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Phase 1 Testing Results of Immobilization of WTP Effluent Management Facility Evaporator Bottoms Core Simulant

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Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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EXECUTIVE SUMMARY

The Hanford Waste Treatment and Immobilization Plant (WTP) Low Activity Waste (LAW) vitrification facility will generate an aqueous condensate recycle stream (LAW Melter Off-Gas Condensate) from the off-gas system. The baseline plan for disposition of this stream during full WTP operations is to send it to the WTP Pretreatment Facility, where it will be blended with LAW, concentrated by evaporation and recycled to the LAW vitrification facility. However, during the Direct Feed LAW (DFLAW) scenario, planned disposition of this stream is to evaporate it in a new evaporator in the Effluent Management Facility (EMF) and then return it to the LAW melter. It is important to understand the composition of the effluents from the melter and new evaporator so that the disposition of these streams can be accurately planned and accommodated. Furthermore, alternate disposition of this stream would eliminate recycling of problematic components, and would enable less integrated operation of the LAW melter and the Pretreatment Facilities. Alternate disposition would also eliminate this stream from recycling within WTP when it begins operations and would decrease the LAW vitrification mission duration and quantity of glass waste.

This LAW Melter Off-Gas Condensate stream will contain components that are volatile at melter temperatures and are problematic for the glass waste form, such as halides and sulfate, along with entrained, volatile, and semi-volatile metals, such as Hg, As, and Se. Because this stream will recycle within WTP, these components accumulate in the Melter Condensate stream, exacerbating their impact on the number of LAW glass containers that must be produced. Diverting the stream reduces the halides and sulfate that get recycled to the melter and is a key objective of this work. This overall program examines the potential treatment and immobilization of this stream to enable alternative disposal. The objective of earlier tasks was to formulate and prepare a simulant of the LAW Melter Off-gas Condensate expected during DFLAW operations and use it in evaporator testing to predict the composition of the effluents from the Effluent Management Facility (EMF) evaporator to aid in planning for their disposition. The objective of this task was to test immobilization options for this evaporator bottoms aqueous stream. This document describes the method used to formulate a simulant of this EMF evaporator bottoms stream, immobilize it, and determine if the immobilized waste forms meet disposal criteria.

Testing examined waste forms created with the simulant. This simulant formulation is designated as the “core simulant”; other additives are included for specific testing, such as volatiles for evaporation or hazardous metals for measuring leaching properties of waste forms. Other contaminants of concern were added prior to immobilization, with arsenic and selenium added in this phase, and others will be added in future testing, such as mercury.

These initial tests successfully produced waste forms that passed the physical parameters and leachability criteria, and all solidification agents treated the metals sufficiently to meet TCLP. This testing demonstrated the Cast Stone dry blend (cement/blast furnace slag/Class F fly ash) is effective in treating all of the metals added, and was most effective at treating the chromium such that it was below the detection limit of 50 µg/L (ppb). Testing also indicated that Aquaset® reagents make a solidified waste form that sequesters the hazardous metals to below the leachability limits, but testing would be needed with an added reductant if it is desired to completely eliminate the chromium leaching. A mixture of ordinary portland cement and fly ash passed the leachability criteria, but was the poorest of the mixtures tested. Further testing is needed to optimize the mixtures.

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LIST OF ABBREVIATIONS

BFS	Ground granulated blast furnace slag
CoC	Contaminants of Concern
DFLAW	Direct Feed Low-Activity Waste
DI	deionized (water)
DL	Detection Limit
DOE	Department Of Energy
EMF	Effluent Management Facility
ETF	Effluent Treatment Facility
FA	Class F fly ash
g	gram
ICP-ES	inductively coupled plasma – emission spectroscopy
L	liter
LAW	low-activity waste
M	molar
mg	milligram
mL	milliliter
OPC	Ordinary portland cement
ppb	Parts per billion
RCRA	Resource Conservation and Recovery Act
RL	Reporting Limit
SBS	submerged bed scrubber
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure
VSL	Vitreous State Laboratory
WESP	wet electrostatic precipitator
WRPS	Washington River Protection Solutions
WTP	Waste Treatment Plant
W/DM	Waste/Dry Mix

1.0 Introduction

1.1 Background

The Hanford Low-Activity Waste Melter Off-Gas Condensate stream will be generated in the Waste Treatment Plant (WTP) by condensation and scrubbing of the Low-Activity Waste (LAW) melter off-gas system by a Submerged Bed Scrubber (SBS) and Wet Electrostatic Precipitator (WESP), as shown in Figure 1-1. This stream, which will contain substantial amounts of chloride, fluoride, ammonium, and sulfate ions, and technetium and other radionuclides will get recycled to the LAW melter after evaporation. During Direct Feed LAW (DFLAW) operations, the evaporation will be performed in the planned Effluent Management Facility (EMF), as shown in Figure 1-2. Most of the evaporator bottoms will be returned to the LAW melter, but some may be returned without evaporation to the tank farms when the EMF evaporator is unavailable. The volatile halide and sulfate components that accumulate in this stream are only marginally soluble in glass, and often dictate the LAW glass waste loading, thereby impacting the total quantity of glass canisters produced. The principal radionuclides present in this stream that are not compatible with current onsite disposal limits are ^{99}Tc and ^{129}I. These radionuclides are volatile in the melter and accumulate in the LAW system. Diverting this EMF evaporator bottoms stream to an alternate disposal path would have substantial beneficial impacts on the cost, life cycle, and operational complexity of WTP,[1] but disposition of ^{99}Tc and ^{129}I must be appropriately managed.

1.2 Testing Basis and Objective

The scope of this task is to support Washington River Protection Solutions (WRPS) in evaluating options for disposition of this EMF evaporator bottoms waste stream. To accomplish this, several steps were performed: (1) a simulant of the SBS/WESP condensate from the LAW melter was generated, (2) the SBS/WESP condensate was evaporated in a laboratory-scale vacuum evaporator, (3) the evaporator bottoms were characterized, (4) a simulant was formulated of the evaporator bottoms (with and without As and Se spikes), (5) the simulant of evaporator bottoms was immobilized, and (6) the immobilized simulant was tested and analyzed for leaching of hazardous metals using the Toxicity Characteristic Leaching Procedure (TCLP).[2] This document describes the last three steps. Results of the first three steps were reported previously.[3,4]

To develop the basis for the simulant of the stream prior to evaporation, analytical results were used from samples obtained of melter off-gas condensate from two DuraMelter-10 (DM-10) tests at Vitreous State Laboratory (VSL) at the Catholic University of America.[5] Preparation and analysis of the dilute simulant has been described elsewhere.[6]

During tests at VSL, the SBS and WESP condensate was found to be near neutral pH. Prior to evaporation in the EMF evaporator, the pH will be raised to 12 to minimize corrosion.[7] Note that a significant cation in the dilute stream is ammonium, which will largely convert to ammonia, equation (1), during this adjustment (>98% at pH=11)[7] and will then largely vaporize in the evaporator.

