LABORATORY SCREENING OF LOW-LEVEL MIXED WASTE FORMS

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ABSTRACT

The Hanford Site is preparing for the future remediation of single-shell waste storage tanks. The present plan for the double-shell storage tanks is to dispose of the low-level waste in grout and the high-level waste in glass. There is no formal plan for disposal of the single-shell tank wastes. Disposal methods and waste forms are being reviewed and studied before preparing a plan for the single-shell tank materials. To support preparation of the plan, low-level mixed waste forms have been screened in the laboratory as potential candidate stabilization forms for the single-shell tank waste residues.

INTRODUCTION

Most of the bulk volume of waste stored in the single-shell tanks (SST) is low-level liquid or slurry waste with some hazardous chemical constituents. There are several significant different SST compositions and they are generally different from the double-shell tank waste. For this reason the disposal methods and waste forms are being reviewed and studied before preparing a disposition plan for the SST materials. This report describes the low-level mixed waste forms and/or matrices being tested in the laboratory for evaluation as a potential stabilization agent for specific SST waste residues. The waste forms being considered and tested include portland, pozzolan, slag, polymer-modified, gypsum, and other cement-based forms. The primary laboratory screen testing includes general waste product characteristics, leach testing, toxicity characteristic leach procedure (TCLP) testing for hazardous constituents, and compression strength measurements. A summary of the results is included and the better-performing waste forms are determined.

DESCRIPTION OF THE WASTE

The tank waste resulted primarily from fuel fabrication and reprocessing operations where nitric acid solutions were used for dissolving fuel, fuel cladding and scrap fuel. The nitric acid aqueous liquid after processing was neutralized with sodium hydroxide to a high pH (generally 12 or greater), and sodium nitrite was generally added as a steel corrosion inhibitor. The caustic liquid was then evaporated (concentrated) and placed in carbon steel tanks for storage. Several different types of SST waste resulted from the (pre-1980) operations. The concentrate formed both solid and liquid phases. The solid phase contained most of the radionuclides and the heavier elements; whereas the liquid fraction contained the light elements, primarily the soluble sodium salts. This liquid fraction can generally be pumped and is termed the interstitial tank liquid. This liquid fraction and other easily water soluble fractions are looked upon as the low-level waste fraction; whereas the more insoluble fraction contains the bulk of the transuranics and radionuclides except for cesium. This pumpable interstitial liquid is used in this report as the representative low-level waste fraction. Figure 1 shows a schematic of a SST and its contents.

Interstitial Tank Liquid Composition

The interstitial tank liquid is composed primarily of the sodium salts of nitrate, nitrite, carbonate, aluminate, and phosphate. There is free sodium hydroxide and also small amounts of hydrous oxides of iron and manganese. The small amounts of iron and manganese were not considered in this work, because they are not expected to exhibit any negative affects on the cement-based waste forms. Table I (1) gives the interstitial tank liquid composition that was used as the representative low-level waste. Trace chromium, cadmium, and barium were added for performing TCLP testing. Trace cerium (plutonium substitute) and strontium were added as chemical tracers for radionuclides for leach testing.

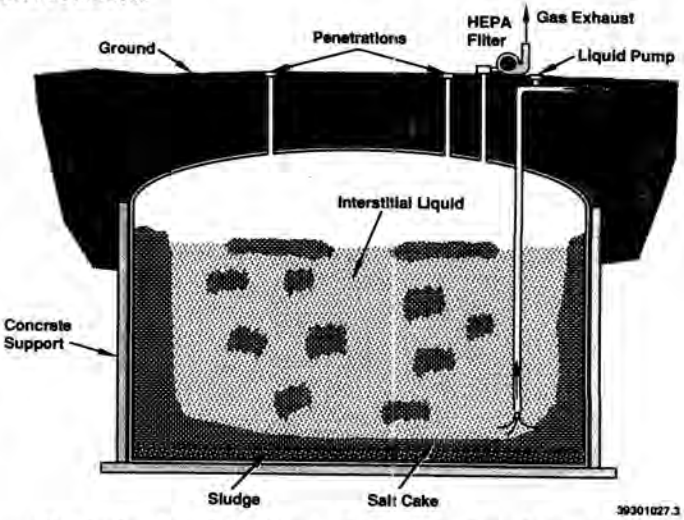

Fig. 1. A schematic of a single-shell tank and contents.

