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DEPARTMENT OF NUCLEAR ENERGY

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1. DESCRIPTION OF THE WASTE FORM DEVELOPMENT PROGRAM

This work is funded under the Department of Energy's National Low-Level Waste Management Program (NLLWMP). The NLLWMP's objective is to "provide an acceptable Low-Level Waste Management System by 1988" which will enable disposal "of materials that have been declared as low-level waste in a manner which will protect public health and safety in the short and long terms." The Waste Form Development program is an integral part of the NLLWMP's program to develop technology applicable to the entire low-level waste stream from generator to disposal.

Low-level wastes (LLW) at nuclear facilities have traditionally been solidified using portland cement (with and without additives). Urea-formaldehyde has been used for LLW solidification while bitumen (asphalt) and thermosetting polymers will be applied to domestic wastes in the near future.

Operational difficulties have been observed with each of these solidification agents. Such difficulties include incompatibility with waste constituents inhibiting solidification, premature setting, free standing water and fires. Some specific waste types have proven difficult to solidify with one or more of the contemporary agents. Similar problems are also anticipated for the solidification of "new" wastes, which are generated using advanced volume reduction technologies, and with the application of additional agents which may be introduced in the near future for the solidification of LLW.

In the Waste Form Development program, contemporary solidification agents are being investigated relative to their potential applications to major fuel cycle and non-fuel cycle LLW streams. The range of conditions under which these solidification agents can be satisfactorily applied to specific LLW streams is being determined. These studies are primarily directed towards defining operating parameters for both improved solidification of "problem" wastes such as ion exchange resins, organic liquids and oils for which prevailing processes, as currently employed, appear to be inadequate, and solidification of "new" LLW streams

including high solids content evaporator concentrates, dry solids, and incinerator ash generated from advanced volume reduction technologies. Solidified waste forms are tested and evaluated to demonstrate compliance with waste form performance and shallow land burial (SLB) acceptance criteria and transportation requirements (both as they currently exist and as they are anticipated to be modified with time).

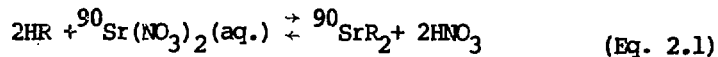
2. SOLIDIFICATION OF ION EXCHANGE RESIN WASTES

2.1 Characterization of Ion Exchange Resin Wastes

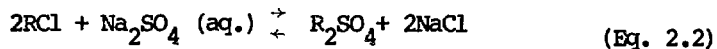
2.1.1 Principles of the Ion Exchange Process.

Ion exchange is a process in which cations and anions dissolved in an electrolytic solution are interchanged with counter ions in a solid phase. Counter ions exchange on a stoichiometrically equivalent basis with dissolved ions of the same sign and charge. The structure of the solid phase ion exchanger is not permanently altered and the process is reversible (through regeneration) as demonstrated by the following typical exchange reactions:

Cation Exchange:



Anion Exchange:



where R represents the insoluble matrix of the exchanger. Equation 2.1 describes the removal of strontium-90 from a waste stream by cation exchange. Equation 2.2 describes the removal of sulfate by anion exchange [1].

Many naturally occurring organic and inorganic materials possess some ion exchange capability. However, with the notable exception of zeolite minerals, few have been utilized on a commercial basis. The majority of ion exchangers available for commercial use today are synthetic organic resins. These resins are made up of a framework of hydrocarbon chains (typically linear polystyrene), which are crosslinked with divinylbenzene (DVB). The degree of crosslinking determines the width of the framework, swelling characteristics, ease of ion movement, hardness, and resistance to mechanical breakdown. The exchange capability is imparted to the resin by introducing fixed ionic groups, or functional groups. One such process for cation exchangers

is sulfonation, in which eight to ten HSO_3 groups are added for each ten benzene rings in the polystyrene structure. In this case, the SO_3 is bonded to the benzene ring and the hydrogen atom becomes the exchangeable counter ion. Figure 2.1 depicts the structure of sulfonated polystyrene cation exchange resin which has been converted to the Na^+ form [2].

2.1.2 Ion Exchange Applications in the Nuclear Industry.

The majority of power reactors operating in this country are light water reactors (LWRs) which utilize water for cooling and neutron moderation. Dissolved ionic species present in this water can lead to increased corrosion, higher radiation doses due to activation products and reduced neutron economy from uncontrolled neutron capture reactions. To alleviate these potential problems, ion exchange resins have been used to [1,3]:

- Provide demineralized make-up water.
- Remove radioactive contaminants such as neutron activation products and fission products which may have leaked from fuel elements.
- Reduce levels of oxygen in coolant.
- Control levels of additives including corrosion inhibitors, neutron poisons and chemical shim (in FWRs).

In order to maximize effective surface area, resins are produced in both bead form (with diameters ranging from 0.35 to 1.15mm) and in powdered form. Powdered resin can have as much as 100 times more surface area than the equivalent weight of bead resin [4].

Bead resin is generally used in columns and ionic solutions are passed through these columns for purification. Resin columns can be set up as individual cation or anion resin columns (either alone or in series), or as a homogenous mixture of both resin types in a single column (mixed bed). Bead resins have the advantage of being easily regenerated. Regeneration of exhausted resins can be accomplished by introducing a flow of an acid solution for cation resins, and an alkali solution for anion resins, which displace the exchanged ions and replace them with fresh counter ions. Mixed bed resin columns are more difficult to regenerate than individual cation or anion resin bed columns.

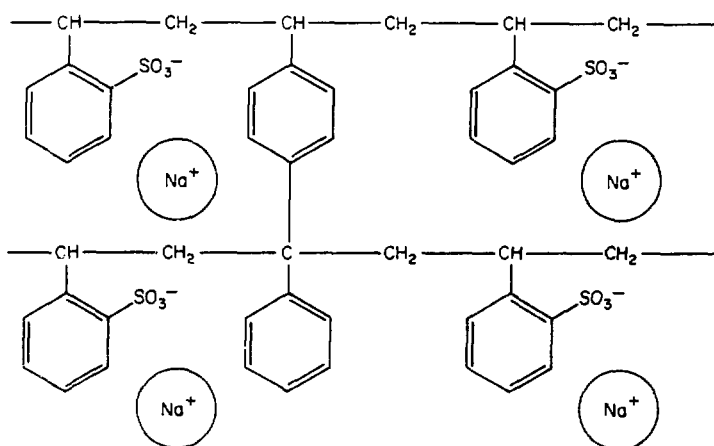


Fig. 2.1 Structure of sulfonated polystyrene cation exchange resin crosslinked with divinylbenzene. (SO_3^- is the functional group and Na^+ is the exchangeable counter ion.

Powdered resins also have the ability to remove suspended solids and therefore are generally used as filter precoat material. Because ion exchange reaction rates are controlled by diffusion, which in turn is proportional to surface area, powdered resins are capable of higher reaction rates than bead resins. This more rapid exchange rate enables higher operating capacity utilization. When powdered resins are expended, they are typically disposed in the form of a sludge. The fact that they are not usually regenerated significantly increases the operating cost of powdered resin demineralization systems.

Cation exchange resins are available in both strongly and weakly acidic forms; anion exchange resins in both strongly and weakly basic forms. For most power plant applications, where ion exchange resins are used for sorbing or separating various ionic species, the strong acid and base type resins are more commonly used due to their ability to dissociate. On the other hand, weakly dissociated resins provide higher regeneration efficiencies [5]. Due to the number of parameters involved, the type and form of resin utilized is determined according to the specific application.

Power reactor bead resin wastes are generally maintained in a wet slurry condition to allow pumping them through waste handling process piping. Typically, a pumpable slurry will contain 70% resin and 30% free standing water, by volume. Prior to disposal, resin waste is often dewatered to remove excess surface water.

2.1.3 Resin Waste Disposal.

Ion exchange resin columns are scheduled for replacement on the basis of one of two criteria. These are either (1) depletion of exchange capacity (breakthrough) or (2) significant personnel dose as a consequence of the contained radioactivity. In many cases, resin columns are scheduled for replacement based on the handling and exposure dose hazards associated with their activity, rather than their useful service life as chemical exchangers. Although ion exchange resin wastes account for a relatively small fraction of all low-level waste produced on a volume basis, they represent a significantly higher percentage from the standpoint of contained radioactivity [6].

Ion exchange resin wastes, as well as other low-level wastes are disposed of by means of shallow land burial. Until recently, the majority of resin wastes in the United States have simply been dewatered and packaged in large carbon steel liners prior to shipment to the burial site. However, at present the United States Nuclear Regulatory Commission (NRC) requires that all new commercial power reactor plants licensed have the capability to solidify ion exchange resin wastes [7]. Additionally, recent license amendments to some commercial shallow land burial sites stipulate either solidification of resin waste or the use of high integrity containers for the disposal of dewatered resins. Draft rule 10CFR61, "Licensing Requirements for Land Disposal of Radioactive Waste," requires either solidification or the use of high integrity containers for the disposal of ion exchange resin waste [8]. However, the NRC has not approved any high integrity containers and, to date, only limited efforts have been applied towards the development and testing of such containers.

Limited operating experience and past studies have indicated instances of poor waste form performance for ion exchange bead resin waste incorporated in a cement matrix. Swelling and cracking of waste forms, resulting in poor product integrity, has been demonstrated [9]. This diminishes the benefits inherent in solidification. Agents investigated for the solidification of bead resin waste include three types of hydraulic cement, Envirostone (a polymer modified gypsum based cement product), and vinyl ester-styrene.

2.1.4 Preparation of Simulated Ion Exchange Resin Waste.

The solidification of cation, anion, and mixed bed resins was investigated. Nuclear Grade Amberlite ion exchange resins manufactured by the Rohm and Haas Company^(a) were selected as representative of those used in the nuclear power industry. These are "gel" type synthetic ion exchange resins formed by crosslinking linear polystyrene with 8% divinylbenzene by weight.

^(a) Rohm and Haas Company, Philadelphia, PA 19105

The cation form, designated IRN-77, is a strongly acidic resin and has sulfonic acid functionality. A minimum of 95% of its exchange sites are in the hydrogen form. The minimum total exchange capacity of Amberlite IRN-77 in the hydrogen form is 1.8 milliequivalents per milliliter (wet) or 4.7 milliequivalents per gram (dry). Anion resin, designated IRN-78, is a strongly basic quaternary ammonium functionality resin, containing a minimum 80% of its exchange sites in the hydroxide form with a maximum of 5% in the chloride form and a maximum of 15% in the carbonate form. The minimum total exchange capacity of Amberlite IRN-78 in the hydroxide form is 0.78 milliequivalents per milliliter (wet) or 3.5 milliequivalents per gram (dry). Mixed bed resin for these studies was formed by combining 2 parts IRN-77 and 1 part IRN-78 by dry weight.

2.1.4.1 Resin Loading: "Cold" (non-radioactive) resins were used for formulation development studies. Cation and anion resins were employed in their fresh, unloaded form (H^+ and OH^- , respectively). Mixed bed resins were used in both their unloaded and loaded forms. The resins were batch loaded in a solution containing sodium sulfate, calcium chloride and aluminum nitrate to provide a mixture of single and multivalent ions. After soaking in this aqueous solution containing equal milliequivalents of the above compounds (in sufficient total concentration to satisfy the resin's theoretical exchange capacity) for at least 18 hours with occasional stirring, the resins were drained and rinsed five times with deionized water.

2.1.4.2 Water Content: Ion exchange resin wastes vary widely in terms of water content. Therefore, methods were employed to measure and characterize the water contents of various forms of resin wastes. Water content of the resins was calculated according to ASTM Standard Test Method D2187-77, "Physical and Chemical Properties of Ion Exchange Resins," [10]. This procedure involves the determination of the mass loss upon drying of resins in a gravity convection oven at $110^{\circ}C$ for 18 ± 2 hours. Water content is then calculated as follows:

$$\text{wt\% water} = \frac{\text{wt. of wet resin} - \text{wt. of dry resin}}{\text{wt. of wet resin}} \times 100 \quad (\text{Eq. 2.3})$$

The water content of as-received resin was measured and compared with values calculated for typical slurry and dewatered bead resin waste streams. To facilitate this comparison, a 70/30 volume ratio of settled resin to free standing water was used to produce a simulated slurry waste in the following manner. Resin saturated to equilibrium in deionized water was placed in a graduated burette. By introducing a flow of deionized water at the bottom of the burette, the resin bed was expanded upwards, classifying particle sizes and removing pockets of air. The flow was removed, allowing the resin to settle by gravity. The volume of the resin bed was measured after settling, and by using the ratio stated above, total volume and free-standing water volume were calculated. The height of the water level was adjusted to the desired value (70/30 volume ratio) by draining the excess water.

For the purposes of this report, dewatered resin will be defined as resin saturated with water to equilibrium, with all observable free standing water decanted from above the settled bead resin surface. Dewatered resin was prepared in the same manner as the resin slurry, with the exception that the excess water above the settled resin bed was removed.

In practice and as defined above, dewatered resin will still contain a substantial amount of water (as much as 66 wt% for IRN-77 and 77 wt% for IRN-78). Most of this moisture is sorbed within the resin beads and when solidifying in a cement media is unavailable for hydration of the cement. The remaining portion (approximately 10-15 wt%) is loosely held by electrostatic forces in the interstitial spaces between resin beads. This interstitial water can be directly utilized by the cement to further the hydration reaction.

In order to present specimen formulations that reflect the actual water available, a method was devised to remove most of the interstitial water. Polymethylpentene containers with tight fitting screw cap lids were modified to accept a low pressure (5-10 psi) air line and a 2.5 cm diameter filtered drain. This apparatus is shown in Figure 2.2. In this method, saturated resin is placed into containers which are inverted and held under pressure (5-10 psi) for at least ten minutes or until no moisture is visibly draining. Resin prepared in this manner is termed "damp resin." Although the



Fig. 2.2 Apparatus used to remove interstitial water from ion exchange resin.

percentage of water in damp resin closely corresponds to measured values for as-received resin, this procedure assures both saturation of the resin with water and uniformity of water content.

As waste handling techniques in actual applications are diverse, the percentage of total water in so-called dewatered and slurry resin wastes may vary. In order to provide waste form formulation data in a consistent manner that can be universally applied, the amount of ion exchange resin in waste form formulations is reported as weight percentage dry resin. Through determination of the dry resin content of any ion exchange resin waste stream, the results determined in this study can be directly applied to actual in-plant conditions. Water content information for the various resin types and forms employed is summarized in Table 2.1.

Table 2.1 Weight Percent Water In Resin Wastes

<u>Resin Type</u>	<u>Weight Percentage Water</u>			
	<u>As-Received</u>	<u>Damp</u> ^(a)	<u>Dewatered</u>	<u>Slurry</u>
IRN-77	53.6	54.9	65.7	75.0
IRN-78	66.5	65.6	77.2	83.6
Mixed Bed	57.9	57.6	72.0	79.6

^(a) represent average values; actual wt % water may vary \pm 3%.

2.1.4.3 Density: Density measurements for these ion exchange resin wastes are listed in Table 2.2.

Table 2.2 Resin Waste Density

Resin Type	Density, g/cm ³			
	As-Received	Damp	Dewatered	Slurry
IRN-77	1.26	1.34	1.17	1.08
IRN-78	1.11	1.23	1.10	1.03
Mixed Bed	1.21	1.28	1.15	1.06

2.1.4.4 pH: The pH of as-received ion exchange resins was measured in a slurry condition with demineralized water. Measured pH values were 3.0 for cation resin (IRN-77), 10.3 for anion resin (IRN-78) and 8.5 for mixed bed resin (two parts cation to one part anion resin by weight). The pH of actual resin wastes depend largely upon the extent of resin depletion. Fully depleted resin wastes will typically have a pH of approximately 7. The pH also depends somewhat upon the pH of the liquid stream being demineralized by the ion exchange resin.

2.2 Solidification with Hydraulic Cements.

2.2.1 Cement Types.

Hydraulic cement is the most widely used solidification agent for low-level wastes in the United States. Portland cement is the primary hydraulic cement produced and is used extensively for radioactive waste solidification. Portland type I and portland type III cements, as well as high alumina cement were selected for examination in these studies.

Portland cement is primarily a mixture of calcium silicates (dicalcium silicate, C_2S , and tricalcium silicate, C_3S) with smaller proportions of tricalcium aluminate and tetracalcium aluminoferrite, as shown in Tables 2.3 and 2.4. Type III cement has a lower C_2S content and higher C_3S content than type I cement. As a result, type III cement exhibits higher strength for shorter set times than type I cement. High alumina cement consists primarily of monocalcium aluminate with a relatively small percentage of

silicate and other materials (Table 2.5). It hardens more rapidly than portland type 1 cement and can achieve strength in one day equivalent to that found in portland type I cement after one month.

Table 2.3 Principal Compounds Present in Portland Cements

Compound	Formula	Abbreviation
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S
Dicalcium silicate	$2\text{CaO} \cdot \text{SiO}_2$	C_2S
Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A
Tetracalcium aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF

Table 2.4 Compound Composition of Portland Cements

Type of Cement	Compound Composition, wt%			
	C_3S	C_2S	C_3A	C_4AF
I. Normal	45	27	11	8
III. High early strength	53	19	10	7

Adapted from: [11]

Table 2.5 Composition of High Alumina Cement

Compound	Formula	Composition, wt. %
Silicate	SiO_2	8-9
Alumina	Al_2O_3	40-41
Lime	CaO	36-37
Ferric Oxide	Fe_2O_3	5-6
Ferrous Oxide	FeO	5-6

Adapted from: [20]

2.2.2 Formulation Development.

Previous work considering the solidification of ion exchange resin wastes with portland cements indicated instances of waste form expansion which resulted in low product integrity and/or waste form disintegration [11,12]. This behavior was shown to be a function of both resin type and resin content in the waste form. This loss of waste form integrity is postulated to be a result of resin swelling/shrinking due to competition between the cement and resin for water and/or the adsorption of soluble cement species during solidification [9].

Studies were performed to determine the range of acceptable formulations for the solidification of ion exchange resin waste in hydraulic cements. The acceptability criteria imposed require the resultant waste form to be a free standing monolithic solid with no drainable free standing water. Waste forms are also required to maintain their integrity during a two week immersion test in demineralized water. The water immersion test is taken to be indicative of long-term waste form integrity. The volume of water employed in this test is based upon the proposed ANS 16.1 leach test which requires that $V_L/S = 10$ cm, where V_L is the water volume and S is the external geometric surface area of the specimen [13].

Formulation specimens were mixed using a 1/6 horsepower planetary action mortar mixer (Hobart Model N-50) in the following manner. Cement was weighed out and placed in a stainless steel mixing bowl. Ion exchange resin and water were weighed separately and then mixed together before being added to the mixing bowl. The constituents were mixed at low speed (approximately 120 rpm) for two minutes. The mixture was then transferred into individual 160 ml cylindrical polyethylene specimen preparation containers and the containers were capped to prevent evaporative water loss. Each specimen container was then placed on a vibration table (operated at low amplitude) for approximately thirty seconds to dislodge any air bubbles that might be present within the formulation. The resultant waste form specimens were approximately 4.7 cm in diameter and 8.5 cm high. At least two replicate specimens of each formulation were prepared.

Formulations were initially evaluated for workability. Sufficient water must be present in any cement-resin waste mixture to provide adequate workability (or mixability). Good workability is required to provide a homogeneous mixture in a reasonable time using conventional cement mixing techniques. When insufficient water is added, the mix is dry and friable and does not have the consistency necessary to produce a homogeneous mixture or waste form after curing. The determination of these mixability limits is somewhat subjective and partially dependent upon the mixing method. These limits were found by taking cement-resin mixes that were not workable and slowly adding water until an adequate mix consistency was achieved.

Twenty-four hours after preparation, formulations were examined for free standing water. Those formulations having any observable free standing water in one or more of the formulation replicates were considered unacceptable. While free standing water in cement systems may decrease after longer cure times due to continuing hydration, this conservative approach was used in order to develop reliable formulations for full-scale waste forms. Those formulations that solidified and had no free standing water after twenty-four hours were cured in their containers for a total of fourteen days at room temperature. After curing for fourteen days, the specimens were removed from their preparation containers to verify formation of a free standing monolithic solid. A number of portland type III cement-cation resin formulations exhibited excessive cracking and swelling and, as such, were considered unacceptable. Acceptable formulation specimens were then subjected to a water immersion test.

A large number of formulations were prepared and tested to determine satisfactory formulations and to investigate the effects of cement type, resin type, resin loading and water content. This information has been put into the form of ternary compositional phase diagrams defining composition envelopes for acceptable formulations. The compositional phase diagrams developed for the solidification of ion exchange resin waste with portland cement are shown in Figures 2.3, 2.4 and 2.6-2.8. The compositional phase diagrams for the solidification of mixed bed ion exchange resin waste with high alumina cement is included as Figure 2.5. These compositional phase diagram express formulations in terms of weight percentages cement, dry resin and water (total

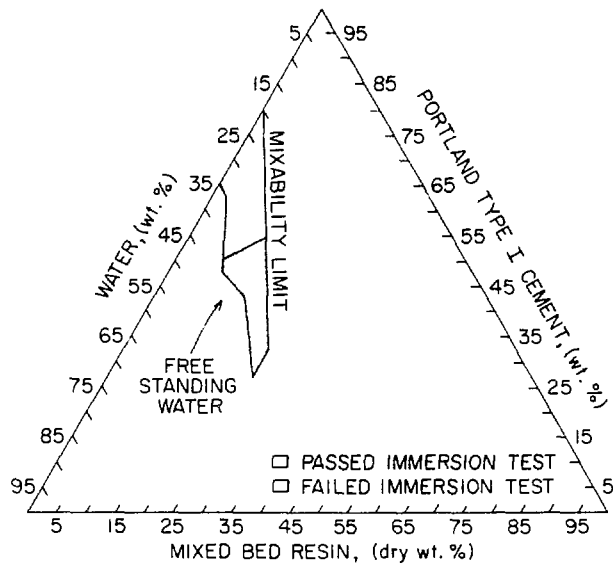


Fig. 2.3 Compositional phase diagram for the solidification of unloaded mixed bed resin with portland type I cement.

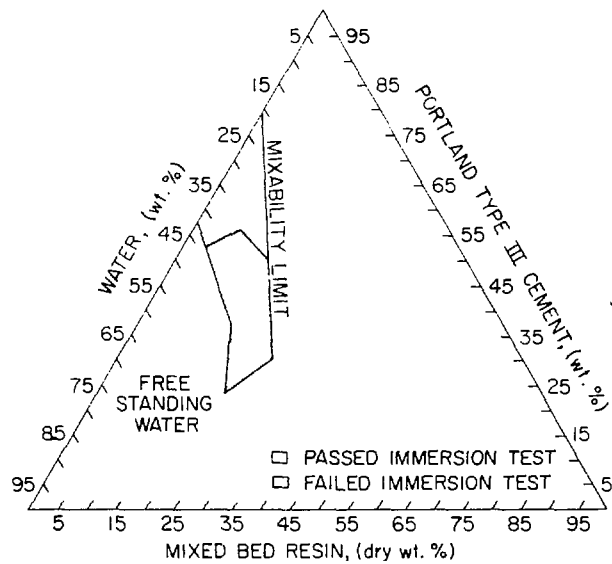


Fig. 2.4 Compositional phase diagram for the solidification of unloaded mixed bed resin with portland type III cement.

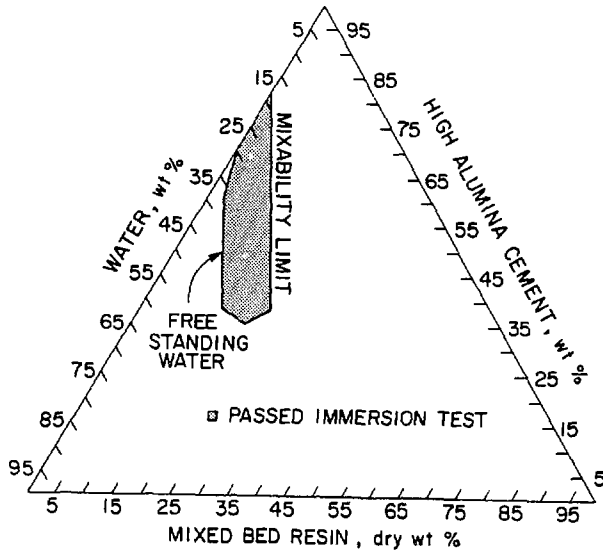


Fig. 2.5 Compositional phase diagram for the solidification of unloaded mixed bed resin with high alumina cement.

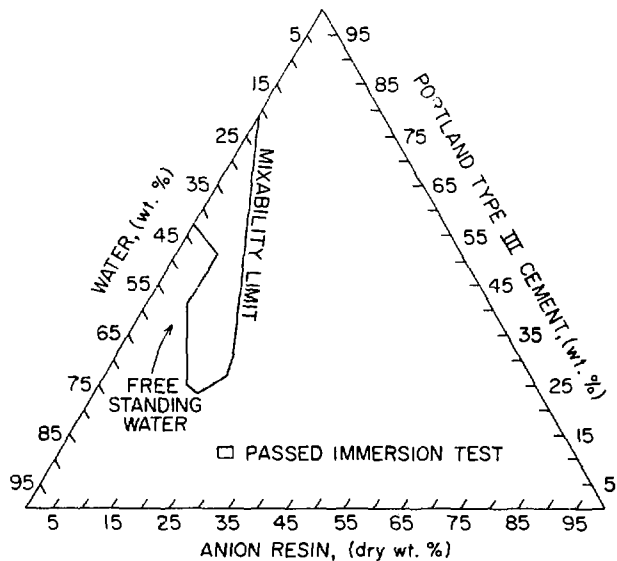


Fig. 2.6 Compositional phase diagram for the solidification of unloaded anion resin with portland type III cement.

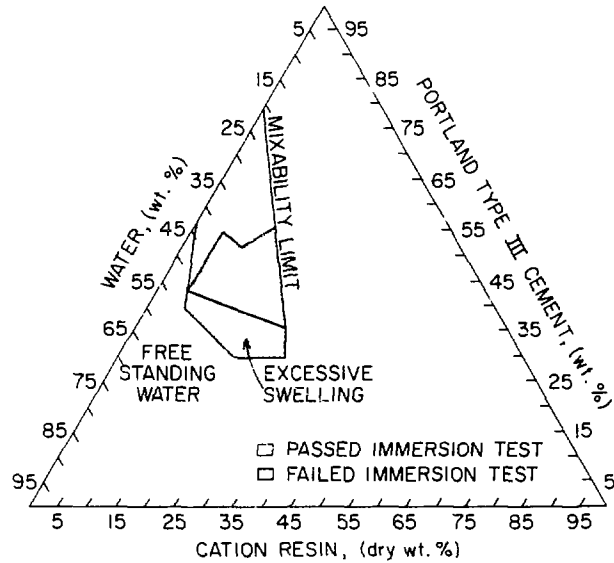


Fig. 2.7 Compositional phase diagram for the solidification of unloaded cation resin with portland type III cement.

