

THE EFFECT OF CURE CONDITIONS ON THE STABILITY OF CEMENT WASTE FORMS AFTER IMMERSION IN WATER*

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ABSTRACT

We investigated the effects of curing conditions on the stability of cement-solidified ion-exchange resins after immersion in water. The test specimens consisted of partially depleted mixed-bed bead resins solidified in one of three vendor-supplied Portland I cement formulations, in a reference cement formulation, or in a gypsum-based binder formulation. We cured samples prepared using each formulation in sealed containers for periods of 7, 14, or 28 days as well as in air or with an accelerated heat cure prior to 90-day immersion in water. Two cement formulations exhibited apparent Portland-cement-like behavior, i.e., compressive strength increased or stabilized with increasing cure time. Two cement formulations exhibited behavior apparently unlike that of Portland cement, i.e., compressive strength decreased with increasing cure time. Such non-Portland-cement-like behavior is correlated with higher waste loadings. The gypsum-based formulation exhibited approximately constant compressive strength with cure time. Accelerated heat cures may not give compressive strengths representative of real-time cures. Some physical deterioration (cracking, spalling) of the waste form occurs during immersion.

INTRODUCTION

According to 10 CFR Part 61, when considering the near-surface disposal of low-level radioactive waste (LLW), Class B and C wastes must meet the structural stability requirements as defined in Section 61.56(b). A stabilized waste form is necessary to limit the loss of trench stability which could lead to water infiltration and possibly radionuclide migration. Further, a stable waste form should maintain its physical dimensions and form for 300 years.

In order to provide guidance to waste generators, NRC has issued a Technical Position on Waste Form which recommends waste form test methods and results acceptable for demonstrating compliance with the waste form stability requirements in 10 CFR Part 61. Included in the test program is the criterion that an acceptable waste form should maintain its gross physical integrity and have a minimum compressive strength of 50 psi following a 90-day period of immersion in water.

Previous studies (1,2) have indicated that the performance of cement-solidified decontamination waste forms in the water immersion test may depend on the cure period prior to water immersion. Curing time has also been reported to affect the release of radionuclides from cemen-

titious wastes. For example, as curing period increased from 0 to 28 days prior to leach testing, the rates of release of cesium, strontium, plutonium and curium decreased (3). Apparently, as the hydration of the cement proceeds, the pore network becomes blocked and thus reduces leaching.

The purpose of this study was to examine the effects of curing conditions on the stability of cement-solidified ion-exchange resins after immersion in water. Test specimens were prepared by solidifying a partially depleted ion-exchange resin mixture in Portland I cement waste forms with nominal 2-in-diam x 4-in-high dimensions using three vendor-supplied formulations--referred to as X, Y, and Z--and a formulation from the literature (1) as a reference (REF). A gypsum-based binder formulation--denoted by G--was also investigated as part of this study although waste forms based on this material are not expected to exhibit Portland-cement-like behavior, i.e., an increase in compressive strength during the first few months of curing. Samples prepared using each formulation were cured for different times or under different conditions prior to immersion in water. The performance of the samples was monitored throughout the immersion period and the compressive

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strengths were measured at the end of the immersion test. Evaluation of the data focused on determining whether or not certain cure conditions can provide more conservative immersion test results.

EXPERIMENTAL

Simulated Mixed Bed Bead Resin Wastes

In this investigation, we used resins typical of the types used for water cleanup in light water reactors, namely, Amberlite IRN-77 (Rohm and Haas) cation exchangers which were supplied in the H^+ form and Amberlite IRN-78 (Rohm & Haas) anion exchange resins which were supplied in the OH form. Since it is likely that power plant resins will be somewhat expended, the cation exchange resins were equilibrated with a mixture of various nonradioactive metal ions to expend approximately 40 percent of the exchange capacity. The compounds in the amounts indicated in Table I were added to 9 kg of IRN-77 resins in 20 L of deionized water:

Cesium was added to the resins to simulate what might be used in qualifying tests to measure Cs release from the waste forms. The use of iron, chromium, nickel, cobalt, and manganese was based on the description of ions present on cation exchange resins used to process the primary coolant of a PWR. It appears that the degree of depletion for that particular resin bed varied as a function of resin bed depth. The reported degree of depletion was 10% in the bottom quarter of the resin bed, 17% and 31% in the next two quarters, and 64% in the top quarter of the bed (4).

After equilibrating the cation exchangers with the mixture of metal ions for three days, the pH of the water solution measured 0.75. The cation exchange resins were rinsed with deionized water (eight times) until the pH of the resin rinse water sample was the same as that of the deionized

TABLE I

Compounds Used to Expend Ion Exchange Resins.

