BNL 51615
UC-70
(Nuclear Waste Management —TIC-4500)

BNL--51615

DE83 005949

# SOLIDIFICATION OF ION-EXCHANGE-RESIN WASTES

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**August 1982**



**Prepared for the**
**NATIONAL LOW-LEVEL WASTE PROGRAM**
**UNITED STATES DEPARTMENT OF ENERGY**

**NUCLEAR WASTE RESEARCH GROUP**
**DEPARTMENT OF NUCLEAR ENERGY**

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## SUMMARY

This topical report describes the results of an investigation at Brookhaven National Laboratory (BNL) of the solidification of ion exchange resin wastes. The work was conducted as part of the Waste Form Development Program, sponsored by the U.S. Department of Energy National Low-Level Waste Management Program.

The solidification media investigated included portland type I, portland type III and high alumina cements, a proprietary gypsum-based polymer modified cement, and a vinyl ester-styrene thermosetting plastic. Work was conducted to determine compositional envelopes which will produce acceptable waste forms. Imposed acceptability criteria required that waste forms be monolithic free standing solids with no free standing water and be able to withstand a two week immersion test without loss of mechanical integrity.

Samples formulated with hydraulic cement were analyzed to investigate the effects of resin type, resin loading, waste-to-cement ratio, and water-to-cement ratio. The solidification of cation resin wastes with portland cement was characterized by excessive swelling and cracking of waste forms, both after curing and during immersion testing. Similarly, mixed bed resin waste formulations were limited by their cation component. Additives to improve the mechanical properties of portland cement-ion exchange resin waste forms were evaluated. Several techniques including resin pretreatment and binder modifications provided significant improvements. High alumina cement formulations displayed a resistance to deterioration of mechanical integrity during immersion testing, thus providing a significant advantage over portland cements for the solidification of resin wastes. The chemical interactions of resins solidified in a cement matrix were explored by means of scanning electron microscopy and energy dispersive x-ray analyses.

Properties of cement-ion exchange resin waste forms including compressive strength, leachability, and radiation stability were examined. An experiment was conducted to study the leachability of cesium-137, strontium-85, and

cobalt-60 from resins modified in portland type III and high alumina cements. The cumulative Cs-137 fraction release was at least an order of magnitude greater than that of either Sr-85 or Co-60. Release rates of Cs-137 in high alumina cement were greater than those in portland type III cement by a fractor of two. Compressive strength and leach testing were also conducted for resin wastes solidified with polymer modified gypsum based cement. Cesium-137, strontium-85, and cobalt-60 fraction releases were approximately one, two and three orders of magnitude higher, respectively, than in equivalent portland type III cement formulations. As much as 28.6 wt% dry ion exchange resin was successfully solidified using vinyl ester-styrene compared with a maximum of 25 wt% in both portland and gypsum-based cement.

TABLE OF CONTENTS

TABLE OF CONTENTS (CON'T)

## LIST OF TABLES

## LIST OF FIGURES

LIST OF FIGURES (CONT.)

LIST OF FIGURES (CONT.)

# 1. CHARACTERIZATION OF ION EXCHANGE RESIN WASTES

## 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:

$$2HR + {}^{90}Sr(NO_3)_2(aq.) \rightleftarrows {}^{90}SrR_2 + 2HNO_3 \qquad \text{(Eq. 1.1)}$$

Anion Exchange:

$$2RCl + Na_2SO_4\ (aq.) \rightleftarrows R_2SO_4 + 2NaCl \qquad \text{(Eq. 1.2)}$$

where R represents the insoluble matrix of the exchanger. Equation 1.1 describes the removal of strontium-90 from a waste stream by cation exchange. Equation 1.2 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 1.1 depicts the structure of sulfonated polystyrene cation exchange resin which has been converted to the $Na^+$ form [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 PWRs).

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.

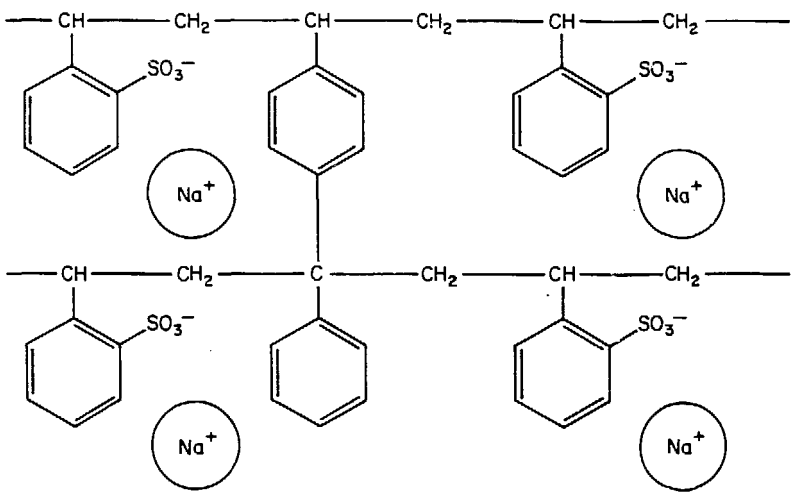


Fig. 1.1 Structure of sulfonated polystyrene cation exchange resin crosslinked with divinylbenzene. ($SO_3^-$ is the functional group and $Na^+$ is the exchangeable counter ion.

Powdered resins 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.

## 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.

## 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. 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

[a] Rohm and Haas Company, Philadelphia, PA 19105

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.

### 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 multivalents 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.

### 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°C for 18±2 hours. Water content is then calculated as follows:

$$\text{wt\% water} = \frac{\text{wt. of wet resin} - \text{wt. of dry resin}}{\text{wt. of wet resin}} \times 100 \qquad \text{(Eq. 1.3)}$$

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 1.2. 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 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 1.1.

Table 1.1 Weight Percent Water In Resin Wastes

| | Weight Percentage Water | | | |
|---|---|---|---|---|
| Resin Type | As-Received | Damp[a] | Dewatered | Slurry |
| 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 ± 3%.

### 1.4.3 Density

Density measurements for these ion exchange resin wastes are listed in Table 1.2.

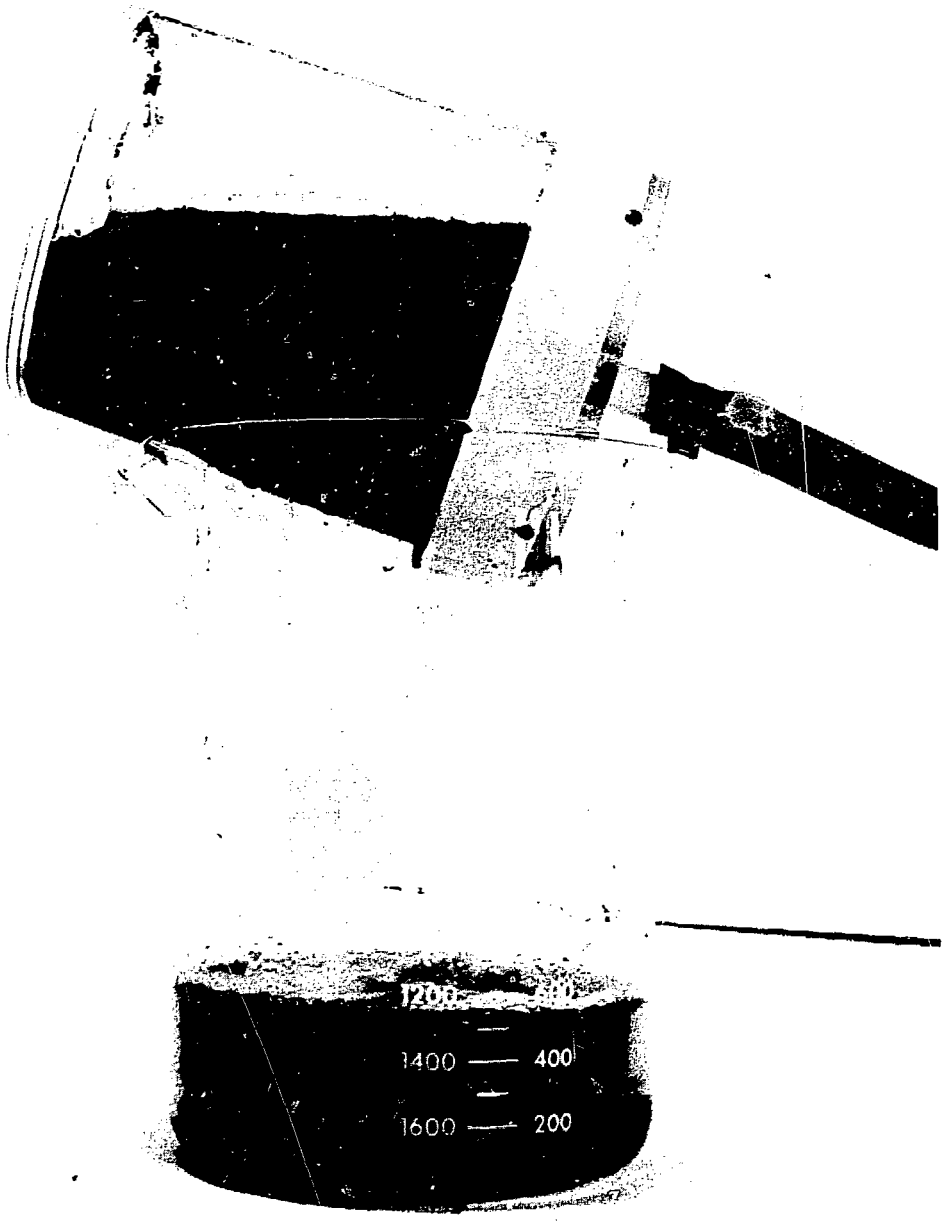


Fig. 1.2 Apparatus used to remove interstitial water from ion exchange resin.

Table 1.2 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 |

### 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. SOLIDIFICATION WITH HYDRAULIC CEMENTS

### 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 2.1 and 2.2. 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 2.3). It hardens more rapidly than portland type I cement and can achieve strength in one day equivalent to that found in portland type I cement after one month.

Table 2.1 Principal Compounds Present in Portland Cements

| Compound | Formula | Abbreviation |
|---|---|---|
| Tricalcium silicate | $3CaO \cdot SiO_2$ | $C_3S$ |
| Dicalcium silicate | $2CaO \cdot SiO_2$ | $C_2S$ |
| Tricalcium aluminate | $3CaO \cdot Al_2O_3$ | $C_3A$ |
| Tetracalcium aluminoferrite | $4CaO \cdot Al_2O_3\ Fe_2O_3$ | $C_4AF$ |

Table 2.2 Compound Composition of Portland Cements

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

Adapted from: [11]

Table 2.3 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 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 homogenous 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.

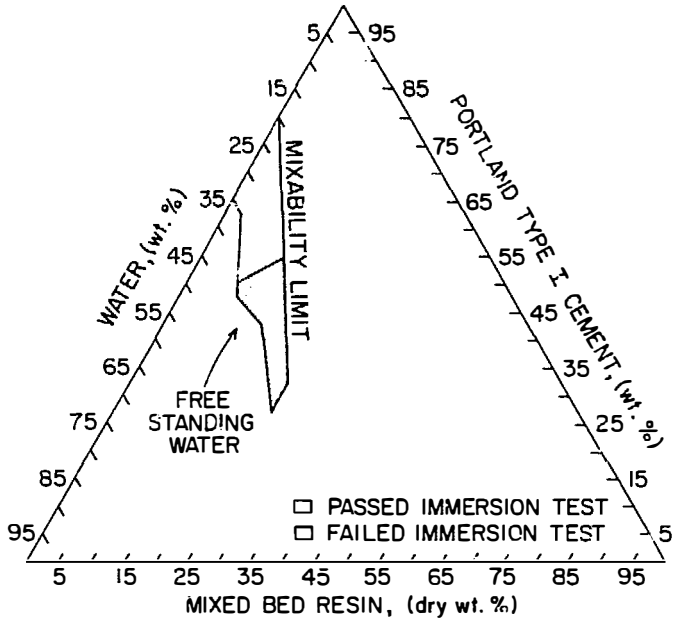


Fig. 2.1 Compositional phase diagram for the solidification of unloaded mixed bed resin with portland type I cement.

