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Formulation and Preparation of Hanford Waste Treatment Plant Direct Feed Low Activity Waste Effluent Management Facility Core Simulant

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EXECUTIVE SUMMARY

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

This LAW Melter Off-Gas Condensate stream will contain components that are volatile at melter temperatures and are problematic for the glass waste form, such as halides and sulfate. Because this stream will recycle within WTP, these components accumulate in the Melter Condensate stream, exacerbating their impact on the number of LAW glass containers that must be produced. Diverting the stream reduces the halides and sulfate in the recycled Condensate and is a key outcome of this work. This overall program examines the potential treatment and immobilization of this stream to enable alternative disposal. The objective of this task was to formulate and prepare a simulant of the LAW Melter Off-gas Condensate expected during DFLAW operations. That simulant can be used in evaporator testing to predict the composition of the effluents from the Effluent Management Facility (EMF) evaporator to aid in planning for their disposition. This document describes the method used to formulate a simulant of this LAW Melter Off-Gas Condensate stream, which, after pH adjustment, is the feed to the evaporator in the EMF.

The origin of this LMOGC stream will be the liquids from the Submerged Bed Scrubber (SBS) and the Wet Electrostatic Precipitator (WESP) from the LAW melter off-gas system. Until the LAW melter in WTP begins radioactive operations, the actual stream is not available for direct characterization, making it challenging to formulate a simulant. Producing the simulant for this task was based on analytical results of condensates from laboratory-scale tests at Vitreous State Laboratory (VSL), which in turn used a simulant. The selected condensate streams were collected during two tests where the simulants being fed to the melter were most like those expected during the DFLAW operational period. The stream is a dilute salt solution with near neutral pH, and will likely contain some insoluble solids from melter carryover. The soluble components are mostly sodium, ammonium, and potassium salts of nitrite, nitrate, chloride, and fluoride. Plans are to raise the pH of the stream prior to evaporation in the new Effluent Management Facility to forestall corrosion of the evaporator components, so the simulant formulation adds caustic to generate an alkaline solution.

Future testing is planned to examine partitioning of components during evaporation and to test creating waste forms with the simulant. Evaporation testing will help to quantify distribution of species in the EMF evaporator, particularly ammonia, which is expected to partition to the evaporator condensate for disposition in the Effluent Treatment Facility (ETF). This simulant formulation is designated as the “core simulant”; other additives will be included for specific testing, such as volatiles for evaporation or hazardous metals for measuring leaching properties of waste forms.

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LIST OF ABBREVIATIONS

AD	Analytical Development Department in SRNL
DFLAW	Direct Feed Low-Activity Waste
DOE	Department of Energy
EMF	Effluent Management Facility
ETF	Effluent Treatment Facility
g	grams
hr	hour
HTWOS	Hanford Tank Waste Operations Simulator
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
Kg	kilogram
L	Liter
LAW	Low-Activity Waste
LMOGC	LAW Melter Off-Gas Condensate
mg	milligram
mL	milliliter
PSAL	Process Science Analytical Laboratory in SRNL
SBS	Submerged Bed Scrubber
Sim	Simulant
SRNL	Savannah River National Laboratory
Std. Dev	Standard Deviation
VSL	Vitreous State Laboratory – Catholic University
WESP	Wet Electrostatic Precipitator
WRPS	Washington River Protection Solutions
WTP	Waste Treatment Plant

1.0 Introduction

The Hanford LMOGC stream will be generated in the WTP by condensation and scrubbing of the LAW melter off-gas system by a SBS and WESP, as shown in Figure 1-1. This stream, which will contain substantial amounts of chloride, fluoride, ammonium, and sulfate ions, will get recycled to the LAW melter after evaporation. During DFLAW operations, the evaporation will be performed in the planned EMF, as shown in Figure 1-2. Most of the evaporator bottoms will be returned to the LAW melter, but some may be returned to the tank farms. The volatile halide and sulfate components that accumulate in this stream are only marginally soluble in glass, and often dictate the waste loading and thereby impact LAW waste glass volume. The principal radionuclides present in this stream that are not compatible with current onsite disposal limits are ^{99}Tc and ^{129}I. These radionuclides are volatile in the melter and accumulate in the LAW system. Diverting this LAW Melter Off-Gas Condensate stream to an alternate disposal path would have substantial beneficial impacts on the cost, life cycle, and operational complexity of WTP [1], but disposition of ^{99}Tc and ^{129}I must be appropriately managed.

