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EVAPORATION OF PRETREATED HANFORD TANK AW-101 SAMPLE MIXED WITH RECYCLE

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LIST OF ACRONYMS

ICP	Inductively Coupled Plasma
LAW	Low Activity Waste
NIST	National Institute of Standards and Technology
NM	Not Measured
QA	Quality Assurance
RPP	River Protection Project
SBS	Submerged Bed Scrubber
SRTC	Savannah River Technology Center
St. Dev.	Standard Deviation
Toc	Total Organic Carbon
WTP	Waste Treatment Plant
XRD	X-ray Diffraction

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1.0 SUMMARY OF TESTING

1.1 OBJECTIVES

This task was undertaken to provide validation data for the Treated Feed Evaporator flowsheet and operating conditions using Hanford Tank 241-AW-101 (Envelope A) pretreated waste blended with simulated River Protection Project Waste Treatment Plant (RPP-WTP) waste recycles. This radioactive task provided the first opportunity to compare performance of blended actual treated waste to the performance of blended treated waste simulants and recycle simulants.[1] Specific objectives were:

1) determining the effect of plant recycles
2) developing solubility data, as well as chemical and physical property data
3) evaluating antifoam effectiveness

These were all accomplished except for antifoam evaluation since foaming did not occur during the majority of evaporation testing. Foaming was only observed well past saturation for one of the blends.

1.2 CONDUCT OF TESTING

The treated AW-101 sample was produced from the composite effluent of Ion Exchange testing carried out at SRTC.[2] Submerged Bed Scrubber (SBS) Recycle (subenvelope A2) was made by Duratek during vitrification melter tests with simulants. These feed streams were blended at two different ratios, 45:55 and 35:65 AW-101 to SBS A2, corresponding to the baseline flowsheet ratio of 40:60.[3] SRTC personnel characterized the feed materials, the blended feed mixtures, and the evaporation products.

A 4-inch ID evaporator was used to concentrate 3-5 L of each blend[4] to the target RPP-WTP design concentration of 8 M Na. Plant design pressure (~60 mm Hg) and temperature (~50-60°C) were used. The evaporator produced 4 ml/min of condensate, which converts to 0.012 gpm/ft^2, or 4% of the maximum RPP-WTP design flux.[5] Samples were taken at nominally 5M Na, 8M Na, and 11M Na (i.e., saturation).

1.3 RESULTS AND PERFORMANCE AGAINST OBJECTIVES

The design basis operating conditions were validated. The evaporator operated at 60 mm Hg, and boiling temperature increased from 45°C for the dilute solution to 52°C (or 59°C at 80 mm Hg) for the target concentration of 8M Na. Precipitation began between 8.7 and 10.4 M Na. Chemical and physical property data were developed for the AW-101 ion exchange effluent, the SBS A2 simulant recycle, two blends (45:55 and 35:65) of AW-101 to SBS A2, as well as condensate and concentrate solutions. Analyses included solids characterization.

During these evaporation tests, no excessive or problematic solids formed. Therefore, it is unlikely that solids will be an issue for evaporation of AW-101 material with recycle in the LAW portion of the RPP-WTP. In general, foaming did not occur. However, foaming was observed during post-saturation boiling of the 45:55 blend of AW-101 and SBS A2. (The post-saturation concentrate included 10.4 M Na, 59 wt.% total solids, and 5.7 wt.% suspended solids.) Foaming was not observed for the 35:65 blend, even after saturation (i.e., 11.0 M Na, 10.4 wt.% suspended solids, and 59 wt.% total solids).

Concentrated solutions of AW-101/SBS A2 at 7.0 and 7.6 M Na had viscosity values of 7-9 cP and a heat capacity of 0.8 cal/g °C. These values for actual AW-101 solutions were significantly higher than those of Envelope A simulants in an earlier study.[1] These differences are due in part to the fact that the simulants were not made to match specific tanks, such as AW-101. Also, the radioactive AW-101 samples were evaluated on different instruments than the non-radioactive simulants, with experimental error of 10% assumed for each instrument. It is important to note that the viscosities of concentrated AW-101 solutions in this study, as well as those of the simulants in the earlier study, all fall well within the expected range of 0.4 to 15 cP, the current bounding conditions for the WTP.[6]

1.4 QUALITY REQUIREMENTS

This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRTC as identified in DOE IWO M0SRLE60. SRTC has provided matrices to WTP demonstrating compliance of the SRTC QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRTC QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices. As noted in the Test Specification,[5] DOE/RW-033P is not applicable to this work. The specific QA requirements associated with this task are outlined in a Task Technical and Quality Assurance Plan.[8]

1.5 ISSUES

These tests did not raise issues for the design and operation of the RPP-WTP. However, experimental vapor flux was only 4% of the maximum design flux. Because higher fluxes were not tested, a foaming issue during evaporation of this material in the RPP-WTP cannot be completely ruled out. Higher fluxes will be tested on a pretreated sample from tank AN-104.

2.0 EXPERIMENTAL DESCRIPTION

2.1 FEED

The key portion of the evaporator feed originated from Hanford Tank 241-AW-101. This tank is in Envelope A, subset A2 of the tanks to be treated by the RPP-WTP. The AW-101 sample was diluted, characterized, and treated for cesium and technetium removal by ion exchange at SRTC. (Pretreatment of AW-101 by ion exchange at SRTC occurred prior to the removal of technetium treatment from the flowsheet.) The resulting pretreated AW-101 sample was used for these experiments, and was blended with a simulated recycle stream, SBS A2, generated by Duratek. SBS stands for Submerged Bed Scrubber, a processing step in the RPP-WTP Low Activity Waste (LAW) vitrification process. Hence, the SBS material contains glass-former solids. A2 is the subenvelope designation for a particular Duratek processing run. Previously, the SBS A2 sample has also been identified as RM-02-163.

The major components of the feed are shown in Table 1 and Table 2. In most cases, these values represent the average of two samples. Radioactive components are in the Results section (Table 5) for comparison with evaporator products. For SBS A2 and the blended solutions, samples were filtered prior to analysis, except for specific gravity and percent solids determinations.

The AW-101 portion of the feed contained 4.76 M sodium (Na), and the SBS A2 portion of the feed contained only 0.12 M Na. Evaporator runs were conducted with two different blends of AW-101 to SBS A2, 45:55 and 35:65. These ratios were chosen in light of the 40:60 blend ratio expected in the RPP-WTP.[3]

In Table 1, almost all measured concentrations in the blended feeds are close to the expected values based on concentrations in the AW-101 and SBS A2 solutions. However, a few blend concentrations indicate a discrepancy. For silicon (Si), calcium (Ca), and zinc (Zn), concentrations in the blends are higher than expected. This is likely due to partial dissolution (after blending) of some of the solids present in SBS A2. Si and Ca were the most predominant elements identified in SBS A2 solids, as discussed later in this section. Si, Ca, and Zn were all present in sufficient quantity in the SBS A2 solids that partial dissolution in the caustic blend matrix would yield the measured increases in dissolved concentration. Other elements in Table 1 which were present in trace quantities did not show a suitable mass balance before and after blending. It is likely that the chemical changes due to blending caused shifts in the equilibrium concentrations of these trace species. On the whole, the reported concentrations in Table 1 and Appendix A, which includes many analyses of evaporator product solutions, show consistent behavior for a wide range of elements.

