CEMENT ENCAPSULATION OF LOW LEVEL RADWASTE STREAMS[a]

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ABSTRACT

Low level waste streams will be generated during the clean-up of the nuclear fuel reprocessing plant at West Valley, New York. A study was conducted on several presently identified waste streams to develop cement encapsulation recipes with maximum waste loadings. First, jar scale tests were performed on simulated wastes to develop and evaluate cement encapsulation recipes. Using the most promising recipe, full-scale encapsulation tests were then performed. Recipes were developed and successfully tested on the following wastes: 39 and 53 weight percent supernatant (i.e., neutralized nitric acid waste), hydroxide and carbonate precipitated sludge, filter precoat sludge, granular weak-acid resin and granular strong-acid resin. One waste stream, dried supernatant, could not be encapsulated at the desired waste loading using the existing full-scale, high shear mixer.

INTRODUCTION

A commercial nuclear fuel reprocessing plant was operated in West Valley, New York at the Western New York Nuclear Service Center from 1966 to 1972. West Valley Nuclear Services Company, Incorporated, a wholly-owned subsidiary of Westinghouse Electric Corporation and a contractor to the U. S. Department of Energy, was formed to carry-out the solidification of the high-level radioactive wastes generated from the reprocessing operation, and to decontaminate and decommission the equipment and facilities. These tasks will generate a large volume and variety of low-level waste streams which will require disposal in an environmentally acceptable manner. A study was undertaken to determine if several identified low level wastes could be disposed according to DOE regulations. The NRC regulation "Licensing Requirements for Land Disposal of Radioactive Waste," 10 CFR, Part 61, has established a waste classification system based on the radionuclide concentrations in the wastes. According to this classification, the more radioactive wastes (Class B and C) should be stabilized prior to disposal. The lower activity liquid wastes (Class A) do not require stabilization, but should be solidified or absorbed to meet the free liquid guidelines (i.e., no more than 1.0 percent of the waste volume as free liquid). Therefore, depending on the exact radioactive composition of the actual waste requiring disposal, it may be necessary, or at least desirable, to produce a stable encapsulated waste. Cement encapsulation tests were thus conducted on each of the identified wastes to determine a recipe that would result in a stable waste form, with maximum waste loadings.

The low level wastes streams studied were those whose composition have thus far been identified. The wastes examined included: 1) the supernatant from West Valley Tank 8D2, which has been treated by ion exchange to remove much of the radioactivity, 2) the ion exchange resin and the sludge from the low level waste treatment facility (LLWTF) and 3) the ion exchange resin and the filter sludge from the fuel receiving and storage (FRS) pool. The supernatant was examined at three concentrations (39 w/o, 53 w/o and 100 w/o) to determine the effects on encapsulation of volume reducing this waste by evaporation. It is hoped that the volume of supernatant requiring disposal can be significantly reduced by concentrating the waste by evaporation. Using each of the simulated wastes, tests were performed to develop the cement formula required to encapsulate each waste.

This study involved first preparing each of the simulated wastes. Jar tests were then performed to determine cement formulas for encapsulating each of the wastes. The recipes tested were evaluated based on mixability, set time, amount of free standing water, and the stability of the cured waste in water. The most promising recipe developed for each waste was then examined in a full-scale encapsulation test using an available high shear mixer. In addition to testing the recipes, the full-scale tests were

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performed to generate samples required for future stability testing.

EXPERIMENTAL METHOD

Simulated Waste Preparation

The composition used to prepare the simulated supernatant is given in Table I. This composition is based on the most recent analysis of samples taken from West Valley Tank 8D2. In addition to this 39 w/o salt solution, a 53 w/o solution was also examined because earlier results indicated that $NaNO_3$, which is the main component of the supernatant, could be successfully concentrated to about 50 w/o in a forced circulation evaporator. Higher concentration solutions produced hard crystals which were abrasive and could result in pumping and plugging problems. The 53 w/o supernatant required for testing was successfully produced in a pilot-scale forced circulation evaporator.