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \qquad (1)$$

It is important to determine the distribution of ammonium and ammonia in the evaporator because the overhead condensate will be dispositioned in the Effluent Treatment Facility (ETF). The EMF evaporator bottoms simulant formulation accounted for this conversion of ammonium to ammonia and subsequent loss of ammonia, replacing it with sodium ions in the formulation. Additionally, a significant component is boric acid, which will consume one equivalent of hydroxide ions to reach pH 11. It was important to experimentally determine the total equivalents of hydroxide consumed by the ammonium to ammonia conversion, and the boric acid reaction, to determine the amount needed to overcome any other buffers, such as forming zinc hydroxides, and actually raise the pH to the target. Since formulation of the EMF evaporator bottoms simulant began with different salts from the SBS/WESP simulant, it was not always possible to simply substitute sodium salts for ammonium salts and end up with the same soluble composition. Further, the directly-made simulant did not then go through a heating and concentrating cycle, so it was important to adjust the chemical mixing steps so that the final composition matched the soluble chemical composition of the evaporated simulant.

1.3 EMF Evaporator Bottoms Simulant Formulation

Evaporator bottoms from the evaporation test were characterized for chemical composition. To dispose of this stream as a low level waste, it would be necessary to immobilize the liquid as a solid and stabilize the hazardous constituents. The goal of this testing was to formulate a waste form that will immobilize the EMF bottoms stream such that it will pass regulatory requirements for disposal. Options for immobilization methods and recommended testing have been investigated. These options included grout-type waste forms and those made with Aquaset® products.[a]

The evaporator testing with the simulated feed to the EMF generated an aqueous stream that was characterized.[4] Most constituents were soluble, but a small amount of lithium fluoride (LiF) and kogarkoite ($Na_3(SO_4)F$) had precipitated. The ammonia had stripped from the bottoms to below the level of detection (50 mg/L). That test generated ~100 mL of EMF bottoms. In order to perform the immobilization testing, a much larger quantity of simulant was needed. To generate this stream, the composition used for the feed to the EMF was increased 11 times higher for all constituents, and the ammonium salts were all replaced with sodium or potassium salts. Compared to the dilute simulant, the order of addition of the chemicals was minimally changed for the first batch (formulation revision #0, or Rev0), but more time was spent on the silica dissolution step to try to increase its soluble concentration. The low solubility of silica and zinc led to extensive changes for batches Revision 1 (Rev1) and Revision 2 (Rev2) in an attempt to dissolve all species and achieve a simulant comparable to that from the EMF evaporator test. Compared to the evaporator feed, the constituents were added at 11X concentration instead of the 12.5X achieved in the test because the 12.5X actually overshot the target density slightly, at 1.217 g/mL vs. the target of 1.20 g/mL. It would also be very challenging to make the simulant at the precipitation point of two constituents and have each batch be consistent. In the facility, it is expected that the evaporator would target running beneath the precipitation point for kogarkoite, since it would tend to scale the evaporator.[8] Arsenic and selenium were added to the Rev2 formulation so that their leachability from the waste form could be determined. It should be noted that in the first batch preparation (Rev0), the total liquid volume target was also exceeded slightly due to inaccurate estimates of density and solubility during the first trial, further diluting the feed by 3%. Future testing will also examine other contaminants of concern, such as mercury.

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[a] Aquaset is a trademark of Fluid Tech, LLC, Knoxville, TN

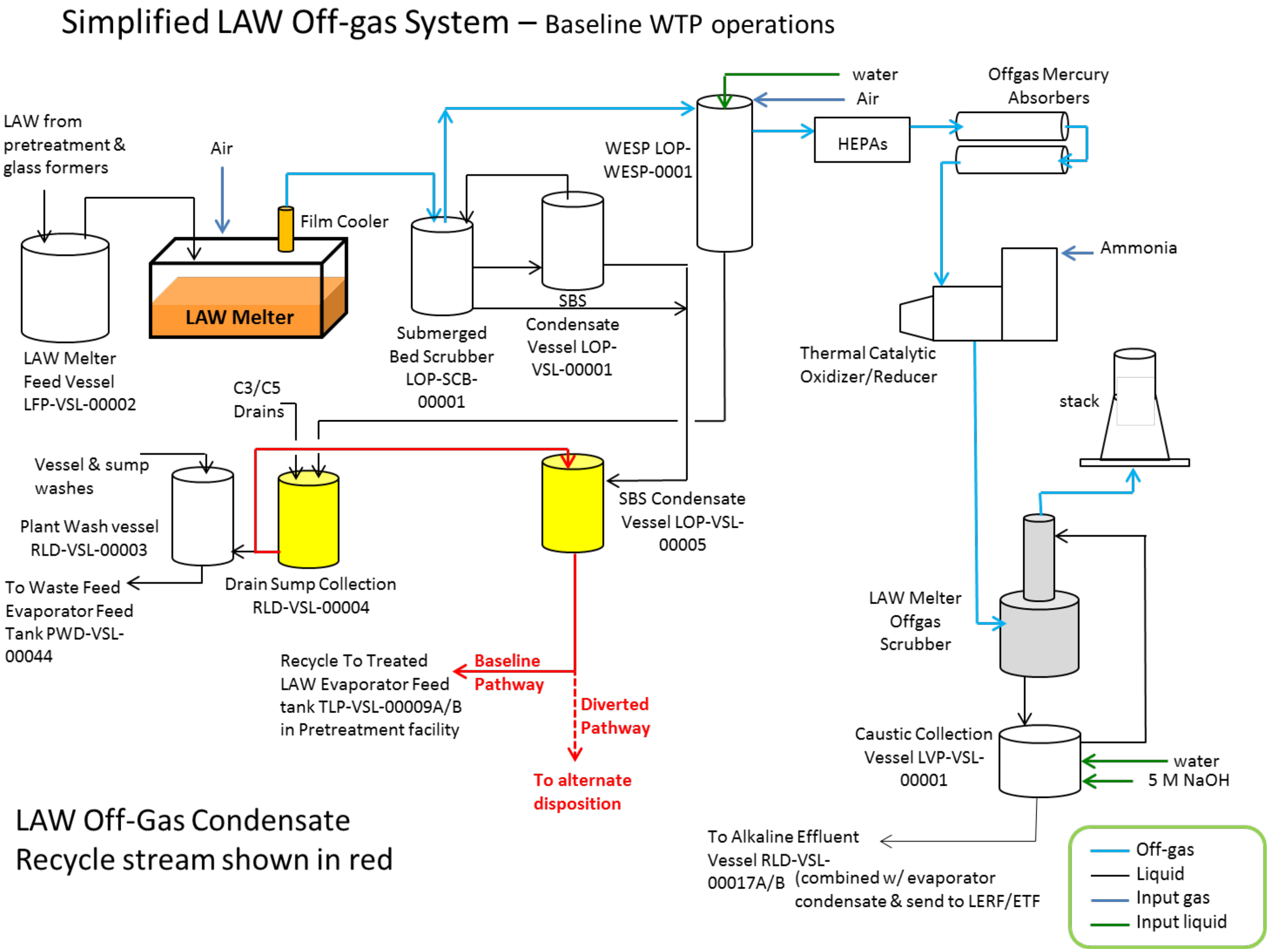

Figure 1-1. Simplified LAW Off-gas System

Note: Yellow indicates SBS/WESP LAW Off-Gas Condensate collection tanks, red lines indicate the collected off-gas condensate pathway, adapted from Reference 9.