Compound	Mass (g)
$FeSO_4 \cdot 7 H_2O$	562.14
$Cr(NO_3)_3 \cdot 9H_2O$	342.95
$Ni(NO_3)_2 \cdot 6H_2O$	57.85
$CoCl_2 \cdot 6H_2O$	23.56
$MnCl_2 \cdot 4H_2O$	11.28
CsCl	85.57

water (pH 5.8). The rinsing was conducted in order to remove the various anions from solution. Since there was little information on the anionic species present in reactor resin waste, the anion exchange resins were used as received (OH-form). Nine kilograms of IRN-78 resins were added to the cation exchangers to make the mixed bed resins. After mixing, the pH of the solution associated with the resins measured 7.4. The resins were stored with sufficient water to cover the surface. The removal of cations from the equilibration solution by the resin was verified by means of atomic absorption spectroscopy; generally, no more than 5% of the metal ions were detected in the solution.

Waste Form Preparation

A small number of samples were prepared using each of the formulations to be included in this study. The samples were prepared, cured, and evaluated according to a vendor's process control program, if available. Based on the results of these solidifications, the quantities of the ingredients needed to prepare 27 forms were determined. It was intended that 25 forms of each formulation would be prepared in a batch mode and the mixture would be poured into molds to make the individual forms. Samples made with vendor Z's formulation were prepared in batches of only two forms at a time because of the rapid set of this formulation. Deionized water was used in each formulation and the composites were prepared with a Blakeslee commercial mixer.

The specimens to be immersion tested were molded in 165-mL polyethylene containers. Each container was sealed with a tight-fitting cap and then wrapped with tape to minimize loss of water vapor while curing. The resulting right cylindrical forms had nominal dimensions of 2-in. diam. and 4-in height. Since the forms were observed to have slightly different heights after removal from the molds, it is likely that a small vapor space with a volume of a few mL above the forms was present in at least some of the containers.

The reference formulation was the same as that used for the preparation of simulated decontamination resin wastes (1). A typical 300 g form consisted of 187.5 g Portland I cement, 75.0 g water, and 37.5 g dewatered resin. The resin was dewatered by means of a vacuum aspirator consisting of a vacuum flask and a Buechner funnel with a dacron filter. The final water content is approximately 50% by weight as determined by oven drying at 90 to 105°C for at least 21 hours, cooling in a desiccator, and weighing. The resin:water slurry was adjusted to pH 12.0 with 1.2 g NaOH. A test solidification was performed to ensure satisfactory solidification. The form was hard with no free liquid after 24 hours.

The batch was scaled to 8400 g, not including the weight of NaOH for the pH adjustment. Forty-three grams of NaOH were added to 1050 g resin in 2100 g water. About 1.5 mL of concentrated HCl was also added for final

adjustment of the solution to pH = 12.0. After equilibrating for about 15 minutes, 5250g Portland I cement was added and the batch mixed for about 4 minutes. Since it was a relatively fluid mix, the batch was stirred after every fifth sample to ensure homogeneity and poured into a mold. There was no evidence of settling out in the reference mix.

The adjustment of the pH to 12 with NaOH is part of a "cookbook" procedure for the reference formulation. Most vendors of cement solidification processes for low-level waste have some similar procedure for raising the pH before incorporation of the resin into cement. Such a procedure will also contribute to loading any unexpended cation-exchange capacity. Based on the experience in the preparation of similar waste forms, such addition of caustic is often necessary to insure good quality waste forms.

The materials and the proportions specified in the vendors' topical reports were used to solidify the mixed bed resins. Because of the proprietary nature of some of that information, we are not providing details here except to indicate the relative waste loadings as follows: Vendor Z Vendor Y Vendor X REF.

Curing Parameters

A set of five replicate waste forms were cured according to five different curing conditions prior to water immersion. Curing conditions were as follows:

1. 7 days at room temperature; forms stored in sealed containers.
2. 14 days at room temperature; forms stored in sealed containers.
3. 28 days at room temperature; forms stored in sealed containers.
4. Air curing; forms stored in sealed containers for 24 hours at room temperature to allow them to set and then removed from containers and stored in an incubator at 20° C and approximately 65% relative humidity for a total of 28 days.

Forms prepared with the Vendor Z's formulation were cured at 60°C for the first 24 h; other samples were cured for 24 h at room temperature.

5. Heat curing

- a. 24 h in a 50°C oven followed by 6 days at room temperature; forms stored in sealed containers.
- b. 48 h in a 60°C oven followed by 5 days at room temperature; forms were stored in sealed containers (Used for vendor Z's formulation samples only)

The heat curing conditions were based upon procedures specified in vendor topical reports. Such conditions were used to cure test samples prior to qualification testing or to cure samples as part of the process control program

to establish an exact formulation for solidification of a specific wastestream.

