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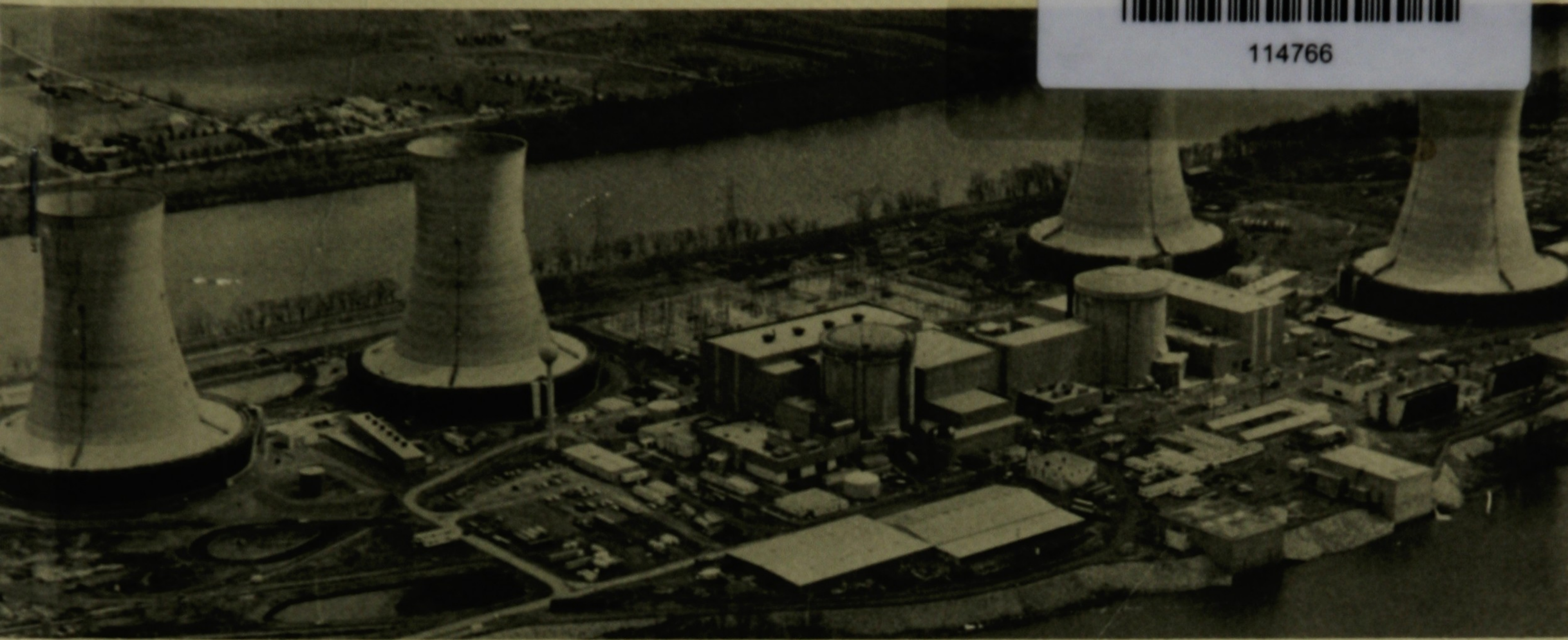

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SOLIDIFICATION OF EPICOR-II RESIN WASTE FORMS

Robert M. Neilson, Jr.
John W. McConnell, Jr.

Prepared for the
U.S. Department of Energy
Three Mile Island Operations Office
Under DOE Contract No. DE-AC07-76ID01570

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ABSTRACT

One goal of the EPICOR-II Research and Disposition Program is to investigate methods of immobilizing ion exchange resin wastes by solidification. Formulations were developed for the solidification of EPICOR-II prefilter wastes from Three Mile Island Unit-2 using Portland type I-II cement and vinyl ester-styrene. The work was accomplished by EG&G Idaho, Inc. at the Idaho National Engineering Laboratory and was funded by the U.S. Department of Energy. In developing formulations, ion exchange resins and zeolite simulating those in EPICOR-II prefilters were used. Once suitable formulations were defined, radioactive wastes from EPICOR-II prefilters PF-7 (organic ion exchange resins) and PF-24 (organic ion exchange resins with zeolite) were solidified. A total of 267 radioactive waste form specimens was prepared in hot cell solidification operations. That total includes 136 Portland cement specimens (72 incorporating prefilter PF-7 waste and 64 with prefilter PF-24 waste) and 131 vinyl ester-styrene specimens (71 incorporating prefilter PF-7 waste and 60 with prefilter PF-24 waste). The methodologies used and products produced are described and evaluated in this report.

ACKNOWLEDGMENTS

The assistance of Ms. K. Messick, for her work in the development of formulations, and the efforts of Messrs. D. C. Sparks and G. A. Rigby during solidification operations using radioactive EPICOR-II prefilter wastes are appreciated.

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SOLIDIFICATION OF EPICOR-II RESIN WASTE FORMS

INTRODUCTION

EPICOR-II prefilters expended in the cleanup of Three Mile Island Unit-2 liquid wastes were transported to the Idaho National Engineering Laboratory as part of the EPICOR-II Research and Disposition Program. That program is investigating degradation and solidification of prefilter wastes, waste form properties, and prefilter liner corrosion. This report describes development of formulations for solidification of EPICOR-II wastes from prefilters PF-7 and -24 using Portland cement and vinyl ester-styrene. The waste forms produced will be used in subsequent evaluations of waste form properties including leachability, mechanical integrity, radiation stability, and biodegradation. The solidification work was accomplished by EG&G Idaho, Inc. and was funded by the U.S. Department of Energy.

Limited operating experience exists for the solidification of commercial low-level ion exchange resin wastes.[1] The majority of waste ion exchange resins have been dewatered and packaged in large carbon steel liners or, more recently, high integrity containers for disposal. Published information concerning the immobilization of ion exchange resins in Portland cement indicates instances of low product integrity, waste form disintegration, and free-standing water.[1-3]

Formulations developed in this study for the immobilization of EPICOR-II prefilter wastes must result in waste forms which meet the regulatory requirements of 10 CFR 61 "Licensing Requirements for Land Disposal of Radioactive Waste."[4] Important requirements are that (a) the wastes have structural stability (which can be provided by the waste, processing the waste to a stable form, or placing the waste in a disposal container or structure that provides stability after disposal) and (b) the waste form contains as little free-standing noncorrosive liquid as is reasonably achievable (in no case shall the liquid exceed 1% by volume of the waste). Guidance for implementing these (and other) waste form requirements is provided by the U.S. Nuclear Regulatory Commission in its "Branch Technical Position on Waste Form."[5] It is the intent of the EPICOR-II Research and Disposition Program to evaluate the waste forms produced in this study relative to the stipulations of the Branch Technical Position.

MATERIALS AND PROCEDURES

EPICOR-II Prefilter Wastes

EPICOR-II prefilter wastes were obtained from prefilters PF-7 and -24. Waste from prefilter PF-7 contained a mixture of synthetic organic ion exchange resin types (phenolic cation, strong acid cation, and strong base anion resins), while prefilter PF-24 contained a mixture of synthetic organic ion exchange resins (strong acid cation and strong base anion resins) with an inorganic zeolite. The organic ion exchange resin types and the zeolite (when present) were layered in the prefilters. The order of layering, specific ion exchange resins employed in this process, and their relative quantities are proprietary. Prefilter wastes were removed from their liners in a coring operation during which a coring tool was inserted through the resin layers, closed, and withdrawn, thereby removing a representative portion of the prefilter waste. The EPICOR-II prefilter wastes used in this study were supplied in 0.0189-m^3 (5-gal.) mild steel buckets labeled "A" (prefilter PF-7 waste) and "B" (prefilter PF-24 waste). As a result of the coring operation, prefilter wastes as supplied in those buckets were not homogeneous. Prefilter wastes from each bucket were homogenized by mixing before solidification. The water content was not known for the EPICOR-II prefilter wastes as supplied for solidification.