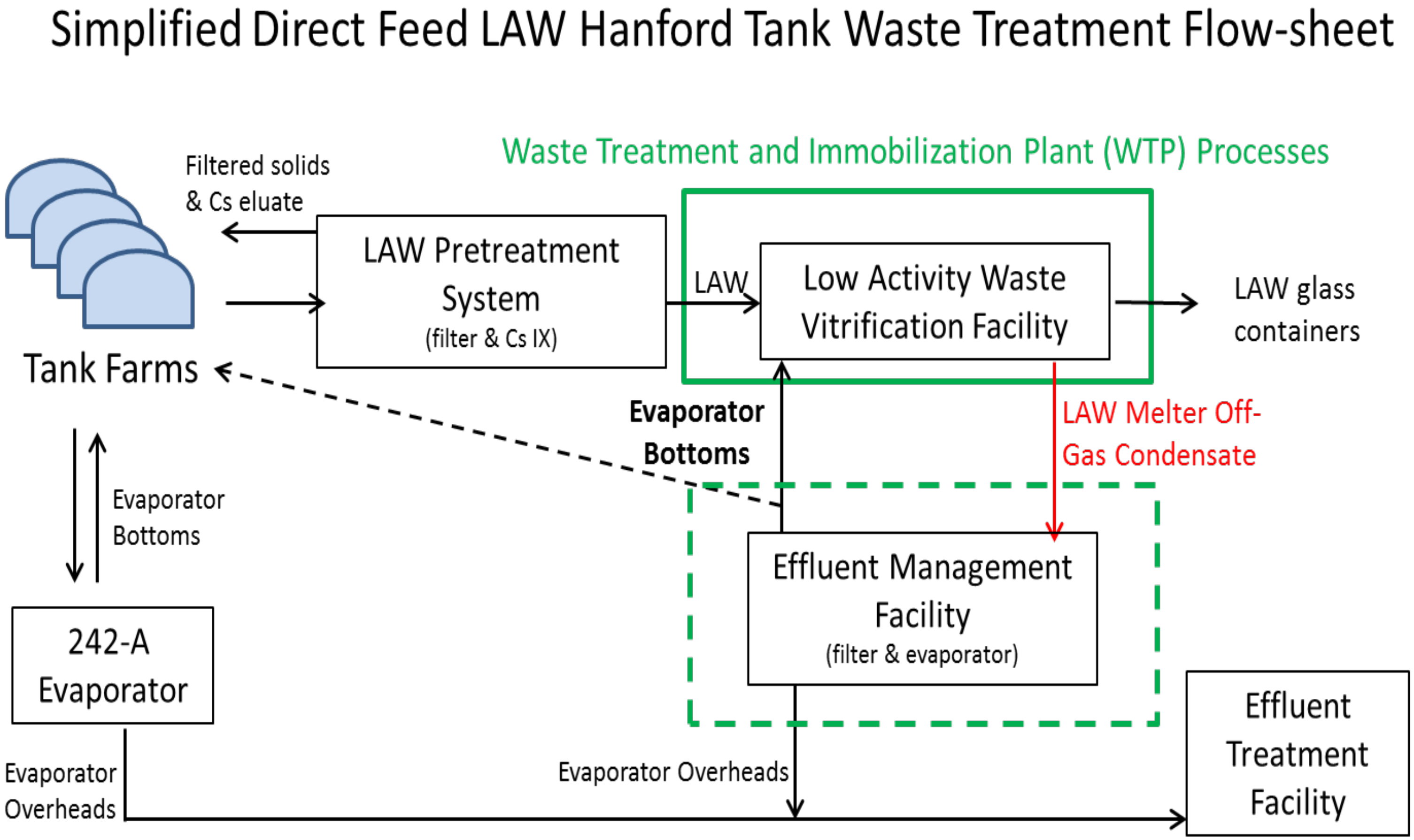

Figure 1-2. Simplified Schematic of the Direct Feed LAW (DFLAW) Scenario.

2.0 Experimental Procedure

2.1 Simulant Formulation

The EMF bottoms simulant was prepared based on the characterization of the bottoms from the evaporation test and from calculations of the concentration of the chemicals from the preparation of the evaporator feed. To actually generate the simulant from available chemicals, constituents were selected as salts, except for boric acid and silica. The amount of sodium was varied to achieve charge balance and the target pH. The concentration was set to 11X the concentration of the EMF evaporator feed simulant. Sodium or potassium salts were adjusted to replace ammonium salts (since there was no ammonia measured in the bottoms). The pH target was set to 12.5-13.

Three formulations of the simulant were prepared before a fully soluble version was achieved. The chemical formulation is shown in Table 2-1. For Rev0, the order of addition was the sequence shown in Table 2-1. Near the end of the preparation, the potassium hydroxide, silica, and a small amount of water were combined in a separate container and stirred in an attempt to first dissolve the silica, but it did not completely dissolve. The slurry of potassium hydroxide and silica was added to the mixture and warmed, but did not dissolve. Other solids were also evidently present. In the Rev1 preparation, the potassium hydroxide, zinc nitrate, and silica were combined first and warmed, but did not dissolve. Next, the boric acid and sodium hydroxide solution were added, but additional solids formed. Addition of the remaining chemicals did not dissolve the solids, and there were insoluble solids visible in the final Rev1 simulant.

For the Rev2 simulant, the amount of sodium hydroxide was increased to the amount that was actually used in the earlier evaporation test (accounting for concentration in the evaporator), and the silica was decreased to the amount that was actually soluble in the earlier evaporation test. The potassium and sodium hydroxides, silica, and zinc nitrate were first dissolved in a small amount of warm water. A warm aqueous solution of dissolved boric acid was then added to that solution. The remaining chemicals were then added, except the potassium fluoride, which was first dissolved in a small amount of water and then added at the end. The final solution was clear yellow.

Table 2-1. EMF Core Condensate Simulant Formulation.

Chemical	Formula	Rev0 and Rev1 Target Mass (g/L)*	Rev0 & Rev1 Target Molarity	Rev2 Target Mass (g/L)	Rev2 Target Molarity
Sodium chloride	NaCl	31.2	0.534	31.2	0.534
Sodium nitrate	$NaNO_3$	11.65	0.137	11.65	0.137
Sodium sulfate	Na_2SO_4	18.2	0.128	18.2	0.128
Potassium sulfate	K_2SO_4	24.2	0.138	24.2	0.138
Boric acid	$B(OH)_3$	57.75	0.934	57.75	0.934
Zinc nitrate	$Zn(NO_3)_2$	2.648	0.014	2.648	0.014
Sodium oxalate	$Na_2C_2O_4$	0.842	0.00628	0.842	0.00628
NaOH (50 wt%)	NaOH	77.1**	0.964	101	1.26
Sodium chromate	Na_2CrO_4	1.183	0.0073	1.183	0.0073
Sodium nitrite	$NaNO_2$	91.85	1.33	91.85	1.33
Lithium carbonate	Li_2CO_3	2.343	0.0317	2.343	0.0317
Potassium hydroxide	KOH	10.78	0.192	10.78	0.192
Silica	SiO_2	3.36	0.056	0.051	0.00085
Potassium Fluoride	KF	13.77	0.237	13.77	0.237

*calculated weights assumes pure anhydrous reagent is used except NaOH

**Rev1 formulation was controlled to pH 12.5-13, requiring 76.53 g of 50 wt% NaOH

The cloudy yellow solutions for Rev0 and Rev1 were filtered and submitted for analysis. The clear yellow Rev2 was not filtered. Samples were analyzed in duplicate by Inductively Coupled Plasma – Emission Spectroscopy, and anion and cation Ion Chromatography at SRNL (Process Science Analytical Laboratory).

