PNWD-3248
WTP-RPT-057, Rev 0

AP-101 Diluted Feed (Envelope A) Simulant Development Report

R. L. Russell
S.K. Fiskum
L.K. Jagoda
A.P. Poloski

February 2003

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Test specification: TSP-W375-01-00020
Test plan: TP-RPP-WTP-078, Rev. 0
Test exceptions: 24590-WTP-TEF-RT-02-028
24590-WTP-TEF-RT-02-029
R&T focus area: Pretreatment
Test Scoping Statement(s): B-29a

Battelle, Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by TSP-W375-01-00020 and TP-RPP-WTP-078, Rev. 0. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager *WTP R&T Support Project*	*Date*

G. Todd Wright, Manager *Research and Technology*	*Date*

Summary

The U.S. Department of Energy (DOE) is tasked with the disposition of high-level radioactive waste stored at the Hanford site. The waste is to be vitrified following specific pretreatment processing, separating the waste into a small-volume high-level waste (HLW) fraction and a large-volume low-activity waste (LAW) fraction in the Waste Treatment Plant (WTP). The River Protection Project-Waste Treatment Plant (RPP-WTP) requires the use of non-radioactive tank waste simulants for process verification, waste form qualification tests, and plant cold commissioning. The RPP-WTP Research and Technology schedule [WTP Request for Proposal reference Standard 2 item (a)(3)(ii)] identifies testing and validating the capability of LAW pretreatment processes for removing entrained solids, ^{137}Cs, ^{99}Tc, ^{90}Sr, and transuranic (TRU) elements, to meet immobilized LAW product requirements. Activities shall address the ability to meet contract requirements, operating requirements, plant throughput requirements, and information for regulatory permits and the authorization basis. The Tank 241-AP-101 (AP-101) simulant will be used for conducting Cs and Tc ion exchange process verification testing.

Battelle, Pacific Northwest Division (PNWD) was contracted to develop AP-101 supernatant simulant under Contract 24590-101-TSA-W000-0004. The AP-101 simulant development is further defined in Technical Scoping Statement B-29a, which is included in Appendix C of the *Research and Technology Plan*[1].

Objectives

The objective of this testing was to develop a procedure for preparing a simulant to mimic the chemical and physical properties of the AP-101 supernatant fraction. There were no entrained solids in this waste. This objective was demonstrated by preparing a 10-L batch of AP-101 simulant. The simulant metals and anionic constituents' concentrations were to agree with actual AP-101 waste concentrations within ±10%, or within analytical error of the method as determined by inductively coupled plasma atomic emission spectrometry (ICPAES) and inorganic ion chromatography (IC). The simulant 10-L batch prepared for this task met all the specified criteria with the following exceptions: Cr was 20% low, oxalate was 44% low, total organic carbon (TOC) was 21% low, and the added Si and Cu were not detected.

Conduct of Test

A simulant recipe was formulated based on the actual tank waste analyses of undiluted AP-101 process feed, diluted AP-101 Cs ion exchange feed, Cs ion exchange effluent, and Tc ion exchange effluent. Three small trial batches of simulant were prepared incorporating incremental improvements to the formulation. A large 10-L simulant batch was prepared, again incorporating incremental improvements to the formulation. The concentrations of the metals and anionic constituents were measured by ICPAES and IC in each trial simulant. Viscosity was determined as a function of temperature for the final 10-L batch.

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[1] S. Barnes, R. Roosa, and R. Peterson. 2002. "Research and Technology Plan," 24590-WTP-PL-RT-01-002, Rev. 1, RPP-WTP project.

Results and Performance Against Objectives

Most major (>0.1 M) and minor (<0.1 M to >0.01 M) cationic and anionic component (Al, K, Na, OH^-, NO_2^-, NO_3^-, PO_4^{3-}[measured as P by ICPAES], Cl^-, and SO_4^{2-}) concentrations met the success criteria of matching the actual AP-101 waste composition within the error (±15%) of the analytical methods. However, oxalate, TOC, and Cr were slightly low, while Si and Cu were not recovered. Trace-element-component compositions were within a factor of three of the actual AP-101 waste composition. The simulant density (1.256 g/mL) matched the actual AP-101 waste density (1.256 g/mL). The total undissolved solids remained constant over a 3-week period at 0.28 wt%. Over a 3-week aging period, the simulant composition was essentially unchanged, except for the NO_2^- concentration. The NO_2^- concentration appeared to have increased 10%, while the corresponding NO_3^- concentration appeared to have decreased 3%, potentially indicating that the simulant solution is reducing. However, both of these changes were within the uncertainty of the analysis method (±15%). Relative recoveries of the major and minor metal and anionic constituents are summarized in Figures S1 and S2, respectively.