Simulated EPICOR-II Prefilter Wastes

Simulated non-radioactive EPICOR-II prefilter wastes were employed in developing formulations used for the solidification of the actual EPICOR-II wastes. The ion exchange resins and zeolite used were representative of those present in prefilters PF-7 and -24 and were employed in the proper ratios to simulate EPICOR-II wastes.[6,7] Table 1 lists the hypothesized structures of the organic ion exchange resins. Simulated wastes were not loaded with the chemical species absorbed on the actual EPICOR-II wastes because information concerning the chemical loading was not available. Use of unloaded resins is, however, a conservative approach in developing formulations. Previous work has shown that cement formulations can accommodate larger quantities of loaded ion exchange resin and maintain integrity in immersion tests; hence, formulations developed using unloaded resins should prove compatible with actual EPICOR-II wastes (Reference 1). Simulated wastes representative of prefilter PF-7 (organic resins) and PF-24 (organic resins with zeolite) wastes are referred to as Type 1 and Type 2 wastes, respectively, in this study.

TABLE 1. STRUCTURES OF ORGANIC ION EXCHANGE RESINS IN SIMULATED EPICOR-II WASTES[7]

Resin Type	Base Material	Active Group
Strong base anion	Styrene, divinylbenzene	$N(CH_3)_3$
Strong acid cation	Styrene, divinylbenzene	SO_3H
Phenolic cation	Phenol, formaldehyde	ArOH[a]

a. ArOH is the symbol for phenol.

Solidification Agents

Portland cement waste forms were prepared using Portland type I-II cement (Oregon Portland Cement Co., Inkom, ID). Portland cement was mixed with prefilter waste and some additional water. Water combined with the cement to form hydrated silicate and aluminate compounds which interact to form a monolithic solid. The ion exchange resin beads and zeolite granules were physically entrapped and acted as aggregate in the Portland cement waste form.

Vinyl ester-styrene is a proprietary solidification agent (thermosetting polymer) developed and supplied by the Dow Chemical Company (Midland, MI). Vinyl ester-styrene was mixed with prefilter waste under high shear mixing conditions. The high shear mixing caused interstitial (non-absorbed) water between the resin beads to form an emulsion with the vinyl ester-styrene binder. Solidification of the emulsion occurred after addition of a polymerization catalyst and a promoter (which allowed the polymerization catalyst to operate at room temperature). The specific catalyst and promoter, as well as the sequence in which constituents were added, are proprietary. The waste form that resulted was a continuous polymer matrix, with fine droplets of water and resin beads homogeneously dispersed throughout.

Telephone contacts and written correspondence were used to obtain pertinent information from commercial waste solidification service, equipment, and supply companies regarding formulations for the solidification of EPICOR-II wastes.[8-10]

Water Content

Ion exchange resins vary widely in terms of water content (i.e., dry, partially saturated, dewatered, decanted, or slurry). Water contents of ion exchange resins and zeolite used in this study were measured according to ASTM Standard Test Method D2187-77, "Physical and Chemical Properties of Ion Exchange Resins." That procedure measured the mass loss of ion exchange resins that had been dried at 110°C for 18 $\pm$ 2 hours in a gravity convection oven. Water content was calculated as

$$\text{wt\% water} = \frac{M_A - M_D}{M_A} \times 100 \qquad (1)$$

where

M_A = mass of as-received resin (g)
M_D = mass of dried resin (g).

Preparation of Decanted Ion Exchange Resin

The water content of ion exchange resins is significant to the solidification operation, particularly when using Portland cement (which requires water for hydration). Experimentation to develop suitable formulations required the use of resins with known water content. Resins were used in the decanted state because they were simple to prepare, had reproducible water contents, and contained water available for cement hydration. In the decanted state, ion exchange resin beads have absorbed water to saturation and the interstitial void space between resin beads has been filled with water. The decanted resins were prepared by placing them in water for several hours and then decanting excess water until the height of the water column in the holding vessel equaled the height of the settled resins.

Homogenization of Resins

The ion exchange resin types comprising both the simulated and actual EPICOR-II resin wastes each had a distinctive appearance. The organic resins consisted of round beads with a particular coloration (strong acid cation--yellow, strong base anion--reddish-brown, or phenolic cation--black). Inorganic zeolite particulates were angular gray granules. Both the simulated and actual EPICOR-II wastes were homogenized by mixing until a uniform distribution of color throughout the resin mass was achieved.

Homogenization of actual EPICOR-II wastes was particularly important because the wastes contained activity unevenly distributed by location within the bed and between the different resin types that made up each waste. Homogenization is also representative of commercial practice for waste solidification. EPICOR-II resin wastes were homogenized at the Auxiliary Reactor Area-I (ARA-I) Hot Cells in the 0.0189-m^3 (5-gal.) buckets in which they were supplied. After removing the ring clamp and lid from a waste bucket, the bucket was placed on a mixing stand and mixed for approximately 10 min at low speed, using a multiple rod blade.

Preparation of Simulated and Actual EPICOR-II Waste Forms

Simulated EPICOR-II waste forms were prepared in polyethylene vials having a diameter of 4.76 cm (1.88 in.) and a height of 10.2 cm (4.0 in.). Portland cement formulations were hand mixed with a stainless steel spatula. Vinyl ester-styrene formulations were mixed using a Cowles type dispersion blade attached to a high speed drill motor. The preparation containers had snap-on lids to prevent water evaporation while curing. Simulated waste form specimens had an average height of 5.6 cm (2.2 in.) and were cured at approximately 20°C (68°F).

Actual EPICOR-II waste forms were prepared in 4.76-cm-diameter by 10.2-cm-height polyethylene vials. Those waste forms were prepared in the ARA-I Hot Cells using solidification equipment specifically designed for remote operation. That equipment (Figure 1) consisted of the following modules: (a) mixing, (b) injection, (c) turntable, and (d) promoter addition and mixing. The mixing module was used to homogenize EPICOR-II resins and mix decanted resin wastes with the appropriate solidification agent. The waste/binder mixture was transferred to an injection apparatus, which dispensed the mixture into individual numbered polyethylene vials located on the turntable. The turntable held 36 vials, which were filled in numerical order for each batch prepared. Sufficient mixture was added to each vial to produce waste forms with an average height of 7.6 cm (3.0 in.) with a tolerance of $\pm$ 0.6 cm (0.3 in.). The promoter addition and mixing module was used only for vinyl ester-styrene waste forms. Snap-on lids were placed on the vials after waste form preparation was complete. The waste forms were cured at approximately 20°C (68°F).

Free-Standing Water

Waste forms were inspected after solidification for the presence of free-standing water. Formulations containing any drainable free liquid in the preparation vial more than 24 hours after solidification were unacceptable. This criterion is more stringent than the free-standing liquid requirement of 10 CFR 61. Conservatism, however, is appropriate because of the small size of the specimens prepared relative to the dimensions of full-scale waste forms.

Immersion Testing

Simulated EPICOR-II resin waste forms were immersion tested. Portland cement specimens were immersion tested 21 days after preparation; vinyl ester-styrene specimens were tested 7 days after preparation. The tests demonstrated the long-term mechanical integrity of the formulations tested and their applicability for lysimeter and leaching experiments. The test consisted of completely immersing individual specimens in demineralized