1.1 Previous Testing Basis

Analysis results from two DM-10 tests at VSL were used as the basis for the simulant of this stream [2]. At the time, the melters were fed simulants of Hanford tanks AN-105 (Test #4) and AN-104 (Test #6). These two tests were selected because the feed compositions are comparable to the feed anticipated for the DFLAW operational period. The purpose of that test program was to track the distribution of technetium in the off-gas system, not to formulate the optimum condensate simulant. However, since extensive characterization data was available, and the SBS and WESP were of the latest design, it was considered a reasonable basis for the composition.

Other simulant formulations of the LMOGC have been prepared [3,4]. Those simulants were primarily based on the calculated output composition generated by the Hanford Tank Waste Operations Simulator (HTWOS), with adjustments based on pilot-scale test results.

The relative production rate of glass versus water used to scrub the off-gas appeared to vary between the VSL lab and pilot and the expected full-scale melters. This impacts the total concentration of the individual species in the condensate stream, but probably not their relative ratios. The DM10 produced 2 Kg/hr of glass and generated ~14.7 L/hr of scrubber water; which is more than the planned ratio for the WTP melter. A more concentrated composition was selected for development than was actually measured in the DM10 testing because of this and because of upcoming testing needs. This is also consistent with more concentrated condensate measured in the DM-1200 tests [5].

During tests at VSL, the SBS and WESP were typically pH of 6-8, with one SBS sample flush that was pH ~3. Prior to evaporation in the EMF evaporator, the pH will be raised to 10-12 to minimize corrosion. Note that a significant cation in the Melter Condensate is ammonium, which will largely convert to ammonia during this adjustment and will then partially vaporize in the evaporator. It is important to determine the distribution of ammonium and ammonia in the evaporator because the overhead condensate will be dispositioned in the ETF.