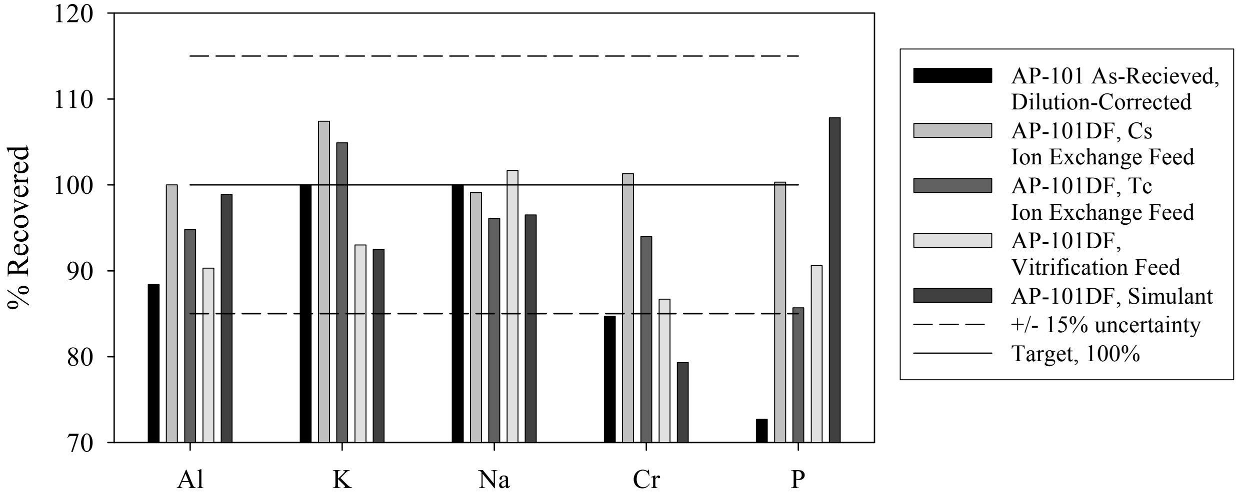

Figure S1. Relative Metal Recoveries of Actual AP-101 Diluted Feed (DF) Tank Waste and AP-101 Diluted Feed Simulant Relative to Targeted Simulant Composition

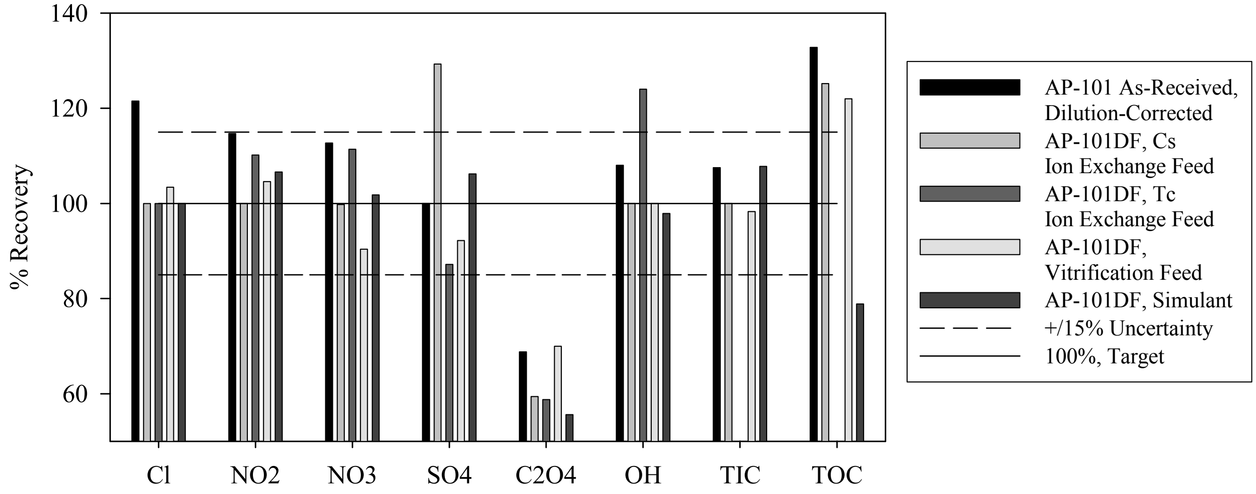

Figure S2. Relative Anionic Recoveries of Actual AP-101 Diluted Feed Tank Waste and AP-101 Diluted Feed Simulant Relative to Targeted Simulant Composition

The simulant viscosity exhibited Newtonian behavior and compared well with the actual AP-101 diluted feed viscosity. The average viscosity results are summarized in Table S1.

Table S1. Viscosity of AP-101 Simulant and AP-101 Diluted Feed

	25°C cP	**40°C cP**	**60°C cP**
AP-101 Simulant (4.80 M Na)	3.5	2.5	1.8
AP-101 Diluted Feed Actual Waste (4.96 M Na)	3.4	2.5	1.8

Quality Requirements

PNWD implemented the RPP-WTP quality requirements in a quality assurance project plan (QAPjP) as approved by the RPP-WTP quality assurance (QA) organization. The first simulant preparation (weighing, mixing, observations, and acid digestion) and analytical analyses including x-ray diffraction XRD were conducted in accordance with PNWD's quality assurance project plan, CHG-QAPjP, Rev.0, which invoked PNWD's Standards Based Management System (SBMS), compliant with DOE Order 414.1a Quality Assurance and 10 CFR 830.120, Energy/Nuclear Safety Management/Quality Assurance Requirements. Due to a change in the contract QA requirements, the remainder of the simulant preparations and analytical activities were conducted in accordance with PNWD's quality assurance project plan, RPP-WTP-QAPjP, Rev.0, which invoked NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Part 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description (WTPSP) Manual.

PNWD addressed verification activities by conducting an Independent Technical Review of the final data report in accordance with procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and the reported work satisfied the Test Plan objectives. The review procedure is part of PNWD's WTPSP Manual.

Issues

The organic composition of the AP-101 diluted feed is not well characterized. Current analysis activities of the actual waste Tc ion exchange effluent will determine the chelator concentrations. Adding these organics to the AP-101 simulant recipe is not anticipated to negatively impact the composition and stability of the simulant because their relative concentrations are low (440 mg C/L). Rheological properties are more sensitive to changes in organic composition and may be affected. The incomplete organic content may explain why some of the potentially complexing cations are at different concentrations than the original additions. While, the TOC difference may not affect results for major constituents, it may have an effect on the behavior of minor and/or trace constituents. The appropriate use of this simulant should consider this phenomenon.

The F^- concentration in the actual AP-101 feed is not well characterized. All F^- analyses were based on inorganic IC where positive interferences were obtained from acetate and formate.