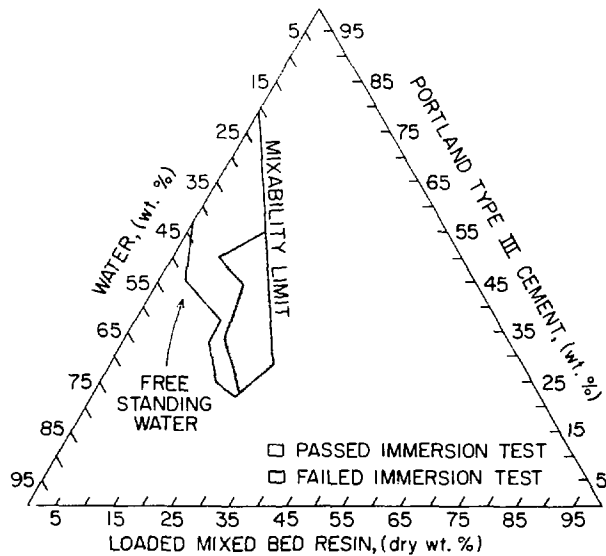


Fig. 2.8 Compositional phase diagram for the solidification of loaded mixed bed resin with portland type III cement.

water consisting of water associated with the resin waste plus added water, if any). Envelopes of those formulations which successfully withstood the two week immersion test are indicated by lightly shaded areas. Those formulations which failed the immersion test or displayed excessive cracking or swelling after curing are indicated by the more heavily shaded areas. Formulations which contain the minimum water necessary to form a homogeneous mixable paste fall on the line labeled "mixability limit". Regions of formulations which yielded observable free standing water after twenty-four hours are also indicated.

Compositional phase diagrams are intended as a guide to assist in determining constituent formulations for successful waste form solidification. Due to the marked variability of results with changes in solidification parameters (resin loading in particular), formulations which fall at the boundaries of acceptable limits may not provide good reproducibility. It is advisable, therefore, to avoid these boundaries whenever possible. In addition, quality assurance testing of full-scale waste forms to demonstrate the applicability of a given cement-water-resin combination is recommended.

Quantities of ion exchange resin waste are reported on the compositional phase diagrams as weight percentages of dry resin. Typical resin waste streams, however, are either dewatered or are in the form of a resin slurry, each of which contains a considerable percentage of their total weight as water. The following procedure may be used to adapt information from compositional phase diagrams to any given bead resin waste stream:

- 1) Select formulation weight percentages of cement (C_F), total water (W_F) and dry resin (R_F) from the appropriate compositional phase diagram.
- 2) Determine the weight percentage of water (wt% W_{waste}) and dry resin (wt% DR) in the resin waste stream according to ASTM standard test D2187-77.
- 3) Determine the quantity of the resin waste stream to be solidified (WS) and calculate the amount of dry resin (DR) and water (W_{waste}) in this quantity of waste:

$$DR = WS \text{ (wt\% DR)} \quad (\text{Eq. 2.4})$$

$$W_{\text{waste}} = WS \text{ (wt\% } W_{\text{waste}} \text{)} \quad (\text{Eq. 2.5})$$

- 4) Calculate the quantity of cement required (C) by applying the following equation:

$$C = \frac{DR}{R_f} (C_f) \quad (\text{Eq. 2.6})$$

- 5) Calculate the formulation water requirements (W) according to:

$$W = \frac{DR}{R_f} (W_f) \quad (\text{Eq. 2.7})$$

- (6) Subtract the quantity of water contained in the waste (W_{waste}) from the formulation water requirement (W) to determine the amount of water which must be added or removed from the waste stream:

$$W_{\text{corr}} = W - W_{\text{waste}} \quad (\text{Eq. 2.8})$$

A positive W_{corr} indicates water must be added, while a negative value indicates excess water must be removed from the waste stream. (Note that application of the W_{corr} term will change the total quantity of the waste stream to be solidified.)

2.2.3 Effect of Cement Type.

Unloaded mixed bed resins were solidified with portland type I, portland type III and with high alumina cements to determine the effect of cement type on acceptable formulations. These compositional phase diagrams are shown in Figures 2.3, 2.4 and 2.5, respectively.

2.2.3.1 Portland Cement: Initial studies indicated that portland type III cement formulations were capable of incorporating larger quantities of water than portland type I cement formulations and meet free standing water and immersion criteria. Therefore, subsequent studies concentrated on the use of portland type III cement. The minimum water requirements for workability (mixability limit) were similar for both cement types. Figure 2.9 compares the results of water immersion tests for unloaded cation resin solidified with portland types I and III cements. These formulations incorporate the same type and form of resin waste and have the same waste-to-cement ratio and water-to cement ratio. Type III cement also appears capable of incorporating more ion exchange resin in waste form formulations than portland type I cement.

2.2.3.2 High Alumina Cement: Formulations of mixed bed resin wastes solidified in high alumina cement exhibited more free standing water than those of portland type III, but somewhat less than those of portland type I. The minimum water requirements necessary to provide adequate workability were similar to those found for the portland cement.

The results of the immersion tests revealed a distinct advantage of high alumina cement for the solidification of ion exchange resin wastes. None of the high alumina cement specimens undergoing two week immersion tests showed any evidence of cracking, swelling or crumbling. Such examples, of failed structural integrity were common in the immersion tests for portland cement formulations.

2.2.4 Effect of Resin Type and Loading

Anion, cation and mixed bed resins yielded unique regions of acceptable formulations. Anion resin produced a wide region of free standing water but was not susceptible to swelling and cracking during immersion testing. The compositional phase diagram for anion resin solidified with portland type III cement appears in Figure 2.6.

Although less restricted by free standing water problems, the performance of cation resin solidified in portland cement was limited by excessive swelling and deterioration of mechanical integrity both after curing and

Portland Type III
Cation Resin: IRN-77
Water / Cement = 0.4
Dry Resin / Cement = 0.13 (by wt)
Days In Water = 8

Portland Type I
Cation Resin: IRN-77
Water / Cement = 0.4 (by wt)
Dry Resin / Cement = 0.13 (by wt)
Days In Water = 7



Fig. 2.9 Water immersion test comparing waste forms incorporating unloaded cation resin waste solidified with portland type III and portland type I cements.

in immersion testing. Based on these results, the phenomenon of swelling and cracking of ion exchange resin waste forms can be directly attributed to the presence of the cation form of the resin. Figure 2.7 is the compositional phase diagram for cation resin solidified with portland type III cement. Figure 2.10 compares the effects of increasing cation resin content in portland type III cement waste forms in immersion testing. As shown in this figure, these specimens have dry resin-to-cement ratios of 0.13, 0.15, and 0.18 which correspond to 7, 8, and 9% dry resin by weight in the formulations.

The ternary compositional phase diagram developed for the solidification of mixed bed resin with portland type III cement is shown in Figure 2.4. The resultant envelope of acceptable formulations is similar to that observed for the cation resin. While the diagram does show some of the characteristics of anion resin solidification, the behavior of mixed bed resin is dominated by its cation resin component.

A much larger acceptable formulations envelope was observed for the solidification of loaded mixed bed resin with portland type III cement. These results are shown in Figure 2.8. Fewer formulations failed by the free standing water criterion than with unloaded mixed bed resin. Figure 2.11 shows the effect of immersion testing for otherwise equivalent formulations of unloaded and loaded mixed bed resin waste forms.

2.2.5 Effect of Waste-to-Cement Ratio.

The ratio of the weight of dry resin to the weight of dry cement is the waste-to-cement ratio, (W/C). The amount of resin that can successfully be incorporated in a given formulation is a function of cement type, resin type, and water-to-cement ratio. Maximum waste-to-binder ratios for various resin-cement combinations are summarized in Tables 2.6 and 2.7. Table 2.6 represents resin loadings compatible with the formulation criteria of a free standing monolithic solid with no free standing water. Table 2.7 represents the maximum waste-to-binder ratios for those formulations which met these criteria and also maintained their integrity after immersion in water for two

Portland Type III
 Cation Resin IRN-77
 Water / Cement = 0.4 (by wt)
 Dry Resin / Cement = 0.13 (by wt)
 Days In Water = 8

Portland Type III
 Cation Resin IRN-77
 Water / Cement = 0.4 (by wt)
 Dry Resin / Cement = 0.15 (by wt)
 Days In Water = 8

Portland Type III
 Cation Resin IRN-77
 Water / Cement = 0.4 (by wt)
 Dry Resin / Cement = 0.18 (by wt)
 Days In Water = 8



Fig. 2.10 Water immersion test indicating the effect of increasing cation resin content for portland type III cement waste forms.

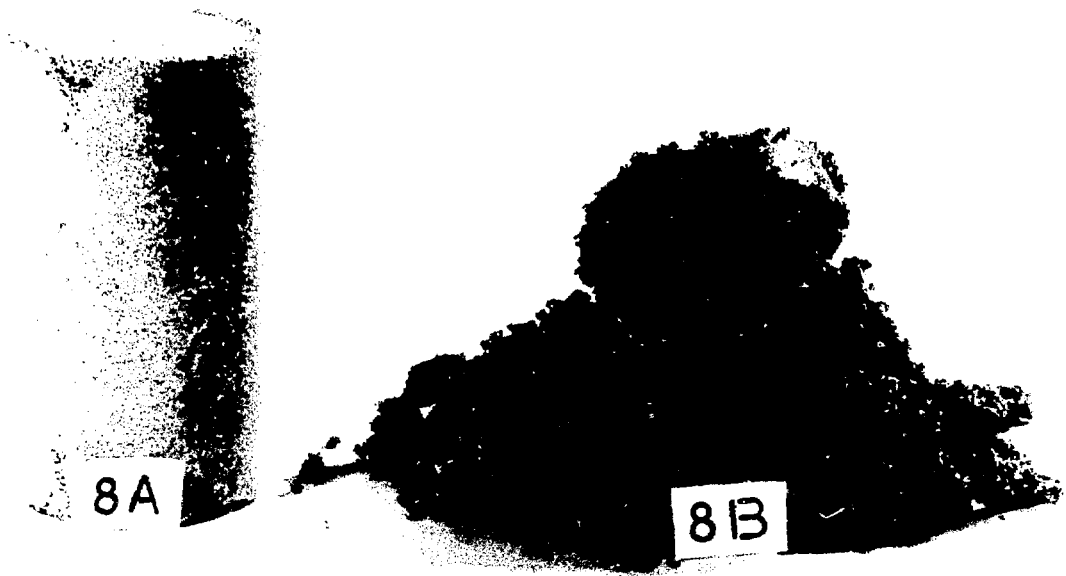


Fig. 2.11 Waste forms after completion of the two week water immersion test comparing the effect of loaded and unloaded mixed bed resin.

TABLE 2.6

Maximum Resin Loadings for Formulations Satisfying Initial Criteria

Cement Type	Resin Type	Cement Wt %	Water Wt %	Dry Resin Wt %	Available Water/Cement Ratio (a)	Waste/Cement Ratio (b)
Portland Type III	loaded mixed bed	25	48	27	.90	1.08
Portland Type III	mixed bed	27	48	25	.58	.93
Portland Type I	mixed bed	27	48	25	.49	.93
Portland Type III	IRN-77	35	39	26	.45	.73
Portland Type III	IRN-78	31	49	20	.80	.63
High Alumina	mixed bed	38	39	23	.15	.59

TABLE 2.7

Maximum Resin Loadings for Various Cement/Resin Combinations
Satisfying Initial Criteria and Passing Two Week Immersion Test

Cement Type	Resin Type	Cement Wt %	Water Wt %	Dry Resin Wt %	Available Water/Cement Ratio (a)	Waste/Cement Ratio (b)
Portland Type III	loaded mixed bed	22	53	25	1.34	1.14
Portland Type III	mixed bed	52	35	13	.32	.25
Portland Type I	mixed bed	58	31	11	.29	.18
Portland Type III	IRN-77	59	29	12	.32	.20
Portland Type III	IRN-78	31	49	20	.80	.63
High Alumina	mixed bed	38	39	23	.15	.59

(a) Water/Cement avail as described in Section 2.2.6.

(b) Dry resin/cement by weight.

weeks. Alternatively, the amount of resin in each formulation is also expressed as a dry resin percentage of the total formulation weight. The waste-to-cement ratio can be derived from compositional phase plots by dividing dry resin weight percent by that of cement. Figure 2.10 is a photograph of an immersion test depicting the effects of increasing waste-to-binder ratios in otherwise equivalent samples.

2.2.6 Effect of Water-to-Cement Ratio.

Water-to-cement weight ratios are typically used to determine the quantities of each constituent in a cement mixture. When solidifying ion exchange resin wastes, however, a portion of the total weight percentage of water contained in the cement-waste mixture is absorbed within the resin beads and thus is not directly available for hydration of the cement. A distinction is made, therefore, between the available water-to-cement ratio, and the true water-to-cement ratio.

The ratio of the weight of all the water included in the formulation to the weight of cement is defined as the true water-to-cement ratio and is expressed by:

$$W/C_{\text{true}} = \frac{(W_{\text{ar}} + W_{\text{iw}} + W_{\text{sw}} + W_{\text{m}})}{\text{cement}} \quad (\text{Eq. 2.9})$$

where,

W_{ar} = water absorbed in the resin

W_{iw} = interstitial water in the waste

W_{sw} = settled water in waste

W_{m} = water added for mixing

The ratio of the weight of water available for cement hydration, to the weight of cement is defined as the available water-to-cement ratio, and is given by the following expression:

$$W/C_{\text{avail.}} = \frac{(W_{iW} + W_{SW} + W_M)}{\text{cement}} \quad (\text{Eq. 2.10})$$

By removing the interstitial and settled water as outlined in Section 1.4.2, these terms (W_{iW} and W_{SW}) can be eliminated from Equations 2.9 and 2.10.

Water-to-cement ratios listed in Tables 2.6 and 2.7 represent available water. True water-to-cement ratios as expressed by Equation 2.9 can be taken directly from compositional phase diagrams by dividing the weight percent of water by that of cement.

Water-to-cement ratios were varied over a wide range to determine the minimum water necessary for mixability and the maximum water allowable without free standing water formation or insufficient mechanical integrity. The effects observed were unique for each resin/cement combination. Figure 2.12 is a photograph of specimens undergoing immersion testing which demonstrates the effect of increasing water-to-cement ratios on mechanical integrity for cation resin wastes solidified with portland type I cement.

2.2.7 Modifications to Improve Waste Form Integrity.

As a result of the relatively narrow range of acceptable formulations determined for the solidification of ion exchange resin waste with portland cement, work was conducted to investigate modified portland cement systems. Attempts to improve the mechanical integrity of portland cement-resin waste forms focused on 1) pretreatment of the resin waste to minimize or prevent shrinking/swelling effects and 2) the modification of the cement matrix itself to provide additional strength.

2.2.7.1 Resin Pretreatment: Since the poor mechanical integrity of solidified ion exchange resins in portland cement is attributed to the shrinking/swelling of the resin beads in the hydrated cement, methods of reducing this phenomenon were investigated. One approach involved coating of the resin beads to limit their interaction with moisture and cationic species available in the cement. To this end, the use of several materials was

Portland Type I
Cation Resin IRN-77
Water / Cement = 0.2 (by wt)
Dry Resin / Cement = 0.13 (by wt)
Days in Water = 7

Portland Type I
Cation Resin IRN-77
Water / Cement = 0.3 (by wt)
Dry Resin / Cement = 0.13 (by wt)
Days in Water = 7

Portland Type I
Cation Resin IRN-77
Water / Cement = 0.4
Dry Resin / Cement = 0.13
Days in Water = 7



Fig. 2.12 Water immersion test comparing the effect of increasing water-to-cement ratio for portland type I cement waste forms incorporating unloaded cation resin.

examined including vinyl ester-styrene, water extendible polyester, sodium silicate, and furfuryl alcohol. A second approach involved the introduction of various calcium compounds to the ion exchange resins prior to solidification to reduce ionic interaction with the cement.

Previous experience indicated that mixed bed ion exchange resins loaded with NaCl, yielded solidified waste forms of poor integrity and which were most susceptible to swelling and cracking in immersion. NaCl loaded mixed bed resins were therefore used to determine if potential modifications or techniques were able to provide significant improvements. The various methods of resin pretreatment are reviewed below and the results of these techniques are summarized in Table 2.8.

1) Vinyl ester-styrene (VES) - This thermosetting polymer marketed by Dow Chemical Co., Midland, MI, is currently being used in conjunction with a promoter/catalyst system to solidify low-level radioactive waste at U.S. nuclear power plants. For this work, however, uninitiated vinyl ester-styrene monomer was utilized to pretreat ion exchange resin prior to solidification with portland cement.

Since the VES is a liquid resin not miscible in water, pretreatment of damp or slurried ion exchange resin waste required the creation of a VES-waste emulsion. This was accomplished using a variable speed air powered laboratory stirrer (Arrow Engineering Co., Hillside, NJ), gradually adding VES to the ion exchange resin slurry and mixing for approximately 10 minutes. This mixture was then added to the portland type III cement and mixed in the same manner as previous cement-resin formulations.

2) Water extendible polyester (WEP) - Use of this uninitiated monomer as an exchange resin pretreatment for portland cement solidification was outlined by Buckley and Speranzini [14]. Aropol WEP 662 (Ashland Chemical Co. Columbus, OH) utilized for this study is also non-miscible with water and required the formation of an emulsion. Mixing procedures and results paralleled those of VES. When quantities of ion exchange resin waste exceeded 15 wt% dry resin, the WEP appeared to interfere with normal water-cement interaction, resulting in samples with drainable free standing liquid.

3) Sodium silicate - Sodium silicates have many properties not shared with other alkaline salts and have many diverse applications in industry including the formation of protective coatings and films [15]. Liquid Sodium Silicate N, (PQ Corp., Valley Forge, PA) was used for this investigation. This product has a syrupy consistency and mixes readily with water, simplifying pretreatment processing. Ion exchange resins were soaked in liquid sodium silicate for one hour prior to solidification in portland type III cement.

4) Furfuryl alcohol (FA) - This monomer marketed by the Quaker Oats Co, Chicago, IL, is a by-product of agricultural wastes. In its polymerized form this product has been used in diverse applications including foundry cores and molds and the production of rapid curing polymer concrete [16,17]. FA dissolves readily in water eliminating the need to form an emulsion. Mixed bed ion exchange resin waste was soaked in furfuryl alcohol monomer for 15 minutes prior to solidification in portland type III cement. As much as 25 wt% dry resin (NaCl loaded, mixed bed) was successfully solidified, i.e. passed free standing water and immersion criteria, by utilizing the FA monomer. This represents a significant improvement over the results of non-treated NaCl loaded resins and approaches the maximum quantities of resin that can physically be incorporated within a cement matrix.

One disadvantage in the use of FA monomer is its inherent instability in the presence of strong acids. Various acids are normally used to initiate the condensation polymerization of FA. Product literature warns that care must be taken even when working in the presence of dilute acid solutions because the inception period of the reaction may lead one to believe that insufficient acid is present to bring on polymerization [16]. No problems were encountered when soaking NaCl loaded resins in FA monomer. When unloaded "as-received" resins were treated in FA monomer a reaction occurred within the resin beads, initiated by free hydrogen ions loosely held at the exchange sites. A large exotherm was observed which eventually led to the deterioration of the resin beads. For this reason, FA pretreatment of unloaded or partially loaded resins which still contain significant amounts of available hydrogen, is not recommended.

5) Calcium pretreatment - In order to minimize the swelling of ion exchange resin beads within the cement, the resin was soaked in solutions containing either calcium hydroxide or calcium chloride prior to solidification in portland type III cement. This technique was found to provide no improvement.

2.2.7.2 Binder Modifications: Two methods of altering the cement matrix itself to provide additional strength were attempted.

1) Sodium metasilicate - This additive has been used in experimental solidification of ion exchange resins used in the Epicor II system at the Three Mile Island, Unit 2 cleanup operation [18]. For this investigation, Metso Bead 2048 (PQ Corp., Valley Forge, PA) was used as an additive to portland type III cement. Both NaCl loaded and fresh unloaded mixed bed resins were solidified with this modified cement system.

Results for both types of ion exchange resins were similar and only moderate improvements were realized for either. Maximum resin incorporated was 10 wt% dry resin for both loaded and unloaded resins. Figure 2.13 is a compositional phase diagram of acceptable formulations for the solidification of unloaded mixed bed resins in portland type III cement plus sodium metasilicate additive. The sodium metasilicate was added at a constant ratio of cement/Metso Beads = 10.

2) Polymer Concrete - Water extendible polyester in conjunction with a promoter/catalyst system was mixed with ion exchange resins and portland type III cement to form a polymer concrete. Aropol WEP 662 polyester resin (Ashland Chemical Co., Columbus, OH) was mixed with cobalt napthanate (CoN) as the promoter along with methyl ethyl ketone peroxide (MEKP) as the catalyst. This mixture was added to the cement-water-ion exchange resin slurry and mixed with an air powered laboratory stirrer for 2 minutes. Formulations of initiated WEP polymer concrete containing as much as 25 wt% dry resin were successfully tested.

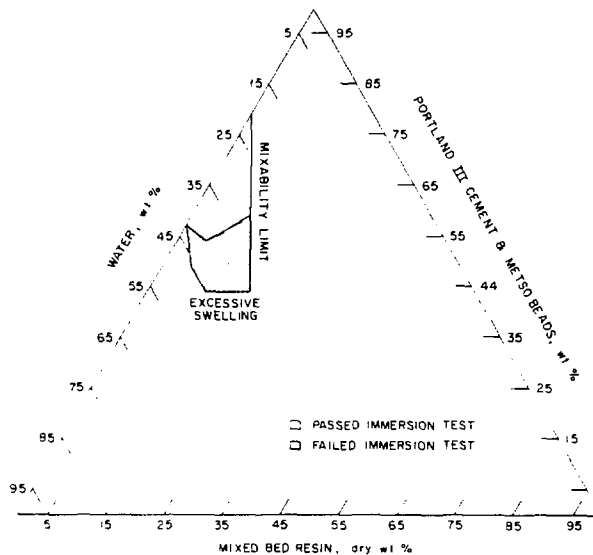


Fig. 2.13 Compositional phase diagram for the solidification of unloaded mixed bed resin with portland type III cement and Metso beads (Na_2SiO_2). Cement/metso beads ratio = 10.

2.2.8 Waste Form Properties.

Work was conducted to determine the physical and chemical properties of cement-ion exchange resin waste formulations within the acceptable ranges developed. The properties of interest include compressive strength, radiation stability, and leachability of waste forms.

2.2.8.1 Compressive Strength: Mechanical integrity of waste forms, is an important consideration in the safe handling and transportation of radioactive waste prior to disposal. Waste form failure under load may result in cracking or friability leading to possible dispersion of activity. Waste form failure also creates a larger effective surface area from which activity can be leached. Therefore, mechanical properties of waste forms are of concern within the disposal environment, as well.

Table 2.8 Maximum Resin Loadings For Various Additives Satisfying Initial Criteria And Passing Two Week Immersion Test

ADDITIVE	DRY RESIN WT% (a)	CEMENT WT% (b)	WATER WT%	ADDITIVE WT%	ADDITIVE/ CEMENT	ADDITIVE/ WASTE
Vinyl Ester Styrene Monomer	15	45	35	5	0.11	0.33
Water Extend- ible Polyester Monomer (WEP)	15	45	35	5	0.11	0.33
Na ₂ SiO ₃ Liquid ²	5	52	30	13	0.24	2.53
Furfuryl Alcohol Monomer	25	30	33	12	0.40	0.48
Na ₂ SiO ₃ Metso Beads	10	54	31	5	0.10	0.57
Polymerized WEP	25	20	30	25	1.25	1.00

(a) NaCl loaded mixed bed resin.

(b) Portland type III cement.

Table 2.9 Compressive Strengths of Typical Cement-Resin Waste Combinations

CEMENT TYPE	WASTE TYPE	CEMENT WT%	WATER WT%	DRY RESIN WT%	COMPRESSIVE STRENGTH, PSI
Portland Type I	Unloaded Mixed Bed Resin	57	38	5	1324
		57	33	10	1327
		58	31	11	1271
		54	33	13	1327
		50	34	16	1329
Portland Type III	Unloaded Mixed Bed Resin	55	37	8	1301
		58	31	11	1329
		52	35	13	1331
		49	35	16	1115
		42	38	20	636
Portland Type III	Fission Product	52	43	5	1316
	Loaded Mixed Bed	55	37	8	1312
	Resin	45	40	15	1193
	(see Sect. 2.1.4.1)	42	38	20	636
High Alumina Cement	Unloaded Mixed Bed Resin	57	38	5	1093
		57	33	10	1160
		53	32	15	1152
		40	40	20	275
		38	39	23	141
Portland Type III	NaCl Loaded Mixed Bed Resin	55	42	3	1292
		52	43	5	896
		52	38	10	1165
		45	40	15	474
		42	38	20	532
Portland Type III	IRN 77 Cation Resin	60	35	5	1338
		55	40	5	933
		55	35	10	1483
		59	29	12	1308
Portland Type III	IRN 78 Anion Resin	60	35	5	1338
		57	33	10	1320
		35	50	15	439
		31	49	20	119

Compression strength testing was conducted as a measure of mechanical integrity. The compressive strengths of typical cement-ion exchange resin waste forms were tested in accordance with the ASTM method C39-72, "Test for the Compressive Strength of Cylindrical Concrete Specimens" [19]. Specimens were cast in 4.7 cm diameter 160 ml cylindrical polyethylene vials which were then capped to prevent evaporative water loss and cured in excess of 90 days. Compression test results are summarized in Table 2.9.

2.2.8.2 Leachability and Radiation Stability: Leachability refers to the release of radionuclides from the waste or solidified waste form into the environment when in contact with liquids. A waste form's ability to resist this release is an important consideration for shallow land burial. Although leachability criteria have yet to be imposed on waste forms within shallow land burial sites, the leaching characteristics of waste forms can be utilized to evaluate their relative potential behavior in the disposal environment.

Radiation stability was examined from the standpoint of the effects of irradiation (from contained activity and that present in the disposal environment) on the leachability characteristics of solidified and unsolidified ion exchange resin wastes.

