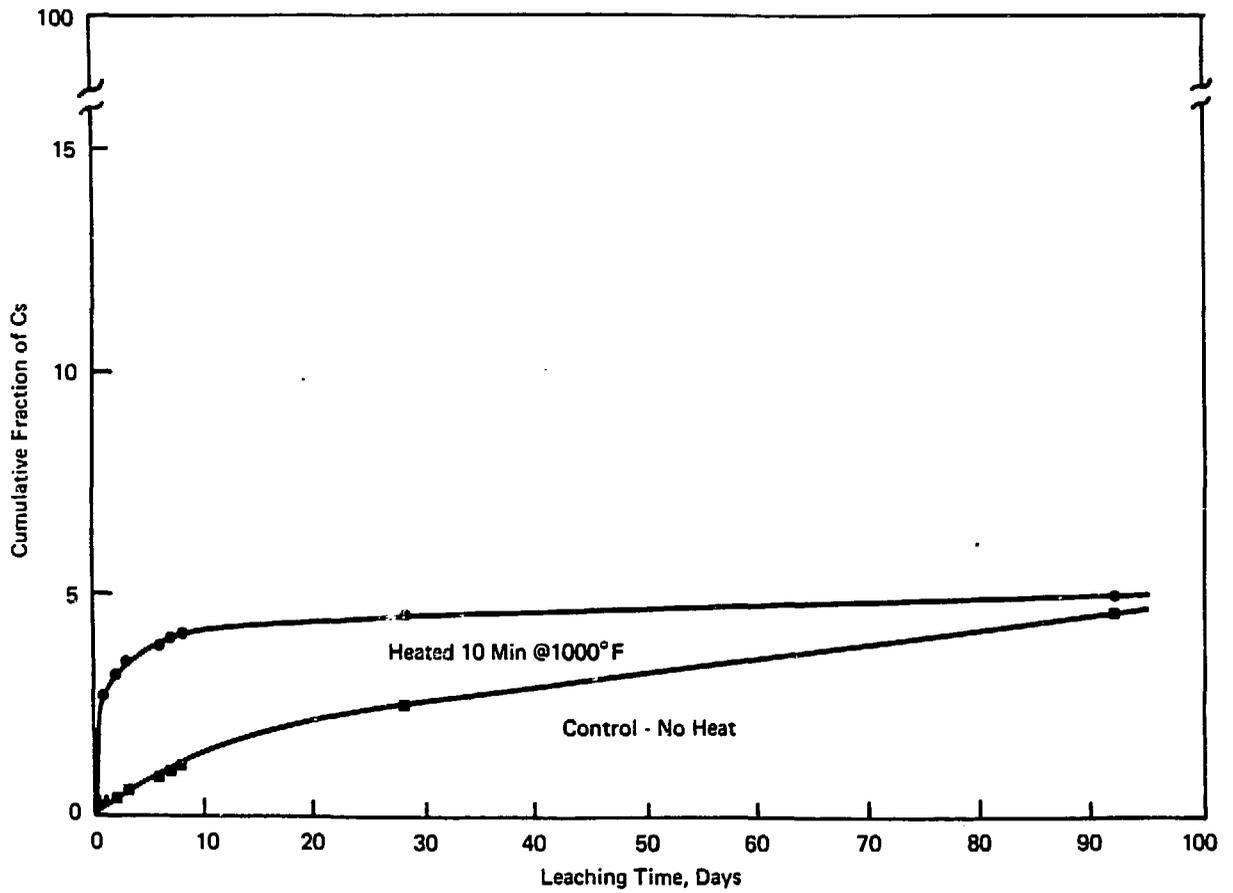


Figure 7.3. Cumulative fraction release of Cs showing the effect of heating the waste form to 1000°F (538°C) for 10 minutes.

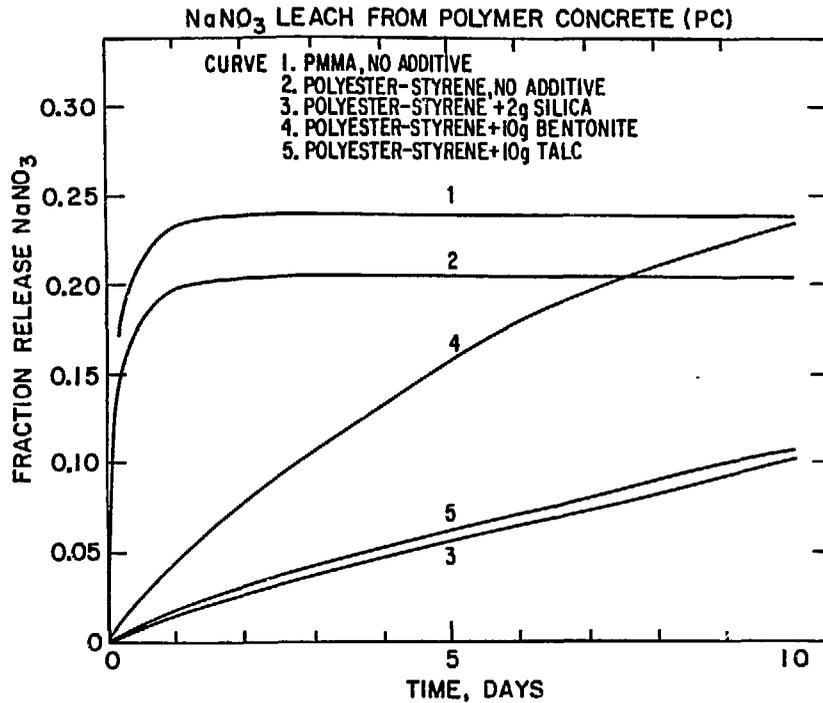


Figure 7.4. Fraction release of NaNO<sub>3</sub> from a polymer concrete containing various additives.

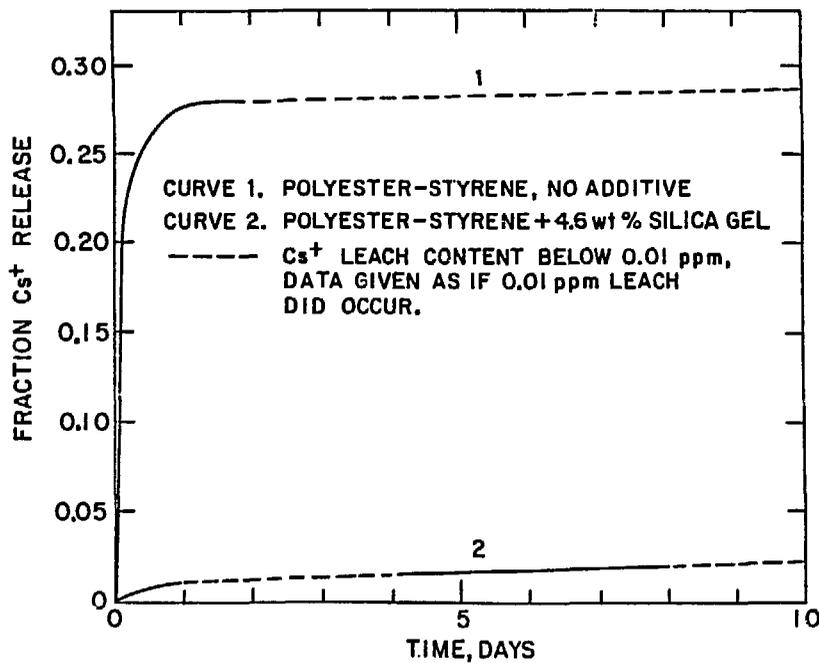


Figure 7.5. Fraction release of Cs from a polymer concrete with and without silica gel added to retain cesium.

of ion sorbers (silica, talc and bentonite) to polyester-styrene significantly decreased the initial rate of leaching (talc and silica samples especially). These samples had not yet equilibrated after 10 days. They reached a fraction release of 0.10 in that time. The additives however are believed, in the case of  $\text{NaNO}_3$ , to act as absorbents of the water, thus slowing the initial leachability but perhaps not affecting the long term leaching. Coating the polymer-concrete composite with polyester-styrene resin (0.15-0.25 mm thick) was found to reduce the fraction release to non-detectable levels.

Cesium release was also measured. The fraction release for this ion in PMMA waste forms was 0.13-0.14 over 10 days; in PS it was 0.29; in PS with silica, bentonite or talc added, the cumulative fraction releases, respectively, were 0.015-0.023, 0.0090-0.015, and 0.072-0.030. This demonstrates significant retention of cesium. These samples had reached equilibrium [7.10].

Polymer concrete was also tested for leachability of  $\text{NaNO}_3$  from  $\text{Al}_2\text{O}_3$  calcine. The fraction release observed was 0.03-0.04 for non-irradiated samples, and about 0.02 for samples irradiated to  $2.5 \times 10^9$  rads. In this case, the calcine absorbed 38% of the styrene monomer; the remaining monomer filled the pore spaces between calcine particles, producing a waste form with a particularly low leachability [7.10].

