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Development and Testing of a Cement-Based Solid Waste Form Using Synthetic UP-1 Groundwater

G. A. Cooke, L. L. Lockrem

CH2M HILL Hanford Group, Inc.

Richland, WA 99352

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Abstract: The Effluent Treatment Facility plans to convert several waste streams from evaporator operations into a solid waste form. This report provides the results of development and testing of cementitious solids formulations to solidify evaporated groundwater brine, identified as UP-1, from Basin 43.

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DEVELOPMENT AND TESTING OF A CEMENT-BASED SOLID WASTE FORM USING SYNTHETIC UP-1 GROUNDWATER

G. A. Cooke
L. L. Lockrem
CH2M HILL Hanford Group, Inc.

M. D. Guthrie
K. J. Lueck
Fluor Hanford, Inc.

M. Avila
RJ Lee Group, Inc.
Center for Laboratory Sciences

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CH2MHILL
Hanford Group, Inc.

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1. OBJECTIVE

The Effluent Treatment Facility (ETF) in the 200 East Area of the Hanford Site is investigating the conversion of several liquid waste streams from evaporator operations into solid cement-based waste forms. The cement/waste mixture will be poured into plastic-lined mold boxes. After solidification the bags will be removed from the molds and sealed for land disposal at the Hanford Site.

The RJ Lee Group, Inc. Center for Laboratory Sciences (CLS) at Columbia Basin College (CBC) was requested to develop and test a cementitious solids (CS) formulation to solidify evaporated groundwater brine, identified as UP-1, from Basin 43. Laboratory testing of cement/simulant mixtures is required to demonstrate the viability of cement formulations that reduce the overall cost, minimize bleed water and expansion, and provide suitable strength and cure temperature.

Technical support provided mixing, testing, and reporting of values for a defined composite solid waste form. In this task, formulations utilizing Basin 43 simulant at varying wt% solids were explored. The initial mixing consisted of making small (~300 g) batches and casting into 500-mL Nalgene^{®1} jars. The mixes were cured under adiabatic conditions and checked for bleed water and consistency at recorded time intervals over a 1-week period. After the results from the preliminary mixing, four formulations were selected for further study. The testing documentation included workability, bleed water analysis (volume and pH) after 24 hours, expansivity/shrinkage, compressive strength, and selected Toxicity Characteristic Leaching Procedure (TCLP) leach analytes of the resulting solid waste form.

2. INTRODUCTION

The ETF plans to convert several liquid waste streams from evaporator operations into a solid waste form. The waste mixture will be poured into solid monolith cubes and sealed for land disposal at the Hanford Site.

Fluor Hanford, Inc. requested the Analytical Technical Services division of CH2M HILL Hanford Group, Inc. (CH2M HILL) and the CLS at CBC to supervise and conduct testing and development of dry reagent formulation (DRF) for mixing with liquid effluent waste from the ETF evaporator operations.

The solidification and stabilization of a variety of liquid radioactive wastes has been a major area of focus for the Office of Environmental Management, U.S. Department of Energy. Solidification of these wastes is a key element of a permanent land disposal solution. The general types of solidified waste forms that have been investigated for waste disposal include grout, glass, ceramics (crystalline or vitreous), polymers, and compacted waste. Cement-based waste forms immobilize the toxic elements of the waste by binding them in a low solubility solid phase and/or encapsulating the soluble toxic elements in a less-soluble, low permeability matrix that resists degradation.

¹ NALGENE[®] is a registered trademark of Nalge Nunc International Corporation, Rochester, New York.

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The focus of this particular testing was the use of Basin 43 brine as the waste of interest. The simulant was used to explore various DRF formulations. Initial mixing consisted of making small (~300 g) batches and casting into 500-mL Nalgene jars. The mixes were cured under adiabatic conditions and checked for bleed water and consistency at recorded time intervals over a 1-week period. The simulant used in this testing will be formulated to match the anticipated UP-1 waste stream from the ETF.

The activities included in this report consist of (1) preparation of a Basin 43 simulant waste mixture, (2) selection of a suitable DRF formulation, (3) mixing of a cast stone/waste mixture at different waste loadings, and (4) testing of the resulting solid waste forms. The testing documentation includes workability, bleed water analysis (volume and pH) after 24 hours, expansivity/shrinkage, cure temperature, compressive strength and selected TCLP leach analytes of the resulting solid waste form. These results are documented in this report.

The CLS is the operational organization for these testing activities. Technical and project oversight was provided by Larry L. Lockrem from the Analytical Process Development (APD) group of the Analytical Technical Services division of CH2M HILL Hanford Group, Inc.

3. PREPARATION OF PRELIMINARY CEMENT/WASTE MIXTURES

To begin preparing CS waste forms, the Basin 43 simulant was prepared according to the anticipated UP-1 waste stream from the ETF (see Table 1). This is a 25 wt% solids formulation.

