Solidification/ Stabilization Treatability Study of a Mixed Waste Sludge

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ABSTRACT

The Department of Energy Oak Ridge Operations Office signed a Federal Facility Compliance Agreement with the U.S. Environmental Protection Agency Region IV regarding mixed wastes from the Oak Ridge Reservation (ORR) subject to the land disposal restriction provisions of the Resource Conservation and Recovery Act (RCRA). This agreement required treatability studies of solidification/stabilization (S/S) on mixed wastes from the ORR. This paper reports the results of the cementitious S/S studies conducted on a waste water treatment sludge generated from biodenitrification and heavy metals precipitation. For the cementitious waste forms, the additives tested were Portland cement, ground granulated blast furnace slag, Class F fly ash, and perlite. The properties measured on the treated waste were density, free-standing liquid, unconfined compressive strength, and TCLP performance. Spiking up to 10,000, 10,000, and 4,400 mg/kg of nickel, lead, and cadmium, respectively, was conducted to test waste composition variability and the stabilization limitations of the binding agents. The results indicated that nickel, lead, and cadmium were stabilized fairly well in the high pH hydroxide-carbonate- "bug bones" sludge, but also clearly confirmed the established stabilization potential of cementitious S/S for these RCRA metals.

INTRODUCTION

The U.S. Department of Energy Oak Ridge Operations Office has signed a Federal Facility Compliance Agreement (FFCA) with the U.S. Environmental Protection Agency Region IV regarding Oak Ridge Reservation (ORR) mixed (radioactive and hazardous) wastes that are subject to the land disposal restrictions (LDR) of the Resource Conservation and Recovery Act (RCRA). The FFCA establishes an aggressive schedule for conducting studies and treatment method development under the treatability exclusion of RCRA (treatability studies) for those mixed wastes for which treatment methods and capabilities have yet to be defined. One of these wastes is a radioactive waste water treatment sludge with the waste codes F001, F002, F006, and F007. This sludge is generated from a facility designed to treat aqueous nitrate waste streams. The waste water treatment steps consist of neutralization, biodenitrification, decanting producing the first sludge solids ("bug bones"), acidification (permitting gasification of carbonates in the decanted liquid), chemical addition [$Fe_2(SO_4)_3$] and pH adjustment [NaOH] leading to precipitation and flocculation of heavy metals, clarification producing the remaining sludge solids, carbon adsorption, and surface water discharge. The sludges are collected and stored in tanks and consist of hydroxides, carbonates, and "bug bones". This paper presents the results of a treatability study of this waste water treatment sludge confirming the established stabilization of the oxides of nickel, lead, and cadmium in cementitious waste forms. As will be seen, this sludge proved an effective stabilizer of the RCRA metals, prior to adding stabilizing agents.

The sample of the waste water treatment sludge obtained for this study was found to be not characteristically hazardous in regard to the RCRA metals, despite the waste codes associated with this waste. This result does not

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guarantee that the stored sludge is not characteristically hazardous, considering the variability that can be expected in the stored sludge. In addition, the listed codes associated with this sludge mandates treatment, despite the performance in the TCLP test. The scope of this study included spiking three RCRA metals up to two orders of magnitude above the initial concentration to test waste composition variability and the limits of cementitious stabilization. Since the sample appeared to contain little of the RCRA metals that was extractable, the decision was made to spike the sludge at three concentration levels expected to give different measurable TCLP performances. Based on prior characterization data of the waste water treatment sludge, the metals selected for spiking were nickel, lead, and cadmium. Nickel was spiked at 2,500, 5,000, and 10,000 mg/kg; lead was spiked at 1,200, 2,370, and 10,000 mg/kg; and cadmium was spiked at 220, 440, and 4,400 mg/kg.

The stabilization of nickel, lead, and cadmium, as well as other metals, can be achieved with grout.[1] The stabilization of nickel can be achieved if proper pH control is exercised and no nickel complexes are involved.[1] Stabilization of nickel concentrations as high as 5,730 mg/kg in electroplating sludge has been reported using cement kiln dust and cement.[1,2] Lead leaching is minimized if the leachate pH is maintained between 8 and 10.[1] The observation that much of the stabilized lead is retained even after all the alkalinity has been leached has led to theoretical speculation that lead hydroxide is respeciated as a silicate.[1,3,4] Stabilization was tested on lead concentrations as high as 450,000 mg/kg in ceramic glaze waste, resulting in EP Toxicity leachate concentrations as low as 38.1 mg/L (a significant retention, but not good enough to meet TCLP LDR limits) using cement, silicate, and ammonium biphosphate.[1,5] Stabilization meeting TCLP LDR limits has been reported for lead concentrations as high as 38,000 mg/kg in arc furnace dust using cement, silicate, lime kiln dust, and/or proprietary agents.[1,6] The primary treatment method for cadmium has been precipitation with alkali/alkaline, usually lime.[1] Complexing agents prevent the precipitation of cadmium, necessitating the destruction of the complexing agent to stabilize cadmium.[1,7] Stabilization of cadmium concentrations as high as 18,980 mg/kg in cadmium nitrate sludge has been reported using Portland cement.[1,8]