#### 7.4.3 Mechanical Strength

The compressive strength of vinyl ester-styrene specimens with varying water to binder weight ratios was measured at Brookhaven National Laboratory [7.7]. The material failed in a brittle manner. Droplets of water were observed on the shattered pieces, apparently squeezed from the waste form. The compressive strengths for waste forms having 1.0, 1.5 and 1.9 water/binder ratios by weight were 2900, 2100 and 1300 psi respectively.

Compressive strength tests were made with polymer concrete (polystyrene-divinylbenzene) waste forms containing  $\text{NaNO}_3$  waste [7.11]. A rapid loss of strength occurred about  $121^\circ\text{C}$ . Upon substitution of silica sand for the  $\text{NaNO}_3$  the loss of strength was significantly less pronounced.

#### 7.4.4 Radiation Stability

Experiments carried out by the Dow Chemical Company showed that their vinyl ester-styrene binder is relatively stable with regard to radiation effects. Figure 7.6 illustrates the cumulative fraction release of  $^{137}\text{Cs}$  plotted as a function of time for a variety of radiation exposures. Low exposures have no significant effect on leachability [7.12]. Exposures of  $4 \times 10^8$  and  $6 \times 10^8$  rads as much as tripled the leachability; however, this was still below a cumulative release of 5% in 100 days [7.12]. Similar doses had no effect on the leachability of  $^{60}\text{Co}$  [7.12].

The effect of irradiation on the compressive strength of the Dow binder was also studied (Figure 7.7). In general, there was an increase in both yield strength and maximum strength up to doses of about  $2 \times 10^6$  rads. The yield strength remains the same as the maximum strength is reduced and meets the yield strength at  $1.8 \times 10^7$  rads. At this point, the compressive strength of all vinyl ester-styrene waste forms began to drop. The initial increase in strength is the result of increased cross-linking of polymer chains induced by irradiation.

Polymer concrete specimens made with polystyrene containing 10% or 30% DVB were irradiated at  $1.2 \times 10^7$  rads/hr with  $^{60}\text{Co}$ . This irradiation caused heating of the center of the waste form to  $155^\circ\text{C}$ . These 3 inch diameter by 6 inch long cylinders received total doses of  $10^9$  rads. Extensive cracking occurred, presumably due to gas generation. This effect may be a consequence of the high radiation dose rate and hence of no concern for actual

<sup>137</sup>Cs Leach Test Results for Irradiated PWR Waste - 1.65/1.0 Waste/Binder Ratio

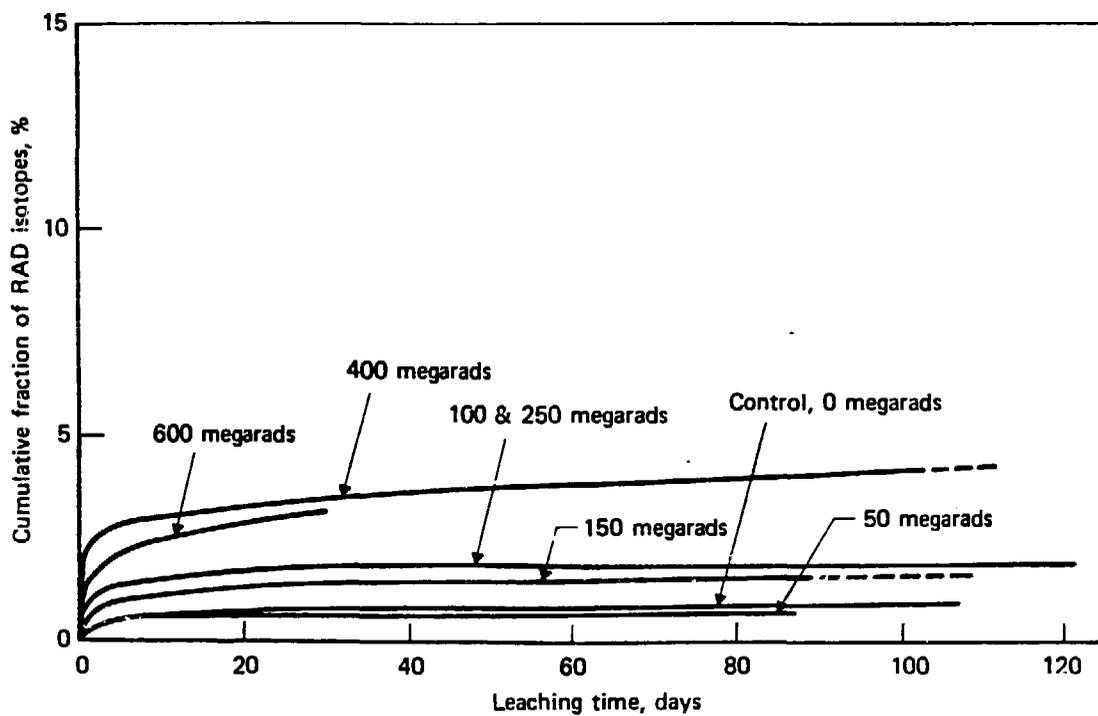


Figure 7.6. Fraction release as a function of irradiation dose.

EFFECT OF RADIATION ON SOLIDIFIED PWR WASTE  
- 1.65/1.0 WASTE/BINDER RATIO

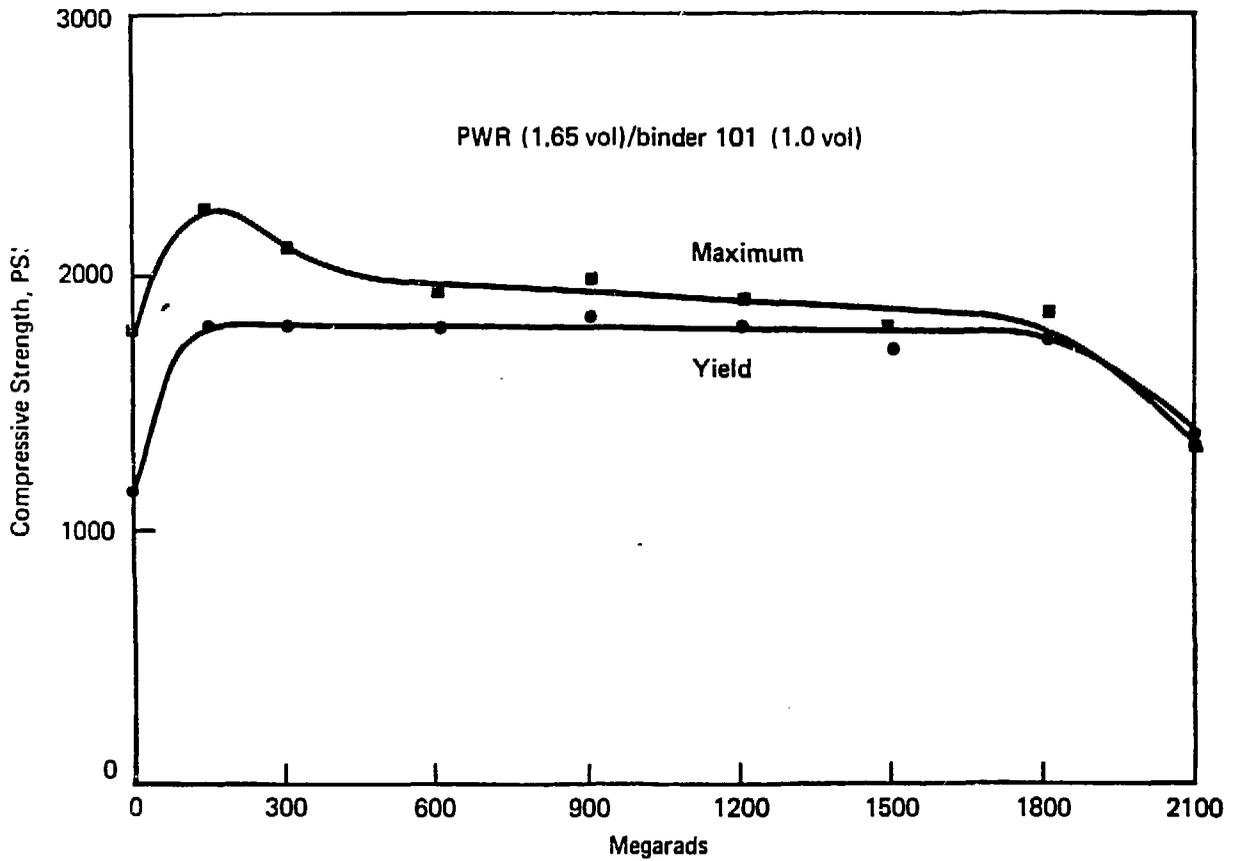


Figure 7.7. Compressive strength as a function of irradiation dose.

wastes. At high dose rates, the radiolytic production of hydrogen may exceed the rate at which it diffuses through the waste form. At more representative (lower) dose rates, such sample pressurization should not occur. An experiment designed to simulate the gamma heating effect of the irradiation experiment produced only slight discoloration of the samples upon heating at 150°C [7.13].