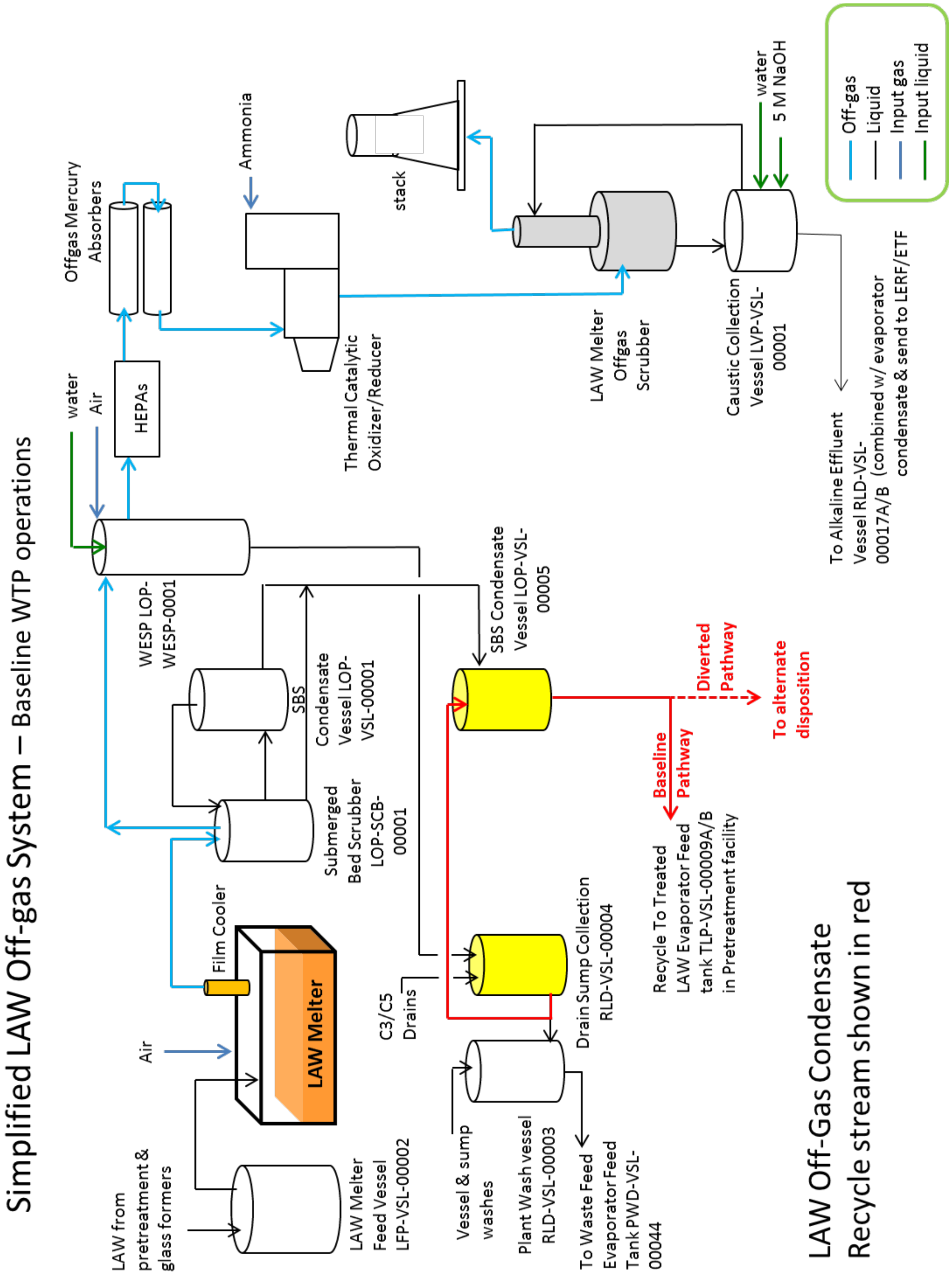

Figure 1-1. Simplified LAW Off-gas System (adapted from 24590-WTP-RPT-PT-02-005, Rev. 6; yellow indicates SBS/WESP LAW Off-Gas Condensate collection tanks, red lines indicate the collected off-gas condensate pathway)

