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Secondary Waste Simulant Development for Cast Stone Formulation Testing

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April 2015

U.S. DEPARTMENT OF ENERGY

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

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[1] Washington River Protection Solutions, Richland, Washington.

Executive Summary

Washington River Protection Solutions, LLC (WRPS) funded Pacific Northwest National Laboratory (PNNL) to conduct a waste form testing program to implement aspects of the Secondary Liquid Waste Treatment Cast Stone Technology Development Plan (Ashley 2012) and the Hanford Site Secondary Waste Roadmap (PNNL 2009) related to the development and qualification of Cast Stone as a potential waste form for the solidification of aqueous wastes from the Hanford Site after the aqueous wastes are treated at the Effluent Treatment Facility (ETF). The current baseline is that the resultant Cast Stone (or grout) solid waste forms would be disposed at the Integrated Disposal Facility (IDF). Data and results of this testing program will be used in the upcoming performance assessment of the IDF and in the design and operation of a solidification treatment unit planned to be added to the ETF. The purpose of the work described in this report is to 1) develop simulants for the waste streams that are currently being fed and future WTP secondary waste streams also to be fed into the ETF and 2) prepare simulants to use for preparation of grout or Cast Stone solid waste forms for testing.

The waste solidification unit to be added to the ETF is expected to receive wastes from three sources on the Hanford Site: 1) the 242-A Evaporator, 2) the ERDF, and 3) the WTP. Chemical simulants were selected to represent each of the three waste streams that the waste solidification unit is expected to receive: 1) condensates from the 242-A Evaporator, 2) leachates from ERDF, and 3) process condensates from the WTP Pretreatment Facility plus the caustic scrubber solution from the WTP LAW melter off-gas treatment system. Chemical simulants of each of the three waste streams were prepared, and will be used in preparing grout specimens for secondary waste grout formulation tests.

Before the larger simulant batches were prepared for the grout waste form tests, smaller one-liter batches were prepared to check for chemical interactions and solids formation at the targeted wt% total solids. The 242-A Evaporator simulant had a layer of solids on the bottom after settling for several days. It appeared that these solids were primarily silicate colloids. The ERDF simulant formed a very significant amount of solids on the bottom of the flask at 30 wt% total solids. This simulant was diluted to 12.3 wt% total solids and there was still a significant layer of solids present on the bottom. These solids were determined by XRD to be gypsum. Because of the amount of solids present and the wt% total solids present in the recent ETF runs of 10-12 wt% due to halide limitations, it was decided to dilute the final ERDF simulant to 10 wt% total solids. This amount of total solids also produced significant undissolved solids. The WTP Off-gas simulant was clear with only a few clear crystals along the container wall present at 18 wt% total solids. However, over time, more crystals appeared to be forming indicating that the solution was at or near saturation.

Acronyms and Abbreviations

DFLAW	Direct Feed Low-Activity Waste
DOE	U.S. Department of Energy
EMF	Effluent Management Facility
ERDF	Environmental Restoration Disposal Facility
ETF	Effluent Treatment Facility
IC	ion chromatography
ICP-OES	inductively coupled plasma-optical emission spectroscopy
IDF	Integrated Disposal Facility
LAW	low-activity waste
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act of 1976
WRPS	Washington River Protection Solutions, LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-ray diffraction

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1.0 Introduction

Washington River Protection Solutions, LLC (WRPS) funded Pacific Northwest National Laboratory (PNNL) to conduct a waste form testing program to implement aspects of the Secondary Liquid Waste Treatment Cast Stone Technology Development Plan (Ashley 2012) and the Hanford Site Secondary Waste Roadmap (PNNL 2009) related to the development and qualification of Cast Stone as a potential waste form for the solidification of aqueous wastes from the Hanford Site after the aqueous wastes are treated at the Effluent Treatment Facility (ETF). The current baseline is that the resultant Cast Stone (or grout) solid waste forms would be disposed at the Integrated Disposal Facility (IDF). Data and results of this testing program will be used in the upcoming performance assessment of the IDF and in the design and operation of a solidification treatment unit planned to be added to the ETF.

