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Review of a Test Program for Qualifying the Solidification of Epicor-II Resins with Cement

Prepared by R. E. Barletta, R. E. Davis

Brookhaven National Laboratory

Prepared for
U.S. Nuclear Regulatory
Commission

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Prepared by
R. E. Barletta, R. E. Davis

Department of Nuclear Energy
Brookhaven National Laboratory
Upton, NY 11973

Prepared for
Division of Waste Management
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
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ABSTRACT

The results and recommendations of the resin solidification test program conducted by Metropolitan Edison Company are reviewed. The original purpose of this program was to recommend a formulation or range of formulations suitable for the cement solidification of first-stage Epicor-II liners generated during cleanup activities at Three Mile Island. This was to be accomplished through a systemmatic laboratory and full-scale testing program using ion-exchange materials supplied by Epicor, Incorporated. Events, however, caused the truncation of the full-scale testing. Hence, a formulation was recommended based upon the results of laboratory scale testing. Failure to achieve satisfactory solidification in a single full-scale test using this formulation was observed. The unqualified conclusion that these tests demonstrate that the Epicor-II spent ion exchange media can be successfully solidified in cement appears to be unwarranted. Through a full-scale testing program, some of the deficiencies of the full-scale waste form may be resolved by simple technical modification or implementation of a process control program. Met-Ed/GPU had recognized the need for additional full-scale testing. Further, conflicting results of the screening and primary phases of the Met-Ed/GPU test program and the general conclusion of the Met-Ed/GPU study are noted in this report.

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REVIEW OF A TEST PROGRAM FOR QUALIFYING THE SOLIDIFICATION OF EPICOR-II RESINS WITH CEMENT

1. INTRODUCTION

In an effort to define the parameters necessary for the solidification of spent ion exchange media generated from the operation of the Epicor-II demineralizer system at Three Mile Island, Metropolitian Edison Company (Met-Ed/GPU) contracted with the Hittman Nuclear and Development Corporation (HNDC) to conduct a test program(1) using ion exchange material supplied by Epicor Incorporated. The goal of this program was to define a formulation which could be used to solidify this ion exchange media according to four acceptance criteria. These criteria included:(2)

1. The formation of a freestanding monolith.

2. The absence of free liquid after solidification.

3. The ability of the solidified composite to withstand immersion in water.

4. A minimum compressive strength of the solidified composite of 500 psi. (It should be noted that this value is an order of magnitude higher than that proposed in the Technical Position on Waste Form(3) (TP).

The material supplied by Epicor for use in the program consisted of six resin mixes denoted by the letters A through F. Two mixes (A and C) were actually single resin types. The A-mix was an anion resin in the OH^- form: the C mix was a cation resin in the H^+ form. The B-mix was a mixed bed resin with the cation component in the H^+ form and the anion component in the OH^- form.(1) Mixes D, E, and F were mixtures of several components. The identity of all components and the amounts of all components in a mixture are considered proprietary by the vendor.

A detailed description of the original Met-Ed/GPU test program is given in Reference 2. In addition, a summary of the program is given in the final report for the program.(1) The original test program regarding waste solidification consisted of four phases. A screening phase was to be conducted to define regions of acceptable solidification (criteria 1 through 3 above) for each of the six mixes. In the second, "primary," phase of the program, the selected formulations based upon the results of the screening phase were tested for compressive strength in order to select an optimum formulation for each mix. The third phase of the program consisted of selective tests to determine the ability of various formulations to solidify ion exchange materials which also contained oil, decontamination chemicals (Radiac Wash) or both, and the sensitivity of the solidification parameters to changing the cement used from Portland Type I to Types II or III. The fourth phase was a full-scale test solidification.

The results of the first three phases of the test program and a recommended formulation for the solidification were reported in Reference 1. During the course of this testing program events, most importantly the acceptance of the highly radioactively loaded Epicor-II liners by the DOE, lead to the truncation of the full-scle testing phase. Results of a single full-scale solidification test were not given in this report.

Taken as a whole, this program represented an ambitious effort by Met-Ed/GPU to provide experimental data which would provide the technical basis for the solidification of Epicor-II resins in cement. A large number of samples (over 2000) were fabricated and tested as a part of this program and the acceptability criteria applied to the selection final mix were in excess of any existing criteria for acceptable waste forms. In this light, it is instructive to compare the goals of this program with the stability requirements for solidified waste set forth in the TP. Since the TP postdates the results of the Met-Ed/GPU study, strict comparison of these TP requirements with the test program goals is unfair. However, with the exception of tests for radiation stability, leachability, thermal stability and biodegradation, the objectives of the test program set forth above meet or exceed the requirements of the TP. Two of the other areas, radiation stability and leachability, have been addressed by BNL(4) for one of the mixes (D-mix) tested by the Met-Ed/GPU study. If one were to combine the programs undertaken in the Met-Ed/GPU study and the BNL study, one would go a long way towards demonstrating the stability of a cement/resin composite according to the requirements set forth in the TP. Beyond these requirements, the large number of samples made in the Met-Ed/GPU study make it possible to estimate failure rates for the formulations investigated. This type of analysis is not required by the NRC, but may provide some insight in predicting long-term waste form performance.