Acronyms

ASR	Analytical Services Request
BS	blank spike
cP	centipoise
DF	diluted feed
DIW	de-ionized water
DOE	U.S. Department of Energy
EQL	estimated quantitation limit
HB	high blank
HLW	high-level waste
IC	ion chromatography
ICPAES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
IDL	instrument detection limit
LAW	low-activity waste
LCS	laboratory control sample
MDL	method detection limit
MS	matrix spike
N-cm	Newton-centimeter
NA	not applicable
NM	not measured
PB	process blank
PNWD	Battelle, Pacific Northwest Division
QA	quality assurance
QAPjP	Quality Assurance Project Plan
QC	quality control
RPD	relative percent difference
rpm	revolutions per minute
RPP-WTP	River Protection Project-Waste Treatment Plant
SBMS	Standards Based Management System
TC	total carbon
TFCOUP	Tank Farm Contractor Operation and Utilization Plan
TIC	total inorganic carbon (specifically carbonate)
TOC	total organic carbon

TP	test plan
TRU	transuranic
UDS	undissolved solids
WTP	Waste Treatment Plant
WTPSP	Waste Treatment Plant Support Project
XRD	x-ray diffraction

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1.0 Introduction

The U.S. Department of Energy (DOE) plans to vitrify tank wastes at the Hanford Site in preparation for permanent disposal. Before vitrification, tank wastes will be divided into low-activity waste (LAW) and high-level waste (HLW) fractions through specific pretreatment processes. The separation into the different waste fractions will be conducted in the Waste Treatment Plant (WTP) using Sr/transuranic (TRU) precipitation, Cs ion exchange, and Tc ion exchange. The products from these processes will be vitrified into a waste glass. Before processing actual tank waste in the plant, various processes will need to be further investigated using less expensive and less hazardous simulants. Also, before the plant can receive actual tank waste, the plant will be commissioned by demonstrating performance using non-radioactive simulants. One of the first wastes to be submitted to the WTP is expected to be from Tank 241-AP-101 (AP-101).

This report summarizes AP-101 simulant recipe development and simulant analysis and testing performed in accordance with test specification TSP-W375-01-00020[1] and Test Plan TP-RPP-WTP-078, Rev. 0.[2] Three small-scale trial batches and one large-scale batch were prepared incorporating optimizations for each batch. The simulant preparations were analyzed for metals by inductively coupled plasma atomic emission spectrometry (ICPAES) and inorganic anions and oxalate by ion chromatography (IC). Physical testing included density and viscosity determination on the final product.

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[1] ME Johnson. 2001. *Test Specification for Preparation of AP-101 Simulant Solution*. CH2M HILL Hanford Group, Inc., Richland, Washington.

[2] NN Bridges. 2001. *Preparation of AP-101 Simulant Solution*. TP-RPP-WTP-078, Rev. 0, Battelle Northwest Division, Richland, Washington.

2.0 Objectives

The objectives of this testing were to prepare AP-101 supernatant simulant mimicking the chemical and physical properties of the actual AP-101 supernatant and to assure that the AP-101 simulant is representative of the actual AP-101 tank waste, which did not contain any entrained solids. The simulant is intended to support Cs and Tc ion exchange pretreatment studies.

2.1 Composition

The simulant composition was to match major, minor, and trace constituents of actual AP-101 waste diluted to 5 M Na. Of specific concern were the constituents that affect ion exchange processing parameters and include Na, Cs, OH^-, NO_3^-, and K concentrations. Solution density and viscosity were also identified as process-affecting (Townson, 2001). Key simulant properties for ion exchange are summarized in Table 2.1.[1]

Table 2.1. Key Properties for Ion Exchange Pretreatment Simulant

Property	Cs Ion Exchange	Tc Ion Exchange
Chemical	Na, Cs, K and others[(a)], pH	NO_2^-, NO_3^-, OH^-, total ionic strength
Physical	density, viscosity	density, viscosity
Rheological	viscosity	viscosity
(a) Other characteristics were not defined.		

2.2 Verification and Validation

Verifying simulants includes determining chemical composition, physical properties, and rheological properties in comparison with actual waste (Townson 2001 and Smith 2002). The simulant chemical composition was evaluated from two independent measurements (freshly prepared simulant and 3-week aged simulant) relative to four independent analyses of actual AP-101 tank waste diluted feed. Major, minor, and trace analyte compositions in the simulant were to match the actual waste composition to within ±10% or within the analytical uncertainty of the analysis method. Physical-property testing specifically included density, again in comparison to actual AP-101 tank waste diluted feed. The rheological properties were tested similarly to the AP-101 diluted-feed tank waste that was processed through the small-scale pretreatment unit operations (Cs and Tc ion exchange).[2]

Simulant validation is confirmed when simulant process behavior is shown to adequately mimic actual waste process behavior (Smith 2002). The simulant Cs and Tc ion exchange performances will be evaluated relative to the actual AP-101 tank waste diluted feed in future work.[3]

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[1] Properties were taken from Townson 2001.

[2] The rheological properties were not tested on the actual AP-101 waste Cs ion exchange feed.

[3] The process performance testing is scheduled to begin in November 2002 under Technical Scoping Statements B-42 and B-43.

3.0 AP-101 Composition

This section describes the basis for the AP-101 diluted feed composition as well as the considerations in the simulant formulation.

3.1 Basis for AP-101 Diluted Feed Composition

Undiluted AP-101 supernatant tank waste (containing no entrained solids) was characterized in 2000 (Fiskum et al. 2000). Additional tank waste was received in 2001 for process testing, including Cs ion exchange, Tc ion exchange, and LAW vitrification. The AP-101 waste was diluted from nominally 5.6 M Na to nominally 5.0 M Na and characterized (Goheen et al. 2002). This diluted AP-101 waste was processed through Cs ion exchange (Fiskum et al. 2002) and then through Tc ion exchange (Burgeson et al. 2002). The AP-101 feed and effluents from both ion exchange operations were characterized. Thus, four independent AP-101 measurements, before, during, and after pretreatment, were used to support the AP-101 simulant development. These results are summarized in Table 3.1. The original undiluted AP-101 analysis is shown with correction for dilution to 5 M Na. The concentrations of the major and minor constituents were fairly constant for the three independent measurements from the pretreatment unit operations. The concentrations did not change significantly because the sample was not mixed with other process solutions during testing, and the ion exchange processes were fairly selective for the targeted components. However, the ion exchange did impact some trace components (U was removed). The anionic concentrations for the undiluted AP-101 sample (correcting for dilution) were generally higher than the other three determinations. This analysis also resulted in a net anionic charge 9% higher than the net cationic charge, indicating that the cationic concentrations were either too low and/or the anionic concentrations were too high. The AP-101 diluted feed for Cs ion exchange measurement achieved good charge balance with a difference of only 1%.

