

**THE USE OF TREATABILITY TESTING TO SUPPORT PROCESS
DECISIONS FOR THE TREATMENT AND DISPOSAL OF
TRANSURANIC/ALPHA LOW LEVEL WASTE**

P. R. Lear, R. G. Bennett, J. M. Young
Shaw Environmental & Infrastructure
304 Directors Drive, Knoxville, TN 37923

ABSTRACT

The Melton Valley Storage Tanks (MVSTs) at Oak Ridge National Laboratory (ORNL) contain transuranic and alpha low level radioactive waste. Anticipated treatment of the supernatant decanted from the tanks will involve evaporation of the water and produce a dried salt material. Since the supernatant from the MVSTs contains metals listed in the Resource Conservation and Recovery Act (RCRA), stabilization treatability testing was conducted to verify that these metals could be immobilized in conjunction with the evaporative treatment. The dried salt material from the supernatant was tested to determine the oxidizer classification by the Department of Transportation (DOT). Treatability testing indicated that dried salt material, without any additional stabilization treatment, would not be considered a characteristically hazardous waste under RCRA. The oxidizing solids testing indicated that the dried salt material produced by evaporative treatment of the supernatant would be considered a Category III oxidizer by DOT.

INTRODUCTION

The Melton Valley Storage Tanks (MVSTs) at Oak Ridge National Laboratory (ORNL) contain transuranic and alpha low level radioactive waste. The supernatant decanted from the MVSTs is a mixture of primarily dissolved sodium nitrate salt and lesser amounts of potassium nitrates, sulfates, phosphates, and carbonates. The anticipated treatment of the supernatant will involve evaporation of the water, leaving salt material which will be approximately 95% sodium nitrate. Since the supernatant from the MVSTs contains metals listed in the Resource Conservation and Recovery Act (RCRA), stabilization of these metals may be required. The dried salt material must also be tested to determine the oxidizer classification by the Department of Transportation (DOT) (1).

Stabilization, or chemical fixation, is a treatment process which reduces the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form (2). The physical nature and handling characteristics of the waste are usually improved by stabilization. A number of factors, characteristics, or mechanisms affect the degree of immobilization, or fixation, of contaminants in the waste. Usually, several are in operation at the same time. The major factors are: pH control, redox potential control, chemical reaction (i.e., precipitation, complexation, chemisorption), adsorption, ion exchange, and encapsulation. Metals can be precipitated as carbonates, hydroxides, sulfates, sulfides, silicates, and other simple species, and also as complexes. The degree of stabilization is measured using leaching tests. One such leaching test is the Toxicity Leaching Characteristic Procedure (TCLP) which is used by the U.S. Environmental Protection Agency to determine that a waste is hazardous (3).

A conical-pile type burning method is used to evaluate the oxidizing hazard posed by a solid waste (4, 5). This method provides a qualitative means to measure the potential of a solid waste to increase the burning rate or burning intensity of a combustible substance, specifically fibrous cellulose. The burning rates for 1:1 and 4:1 (w/w) waste:cellulose mixtures are compared to the burning rates for 3:7, 2:3, and 3:2 potassium bromate:cellulose mixtures.

Potassium bromate is used as the reference oxidizing standard. The three mixing ratios provide a range of burning times by which the waste is classified. The 3:7 mixture ratio provides the longest burning time, the 3:2 mixture ratio provides the shortest burning time, and the 2:3 mixture ratio provides an intermediate burning time. The burning times for the potassium bromate:cellulose mixtures are correlated to their relative oxidizing strengths; i.e., the shorter the burning time, the greater the relative oxidizing strength.

MATERIALS

A 2.55 L sample of the supernatant decanted from the MVSTs was obtained from the Capacity Increase Storage Tanks, where the supernatant is now stored, at ORNL. The radioactive sample was packaged and transported to Shaw Environmental's Environmental Technology Development Center in Oak Ridge, Tennessee.

