INEL/CON-97-00334
CONF-970537--

OPTIMIZATION OF HYDRAULIC CEMENT ADMIXTURE WASTE FORMS FOR SODIUM-BEARING, HIGH ALUMINUM, AND HIGH ZIRCONIUM WASTES

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ABSTRACT

A three-way blend of portland cement, blast furnace slag, and fly ash was successfully tested on simulated acidic high sodium, aluminum, and zirconium low-level wastes (LLW). Grout cubes were prepared at various waste loadings to maximize loading while meeting compressive strength and leach resistance requirements. For sodium LLW, a 21% waste loading achieves a volume reduction of 3.3 and a compressive strength of 2750 pounds per square inch while meeting leach, mix, and flow requirements. It was found that the sulfur in the slag reduces the chromium leach rate below regulatory limits. For aluminum LLW, a 10% waste loading achieves a volume reduction of 8.5 and a compressive strength of 4350 pounds per square inch while meeting leach requirements. Likewise for zirconium LLW, a 21% waste loading achieves a volume reduction of 8.3 and a compressive strength of 3570 pounds per square inch.

INTRODUCTION

High-activity wastes at the Idaho Chemical Processing Plant (ICPP) include about 6800 m^3 of aqueous acidic tank waste and 3800 m^3 of solid dry calcine. The High-Level Waste Program Plan calls for the tank waste to be separated via solvent extraction and ion exchange into high-activity and low-level radioactive wastes. The calcine is to be retrieved from storage bins, dissolved in nitric acid, and separated. The small volume, high-activity waste will be vitrified and disposed of in a geological repository. The large volume, low-level waste (LLW) will be grouted and sent to a near-surface low-level disposal facility.

The projected low-level wastes are acidic, high in nitrates, and may contain heavy metals and organics, as well as radionuclides. All of these attributes can be detrimental to grout stability. This research is part of a program to develop processing methods and grout formulations to treat these wastes. Optimal grout formulations should maximize waste loading, reduce waste volume, and produce a viable waste form, i.e., the waste form must be solid and restrict the leaching of radionuclides and hazardous metals. The Department of Energy Order 5820.2a, "Radioactive Waste Management," does not contain specific waste form criteria. Therefore, the guiding document for this research is the "Technical Position on Waste Form," published by the Low-Level Waste Management Branch of the U.S. Nuclear Regulatory Commission.[2] Waste form qualifications include compressive strength, leach resistance, thermal cycling, and immersion testing. Only compressive strength and leach resistance are addressed in this study.

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The low-level waste derived from separation of liquid sodium-bearing waste is designated as Na LLW. (A listing of simulant components can be found in Reference 1.) The Na LLW simulant has a density of 1.1 g/mL. Of the 1130 g per liter, about 900 g are acids and water and 230 g are dissolved solids. The 230 g dissolved solids contain 185 g nitrate. The LLW from aluminum calcine is designated as Al LLW. The simulant has a similar density and has about 190 g dissolved solids with 174 g nitrate. The zirconium low-level waste (Zr LLW) has 215 g dissolved solids of which 170 g is nitrates.

Prior to grouting, the LLW simulants are preconditioned using thermal calcination. This process, called denitration, heats the waste to 650°C, volatilizes or decomposes the nitrates, and solidifies the waste.[1] The Na LLW results in 120 g solids per liter of liquid with no additives. If clay is added, the Na LLW results in 65 g/L from the waste plus the 137 g/L clay. For Al LLW, 23 g/L are produced with and without clay. Zr LLW yields 47 g/L without additives and 48 g/L with clay. By driving off the liquids and nitrates, the waste volume is reduced significantly and an aggregate is provided for grouting.

GROUT PREPARATION, CURING, AND COMPRESSIVE STRENGTH

The Pennsylvania State University Materials Testing Laboratory recommended a grout formulation of 1/3 portland cement, 1/3 blast furnace slag, and 1/3 silica fume. This produced a very pasty mix that required high water to cement ratios. Class F fly ash was substituted for silica fume to achieve a grout that could be poured or pumped and still provide silica to the mix. The three-way blend was used for LLW solids denitrated without additives. The LLW denitrated with clay was initially grouted with only portland cement; however, to improve leach resistance the clay-denitrated solids were grouted with portland cement and blast furnace slag.

For Na LLW without additives, waste loadings of 10 to 25 weight percent (wt%) by were studied while waste loadings of 9 to 16 wt% were studied for Na LLW denitrated with clay. Waste loadings from 7 to 24 wt% were studied for Al and Zr LLW. Grout mix properties were qualitatively noted for ease of mixing and pouring. Grout specimens were prepared in 2x2x2 inch molds as required by ASTM C109-93, "Standard Test Method for Compressive Strength of Hydraulic Mortars (Using 2-in. or 50-mm Cube Specimens)". Since cube specimens were prepared individually, mixing was done by hand for the small batches.