In order to assess whether the conclusions reached in Reference 1 are reasonable and whether the information generated in the test program would be sufficient to qualify a process control program for the solidification of Epicor-II wastes, the authors have reviewed the results of the Met Ed/GPU test solidification program. The principal data base for this assessment was volume 1 of Reference 1. The "raw" test data contained in volumes 2 and 3 of the report were not reviewed. The results presented in Reference 1 clearly demonstrate that, with respect to self-imposed acceptance criteria, successful solidification of Epicor-II ion-exchange media in cement can be accomplished at laboratory scale (i.e., approximately 1-L size specimens). It was unfortunate that the full-scale testing phase to verify these laboratory results was not carried out. However, the memorandum of understanding between the DOE and NRC(5) rendered the investigation moot as the Epicor-II prefilters were accepted for disposal by the DOE. Since it is possible to dispose of the second- and third-stage liners as dewatered resin, solidification of Epicor-II liners was not pursued by Met-Ed/GPU. This report concentrated on those areas where insufficient data, which may invalidate the conclusion that a single formulation could be used to solidify actual Epicor-II resins using cement, existed. From this standpoint, the results of the single full-scale test discussed in Section 4 demonstrate the need to perform full-scale testing to demonstrate the acceptability of waste forms. This perspective is consistent with the TP in that it requires testing be done to correlate the properties of small-scale specimens with full-scale waste forms, and, in particular, that the minimum compressive strength of 50 psi be demonstrable throughout full-scale waste forms.

Barletta et al.[6] have stated that the existing literature on the properties of resin/cement composites indicates that these properties are dependent upon the particular resin solidified, as well as the formulation used for solidification. Thus, for completeness, any assessment concerning whether the data base presented by Met-Ed/GPU is sufficient to ensure that satisfactory solidification of actual Epicor-II resins in cement must include a judgment as to whether the material used in that study was representative of the Epicor-II experience. This assessment was not within the scope of the Met-Ed/GPU study. However, information provided by Epicor during the course of the test program resulted in a de-emphasis of work on the C-mix and hence, guided the direction of the test program.

With respect to the solidification of first-stage Epicor-II liners, the question of representativeness of the ion-exchange media tested has, however, been addressed by Barletta, Davis, and Weiss[7] in the form of a proprietary report. They concluded that insufficient information existed to address whether or not the mixes are representative with respect to solidification. It is the authors' judgment that the representativeness issue would need to be resolved to conclude that the Met-Ed/GPU data base is valid for actual Epicor-II resin waste.

2. ANALYSIS OF THE CONCLUSIONS OF THE MET-ED/GPU STUDY

Reference 1 concludes that, based on the testing program, "the resins used in the Epicor-II system at Three Mile Island Unit-II can be adequately immobilized in cement of Types I, II, and III." It further recommends a formulation containing resin, water, cement, and sodium metasilicate ("metso beads") in the following weight ratio 350: 153 (±25): 525 (±25): 52.5 (±2.5). The rationale for choosing this particular formulation is not explicitly discussed in Reference 1. It must be assumed that this conclusion is based upon the results of the screening and primary phases of the program. The formulation recommended from both the screening and primary phases of the test program are listed in Table 2.1. It can be seen from Table 2.1 that this formulation corresponds to that recommended for mixes D, E, and F from the primary phase. Based on the analyses of the screening tests, this formulation is outside the recommended range for solidification of both the A and B mixes. No formulation was recommended for C-mix. During the course of the test program, it was learned that D, E, and F mixes were "representative" of the actual Epicor-II liners. The test program therefore, changed direction to emphasize the D, E, and F mixes. It would appear, however, that the formulation generally recommended by Met-Ed/GPU in the conclusion section is inconsistent with the results of the primary and screening tests for the A-, B-, and C-mixes.

In general, the results of the screening and primary test phases provide substantial evidence that A, B, D, E, and F mixes can be solidified at laboratory scale with cement. C-mix might be solidified with cement, but not within the range of compositions explored within the test program. The "generally" recommended formulation, it would appear, was based upon the D, E, and F mix results, as these mixes were believed to be more "representative" of the actual Epicor-II resin waste.

It may be that there is no unique formulation which can be used to assure successful solidification of a wide range of ion-exchange media at high packing efficiency. Such a conclusion may be drawn from the results of both the primary and screening phases of the testing program. This result is consistent with the conclusion reached by Barletta et al.(6) based upon the existing literature. It may also be seen by comparing the solidification region studied by Met-Ed/GPU with several other studies of organic resin/cement compatibility available in the literature. The information assembled to date is summarized in the three-component diagram shown in Figure 2.1. Three regions of compositions are shown: the solidification region of the Hanford Engineering Development Laboratory (HEDL),(8,9) the solidification region reported by Christensen,(10,11) and that explored by Met-Ed/GPU.(2)

The results of the HEDL investigation(8) of resin/cement compatibility are replotted. The region between the maximum and minimum water lines were reported to produce a solidified product. The only stated criterion for solidification was that enough water was present to mix (minimum water line) but not enough water to cause free water (maximum water line) to exist after solidification. It should be noted that this is a much less stringent criterion than those applied in the Met-Ed/GPU study. Compressive strengths of solidified composites varied over the range of 20 to 1500 psi. In general for a given loading of dewatered resin and cement, the minimum water composites exhibited higher compressive strengths than the maximum water composites. In this reference and the subsequent progress report,[9] which summarized the results of ancillary leaching experiments, it was stated that some composites made within these limits of acceptability expanded and fragmented upon immersion in water. Unfortunately, a detailed reporting of those compositions which failed was not made. One failed composition was reported. It is represented on the diagram by a circular point. Two other compositions, obtained from Reference 8, for specimens which were used in leach testing, are represented on the diagram by the square and triangular points.