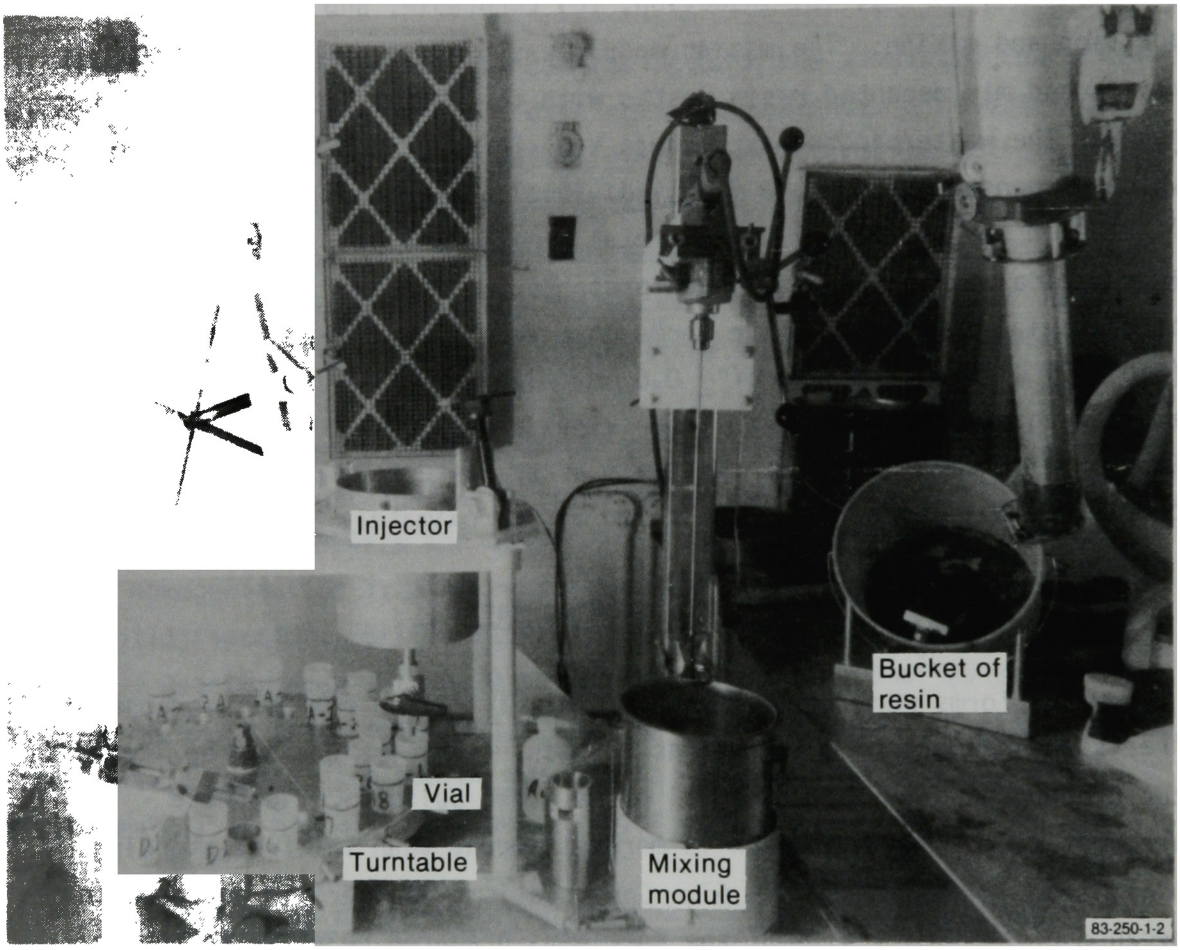


Figure 1. Photograph of the remotely operated equipment used to produce Portland cement and vinyl ester-styrene waste forms incorporating actual EPICOR-II ion exchange wastes.

water for 21 days. The amount of water used was that prescribed by the American Nuclear Society 16.1 leach test procedure, namely a leachant volume to specimen external geometric surface area ratio of 10 ± 0.2 cm.[11] Those specimens that passed the test maintained their mechanical integrities for the duration of immersion.

Contact Gamma Dose Rate

Contact gamma dose rates were measured for individual EPICOR-II waste forms in their preparation vials. The measurements were taken at approximately the mid-height of the waste form cylinder using an Eberline Model RD-3A ion chamber. The center of the ion chamber was located approximately 3.2 cm (1.3 in.) from the side of the waste form during the measuring operations.

RESULTS AND DISCUSSION

Throughout this section of the report, results of the solidification of simulated and actual EPICOR-II resin wastes are discussed. Several formulations and batches were mixed and examined. The series and batch numbering system is presented below:

- Series 93, 94, 111, 112, and 113 used both organic and organic/zeolite simulated waste solidified in Portland cement
- Series 120, 121, and 122 used both organic and organic/zeolite simulated waste solidified in vinyl ester-styrene
- Batches C1 and C1A used actual organic waste solidified in Portland cement
- Batches C2A and C2B used actual organic/zeolite waste solidified in Portland cement
- Batches D1 and D1A used actual organic waste solidified in vinyl ester-styrene
- Batches D2 and D2A used actual organic/zeolite waste solidified in vinyl ester-styrene.

Formulation Development

The water content of ion exchange resin wastes significantly affects the mixability and free-standing water in Portland cement formulations (References 1 through 3). Measurements were made to determine water contents of the individual resin types that comprised the simulated EPICOR-II wastes (Table 2). These data were used subsequently to facilitate the preparation of decanted simulated resin. They also permitted calculation of the dry resin content of the waste form formulations prepared.

TABLE 2. WATER CONTENTS OF ION EXCHANGE RESIN TYPES AND ZEOLITE PRESENT IN SIMULATED EPICOR-II WASTES

	Percent Water Content (wt%)		
	Dry	As-Received	Decanted
Strong base anion	0	63.6	74.2
Strong acid cation	0	45.0	60.6
Phenolic cation	0	44.5	64.4
Zeolite	0	5.9	48.0

The formulations used for the solidification of simulated EPICOR-II wastes in Portland cement are listed in Table 3. Portland cement with additive formulations were not considered. These different formulations are referred to as "Series" in this report. Series 111 and 112 formulations differed slightly for the two EPICOR-II waste types: Type 1 (organic resin mix) and Type 2 (organic resin with zeolite). Series 111 and 112 formulations were based on commercial operations in which water is removed from a settled resin slurry in a decant tank until a layer of free-standing water equivalent to 20% of the total waste volume remains above the settled resin. Because the densities of the decanted resin wastes were different (Type 1 = 1.09 g/cm^3 and Type 2 = 1.13 g/cm^3), the weight fraction of decanted resin varied at 20 vol% free-standing water for each waste type. One vendor suggested adjustment of the waste pH to 9 before solidification. Series 111 and 113 formulations incorporated resin wastes with pH adjusted to approximately 9 by the addition of 8M NaOH. Waste pH was not adjusted for Series 93, 94, and 112 formulations. In addition, a set of specimens based on the Series 93 formulations was prepared which incorporated a range of additional water contents (7.0 to 29.6 g) to 30.0 g decanted resin and 60.0 g of Portland cement. This was done to determine the range of additional water contents that resulted in acceptable waste forms. Decanted resin wastes, either with or without pH adjustment, were used for these specimens.

TABLE 3. PORTLAND CEMENT FORMULATIONS FOR THE SOLIDIFICATION OF SIMULATED EPICOR-II WASTES

		Formulation Weight Percentage		
Series	Waste Type	Decanted Resin	Portland Cement	Additional Water
93	1,2	30.0	60.0	10.0
94	1,2	19.2	65.9	14.9
111	1	46.0	43.4	10.6
111	2	48.0	41.3	10.7
112	1	46.0	43.4	10.6
112	2	48.0	41.3	10.7
113	1,2	30.0	60.0	10.0

Vinyl ester-styrene formulations were prepared using decanted resin waste/binder volume ratios of 1.0, 1.5, 2.0. Those formulations are listed in Table 4 as Series 120, 121, and 122, respectively. The density of the vinyl ester-styrene binder was 1.03 g/cm^3.

TABLE 4. VINYL ESTER-STYRENE FORMULATIONS FOR THE SOLIDIFICATION OF SIMULATED EPICOR-II WASTES

			Formulation Weight Percentage[a]	
Series	Waste Type	Waste/Binder Volume Ratio	Decanted Resin	Vinyl Ester-Styrene
120	1	1.0	51.4	48.6
120	2	1.0	52.3	47.7
121	1	1.5	61.3	38.7
121	2	1.5	62.2	37.8
122	1	2.0	67.9	32.1
122	2	2.0	68.7	31.3

a. Formulation percentages do not include catalyst or promoter. Additions of catalyst and promoter are proprietary and based on the amount of vinyl ester-styrene binder present. For the formulations tested, tne combined catalyst and promoter additions ranged from 0.8 to 1.2 wt% of the formulation.