Table 1. Basin 43 Simulant Recipe.

Reagent	Moles	Molecular Weight	grams/L
Na ₂ SO ₄	0.273	142	38.7
CaSO ₄ ·2H ₂ O	0.733	172	126.1
Ca(NO ₃) ₂ ·4H ₂ O	0.363	236	85.7
Mg(NO ₃) ₂ ·6H ₂ O	0.497	256.3	127.4
MgCl ₂ ·6H ₂ O	0.078	203.3	15.9
KCl	0.079	74.5	5.9
H ₂ O	41.132	18	740.4
Total			1,139.9

Note: Mixture adjusted to a pH between 10-11 with 50% NaOH

A 2-L batch of the Basin 43 was prepared at room temperature. Small ~300-g batches were mixed using the simulant heated at ~100 °F. The cementitious dry ingredients were added to the heated simulant and mixed. All of the mixes were mixed for 10 minutes and their consistency on mixing was recorded. The mixes were poured into 500-mL Nalgene bottles and sealed tight.

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They were each placed in a 60 °C oven for a minimum of 24 hours, unless otherwise noted. All the mixes contained Basin 43 simulant along with portland cement. The mixes contained some or all of the following dry ingredients in varying amounts: blast furnace slag and fly ash.

4. PHYSICAL ANALYSIS OF PRELIMINARY CEMENT/WASTE SAMPLES

All mixes were prepared with 25 wt% solids Basin 43 simulant. The simulant was heated to 100 °F or greater prior to mixing. All dry ingredients were added to the simulant and then mixed for approximately 10 minutes each. Each formulation was then placed in a 500-mL plastic bottle and screwed tight with a lid.

All mixes were placed in a 60 °C oven for curing. After 24 hours in the oven, each mix was observed for relative hardness and bleed water. All observations were made from outside the bottle and recorded. Those mixes determined to be set were removed from the bottle and tested for hardness using a penetrometer. All of these results are provided in Table 2.

All of these formulations provided great results regarding penetrometer tests and the set-time. Each mix was easy to mix and pour. The consistency was similar for each mix; the only variation between each appeared to be the brine/solids loading. The mixes all set hard and no visible cracking was observed. Also, bleed water was not an issue for any of the batches.

5. FINAL FORMULATIONS

Based on the preliminary mixes, four mixes provided the best physical properties and were chosen to perform TCLP leaching tests: 7, 8, 9, and 10 noted in Table 2 but with a brine to solids ratio (B/S) of 1.3 for all of them as shown in Table 3.

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Table 2. Basin 43 Preliminary Mixtures. (2 sheets)

Date mixed	8-Aug	8-Aug	8-Aug	8-Aug	8-Aug	8-Aug
Batch	1	2	3	4	5	6
B/S	1.2	1.3	1.3	1.2	1.2	1.2
DI H ₂ O	NA	NA	NA	NA	NA	NA
Basin 43	360	250	250	250	250	250
Portland cement	150	96	96	104	69	69
Slag	150	96	NA	NA	139	
Fly ash	NA	NA	96	104	NA	139
Heated @ 60 °C	Yes	Yes	Yes	Yes	Yes	Yes
Consistency on pouring	Very easy to mix, very smooth texture, very pourable	Very easy to mix, very smooth texture, very pourable	Very easy to mix, very smooth texture, very pourable	Very easy to mix, very smooth texture, very pourable	Very easy to mix, very smooth texture, doesn't pour as readily as FA mix, any thicker wouldn't pour out freely	Very easy to mix, very smooth texture, very pourable, easier to pour than batch 5
24 hr	Hard, very solid	Hard, very solid	Hard, very solid	Hard, very solid	Hard, very solid	Hard, very solid
Bleed water	Trace amt	Trace amount	None	None	None	None
48 hr	Same, but no bleed water	Same, but no bleed water	Same	Same	Same	Same
Penitrometer reading (psi)	>2000	>2000	>2000	>2000	>2000	>2000

NA = not applicable

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Table 2 Basin 43 Preliminary Mixture (2 sheets).

Date mixed	9-Ang 7"	9-Ang 8"	9-Ang 9"	9-Ang 10"	8-Ang 11	10-Ang 12	10-Ang 13
Batch							
B/S	1.2	1.4	1.4	1.4	1.2	1.2	1.2
DI H ₂ O	NA	NA	NA	NA	NA	100	100
Basin 43	250	250	250	250	250	150	150
Portland cement	69.4	89.3	89.3	59.5	59.5	104	104
Slag	69.4	89.3	NA	119	NA	NA	104
Fly ash	69.4	NA	89.3	NA	119	104	NA
Heated @ 60 °C	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Consistency on pouring	Same thickness as other B/S 1.2 mixes made above, very easy to mix and easy to pour	Very easy to mix, very smooth texture, very runny mixture, but does not splash when poured	Very easy to mix, very smooth texture, very runny mixture, but does not splash when poured	Very easy to mix, slightly thicker than batch 8, easy to pour	Very easy to mix, slightly thicker than batch 9, easy to pour	Very easy to mix, very smooth texture, slightly thinner than the mixtures above	Very easy to mix, very smooth texture, slightly thinner than the mixtures above
24 hr	Hard, very solid	Hard, very solid	Hard, very solid	Hard, very solid	Hard, very solid	Hard, very solid	Hard, very solid
Bleed water	None	None	None	None	None	None	1 mL
48 hr							
Bleed water	Same	Same	Same	Same	Same	Same	Same
Penitrometer reading (psi)	>2000	>2000	>2000	>2000	>2000	>2000	NA