Table 2.1

Recommended Formulation From the Primary and Screening Phases of the Test Program

Mix	Component	Weight (g)	
		Screening Phase	Primary Phase
A	Resin	350	350
	Water	131-146	146
	Cement	340-450	450
	Metso beads	0	0
B	Resin	350	350
	Water	131-146	146
	Cement	300-450	525
	Metso beads	30-45	52.5
C[a]	Resin	350	---
	Water	146-161	---
	Cement	375-495	---
	Metso beads	75-99	---
D	Resin	350	350
	Water	146-161	153
	Cement	450-660	525
	Metso beads	45-66	52
E	Resin	350	350
	Water	146-161	153
	Cement	450-660	525
	Metso beads	45-66	52
F	Resin	350	350
	Water	146-161	153
	Cement	450-660	525
	Metso beads	45-66	52

[a]No formulations were recommended for C mix in Reference 1. Ranges given are those of the region of highest success in the screening test phase. Additional effort was not invested to determine a formulation for C-mix since it was learned after the test program began that C mix was not representative of actual Epicor-II resin waste.

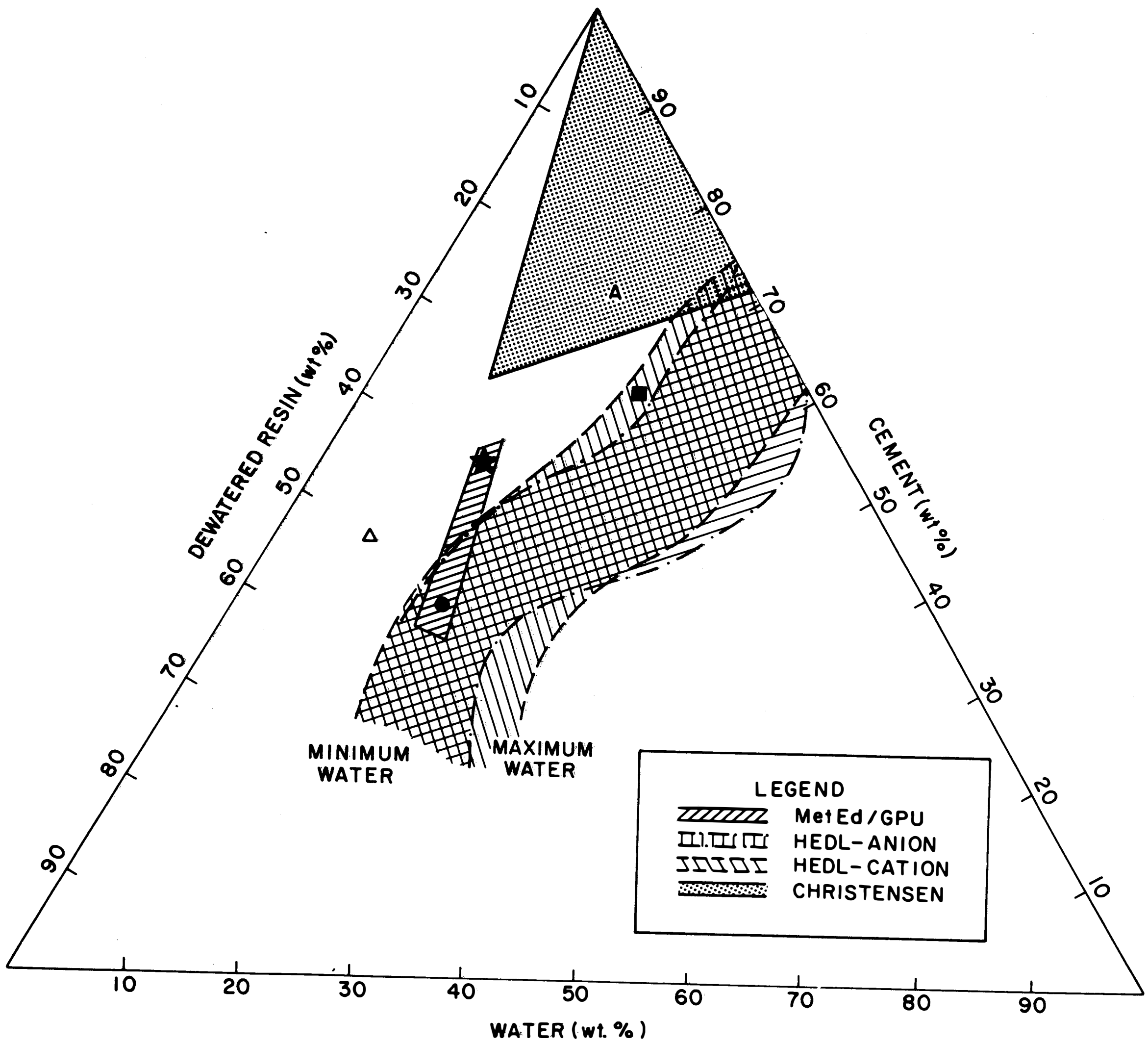

Figure 2.1 Plot of solidification regions studied by HNDC,[1] HEDL,[4,6] and Christensen.[10,11]

Triangle A in the diagram represents the region of acceptable resin/water/cement compositions reported by Christensen.[10,11] This region was constructed from data given in both References 10 and 11. To replot the data of Reference 9, reported as percent dry resin, a weight increase for the swollen resin of a factor of two was assumed, and the water content was correspondingly decreased. For example, Christensen[10] reported the following specific composition: 65 weight percent cement, 22 weight percent water, and 12 weight percent dry resins (calculated). The following composition variables were used in preparing the diagram: 65 weight percent cement, 10 weight percent water, 24 weight percent dewatered resin.

Christensen states that the triangular region A reflects the operating experience in the solidification of actual PWR and BWR organic ion exchange resins. It should be noted that this cement solidification process includes the addition of properietary chemical(s) and an "integral waterproofer" (possibly an organic polymer). This water proofing is claimed to reduce the water permeability of the resulting waste form and thereby eliminate swelling and cracking of the waste form due to absorption of water. These additional components in the mixture may well enhance the mixability of the low water composites in this region. The following observations were also reported. Core samples (0.1 m diam. x 1 m length) taken from solidified resin/cement composites did not exhibit any change or tendency to disintegrate after two years of water immersion. Compressive strengths varied over the range of 5000 to 7000 psi. A sectioned full-scale (1.2 m cube) waste form appeared to have a homogeneous distribution of resin in cement. Unfortunately, the specific types of resin solidified and the details of testing were not reported.