Immersion Testing

After curing under controlled conditions, the mass, diameter, and height of each specimen were measured before immersion in water. Five replicate forms from each formulation and cure condition were immersed in deionized water, which had been equilibrated to ambient temperature. Since the Technical Position on Waste Form allows immersion testing to be performed in conjunction with leach testing, the immersion water was changed according to the schedule prescribed in the leach test, ANS 16.1. The quantity of water used in all cases was 1750 mL, which is approximately 10 cm x surface area, as specified in ANS 16.1. The water change schedule was as follows: 30 s, 2 h, 7 h, 24 h, 2 d, 3 d, 4 d, 5 d, 19 ± 1 d, 47 ± 1 d, and 90 ± 1 d.

Compression Testing

At the end of the 90-day immersion period, the forms were weighed, measured, photographed, and compression-tested. When removed from the leachate, a sample was wrapped in a damp paper towel for 60 s, then air-dried for 60 s prior to weighing. Diameter measurements were recorded for the top, middle, and bottom of each form. The average of these six values was the mean diameter. The forms were capped with a sulfur mortar capping compound manufactured by Soiltest, Inc. and tested using a Soiltest Compression Tester with a 6-1/8 in. ram. The standard procedure ASTM C39-80 was used to measure the compressive load at failure. Loading rate was calibrated prior to every test and varied from 98 to 158 lbs/s.

The ASTM method C472-79, "Standard Methods for Physical Testing of Gypsum Plasters and Gypsum Concrete" is used for measuring various physical properties, including compressive strength, of gypsum based materials. It is not likely that these procedures would be directly suitable for testing wastefoms since, for example, samples for compression testing are to be dried to a constant weight prior to testing. This procedure might not give an indication of the waste form performance under conditions in actual disposal facilities.

RESULTS

Effect of Curing on Compressive Strength

The observations of degradation of the cured specimens which were made during the 90-day immersion period may be summarized as follows:

- REF Fine cracks in air-cured and 7-day specimens
- X Narrow cracks in heat-cured specimens
 - Hairline cracks in 28-day specimens
 - Bubbling and cracking in air-cured specimens
- Y Extensive cracking

- Z Extensive cracking, spalling, and flaking in most specimens
 - Bubbling and cracking of air-cured specimens
- G No cracking or spalling but surface softening

The mean values and standard deviations of the compressive strength data obtained as described above are summarized in Table II and are discussed in the following sections. Each mean value was the result of averaging five replicates.

DISCUSSION

Based on the observed dependence of post-immersion compressive strength on cure time for specimens cured at room temperature in sealed containers, the five formulations investigated fell into three categories as indicated in Tables III, IV, and V.

The numbers in parentheses refer to the average of four values when the fifth value could be rejected as an extreme

TABLE II

Average Compressive Strength (psi) of Waste Forms Measured After 90 Days Immersion in Water.

	Heat	7-day	14-day	28-day	Air
REF	3240 ± 60	1650 ± 620	2870 ± 400	3140 ± 140	3350 ± 80
X	1300 ± 100	470 ± 50	680 ± 470	710 ± 580	1050 ± 250
Y	820 ± 100	1140 ± 50	1080 ± 50	720 ± 200	750 ± 110
Z	960 ± 330	1000 ± 210	820 ± 170	330 ± 70	700 ± 70
G	90 ± 20	80 ± 10	90 ± 10	80 ± 10	120 ± 30

outlier by means of statistical testing. These outlier values are attributed to inhomogeneous samples resulting from rapid set times and inadequate mixing.

Reference Samples

The compressive strengths of samples cured in sealed containers increased with increasing cure time as might be expected for a typical concrete mix. The compressive strength of the samples cured for 28 days is about the same as those of the heat-cured and air-cured specimens. In part, this is not surprising, since heat cure does, in general, provide a high early strength for concrete. Of particular interest, however, is the high strength of the forms that were cured in air, since some loss of water would be expected

TABLE III

Formulations with Apparent Portland-Cement-Like Behavior Compressive Strength (psi).

	7 Days	14 Days	28 Days
REF	1650	2870	3140
X	470	680 (470)	710 (463)

TABLE IV

Formulations with Behavior Apparently Unlike Portland Cement Compressive Strength (psi).

	7 Days	14 Days	28 Days
Y	1140	1080	720
Z	1000	820	330

TABLE V

Formulation Not Expected to Behave Like Portland Cement Compressive Strength (psi).

	7 Days	14 Days	28 Days
G	80	90	80

during air curing. The loss of mass (presumably water) during curing did not affect the strength of the form but did change the fracture pattern of the forms.