As a prime contractor to the U. S. Department of Energy (DOE), WRPS has responsibility for the design and construction of a solidification treatment unit to be added to the ETF. The ETF is an existing operating facility on the Hanford Site and is a Resource Conservation and Recovery Act (RCRA)-permitted multi-waste treatment and storage facility that can accept Washington State-regulated dangerous, low-level, and mixed wastewaters for treatment. The ETF currently treats aqueous waste streams including evaporator condensates from the 242-A Evaporator, Environmental Restoration Disposal Facility (ERDF) and future IDF leachates, laboratory wastes, and groundwater liquid wastes. The solidification treatment unit will be added to provide the additional capacity needed for secondary liquid wastes when the Hanford Tank Waste Treatment and Immobilization Plant (WTP) begins waste treatment operations. The solidification treatment unit will also be used to solidify the ETF process streams currently being fed to the rotary evaporator, which dries the ETF process liquid wastes forming a powder. The powders are currently placed in drums and disposed of on-site at the ERDF. WRPS and one of its subcontractors have developed a conceptual design for the ETF upgrade. The solidification treatment unit needs to be operational in time to receive secondary liquid wastes from the WTP Low Activity Waste (LAW) Vitrification Facility.

The WTP is being constructed on the Hanford Site to treat and vitrify 56 million gallons of radioactive wastes stored on site. When operational, the WTP will generate secondary aqueous liquid waste streams from primary and secondary off-gas capture systems that will be sent to the ETF for treatment and solidification. In preparation for the processing of these secondary wastes, the ETF will be upgraded to include a waste solidification unit for immobilizing all of the wastes processed in ETF into a low-temperature grout waste form called Cast Stone.

The purpose of the work described in this report is to 1) develop simulants for the waste streams that are currently being fed and future WTP secondary waste streams also to be fed into the ETF and 2) prepare simulants to use for preparation of grout or Cast Stone solid waste forms for testing. The grout/Cast Stone prepared with these simulants of the selected ETF process streams will be cured for appropriate time periods then tested for waste form properties such as contaminant leach rates and physical stability attributes. The waste form preparation and property testing details will be addressed in another report.

1.1 Quality Assurance

This work was conducted with funding from WRPS under contract 36437-168, Secondary Waste Cast Stone Formulation and Waste Form Qualification. The work was conducted as part of PNNL Project 66595.

All research and development (R&D) work at PNNL is 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*, to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this 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 work described in this report was assigned the technology level “Applied Research,” and was planned, performed, documented, and reported in accordance with Procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work.

2.0 Secondary Waste Simulant Compositions

The waste solidification unit to be added to the ETF is expected to receive wastes from three sources on the Hanford Site: 1) the 242-A Evaporator, 2) the ERDF, and 3) the WTP. Chemical simulants were selected to represent each of the three waste streams that the waste solidification unit is expected to receive: 1) condensates from the 242-A Evaporator, 2) leachates from ERDF, and 3) process condensates from the WTP Pretreatment Facility plus the caustic scrubber solution from the WTP LAW melter off-gas treatment system. These simulant compositions were based on the ETF output after treatment with sulfuric acid to adjust the pH and subsequent evaporation in the ETF secondary waste treatment train. To support the Direct Feed Low Activity Waste (DFLAW) initiative, an Effluent Management Facility (EMF) is planned to handle off-gas condensates from the LAW Vitrification facility. The resulting feed stream to the ETF will have a composition similar to that expected from the WTP once it achieves full operations and therefore is considered a representative simulant for this study. Chemical simulants of each of the three different waste streams will be used in preparing the grout specimens for these secondary waste grout formulation tests. Each of these simulant formulations is described in the following sections.

2.1 242-A Evaporator Simulant

The 242-A Evaporator simulant is derived from the composition of a 2013 ETF process campaign (Halgren 2013). The input feed is pH-adjusted with sulfuric acid resulting in a high sulfate concentration in the ETF secondary waste evaporator brine. Table 2.1 shows a nominal 242-A Evaporator simulant composition that was formulated for this task. The total solids composition was limited to 10 wt% to minimize corrosion of ETF evaporator components by limiting halide concentrations. The primary elements from this waste stream were selected and their concentrations were adjusted to create a charge balanced composition that was used to produce the simulant.