The last region shown in Figure 2.1 has been explored by the Met-Ed/GPU study. Only those resin/ water/cement compositions without additives are represented by the shaded region. Inclusion of an additive (sodium metasilicate) with the cement (that is, the sum of cement plus additive plotted versus dewatered resin and water) extends the region slightly toward the 100% cement apex on the diagram. The point marked by a star is the formulation recommended by HNDC in the conclusion of Reference 1. For this specific point, the weight of additive has been included in the amount of cement plotted.

Based upon the data shown in Figure 2.1, the following observations have been made.

- The HEDL and Christensen regions only marginally intersect. On available information, a definite explanation of this apparent discrepancy cannot be constructed. It may depend on the following: HEDL minimum water mix criteria, types of cement and resin used in the studies, and "additives" (type(s) and amount(s) are proprietary and not accounted for in the diagram) in Christensen study.

- The Met-Ed/GPU region of investigation is based on HNDC operating experience.[2] The region being investigated by Met-ED/GPU only partially intersects with the HEDL region. Further, the region of the Met-Ed/ GPU test appears to include the reported HEDL composition, which underwent catastrophic failure (see Figure 2.2). The intersection occurs in a region of low compressive strengths as reported by HEDL. However, low water composites generally exhibit higher compressive strength than high water composites of equivalent resin/cement loading. This variation in behavior may be due to the differences in the resin solidified in both studies.

- There is no overlap between the Met-Ed/GPU tests and the stability region located by Christensen. Investigation in this area would have most certainly reduced the packing efficiency below the 70% criterion used by Met-Ed/GPU for an acceptable solidification formula.[1] However, no technical basis exists for maintaining this criterion.

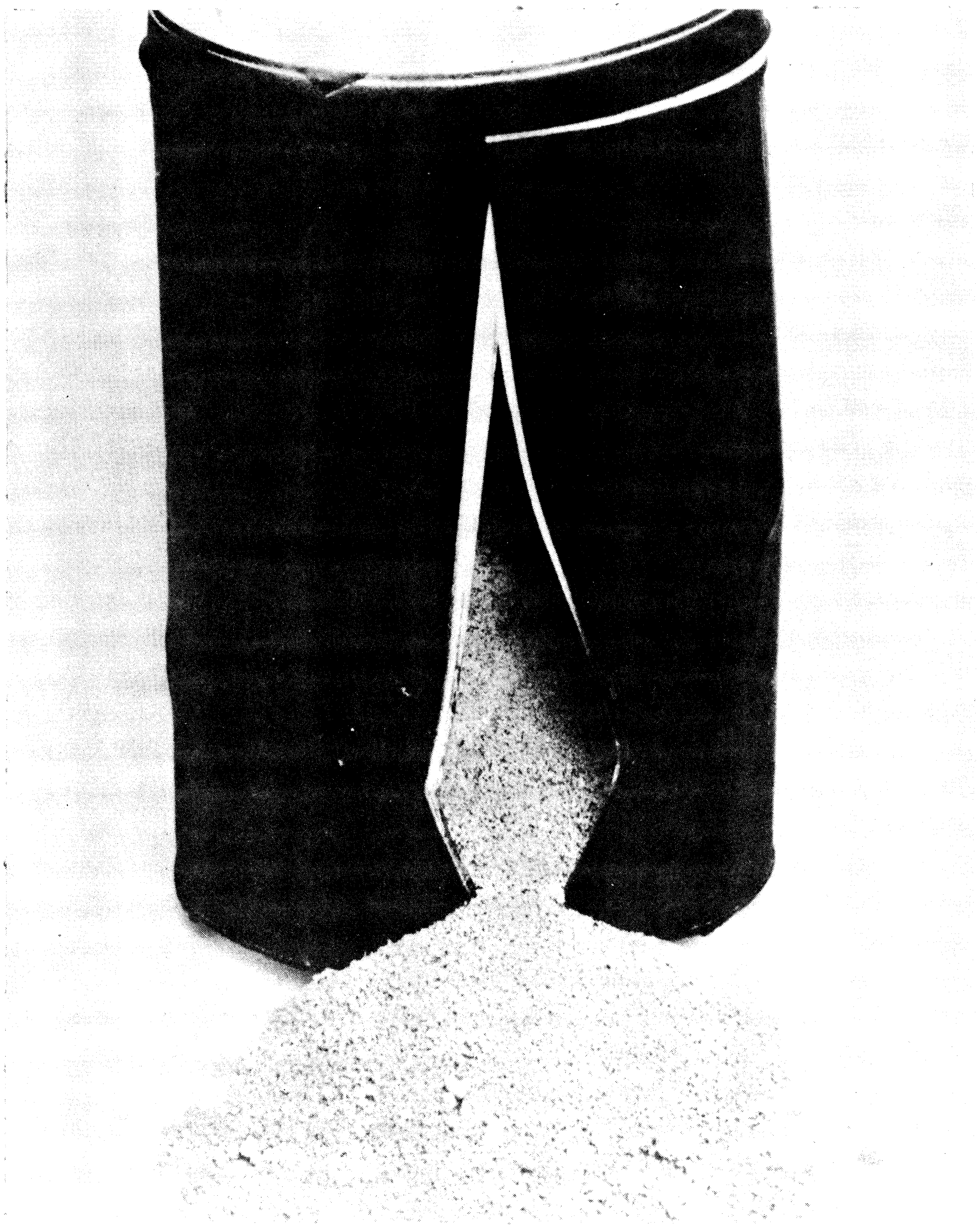

Figure 2.2 Ruptured can and pulverized cement due to swelling of anion exchange resin. Taken from HEDL-TME-77-74.

