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Effluent Management Facility Evaporator Bottoms-Waste Streams Formulation and Waste Form Qualification Testing

August 2017

SA Saslow
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U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

This report describes the results from grout formulation and cementitious waste form testing performed by Pacific Northwest National Laboratory (PNNL) for Washington River Protection Solutions, LLC (WRPS). These results are part of a screening test that investigates grout formulations proposed for encapsulating a wide-range of waste compositions predicted to be present in evaporator bottoms wastes from the Hanford Effluent Management Facility (EMF) bottoms. This work supports the technical development need for alternative treatment and disposition paths for the EMF evaporator bottoms waste and future direct-feed low-activity waste (DFLAW) operations at the Hanford Site. High-priority activities included simulant production, grout formulation, and cementitious waste form testing. The work contained within this report relates to waste form development and testing, but does not directly support the 2017 Integrated Disposal Facility (IDF) performance assessment (PA). However, this work contains valuable information useful for PA maintenance (past FY 2017) and future waste form development efforts. These analytical results can be used by (1) cementitious waste form scientists to further the understanding of cementitious leach behavior of contaminants of concern (COCs), (2) decision makers interested in off-site waste form disposal, and (3) the U.S. Department of Energy, their Hanford Site contractors, and stakeholders as they continue to assess the IDF PA program at the Hanford Site. The reported results help fill existing data gaps, support final selection of a cementitious waste form for the EMF evaporator bottoms waste, and improve the technical defensibility of long-term waste form risk estimates.

Specific grout formulation and waste form testing efforts described in this report include

- Preparation of eight EMF evaporator bottoms waste simulants containing a range of major salt species concentrations (boron, chloride, nitrite, and sulfate);
- formulation and characterization of cementitious waste forms for treatment of the eight EMF evaporator bottoms waste simulants using three dry material ingredient recipes including: the original Cast Stone recipe (8% ordinary Portland cement [OPC], 45% fly ash [FA], and 47% blast furnace slag [BFS]), 20% Aquaset II-GH®/80% BFS, and 20% OPC/80% BFS;
- residual free liquid observations of the cementitious waste forms, for up to 30 days, to assess the storage time necessary for disposal according to Hanford Site solid waste acceptance criteria, HNF-EP-0063, Rev. 14 (Ramirez, 2008); and
- Toxicity Characteristic Leaching Procedure (EPA, 1992) testing to demonstrate that these cementitious waste form(s) will meet Resource Conservation and Recovery Act (RCRA, 1976) land disposal restrictions (LDRs) for hazardous wastes when compared to the Universal Treatment Standards (40 CFR 268, 2015).

The key findings from this work are listed below and supported by the following details:

1. **The Cast Stone formulation was best at re-absorbing residual free liquids to within acceptable criteria for waste form disposal for seven of the eight simulants.** For these seven simulants, free liquids were re-absorbed within three to five days after monolith production. The Aquaset/BFS formulation was successful at treating all eight simulants, but required 10 to 18 days before free liquids were re-absorbed into the grout.
2. **All test batches passed TCLP testing,** meeting Universal Treatment Standards (40 CFR 268) used for LDRs.

Eight simulant solutions were prepared according to a test matrix provided by the client (WRPS) that requires only a small set of simulants to be generated for this screening phase of grout-based waste form development. Simulants were prepared with varying boron, chloride, nitrite, and sulfate concentrations with a composition range based on wet electrostatic precipitator (WESP) and submerged bed scrubber (SBS) condensates estimated by DM10 melter and off-gas system campaigns documented in VSL-12R2640-1, Rev. 0 (Abramowitz et al. 2012). Additionally, all simulants were spiked with Zn (700 ppm) and RCRA metals, As (180 ppm), Se (180 ppm), Cr (300 ppm), and Hg (>30 ppm). All simulant solutions contained variable amounts of visible precipitates when observed several days after preparation. A decrease in soluble Zn was observed to correlate with those simulants containing low initial boron levels, as determined by solution analysis. Due to the presence of precipitates, simulants were continuously mixed immediately before and during grout production to obtain the highest level of homogeneity.

Twenty-four grout formulations were prepared using the eight simulant solutions and three dry material recipes: the original Cast Stone recipe (8% OPC, 45% FA, and 47% BFS), 20% Aquaset II-GH®/80% BFS, and 20% OPC/80% BFS. For all formulations, a water-to-dry-mix (w/dm) ratio of 0.5 was used and a water-reducing agent (MasterGlenium 3030 from BASF Corp.; Beachwood, Ohio.) was added when necessary to reduce viscosity and improve flowability of the mix. Eight monolith specimens were made from each of the 24 grout formulation test batches and were allowed to cure for at least 7 days.

Residual free liquids were monitored for one monolith specimen from each test batch for at least 28 days or until no free liquids (<1% of the total waste volume) were observed. Test batches using the original Cast Stone formulation recipe re-absorbed all residual free liquid within three to five days for all simulants except Simulant 7 (low Cl and B, high NO_2 and SO_4). Alternatively, the Aquaset (20 wt%) and BFS (80 wt%) formulation was suitable for treating all simulants (i.e. <1% total waste volume), but required 10 to 18 days after monolith production to re-absorb the residual free liquid. Simulant immobilization by OPC (20 wt%) and BFS (80 wt%) is not recommended as a treatment since simulants were treated equally or better with the Cast Stone dry material recipe, with the exception of Simulant 7. These results, once confirmed by replicate observations, should guide future formulations for scale-up tests and provide baseline guidance for the time required before waste forms may be disposed of in the IDF.

The TCLP test results when compared to Universal Treatment Standards (40 CFR 268, 2015) for hazardous wastes show that all test batches pass LDRs (40 CFR 268) for each COC. A comparison of TCLP leachate concentrations across the three dry ingredient formulations for Zn and RCRA metals As, Cr, Hg, and Se reveals that a single formulation cannot be singled out as the best for immobilizing all COCs. For instance, the OPC/BFS formulation is adequate for immobilizing Zn, As, Se, and Hg for the majority of the simulants tested, but for Cr treatment the Aquaset/BFS formulation is preferred. An observation worth noting is that all Hg levels were non-detectable in the leachate despite being present in the simulants used to make the cementitious waste forms at elevated concentrations (≥38 ppm in each). These initial TCLP trends, however, are based on the analysis of one specimen from each test batch and replicate specimen analysis by TCLP is recommended for formulations studied in future testing.

The appendices of this report provide photographic evidence of residual free liquids seen immediately after formulation and at the end of the residual free liquids testing period. Also in the appendices are solid digest concentrations of major and select trace constituents from individual dry materials used to produce the cementitious waste forms and from the specimens after TCLP analysis.

The results in this report fill existing data gaps, support final selection of cementitious waste forms for EMF evaporator bottoms waste, and improve the technical defensibility of long-term waste form risk estimates. Future work, quantifying the effective (observed) diffusivity of ^{99}Tc and ^{129}I using U.S. Environmental Protection Agency Method 1315 and ^{99}Tc desorption coefficient (K_d), will provide additional information that can be used to support future maintenance of the IDF PA and waste form selection. These additional data and results will be documented in an update to this report in FY 2018.

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Acronyms and Abbreviations

ASTM	ASTM International (West Conshohocken, PA)
BFS	blast furnace slag
COC	contaminant of concern
CVAA	cold vapor atomic absorption
DFLAW	Direct Feed Low-Activity Waste
DIW	deionized water (18.2 MΩ·cm)
EMF	Effluent Management Facility
EPA	U.S. Environmental Protection Agency
FA	fly ash
FY	fiscal year
HL	hydrated lime
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
IDF	Integrated Disposal Facility
K_d	distribution coefficient
K_{sat}	saturated hydraulic conductivity
LAW	low-activity waste (Hanford)
LDR	land disposal restriction
MG 3030	MasterGlenium 3030, water-reducing additive
ND	not detected
OPC	ordinary Portland cement
PA	performance assessment
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
RCRA	Resource Conservation and Recovery Act of 1976
SRNL	Savannah River National Laboratory
SWCS	secondary waste Cast Stone
SwRI	Southwest Research Institute
TCLP	Toxicity Characteristic Leaching Procedure
TDS	total dissolved solids
TG1	test group one
TG2	test group two
TS	total solids
VSL	Vitreous State Laboratory

w/dm	free water-to-dry-mix (ratio)
WESP-SBS	wet electrostatic precipitator–submerged bed scrubber
WRA	water-reducing additive
WRPS	Washington River Protection Solutions, LLC
WWFTP	WRPS waste form testing program

Units of Measure

°C	temperature in degree Celsius [$T(°C) = T(K) - 273.15$]
d	day(s)
g	gram(s)
L	liter(s)
M	molarity, mole(s)/liter
mL	milliliter(s)
ppm	parts per million
rpm	revolutions per minute
vol%	volume percent
wt%	weight percent
µ	micro (prefix, 10^{-6})

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1.0 Introduction

The direct feed low-activity waste (DFLAW) operations involve concentrating the Hanford Low-Activity Waste (LAW) melter off-gas condensate by evaporation in the Effluent Management Facility (EMF). The concentrated condensate will then be sent back to the LAW melter for recycling. However, the concentrate is expected to contain high levels of halides and sulfate that require dilution to ensure solubility in the glass melt and minimize potential for corrosion of the melter's refractory lining. As consequence, dilution could strain LAW melter performance and final LAW glass production by decreasing glass waste loading. Furthermore, radionuclides technetium-99 (^{99}Tc) and iodine-129 (^{129}I) are expected to accumulate in the recycled captured off-gas waste stream. To this end, the purpose of this research program is to examine alternative disposition paths for the EMF evaporator concentrate waste stream that bypass recycling to the LAW melter (McCabe et al. 2016), thus eliminating recycling of the identified problematic components and decreasing the need for integrated operations with the LAW melter. Technology development and maturation activities conducted within this program will support alternative disposition path investigations for the EMF evaporator bottoms wastes and the results will be used to verify whether developed waste forms can meet off-site disposal acceptance criteria and/or on-site Hanford Integrated Disposal Facility (IDF) waste acceptance criteria.

In fiscal year 2017 (FY 2017), Washington River Protection Solutions, LLC (WRPS) contracted with Pacific Northwest National Laboratory (PNNL) to conduct screening tests to determine whether variation in the bulk EMF evaporator bottoms waste stream composition is a factor in producing an acceptable solidified waste form. High-priority activities include EMF evaporator bottoms-waste simulant production, grout-based waste form formulation development, and waste form performance testing. This work supports the WRPS One System Chief Technology Office's Technology Maturation and Analysis Group in identifying options for alternative treatments and dispositions for Hanford Tank Waste Treatment and Immobilization Plant (WTP) secondary liquid wastes from the DFLAW process.

A waste form test matrix for the EMF evaporator bottoms-waste simulants was prepared based on the lessons learned from previous testing programs and results (Westsik et al. 2013; Serne et al. 2015; Um et al. 2016). PNNL's FY 2017 scope of work focused on EMF evaporator bottoms-waste simulant production as well as preparation and characterization of cementitious waste forms spiked with selected metals regulated by the Resource Conservation and Recovery Act of 1976 (RCRA, 1976) (i.e., Cr, Hg, As, and Se), Zn, technetium-99 (^{99}Tc), and iodine-127 (^{127}I). In addition, PNNL FY 2017 testing has been split into two groups: test group one (TG1) and test group two (TG2).[1]

For TG1, a total of eight EMF bottoms-waste simulants, spiked with Zn and the selected RCRA metals Cr, As, Se, and Hg, were solidified at PNNL using three dry material formulations with baseline dry ingredients, ordinary Portland cement (OPC), fly ash (FA), blast furnace slag (BFS) and Aquaet II-GH (Aquaset). This test matrix thus generates a total of 24 grout formulations to be cured as cementitious waste forms. Waste form specimens from each TG1 grout formulation were used for two testing procedures: (1) residual free liquid of the freshly prepared waste form paste/slurry, performed at PNNL, and (2) Toxicity Characteristic Leaching Procedure (TCLP, EPA 1992) of the cured waste form specimens, preparation and analysis performed at SwRI. The results of these tests were used to assess which TG1 waste form specimens comply with land disposal restrictions (LDRs) (40 CFR 268, 2015) and are the focus of this report.

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[1] In the governing test plan for this report, TP-SWCS-019, Rev 0.1, test group one is referred to as the "off-site" testing group, where "off-site" is meant to indicate that the developed waste forms were tested primarily through a PNNL contract with EPA accredited Southwest Research Institute (SwRI). Furthermore, test group two is referred to as the "on-site" waste forms characterized and tested primarily at PNNL.

Waste form specimens generated as part of the TG2 testing group were prepared for use in additional testing procedures (the majority performed at PNNL) that will provide qualification information for future IDF performance assessments (PAs) and maintenance. The TG2 waste form specimens were generated using a ninth simulant, with a composition matching the average of the eight TG1 simulants. Two dry material formulations were tested to solidify the average EMF evaporator bottoms-waste simulant: the original Cast Stone dry material formulation and a hydrated lime (HL)/OPC/BFS formulation down-selected from three formulations containing different amounts of HL. The selection of the final HL-containing formulation was based on examination for mixture flow and residual free liquids. Two batches of TG2 waste form specimens were generated for each of the two final dry material formulations, one batch with added ^{99}Tc and one without, for a total of four waste form specimen test batches. All TG2 specimens were spiked with select RCRA metals, Zn, and ^{127}I (as an analog to ^{129}I). In FY 2017, non-^{99}Tc specimens were used to assess processing properties of the freshly prepared waste form paste or slurry, including residual free liquids and set time by Vicat needle, which provides an indication of specimen structure development due to hydration reactions (ASTM C191-13). Saturated hydraulic conductivity (K_{sat}) and compressive strength tests were performed at PNNL, and TCLP testing and analysis was performed at SwRI. Additional tests to determine ^{99}Tc desorption distribution coefficient (K_d) and U.S. Environmental Protection Agency (EPA) Method 1315 (EPA 2013) for observed diffusivity of contaminants will be conducted at PNNL in FY 2018. All TG2 testing results will be added in an update to this current report in FY 2018.

1.1 Objectives

The overall objectives of the EMF evaporator bottoms waste form testing program are to

- produce EMF evaporator bottoms-waste simulants based on simulant recipes provided by WRPS that cover the range of expected EMF evaporator waste streams,
- determine a formulation(s) for a grout-based waste form that meets off-site and/or on-site disposal facility acceptance criteria for the EMF evaporator bottoms wastes, and
- provide contaminant release data on the grout-based EMF evaporator bottoms waste form for future PA maintenance and risk assessment evaluations.

1.2 Report Contents and Organization

This report contains only TG1 testing results, consisting of six sections and one appendix. Section 1 provides an introduction and describes key objectives and quality assurance procedures of the tests conducted for this study. Section 2 summarizes simulant production and analysis. Section 3 describes grout waste form formulation and characterization. Section 4 presents the results of residual free liquid and TCLP tests of the TG1 waste form specimens. Section 5 provides a summary, including conclusions and recommendations for future work, and finally Section 6 contains a list of references cited throughout the report. Photos taken during residual free liquid observations and additional data and information for TCLP tests are included in Appendix A.

1.3 Quality Assurance

This work was funded by WRPS under contract 36437-161, *Secondary Waste Cast Stone Formulation and Waste Form Qualification*. The work was conducted as part of PNNL Project 68334, Liquid Secondary Waste Formulation Development. SwRI testing is approved under contract 348272.

All research and development (R&D) work at PNNL was performed in accordance with PNNL's Laboratory-level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2000), to R&D activities. In addition to the PNNL-wide quality assurance (QA) controls, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for the work. The WWFTP QA program consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work. The WWFTP QA program is based on the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008 Quality Assurance Requirements for Nuclear Facility Applications*, graded on the approach presented in NQA-1-2008, Part IV, Subpart 4.2, "Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development."