Table 2.1. 242-A Evaporator Simulant Composition

Waste Constituent	Molar Fractions
Ca	0.023
K	0.003
Mg	0.009
Na	0.075
Si	0.011
Cl	0.013
SO_4	0.324
NH_4	0.541

2.2 ERDF Leachate Simulant

The ERDF leachate simulant is based on the composition of the ERDF portion of the ETF 2012 campaign (Halgren 2012). Although this waste stream is not expected to be processed at the, the composition is a reasonable representation of other waste disposal facility leachates that will be routed to the ETF in the future. Since the input feed is pH-adjusted with sulfuric acid before treatment, there is a high sulfate concentration and a low pH present. Table 2.2 shows the nominal ERDF leachate simulant composition that was formulated for this task from the ETF 2012 campaign. The primary elements from this waste stream were selected and their concentrations were adjusted to create a charge balanced composition that was used to produce the simulant. The target total solids content for this simulant was 10-wt% based on halide limitations of the plant.

Table 2.2. ERDF Leachate Simulant Composition

Waste Constituent	Molar Fractions
Ca	0.171
Mg	0.092
Na	0.222
Cl	0.162
NO_3	0.117
SO_4	0.235

2.3 WTP Off-gas Condensate Simulant

The WTP off-gas condensate simulant is based on an estimated average composition of condensate from the first eight years of DFLAW operations. The composition is dominated by sodium additions for pH control in the caustic scrubber and sulfuric acid additions in the ETF, and is similar to the composition expected for this waste stream during WTP operations once the facility is fully operational. Table 2.3 shows the nominal WTP future condensate simulant composition that was formulated for this task. The primary elements from this waste stream were selected and their concentrations were adjusted to create a charge-balanced composition that was used to produce the simulant. The target total solids content for this simulant is 18 wt%.

Table 2.3. WTP Off-gas Condensate Simulant Composition

Waste Constituent	Molar Fractions
NO_3	0.117
NO_2	0.001
Na	0.295
Cl	0.006
SO_4	0.250
NH_4	0.330
F	0.001

3.0 Simulant Preparation

The three chemical simulants described in Sections 2.1 through 2.3 were prepared for use in this testing. Each simulant was initially prepared in a 1-L flask at the target total solids concentration. The order of chemical addition was determined based on chemical solubility knowledge.

Once satisfactory recipes were determined, larger, multi-liter size batches of each of the simulants were prepared for use in the grout waste form preparation. The results of the 1-L preparations are discussed below for each simulant.

3.1 242-A Evaporator Simulant Results

When the initial simulant was prepared in a 1-L flask at 10 wt% total solids, white solids formed and settled to the bottom slowly. The solution remained cloudy throughout the day as shown in Figure 3.1 and took until the next morning to clear as shown in Figure 3.2. It appeared that the cloudy solution was due to colloidal silica from the silicate added to this simulant. It was also found that the majority of the solids in the solution went through a 0.45-micron filter which confirms the formation of colloidal silica as it tends to form in the nanometer size and remain suspended. The solids were easily re-suspended in the simulant solution with stirring. After settling overnight, significant floating crystals remained on top of the simulant as shown in Figure 3.3.