The dried, or 100 w/o, supernatant was studied because it can be produced in an evaporator such as a scraped-film type. The dried supernatant required for testing was prepared by evaporating the solution listed in Table I to dryness. The dried crystals were then ground to minus 10 mesh. Handling of the dry product was difficult because it was hygroscopic. Even a small amount of moisture pick-up caused the dried supernatant to cake, which would prevent it from being easily transported. To maintain a dry product, it will be necessary to keep it in a moisture-free environment.

The simulated LLWTF sludge was produced by adding, in sequence, the chemicals listed in Table II. The resultant hydroxide and carbonate precipitates and solids were allowed to settle for several days. The top layer of solution was then pumped off. The settled sludge typically contained 5 to 7 w/o total solids. The sludge was then concentrated by evaporation to about 19 w/o. This is the approximate concentration which is presently produced and drummed in the actual system.

TABLE I

Simulated Supernatant

Compound	Wt% (Dry Basis)
$NaNO_3$	53.47
$NaNO_2$	27.62
Na_2SO_4	6.77
$NaHCO_3$	3.78
KNO_3	3.22
Na_2CO_3	2.24
NaOH	1.56
K_2CrO_4	0.45
NaCl	0.42
Na_3PO_4	0.34
Na_2MoO_4	0.06
NaF	0.04
Na_3BO_3	0.05

TABLE II

LLWTF Sludge Waste Compositions

Chemical	Concentration
$Mg(NO_3)_2$	14.8 g/l
$Ca(NO_3)_2$	9.84 g/l
$FeSO_4$	2.44 g/l
NaOH	10.0 g/l
Na_2CO_3	6.36 g/l
Clay	0.90 g/l
Polyelectrolyte	1 mg/l

The LLWTF resin (Duolite CS-100)[b] a granular weak acid resin containing both carboxylic and phenolic hydroxyl groups, was converted from the H^+- to the Na^+-form prior to testing because the actual resin requiring disposal will be in this form. Each liter of resin was contacted with 8 liters of 2M NaOH and then rinsed with deionized water.

The simulated fuel receiving and storage (FRS) sludge was initially produced by mixing water with the filter precoat material (HyFlo Super Cell[b]) and then allowing the mixture to settle for about 1 day. The water layer was then decanted from the settled sludge. The settled sludge contained about 29 w/o solids. A 29 w/o sludge was used in the encapsulation testing.

The FRS resin (Duolite ARC[b]), a granular, strong-acid, phenolic resin was received in the H-form and will require encapsulation in this form. No preparation of this waste was thus required.

Jar Scale Testing

Jar scale tests using a laboratory mixer were performed to evaluate different recipes for encapsulating each of the wastes. For all waste streams, it was attempted to maximize the waste loading in the cement. For liquid wastes, this meant maintaining as high a water to cement ratio (w/c) as possible. The recipes were evaluated based on mixability, set time, absence of free standing liquid, and the physical stability of the final product. The set time of the mix was qualitatively determined by measuring penetration resistance with time. It was desired that the mixture have a penetration resistance of less than 10 psi in the first hour after the start of mixing. This was desired because once the mixture has reached 10 psi resistance it cannot be readily transported. This requirement thus allows sufficient time for the mixture to be discharged from the mixer. It is important to note that experience has shown that the mixture will set more rapidly in a full-scale test. Thus, recipes which set too rapidly in the jar tests could result in a mixture which would set in the full-scale mixer before it could even be discharged.

To evaluate the stability of each of the jar mixtures, two 2.54 cm diameter by 7.62 cm long cylinders were made and fast cured in a warm water bath (@ ~35°C). One of the fast cured samples was then placed in deionized water for 1 week, and any physical changes noted. A mixture was not acceptable if the sample showed any significant deterioration during this immersion test. The most acceptable recipe determined in the jar tests for each of the waste streams was then examined in a full-scale encapsulation test.