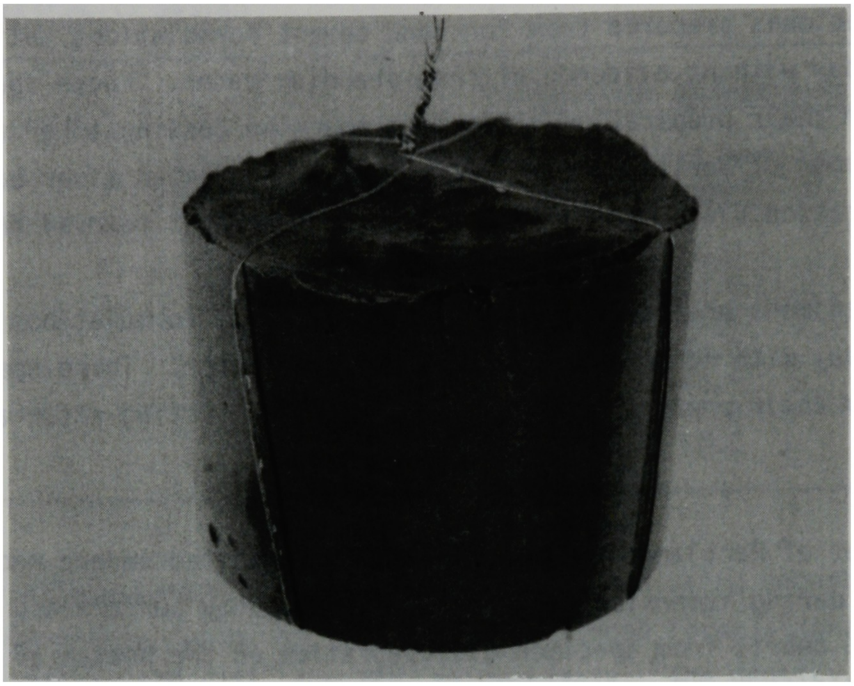
All specimens prepared from Portland cement formulations solidified within one day with no evidence of free-standing water. Those specimens were removed from their preparation vials for immersion testing after a 21-day cure time. A number of Series 111 and 112 specimens exhibited minor bulging of their preparation vials and slight surface cracks after removal from the vials.

All specimens prepared from vinyl ester-styrene formulations solidified within one day with no evidence of free-standing water. Those specimens were removed from their preparation vials for immersion testing after a 7-day cure time.

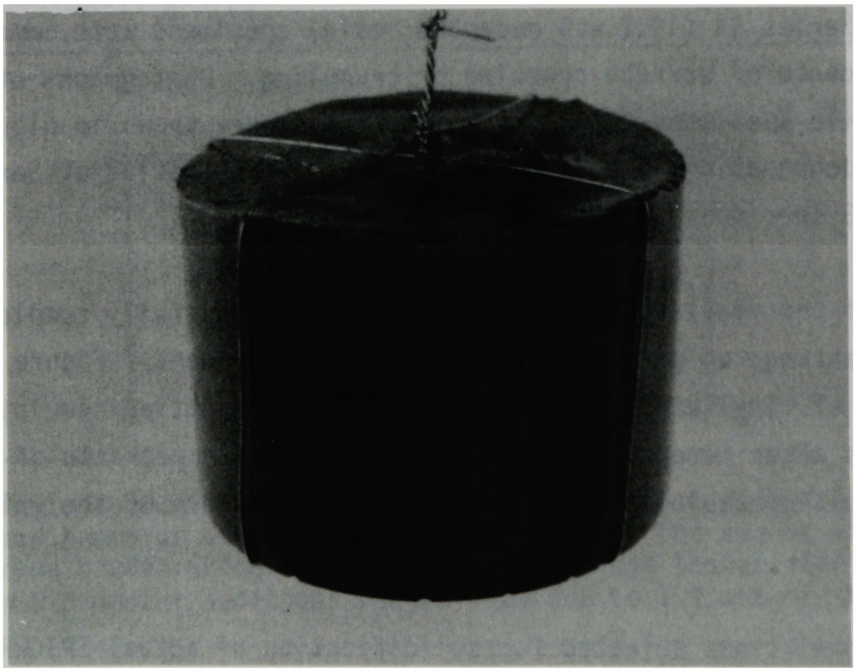
A number of Portland cement formulations exhibited severe mechanical degradation during immersion testing, as evidenced by surface and interior cracking and debris from specimen disintegration on the bottom of the test vessel. All Series 111 and 112 (having from 46.0 to 48.0 wt% decanted resin) specimens and all Series 113 (30 wt% decanted resin) specimens exhibited some degree of degradation. These formulations incorporated high resin loadings and/or pH adjusted resin wastes. Each of the Series 93 (30 wt% decanted resin) and Series 94 (19.2 wt% decanted resin) specimens were immersion tested with no evidence of surface cracking or crumbling. Photographs of representative specimens after immersion testing are shown in Figure 2. The mechanical degradation that resulted from immersion testing of Series 111, 112, and 113 specimens is clearly evident.

Each of the vinyl ester-styrene specimens successfully completed immersion testing; no mechanical degradation was evident. Figure 3 shows photographs of vinyl ester-styrene specimens incorporating simulated EPICOR-II resin wastes after immersion testing. The speckled appearance of those specimens is the result of resin beads near the surface of the white polymer matrix.

The formulations selected for solidification of actual EPICOR-II resin wastes are listed in Table 5. Both the Portland cement and vinyl ester-styrene formulations selected are representative of commercial formulations and, as a result of immersion testing, are expected to withstand

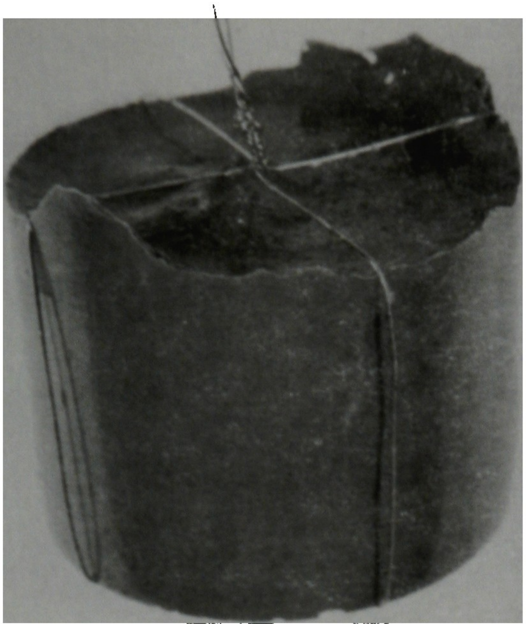


(a) Series 93-Type 1 waste (30.0 wt% decanted organic resin)



(b) Series 93-Type 2 waste (30.0 wt% decanted organic resin with zeolite)

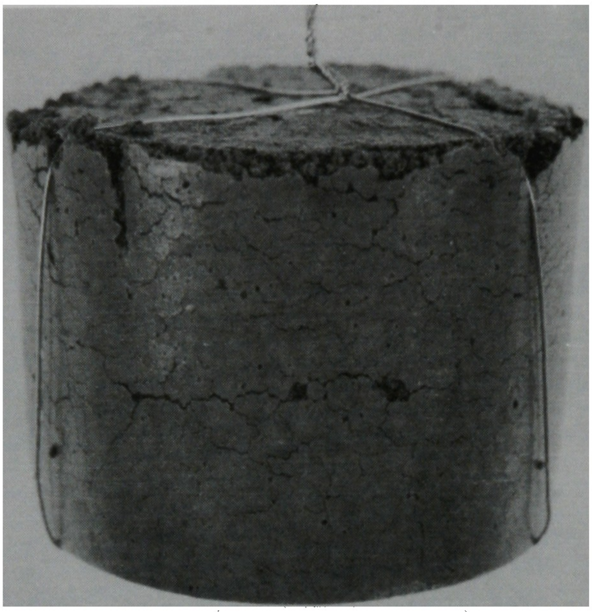
Figure 2. Appearance of Portland type I-II cement specimens incorporating simulated EPICOR-II wastes, after immersion testing.