METHODS

Characterization

The supernatant sample supplied was characterized for specific gravity, total suspended solids (TSS), total dissolved solids, pH, and total metals. The TSS and TDS were determined using Standards Methods 2450D and 2450C, respectively. The pH was determined using SW-846 Method 9040B. Total metals were determined using SW-846 Method 6010, with the exception of mercury, which was determined using SW-846 Method 7470A.

A portion of the supernatant material was dried at 140°C until greater than 90% solids to simulate the evaporative treatment process. The dried salt material was subjected to the Toxicity Characterization Leaching Procedure (TCLP) (6). The TCLP extract was analyzed for total metals using SW-846 Method 6010, with the exception of mercury, which was determined using SW-846 Method 7470A.

Stabilization Treatability

The stabilization treatability involved testing a number of potential treatment sequences: neutralization, sulfide precipitation, and evaporation; sulfide precipitation and evaporation; amalgamation and evaporation; sulfide and hydroxide precipitation and evaporation; and hydroxide precipitation and evaporation.

For the neutralization, sulfide precipitation, and evaporation treatment, a portion of the supernatant material were neutralized to pH 8.0 using 0.1 mL of 5% (v:v) nitric acid solution per mL of supernatant. The neutralized supernatant was allowed to evaporate to approximately 45% solids under ambient conditions. The partially-dried salt material was split. One-half of the partially-dried salt material was treated with a 0.1 wt % addition of Thio-Red, a commercially available calcium polysulfide solution, to precipitate available metals as sulfides. The other half of the partially-dried salt material was treated with 50 µg/g ferrous sulfide, followed by 3 wt % magnesium hydroxide. The treated partially-dried salts were then dried to greater than 90% solids at 140°C and subjected to the TCLP. Metals analysis was conducted on the TCLP extract.

For sulfide precipitation and evaporation, a portion of the supernatant was allowed to evaporate to approximately 45% solids under ambient conditions. The partially-dried salt material was split. One-half of the partially-dried salt material was treated with a 0.1 wt % addition of Thio-Red. The other half of the partially-dried salt material was treated with 50 µg/g of ferrous sulfide, followed by 3 wt % of magnesium

hydroxide. The treated partially-dried salts were then dried to greater than 90% solids at 140°C and subjected to the TCLP. Metals analysis was conducted on the TCLP extract.

For mercury amalgamation and evaporation, a portion of the supernatant was allowed to evaporate to approximately 45% solids under ambient conditions. The partially-dried salt material was treated with a 1 wt % addition of zinc powder. The treated partially-dried salts were then dried to greater than 90% solids at 140°C and subjected to the TCLP. Metals analysis was conducted on the TCLP extract.

For sulfide and hydroxide precipitation and evaporation, a portion of the supernatant was allowed to evaporate to approximately 45% solids under ambient conditions. The partially-dried salt material was treated with a 0.1 wt % addition of Thio-Red, followed by 4.5 wt % of magnesium hydroxide. The treated partially-dried salts were then dried to greater than 90% solids at 140°C and subjected to the TCLP. Metals analysis was conducted on the TCLP extract.

For hydroxide precipitation and evaporation, a portion of the supernatant was allowed to evaporate to approximately 45% solids under ambient conditions. The partially-dried salt material was treated with a 4.5 wt % addition of magnesium hydroxide. The treated partially-dried salts were then dried to greater than 90% solids at 140°C and subjected to the TCLP. Metals analysis was conducted on the TCLP extract.

Oxidizing Solids Testing

A portion of the supernatant was dried at 140°C to greater than 90% solids to simulate the evaporation treatment process. Aliquots of the dried salt material were mixed thoroughly with fibrous cellulose in both 1:1 and 4:1 weight-to-weight ratios. A 30 g aliquot of the dried salt:cellulose mixture was formed into a truncated conical pile, using glass funnel with a 70 mm diameter base, on a cool, impervious surface. A wire was inserted into the base of the pile and electrically heated. The burning time (in seconds) of each dried salt:cellulose ratio mixture was measured and recorded. The test was repeated five times for each dried salt:cellulose ratio mixture.