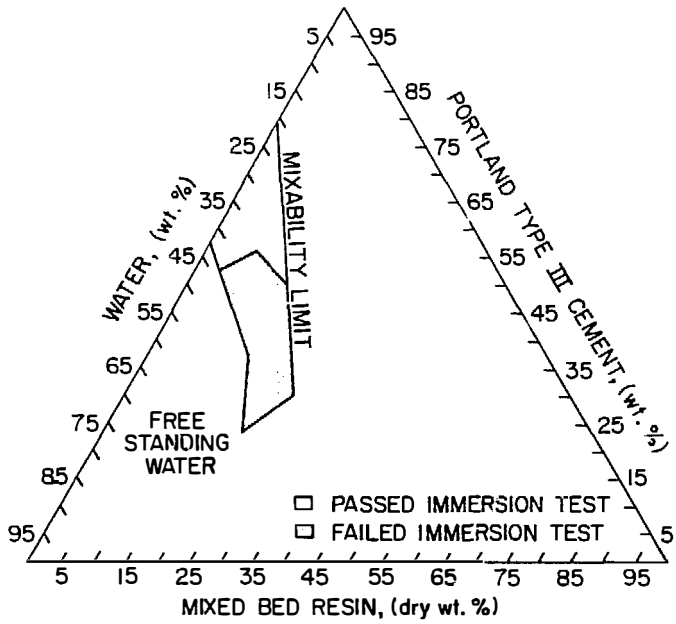


Fig. 2.2 Compositional phase diagram for the solidification of unloaded mixed bed resin with portland type III cement.

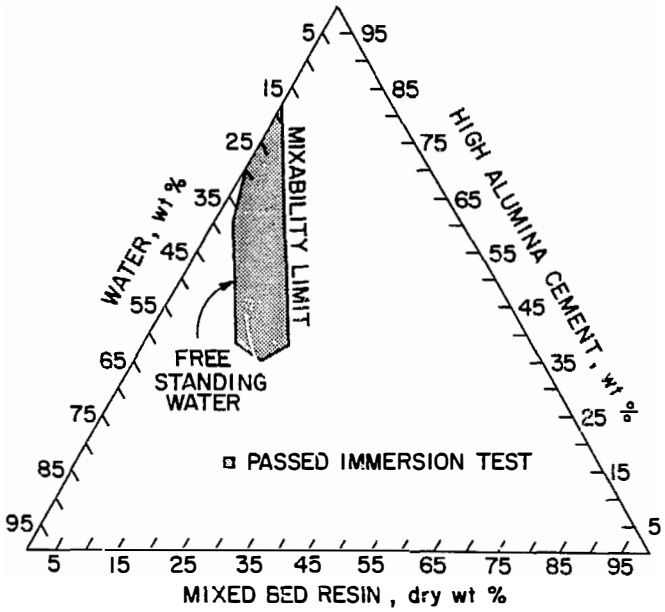


Fig. 2.3 Compositional phase diagram for the solidification of unloaded mixed bed resin with high alumina cement.

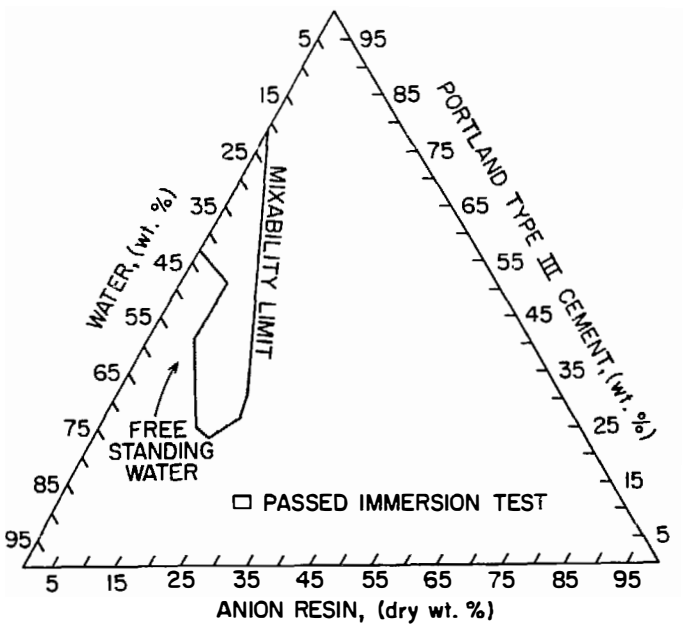


Fig. 2.4 Compositional phase diagram for the solidification of unloaded anion resin with portland type III cement.

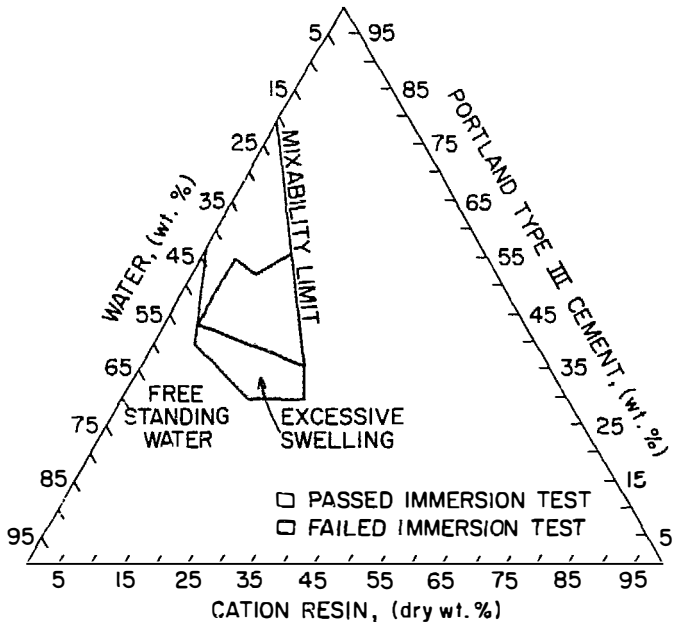


Fig. 2.5 Compositional phase diagram for the solidification of unloaded cation resin with portland type III cement.

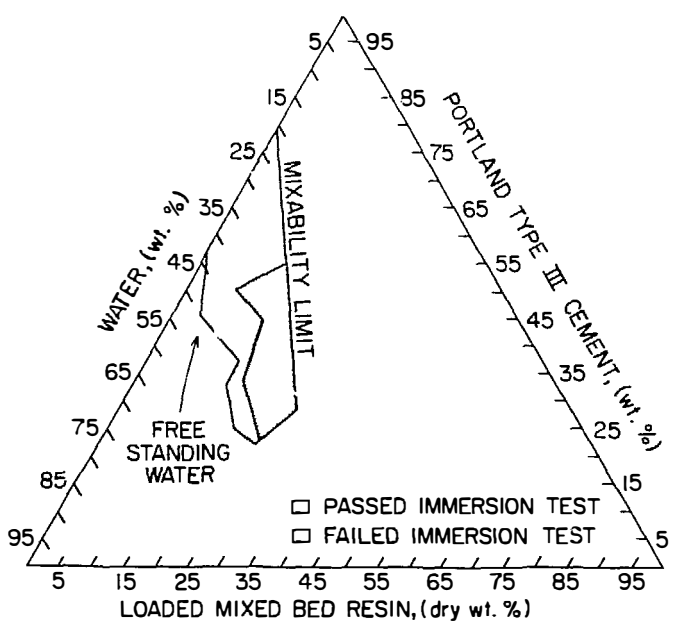


Fig. 2.6 Compositional phase diagram for the solidification of loaded mixed bed resin with portland type III cement.

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 2.1, 2.2 and 2.4-2.6. The compositional phase diagrams for the solidification of mixed bed ion exchange resin waste with high alumina cement is included as Figure 2.3. These compositional phase diagram express formulations in terms of weight percentages cement, dry resin and water (total 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 steam 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:

$$DR = WS\ (wt\%\ DR) \qquad \text{(Eq. 2.1)}$$

$$W_{waste} = WS\ (wt\%\ W_{waste}) \qquad \text{(Eq. 2.2)}$$

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

$$C = \frac{DR}{Rf} (C_f) \qquad \text{(Eq. 2.3)}$$

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

$$W = \frac{DR}{Rf} (W_f) \qquad \text{(Eq. 2.4)}$$

(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:

$$W_{corr} = W - W_{waste} \qquad \text{(Eq. 2.5)}$$

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.)

## 2.3 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 2.1 , 2.2 and 2.3, respectively.

### 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 2.7 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.

### 2.3.2 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.

## 2.4 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 2.4.

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 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

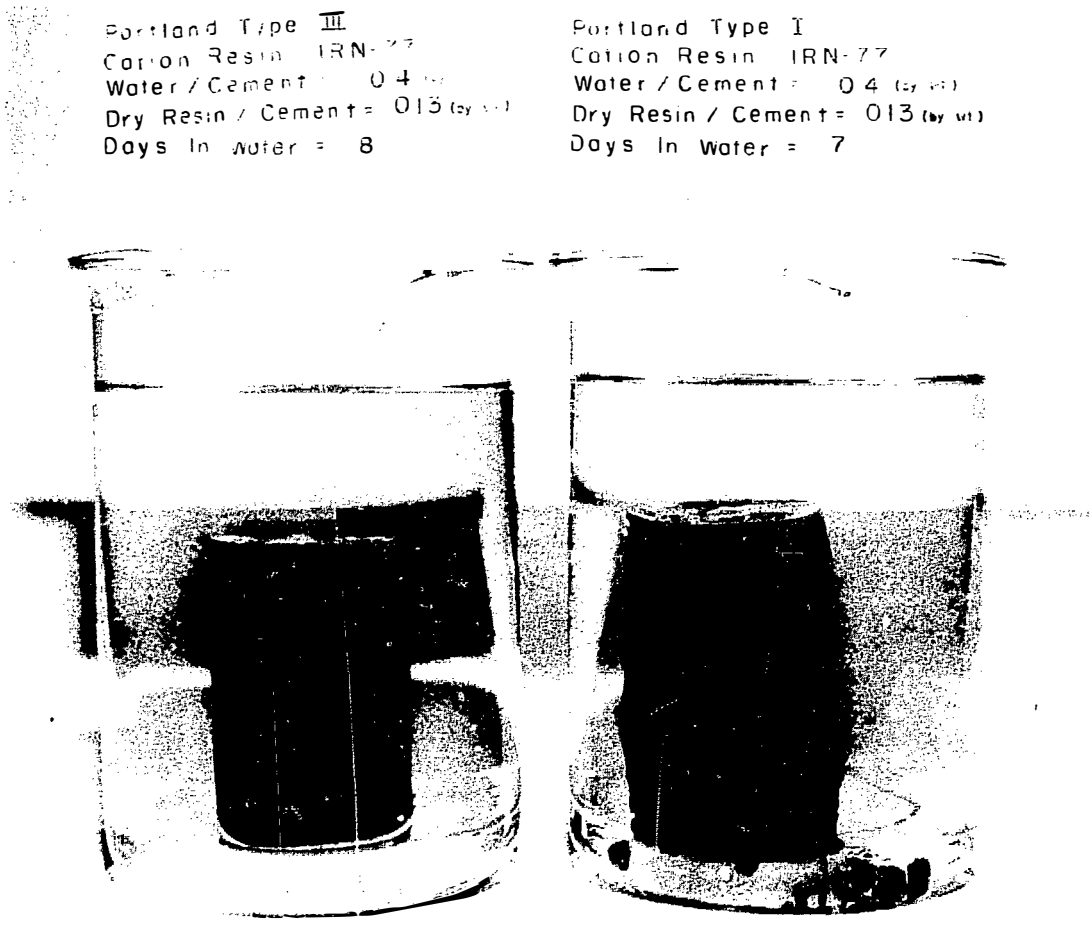


Fig. 2.7 Water immersion test comparing waste forms incorporating unloaded cation resin waste solidified with portland type III and portland type I cements.

of the cation form of the resin. Figure 2.5 is the compositional phase diagram for cation resin solidified with portland type III cement. Figure 2.8 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 2.2. 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 2.6. Fewer formulations failed by the free standing water criterion than with unloaded mixed bed resin. Figure 2.9 shows the effect of immersion testing for otherwise equivalent formulations of unloaded and loaded mixed bed resin waste forms.