(c) Series 94-Type 1 (19.2 wt% decanted organic resin)

(d) Series 94-Type 2 (19.2 wt% decanted organic resin with zeolite)

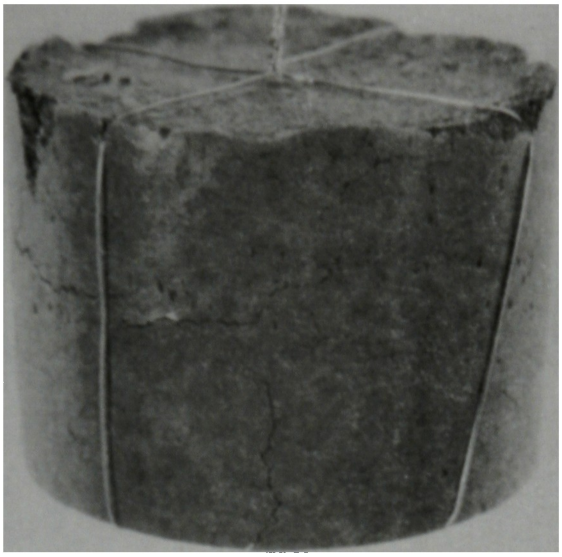
Figure 2. (continued)



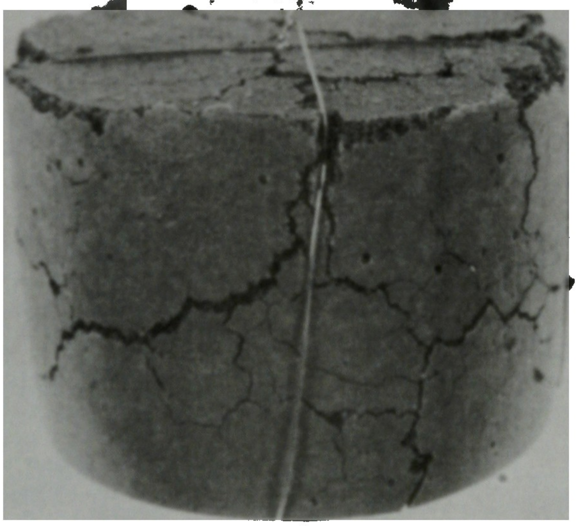
(e) Series 111-Type 1 waste (46.0 wt% decanted organic resin, pH adjusted)

(f) Series 111-Type 2 waste (48.0 wt% decanted organic resin with zeolite, pH adjusted)

Figure 2. (continued)

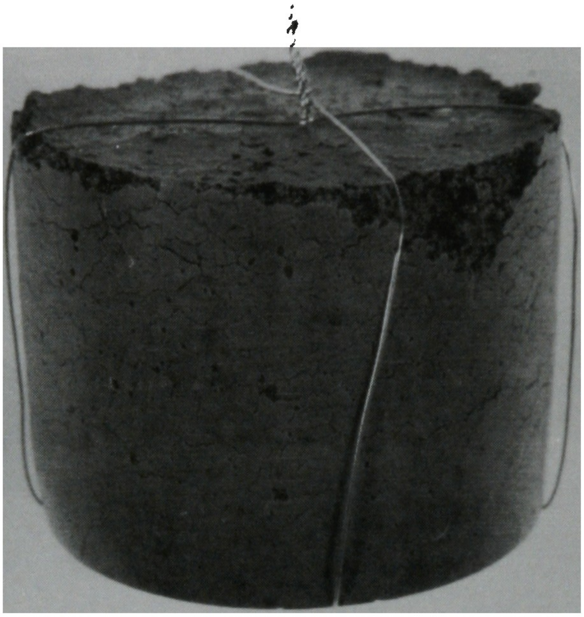


(g) Series 112-Type 1 waste (46.0 wt% decanted organic resin)

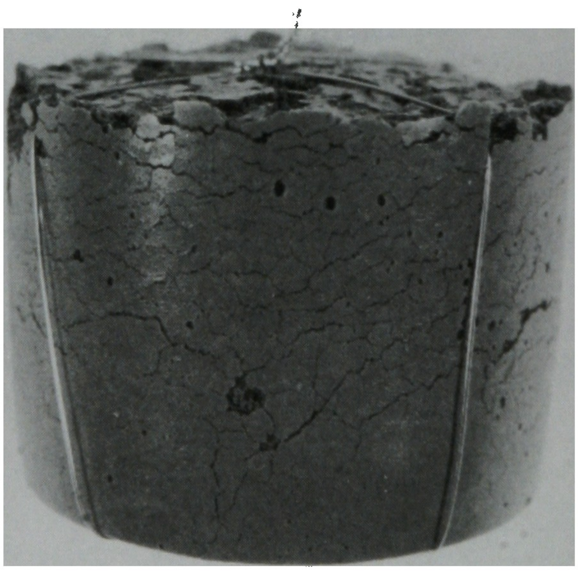


(h) Series 112-Type 2 waste (48.0 wt% decanted organic resin with zeolite)

Figure 2. (continued)



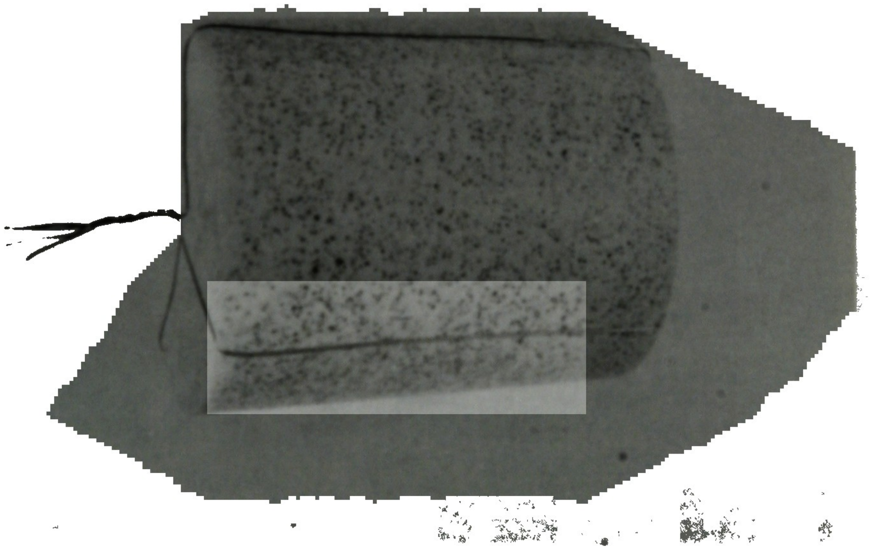
(i) Series 113-Type 1 waste (30.0 wt% decanted organic resin, pH adjusted)



(j) Series 113-Type 2 waste (30.0 wt% decanted organic resin with zeolite, pH adjusted)

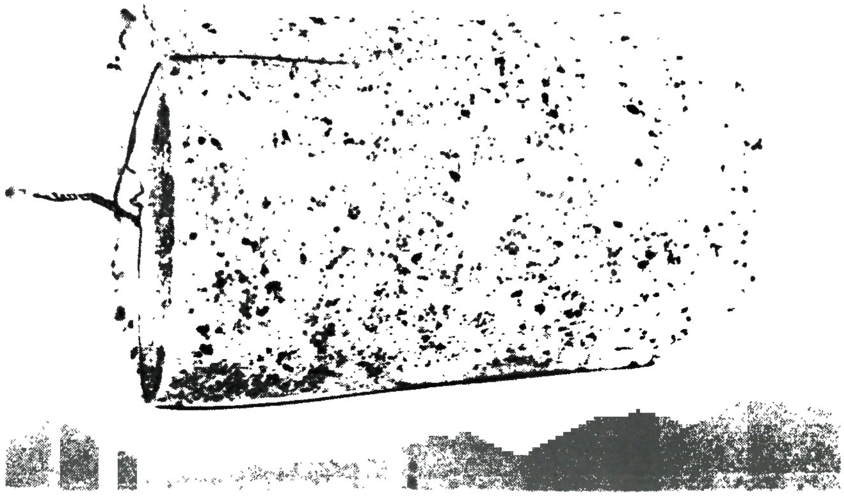
Figure 2. (continued)

(a) Series 120-Type 1 waste (51.4 wt% decanted organic resin)

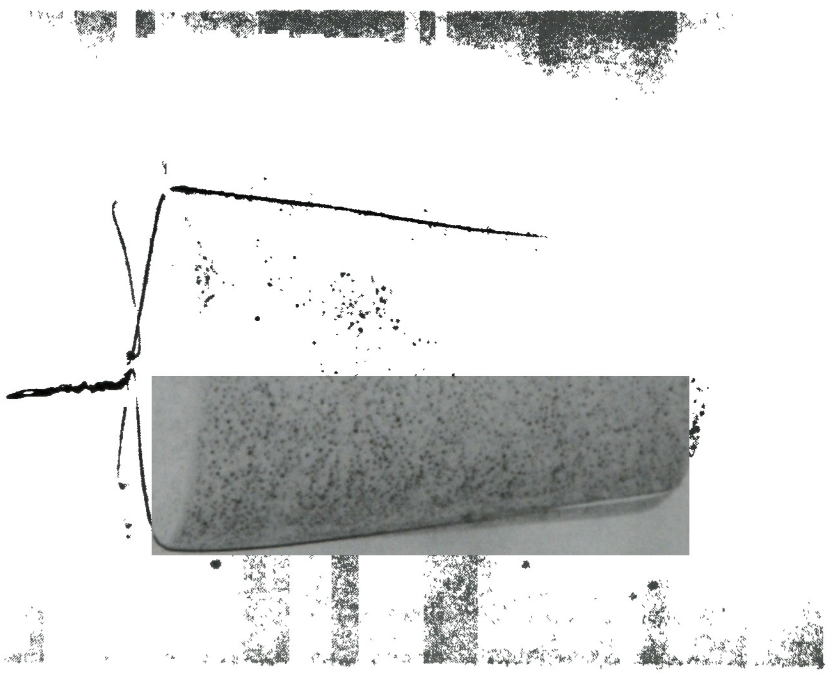


(b) Series 120-Type 2 waste (52.3 wt% decanted organic resin with zeolite)

Figure 3. Appearance of vinyl ester-styrene specimens incorporating simulated EPICOR-II wastes, after immersion testing.