2.2 Rev1 Simulant Immobilization Tests

Phase 1 testing utilized Rev1 simulant and evaluated formulations which meet the treatment technology for stabilization as defined in the U.S. Code of Federal Regulations governing the U.S. Environmental Protection Agency, which specifies the addition of: (1) ordinary portland cement; or (2) lime / pozzolans (e.g., fly ash and cement kiln dust) as the reagents (or waste reagents) or combinations of reagents to achieve stabilization.[10] The properties of the waste simulant pertinent to solidification are shown in Table 2-2.

Table 2-2. Rev1 Simulant Properties for Solidification.

Property	Value
pH	12.8
Density	1.196 g/ml
Wt % total solids	24.3

Six mixes were prepared using the solidification agents. The client, WRPS, requested that solidification agents from the Aquaset® family be tested. Aquaset® II-H is a blend of sepiolite powder, a non-swelling clay, and ordinary portland cement (OPC). Aquaset® II-GH is similar in composition; however the sepiolite is in a granular form rather than powder. The Aquaset® products were tested as received, and were also blended with 10% ground granulated blast furnace slag (BFS). OPC combined with Class F fly ash (FA) and the Hanford Supplemental LAW Cast Stone dry blend, 8% OPC, 47% BFS, and 45% FA are the other mixes tested. Table 2-3 shows the makeup of each of the solidification agent blends used for initial testing. For the grout type mixes, W/DM refers to the water content of the waste simulant to dry materials ratio.

Table 2-3. Dry Blends Used for Initial Testing.

Solidification Reagent	Mass Fraction	Typical Reagent/ waste Ratio	Typical Reagent/ waste (g/ml)
Aquaset® II-H	100	5-8 lb/gal W/DM 1.5-0.94	0.6-1
Aquaset® II-GH	100	6-8 lb/gal W/DM 1.3-0.94	0.7-1
Aquaset® II-H + BFS	90/10	5-8 lb/gal W/DM 1.5-0.94	0.6-1
Aquaset® II-GH + BFS	90/10	6-8 lb/gal W/DM 1.3-0.94	0.7-1
OPC + Class F fly ash	20/80	W/DM 0.4-0.6	*
Cast Stone OPC/BFS/FA	8/47/45	W/DM 0.4-0.6	*

*dependent on total solids content of aqueous waste.

For these tests, the pH adjustment step recommended in the Aquaset® Process Control Program was omitted to evaluate the reagents ability to solidify the projected waste simulant without additional operations, vapor production, or increase in waste volume. Mixes containing Aquaset® reagents were prepared following the sample preparation method in the vendor's Process Control Program.[11] However, because of limited availability of the simulant, 75 ml of simulant was used for each mix rather than the recommended 200 ml. The waste simulant was measured into a polycarbonate container. Initially, 80 g of reagent blend was cast over the surface of the waste simulant. The mix was monitored for approximately five minutes to allow for absorption/swelling of the reagents. After approximately five minutes, additional solidification reagent was cast over the simulant until no observable free water was observed and the mass of solidification reagent used was noted. Mixes not containing Aquaset® reagents were prepared by adding the premeasured dry materials into the waste simulant and mixing in a resonant acoustic mixer.[b] The mixer was operated for approximately one minute after it was observed that the dry materials were incorporated in to the waste simulant.

2.3 Rev2 Simulant Immobilization Tests - Phase 1

In the Rev1 simulant testing in Section 2.2, the goal was to determine the minimum mass of solidification agent required to eliminate residual free liquid. For Phase 1 testing with the Rev2 simulant, a consistent ratio of sorbents to waste simulants were used based on the Aquaset® II-GH + BFS formulation, which required the most solids to eliminate free liquids, 134.8 grams (the OPC/FA and Cast Stone mixes used more solids, however the solids additions were predetermined and, based on previous testing in other systems, less solids would have been sufficient to eliminate free liquids). For these tests, additional dry materials were added to ensure that no free liquids would be present—as free liquids would preclude the samples from moving forward in testing. To prepare the samples, Rev2 waste simulant was measured into 200 ml polycarbonate jars. Table 2-4 shows the measured properties of the waste simulant used. For the samples containing Aquaset®, the solidification reagents were cast across the surface of the waste simulant. Intermittently, the container was tapped on the side to remove entrapped air and mitigate layering of the additions. Additions of the reagents continued until all 150 grams were added. As opposed to the testing in Section 2.2, solidification agents were deliberately added after free liquids were no longer present. The mixtures that did not contain Aquaset® reagents were prepared using the resonant mixer as described in Section 2.2. Table 2-5 shows the formulations used to prepare samples for testing. After the samples were prepared, the set time of each mix was monitored using the ASTM method for setting of cement.[12] The heat of hydration will be measured by isothermal calorimetry at 25 °C.[13] Hydration continues almost indefinitely. In these tests, the data will be collected for at least seven days—this corresponds to the time samples will be held prior to TCLP analysis.[c] The total heat generated will be normalized to the amount of solidification agent in the sample.

Table 2-4. Rev2 Simulant Properties for Solidification.

Property	Value
pH	12.7
Density	1.208 g/ml
Wt % total solids	25.2

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[b] LabRAM , Resodyne™ Acoustic Mixers, Inc., Butte, MO

[c] FluidTech recommends 7 days prior to analysis for treatment against waste acceptance criteria [Fluidtech]

Table 2-5. Formulations with the Same Waste Simulant to Solidification Reagent Ratios to Compare Properties.

Solidification Reagent	Waste Simulant (ml)	Waste Simulant (g)	Reagent Mass (g)	Reagent/Waste Simulant (g/ml)	W/DM
Aquaset® II-H	74	89.4	150	2	0.45
Aquaset® II-GH	74	89.4	150	2	0.45
Aquaset® II-H + BFS	74	89.4	150	2	0.45
Aquaset® II-GH + BFS	74	89.4	150	2	0.45
OPC + Class F fly ash	74	89.4	150	2	0.45
Cast Stone OPC/BFS/FA	74	89.4	150	2	0.45

2.4 Spiking Rev2 Simulant with Arsenic and Selenium

A portion of the Rev2 simulant was spiked with 5 mg/L each of arsenic and selenium to prepare immobilized waste form samples for leaching and analysis by the TCLP.[2] The arsenic and selenium were from analytical standards that had been prepared by dissolution of the metal in 2% nitric acid. This dissolution is expected to have converted the metals to arsenous (As(IV)) and selenic (Se(VI)) acids.[14] After spiking, duplicate subsamples were removed and sent for analysis. The remainder of the simulant was spiked with an equivalent amount of 2% nitric acid that did not contain As and Se in order to have an identical solution for use to prepare immobilized samples for the physical properties testing. This diluted the simulant by one volume percent.