Performance of this work and preparation of this report were assigned the technology level "Applied Research" by PNNL and were conducted in accordance with WWFTP procedure QA-NSLW-1102, *Scientific Investigation for Applied Research.* All staff members contributing to the work have technical expertise in the subject matter and received QA training before performing quality-affecting work. The "Applied Research" technology level provides adequate controls to ensure that the activities were performed correctly. Use of both the PNNL-wide and WWFTP QA controls ensured that all client QA expectations were addressed in performing the work.

2.0 Simulant Preparation and Analysis

This section describes the simulant production of the EMF evaporator bottoms waste. Simulant preparation details and solution analyses are included.

2.1 Simulant Composition

A screening test was needed to develop cementitious waste forms for EMF evaporator bottoms slurry waste streams that cover a wide range of wet electrostatic precipitator–submerged bed scrubber (WESP-SBS) concentrate compositions and to assess whether cured EMF-based waste forms met LDRs. Eight TG1 EMF evaporator bottoms-waste simulants were prepared with varying boron, chloride, nitrite, and sulfate concentrations. These eight TG1 simulants cover a wide range of major salt compositions projected to be generated by DFLAW operations. The range is based on the WESP-SBS concentrates associated with the Vitreous State Laboratory (VSL) DM10 melter and prototypical off-gas system campaigns documented in VSL-12R2640-1, Rev. 0 (Abramowitz et al. 2012). Mathematical estimates of pH adjustments, to attain a caustic pH (~12.7), and concentrations of the eight simulants to achieve ~15% total dissolved solids (TDS) were made to estimate the final composition of the EMF evaporator concentrates. The final chemical composition, total solids (dissolved and precipitated), and density of the eight simulant solutions were measured directly (Table 2.4).

A test matrix for simulant development was provided by WRPS to allow a small set of simulants to be generated for this screening phase of cementitious waste form development. The simulant test matrix was drawn from the National Institute of Standards and Technology's website for fractional factorial design (http://www.itl.nist.gov/div898/handbook/pri/section3/pri334.htm), and the test matrix for a partial factorial design included nominal high and low ranges in combination with each of the four major salt components. The proposed simulant matrix provided by WRPS for the eight TG1 simulants is shown in Table 2.1.

Table 2.1. Simulant Design Matrix

Test	Cl	NO_2	SO_4	B
T1	Low	Low	Low	High
T2	High	Low	Low	Low
T3	Low	High	Low	Low
T4	High	High	Low	High
T5	Low	Low	High	High
T6	High	Low	High	Low
T7	Low	High	High	Low
T8	High	High	High	High

The species selected for the simulant matrix are those that are both the most significant contributors to the total salt content and also showed a wide range of concentrations in VSL off-gas results that were projected to be in the EMF evaporator bottoms-waste concentrate process. For example, VSL concentrates were observed to contain a range of nitrite levels, from non-detect to 30%. Variable nitrite is expected due to nitrate reduction by organic reductants (e.g. sucrose) added to the vitrification feed. Because some species were present at relatively consistent low levels, such as fluoride, they were not selected as key factors for simulant testing. Once beyond the screening phase of testing, however, fluoride and other constituents must be included in future simulants.

For this test, it was assumed that the nominal density for the 15% TDS EMF evaporator bottoms-waste concentrate is 1,090 g/L.[2] The 15% TDS is the maximum indicated in the Bechtel National, Inc. specification for the EMF evaporator bottoms-waste stream.[3] The major salt portion of this solution is 15% × 1,090 = 164 g/L and divided into fourths. The estimated concentrations of each major salt constituent in the test simulants proposed are shown in Table 2.2. The column labeled "Final B ions, Na^+ & OH^-" represents the estimated ionic species present at the final pH condition after boric acid neutralization with sodium hydroxide.

Table 2.2. Estimated Concentration (g/L) of Variable Simulant Species in the Eight TG1 Simulants [(a)]

Test	NaCl	$NaNO_2$	Na_2SO_4	Final B Ions, Na^+ & OH^-	Sum
T1	60	0	15	89	164
T2	119	0	15	30	164
T3	55	68	14	27	164
T4	65	41	8	49	163
T5	41	0	61	61	163
T6	82	0	61	20	163
T7	36	55	55	18	164
T8	41	41	41	41	164

[(a)] Analytically measured simulant concentrations are provided in Table 2.4

Since LDR compliance of the final solidified waste forms is a key disposal requirement, the metals of concern identified to-date are Zn, Cr, Hg, As, and Se. The first two of these metals were added as salts to the eight TG1 simulants at levels of 0.7 g/L of Zn as $Zn(NO_3)_2$ and 0.3 g/L of Cr as Na_2CrO_4. The latter three metals, Hg, As, and Se, were also added in solid form as a salt (see next section for details). The estimated spike levels of Hg (~30 mg/L), As (~180 mg/L), and Se (~180 mg/L) in the simulants are based on calculations of spike levels sufficient to allow sample quantification of the concentrate and the TCLP leachates and may be higher than the concentrations expected in the concentrate waste stream.

2.2 Simulant Preparation

The simulants described in Section 2.1 were prepared in 5 kg quantities. The target TDS concentration for each of the eight simulants was 15 wt% TDS. Due to precipitation of some simulant constituents with time, the term "total solids" (TS) is used to encompass dissolved and precipitated simulant solids. The order of chemical addition was determined to be important in preparing these simulants (Cozzi and McCabe 2016) as explained below.

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[2] Target density decided by WRPS and communicated in an email sent on November 17th, 2016 between Ridha Mabrouki, David Swanberg, John Mahoney (WRPS), Sarah Saslow, Renee Russell, Wooyong Um, Melanie Chiaradia, and Gary Smith (PNNL).

[3] From WTP report 24590-BOF-3PS-MEVV-T0001, Rev 0, "DFLAW Effluent Management Facility Process System (DEP) Evaporator System" referenced by WRPS in an email sent on November 28th, 2016 between Ridha Mabrouki (WRPS) and Sarah Saslow, Wooyong Um, and Renee Russell (PNNL).

Zinc nitrate was first dissolved in ~100 mL of deionized water (DIW). Then the required amount of 50 wt% NaOH solution (120 to 600 g) was heated to 40°C to 50°C. Once the 50 wt% NaOH solution was at temperature, the zinc nitrate solution was added while stirring.

In another beaker, DIW (600 to 2900 g) was heated to 50°C and the required amount of H_3BO_3 was dissolved while maintaining temperature and with constant stirring. Once the H_3BO_3 dissolved, this solution was slowly combined over the course of ~10 to 15 minutes with the NaOH solution held at 50°C and with continuous mixing. Once these two solutions were combined and mixed, the resultant solution was transferred to a larger container and ~1 L of DIW was added.

Then NaCl and Na_2SO_4 were added to the solution and mixed until fully dissolved. The pH of the solution was then measured using an ORION Star A215 pH meter to assure that it was basic, $\geq$12.7. Once this was confirmed, the Na_2CrO_4, $NaNO_2$, As_2O_3, SeO_2, and $Hg(NO_3)_2{\bullet}H_2O$ were added individually to the solution in the order listed and mixed until fully dissolved before adding the next salt. However, the $Hg(NO_3)_2{\bullet}H_2O$ precipitated almost immediately after addition to the simulant. Once all salts (except $Hg(NO_3)_2{\bullet}H_2O$) were dissolved, DIW was added to just below the target weight and allowed to cool to room temperature overnight.

Once at room temperature, the pH was measured again to assure the pH was $\geq$12.7. DIW was then added to reach the target weight, and the pH checked again to assure that the pH was still $\geq$12.7. At this point, the simulant was mixed for several hours before subsamples were taken for analysis by ion chromatography (IC), inductively coupled plasma optical emission spectroscopy (ICP-OES), and to determine the simulant density and TS. The final simulant was then transferred to a 10-L carboy.

2.3 Simulant Observations and Analytical Results

It was noticed during the preparation of the eight TG1 simulants that the Hg compound precipitated out of solution almost immediately after addition. This is likely due to the high levels of hydroxide present that are known to precipitate Hg as HgO (Qian, 2003), which is resistant to redissolution. Furthermore, after allowing the simulants to sit for several days, another dark precipitate began to form at the bottom of each of the eight TG1 simulant carboys. Low analytical Zn values in simulants with longer wait times between preparation and analysis suggest that zinc compounds precipitated over this course of time. This suggests that the amount of zinc added to the simulants is above the solubility limit for some Zn compound(s), thus causing it to precipitate. Additionally, Zn precipitation was most evident in simulants with low boron levels.

In Table 2.3, the measured pH, density, and wt% TS for each simulant are provided. The measured simulant compositions were all within the expected range and showed no peculiarities. Table 2.4 shows the IC and ICP-OES analytical data for the simulants. Results are reported as “Batched”, “Initial Analytical” or “Final Analytical”. The “Batched” concentrations are the expected concentrations for each simulant according to mass balance calculations. “Initial Analytical” results were determined from simulant aliquots directly, whereas the “Final Analytical” results were determined from acid digested simulant aliquots as described later in this section. The final analytical results for constituents Cr, As, and Se were within 15% of the batched values along with the major salt components (B, Cl, SO_4, and NO_2). When the simulant had a short wait time (<3 days, Table 2.5) between preparation and the initial analytical measurement, the Zn values were within 10% of the target. However, as this time increased to >3 days, the amount of Zn measured in the supernatant decreased, likely due to Zn precipitation. In some cases this decrease in the initial analytical value was greater than 200 mg/L. However, for the final analytical measurements a decrease in Zn to as low as 132 mg/L was measured (Simulant 7). Low simulant Zn concentrations were observed to correlate with low boron simulants, where the Zn concentration measured in Simulant 7 was 132 mg/L and the boron concentration was 1,612 mg/L. This trend is also observed in Simulants 2, 3, and 6. These four low boron simulants were also observed to contain the most precipitates. One challenge with precipitation is collecting a representative simulant sub-sample for solution analysis and may contribute to the low concentrations reported in Table 2.4.

The initial Hg concentration measured in all eight TG1 simulants differed from the target Hg concentration, 30 mg/L, by more than 10% (regarded here as a reasonable uncertainy range) regardless of the time between preparation and analysis. While the exact cause for the low measured Hg concentrations remains unclear, Hg loss could be attributed adhesion to reaction, containment, and analysis vessels or sampling errors due to the low Hg concentration relative to other constituents and immediate precipitation of Hg.

To determine whether Hg loss was due to precipitation or subsequent inaccurate sampling/analysis, the simulant aqueous phase (filtrate) and solid phase (precipitate) were analyzed separately. Simulants were thoroughly mixed before a 10 mL slurry aliquot was taken. The slurry aliquot was filtered using pre-weighed filter paper for mass-balance calculations. The supernate was analyzed within 24 h and the solids were dried at room temperature for over 24 h, with the mass checked periodically to make sure drying was complete after the 24 h drying period. The solid (14 – 38 mg) was then digested in 10 mL of concentrated nitric acid and 10 mL of DIW, and analyzed within 24 h. Unfortunately, the calculated Hg concentration was still determined to be very low, as shown in Table 2.6 for Simulant 1. This is likely due to inaccuracy in the testing method, since Zn was also determined to be almost an order of magnitude less than the target concentration (700 mg/L, Table 2.6). Since Zn is not expected to volatilize or react with the containment vessels, all Zn should have been accounted for between the solid and filtrate phases if the mass balance test method was successful.

Table 2.3. Final Measured Simulant pH, Density, and wt% TS Results

	pH	Density (g/mL)	Wt% TS
Simulant	Target pH ≥ 12.7	Target = 1.09 g/mL	Target = 15 wt%
Simulant 1	13.55	1.14	16.02
Simulant 2	13.02	1.12	15.70
Simulant 3	13.03	1.12	15.48
Simulant 4	13.27	1.12	15.47
Simulant 5	13.35	1.14	16.07
Simulant 6	12.92	1.12	15.52
Simulant 7	12.82	1.12	15.33
Simulant 8	13.15	1.12	15.30

As a second approach for determining the actual concentration of Hg and Zn in the simulants, acid digestion of an aliquot of the total slurry was performed. Three separate, homogeneous slurry aliquots were taken from Simulant 1. Two aliquots were spiked with an additional 21.5 mg/L Hg and 30 mg/L Hg, respectively, from a 1000 mg/L Hg-spike solution made from $Hg(NO_3)_2 \cdot H_2O$ in 2% HNO_3. The first spike concentration, 21.5 mg/L Hg, was selected to increase the simulant Hg concentration to the target concentration, 30 mg/L Hg, while accounting for the Hg already present in Simulant 1, 8.5 mg/L Hg, according to results reported in Table 2.6. The second spike concentration, 30 mg/L Hg, was selected to test the accuracy of the spiking procedure and evaluate possible matrix effects. A third total slurry aliquot did not receive any Hg spike and was used to cross-check the initial Hg concentration in Simulant 1. The slurry samples were directly acid digested with dilute nitric acid, to a final HNO_3 level of ~6% in the subsample, and analyzed for Hg and Zn within 24 to 48 h of preparation (Table 2.7). These results showed that Zn was present within ±10% of the target value, 700 mg/L. For the subsamples spiked with Hg, results show that the final Hg concentration was within ±10% of the spike target (30 mg/L or 38.5 mg/L) and suggest that the Hg-spike method can be used to adjust the simulant Hg concentration as needed. For the subsample analyzed without added Hg spike, Hg was present at 14.7 ppm, slightly higher than originally determined (8.5 ppm).

Based on these results, it is evident that by spiking the simulant with $Hg(NO_3)_2 \bullet H_2O$ in 2% HNO_3 immediately before waste form production or analysis, the target Hg concentration can be obtained. Since the direct cause of Hg loss remains unknown, each simulant aliquot prepared for TG1 test batches was spiked separately, immediately before adding dry ingredients during waste form formulation. A spike solution of 10,000 mg/L Hg (added as $Hg(NO_3)_2 \bullet H_2O$) in 2% HNO_3 was used to decrease the total spike volume added to the TG1 simulants and to keep the water/dry mix ratio within the target range. The Hg spike increased the initial Hg concentration in the simulant aliquot by 40 mg/L to account for possible loss during waste form development. The final Hg concentration in the simulant aliquot was determined from a subsample taken while mixing and within one minute after adding the Hg spike. Exceeding the target Hg concentration (30 mg/L) helped make sure that the final concentration met the target concentration necessary for TCLP analysis. The final measured compositions of the eight Hg-spiked simulants at the time of grout production are shown in Table 2.4 under “Final Analytical”.