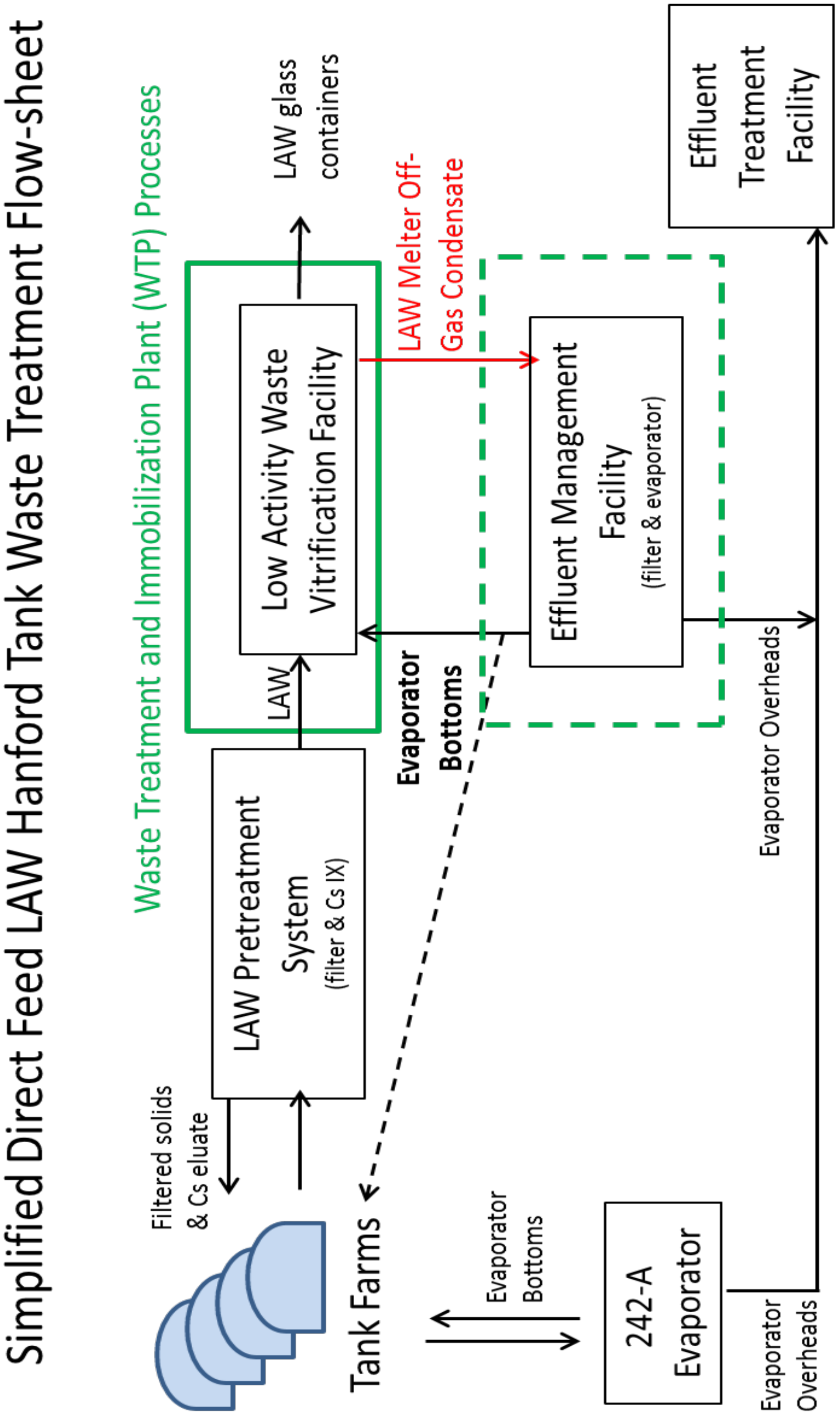

Figure 1-2. Simplified Schematic of the Direct Feed LAW (DFLAW) Scenario

1.2 Simulant Formulation Adjustments

Results of the Off-Gas Condensate stream analysis from VSL tests 4 and 6 were used as the basis for the chemical composition [2]. Aqueous stream samples were collected both during the tests, and when the SBS and WESP were flushed/deluged at the conclusion of each test. Note that tap water was used for the SBS and WESP, not deionized water. This contributed primarily calcium, magnesium, chloride, and sulfate to the stream. Analysis of the tap water was not performed by VSL, so a Washington D.C. municipal water system analysis report was used as a basis for the background concentration of these species [6].

Melter Condensate chemical composition data was obtained from the VSL report [2]. Species included in the simulant formulation were selected based on their (1) concentration (>1 mg/L), and (2) origin (i.e., background from water vs. LAW melter feed chemicals). Boron, chromium, potassium, lithium, sodium, silicon, zinc, chloride, fluoride, nitrite, nitrate, and sulfate were included. Although rhenium and iodine were high in the Condensate, they had been added to the LAW feed in disproportionately high concentration to enable their analysis, and were therefore excluded from this formulation. The calcium and magnesium were excluded from the simulant formulation because they originated primarily from the tap water. The composition was then calculated by using the concentrations in each sample, and included adjusting for the volume of Melter Condensate generated during operation for each device versus during the flush/deluge (note that the SBS volume is much larger than WESP). The concentrations of the species were decreased to subtract the amount contributed by the tap water, based on the Washington D.C. water quality report [5], which only significantly impacted chloride and sulfate concentrations (42 and 44 mg/L, respectively). Results are shown in Table 1-1. Individual component analysis results that exceeded 10X the average of the other samples were discarded as an outlier. Only a few analyses exceeded this threshold (One each of nitrite, nitrate, and potassium for Test 4, and three measurements of potassium for Test 6). Since ammonium ion was not analyzed, it was calculated based on the anion-cation imbalance. Any samples that resulted in a negative value for ammonium were set to zero. All results reported as “less than” the detection limits were set to zero. The analysis results from the two tests were averaged (i.e., the concentration of each component was averaged between the two tests). Although oxalate and carbonate were not analyzed by VSL, they were added to the simulant in small amounts. Oxalate has been observed in off-gas condensate samples previously [7,8], and carbonate is present in the waste, where it could be carried over by entrainment, and it is produced in the destruction of sugar in the melter as carbon dioxide. To enable tracking the fate of these species, a small amount of each (173 mg/L CO_3^{-2} and 50 mg/L $C_2O_4^{-2}$) was added to the simulant despite the absence of analyses from these VSL tests to support their inclusion. Similarly, ammonia was included based on prior observations [5].