TABLE I
Representative Low-Level Tank Waste
(Interstitial Tank Liquid)

Component	Content (moles/L)
Sodium cation	9.7
Nitrate anion	3.0
Nitrite anion	1.9
Carbonate anion	0.16
Aluminum cation	1.4
Phosphate anion	0.05
Hydroxide anion	3.0

Cement-Based Waste Formulations

The interstitial tank liquid was diluted by taking 666 ml and diluting it to 1 L. This diluted liquid was used as the waste fraction. The cement to be tested was typically added to the diluted waste fraction until a moderate cement slurry (about 50% slump) was produced. Then the slurry was placed in a standard 5.08-cm (2-in) cube or other standard size mold to cure. A 5.08-cm (2-in) specimen was used to minimize the amount of simulant and test cement needed for the comparative tests. Table II gives the liquid-to-cement ratio used, the density of the resulting product, and the diluted liquid and the original interstitial tank waste loadings achieved on a volume basis. Grout for comparison basis typically takes 1.9 million L (0.5 million gal) of tank waste, dilutes it to 3.8 million L (1 million gal), and then produces 4.9 million L (1.3 million gal) of solid. The diluted liquid loading is about 77% and the original tank waste loading about 38%. Figure 2 shows waste loading comparisons for grout and the cement-based waste form candidates.

WASTE FORM TESTING

Samples of the cement-based waste forms listed in Table II were tested for compression strength, leachability (American Nuclear Society [ANS] 16.1), and the U.S. Environmental Protection Agency TCLP (2,3). The U.S. Department of Energy does not require a specific compression strength, only requiring the material to be a solid. The U.S. Nuclear Regulatory Commission (NRC) position test requirement is 0.4 MPa (>60 lbf/in^2) for compression strength on all solids except cement and 3.4 MPa (500 lbf/in^2) or greater is recommended for cement solids cured 28 days. This value was established to ensure there is sufficient cement in the waste form to stabilize radioactive species since structure concrete can reach 34.5 MPa to 41.4 MPa (5,000 to 6,000 lbf/in^2). The higher value also was established as a "maximum practical compressive strength" not just the "minimum acceptable compressive strength" (4).

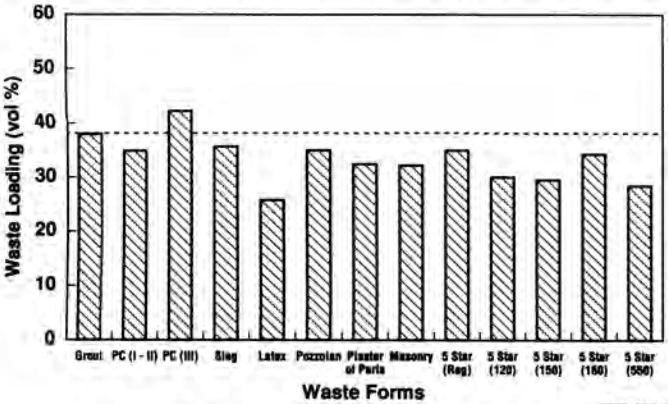

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Fig. 2. Typical loadings for waste form candidates.

The compressive strength results are given in Table III in both lbf/in^2 and the international MPa units and shown in Fig. 3.