Table 1. Metals in Feed

	AW101 IX Effl. mg/L	SBS A2 Recycle mg/L	Blend 45:55 mg/L	Blend 35:65 mg/L
ICP-Emission Spectrometry				
Ag	0.27	1.03	<0.16	<0.16
Al	12950	0.86	5910	4060
B	15.8	838	449	530
Ba	0.42	<0.02	<0.38	<0.38
Ca	4.11	0.53	4.27	5.23
Cd	1.03	<0.03	0.086	<0.08
Ce	3.67	<1.5	1.08	2.56
Cr	39.6	40.7	39.4	40.1
Cu	2.41	<0.1	0.71	0.54
Fe	1.72	<0.09	0.48	0.14
Gd	<0.47	NM	<0.47	<0.47
K	19150	1117	9250	6080
La	0.51	<1.4	<0.14	0.46
Li	<0.86	1.49	<0.86	1.44
Mg	<0.11	0.88	<0.11	<0.11
Mn	<0.02	0.03	<0.02	<0.02
Mo	38	0.2	17.3	9.32
Na	109000	2761	50550	46400
Na (M)	4.76	0.12	2.21	2.02
Ni	2.29	<0.12	1.06	1.33
P	143	<1.4	61.6	48.1
Pb	18.2	<1.4	2.16	<0.67
S	199	237	226	218
Sb	35.7	NM	15.3	12.0
Si	63.9	49.3	84.8	72.2
Sn	64	<0.52	30.5	23.3
Sr	1.41	0.01	1.05	1.35
Ti	<0.15	<0.28	<0.15	<0.15
U	<4.54	NM	<4.5	5.47
V	0.10	0.47	<0.04	NM
Zn	4.39	3.96	30.5	34.2
Zr	5.34	<0.10	<0.46	<0.46
Atomic Absorption				
Na	NM	2770	NM	NM

NM = Not Measured

Table 2. Non-metals in Feed

	AW101 IX Effluent mg/L	SBS A2 Recycle mg/L	Blend 45:55 mg/L	Blend 35:65 mg/L
IC Anions				
Chloride	1980	1850	2020	1840
Fluoride	275	1090	382	744
Formate	1020	100	607	323
Nitrate	92100	1630	36700	25000
Nitrite	45200	4710	22800	16200
Oxalate	226	19	131	86
Phosphate	154	<10	66	96
Sulfate	172	864	429	400
Total Carbon	2300	377	1250	NM
Organic Carbon	878	356	822	NM
Inorganic Carbon	1420	21	418	NM
	Mol/L	**Mol/L**	**Mol/L**	**Mol/L**
Total Base	2.81	NM	1.25	0.888
Free OH	2.02	NM	0.858	0.584
Other Base excl. CO_3	0.66	NM	0.375	0.155
Carbonate	NM	NM	0.043	NM
pH	NM	7	NM	NM
Specific Gravity	1.23[9]	1.013	1.095	1.08
	wt.%	**wt.%**	**wt.%**	**wt.%**
Suspended Solids	None visible	0.42	0.20	0.39
Total Solids	32.0[9]	1.64	15.7	11.8

NM = Not Measured

For AW-101 Ion Exchange Effluent, simulated SBS A2 recycle, blended feeds, and concentrate, the filtrate was clear yellow and the filtered solids were brown. Photographs of both settled and mixed SBS A2 are shown in Figure 1.

Figure 1. Settled (left) and mixed solutions of SBS A2 simulant recycle

The AW-101 portion of the feed contained no observable solids and, as shown in Table 2, SBS A2 had 0.4 wt. % suspended or insoluble solids. The crystal structures of SBS A2 solids were identified by x-ray diffraction (XRD) as SiO_2 (quartz), Fe_2O_3, $ZrSiO_4$, K_2NaAlF_6, TiO_2, and CaF_2. SiO_2, Fe_2O_3, and TiO_2 are glass formers that were entrained in the Duratek melter offgas. The $ZrSiO_4$, CaF_2, and K_2NaAlF_6 are likely to be precipitation products when the offgas was contacted with water in the submerged bed scrubber. It should be noted that CaF_2 is only sparingly soluble in water, and not appreciably more soluble in caustic solution.

Attempts to completely dissolve these SBS A2 solids in hot nitric acid or hot sodium hydroxide for further analysis were unsuccessful. However, a fusion (digestion) technique using cesium hydroxide and hydrochloric acid did dissolve the solids. Analysis of the resulting digested solution provided quantitative results on their relative abundance: silicon (11 wt. % of dry solids), calcium (9.4%), zirconium (8.7%), potassium (6.5%), iron (4.2%), aluminum (4.2%), sodium (3.2%), zinc (2.2%), titanium (1.9%), magnesium (1.8%), chromium (0.6%), sulfur (0.2%), and other trace components.

2.2 SYSTEM CONFIGURATION

A photograph of the experimental setup is included in Figure 2. The evaporator, condensers, and condensate collection vessels were fabricated in the SRTC Glass Shop. The evaporator is a 4-in. diameter, 19-in. tall vessel with a volume of 2200 mL. The main evaporator body is quartz, and the lid with multiple entry ports is borosilicate glass. Heat was supplied through a Corning stirrer/hot plate. Feed was drawn into the evaporator by the vacuum in the system and was added periodically to maintain a liquid level between 700 and 1500 mL. The liquid level dropped below this range at the end of each experiment.

The evaporator temperature was monitored using a Cole-Parmer Type K thermocouple and thermocouple readout (model 91100-50). The evaporator pressure was measured using a calibrated SPER Scientific pressure transducer (model PS100) and readout (model 840065). All equipment used to measure temperature and pressure were calibrated with NIST-traceable standards prior to use by the Savannah River Standards Laboratory and logged as Measuring and Test Equipment (M&TE). Vacuum is pulled on the system using a Vacuubrand MZ 2C Pump, a Teflon® diaphragm pump. The tubing between the evaporator and the vacuum pump was equipped with an air bleed valve to control evaporator pressure.

The two jacketed condensers used were approximately 3 in. diameter, and were cooled using a Neslab Coolflow DC-25 chiller, operated at nominally 18°C. The first condensate collection vessel had graduations up to 3250 mL. The second condensate vessel was only 250 mL.

Many samples of feed and concentrate required filtering for analysis of the filtrate and/or the solids. Small samples were filtered using Gelman Acrodisc 25 mm syringe filters with 0.45 μm Versapor Membrane. Large samples and all samples requiring solids analysis were vacuum-filtered using Nalgene cellulose nitrate filters, 47 mm diameter, 0.45 μm pore diameter.

The evaporator concentrate samples taken at approximately 8 M Na were in duplicate. A portion of each sample was submitted for density, suspended solids, and total solids, and another portion was filtered. The filtrate was analyzed for cations (ICPES), anions (IC), hydroxide/base content, and carbon content. In addition, solids were analyzed using x-ray diffraction (XRD) and, in some cases, scanning electron microscopy (SEM).