#### 7.4.5 Thermal Effects

Vinyl ester-styrene waste forms, upon exposure to burning fuel oil, will char and lose weight. They will not, however, sustain combustion [7.13]. Weight loss occurs due to evaporation of contained water and some polymer decomposition at the surface of the waste form. This water loss can occur at low temperatures as well, although at a much reduced rate.

Experiments have demonstrated that significant quantities of water are evaporated from solidified Dow material in ambient air. Figure 7.8 shows sample weight as a function of time for various water to binder ratios. These specimens were disks, 4.68 cm diameter and 1.20 cm thick ( $V/S = 0.40$  cm). Not surprisingly, the sample with the greatest water to binder ratio demonstrates the greatest weight loss; about 40% after 70 days [7.7]. This weight loss is much slower than that observed for urea-formaldehyde.

#### 7.5 Advantages and Disadvantages

Tables 7.1 and 7.2 present the advantages and disadvantages of polyester type polymers for the solidification of low-level waste. Table 7.1 is for the Dow process, while Table 7.2 considers polymer-concrete. Actual operating experience with the Dow process is somewhat limited. Polymer concrete has been made only on a laboratory scale in this country. Both have the advantages of the low leachability and high strength.

WEIGHT LOSS VERSUS TIME IN AMBIENT AIR FOR DOW  
SOLIDIFICATION AGENT SPECIMENS (72° F, 57% RH)

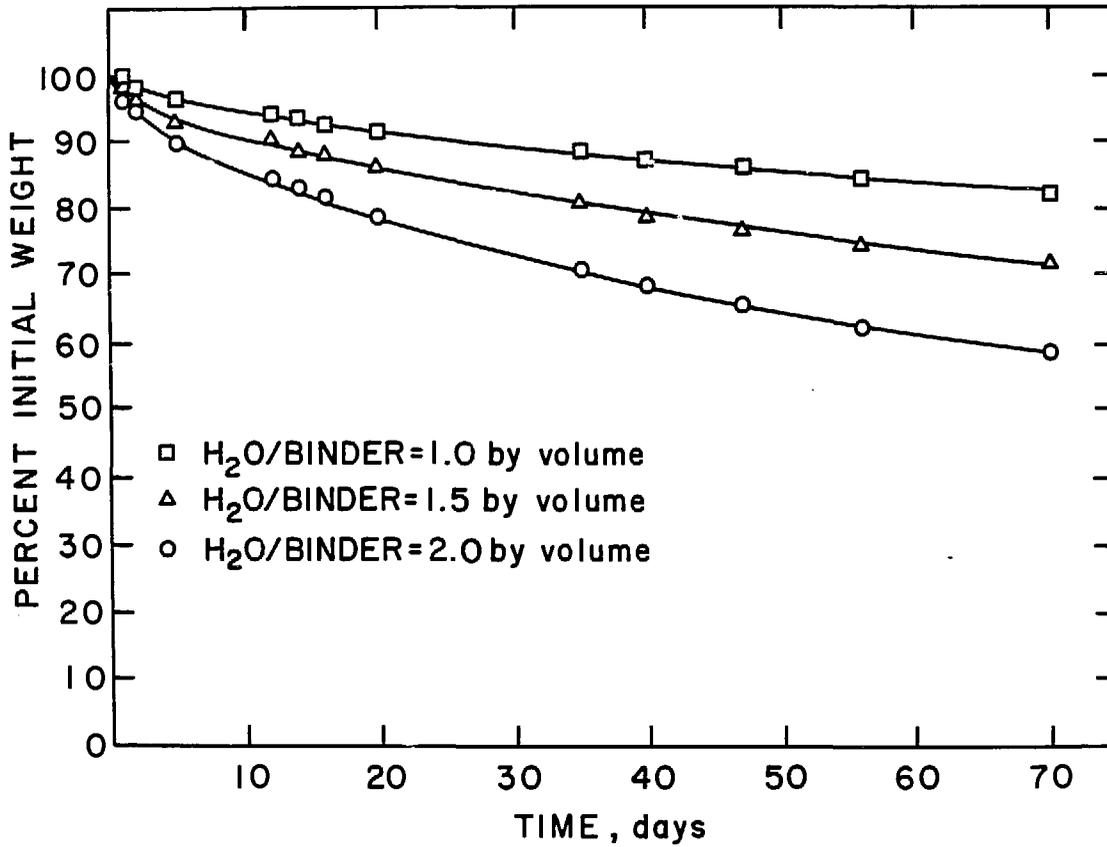


Figure 7.8. Sample weight as a function of time for three samples at various water to binder ratios.

Table 7.1  
 Advantages and Disadvantages of Vinyl Ester Styrene  
 Dow Process Solidification

Advantages	Disadvantages
1. Adaptable to many wastes-both solid and liquid	1. Limited binder shelf-life
2. No free-standing water	2. Hazards associated with the monomer, catalyst and promotor handling
3. Relatively low leachability	3. Some wastes may interact chemically and prevent/affect polymerization
4. High compressive and impact strength	4. Relatively expensive materials
5. Good radiation stability	5. Mixing method important
6. Ease of working with liquid components	
7. In-container mixing available	
8. Available in mobile systems	

Table 7.2

Advantages and Disadvantages of Polymer Concrete Solidification

Advantages	Disadvantages
1. High waste loading with negligible volume increase	1. Applicable only to dry wastes
2. Low leachability	2. Limited binder shelf-life
3. High compressive and impact strength	3. Hazards associated with monomer handling
4. No free standing water	4. Relatively expensive materials
5. Relatively insensitive to chemical nature of waste	5. Some wastes may interact chemically and prevent/affect polymerization
6. Simple process for combining waste and binder	6. Not commercialized to full-scale use

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## 8. EPOXY AS AN AGENT FOR LOW-LEVEL WASTE SOLIDIFICATION

United Technologies Corporation is developing a volume reduction/solidification process that utilizes epoxy resin as the waste form binder. Solidification in epoxy is one step of this integrated volume reduction and solidification process called the inert carrier process. This process also uses epoxy resin to remove waste solids from an inert silicone carrier. This system is discussed in the context of the process in which it is used, although viewed only in the solidification aspect, the resultant waste form is similar to the polymer-concretes described in a previous section.

### 8.1 Description of the Inert Carrier Process

The Inert Carrier Radwaste Process (ICRP) utilizes an inactive liquid silicone which is maintained at 150°C in the evaporator. As liquid radioactive waste is added to the heated silicone, the high turbulence and temperature of the fluid causes the water to evaporate instantly. The waste solids residue remains as suspended solids in the silicone carrier. With the addition of an immiscible epoxy monomer, the particulates are removed from the silicone carrier. The epoxy monomer-waste solids mixture then falls to the bottom of a separation column and is drawn off. A catalyst is added through a static mixer to induce polymerization of the epoxy monomer and the mixture is deposited into the waste container. The waste form cures in approximately 3 hours. There is no carryover of waste into the carrier which is reused, nor is there any accumulation of epoxy within the system. Figure 8.1 is a schematic of the ICRP System [8.1].