Table 2.4. Analytical (Measured) Results of Final Simulants

	Simulant 1				Simulant 2				Simulant 3			
Constituent (a)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)
B	8,410	7,660	7,838	-7	2,692	2,500	2,506	-7	2,508	2,330	2,495	-1
Na	69,355	68,600	63,664	-8	65,855	62,500	60,720	-8	62,676	62,600(b)	59,248	-5
Zn	732	679	673	-8	718	686	375	-48	718	638	294	-59
Cr	313	302	296	-5	308	289	286	-7	308	278	263	-15
As	188	179	194	3	185	178	191	3	184	187	193	5
Se	189	196	185	-2	185	185	180	-3	184	174	182	-1
Hg	31	18.7	39	27	31	16	38	23	32	9.61	60	86
Cl	38,064	38,300	38,300	0.6	74,091	76,500	76,500	3.3	34,191	34,900	34,900	2.1
NO_2	0	ND(c)	ND(c)	-	0	ND(c)	ND(c)	-	46,459	42,200(b)	42,200	-9.2
SO_4	10,611	10,600	10,600	-0.1	10,412	10,400	10,400	-0.1	9,702	9,970	9,970	2.8

	Simulant 4				Simulant 5				Simulant 6			
Constituent (a)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)
B	4,500	4,120	4,269	-5	5,650	5,470	5,299	-6	1,797	1,680	1,777	-1
Na	65,855	63,400(b)	61,088	-7	63,848	64,200(b)	59,984	-6	62,802	58,100(b)	58,880	-6
Zn	721	698(b)	644	-11	730	725	651	-11	720	471	221	-69
Cr	309	288	262	-15	313	313	290	-7	309	310	289	-7
As	186	195	192	3	188	194	195	4	186	191	194	4
Se	186	184	180	-3	188	181	191	1	186	186	191	3
Hg	31	5	46	48	31	12	60	95	31	2	43	38

Constituent (a)	Simulant 4				Simulant 5				Simulant 6			
	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)
Cl	40,634	41,400	41,400	1.9	25,922	27,100	27,100	4.5	51,161	52,500	52,500	2.6
NO_2	28,149	27,000	27,000	-4.1	0	ND(c)	ND(c)	-	0	ND(c)	ND(c)	-
SO_4	5,584	5,670	5,670	1.5	42,993	44,700	44,700	4.0	42,426	43,400	43,400	2.3

Constituent (a)	Simulant 7				Simulant 8			
	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)	Batched (mg/L)	Initial Analytical (mg/L)	Final Analytical (mg/L)	% Difference (Final vs. Batched)
B	1,614	1,560	1,612	0	3,787	3,550	3,533	-7
Na	59,597	57,800	57,040	-4	62,137	59,700	58,880	-5
Zn	718	488	132	-82	722	675	648	-10
Cr	308	316	291	-5	309	300	289	-7
As	185	186	198	7	186	182	195	5
Se	185	192	196	6	186	195	190	2
Hg	31	19.3	65	109	31	45	53	71
Cl	22,395	23,400	23,400	4.5	25,649	26,200	26,200	2.1
NO_2	37,600	32,900	32,900	-12.5	28,189	26,900	26,900	-4.6
SO_4	38,141	39,700	39,700	4.1	28,593	29,300	29,300	2.5

(a) RCRA metals Cr, As, Se, and Hg added as Na_2CrO_4, As_2O_3, SeO_2, and $Hg(NO_3)_2 \cdot H_2O$ salts. Additional Hg added as $Hg(NO_3)_2 \cdot H_2O$ in 2% HNO_3.

(b) Concentration from replicate sample analyzed four days after preparation for analysis (Table 2.5)

(c) ND = not detected

Table 2.5. Time Between Preparation and Analysis of Simulant Subsamples

Simulant	Prepared	Received	Analytical Sample Prepared	Analytical Sample Analyzed
1	Feb. 6	Feb. 9	Feb. 10	Feb. 10
2	Feb. 7	Feb. 9	Feb. 10	Feb. 10
3 (Replicate)	Jan. 31	Feb. 3 (Feb. 3)	Feb. 6 (Feb. 6)	Feb. 6 (Feb. 10)
4 (Replicate)	Feb. 1	Feb. 3 (Feb. 3)	Feb. 6 (Feb. 6)	Feb. 6 (Feb. 10)
5 (Replicate)	Feb. 1	Feb. 3 (Feb. 3)	Feb. 6 (Feb. 6)	Feb. 6 (Feb. 10)
6 (Replicate)	Feb. 2	Feb. 3 (Feb. 3)	Feb. 6 (Feb. 6)	Feb. 6 (Feb. 10)
7	Feb. 6	Feb. 9	Feb. 10	Feb. 10
8	Feb. 7	Feb. 9	Feb. 10	Feb. 10

Replicate samples indicate two sub-samples analyzed from the original simulant aliquot taken for analysis. Replicate sub-samples were analyzed four days after the original sub-sample.

Table 2.6. Solution and Solid Phase Analysis on Simulant 1

	Simulant 1		
Chemical	Target[a] (ppm)	Batched[b] (ppm)	Filtrate + Solids Phase[c] (ppm)
Zn	700	732	84 (±15)
Hg	30	33	8.5 (±1.1)

(a) Target: the concentration outlined in TP-SWCS-0019, Rev. 0.1
(b) Batched: the concentration calculated from the chemical mass added during simulant production
(c) Average of duplicate samples

Table 2.7. Acid Digest of Simulant 1 with Hg Spike

	Simulant 1				
Chemical	Target (ppm)	Batched (ppm)	Acid Digest No Spike (ppm)	Acid Digest 21.5 ppm Hg Spike (ppm)	Acid Digest 30 ppm Hg Spike (ppm)
Zn	700	732	722	711	708
Hg	30	33	14.7	30.4[a]	36.8[b]

(a) Target concentration was 30 ppm (21.5 ppm spike + 8.5 ppm [Table 2.6])
(b) Target concentration was 38.5 ppm (30 ppm spike + 8.5 ppm [Table 2.6])

Efforts were made to maintain TG1 simulants without precipitates, to avoid precipitates settling during preparation of the grout waste forms and to achieve more homogeneous waste forms. This was especially important since contaminants leach differently depending on whether they are immobilized within the waste form as part of the aqueous phase or as precipitates. Unfortunately, without altering the chemistry of the simulants already prepared, precipitate dissolution via heating was the least disruptive method available to minimize impacts of precipitates in the simulants. A subsample of Simulant 6, which visually appeared to have the most precipitates present, was heated in a glass beaker covered with a watch glass at ~50°C for several hours while stirring. After heating, some precipitates still remained; however, the precipitate had turned from black to white in color, as shown in Figure 2.1. Since the majority of the precipitate is hypothesized to be Zn compounds, and zinc chromate ($ZnCrO_4$) is dark in color, this observation suggests that heating the simulant may cause the $ZnCrO_4$ to react and/or dissolve into solution. If Zn bound in $ZnCrO_4$ precipitates does not dissolve, it likely forms ZnO (white) following Cr dissolution. However, it is difficult to conclude whether the white precipitates remaining after heat treatment, proposed to be ZnO, formed as a result of $ZnCrO_4$ reactions or were already present.

Figure 2.1. Simulant 6 Precipitate after Heating at ~50°C for Several Hours

Since the precipitates could not be dissolved by heating, kinetic information was needed to determine how soon a simulant needed to be used before precipitate formation occurred. To do this, a 1 L batch of Simulant 6 was prepared without Hg and observed over time. Simulant 6 was chosen, again, since it visually appeared to be one of the simulants with the most precipitates present. Three hours after preparation, no precipitates were observed; however, the next morning (~20 hours after preparation) precipitates had started to form and the amount of precipitate increased with time (Figure 2.2). After 70 hours, 40 ppm of Hg ($Hg(NO_3)_2 \cdot H_2O$ in 2% HNO_3) was added to visually determine if the presence of the Hg had an effect on the Zn precipitation, but no effect was observed. Based on this test it was determined that the cumulative time required to make fresh simulants, allow the simulants to cool to room temperature, and complete grout production would be more than the project schedule and budget could allow and that the original simulants would be used.

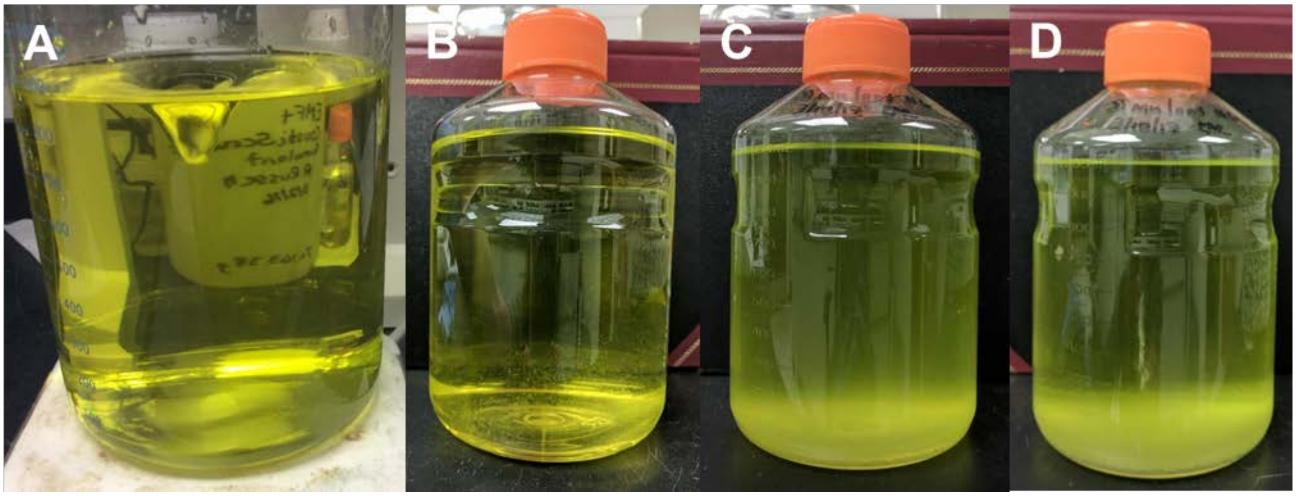

Figure 2.2. Precipitate Formation in a 1 L Batch of Simulant 6 as a Function of Time. Photos taken (A) immediately after simulant preparation was complete and (B) 20 hours, (C) 49 hours, and (D) 70 hours after simulant production. After 70 hours (D), 40 ppm of Hg was spiked into the simulant before observation.

It is important to note that the precipitates observed in the eight TG1 simulants were not observed in the average simulant used to prepare TG2 waste forms. Simulant preparation and analytical results for the average TG2 simulant will be described in detail in the FY 2018 update of this current report.

2.4 Simulant Preparation Conclusions

All TG1 simulants contained precipitates, of varying amounts, that could not be completely redissolved with heat and mixing. This suggests that the composition matrix of the TG1 simulants exceeded the Zn solubility limit, causing Zn to precipitate at room temperature over time. Low simulant Zn concentrations were observed to correlate with low boron simulants, Simulants 2, 3, 6, and 7. These four low boron simulants were also observed to contain the most precipitates. The TG2 average simulant, however, did not contain precipitates despite containing ~700 ppm Zn.

Initial analytical results for the eight TG1 simulants indicate varying degrees of Hg loss from all but one simulant. The exact cause for Hg loss remains unclear, but could be attributed to: 1) Hg adhesion to reaction, containment, and analysis vessels, 2) sampling errors due to the low Hg concentration relative to other constituents, or finally 3) immediate precipitation of Hg. Based on subsequent testing, using a spike of $Hg(NO_3)_2 \bullet H_2O$ in 2% HNO_3 to increase the total Hg concentration in simulant aliquots, it was decided that each simulant aliquot would be spiked with 40 ppm of Hg immediately before grout formulation to help make sure the correct concentration of Hg was present in the simulant during waste form production. An aliquot of the final Hg-spiked simulant was taken and preserved in nitric acid for final metal and compositional analysis.

Efforts to prepare TG1 simulants without precipitates, either by heating to dissolve precipitates or by preparing fresh simulant batches for use before the formation of precipitates, were unsuccessful. Future work should evaluate precipitate formation as a function of the variables tested in the test matrix provided by WRPS, both by computational modeling and by additional liquid- and solid-phase analytical methods.

3.0 EMF Evaporator Bottoms-Waste Grout Formulation and Characterization

Twenty four TG1 EMF evaporator bottoms-waste grout batches were prepared for the EMF evaporator bottoms-waste streams formulation and waste form testing activities performed in FY 2017. A designed grout test matrix (Table 3.1) was used to evaluate the effects of key EMF simulant and grout mix parameters on the properties of the grout during and after curing. Each of the 24 unique monolith formulations prepared varies at least one key parameter. Parameters tested include simulant composition (see Section 2) and dry ingredient composition. Dry ingredients include OPC, FA, Aquaset II-GH® (Aquaset), and BFS. The OPC, FA, and BFS are the baseline dry ingredients used in the original Cast Stone formulation, while the new grout formulations were prepared with 1:4 ratios of either Aquaset or OPC mixed with BFS. For all 24 formulations, the dry ingredients listed in Table 3.1 were thoroughly mixed and then added to the identified liquid simulant.

The baseline grout dry mix was the original Cast Stone formulation, containing 8 wt% OPC, 45 wt% FA, and 47 wt% BFS, and was used to form monolith test batches 1 through 8. Test batches 9 through 16 contained a 1:4 ratio of Aquaset and BFS (20 wt% Aquaset and 80 wt% BFS) and test batches 17 through 24 contained a 1:4 ratio of OPC and BFS (20 wt% OPC and 80 wt% BFS). To improve slurry flowability, a water-reducing additive (WRA; MasterGlenium 3030 from BASF) was added (as needed), based on a ratio of 0.6 mL of WRA per 100 grams of dry mix (maximum total in any grout batch = 10.5 mL), to monolith formulations immediately after mixing the dry ingredients and selected simulant.

Each of the three dry ingredient formulations was tested against all eight simulant compositions (Table 2.4), which had varying boron, chloride, nitrite, and sulfate concentrations. All of the TG1 grout monolith specimens were cured at least 7 days and up to 28 days at room temperature and 80–100% relative humidity. One specimen from each test batch was visually monitored over the course of this curing period for the presence of free liquids (see Section 4 for details). After 7 days of curing, one monolith specimen from each of the 24 formulations was sent to SwRI, an EPA certified laboratory for TCLP analysis. Other 28-day cured TG1 monolith specimens were archieved for future testing and characterization.

Table 3.1. Liquid Secondary Waste Grout Test Matrix

Test Batch #	Simulant	Water-to-Dry Mix (w/dm) Ratio	Dry Blend Addition	Dry Materials	FA(a) (g)	OPC(a) (g)	BFS(a) (g)	Aquaset II-GH (a) (g)	Simulant Mass (b) (g)	WRA(c)
1	T1	0.5	8%, 45%, 47%	OPC, FA, BFS	787.50	140.00	822.50	0.00	1029.4	3030
2	T2	0.5	8%, 45%, 47%	OPC, FA, BFS	787.50	140.00	822.50	0.00	1029.4	3030
3	T3	0.5	8%, 45%, 47%	OPC, FA, BFS	787.50	140.00	822.50	0.00	1029.4	3030
4	T4	0.5	8%, 45%, 47%	OPC, FA, BFS	787.50	140.00	822.50	0.00	1029.4	3030
5	T5	0.5	8%, 45%, 47%	OPC, FA, BFS	787.50	140.00	822.50	0.00	1029.4	3030
6	T6	0.5	8%, 45%, 47%	OPC, FA, BFS	787.50	140.00	822.50	0.00	1029.4	3030
7	T7	0.5	8%, 45%, 47%	OPC, FA, BFS	787.50	140.00	822.50	0.00	1029.4	3030
8	T8	0.5	8%, 45%, 47%	OPC, FA, BFS	787.50	140.00	822.50	0.00	1029.4	3030
9	T1	0.5	20%, 80%	Aquaset [d], BFS	0.00	0.00	1400.00	350.00	1029.4	3030
10	T2	0.5	20%, 80%	Aquaset [d], BFS	0.00	0.00	1400.00	350.00	1029.4	3030
11	T3	0.5	20%, 80%	Aquaset [d], BFS	0.00	0.00	1400.00	350.00	1029.4	3030
12	T4	0.5	20%, 80%	Aquaset [d], BFS	0.00	0.00	1400.00	350.00	1029.4	3030
13	T5	0.5	20%, 80%	Aquaset [d], BFS	0.00	0.00	1400.00	350.00	1029.4	3030
14	T6	0.5	20%, 80%	Aquaset [d], BFS	0.00	0.00	1400.00	350.00	1029.4	3030
15	T7	0.5	20%, 80%	Aquaset [d], BFS	0.00	0.00	1400.00	350.00	1029.4	3030
16	T8	0.5	20%, 80%	Aquaset [d], BFS	0.00	0.00	1400.00	350.00	1029.4	3030
17	T1	0.5	20%, 80%	OPC, BFS	1750	0.00	350.00	1400.00	1029.4	3030
18	T2	0.5	20%, 80%	OPC, BFS	1750	0.00	350.00	1400.00	1029.4	3030
19	T3	0.5	20%, 80%	OPC, BFS	1750	0.00	350.00	1400.00	1029.4	3030
20	T4	0.5	20%, 80%	OPC, BFS	1750	0.00	350.00	1400.00	1029.4	3030
21	T5	0.5	20%, 80%	OPC, BFS	1750	0.00	350.00	1400.00	1029.4	3030
22	T6	0.5	20%, 80%	OPC, BFS	1750	0.00	350.00	1400.00	1029.4	3030
23	T7	0.5	20%, 80%	OPC, BFS	1750	0.00	350.00	1400.00	1029.4	3030
24	T8	0.5	20%, 80%	OPC, BFS	1750	0.00	350.00	1400.00	1029.4	3030

(a) Dry ingredients are mixed together in a closed plastic bag, and the bag was manipulated until the dry mixture appeared to be homogeneous.