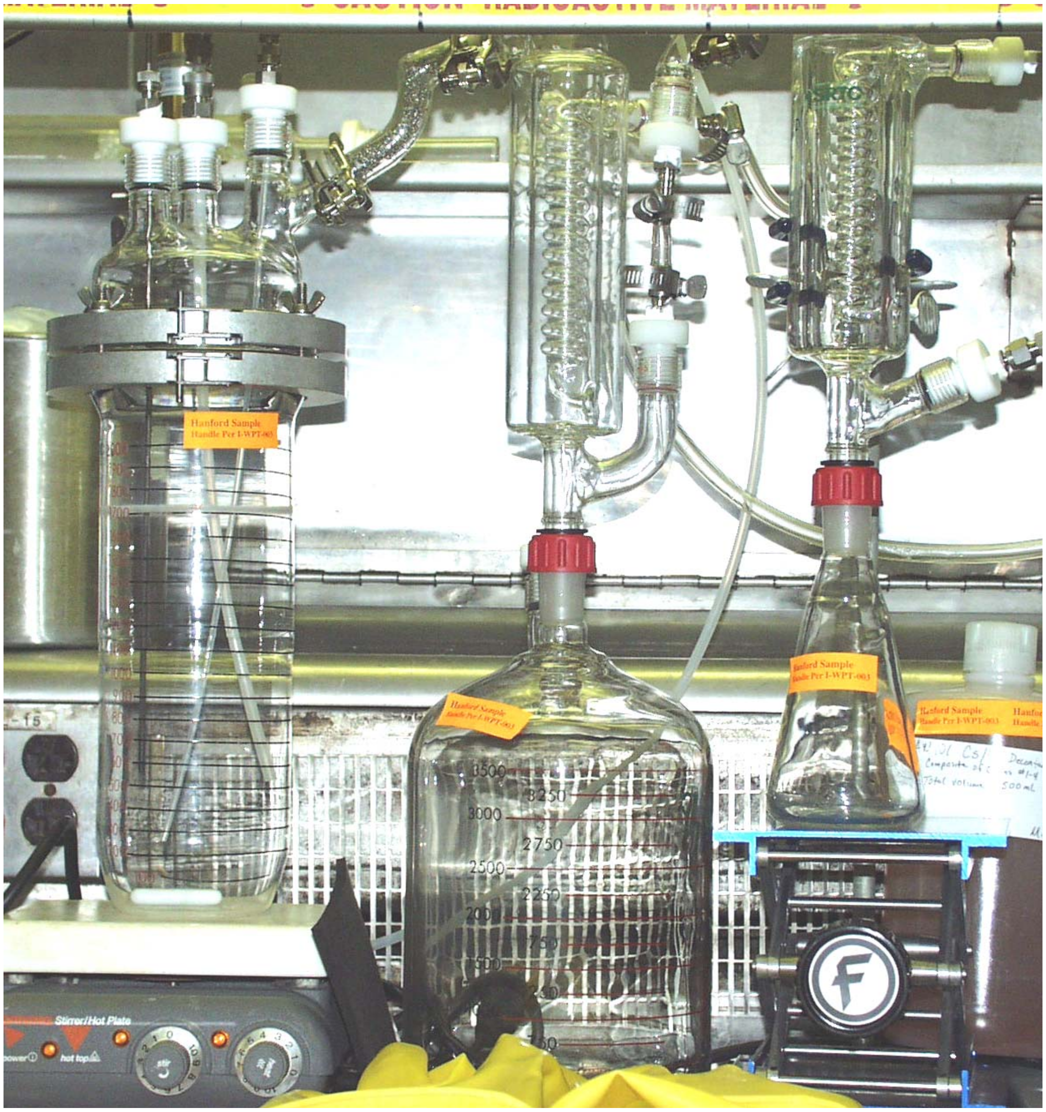


Figure 2. Evaporator Apparatus

3.0 RESULTS AND DISCUSSION

3.1 EXPERIMENTAL OBSERVATIONS

3.1.1 Blend Ratio: 45:55

In the first experiment, a 45:55 blend of AW-101 to SBS A2 was used as feed (i.e., 1.5 L of treated AW-101 and 1.8 L of SBS A2). The evaporator was charged with 1000 mL of feed. The hot plate was turned on and gradually increased to full power. Pressure was maintained via a bleed valve at 27.55+/-0.2 in Hg vacuum (i.e., 60+/-5 mm Hg absolute). During testing, condensate was collected at nominally 4 mL/min. Only one drop of condensate was observed/collected in the secondary (250 mL) flask. A plot of the temperature and pressure of the evaporator is shown in Figure 3. Initial rises in temperature were due to startup. Day 3 behavior differed because the bleed valve allowed a consistent, gradual rise in pressure.

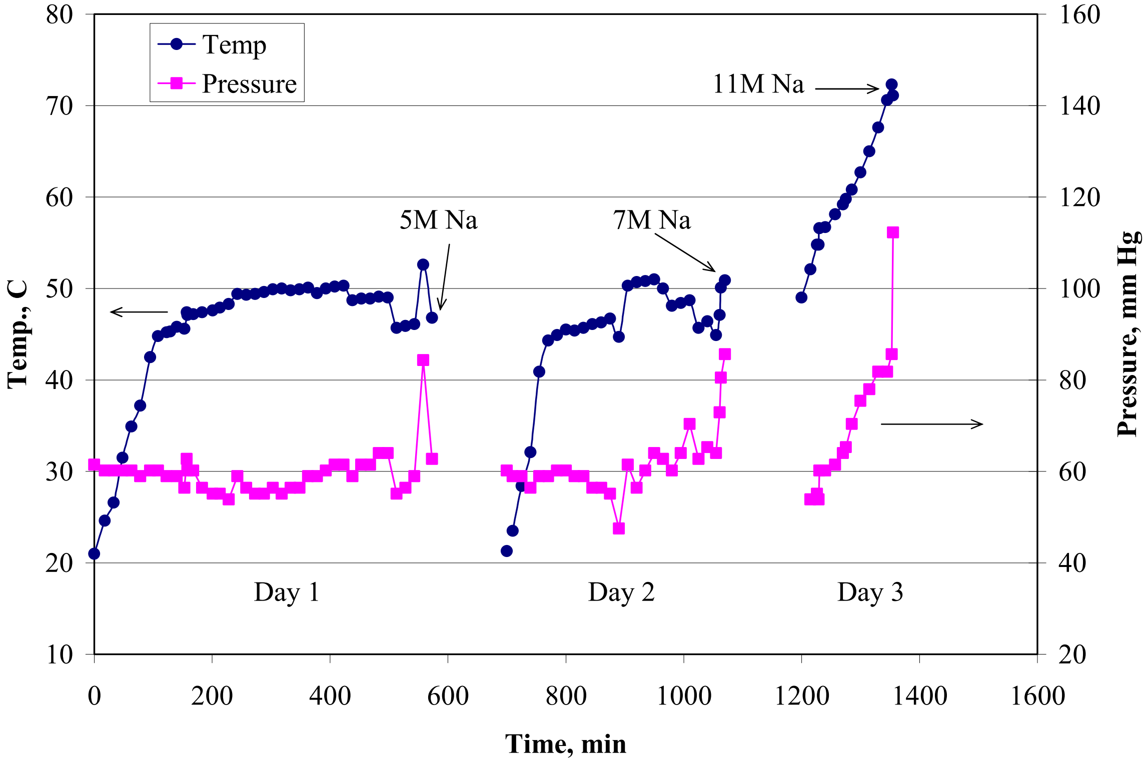
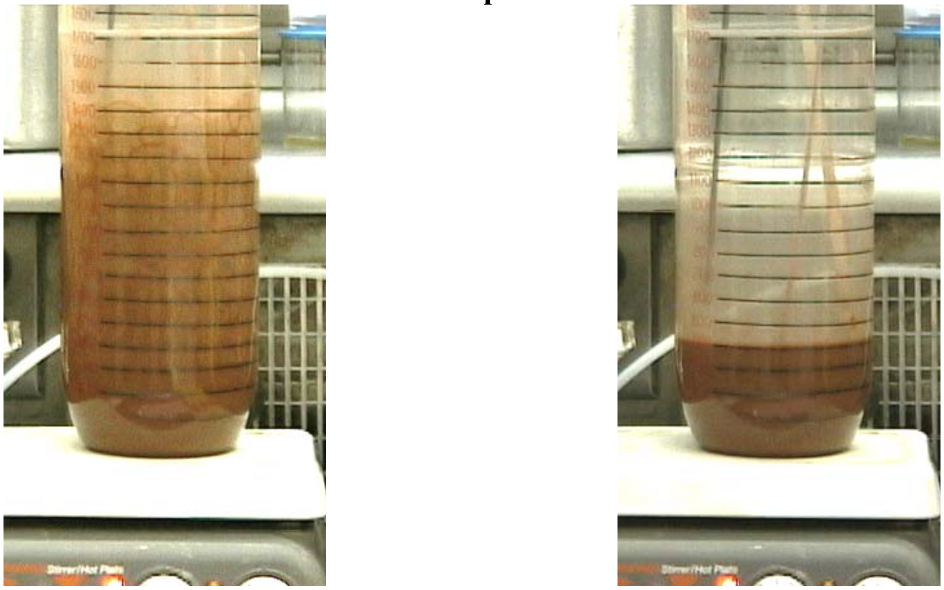