* Provided the best physical properties and were chosen to perform TCLP leaching tests.
 NA = not applicable

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Table 3. Formulations for Toxicity Characteristic Leaching Procedure Testing.

Date Mixed	18-Aug	18-Aug	18-Aug	18-Aug	18-Aug
Batch	7A ^a	8A ^a	9A ^a	10A ^a	Control ^a
B/S	1.3	1.3	1.3	1.3	1.3
Basin 43	100	100	100	100	100
Portland cement	25.6	38.5	38.5	25.6	25.6
Slag	25.6	38.5	NA	51.3	25.6
Fly ash	25.6	NA	38.5	NA	25.6

^a Provided the best physical properties and were chosen to perform TCLP leaching tests.

NA = not applicable

6. TOXICITY CHARACTERISTIC LEACHING PROCEDURE RESULTS

The U.S. Environmental Protection Agency (EPA) SW-846² Method 1311 test is the TCLP from a size-reduced sample. The TCLP testing was performed on selected formulations after 28 days of curing. The formulations tested were formulations 7A, 8A, 9A, 10A, and a control. The performance of the test is based on land disposal restrictions mandated by Washington State Department of Ecology (Ecology) and the *Code of Federal Regulations*. In this testing, the samples were crushed to $<3/8$ inch. The samples were leached glacial acetic acid as the extraction solution.

The EPA SW-846 test determines the characteristic leaching of metals from a crushed ($<3/8$ inch) sample. The leach solution will be analyzed for antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr, total), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Th), and zinc (Zn). The acceptance levels for inorganic elements are (as prescribed by Ecology) shown in Table 4.

Table 4. Toxicity Characteristic Leaching Procedure. Acceptance Levels

Element	TCLP (mg/L)
Sb	<0.10
As	<0.50
Ba	<7.6
Be	<0.010
Cd	<0.050
Cr	<0.33
Pb	<0.15
Hg	<0.009
Ni	<1.0
Se	<0.16
Ag	<0.30

² SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, Third Edition, as amended, U.S. Environmental Protection Agency, Washington, D.C., September 1986.

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The TCLP test results are presented in Table 5. The values in the shaded cells exceed the acceptance levels presented in Table 4. The only mixture that passed all the acceptance levels is 8A, which is a portland cement, slag mixture as shown in Table 3.

**Table 5. Toxicity Characteristic Leaching Procedure Results
(100 ppm spike levels) (mg/L).**

Element	Control	7A	8A	9A	10A
Be	0.00326	0.01031 ^a	0.00880	0.01212 ^a	0.01151 ^a
Cr	0.03673	0.04820	0.04190	0.06889	0.04949
Ni	0.01844	0.03414	0.01870	0.06377	0.02516
Zn	-0.10750	-0.07583	-0.06921	0.02892	-0.07070
As	0.00744	0.01560	0.01019	0.02724	0.01163
Se	0.00131	0.00506	0.00695	0.00764	0.00778
Ag	-0.00132	0.00615	0.00487	0.00866	0.00689
Cd	0.00024	0.00657	0.00555	0.00947	0.00770
Sb	-0.00458	0.00217	0.00308	0.00755	0.00426
Ba	1.59601	1.68353	0.61396	3.03741	0.70151
Hg	-0.00241	-0.00206	-0.00217	-0.00213	-0.00221
Tl	0.00067	0.01929	0.01557	0.02767 ^a	0.02070 ^a
Pb	0.03211	0.03915	0.00960	0.06909	0.01421

^a Values exceed the acceptance levels presented in Table 4.

7. SUMMARY

Based on the results from the preliminary formulations and the TCLP, these formulations proved promising in preparation as a CS monolith. None of the formulations did not had excessive expansion or bleed water. Also, the strength exhibited from each formulation surpassed the 50-psi strength requirements, which was the original goal. The use of Basin 43 and portland cement, with a mixture of either fly ash or slag, exhibited similar results regarding workability; however, the TCLP for the slag mixture in equal amounts with portland cement (8A) passed all the leaching acceptance levels.

In all, the use of relatively cheap, easy to access materials, provided a formulation that has proven great promise and is fully usable for stabilizing the Basin 43 waste stream.