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ABSTRACT

Work has been conducted to investigate the solidification of ion exchange resin wastes with portland cements. These efforts have been directed toward the development of acceptable formulations for the solidification of ion exchange resin wastes and the characterization of the resultant waste forms. This paper describes formulation development work and defines acceptable formulations in terms of ternary phase compositional diagrams. The effects of cement type, resin type, resin loading, waste/cement ratio and water/cement ratio are described. The leachability of unsolidified and solidified resin waste forms and its relationship to full-scale waste form behavior is discussed. Gamma irradiation was found to improve waste form integrity, apparently as a result of increased resin crosslinking. Modifications to improve waste form integrity are described.

INTRODUCTION

This paper describes work directed towards the development of formulations for the solidification of ion exchange resin wastes in portland cements and the characterization of the resultant waste form products. This work is a part of the Waste Form Development/Test program conducted at Brookhaven National Laboratory (BNL) under funding from the Department of Energy's Low-Level Waste Management Program. In this effort, BNL is investigating contemporary solidification agents relative to their potential applications to various low-level waste streams.

The majority of ion exchange resin wastes in the United States are not solidified prior to disposal. Instead, these wastes are typically dewatered and disposed of in large carbon steel liners. However, the United States Nuclear Regulatory Commission does require that commercial nuclear power plants undergoing licensing reviews provide the capability to solidify ion exchange resin wastes.[1] Proposed rule 10CFR61, Licensing Requirements for Land Disposal of Radioactive Wastes, necessitates that all but low activity content ion exchange resin wastes meet certain waste stability requirements. These requirements can be provided by the waste form itself (which entails solidification of ion exchange resin waste) or by use of a suitable disposal container.[2] In addition, conditions are being imposed by the operators of shallow land burial disposal sites which require either the solidification of ion exchange resin wastes or the use of high integrity containers for the disposal of dewatered resin wastes.

PREPARATION OF SIMULATED ION EXCHANGE RESIN WASTES

RESIN TYPES AND LOADING

The solidification of cation, anion and mixed bed bead resin wastes has been studied. Nuclear Grade Amberlite ion exchange resins, manufactured by the Rohm and Haas Company, Philadelphia, PA, 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 wt% divinylbenzene. The cation form, designated IRN-77, is a strongly acidic resin with sulfonic acid functionality. A minimum of 95% of its exchange sites are in the hydrogen form. The minimum total exchange capacity of Amberlite IRN-77 is 1.8 milliequivalents per milliliter in the hydrogen form. Anion resin, designated IRN-78, is a strongly basic quarternary ammonium functionality resin, containing a minimum of 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 is 0.78 milliequivalents per milliliter in the hydroxide form. Mixed bed resin used in this work is formed by combining 2 parts IRN-77 and 1 part IRN-78 by dry weight.

"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. Resins were loaded by a batch technique in a solution containing equal milliequivalent amounts of sodium sulfate, calcium chloride and aluminum nitrate in sufficient total concentration to satisfy the resin's exchange capacity. Both unloaded and loaded forms were employed in order to span the range of actual resin conditions.

Resins used in leaching experiments were batch loaded in a solution containing Cs-137, Sr-85 and Co-60 after having been first converted to Na^+ (cation resin) and Cl^- (anion resin) forms. Essentially all the activity was adsorbed by the resins during batch loading, providing an average concentration of 3.7 Ci/g dry resin for each of the radionuclides. The resins were stirred during batch loading to provide a uniform distribution of activity.

RESIN WASTE CHARACTERISTICS

Ion exchange resin wastes vary widely in terms of water content. Water content was determined according to ASTM Standard Test Method D2187-77.[3] This procedure involves measurement of mass loss upon drying at 110°C.

The water content of as-received resins was compared with values determined for slurry and dewatered resin wastes. A 70/30 volume ratio of settled resin to free standing water was employed for simulated resin slurry waste. Dewatered resin was produced by decanting all observable free standing water above settled resin saturated with water to equilibrium.

In actual practice, dewatered resin still contains a significant quantity of water. Most of this water is sorbed within the resin beads and, when solidified in a cement matrix, is directly unavailable for cement hydration. The remaining portion is loosely held in the interstitial spaces between resin beads. This interstitial water can be directly utilized by the cement to further the hydration reaction. A method was devised to remove most of this interstitial water from dewatered resin. Resin prepared in this manner is termed "damp resin". This procedure has been used to assure both saturation of the resin with water and uniformity of water content (as opposed to use of as-received resin which can exhibit variations in water content depending upon storage mode, etc.).

Since waste handling techniques in actual applications are diverse, the percentage of total water in so-called dewatered and slurry wastes may vary. In order to provide waste form formulation data in a consistent manner, 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. The average percentage of water contained in various waste streams as defined in this work is shown in Table 1.

SOLIDIFICATION WITH PORTLAND CEMENTS

CEMENT TYPES

Hydraulic cement is the most widely used solidification agent in the United States. Portland cement is the primary hydraulic cement produced and is used extensively for radioactive waste solidification. For these reasons, portland type I and type III cements have been selected for use 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 (C_3A) and tetracalcium aluminoferrite (C_4AF). 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.

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.[5,6] 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/shrinkage due to competition between the cement and resin for water and/or the adsorption of soluble cement species during solidification.[7]

Studies were performed to determine the range of acceptable formulations for the solidification of ion exchange resin waste in portland cements. The acceptability criteria imposed require that the resultant waste form 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 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.[8] The water immersion test has been shown to be indicative of long-term waste form integrity.