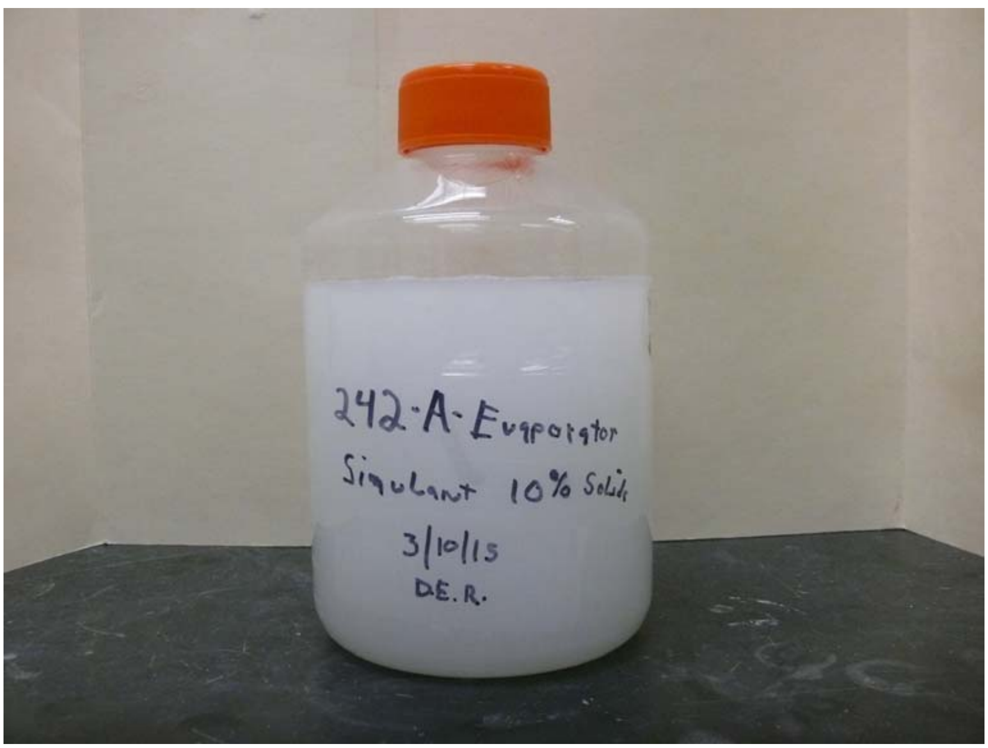

Figure 3.1. 242-A Evaporator Simulant at 10 wt% Solids

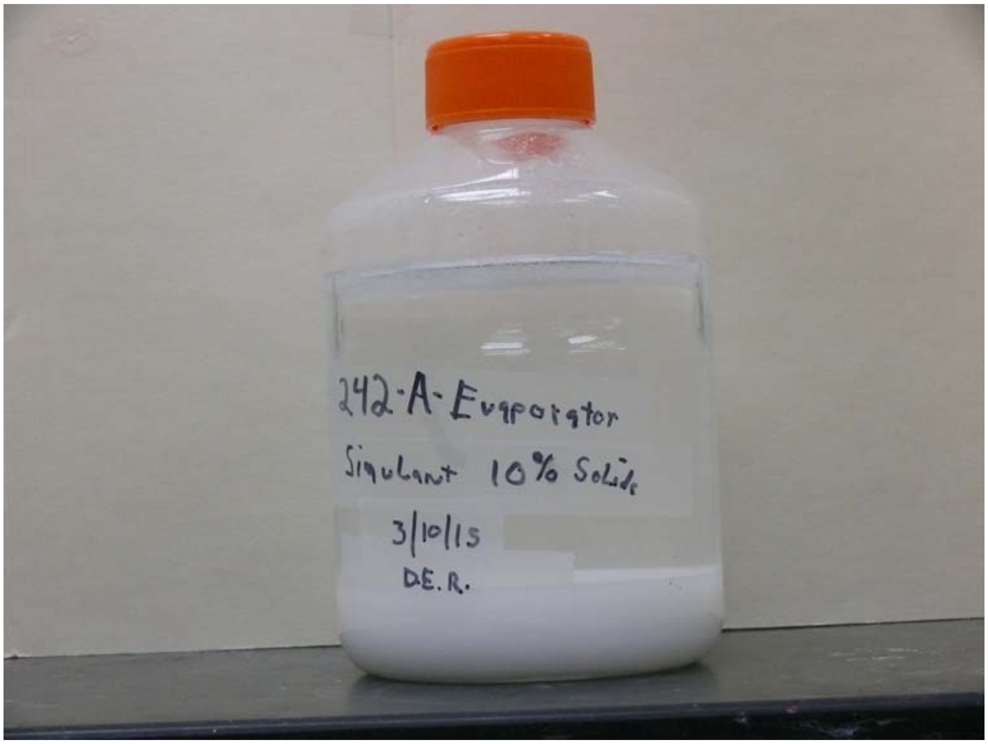

Figure 3.2. 242-A Evaporator Simulant at 10 wt% Solids after Settling Overnight

Figure 3.3. 242-A Evaporator Simulant at 10 wt% Solids after Settling Overnight with Floating Crystals

The actual recipe used based on 1 kg of simulant is given in Table 3.1. The wt% solids values shown in Table 3.1 include both the dissolved solids and any undissolved solids that formed. The wt% solids were based on direct measurements of small aliquots of the simulant suspensions. The weights of the aliquots of suspension before drying and after drying were used to calculate the wt% solids.

Table 3.1. Recipe for 242-A Evaporator Simulant Based on 1 kg

Chemical	Amount Needed (g) Rounded to Two Decimal Places
$CaCl_2$	1.63
$(NH_4)_2SO_4$	80.83
Na_2SiO_3-$9H_2O$	6.75
K_2SO_4	0.65
$MgSO_4$	2.45
$CaSO_4$	5.04
Na_2SO_4-$10H_2O$	19.67
Density (g/cm^3)	1.06
pH	8.25
Wt% total solids	10.03

3.2 ERDF Leachate Simulant Results

When the initial simulant was prepared in a 1-L flask at 30 wt% solids, significant solids formed leaving an ~7/8-inch layer of settled solids on the bottom of the flask. The simulant was then heated to 70 °C for about 2.5 hours and the simulant appeared to contain more solids than at the beginning. After cooling overnight, the solids settled much faster than before indicating that heating may have changed the solids.