Figure 3. Operating conditions for evaporation of 45:55 blend of AW101/SBS A2

At the end of each day, boiling point data were collected. The system pressure was sequentially increased from approximately 60 to 70 to 80 mm Hg. At each pressure reading the system temperature was allowed to stabilize during boiling to determine the boiling point. The system was then allowed to cool and samples were taken to determine exact concentrations.

After the concentration in the evaporator passed 8 M Na, experimenters watched closely to identify a precipitation event. However, no dramatic increases in solids content were observed. Toward the end of the evaporation, the pressure gradually increased in the vessel and the boiling temperature also increased. (The bleed valve may have been open slightly too much.) Foaming was also observed at the end of the evaporation, as shown in Figure 4, with the foam height reaching 2 to 4 times the liquid height. As determined later and shown in Table 9, foaming occurred at a concentration of 10.4 M Na, 59 wt. % total solids, and 5.7 wt. % suspended solids.

Normal Operation



Post-Saturation Foaming **Liquid Level During Foaming**

Figure 4. Photographs of Evaporator Operation

3.1.2 Blend Ratio: 35:65

The second experiment involved a 35:65 blend of AW-101 to SBS A2 (i.e., 1.5 L of treated AW-101 and 2.79 L of SBS A2). The experimental method and sampling schedule were the same as the previous evaporation of a 45:55 blend. However, no foaming was observed, even after the concentrate was well past saturation. The evaporator operating conditions for this blended sample is in Figure 5. Sharp drops in temperature in Figure 5 were due to either feed additions or brief suspensions in heating for sampling purposes. Pressure changes were made for boiling point determinations.

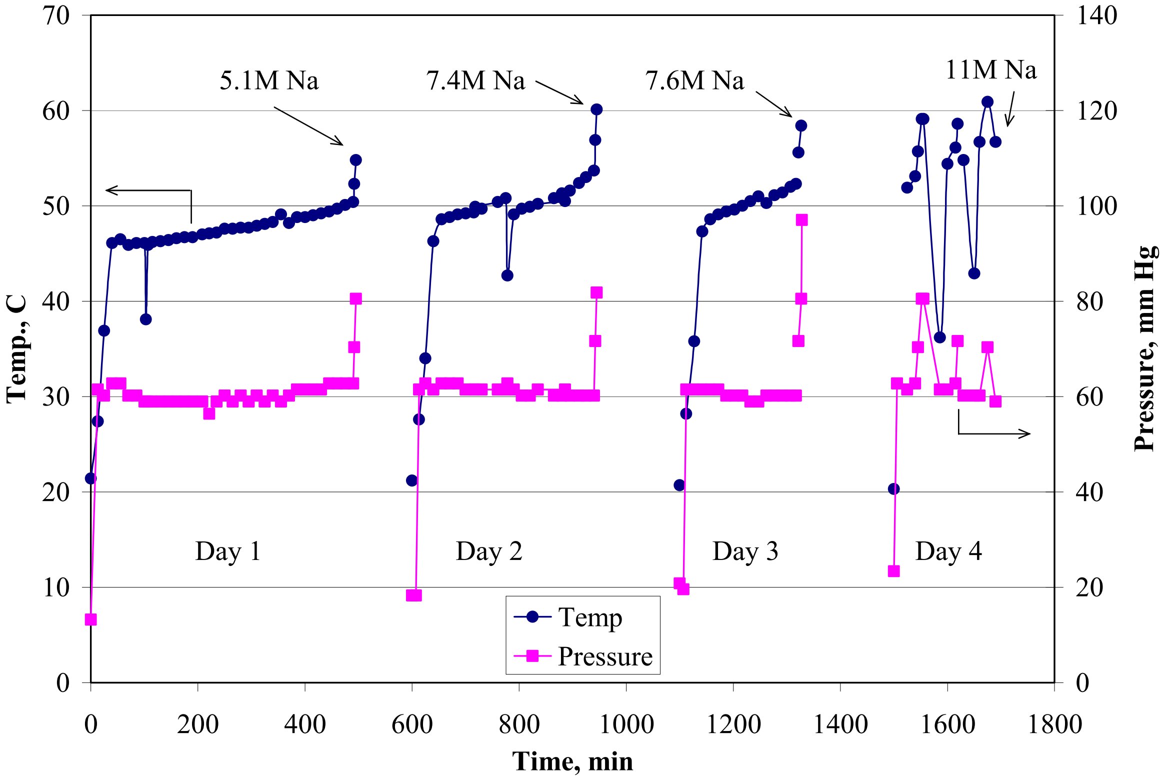


Figure 5. Operating conditions for evaporation of 35:65 blend of AW101/SBS A2

3.2 BOILING POINT

As mentioned previously, boiling points were measured at a range of concentrations and pressures. In addition, estimated boiling points were calculated with an OLI model. For the 35:65 blend, these boiling points are presented in Figure 6. As seen in Figure 6, the experimental boiling points are nominally 5-10°C higher than model values for most temperatures and pressures. The reason for the offset between experimental and model results is not clear. In addition, experimental concentrations represent the filtered supernate at room temperature. Precipitation may have occurred during or after boiling point measurements, especially for 11 M Na solutions. This would cause a difference between the actual Na concentrations and those used in the model, and lead to lower model predictions. Experimental data for the 45:55 blend were similar to those for the 35:65 blend, but were not taken at consistent pressures.