2.2.8.3 Leachability as a Function of Cement Type: The leachability of ion exchange resin waste solidified in portland type III and high alumina cements was evaluated according to the proposed ANS 16.1 standard leach test [13]. Cation exchange resins were chemically loaded to 25% of their theoretical exchange capacity with a non-radioactive mixture of strontium, cesium and cobalt compounds, to better simulate partially expended resin waste. The resins were then loaded with a tracer solution containing 10.5 μCi of Sr-85, 12.2 μCi of Cs-137, and 9.8 μCi of Co-60. Two replicate waste forms of each cement type were formulated using 59.6 wt% cement, 34.6 wt% water and 5.8 wt% dry cation exchange resin. The solidified specimens were right cylinders with a diameter of 4.7 cm, height of 6.8 cm and a mass of 167.9 grams. Specimens were cured for 55 days prior to initiation of the leaching test.

Leaching was performed in 1380 ml of demineralized water determined according to the recommended ratio of leachant volume to exposed waste form surface area of 10 cm. Leachant was renewed prior to each sampling. 10 ml aliquots were sampled at the prescribed cumulative leaching intervals of 30 seconds, 2 hours, 7 hours, 24 hours, 2, 3, and 4 days. In addition, samples were taken at 7, 14 and 21 days.

The results of leaching studies for ion exchange resin waste solidified in portland type III and high alumina cements are shown in Figures 2.14 through 2.17. Cumulative fraction release is plotted versus time for Cs-137 in Figure 2.14 and for Sr-85 in Figure 2.15. Plotting the fraction release vs. $t^{1/2}$ as in Figure 2.16 and 2.17 provides a linear representation of activity release. The release of Co-60 from waste forms of both cement types was below detection limits.

For the retention of Cs-137 portland type III cement appears to have a slight advantage over high alumina cement. For the duration of the 21 day leach test, the release of Cs-137 from the high alumina cement specimens was greater by a factor of approximately 2. However, this slight advantage is more than offset by the ability of high alumina cement to resist mechanical integrity failure. When a waste form cracks or crumbles, the surface area from which leaching can occur greatly increases.

The release rate for Sr-85 was slightly lower for the high alumina cement during the first week. However, for times greater than 7 days, fraction release of Sr-85 was approximately equivalent in both cement types.

2.2.8.4 Leachability of Irradiated Waste Forms: The formulation selected for this leaching study contained 7.4 wt% dry mixed bed resin, 37.6 wt% water, and 55.0 wt% portland type III cement. These specimens were right cylinders with a diameter of 4.7 cm, a height of 6.5 cm, and a mass of 181.8 grams. Corresponding specimens of damp mixed bed resin waste were also prepared. These specimens consisted of 9.4 grams anion resin and 18.8 grams cation resin in their damp forms (for a total of 13.5 grams resin on a dry basis). Both resin and waste form specimens each contained 53 μ Ci of Cs-137, 42 μ Ci of Sr-85, and 55 μ Ci of Co-60.

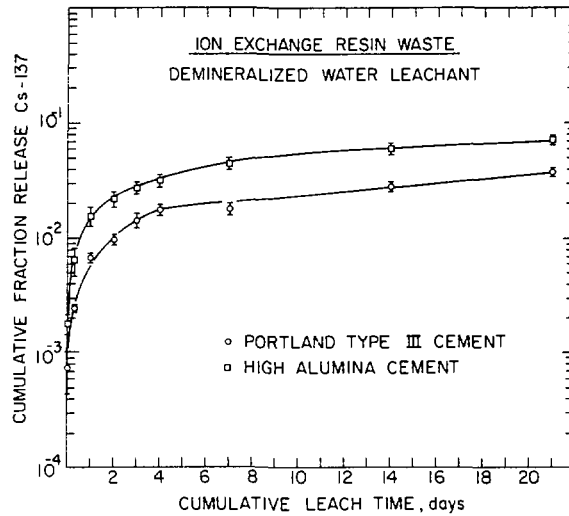


Fig. 2.14 Cs-137 cumulative fraction activity release from solidified ion exchange resins leaching in demineralized water.

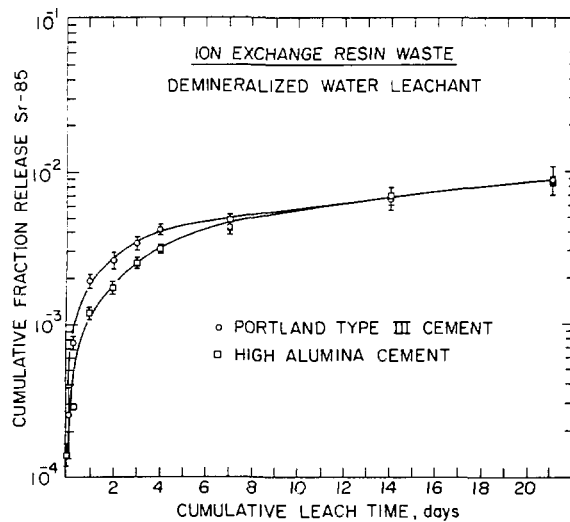


Fig. 2.15 Sr-85 cumulative fraction activity release from solidified ion exchange resins leaching in demineralized water.

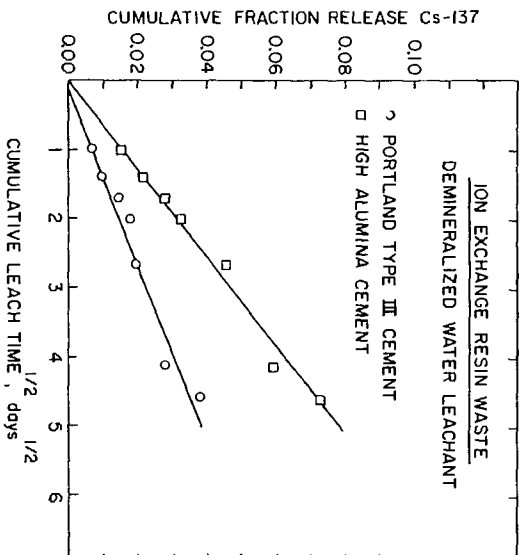


Fig. 2.16 Cs-137 cumulative fraction activity release as a function of $t_2^{1/2}$.

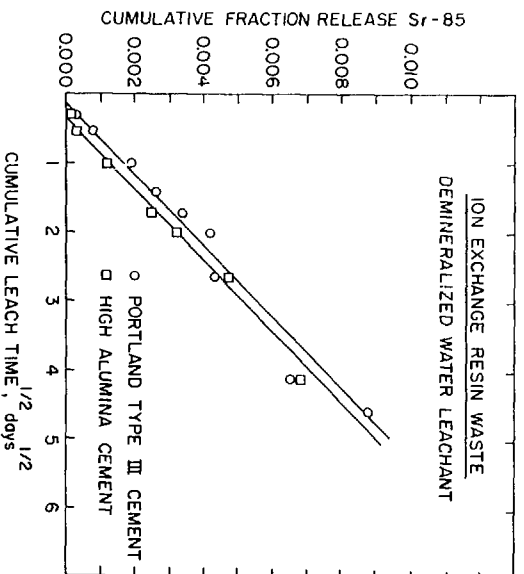


Fig. 2.17 Sr-85 cumulative fraction activity release as a function of $t_2^{1/2}$.

After a two week cure time, these specimens were placed into a Co-60 gamma irradiation facility and irradiated to total doses of 10^4 to 10^8 rads at dose rate of 1.5×10^6 rads/hr. The 10^8 rads dose was selected as representative of the typical maximum long-term dose accumulated in resin wastes.

After all resin and waste form specimens had been irradiated to the desired total dose, they were subjected to static leach tests utilizing both demineralized water and synthetic seawater leachants for cement-resin waste forms. So-called "cement water" and synthetic seawater were used for unsolidified resin. The "cement water" was used in order to employ leachants of similar composition to those in which activity release from cement waste forms occurred. (Soluble cement constituents are released rapidly into demineralized water during leaching so that the water is demineralized only at the initiation of the test.) The "cement water" was prepared by leaching non-radioactive neat portland type III cement cylinders in demineralized water for one week. This was then filtered. The volume of water used was selected to provide a ratio of water volume to cement cylinder external geometric surface area (V_L/S) of 10 cm. Sufficient cement water leachate was prepared in this manner to support leachability testing. Ion exchange resins were leached while contained in a closed mesh nylon bag. The ratio of volume to exposed geometric surface area (V/S) for unsolidified resin waste specimens was 0.8 cm. The V/S ratio for cement-resin waste forms was 0.84 cm. Sufficient leachant was used to provide a leachant volume to exposed geometric surface area ratio of 10 cm.

Leaching of ion exchange resins exposed to total doses of 0 (control), 10^4 , 10^6 and 10^8 rads did not indicate any apparent effect of irradiation on resin waste activity release in cement water.

Figures 2.18 and 2.19 show initial Cs-137 cumulative fractional activity releases as a function of leach time in demineralized/cement water leachants and seawater leachant, respectively, for waste forms exposed to a total dose of 10^8 rads. The Cs-137 fraction release from unsolidified ion exchange resin in cement water was significantly lower than that observed for the cement-resin waste forms in demineralized water. Cesium, however, is known to be one of the most easily leachable species from cement matrices.

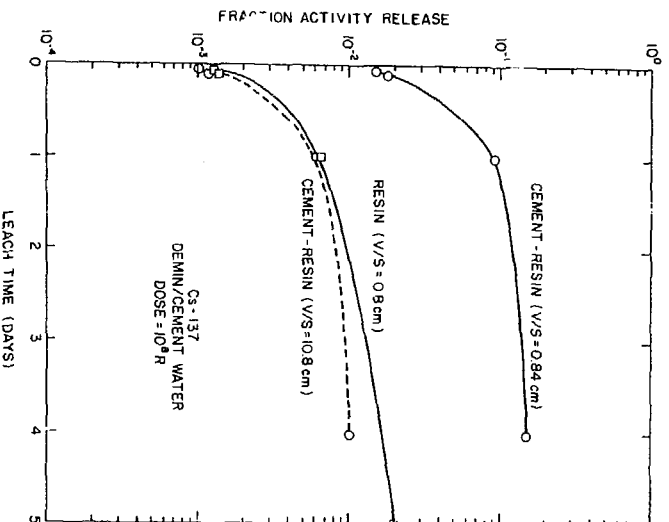


Fig. 2.18 Cs-137 release for specimens irradiated for a total dose of 10^8 rads and leached in demin/cement water.

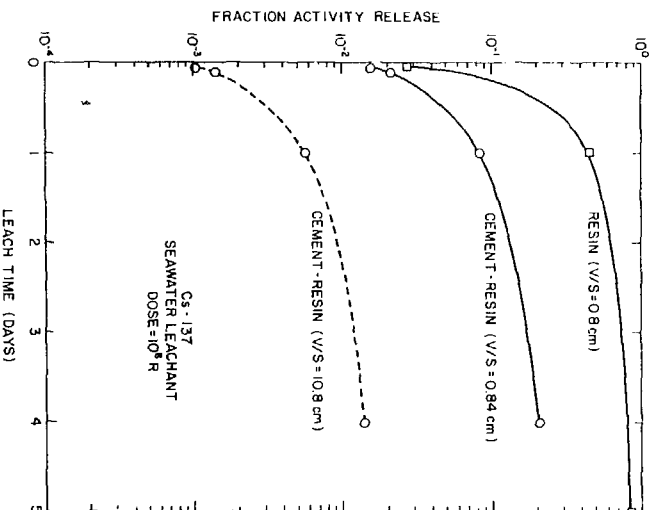


Fig. 2.19 Cs-137 release for specimens irradiated for a total dose of 10^8 rads and leached in seawater.

In synthetic seawater, Cs-137 is released significantly more rapidly from the unsolidified ion exchange resin than from resin solidified in cement. It is not unexpected to observe the rapid release of activity from ion exchange resin in high ionic strength solutions such as seawater. Data were also obtained for Sr-85 and Co-60 releases.

Leaching may proceed by a number of mechanisms. Often leaching is dominated by diffusion, although other mechanisms may include dissolution, chemical reactions and combinations thereof. Diffusion in particular and other mechanisms as well are sensitive to the specific surface area of the waste form exposed to the leachant. For example, the semi-infinite solution for mass transport by diffusion from a homogeneous medium having a zero surface contamination for all $t \geq 0$ is (neglecting decay):

$$(\Sigma a_n / A_0) (V/S) = 2(D_e / \pi)^{1/2} t^{1/2} \quad (\text{Eqn 2.11})$$

where,

Σa_n = cumulative activity removed,

A_0 = initial activity,

V = specimen volume

S = specimen geometric surface area,

D_e = effective diffusivity, and

t = cumulative leach time.

The effective diffusivity is a material constant for the waste form and radionuclide considered under the constraints of the test procedure [11].

Laboratory leach test data can then be extrapolated to full-scale waste forms by appropriate use of the V/S ratio. A 210 liter (55 gallon) waste form has a V/S ratio of 10.8 cm. Therefore, Eqn 2.11 predicts that leaching of a 210 liter cement-resin form under similar conditions would provide cumulative fractional activity releases only 7.8% of those observed in laboratory leaching experiments ($V/S = 0.84$ cm) for any given leach time. Calculated cumulative fractional activity release curves have been included in Figures 2.18 and 2.19 to estimate releases from 210 liter cement-resin waste

forms. Unsolidified ion exchange resin waste has the same effective V/S ratio independent of waste quantity or container size, since the leachant can contact each individual resin bead. The resin waste V/S ratio is determined by the average resin bead volume and its average external surface area. A V/S ratio of 0.8 cm was calculated for the resin waste used in this work. Fractional activity releases in leaching from unsolidified resins are not dependent upon the quantity of the resin waste disposed. Although laboratory experiments showed a significantly greater Cs-137 release from cement-resin waste forms than from unsolidified resin in demineralized/cement water leachants, application of respective V/S ratios indicate that this would not be the case for 210 liter cement-resin waste forms. Thus, it appears solidification of resin wastes can provide decreased leachability in disposal environments.

Another interesting effect of Co-60 irradiation on cement-resin waste forms was noted. Portland type III cement-mixed bed resin waste forms were prepared using a formulation that passed initial acceptability criteria, but did not pass the two week water immersion test. After curing for two weeks, specimens were irradiated in triplicate to total doses of 0 (control), 10^4 , 10^6 and 10^8 rads at 1.5×10^6 rads/hr. After all specimens had been irradiated, they were then subjected to the water immersion test. The control, 10^4 and 10^6 rads total dose specimens failed the immersion test; however, the 10^8 rads specimens passed. Also, the 10^6 rads specimens did have notably better specimen integrity in immersion than the control and 10^4 rads specimens. No difference in behavior was evident between the control and 10^4 specimens.

It is presumed that this behavior is due either to increased cross-linking of the resins, thereby reducing their ability to shrink and swell, or the reduction of the number of functional exchange sites on the resin, limiting its capacity for ionic sorption.

2.3 Electron Microscope Analysis of Resin-Cement Interactions.

2.3.1 Introduction.

Chemical interactions between ion exchange resin and portland type III cement were explored by means of an AMRAY 1000A scanning electron microscope (SEM) and a Tracor Northern 2000 x-ray energy analyzer for energy dispersive x-ray analysis. Single resin beads solidified within a cement matrix were examined and compared with unsolidified beads and a section of neat, portland type III cement. This allowed the semi-quantitative determination of chemical interactions between the bead and the cement in the immediate region of the resin beads.

Cation (IRN-77) and anion (IRN-78) exchange resins manufactured by Rohm and Haas were used. Samples were prepared for SEM analysis by application of carbon coatings in order to provide a conductive surface.

A preliminary investigation demonstrated that, at the magnifications employed, the x-ray analysis provided a spectrum which was reproducible at various positions on a neat cement sample. In this way, it was confirmed that the spectra obtained were not those of individual mineral crystals within the cement, but an average of a discrete region of the binder.

2.3.2 Spectral Analysis.

Analysis of an unsolidified NaCl loaded cation resin bead yielded a spectrum showing only the strong sulfur line which is ubiquitous in the cation form of this resin plus a clear sodium line (Figure 2.20). Similarly the anion form of the resin gave spectra showing the presence of only chlorine. The technique therefore was able to determine qualitatively, the loading of the beads.

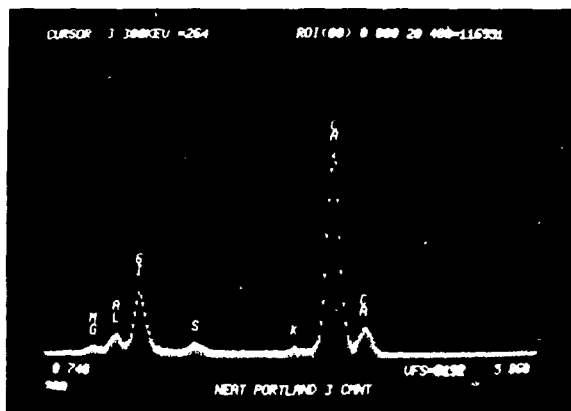


Fig. 2.20 Spectrum from x-ray excitation analysis of neat portland type III cement.

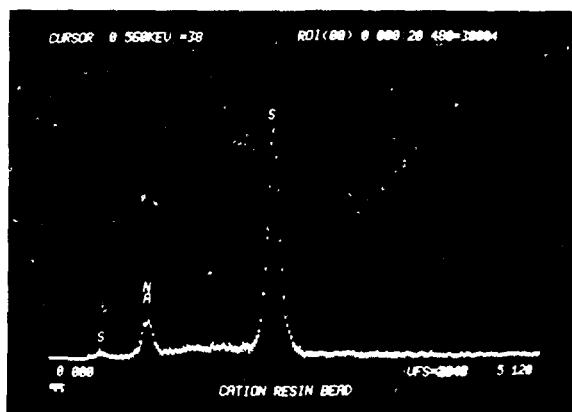


Fig. 2.21 Spectrum from x-ray excitation analysis of individual sodium loaded cation resin bead.

Figure 2.21 is a spectrum of a neat portland type III cement sample. There is a strong calcium peak followed in intensity by silicon and aluminum. Traces of sulfur, potassium and magnesium are also present. The ratios of the peak heights of the major elements are given in Table 2.10.

Figure 2.22 is an SEM photomicrograph (60x magnification) of a portion of a laboratory scale portland type III cement waste form containing a mixture of two parts cation resin and one part anion resin. This waste form successfully completed a two week water immersion test. The beads have shrunk away from the cement leaving voids. This is very likely an artifact of the microscopy process because the chamber of the SEM, in which the samples are examined, is

Table 2.10

Ratios of Elements in Ion Exchange Resin and Portland Cement Samples
Determined by Energy Dispersive X-Ray Analysis

	Sample	Al/Ca	Si/Ca	S/Ca	Al/Ca
1.	Neat Cement	0.08	0.32	0.05	0.25
2.	Resin Bead in Cement	0.24	0.08	0.97	3.00
3.	Cement on Resin Bead	0.20	0.15	0.53	1.33
4.	Cement away from Bead	0.07	0.41	0.08	0.60

evacuated. This would dry the beads and cause them to shrink. Each bead in the photo appears to be coated with cementitious material which adheres to the surface.

The resin bead on the right hand margin of Figure 2.22 was subjected to x-ray analysis. On the upper region of the bead a clear space, uncontaminated by cement, was found which revealed the smooth surface of the bead itself. Figure 2.23 shows the x-ray spectrum obtained from this position. The very high sulfur peak, typical of exchange resins, was present. So too,



Fig. 2.22 SEM photograph of resin beads in cement which had passed the immersion test. The bead in the upper right-hand corner was subjected to x-ray excitation analysis. Magnification: 60x
Scale: 1cm = 125 μ .

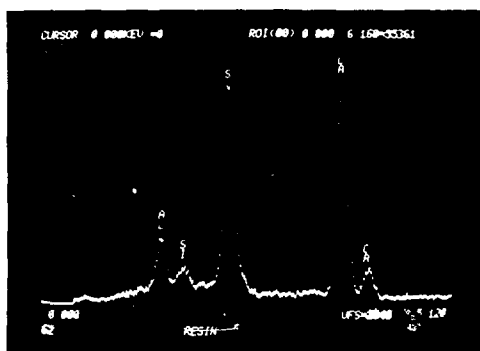


Fig. 2.23 X-ray excitation spectrum for a portion of the resin bead depicted in Figure 3.3.

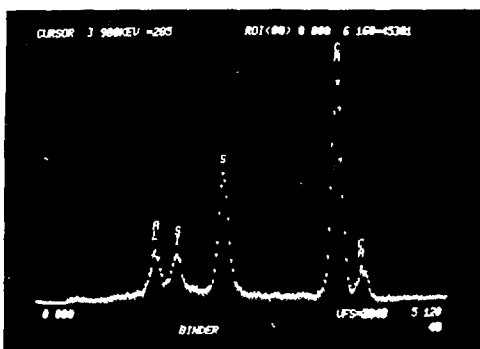


Fig. 2.24 X-ray excitation spectrum for a portion of the cement adhering to the resin bead depicted in Figure 3.3.

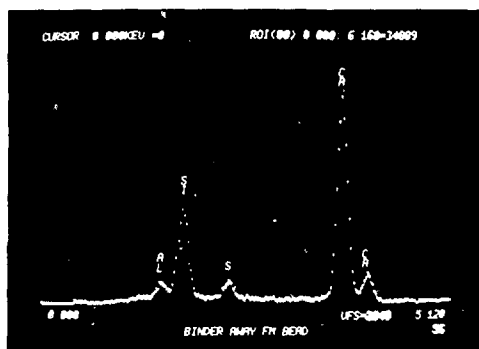


Fig. 2.25 X-ray excitation spectrum for a portion of the cement located approximately 100 microns from any bead.

was a strong calcium peak, typical of cement. Aluminum and silicon were also present with aluminum exhibiting a peak height which was three times greater than that of silicon. The resin bead had taken up components of the cement and, in the case of aluminum, had concentrated it by a factor of 12 relative to silicon. The ratio of these peaks are shown as Sample 2 in Table 2.10.

On the same resin bead (Figure 2.22) a portion of the bright white surface coating was analyzed. The spectrum is shown in Figure 2.24. Here the peak heights for aluminum and silicon are of similar magnitude while the sulfur peak is much reduced from that of Figure 2.23. Compared to neat cement this sample is enriched in aluminum by factors of 3 to 5. It is depleted in silicon and strongly enriched in sulfur by a factor of 10. The resin bead appears to have given up some sulfur to the binder. It should be cautioned that the strong peak of sulfur may be due in part to excitation of sulfur within the bead itself, beneath the cement coating. The ratio of peak heights are given as Sample 3 in Table 2.10.

The last spectrum (Figure 2.25) shows the composition of a portion of the cement matrix which is at a position distant from any resin bead. The spectrum is similar to that of neat cement. However, sulfur is enriched in the binder by a factor of 1.6. Aluminum, relative to calcium, is very similar while silicon is slightly enriched. Apparent enrichment of silicon may be due to slight depletion of calcium. Peak height ratios are shown for Sample 4 in Table 2.10.

From these analyses a trend appears. Resin beads when cast in cement interact with the components of the cement. The resin appears to sorb calcium and aluminum preferentially but also some silicon. Moreover, because sulfur is enriched in cement sampled close to resin beads, the resin beads may be giving up sulfur to the cement. The only way that this could occur is if the bead itself were being destroyed. The sulfonate groups, which are the cation exchange sites of the resin and the source of sulfur are integral parts of the exchange resin. If sulfur is indeed being released from the beads then it would appear that the high pH of the cement may cause the resin to break down.

A micrograph of a resin bead magnified 2100 times is shown in Figure 2.26. Very little pitting is seen on the surface. In contrast, Figure 2.27 shows a resin bead magnified 1500 times in a cement sample which failed the water immersion test. Here the surface of the bead is heavily pitted and fibrous crystals have grown on the resin. An overview of the entire bead is shown in Figure 2.28. Based on limited sampling this pitting has only been observed in cement samples that failed the water immersion test. Almost no pitting was found in resin beads from stable cement waste forms.

2.4 Solidification with Polymer Modified Gypsum Cement (Envirostone).

2.4.1 Description of Envirostone.

Envirostone is the trade name given a polymer modified gypsum based cement product, recently developed by United States Gypsum Company, Chicago, Illinois, for the solidification of low-level radioactive waste. According to manufacturer's claims its advantages include: fast controllable set time, easy clean-up of equipment, applicability to a wide variety of waste streams, an exothermic temperature rise for determining set, high packaging efficiencies and relatively low cast densities [21]. In tests conducted by U.S. Gypsum Co., Envirostone was successfully used to solidify boric acid, organic liquids including lubricating oils and scintillation fluids, and ion exchange bead resin waste streams [22].

Envirostone is a finely ground, nonflammable white powder consisting of gypsum plaster with resin polymer and catalyst additives. Gypsum plaster is the hemihydrate form of calcium sulfate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$). Envirostone was found to have a rapid set time, forming a white plaster in the solid phase. A minimum of 18 wt% water is necessary for complete hydration of the gypsum plaster.

2.4.2 Formulation Development.

Unloaded mixed bed ion exchange resin was prepared with interstitial water removed as discussed in Section 2.1.4.2. The average water content of this damp resin was 58% by weight. Other resin properties apply as stated previously.



Fig. 2.26 SEM photograph of a resin bead which had not been placed in cement. Magnification: 2100x Scale: 1cm = 3.6 μ .

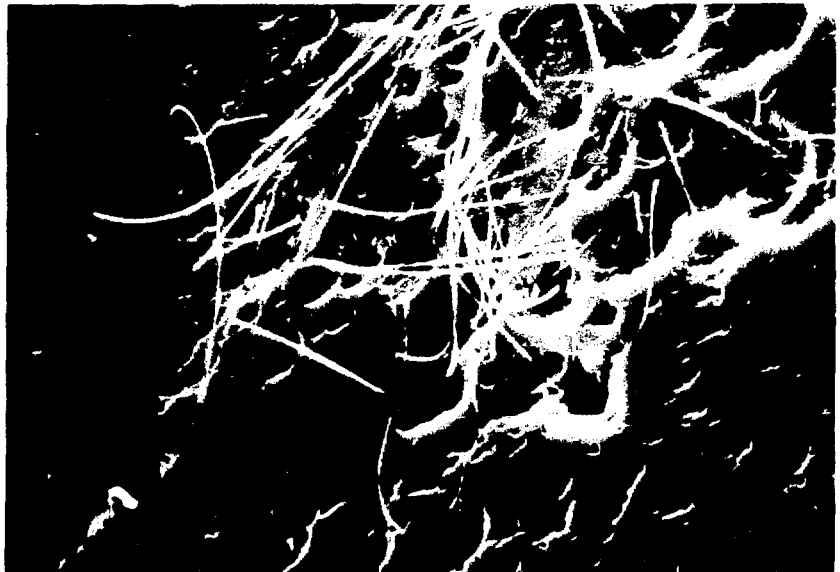


Fig. 2.27 SEM photograph of the surface of a resin bead from a cement sample which failed the immersion test. Magnification: 1500x Scale: 1cm = 6.7 μ .



Fig. 2.28 SEM photograph giving an overview of the resin bead depicted above and the cement matrix. Magnification: 160 x Scale: 1cm = 67 μ .