Formulation specimens were mixed using a 1/6 horsepower planetary mortar mixer (Hobart Model N-50). The mixture was then transferred into individual 160 ml cylindrical polyethylene specimen preparation containers. The containers were capped to prevent evaporative water loss. Resultant waste form specimens were approximately 4.7 cm in diameter and 8.5 cm high. At least two replicate specimens of each formulation were prepared.

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

Twenty-four hours after preparation, formulations were examined for free standing water. Those formulations having any drainable 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 24 hours were cured in their containers for a total of 14 days at room temperature. After curing for 14 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 subjectd to the 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 1-5. These compositional phase diagrams 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 24 hours are also indicated.

These 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 to avoid these boundaries whenever possible. Full-scale testing will be performed to demonstrate the applicability of the formulations determined.

Effect of Cement Type

Unloaded mixed bed resins were solidified with both portland type I and type III cements. These compositional phase diagrams are shown in Figures 1 and 2, respectively.

Initial studies indicated that portland type III cement formulations were capable of incorporating larger quantities of water than portland Type I cement and pass free standing water and immersion criteria. The minimum water requirements for workability (mixability limit) were similar for both cement types. Type III cement also appears capable of incorporating larger quantities of ion exchange resin in acceptable formulations. As a result of these findings, subsequent work concentrated on the use of portland type III cement.

Effect of Resin Type and Loading

Anion, cation and mixed bed resins yielded unique regions of acceptable formulations. Anion resin formulations indicated a wide region of free standing water but initially acceptable formulations were not susceptible to degradation in the water immersion test. The compositional phase diagram for anion resin solidified with portland type III cement is shown in Figure 3.

Although less restricted by free standing water problems, the performance of cation resin formulations was limited by excessive swelling and deterioration of mechanical integrity both after curing and in immersion testing. Based upon these results, the swelling and cracking of the ion exchange resin waste forms studied can be directly attributed to the cation form of the resin. Figure 4 is the compositional phase diagram 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 Ci of Cs-137, 42 Ci of Sr-85, and 55 Ci of Co-60.

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 rad at a dose rate of 1.5×10^6 rad/hr. The 10^8 rad 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/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 close mesh nylon bag. The ratio of waste form volume to exposed geometric surface area (V/S) for resin 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 rad did not indicate any apparent effect of irradiation on resin waste activity release in cement water.

Figures 6 and 7 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 rad. The Cs-137 fraction release from unsolidified ion exchange resin in cement water was significantly lower than that observed for the cement-resin waste forms in demineralized water. Cesium, however, is known to be one of the most easily leachable species from cement matrices. In synthetic seawater, Cs-137 is released significantly more rapidly from the ion exchange resin. 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):

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

where

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.[6]

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. 1 predicts that leaching of a 210 liter cement-resin waste 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 6 and 7 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 such 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 rad at 1.5 x 10^6 rad/hr. After all specimens had been irradiated, they were then subjected to the water immersion test. The control, 10^4 and 10^6 rad total dose specimens failed the immersion test; however, the 10^8 rad specimens passed. Also, the 10^6 rad specimens did have notably better specimen integrity in immersion than the control and 10^4 rad specimens. No difference in behavior was evident between the control and 10^4 rad 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.

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 is being conducted to investigate modified cement systems. Attempts to improve the mechanical integrity of cement-resin waste forms has focused on pretreatment of the resin waste to minimize or prevent shrinkage/swelling effects and the use of direct additives to the cement itself.

Some methods under investigation to reduce resin shrinkage/swelling involve pretreatment of the resin bead waste to minimize subsequent moisture absorption/desorption and/or ion exchange within the cement matrix. Other techniques include the direct combination of additives with cement. The use of several materials including vinyl ester-styrene, water extendable polyester, sodium silicate and sodium metasilicate are currently being investigated. Some additives may also provide benefits by improving the strength properties of the cement matrix. Early results from these studies have indicated improved waste form integrity and suggest that increased waste loadings should be attainable.

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TABLE 1. Weight Percentage Water Content in Resin Wastes.

	Weight Percentage Water			
Resin Type	As-Received	Damp	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

TABLE 2. Maximum Resin Loadings Satisfying Initial Criteria.

Portland Cement Type	Resin Type	Cement Wt %	Water Wt %	Dry Resin Wt %	Available Water/Cemnent Ratio	Waste/ Cement Ratio
III	loaded M.B.	25	48	27	.90	1.08
III	M.B.	27	48	25	.58	.93
I	M.B.	27	48	25	.49	.93
III	IRN-77	35	39	26	.45	.73
III	IRN-77	31	49	20	.80	.63

M.B. = mixed bed; (a) Dry resin/cement by weight

TABLE 3. Maximum Resin Loadings for Various Cemen/Resin Combinations Satisfying Initial Criteria and Passing Two-Week Immersion Test.

Portland Cement Type	Resin Type	Cement Wt %	Water Wt %	Resin Wt %	Available Water/Cement Ratio	Waste/ Cement Ratio
III	loaded M.B.	22	53	25	1.34	1.14
III	M.B.	52	35	13	.32	.25
I	M.B.	58	31	11	.29	.18
III	IRN-77	59	29	12	.32	.20
III	IRN-78	31	49	20	.80	.63

M.B. = mixed bed; (a) Dry resin/cement by weight

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