## 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 2.4 and 2.5. Table 2.4 represents resin loadings compatible with the formulation criteria of a free standing monolithic solid with no free standing water. Table 2.5 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 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

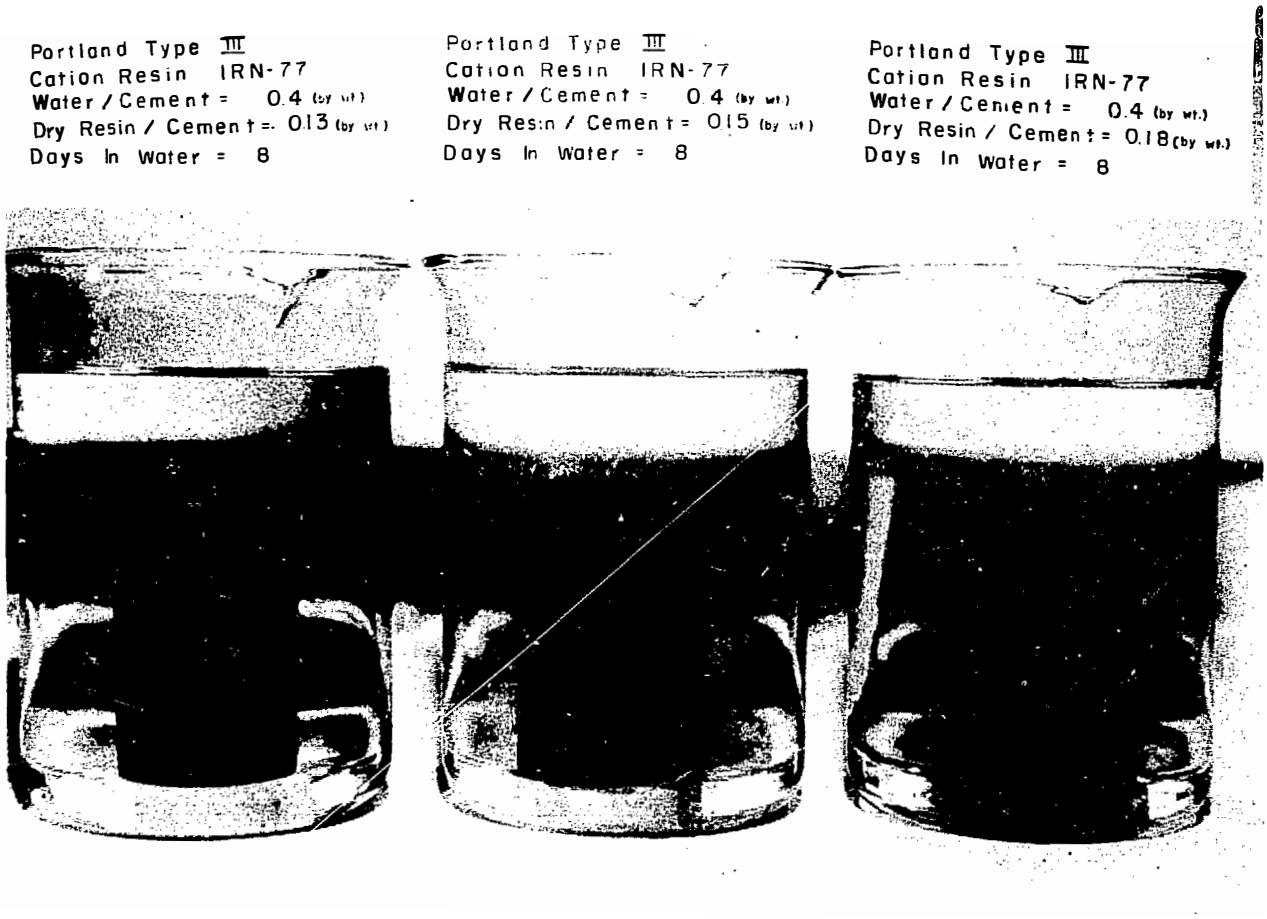


Fig. 2.8 Water immersion test indicating the effect of increasing cation resin for portland type III cement waste forms.

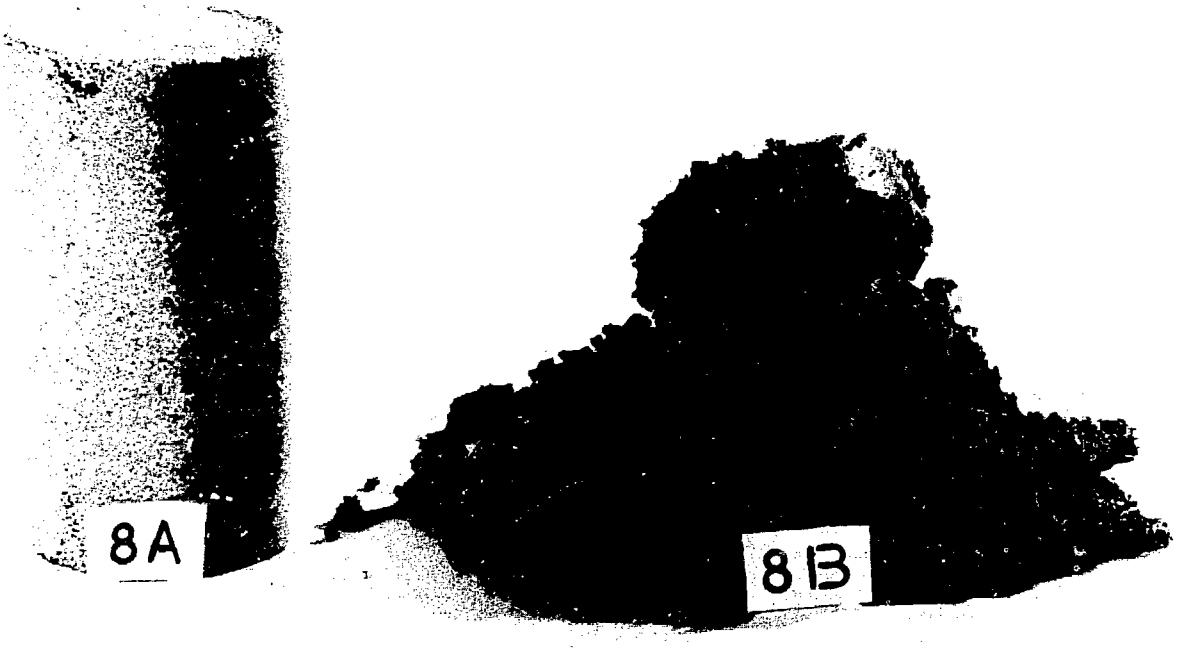


Fig. 2.9 Waste forms after completion of the two week water immersion test comparing the effect of loaded and unloaded mixed bed resin. (Specimen 8A consists of 28 wt% portland type III cement, 52 wt% water and 20 wt% dry load mixed bed resin. Specimen 8B is the equivalent formulation using loaded mixed bed resin.)

TABLE 2.4

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 2.5

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 2.6.
[b] Dry resin/cement by weight.

weight percent by that of cement. Figure 2.8 is a photograph of an immersion test depicting the effects of increasing waste-to-binder ratios in otherwise equivalent samples.

## 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:

$$W/C_{true} = \frac{(W_{ar} + W_{iw} + W_{sw} + W_m)}{cement} \qquad \text{(Eq. 2.6)}$$

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:

$$W/C_{avail.} = \frac{(W_{iw} + W_{sw} + W_m)}{cement} \qquad \text{(Eq. 2.7)}$$

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 2.6 and 2.7.

Water-to-cement ratios listed in Tables 2.4 and 2.5 represent available water. True water-to-cement ratios as expressed by Equation 2.6 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 2.10 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.

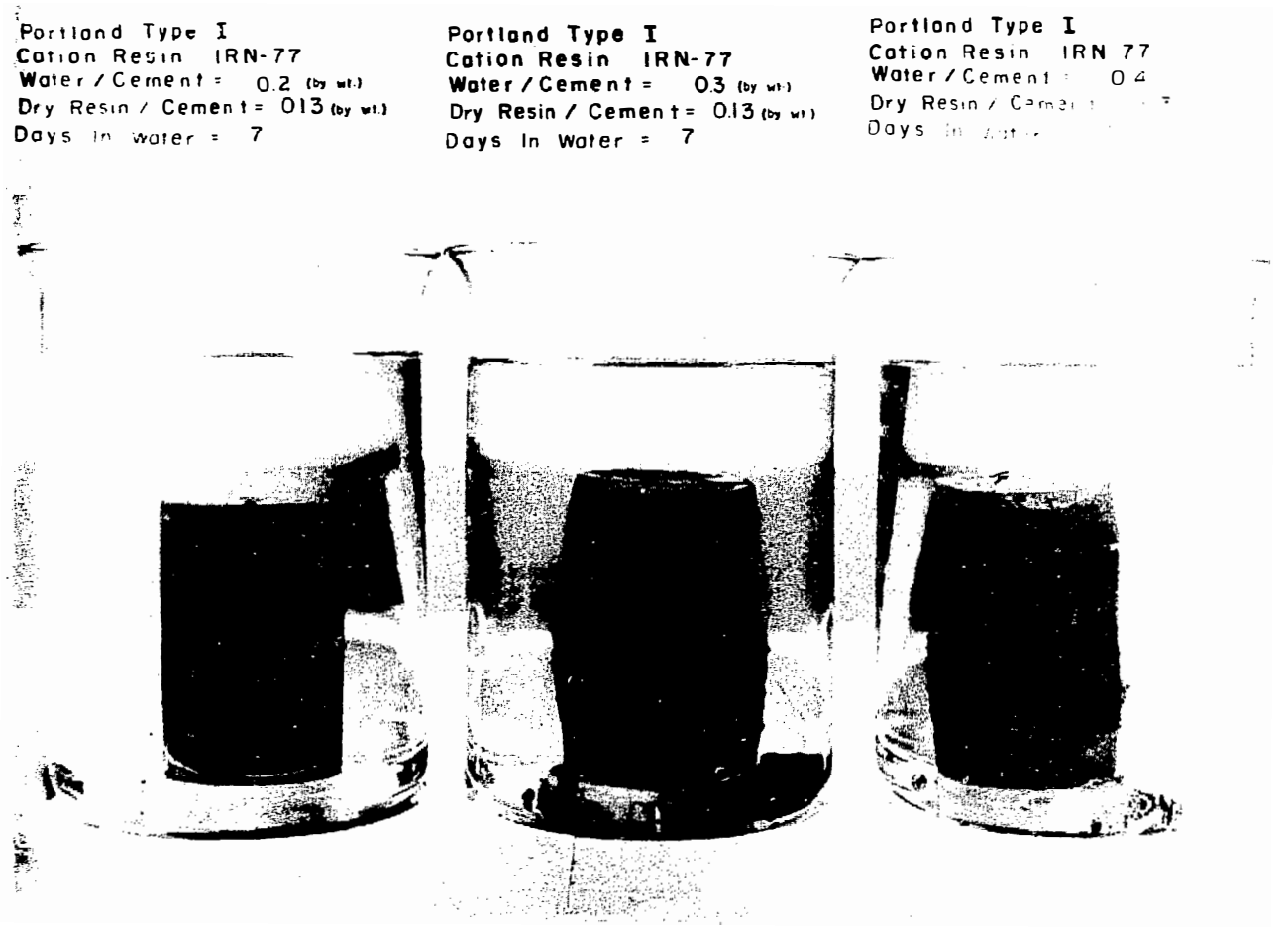


Fig. 2.10 Water immersion test comparing the effect of increasing water-to-cement ratio for portland type I cement waste forms incorporating unloaded cation resin.

## 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.

### 2.7.1 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 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 2.6.

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, uniniated 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.

### 2.7.2 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 2.11 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.

## 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.

### 2.8.1 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.

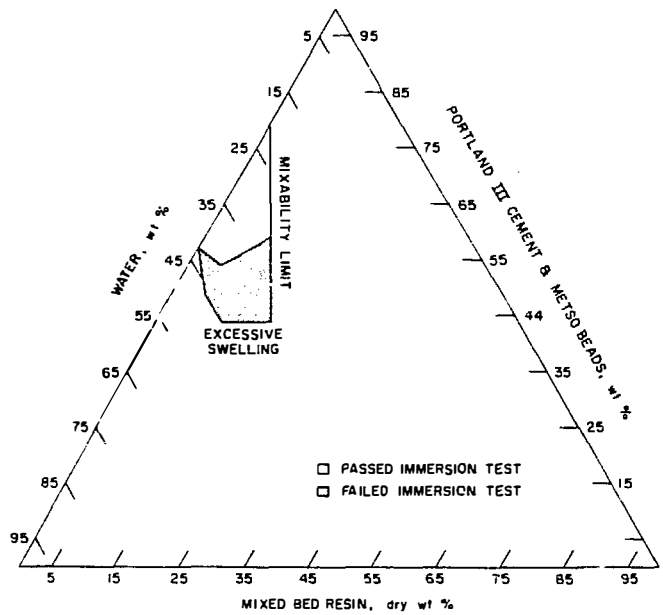


Fig. 2.11 Compositional phase diagram for the solidification of unloaded mixed bed resin with portland type III cement and Metso beads ($Na_2SiO_2$). Cement/Metso beads ratio = 10.