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[b] Diamond-Shamrock Corporation

Full-Scale Testing

The full-scale tests were performed in a batch type, high shear mixer that was available at the R&D Center and which will be used at West Valley. A 3600 RPM, 30 hp motor is connected to the mixer impeller shaft through a belt drive that reduces the speed of the impeller to ~2000 RPM. The impeller rotates inside of a bottom casting, shaped like a convolute, similar to a centrifugal pump. This causes the contents of the mixer body to be drawn into the center of the casting and then forced between the impeller and the casting (clearance of ~2 mm), causing a zone of high shear forces. This insures intimate mixing of the various components of the mixture. All of the components for a test were individually weighed out. Generally, the liquid components would be added to the mixer first. The mixer would then be started and the dry components and/or cement would be added manually. The mixer would then be run for, typically, 5 minutes. At the end of the mixing period, the peristaltic valve, at the exit end of the convolute, would be opened and the mixture would be pumped out of the mixer and into a drum. Discharge times of 10 - 20 seconds were typical. The peristaltic valve would then be closed and the mixer rinsed. The mixture was then transferred from the drum into sample molds for subsequent waste form qualification testing.

RESULTS

Jar Tests

Initially, to encapsulate the 39 w/o supernatant relatively small water to cement weight ratios (w/c) were examined because an initial scoping test with sodium nitrate had indicated that the supernatant might act like a water reducing agent. Using a w/c from 0.2 to 0.4, the mixes had poor mixability and excessively rapid set time. To improve mixability, the use of a dispersing agent, Stepantan A[c], was examined. The agent at level of 4 w/o (based on cement weight) did improve mixability and set time but increased the final encapsulation volume by over 40%.

The next two tests were performed to determine if increasing the w/c would improve the set time and mixability, while also increasing the waste loading. At a w/c of 0.6 and 0.7, the mixture showed the desired mixability and set time (i.e., penetration resistance of 10 psi in greater than 90 minutes). Also, samples of these mixtures showed no deterioration during immersion in water for one week. The recipe using the w/c of 0.7 was used in the full-scale tests because of the higher waste loading. The w/c was not increased further to avoid producing a relatively weak product and bleed water.

The initial tests performed on the volume reduced (53 w/o) supernatnat showed that up to a w/c of 0.4 the mixture set up too rapidly. Stepantan A at 2 w/o (based on cement weight) did not improve the set time. Increasing the w/c to 0.6 and 0.7 resulted in acceptable mix time and set times. In addition, cured samples of both recipes showed no deterioration during immersion in water. The recipe with a w/c of 0.7 was used in the full-scale test because of its higher waste loading. Again the w/c was not increased further to minimize the risk of producing bleed water and a weak product.

To maximize the waste loading for the dry supernatant waste, the w/c was kept as small as possible. At a w/c of 0.3 and 0.4 the mixtures became too thick to mix during cement addition. Even the addition of Stepantan A did not help. However, it was found that with both a w/c of 0.4 and 0.5 that by first mixing the water with the cement and Stepantan A and then adding the dry waste, the mixture was mixable, had an acceptable set time and, when cured, was stable in water. The recipe with a w/c of 0.4 and a 4 w/o Stepantan A addition was tested in the full-scale test to maximize the waste loading.

The LLWTF sludge encapsulation tests examined increasing the waste loading by increasing the w/c from 0.4 to 0.9. All recipes showed acceptable mixability and set time. Cured samples of all the mixes showed no physical deterioration during immersion in deionized water for 1 week. Although the mix with a w/c of 0.9 showed acceptable characteristics, the full-scale test was performed using a w/c of 0.8 to avoid the possibility of forming a weak final product.