LEACH INDICES

Phillips (5) recommended the application of the ANS 16.1 (2) leach test for determining the leachability of commercial nuclear type waste forms covered under Code of Federal Regulations 10 CFR 61 (6). The NRC accepted this recommendation and presently uses this leach test as a part of their Waste Form Technical Position letter (4). This leach test was used as a waste form screening technique. It was applied to each of the cement waste forms tested for compression strength. The NRC position paper calls for a leach index minimum of 6 or greater. The results for the screened cement samples are given in Table IV.

The leach index for sodium represented the leachability of the sodium hydroxide caustic, but also should provide an indication of cesium (^{135}Cs or ^{137}Cs) performance. Cerium chemical tracer was added as a stand-in for plutonium (transuranics). Strontium was added as a chemical tracer for ^{90}Sr. All of the leach indices were above the minimum acceptable level of 6. The highest index average was exhibited by the slag cement. There is actually very little difference in values, but the leach index is a log function, which does tend to minimize differences. The leach index is roughly defined as the log of the reciprocal of diffusivity of the specific ion (nuclide). The index becomes a whole number or decimal rather than an exponential figure, which makes comparisons and listings easy and convenient.

TOXICITY CHARACTERISTIC LEACH PROCEDURE RESULTS

The TCLP tests are necessary to screen for waste forms that are able to stabilize the hazardous chemical components

TABLE II

Cement-Based Waste Form Compositions

Cement Description	Liquid Cement ratio	Density (g/cc)	Liquid Loading (vol%)	Tank Waste (vol%)
Portland type I-II	0.58	1.75	52.4	34.9
Portland type III	0.59	1.85	63.4	42.2
Slag cement	0.67	1.62	53.6	35.7
Latex cement	0.33	1.91	38.8	25.8
Pozzolan	0.56	1.8	53	35
Plaster of paris	0.69	1.45	48.7	32.5
Masonry	0.59	1.59	48.3	32.2
5 Star Grout*	0.40	1.8	52.6	35.0
5 Star Grout (no. 120)	0.41	1.81	43.5	30.0
5 Star Grout (no. 150)	0.42	1.82	44.3	29.5
5 Star Grout (no. 160)	0.24	2.18	51.5	34.3
5 Star Grout (no. 550)	0.41	1.81	42.6	28.4

*5 Star Grout is a trademark of Five Star Products, Inc.

of the mixed waste. The primary toxic elements in the Hanford Site tank waste is typically chromium and lead and sometimes barium, mercury, or silver. The tanks also contain organic species, some of which are toxic; however, pretreatment methods for destroying the organics are being investigated. For this preliminary screening, it is assumed that the toxic organics will have been treated and removed to non-toxic levels.

TABLE III

Compression Strengths of Cement-Based Waste Forms

Cement Description	Compression Strength (lbf/in^2)	Compression Strength MPa
Portland type I-II	1,000	6.9
Portland type III	1,630	11.2
Slag cement	4,250	29.3
Latex cement	630 - 750	4.3 - 5.2
Pozzolan	1,750	12.1
Plaster of paris	130	0.9
Masonry	630	4.3
5 Star Grout	1,130	7.8
5 Star Grout (120)	1,130	7.8
5 Star Grout (150)	1,250	8.6
5 Star Grout (160)	750	5.2
5 Star Grout (550)	1,250	8.6

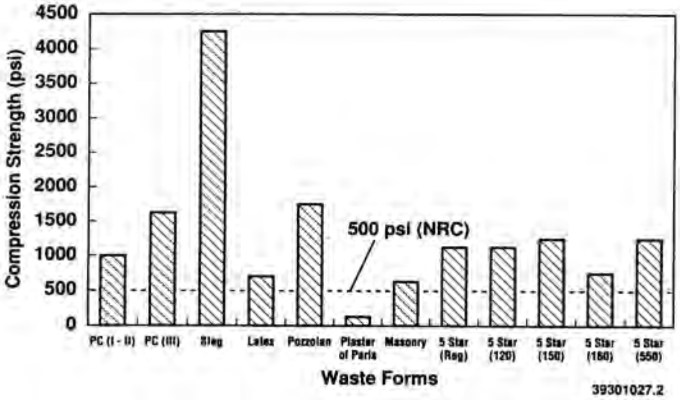

Fig. 3. Compression strength measurements for waste form candidates.