3. ADDITIONAL COMMENTS ON THE SCREENING TESTS, THE PRIMARY TESTS, AND THE SOLIDIFICATION OF ION-EXCHANGE MEDIA CONTAMINATED WITH OIL AND RADIAC WASH

In addition to the evaluation of the conclusions and recommendations of the Met-Ed/GPU solidification test program presented in the previous section, specific comments on the screening and primary test phases of the program as well as the solidification tests for resins contaminated with oil and Radiac Wash are presented here. These comments result from an evaluation of the data presented to determine if the recommended formulations were consistent with both the small-scale test results and the Med-Ed/GPU acceptability criteria given in Section 1. It should be noted, however, that such an evaluation is secondary to the issues discussed in the preceding section.

3.1 Screening Test Phase

The purpose of this phase was "to determine a broad range of cement ratios ...that would produce a freestanding monolith with no free water."(1) A range was recommended for all mixes except the C-mix (see Table 2.1). Review of the results of screening tests, however, raises a number of questions. Within the recommended ranges, samples were fabricated which were hard to mix or which fell apart upon immersion in water. For example, replicate samples containing A-mix at specific formulations, which were reported to be hard to mix in one experiment (two-day cure), were not reported to be hard to mix in another experiment (nine-day cure). As another example, for B-mix, one out of three samples failed the immersion test after a two-day cure, while only 1 out of 18 fabricated using D-mix failed the immersion test. Based upon this data and the acceptability criteria used for these tests, the reasons for recommending any particular region for the primary phase testing, seem arbitrary. Given the observed failures, narrower regions containing less or no failures might have been preferable for study in the primary phase.

The existence of failed samples within the regions recommended for the primary test, points to a key problem with both the screening and primary test phases. In the screening tests, the maximum number of replicates was three. These replicates were an accident of the original depletion procedure which varied the chemical loadings on the resins only slightly. Given the results of the screening phase, it is unclear what the expected failure rate might be for any series of samples prepared in the recommended range. This is an assessment which should have been provided by Met-Ed/GPU as a part of the program. Indeed, an experiment which might allow for such an assessment was performed as a part of the screening phase tests. For a single formulation of D-mix (350:146:450:10), 10 identical samples were fabricated and immersed in water after curing two days. One of the samples crumbled. Assuming the process could be scaled to full size, this suggests that a failure rate of about 10% might be anticipated.

This failure rate is only inferred from the Met-Ed/GPU study. Consideration of the process and quality assurance procedures required was clearly outside the scope of that study. However, these results point an important issue not addressed in the interpretation of the results of the testing program by Met-Ed/GPU nor, for that matter, in the TP. The TP recommends a number of tests which should be performed in order to assure the long-term stability of Class B and C wastes. The implication is that all such waste forms disposed of in shallow land burial must meet the stability criteria. Since non-destructive testing of all waste is clearly impossible, this compliance must be demonstrated statistically and ensured by quality assurance procedures. Thus, as parameters relevant to the long-term stability are measured, e.g., compressive strength, the variation in these parameters become a part of the reliability assessment necessary to estimate the lifetime of the stabilized waste after burial. Acceptable variation in these parameters would then be tied to the particular failure analyses performed. It must be noted that this reliability assessment is <u>not</u> required by the TP, however, given the absence of realistic testing from which long-term behavior can be predicted, reliability assessment may be a means to provide reasonable assurance that long-term stability can be expected for a given solidified waste.

For the Epicor-II prefilters, once they have been solidified in cement, these liners would be considered as Class C, intruder waste, according to 10 CFR Part 61. As such, stability for 300 years would be needed for this waste. A risk assessment for these wastes is also outside the scope of this work, however, if the failure rate observed in the screening phase were applicable to the full-scale waste forms produced at the recommended formulation, it is our concern that a 10% failure rate may not provide reasonable assurance of long-term stability.

3.2 Primary Test Phase

The purpose of the primary test phase was to select a final mix ratio for each of the six mixes within the ranges recommended as a result of the screening test phase. The chief criterion to be used in this phase was the compressive strength of the composites. With this purpose in mind, the recommended mix ratios from this phase were reviewed. Two inconsistencies between the results of the primary and screening phases were evident. With respect to the solidification of A mix, one-third of the samples prepared at the formulation recommended in the primary test phase failed in the screening test phase after a two-day cure. The sample was characterized as crumbly and was reported to have crumbled during water immersion. For the B-mix, the formulation recommended in the primary phase falls outside the region recommended in the screening phase. In the screening phase, one sample fabricated at this particular formulation was characterized as hard to mix and one nine-day cure specimen crumbled in water. These discrepancies were not addressed in the summary report on the test program. Given the failures observed for samples fabricated using the recommended formulation during the screening phase, it is difficult to see how the formulations selected for A-and B-mixes can be recommended as an optimum to achieve solidification.

With respect to the tests on composites fabricated with the D-, E-, and F-mixes, no apparent discrepancies between the screening and primary test phases were noted. The test procedure used, however, did not generate data on the compressive strength of a significant number of samples having identical formulations, curing, and post-cure treatment to enable an estimation of the variation to be expected in the compressive strength. A single, unidentified formulation of D-mix was tested using 24 replicate samples. This test showed a range in compressive strength from 910 psi to 1800 psi.(2) The mean compressive strength observed was 1470 $\pm$ 200 psi. This test indicates that, for the particular formulation tested, a variation in compressive strength is to be expected. It should be noted that without additional verification this result should not be used to predict the variation in the compressive strength that can be expected for composites fabricated from other resin mixes. However, all compressive strengths measured in the Met-Ed/GPU test program are far in excess of the 50 psi value specified in the TP.