Based on the preceding considerations, Portland cement, Class F fly ash, and slag were selected as stabilizing agents in the present study. Perlite, a fine, porous volcanic rock commonly used as a filter aid, was used as a water-sorptive agent in this study in order to control bleed water for high water contents. The highly porous perlite dust absorbs large amounts of water by capillary action and does not present the handling and processing problems exhibited by clays used for bleed water control.

EXPERIMENTAL

The study scope included controlling the sludge water content and varying this water content over a wide range. For this reason, the waste water treatment sludge was first oven dried at 105 °C. The dried sludge was then sieved through 4.75-mm sieve openings and homogenized to provide the feed sludge solids for the experimental design (see Table I). Homogeneity was tested by standard total analysis (EPA Method 3051) of a marker element (uranium) in five subsamples of the dried-sieved homogenized sludge. The percentage relative standard deviation (% RSD, i.e., standard deviation divided by the mean times 100) for uranium was 3.5% after homogenizing this dried, sieved sludge.

Grout Preparation

The grout preparation consisted of first mixing the sludge solids with water and the spike compounds and then mixing with the stabilizing agents. The treated sludge (grout) was cured in a humid environment at room temperature for 28 d to make the cementitious waste form. The spiking procedure consisted of mixing the spike compounds with some of the water overnight, adding this slurry to the sludge solids, rinsing the slurry container with the remainder of the water and adding this rinsate to the sludge solids, and mixing this concoction for 20 min with a Kitchen Aid mixer using a wire whip on low speed. The spiked, wet sludge was then mixed with a dry blend of the stabilizing additives for 4 min in the mixer. The compounds used for spiking were NiO, PbO, and CdO.

The dry blend consisted of as many as four additives blended for 2 h in a twin-shell blender. The four dry blend additives consisted of (1) Type I-II Portland cement (cement) from the Dixie Cement Co., (2) Class F fly ash (fly ash) from the American Fly Ash Co., (3) ground granulated blast furnace slag (slag) (Blaine fineness of 6220 cm^2/g) from the Koch Minerals Co., and (4) perlite (Grade H-200) from the Harborlite Corp. The composition of each of these dry additives was varied over a wide range, and only cement was present in every dry blend. Slag is a cement substitute, but requires activation by a base. Thus, when slag was used as the main binder, a small amount of cement was also added to activate the slag. The grout compositions were chosen in a statistical design (mixture experiment), but this statistical approach is not discussed in this paper.

Modified TCLP Measurements

Both the sludge solids (unspiked and spiked at the three levels) and cementitious waste forms were extracted using a modified TCLP. The modifications to the TCLP consisted of (1) extracting a 10-g sample in 200 mL of extraction fluid; (2) size reduction to <4.75-mm particles; and (3) analysis of the extract by an inductively coupled plasma (ICP) spectrometer (acceptable for most of the RCRA metals, but the standard technique requires graphite atomic absorption for arsenic and selenium). (EPA accepts the sensitivity for these two by the Thermo Jarrel Ash 61E Trace ICP used in this study). TCLP extraction fluid #2 (an aqueous solution of acetic acid at a pH of about 2.8) was required for half of the TCLP extractions of grout samples and TCLP extraction fluid #1 (same aqueous solution of acetic acid adjusted to a pH of about 4.9 with NaOH) was required for the other half.

Density Measurements

The bulk density of the as-received sludge and dried-sieved homogenized sludge was determined by weighing a known volume (using a graduated cylinder) of the granular sludge and calculating the bulk density. The bulk density of the cementitious waste forms was measured by packing a 2-in. cube mold with the freshly made grout, determining the net weight of the grout, and calculating the bulk density. The corresponding volume of the dried-sieved homogenized sludge were calculated along with each grout volume. The percentage volume increase of the dried-sieved homogenized sludge (bulking factor) gives the volume increase over the dried sludge after adding water and the cementitious additives.