The cationic and anionic charges need to balance in the actual simulant. Based on the analytical results, there will probably be some charge discrepancy because of analytical error. Other reasons for the charges not balancing are that the ionic species in the solution are not correctly predicted or that some minor components have been ignored. Because of these charge discrepancies, some adjustments must be made to the predicted composition by modifying the composition of the components that are not expected to be important in the simulant applications. The AP-101 diluted feed Na concentration is an important factor for vitrification testing; thus Na concentration was not compromised to establish charge balance. The OH^- and alkali metals (e.g., K) concentrations were shown to affect Cs ion exchange. The OH^- and NO_3^- concentrations have been shown to affect Tc ion exchange. Thus the OH^-, K, and NO_3^- concentrations in the simulant had to closely mimic that of the actual waste. Therefore, every effort was made to assure that these constituents were kept at the actual feed-measured levels and were not compromised in simulant formulation. Additionally the NO_2^-, NO_3^-, and CO_3^{-2} concentrations found for the Cs ion exchange feed were targeted in the simulant composition because the corresponding concentrations derived from the original AP-101 analysis appeared too high based on the charge balance, and based on comparison to subsequent analysis results.

Table 3.1. AP-101 Actual Waste Composition

Element	AP-101 Dilution-corrected$^{(a)}$ mg/L	AP-101DF Cs IX diluted feed mg/L	AP-101DF Tc IX diluted feed mg/L	AP-101DF Tc IX effluent $^{(b)}$ mg/L
ICP-AES Analytes				
Al	6170	6980	6620	6305
B	14.2 HB	[55] HB	210 HB	84.2 HB
Ba	[0.29]	<1	<1.3	[0.33]
Be	1.17$^{(c)}$	<2	<1.3	[0.91]
Ca	[6.8]	[210]	<31	[12]
Cd	[1.7]	<2	<2	2.1 HB
Co	0.31$^{(c)}$	<7	<7	<2
Cr	127	152	141	130
Cs (total)	6.0^{c}	4.89$^{(c)}$	(removed)	(removed)
Cu	[1.4] HB	<4	<3	<0.7
Fe	[2.2] HB	[3.8] HB	<3	[1.2]
K	27,740	29,800	29,100	25,800
La	<2	<7	<7	<2
Li	0.30$^{(c)}$	<4	<4	<8
Mg	<2	<14	<13	<3
Mo	12.9$^{(c)}$	[14]	[12]	[12]
Na	115,000	114,000	110,500	117,000
Ni	7.04 HB	[4.4] HB	[5.8] HB	[3.0] HB
P	279	385	329	348
Pb	[13]	<10	<13	[5.8]
Rb	3.53$^{(c)}$	3.9$^{(c)}$	NM	2.58$^{(c)}$
Si	122	[360] HB	[315] HB	380 HB
W	25.4$^{(c)}$	<270	<250	<51
Zn	[4.9]	[8.0]	<6	[4.6]
Inorganic ion chromatography				
F$^{(d)}$	2580	2300	1850	2330
Cl	1762	1450	1450	1500
NO_2	37,280	32,500	35,800	34,000
NO_3	117,400	104,000	116,000	94,200
PO_4	907	<950	690	1210
SO_4	3580	4630	3120	3300
C_2O_4	1100	<950	940	1120
Organic ion chromatography				
Oxalate	1601	NM	NM	NM
Formate	1070	NM	NM	NM
Acetate	1460	NM	NM	NM
Citrate	<890	NM	NM	NM
Titration				
OH	2.1 M	1.94 M	2.40 M	1.94 M
CO_3	NM	0.56 M	0.51 M	0.50 M

Table 3.1 (Contd)

Element	AP-101 Dilution-corrected[(a)] mg/L	AP-101DF Cs IX diluted feed mg/L	AP-101DF Tc IX diluted feed mg/L	AP-101DF Tc IX effluent [(b)] mg/L
Combustion				
TOC-P[(e)]	1740	1640	NM	1630
TOC-F[(e)]	NM	7950	NM	3450
TIC-P[(e)]	5750	5350	NM	5260
TIC-F[(e)]	NM	<170	NM	3450
TC-P[(e)]	7490	6990	NM	6860
TC-F[(e)]	7660	7950	NM	6900
Density g/mL	1.256	1.256	1.257	1.258

(a) AP-101 characterization on undiluted tank waste corrected for dilution to 5 M Na.
(b) Also LAW vitrification feed.
(c) Analysis result based on inductively coupled plasma-mass spectrometry (ICP-MS).
(d) Fluoride results should be considered the upper-bound concentration. Significant peak distortion of the F peak suggests the presence of co-eluting anion(s), possibly formate or acetate.
(e) For TOC and TIC: P = by hot persulfate method; F = by furnace method/TIC by difference (TIC = TC-TOC); units are in mg C/L.
High blank (HB) indicates that a high preparative blank resulted in batch preparation and also indicates that the sample concentration may be biased high.
Bracketed results indicate that the result was within 10 times the instrument detection limit, and errors are likely to exceed ±15% 2-σ.
NM = not measured; DF = diluted feed

The PO_4^{-3} results by IC ranged from 690 μg/mL to 1210 μg/mL (0.0073 M to 0.0127 M). The scatter was in part attributed to the low PO_4^{-3} concentration and the large dilutions required for IC analysis of this matrix. The PO_4^{-3} results were close to the estimated quantitation limit (EQL) for IC. The total P results by ICPAES ranged from 279 to 385 μg/mL (0.0090M to 0.012M), indicating a possible high bias by IC. The PO_4^{-3} molarity was set equal to the total P molarity as determined by ICPAES.