Table 1-1 Initial Averaged Compositions of SBS and WESP Streams from VSL Tests 4 & 6

specie	Test 4 average SBS (M)	Test 4 average WESP (M)	Test 4 Volume-weighted average (M) SBS+WESP	Test 6 average SBS (M)	Test 6 average WESP (M)	Test 6 Volume-weighted average (M) SBS+WESP	Overall average (M)
B	3.20E-03	1.42E-03	2.95E-03	7.25E-03	1.00E-02	7.65E-03	5.29E-03
Cr	1.70E-07	4.50E-06	7.60E-07	6.70E-05	1.70E-04	8.20E-05	4.13E-05
K	2.00E-04	2.43E-03	5.10E-04	5.75E-03	1.78E-02	7.49E-03	3.99E-03
Li	4.40E-04	2.13E-03	6.80E-04	3.90E-05	6.10E-05	4.20E-05	3.59E-04
Na	6.70E-04	5.77E-03	1.37E-03	9.40E-03	1.99E-02	1.09E-02	6.12E-03
Si	5.80E-04	3.00E-04	5.40E-04	7.50E-05	1.70E-04	8.90E-05	3.16E-04
Zn	1.60E-04	1.00E-04	1.50E-04	6.20E-06	2.80E-05	9.40E-06	7.96E-05
Cl	1.49E-03	4.34E-03	1.88E-03	2.82E-03	1.23E-02	4.19E-03	3.02E-03
F	1.39E-03	6.60E-04	1.29E-03	1.26E-03	2.62E-03	1.46E-03	1.37E-03
NO_2^-	1.60E-04	1.80E-04	1.70E-04	1.46E-02	1.75E-02	1.50E-02	7.57E-03
NO_3^-	4.50E-05	4.20E-04	9.70E-05	7.10E-04	8.13E-03	1.79E-03	9.33E-04
SO_4^{-2}	2.54E-03	1.95E-03	2.46E-03	4.60E-04	1.23E-03	5.70E-04	1.51E-03
Calc'd NH_4^+	6.02E-03	2.40E-04	5.19E-03	2.40E-03	6.11E-03	2.94E-03	4.07E-03

Column 8 is the Overall compositional average, i.e., the average of Columns 4 and 7.

2.0 Experimental Procedure

2.1 Simulant Preparation

To actually generate the simulant from available chemicals, constituents were selected as salts, except for boric acid and silica. The amount of sodium was varied to achieve charge balance and the target pH. The sodium concentration was initially set to 0.1 M and other components were normalized to it. The sodium was then varied to achieve a final charge balancing and pH adjustment. The pH target was set to 11.9, requiring an additional quantity of sodium hydroxide. This pH adjustment was made because the EMF evaporator will require corrosion control, and this pH was calculated as the target to convert enough of the ammonium ion to ammonia to allow adequate margin to prevent the pH from decreasing during evaporation due to the vaporization of ammonia and resulting shift in equilibrium.

The chemical formulation is shown in Table 2-1. The chemicals were added in the order shown, adding the chromate, nitrite, and carbonate after pH adjustment to avoid reaction or lost as a vapor. The mixture was stirred overnight, and a final pH adjustment was then made to reach 11.8-11.9.

Table 2-1. EMF Core Condensate Simulant Formulation

Chemical	Formula	Target Mass (g)/L simulant*	Target Molarity
Potassium fluoride	KF	1.252	0.0216
Sodium chloride	NaCl	0.275	0.0047
Ammonium nitrate	NH_4NO_3	0.910	0.0114
Ammonium sulfate	$(NH_4)_2SO_4$	0.642	0.0049
Sodium sulfate	Na_2SO_4	0.963	0.0068
Potassium sulfate	K_2SO_4	2.20	0.0125
Ammonium chloride	NH_4Cl	2.343	0.0438
Silica	SiO_2	0.305	0.0052
Boric acid	$B(OH)_3$	5.250	0.0849
Zinc nitrate	$Zn(NO_3)_2$	0.241	0.0013
Sodium oxalate	$Na_2C_2O_4$	0.077	0.0006
Potassium hydroxide	KOH	0.980	0.0175
NaOH (50 wt%)	NaOH	Adjust to pH 11.9	
Sodium chromate	Na_2CrO_4	0.108	0.0007
Sodium nitrite	$NaNO_2$	8.350	0.1210
Lithium carbonate	Li_2CO_3	0.213	0.0029

*calculated weights assumes anhydrous reagent is used

The cloudy yellow solution was filtered and submitted for analysis. Samples were analyzed three times by Inductively Coupled Plasma – Emission Spectroscopy, and anion and cation Ion Chromatography at SRNL (two samples at the Process Science Analytical Laboratory, and once at the SRNL Analytical Development laboratory).