Table 2.6 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 Extendible Polyester Monomer (WEP) | 15 | 45 | 35 | 5 | 0.11 | 0.33 |
| $Na_2SiO_2$ Liquid | 5 | 52 | 30 | 13 | 0.24 | 2.53 |
| Furfuryl Alcohol Monomer | 25 | 30 | 33 | 12 | 0.40 | 0.48 |
| $Na_2SiO_2$ 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.

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 2.7.

### 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.

2.8.2.1 Leachability as a Function of Cement Type: The leachability of ion exchange resin waste solidified in portlant 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.

Table 2.7 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 Loaded Mixed Bed Resin (see Sect. 1.4.1) | 52 | 43 | 5 | 1316 |
| | | 55 | 37 | 8 | 1312 |
| | | 45 | 40 | 15 | 1193 |
| | | 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 |

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 2.12 through 2.15. Cumulative fraction release is plotted versus time for Cs-137 in Figure 2.12 and for Sr-85 in Figure 2.13. Plotting the fraction release vs. $t^{1/2}$ as in Figure 2.14 and 2.15 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.

2.8.2.2 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 μCi of Cs-137, 42 μCi of Sr-85, and 55 μCi of Co-60.

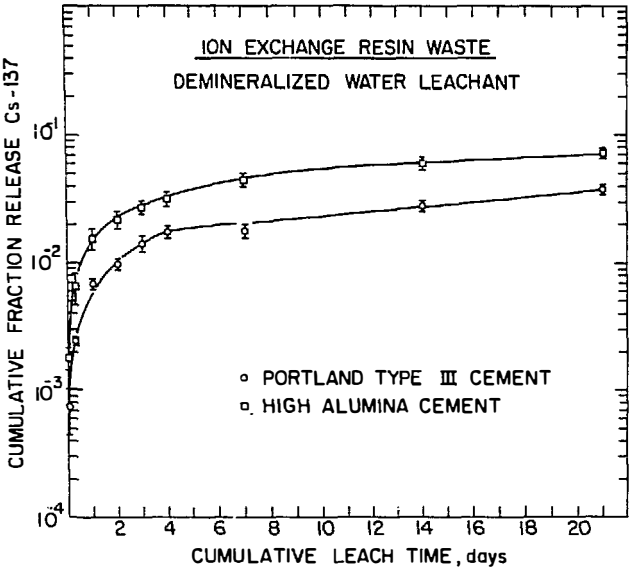


Fig. 2.12 Cs-137 cumulative fraction activity release from solidified ion exchange resins leaching in demineralized water.

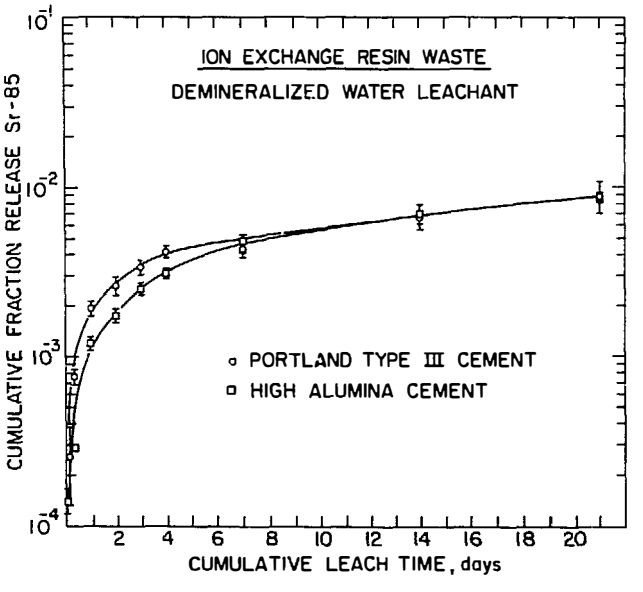


Fig. 2.13 Sr-85 cumulative fraction activity release from solidified ion exchange resins leaching in demineralized water.

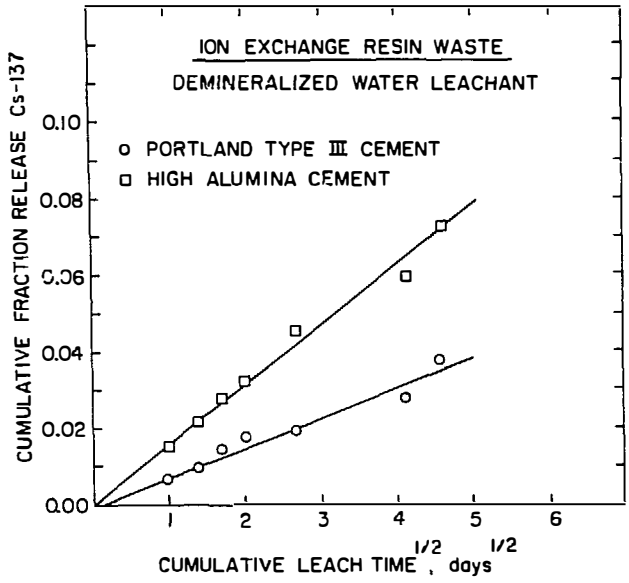


Fig. 2.14 Cs-137 cumulative fraction activity release as a function of $t^{\frac{1}{2}}$.

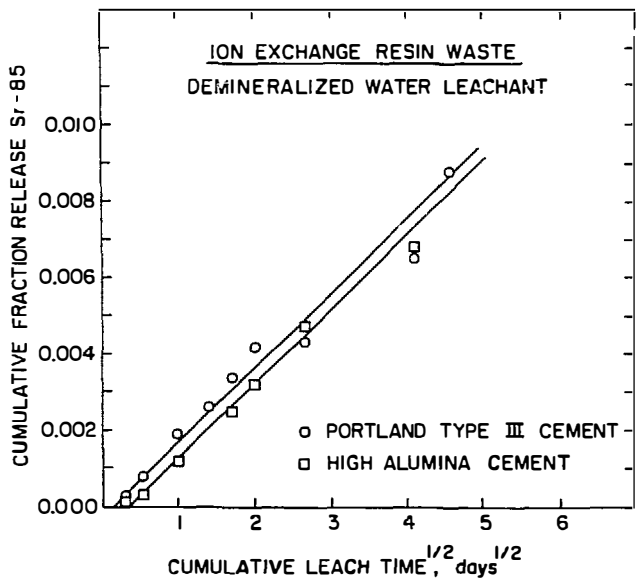


Fig. 2.15 Sr-85 cumulative fraction activity release as a function of $t^{\frac{1}{2}}$.

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 a dose rate of $1.5 \times 10^6$ 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 2.16 and 2.17 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

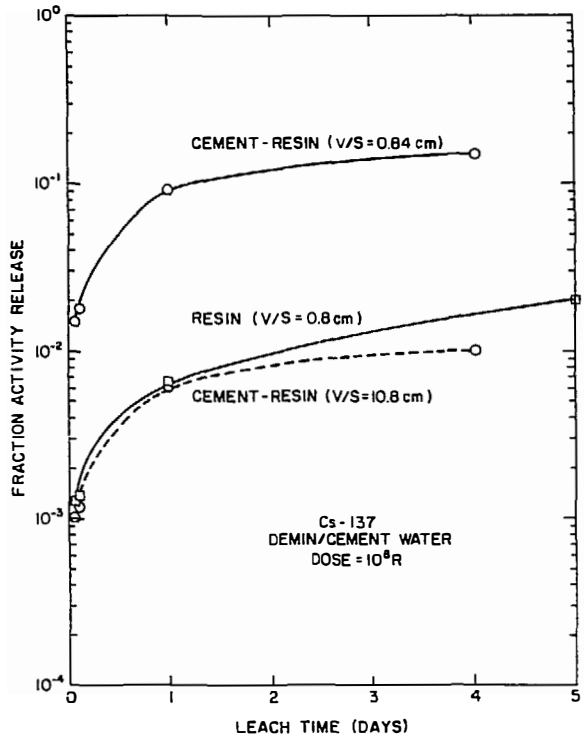


Fig. 2.16 Cs-137 release for specimens irradiated for a total dose of $10^8$ rads and leached in demin/cement water.

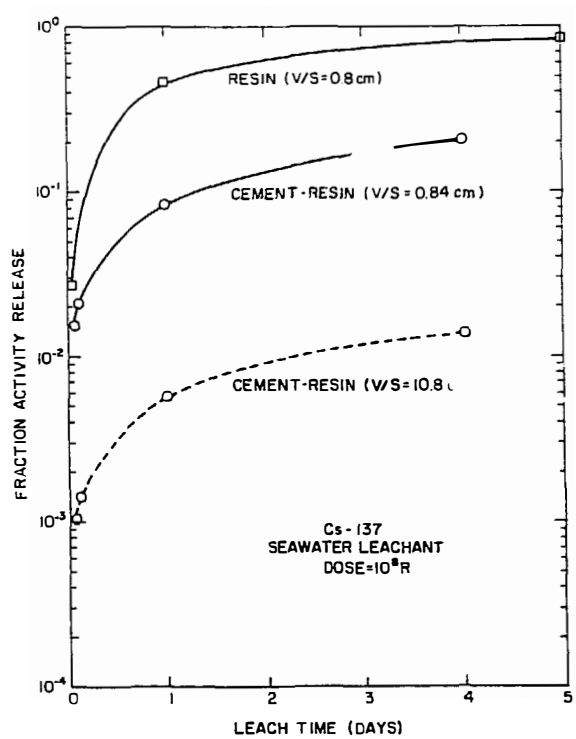


Fig. 2.17 Cs-137 release for specimens irradiated for a total dose of $10^8$ rads and leached in seawater.

known to be one of the most easily leachable species from cement matrices. 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 $t > 0$ is (neglecting decay):

$$(\Sigma a_n/A_o)(V/S) = 2(D_e/\pi)^{1/2}t^{1/2} \qquad \text{(Eqn. 2.8)}$$

where,

$\Sigma a_n$ = cumulative activity removed,

$A_o$ = 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 2.8 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 2.16 and 2.17 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 $1.5 \times 10^6$ 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 crosslinking 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.

# 3. ELECTRON MICROSCOPE ANALYSIS OF RESIN-CEMENT INTERACTIONS

## 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.

## 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 3.1). Similarly the anion form of the resin gave spectra showing the presence of only chlorine. The technique therefore was able to determine qualitativley, the loading of the beads.

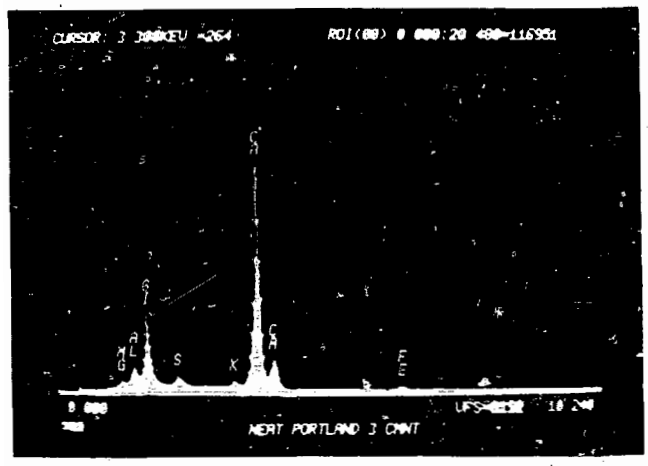


Fig. 3.1 Spectrum from x-ray excitation analysis of neat portland type III cement.