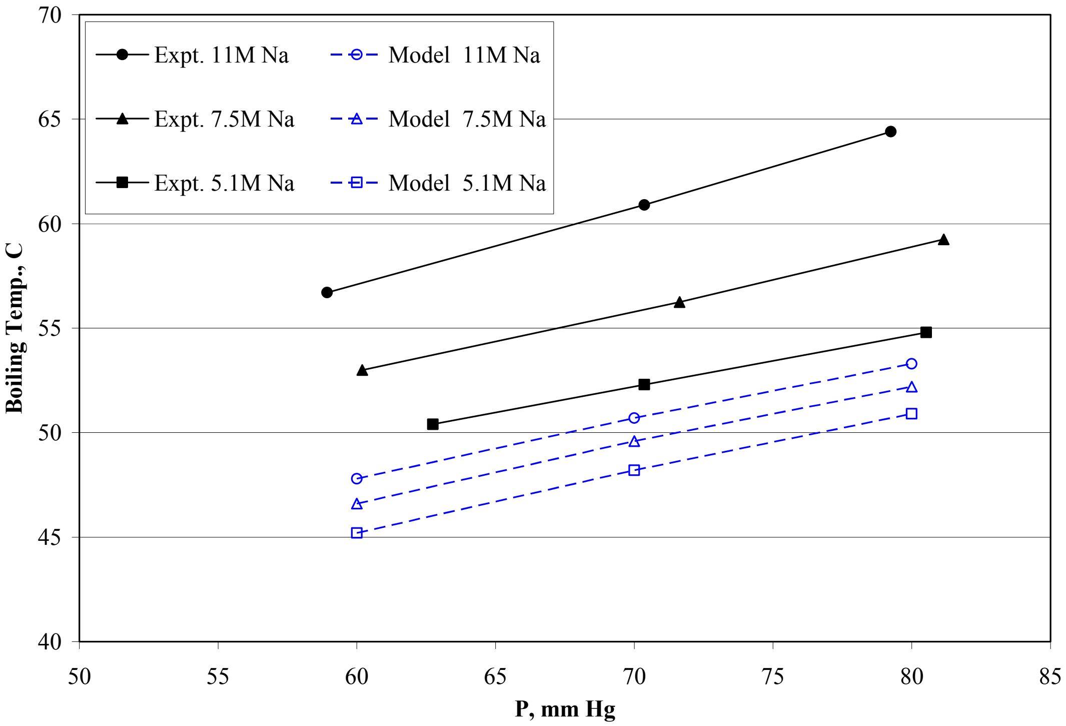


Figure 6. Experimental and model boiling points for 35:65 blend of AW101/SBS A2

3.3 PRODUCT COMPOSITION

Composition of concentrate and condensate products of the two evaporated blends are shown in Table 3 through Table 7. Solids analyses are included in the next section. Note that the 45:55 blend condensates in Table 3 were diluted, which increased the detection limits. Condensate samples from the 35:65 blend (Table 6) were not diluted.

Table 3. Products from Evaporation of 45:55 Blend (AW-101:SBS A2)

ICP-Emission Spectrometry					
	Feed mg/L	**Concentrate mg/L**	**CF**	**Condensate mg/L**	**DF**
Ag	<0.16	<1.60	–	<1.60	–
Al	5910	20750	3.51	<11.4	> 518
B	449	1650	3.68	<5.60	> 80
Ba	<0.38	<3.80	–	<3.80	–
Ca	4.27	<4.60	–	<4.60	–
Cd	0.09	<0.84	–	<0.84	–
Ce	1.08	18.1	–	12.9	–
Cr	39.35	140.5	3.57	<1.20	> 33
Cu	0.71	3.23	–	2.56	–
Fe	0.48	3.21	–	<0.72	–
Gd	<0.47	<4.68	–	<4.68	–
K	9250	32500	3.51	<188	> 49
La	<0.14	<1.44	–	<1.44	–
Li	<0.86	<8.60	–	<8.60	–
Mg	<0.11	<1.06	–	<1.06	–
Mn	<0.02	<0.16	–	<0.16	–
Mo	17.25	61.9	3.59	<10.6	–
Na	50550	160000	3.17	<4.40	>1.15E+04
Na (M)	2.21	6.96	3.17	< 0.0002	> 1.1E+04
Ni	1.06	<2.70	–	<2.70	–
P	61.55	212	3.44	<13.8	> 4
Pb	2.16	6.98	3.24	<6.38	–
S	226	772.5	3.42	<27.4	> 8
Sb	15.3	<75.6	–	<75.6	–
Si	84.75	378	4.46	<3.34	> 25
Sn	30.45	112.5	3.69	10.5	2.9
Sr	1.05	<1.52	–	<1.52	–
Ti	<0.15	<1.54	–	<1.54	–
U	<4.54	<45.4	–	<45.4	–
V	<0.04	1.33	–	1.11	–
Zn	30.45	190	6.2	<0.64	> 48
Zr	<0.46	<4.56	–	<4.56	–
Average			3.45	(without Si and Zn)	
St. Dev.			0.19		

In this study, the concentration factor (CF) is defined as the concentration in the concentrate divided by that of the feed. The decontamination factor (DF) is the concentration in the feed divided by that of the condensate. In Table 3, the CFs for silicon (Si) and Zn are significantly higher than those of other species. This may be due to dissolution of SBS A2 solids in the caustic matrix of the concentrate. In addition, elevated Si in the concentrate may be due to leaching from the glassware. Excluding Si and Zn, the average CF for the predominant species was 3.45 with a standard deviation of 0.19. The decontamination factor for sodium was over 10,000. This is consistent with the DFs for anions (in Table 4), which were also greater than 10,000. DFs for nearly all other components were as high as allowed by instrument detection. However, significantly more cerium in both products than in the feed indicates a likely sample contamination or instrument problem for this element.