A super-plasticizer was added to the mix to improve fluid properties of the wet grout. One-half milliliter was added per cube batch, which is equivalent to 20 ounces per 100 pounds of portland cement. The target water-to-solids ratio was 0.40 where the solids is the sum of the weight for waste solids, cement, slag, and fly ash. In general, for waste loadings from 7 to 17 wt%, the grout was fluid and could be poured into the molds. For waste loadings of 21 to 24 wt%, the grout had a lower slump (piled up in the mold rather than leveling off). If higher waste loadings are pursued, this problem may be resolved by vibrating the mold or drum to cause the grout to settle. It is further noted that the Na LLW denitrated with clay was very hygroscopic during mixing; however, during curing the excess water would "bleed" out.

Three types of curing were tested: 1) natural curing for 28 days in a closed plastic bag to simulate capped storage drum conditions, (Enclosed Cured), 2) natural curing for 28 days over a water bath to simulant moist, humid conditions (Humid Cured), and 3) fast curing at elevated temperature and pressure in an autoclave at 200°C and 200 psi for 2 hours (Autoclave Cured).

The curing method did have an effect on the subsequent density and compressive strength as noted in Tables 1 to 4. The results clearly show that the cubes cured in closed plastic bags have higher compressive strengths. The improved strength is sustained over a broader range of waste loading. The cubes cured in the humid enclosure and the plastic bags have similar densities; however, the density of the autoclaved cubes is much lower.

There does not appear to be a correlation between waste loading and density. However, compressive strength decreases as waste loading increases. The latter may be more a function of the amount of water added to make the mixed grout more fluid.

Table 1: Grout Density and Compressive Strength as a Function of Waste Loading and Curing Method for Sodium-Bearing LLW Denitrated without Additives

Na LLW w/o clay		Humid Cured		Enclosed Cured		Autoclave Cured	
Waste Wt. %	Volume Reduct.	Density (g/cm^3)	Comp. Str. (psi)	Density (g/cm^3)	Comp. Str. (psi)	Density (g/cm^3)	Comp. Str. (psi)
10.7%	1.6	na	na	1.82	3170	na	na
14.2%	2.1	na	na	1.80	3000	na	na
17.7%	2.7	na	na	1.80	2830	1.40	2450
21.4%	3.3	1.78	1970	1.80	2750	1.36	1850
25.2%	3.8	1.80	1850	1.82	2440	1.32	1260

Table 2: Grout Density and Compressive Strength as a Function of Waste Loading and Curing Method for Sodium-Bearing LLW Denitrated with Clay

Na LLW with clay		Humid Cured		Enclosed Cured		Autoclave Cured	
Waste Wt. %	Volume Reduct.	Density (g/cm^3)	Comp. Str. (psi)	Density (g/cm^3)	Comp. Str. (psi)	Density (g/cm^3)	Comp. Str. (psi)
9.2%	2.3	1.69	2340	1.61	3150	1.27	2380
12.6%	3.2	1.69	2830	1.69	3140	1.17	1860
16.0%	3.9	1.60	100	1.59	1650	1.10	1040

Table 3: Grout Density and Compressive Strength as a Function of Waste Loading and Curing Method for Aluminum LLW Denitrated without Additives

Al LLW		Humid Cured		Enclosed Cured		Autoclave Cured	
Waste Wt. %	Volume Reduct.	Density (g/cm^3)	Comp. Str. (psi)	Density (g/cm^3)	Comp. Str. (psi)	Density (g/cm^3)	Comp. Str. (psi)
7.0%	5.5	1.81	4070	1.79	4040	1.39	470
10.5%	8.5	1.84	2860	1.79	4350	1.44	1590
14.0%	11.0	1.75	1880	1.78	3450	1.48	2030
17.6%	13.6	1.82	2240	1.76	2610	1.46	1760
21.2%	16.2	1.81	1840	1.74	2360	1.46	1710
24.3%	20.1	1.67	310	1.71	2170	1.38	1050

Table 4: Grout Density and Compressive Strength as a Function of Waste Loading and Curing Method for Zirconium LLW Denitrated without Additives

Zr LLW		Humid Cured		Enclosed Cured		Autoclave Cured	
Waste Wt. %	Volume Reduct.	Density (g/cm^3)	Comp. Str. (psi)	Density (g/cm^3)	Comp. Str. (psi)	Density (g/cm^3)	Comp. Str. (psi)
7.0%	2.7	n/a	n/a	1.81	4920	1.59	3860
10.5%	4.1	1.81	3810	1.82	4800	1.50	2400
14.0%	5.5	1.77	2240	1.81	3520	1.53	1840
17.6%	6.9	1.83	2450	1.84	3930	1.44	1830
21.2%	8.3	1.97	3550	1.84	3570	1.56	1290
24.3%	9.6	1.81	2410	1.83	3430	1.53	1150

The volume reduction factors noted in the tables indicate the change in volume from the original liquid LLW to the solid grout waste form. For example, a volume reduction factor of 6 would mean that six cubic meters of liquid LLW would yield one cubic meter of waste grout following denitration. The volume reduction factors are derived experimentally from the simulated waste and grout. The volume reduction is directly related to the denitration process. Since Al LLW has only 23 grams denitrated solids per liter of liquid waste while Zr LLW has 47 grams, the Al LLW volume reduction factors in Table 3 are about twice those of the Zr LLW noted in Table 4.