Numerous formulations were prepared covering a wide range of Envirostone-water-resin proportions. The same procedure was followed for each specimen: specified amounts of Envirostone, water, and damp resin were combined to provide the proper weight percentage compositions. The materials were then placed into a stainless steel mixing bowl and mixed at low speed for two minutes with a Hobart mixer. After mixing, the material was quickly poured into 160 ml polyethylene specimen preparation containers. Two samples were made from each formulation. Waste form specimens were cylindrical, with average dimensions of 4.7 cm in diameter and 8.5 cm in height. After weight measurements were recorded, the specimen containers were covered to minimize evaporative water losses and were then set aside to cure at 25°C. Daily checks were made for the presence of observable free standing water.

The varied formulations led to a wide range of specimen consistencies, from very dry (not pourable) to thin and frothy. Many of the drier formulations (less than 40 wt% water) began setting up before the specimen containers could be filled. This is noted as a potential problem with the large-scale use of Envirostone as a waste solidification agent. Set time for Envirostone was determined by use of the Vicat needle apparatus as described in ASTM Test Method C472-73 for Physical Testing of Gypsum Plasters and Gypsum Concrete [23]. The average set time was 17 minutes. However, specimens typically lost their workability within five minutes or less.

Figure 2.29 is the compositional phase diagram illustrating regions of acceptable formulations for the solidification of unloaded mixed bed resin waste with Envirostone. Constituents are expressed as weight percentages of Envirostone, dry resin, and water. All acceptable formulations produced specimens which were free standing solids. Some formulations, however, were too dry to mix. These represent formulations in which the available water was insufficient. As a result the specimens remained powdery and did not solidify.

In Figure 2.29 acceptable formulations for a twenty-four hour cure time are indicated by the lightly shaded areas. None of these specimens exhibited free standing water after this time. For formulations just outside the acceptable region, some specimens showed a statistical variation in the

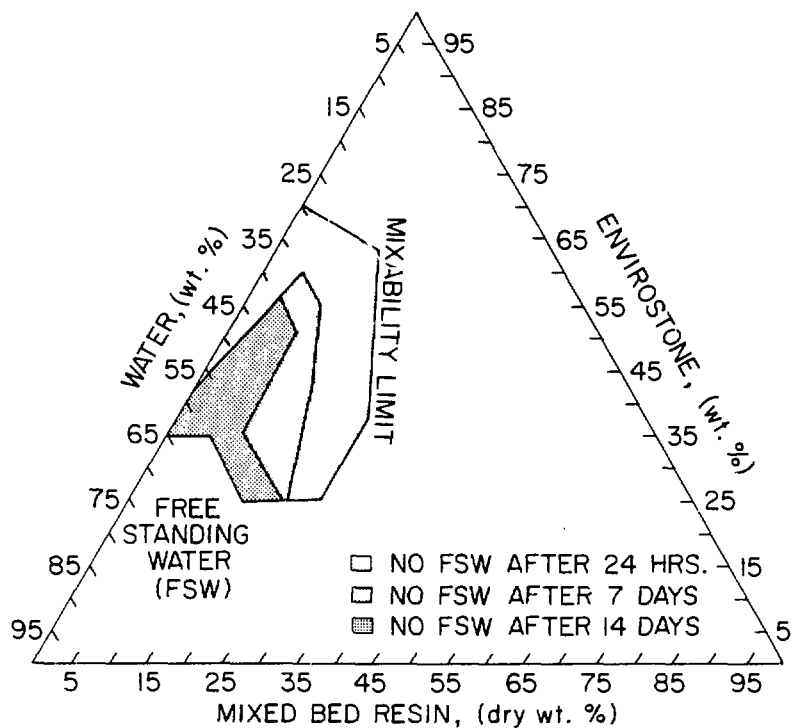


Fig. 2.29 Compositional phase diagram for the solidification of unloaded mixed bed resin with Envirostone.

presence of free standing water. For example, in some cases one sample of a pair produced free standing water while the other did not. Duplications of such formulations also showed similar variations. These formulations are unacceptable. Medium and heavily shaded areas represent the formulations for which free standing water was absorbed or combined in the waste form within one week and two weeks, respectively.

Those specimens which had no free-standing water present after one week were then subjected to an immersion test. One waste form of each formulation was removed from the specimen container and individually submersed in demineralized water. 1750 ml of water was used, based on the proposed ANS 16.1 standard leach test as discussed in Section 2.2.2. The immersion containers were left undisturbed for two weeks. After this time, specimens were removed from the water and examined.

These tests were conducted to examine the possible effects of swelling and/or shrinking of the specimens when contacted with water and to indicate their longer term integrity. As discussed in Section 2.2.2 waste forms containing ion exchange resins solidified in a portland cement matrix were subject to swelling, cracking and crumbling when immersed in water. This behavior was not observed for any of the Envirostone formulations. None of the specimens exhibited any cracking while immersed. A few resin beads (<1 gram) were found in the bottom of some containers which held specimens whose compositions contained in excess of 10 wt% dry resin.

This phenomenon might be explained in either of two ways. One possibility is that the swelling of the resin beads due to additional water absorption or chemical exchange, caused surface beads to "pop" out of the sample. The second possibility is related to the solubility of gypsum in water. Gypsum dissolves at a rate of 0.24gm/100cc of water at 25°C [24]. For the immersion test specimens, this corresponds to a loss of about 4.2 grams of Envirostone per specimen. The thickness of the outer specimen layer which would be dissolved to correspond to this weight loss ranges from about 0.2-0.3 mm. This thickness is comparable to resin bead radii, indicating that surface beads may be released due to Envirostone dissolution. Figure 2.30 is a photograph of two Envirostone samples before and after immersion testing. Figure 2.31 depicts the effects of immersion as a function of resin content.

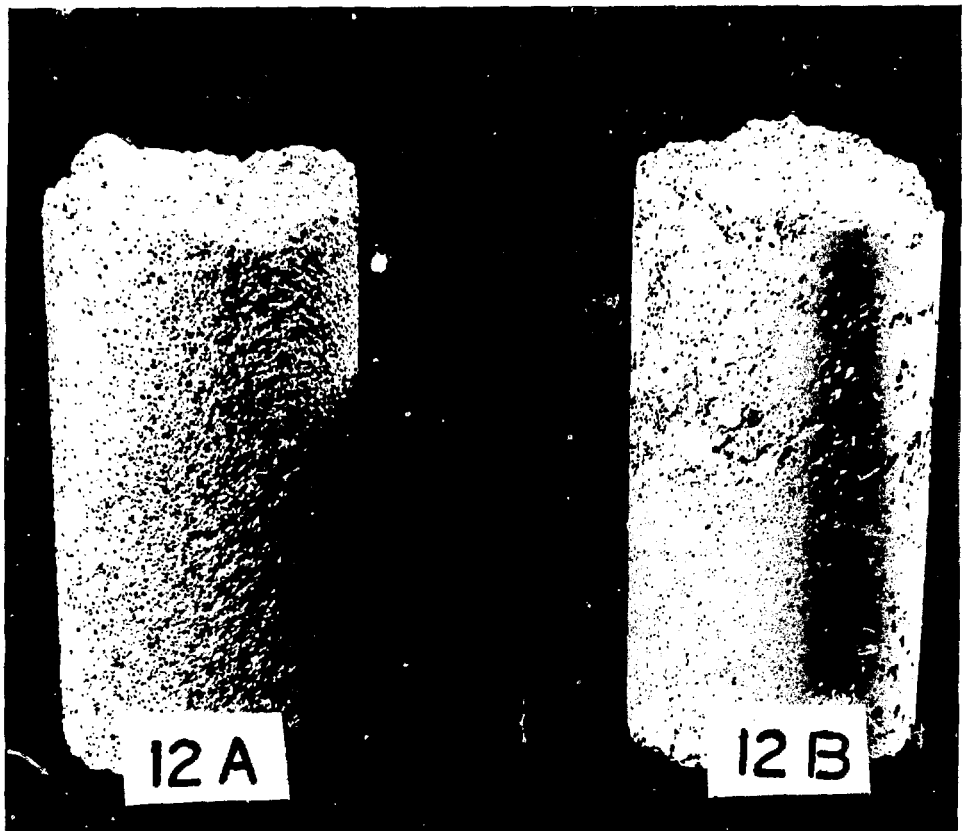


Fig. 2.30 Effect of immersion testing on Envirostone waste forms containing unloaded mixed bed resin.

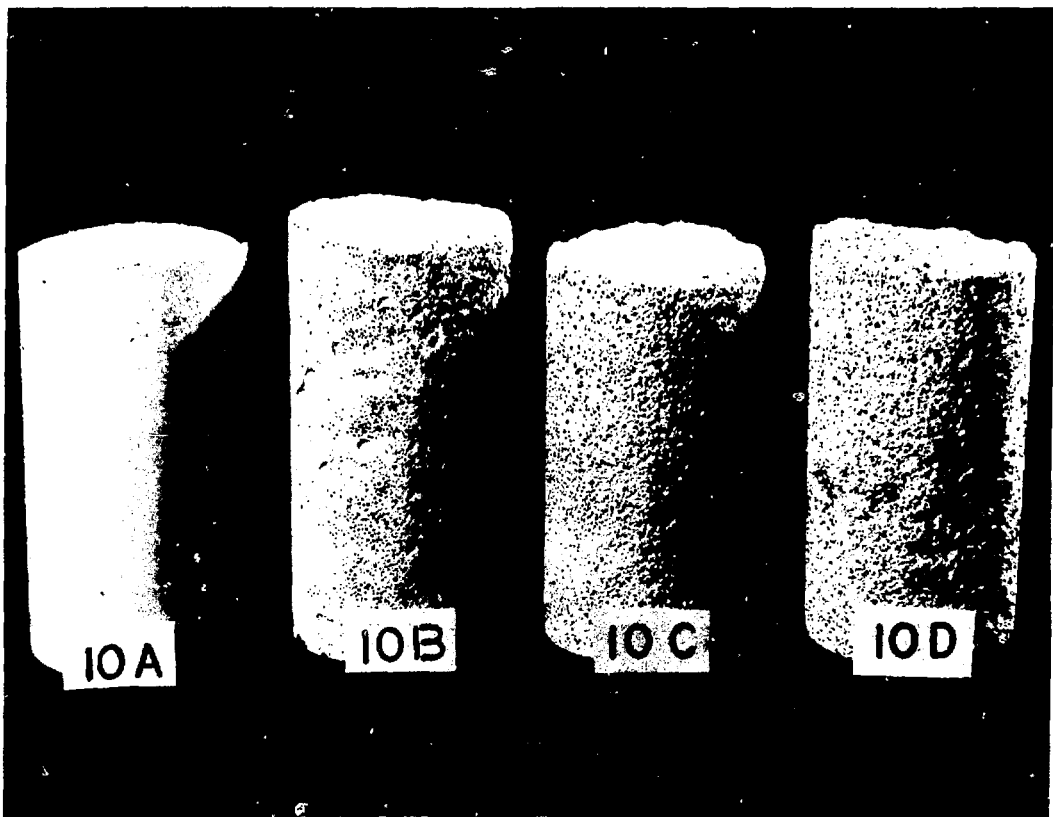


Fig. 2.31 Effect of unloading mixed bed resin contents on Envirostone waste forms after immersion testing. (Specimens 10A-10D contain 5, 10, 11, 15 wt% dry resin, respectively.)

Although no precise measurements were made, many samples exhibited about a 10% swelling in volume while undergoing the immersion test. Swelling was more pronounced in those formulations with resin loadings greater than 10 wt%. It was also noted that surface hardness decreased after the immersion test. Although remaining intact for the duration of the two week immersion test, those samples with high resin contents (>20 wt%) tended to become brittle and have poor mechanical strength when removed from the water. The ability of the matrix to swell, thus conforming to resin bead volume increases may account for the absence of cracking and crumbling behavior in immersion (since like portland cement, Envirostone has a relatively poor tensile strength).

Density measurements were made to examine the correlation between sample swelling, loosening of resin beads, and formulation percentages. Figure 2.32 shows specimen density as a function of resin loading for three different Envirostone/water ratios. Figure 2.33 represents density as a function of the weight percentage Envirostone in the specimen. Both graphs illustrate that waste form density decreases with increased resin loading, and that density increases with increased Envirostone content. These two factors correspond to the immersion test results; specimens with high resin loadings had lower densities and more capacity for water absorption, which in turn led to increased swelling.

2.4.3 Waste Form Properties.

2.4.3.1 Compressive Strength: The mechanical strength of waste forms with Envirostone was examined using a Soiltest (Model 2520) compression test machine in accordance with ASTM procedures [23]. Specimens encompassing twenty-two different formulations were made in triplicate following the same procedure described earlier. The average specimen diameter was 4.7 cm and average height was 7.5 cm. Specimens were then cured for 1 or 3 weeks, as indicated on the graphs which follow. The formulations were chosen to examine three items:

- the effect of increased resin loadings for three different Envirostone/water ratios, (Figure 2.34).
- the effect of increased Envirostone content for given resin loadings (Figure 2.35).
- the effect of a three week vs. one week cure time (Figure 2.36).

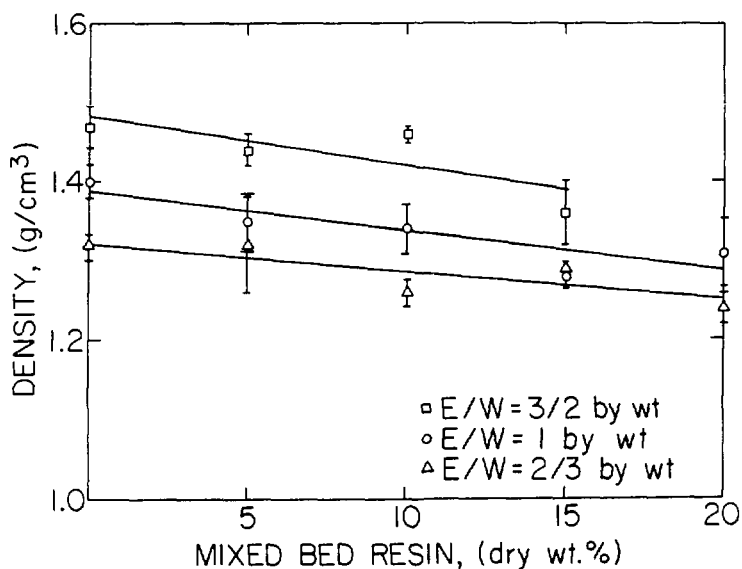


Fig. 2.32 Envirostone waste form density as a function of unloaded mixed bed resin content.

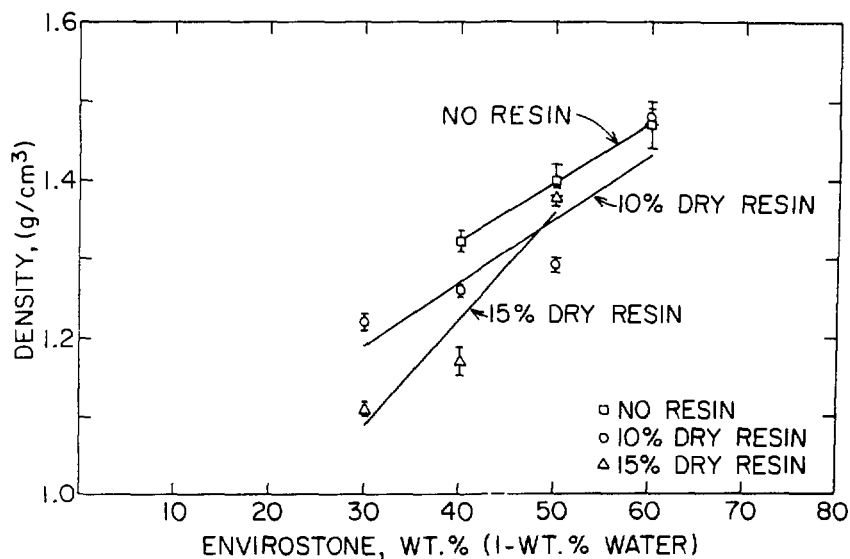


Fig. 2.33 Density of Envirostone-mixed bed resin waste forms as a function of wt% Envirostone.

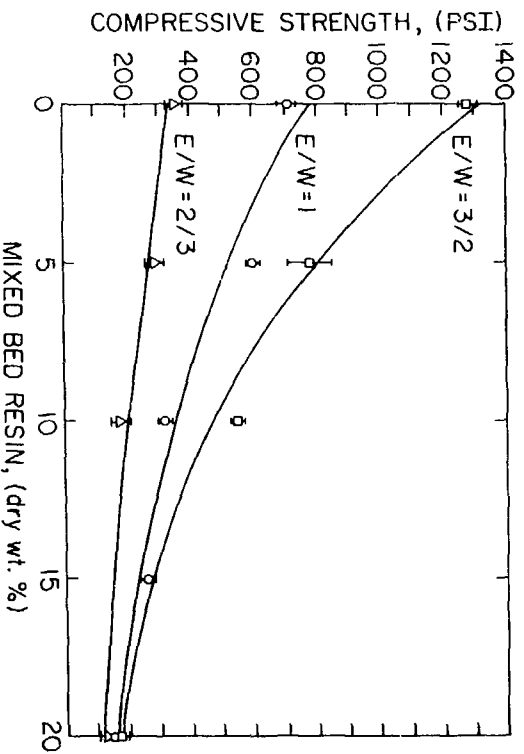


Fig. 2.34 Compressive strength of Envirostone-mixed bed resin waste forms as a function of resin content at various Envirostone/water ratios.

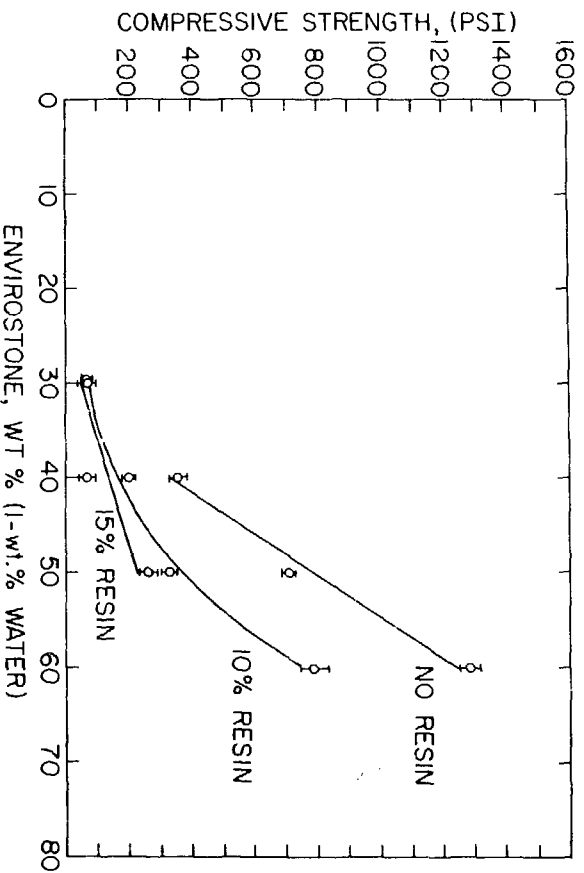


Fig. 2.35 Compressive strength of Envirostone-mixed bed resin waste forms as a function of Envirostone content for various resin contents.

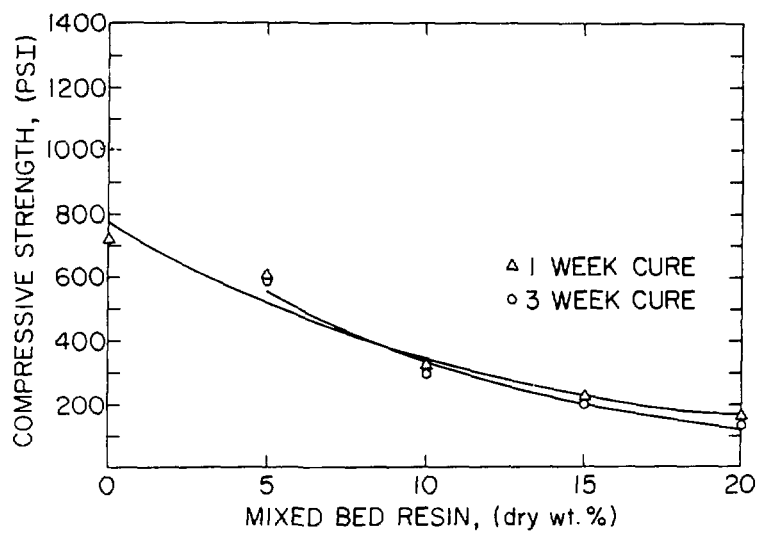


Fig. 2.36 Compressive strength of Envirostone-mixed bed resin waste forms as a function of resin content for one week cure times.

There are three general conclusions which can be drawn by examining this data. The first is that the compressive strength of the formulations decreases as resin content increases for a given Envirostone/water ratio. Similarly, increasing the Envirostone/water ratio for a given resin loading increases formulation strength. The effect of increased cure time (3 weeks instead of one week) is seen to be negligible for the formulations tested.

2.4.3.2 Leachability: The leaching properties of Envirostone waste forms containing mixed bed ion exchange resins were examined. The specimens used to conduct the leach tests were spiked with radioactive tracers, and thus they required a modification of the mixing procedure. Specified amounts of resin and water were measured and added to specimen preparation vials. Four milliliters of a tracer solution were then added to each vial. Each specimen contained approximately 140 μ Ci of activity of each of three isotopes: cesium-137, strontium-85 and cobalt-60. After addition of the tracer solution, the vials were covered and left undisturbed for 72 hours. This allowed time for the resin to adsorb the radionuclides and thus more aptly represent an actual waste stream.

After 72 hours, a premeasured amount of Envirostone was added to the resin and water slurry. Each specimen mixture was stirred in the preparation container for two minutes. Stirring was done by hand with a stainless steel stirring rod. After mixing, the specimen containers were covered and left to cure for one week at 25°C before the initiation of the leach test.

Three different formulations were used: two specimens were made with no resin, two with 5 wt% dry resin, and four with 10 wt% dry resin. Two of the 10 wt% dry resin specimens were leached in synthetic seawater, while the other specimen formulations were leached in deionized water. Leach test specimens measured 4.7 cm in diameter and 8.7 cm high. After they had cured for one week, each specimen was removed from its preparation container and suspended with monofilament cord in the center of the leachant.

The leach test complied with the proposed ANS 16.1 standard for the measurement of leachability of low-level radioactive waste forms with the following modifications. The ANS 16.1 test calls for leachate sampling and replacement at cumulative intervals of 30 seconds, 2 hours, 7 hours, 24 hours,

2, 3, and 4 days. These intervals were paralleled through the fourth day, after which aliquots were taken on the eighth day of leaching and weekly thereafter for 6 weeks. After six weeks of cumulative leach time, sampling continued at the rate of once per month.

Figure 2.37 shows the leaching data in deionized water for each of the three sets of Envirostone specimens containing 0, 5 wt% and 10 wt% dry mixed bed ion exchange resin respectively. Figure 2.38 shows leachability for samples containing 10 wt% dry resin in synthetic seawater. Each figure indicates the cumulative fraction releases for strontium-85, cobalt-60 and cesium-137 for 44 days of leaching. The cumulative fraction release for cesium was between 83% and 91% in deionized water and was 98% for leaching in seawater. Cumulative cobalt fraction releases ranged between 68% and 78% in deionized water while in seawater it was 87%. Strontium releases exhibited the greatest variability, showing apparent sensitivity to the presence of ion exchange resin in the specimens. The two sets of specimens containing 5 wt% and 10 wt% resin released 57% and 49% strontium respectively while the set of samples containing no resin gave a 27% cumulative fraction release after 44 days. In seawater, the cumulative fraction release for strontium was 73%.

2.5 Solidification with Thermosetting Polymers.

2.5.1 Description of Vinyl Ester-Styrene.

Solidification of ion exchange resin wastes with thermosetting polymers was performed using the vinyl ester-styrene binder developed by Dow Industrial Services.^(a) The Dow binder is currently being employed to solidify low-level radioactive waste at U.S. nuclear power plants utilizing both installed and mobile solidification equipment. Vinyl ester-styrene has been used to solidify a variety of wet solid waste streams including ion exchange resins, evaporator bottoms, filter aid materials and decontamination solvents [25, 26].

^(a) Dow Chemical Company, Midland, MI 48640

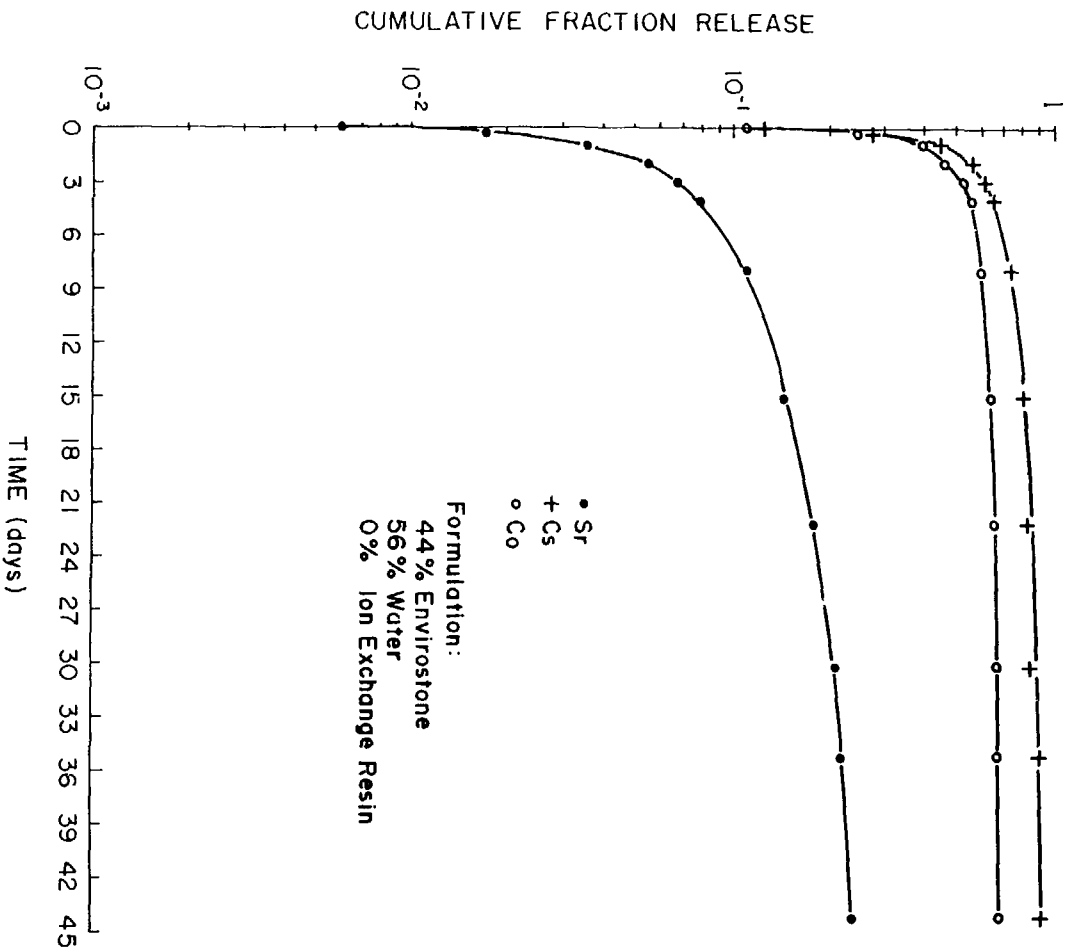


Fig. 2.37(a) Average cumulative fraction release Sr-85, Cs-137 and Co-60 vs. time for deionized water leaching of Envirostone.