The wt% dissolved solids was measured and found to only be 14.5 wt%. Therefore, it was decided to prepare a simulant with only 12.3 wt% total solids in order to help the solids go into solution without precipitating. However, it was found that just as many solids precipitated out and behaved just the same as before. This simulant is shown in Figure 3.4 with the two simulants compared in Figure 3.5.

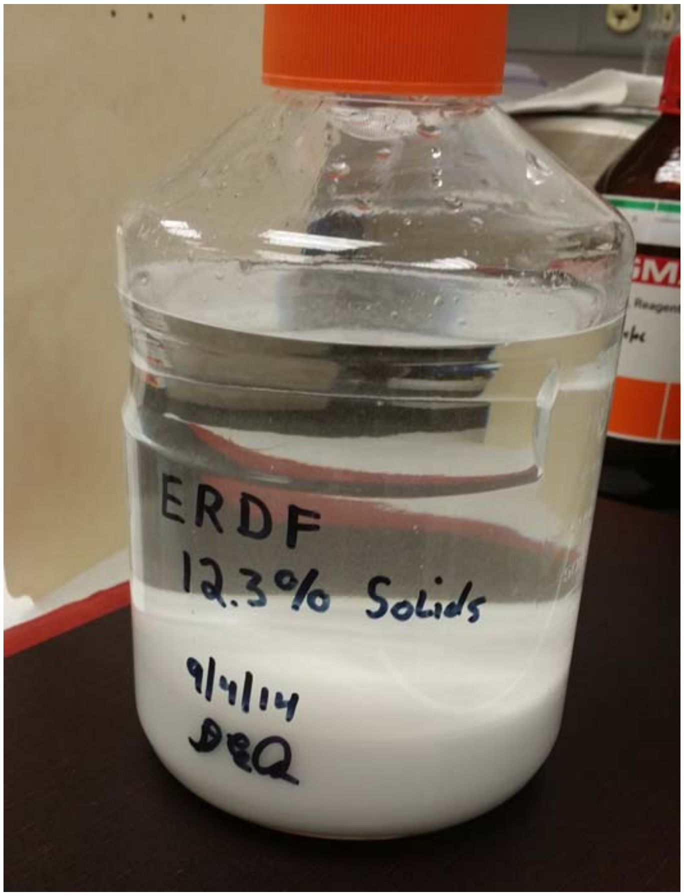

Figure 3.4. ERDF Leachate Simulant at 12.3 wt% Total Solids

Figure 3.5. ERDF Leachate Simulant Compared at 12.3 wt% Solids and 30 wt% Solids

It was then determined that based on the past several years of ETF campaign reports (Halgren 2012 and Halgren 2013), the treated brine was only 10-12 wt% total solids due to a halide limitation of 10,000 ppm in the feed. Based on these results, it was decided to proceed with the large batch simulant needed for the grout preparation at 10 wt% total solids. A 6.1 kg batch of ERDF Leachate simulant was then prepared for the grout formation work. However, after the simulant was prepared, it was discovered that the sodium sulfate added to the simulant contained 10 waters of hydration which made the actual total wt% solids of the simulant 8.23. The wt% solids values cited in Table 3.2 include both the dissolved solids and any undissolved solids that formed upon cooling. The wt% solids were based on direct measurements of small aliquots of the simulant suspensions. The weights of the aliquots of suspension before drying and after drying were used to calculate the wt% solids. However, the final simulant used for the Cast Stone monolith preparation was prepared correctly accounting for the waters of hydration. The actual recipe based on 1 kg of simulant is given in Table 3.2.

The amount of undissolved solids in the simulant was measured and found to be ~3.5 wt%. The solids were analyzed by XRD and seen to contain only gypsum ($CaSO_4$) as shown in Figure 3.6.