The F^- is co-eluted from the IC system with acetate and formate. Thus, the reported F^- peak was biased high and should be considered an upper bound. If the detection sensitivity was comparable for acetate, formate, and fluoride, then a gross F^- concentration could be estimated by subtracting the formate and acetate component concentrations from the F^- concentration. The F^- concentration was then estimated to be present at 53 μg/mL (0.0028 M).

Oxalate was measured by two different techniques. The organic IC method resulted in an average concentration of 1,600 μg/mL (dilution-corrected). The inorganic IC method resulted in significantly lower oxalate concentrations of nominally 1050 μg/mL. The higher oxalate concentration was conservatively targeted for the simulant composition in an effort to better complex the metals in solution.

The TOC in the AP-101 diluted feed was uncertain. The hot persulfate analytical method for TOC resulted in 1640 μg C/mL in the actual diluted AP-101 feed. The furnace analytical method was not considered reliable for TOC and total inorganic carbon (TIC); however, the total carbon (TC) results agreed with that of the hot-persulfate analytical method. Only four organic anions (acetate, oxalate, formate, and citrate) were measured in this waste, and citrate was below the instrument detection limit

(IDL). The TOC sum of these analytes resulted in 1320 µg C/mL. Thus, only approximately 75% to 80% of the organics in the actual AP-101 diluted feed had been identified and/or quantified.[1]

3.2 AP-101 Diluted Feed Simulant Composition

All radioactive components were deleted from the simulant composition. Radioactive Cs was replaced with non-radioactive Cs and added at the total Cs concentration. Subsequent testing through Cs ion exchange will require analysis by ICP-MS for ^{133}Cs or addition of ^{137}Cs tracer for GEA analysis. Subsequent testing through Tc ion exchange will require addition of pertechnetate (radioactive test) or perrhenate (non-radioactive test). Trace components As, Co, Sb, Tl, and Zn were not added to the simulant since they were present in small quantities in the actual waste and were not vital to the pretreatment testing to be performed with this simulant. No appropriate surrogate for U was identified; U was present in the actual waste at nominally 45 µg/mL.[2]

Thus, the 10-L batch AP-101 simulant composition was targeted to contain the metals and anions as shown in Table 3.2. This was based largely on the detailed, original AP-101 analysis corrected for dilution and with specific analytes (Al, Cl^-, Cr, NO_3^-, and NO_2^-) amended to the as-found concentration in the Cs ion exchange feed analysis, obtaining charge balance.

The major anionic and cationic complexes of the targeted AP-101 simulant composition are shown in Table 3.3, not taking into account the minor constituents. In some cases (such as AlO_2^-), the chemical form is assumed and is based on generally known aqueous chemistry. The cationic and anionic charges are well balanced.

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[1] Current analysis activities for AP-101 Tc ion exchange effluent includes organic speciation for organic anions (including citrate, formate, acetate, oxalate, glycolate) and chelators.

[2] U has been shown to exchange onto SL-644 (Fiskum et al. 2002).

Table 3.2. Targeted 10-L Batch AP-101 Simulant Composition

Element	Targeted mg/L	Targeted M	Element	Targeted mg/L	Targeted M
Metals					
Al	6980	2.59E-1	Li	0.30	4.4 E-5
B	14.2	1.32E-3	Mo	12.9	1.34E-4
Ba	0.29	2.1 E-6	**Na**	**115,000**	**5.00E+0**
Be	1.2	1.3 E-4	Ni	7.0	1.2 E-4
Ca	6.8	1.7E-4	P[a]	384	1.24E-2
Cd	1.7	1.6E-5	Pb	13	6.4 E-5
Cr	150	2.92E-3	Rb	3.5	4.1 E-5
Cs	**5.99**	**4.51E-5**	S[b]	1200	3.73E-2
Cu	1.4	2.2E-5	Si	122	4.34E-3
Fe	2.2	4.0E-5	W	25	1.4 E-4
K	**27,740**	**7.10E-1**	Zn	5.0	7.6 E-5
Anions					
F^-	53	2.8 E-3	PO_4^{3-}	1180	1.24E-2
Cl^-	1450	4.09E-2	SO_4^{2-}	3580	3.73E-2
NO_2^-	32,500	7.07E-1	**OH^-**	**33,000**	**1.94E+0**
NO_3^-	**104,160**	**1.68E+0**	CO_3^{2-}	5350	4.46E-1
Organics					
Formate	1070	2.37E-2	Oxalate	1600	1.78E-2
Acetate	1460	2.47E-2	TOC	1310 mg C/L	1.09 E-1

(a) P added as PO_4^-

(b) S added as SO_4^-

Bolded values indicate components of special concern to successfully duplicating pre-treatment activities.

Table 3.3. Charge Balance for 10-L Batch AP-101 Simulant

Ionic Complex	Targeted M	Molar charge	Ionic Complex	Targeted M	Molar charge
Cations					
Na^+	5.00E+0	+5.00E+0	K^+	7.10E-1	+7.10E-1
Total cationic molar charge			**+5.71**		
Anions					
OH^-	1.94E+0	-1.94E+0	$C_2O_4^{2-}$	1.78E-2	-3.56E-2
NO_3^-	1.68E+0	-1.68E+0	PO_4^{3-}	1.24E-2	-3.72E-2
CO_3^{2-}	4.46E-1	-8.92E-1	Acetate	2.47E-2	-2.47E-2
NO_2^-	7.07E-1	-7.07E-1	Formate	2.37E-2	-2.37E-2
AlO_2^-	2.59E-1	-2.59E-1	CrO_4^{2-}	2.92E-3	-5.84E-3
SO_4^{2-}	3.73E-2	-7.46E-2	F^-	2.81E-3	-2.81E-3
Cl^-	4.09E-2	-4.09E-2	Not Applicable		
Total anionic molar charge			**-5.72**		

3.3 Derivation of AP-101 Formulation

Reagent-grade salts and chemical forms were carefully selected to best mimic the actual waste composition. If this simulant is prepared with lesser grade chemicals, it may need to be verified and validated again. Cost, chemical availability, and ease of scale up were considered in choosing which chemicals to use.