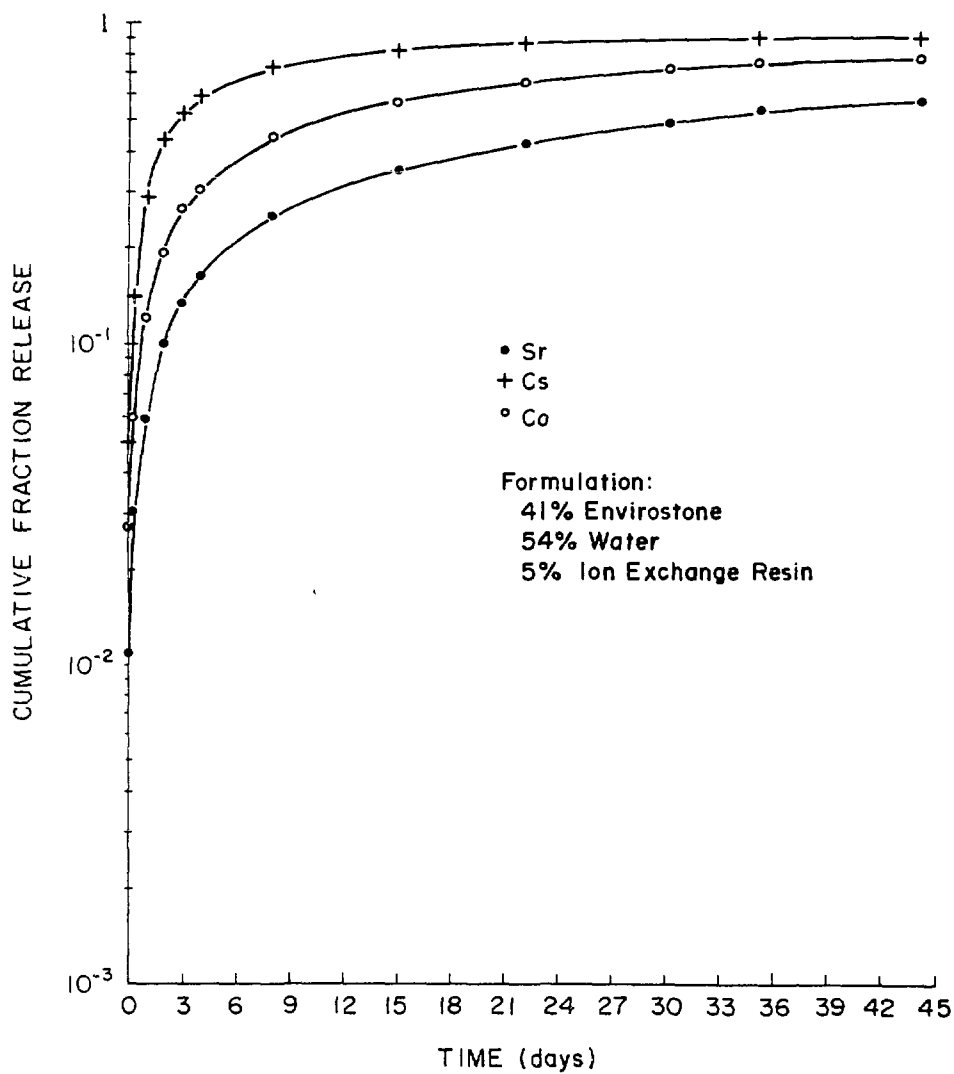


Fig. 2.37(b) Average cumulative fraction release Sr-85, Cs-137 and Co-60 vs. time for deionized water leaching of Envirostone waste forms containing 5 wt% dry mixed bed resin.

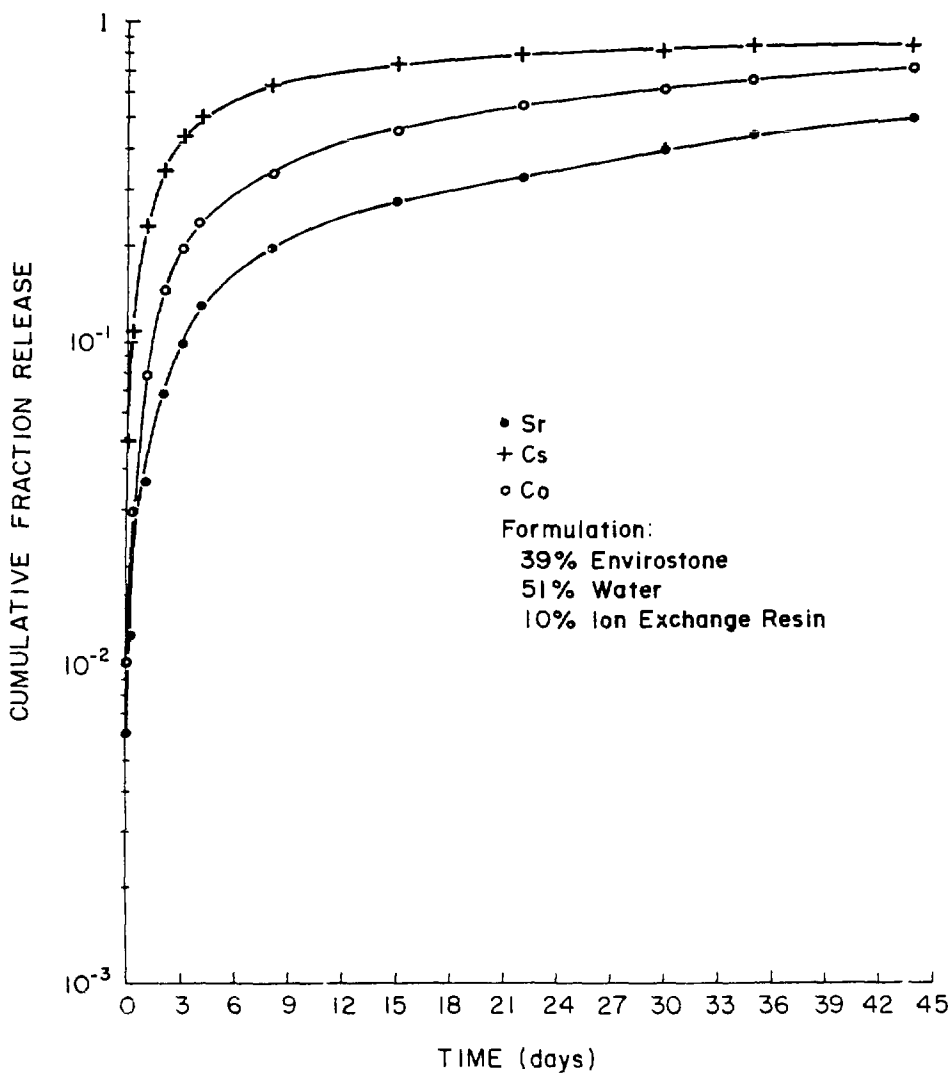


Fig. 2.37(c) Average cumulative fraction release Sr-85, Cs-137 and Co-60 vs. time for deionized water leaching of Envirostone waste forms containing 10 wt% dry mixed bed resin.

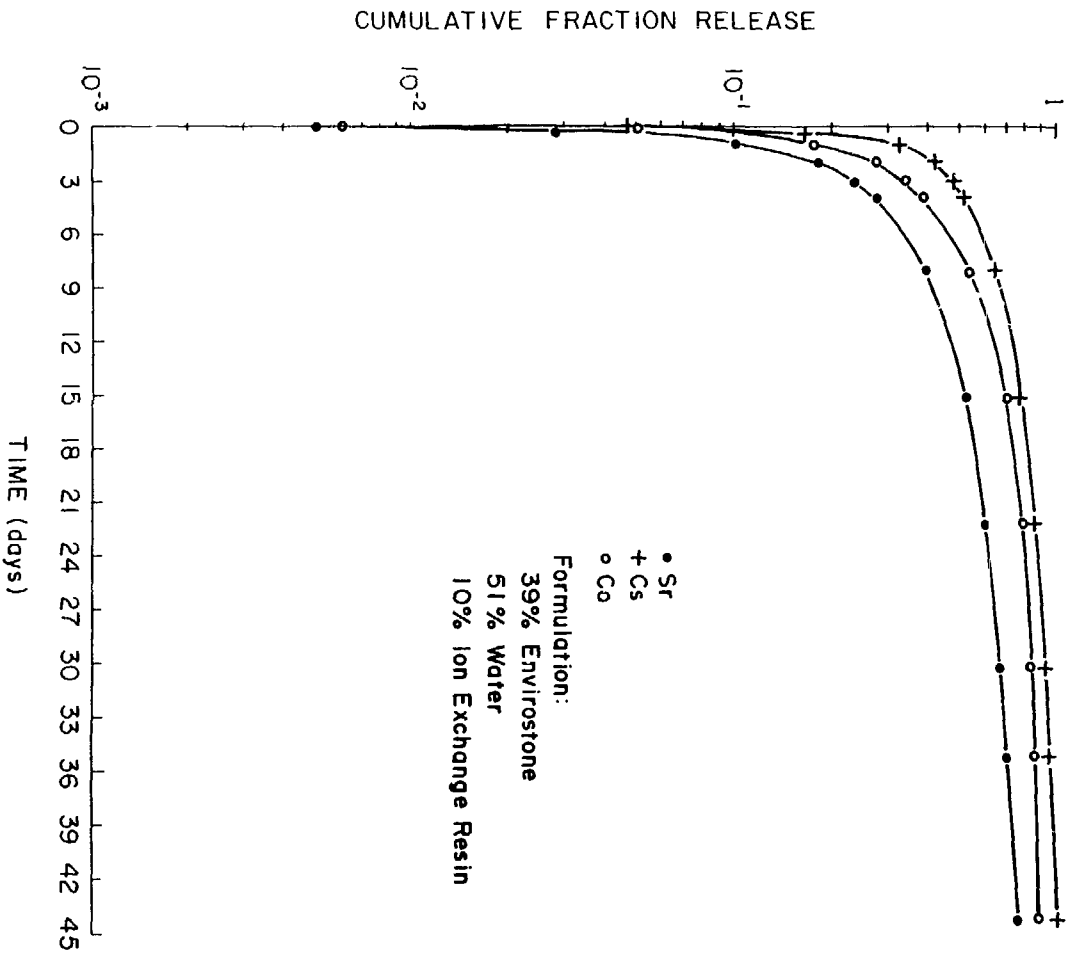


Fig. 2.38 Average cumulative fraction release Sr-85, Cs-137 and Co-60 vs. time for Envirostone waste forms containing 10 wt% dry mixed bed resin leached in synthetic seawater.

The application of vinyl ester-styrene is based upon the encapsulation of the waste stream within a polymerized matrix. There is no chemical bonding between the waste and solidification agent. An emulsion is formed between the aqueous waste stream and the vinyl ester-styrene by high shear mixing. Polymerization and subsequent curing take place upon the addition of a catalyst and promoter, yielding a continuous matrix of cured polymer with fine droplets of aqueous waste and waste solids dispersed throughout.

2.5.2 Formulation Development

Laboratory scale specimens were prepared to examine the formulation parameters for the solidification of ion exchange resin wastes with vinyl ester-styrene. Unloaded mixed bed resins containing 2 parts cation and 1 part anion resin by weight as described in Section 2.1.4 were employed.

Formulations were mixed using a variable speed air powered stirrer (Arrow Engineering Co., Hillside, NJ) with a two inch diameter, triple bladed propeller type stirring blade. Specimens were mixed in 32 ounce coated paper containers (6.5cm ID x 15.5cm ht.) in the following manner. (Specified promoter/catalyst types used and amounts added are proprietary.) A measured quantity of vinyl ester-styrene binder was placed in the mixing container which was positioned under the stirrer so that the blades were approximately centered. The stirrer was started and the speed and blade height were adjusted for adequate mixing. Catalyst was added and stirred for approximately one minute.

Simulated resin waste was added slowly and at a constant rate over a period of approximately two minutes. Both damp and slurry forms of unloaded mixed bed ion exchange resin were used. The stirrer speed was adjusted to maintain high shear mixing. Care must be exercised during this operation to ensure formation of a waste-binder emulsion. This is evidenced by the appearance of a lightly colored, homogenous mixture. The emulsion will break down if 1) the waste is added too quickly, 2) the high shear action is not maintained, or 3) an excessive quantity of waste is added. The appearance of streaking in the mixture is an indication of the onset of one or more of these conditions. Once the emulsion has broken, the ability of the binder to encapsulate the liquid waste is lost.

Finally, the promoter was added and stirring continued for approximately one additional minute. After mixing was completed, the stirrer was removed and the mixture was transferred to 160 ml polyethylene specimen preparation containers (4.7 cm ID x 9.7 cm height) for curing. In most cases, the gel time was approximately 15 minutes. Within one hour a distinct exothermic reaction was observed. Specimens were allowed to cure overnight and were then removed from their containers for inspection.

The final product was a hard, monolithic solid and in no case was there any evidence of free standing water for the formulations employed. The limiting constraint in solidifying resin slurry wastes was the amount of water that could successfully be held within the emulsion while mixing. The maximum resin content of solidified resin slurry waste forms was 18.4 wt% dry resin. By solidifying ion exchange resins which had excess and interstitial water removed (damp resin) higher waste-to-binder ratios could be achieved, resulting in improved volumetric efficiency. As much as 28.6 wt% dry resin was successfully solidified using damp resin. Maximum loadings of damp resin were limited by the volume of binder available to provide mechanical integrity of the waste form. Waste-to-binder ratios and weight percentages of dry resin for formulations prepared are summarized in Table 2.11. Vinyl ester-styrene waste form specimens incorporating various amounts of mixed bed ion exchange resins are shown in Figure 2.39.

Table 2.11 Vinyl Ester-Styrene Formulations for the Solidification of Mixed Bed Ion Exchange Resin Wastes

<u>Waste Stream Type</u>	<u>Waste/Binder Ratio (by wt.)</u>	<u>Dry Resin Wt%</u>
Resin slurry	2.0	12.3
Resin slurry	2.5	18.4
Damp resin	1.0	18.4
Damp resin	1.5	22.1
Damp resin	2.0	24.6
Damp resin	2.5	26.3
Damp resin	3.0	27.6
Damp resin	3.5	28.6

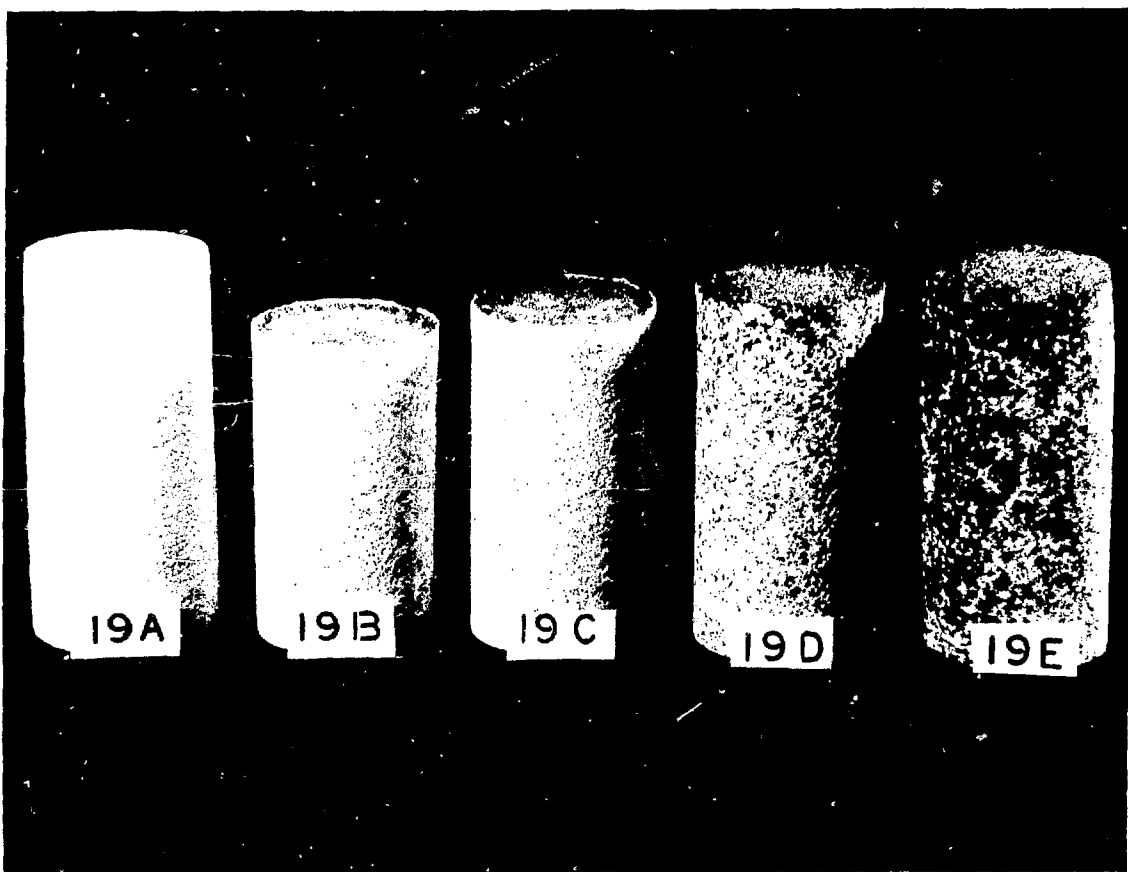


Fig. 2.39 Vinyl ester-styrene waste forms incorporating unloaded mixed bed resin.

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3. SOLIDIFICATION OF OIL AND ORGANIC LIQUID WASTES

Oils and other organic liquid wastes represent a particularly troublesome radioactive waste category for producers of low-level wastes (LLWs). Typically, these organic wastes are generated in low volume quantities at both government and commercial facilities, and often contain relatively low levels of radioactive contamination. Little success has been reported in the past for the immobilization of these wastes in acceptable waste forms with reasonably high loadings (≥ 20 volume%). In the past, oils and other organic liquid LLWs have commonly been immobilized by sorption onto solid adsorbents such as vermiculite or diatomaceous earth. However, evolving regulations regarding the disposal of these materials encourage solidification. As a result, there is a need to identify appropriate solidification agents and determine how they can be best applied. Alternatively, and where it is available for this application, incineration may be an acceptable treatment option for these wastes.

The following solidification agents were investigated:

Portland type I cement, with and without additives and including vermiculite

NUTEK 380-cement^(a)

DCM cement shale silicate^(b)

Envirostone polymer-modified gypsum cement^(c)

The simulated liquid organic wastes which were used to prepare the waste form samples include a lubricating (vacuum pump) oil and an organic solution ("NEN") containing selected alcohols, alkanes, ketones, aldehydes, esters, aromatics, and chlorinated hydrocarbons. The experimental matrix for this study is given in Table 3.1.

^(a) Nuclear Technology Corp., Amston, Connecticut.

^(b) Delaware Custom Material, Inc., State College, Pennsylvania.

^(c) U.S. Gypsum Co., Chicago, Illinois.

Table 3.1 Solidification Media Investigated

	<u>Immobilization of Oil</u>	<u>Immobilization of "NEN"</u>
Portland Type I Cement	X	
Vermiculite and Portland Type I Cement	X	
Nutek 380-Cement	X	X
Emulsifier, Portland Type I Cement, and Silicate	X	
DCM Cement	X	
Envirostone Cement	X	X

The solidified waste forms were evaluated in terms of being free-standing monolithic solids and having no free liquid following solidification. Other testing was applied to selected specimens, viz immersion testing, vibratory shock testing, and flame testing. Immersion testing involved placement of the waste form specimens in water at ambient temperature for periods of 72 hours or longer. If there was no evidence of a loss of sample integrity, the specimens were judged to have passed the immersion test. Vibratory shock testing was intended to simulate transportation conditions which the waste forms might experience when shipped to a burial site. Specimens were considered to have passed this test if they exhibited little in the way of physical breakup or deterioration of sample integrity. Flame testing involved determining the response when the sample was subjected to an open flame propane torch and noting whether any burning of the specimen was sustained when the torch was removed.

This work concentrated on high waste loading formulations which are assumed to be representative of actual practice of LLW generators. At lower waste loadings (≤ 10 volume%), improved waste form properties should result.

3.2 Solidification of Simulated Oil Wastes.

A representative hydrocarbon lubricating oil was chosen for use as a simulated oil waste in this study (Inland Vacuum Industries #19 Vacuum Pump Oil). This oil is in common use as a vacuum pump oil at BNL and has a density of 0.86 g/ml at ambient temperature. As discussed in the following sections, simulated waste form specimens of this oil and the various solidification media were prepared and evaluated as to their suitability for immobilizing oil wastes.

Samples were prepared on a batch basis and were mixed by hand or by laboratory mixer. A Hobart Model N-50, 3-speed, heavy duty electric mixer was used for many of the preparations. For those preparations in

which an emulsifier was used for incorporating the organic waste in solution, a Gast Model 1-AM, 2-inch air-powered mixer was used. This air-powered mixer was capable of delivering a high speed, high shear mixing action.

For each formulation batch, at least two specimens in the form of right circular cylinders were prepared in polyethylene containers which were then capped during the period of curing. Two specimen sizes were employed with nominal diameters of approximately 31 and 47 mm, respectively. Typical specimen heights were two or three times the diameters. The resultant solids had nominal volumes in the ranges of 40-60 ml and 140-160 ml, respectively. After curing for at least a two week period, the specimens were removed from the plastic containers and subjected to property testing.

3.2.1 Portland Type I Cement.

Portland type I cement has been widely used as a solidification agent for LLW. The use of this agent by the nuclear waste industry and its advantages and disadvantages has been discussed recently by Fuhrmann et al. [1].

Formulations of oil, Portland type I cement, and water which were prepared for this study are given in Table 3.2. Samples 11 and 16 contained relatively large fractions of free liquid, whereas samples 12 and 13 exhibited relatively little free liquid. Only a trace quantity of free oil remained on the surface of sample 14, while sample 15 cured to an essentially dry solid. All of the specimens were wiped dry and allowed to cure in air following the initial 3-day curing period in the containers. The specimens were placed on a paper mat during the subsequent air curing period and it was observed that oil ran out of the specimens and spread along the paper mat.

From the standpoint of general appearance and its lack of free liquid, the best performance rating for these samples was assigned to formulation number 15. This formulation, with a water/cement ratio of

Table 3.2 Solidification of Oil With Portland Type I Cement

<u>Sample I.D.</u>	<u>Formulation Weight Percentage</u>			<u>Volume%</u> <u>Oil</u>	<u>% Weight Loss</u> <u>on Curing in Air</u>
	<u>Oil</u>	<u>Portland I Cement</u>	<u>Water</u>		
11	10	30	60	(a)	(a)
12	30	35	35	45	25
13	30	50	20	50	7
14	20	50	30	34	14
15 ^(b)	5	75	20	12	2
16	50	30	20	(a)	(a)

(a) Not determined.

(b) Formulation judged to yield the most satisfactory solid in this group.

0.27, also exhibited the least weight loss on curing in air. The weight loss includes both water lost through evaporation and oil lost by seepage onto the paper mat, although the relative amounts of each were unassignable. While rated best among the oil/Portland type I cement specimens, sample number 15 represented an oil loading efficiency of only 12 vol%, however, indicating that this solidification media is not very effective for oil wastes.

3.2.2 Vermiculite and Portland Type I Cement.

Many nuclear facilities routinely dispose of oil and other organic liquid LLWs by sorbing them onto solid sorbents such as vermiculite which are then packaged for burial [2]. These materials may then be further immobilized by incorporating them into cemented solids.

In order to determine some suitable formulations, samples of unloaded (with oil) vermiculite plus water and Portland type I cement were prepared as shown in Tables 3.3 (for untreated vermiculite) and 3.4 (for water-saturated vermiculite). Good solid specimens were obtained with all of the formulations. In the case of untreated vermiculite, an excess of water over that required for cementation was added in order to saturate the vermiculite, since the cement and vermiculite would otherwise compete for the limited water which was present. According to Lin and MacKenzie [2], under near neutral to highly basic conditions, vermiculite will absorb water up to about 4 g per gram of absorbent. In terms of the total amount of water added and hence available for cementation (over that required by the vermiculite) in each case, samples 20-25 are thus directly comparable to samples 26-31, respectively. This appears to be reflected in the similar degree of weight loss on curing in air for the comparable samples, suggesting that the manner and order in which the ingredients are added is unimportant in this case. The minimum amount of weight loss for these specimens on curing in air is exhibited for a water/cement ratio of 0.28 by weight.

TABLE 3.3 Solidification of Untreated Vermiculite With Portland Type I Cement

Sample I.D.	<u>Formulation Weight Percentage</u>			<u>% Weight Loss on Curing in Air</u>
	<u>Untreated Vermiculite</u>	<u>Portland I Cement</u>	<u>Water</u>	
26	5.6	45	49	33
27	7.7	38	54	38
28	5.5	57	38	14
29	7.4	48	44	29
30	5.5	50	45	30
31	7.7	42	50	53

TABLE 3.4 Solidification of Water-Saturated Vermiculite With Portland Type I Cement

Sample I.D.	<u>Formulation Weight Percentage</u>			<u>% Weight Loss on Curing in Air</u>
	<u>Water-Saturated Vermiculite</u> (a)	<u>Portland I Cement</u>	<u>Added Water</u>	
20	28	45	27	32
21	38	38	23	37
22	27	57	16	14
23	38	48	13	23
24	27	50	23	25
25	36	42	19	33

(a) 80 wt% water

Samples were prepared using vermiculite which had been partially loaded with oil (50% saturated) plus water and Portland type I cement. The formulations are given in Table 3.5. With these samples, there was insufficient water to both saturate the sorbing capacity of the vermiculite and also provide a water/cement ratio sufficient for a good cement product. For example, only for sample number 47 was there an excess of water over that which would be required to saturate the vermiculite. In this case a water/cement ratio of only 0.10 would result if all of the water so available were to be sorbed onto the vermiculite. Adequate cement hydration occurred, indicating that Portland type I cement is able to compete with vermiculite for the available water. However, due to the relatively small amounts of water available for solidification, samples 6-10 and 41-46 were too dry to give solids. Samples 47-52 did give good solid specimens, however, and the best overall specimen was judged to be number 49. However, the volumetric loading efficiency (11 vol% oil) for this sample is rather low.