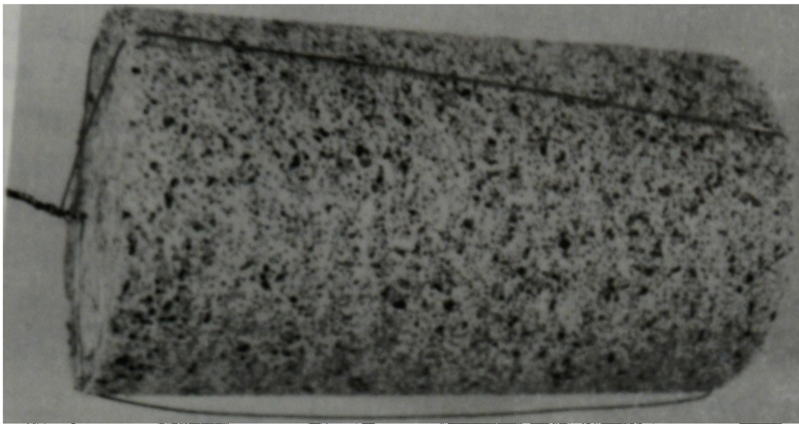


(c) Series 121-Type 1 waste (61.3 wt% decanted organic resin)

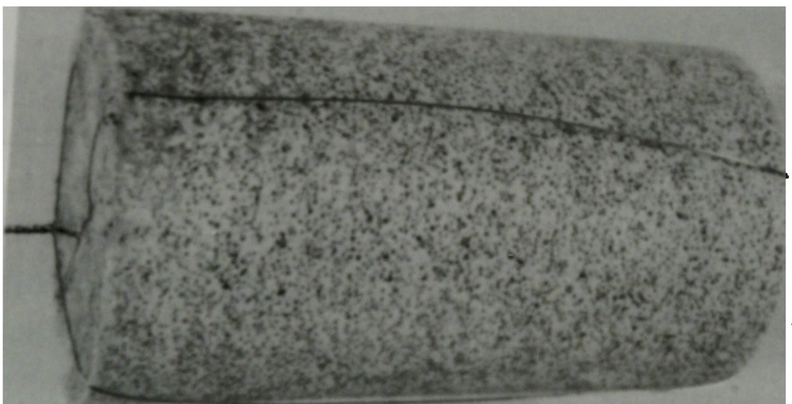


(d) Series 121-Type 2 waste (62.2 wt% decanted organic resin with zeolite)

Figure 3. (continued)



(e) Series 122-Type 1 waste (67.9 wt% decanted organic resin)



(f) Series 122-Type 2 waste (68.7 wt% decanted organic resin with zeolite)

Figure 3. (continued)

the conditions of lysimeter and leach testing. The formulation chosen for solidification with Portland cement was that used for Series 93 (30 wt% decanted resin) waste forms. Immersion testing indicated that waste forms prepared to this formulation may contain a substantial range of additional water content and be acceptable for subsequent testing. The Series 121 (61.3 wt% decanted resin) formulation was selected for solidification of actual EPICOR-II wastes with vinyl ester-styrene. Because the differences in Series 121 formulations for Type 1 and Type 2 wastes were small (see Table 4), and because the densities of the actual EPICOR-II wastes were not known, the Type 1 waste formulation was selected for both wastes.

TABLE 5. FORMULATIONS SELECTED FOR THE SOLIDIFICATION OF ACTUAL EPICOR-II RESIN WASTES

	Formulation Weight Percentage[a]		
Solidification Agent	Decanted Resin	Binder	Additional Water
Portland type I-II cement	30.0	60.0	10.0
Vinyl ester-styrene	61.3	38.7	0.0

a. Does not include catalyst and promoter in the vinyl ester-styrene formulation, which constitute less than 1% of the final formulation weight.

As Table 5 indicates, the vinyl ester-styrene formulation selected (61.3 wt% decanted resin) contained more than twice the amount of decanted resin waste on a weight basis than the Portland cement formulation (30.0 wt% decanted resin). Table 6 considers simulated EPICOR-II waste loading in terms of packaging efficiency, which is more meaningful for this comparison. Packaging efficiency is the volume of dewatered resin waste incorporated per unit volume of the solidified waste form. The packaging efficiency of the vinyl ester-styrene formulation was 20% higher than that of the Portland cement formulation.

TABLE 6. DENSITY AND PACKAGING EFFICIENCY OF THE SELECTED FORMULATIONS FOR THE SOLIDIFICATION OF SIMULATED EPICOR-II WASTES

Binder	Decanted Resin Type	Waste Form Density (g/cm^3)	Waste Form Packaging[a] Efficiency
Portland type I-II cement	Type 1	1.75	0.48
	Type 2	1.81	0.48
Vinyl ester-styrene	Type 1	1.07	0.60
	Type 2	1.10	0.60

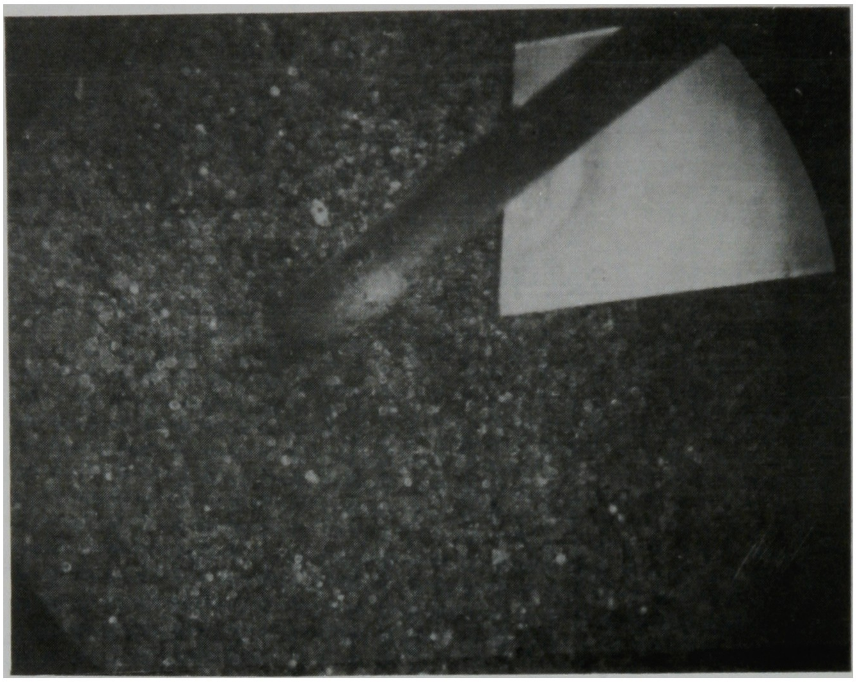
a. Packaging efficiency is the ratio of the waste volume to the volume of the resultant waste form.