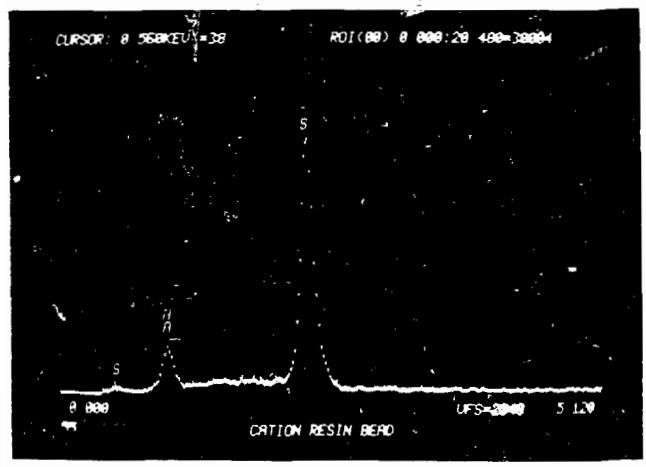


Fig. 3.2 Spectrum from x-ray excitation analysis of individual sodium loaded cation resin bead.

Fig. 3.3 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 = 125μ.

Figure 3.2 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 3.1.

Table 3.1

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 |

Figure 3.3 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 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 3.3 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 3.4 shows the x-ray spectrum obtained from this position. The very

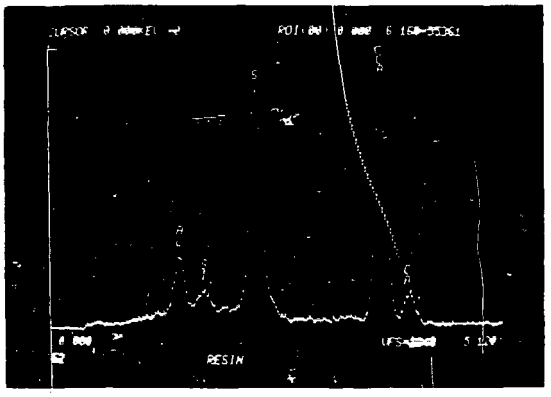


Fig. 3.4 X-ray excitation spectrum for a portion of the resin bead depicted in Figure 3.3.

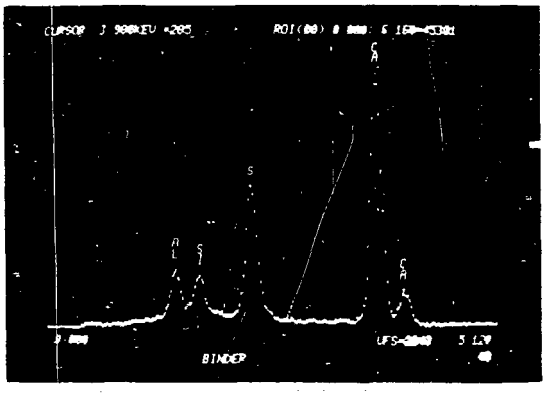


Fig. 3.5 X-ray excitation spectrum for a portion of the cement adhering to the resin bead depicted in Figure 3.3.

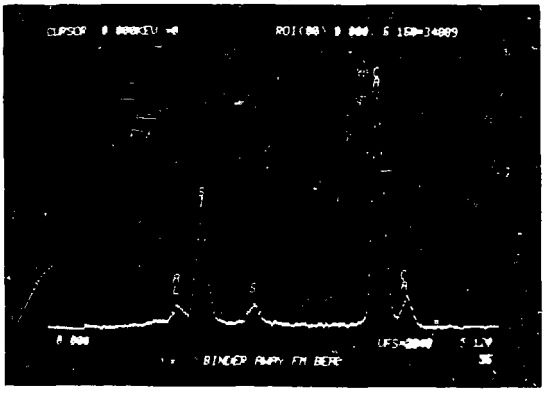

Fig. 3.6 X-ray excitation spectrum for a portion of the cement matrix located approximately 100 microns from any bead.

high sulfur peak, typical of exchange resins, was present. So too, 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 3.1

On the same resin bead (Figure 3.3) a portion of the bright white surface coating was anlayzed. The spectrum is shown in Figure 3.5. Here the peak heights for aluminum and silicon are of similar magnitude while the sulfur peak is much reduced from that of Figure 3.4. 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 3.1.

The last spectrum (Figure 3.6) 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 3.1.

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 3.7. Very little pitting is seen on the surface. In contrast, Figure 3.8 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 3.9. 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.

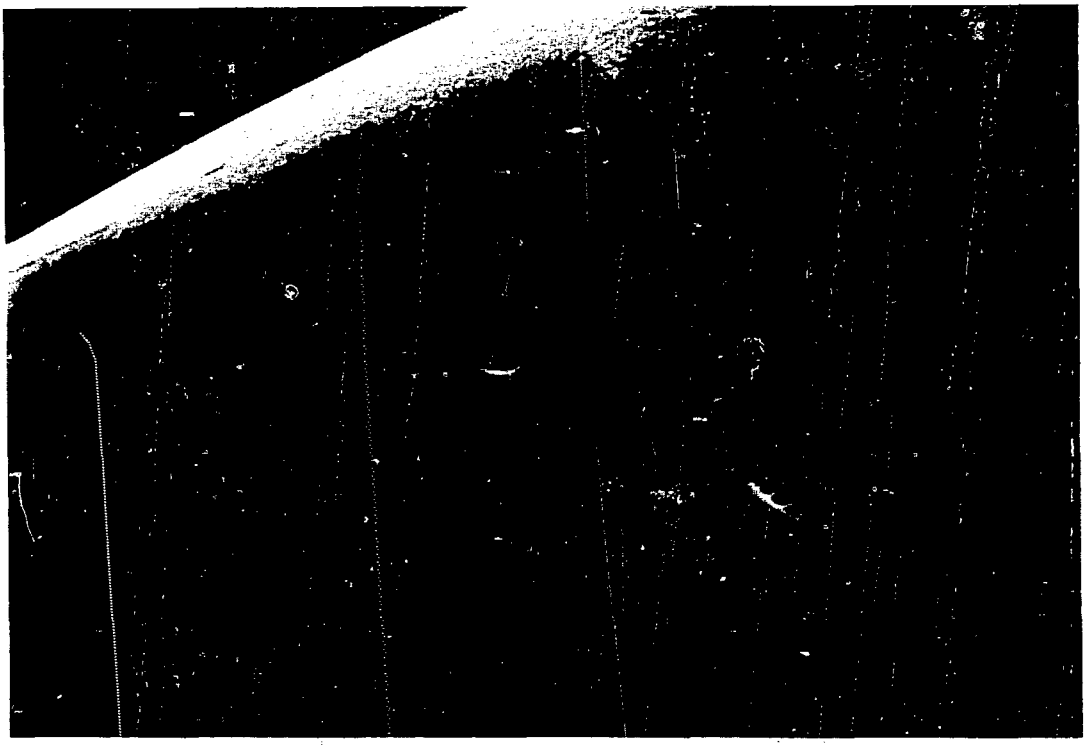

Fig. 3.7 SEM photograph of a resin bead which had not been placed in cement. Magnification: 2100x Scale: 1cm = 3.6μ

Fig. 3.8 SEM photograph of the surface of a resin bead from a cement sample which failed the immersion test.
Magnification: 1500x Scale: 1cm = 6.7μ

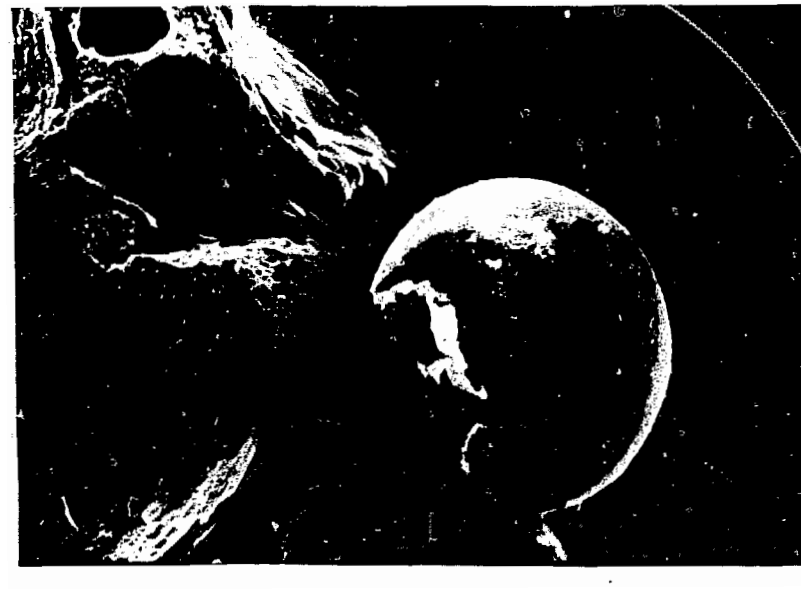

Fig. 3.9 SEM photograph giving an overview of the resin bead depicted above and the cement matrix.
Magnification: 160x Scale: 1cm = 67μ

## 4. SOLIDIFICATION WITH POLYMER MODIFIED GYPSUM CEMENT (ENVIROSTONE)

### 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 temperture 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 power consisting of gypsum plaster with resin polymer and catalyst additives. Gypsum plaster is the hemihydrate form of calcium sulfate ($CaSO_4 \cdot 1/2H_2O$). 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.

### 4.2 Formulation Development

Unloaded mixed bed ion exchange resin was prepared with interstitial water removed as discussed in Section 1.4.2. The average water content of this damp resin was 58% by weight. Other resin properties apply as stated previously.

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 4.1 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 4.1, 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 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.

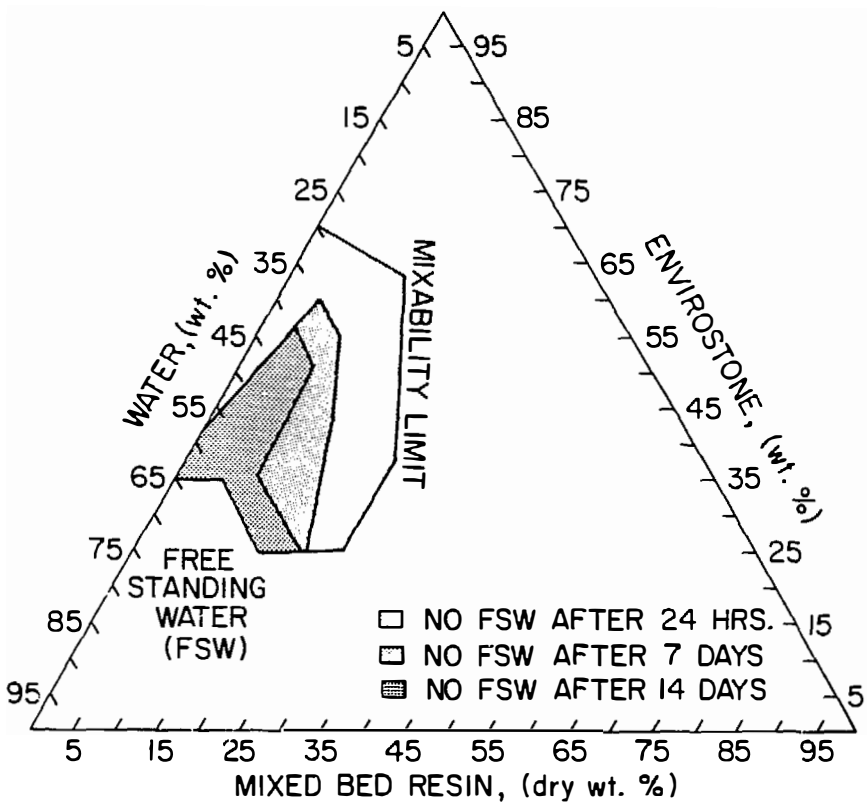


Fig. 4.1 Compositional phase diagram for the solidification of unloaded mixed bed resin with Envirostone.

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. 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., 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$^{o}$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 4.2 is a photograph of two Envirostone samples before and after immersion testing. Figure 4.3 depicts the effects of immersion as a function of resin content.