Table 3.2. ERDF Leachate Simulant Based on 1 kg

Chemical	Amount Needed (g) Rounded to Two Decimal Places
$Ca(NO_3)_2$	19.31
$CaCl_2$	18.00
$CaSO_4$	8.73
$MgSO_4$	22.33
Na_2SO_4	31.62
Density (g/cm^3)	1.05
pH	9.4
Wt% total solids	7.90

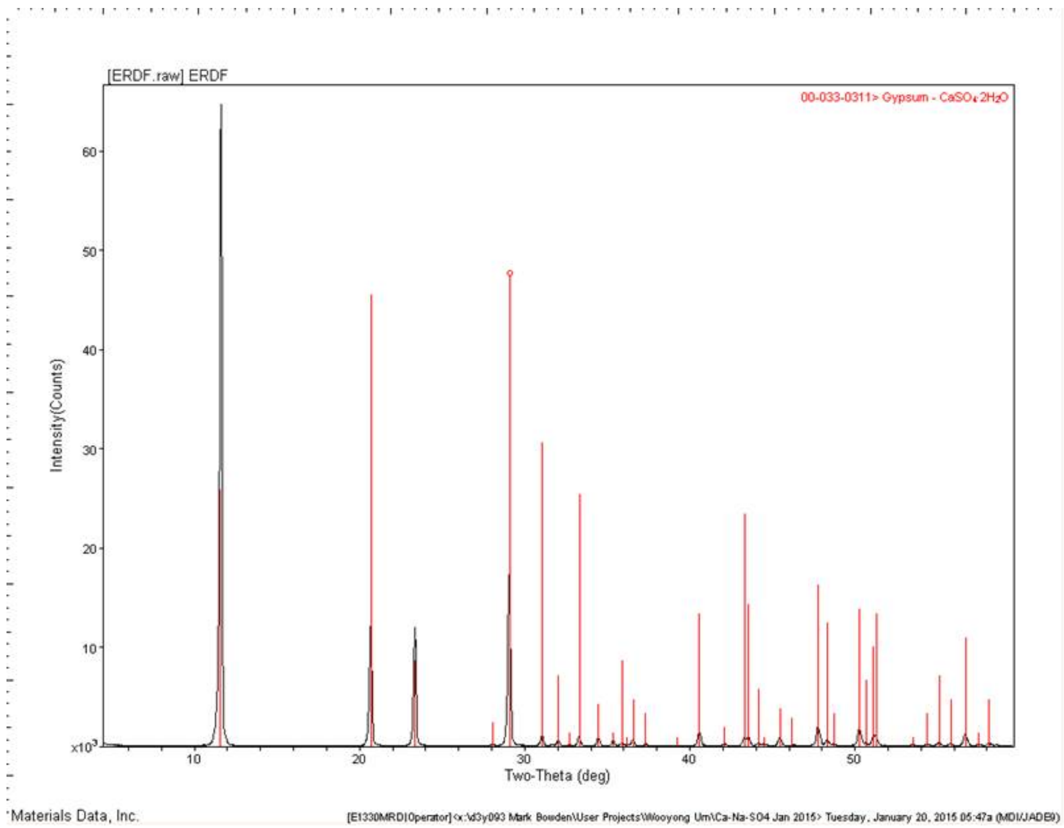

Figure 3.6. XRD Pattern of ERDF Leachate Simulant Solids

3.3 WTP Off-gas Condensate Simulant Results

When the initial simulant was prepared in a 1-L flask at 18 wt% total solids, the chemicals went into solution easily and no heating was required. After sitting overnight, a few clear crystals had formed on the surface of the container along the top. Over time more clear crystals formed along the container walls indicating that the solution was at or near saturation. This simulant is shown in Figure 3.1.