Characterization of Actual EPICOR-II Wastes

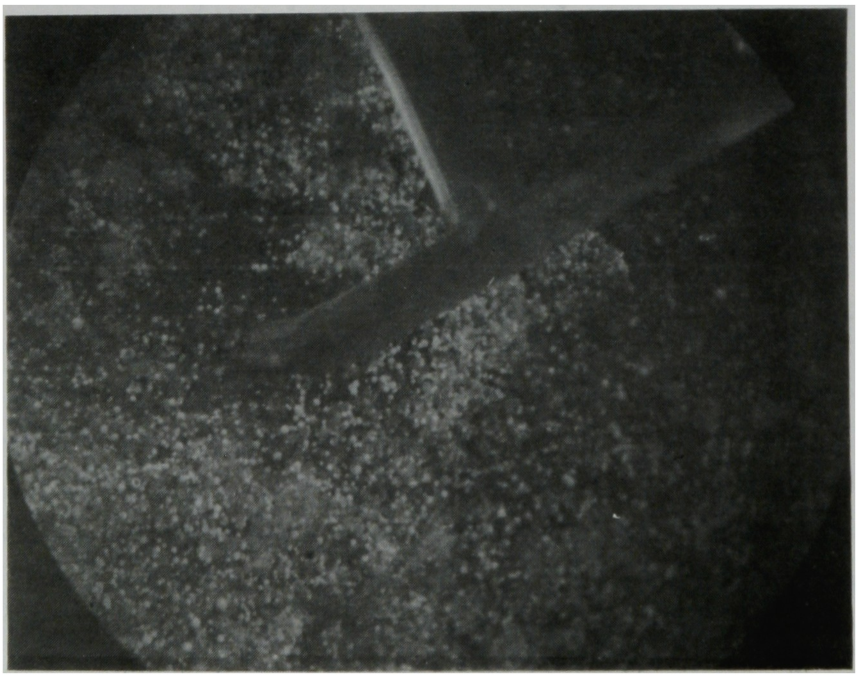
Ion exchange resin waste from prefilter PF-7 (organic resin), as supplied from prefilter coring, appeared dry with several small chunks of a white material on the surface. Mixing during homogenization easily broke up these chunks and dispersed them throughout the resin. Resin waste from prefilter PF-24 (organic resin with zeolite) appeared wetter than the prefilter PF-7 waste, as evidenced by clumping of the bead resins. No white chunks of material were noted in prefilter PF-24 waste.

Although EPICOR-II wastes appeared homogeneous after 2 to 5 min of mixing, the resin wastes were each mixed for a total of 10 min to assure homogeneity. Figure 4(a) is a photograph of the prefilter PF-7 waste after 5 min of mixing. In contrast, Figure 4(b) shows the surface of the prefilter PF-24 waste after two turns of the mixing blade, which brought other layered resin types to the surface.

Prefilter PF-7 and -24 waste samples, approximately 20 g each, were posted out of the hot cell after homogenization to determine water contents. Water content measurements were made using two samples of each waste (Table 7).



(a) Prefilter PF-7 waste (organic resin) after five minutes of mixing



(b) Prefilter PF-24 waste (organic resin with zeolite) before significant mixing

Figure 4. Surface appearance of actual EPICOR-II wastes.

TABLE 7. WATER CONTENTS OF AS-RECEIVED EPICOR-II WASTES

Waste Type	Prefilter	Initial Mass (g)	Final Mass (g)	Initial Water Content (wt%)
1	PF-7	5.29	3.38	36.1
1	PF-7	5.56	3.50	37.1
				Average = 36.6
2	PF-24	5.08	2.90	42.9
2	PF-24	6.48	3.86	40.4
				Average = 41.7

Water was added to measured quantities of EPICOR-II wastes to prepare decanted resin for solidification. It was determined from water addition measurements that prefilter PF-7 (Type 1) waste required an average of 0.542 g of added water per gram of as-received waste to provide decanted waste. For prefilter PF-24 (Type 2) waste, this average ratio was 0.425. Table 8 gives water content and grams of dry waste/grams decanted waste calculated for simulated and actual EPICOR-II wastes. This information indicates that a given quantity of actual EPICOR-II waste contained more dry waste and less total water than the respective simulated waste.

TABLE 8. WATER CONTENTS OF EPICOR-II RESIN WASTES

	Water Content (wt%)		
Waste Type	As-Received	Decanted	g Dry Waste/g Decanted Waste
Type 1 simulated	52.3	66.8	0.332
Type 1 actual	36.6	58.9	0.410
Type 2 simulated	44.6	63.5	0.368
Type 2 actual	41.7	59.1	0.408

Solidification of EPICOR-II Wastes

Because the actual EPICOR-II wastes contained more dry waste per gram of decanted waste than the simulated wastes used in formulation development, the selected Portland cement formulation was modified to provide 10.0 wt% dry waste in the resultant waste form. [The selected formulation shown in Table 5 contained 10.0 wt% dry waste with simulated Type 1 waste and 10.9 wt% dry waste with simulated Type 2 waste.] Because less decanted waste was used in the Portland cement formulations incorporating actual EPICOR-II wastes, an increase in the additional water content also was required to compensate for the loss of interstitial water to the mix.

Production of Portland cement waste forms with prefilter PF-7 waste was fairly routine. When a similar procedure was used for the solidification of prefilter PF-24 waste, there was insufficient time to cast individual specimens before the mixture would thicken appreciably. This was readily apparent in the first batch. Specimens in this batch contained considerable void space as the mixture was consolidated in individual preparation vials. This sample batch was ultimately discarded. For subsequent batches, more additional water was used and the mixing operation shortened to reduce the time required to prepare the batch specimens. A total of four batches of Portland cement waste forms was prepared and retained: two batches for each waste type. Table 9 lists the formulations used for the Portland cement waste form batches. The masses of the individual specimens prepared within each batch are given in Table 10. Contact gamma doses for the individual specimens are listed in Table 11.

The difference between the water contents of decanted EPICOR-II wastes and decanted simulated wastes was not significant for solidification with vinyl ester-styrene. The formulation selected from developmental studies was used for solidification using this binder (with the exception of Batch D2A where a larger quantity of vinyl ester-styrene than required was accidentally posted into the hot cell). Formulations for vinyl ester-styrene batches incorporating EPICOR-II wastes are listed in Table 12.

TABLE 9. FORMULATIONS FOR PORTLAND CEMENT WASTE FORM BATCHES INCORPORATING EPICOR-II WASTES

Batch	Waste[a] Type	Formulation Weight Percentage				
		As-Received Waste	Added Water	Decanted[b] Waste Total	Portland Type I-II Cement	Additional Water
C1	1	15.6	8.5	24.1	62.7	13.2
C1A	1	15.6	8.5	24.1	62.7	13.2
C2A	2	16.8	7.1	24.0	62.5	13.5
C2B	2	16.5	7.1	23.6	61.4	15.1

a. Waste Type 1 is organic resin from prefilter PF-7. Waste Type 2 is organic resin with zeolite from prefilter PF-24.

b. Decanted waste total is the as-received waste and added water weight percentage.

While production of vinyl ester-styrene waste forms proceeded smoothly, there was a problem with ion exchange resin settling in the injector. The density of the ion exchange resin was higher than the vinyl ester-styrene binder. Settling was noticed in individual preparation vials before the addition of promoter. The amount of ion exchange resin in each specimen was related to the height of the resin in the mix after settling. Typically, approximately the first 1/4 to 1/2 of the specimens in each batch had similar settled resin levels. The settled resin level decreased for subsequent specimens, reached a minimum, and then increased. The settled resin levels in the last specimens in a batch usually were higher than those in the first specimens. This behavior was related to the size of the sample batch. The relative ion exchange resin content is also evident from specimen mass and contact gamma dose measurements (Tables 13 and 14, respectively). The ion exchange resin in individual specimens was homogeneously dispersed by mixing the individual specimens after promoter addition.