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,

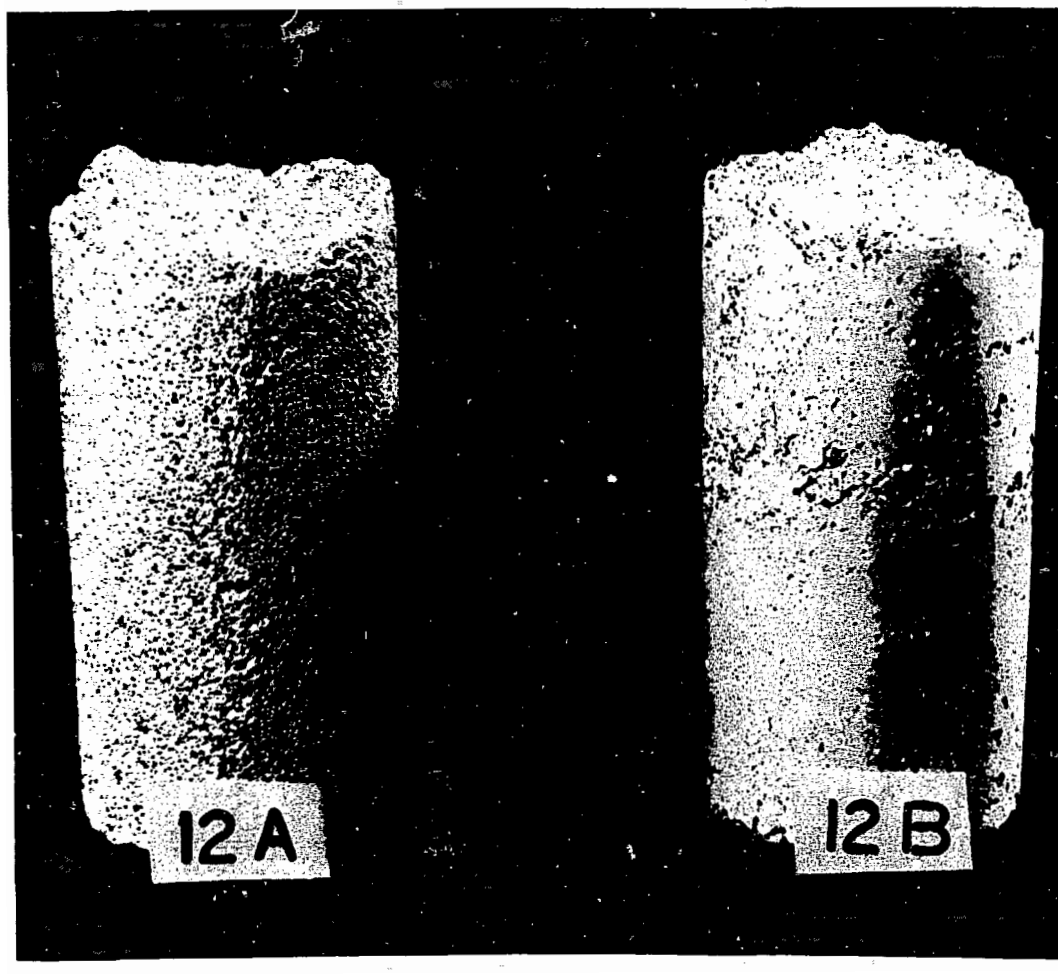


Fig. 4.2 Effect of immersion testing on Envirostone waste forms containing unloaded mixed bed resin. (Specimen 12A underwent the two week immersion test. Specimen 12B is a replicate specimen which was not immersion test.)

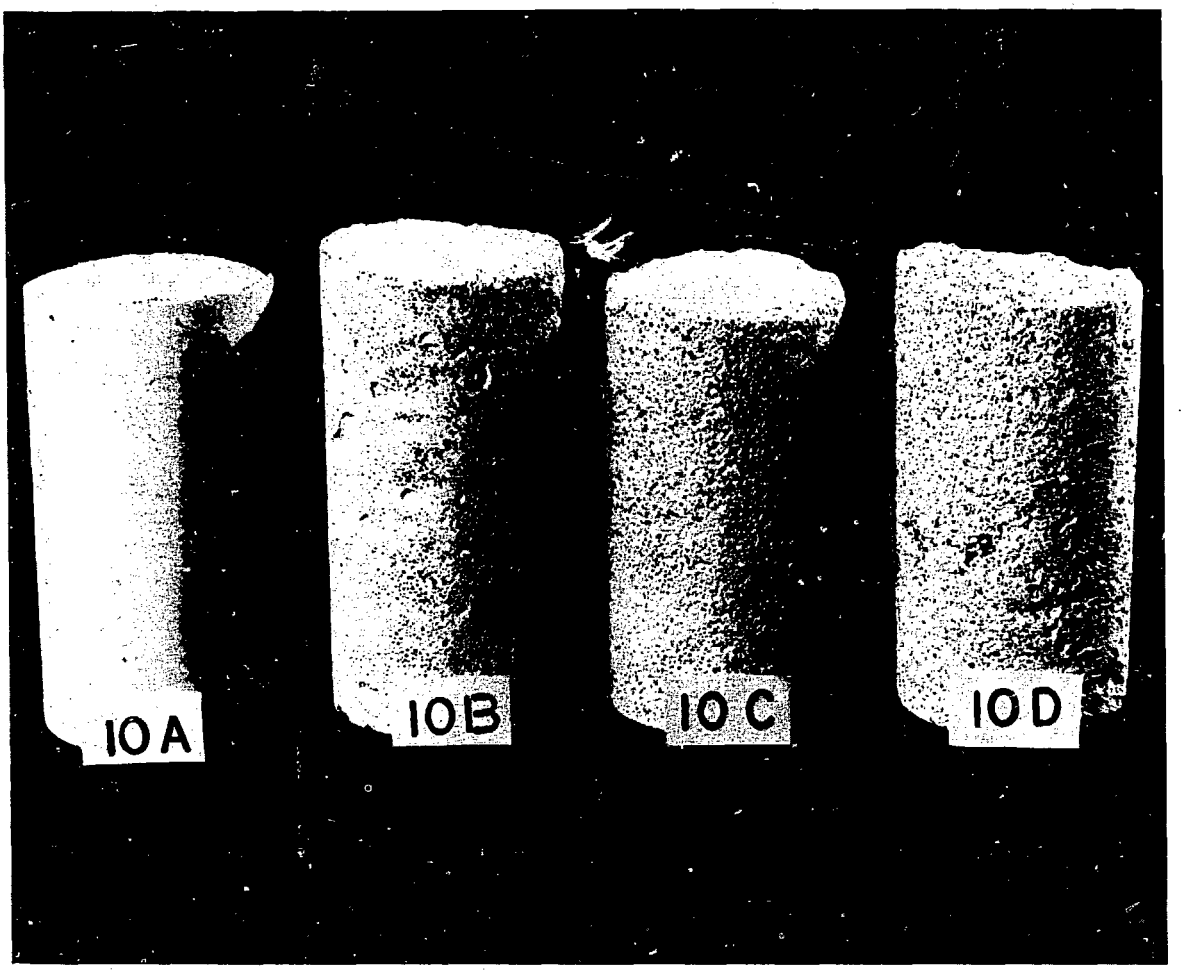


Fig. 4.3 Effect of unloaded mixed bed resin content on Envirostone water forms after immersion testing. (Specimens 10A-10D contain 5, 10, 11, 15 wt% dry resin, respectively.)

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 4.4 shows specimen density as a function of resin loading for three different Envirostone/water ratios. Figure 4.5 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.

## 4.3 Waste Form Properties

### 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 4.6)
- the effect of increased Envirostone content for given resin loadings (Figure 4.7)
- the effect of a three week vs. one week cure time (Figure 4.8).

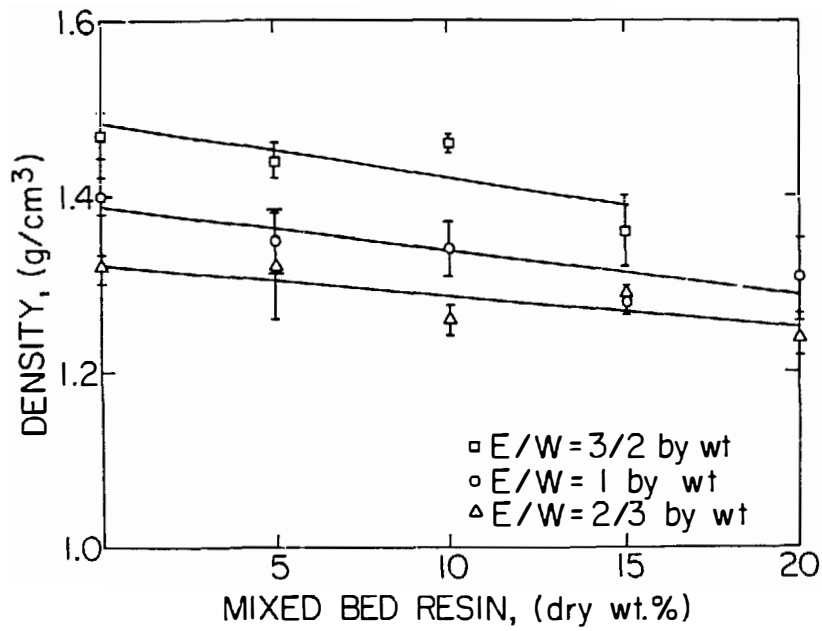


Fig. 4.4 Envirostone waste form density as a function of unloaded mixed bed resin content.

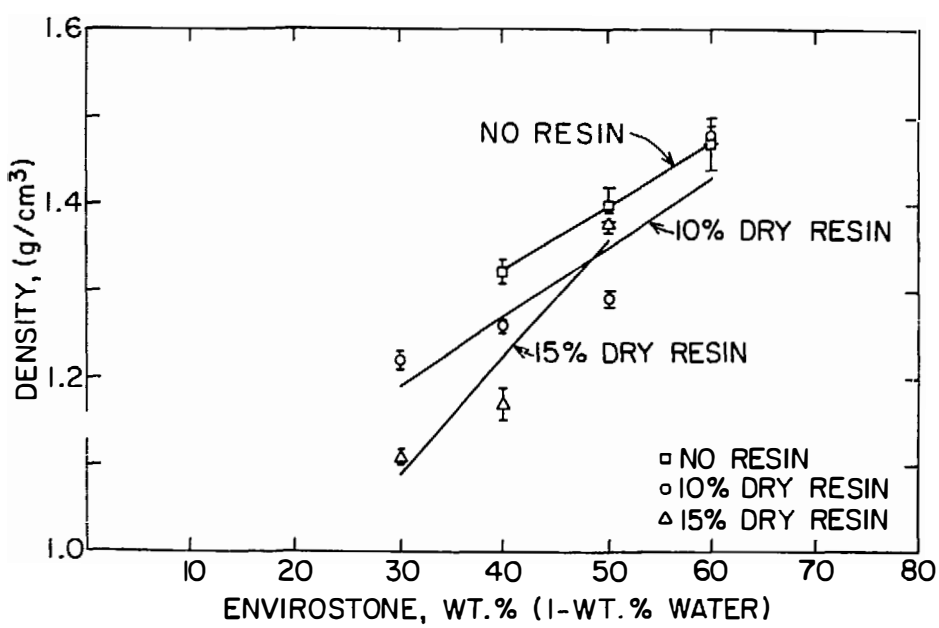


Fig. 4.5 Density of Envirostone-mixed bed resin waste forms as a function of wt% Envirostone.

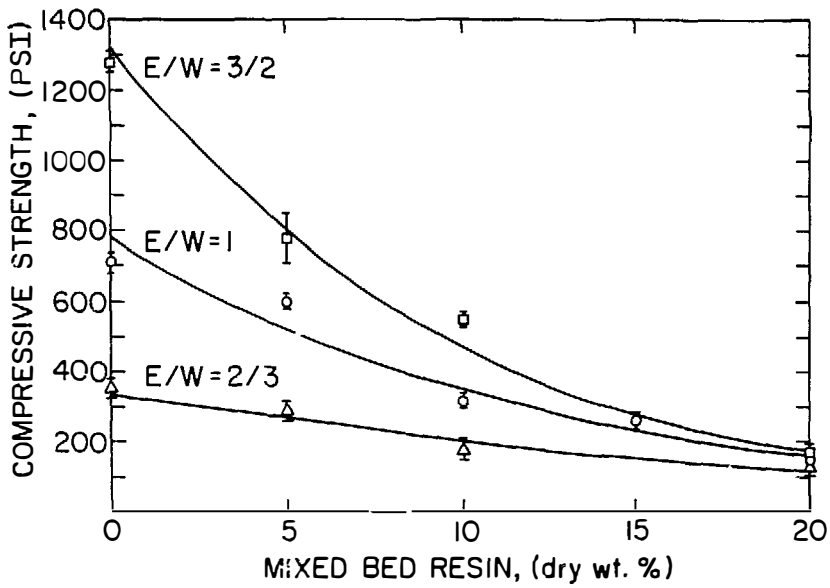


Fig. 4.6 Compressive strength of Envirostone-mixed bed waste forms as a function of resin content at various Envirostone/water ratios.