Table 4. Anions and Other Evaporation Products of the 45:55 Blend

IC Anions					
	Feed mg/L	**Concentrate mg/L**	**CF**	**Condensate mg/L**	**DF**
Chloride	2015	6475	3.2	<0.2	>10000
Fluoride	382	694	1.8	<0.2	>1900
Formate	607	543	0.9	<1	>600
Nitrate	36700	123000	3.4	<1	>36700
Nitrite	22750	78400	3.4	<1	>22800
Oxalate	131	323	2.5	<1	>130
Phosphate	66	330	5.0	<1	>66
Sulfate	429	1355	3.2	<0.5	>860
Carbonate	0.043	0.105	2.5	<0.002	>21
Total Carbon	1250	3820	3.1	47	27
Organic Carbon	822	2385	2.9	28	29
Inorganic Carbon	418	1435	3.4	19	23
	Mol/L	**Mol/L**		**Mol/L**	
Total Base	1.25	4.13	3.3	0.046	27
Free OH	0.858	2.94	3.4	0.041	21
Other Base	0.375	1.1	3.0	<0.002	>188

Radioactive components were measured for the products of the 45:55 blend. As shown in Table 5, the CF for gamma emitters was 2.1-3.5, which matches that of the major cations and anions. DF values were limited by instrument detection. Liquid scintillation analyses provided gross alpha and beta values, but these were measured with a screening method. Though quantitative, the method does not yield the accuracy of separation techniques. Analyses for some trace components were not completed due to a related programmatic decision.[4]

Table 5. Radioactive and Trace Metal Components in Evaporation of 45:55 Blend

Gamma Pulse Height Analysis						
	AW101 IX Effl. µCi/mL	**45:55 Blend µCi/mL**	**Concentrate µCi/mL**	**CF**	**Condensate µCi/mL**	**DF**
Co-60	1.83E-04	8.77E-05	2.13E-04	2.4	<1.23E-5	>7.1
Sb-126	2.52E-04	1.08E-04	3.80E-04	3.5	<9.38E-6	>11.5
Sn-126	2.75E-04	1.27E-04	2.70E-04	2.1	<1.59E-5	>8.0
Cs-137	2.91E-03	1.28E-03	4.48E-03	3.5	<1.22E-5	>116
Liquid Scintillation Analysis						
	dpm/mL		**dpm/mL**		**dpm/mL**	
Alpha	759	NM	270	–	<46.4	–
Beta	1.80E+05	NM	5.45E+04	–	461	~300
Atomic Absorption						
	mg/L	**mg/L**	**mg/L**	–	**mg/L**	–
As	0.49	0.17	1.48	–	<0.025	>6.8
Se	0.73	<0.055	0.45	–	<0.025	–
Hg	<0.11	NM	<0.11	–	<0.11	–
ICP-Mass Spectrometry						
Element	**mg/L**	**mg/L**	**mg/L**		**mg/L**	
Ru	3	1	4	–	<0.05	–
Rh	4.0	2.0	7.1	–	0.01	–
Pd	0.2	0.1	0.2	–	<0.01	–
Ta	<0.1	<0.1	<0.1	–	<0.00001	–
Pt	<0.1	<0.0001	<0.01	–	<0.01	–
Pr	<0.01	<0.0001	<0.0001	–	<0.000003	–
Isotope						
U-235	<0.00006	<0.00002	0.08	–	0.001	–
Np-237	<0.00006	0.02	<0.00002	–	<0.000008	–
U/Pu-238	0.01	0.03	0.05	–	0.003	–
All other actinides	<0.00006	<0.00002	<0.00002	–	<0.000008	–

NM = Not Measured

Table 6. Products from Evaporation of 35:65 Blend (AW-101:SBS A2)

ICP-Emission Spectrometry					
	Feed mg/L	Concentrate mg/L	CF	Condensate mg/L	DF
Ag	<0.16	0.21	–	<0.01	–
Al	4100	27350	6.7	0.08	52600
B	526	2300	4.4	0.14	3700
Ba	<0.38	0.383	–	<0.02	–
Ca	5.19	11.9	–	<0.03	–
Cd	<0.08	1.27	–	<0.01	–
Ce	2.41	3.56	–	0.1	–
Cr	39.9	166	4.1	<0.01	>5700
Cu	0.54	1.42	–	0.02	–
Fe	0.14	4.86	–	<0.002	–
Gd	<0.47	<0.47	–	<0.03	–
K	6035	34400	5.7	NM	–
La	0.42	0.53	–	0.01	–
Li	1.35	3.92	–	<0.03	–
Mg	<0.11	<0.11	–	<0.02	–
Mn	<0.02	<0.02	–	<0.001	–
Mo	9.81	53.2	5.4	<0.06	> 164
Na	48900	175000	3.6	0.28	176000
Na (M)	2.13	7.61	3.6	0.000012	176000
Ni	1.30	3.52	–	<0.02	–
P	47.8	225	4.7	<0.08	>630
Pb	<0.67	9.53	–	<0.04	–
S	217	928	4.3	0.16	1400
Sb	11.9	50.8	4.3	<0.42	> 28
Si	71.8	233	3.2	1.31	22
Sn	22.2	96.3	4.3	0.07	317
Sr	1.35	0.02	–	<0.001	–
Ti	<0.15	0.53	–	<0.008	–
U	5.47	8.31	–	0.26	–
V	NM	7.05	–	0.009	–
Zn	34.2	291	8.5	0.005	6840
Zr	<0.46	2.01	–	<0.03	–

NM = Not Measured

Table 7. More Products of Evaporation of 35:65 Blend

IC Anions				
	Feed mg/L	**Concentrate mg/L**	**CF**	**Condensate mg/L**
Chloride	1840	10900	5.9	<2
Fluoride	744	272	0.4	<2
Formate	323	2400	7.4	<10
Nitrate	25000	169000	6.8	<10
Nitrite	16150	104400	6.5	<10
Oxalate	86	185	2.2	<10
Phosphate	96	250	2.6	<10
Sulfate	400	1405	3.5	<5
	Mol/L	**Mol/L**		**Mol/L**
Total Base	0.888	4.16	4.7	0.056
Free OH	0.58	2.73	4.7	0.053
Other Base	0.15	1.18	7.6	<0.02

3.4 SOLIDS

The solids found in AW-101/SBS A2 concentrate were identified by XRD. Four filter cake samples from different blend ratios and concentrations were analyzed. The solids found in all four samples, in order of decreasing concentration, were: SiO_2 (quartz), NaF, $NaNO_3$, K_2NaAlF_6, $Na_2CO_3•H_2O$, Fe_2O_3, and $ZrSiO_4$. In addition, CaF_2, $Na_2Ca(CO_3)_2•2H_2O$, and PuO_2 were each detected at trace levels in two samples. Since mass spectrometry showed very low levels of plutonium in feed and concentrate solutions, the detection of PuO_2 is likely due to cross-contamination during laboratory handling.

Table 8 and Table 9 contain data for the weight percent solids, specific gravity, and sodium concentration of the feed and a range of concentrate samples. The data follows expected trends, except the insoluble solids values for 5.1 M and 8.7 M Na concentrate. In these cases, the samples may not have been representative of the well-mixed concentrate. More likely, the low values are due to analytical variability because weight percent insoluble solids is determined by the difference of two large numbers – wt. % total solids and wt. % solids in filtrate. Nevertheless, as shown in Figure 7, the data for the 35:65 blend indicates that precipitation begins between 8.7 and 10.4 M Na.