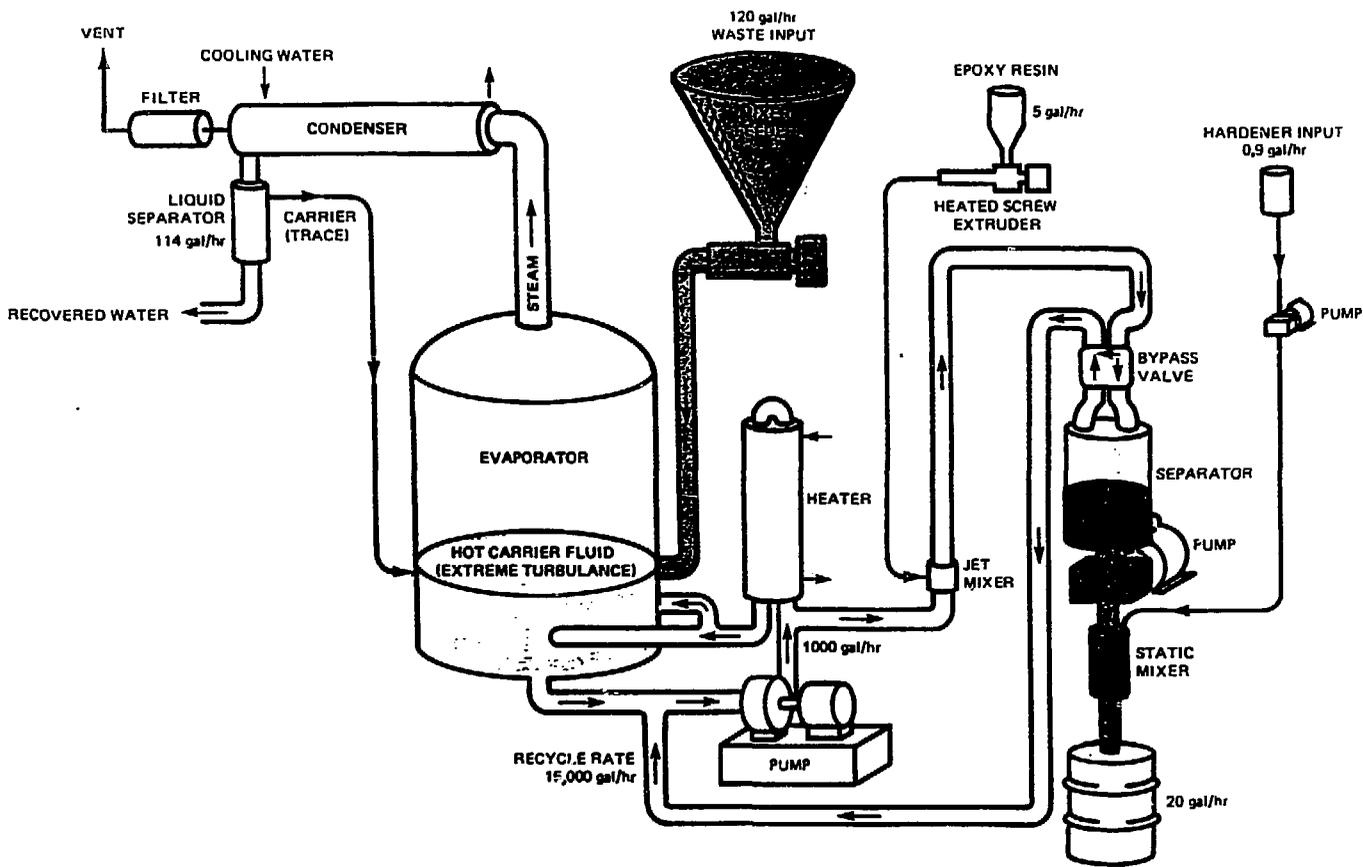


Figure 8.1. Schematic of the inert carrier process [8.1].

## 8.2 Waste Form Characteristics

There is little available data describing the characteristics of the waste form produced by this process. Tests run by United Technologies show leachabilities for waste forms containing 70 wt% dry  $\text{NaSO}_4$  in epoxy resin are less than 1% over a period of 7 days [8.1]. Tensile strengths of 3100 to 4200 psi were measured for similar waste forms. Upon exposure to a flame for 3 minutes, the material smoldered and then self-extinguished within one minute.

## 8.3 Advantages and Disadvantages

The principal advantages of the ICRP is the volume reduction for liquid wastes which is an integral part of the solidification system. A disadvantage of the process is its use of elevated temperatures.

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## 9. MINERALIZATION PROCESSES FOR LOW-LEVEL WASTE SOLIDIFICATION

A variety of mineralization processes have been developed, which fix radionuclides within a crystal lattice. These processes are generally not in use commercially, although silica polymerization of bulk industrial wastes has been developed commercially. While there is, in some cases, a great deal of literature involving the mineralogy and geochemistry of these materials, there is relatively little information specifically addressing their use for radioactive waste disposal. Most considerations for these processes are for high-level and industrial chemical wastes, but in many cases they could be suitable for specific low-level waste streams. The applicability of these processes is highly dependent upon the chemical composition of the waste streams.

### 9.1 Description of Waste Bearing Minerals

There are four principal processes which are considered in this section. Each has, to varying degrees, been experimented with as a solidification agent for radioactive wastes. The reactions in each process result in formation of new minerals. These minerals are, in every case, analogous to naturally occurring minerals although the particular salts within them may be found only in radioactive waste. The materials which enter into these processes are clay minerals and nitrates and/or hydroxides of sodium and aluminum. Aluminosilicate lattices are formed which can strongly retain waste salts forming feldspathoid minerals such as nepheline, sodalite and cancrinite, depending on the content and proportions of the input materials and waste.

## 9.2 Solidification Using Mineralization Processes

### 9.2.1 Clay Reaction Processes

Experiments at Atlantic Richfield Hanford Company [9.1] have resulted in three processes which utilize the reactions between clay minerals (calcined and uncalcined bentonite and kaolinite) and certain radioactive wastes (caustic liquors, salt cake or dissolved salt cake). In particular, the reactions involve the sodium nitrate, sodium nitrite, sodium hydroxide and aluminum hydroxide within the waste. The reaction products are feldspathoid minerals, sodium nitrate cancrinite and sodalite which may be represented by  $6(\text{NaAlSiO}_4) \cdot x \text{ salt} \cdot y \text{ H}_2\text{O}$ , where  $x < 2$  and  $y$  is small when salts are present. Sodium hydroxide is also formed. At low concentrations of  $\text{NaOH}$  and  $\text{NaNO}_3$ , the mineral sodalite will form concurrently with cancrinite, both containing a wide range of salts [9.3]. The low temperature reactions were carried out at temperatures between  $50^\circ$  and  $100^\circ\text{C}$ . Calcined bentonite reacted most rapidly going to completion (at  $100^\circ\text{C}$ ) in less than an hour [9.1].

The Rich Clay process utilizes a stoichiometric excess of clay mixed with liquid waste, producing a cancrinite, clay and waste salt mixture. The Lean Clay process produces relatively pure, small cancrinite crystals by controlling the ratios of the reactants. A binder must be used to solidify the crystalline product. The Clay Calcination process mixes clay with either solid or liquid waste, first producing cancrinite. This product is then heated to  $600^\circ - 1000^\circ\text{C}$  forming nepheline. A flow sheet for these processes is shown as Figure 9.1 [9.1]. It should be noted that none of these processes result in any significant volume reduction and some show as much as a sixfold increase in volume. During the crystallization of cancrinite and sodalite, the salts present, as well as the  $\text{NaOH}$  and the zeolitic water, are important

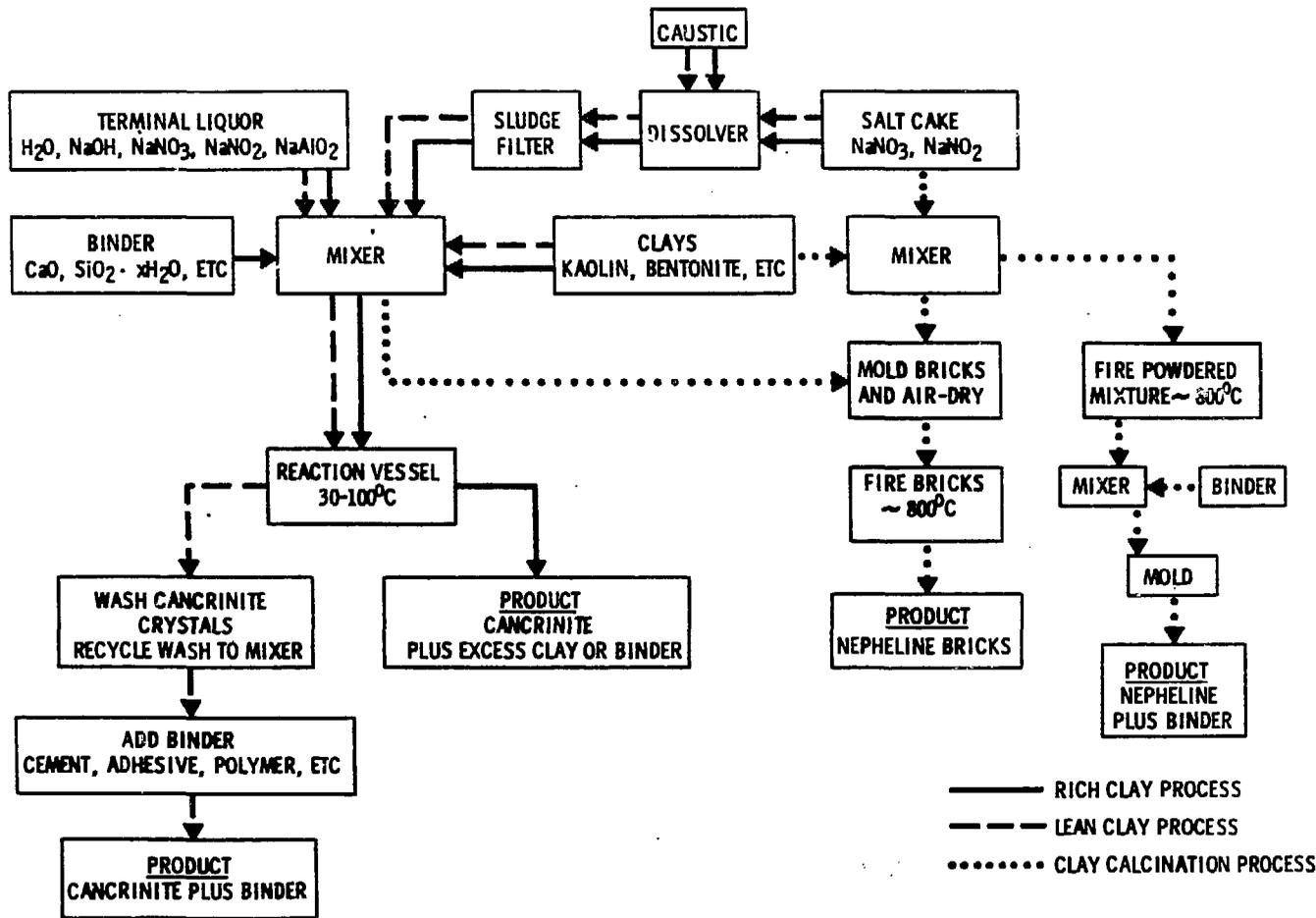


Figure 9.1. Flow charts for three processes: The rich clay process, the lean clay process and the clay calcination process.