(b) Simulant mass calculated assuming 15 wt% total solids, a density of 1.09 g/mL, and a required water mass of 875 g.

(c) Water-reducing additive (WRA): MasterGlenium 3030 (MG 3030) from BASF used as needed, up to 0.6 mL of MG 3030 per 100 g of dry mix, to enhance the cement rheology

(d) Aquaset II-GH® (Fluid Tech, LLC.) is a 1:1 blend of granular sepiolite and OPC with <3% quartz.

3.1 Preparation of EMF Evaporator Bottoms-Waste Monoliths

Liquid simulant and homogenized dry ingredients were prepared separately and then combined to prepare the grout specimens. The select dry materials (either [1] OPC, FA, and BFS, [2] Aquaset and BFS, or [3] OPC and BFS) were measured, according to the masses specified in advance, into a plastic bag and mixed by manipulating the closed plastic bag until the dry mixture appeared to be homogeneous by visual observation. Aliquots of simulants were also taken from each respective batch at the masses specified in TI-SWCS-024.[1] One target w/dm ratio of 0.5 was used for all TG1 monoliths.

3.1.1 Dry Ingredients

The grout monoliths were made using two or three of the four primary dry ingredients, blended together in different ratios. OPC and BFS used in this work were supplied by Lafarge North America, Inc., in Pasco, Washington. According to the OPC mill test report, R-TI-15-04, this is a Type I/II Portland cement produced in Richmond, British Columbia. The BFS, commonly referred to by the trade name NewCem®, meets ASTM C989-14 requirements for class 100 ground granulated BFS and was processed at Lafarge's Seattle, Washington plant. The FA used in this work qualifies as both class F and class C FA and was sourced from the Centralia, Washington power plant. The OPC, BFS, and FA are the same materials used in previous work detailed in Westsik et al. (2013), Serne et al. (2015), and Um et al. (2016). Aquaset II-GH® (Aquaset) is a primary blend of granular sepiolite and OPC and was purchased from Fluid Tech, LLC in Montpelier, Idaho. Each of the dry materials were sent to SwRI to be digested and analyzed for total metals in order to determine the material composition. Dry material compositions are reported in Appendix A.2.

3.1.2 Grout Mixing/Monolith Production

Grout mixing and monolith production followed the procedure outlined in Westsik et al. (2013) and Um et al. (2016).

3.1.2.1 Grout Mixing Summary

Grout mixing and monolith production followed this general outline;

1. addition of dry ingredients to stirring simulant, 5 minute target duration
2. addition of MG 3030 (if needed) to wetted dry-blend–simulant slurry
3. continued mixing, total of 15 minutes from start of step 1 above
4. filling of monolith plastic forms with the well mixed slurry
5. de-airing of filled plastic forms
6. at least 7 day curing in a humid environment at room temperature.

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[1] TI-SWCS-024. 2017. "Production of off-site EMF evaporator bottom waste grout specimens," Pacific Northwest National Laboratory, Richland, Washington.

3.1.2.2 Grout Monolith Production

Grout mixing was performed with a Caframo BDC1850 variable speed overhead stirrer. This style of mixer was used to accommodate a custom 3.5" diameter impeller designed and provided by SRNL. The impeller and mixer head were joined by a 3/8" shaft and the combined mixer apparatus was supported by a Caframo A210 heavy-duty stand and A120 heavy-duty clamp. The mixer shaft was lowered into a 2-L plastic mixing beaker until the bottom of the impeller was between 0.75" and 1.25" from the bottom of the beaker. The beaker was offset from the mixer shaft so that the impeller was between 0.25" and 0.5" from one sidewall. This offset helped to minimize the creation of a central vortex, and thus air entrainment, during mixing. With the beaker of simulant in place under the mixer, the mixer's stirrer was started at about 200 rpm. Vortex creation and modest air entrainment was acceptable at this point. With the mixer's stirrer turning at about 200 rpm, 4.545 mL of 10,000 ppm Hg spike (in 2% nitric acid) solution was added to the simulant and allowed to mix for ~1 minute. Then a 10 mL subsample was taken for additional simulant characterization (Figure 3.1, left) before slowly adding the bag of homogenized dry ingredients to the Hg-spiked simulant. To facilitate clean transfer from the bag to the beaker, a 2" diagonal cut was made across one corner of the bag. This corner opening funnels the dry pre-mix into the desired location in the beaker and allows for good control during addition to the beaker. A timer was used to make sure that all dry ingredients were added to the mixing beaker within approximately 5 minutes. As the dry ingredients were added, the mixer rotation speed was increased to maintain obvious surface movement in the slurry with minimal formation of a central vortex and associated air entrainment.

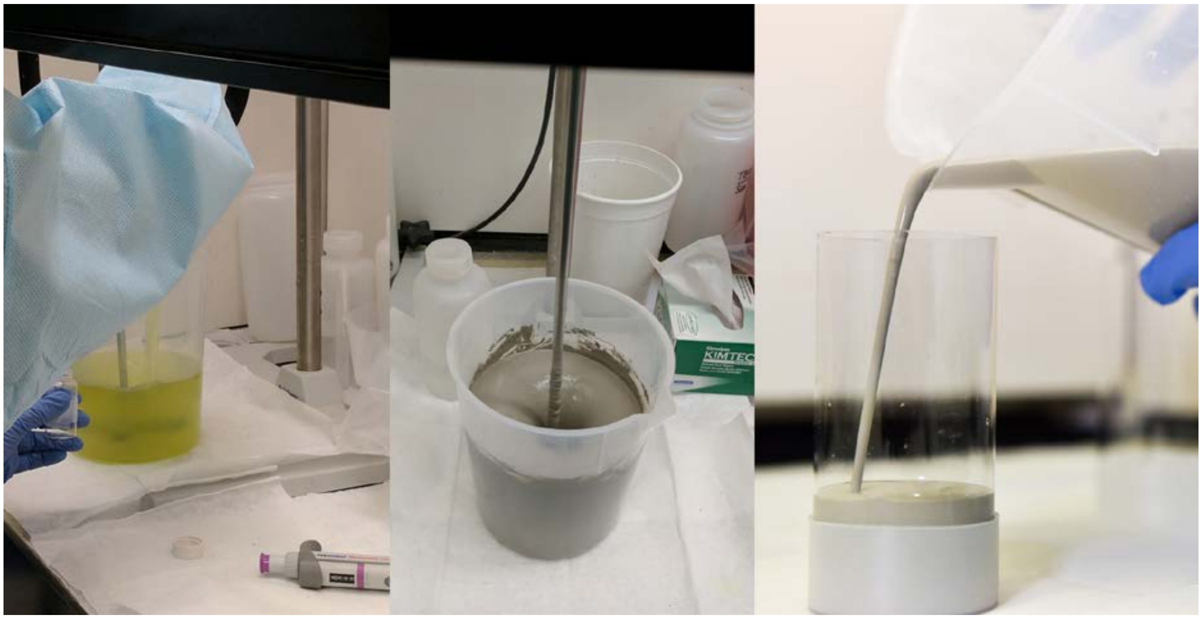

Figure 3.1. Taking Simulant Subsample while Mixing before Dry Ingredient Addition (left), Mixing Grout after Combining Simulant and Dry Ingredients (middle), and Pouring Grout into Plastic Waste Form Mold (right)

As soon as all of the dry ingredients had been added to the mixing beaker, the grout was visually assessed for low flowability. If reduced flowability was determined, MG 3030 was added step-wise to the grout near the vortex. WRA addition was based on operator experience and awareness that flowability is an important process characteristic when pouring grout waste forms. The MG 3030 significantly reduced viscosity and allowed the grout to be "burped" to release entrained air by stopping the mixer for 15–30 seconds and tapping the beaker on the benchtop. In the end, only test batch 9 required addition of the WRA, needing 8 mL of WRA to improve grout flowability. Mixing continued until 15 minutes had elapsed since the beginning of dry pre-mix addition (Figure 3.1, middle). This time was spent promoting grout homogeneity by scraping the beaker sides and mixer shaft with a spatula as needed. Mixer speed was adjusted to the highest possible level without risking additional air entrainment. This speed varied from batch to batch and was occasionally decreased during mixing as grout shear properties changed over time.

At the end of the mixing period, the grout slurry was poured into 2" internal diameter × 4" high cylindrical forms (Figure 3.1, right). These forms consist of thin-walled plastic mailing tubes with push-on plastic caps (Icon Plastics in Costa Mesa, California). Each batch of grout was expected to fill approximately six to eight forms. The forms were initially filled about three-quarters full to minimize risk of spillage during mechanical agitation with a vortex mixer to release entrained air in the grout material. Not all grouts appeared to have entrained air, but all monoliths were agitated to make sure that minimal entrained air was cured into the monoliths. De-airing required a minute or less per monolith, which helped minimize the effects of grout stratification. De-airing was considered complete when visual inspection detected the cessation of new bubbles rising to the surface of the grout slurry. The forms were then completely filled, gently de-aired, and covered with perforated caps. The caps were left a few millimeters higher than the upper surface of the grout in order to allow a level grout surface to form and to minimize surface imperfections induced by contact with the cap during the slurry setting. One additional form, filled one-quarter to one-half full, was also prepared for each grout formulation and used for residual free liquds observations. All forms were labeled with the year and sample identifier of the following format:

17-EMF-TB#-N

where 17 = last two digits of calendar year
EMF = EMF Evaporator Bottoms
TB# = Test Batch # from Table 3.1
N = monolith number (starting with 1).

The filled and capped forms were placed into racks, which were stacked into 5-gallon buckets. Before the racks were installed, the buckets were preloaded with 3/8" to 1" of DIW to maintain a humid environment (relative humidity: ~80–100 %) inside the sealed bucket at room temperature. Monoliths were allowed to cure at room temperature and with high humidity for a minimum of 7 days inside the sealed buckets. During this period, free-liquid observations were made on at least one monolith from each of the 24 test batches (see Section 4.1 for free liquids results). After at least 7 (or 28) days of curing, each cured monolith was removed from its mold and physically observed for cracks, surface voids, irregular shapes, and loose chips. Any loose chips were removed from the monolith and notes on the physical description of each monolith were recorded. The 7-day cured monoliths were used for TCLP testing, while 28-day cured monoliths were archived for future testing. Archived samples were packaged in an open Ziploc bag that was then enclosed in a second, sealed Ziploc bag containing a wet paper towel to maintain relative humidity conditions, >80%.

4.0 Residual Free Liquids and TCLP Tests

The freshly prepared wet pastes of waste form specimens were characterized for free liquid content during the initial curing stage. In addition, after curing, select TG1 waste form specimens were characterized with respect to TCLP testing. The free liquids and TCLP testing methods and results are described in this section.

4.1 Free Liquids Testing

4.1.1 Methods and Materials

All TG1 waste form specimens were monitored for the presence of free liquids during the 28-day cure period. Observations were made every day for the first 7 days post-production of monolith specimens and at least twice a week until the 28-day cure period was reached or until no free liquids remained. Visual inspection identified free liquids from curing waste form specimens. Per *Hanford Site Solid Waste Acceptance Criteria* (Ramirez 2008), free liquids must not exceed 1% of the total waste volume. Visual observations of a few drops of liquid on the surface or less are considered less than 1% of the total waste volume.

4.1.2 Results and Discussion

The presence of free liquids was monitored on one monolith selected from each TG1 test batch, TB1 through TB24. On each observation day, a photo was taken to document the presence of free liquids. Photos taken on production day compared to the final observation for each monolith are provided in Appendix A.1. For all monoliths, yellow free liquid was initially observed on the top surface of the grout monolith. In many instances, the free liquid turned colorless, with some monolith specimens absorbing the free liquid over the course of 3 to 18 days. However, for test batches TB7, TB19, and TB22, free liquids remained throughout the 28- to 30-day observation period. The time required for free liquids to reduce to less than 1% of the total waste volume is illustrated in Figure 4.1 and tabulated in Table 4.1.

Additionally, cured cementitious waste forms containing low boron concentrations (simulants 2, 3, 6, and 7) were observed to be darker in color (green/grey) and in some cases contained white precipitates on the exterior surfaces. This contrasts to the tan color typical for cementitious waste forms produced in previous FY testing activities or with relatively high boron levels in this study (simulants 1, 4, 5, and 8). Solid phase characterization of the cured waste forms and any surface precipitates will be included in the FY18 update to this report.

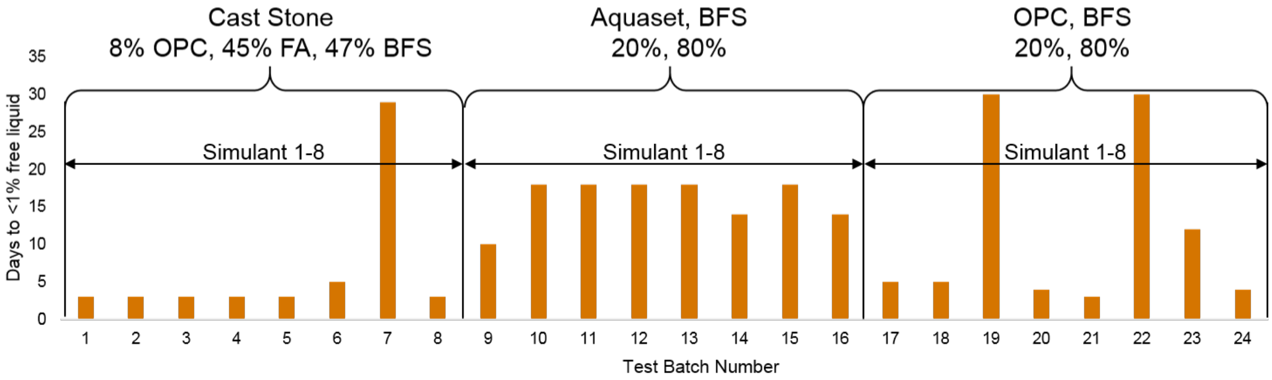

Figure 4.1. Number of Days after Monolith Production for Free Liquids to Decrease to Less Than 1% of the Total Waste Volume for All TG1 Test Batches

Table 4.1. Days Required for Free Liquids to Reach Less Than 1% of Total Waste Volume

Simulant	Cast Stone 8% OPC, 45% FA, 47% BFS	Aquaset, BFS 20%, 80%	OPC, BFS 20%, 80%
	(days)	(days)	(days)
1	3	10	5
2	3	18	5
3	3	18	30
4	3	18	4
5	3	18	3
6	5	14	30
7	29	18	12
8	3	14	4

Based on free-liquids analysis alone, the Cast Stone formulation recipe re-absorbs free liquids within three to five days for all simulants except Simulant 7 (low Cl and B, high NO_2 and SO_4). Free liquids were still present at the end of the observation period (29 days) for TB7, which treated Simulant 7 with the Cast Stone formulation. So while the Cast Stone formulation yielded the most promising results for the majority of the simulants tested, implementation of that recipe may not recommended for waste streams similar to Simulant 7. The Aquaset (20 wt%) and BFS (80 wt%) waste form formulaton is recommended for treatment of all simulated wastes, including Simulant 7, based on observations of this study. Free liquid was observed up to 18 days after monolith production using the Aquaset/BFS formulation, however, the presence of free liquids diminished to less than 1% of the total waste volume for all simulants tested after 18 days. Finally, the formulation of OPC (20 wt%) and BFS (80 wt%) is not recommended for treatment because two of the treated simulants (Simulants 3 and 6) had free liquids remaining even after 30 days. Those simulants successfully treated with the OPC/BFS formulation are treated as well or better with the current Cast Stone formulation, with the exception of Simulant 7.