Table 8. Solids and Sodium Concentrations during Evaporation of 35:65 Blend

	Feed	Concentrate					
				Target			Sat'd
Na, M	2.13*	5.13	7.39	7.61*	8.74	10.0	11.0
Specific Gravity	1.08*	NM	NM	1.38*	NM	NM	NM
Insoluble Solids, wt%	0.39	0.12	0.92	1.25*	0.7	4.4*	10.4
Total Solids, wt%	11.8*	31.4	42.2	43.5*	49.4	54.5*	59.3

*Average of two samples. NM = Not measured

Table 9. Solids and Sodium Concentrations during Evaporation of 45:55 Blend

	Feed	Concentrate			Condensate
			Target	Sat'd	
Na, M	2.20	5.09	6.96	10.4	<0.0002
Specific Gravity	1.10	NM	1.36	1.57	0.993
Insoluble Solids, wt.%	0.20	0.36	0.67	5.73	None visible
Total Solids, wt.%	15.7	36.8	47.2	58.8	0.20

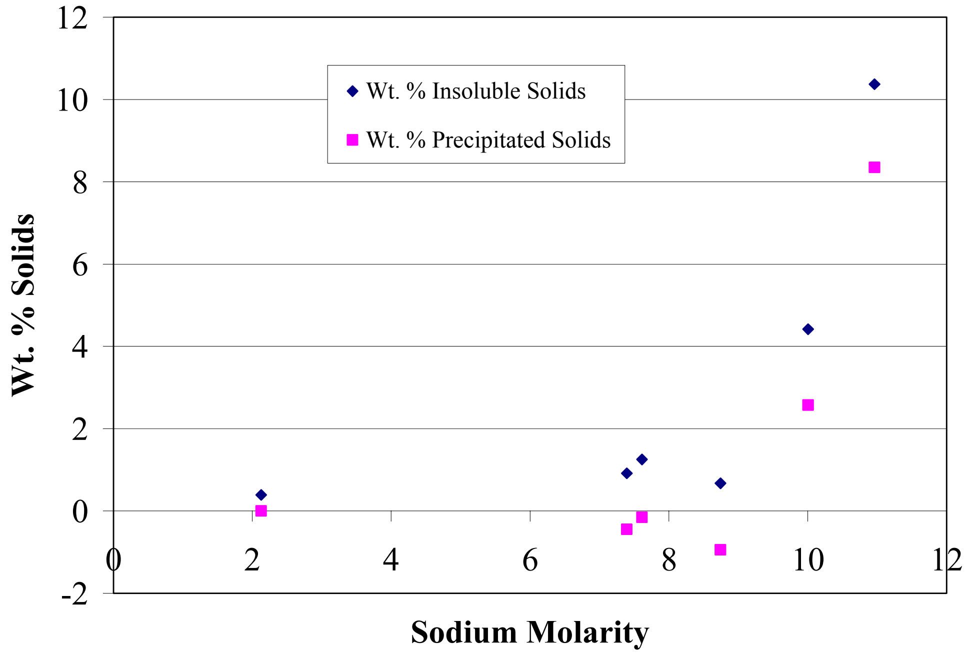


Figure 7. Wt. % Total and Insoluble Solids for 35:65 Blend of AW-101/SBS A2

3.5 RHEOLOGY

The rheology was measured with a Haake RV20/M5 rheometer. An MV1 concentric cylinder geometry head was used for the measurement, due to solids in the feed material. Prior to analyzing the sample, the MV1 bob was inspected for damage, and installed onto the rheometer after passing the visual inspection. A flow curve program reflecting the requirements in the RPP-WTP physical and rheological procedure was used. Per RPP-WTP requirements, the rheometer functionality must be checked using a NIST-traceable Newtonian oil standard and the measured viscosity must be within +/-10% of the standard. A N35 oil standard was used and the resulting viscosity was within the stated requirements.

The two AW-101 concentrated samples were analyzed at 25°C, in duplicate. Both samples behaved liked Newtonian fluids and a representative flow curve can be seen in Figure 8. No settling issues were observed in the flow curve measurements. The average viscosities of the samples are listed below:

45:55 Blend of AW101/SBS A2 at 7.0M Na = 7.1 cP (or mPa-sec)
35:65 Blend of AW101/SBS A2 at 7.6M Na = 8.7 cP (or mPa-sec)

For twelve different Envelope A simulants[1], the measured viscosity at 7M Na had a median value of 3.5 cP and a high of 6 cP. The AW101/SBS A2 value of 7.1 cP is twice as large as the median simulant value. Similarly, at 7.6M Na, the simulant viscosity median was about 4.3 cP. The AW101/SBS A2 value of 8.7 cP is twice as large. The reason for higher viscosities in the real waste material is not clear. Determining the cause for these differences is outside the scope of this task. However, total organic carbon (TOC) levels may have contributed to higher viscosity values. The 45:55 blend, for example, had 2400 mg TOC/L. It is important to note that the viscosities of concentrated AW-101 solutions in this study, as well as those of the simulants in the earlier study, all fall well within the expected range of 0.4 to 15 cP, the current bounding conditions for the WTP.[6]

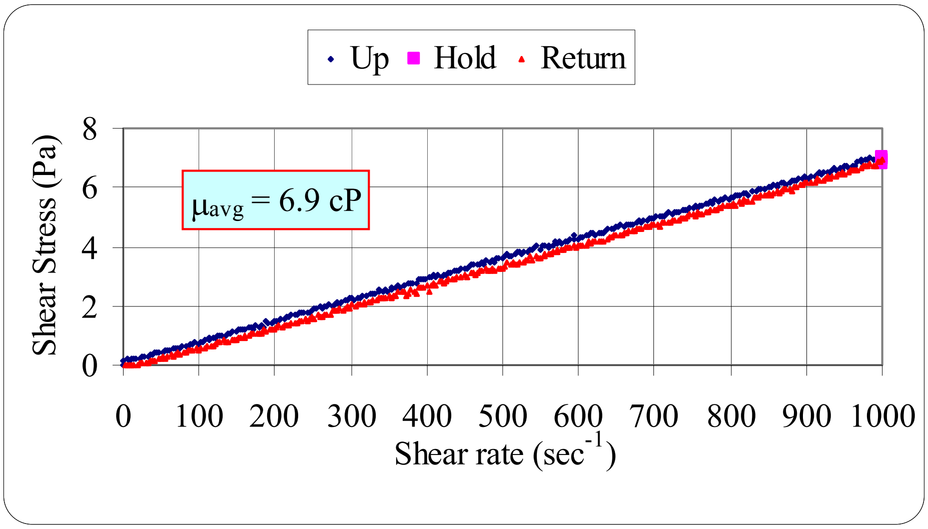


Figure 8. Flow Curve for 45:55 Blend of AW-101 to SBS A2 at 7 M sodium

3.6 HEAT CAPACITY

Heat capacity of concentrates was measured with an Instrument Specialist, Inc. DSC 500 with an indium reference. Both water and sapphire (Al_2O_3 – aluminum oxide) standards were tested to ensure equipment accuracy. The instrument is a Differential Scanning Calorimeter operated according to the applicable ASTM Standard[9]. Reported results are the average of two samples and represent the heat capacity at 50°C. For Blend 1, the concentrate supernate and slurry values were 0.78 and 0.81 cal/g °C, respectively (i.e., 3.3 and 3.4 J/g °C). For Blend 2, the supernate and slurry values were 0.79 and 0.76 cal/g °C, respectively (i.e., 3.3 and 3.2 J/g °C). In both cases, the presence of insoluble solids had no significant effect on heat capacity.

Heat capacities for AW-101/SBS A2 concentrates are similar to that of the as-received AN-107 sample (9.0 M Na, 49.5 wt.% total solids, 0.48% insoluble solids), which had a heat capacity of 0.82 J/g°C[10]. However, the heat capacities observed for Envelope A simulants were consistently 0.6 cal/g°C (or slightly less) for both 6M and 8M Na concentrates.