2.5 Rev2 Simulant Immobilization Tests - Phase 2

For Phase 2 of the testing with the Rev2 simulant, the same formulations in Table 2-5 were used to prepare samples for TCLP testing. To evaluate retention of contaminants of concern (COC), each of the mixes in Section 2.4 were replicated. After all of the samples had set —as determined by the ASTM method as explained in Section 2.4—the samples were sent to an offsite laboratory for Resource Conservation and Recovery Act (RCRA) metals and Underlying Hazardous Constituents (UHC) retention via TCLP testing and analysis.[d]

2.6 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Results are recorded in Electronic Laboratory Notebooks #E7518-00159 and B7899-00070. This report documents completion of scope for FY16 for Task 3.4 in the Task Technical and Quality Assurance Plan.[6]

3.0 Results and Discussion

3.1 Simulant Analysis Results

Previously reported analysis results of the bottoms from the EMF evaporation test are shown in Table 3-1, along with the simulant formulation targets and the results from the three simulant formulations. Preparation of the first batch of EMF Bottoms simulant (Rev0) yielded significant insoluble solids. During the preparation, it was evident that some of the boric acid precipitated, presumably as sodium tetraborate. However the analysis indicated that eventually this dissolved. The analysis of the soluble boron exceeded the calculated concentration, probably due to analytical uncertainty. The silica either did not completely dissolve or had dissolved and partially re-precipitated in the final mixture. The zinc was

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[d] Gel Laboratories, LLC, Charleston, SC.

only ~38% of the target composition, likely precipitating as zinc hydroxide. Regardless of this, the simulant was used in the first phase of immobilization testing. The objective of the first phase was to get an estimate of waste loading, gain experience with handling the Aquaset® products, and ensure that no unusual reactions occurred. No property measurements or chemical analyses from that phase are reported here. The partial insolubility of the zinc or silica was not expected to play a major role in meeting these initial objectives.

Preparation of the Rev1 batch of EMF Bottoms simulant also exhibited a small amount of insoluble solids. Analysis of the filtrate is shown in Table 3-1. The principal challenges in obtaining a solution that was similar to the evaporator bottoms was dissolving and converting the zinc nitrate to zinc tri- and tetra-hydroxides, and to convert the boric acid to boron tetrahydroxide without precipitating it as sodium tetraborate. These were addressed by adjusting the sequence of chemical additions, creating sub-batches of mixtures that were blended together later, and raising the temperature of several steps. Again in the second batch, the silica did not completely dissolve, or perhaps partially dissolved and then re-precipitated later. Likewise, the zinc did not entirely dissolve.

Preparation of the Rev2 batch of EMF simulant resulted in a completely clear yellow solution with no insoluble solids. To prepare this batch, the sodium hydroxide content was increased from 0.94 M to 1.26 M. This matches the actual amount added during the EMF feed batch preparation after adjusting for concentration in the evaporator and adjusting to 11X concentration. Similarly, the silica was decreased from 0.056 M to 0.00085 M, which matches the amount found soluble in the EMF evaporator bottoms. Additionally, the zinc nitrate was first dissolved in water and then added to a warm, concentrated potassium hydroxide and sodium hydroxide solution. Then, the boric acid solution was prepared at 50 °C and then added to that caustic mixture in order to maintain the zinc in the soluble state, and avoid generating insoluble sodium tetraborate. These concentration adjustments and the sequence of addition of chemicals produced a simulant that closely resembled the target formulation. Results of the analysis are shown in Table 3-1. Most components are within 12% of the target, except zinc and lithium, which are high by 30-50% which is attributed to analytical instrument variability. Unlike the bottoms from the EMF evaporator, no insoluble lithium fluoride or kogarkoite formed, presumably due to the slightly more dilute solution than in the EMF bottoms.

Table 3-1. Compositions of EMF Bottoms Simulants Targets and Analysis Results.*

	Filtered EMF Evaporator bottoms (mg/L)	**Simulant preparation Formulation target (mg/L)**	**Filtered Bottoms Simulant Batch Rev0 (mg/L)**	**Filtered Bottoms Simulant Batch Rev1 (mg/L)**	**Bottoms Simulant Batch Rev2 (mg/L)**
B	13150	10097	14900	10775	11750
Cr	512	380	398	343	560
K	35600	27639	26850	27200	30500
Li	326	440	504	434	658
Na	99350	74701**	73700	72550	93200
Si	27	1568**	45	24	21
Zn	1145	914	349	268	1180
NH_4	<50	0	NA	NA	NA
Cl	24900	18928	18900	18000	17900
F	2600	4503	4270	4368	4290
NO_3	12400	10231	9665	9810	9395
NO_2	85150	61247	67400	64625	62550
SO_4	21150	25649	24350	25900	28300
PO_4	0	0	<100	<100	<100
TIC	748	381	NA	NA	NA
oxalate	687	553	506.5	508	556
pH	13.01	12.5-13.0	12.8	12.8	12.7
Density	1.217	1.20	NA	1.196	1.208
Wt% solids	NA	29.2	NA	24.3	25.1

*Average of duplicate analyses shown
**targets for Rev2 for Na and Si were 81,650 and 24 mg/L, respectively
NA = not analyzed

After the Rev2 simulant was spiked with As and Se, ICP-ES analysis of duplicate samples was performed. Results are shown in Table 3-2. All analytes are within expected ranges, except the lithium and silica are low. The fluoride is also low, suggesting that LiF had precipitated, but no solids were visible in the solution. The original analysis, prior to spiking with As and Se, are somewhat above the target for Li and very near the target for Si, indicating that this is just analytical variability.

Table 3-2. As-Se spiked EMF Bottoms Simulants Targets and Analysis Results.*

	Simulant preparation Formulation target (mg/L)	As-Se spiked Bottoms Simulant Batch Rev2 (mg/L)	Standard Deviation of duplicate analyses
As	5	7	0.12
B	10097	10200	0.0
Cr	380	434	15
K	27639	29750	150
Li	440	286	10
Na	81650	85350	450
Se	5	6	0.02
Si	24	13	0.06
Zn	914	965	0.68
Cl	18928	18150	150
F	4503	3750	0.0
NO_3	10231	10150	250
NO_2	61247	63450	250
SO_4	25649	24900	100
PO_4	0	<100	NA
oxalate	553	482	18

*Average of duplicate analyses shown

3.2 Immobilization Tests

Testing with the Rev1 waste simulant was used to determine the amount of solidification reagents necessary to eliminate free liquid. In Figure 3-1, it can be seen that the initial 80 gram addition of solidification agents to the 75 mL of Rev.1 simulant is not sufficient to preclude the presence of free liquids. Continued additions of solidification agents resulted in the elimination of free liquids, Figure 3-2. Figure 3-3 shows the formulations of OPC/fly ash and Cast Stone materials (i.e., no Aquaset®). The final formulations used to eliminate the formation of free liquids are shown in Table 3-3.