A word of caution concerning the volume reduction factors is that these factors are for the low-level waste stream only. In taking the original calcine from "cradle to grave" there is actually a volume increase. This occurs in the separation process where dilutions are made when nitric acid is added to dissolve the calcine and when other solvents or water are added in the extraction processes. For example, 1 kilogram of Al calcine has a volume of 0.9 liters. Following the separation processes, a total of 45.6 liters of LLW are produced. If the Al LLW is denitrated and grouted at 10.5 wt% waste loading and the LLW volume is reduced by a factor of 8.5 (Table 3), 5.4 liters (45.6/8.5) of grout would be produced. Thus, the overall volume change from Al calcine to Al grout is an increase from 0.9 to 5.4 liters. For Zr calcine, the overall volume change is not as dramatic as 1 liter of Zr calcine yields 3.5 liters of LLW grout at 21.2 wt% waste loading. Grouting the liquid sodium-bearing waste achieves a volume reduction from 1 liter to 0.6 liters.

LEACH RESULTS

Following strength testing, the grout cubes were submitted for leach testing to determine the amount of hazardous metals that may leach from the grout. This is completed using the U. S. Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP). For the grout to pass TCLP, the resulting leach values must be less than the regulatory levels specified in 40 CFR 261.24, Table 1, "Maximum Concentration of Contaminants for the Toxicity Characteristic." The TCLP is a rather aggressive leaching procedure. Each grout sample (up to 100 grams) is crushed to a maximum sieve size of 9.4 millimeters. Because the samples are basic, the procedure requires that a solution of acetic acid as the extraction fluid (TCLP Extraction Fluid #2). The solid phase is extracted with a volume of extraction fluid equal to 20 times the weight of the solid phase. The sample and extraction fluid are agitated together by rotating the extraction vessel in an end-over-end manner at 30 revolutions per minute for 18 hours. The extraction fluid is then submitted for analysis of cadmium, chromium, lead, and mercury. The 40 CFR Section 261.24 limits for chromium and lead are 5.0 milligram per liter (mg/L). The limit for cadmium is 1.0 mg/L and the limit for mercury is 0.2 mg/L.

The TCLP results are presented in Table 5 for the various LLW streams tested to date. A sample of portland cement was leached as a blank. Three types of Na LLW grout cubes were leach tested: 1) Na LLW denitrated without additives, 2) Na LLW denitrated with clay and grouted with portland cement, and 3) Na LLW denitrated with clay and grouted with portland cement and blast furnace slag. Past research and these data show that lead and mercury are usually below detectable limits. These elements are either well contained in the cement matrix or are driven off during the denitration process. An elemental material balance is needed to determine their disposition. For the Na LLW denitrated without additives, lead, mercury, and cadmium are below detection limits and chromium leaches well below regulatory limits.

When Na LLW is denitrated with clay and grouted with portland cement, chromium leaches at much higher levels. At 16 wt% waste loading, the chromium leach is above the regulatory limit of 5 milligrams per liter. Thermal denitration oxidizes chromium to the +6 oxidation state and the sulfur in the blast furnace slag reduces it to an oxidation state of +3.[3-5] The +3 chromium does not leach as much as the +6. Thus, slag was added to later grout mixes as shown in the third Na LLW set. The slag reduced the chromium leach levels below regulatory limits. These leach results show that the addition of clay is not an advantage over the waste processed without additives. The denitration results indicate that the clay facilitates nitrate destruction for Na LLW, but adds extra volume to the grout. Therefore, clay addition is not recommended unless future studies indicate excessive nitrate leachability without the clay.