Results for samples prepared using oil-saturated vermiculite plus water and Portland type I cement are given in Table 3.6. Oil-saturated vermiculite contains approximately 3 g of oil per gram of absorbent (density of untreated vermiculite is 0.099 g/ml) [2]. These samples set up in about three days to give good free standing monolithic solids, however, all had an initial oily appearance and traces of free liquid were observed with all samples. Sample 38 was judged to be the best overall specimen, with a volumetric loading efficiency of 30% and only a 10% weight loss on curing in air.

If oil wastes are to be disposed of by first sorbing on vermiculite and then solidifying with Portland type I cement, it appears that best results are obtained by saturating the vermiculite with oil prior to solidification. With unsaturated oil-vermiculite, lower volumetric efficiencies for waste loading are obtained and poorer solids result due to competition for the water between cement and the absorbent.

TABLE 3.5 Solidification of Partially (50%) Saturated (Oil)
Vermiculite With Portland Type I Cement

Sample I.D.	<u>Formulation Weight Percentage</u>			<u>Volume%</u> <u>Oil</u>	<u>% Weight Loss</u> <u>on Curing in Air</u>
	<u>Oil (50% Sat'd)</u> <u>Vermiculite^(a)</u>	<u>Portland I</u> <u>Cement</u>	<u>Water</u>		
6	17	59	24	10	9
7	28	48	24	12	13
8	40	36	24	13	18
9	45	30	24	15	20
10	51	25	24	16	20
41	19	51	30	13	12
42	27	45	27	16	19
43	19	63	18	(b)	(b)
44	19	63	18	(b)	(b)
45	19	56	25	13	10
46	27	50	23	14	13
47	17	45	38	10	26
48	23	38	38	13	30
49 ^(c)	17	55	28	11	13
50	23	48	29	14	17
51	17	50	33	11	16
52	23	42	35	14	29

(a) 37.5 wt% oil.

(b) Not determined

(c) Formulation judged to yield the most satisfactory solid in this group.

TABLE 3.6 Solidification of Oil-Saturated Vermiculite With Portland Type I Cement

<u>Sample I.D.</u>	<u>Formulation Weight Percentage</u>			<u>Volume% Oil</u>	<u>% Weight Loss on Curing in air</u>
	<u>Oil-Saturated Vermiculite</u>	<u>(a)</u> <u>Portland I Cement</u>	<u>Water</u>		
1	24	48	29	27	11
2	35	35	30	34	22
3	47	24	29	40	29
4	50	20	30	45	30
5	51	17	31	43	33
32	20	50	30	26	17
33	27	45	27	35	15
34	33	42	25	40	18
35	20	63	18	24	7
36	27	57	16	29	7
37	33	52	15	34	8
38 ^(b)	20	55	25	30	10
39	27	50	23	36	12
40	33	46	21	39	14

(a) 75 wt% oil.

(b) Formulation judged to yield the most satisfactory solid in this group.

3.2.3 Nutek 380-Cement.

The Nuclear Technology Corporation (NUTEK) has developed a proprietary chemical process to solidify radioactive waste oils [3]. Ingredients and details concerning waste formulations were obtained from NUTEK. Samples prepared for this study are listed in Table 3.7. The ingredient Nutek 380A serves as an emulsifying agent; Nutek 380B serves to accelerate the set time.

In this procedure, oil and Nutek 380A are mixed to a creamy emulsion consistency, then added to a mixture of Portland cement and slaked lime and stirred until homogeneous. (The amount of lime added to the cement is less than that which yields a masonry cement.) The Nutek 380B is then slowly added and the composition is stirred slowly for a short period and allowed to set (48 hours).

Good solid monoliths were obtained with this procedure and there were no instances of free liquid formation with these compositions. Samples 78 and 80 were judged to be best in appearance and apparent strength, followed by 79 (which was somewhat softer) and 81 (which was softest). It appears that this process yields good solid waste forms at volumetric oil loadings of about 30%.

3.2.4 Emulsifier, Portland Type I Cement, and Sodium Silicate.

Simulated waste specimens were prepared from batch mixtures of oil, emulsifier (Nutek 316, also available from Nuclear Technology Corporation), Portland type I cement, and sodium silicate. An aqueous solution of sodium silicate (weight ratio of 3.22; density of 41.0⁰Bé) was used in Table 3.8. No free standing liquid was observed with any of these specimens.

TABLE 3.7 Solidification of Oil With NUTEK 380-Cement

Sample I.D.	<u>Formulation Weight Percentage</u>						Volume% Oil
	<u>Oil</u>	<u>Portland I Cement</u>	<u>Lime</u>	<u>Nutek 380A</u>	<u>Nutek 380B</u>	<u>Water</u>	
77	20	46	6.2	25	3.7	0.0	29
78 ^(a)	18	42	5.7	23	3.4	8.4	29
79	22	36	4.9	28	4.2	5.1	32
80 ^(a)	19	50	0.0	24	3.6	4.4	30
81	25	29	4.0	31.4	4.8	5.8	43

(a) Formulations judged to yield the most satisfactory solids in this group.

TABLE 3.8 Solidification of Oil Plus Emulsifier (NUTEK 316) With Portland
Type I Cement - Sodium Silicate

Sample I.D.	Formulation Weight Percentage					Volume% Oil
	Oil	Portland Cement	Emulsifier	Sodium Silicate	Water	
82	18	51	0.0	2.5	28	30
83 ^(a)	23	46	2.0	3.8	25	39
84	29	41	2.9	4.6	23	45
85	33	38	3.5	5.3	21	49
86	36	35	3.8	5.9	19	44
87	38	34	4.0	6.1	19	(b)

(a) Formulation judged to yield the most satisfactory solid in this group.

(b) Not determined.

In this procedure, oil was first added to water and mixed with high speed mixer for 4 minutes. Cement was then added and the mixture was mixed for 2 minutes. Emulsifier was added and mixing was maintained until a good homogeneous mix was obtained. Then, sodium silicate was added. The specimens cured to firm, monolithic solids in about 24 hours.

Sample 83, with a volumetric loading of 39% oil, was judged to be the best composition of this set, followed by 84. Samples 85 and 86 were soft, and 87 was very soft and crumbly.

3.2.5 DCM Cement Shale Silicate.

DCM cement shale silicate, a proprietary process, is available in kit form from the manufacturer, Delaware Custom Materiel, Inc., State College, Pennsylvania. For the tests done for this study, the manufacturer's directions were followed. Oil and then cement were added to water and mixed for 4-5 minutes. The emulsifier was then added and the composite mixture was mixed for 4 minutes. Then, sodium silicate was added while the mixing was continued until a creamy composition was obtained (in less than one minute).

Sample compositions made up with the DCM cement are given in Table 3.9. In this set, sample 88 was judged to be best with a 30 vol% loading of oil; specimens of this composition exhibited dry hard surfaces. Sample 89 had firm surfaces but evidenced some oily appearance. Sample 90 produced specimens with soft and oily surfaces, while those of 91 were very soft and oily. Specimens from sample 92 were soft and could be crushed easily by hand, while those of number 93 were too soft to handle.

3.2.6 Envirostone Cement.

Envirostone polymer-modified gypsum cement is manufactured and marketed by the U.S. Gypsum Company, Chicago, Illinois. The manufacturer's directions were used in preparing the formulations in this study.

TABLE 3.9 Solidification of Oil Plus Emulsifier With DCM Cement - Sodium Silicate

Sample I.D.	Formulation Weight Percentage					Volume% Oil	Oil Loss on Immersion mL Oil/mL Specimen
	Oil	DCM Cement	Emulsifier	Sodium Silicate	Water		
88 (a)	17	51	1.6	2.8	27	30	9/199
89	24	46	2.0	3.8	25	38	16/210
90	29	41	2.9	4.6	23	44	22/198
91	33	38	3.3	5.3	21	48	30/190
92	37	36	3.1	5.0	20	(b)	19/ (b)
93	38	34	3.8	6.1	19	(b)	(b)

(a) Formulation judged to yield the most satisfactory solid in this group.

(b) Not determined.

Liquid emulsifier, water, and oil were added to the Envirostone cement in that order and mixed at high speed with the air-powered mixer for 2 minutes. All samples set within about 10 minutes without any evidence of free liquid remaining on any of the specimens.

Sample compositions of oil and Envirostone cement are given in Table 3.10. The specimens for formulations 53 and 54 produced firm solids, while those for 55 through 58 progressively ranged from soft to very soft. Overall, sample 54 was judged to have the best performance characteristics of this set (this represents a volumetric loading efficiency of 36%).

TABLE 3.10 Solidification of Oil With Envirostone Cement

Sample I.D.	Formulation Weight Percentage				Volume% Oil	% Weight Loss on Curing in Air
	Oil	Envirostone Cement	Liquid Additive	Water		
53	18	52	2.2	28	28	21
54 ^(a)	24	47	3.0	26	36	21
55	30	43	3.7	24	43	16
56	34	40	4.3	22	48	13
57	38	37	4.8	20	50	12
58	40	36	5.0	20	50	12

(a) Formulation judged to yield the most satisfactory solid in this group.

3.3 Solidification of Simulated Organic Liquid Wastes.

Candidate solidification media for organic liquid wastes were surveyed and two were chosen for further study: Nutek-380 cement and DCM cement shale silicate. A simulated organic liquid waste, "NEN" solution, was prepared for this study. This solution, intended to simulate as

closely as possible the organic liquid waste stream produced at a typical radiopharmaceutical/labeled compound manufacturing facility, was prepared according to a compositional recipe suggested by a representative of New England Nuclear, Boston, Massachusetts. The composition of "NEN" solution is given in Table 3.11. The density of this solution is 0.81 g/ml at ambient temperature.

3.3.1 Nutek 380-Cement.

Samples were prepared using "NEN" solution and the Nutek process described in Section 3.2.3. The sample compositions which were used for this study are given in Table 3.12.

Samples 96-98 were unacceptable in that specimens contained considerable quantities of free liquid (ranging to 30% of the specimen volume for number 98). Specimens from samples 101-103 eventually set up and gave dry monolithic solids after curing for several days in closed containers. An acceptable solid was obtained with sample 102 which contained 6 weight percent "NEN" (about 10 vol%). Sample 101 gave softer, more crumbly specimens, while number 103 was intermediate between the two (101 and 102). In all cases, the odor of organic vapors, particularly that of diethyl ether, was quite strong.

3.3.2 Envirostone Cement.

Samples were prepared using "NEN" solution and the Envirostone process described in Section 3.2.6. Sample compositions are given in Table 3.13.

Eventually, all of the "NEN"-Envirostone specimens solidified, although free liquid persisted in some cases. Sample T4 was judged to give the best overall product (at 11 vol% "NEN") on the basis of general appearance and the firmness of the solid which was formed. Number 59 (26 vol% "NEN") was judged to be much less acceptable due to its soft nature, followed by number T1 (28 vol% "NEN"). With samples 60 and 61, the top portions of the specimens were cracked and tended to flake off. Samples 62, 63 and 64 retained substantial portions of free liquid and were

considered to be unacceptable. All of the "NEN" - Envirostone specimens initially had a free liquid layer but samples 59-62 and T1-T4 eventually cured to form solids without any free liquid.

As with samples of "NEN" plus Nutek 380-cement, the Envirostone samples exhibited strong odor of the organic mixture when kept in closed containers. However, this diminished on standing for specimens which were removed from their containers due to evaporation of volatile organic constituents in the simulated waste.

3.4 Testing of Solidified Waste Forms.

Selected solidified waste form specimens were subjected to immersion testing in water, vibratory shock testing, and flame testing. Discussion of the performance of these specimens under various testing conditions is described.

3.4.1 Immersion Testing.

Specimens representing all of the solidified oil formulations were subjected to immersion testing for periods ranging from 72 hours to more than 1 week. The test consisted of immersing each of the solid specimens (which were cylindrical and typically 47 mm in diameter and approximately 100 mm long) in 1750 ml of tap water at ambient temperature. All of the specimens tested passed the immersion test in that there was little if any loss of sample integrity over the period they were immersed. However, in most cases some oil was released from the solids as evidenced by a film on top of the immersion solution. This amount of released oil was determined in a few cases, such as shown in Table 3.9 for samples of oil plus emulsifier, DCM cement shale, and sodium silicate.

The loss of oil from solidified waste forms, whether on draining out of the specimens when removed from containers and placed on paper mats, or on being immersed in water, may bear little or no relation to the containment of radioactivity by actual solidified LLW forms. Actual LLW specimens will contain various radioactive elements in a

TABLE 3.11 Composition of "NEN" Simulated Organic Liquid Waste Stream

Simulated Organic Liquid Waste Stream		
<u>Composition</u>		
<u>Component</u>	<u>Vol%</u>	<u>Component Formula</u>
Methanol	22	CH_3OH
Ethanol	22	$\text{C}_2\text{H}_5\text{OH}$
Acetone	9	CH_3COCH_3
Isopropanol	5	$\text{CH}_3\text{CHOHCH}_3$
Diethyl ether	9	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
Ethyl acetate	4	$\text{C}_2\text{H}_5\text{COOCH}_3$
n-Hexane	9	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
Benzene	4	C_6H_6
Toluene	4	$\text{C}_6\text{H}_5\text{CH}_3$
Acetonitrile	4	CH_3CN
1,2-Ethylene dichloride	4	$\text{C}_2\text{H}_4\text{Cl}_2$
Chloroform	4	CHCl_3
	<hr/> 100	

TABLE 3.12 Solidification of Simulated Organic Liquid Waste ("NEN") With
NUTEK 380-Cement

Sample I.D.	Formulation Weight Percentage					
	"NEN"	Portland Cement	Lime	Nutek 380A	Nutek 380B	Water
96	20	49	6.7	21	2.5	0.0
97	18	45	6.1	19	2.9	8.9
98	23	39	5.3	24	3.6	5.6
101	13	63	8.5	14	2.3	0.0
102	6.1	58	7.9	6.3	1.1	21
103	10	59	8.0	11	1.6	11

TABLE 3.13 Solidification of Simulated Organic Liquid Waste ("NEN") With Envirostone

Sample I.D.	<u>Formulation Weight Percentage</u>				Volume% "NEN"
	<u>"NEN"</u>	<u>Envirostone Cement</u>	<u>Liquid Additive</u>	<u>Water</u>	
59	17	52	2.2	29	26
60	23	48	3.1	26	36
61	28	44	3.8	24	43
62	33	41	4.4	22	50
63	37	38	4.9	21	(a)
64	38	36	5.1	20	(a)
T1	18	57	2.5	23	28
T2	14	66	1.9	18	25
T3	0.0	55	7.1	38	0.0
T4	8.1	50	6.5	35	11

(a) not determined

multitude of chemical states and physical forms. These radionuclides may be activation products, fission products, or natural radioactive isotopes and transuranics (if present at less than 10 nanocuries/g). These radioactive elements may be present as particulates, or as dissolved species, or as sorbed species. In order to ascertain the effectiveness of the various solidification media in containing such materials and to predict the releases of radioactivity under various scenarios, extensive leach testing of the solidified products would be essential. The observations noted here simply relate to the release of fluids (water, oil, etc.) from the waste form specimens.

3.4.2 Vibratory Shock Testing.

Selected waste specimens were subjected to vibratory shock testing in order to simulate transportation conditions which might be experienced by LLW forms when shipped to burial sites. For this test, an electromagnetic vibrating table (FMC Corporation Model J-50-B) was modified by construction of a metal fence around the outer edge of the platform. The vibrating frequency of this table was 236 revolutions per minute (3.9 Hz). The vibratory table top was loaded with formulations representing a wide range of oil content and solidification media as follows:

- 1 to 58 Free-standing solids, had undergone immersion testing.
- 1 to 58 Free-standing solids, not subjected to prior immersion testing.
- 65 to 70 Solids contained in closed vials.
- 82 to 87 Solids contained in closed vials.

These samples were tested simultaneously for a one-hour period after which only a very small amount of loose material (vermiculite and cement dust) was observed to be present on the vibratory table top. No

free liquid was observed. Thus, all samples appeared to perform adequately in this simulated transportation mode.

Another smaller group of waste specimens was likewise tested. These included solids contained in closed vials (the specimens from formulations 82 to 93). After one hour of testing, two specimens (87 and 93, each containing 223 g oil to 200 g cement) did exhibit a very thin layer of free liquid on the top.

3.4.3 Flame Testing.

An open flame test was applied to selected waste specimens. In this test, the specimens were contacted with an open flame from a propane torch. In most cases, it was observed that vapors above the samples would ignite and burn as long as contact was maintained with the open flame. With the exception of two specimens, as discussed below, the flames were extinguished as soon as the propane torch was removed. The samples which were tested are listed in Table 3.14

Two specimens, samples number 12 and 32, were observed to continue to sustain combustion after the propane torch was removed. Sample 12 was an oil/cement composition. Sample 32 was an oil-saturated vermiculite/cement composition. With both of these specimens, as well as one from sample number 77 (oil/Nutek 380-cement), oil was observed to flow out of the solid when heated. These results are not definitive since several weeks had passed since the specimens had been prepared and varying amounts of oil had already been released from these waste forms. However, it appeared that the Envirostone specimens showed the least tendency to lose oil or sustain a flame under these conditions.

3.5 Conclusions.

The results obtained in this study indicate that there are several options available for the solidification of oil or organic liquid LLWs at low waste loadings (≤ 10 volume%). For higher waste loadings, the choices are more limited and there is greater probability of obtaining

TABLE 3.14 Flame Testing of Selected Simulated Waste Specimens

<u>Sample I.D.</u>	<u>Flame Test Result: Flame Extinguished When Propane Torch Removed</u>		<u>COMMENTS</u>
	<u>YES</u>	<u>NO</u>	
3	X		
12		X	When heated, oil flowed out of the solid.
21	X		
25	X		
32		X	When heated, oil flowed out of the solid.
36	X		
47	X		
51	X		
54	X		
58	X		
77	X		When heated, oil flowed out of the solid.
81	X		
82	X		
83	X		
84	X		
85	X		
86	X		
94	X		

unsatisfactory solids. This study concentrated on high waste loading formulations which are assumed to be more representative of actual LLW generators' practices. Based on the criteria applied in this study, acceptable solids were obtained (i.e., selected formulations yielded free-standing monolithic solids with < 1 vol% free liquid, which passed a water immersion test). However, there are indications that these formulations may not be completely satisfactory on the basis of other or evolving LLW acceptance criteria. Further work would be required in order to more fully characterize these various waste forms including leach testing of selected radionuclides.

Formulations judged to yield the most satisfactory solids for each solidification media with oil and "NEN" solution are summarized in Table 3.15. In the case of oil, volumetric waste loadings of the order of 30-40 volume% may be realized with specimens of reasonable physical integrity. For "NEN", however, acceptable formulations are generally below about 10 volume%. Especially for organic liquid wastes, alternative treatments such as incineration may be preferable to direct immobilization.

TABLE 3.15 Formulations Judged to Yield the Most Satisfactory Solids

<u>Immobilization Media</u>	<u>Oil Waste</u>	<u>Organic Liquid Waste ("NEN")</u>
Portland Type I Cement	#15 (12 vol%)	
Vermiculite plus Portland Type I Cement	#38 (30 vol%), sat'd. #49 (11 vol%), 50% sat'd.	
Nutek 380-Cement	#78 (29 vol%) #80 (30 vol%)	#102 (6 wt%)
Emulsifier, Portland Type I Cement, and Sodium Silicate	#83 (39 vol%)	
DCM Cement	#88 (30 vol%)	
Envirostone Cement	#54 (36 vol%)	#T4 (11 vol%)

REFERENCES SECTION 3

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4. SOLIDIFICATION OF NITRATE SALT WASTES

4.1 Description of Nitrate Salt Wastes.

Work was conducted to investigate the solidification of dry and aqueous sodium nitrate wastes. Aqueous wastes over the range of 30-80 wt% sodium nitrate were used. As sodium nitrate is typically the major solute component in nitrate wastes, other less prevalent solutes were not included in simulated wastes for this study.

4.2 Formulation Development.

Portland type I cement, high alumina cement and vinyl ester-styrene were investigated for the solidification of nitrate salt wastes. Formulation acceptability required the production of a free standing monolithic solid with no drainable free standing water after a cure time of one week or less. After curing at room temperature for fourteen days, waste forms were removed from their preparation containers to verify the formation of a free standing monolithic solid. Acceptable specimens were then subjected to a two week immersion test in demineralized water (described in Section 2.2.2) during and after which they were required to maintain their mechanical integrity.

4.2.1 Solidification with Portland Type I Cement.

Water must be present when solidifying sodium nitrate waste for cement hydration. Typically, this water would be a component of an aqueous nitrate waste although water could be added to solidify an initially dry nitrate waste. The amount of water is also important. Water must be present in a sufficient quantity to provide adequate workability to the cement-waste mixture. However, attempts to incorporate an excessive amount of waste (or water) can result in the presence of free standing water after solidification. There must also be sufficient cement present to adequately immobilize the waste in a monolithic waste form.

Portland type I cement waste forms were prepared using a Hobart model N-50 planetary action mortar mixer. The minimum water-to-cement ratio producing an adequately workable mixture with portland type I cement was 0.25 by weight. This mixture contains 20 wt% water and 80 wt% cement. The maximum water-to-cement ratio not resulting in free standing water was 0.50 by weight. A range of formulations were initially prepared with each of the following aqueous waste streams.: 10, 25, 35, 45, 50 and 70 wt% sodium nitrate. Triplicate specimens of various waste/binder formulations were prepared for each of these waste streams to define the compositional envelope for acceptable formulations. The 70 wt% sodium nitrate waste stream was heated to provide a homogeneous, unsaturated waste solution (all others were unsaturated at room temperature). Formulations were cast into 4.7 cm diameter polyethylene containers for curing. These containers were capped to prevent evaporative water loss. After curing at room temperature for seven days, the specimens were examined for free standing water. After fourteen days, the specimens were removed from their containers to verify the formation of a free standing monolithic solid waste form. Acceptable formulations were then subjected to the two week water immersion test. No formulations failed the water immersion test.

Figure 4.1 is the ternary compositional phase diagram for the production of acceptable aqueous sodium nitrate waste forms with portland type I cement. This diagram also indicates formulational regimes which result in unworkable mixtures and in free standing water. The maximum amount of sodium nitrate in an acceptable formulation was found to be 68 wt%. This information is shown in a different form in Figure 4.2. In this figure, waste/cement ratios for acceptable formulations are plotted as a function of the weight percentage sodium nitrate in the waste. Aqueous wastes containing greater than 85% sodium nitrate could not be solidified since they do not contain sufficient water to hydrate the quantity of cement necessary to produce a monolithic solid. In areas above the acceptable ranges, free standing water results, in areas below, insufficient mixability occurs.

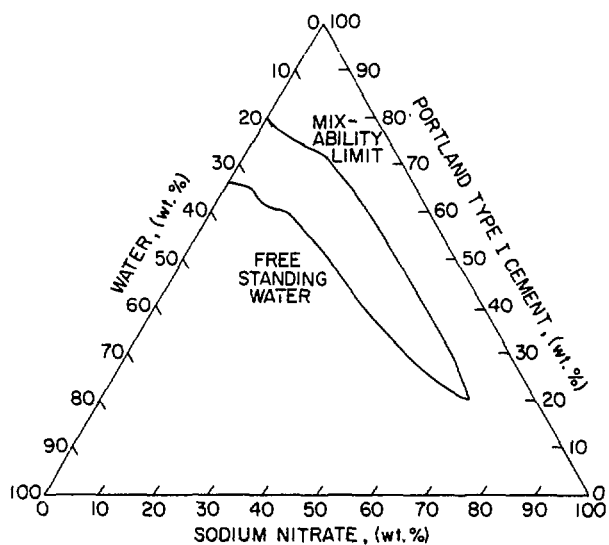


Fig. 4.1 Ternary compositional phase diagram for the solidification of aqueous sodium nitrate waste in portland type I cement.

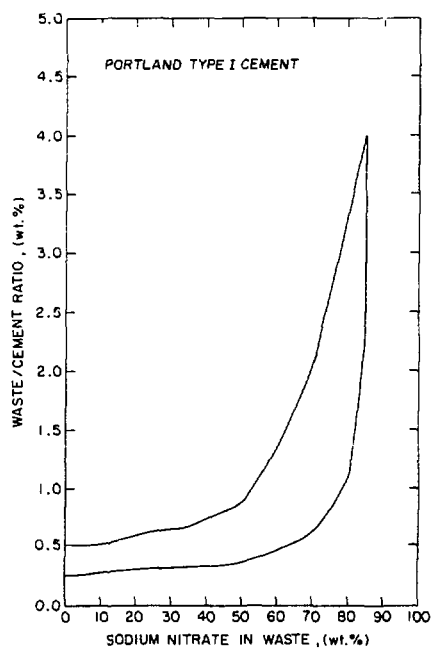


Fig. 4.2 Acceptable waste/cement ratios for solidification in portland type I cement, versus weight percentage sodium nitrate in the waste.

4.2.2 Solidification With High Alumina Cement.

The use of high alumina cement as a solidification agent for aqueous nitrate wastes is similar to that for portland type I cement. However, since it is chemically different from portland type I cement and forms other cement hydrates, it is not unexpected that it should have a unique compositional envelope for acceptable formulations. The procedure employed to determine the range of acceptable formulations and the methods of specimen preparation were identical to those employed with portland type I cement.

Figure 4.3 is the ternary compositional phase diagram for the solidification of aqueous sodium nitrate waste with high alumina cement. As compared to portland type I cement (Figure 4.1), the high alumina cement has a smaller range of acceptable formulations. This is also apparent in Figure 4.4 which indicates the ranges of waste/cement ratios which result in acceptable formulations for various sodium nitrate contents in the waste. On the basis of the acceptability criteria employed, there appears to be no obvious benefit to the use of high alumina cement over portland type I cement for the solidification of aqueous nitrate waste.

4.2.3 Solidification With Vinyl Ester-Styrene.

Vinyl ester-styrene (VES) is a proprietary^(a) water extendable binder used for the solidification of wet solid wastes. Sodium nitrate wastes were mixed with vinyl ester-styrene under high shear mixing conditions. Vinyl ester-styrene is a water extendable monomer and under the proper mixing conditions, water in the waste forms a stable emulsion with the monomer. Waste solids are physically entrapped after polymerization of the monomer. The VES-waste emulsion is polymerized at room temperature with a catalyst-promoter. High shear mixing is not required for the incorporation of dry solid wastes since the formation of an emulsion with waste water is unnecessary.