The residual free liquid results discussed here are based off of observations collected for one specimen from each test batch. Replicate sample observations are needed to confirm these assessments. Once confirmed the results of this work can be used to select formulations for scale-up tests and to provide baseline guidance for the time required before waste forms may be moved to and be disposed of in the IDF.

4.2 TCLP Testing

4.2.1 Methods and Materials

The TCLP testing, EPA Method 1311 (EPA 1992), was conducted to demonstrate that the cementitious waste forms developed would meet RCRA LDRs (40 CFR 268, 2015) for hazardous wastes. The EMF evaporator bottoms-waste simulants contain RCRA metals, including As, Cr, Hg, and Se, and potentially high concentrations of Zn. In addition, some of the dry materials may include these and other hazardous materials, e.g. As, Se, Hg, Cr, and Pb. Waste form specimens from test batches 1 through 24 (TB1–TB24) were sent to the EPA-accredited SwRI for the TCLP testing. The results were compared with the Universal Treatment Standards (UTS) in 40 CFR 268, *Land Disposal Restrictions* (40 CFR 268, 2015).

From each test batch, TB1 through TB24, one monolith specimen was selected for analysis by the TCLP at SwRI. The monolith numbers are provided in Table 4.3, Table 4.4, and Table 4.5 according to the dry ingredient recipe used. Each monolith was removed from its form 7 days after monolith production and packaged in an open Ziploc bag that was then enclosed in a second, sealed Ziploc bag containing a wet paper towel to maintain relative humidity conditions, >80%. Monolith specimens were then shipped overnight to SwRI to make sure that the specimens were ready for TCLP testing 14 days after monolith production. This schedule is summarized in Table 4.2 and matches the timeline used by SRNL for TCLP testing that they performed. In some instances, the monolith specimen was still soft, determined by squeezing the outer plastic wall, on the 7-day opening date. This was noted for TB12, TB13, and TB16. For these specimens, the plastic form was left on the monolith specimen so that the monolith could continue to cure and maintain its shape until the TCLP testing start date. These specimens were packaged within Ziploc bags and sent to SwRI upright to contain any free liquids present within the plastic form as well as possible. The plastic form was removed on the TCLP test start date by SwRI. For monolith 17-EMF-TB13-1, the monolith still had not completely cured by the 14th day and the TCLP test was conducted using the bottom, solidified portion of the monolith.

Table 4.2. Specimen Preparation and TCLP Testing Schedule

Test Batch #	SwRI ID#	Production Date	Monolith Opening Date	Ship Date	TCLP Test Start Date	TCLP Filtration Date
TB1	613739	03/27/2017	04/03/2017	04/05/2017	4/10/2017	4/11/2017
TB2	613748	03/27/2017	04/03/2017	04/05/2017	4/10/2017	4/11/2017
TB3	613749	03/27/2017	04/03/2017	04/05/2017	4/10/2017	4/11/2017
TB4	613750	03/27/2017	04/03/2017	04/05/2017	4/10/2017	4/11/2017
TB5	613751	03/27/2017	04/03/2017	04/05/2017	4/10/2017	4/11/2017
TB6	613752	03/27/2017	04/03/2017	04/05/2017	4/10/2017	4/11/2017
TB7	613753	03/28/2017	04/04/2017	04/05/2017	4/11/2017	4/12/2017
TB8	613754	03/28/2017	04/04/2017	04/05/2017	4/11/2017	4/12/2017
TB9	613755	03/28/2017	04/04/2017	04/05/2017	4/11/2017	4/12/2017
TB10	613738	03/28/2017	04/04/2017	04/05/2017	4/11/2017	4/12/2017
TB11	613740	03/28/2017	04/04/2017	04/05/2017	4/11/2017	4/12/2017
TB12	613741	03/28/2017	04/04/2017(a)	04/05/2017	4/11/2017	4/12/2017
TB13	613742	03/29/2017	04/05/2017(a)	04/05/2017	4/12/2017	4/13/2017
TB14	613743	03/29/2017	04/05/2017	04/05/2017	4/12/2017	4/13/2017
TB15	613744	03/29/2017	04/05/2017	04/05/2017	4/12/2017	4/13/2017
TB16	613745	03/29/2017	04/05/2017(a)	04/05/2017	4/12/2017	4/13/2017
TB17	613746	03/29/2017	04/05/2017	04/05/2017	4/12/2017	4/13/2017
TB18	613747	03/29/2017	04/05/2017	04/05/2017	4/12/2017	4/13/2017
TB19	614014	04/03/2017	04/10/2017	04/11/2017	4/17/2017	4/18/2017
TB20	614015	04/03/2017	04/10/2017	04/11/2017	4/17/2017	4/18/2017
TB21	614016	04/03/2017	04/10/2017	04/11/2017	4/17/2017	4/18/2017
TB22	614017	04/03/2017	04/10/2017	04/11/2017	4/17/2017	4/18/2017
TB23	614018	04/03/2017	04/10/2017	04/11/2017	4/17/2017	4/18/2017
TB24	614019	04/03/2017	04/10/2017	04/11/2017	4/17/2017	4/18/2017

(a) Plastic form was not removed from monolith specimen before shipment due to incomplete curing (monolith was still soft and/or free liquids were present).

4.2.2 Results and Discussion

The TCLP test results for the Cast Stone formulation are shown in Table 4.3 along with the UTS (40 CFR 268, 2015) concentrations for hazardous waste constituents required by LDRs. Similarly, Tables 4.4 and Table 4.5 show the TCLP concentrations from the Aquaset/BFS and OPC/BFS formulations, respectively. All 24 grout test batches analyzed passed LDRs when compared to the UTS limit for each contaminant of concern (COC). However, these results are non-conservative due to the presence of precipitates in the starting simulants and that COCs immobilized as a solid (precipitate) rather than in the aqueous phase may exhibit different leach behaviors.

A comparison of TCLP leachate concentrations across the three dry ingredient formulations for Zn and RCRA metals As, Cr, Hg, and Se reveals that a single formulation cannot be singled out as the best for immobilizing all COCs. For instance, both the Cast Stone recipe and the OPC/BFS formulation are better for immobilizing Zn compared to the Aquaset/BFS formulation. This trend is reversed for Cr and overall the Aquaset/BFS formulation is best for Cr immobilization in all treated simulants. For As and Se, the OPC/BFS formulation is the best option for the majority of the simulants tested and for Hg all dry ingredient formulations are adequate for Hg immobilization. These trends have been determined assuming constituents with non-detect concentrations are equal to the analytical detection limit and by considering whether the leachate COC concentration for one formulation is more or less than another for the majority of immobilized simulants. However, these initial TCLP trends are based on the analysis of one specimen from each test batch and replicate specimen analysis by TCLP is recommended for formulations studied in future testing.

It is important to note that all Hg levels were non-detectable or below the detection limit for cold vapor atomic absorption (CVAA) analysis despite being present in the simulant at elevated concentrations (between 38 ppm and 65 ppm, Table 2.4). The retention of Hg at elevated levels is further supported by the concentration of Hg in the monolith specimen after TCLP testing. All specimens analyzed by TCLP were completely digested at SwRI, using a series of acid and fusion digestion methods, to determine the remaining concentration of constituents in the waste form and to better benchmark the starting composition within each grout formulation. Solid digestion results are provided in Appendix A.2. From these solid digestion results, the Hg remaining in the waste form ranged from 21.8 ppm to 29.9 ppm. This range is approximately what one would expect assuming little Hg was present in the initial dry ingredients (Appendix A.2), which dilutes the total Hg concentration in the waste form once the dry ingredients (~1750 g total) and simulant aliquot (~1029.4 g) are mixed.

Table 4.3. TCLP Results for Simulants Treated with Cast Stone Formulation Recipe

Simulant	1	2	3	4	5	6	7	8	UTS Limit (mg/L)*	Pass/Fail 40 CFR 268
Sample ID	17-EMF-TB1-04	17-EMF-TB2-02	17-EMF-TB3-02	17-EMF-TB4-02	17-EMF-TB5-02	17-EMF-TB6-02	17-EMF-TB7-02	17-EMF-TB8-02		
RCRA Metals, (mg/L)										
As	0.0254	0.0416	0.0428	0.0397	0.0487	0.0421	0.0511	0.0504	5.0	Pass
Ba	0.238	0.295	0.271	0.266	0.164	0.181	0.204	0.19	21	Pass
Cd	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.11	Pass
Cr	0.0533	<0.00500	0.0196	0.0265	0.0166	<0.00500	0.00834	0.0427	0.60	Pass
Pb	<0.00500	<0.00500	<0.00500	0.0342	<0.00500	<0.00500	<0.00500	<0.00500	0.75	Pass
Hg	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	0.025	Pass
Se	0.357	0.275	0.577	0.603	0.347	0.256	0.472	0.591	5.7	Pass
Ag	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.14	Pass
Underlying Hazardous Constituents, (mg/L)										
Sb	0.0106	0.0116	0.0111	0.0114	0.0119	0.0103	0.0105	0.0111	1.15	Pass
Be	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	1.22	Pass
Ni	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.00643	<0.00500	11	Pass
Tl	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.20	Pass
Other Metals, (mg/L)										
Zn	<0.00500	<0.00500	<0.00500	0.00977	<0.00500	<0.00500	0.0277	<0.00500	4.3	Pass

*As reported in 40 CFR 268, 2015

Table 4.4. TCLP Results for Simulants Treated with Aquaset and BFS Formulation Recipe

Simulant	1	2	3	4	5	6	7	8	UTS Limit (ppm)*	Pass/Fail 40 CFR 268
Sample ID	17-EMF-TB9-02	17-EMF-TB10-02	17-EMF-TB11-02	17-EMF-TB12-02	17-EMF-TB13-01	17-EMF-TB14-01	17-EMF-TB15-01	17-EMF-TB16-01		
RCRA Metals, (mg/L)										
As	0.0369	0.0503	0.0573	0.103	0.0916	0.0693	0.0749	0.0748	5.0	Pass
Ba	0.284	0.329	0.335	0.274	0.208	0.218	0.215	0.243	21	Pass
Cd	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.11	Pass
Cr	0.00634	<0.00500	<0.00500	<0.00500	0.00989	<0.00500	<0.00500	0.005	0.60	Pass
Pb	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.75	Pass
Hg	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	0.025	Pass
Se	0.525	0.224	0.387	0.513	0.358	0.252	0.363	0.364	5.7	Pass
Ag	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.14	Pass
Underlying Hazardous Constituents, (mg/L)										
Sb	<0.00500	<0.00500	<0.00500	0.00501	<0.00500	<0.00500	0.00507	<0.00500	1.15	Pass
Be	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	1.22	Pass
Ni	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	11	Pass
Tl	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.20	Pass
Other Metals, (mg/L)										
Zn	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.0107	<0.00500	4.3	Pass

*As reported in 40 CFR 268, 2015

Table 4.5. TCLP Results for Simulants Treated with OPC and BFS Formulation Recipe

Simulant	1	2	3	4	5	6	7	8	UTS Limit (ppm)*	Pass/Fail 40 CFR 268
Sample ID	17-EMF-TB17-01	17-EMF-TB18-01	17-EMF-TB19-01	17-EMF-TB20-01	17-EMF-TB21-01	17-EMF-TB22-01	17-EMF-TB23-01	17-EMF-TB24-01		
RCRA Metals, (mg/L)										
As	0.0311	0.0525	0.025	0.0196	0.0164	0.0202	0.0227	0.0194	5.0	Pass
Ba	0.309	0.315	0.297	0.304	0.269	0.265	0.272	0.306	21	Pass
Cd	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.11	Pass
Cr	0.0105	0.00507	0.00824	0.0182	0.0202	0.00591	0.00991	0.0189	0.60	Pass
Pb	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.75	Pass
Hg	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	0.025	Pass
Se	0.388	0.245	0.253	0.283	0.309	0.203	0.269	0.316	5.7	Pass
Ag	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.14	Pass
Underlying Hazardous Constituents, (mg/L)										
Sb	0.0108	0.0131	0.0067	0.00607	0.00566	0.00808	0.00681	0.00662	1.15	Pass
Be	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	1.22	Pass
Ni	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	11	Pass
Tl	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	0.20	Pass
Other Metals, (mg/L)										
Zn	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	<0.00500	4.3	Pass

*As reported in 40 CFR 268, 2015

5.0 Summary and Recommendations

This section summarizes the key conclusions from each activity performed during FY 2017 for EMF TG1 cementitious waste form formulation and testing. The results obtained help fill existing data gaps, support final selection of a cementitious waste form for the future EMF evaporator bottoms waste stream, and improve the technical defensibility of long-term waste form performance estimates. Recommendations for further testing needed, to provide additional information for waste form development and to support future IDF PA maintenance, are also addressed.

Specific formulation and waste form qualification testing efforts described in this report include

1. production of eight EMF evaporator bottoms-waste simulant solutions containing a range of major salt species (boron, chloride, nitrite, and sulfate),
2. formulation and characterization of cementitious waste forms for treatment of the eight simulants using three dry ingredient recipes: the original Cast Stone recipe (8% OPC, 45% FA, and 47% BFS), 20% Aquaset II-GH®/80% BFS, and 20% OPC/80% BFS,
3. observations of residual free liquid from the cementitious waste forms over the 28-day cure period to assess the storage time necessary before disposal according to Hanford Site solid waste acceptance criteria (Ramirez 2008),
4. TCLP testing to demonstrate that waste form(s) will meet RCRA LDRs for hazardous wastes when compared to the Universal Treatment Standards in 40 CFR 268 (2015).

5.1 Conclusions

The eight simulants used in this report were developed according to a test matrix to allow a small set of simulants to be prepared with varying boron, chloride, nitrite, and sulfate concentrations. All TG1 simulants were spiked with Zn (700 ppm) and RCRA metals, As (180 ppm), Se (180 ppm), Cr (300 ppm), and Hg (>30 ppm). All TG1 simulants contained precipitates, of varying amounts, that could not be completely redissolved with heat and vigorous mixing. This suggests that the composition matrix of the TG1 simulants exceeded the Zn solubility limit, causing Zn to precipitate at room temperature over time. Zn precipitation was most evident in simulants with low boron levels, with analytical values significantly lower than the concentration expected by mass-balance calculations. Furthermore, maintaining the target Hg concentrations proved especially difficult, with none of the simulants meeting the target concentration (30 ppm) within 10%. The exact cause for the Hg variation remains unclear, but it could be attributed to Hg adhesion to reaction, containment, and analysis vessels, or sampling errors due to the low Hg concentration relative to other constituents and/or immediate precipitation of some insoluble Hg compound. Consequently, 40 ppm Hg was added to each simulant aliquot, as $Hg(NO_3)_2 \cdot H_2O$ in 2% HNO_3, in addition to the Hg already present in order to increase the total Hg concentration and make sure the correct level of Hg was present during waste form preparation. Analytical results from an aliquot of the final Hg-spiked simulant showed that for each simulant aliquot, the target concentration (30 ppm) was met and often exceeded.