to the formation and stability of the lattice. Indeed, the anions in the alkaline solution determine which of the two minerals is formed [9.3]. These entrained salts are strongly held within the aluminosilicate lattice and are not released until the crystal lattice is decomposed [9.4].

Another clay reaction process involves the formation of the mineral pollucite. This is a cesium silicate with the formulation  $Cs[AlSiO_6]H_2O$ . This mineral, those mentioned above and the zeolites, are all structurally similar, belonging to the tectosilicate group of silicate minerals. Pollucite is formed by reacting bentonite, pyrophyllite or kaolinite plus silica gel with a cesium salt in an alkaline solution at  $80^\circ - 100^\circ C$ . The aluminum and silicon are dissolved and the clay falls to an amorphous state. Spherical crystals of pollucite form out of the slurry over a period of about two days [9.4]. The formation of pollucite is dependent on the presence of cesium.

### 9.2.2 Silica Processes

There are a variety of industrial processes which utilize silica reactions with waste to form solids. One such proprietary method is the Chemfix process (Chemfix, Inc., Kenner, La.). This process is based on the formation of crosslinked chain silicates similar to natural pyroxene minerals [9.5]. The Chemfix process mixes less than 10 volume % of silica and setting agent with the waste. This is accomplished by pumping liquid waste through the processing equipment, housed in a trailer, where the mixing takes place. Typically the waste is then pumped back to a holding lagoon where it solidifies over a period of several days. The Chemfix process is primarily intended for solidifying large volumes of heavy metal bearing industrial wastes and as cover and sealer for land fills. Leach tests by Chemfix have shown significant retention of metals. Physically this material resembles a friable soil.

It loses 16 wt% water over a 100 hour period at ambient temperatures, shrinking considerably, but apparently this does not affect the leaching properties [9.5]. In several years of use, over 100 million gallons of waste have been treated with this material. What is apparently a similar product based on a silica-alkaline reaction was patented in Canada (Canadian Patent No. 1024277, issued January 10, 1978). Concentrations of heavy metals observed in the leachate were generally less than 1 ppm, reaching steady state values within several days [9.6]. Neither of these solidification techniques have been applied to radioactive waste disposal. It should be noted, however, that the physical form of these solids may not meet waste form criteria.

Workers at Savannah River Laboratory have experimented with the use of silica gels and silica flour as a possible in-tank solidification process [9.7]. This too is a silica-alkali reaction resulting in the formation of insoluble polysilicates. It was found that best results were obtained when precise proportions of silica to NaOH were mixed. An excess of either reactant does not produce a monolithic solid. Ratios of 3 g of silica gel or 4 g of silica flour reacted with 1 ml of 8M NaOH provided the best waste form. Aluminate ions present in SRP waste react readily with silicates to form insoluble aluminosilicates. This reaction required 1 week at 100°C and 1 month at 25°C. It was found that solidification with this method increased the volume of the waste by a factor of 6, a definite drawback. No leaching data are available for these experiments. It should be noted that silica gel has been used as an additive in cement waste forms to improve leachability.

### 9.3 Mineralization Process Waste Form Characteristics

There is relatively little that is known about the characteristics of these materials as waste forms. Table 9.1 [9.1] reviews the properties of the minerals. There is little or no volume advantage achieved with these processes. Indeed there may in some cases be substantial volume increases.

Table 9.1

## Comparison of Alternative Clay Fixation Processes [9.1]

<u>Product Characteristics</u>	<u>Rich Clay Process</u>	<u>Lean Clay Process</u>	<u>Clay Calcination Process</u>
Mineral form	Cancrinite	Cancrinite	Nepheline
Volume	1.3 x caustic terminal liquor 3 x salt cake	2 x caustic terminal liquor 6 x salt cake	0.8 x caustic terminal liquor 1.5 x salt cake
Leachability, g/cm <sup>2</sup> -day	10 <sup>-4</sup> to 10 <sup>-2</sup>	10 <sup>-5</sup> to 10 <sup>-3</sup>	10 <sup>-5</sup> to 10 <sup>-3</sup>
Thermal and radiolytic stability	Good	Good	Excellent
Mechanical strength	Poor-to-good	Excellent	Excellent
Bulk density, g/ml	1.5 to 1.7	1.6 to 2.0	1.6 to 2.0

### 9.3.1 Chemical Compatibility of Wastes

There are relatively few wastes with which these processes, particularly those forming the feldsparthoids, are compatible. Their formation requires high alkalinity, together with the presence of very precise types and amounts of waste, as described above. This makes these processes inappropriate for most types of waste. Silicate type processes appear to be somewhat more universally applicable, but there is little information available.

### 9.3.2 Leachability

Leachability information for the minerals produced by the clay fixation process is given in Table 9.1. Fraction release of cesium from cancrinite and sodalite are shown in Figure 9.2 as a function of kaolinite: salt ratio. Sodalite had a fraction release of 1% Cs over a one week period. The leachabilities measured were  $1.2 \times 10^{-3}$  g/(cm<sup>2</sup>)(day) for cancrinite, and  $3.4 \times 10^{-4}$  g/(cm<sup>2</sup>)(day) for sodalite, as determined on powders at SRL [9.2]. These leach rates are similar to those reported from Hanford Engineering Development Laboratory. Increases of volume for both minerals were observed to be about 50% for NaOH: Kaolinite: salt mole ratios of 4:2:1 [9.2].

### 9.4. Advantages and Disadvantages

Table 9.2 presents advantages and disadvantages associated with mineralization processes as represented by the clay reaction processes. Leachability and long term stability of these materials is good. However, aside from the many production limitations with these processes, there is generally a large volume increase with this type of waste form.

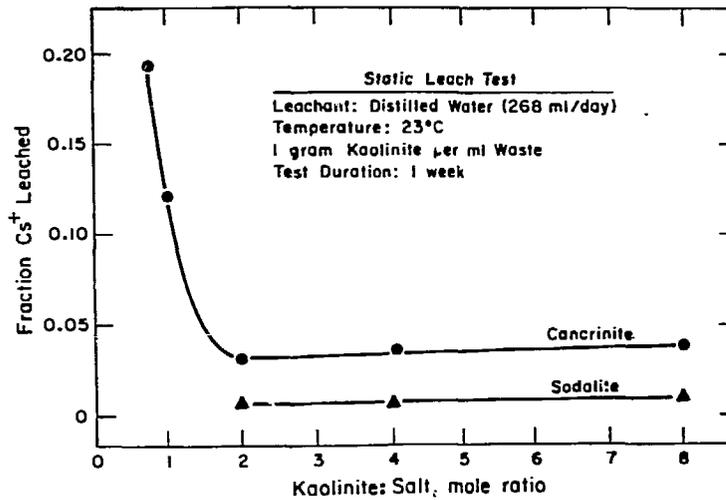


Figure 9.2. Fraction release from two minerals as a function of the kaolinite:salt ratio.

Table 9.2

**Advantages and Disadvantages of  
Mineralization Processes (Clay Reaction Processes)**

Advantages	Disadvantages
1. Low leachability	1. Applicable only to very specific waste types and requires precise ratios of waste constituents and mineralization additives.
2. Long-term stability	2. Results in as much as a 6 fold volume increase
	3. Minerals formed would require incorporation into another matrix in order to make a monolithic waste form
	4. Has not been demonstrated in actual usage

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## 10. GLASS AS AN AGENT FOR LOW-LEVEL WASTE SOLIDIFICATION

Glass processes are typically thought of for the solidification of high-level waste. However, there are two processes which produce glassy waste forms while concurrently providing volume reduction for many types of low-level waste. Although these processes are beginning to be commercialized, relatively little information is available for these processes. Other glass systems developed for the solidification of high-level waste are not considered.