The initial tests performed on the FRS sludge indicated that at a w/c of 0.3 and 0.4 the recipes were not mixable even with the addition of the dispersing agent, Stepantan A. It should be noted that the sludge itself will not mix until sufficient force is applied to produce movement. Once this yield stress is reached, the sludge will mix freely. In order to mix and encapsulate this waste, it is thus necessary that the mixing device has sufficient shear force. The next tests on the FRS sludge examined adding additional water and Stepantan A to the mixture. Both recipes were mixable; however, the final product had bleed water and was thus unacceptable. The last set of tests examined a w/c from 0.7 to 0.9. The mixtures with a w/c of 0.8 and 0.9 had bleed water. The mixture with a w/c of 0.7 was mixable, had an acceptable set time and did not have any bleed water. The immersion test on this sample showed no deterioration. This recipe was thus used in the full-scale test.

The jar tests performed to encapsulate the CS-100 resin, which is used in the LLWTF, examined increasing the resin to water ratio (r/w) from 1.0 to 1.75 while also increasing the w/c from 0.4 to 0.6. The higher the r/w the greater the waste loading and the thicker the mixture. The w/c was thus also increased to improve the mixability of the mixture. The w/c was not increased above 0.6 because it was felt that a weak product would likely result. In the initial tests, a proprietary agent was also added to the mix. Previous experience has shown that adding this agent to a resin waste will prevent the adverse effects of resin swelling during immersion of the encapsulated waste. That is, without this agent addition some encapsulated resins will swell during immersion in water which results in severe cracking and deterioration of the cement. As well as showing acceptable mixability and set times, fast-cured samples of all the mixtures tested here were stable in water. The recipe with a r/w of 1.75 and a w/c of 0.6 had the highest waste loading, and is thus the most attractive. A test was then performed to determine if this sample recipe could be used without the proprietary agent. A fast cured sample of this mix showed no deterioration during water immersion. The agent was thus not required with this resin. This mixture was retested on a different batch of CS-100 resin, which appeared to be significantly larger in size. Previous experience has shown that the size of resin can effect the characteristics of the encapsulated waste. That is, smaller resin particles tend to

[c] Stephan Chemical Company

result in a more stable encapsulated waste. A fast-cured sample of this mixture was found to be stable in water. Variations in batches of CS-100 resin should not seriously effect the encapsulated product. The full-scale test was performed using a r/w of 1.75, a w/c of 0.6, and no proprietary agent. It should be noted that r/w of 2 was examined, but the resin/water mixture alone was not mixable.

The initial tests performed to encapsulate the FRS ARC resin examined varying the r/w from 1.0 to 1.5 and varying the w/c between 0.4 and 0.6. All of the mixtures set-up too rapidly (i.e., 10 psi penetration resistance in less than 50 minutes). To increase the set time, the use of a retarding agent (Pozzolith 100XR) was examined. The use of the agent at a level of 0.006 ml/g of cement resulted in a set time which was too slow. That is, some of the resin seemed to rise to the top of the waste form, which resulted in a weak top layer. Reducing the additive concentration to 0.003 ml/g of cement seemed to prevent this and thus produce a more uniform product. Again, the proprietary stabilizing agent was used in the initial tests, and the fast-cured samples of all of the mixtures were stable in water. An additional test was performed without this stabilizing agent. The sample produced in this test was stable in water. Based on these results, the recipe for the full-scale test used a w/c of 0.6, a r/w of 1.5 and 0.003 ml of Pozzolith 100XR/g of cement. No stabilizing agent was required.

Full-Scale Tests

A brief summary of the full-scale tests that were run using the most promising recipe for each waste type is given in Table III. The full-scale tests were run primarily to generate samples for the waste form qualification testing that was required. A secondary purpose was to insure that the waste/cement mixtures could be mixed in a high shear type mixer that was available at the R&D Center and is to be used for the actual wastes at West Valley.

From the summary given in Table III, it can be seen that all of the full-scale tests gave acceptable results, except for the test using the dried supernatant and the first test using the LLWTF resin (Test A). The dry supernatant mixture became too thick to mix after only ~36% of the dried supernatant powder had been added to the cement/water/dispersing agent mixture. This amount of material is roughly equivalent to the supernatant without any volume reduction. From the observation of the test, it is felt that the high shear mixer is not the type of mixer to be used to solidify this type of waste, and therefore, no additional testing was done.