Grout formulation for immobilization of each of the eight simulants was tested with three dry ingredient recipes: the original Cast Stone recipe (8% OPC, 45% FA, and 47% BFS), 20% Aquaset II-GH®/80% BFS, and 20% OPC/80% BFS. For all formulations, a w/dm ratio of 0.5 was used and a WRA (MasterGlenium 3030 from BASF Corp.) was added when necessary to reduce viscosity and improve flowability of the mix. A total of 24 grout test batches were produced and used to make eight monolith specimens from each simulant-dry blend formulation. Monolith specimens for TCLP analysis were cured for 7 days before being packaged at >80% relative humidity for transport to SwRI for analysis. The remaining cementitious waste forms were cured for at least 28 days before they were opened and archived for use in additional tests in the last quarter of FY 2017 or in FY 2018.

Residual free liquids were monitored for one monolith specimen from each grout test batch for at least 28 days or until no free liquids (<1% of the total waste volume) were observed. Test batches using the original Cast Stone formulation recipe re-absorbed residual free liquids to below 1 vol% within three to five days for all simulants except Simulant 7 (low Cl and B, high NO_2 and SO_4). Only the Aquaset/BFS formulation re-absorbed residual free liquids from all eight treated simulants, but required up to 18 days to achieve <1 vol% residual free liquid. Simulant immobilization by OPC (20 wt%) and BFS (80 wt%) is not recommended for EMF evaporator bottoms waste stream solidification, since simulants were treated as well or better with the Cast Stone dry-blend formulation, with the exception of Simulant 7. However, residual free liquid observations are based on observations collected for one specimen from each test batch and replicate sample observations in future tests are recommended to confirm these assessments. Once confirmed, these results should be considered when selecting formulations for scale-up tests and to provide baseline guidance for the time required before waste forms may be transported to and disposed of in the IDF.

Monoliths were analyzed by TCLP 14 days after production to match the TCLP analysis timeline used by SRNL (Cozzi and McCabe 2016). The TCLP test results, when compared to the UTS limits used to meet LDRs (40 CFR 268, 2015) for hazardous wastes, show that all 24 grout test batches passed LDRs for each COC. However, a single dry ingredient formulation cannot be singled out as the best for immobilizing all COCs in the majority of simulants tested. For instance, the OPC/BFS formulation is adequate for immobilizing Zn, As, Se, and Hg for the majority of the simulants tested, but for Cr treatment the Aquaset/BFS formulation is preferred. These initial TCLP trends, however, are based on the analysis of one specimen from each test batch and replicate specimen analysis by TCLP is recommended for formulations studied in future testing. A final observation worth noting is that all Hg levels were non-detectable in the leachate despite being present in the simulants used to make the cementitious waste forms at elevated concentrations (≥38 ppm in each).

5.2 Recommendations

The results described herein help fill existing data gaps and should support final selection of a cementitious waste form for incorporating EMF evaporator bottoms waste streams. Recommendations for additional studies to provide more technical defensibility for long-term waste form performance are listed below:

1. Precipitate formation as a function of the variables tested in the test matrix provided by WRPS, both by computational modeling and by additional liquid- and solid-phase analytical methods, should be performed to better understand the chemical and physical properties of the EMF evaporator bottoms-waste stream and how these properties might influence waste form selection for immobilization.
2. The dry-blend formulation should be optimized to improve setting times and physical properties that meet LDRs for contaminant and radionuclide (^{99}Tc and ^{129}I) retention. Variables to consider include increasing the w/dm ratio, which will increase waste loading; alternative dry blend formulations (e.g., magnesium phosphate- and wollastonite-based cement currently under investigation by the French Alternative Energies and Atomic Energy Commission, CEA France (Cau Dit Coumes, 2014 and Lambertin, 2017)); and the incorporation of getters for retention of ^{99}Tc and redox sensitive contaminants such as Cr.

3. Qualification testing for monoliths cured for a range of cure times (e.g., 7 days, 28 days, 60 days) should be performed to improve waste form production and efficiency. Testing scope should include additional TCLP testing and methods to determine the effective (observed) diffusivity of COCs (e.g., ^{99}Tc and ^{129}I) and desorption coefficients (K_d) for the same key COCs. Results from these recommended studies would help support future maintenance of the IDF PA and guide waste form selection to support the implementation of alternative waste pathways for DFLAW waste streams.

6.0 References

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Appendix A

Additional Data

Appendix A

Additional Data

A.1 Free Liquids Photos

For each TG1 monolith monitored for free liquids, a photo was taken for every day an observation was made. The photos taken on the day of production and on the final observation day are provided in this section as Figure A.1–Figure A.24.

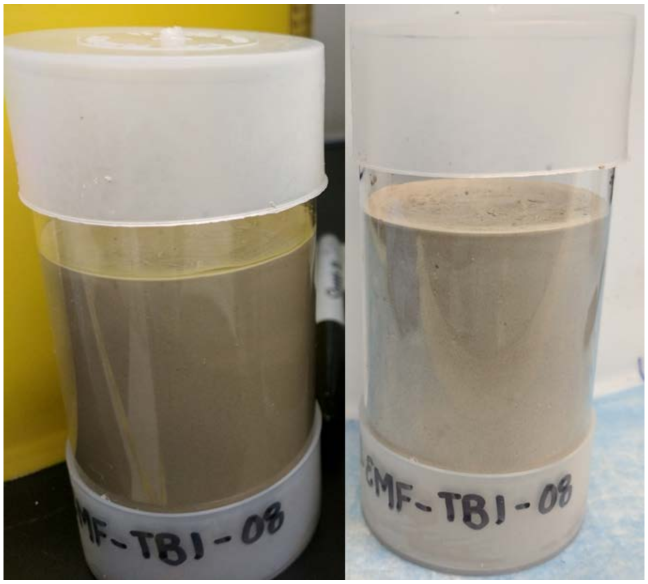

Figure A.1. Free liquid photos for TB1 (Simulant 1, Cast Stone) on the day of production (left) and three days after production, when no free liquids were observed, (right).

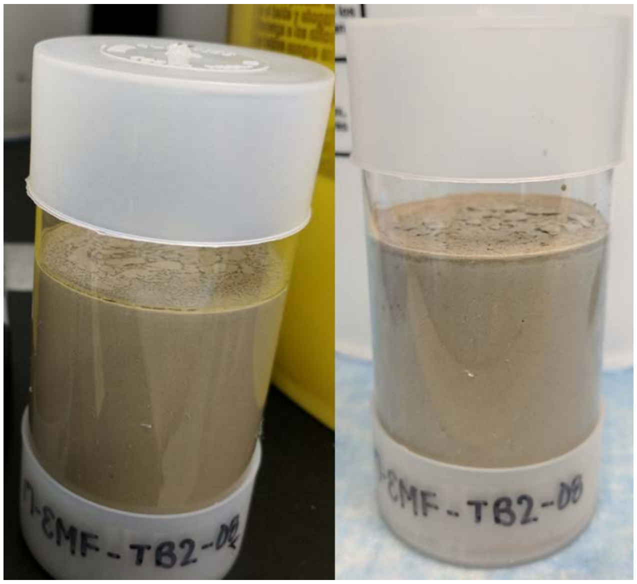

Figure A.2. Free liquid photos for TB2 (Simulant 2, Cast Stone) on the day of production (left) and three days after production, when no free liquids were observed, (right).

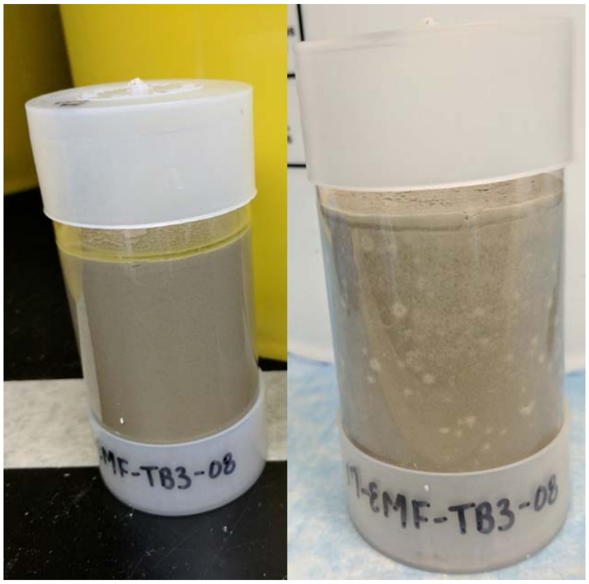

Figure A.3. Free liquid photos for TB3 (Simulant 3, Cast Stone) on the day of production (left) and three days after production, when no free liquids were observed, (right).

Figure A.4. Free liquid photos for TB4 (Simulant 4, Cast Stone) on the day of production (left) and three days after production, when no free liquids were observed, (right).

Figure A.5. Free liquid photos for TB5 (Simulant 5, Cast Stone) on the day of production (left) and three days after production, when no free liquids were observed, (right).

Figure A.6. Free liquid photos for TB6 (Simulant 6, Cast Stone) on the day of production (left) and five days after production, when no free liquids were observed, (right).

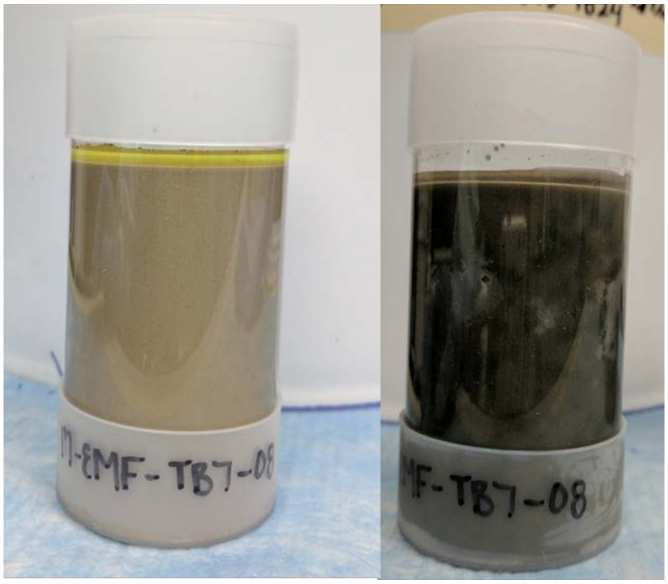

Figure A.7. Free liquid photos for TB7 (Simulant 7, Cast Stone) on the day of production (left) and on the final observation day, 29 days after production, with free liquids still present (right).

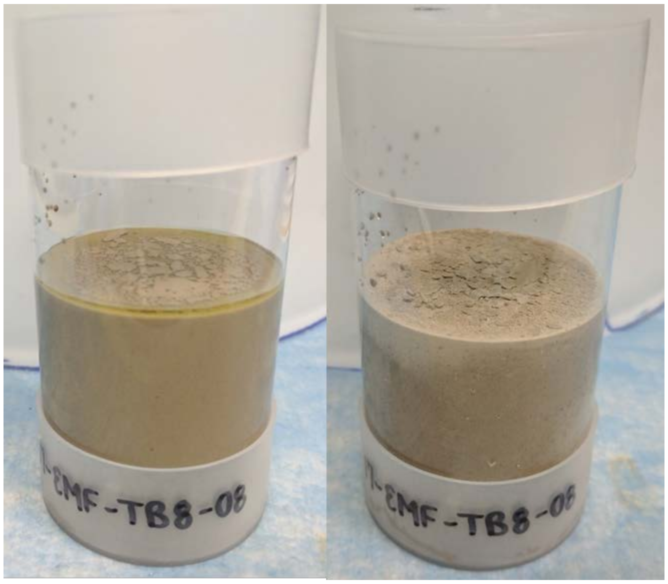

Figure A.8. Free liquid photos for TB8 (Simulant 8, Cast Stone) on the day of production (left) and three days after production, when no free liquids were observed, (right).

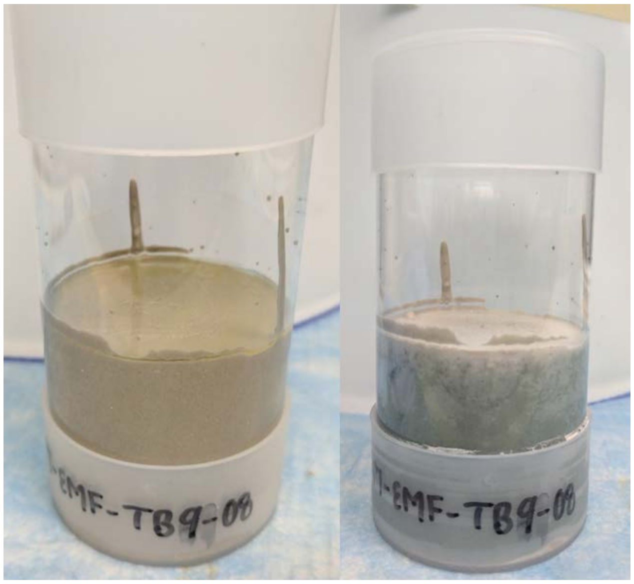

Figure A.9. Free Liquid Photos for TB9 (Simulant 1, Aquaset/Blast Furnace Slag **[**BFS]) on the day of production (left) and ten days after production, when no free liquids were observed, (right).

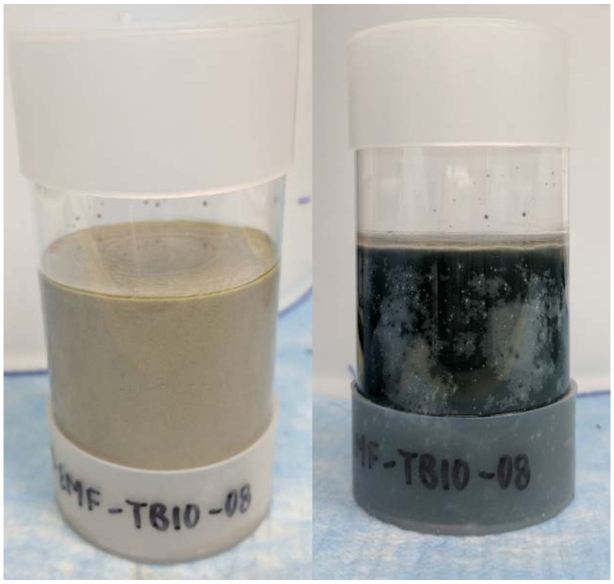

Figure A.10. Free liquid photos for TB10 (Simulant 2, Aquaset/BFS) on the day of production (left) and eighteen days after production, when <1 vol. % free liquids were observed, (right).

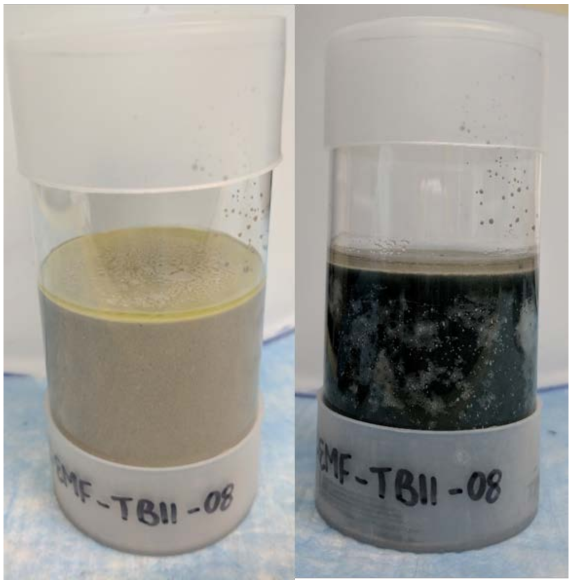

Figure A.11. Free liquid photos for TB11 (Simulant 3, Aquaset/BFS) on the day of production (left) and eighteen days after production, when <1 vol. % free liquids were observed, (right).

Figure A.12. Free liquid photos for TB12 (Simulant 4, Aquaset/BFS) on the day of production (left) and eighteen days after production, when no free liquids were observed, (right).