RESULTS

The characterization results for the Melton Valley Storage Tanks supernatant are contained in Table I. The density and TDS is consistent with the supernatant being a mixture of dissolved sodium and potassium nitrates, sulfates, phosphates, and carbonates. The total metals content indicate that Cd and Cr were above the RCRA Toxicity Characteristic (RCRA TC) levels of 1.0 mg/L and 5.0 mg/L, respectively. When the supernatant is dried to greater than 90% solids, none of the RCRA metals exceeded the RCRA TC (Table II). The dried salt material, even without any stabilization treatment, would not be considered a RCRA characteristically hazardous waste.

Table I Characterization Results for the Melton Valley Storage Tanks Supernatant

Data	Method	Results
Density (g/mL)	NA	1.192
TSS (mg/mL)	Standard Methods (1992 ed) 2540 D	4.70
TDS (mg/mL)	Standard Methods (1992 ed) 2540 C	351.6
TS (mg/mL)	TDS plus TSS	356.3
Untreated pH (s.u.)	SW846 9040B	11.02
Total Hg (mg/L)	SW846 7470A	0.152
Total Cr (mg/L)	SW846 6010	5.81
Total Pb (mg/L)	SW846 6010	1.40
Total Cd (mg/L)	SW846 6010	1.42
Total As (mg/L)	SW846 6010	0.71
Total Ba (mg/L)	SW846 6010	0.611
Total Se (mg/L)	SW846 6010	< 2.25
Total Ag (mg/L)	SW846 6010	0.319

Table II. TCLP Results for the Dried Salt Material from the Melton Valley Supernatant Sample

Parameter	Methodology	Result
TCLP Leachant Used	SW846 1311	Extraction Fluid #1
Extractant pH	SW846 1311	4.86
Extracted Hg (mg/L)	SW846 7470A	0.0061
Extracted Cr (mg/L)	SW846 6010	0.135
Extracted Pb (mg/L)	SW846 6010	0.195
Extracted Cd (mg/L)	SW846 6010	0.155
Extracted As (mg/L)	SW846 6010	<0.135
Extracted Ba (mg/L)	SW846 6010	0.087
Extracted Se (mg/L)	SW846 6010	<0.246
Extracted Ag (mg/L)	SW846 6010	0.020

The stabilization treatability results are summarized in Tables III through VI. Since the dried salts had low level of leachable metals, the stabilization treatments appeared to have little to no effect on the levels of leachable metals in the dried salts.

Table III TCLP Results for the Neutralized and Sulfide Immobilized Dried Salt Material

Parameter	Methodology	Stabilized with ThioRed	Stabilized with Iron Sulfide
		Result	Result
TCLP Leachant Used	SW846 1311	Extraction Fluid #1	Extraction Fluid #1
Extractant pH	SW846 1311	6.1	6.4
Extracted Hg (mg/L)	SW846 7470A	0.0064	0.0084
Extracted Cr (mg/L)	SW846 6010	0.272	0.512
Extracted Pb (mg/L)	SW846 6010	< 0.138	0.159
Extracted Cd (mg/L)	SW846 6010	0.155	0.155
Extracted As (mg/L)	SW846 6010	< 0.125	< 0.125
Extracted Ba (mg/L)	SW846 6010	0.0963	0.0989
Extracted Se (mg/L)	SW846 6010	< 0.222	< 0.222
Extracted Ag (mg/L)	SW846 6010	< 0.014	0.02

Table IV TCLP Results for the Sulfide Immobilized Dried Salt Material

Parameter	Methodology	Stabilized with ThioRed	Stabilized with Iron Sulfide
		Result	Result
TCLP Leachant Used	SW846 1311	Extraction Fluid #1	Extraction Fluid #1
Extractant pH	SW846 1311	6.8	6.6
Extracted Hg (mg/L)	SW846 7470A	0.0039	0.0074
Extracted Cr (mg/L)	SW846 6010	0.236	0.512
Extracted Pb (mg/L)	SW846 6010	< 0.138	< 0.138
Extracted Cd (mg/L)	SW846 6010	0.150	0.165
Extracted As (mg/L)	SW846 6010	< 0.125	< 0.125
Extracted Ba (mg/L)	SW846 6010	0.0988	0.155
Extracted Se (mg/L)	SW846 6010	< 0.222	< 0.222
Extracted Ag (mg/L)	SW846 6010	0.04	0.03