TABLE 10. MASSES OF PORTLAND CEMENT WASTE FORM SPECIMENS

Sample Number	Specimen Mass[a] (g) Batch C1	Batch C1A	Batch C2A	Batch C2B[b]
1	244.66	235.42	240.52	--[c]
2	246.88	241.47	247.48	264.13
3	241.12	251.35	242.88	260.51
4	258.39	231.68	246.44	243.65
5	240.94	252.83	251.41	255.23
6	242.80	245.82	259.24	244.01
7	250.25	240.18	258.22	237.05
8	243.53	243.17	253.15	243.38
9	246.22	246.66	254.52	250.55
10	248.11	235.57	251.06	247.54
11	244.48	246.56	247.68	230.56
12	249.48	237.70	256.08	217.97
13	244.73	238.91	243.47	226.11
14	250.99	245.60	255.06	233.99
15	241.97	242.14	247.43	226.85
16	249.24	237.68	242.31	234.29
17	246.97	240.70	242.38	243.55
18	247.76	240.26	253.08	253.66
19	247.16	236.77	248.29	219.50
20	246.14	265.68	256.73	229.47
21	253.88	240.12	264.71	226.50
22	245.13	243.99	246.28	246.53
23	249.52	245.25	248.92	234.48
24	247.20	241.90	254.97	243.63
25	245.11	240.76	244.93	228.48
26	255.54	235.05	248.14	238.92
27	249.47	241.18	249.88	242.72
28	235.01	247.25	248.79	250.58
29	255.53	239.48	251.84	249.73
30	246.53	228.98	247.15	--
31	253.21	245.60	253.05	--
32	248.56	240.00	252.63	--
33	229.64	226.70	250.25	--
34	244.23	243.82	250.71	--
35	249.90	241.71	245.36	--
36	230.71	239.11	255.71	--
Average	246.41	241.53	250.31	240.13
Standard Deviation	4.42	6.91	5.35	11.88

a. Assumes container mass = 25.32 g.

b. Partial batch.

c. Sample 1 in Batch C2B was discarded because the preparation vial was overfilled.

TABLE 11. CONTACT GAMMA DOSES FOR PORTLAND CEMENT WASTE FORMS INCORPORATING EPICOR-II WASTES

Sample Number	Contact Gamma Dose (R/h)			
	Batch C1	Batch C1A	Batch C2A	Batch C2B[a]
1	2.1	2.0	10.0	--[b]
2	2.1	2.0	10.5	10.0
3	2.0	2.1	10.0	10.0
4	2.3	2.0	10.0	10.0
5	2.2	2.1	10.5	10.0
6	2.2	2.1	10.5	10.0
7	2.2	2.1	11.0	10.0
8	2.2	2.1	11.0	10.0
9	2.1	2.1	11.0	10.0
10	2.2	2.0	11.0	10.0
11	2.2	2.1	11.0	10.0
12	2.2	2.1	11.0	10.0
13	2.2	2.1	11.0	10.0
14	2.2	2.1	10.5	10.0
15	2.2	2.1	10.5	10.0
16	2.2	2.1	11.0	10.0
17	2.2	2.1	10.5	10.0
18	2.1	2.1	11.0	10.0
19	2.0	2.1	11.0	10.0
20	2.1	2.2	11.0	10.0
21	2.2	2.1	11.0	10.0
22	2.1	2.1	11.0	10.0
23	2.2	2.2	11.0	10.0
24	2.2	2.1	10.5	10.0
25	2.1	2.1	11.0	10.0
26	2.0	2.1	10.5	10.0
27	2.0	2.2	10.5	10.0
28	2.0	2.2	10.5	10.0
29	2.0	2.2	10.5	10.0
30	2.0	2.1	10.5	--
31	2.0	2.1	11.0	--
32	2.0	2.0	11.0	--
33	2.0	2.0	10.5	--
34	2.0	2.0	11.0	--
35	2.1	2.0	10.5	--
36	2.0	2.0	11.0	--

a. Partial batch.

b. Sample misplaced during loading of storage cask.

TABLE 12. FORMULATIONS FOR VINYL ESTER-STYRENE WASTE FORM BATCHES INCORPORATING EPICOR-II WASTES

		Formulation Weight Percentage[a]			
Batch	Waste[b] Type	As-Received Waste	Added Water	Decanted[c] Waste Total	Vinyl Ester-Styrene
D1	1	40.9	20.3	61.3	38.7
D1A	1	38.9	22.6	61.5	38.5
D2	2	43.1	18.3	61.4	38.6
D2A	2	34.9	14.9	49.8	50.2

a. Does not include catalyst and promoter, which constitute a total of approximately 1 wt%.

b. Waste Type 1 is organic resin from prefilter PF-7. Waste Type 2 is organic resin with zeolite from prefilter PF-24.

c. Decanted waste total is the as-received waste and added water weight percentage.

TABLE 13. MASSES OF VINYL ESTER-STYRENE WASTE FORM SPECIMENS

Sample Number	Specimen Mass[a] (g)			
	Batch D1	Batch D1A	Batch D2	Batch D2A[b]
1	148.92	146.59	148.92	150.01
2	165.58	152.62	145.76	149.80
3	148.64	140.42	150.50	146.75
4	149.76	140.66	145.92	144.68
5	144.73	139.66	143.29	147.94
6	151.58	138.56	146.25	143.39
7	145.38	138.10	147.80	138.88
8	144.58	138.18	150.02	140.81
9	143.88	140.95	148.68	140.73
10	146.58	139.06	152.28	141.12
11	145.48	140.85	147.03	142.27
12	144.32	141.94	154.33	142.04
13	149.62	141.48	146.44	134.95
14	144.43	140.77	145.11	131.50
15	144.97	140.63	145.28	125.02
16	140.98	144.54	145.33	127.96
17	138.80	139.62	143.58	127.99
18	147.01	139.48	144.00	129.68
19	141.17	143.28	145.63	125.70
20	138.04	142.82	140.41	128.29
21	138.18	139.48	140.08	129.80
22	137.52	141.73	141.43	137.01
23	141.83	140.35	145.58	164.42
24	140.38	144.43	145.99	160.79
25	135.11	143.33	138.88	--
26	136.15	136.61	141.06	--
27	135.82	138.58	140.19	--
28	135.72	138.99	140.96	--
29	--[c]	137.90	132.48	--
30	132.95	134.98	138.81	--
31	135.05	131.84	133.16	--
32	144.85	134.15	132.99	--
33	144.17	130.79	134.50	--
34	149.63	129.97	135.99	--
35	147.98	133.53	141.28	--
36	151.26	144.35	143.70	--
Average	143.75	139.76	143.43	139.65
Standard Deviation	6.43	4.42	5.34	10.53

a. Assumes container mass = 25.32 g.

b. Partial batch.

c. Sample number 29 in Batch D1 was discarded because the preparation vial was cut by the mixing blade during promoter addition.

TABLE 14. CONTACT GAMMA DOSES FOR VINYL ESTER-STYRENE WASTE FORMS INCORPORATING EPICOR-II WASTES

	Contact Gamma Dose (R/h)			
Sample Number	Batch D1	Batch D1A	Batch D2	Batch D2A[a]
1	4.8	4.5	19.0	17.0
2	6.0	5.0	18.5	16.5
3	4.7	4.5	18.0	16.0
4	4.4	4.5	18.0	14.5
5	4.4	4.5	18.0	13.5
6	4.4	4.5	18.0	13.5
7	4.2	4.5	18.0	11.5
8	4.0	4.5	18.0	11.0
9	3.7	4.5	18.0	9.0
10	3.6	4.5	18.0	9.5
11	3.4	4.5	18.5	9.0
12	3.1	4.5	18.5	7.0
13	3.1	4.0	17.0	5.5
14	2.7	4.0	17.0	4.5
15	2.5	4.0	17.0	4.0
16	2.5	4.0	17.0	3.5
17	2.3	3.5	17.0	3.0
18	2.2	4.0	17.0	3.0
19	2.2	3.5	16.5	3.0
20	2.0	3.5	16.5	2.5
21	1.7	3.5	16.5	3.5
22	1.7	3.0	16.0	10.5
23	1.5	2.5	16.5	22.0
24	1.5	2.5	16.0	27.0
25	1.1	2.5	15.0	--
26	0.9	2.4	15.5	--
27	0.7	2.5	14.5	--
28	0.7	2.3	13.5	--
29	--[b]	2.0	12.0	--
30	0.5	1.5	10.0	--
31	0.8	1.0	9.5	--
32	2.2	0.8	8.5	--
33	6.0	0.7	9.5	--
34	6.5	0.7	11.5	--
35	6.5	1.2	14.5	--
36	6.5	3.4	15.5	--

a. Partial batch.

b. Sample misplaced during loading of storage cask.

SUMMARY

Formulations were developed for the solidification of EPICOR-II wastes in Portland cement and vinyl ester-styrene. Specimens prepared from these formulations using simulated EPICOR-II wastes were immersion tested with no evidence of mechanical integrity degradation. A total of 267 waste form specimens was prepared using actual EPICOR-II wastes. This total includes 136 Portland cement specimens (72 incorporating Type 1 waste and 64 with Type 2 waste) and 131 vinyl ester-styrene specimens (71 incorporating Type 1 waste and 60 with Type 2 waste).

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