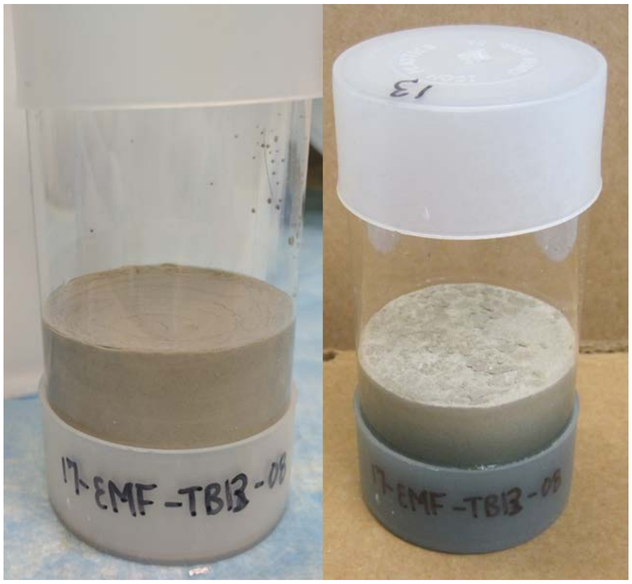

Figure A.13. Free liquid photos for TB13 (Simulant 5, Aquaset/BFS) on the day of production (left) and eighteen days after production, when no free liquids were observed, (right).

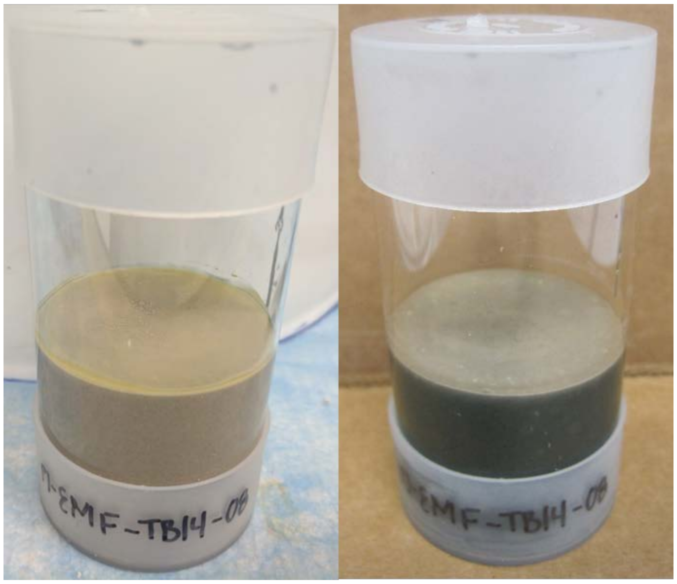

Figure A.14. Free liquid photos for TB14 (Simulant 6, Aquaset/BFS) on the day of production (left) and fourteen days after production, when no free liquids were observed, (right).

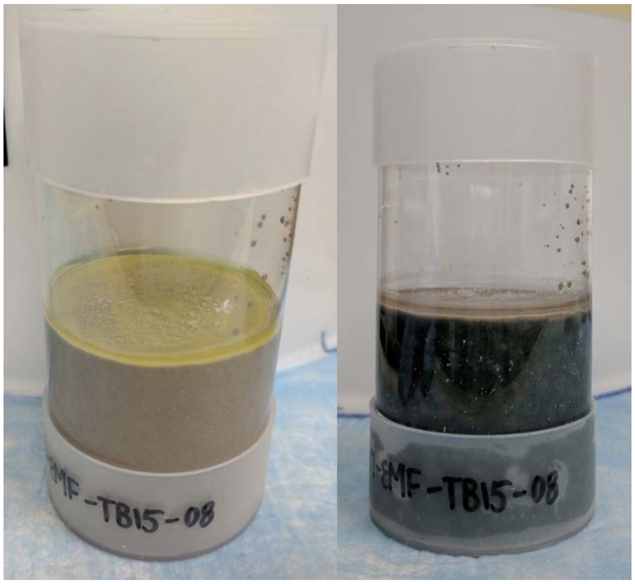

Figure A.15. Free liquid photos for TB15 (Simulant 7, Aquaset/BFS) on the day of production (left) and eighteen days after production, when <1 vol. % free liquids were observed, (right).

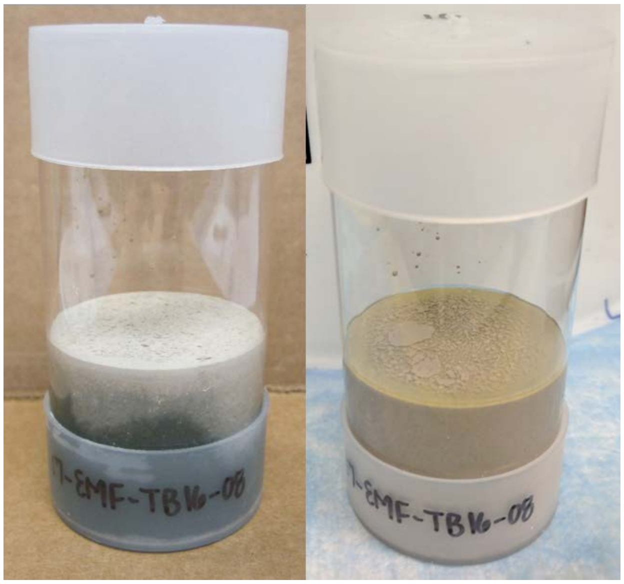

Figure A.16. Free liquid photos for TB16 (Simulant 8, Aquaset/BFS) on the day of production (left) and fourteen days after production, when no free liquids were observed, (right).

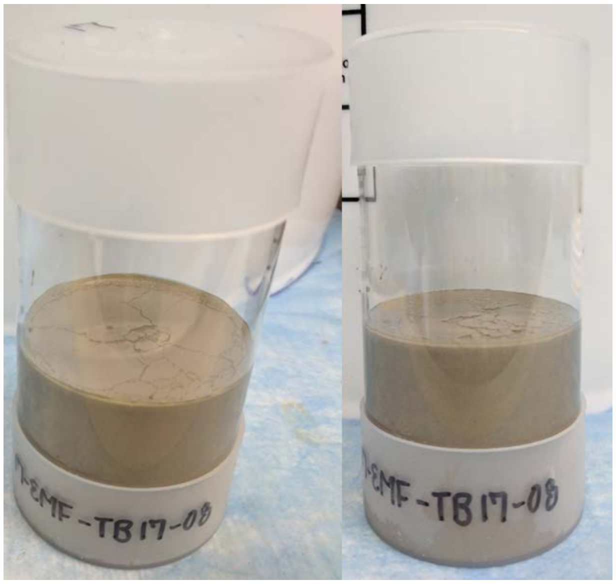

Figure A.17. Free liquid photos for TB17 (Simulant 1, Ordinary Portland Cement [OPC]/BFS) on the day of production (left) and five days after production, when no free liquids were observed, (right).

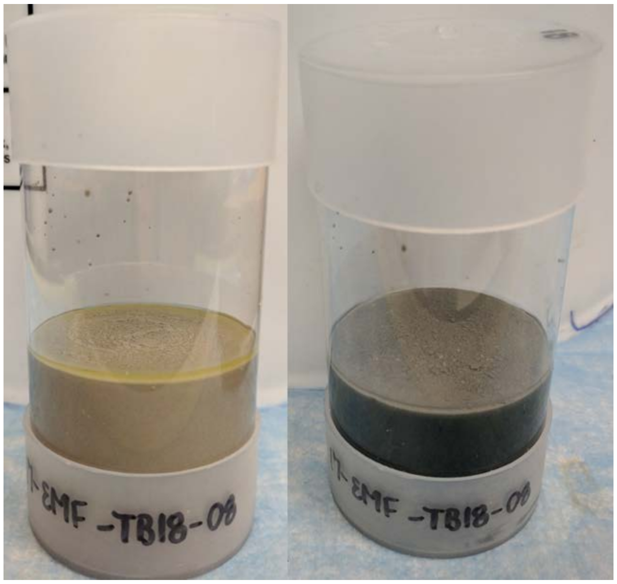

Figure A.18. Free liquid photos for TB18 (Simulant 2, OPC/BFS) on the day of production (left) and five days after production, when no free liquids were observed, (right).

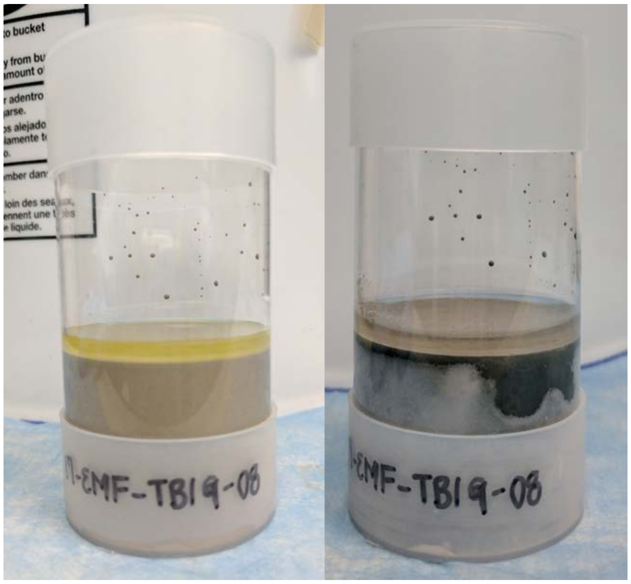

Figure A.19. Free liquid photos for TB19 (Simulant 3, OPC/BFS) on the day of production (left) and on the final observation day, 30 days after production, with free liquids still present (right).

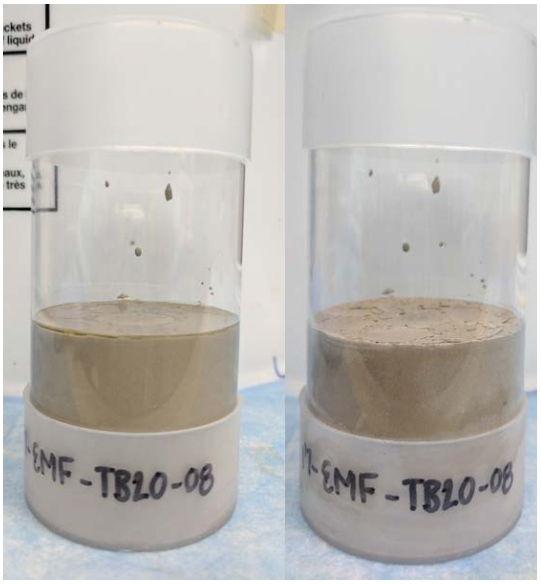

Figure A.20. Free liquid photos for TB20 (Simulant 4, OPC/BFS) on the day of production (left) and four days after production, when no free liquids were observed, (right).

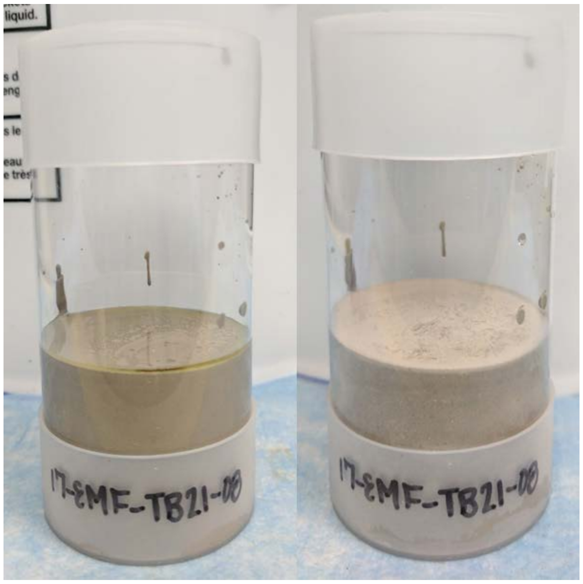

Figure A.21. Free liquid photos for TB21 (Simulant 5, OPC/BFS) on the day of production (left) and three days after production, when no free liquids were observed, (right).

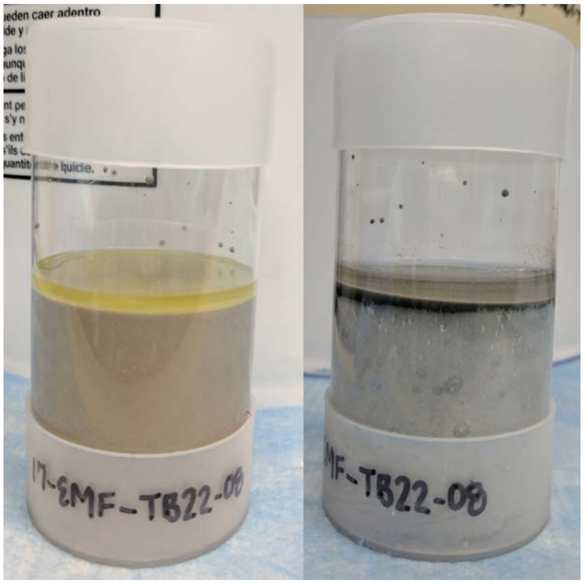

Figure A.22. Free liquid photos for TB22 (Simulant 6, OPC/BFS) on the day of production (left) and on the final observation day, 30 days after production, with free liquids still present (right).

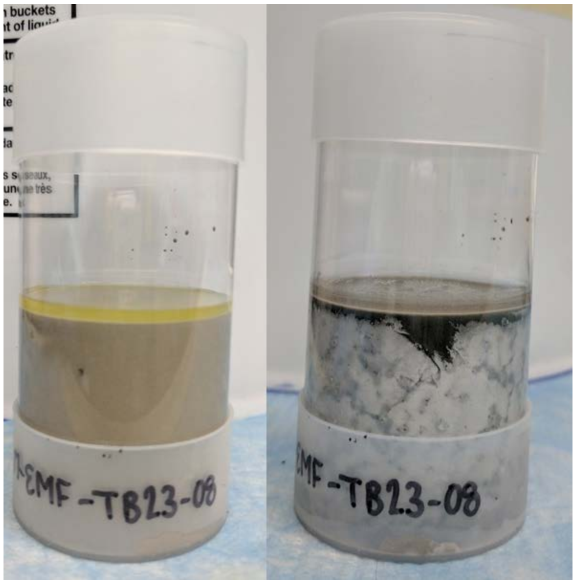

Figure A.23. Free liquid photos for TB23 (Simulant 7, OPC/BFS) on the day of production (left) and twelve days after production, when <1 vol% free liquids were observed, (right).

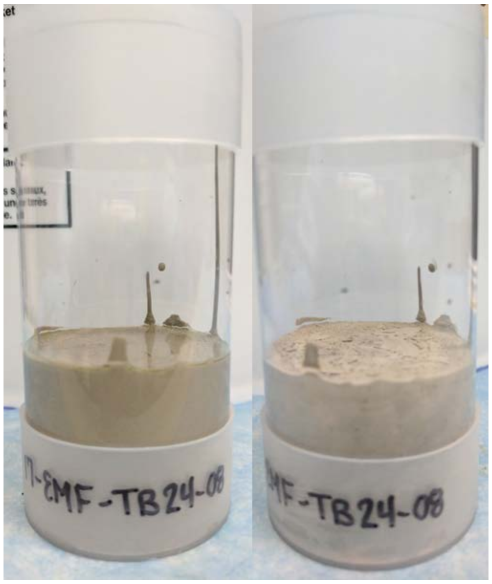

Figure A.24. Free liquid photos for TB24 (Simulant 8, OPC/BFS) on the Day of Production (left) on the day of production (left) and four days after production, when no free liquids were observed, (right).

A.2 Solid Digest Data

The composition of the dry ingredients used in this report was determined by solid digestion methods at Southwest Research Institute (SwRI) (Table A.1). To determine the composition of the monoliths after Toxicity Characteristic Leaching Procedure (TCLP) testing, solid digestion was performed, and the results provided in Table A.2 (Cast Stone), Table A.3 (Aquaset/BFS), and Table A.4 (OPC/BFS).