Table V TCLP Results for the Zinc Amalgamated Dried Salt Material

Parameter	Method	Result
TCLP Leachant Used	SW846 1311	Extraction Fluid #1
Extractant pH	SW846 1311	5.3
Extracted Hg (mg/L)	SW846 7470A	0.0079
Extracted Cr (mg/L)	SW846 6010	0.485
Extracted Pb (mg/L)	SW846 6010	< 0.138
Extracted Cd (mg/L)	SW846 6010	0.171
Extracted As (mg/L)	SW846 6010	< 0.125
Extracted Ba (mg/L)	SW846 6010	0.172
Extracted Se (mg/L)	SW846 6010	<0.222
Extracted Ag (mg/L)	SW846 6010	0.04

Table VI TCLP Results for the Magnesium Hydroxide Immobilized Dried Salt Material

Parameter	Method	Stabilized ThioRed Magnesium Hydroxide with and	Stabilized Magnesium Hydroxide with
		Result	Result
TCLP Leachate Used	SW846 1311	Extraction Fluid #1	Extraction Fluid #1
Extractant pH	SW846 1311	8.5	8.7
Extracted Hg (mg/L)	SW846 7470A	0.0079	0.0015
Extracted Cr (mg/L)	SW846 6010	0.71	0.27
Extracted Pb (mg/L)	SW846 6010	<0.138	< 0.138
Extracted Cd (mg/L)	SW846 6010	0.2	0.033
Extracted As (mg/L)	SW846 6010	< 0.125	< 0.125
Extracted Ba (mg/L)	SW846 6010	0.3	0.15
Extracted Se (mg/L)	SW846 6010	< 0.222	< 0.222
Extracted Ag (mg/L)	SW846 6010	0.038	0.038

Table VII summarizes the oxidizing solids testing results. Since the burn times for the dried salt material is less than the 3:7 potassium bromate:cellulose standard and greater than the 2:3 potassium bromate:cellulose standard, the dried salt material would be considered a Category III oxidizer by DOT.

Table VII Oxidizing Solid Testing Results

Potassium Bromate:Cellulose			
Ratio	3:7	2:3	3:2
Burn Time (sec)	205.6	95.8	29
Dried Salt Material:Cellulose			
Ratio	4:1	1:1	
Burn Time (sec)	122.4	149.8	

CONCLUSIONS

Treatment of the transuranic and alpha low level radioactive waste supernatant decanted from the MVSTs will involve evaporation of the water, leaving salt material which will be approximately 95% sodium nitrate. Though the supernatant from the MVSTs contains metals listed in the Resource Conservation and Recovery Act (RCRA), stabilization of these metals should not be required during the evaporative.

The dried salt material should be considered a Category III oxidizer by the DOT.

REFERENCES

- 1 Code of Federal Regulations, Title 49, Part 173, Appendix F, Guidelines for the Classification and Packaging Group Assignments of Division 5.1 Materials
- 2 Conner, J. R., Chemical Fixation and Solidification of Hazardous Waste, Van Nostrand Reinhold, New York, 1990.
- 3 Code of Federal Regulations, Title 40, Part 264.26
- 4 United Nations, Recommendations on the Transportation of Dangerous Goods, Manual of Tests and Criteria, ST/SG/AC.10/11/Rev 2, Section 34, Classification Procedures, Test Methods and Criteria Relating to Oxidizing Substances of Division 5.1, Test O.1: Test for Oxidizing Solids, 1995.
- 5 US Environmental Protection Agency, Publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Method 1040.
- 6 US Environmental Protection Agency, Publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Method 1311.