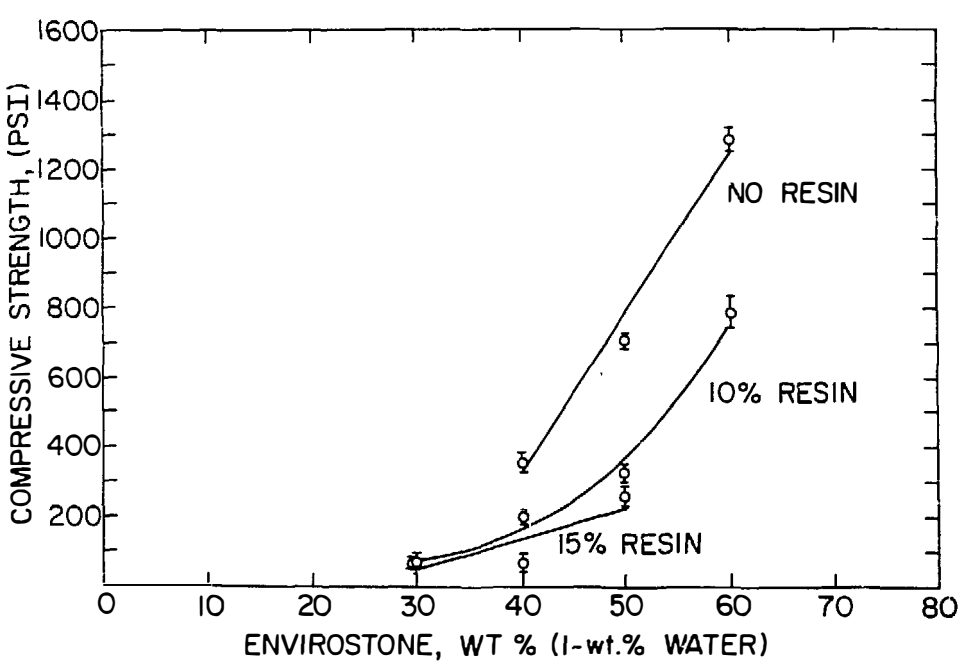


Fig. 4.7 Compressive strength of Envirostone-mixed bed resin waste forms as a function of Envirostone content for various resin contents.

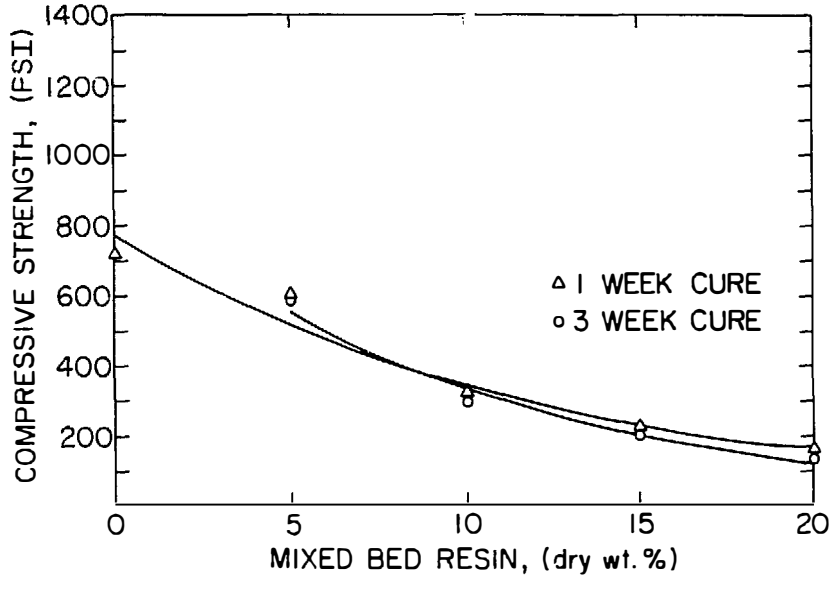


Fig. 4.8 Compressive strength of Envirostone-mixed bed resin waste forms as a function of resin content for one week and three week cure times.

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.

### 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 μCi 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 4.9 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 4.10 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%.

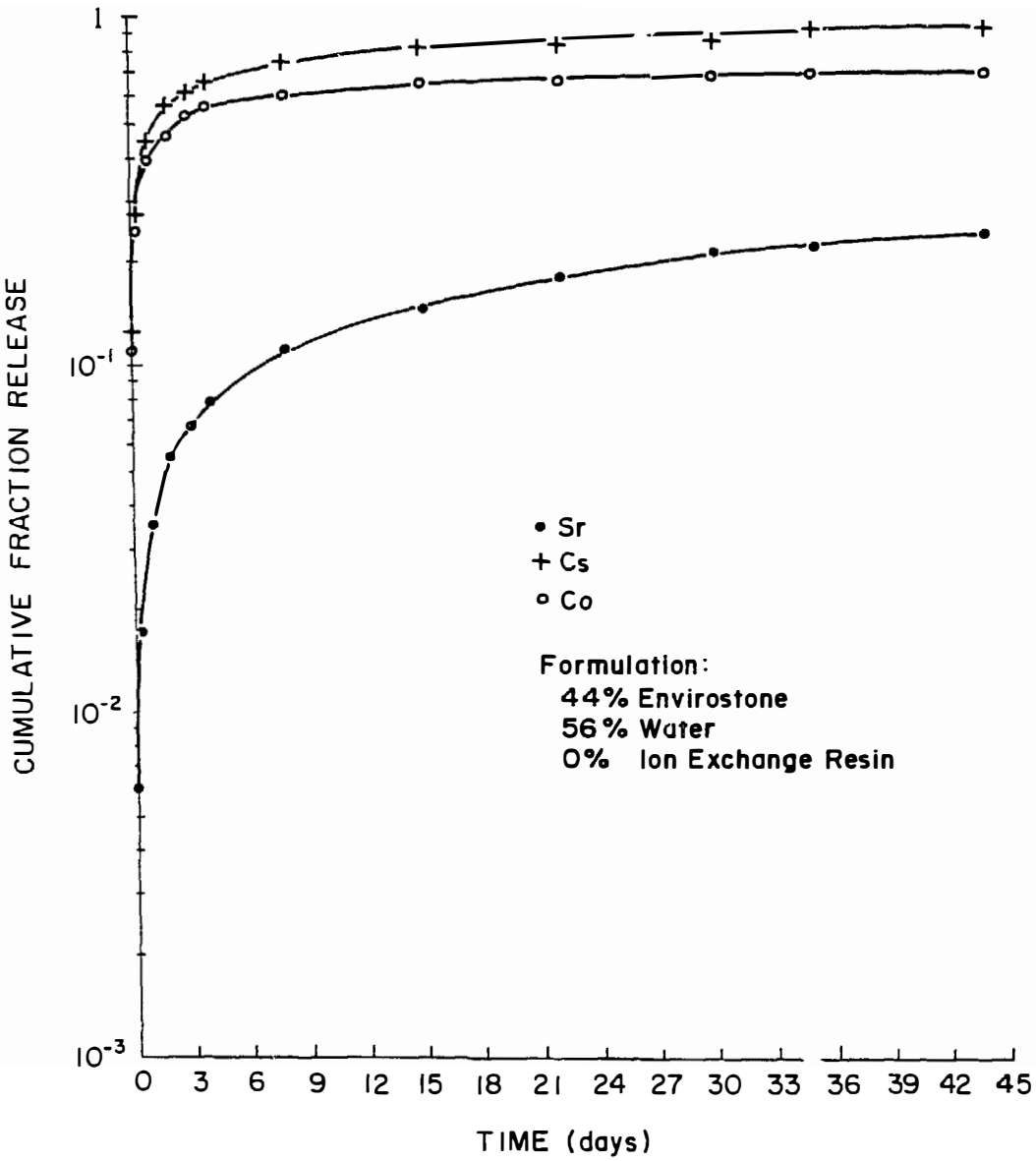


Fig. 4.9(a) Average cumulative fraction release Sr-85, Cs-137 and Co-60 vs. time for deionized water leaching of Envirostone.

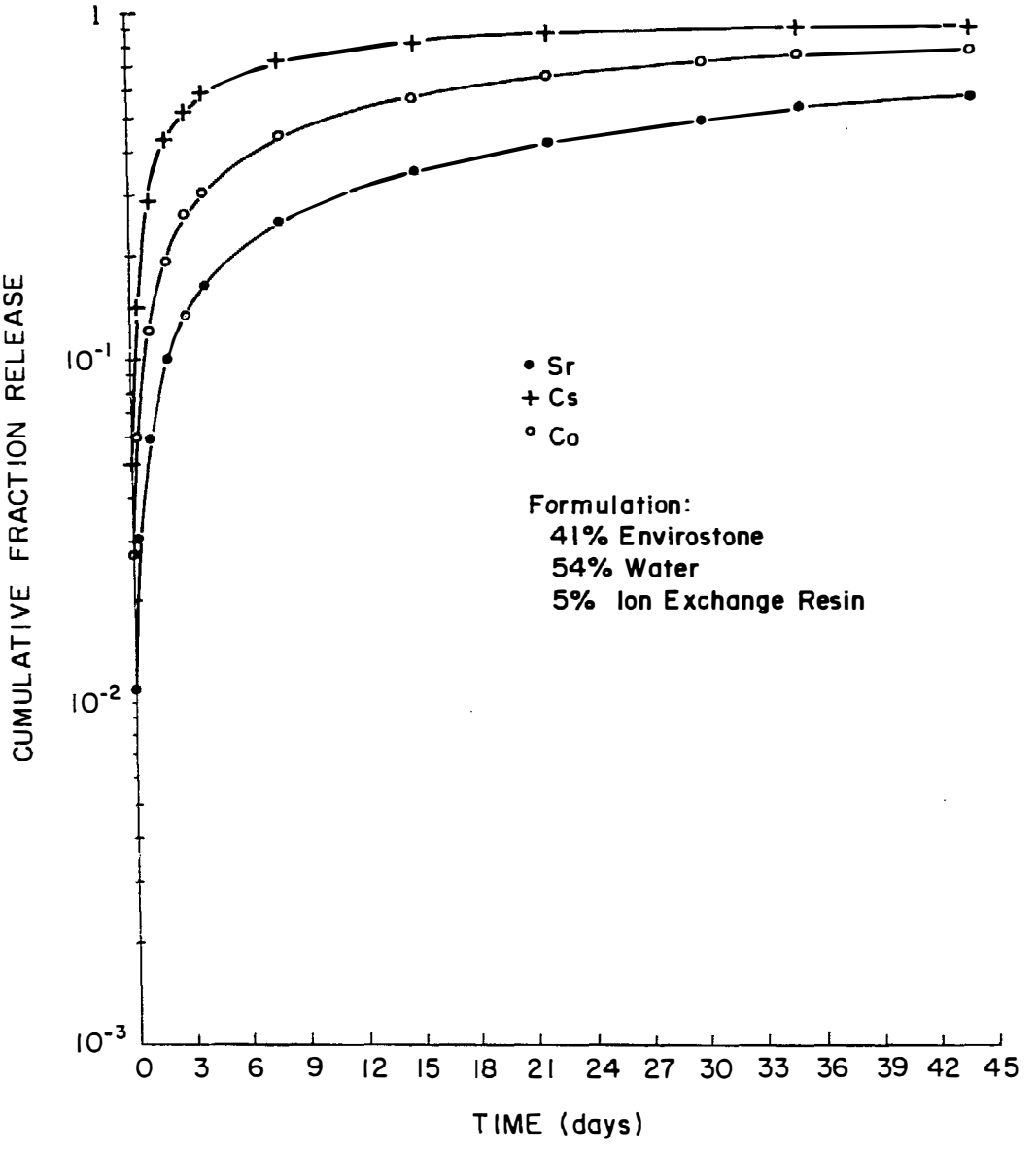


Fig. 4.9(b) Average cumulative fraction release Sr-85, Cs-137 and Co-60 vs. time for deionized water leaching of Envirostone waste forms containing 5 wt% dry mixed bed resin.