Table 5: Leach Results

Grout Sample	Waste Loading Wt. %	Hg 0.2 mg/L max.	Pb 5 mg/L max.	Cd 1 mg/L max.	Cr 5 mg/L max.
Portland cement	0	<0.005	<0.060	<0.004	<0.006
Na LLW at 650°C grouted with 3-way blend (no clay).	17.7	<0.005	<0.060	<0.004	0.022
	21.4	<0.005	<0.060	<0.004	0.028
	25.2	<0.005	<0.060	<0.004	0.067
Na LLW + Clay at 650°C grouted with cement only	9.2	*	<0.033	0.0056	1.80
	12.6	*	<0.033	0.0057	3.51
	16.0	*	<0.033	0.0066	6.14
Na LLW + Clay at 650°C grouted with cement and slag	9.2	*	<0.033	0.0182	0.1816
	12.6	*	<0.033	0.0841	0.6189
	16.0	*	<0.033	0.1230	3.136
Al LLW at 650°C	7 to 24	**	**	**	**
Zr LLW at 650°C grouted with 3-way blend	7.0	**	**	<0.0030	**
	10.5	**	**	0.0080	**
	14.0	**	**	0.0183	**
	17.6	**	**	<0.0030	**
	21.2	**	**	0.0893	**
	24.3	**	**	0.2621	**

* Sample not analyzed for component
** Projected LLW does not contain component

The Al LLW does not contain any hazardous components and the Zr LLW contains only cadmium. The cadmium leaches below the regulatory limit for all Zr LLW waste loadings and is one-tenth the limit at 21.2 wt% waste loading. For this particular sample, 34.24 grams were leached, which contained a total of 274 milligrams cadmium and the leachant volume was 685 milliliters. The results from Table 5 show 0.0893 micrograms per milliliter leached for a total of 0.061 milligrams cadmium. Thus, only 0.03% of the cadmium leached out of the Zr LLW grout cube.

CONCLUSIONS AND RECOMMENDED FORMULATIONS

Based on these laboratory tests, the projected low-level wastes derived from liquid sodium-bearing waste and from aluminum and zirconium calcines can be successfully grouted using denitration and a blended grout. Thermal denitration is effective in destroying the nitrates and provides a solid product that is compatible with portland cement grout. Denitration reduces the waste volume, which should result in lower disposal costs. However, denitration of sodium-bearing waste may cause heavy metals to volatilize, especially mercury. If so, the off-gas system design may be significantly impacted.

The three-way blend of portland cement, blast furnace slag, and fly ash is recommended for ICPP low-level wastes. Waste loadings up to 25 wt% produced acceptable compressive strengths and leach resistances. The leach rate of chromium can be controlled by using blast furnace slag in the grout. The higher loadings produced thicker grouts; therefore, a maximum of 17 to 21 wt% waste loading is recommended to provide good fluid properties, such that the grout can be poured from mixer to storage drums. Natural curing in closed storage drums is preferred over curing at elevated temperatures and pressures based on the higher compressive strength results of natural curing. In summary, the formulations prepared with LLW denitrated without additives and grouted with the three-way blend produced the highest waste loadings and the lowest leach rates.

FUTURE STUDIES / ISSUES

Continued laboratory studies are recommended to develop a material and energy balance for the denitration and grouting processes. Knowledge of the disposition of each component/element in the waste is needed. For example, mercury and lead do not show up on leach tests. One study indicates that cadmium nitrate and lead nitrate volatilize during incineration.[6] Mercury volatilization is accounted for in the off-gas design; however, if other heavy metals volatilize, it must be determined whether they can be captured and treated. Also, an energy balance for the denitration, grouting, and curing processes is needed to determine overall costs and where heat could be recovered and recycled.

If the denitration process is run full-scale, up to 500 gallons of liquid Al LLW could be processed and grouted in a single 55 gallon drum. This efficient volume reduction may have a penalty in gaseous emissions. The 500 gallons of liquid waste would result in approximately 720 pounds of NO_x and 3800 pounds of acidic water vapor. This amount of NO_x would need to be released over a minimum period of two hours to remain below the current release limits of 472 pounds per hour. Thus, only 10 to 12 drums could be produced per day, but this would represent 5000 to 6000 gallons of waste treated per day. To become a viable process, denitration equipment must be located and tested, as well as materials of construction that can withstand the corrosive off-gas.

Additional waste form qualification is needed to complete the tests required by the Nuclear Regulatory Committee. This includes, in part, compressive strength testing following 90 day immersion and after 30 freeze-thaw cycles. Chemical leach resistance studies will continue for toxic chemicals and radionuclides. To date, only laboratory size samples have been tested. Full size drums of grout will need to be grouted, core sampled, and subjected to the qualification tests. All of this is a iterative process to achieve a viable waste form.

ACKNOWLEDGEMENTS

The author expresses his gratitude to the following persons for their assistance in this program:

Dr. Barry Sheetz, Materials Research Laboratory, Pennsylvania State University
Eric Olson, S. M. Stoller Corp., Boulder, Colorado
Toshinori Shigemitsu, Nuclear Fuel Industries, Ltd, Osaka, Japan
Darrell Dietz, Ash Grove Cement Company, Inkom, Idaho
Jerry Rose, Blue Circle Cement, Inc., Sparrows Point, Maryland
Cary Sargent, Valley Ready Mix, Inc., Idaho Falls, Idaho

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