A related comment might be made regarding the recommendation made on the use of Portland types II and III cement.(1) Again, this recommendation was based on the results of 24 replicates fabricated from D-mix at some unspecified formulation. Given the variation in the properties of resin/cement composites observed in the Met-Ed/GPU solidification test program, extrapolation of the results of this test to other resin mixes and/or formulations may be unwarranted. Thus, the conclusion in Reference 1 that actual Epicor-II resin wastes can be "adequately immobilized in Portland cement of types ...II and III," requires further verification by experiment.

3.3 Resin Solidification Tests With Oil and Radiac Wash Contaminants

Tests in this category are comprised of a very limited number of experiments. For the solidification tests with oil, samples of D, E, and F mixes were solidified along with an oil contaminat comprised of 50 volume percent turbine lube oil and 50 volume percent hydraulic oil. Solidifications were performed at two levels of oil contamination: "trace oil" which contained 1 weight percent of the resin weight as oil (six samples) and "maximum oil" which contained between 17 and 23 weight percent of the resin weight as oil (8 samples). In the "maximum oil" tests, only E mix was used and samples were solidified with and without an emulsifier.

Samples were also prepared by first passing 660-mL Radiac Wash through either D, E, or F mix prior to solidification. A total of 28 samples were prepared. Twelve of the samples were rinsed with Radiac alone. A second set of 16 specimens had "trace levels" of oil (1 weight percent) added to the mix prior to solidification.

Given the limited number of samples and tests performed, the conclusions drawn by Met-Ed/GPU in this section of Reference 1 can, therefore, only be regarded as tentative. Samples contaminated with oil were only tested for stability will respect to water immersion. Based on these tests, it was concluded that up to 17% oil with respect to the weight of the resin could be solidified. No experimental evidence was provided for the maximum amount of oil that could be incorporated with mixes other than E mix.

The results of the limited scoping experiments indicated a potential problem in solidifying resins contaminated with Radiac Wash. The results of compression tests carried out on four samples of D-mix containing oil and contacted with Radiac Wash indicated that for the particular formulation tested high strength (1400 to 1920 psi) can be obtained however. Since no chemical analysis was done on the Radiac Wash solutions before and after contact with the mixes, the amount of Radiac Wash incorporated in the composites is unknown. The extent of the problem in solidification, as well as potential solutions to it, need to be investigated quantitatively before the numerical tolerance of the solidification process to the contamination by Radiac Wash can be determined.

4. FULL-SIZE LINER SOLIDIFICATION

Any acceptable formulation for the cement solidification of Epicor-II resins would have to be verified by full-scale testing. As has been already noted, based upon events that transpired during the test program, the full-scale test phase was not completed. Only one attempt was made to solidify the contents of a 4-ft-diameter by 4-ft-high prototypic cylindrical liner by Met-Ed/GPU as a part of this test program. Since the test procedure and the results of this full-scale test were not reported in Reference 1, a brief description of the test will be given. In addition, we have included copies of the pertinent progress reports on the solidification test program prepared by GPU concerning the full-scale solidification test in Appendix A. This work is reviewed here to indicate the need to perform full-scale testing.

The full-scale solidification of a modified liner containing Epicor-II type ion exchange material was conducted on November 12, 1980. This liner had previously been used for flow testing as a part of the Met-Ed/GPU resin test program. The solidification composition used in this test contained ion exchange material, water, cement (Portland Type I) and sodium metasilicate in the weight ratio of 350:153.5:514:51.4. Although this formulation contained slightly less cement and sodium metasilicate than the optimum formulation recommended in the conclusion of the final report on the Met-Ed/GPU solidification test program,[1] it is within the recommended ranges for all waste form constituents. It was expected that this formulation would result in a packaging efficiency of between 68 and 69%. Based on the history of this prototypic liner in the flow testing program and the liner design itself, Met-Ed/GPU and its contractor do not believe this full-scale testing provided a reasonable simulation of actual Epicor-II liners. Given this belief, the results of this full-scale solidification test map have limited applicability to assessing if the formulation recommended in the screening and the primary phases of the test program can be scaled to full-scale. Nonetheless, the specifics of the test are presented below.

Although a part of the resin solidification program, this test was not representative of the actual solidification process proposed for use at TMI. It differed in three major respects. First, solidification of Epicor-II ion-exchange media would most likely be accomplished by first sluicing the media from the existing liners into new liners or by a modification of the existing liners to allow for mixing. Hence, the specifics of the liner design, underdrain, and mixing systems cannot be specified, and the design tested is just one of many possible configurations. Second, modification in both the Hittman procedure and the liner configuration were made in the actual input connections for material and for recirculation of liquid through the underdrain. These modifications were made for the purpose of the test and were not claimed to reflect what would be the expected configuration or procedure used for actual Epicor-II liner solidification. The third distinction was that during this test a water-cement slurry was circulated through the underdrain. This was done in an effort to remove or fix any water left in the underdrain after dewatering. It was expected that this method would be inadequate for the actual TMI liners. Grout injection has been suggested as a preferable alternative for handling any problems with the underdrain liquid. However, this alternative would need to be demonstrated as practical for either the Hittman liner underdrains or those in the Epicor-II liners.

In the full-scale test, the addition of the cement, metso beads, and water took a little over an hour, which was somewhat longer than expected. This was due mainly to problems encountered in the cement feed. After solidification, the top of the liner was removed and the surface of the cement inspected. The surface of the cement form had not completely hardened at this time. Traces of cement powder could be seen in the center of the liner, around the mixing shaft. While the presence of unsolidified cement is an indication that the desired formulation may not have been achieved, the observed quantity of dry cement was small compared with the total quantity of cement. Hence, the formulation was probably well within the process tolerance for the amount of cement ($\pm 5\%$).