Table A.1. Composition of Dry Ingredients

Constituent	Hydrated Lime	OPC	OPC (Westsik, 2013)	FA	FA (Westsik, 2013)	BFS	BFS (Westsik, 2013)	Aquaset® II-GH
	(mg/kg)	(mg/kg)	(µg/g)	(mg/kg)	(µg/g)	(mg/kg)	(µg/g)	(mg/kg)
Aluminum	1630	27,000	27,600	98,300	103,000	77,800	77,700	20,600
Antimony	0.987	53.7	<2,320	2.85	<2,320	0.533	<2,340	1.08
Arsenic	<1.48	37.4	<28.3	30.5	<28.3	<1.48	<28.6	9.03
Barium	13	602	492	5570	6,960	484	523	176
Beryllium	<0.493	0.708	-	2.88	-	8.81	-	0.556
Bismuth	<29.6	<29.6	-	<29.7	-	<29.5	-	<29.7
Boron	<976	<935	-	<903	-	<962	-	<903
Cadmium	<0.247	0.379	<4.67	1.16	<4.68	<0.246	<4.72	<0.246
Calcium	523,000	475,000	486,000	97,100	114,000	314,000	356,000	274,000
Chromium	<43.8	76.2	165	85.4	<65.0	<43.3	<65.6	<47.4
Cobalt	<0.493	23.8	-	17.6	-	<0.492	-	4.75
Copper	<0.493	254	242	118	<112	5.58	<113	17.7
Iron	841	22,600	27,800	41,900	52,700	6340	6,200	15,000
Lanthanum	1.92	8.66	-	44	-	44	-	12.8
Lead	<0.493	29.9	37.9	25.4	31.3	1.35	<17.9	7.19
Lithium	2.37	18.5	-	57.5	-	59.3	-	130
Magnesium	5570	5300	5,010	25,700	30,000	30,200	27,700	52,600
Manganese	26.2	699	614	598	557	1400	2,130	289
Mercury	<0.00988	<0.00986	<15.8	0.139	<15.8	<0.00971	<15.9	<0.00992
Molybdenum	<0.740	9.37	<31.1	9.12	<31.1	0.912	<31.4	1.25
Nickel	0.859	24.5	<484	48.3	<484	1.44	<488	9.09
Palladium	<24.7	<24.6	-	<24.7	-	<24.6	-	<24.8
Phosphorus	27.4	261	<3,080	1340	<3,080	83.6	<3110	286
Potassium	336	2550	<8,930	14,000	16,800	3850	<9010	6610
Selenium	<1.97	<1.97	<5,920	6.01	<5,920	<1.97	<5980	<1.97
Silicon	5000	91,700	110,000	214,000	270,000	141,000	181,000	131,000
Silver	<0.987	<0.985	1.79	<0.989	2.18	<0.984	<1.79	<0.984
Sodium	237	2250	<6,570	27,800	34,100	1550	<6630	3360
Strontium	376	1260	1,480	2930	3,730	466	670	903
Sulfur	195	13,200	14,000	3280	<11,100	13,500	23,800	5480
Thallium	<0.247	<0.246	-	1	-	0.282	-	0.257
Thorium	<19.7	<19.7	-	<19.8	-	<19.7	-	<19.8

Constituent	Hydrated Lime	OPC	OPC (Westsik, 2013)	FA	FA (Westsik, 2013)	BFS	BFS (Westsik, 2013)	Aquaset® II-GH
	(mg/kg)	(mg/kg)	(µg/g)	(mg/kg)	(µg/g)	(mg/kg)	(µg/g)	(mg/kg)
Tin	<3.45	55.9	-	3.49	-	<3.44	-	<3.47
Titanium	85.1	1770	-	5750	-	2850	-	1000
Tungsten	<1.97	10.8	-	2.75	-	<1.97	-	2.81
Uranium	<197	<197	-	<198	-	<197	-	<198
Vanadium	1.77	72.9	-	176	-	20.2	-	23
Yttrium	5.59	13.9	-	39.6	-	63.6	-	9.39
Zinc	4.76	991	-	142	-	13.3	-	228
Zirconium	6.42	66.9	-	187	-	218	-	48.4

-: Not measure or not detected

Table A.2. Waste Form Composition after TCLP Testing, Cast Stone

Sample	17-EMF-TB1-04	17-EMF-TB2-02	17-EMF-TB3-02	17-EMF-TB4-02	17-EMF-TB5-02	17-EMF-TB6-02	17-EMF-TB7-02	17-EMF-TB8-02
Simulant	1	2	3	4	5	6	7	8
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Aluminum	43,800	43,900	43,200	44,200	45,100	44,600	44,500	44,600
Antimony	4.09	4.19	4.17	4.08	4.08	4.11	4.11	4.17
Arsenic	77.3	76.8	79.9	79	80.7	80.5	79.7	80.8
Barium	1690	1680	1670	1720	1800	1750	1780	1790
Beryllium	3.49	3.48	3.63	3.61	3.56	3.54	3.58	3.58
Bismuth	<29.7	<29.6	<29.4	<29.6	<29.8	<29.6	<29.8	<29.2
Boron	2830	<967	1070	1580	1890	<988	<781	1290
Cadmium	0.432	0.426	0.509	0.497	0.513	0.432	0.43	0.453
Calcium	137,000	138,000	134,000	139,000	136,000	140,000	139,000	138,000
Chromium	134	137	125	125	149	135	144	132
Cobalt	6.69	6.65	6.9	6.5	7.32	6.84	7.51	6.85
Copper	48.3	47.9	48.8	48.4	49	49	52.7	50.3
Iron	15,600	15,800	15,800	15,700	15,600	15,800	15,700	15,300
Lanthanum	25.9	26.4	26.4	26.6	25.8	26.2	26	26.3
Lead	10.2	10.2	10.1	10.5	10.1	9.97	9.95	10.2
Lithium	34.4	34.6	34.7	34.4	35	35.1	35	35.1
Magnesium	17,200	17,300	17,300	17,300	17,300	17,100	17,200	17,200
Manganese	636	641	641	639	639	631	635	634
Mercury	26.2	28	29.3	25.5	24.3	28.8	27.6	27.5
Molybdenum	3.56	3.33	3.77	3.88	3.68	3.24	3.89	3.73
Nickel	16.4	16.6	16.7	16.4	16.5	16.4	16.7	16.5
Palladium	<24.7	<24.7	<24.5	<24.7	<24.8	<24.7	<24.8	<24.4
Phosphorus	436	417	417	425	427	416	423	428
Potassium	5220	5260	5260	5180	5230	5270	5190	5220
Selenium	65.1	64.5	64.1	65.3	63.8	66.2	64.9	66.6

Sample	17-EMF-TB1-04	17-EMF-TB2-02	17-EMF-TB3-02	17-EMF-TB4-02	17-EMF-TB5-02	17-EMF-TB6-02	17-EMF-TB7-02	17-EMF-TB8-02
Simulant	1	2	3	4	5	6	7	8
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Silicon	115,000	113,000	111,000	112,000	114,000	114,000	114,000	113,000
Silver	<0.989	<0.987	<0.979	<0.988	<0.993	<0.987	<0.992	<0.975
Sodium	30,600	30,000	29,200	29,900	29,000	29,300	28,300	28,800
Strontium	1020	1020	1030	1040	1040	1030	1040	1040
Sulfur	6730	6810	6810	6290	10,300	10,300	9890	8810
Thallium	0.333	0.331	0.334	0.368	0.351	0.349	0.353	0.352
Thorium	<19.8	<19.7	<19.6	<19.8	<19.9	<19.7	<19.8	<19.5
Tin	3.55	<3.46	<3.43	<3.46	<3.48	<3.45	<3.47	<3.41
Titanium	2610	2600	2560	2640	2650	2640	2650	2640
Tungsten	6.34	6.51	12.1	3.83	13.1	5.31	13.9	4.59
Uranium	<198	<197	<196	<198	<199	<197	<198	<195
Vanadium	59.8	59.8	60.5	60.5	60.4	60.1	60.7	60.6
Yttrium	30.9	30.8	31.1	31.2	31.2	31.1	31.1	31.2
Zinc	337	241	282	344	341	270	297	339
Zirconium	124	123	122	123	123	123	124	124

Table A.3. Waste Form Composition after TCLP Testing, Aquaset/BFS

Sample	17-EMF-TB9-02	17-EMF-TB10-02	17-EMF-TB11-02	17-EMF-TB12-02	17-EMF-TB13-01	17-EMF-TB14-01	17-EMF-TB15-01	17-EMF-TB16-01
Simulant	1	2	3	4	5	6	7	8
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Aluminum	35,600	35,700	34,900	33,900	34,000	33,400	33,700	33,400
Antimony	0.716	0.693	0.637	1.14	1.21	1.13	1.14	1.1
Arsenic	68.9	70.4	66.4	70.3	73	71.6	72.1	72.5
Barium	285	282	279	246	261	248	249	243
Beryllium	4.75	4.81	4.33	4.62	4.49	4.55	4.49	4.43
Bismuth	<29.6	<29.8	<29.4	<29.9	<29.4	<29.5	<29.6	<29.5
Boron	2650	<963	1000	1510	1780	<946	<927	1190
Cadmium	<0.247	<0.246	0.252	0.343	0.339	0.268	0.25	0.256
Calcium	181,000	182,000	178,000	186,000	187,000	185,000	184,000	183,000
Chromium	113	117	108	112	119	127	131	122
Cobalt	1.39	0.984	0.94	1.56	1.33	1.51	1.26	1.64
Copper	7.37	6.21	6.07	8.99	8.45	8.33	7.99	8.38
Iron	5580	5730	5540	5470	5310	5380	5440	5430
Lanthanum	24.5	24.7	22.0	24.5	24.2	24.2	24.4	24.1
Lead	2.56	2.25	2.26	9.73	9.81	10.1	9.68	9.87
Lithium	46.8	47	47.2	46.7	46	46.4	46.5	45.7
Magnesium	23,000	23,100	23,000	18,900	18,600	18,700	19,000	18,500
Manganese	770	777	772	928	914	908	932	917
Mercury	26	29.7	29.9	26.9	27.6	27.8	27.6	27.9
Molybdenum	1.16	1.11	0.862	1.6	<0.736	1.27	<0.740	1.2
Nickel	2.54	2.57	2.49	2.99	2.28	2.39	2.11	2.32
Palladium	<24.7	<24.8	<24.5	<24.9	<24.5	<24.6	<24.7	<24.5
Phosphorus	78.7	95.8	74.3	89.5	87.8	89.7	82.9	82.2
Potassium	2820	2870	2830	2970	2960	2980	2960	2960
Selenium	62.1	63	58.3	64.3	63.8	66.5	66.6	65.2
Silicon	92,200	93,600	93,400	94,400	94,900	94,500	93,100	92,700
Silver	<0.987	<0.984	<0.981	<0.997	<0.981	<0.983	<0.987	<0.982
Sodium	23,900	23,600	22,300	22,700	22,200	22,200	20,700	22,000
Strontium	364	363	367	409	403	406	411	404
Sulfur	8800	8800	8740	11,700	15,700	15,700	15,400	14,200
Thallium	<0.247	<0.246	<0.245	0.259	0.251	0.262	0.26	0.246
Thorium	<19.7	<19.8	<19.6	<19.9	<19.6	<19.7	<19.7	<19.6
Tin	<3.46	<3.47	<3.43	<3.49	<3.43	<3.44	<3.45	<3.44
Titanium	1590	1600	1570	1530	1540	1510	1530	1520
Tungsten	10.2	5.13	4.76	11.5	5.25	9.09	3.93	10.7
Uranium	<197	<198	<196	<199	<196	<197	<197	<196
Vanadium	13.8	13.8	12.6	14.8	14.7	14.7	14.6	14.5
Yttrium	33.4	33.4	30.2	35.1	34.3	34.4	34.7	34.2
Zinc	282	179	206	298	296	158	265	289
Zirconium	116	119	106	114	112	113	114	111

Table A.4. Waste Form Composition after TCLP Testing, OPC/BFS

Sample	17-EMF-TB17-01	17-EMF-TB18-01	17-EMF-TB19-01	17-EMF-TB20-01	17-EMF-TB21-01	17-EMF-TB22-01	17-EMF-TB23-01	17-EMF-TB24-01
Simulant	1	2	3	4	5	6	7	8
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Aluminum	34,600	34,900	33,900	34,400	36,200	36,400	36,200	36,300
Antimony	8.41	8.45	6.85	8.22	7.66	7.62	7.5	7.62
Arsenic	73.1	76.5	66.3	73.8	73.2	74.2	73	74.6
Barium	299	300	298	309	331	338	337	336
Beryllium	4.48	4.52	4.53	4.49	4.74	4.76	4.64	4.7
Bismuth	<29.2	<29.2	<29.7	<29.8	<29.7	<29.7	<29.3	<29.4
Boron	2630	<935	<970	1490	2020	<977	<981	1230
Cadmium	0.276	0.282	0.324	0.359	0.261	<0.248	<0.244	<0.245
Calcium	208,000	209,000	205,000	205,000	203,000	204,000	202,000	204,000
Chromium	132	162	123	126	124	127	128	127
Cobalt	3.69	3.82	3.54	3.75	3.41	3.65	3.4	3.57
Copper	38.2	39.7	37	38.5	35.7	36.7	40.3	37
Iron	6330	6350	5920	6100	6220	6240	6210	6350
Lanthanum	23.7	23.8	24.1	23.7	23.8	23.9	23.9	24
Lead	12.8	12.7	12.7	11.3	5.03	5.1	5.61	4.94
Lithium	31.6	31.9	30.9	31.9	32.7	32.6	32	32.4
Magnesium	12,400	12,800	12,100	13,100	16,800	16,700	16,400	16,900
Manganese	955	995	965	938	817	824	818	831
Mercury	24.7	27.3	29.5	21.8	26.6	28.4	28.4	28.2
Molybdenum	1.94	2.14	1.89	2.13	2.11	1.94	2.22	1.99
Nickel	4.02	7.47	4.06	4.43	4.24	4.62	6.11	4.36
Palladium	<24.3	<24.3	<24.8	<24.9	<24.7	<24.8	<24.4	<24.5
Phosphorus	85.9	84.7	92.7	88.8	79	77.9	80.3	81.7
Potassium	2450	2480	2470	2430	2310	2310	2290	2300
Selenium	63.9	65.4	61.4	66.3	62.1	65.4	63.6	64
Silicon	87,700	88,400	82,500	87,000	86,600	87,100	84,000	87,000
Silver	<0.973	<0.974	<0.985	<0.994	<0.989	<0.990	<0.977	<0.980
Sodium	23,900	23,400	22,400	23,000	22,300	22,300	20,900	21,800
Strontium	448	457	445	448	410	412	409	414
Sulfur	13,000	13,200	12,800	12,000	13,300	13,300	12,900	11,900
Thallium	<0.243	<0.243	<0.246	<0.249	<0.247	<0.248	<0.244	<0.245
Thorium	<19.5	<19.5	<19.8	<19.9	<19.8	<19.8	<19.5	<19.6
Tin	7.15	6.46	6.93	7.42	7.3	6.97	7.36	6.93
Titanium	1640	1650	1610	1640	1690	1700	1690	1700
Tungsten	5.25	6.71	3.01	5.68	4.59	6.41	5.85	7.42
Uranium	<195	<195	<198	<199	<198	<198	<195	<196
Vanadium	20.9	20.9	19.4	20.8	19.9	20.3	20	20.1
Yttrium	35.1	35.2	34.9	34.9	34	34.2	34	34.2
Zinc	385	295	313	379	371	294	340	377
Zirconium	116	115	113	117	120	122	122	123

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