RESULTS

Table I lists the compositions (including the spike levels of nickel, lead, and cadmium in the dried-sieved homogenized sludge solids) of the cementitious waste forms made from the waste water treatment sludge. Table II lists the RCRA metal concentrations of the TCLP extracts for the dried-sieved homogenized sludge (low spike, medium spike, and high spike). Table III lists the TCLP extract concentrations of the cementitious waste forms made from the waste water treatment sludge according to the compositions listed in Table I. The TCLP performance of the grouts proved to be sensitive to the final extract pH.

Table IV lists the following other properties measured for the cementitious waste forms: 28-d free standing liquid, 28-d unconfined compressive strength, grout bulk density, and bulking factor. The bulking factors give the percentage volume increases for the cementitious waste forms over the dried sludge, not the wet sludge.

Place Table I here.

Place Table II here.

Place Table III here.

Place Table IV here.

DISCUSSION

The compositions of the grouts in this study were intentionally varied over a wide range, including variations from high waste loadings to low waste loadings and from high water contents to low water contents. Most of the grouts listed in Table I formed relatively weak waste forms. Only a few with higher binder content formed strong cementitious monoliths. The grouts with high waste loadings resulted in wet, soft products that flowed under their own weight, even after a 28-d cure. The higher water content resulted in considerable bleed water in some grouts, but perlite did prove capable of handling high water content.

One of the more important results is that most of the untreated and treated samples of this waste water treatment sludge did meet the TCLP LDR limits for nickel, lead and cadmium, even at the highest spike levels. For the untreated sludge, only the high cadmium spike failed to pass the TCLP LDR criteria. For the treated sludge, only Grout No. 14 failed the TCLP LDR criteria, once again for cadmium. Grout No. 14 had a combination of a high cadmium spike and high waste solids content. Grout No. 14 was a replicate of Grout No. 2, but Grout No. 2 passed the TCLP criteria for cadmium. The other grouts with high cadmium spikes (Grout No.s 1, 4, 10, 15, and 19) passed the TCLP LDR criteria, but only Grout No.s 2 and 14 had the combination of high cadmium spike and high waste solids content.

Treatment usually improved the TCLP performance and, for those few cases which did not, the grout was extracted with the more aggressive TCLP Fluid No. 2 (whereas, the untreated spiked dry sludge was extracted with TCLP Fluid No.1).

CONCLUSIONS

The most significant finding was that this waste water treatment sludge performed well in the TCLP test treated or untreated, even when spiked with nickel, lead and/or cadmium as high as 10,000, 10,000, and 4,400 mg/kg, respectively. The waste water treatment included bioremediation as well as lime and flocculent treatment. Apparently, the combination of "bug bones", calcium carbonate, and iron hydroxides serves to retain the nickel, lead, and cadmium in the sludge quite well, even when spiked to quite high levels. The correct blend of cement, slag, fly ash, and perlite can stabilize this waste water treatment sludge for a wide range of water contents and concentrations of nickel, lead and cadmium. The free water can be controlled, even if the sludge contains high levels of water. Nickel, lead and cadmium can be stabilized, even if the final waste form is relatively weak physically; however, a physically stronger waste form can be produced, if desired, by adding more binder, resulting in more volume increase in the final waste form. Therefore, once the composition required to stabilize the RCRA metals is determined, choosing how much blend to use in treating a given waste means balancing the physical strength desired against the volume increase allowed.

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Table I. Composition of the cementitious waste forms for the waste water treatment sludge.

Grout No.	Mass Fraction in Waste Form						Spike Concentration in Waste Solids (mg/kg)		
	Waste Solids	Water	Cement	Fly Ash	Slag	Perlite	Nickel	Lead	Cadmium
1	0.100	0.583	0.029	0.000	0.288	0.000	2,500	10,000	4,400
2	0.600	0.298	0.009	0.000	0.093	0.000	2,500	2,370	4,400
3	0.100	0.574	0.009	0.000	0.091	0.226	2,500	1,200	440
4	0.100	0.583	0.115	0.000	0.000	0.202	10,000	2,370	4,400
5	0.100	0.286	0.112	0.503	0.000	0.000	2,500	2,370	440
6	0.100	0.286	0.111	0.000	0.503	0.000	5,000	2,370	440
7	0.100	0.583	0.317	0.000	0.000	0.000	10,000	10,000	440
8	0.324	0.576	0.044	0.000	0.056	0.000	5,000	1,200	440
9	0.600	0.286	0.087	0.012	0.014	0.000	10,000	10,000	440
10	0.100	0.286	0.009	0.514	0.091	0.000	5,000	10,000	4,400
11	0.100	0.414	0.100	0.386	0.000	0.000	10,000	1,200	220
12	0.302	0.422	0.092	0.068	0.076	0.041	5,000	2,370	440
13	0.100	0.583	0.317	0.000	0.000	0.000	10,000	10,000	440
14	0.600	0.298	0.009	0.000	0.093	0.000	2,500	2,370	4,400
15	0.100	0.286	0.614	0.000	0.000	0.000	5,000	1,200	4,400
16	0.317	0.583	0.038	0.000	0.063	0.000	5,000	2,370	220
17	0.100	0.286	0.614	0.000	0.000	0.000	2,500	10,000	220
18	0.100	0.286	0.056	0.000	0.558	0.000	10,000	1,200	220
19	0.100	0.286	0.614	0.000	0.000	0.000	5,000	1,200	4,400
20	0.173	0.533	0.009	0.000	0.091	0.194	5,000	10,000	220