### 10.1 Solidification Processes Using Glass

#### 10.1.1 Slag Fusion Process

A system was developed at Eurochemic (Mol, Belgium) to produce a highly insoluble, basalt-like glass [10.1]. This procedure utilizes high temperature incineration at temperatures of 1500-1600°C. The waste is reduced not to ash but to molten slag. The high temperatures eliminate many of the off-gas problems associated with plastics combustion. The waste itself may consist of both combustible and incombustible materials as long as there is at least 10-15% mineral material to form the slag. The slag fusion system is composed of three parts: glove boxes for sorting, a high temperature incinerator, and an off-gas purification system. Combustion gases are blown through a layer of molten slag in order to remove particulates from the gaseous effluent (Fig. 10.1). The slag slowly drains from the bottom of the incinerator and can be formed either into granules or a solid monolith.

#### 10.1.2 Penberthy Pyro-Converter Process

A system for incinerating and solidifying low-level waste in a glass matrix has been developed by Penberthy Electromelt International, Inc.

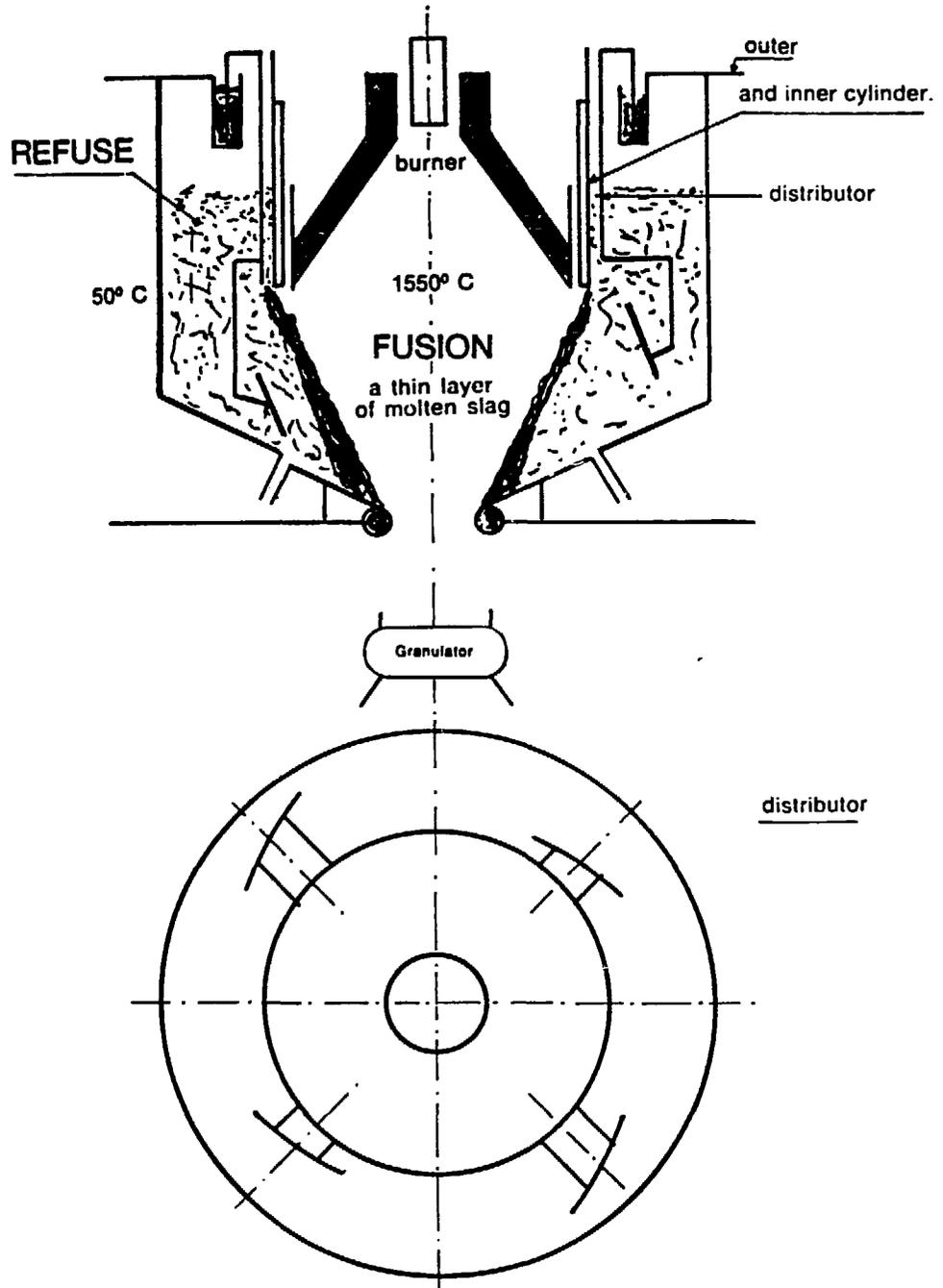


Figure 10.1. A schematic of a portion of the slag fusion process.

(Seattle, Washington) [10.2]. The process utilizes an electric immersion heated glass furnace (Fig. 10.2) similar to that used in the commercial glass industry. The waste is charged at one end of the furnace where it is incinerated in the air space above a pool of molten glass. Continuous addition of raw material for the glass provides an uncontaminated barrier, on the surface of the melt, to any volatilized radionuclides. The glass composition employed can be regulated to best accommodate the waste. For instance, the sodium oxide content of the waste controls the amount of waste which can be loaded in the glass. Alumina and calcia can be added to the raw materials for the glass to increase the chemical durability of the product. As combustible waste is added, it burns with the residue falling into the glass melt, giving very substantial volume reduction factors. Processing temperatures are approximately 1260°C. The mixture of molten glass and incinerated ash is discharged from the low end of the furnace into cooled drums. Spent fiberglass filter pads for dust collection can be pushed into the melt by the fresh replacement pad.

### 10.2 Glass Waste Form Characteristics

There is little information directly available on the relevant characteristics of the waste forms produced by these processes. A considerable body of information for glasses similar to the Penberthy process product may be found in commercial glass property literature. A large amount of data has been developed for high-level waste glasses. However, most of this information deals with different glass compositions, waste types and high activity loadings which are not relevant to low-level waste processing.

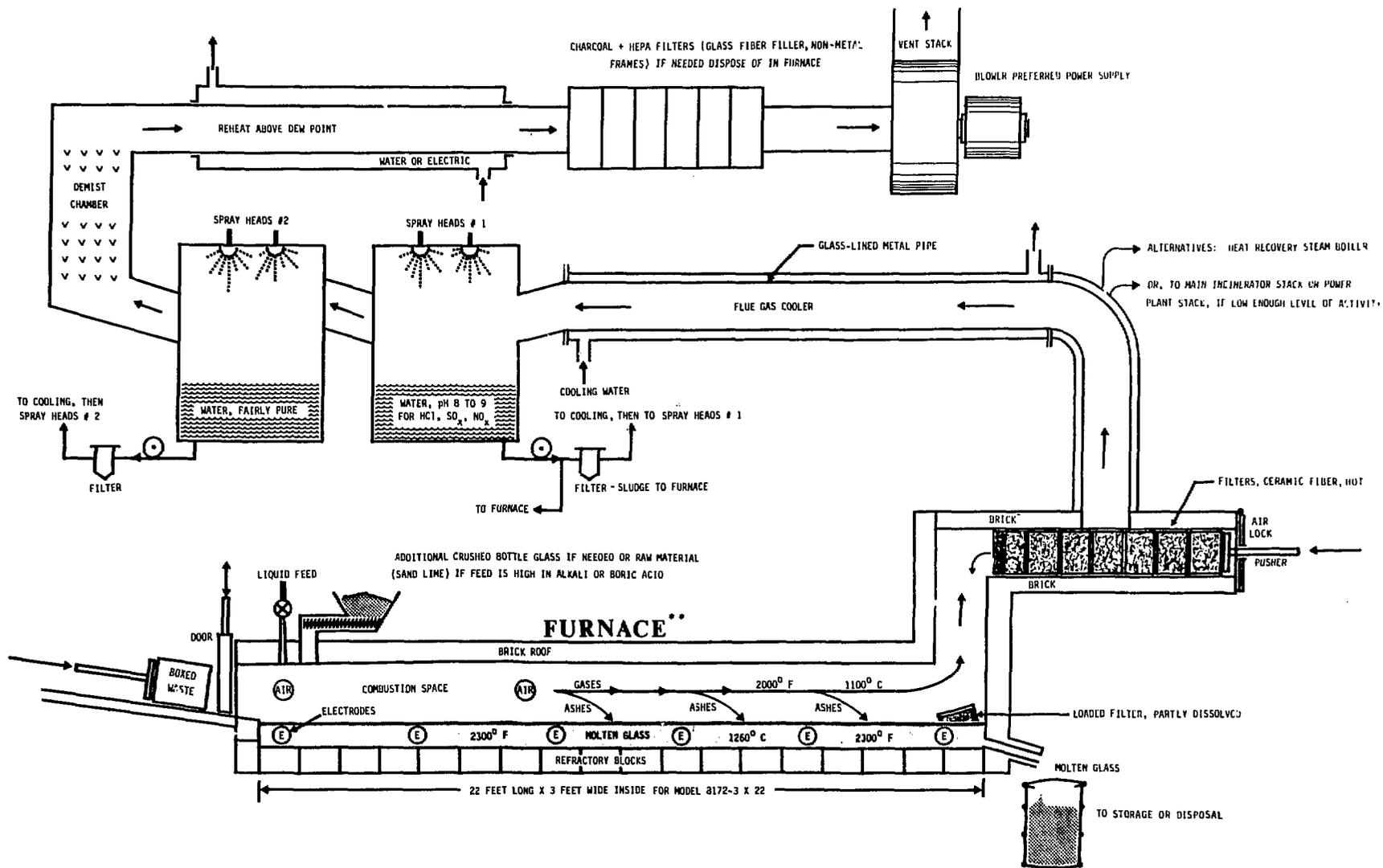


Figure 10.2. The Penberthy pyro-converter glass system.