2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Results are recorded in Electronic Laboratory Notebook #E7518-00159. This report documents completion of Task 3.2 in the Task Technical and Quality Assurance Plan SRNL-RP-2015-01038, Rev. 0 [9].

3.0 Results and Discussion

3.1 Simulant Compositions

A 2 L sample of the simulant was prepared and three subsamples were filtered and analyzed. An average and standard deviation of the chemical analysis results for the three sub- samples of the neutralized and filtered simulant are shown in Table 3-1, and details are shown in appendix A. This shows the calculated target concentration of species based on the formulation shown in Table 1-1 versus the average result from three analyses for most species. Ammonium was only measured once, and carbonate was not measured.

Table 3-1. EMF Core Condensate Simulant Filtrate Analysis Results

Species	Target (mg/L)	Result average (mg/L)	Std. Dev.*
B	918	893	31
Cr	34	34	0.3
K	2512	2705	157
Li	40	47	6.6
Na	6765	7688	468
Si	143	2	1.2
Zn	83	87	6.6
NH_4^+	1169	1120	**
Cl^-	1721	1710	20
F^-	409	404	2.5
NO_3^-	862	949	77
NO_2^-	5568	5763	67
SO_4^{-2}	2330	2173	92.9
CO_3^{-2}	173	NA	-
oxalate	50	43	5.5

* std deviation of 3 values shown in table A-1
**single measurement
NA = not analyzed

This simulant was slightly cloudy prior to filtration, which was evidently due to the insoluble silica. To prepare the simulant, an amorphous form of silica had been used, and it was first mixed with concentrated potassium hydroxide in an attempt to dissolve it. However, it did not completely dissolve in the potassium hydroxide solution, and evidently did not dissolve or further precipitated in the final simulant mixture. Sodium is slightly higher than calculated, but variance in sodium concentration was expected, since sodium hydroxide was used to adjust the pH. The final, measured pH was 12.2.

4.0 Conclusions

A simulant of the feed expected for the feed to the evaporator in the EMF at WTP was formulated based on analytical results of melter off-gas condensate from tests conducted at Vitreous State Laboratory. The calculated composition of the LMOGC stream was adjusted to pH ~12 to represent the feed to the EMF evaporator. The aqueous simulant was prepared using laboratory grade chemicals. All of the components dissolved except for the silica. All the analysis average results matched the target concentrations within two standard deviations except nitrite, which was within three standard deviations. However, silica did not match because of its precipitation and removal through filtration.

5.0 Future Work

Further testing is planned to evaporate this simulant in a vacuum evaporator and measure the distribution of species and examine the achievable concentration factor prior to formation of significant insoluble solids.

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Appendix A. Detailed Results

Table A-1. Individual Sample Analysis Results

	PSAL*	PSAL	AD**
	EMF Sim Apr25	**EMF Sim Apr26**	**EMF Sim Apr26**
	Sample i.d. S-5452	Sample i.d. S-5453	Sample i.d. LW948
Al	<0.100	<0.100	< 0.76
B	861	923	894
Ca	0.43	0.44	0.301
Cr	34	33	33.8
K	2750	2834	2530
Li	51	50	38.9
Mg	<0.100	<0.100	< 0.0253
Na	7852	8053	7160
P	<0.500	<0.500	< 0.448
S	784	778	816
Si	2	2	3.59
Zn	79	90	91.3
F	407	402	404
Cl	1730	1710	1690
NO2	5820	5780	5690
NO3	1000	987	861
SO4	2130	2110	2280
oxalate	39.7	39.2	49
pH	12.2	-	NA
NH4	NA	NA	1120

*PSAL refers to analysis performed at the Process Science Analytical Laboratory
**AD refers to analysis performed by the Analytical Development department in SRNL

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