After a two-day cure, the underdrain was sampled for liquid, the liner was removed and the form sectioned. Approximately two liters of water were released from the underdrain. The water was presumably due to residual water remaining in the underdrain during either the filling of the liner or the recirculation during the mixing. This water was analyzed by both Hittman(12) and BNL for various constituents (Ca^{+2}, Cs^{+}, Na^{+}, K^{+}, and B) and pH. The results of these analyses are given in Table 4.1.

Table 4.1

Results of Analysis of Water Samples From Full-Scale Solidification

	BNL	HNDC
pH	12.3	12.5
Ca^{+2}	0.13 ppm	2.7 ppm
Cs^{+}	0.7 ppm	3.8 ppm
Na^{+}	1.46×10^{4} ppm	1.3×10^{4} ppm
K^{+}	750 ppm	----
B	300 ppm	----

Comparison of these water analyses show large differences in the concentrations of Ca^{+2} and Cs^{+}. The source of this discrepancy is not known. However, both studies reveal significant quantities of Cs in the underdrain liquid. In terms of ^{137}Cs, these concentrations measured by BNL and HNDC would correspond to 0.12 and 0.66 Ci, respectively. Thus, the level of activity which would be present in this liquid (60 to 330 μCi/mL) indicates that had the program proceeded some effort should be made to solidify the liquid in the underdrain. Solidification of the underdrain liquid was not a part of the original test program and is one area which would need further work.

Sectioning of the waste form revealed a 6-in.-high x 4-in.-deep triangular section at the bottom of the resin bed which was unsolidified. This unsolidified area reflects inhomogeneous mixing which could most likely be remedied by a redesign of the mixing system and/or liner.

Core samples which were compressively tested after a two-week cure gave compressive strengths in the range of 514 to 742 psi with an average strength of 618 psi. This strength is above the 500 psi minimum Met-Ed/GPU criterion of the test program, and appears to be consistent with the results obtained for the 7-day cured specimens in the primary phase of the test program at the average chemical loading for resin mixes D, E and F. Further, these compressive strengths are at least 10 times the minimum 50 psi requirement in the TP.

In addition to the compression tests, six specimens from the solidified liner were immersed in water after a two-week air cure. According to the progress report on this experiment (see Appendix A), these samples began "to disintegrate within 15 minutes of immersion." This result is inconsistent with the results of immersion tests on small-scale samples. Since the specimens from the full-size form disintegrated during the immerison test, it is obvious that they would not pass a compression test after immersion. Aside from this study, there is little data in the literature to indicate how the properties determined for laboratory scale specimens scale compare to those of full scale forms. Clearly, from the standpoint of disposal, the properties of the full-scale waste form are of principal interest. Yet, testing to demonstrate these properties is most often done on small-scale forms. This inconsistency is recognized in the TP[3], which requires destructive testing on full-scale waste forms for homogeniety and compressive strength. In this light, the results of immersion tests and compressive strength tests performed on the full-scale waste form in the Met-Ed/GPU study provide a clear indication of how important full-scale verification is. The compression test verified the laboratory-scale testing while the immersion test did not. GPU[13] has recognized the need for additional full-scale testing.

Although this single full-scale test is not believed to simulate actual Epicor-II liners, the results of the full-scale solidification test indicate that the solidification using a composition based on the screening and primary results did not produce an acceptable waste form. The full-scale waste form must be judged as unacceptable based on the Met-Ed/GPU criteria for acceptability given in Section 1. In light of the failure to produce an acceptable solid form in the full-scale test, the conclusion that Epicor-II media can be successfully solidified using the formulation recommended in Reference 2 appears unwarranted. Further, the results of this test indicate that further work to solidify residual liquid in the underdrain should be performed. Some of the shortcomings of the full-scale waste form may be resolved by simple technical modification or implementation of a process control program. Met-Ed/GPU has recognized the need for additional full-scale testing.

5. SUMMARY AND CONCLUSION

The Met-Ed/GPU solidification test program was designed to demonstrate the adequacy of cement solidification for TMI type resin waste. The program's ultimate product was to recommend a formulation or range of formulations for solidification and to provide sufficient technical documentation to assure the formulation(s) ability to fix actual TMI resin waste. This was to be accomplished through a four-phase program including full-scale solidification demonstration. It should be noted that due to the course of events, the program was not completed.

Ion-exchange materials for the program were supplied by the vendor of the Epicor-II demineralizer system. These materials are claimed by the vendor to be representative of the Epicor-II/TMI experience. As discussed in Section 1, the question of representativeness of the materials was outside the scope of the Met-Ed/GPU study. This question has been addressed elsewhere.[3] The effect of property changes that organic ion exchange resins undergo as a result of irradiation to high dose was outside the scope of the Met-Ed/GPU investigation. The consequences to solidification in cement of radiation damage to TMI-type resins has also been addressed elsewhere.[4]

The following observations summarize the conclusions that have resulted from this review.

Screening Test Phase

- The test results, evaluated with regard to the acceptance criteria for this phase, identified regions of high success to be explored in subsequent program phases.
- The results lead to a recommendation, in some cases, of different composition ranges for specific resin types. No recommendation was made for C-type (i.e., cation) resin.
- The results (failures of some replicate specimens) indicate failure may occur in the regions identified for further study.
- Taken as a whole, the results provide additional evidence that no unique compositional range exists that assures adequate solidification of all resin types at high resin/cement loadings. The results corroborate those of other resin/cement solidification studies, and indicate that the formulations recommended are not generic. Thus, as the type of resin to be solidified changes, a reevalution of solidification parameters should be conducted.