### 10.2.1 Chemical Compatibility of Waste

The two systems discussed here, which produce glassy waste forms, also provide volume reduction by incinerating combustible wastes. As a result, most materials which may be directly incompatible with glass are converted to oxides. Some compatibility considerations are anticipated if a single phase glass is desired. In addition, the amount of waste oxides that can be incorporated is limited. The major requirement of the slag fusion process is that there must be sufficient mineral content in the waste to produce slag.

### 10.2.2 Leachability

Relatively little information has been published on the leaching characteristics of the products discussed here. The slag fusion material has been shown to exhibit low leachability in limited testing. Leach tests (24 hour duration, running water) with non-radioactive materials have resulted in leach rates of  $10^{-10}$  g/(cm<sup>2</sup>)(day) for copper,  $10^{-8}$  g/(cm<sup>2</sup>)(day) for iron, and  $10^{-5}$  g/(cm<sup>2</sup>)(day) for sodium. The glassy granules are composed primarily of silicon and iron oxides and range in diameter from 0.5 mm to 5 mm. The off-gases are relatively dust-free even before filtering [10.1].

Pertimer et al. [10.3] at the University of Maryland have tested products of the pyro-converter process. Leach tests in distilled water indicated no leaching above detectable limits in up to 35 days; two samples showed some leaching at 35 days and all samples indicated leaching after 56 days. Concentrations within samples, concentrations within leachates and detection limits were not given. More complete information is expected to be available in the near future.

### 10.2.3 Mechanical Strength

Samples of the pyro-converter product were analyzed for compressive strength and homogeneity for solidification of a non-radioactive ash [10.3]. As much as 34 kg of ash were charged into 68 kg of molten borosilicate glass in 6.8 kg loads. Various ash contents in the glass were obtained. While a few of the samples were homogeneous, most samples, particularly those at high concentrations (1 part ash to 2 parts glass), showed stratification of the ash within the glass. The samples also contained voids in the cooled product. Compressive strengths of two samples of the glass-waste product were 29,300 psi and 32,700 psi. In comparison, the glass without waste had a compressive strength of 118,900 psi. Even samples with the ash, however, have an exceptionally high compressive strength. Breakage occurs along the strata of ash.

### 10.2.4 Radiation and Thermal Stability

While a large body of information exists for the thermal and radiation stability properties of various glasses, little is available for glasses of the compositions discussed here.

### 10.3 Advantages and Disadvantages

Table 10.1 presents the advantages and disadvantages of glass processes for the solidification of low-level wastes. Relatively little work has been performed in this area although a large body of information exists for glass as a high-level waste form. A major advantage of these processes is the concurrent volume reduction of waste as it is incorporated into the matrix. A major disadvantage is the elevated temperature required for the process.

Table 10.1

Advantages and Disadvantages of Glass Solidification

Advantages	Disadvantages
1. Provides volume reduction as well as solidification	1. High temperature process
2. Waste form probably has very low leachability	2. Relatively expensive processing equipment and associated systems
3. Raw materials are inexpensive and readily available	3. Applicability to specific wastes is not well defined
	4. Inhomogeneous product

REFERENCES FOR SECTION 10

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## 11. POLYMER MODIFIED GYPSUM CEMENT (ENVIROSTONE)

Gypsum type materials have been used to solidify low-level aqueous wastes. For instance, plaster of paris ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ) has been employed at the university of Illinois at Urbana-Champaign to solidify small batches (approximately gallon size) of liquid wastes [11.1]. The Mound Facility at Miamisburg, Ohio has used plaster of paris and vermiculite for the solidification of aqueous tritiated wastes.

When gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ) is heated to between  $128^\circ\text{C}$  and  $163^\circ\text{C}$ , one and a half molecules of water are driven off to form the hemihydrate, plaster of paris ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ). If heated to  $163^\circ\text{C}$  or higher, all hydration water is lost, forming the anhydrite. When the hemihydrate powder is mixed with water, it becomes hydrated, forming the less soluble dihydrate, gypsum. The gypsum falls out of solution and forms radiating networks of interlocking crystals.

### 11.1 Description of Envirostone

United States Gypsum Company has recently developed a proprietary solidification agent which is a polymer modified cement called Envirostone. This material was developed in particular for problem wastes such as boric acid wastes, oils and other organic liquids. Envirostone powder, the waste and, depending on the waste type, water are blended into a relatively fluid "cream." When organic liquids are being solidified, a proprietary additive is also employed to condition the organic material. Envirostone can be prepared using standard cement mixing equipment. In-line mixing may be less troublesome than with cement because of the greater fluidity of the mixed product. Setting generally takes place in about an hour and is an exothermic reaction. Envirostone solidifies best at a mixture pH of 6 or less.

## 11.2 Waste Form Characterization

Some characterization of Envirostone waste forms has been undertaken by U.S. Gypsum Company [10.1]. A full-scale (55 gallon drum) test of Envirostone for the solidification of boric acid waste was prepared, mixing (for 13 minutes) 345 lbs. of 12 wt% boric acid solution with 380 lbs. of the Envirostone agent. Maximum internal temperature elevation for this full-scale waste form was 30°C. Gypsum products typically increase in volume slightly (0.5%) on setting but no drum distortion was observed. Setting required 20 minutes.

### 11.2.1 Leachability

Leaching of Envirostone samples employing the ANS 16.1 test demonstrated that Envirostone leachability is relatively insensitive to the waste streams. Typical values for laboratory size specimens (279g and surface areas of 40.6 cm<sup>2</sup>) leached for 5.9 days are:  $9 \times 10^{-2}$  g/(cm<sup>2</sup>)(day) for <sup>60</sup>Co,  $6 \times 10^{-3}$  g/(cm<sup>2</sup>)(day) for <sup>85</sup>Sr,  $1 \times 10^{-1}$  g/(cm<sup>2</sup>)(day) for <sup>137</sup>Cs and  $8 \times 10^{-3}$  g/(cm<sup>2</sup>)(day) for <sup>144</sup>Ce (calculated from [11.1]).

### 11.2.2 Compressive Strength

Compressive strengths of Envirostone samples were measured to range from 1450 psi for a laboratory size waste form containing 58.8 wt% of a 12 wt% boric acid concentrate waste to 600 psi for a waste form containing 66.7 wt% boric acid waste [11.1]. Waste forms containing dewatered ion exchange resin had compressive strengths ranging from 700 psi to 120 psi for samples containing 50 wt% and 80 wt% waste respectively. Samples made with oil as waste had compressive strengths that ranged from 615 psi for 28% waste to 100 psi for 57% waste.

### 11.3 Advantages and Disadvantages

While there is relatively little known about Envirostone as a waste form, certain advantages are evident from the laboratory work that has been done. This material can accept significant quantities of organic liquids or acidic waste and still form a monolithic solid.

#### References for Section 11

- [11.1] Joss, M.D., Lange, R.G. and Rosenstiel, T.L., Envirostone Gypsum Cement: Formulated Gypsum Product for Solidification of Low-Level Radioactive Waste From Nuclear Power Stations, United States Gypsum Company, Chicago.

## 12. POLYMER IMPREGNATED CONCRETE AS AN AGENT FOR LOW-LEVEL WASTE SOLIDIFICATION

In the early 1970's, a "hybrid" waste form was developed at Brookhaven National Laboratory which utilized polymers to improve the properties of concrete waste forms. This concept first incorporates the waste in a cement matrix and then impregnates this waste form with a polymerizable material to seal off cement porosity. Resultant properties begin to approach those of multibarrier waste forms employed for high-level wastes.