3.3.1 Sodium Hydroxide

The NaOH was obtained and added as a 50-wt % solution. This is readily obtainable from a variety of manufacturers (e.g., Fisher Scientific, JT Baker, Spectrum, etc.) and in a variety of quantities. Adding NaOH as a solution has distinct advantages. Solid NaOH is extremely hygroscopic. Measuring solid NaOH by mass results in a mass biased with an unknown amount of water. This has been found to cause a negative Na concentration bias as much as 20%. The dissolution of solid NaOH generates heat. The heat generated from using NaOH in solution is greatly reduced by virtue of the fact that it is already in solution. However, because the simulant preparation procedure begins with acidic solutions, the dilution and acid neutralization process results in some heat production. Using a NaOH solution is also more practical for large-scale simulant production.

3.3.2 Aluminum Nitrate

The $Al(NO_3)_3$-$9H_2O$ was also obtained and added as a 60-wt% solution. This solution was available from Noah Chemical Corporation and available in a variety of quantities. Adding $Al(NO_3)_3$-$9H_2O$ as a solution has advantages similar to those discussed for NaOH. The $Al(NO_3)_3$-$9H_2O$ is extremely hygroscopic, and storing and measuring the crystals introduces mass uncertainty from adsorbed water. The composition of 60-wt% $Al(NO_3)_3$-$9H_2O$ solution is comparatively stable. The solution is also more practical for large-scale simulant production. In a base solution, Al will form a hydroxy complex as tetrahedral $Al(OH)_4^-$.

3.3.3 General Salts

Most metals (Ba, Cd, Ca, Cs, Cu, Fe, Pb, Li, Ni, Zn, and Rb) were added as nitrate salts. The nitrate salts are easily available and generally very water-soluble. The transition metals usually precipitate as insoluble hydroxides in base solution, and Ca and Ba precipitate as carbonates when carbonate is present. Complexing agents (oxalate, acetate, and formate) in the simulant were used in an attempt to maintain these metals in solution. Most anions (Cl^-, F^-, PO_4^{3-}, SO_4^{2-}, NO_3^-, NO_2^-, OH^-, SiO_3^{2-}, formate, acetate, and oxalate) were added as Na salts. Again, these have high water solubility and serve to boost the Na concentration to 5 M while minimizing the acid H^+ contribution. Molybdenum was added as MoO_3, which is very soluble in base solution as the MoO_4^{2-} tetrahedron. Molybdenum oxyhalides could probably be used successfully, although they were not tested. Tungsten was also added as WO_3 and behaves similarly to MoO_3, forming the tetrahedral WO_4^{2-}. Boron was added as boric acid, H_3BO_3, existing in base solution as $B(OH)_4^-$. Carbonate was added as the Na and K salts.

3.3.4 Addition Order

The organic complexing reagents (sodium acetate and sodium oxalate) were first completely dissolved in a large excess of water. Full dissolution is necessary to maximize availability for subsequent cation metal complexing. All nitrate salts were then added and dissolved in solution. The specific addition order of the nitrate salts is not expected to be critical.

The Na salts of the targeted anionic species were then added to solution assuring that metasilicate (SiO_3^{2-}), CrO_4^{2-}, NO_2^-, and carbonate salts were added after the pH adjustment with NaOH. The carbonate salts were added after the NaOH to avoid carbonate decomposition. The sodium formate was added after the NaOH to prevent any redox reactions from occurring. The acid form of formic acid is a fairly strong reducing agent and can react with nitric acid and other possible oxidizers. The sodium chromate was also added after the NaOH. In acid, the chromate converts to dichromate, which is a very strong oxidizer and can react with acetate, formate, and oxalate. The specific chemical addition order is shown in Table 4.2.

3.3.5 Hazardous Constituents

Hazardous constituents for regulatory purposes include Ag, As, Cd, CN, Cu, Cr, Hg, Ni, Pb, Sb, Se, Tl, V, and selected organic compounds. All of the inorganic hazardous components were measured in AP-101 actual waste (Fiskum et al. 2002). The concentrations of Ag, Hg, Se, and V were below the detection limit of the analytical method. The Cd, Cu, Cr, Ni, and Pb were added to the simulant as indicated by the actual waste analysis. The hazardous constituents As (1.1 mg/L), CN (5.7 mg/L), Sb (0.037 mg/L), and Tl (0.016 mg/L) are not represented in the simulant. The CN and As were specifically excluded from the formulation because of their significant health hazards.[1] The Sb and Tl were excluded because of their extremely low concentration.

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[1] Per TP-RPP-WTP-078, Rev. 0, CN and As were specifically excluded from the formulation because of their significant health hazards.

4.0 Experimental Procedure

This section describes the experimental simulant preparations and incremental changes to the formulation as part of the process of continuous improvement.

4.1 Simulant Trial Batches

Three trial batches of simulant were prepared based on the original sample results from the as-received AP-101 tank waste, corrected for dilution to 5 M Na. The simulant recipe, order of addition, and chemicals used were continually optimized with each batch preparation to better mimic the actual composition of diluted AP-101 process feed. Table 4.1 summarizes the simulant preparations with reagent addition order and mass.

In all cases, water, corresponding to 30% of the final targeted simulant volume, was initially added to a tared plastic bottle. Each reagent was added directly to the water with stirring until completely dissolved. Additional water was added as needed to maintain elements in solution. In all cases, fine white solids formed when NaOH was added. A fraction of insoluble solids remained after bringing the solution to volume.