Primary Phase

- The test results indicate that, of the formulations tested, it is possible to fabricate small-scale composites which are freestanding, have no free liquid, have compressive strengths significantly higher than those recommended by the TP (50 psi) and can withstand water immersion testing.

- Variations in the compressive strength at the recommended formulation were found and depended on the resin type tested.

- Inconsistencies were found between the results of the screening and primary phase. These are noted in the text of the report.

- The recommendations made in the primary phase of the program, to a certain extent, conflict with the final recommendation of a single, optimum formulation. In particular, descrepancies were noted between the final recommended optimum formulation and the formulations recommended in the primary phase for the A-, B-, and C-mixes.

Full-Scale Tests

- The solidification tests of a single, full-scale sample using a formulation near the recommended formulation produced a composite which could not meet the Met-Ed/GPU acceptance criteria of homogeneity or ability to survive immersion in water. It is likely that a redesign of the mixing system and/or modification of the liner used could ensure a homogeneous waste form. The lack of agreement of the results from the small-scale tests with that of the full-scale test with respect to water immersion is a different matter, however, and points to the need for additional full-scale testing. This need has been recognized by Met-Ed/GPU.

- The test revealed that large amounts of Cs (in terms of ^{137}Cs, 0.12 to 0.66 Ci) can be expected to be released to the underdrain during solidification. Solidification of any liquid in the underdrain, then, is a problem which must be solved if cement solidification of first-stage Epicor-II liners is to be considered an option. The prototypic liner design used in the solidification test resulted in approximately 2 L of free liquid in the underdrain. This volume of liquid is expected to be dependent upon the particular solidification liner used. Hence, the question of free liquid in the underdrain can only be addressed realistically once a liner design is chosen.

General

- The use of a failure rate, for example, the number of waste forms in a set which failed to pass an immersion test, to judge a waste forms' acceptability for shallow land burial or to act as input into a reliability analysis, was not a part of the GPU/Met-Ed solidification test program nor could it be addressed adequately in the present review. Further, it is not a requirement for waste disposal. It is felt, however, that this generic subject should be addressed and we recommend additional work be performed (by DOE, etc.) in this area.

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APPENDIX A

PROGRESS REPORTS FOR THE SOLIDIFICATION TEST PROGRAM

1. Week Ending November 14, 1980.
2. Week Ending November 26, 1980.

HITTMAN TEST PROGRAM

Progress Report

for

Week Ending November 14, 1980

1. On November 12, 1980, the modified 4x4 EPICOR II liner underwent solidification. Minor problems were encountered during the demonstration but were rectified. Water, cement, and metso addition were simulated to approximate the field solidification process as closely as possible.

2. On November 14, 1980, the shell of the liner was removed by cutting. The wasteform observed was a monolith with the following characteristics:

   a. Approximately two (2) liters of water were released when the liner was cut.

   b. A 6" high, 4" deep area around the bottom of the monolith remained unsolidified. It appeared that the resin never mixed with the cement in this area. Suface crumbled when touched by hand.

   c. Triangular sections from the side showed the presence of air bubbles within the monolith. While these are small enough and would probably not effect the compressive strength of the monolith, they do not, however, meet the "No Voids" criteria of the test document.

   d. The top of the liner appeared to have a crusty layer rather than a firm, hard surface found in the middle.

   e. Resin distribution within the solidified part of the monolith seemed fairly uniform.

3. Four (4) vertical and four (4) horizontal core samples, 3" in diameter and 6" high, will be taken from the monolith. Of these, some will be immersed in water and others compressively tested to compare the properties of the monolith with the results of the screening and primary tests.

Arshad Nawaz
November 17, 1980

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HITTMAN TEST PROGRAM

Progress Report

for

Period Ending November 26, 1980

1. The core samples (6" high x 3" diameter) were allowed to cure in air for approximately two weeks (11/12/80 through 11/26/80) to simulate the screening and primary tests.

2. Six samples were immersed in water on 11/26/80 and started to disintegrate within 15 minutes of immersion.

3. Seven samples were compressively tested to destruction. Compressive strength varied from 514 psi to 742 psi, with the average around 618 psi.

4. The examination of the crushed samples showed a discoloration of the core. Since water was used to provide cooling for the bits during coring, it was assumed that the discoloration was due to water that had penetrated the center. Hittman was directed to let the remaining samples cure in air for a further seven days before compressively testing.

5. A draft of the final report is tentatively scheduled to be distributed by the end of December.

Arshad Nawaz
Arshad Nawaz
December 1, 1980

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The results and recommendations of the resin solidification test program conducted by Metropolitan Edison Company are reviewed. The original purpose of this program was to recommend a formulation or range of formulations suitable for the cement solidification of first-stage Epicor-II liners generated during cleanup activities at Three Mile Island. This was to be accomplished through a systemmatic laboratory and full-scale testing program using ion-exchange materials supplied by Epicor, Incorporated. Events, however, caused the truncation of the full-scale testing. Hence, a formulation was recommended based upon the results of laboratory scale testing. Failure to achieve satisfactory solidification in a single full-scale test using this formulation was observed. The unqualified conclusion that these tests demonstrate that the Epicor-II spent ion exchange media can be successfully solidified in cement appears to be unwarranted. Through a full-scale testing program, some of the deficiencies of the full-scale waste form may be resolved by simple technical modification or implementation of a process control program. Met-Ed/GPU had recognized the need for additional full-scale testing. Further, conflicting results of the screening and primary phases of the Met-Ed/GPU test program and the general conclusion of the Met-Ed/GPU study are noted in this report.

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