(a) Dow Chemical Company, Midland, MI

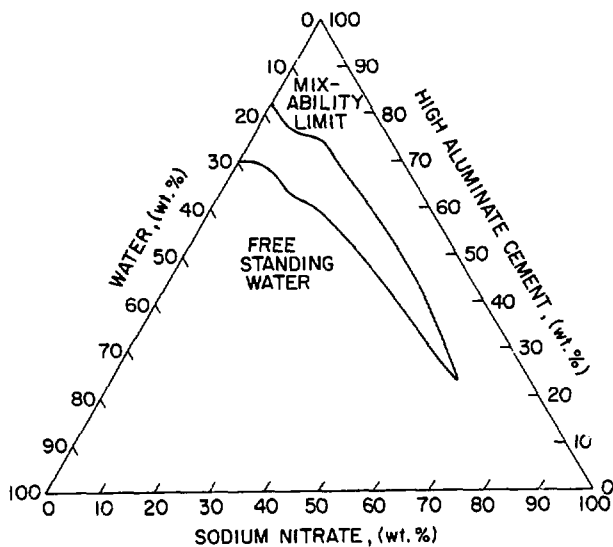


Fig. 4.3 Ternary compositional phase diagram for the solidification of aqueous sodium nitrate waste in high alumina cement.

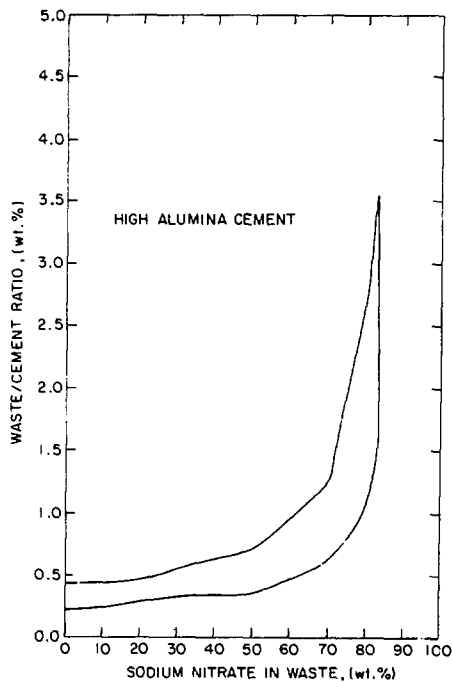


Fig. 4.4 Acceptable waste/cement ratios for solidification in high alumina cement versus weight percentage sodium nitrate in the waste.

Vinyl ester-styrene waste forms were prepared using a high speed electric mixer with a propeller type blade. Appropriate additions of catalyst and promoter were made during the proper stages of the process. After component addition and mixing, the mixture was transferred to polyethylene vials (4.7 cm diameter by 9.8 cm high) for room temperature polymerization. The formation of a stable emulsion and polymerization of VES waste forms are dependent upon the quantity of promoter and catalyst added, the quantity of waste added, the rate of waste addition, the order of addition of components, and the establishment of high shear mixing conditions.

Figure 4.5 is the ternary compositional phase diagram for the solidification of aqueous sodium nitrate waste (up to 70 wt% sodium nitrate) with vinyl ester-styrene. At concentrations above 70 wt% sodium nitrate in the waste, it was difficult to maintain proper mixing conditions to form a stable emulsion as a result of the high viscosity of the mixture. A maximum sodium nitrate content of 57 wt% was determined. While this sodium nitrate loading is lower than those achieved with portland type I or high alumina cements, the vinyl ester-styrene binder exhibited an ability to incorporate large quantities of water in the waste stream. This is indicated in Figure 4.6, by the broad range of acceptable waste/binder ratios for a given waste stream. This figure also indicates the maximum waste/binder ratio achievable for the solidification of dry sodium nitrate; 4.25 by weight. This corresponds to a sodium nitrate loading of approximately 81 wt% in the waste form.

4.3 Compression Strength.

Compression strengths were determined for portland type I cement, high alumina cement and vinyl ester-styrene waste forms containing sodium nitrate waste. This testing was performed using a Soiltest^(a) Model CT-2520 compression tester and ASTM test method C39-72, "Test for the Compressive Strength of Cylindrical Concrete Specimens."

^(a) Soiltest, Inc., Evanston, IL

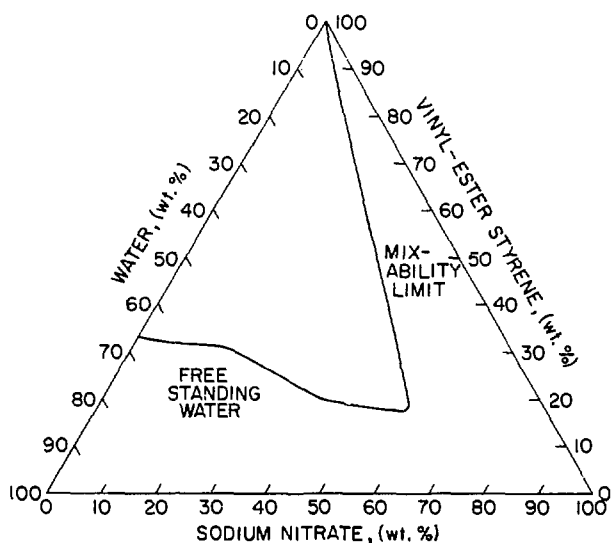


Fig. 4.5 Ternary compositional phase diagram for the solidification of aqueous sodium nitrate waste in vinyl ester-styrene.

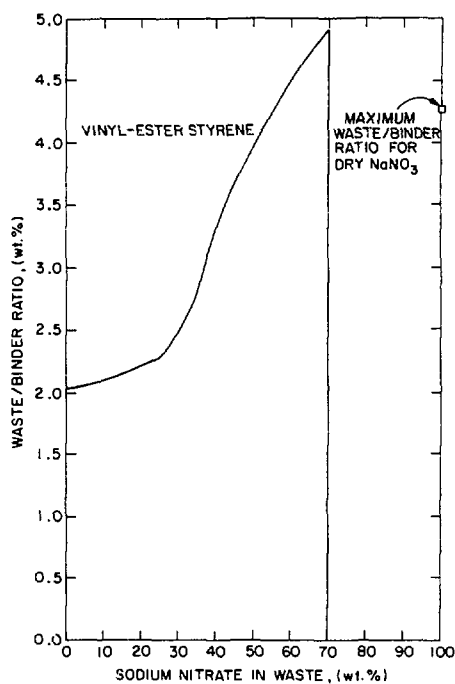


Fig. 4.6 Acceptable waste/binder ratios for solidification in vinyl ester-styrene versus weight percentage sodium nitrate in the waste.

4.3.1 Portland Type I Cement.

Compression test specimens were right circular cylinders, 4.7 cm in diameter by approximately 9.8 cm long. Specimens were prepared as described earlier with aqueous waste streams containing 35, 55 and 80 wt% sodium nitrate. Various waste/cement ratios were used for each waste stream as indicated by earlier formulation development work (see Figure 4.2). A cure time of 29 days at room temperature was used. Three replicate specimens of each formulation were tested.

Measured compression strengths are shown in Figure 4.7. In this figure, compression strength is plotted versus $(\text{NaNO}_3 + \text{water})/\text{cement}$ ratio by weight where $(\text{NaNO}_3 + \text{water})$ is the total waste composition. Compression strength was observed to decrease with increasing waste/cement ratio. The rate of decrease as a function of waste/cement ratio was slower as the water content of the waste decreased. Compression strengths of 5,000-6,000 psi were measured for each waste stream using waste/cement ratios producing acceptable formulations near the mixability limit. The compression strength decreased with increasing waste/cement ratios. However, at waste/cement ratios near the free standing water limit, compression strengths were still in the range of 600-1,400 psi.

4.3.2 High Alumina Cement.

Compression test specimens were right circular cylinders 4.7 cm diameter by approximately 9.8 cm long. Specimens were prepared as described earlier using aqueous waste streams containing 35, 55 and 80 wt% sodium nitrate. Various waste/cement ratios were employed for each waste stream as indicated by earlier formulation development work (see Figure 4.4). A cure time of 36 days was used. Three replicate specimens of each formulation were tested.

Measured compression strengths are shown in Figure 4.8. Compression strengths were observed to be essentially independent of waste/cement ratio for each waste type and sodium nitrate content in the waste for the formulations tested. Compression strengths of 1,250-1,350 were measured.

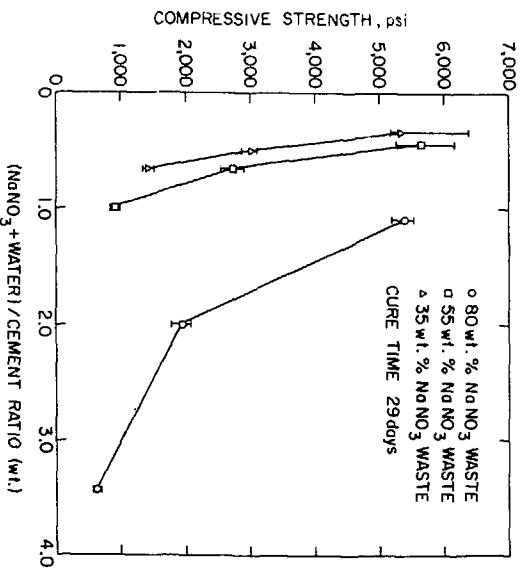


Fig. 4.7 Compression strength of sodium nitrate waste - portland type I cement waste forms.

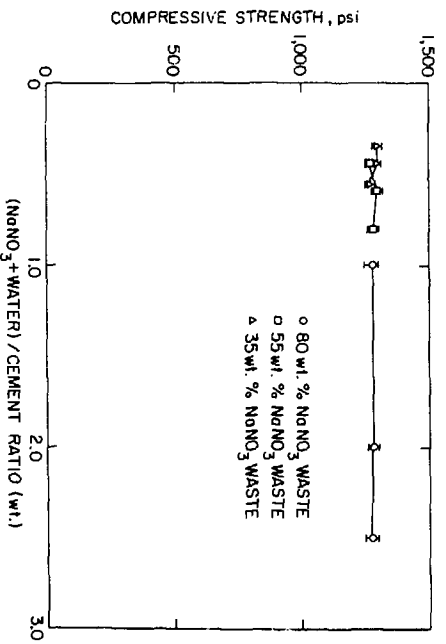


Fig. 4.8 Compression strength of sodium nitrate - high alumina cement waste forms.

4.3.3 Vinyl Ester-Styrene.

Compression testing was also performed using vinyl ester-styrene waste forms. These specimens were prepared as described earlier using waste streams containing 35, 55, 70 and 80 wt% sodium nitrate. Three replicate specimens of each formulation which were right circular cylinders, 4.7 cm in diameter and approximately 9.8 cm long were tested. Formulations used were determined as a result of earlier formulation development studies (see Figure 4.6). These waste forms were tested 28 days after specimen preparation.

Compression strengths measured are shown as a function of waste/binder ratio in Figure 4.9. Compressive strengths were found to decrease with increasing waste/binder ratio for each waste stream. For a given waste/binder ratio, compression strength increased with increasing sodium nitrate content (and hence decreasing water content) in the waste stream. The highest compression strengths, 3,400-3,800 psi were observed for formulations containing dry sodium nitrate waste. Aqueous sodium nitrate formulations had compression strengths of 700-2,300 psi.

4.4 Leachability.

Leach testing to determine the rate of nitrate release was performed for portland type I cement, high alumina cement, and vinyl ester-styrene waste forms. Two specimens of each formulation were leach tested. The test employed was an extension of the ANS 16.1 leach test described previously in Section 2.2.8.2. In this test, demineralized water leachant is used. The leachate is sampled and replaced at cumulative leach time intervals of 2 hours, 7 hours, 24 hours, 48 hours, 72 hours, 96 hours and 120 hours. Subsequently, leachate sampling and replacement was performed at cumulative leach times of 8 days, 11 days, 18 days and each seven days thereafter for a total leach time of 81 days. Leach specimens were right circular cylinders, 4.7 cm in diameter and 9.8 cm long. A leachant volume to sample external geometric surface area ratio of 10 cm was used.

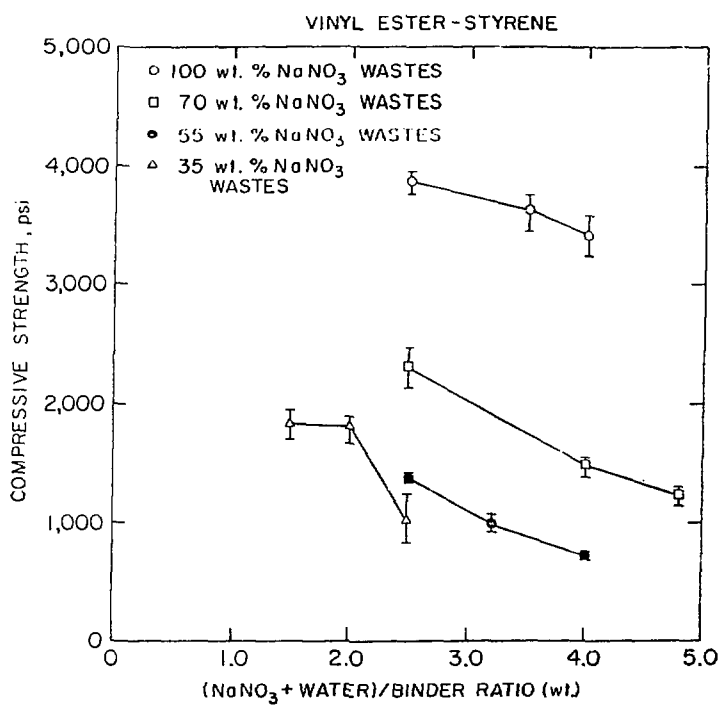


Fig. 4.9 Compression strength of sodium nitrate - vinyl ester-styrene waste forms.

Leachate samples were measured colorimetrically for nitrate content using a Technicon autoanalyzer^(a). The nitrate content of the leachate aliquot was related to the total leachate volume to determine the quantity of nitrate released from the waste form. This value was compared to the original nitrate content of the leach specimen in order to determine the fraction nitrate release. In graphical presentations of the data obtained, the cumulative fraction nitrate release is multiplied by the factor (V/S) where V is the specimen volume and S is its external geometric surface area. If leaching occurs by diffusion from a semi-infinite homogeneous medium having a zero surface concentration for all $t > 0$, then (neglecting decay):

$$(a_n/A_o)(V/S) = 2(D_e/t)^{1/2}t^{1/2} \quad \text{Eqn. 4.1}$$

where,

a_n = cumulative nitrate release

A_o = initial nitrate content

V = specimen volume

S = specimen external geometric surface area

D_e = effective diffusivity and

t = cumulative leach time.

The factor (V/S) is then a normalizing factor for different waste geometries and sizes. The effective diffusivity is a material constant.

Nitrate leaching data is shown in Figure 4.10-4.12 for portland type I cement waste forms, Figure 4.13 for high alumina cement waste forms and Figures 4.14-4.17 for vinyl ester-styrene waste forms. These figures include data for waste forms produced using different aqueous sodium nitrate waste streams and a range of waste/binder ratios as suggested by formulation development work. For portland type I cement, 30, 50 and 70

(a) Technicon, Inc., White Plains, NY

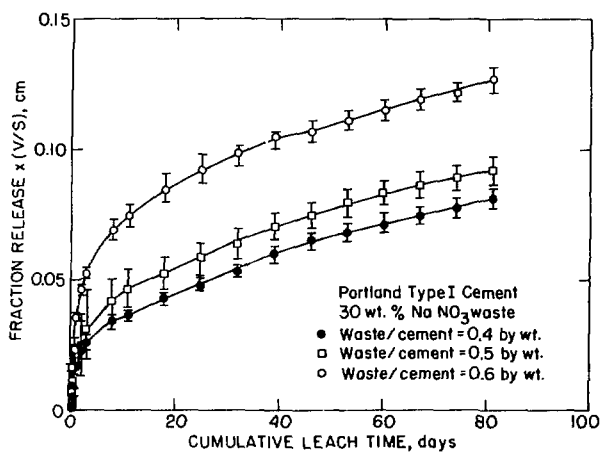


Fig. 4.10 Nitrate leachability for portland type I cement waste forms incorporating 30 wt% sodium nitrate waste.

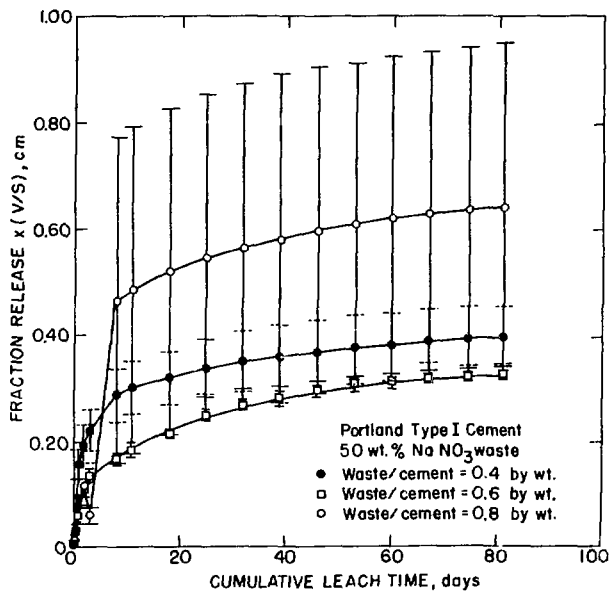


Fig. 4.11 Nitrate leachability for portland type I cement waste forms incorporating 50 wt% sodium nitrate waste.

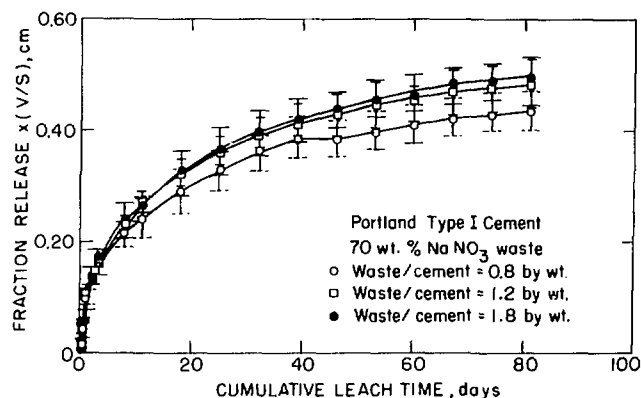


Fig. 4.12 Nitrate leachability for portland type I cement waste forms incorporating 70 wt% sodium nitrate waste.

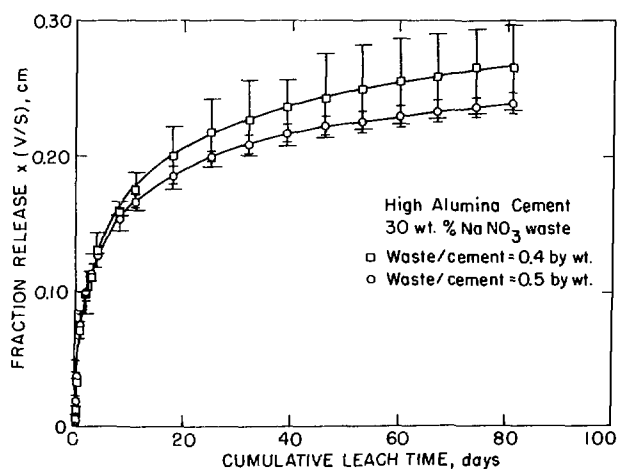


Fig. 4.13 Nitrate leachability for high alumina cement waste forms incorporating 30 wt% sodium nitrate waste.

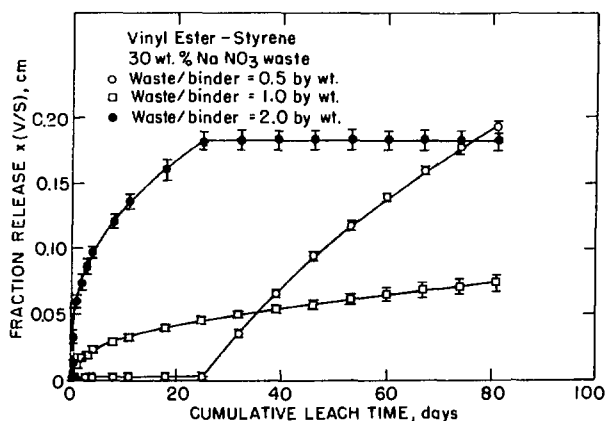


Fig. 4.14 Nitrate leachability for vinyl ester-styrene waste forms incorporating 30 wt% sodium nitrate waste.

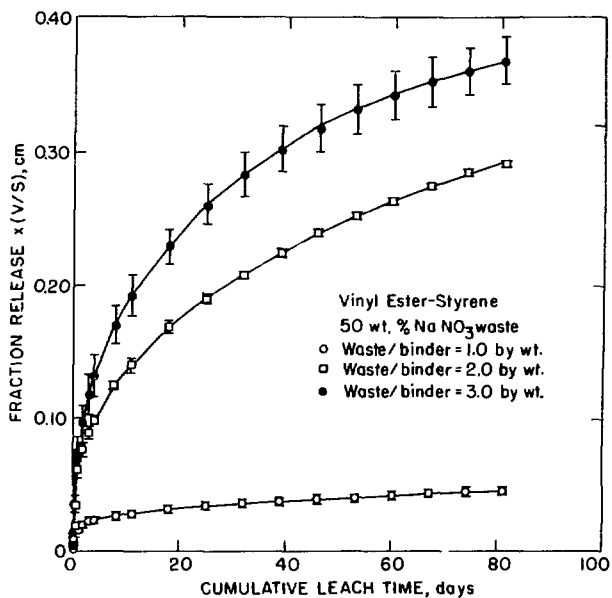


Fig. 4.15 Nitrate leachability for vinyl ester-styrene waste forms incorporating 50 wt% sodium nitrate waste.

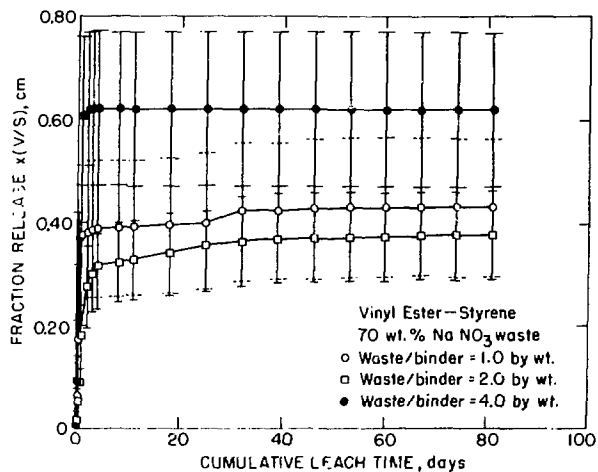


Fig. 4.16 Nitrate leachability for vinyl ester-styrene waste forms incorporating 70 wt% sodium nitrate waste.

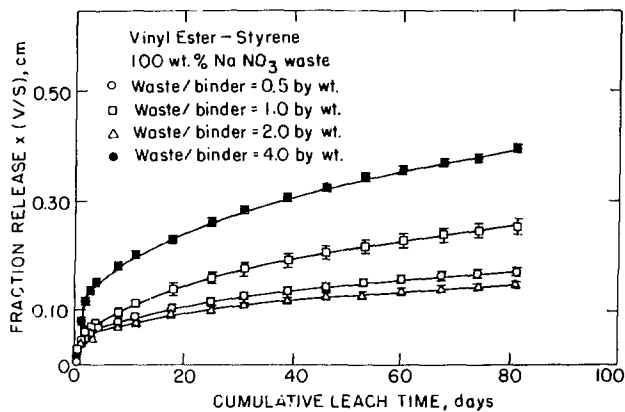


Fig. 4.17 Nitrate leachability for vinyl ester-styrene waste forms incorporating 100 wt% (dry) sodium nitrate waste.

wt% sodium nitrate waste streams were used. 30 wt% sodium nitrate waste was incorporated for leaching of high alumina cement specimens. Vinyl ester-styrene waste forms utilized 30, 50, 70 and 100 wt% sodium nitrate waste.

The data shown in Figures 4.10-4.17 can be directly compared with each other to indicate the effect of binder type, sodium nitrate content in the waste, and waste/binder ratio. In general, leachability was found to increase with increasing sodium nitrate content in the waste form. Sodium nitrate content in the waste form is increased by incorporation of higher sodium nitrate content waste streams and/or use of higher waste/binder ratios. On the basis of the data generated, high alumina cement waste forms appear to have significantly higher leachability for nitrate waste (for total sodium nitrate contents of approximately 0.1 wt%). The leachability of vinyl ester-styrene waste forms is lower than portland type I cement waste forms. However, rapid releases can occur from vinyl ester-styrene waste forms after some time at lower leach rates (see Figure 4.14). This can occur due to the establishment of substantial water pathways into the waste form. This type of behavior can be worsened in actual practice if the waste form is not homogeneous and water can reach large pockets of waste solids. Note however, that many of the vinyl ester-styrene waste forms tested had sodium nitrate contents considerably higher than in the cement waste forms.

5. SOLIDIFICATION OF INCINERATOR ASH WASTE

5.1 Description of Incinerator Ash Wastes.

A large fraction of solid radioactive waste consists of combustible materials. Such combustible solids include protective clothing, rubber boots and gloves, paper, rags, filter aid materials, and ion exchange resins. Volume reduction of these wastes assumes considerable importance relative to the potential for reducing disposal costs and conserving existing shallow land burial site capacity. While a number of volume reduction options are available for combustible solid wastes, the most attractive option is some form of incineration. However, while incineration does result in a large volume reduction for these wastes, the incinerator ash residue produced is highly dispersible. As a result, the immobilization of incinerator ash waste by solidification is important.

Solidification studies have utilized an incinerator ash produced by the rotary kiln incinerator developed at the Rockwell International Rocky Flats plant. This incinerator was used to burn a non-radioactive waste feed whose composition is representative of the combustible low-level wastes generated at the plant. This waste feed composition is listed in Table 5.1.

Table 5.1. Rotary Kiln Feed Composition

<u>Constituent</u>	<u>Weight %</u>
Paper	40.0
Polyethylene	22.8
Neoprene	18.8
Kerosene	9.5
Polyvinyl Chloride	7.9
Tributyl Phosphate	1.0

The feed rate to the incinerator for waste solids was 6.8 kg/hr; waste liquids were fed at a rate of 0.45 liter/hr. The incinerator was operated at a temperature of $1000^{\circ}\text{C} \pm 100^{\circ}\text{C}$ with an after-burner temperature of $1400^{\circ}\text{C} \pm 100^{\circ}\text{C}$. The chemical composition of the resultant ash,

as measured by DC arc emission spectroscopy, is shown in Table 5.2. Confidence limits for this analysis are approximately $\pm 10\%$ for concentrations above one weight percent and $\pm 50\%$ for lower concentrations. While the silicon content of the ash is listed as >10 wt%, an analysis at the Rocky Flats plant gave a silicon content of 15 wt%. The elements listed, with the exception of carbon, are largely present as oxides. The ash contained no significant radioactivity content above background levels.