4.2 10-L Simulant Batch

Following the third trial batch of simulant, a 10-L batch of AP-101 simulant was prepared using a better-optimized composition, as discussed in Section 3.0, using additional data obtained from analyzing the AP-101 actual waste during the unit-operations pretreatment tests. Table 4.2 shows the actual chemical addition order and amounts for the 10-L batch simulant. The simulant was prepared with all of the hydroxide added as 50-wt% NaOH solution and all of the K added as KNO_3 and K_2CO_3. This simulant was prepared in a 10-L carboy with a mechanical mixer to constantly stir the simulant as the chemicals were added. First, the sodium acetate and the sodium oxalate were added to approximately 2 L of de-ionized water (DIW) and allowed to completely dissolve. Then the 60-wt% $Al(NO_3)_3$-$9H_2O$ solution was added along with each of the nitrate salts, boric acid, beryllium oxide, and molybdenum oxide. Each chemical was added and allowed to completely dissolve before the next chemical was added to the simulant.

The sodium salts of the anions were added one at a time and allowed to completely dissolve. Then the 50-wt% NaOH solution was slowly added. Immediately upon adding the 50-wt% NaOH solution, white solids formed, and the simulant turned milky white. As more caustic solution was added and a neutral pH was approached, the simulant began to become increasingly viscous and difficult to stir, probably because of increasing quantities of precipitated $Al(OH)_3$-xH_2O. As the neutral pH point was passed and the simulant became basic, $Al(OH)_3$-xH_2O dissolved, forming $Al(OH)_4^-$, and the simulant became less viscous and stirred well. The neutralization with NaOH addition and caustic dilution was exothermic, causing heating of the entire simulant volume. A fine white precipitate remained in the simulant, however, and never re-dissolved.

Following the caustic addition, WO_3, Na_2SiO_3, Na_2CrO_4, HCOONa, $NaNO_2$, $NaCO_3$, and K_2CO_3 were added to the simulant. The Na_2CrO_4 addition caused the simulant to turn a bright yellow that did not change with time. The color closely emulated the actual AP-101 waste.

Table 4.1. AP-101 Trial Preparations

Trial 1		**Trial 2**		**Trial 3**	
Chemical	**Amount Added (g)**	**Chemical**	**Amount Added (g)**	**Chemical**	**Amount Added (g)**
$NaCH_3CO_2$	2.0290	$NaCH_3CO_2$	1.0148	$NaCH_3CO_2$	1.0142
HCOONa	1.6136	$Na_2C_2O_4$	1.1923	$Na_2C_2O_4$	1.1922
$Na_2C_2O_4$	2.3852	$Al(NO_3)_3\text{-}9H_2O$ (60% soln)	71.54	$Al(NO_3)_3\text{-}9H_2O$ (60% soln)	71.5436
10,044 mg/L Ba(a)	0.0294 mL	10,044 mg/L Ba(a)	0.015 mL	10,044 mg/L Ba(a)	0.015 mL
1006 mg/L Be(a)	1.1495 mL	1006 mg/L Be(a)	0.58 mL	1006 mg/L Be(a)	0.58 mL
$Cd(NO_3)_2\text{-}4H_2O$	0.0049	$Cd(NO_3)_2\text{-}4H_2O$	0.0026	$Cd(NO_3)_2\text{-}4H_2O$	0.0029
$Ca(NO_3)_2\text{-}4H_2O$	0.0406	$Ca(NO_3)_2\text{-}4H_2O$	0.0207	$Ca(NO_3)_2\text{-}4H_2O$	0.0205
$CsNO_3$	0.0091	$CsNO_3$	0.0042	$CsNO_3$	0.0044
$RbNO_3$	0.0064	$RbNO_3$	0.0064	$RbNO_3$	0.0064
10,017 mg/L Cu(a)	0.142 mL	10,017 mg/L Cu(a)	0.071 mL	10,017 mg/L Cu(a)	0.071 mL
$Fe(NO_3)_3\text{-}9H_2O$	0.0164	$Fe(NO_3)_3\text{-}9H_2O$	0.0079	$Fe(NO_3)_3\text{-}9H_2O$	0.0081
$Pb(NO_3)_2$	0.0217	$Pb(NO_3)_2$	0.0109	$Pb(NO_3)_2$	0.0108
$LiNO_3$	0.0033	$LiNO_3$	0.0016	$LiNO_3$	0.0014
$Ni(NO_3)_2\text{-}6H_2O$	0.0351	$Ni(NO_3)_2\text{-}6H_2O$	0.0179	$Ni(NO_3)_2\text{-}6H_2O$	0.0175
$Zn(NO_3)_2\text{-}6H_2O$	0.0228	$Zn(NO_3)_2\text{-}6H_2O$	0.0115	$Zn(NO_3)_2\text{-}6H_2O$	0.0116
H_3BO_3	0.0817	H_3BO_3	0.0408	H_3BO_3	0.0410
MoO_3	0.0196	MoO_3	0.0096	MoO_3	0.0099
$Na_2CrO_4\text{-}4H_2O$	0.5729	NaCl	1.4521	NaCl	1.4523
NaCl	2.9044	NaF	0.0588	NaF	0.0590
NaF	0.1186	$Na_2H_2PO_4\text{-}7H_2O$	1.0470	$Na_2H_2PO_4$	0.5412
$Na_2H_2PO_4\text{-}7H_2O$	2.4187	Na_2SO_4	2.6510	Na_2SO_4	2.6511
Na_2SO_4	5.3017	$NaNO_3$	42.93	$NaNO_3$	42.93
$NaNO_3$	80.0000	KOH	4.4328	KOH (50% soln)	6.0628
KOH	10.0007	KNO_3	9.3531	KNO_3	9.3513
KNO_3	20.0005	NaOH	48.01	NaOH (50% soln)	96.02
NaOH	125.0011	$H_2WO_4\text{-}H_2O$	0.0190	WO_3	0.0162
$H_2WO_4\text{-}H_2O$	0.0372	$Na_2SiO_3\text{-}9H_2O$	0.6169	$Na_2SiO_3\text{-}9H_2O$	0.6167
$Na_2SiO_3\text{-}9H_2O$	1.2335	HCOONa	0.8062	HCOONa	0.8062
$Al(NO_3)_3\text{-}9H_2O$	85.8484	$Na_2CrO_4\text{-}4\ H_2O$	0.2861	Na_2CrO_4	0.1985
$NaNO_2$	55.9162	$NaNO_2$	27.9590	$NaNO_2$	27.9577
Na_2CO_3	28.0007	Na_2CO_3	14.3082	Na_2CO_3	14.31
K_2CO_3	28.0009	K_2CO_3	14.00	K_2CO_3	14.51
Final volume	1-L	Final volume	0.5-L	Final volume	0.5-L
Density	1.277 g/mL	Density	1.26	Density	1.26