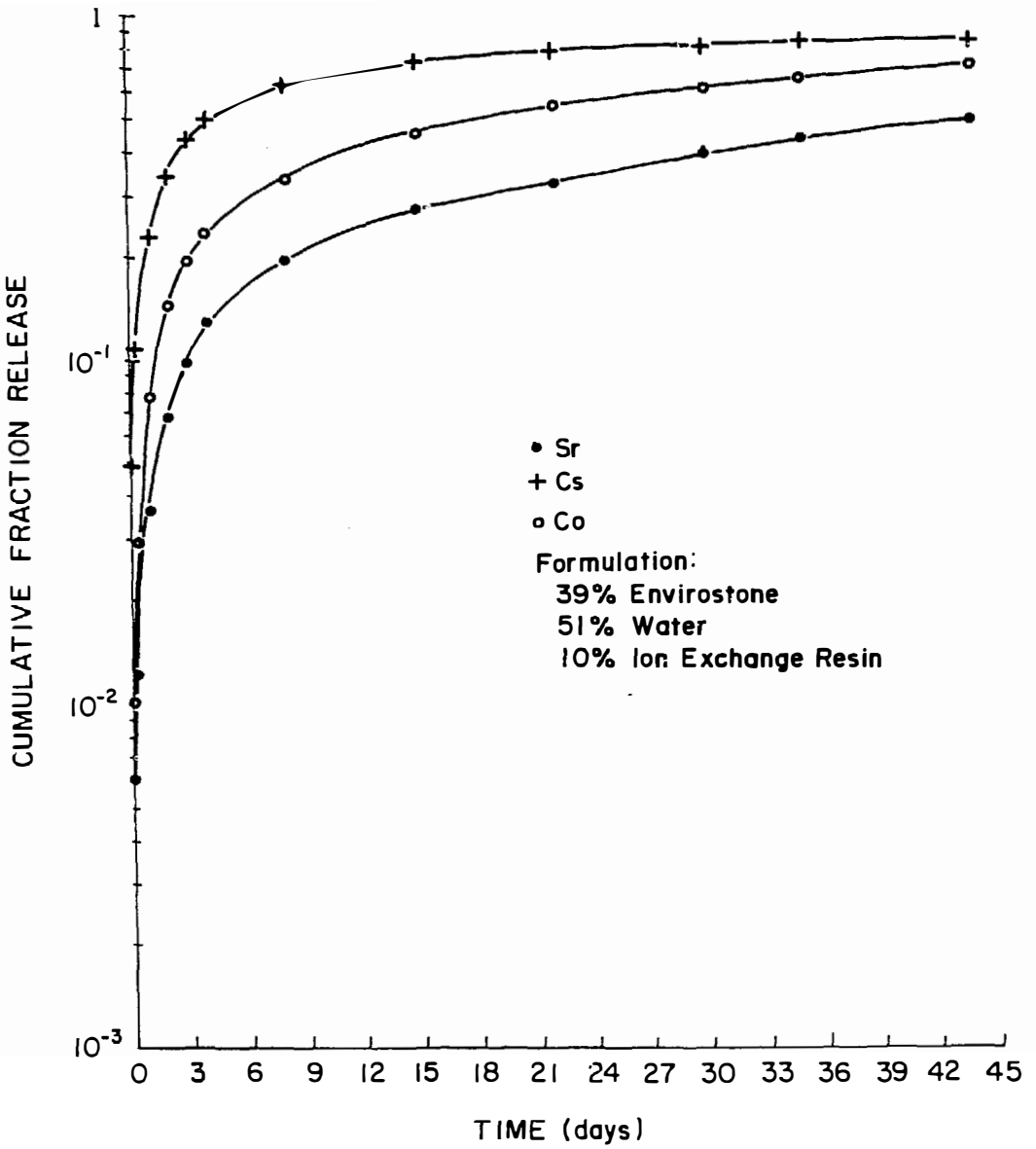


Fig. 4.9(c) Average cumulative fraction release Sr-85, Cs-137 and Co-60 vs. time for deionized water leaching of Envirostone waste forms containing 10 wt% dry mixed bed resin.

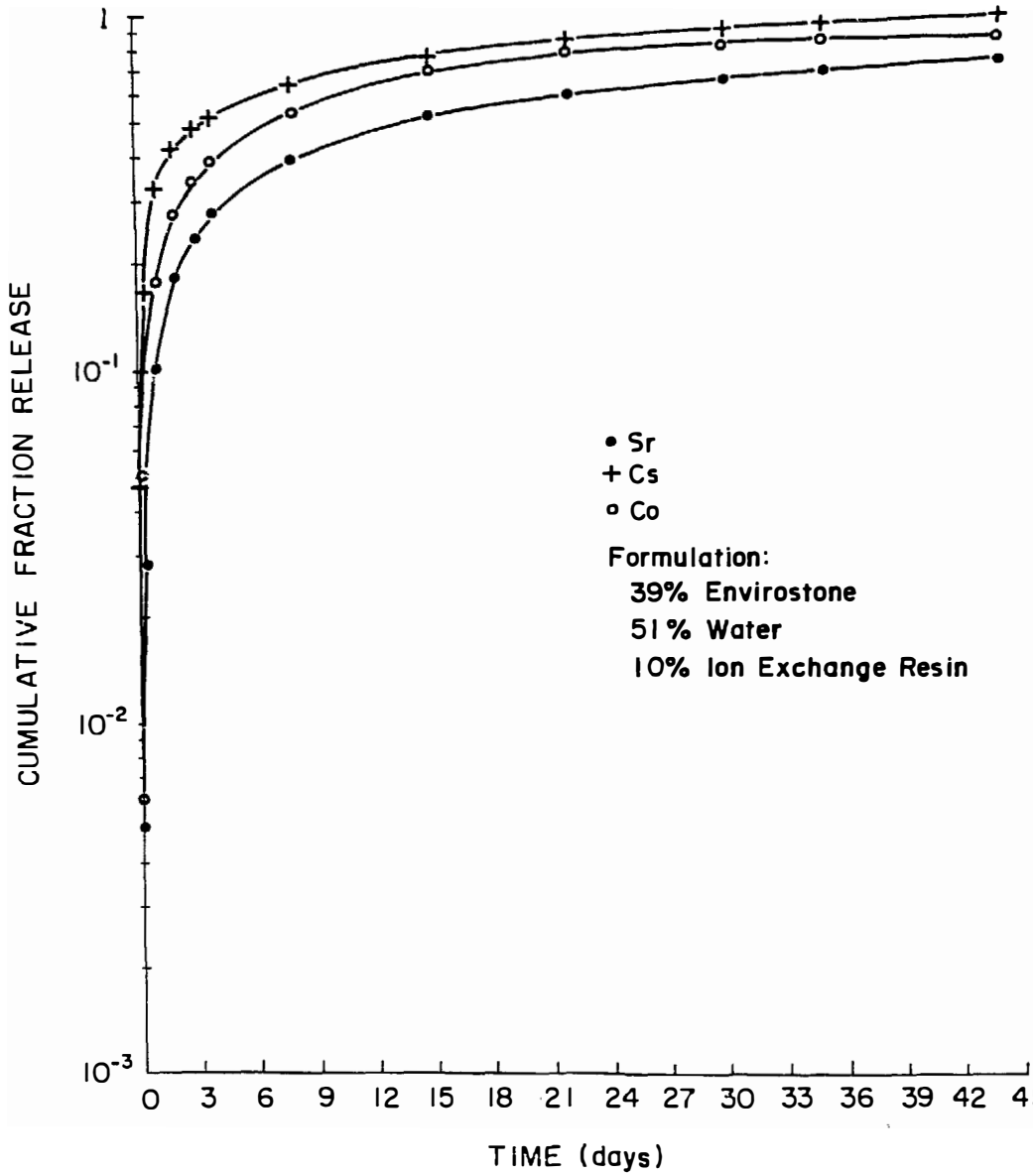


Fig. 4.10 Average cumulative fraction release of Sr-85, Cs-137 and Co-60 vs. time for Envirostone waste forms containing 10 wt% dry mixed bed resin leached in synthetic seawater.

# 5. SOLIDIFICATION WITH THERMOSETTING POLYMERS

## 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].

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.

## 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 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

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[a] Dow Chemical Company, Midland, MI 48640

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 5.1. Vinyl ester-styrene waste form specimens incorporating various amounts of mixed bed ion exchange resins are shown in Figure 5.1.

Table 5.1 Vinyl Ester-Styrene Formulations for the Solidification of Mixed Bed Ion Exchange Resin Wastes

| Waste Stream Type | Waste/Binder Ratio (by wt.) | Dry Resin Wt% |
|---|---|---|
| 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 |

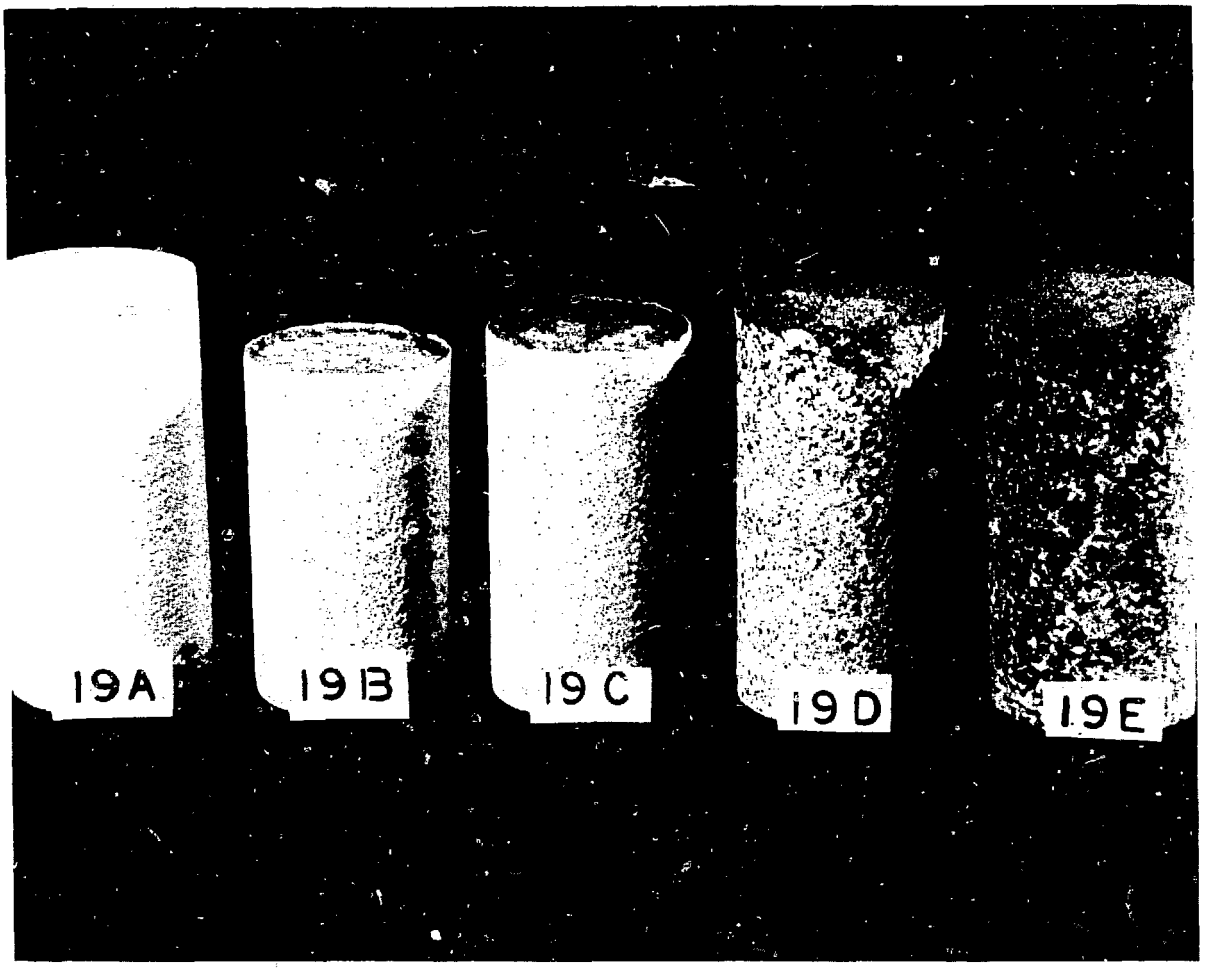


Fig. 5.1 Vinyl ester-styrene waste forms incorporating unloaded mixed bed resin.

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