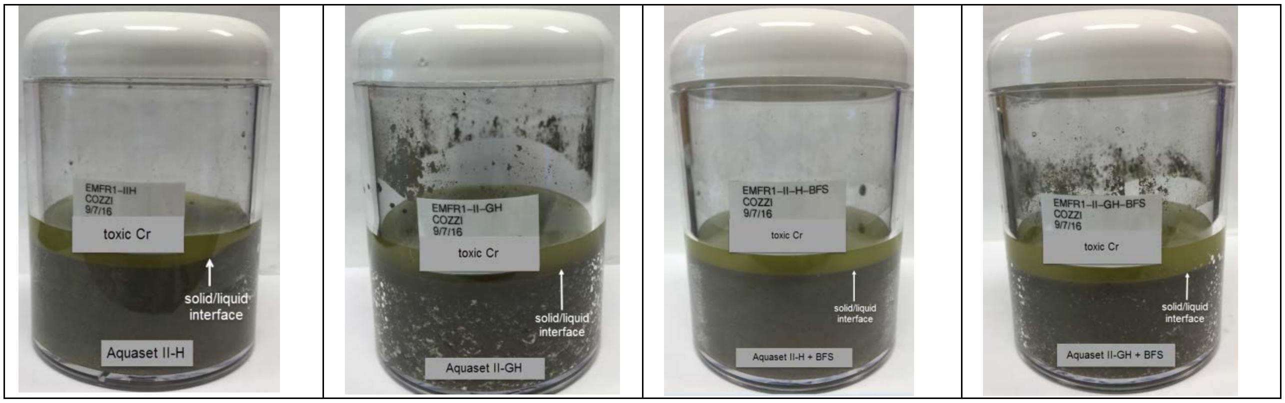

Figure 3-1. Mixes prepared with Aquaset® reagents after initial reagent addition.

Figure 3-2. Mixes prepared with Aquaset® reagents after final reagent addition with no free liquids.

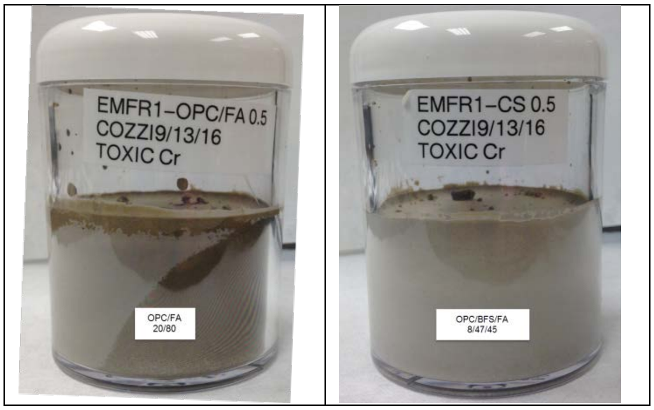

Figure 3-3. Solidification blends prepared with OPC/fly ash and Cast Stone materials (no Aquaset®).

Table 3-3. Formulations to Eliminate Free Liquid.

Solidification Reagent	Waste Simulant (ml)	Waste Simulant (g)	Initial Reagent (g)	Initial Reagent/ Waste Simulant (g/ml)	Final Reagent (g)	Final Reagent/ Waste Simulant (g/ml)	W/ DM
Aquaset® II-H	75	89.7	80	1.07	109.2	1.46	0.62
Aquaset® II-GH	75	89.7	80	1.07	124.5	1.66	0.54
Aquaset® II-H + BFS	75	89.7	80	1.07	119.9	1.60	0.56
Aquaset® II-GH + BFS	75	89.7	80	1.07	134.8	1.80	0.50
OPC + Class F fly ash	75	89.7	--	--	135.4	1.81	0.50
Cast Stone OPC/BFS/FA	75	89.7	--	--	135.4	1.81	0.50

Final set times for the mixes were measured using the ASTM method for hydraulic cements as mentioned in Section 2.3, albeit with a lower measurement frequency. Whereas the method was developed for hydraulic cements that reach final set within the first day, waste forms often take several days to set, and therefore the measurements are not as frequent as prescribed in the method. Set measurments were perfomed once or twice daily, depending on shift schedules. The scheduled measurement at 72 h was not performed. Table 3-4 shows the elapsed time (in hours) to set determination via penetration by the Vicat needle. The penetration depth of the Vicat needle reported are relative as the ASTM method specifies “unset” or “set”. It can be seen from the set times that “time to set” is influenced by the amount of solidification reagent as well as the type of solidification reagent used. The mixes made with Aquaset II-GH/10%BFS, OPC/FA, and the Cast Stone dry blend had similar amounts of solidification agents added. The formulation containing the least amount of material reactive in a caustic solution, 20% OPC, had a longer time to set than the other two mixes that contained greater than 40% hyraulic material (in Section 2.2 the Aquaset® products were noted to contain ~50% OPC and BFS performs as a hydraulic material when the pH >12).

Table 3-4. Set Time Measurements for each of the Formulations Tested with Rev1 Waste Simulant.

Elapsed Time	Aquaset® II-H	Aquaset® II-GH	Aquaset® II-H/10%BFS	Aquaset® II-GH/10%BFS	OPC/FA 20/80	OPC/BFS/FA 8/47/45
(h)	Set (mm)					
9	∞	∞	∞	∞	38	13
18	∞	∞	∞	42	—	—
26	∞	∞	∞	27	∞	30
33	∞	∞	∞	—	∞	30
40	∞	∞	∞	7	—	—
48	∞	36	∞	3	—	—
50	∞	—	—	—	∞	24
67	∞	15	41	5	—	—
92	∞	30	30	5	—	—
107	∞	—	—	—	25	SET
112	∞	10	13	SET	—	
121	34	9	9		35	
136	∞	9	2		—	
145	39	5	SET		16	
153	3	—			10	
162	1	1			—	
170	—	SET			SET	
187	SET					

∞ - Infinite penetration – Vicat needle extended full scale
— - No measurement taken at time interval

Immobilization tests with Rev2 simulant were based on the results in Table 3-3. The Aquaset® II-GH + BFS mix required the most solidification reagent to eliminate free liquids. The formulation in Table 2-5 added at least 10% additional solidification reagent to ensure no free liquids would be present during testing. Set measurments were perfomed once daily. The scheduled measurement at 48 h was not performed. Table 3-5 shows the elapsed time (in hours) to set determination via penetration by the Vicat needle. Usually shorter times measured in this test than the prior test using the Rev1 simulant can be attributed to the additional mass solidification agent used for each test, ~10% increase for Aquaset® II-GH/10%BFS, OPC/FA 20/80, and OPC/BFS/FA 8/47/45, up to >35% additional mass of solidification agent for Aquaset® II-H.

Table 3-5. Set Time Measurements for each of the Formulations Tested with Rev2 Waste Simulant.

Elapsed Time	Aquaset® II-H	Aquaset® II-GH	Aquaset® II-H/10%BFS	Aquaset® II-GH/10%BFS	OPC/FA 20/80	OPC/BFS/FA 8/47/45
(h)	Set (mm)					
23	16	14	2	7	22	24
71	SET	6	15	5	1	SET
95		SET	SET	SET	SET	

Figure 3-4 shows both the side view and top of each of the formulations. The formulations prepared containing Aquaset® solidification reagents all showed signs of layering and air entrapment. The OPC/FA and Cast Stone based formulations showed signs of limited air entrainment.