4.0 CONCLUSIONS

Blended solutions of pretreated Hanford Tank 241-AW-101 and simulated SBS A2 recycle boiled at expected RPP-WTP flowsheet conditions: 60 mm Hg and 50°C. As expected, boiling point increased with concentration. Specifically, the 35:65 blend of AW-101 to SBS A2 at 7.5 M sodium had boiling points of 53°C at 60 mm Hg and 59°C at 80 mm Hg. These were 6-7°C higher than those estimated by an OLI model.

Precipitation of solids in the AW-101/SBS A2 matrix began between 8.7 M and 10.4 M sodium. No problematic or excessive solids were observed. Therefore, SBS recycles are not expected to have any adverse effect on the evaporation process in the RPP-WTP.

In general, foaming did not occur. However, foaming was observed during post-saturation boiling of the 45:55 blend of AW-101 and SBS A2. (The post-saturation concentrate included 10.4 M Na, 59 wt.% total solids, and 5.7 wt.% suspended solids.) Foaming was not observed for the 35:65 blend, even after saturation (i.e., 11.0 M Na, 10.4 wt.% suspended solids, and 59 wt.% total solids).

The target concentrates of AW-101/SBS A2 (i.e., 7 M Na for the 45:55 blend and 7.6 M Na for the 35:55 blend) had the following physical properties: viscosity (7-9 cP), heat capacity (0.8 cal g°C), and specific gravity (1.36-1.38). These values are all higher than those observed for Envelope A simulants.[1]

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5.0 FUTURE WORK

Future evaporation studies with Hanford samples will include vapor fluxes closer to design conditions. For the evaporation of AN104, a heating coil was added inside the evaporator that will yield a vapor flux rate that is 20% of the maximum design value. This five-fold increase should allow a more complete answer on the occurrence of foaming and effectiveness of antifoam treatments.

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APPENDIX A. METALS DATA

Table A- 1. Metals in Feed and Condensate for 35:65 Blend of AW-101/SBS A2

	Feed (35:65 Blend)			**Condensate**		
Sample#	**193464**	**193465**	**Avg.**	**193466**	**193467**	**Avg.**
Analyte	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Ag	<0.160	<0.160	<0.160	<0.009	<0.009	<0.009
Al	4140	4060	4100	0.1	0.056	0.078
B	522	530	526	0.1	0.141	0.143
Ba	<0.380	<0.380	<0.380	<0.021	<0.021	<0.021
Ca	5.15	5.23	5.19	<0.025	<0.025	<0.025
Cd	<0.084	<0.084	<0.084	<0.005	<0.005	<0.005
Ce	2.25	2.56	2.41	0.139	<0.030	0.085
Cr	39.7	40.1	39.9	<0.007	<0.007	<0.007
Cu	0.529	0.54	0.535	0.018	0.014	0.016
Fe	0.136	0.14	0.138	<0.002	<0.002	<0.002
Gd	<0.468	<0.468	<0.468	<0.026	<0.026	<0.026
K	5990	6080	6035	NM	NM	NM
La	0.383	0.456	0.420	0.013	<0.008	0.010
Li	1.26	1.44	1.35	<0.047	<0.002	<0.002
Mg	<0.106	<0.106	<0.106	<0.006	<0.026	<0.026
Mn	<0.016	<0.016	<0.016	<0.001	<0.001	<0.001
Mo	10.3	9.32	9.81	<0.058	<0.058	<0.058
Na	51400	46400	48900	0.341	0.214	0.278
Ni	1.27	1.33	1.30	<0.015	<0.015	<0.015
P	47.5	48.1	47.800	<0.076	<0.076	<0.076
Pb	0.703	<0.638	<0.671	<0.035	<0.035	<0.035
S	216	218	217	0.2	<0.151	0.155
Sb	11.8	12	11.9	<0.416	<0.416	<0.416
Si	71.4	72.2	71.8	1.4	1.24	1.305
Sn	21.1	23.3	22.2	0.1	<0.050	0.1
Sr	1.35	1.35	1.35	<0.001	<0.001	<0.001
Ti	<0.154	<0.154	<0.154	<0.008	<0.008	<0.008
U	5.46	5.47	5.47	0.3	<0.250	0.257
V	NM	NM	NM	0.0	0.008	0.009
Zn	34.1	34.2	34.2	0.0	<0.004	0.005
Zr	<0.456	<0.456	<0.456	<0.025	<0.025	<0.025

Table A- 2. Metals in Concentrate Solutions from 35:65 Blend of AW-101/SBS A2

	Conc. 5M Na	**Conc. 7M Na**	**Concentrate**			**Conc. 9M Na**	**Conc. 10M**	**Conc. Sat'd**
Sample#	**193472**	**193475**	**193470**	**193471**	**Avg.**	**193473**	**193474**	**193476**
Analyte	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Ag	<0.160	<0.160	0.175	0.243	0.21	0.34	0.198	0.514
Al	15000	28800	26600	28100	27350	19700	23400	27400
B	1620	2080	2200	2400	2300	2590	2880	3840
Ba	<0.380	<0.380	0.387	<0.380	0.383	0.459	0.506	0.848
Ca	6.92	7.65	11.5	12.3	11.9	11	16.2	6.78
Cd	0.564	1.07	1.25	1.28	1.27	1.48	1.29	1.24
Ce	1.76	<0.540	3.28	3.83	3.56	5.1	3.76	7.27
Cr	121	154	166	165	165.5	184	201	235
Cu	1.88	2.91	1.35	1.48	1.42	2.99	3.32	3.81
Fe	8.59	22.7	4.95	4.76	4.86	22	13.3	11.8
Gd	<0.468	<0.468	<0.468	<0.468	<0.468	0.606	<0.468	0.888
K	25400	41100	33000	35800	34400	39400	46000	49000
La	0.173	<0.144	0.481	0.57	0.53	0.813	0.601	1.14
Li	2.71	2.52	3.43	4.4	3.92	4.59	4.87	8.09
Mg	<0.106	<0.106	<0.106	<0.106	<0.106	<0.106	0.15	<0.106
Mn	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016
Mo	37.1	49.6	54.3	52	53.2	52	63.7	67.4
Na	118000	170000	174000	176000	175000	201000	230000	252000
Ni	4.05	3.05	3.42	3.62	3.52	4.52	4.48	4.79
P	151	215	227	223	225	204	298	328
Pb	12.4	23.4	10.8	8.26	9.53	32.9	38.4	54.7
S	665	914	915	940	928	501	489	517
Sb	35.5	46.5	50.8	50.8	50.8	56.4	67.7	81.9
Si	311	293	226	239	233	220	247	291
Sn	61.6	88.7	98.2	94.3	96.3	100	116	129
Sr	<0.020	<0.020	0.026	<0.020	0.023	3.56	4.33	2.97
Ti	0.369	1.1	0.527	0.528	0.53	1.39	2.01	1.62
U	6.54	<4.54	6.99	9.62	8.31	11.7	9.49	19.9
V	4.65	6.91	7.02	7.08	7.05	NM	NM	NM
Zn	148	249	279	303	291	339	388	528
Zr	1.1	4.24	1.98	2.03	2.01	5.47	7.7	9.58