### 12.1 Description of Polymer Impregnated Concrete

Polymer impregnated concrete (PIC) is a precast concrete composite, containing liquid or solid radioactive waste, which has been impregnated with a monomer which is subsequently polymerized [12.1]. In this way void spaces within the cement are filled, reducing leachability and improving mechanical properties. This waste form has been used for the solidification of various waste types, including tritiated water,  $Al_2O_3$  calcine composites, sodium nitrate and zeolites. Polymer impregnated concrete processes have also been applied to waste solidification in Europe [12.2].

### 12.2 Solidification Process Using Polymer Impregnated Concrete

Processes using polymer impregnated concrete waste forms start with typical cement waste forms. The cement is then dried at  $120^{\circ}C$  to drive off any unreacted moisture. Weight losses of about 2.5 wt% are observed [12.3]. The dried cement waste form is placed in a chamber which is evacuated and then filled with monomer. Drying improves impregnation by removing water from cement porosity. Waste forms can be impregnated without drying, however, to be successful, the waste form formulations must be properly selected. The monomer employed is typically composed of 70% styrene and 30% divinylbenzene (DVB).

Other monomers can be used, however, the monomer should have a low viscosity. Benzoyl peroxide (0.5 wt%) is added to the monomer as a polymerization catalyst. The styrene-DVB mixture was chosen because of its low viscosity, and also its thermal and radiation stability. The waste form is allowed to soak in the monomer for about four hours and is then placed in a curing oven for another four hours at 50-70°C. One-inch diameter by three-inch long cylindrical specimens absorbed 56 wt% of the monomer. Waste forms incorporating Al<sub>2</sub>O<sub>3</sub> calcine took up about 14 wt% of the monomer because of the high porosity of the calcine [12.4]. Additional curing may be achieved by exposing the waste form to radiation. Crosslinking of the polymer chains becomes more complete in this manner, improving the strength of the product by about 10% [12.1, 12.3]. A schematic of the process is given in Figure 12.1.

### 12.3 Chemical Compatibility of the Wastes

Polymer impregnated concrete waste forms can be produced, incorporating any wastes that can be solidified in concrete.

### 12.4 Waste Form Characteristics

#### 12.4.1 Leachability

The bulk leach rates for cesium and strontium are shown in Table 12.1 [12.5] for two types of waste in cement and in polymer impregnated concrete waste forms. The PIC bulk leach rate was at least 2 orders of magnitude less than the respective cement waste form. Indeed, the activity levels of the PIC leachants were often below detection limits, accounting for the "less than" values in Table 12.1 [12.5]. Additional leach resistance can be obtained by providing a thin polymer film on the waste form surface by a subsequent treatment step.

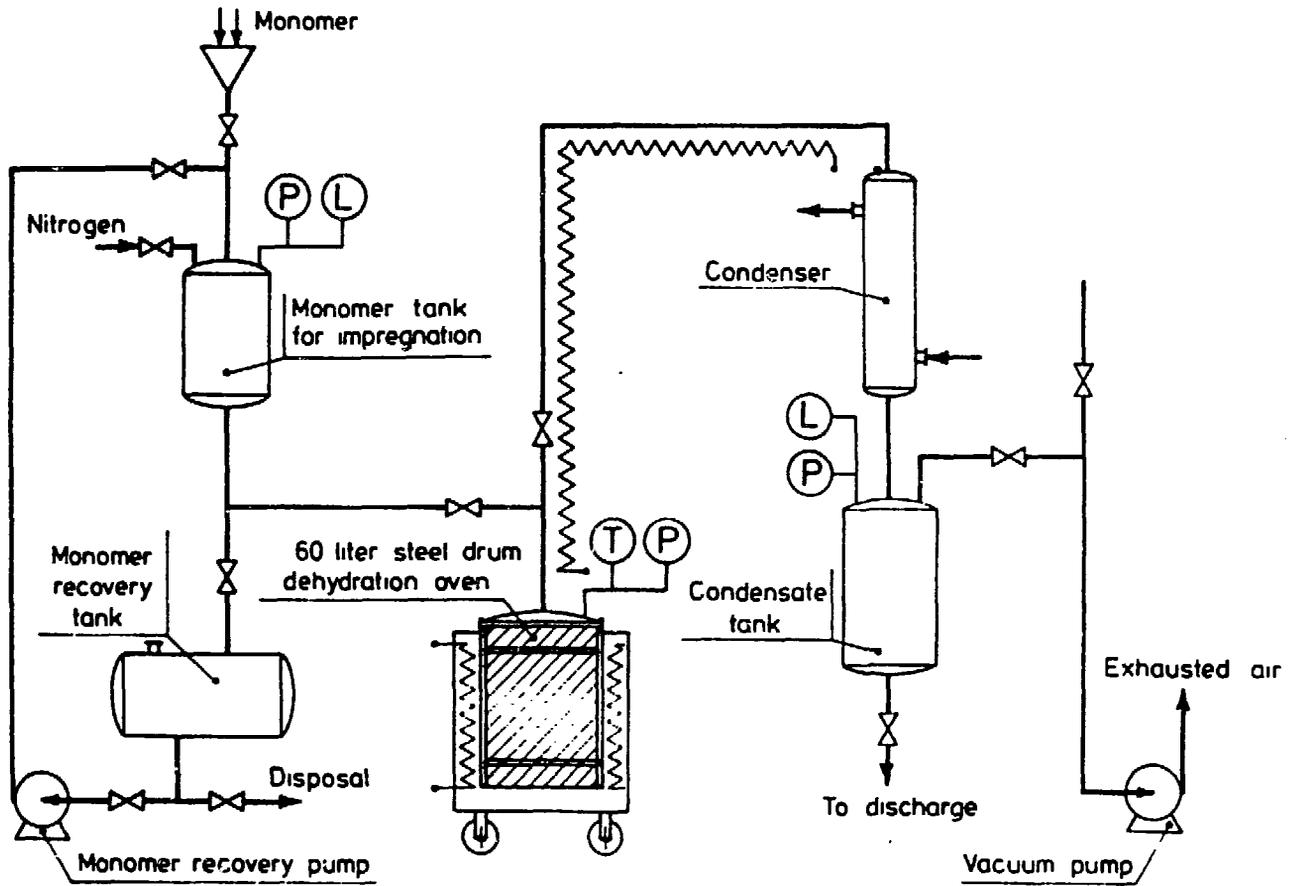


Figure 12.1. Polymer impregnated concrete system.

TABLE 12.1

Cesium and Strontium Leach Rates for Selected Concrete and PIC Formulations

Formulation, wt%					Polymer Loading wt%	Bulk Leach Rate after 143 days g/(cm <sup>2</sup> day)	
Cement	Zeolite	Sludge	Sand	Water		Cesium	Strontium
35.0	12.5 <sup>a</sup>	---	35.0	17.5	---	$6.82 \times 10^{-6}$	$2.50 \times 10^{-5}$
35.0	12.5 <sup>a</sup>	---	35.0	17.5	8.69	$9.95 \times 10^{-8}$	$9.61 \times 10^{-8}$
36.3	4.2 <sup>b</sup>	8.3 <sup>c</sup>	35.0	16.2	---	$4.63 \times 10^{-5}$	$9.27 \times 10^{-7}$
36.3	4.2 <sup>b</sup>	8.3 <sup>c</sup>	35.0	16.2	8.18	$<1.04 \times 10^{-7}$	$<9.72 \times 10^{-8}$

<sup>a</sup>Contains 0.11 meq cesium/g and 0.34 meq strontium/g.<sup>b</sup>Contains 0.32 meq cesium/g.<sup>c</sup>Contains 0.50 meq strontium/g.

#### 12.4.2 Radiation Stability

Samples of polymer impregnated concrete were gamma irradiated to a total dose of  $10^{10}$  rads using  $^{60}\text{Co}$ . The compressive strength of PIC was not significantly affected. The irradiated sample had values of 12,000 psi, while the compressive strength of the control was 12,100 psi. Leachability of the control was  $4.5 \times 10^{-4}$  g/(cm<sup>2</sup>)(day) while the irradiated sample was  $2.6 \times 10^{-4}$  g/(cm<sup>2</sup>)(day). Radiolytic gas production for a dose of  $10^{10}$  rads was  $G(\text{H}_2) = 0.016$  molecules/100eV absorbed, and  $G(\text{CO}_2) = 0.0031$  molecules/100eV absorbed. The radiolytic hydrogen generation ratio observed was lower than that expected for the amount of polystyrene in the waste form. It is believed that much of the hydrogen is absorbed on the cement surfaces [12.6].

#### 12.5 Advantages and Disadvantages

The principal advantage of a polymer impregnated concrete waste form is the significantly decreased leachability. Very large improvements in mechanical properties also result. Such high strengths probably provide little benefit in disposal, however, the improvements over untreated cement waste forms in many cases is significant. The major disadvantage is the increased complexity of the process.

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