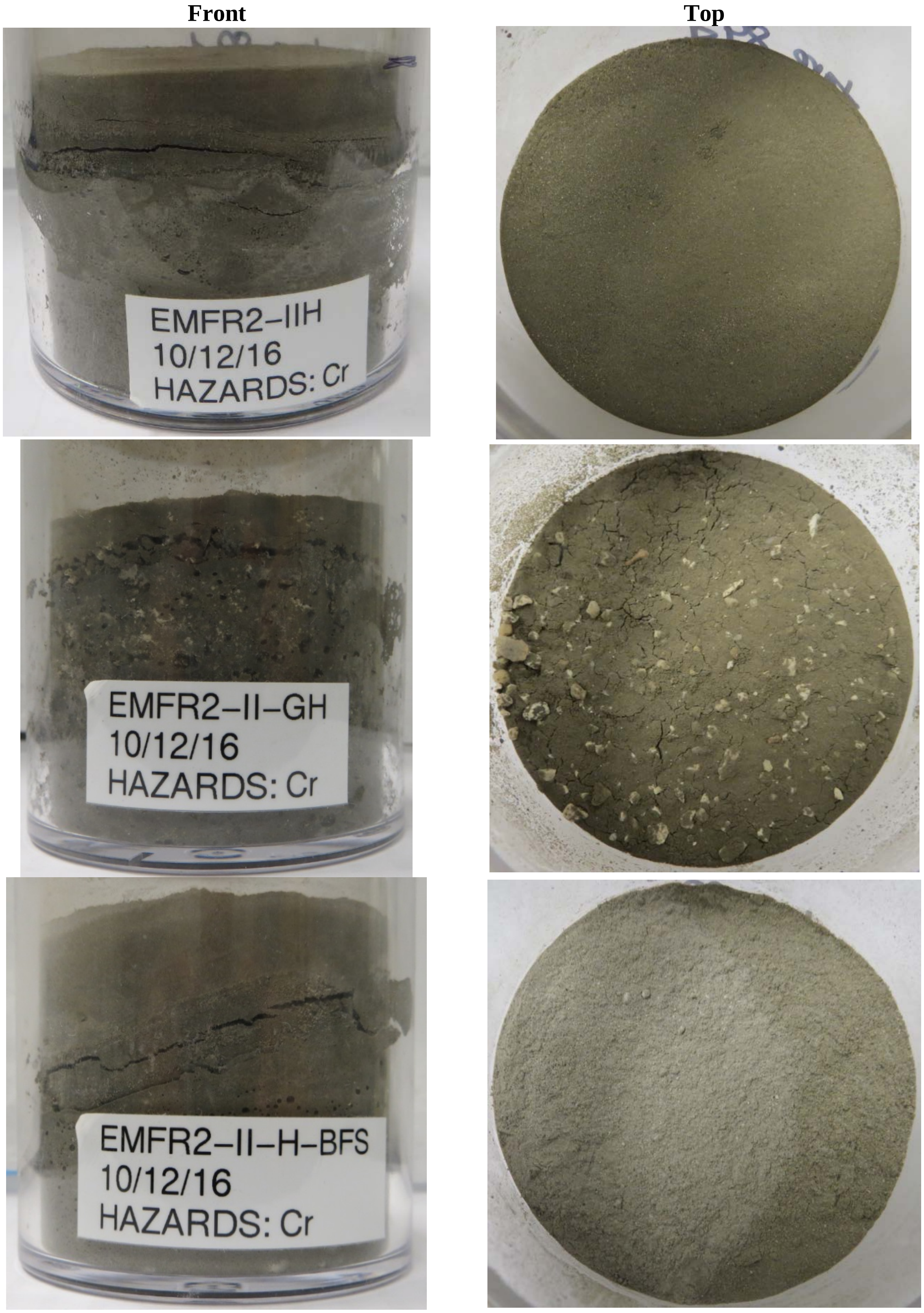

Figure 3-4. –continued, Photographs of formulations prepared with the Rev2 simulant.

Figure 3-4. –continued, Photographs of formulations prepared with the Rev2 simulant.

The heat of hydration was measured over 27 days for each formulation rather than the 7 days as described in Section 2.3. Data collection continued because it was apparent from the plot that the hydration reactions were ongoing at 7 days (168 hours). Figure 3-5 shows the heat generated per gram of solidification reagent using the Rev2 simulant and the ratios shown in Table 2-5. The formulations containing Aquaset® produced similar amounts of heat to each other and to the Cast Stone dry blend. The formulation containing only OPC and fly ash produced about half of the heat of the other formulations. This is consistent with the behavior of mixes containing Class F fly ash, as it is slow to react.

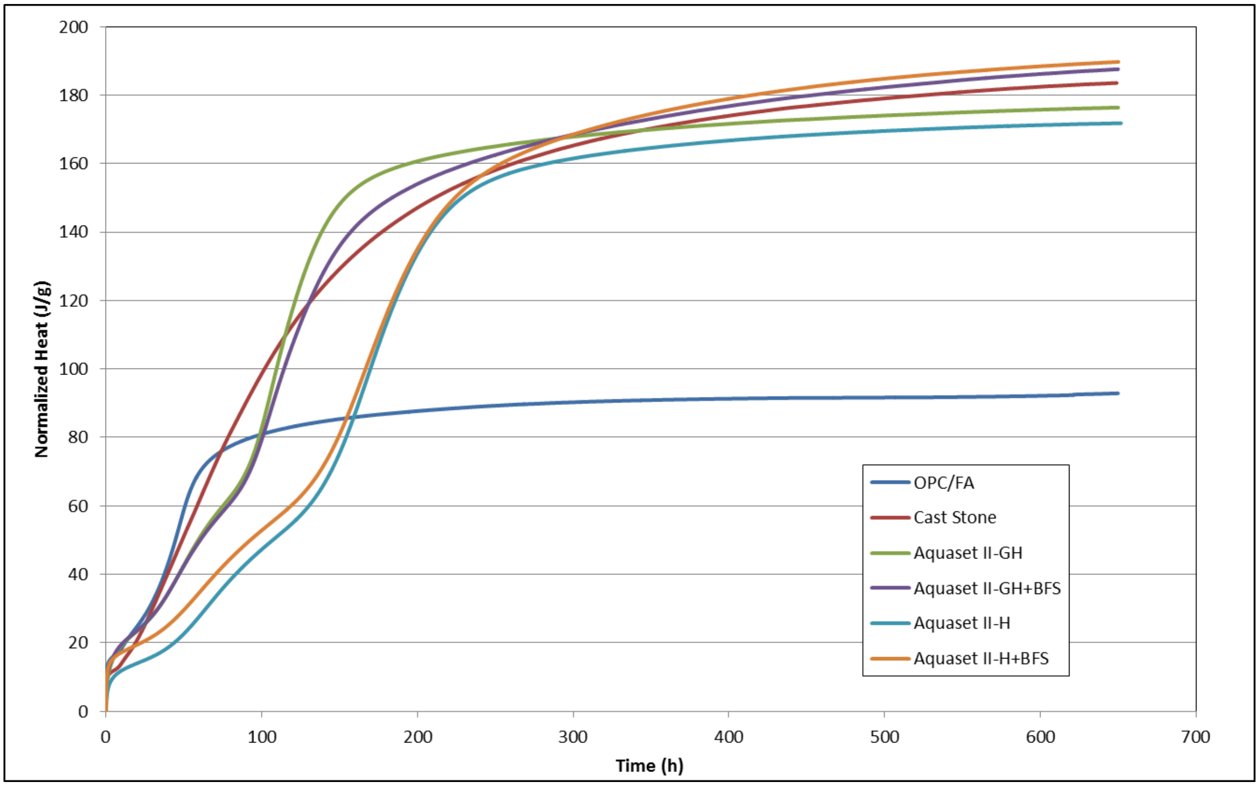

Figure 3-5. Heat of hydration as measured in an isothermal calorimeter at 25 ºC.