Table II. TCLP extract concentrations for the dried-sieved homogenized waste water treatment sludge, mg/L.

Analyte	Low Spike[a]	Medium Spike[b]	High Spike[c]	TCLP LDR Limits
Nickel	0.15	0.12	0.19	0.32
Lead	0.14	0.14	0.34	0.51
Cadmium	0.04	0.08	1.27	0.066
Arsenic	<0.15	<0.15	<0.15	5
Chromium	0.08	0.07	0.02	5.2
Selenium	<0.14	<0.14	<0.14	5.7
Silver	<0.02	<0.02	<0.02	0.072
Barium	0.47	0.56	0.83	100
Extract pH	7.1	7.24	6.95	
Fluid No.	1	1	1	

[a] Values of 2,500, 1,200, and 220 mg/kg, respectively, of nickel, lead and cadmium in the dried-sieved homogenized sludge.

[b] Values of 5,000, 2,370, and 440 mg/kg, respectively, of nickel, lead and cadmium in the dried-sieved homogenized sludge.

[c] Values of 10,000, 10,000, and 4,400 mg/kg, respectively, of nickel, lead and cadmium in the dried-sieved homogenized sludge.

Table III. Concentrations in the TCLP extract of the cementitious waste forms

Grout No.	TCLP Extract Concentration (mg/L)			TCLP Extract pH	TCLP Extract Fluid No.
	Nickel	Lead	Cadmium		
1	<0.05	<0.13	<0.02	10.60	1
2	<0.05	<0.13	<0.02	6.97	1
3	<0.05	<0.13	<0.02	6.70	1
4	<0.05	<0.13	<0.02	9.57	1
5	<0.05	<0.13	<0.02	10.71	1
6	<0.05	<0.13	<0.02	11.15	1
7	<0.05	<0.13	<0.02	11.70	2
8	0.27	<0.13	0.04	7.27	2
9	0.13	0.26	0.05	6.66	2
10	<0.05	<0.13	<0.02	6.43	1
11	<0.05	<0.13	<0.02	10.56	1
12	0.08	<0.13	<0.02	5.96	2
13	<0.05	<0.13	<0.02	11.71	2
14	0.23	<0.13	0.08	7.18	2
15	<0.05	<0.13	<0.02	11.56	2
16	0.25	<0.13	<0.02	6.97	2
17	<0.05	<0.13	<0.02	11.95	2
18	<0.05	<0.13	<0.02	11.09	1
19	<0.05	<0.13	<0.02	11.94	2
20	<0.05	<0.13	<0.02	8.34	1

Table IV. Other properties of the cementitious waste forms.

Grout No.	28-d Free Standing Liquid (vol%)	28-d Unconfined Compressive Strength (kPa)	Grout Bulk Density (kg/L)	Bulking Factor[a] (vol%)
1	0	7	1.3	570
2	0	345	1.6	-15
3	0	152	1.3	552
4	0	517	1.3	554
5	0	7,050	1.8	321
6	0	27,000	1.8	364
7	26	3,606	1.3	547
8	0	35	1.3	103
9	0	248	1.4	4
10	0	324	1.7	390
11	0	1,230	1.5	456
12	0	655	1.5	61
13	18	3,690	1.3	538
14	0	103	1.4	-4
15	0	>34,500	1.9	335
16	0	41	1.2	121
17	0	>34,500	1.9	334
18	0	5,650	1.6	414
19	0	>34,500	1.9	338
20	0	83	1.3	278

[a] Bulking factor is the percent bulk volume increase over the bulk volume of the dried-sieved homogenized sludge (i.e., the grout bulk volume minus the bulk volume of the dried-sieved homogenized sludge used in making the grout divided by the bulk volume of the dried-sieved homogenized sludge times 100).