The first test using the LLWTF resin (CS-100) was unsuccessful due to the mixture setting-up in the mixer. This could have been caused by the resin loading being too high, or an incomplete rising of the resin after being converted to the sodium form with sodium hydroxide in the mixer. To prevent this happening a second time, the resin loading was reduced to a r/w of 1.5, and the resin was treated with sodium hydroxide in a separate tank so that a flow-through rinsing method could be used. (It should be noted that this procedure would not be necessary with the actual resin, since it is normally in the sodium form when it is exhausted.) The test gave acceptable results.

The tests using the FRS precoat sludge were run on a smaller batch size (37.5 ℓ vs. 75 ℓ) because of the high viscosity of this mixture and the 30 HP motor on the particular mixer used. The normal mixers use a 40 HP motor that would be able to handle a larger batch size.

TABLE III

Summary of Full Scale Test Results

Waste		Set Time To 10 psi Resistance, Hours	Set Time To 6000 psi Resistance, Days	Bleed Water After 1 Day
39 w/o Supernatant		<10	<5	No
53 w/o Supernatant		< 8	<5	No
100 w/o Supernatant[a]		< 1	<5	No
LLWTF Sludge		< 3	<1	No
FRS Sludge		< 1	<1	No
LLWTF Resin	Test A[b]	-	-	-
	Test B	< 3	<1	No
FRS Resin		< 1	<1	No

[a] Too thick to mix before all dried supernatant was added.

[b] Set-up in mixer.

The summary of the successfully run full-scale test recipes is given in Table IV. These can be used to scale up, in a linear relationship, to the desired batch size for these six waste streams.

DISCUSSION

The following waste streams were successfully encapsulated in cement using a full-scale high shear mixer: 39 w/o supernatant, 53 w/o supernatant, hydroxide and carbonate precipitated sludge, a precoat filter (i.e., diatomaceous earth) sludge, a strong-acid granular phenolic resin, and a weak-acid granular phenolic, carboxyl resin. In this study the high shear mixer demonstrated its ability to handle a variety of wastes. This is particularly important at West Valley because it is anticipated that a number of other streams (e.g., uranyl nitrate solution, decontamination solutions, and other ion exchange media) will be generated and require disposal. As these additional waste streams are identified, the same recipe development tests discussed here will be performed.

Testing has been performed on samples generated from the full-scale tests to determine the stability of the waste form. The testing performed followed the technical position developed by the NRC staff to provide guidance on test methods and criteria for demonstrating that the encapsulated waste complies with 10 CFR, Part 61 waste stability guideline. The results of this testing, which are detailed in other papers[1,2,3,4] indicate that the waste forms produced from the high shear mixer using the recipes developed have acceptable stability.

TABLE IV

Summary of Full Scale Test Recipes

WASTE TEST SERIES	WASTE		CEMENT Kg	ADDITIONAL WATER, Kg	ADDITIVES	CALCULATED VOLUME, l	PACKAGING EFF., %[b]
	Kg	l					
39 w/o supernatant	69.44	53.0	60.51	-	-	75	71
53/ w/o supernatant	76.53	54.3	54.67	-	-	75	72[a]
LLWTF sludge	61.31	56.2	62.84	-	-	75	75
FRS sludge	32.05	26.1	32.05	-	-	37.5	69
LLWTF Resin (CS-100)	45.98	41.8	47.36	11.36	-	75	56
FRS Resin (ARC)	49.54	41.8	46.56	15.34	Pozzolith 100XR 139.4 ml	75	56

[a] 106% when based on non-volume reduced supernate.

[b] Packaging Efficiency $= \frac{\text{Original Waste Volume}}{\text{Final Encapsulated Volume}} \times 100$

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