Vendor X

The forms that were cured in sealed containers showed an increase in compressive strength with increasing cure period. This is consistent with changes in compressive strength expected for a typical concrete cured for different periods. The standard deviations associated with the 14 d and 28 d cured samples were large because in each set of samples, one form had an unexpectedly large compressive strength. Heat-cured samples did have higher strengths than those cured 28 days and did not degrade as badly as samples cured under the other conditions. Although the air cured samples were fractured after immersion, they also had higher compressive strengths than the 28-day cured samples.

Vendor Y

The compressive strengths of samples cured in sealed containers decreased with increasing cure period. This is the opposite of what would be expected of a typical concrete, however, considering the amount of the proprietary additive used in the formulation, these forms may indeed not perform like a typical concrete. Samples cured in air had comparable compressive strengths to those cured 28 days, however, they did show the most severe fracturing of the forms. Heat cured samples had compressive strengths comparable to those of forms cured 28 days in sealed containers.

Vendor Z

Compressive strengths of the samples that were cured in sealed containers for 7 d, 14 d, and 28 d decreased with increasing cure period. Since the formulation uses predominantly Portland cement as a binder, the mechanical strengths of the resulting forms might be expected to increase with increasing cure period as for a typical concrete. It appears that this formulation does not produce a concrete-like matrix. The heat-cured samples had compressive strengths which were no larger than those for forms cured 7 days. Air-cured samples did show a relatively large compressive strength even though the samples fractured after the immersion period.

Vendor G

The compressive strengths of the samples were nearly all equal regardless of curing condition. Samples cured in air did have slightly higher compressive strengths than the others. This may be related to the large weight loss of the air cured samples since gypsum plasters and gypsum concretes are tested after curing in a relatively low humidity environment. The air curing procedure resulted in stronger forms than did cure conditions typical of concrete.

The binder material used for the samples contains gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, whereas Portland cement contains cal-

cium silicates; thus the two binders are considerably different. Evidence of this is the observed difference in the pH of the immersion solutions.

Other Considerations

The percentage change in post-immersion compressive strength of the four Portland-cement-based waste formulations with increasing cure time is correlated with the weight percent waste loading. The formulation which exhibits the greatest percentage increase in compressive strength with increasing cure time -- and which is therefore the formulation which exhibits the greatest degree of Portland-cement-like behavior -- is the reference formulation, which is the formulation with the smallest waste loading. The formulation exhibiting the greatest percentage decrease in compressive strength with increasing cure time -- and which is therefore the formulation which exhibits the greatest degree of non-Portland-cement-like behavior -- is vendor Z's formulation, which is the formulation with the highest waste loading. The two other Portland-cement-based formulations, which exhibit intermediate behavior, are formulations with intermediate values of the waste loading. We conclude that at some waste loading (which very likely depends on the particular binder formulation as well as on the particular waste) Portland-cement-based waste forms no longer exhibit Portland-cement-like behavior. (Since waste loadings may constitute proprietary information, we cannot present waste loading data in this paper and must confine ourselves to a qualitative discussion of this matter.)

For some formulations, post-immersion compressive strength testing of heat-cured specimens gives values much larger than similar testing of 28-day-cured specimens, as indicated in Table VI

CONCLUSION

The following conclusions may be drawn from this study:

- Various formulations for Portland-cement-solidified mixed-bed bead resins can result in waste forms which meet the post-90-day-immersion minimum compressive strength criterion of 50 psi.
- Not all Portland-cement-based mixed-bed bead-resin waste forms exhibit Portland-cement-like behavior after immersion (that is, they do not exhibit rapid increase in strength for 25 to 30 days, which is the basis for the 28-day cure time for Portland-cement concretes used in construction).
- Such non-Portland-cement-like behavior is correlated with higher waste loadings.
- Accelerated cures may not give results representative of real-time cures.

TABLE VI

Comparison of Heat-Cured and 28-Day-Cured Specimens Compressive Strength (psi).

	Heat (accelerated cure)	28 Days
REF	3240	3140
X	1300	710 (463)
Y	820 (860)	720
Z	960	330
G	90	80

- Cracked specimens may have compressive strengths above the minimum specified in the Technical Position on Waste Form.
- If the post-immersion compressive strength decreases as the cure time increases, then it may be necessary to show that the compressive strength eventually levels off at some acceptable value.
- Post-immersion compressive strength criteria may need to be supplemented by criteria related to

cracking, spalling, and mode of failure since all of these may be related to leaching and integrity of the waste form.

- Set times should be sufficient to allow for adequate mixing of waste formulation constituents, particularly for full-sized waste forms in the field.
- The nature of the failure under compression may need to be addressed since certain modes (e.g., crumbling) could lead to greater leaching than others (e.g., shearing fracture).

Further details are available in a Brookhaven National Laboratory Technical Report (5).

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