Trace metal compounds were added to provide TCLP test capability. Trace levels of 66 (mg/L) barium, 3.2 (mg/L) chromium, and 0.2 (mg/L) mercury were added to the simulant tank waste. The TCLP extraction limits are 100 (mg/L) for barium, 5 for chromium, and 0.2 for mercury. The TCLP tests were performed on extracts of the crushed cement waste form after a 7-day cure. Even though analytical uncertainty could be at least 20%, the short cure time (7 days compared with 28 days or more) should give conservative results. The results are given in Table V as the maximum computed metal level for the listed TCLP limits.

TABLE V

TCLP Test Results for Cement-Based Waste Forms

	Maximum Computed Metal Content (mg/L)		
Waste Form	Ba	Cr	Hg
Portland type I-II	4,100	33	1,500
Portland type III	5,100	160	1,100
Slag cement	7,900	800	95
Latex cement	8,800	80	290
Pozzolan	3,000	42	1,100
Plaster of paris	31,000	530	143
Masonry	8,700	270	870
5 Star Grout	4,700	64	2,000

SUMMARY AND CONCLUSIONS

The waste stabilization agents screened in this report generally exhibited the following characteristics:

- Moderate to low waste loadings
- Good to excellent compression strengths
- Good leachability
- Acceptable TCLP tests.

The reference waste used in this study (interstitial tank liquid) is considered a "worst case," low-level type waste because of the high chemical content. The high quantity of sodium ion in the waste appears to be at or near the limit that

TABLE IV

Leach Indices for Cement-Based Waste Forms

		Leach Index			
No.	Waste Form Description	Na	Ce	Sr	Avg.
1.	Portland type I-II	10.3	10.0	8.8	9.7
2.	Portland type III	8.7	10.1	9.2	9.3
3.	Slag cement (type III init.)	9.3	10.1	10.8	10.1
4.	Plaster of paris	9.0	10.1	9.7	9.6
5.	Pozzolan	8.6	10.0	9.5	9.4
6.	Latex cement	8.1	9.7	8.7	8.8
7.	5 Star Grout	8.6	10.0	9.2	9.3
8.	5 Star Grout (120)	8.5	9.8	9.2	9.2
9.	5 Star Grout (150)	8.6	9.8	9.3	9.2
10.	5 Star Grout (160)	8.4	9.6	8.5	8.8
11.	5 Star Grout (550)	8.9	9.8	9.7	9.5
12.	Masonry cement	8.7	10.0	9.7	9.5

can be incorporated in cement type stabilization agents. Also, the 3M hydroxide content can limit the amount of other chemicals that can be immobilized by the cements. Therefore, the results reported here are considered conservative.

Waste loadings were compared with grout for comparison purposes. Type III portland cement exhibited the best waste loading and was the only one that exceeded that of grout. Slag, portland type I-II, pozzolan, and a few 5 Star cements exhibited waste loadings at or near 35% compared with 38% for grout. Candidates with waste loadings less than 30% would be difficult to accommodate or justify; other candidates loadings could probably be increased or optimized to higher loadings.

The compression strengths listed in either Table III or Fig. 3 show most candidates exceeded the NRC recommended limit of 3.4 MPa (500 lbf/in^2). Slag cement exhibited the best strength and appears to perform well with the high caustic material. Plaster of paris material was the only candidate exhibiting test samples less than 3.4 MPa (500 lbf/in^2), but it exhibited good TCLP results.

The leach indices measured were all greater than the NRC recommended minimum of 6.0. Slag cement performed best, but all performed adequately. The TCLP results showed generally good stabilization for barium, mercury, and some chromium samples.

Overall the slag cement appears to be the best stabilizer candidate for the simulated interstitial waste liquid. Type III portland cement appeared to be second best.

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