Table 5.2 Rotary Kiln Incinerator Ash Compositional Analysis

<u>Element</u>	<u>Weight%</u>
Al	18
C	13.1
Si	>10
Ca	5
Ti	4.8
Zn	2.6
Mg	1
Na	0.5
Fe	0.3
K	0.1
Ni	0.1
Cu	0.08
Cr	0.05
Sr	0.05
Mn	0.03
Pb	0.03

The rotary kiln ash has a bulk density of approximately 0.23 g/cm^3 . It has a visual appearance similar to cigarette ash (gray-white in color), but exhibits color gradations and has carbon present as a distinct particulate. In the presence of water the ash exhibits a pH of approximately 6.

5.2 Formulation Development.

The use of portland cement, high alumina cement, polyester-styrene and vinyl ester-styrene for the solidification of rotary kiln incinerator ash was studied. Formulation acceptability required the production of a free standing monolithic solid with no drainable free standing water after a cure time of one week or less. After curing in their containers for 14 days, waste forms were removed from their containers to verify formation of a free standing monolithic solid. Acceptable specimens were then subjected to a two week immersion test in demineralized water (described in Section 2.2.2) during and after which they were required to maintain their mechanical integrity. Specimens were cured at ambient room temperature in sealed polyethylene containers.

5.2.1 Portland Type I Cement.

Portland type I cement was used to solidify the rotary kiln incinerator ash. Since the ash itself is dry, water must be added to this system for cement hydration. The amount of water added is important since sufficient water must be present to form a workable and pourable cement mix. However, the addition of an excessive amount of water can result in the presence of free standing water after solidification. While it is also desirable to incorporate as much incinerator ash as possible into the final waste form, sufficient cement must be included in the formulation to hold the waste form together producing a monolithic mass. Also, the cement-waste mixture must have a sufficiently long set time to allow complete mixing and transfer from the mixing equipment to the container in which the mixture is cast.

Sufficient water must be added to any given cement-ash waste mixture to provide adequate workability during mixing. Good workability is required to provide a homogeneous, pourable mixture in a reasonable time using conventional mechanical cement mixing techniques. A Hobart Model N-50 planetary action mortar mixer was used for this study. The minimum water-to-cement ratio producing an adequately workable mixture with portland type I cement alone (no ash) was 0.25 by weight. This

corresponds to a mixture containing 20 wt% water and 80 wt% cement. When incinerator ash was added to this mixture, it "balled up" and adequate workability was lost, apparently due to insufficient water in the mix. This was indicative of the ash itself absorbing water from the mixture.

It was subsequently determined that the ash has considerable water absorption capacity which was partially attributed to its large particle size and porosity. The ash was difficult to mix directly with a cement-water mixture, unless sufficient water was first added to satisfy the ash's absorptive requirements. Conversely, adequate workability was only achieved when cement powder was added to wetted ash with sufficient water present to satisfy both ash absorption and cement workability requirements. However, the water required to saturate the ash is weakly held since when sufficient water is added, a minimum of mixing typically results in an excessively wet mixture in which some water separates to the top.

Prior ball milling of the ash was found to minimize these tendencies. Ball milling decreases the ash particle size and changes its geometry, lowers ash water absorption requirements and results in a more homogeneous ash waste with a bulk density of approximately 0.37 g/cm^3 . The increased ash bulk density also facilitates fabrication of the waste form and appears to permit an increase in the amount of ash waste that can be incorporated.

A ternary compositional phase diagram was developed for the solidification of the ball milled rotary kiln ash in portland type I cement (see Figure 5.1). The area indicated represents those formulations meeting acceptability criteria. Also indicated are those regions where free standing water was observed after curing or insufficient water was present in the formulation for adequate workability (mixability limit). Note that acceptable waste forms were obtained from formulations containing up to 50 wt% incinerator ash and as little as 3 wt% portland type I cement. A maximum incinerator ash loading of 40 wt% was obtained using the as-received (not ball milled) ash.

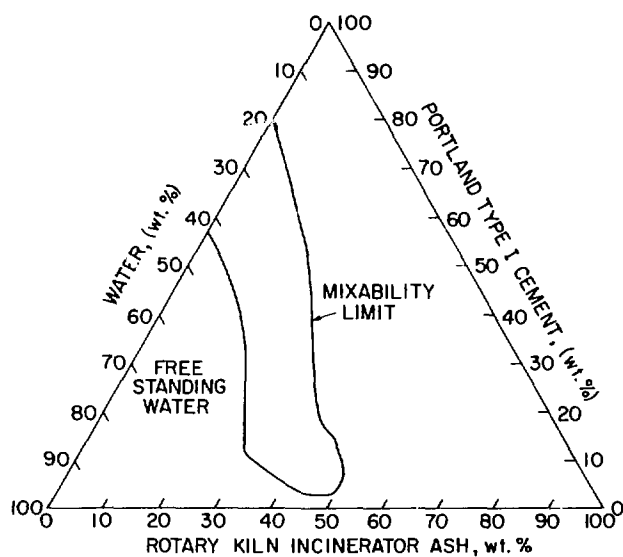


Fig. 5.1 Ternary compositional phase diagram for the solidification of ball milled rotary kiln incinerator ash in portland type I cement.

5.2.2 High Alumina Cement.

Limited formulational development work was conducted using high alumina cement to determine if there were any obvious advantages to its use over portland type I cement. High alumina cement is a high early strength (rapid curing) cement which is composed primarily of monocalcium aluminate ($\text{CaO Al}_2\text{O}_3$). A maximum loading of 50 wt% ash was achieved using the ball milled rotary kiln ash. With the as-received ash, a maximum loading of 45 wt% ash was obtained. While an apparent advantage of using high alumina cement was observed for solidification of the as-received ash, no additional work was conducted. Only minimal processing (ball milling) is required to provide increased waste loadings using portland type I cement which is less expensive and more readily available than high alumina cement.

5.2.3 Polyester-Styrene.

Formulation development work was conducted for the solidification of the rotary kiln incinerator ash with thermosetting polymers. Most of this work utilized a commercial grade polyester-styrene (LB183-18) marketed by the United States Steel Chemical Company, Linden, New Jersey. This resin contains 50 wt% styrene; the remainder consists of equal parts of two different polyester resins. A catalyst-promoter system was used to initiate polymerization of this resin at room temperatures. The promoter (cobalt napthenate) acts to cause the catalyst (methylethylketone peroxide) to decompose, forming free radicals, at room temperatures. These free radicals initiate polymerization of the polyester-styrene monomer. Without use of a promoter, temperatures of 50°C or higher are required to initiate monomer polymerization using this catalyst.

Polyester-styrene formulations containing as much as 55 wt% ball milled rotary kiln incinerator ash were prepared. The ball milled ash was initially used rather than the as-received ash as a result of the work conducted with portland cement which suggested that prior ball-milling would facilitate mixing operations.

Formulation of polyester-styrene waste forms is performed by (1) addition of the catalyst to the polyester-styrene monomer, (2) addition of the incinerator ash waste to the monomer containing catalyst and (3) addition of the promoter to the monomer-ash mixture. (A promoter addition of 0.5% of the weight of polyester-styrene and a catalyst addition of 1.2% of the weight of polyester-styrene were used.) Each step requires thorough mixing to insure uniform distribution of the components. Normally in this type of system, the promoter is added last to prevent premature polymerization of the monomer although under certain conditions a change in the order of addition may be useful. Mixing was performed in a mixing vessel using a high speed pneumatic mixer with a propeller type blade. After component addition and mixing, the mixture was transferred to solidification containers which were low density polyethylene vials with nominal dimensions of 4.7 cm I.D. and 9.8 cm height. A vibration table was used to remove air voids from viscous mixtures.

Attempts to incorporate greater than 55 wt% ball milled ash resulted in an excessively dry mixture which tended to "ball up". The 20 wt% ash formulations cured rapidly (approximately 2 hours) and exhibited a significant curing exotherm, due to the high monomer content. Using the as-received incinerator ash, a maximum of about 45 wt% ash was successfully solidified.

The maximum quantity of ash that can be incorporated is related to the viscosity of the monomer used. Styrene content can be increased in polyester-styrene systems to reduce monomer viscosity. The maximum ash that could be incorporated in a polyester monomer (containing no styrene) was found to be about 20 wt% before the mixture became too viscous during mixing to add additional ash. When a polyester-styrene mixture containing 20 wt% styrene was used, 50 wt% ash could be incorporated. As mentioned previously, polyester-styrene containing 50 wt% styrene produced formulations with up to 55 wt% incinerator ash. While the addition of styrene to polyester monomer increases the amount of ash which can be incorporated, styrene additions in excess of 20 wt% have relatively little effect in allowing further increases in incinerator ash waste content.

5.2.4 Vinyl Ester-Styrene.

Vinyl ester-styrene^(a) is a proprietary water extendable binder used for the solidification of wet solid wastes. The monomer is capable of forming a stable emulsion with water in waste under high shear mixing. The resin-waste emulsion is then polymerized at room temperature by use of a catalyst-promoter system. Water in the waste is immobilized as small discrete droplets in the solid matrix while solids in the waste are mechanically held as particulate in the matrix. While a prime attribute of the vinyl ester-styrene system is its ability to solidify aqueous wastes through the formation of a stable emulsion, this behavior is not relevant to the solidification of dry incinerator ash wastes.

Wastes forms incorporating rotary kiln incinerator ash were prepared in a manner similar to that described for polyester-styrene. A maximum ash loading of 50 wt% ball milled ash was achieved; however, this mixture would not completely polymerize. An elastic solid resulted instead of the desired hard, rigid solid. A maximum of <30 wt% ball milled ash could be incorporated to form a hard, rigid solid with suggested catalyst and promoter additions. Apparently components in the incinerator ash reacted with the catalyst and/or promoter and inhibited more complete polymerization. To improve polymerization, catalyst and/or promoter additions could be increased. However, it was noted that the maximum ash loading producing a workable mixture (50 wt% ash) was less than that obtained with polyester-styrene. As a result, and since polyester styrene is a less expensive base material, no attempt was made to further investigate changes which would enhance polymerization of vinyl ester-styrene.

^(a) Dow Chemical Company, Midland, MI

5.3 Compression Strength.

Compression strengths were determined for portland type I cement, polyester-styrene, and vinyl ester-styrene waste forms incorporating ball milled rotary kiln incinerator ash. ASTM method C39-72 ("Test for the Compressive Strength of Cylindrical Concrete Specimens") and a Soiltest^(a) Model CT-2520 compression tester were employed.

5.3.1 Portland Type I Cement.

Compression test specimens were right circular cylinders, 4.7 cm diameter by 9.8 cm long. Specimens were prepared as described earlier using formulations containing 20, 30, 40, and 50 wt% incinerator ash and employing various (ash + water)/cement weight ratios. Increasing (ash + water)/cement ratios at a constant incinerator ash content are indicative of increasing water/cement ratios. Specimens were prepared in polyethylene vials which were sealed during curing to prevent evaporative water loss. A cure time of 34 days was used. Three replicate specimens were compression tested for each waste form formulation.

Figure 5.2 indicates compressive strength as a function of (ash + water)/cement ratio for waste form incinerator ash contents of 20, 30, 40 and 50 wt%. The parameters of weight percentage incinerator ash and (ash + water)/cement weight ratio are sufficient to specify the composition of the waste form. In general, compression strengths were observed to decrease with increasing ash content and increasing water content in the waste forms. Compression strengths of 1,000 psi or more were obtained for waste forms containing as much as 40 wt% incinerator ash. Compression strengths of portland type I cement waste forms containing 50 wt% ash were low (50-100 psi), however, these waste forms only contained between 5.0 and 7.0 wt% cement and had water/cement weight ratios of

^(a) Soiltest, Inc., Evanston, IL

between 9.5 and 6.6 respectively. These water contents are far above those necessary for hydration of the cement, but are required to satisfy the ash's absorptive requirements and to provide a workable cement-ash mixture. Obviously, in practice, water contents as low as practicable but meeting workability requirements would be used.

5.3.2 Vinyl Ester-Styrene and Polyester-Styrene.

Compression testing was also performed with vinyl ester-styrene and polyester-styrene waste forms containing 20-40 wt% and 30-50 wt% rotary kiln incinerator ash, respectively. Specimens were right circular cylinders, 4.7 cm in diameter and 9.8 cm long. Three replicate specimens were prepared in polyethylene vials as described earlier. Compression testing was performed 29 days after specimen preparation.

The results of compression testing for these waste forms are shown in Figure 5.3. Polyester-styrene waste forms containing 30-50 wt% incinerator ash demonstrated average compression strengths between 1,250-1,300 psi, with only a small decrease observed with increasing ash content. Similarly, vinyl ester-styrene waste forms containing 20 wt% incinerator ash had an average compression strength of 1,350 psi. However, as described previously, vinyl ester-styrene waste forms containing 30 wt% incinerator ash or more did not polymerize sufficiently to form a hard rigid waste form. Resultant average compression strengths of 100 psi and 60 psi were obtained for vinyl ester-styrene waste forms containing 30 wt% and 40 wt% incinerator ash, respectively.

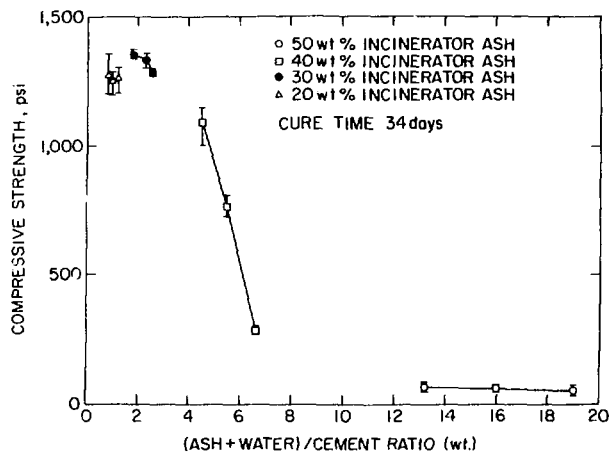


Fig. 5.2 Compression strength of portland type I cement waste forms containing rotary kiln incinerator ash.

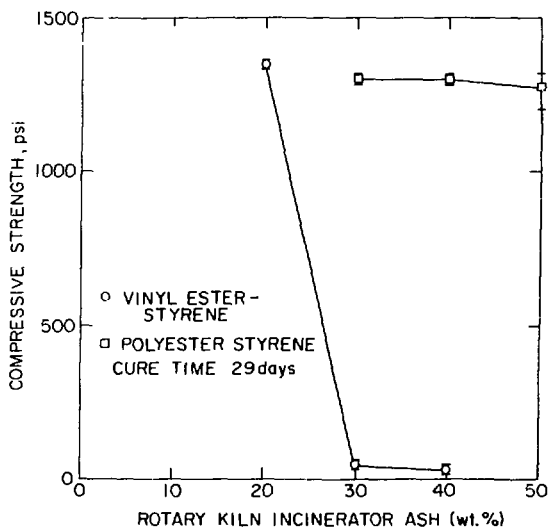


Fig. 5.3 Compression strength of vinyl ester-styrene and polyester-styrene waste forms containing rotary kiln incinerator ash.

6. USE OF ADDITIVES FOR IMPROVED ACTIVITY RETENTION

6.1 Introduction.

Previous work [1] with additives had identified a variety of materials intended to increase the retention of radioactive materials in waste forms. In this work, materials were screened for uptake capacities of cesium and strontium by the measurement of distribution ratios (R_d). Those additives exhibiting the greatest R_d (uptake) were incorporated into laboratory scale portland type III cement waste forms which contained ^{60}Co , ^{137}Cs and ^{85}Sr tracers. A leach test was employed to determine the rate of activity release from the waste forms.

Mineral colloid BP and adsorption alumina were used as additives comprising 5 weight percent of the waste form solids. Alumina showed no effect on the leachability of either cesium or strontium even though it had a very high R_d for these elements. Mineral colloid BP, a montmorillonite clay product of Georgia Kaolin Company, reduced the rate of release of cesium by a factor of 2 but increased the rate of release of strontium by a similar factor. In neither case did the results of the initial uptake screening (measurement of R_d) adequately reflect the results of the leach tests. Therefore, a new approach was taken. A leach test alone was used to determine the efficacy of additives.

6.2 Experimental Method.

Laboratory scale waste forms, measuring 4.7 cm in diameter and 7.0 cm in height were prepared using portland type III cement. The formulation used consisted of: 131 g portland type III cement, 6.6 g additive, 70 g water and 1 ml of mixed tracer solution. The tracer solution contained 12.2 $\mu\text{Ci/ml}$ of ^{137}Cs , 9.76 Ci of ^{60}Co and 3.36 μCi of ^{85}Sr . The additives tested in these formulations and subsequent static leach tests were:

ZBS-3, chabazite
(Source: Oxidental Minerals Corp., Lakewood, CO)

ZBS-4, mordenite
(Source: Oxidental Minerals Corp., Lakewood, CO)

ZBS-5, erionite
(Source: Oxidental Minerals Corp., Lakewood, CO)

ZBS-14, clinoptilolite
(Source: Oxidental Minerals Corp., Lakewood, CO)

Chiton,
(Source: ground shrimp shells)

Thixojel #1, a montmorillonite clay product,
(Source: Georgia Kaolin Company, Elizabeth, NJ)

Ionsiv A-51, a synthetic zeolite
(Source: Union Carbide Corp., Linde Division, Moorestown, NJ)

Ionsiv IE-95, a synthetic zeolite
(Source: Union Carbide Corp., Linde Division, Moorestown, NJ)

Mineral Colloid BP, a montmorillonite clay product,
(Source: Georgia Kaolin Company, Elizabeth, NJ)

Coal Fly Ash
(Source: Colstrip Coal, MT)

Silica Powder
(Source: Fisher Scientific Company, Pittsburgh, PA)

The waste forms were prepared by first measuring out the water into the plastic specimen preparation containers. The tracer solution was then pipetted into each container. Preweighed mixtures of cement and additives were slowly mixed by hand into the water-tracer solution mixture. Small, steel wire hooks were placed into the wet cement for use as lifting eyes to suspend the waste forms during the subsequent leach tests. The waste forms were covered and allowed to cure at room temperature for two weeks. Two portland type III cement specimens containing water and tracer solution, but no additive, were prepared for each leach test series.

Static leach tests were conducted using distilled water leachant. A leachant volume to specimen external geometric surface area ratio of 10 cm was employed. 10 ml of water were withdrawn for each sampling. The

sampling intervals were 0.25, 1, 2, 3, 4 and 8 days. The leachate samples were placed into plastic test-tubes and centrifuged prior to analysis. Aliquots of 5 ml each were taken for gamma spectroscopy on a Tracer Northern 4000 system using an intrinsic germanium gamma detector. From the counting results, fraction activity release data were calculated and plotted for averages of the duplicate samples.

6.3 Experimental Results.

Cesium leaching curves for portland type III cement waste forms containing each of the additives tested are shown in Figures 6.1a and 6.1b. Two sets of samples were prepared and tested at different times. Therefore, each group must be compared to its own reference neat-cement sample (no additive).

As shown in Figure 6.1a, the neat cement, as expected, had the greatest leach rate. Samples containing fly ash and silica powder as additives fell very near the neat cement curve and are not shown. The formulation containing thixo-jel #1 leached less than the neat cement samples while the two synthetic zeolite-containing samples had even lower fraction releases. In Figure 6.1b, which also compares the ^{137}Cs fraction releases of additive samples with those of neat cement, the fraction release from the neat cement samples is slightly higher than that of the previous set. All of the additive containing samples in Figure 6.1b fall into a relatively narrow range. These additive materials are all natural zeolites.

The synthetic zeolite IE-95 had the lowest cesium fraction release of any additive (1.48×10^{-2} after ten days leaching). This material is a zeolite composed primarily of the chabazite structure type. It is supplied in a mixed ion form containing Na^+ , Mg^{+2} and Ca^{+2} ions.

The natural zeolites all have good retention capabilities for cesium. A typical fraction release for these minerals is approximately 2.7×10^{-2} after ten days of leaching, about double that of the synthetic

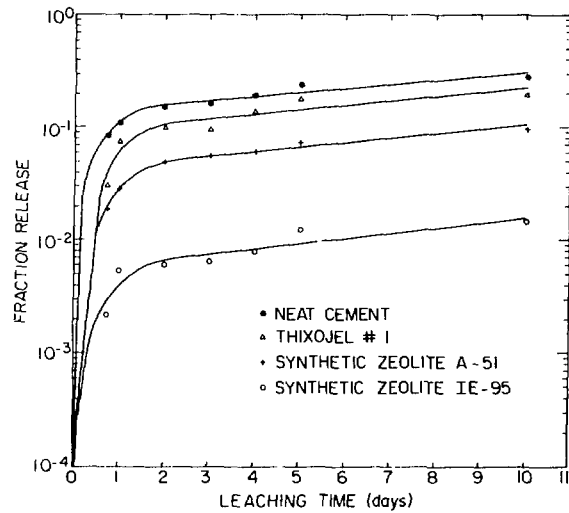


Fig. 6.1(a) Cesium leach rates are shown for neat cement samples and cement with additives.

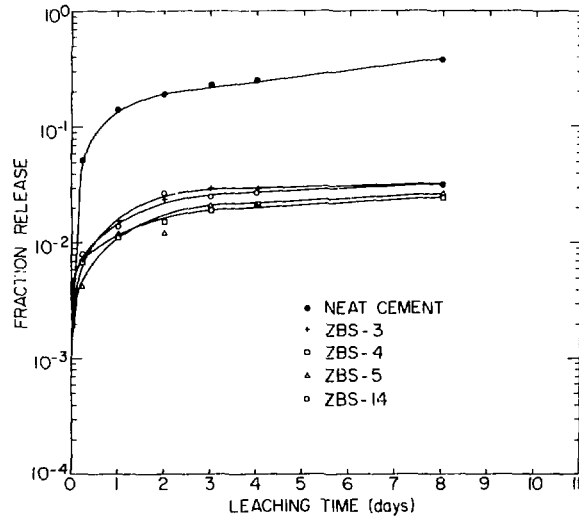


Fig. 6.1(b) Cesium leach rates are shown for neat cement and cement with natural zeolite additives.

zeolite. However, large quantities of these natural zeolitic materials presumably could be obtained at a much lower price than could the IE-95 zeolite.

Curves showing the fraction release of strontium from the waste forms tested are given in Figures 6.2a and 6.2b. Of the materials shown in Figure 6.2a, only the synthetic zeolite A-51 provided any reduction of strontium fraction release over that of the neat cement samples. The other additives shown in Figure 6.2a produced higher strontium fraction releases. All of the natural zeolites reduced strontium leachability somewhat. The greatest change was only a 2-fold decrease by the ZBS-4 and ZBS-5 additive sample. Strontium releases from these samples were still slightly higher than the neat cement and the A-51 zeolite as shown in Figure 6.2a. It is concluded that none of the additives tested made any significant differences in the leachability of strontium from cement waste forms. It should be noted that strontium fraction releases are typically an order of magnitude lower than those of cesium from neat cement samples.

In summary, additive screening tests which determine R_d are not effective in predicting the usefulness of a material in reducing leachability from a waste form. A simple static leaching test of the additive in an appropriate binder provides a more accurate determination of additive effectiveness. None of the materials tested were found to significantly reduce strontium leaching. Some of the additives tested showed promise in reducing cesium release from cement waste forms. One material, a synthetic zeolite, provided an order of magnitude reduction in cesium fraction release. Other natural zeolites, while not quite as effective are promising because they may be available at lower prices.

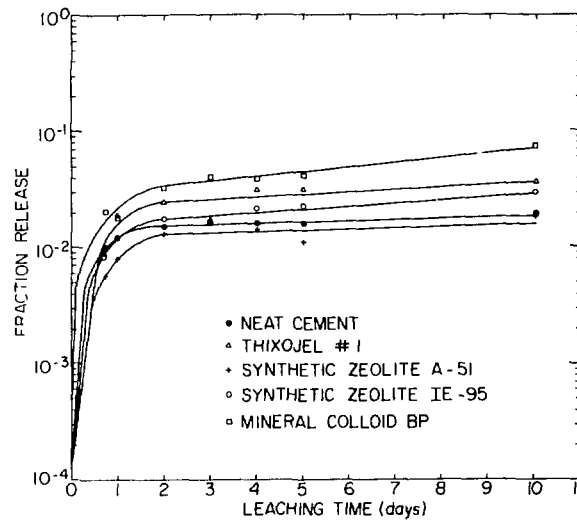


Fig. 6.2(a) Strontium leach rates are shown for neat cement and cement with additives.

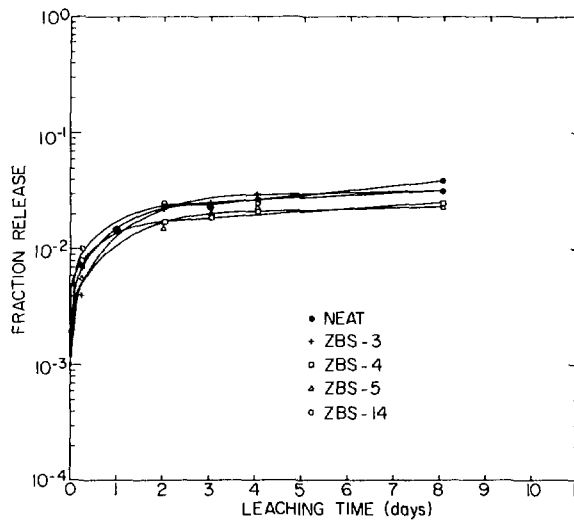


Fig. 6.2(b) Strontium leach rates are shown for neat cement and cement plus natural zeolite additives.

REFERENCE SECTION 6

1. Neilson, R.M. Jr. and P. Colombo, Waste Form Development Program Annual Progress Report, October 1980-September 1981, BNL-51517, Brookhaven National Laboratory, Upton, NY 11973.

7. TECHNICAL ASSISTANCE

The Waste Form Development program also provides technical assistance as required by the Low-Level Waste Management Program (LLWMP). During FY 1982, technical assistance efforts consisted of participation in two working committees organized by EG&G Idaho, Inc. The first committee worked to develop waste acceptance criteria for shallow land burial. The second committee considered the development of environmental release criteria for solid radioactive waste. EG&G, Inc. is responsible for writing the criteria documents resulting from these efforts.