3.3 TCLP Test Results

The waste form formulations using the RCRA-spiked waste simulant were produced in individual sample jars and submitted for TCLP analysis as described in Section 2.5. Table 3-6 shows the maximum leachate concentration of contaminants of concern calculated from the measured concentrations in the spiked Rev2 simulant, the waste loading in the waste form, and the dilutions associated with the TCLP test. Table 3-7 shows the results of the TCLP leachate analysis for each of the formulations tested. The table also contains the detection limit, DL, and reporting limit, RL, of the analytical laboratory, along with the TCLP limit. Arsenic, selenium, and zinc results reported for all of the formulations were below the laboratory detection limits. Whereas all solidification agents treated the chromium to meet TCLP, only the Cast Stone formulation treated the waste simulant for chromium to below the analytical detection limit. This is expected as chromium can substitute for aluminum in cement phases, immobilizing a portion of the chromium. The formulations containing 10 wt% BFS added to the Aquaset® solidification reagents retained more chromium than the Aquaset® solidification reagents alone. Barium was detected at non-hazardous levels in every sample as barium is a known component in cement.

Table 3-6. Maximum Potential TCLP Leachate Concentration

CoC	µg/L
As	110
Se	100
Cr	6,720
Zn	14,940

CoC = contaminant of concern

Table 3-7. TCLP Results for Formulations Prepared with RCRA Spiked Rev2 Waste Simulant.

CoC	Aquaset® II-H	Aquaset® II-GH	Aquaset® II-H/ 10%BFS	Aquaset® II-GH/ 10%BFS	OPC/ FA 20/80	OPC/BFS /FA 8/47/45	DL/RL	TCLP Limit
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Hg	ND	ND	ND	ND	ND	ND	0.67/2	200
As	ND	ND	ND	ND	ND	ND	50/300	5000
Ba	312	275	311	285	200	426	10/50	100,000
Cd	ND	ND	ND	ND	ND	ND	10/50	1000
Cr	2940	2100	2230	1310	3900	ND	10/50	5000
Pb	ND	ND	ND	ND	ND	ND	33/100	5000
Se	ND	ND	ND	ND	ND	ND	60/300	1000
Ag	ND	ND	ND	ND	ND	ND	10/50	5000
Zn	ND	ND	ND	ND	ND	ND	33/100	4,300

DL –Detection Limit; The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the concentration is above zero.
RL – Reporting Limit; The lowest level at which an analyte may be accurately and reproducibly quantitated.

4.0 Conclusions

These initial tests successfully produced waste forms that passed the physical parameters and leachability criteria, with all solidification agents treating the metals, including chromium, to meet TCLP. This testing demonstrated the Cast Stone dry blend (cement/blast furnace slag/Class F fly ash) is effective in treating all of the metals added, and was most effective in treating the chromium by reducing it to below the detection limit of 50 µg/L (ppb). Testing also indicated that Aquaset® reagents make a solidified waste form that sequesters the hazardous metals, but testing is needed with an added reductant, such as more blast furnace slag, if there is a desire to completely eliminate the chromium leaching. Manually rapping the side of the plastic container during preparation of waste forms using Aquaset® solidification reagents was done to release trapped air, compact and level the solids, and to incorporate the waste simulant and remove pockets of liquid simulant. While this step is not in the vendors' instructions, it was used here to optimize the lab samples and may or may not be needed at large scale. Conversely, the Cast Stone formulation and the OPC/FA mixture utilized a resonant acoustic mixer to completely homogenize the samples. A mixture of ordinary portland cement and fly ash also had good performance with most added metals, but was poorest for retaining chromium.

5.0 Future Work

All of these mixtures met the criteria for disposal, so optimization and contaminant variability testing would be the next step. If there is a need to further reduce the chromium leaching from the Aquaset® solidification reagents or OPC/FA mixture, testing would be required to determine the appropriate amount of BFS added. If the Cast Stone dry blend formulation is to be considered further, testing should encompass increasing the waste loading of the EMF bottoms simulant in the waste form and potentially reducing the amount of BFS to just that required for the treatment of chromium. Replacing BFS with fly ash is known to increase flowability of the mix and reduce the initial heat generated during curing, so testing could find the optimum ratio of the components and maximum waste loading.

6.0 References

[1] McCabe, D.J., Wilmarth, W.J., and Nash, C.A., Waste Treatment Technology Process Development Plan for Hanford Waste Treatment Plant Low Activity Waste Recycle SRNL-STI-2013-00351, Rev. 0, July, 2013.

[2] EPA Manual SW-846 Method 1311, Toxicity Characteristic leaching Procedure, U.S. Environmental Protection Agency, 1992.

[3] McCabe, D.J., Nash, C.A., Adamson, D.J., Formulation and Preparation of Hanford Waste Treatment Plant Direct Feed Low Activity Waste Effluent Management Facility Core Simulant, SRNL-STI-2016-00313, Rev. 0, June, 2016.

[4] Adamson, D.J., Nash, C.A., McClane, D.L., McCabe, D.J., Evaporation of Hanford Waste Treatment Plant Direct Feed Low Activity Waste Effluent Management Facility Core Simulant, SRNL-STI-2016-00408, Rev. 0, September, 2016

[5] Abramowitz, H., Brandys, M., Cecil, D'Angelo, N., Matlack, K.S., Muller, I.S., Pegg, I.L., Callow, R.A., Joseph, I., Technetium Retention in WTP LAW Glass with Recycle Flow-Sheet: DM10 Melter Testing, VSL-12R2640-1, Rev. 0, RPP-54130, September, 2012.

[6] McCabe, D.J., Task Technical and Quality Assurance Plan for (ICP) Secondary Liquid Waste Stream Technology Maturation, SRNL-RP-2015-01038, Rev. 0, December 30, 2015.

[7] 24590-BOF-3PS-MEVV-T0001, Rev 0, DFLAW Effluent Management Facility Process System (DEP) Evaporator System

[8] Qureshi, Z.H., Adamson, D., Daniel, W.E., Stone, M.E., Williams, M.R., WTP Pilot-scale Evaporation Tests, WSRC-TR-2003-00561, March, 2004.

[9] Jenkins, K.D., Chen, R.C., Gimpel, R., Deng, Y., Gross, M.R., and Peredo, C., Flowsheet Bases, Assumptions, and Requirements, 24590-WTP-RPT-PT-02-005, Rev. 7, March 29, 2013.

[10] Applicability of treatment standards. Code of Federal regulations, Part 268.40, Title 40, 2017.

[11] FluidTec LLC, "Standard Operating Procedure Fluid Tech Process Control Program," FT-001Rev. 0, July 2013.

[12] ASTM C 191-13, Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle, ASTM, West Conshohocken, PA.

[13] ASTM C 1679-09, Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry, ASTM, West Conshohocken, PA.

[14] Greenwood, N.N. and Earnshaw, A., Chemistry of the Elements, Pergamon Press, 1984.

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