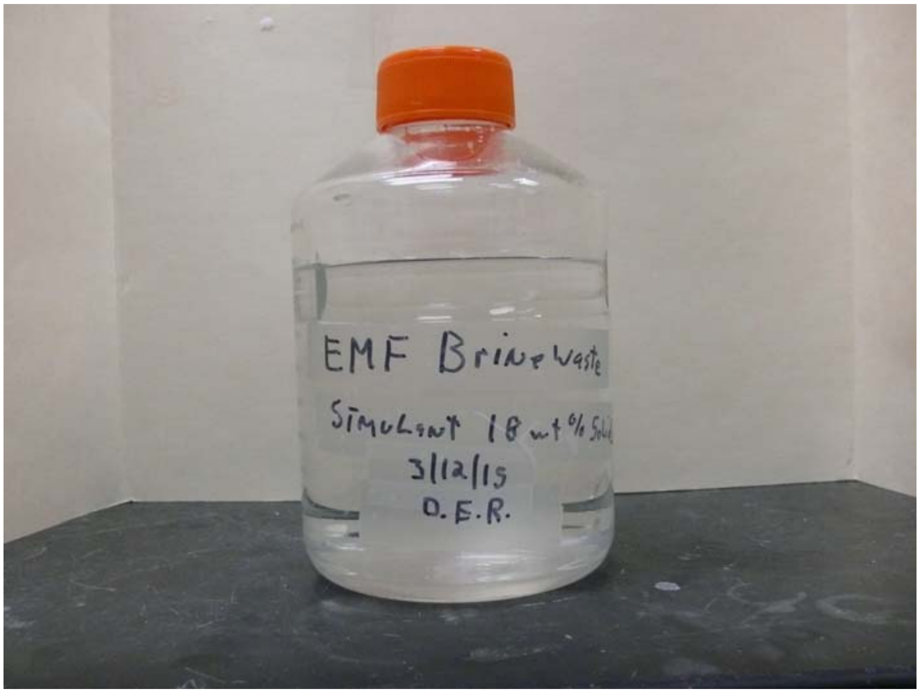

Figure 3.7. WTP Off-gas Condensate Simulant at 18 wt% Solids

The actual recipe based on 1 kg of simulant is shown in Table 3.3. The wt% solids values shown in Table 3.3 include both the dissolved solids and any undissolved solids that formed. The wt% solids were based on direct measurements of small aliquots of the simulant suspensions. The weights of the aliquots of suspension before drying and after drying were used to calculate the wt% solids.

Table 3.3. Recipe for WTP Off-gas Condensate Simulant Based on 1 kg

Chemical	Amount Needed (g) Rounded to Two Decimal Places
$NaNO_3$	42.53
NaF	0.18
NaCl	1.50
$NaNO_2$	0.30
$(NH_4)_2SO_4$	93.24
Na_2SO_4-$10H_2O$	117.12
Density (g/cm^3)	1.13
pH	5.6
Wt% total solids	18.89

4.0 Summary

The waste solidification unit to be added to the ETF is expected to receive wastes from three sources on the Hanford Site: 1) the 242-A Evaporator, 2) the ERDF, and 3) the WTP. Chemical simulants were selected to represent each of the three waste streams that the waste solidification unit is expected to receive: 1) condensates from the 242-A Evaporator, 2) leachates from ERDF, and 3) process condensates from the WTP Pretreatment Facility plus the caustic scrubber solution from the WTP LAW melter off-gas treatment system. Chemical simulants of each of the three waste streams were prepared, and will be used in preparing grout specimens for secondary waste grout formulation tests.

Before the larger simulant batches were prepared for the grout waste form tests, smaller one-liter batches were prepared to check for chemical interactions and solids formation at the targeted wt% total solids. The 242-A Evaporator simulant had a layer of solids on the bottom after settling for several days. It appeared that these solids were primarily silicate colloids. The ERDF simulant formed a very significant amount of solids on the bottom of the flask at 30 wt% total solids. This simulant was diluted to 12.3 wt% total solids and there was still a significant layer of solids present on the bottom. These solids were determined by XRD to be gypsum. Because of the amount of solids present and the wt% total solids present in the recent ETF runs of 10-12 wt% due to halide limitations, it was decided to dilute the final ERDF simulant to 10 wt% total solids. This wt% total solids also produced significant undissolved solids. The WTP Off-gas simulant was clear with only a few clear crystals along the container wall present at 18 wt% total solids. However, over time, more crystals appeared to be forming indicating that the solution was at or near saturation.

Table 4.1 shows the final simulant target moles/mole Na concentrations for the major constituents in the three simulants that will be used for the grout waste form tests. The target concentrations in Table 4.1 have been charge-balanced.

Table 4.1. Final Secondary Waste Simulants for Cast Stone Screening Tests

Waste Constituent	242-A Evaporator	ERDF Leachate	WTP Off-gas
	Concentration (moles/mole Na)[(a)]		
Na	1.000	1.000	1.000
K	0.044	--	--
Ca	0.305	0.773	--
Mg	0.120	0.417	--
Si	0.140	--	--
NH_4	7.213	--	1.119
Cl	0.173	0.729	0.020
F	--	--	0.003
SO_4	4.320	1.061	0.847
NO_3	--	0.529	0.397
NO_2	--	--	0.003

(a) After charge balancing.

5.0 References

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