(a) Ba, Be, and Cu were added as atomic absorption (AA) standards because the mass of nitrate salts for small-scale batches was too low to measure accurately. The AA standards matrices were 2% HNO_3.

Table 4.2. Chemical Addition Order and Amounts for 10-L Simulant Preparation

Compound Name	Formula	Amount Added (g)
Sodium acetate	$NaCH_3CO_2$	20.29
Sodium oxalate	$Na_2C_2O_4$	23.85
Aluminum nitrate nonahydrate (60% soln)	$Al(NO_3)_3$-$9H_2O$	1617.5
Barium nitrate	$Ba(NO_3)_2$	0.0054
Beryllium oxide	BeO	0.0325
Cadmium nitrate tetrahydrate	$Cd(NO_3)_2$-$4H_2O$	0.0487
Calcium nitrate tetrahydrate	$Ca(NO_3)_2$-$4H_2O$	0.4034
Cesium nitrate	$CsNO_3$	0.0878
Rubidium nitrate	$RbNO_3$	0.0062(1)
Copper nitrate trihydrate	$Cu(NO_3)_2$-$3H_2O$	0.0539
Iron nitrate nonahydrate	$Fe(NO_3)_3$-$9H_2O$	0.1606
Lead nitrate	$Pb(NO_3)_2$	0.2131
Lithium nitrate	$LiNO_3$	0.0296
Nickel nitrate hexahydrate	$Ni(NO_3)_2$-$6H_2O$	0.3486
Zinc nitrate hexahydrate	$Zn(NO_3)_2$-$6H_2O$	0.2263
Boric acid	H_3BO_3	0.8165
Molybdenum oxide	MoO_3	0.1928
Sodium chloride	NaCl	23.90
Sodium fluoride	NaF	1.1801
Sodium dihydrogen phosphate	$Na_2H_2PO_4$	14.92
Sodium sulfate	Na_2SO_4	52.98
Sodium nitrate	$NaNO_3$	600.0
Potassium nitrate	KNO_3	200.2
Sodium hydroxide (50% soln)	NaOH	2384
Tungstic acid	H_2WO_4-H_2O	0.3201
Sodium meta-silicate	Na_2SiO_3-$9H_2O$	12.34
Sodium chromate	Na_2CrO_4	4.735
Sodium formate	HCOONa	16.14
Sodium nitrite	$NaNO_2$	487.8
Sodium carbonate	Na_2CO_3	200.3
Potassium carbonate	K_2CO_3	355.2
Final volume = 10 L		

(1) Amount added was 105% of that actually needed due to an oversight.

4.3 Physical Characterization

The density of the AP-101 simulant solution was determined by measuring the net mass brought to volume in a 25-mL volumetric flask.

The total undissolved solids were determined by vacuum filtering a known mass (nominally 50-mL) of simulant through a tared Millipore 0.45-µm nylon filter. The filter was dried at 95°C to constant mass and weighed. The wt% undissolved dried solids was calculated by dividing the dried solids mass by the mass of the filtered simulant slurry.

A 10-mL sample aliquot was filtered into a glass vial for observation over time, specifically to evaluate if additional solids formed.

4.4 Chemical Characterization

The three small-scale trial simulant preparations were analyzed by ICPAES (metals) and IC (inorganic anions and oxalate) only. The large-scale simulant preparation was analyzed for metals (ICPAES), inorganic anions and oxalate (IC), OH^- (titration), and TOC and TIC (furnace combustion and hot-persulfate oxidation followed by combustion). The undissolved solids compositions from the first small-scale and aged 10-L preparations were analyzed by x-ray diffraction (XRD).

Neither Cs nor Rb were measured in the simulants; these analytes required analysis by inductively coupled plasma-mass spectrometry (ICP-MS), which was not performed. Formate and acetate concentrations were also not specifically determined.

4.5 Rheology of 10-L Batch of Simulant

Viscosity is the internal resistance to flow of a fluid against external forces. Viscosity is mathematically defined as the shear stress divided by the shear rate. For a Newtonian fluid, this ratio is constant. For non-Newtonian fluids, this ratio changes based on flow conditions and shear history. The rheological data are typically provided as a rheogram or flow curve. Rheograms and flow curves provide flow data as the fluid is subjected to changes in applied shear, time, temperature, or other conditions. Typically, rheograms and flow curves are presented as plots of shear stress versus shear rate. For the work reported here, the shear rate applied to the samples was linearly increased then decreased over time at several fixed temperatures while measuring the resulting shear stress. There are several types of flow curves that have been well studied, and researchers have created several mathematical models to describe flow behavior. For example, the flow behavior of a Newtonian fluid can be described through the following equation:

$$\tau = \eta K \tag{3.1}$$

where: τ = shear stress (Pa)

η = viscosity (Pa·s)

K = shear rate (s^{-1}).

4.5.1 Equipment

The Haake RS300 rheometer system was used for the measurements described in this report. The RS300 employed a concentric-cylinder geometry sensor system. The inner cylinder of the sensor system rotated while immersed in a fluid sample. The resulting torque on the inner cylinder, caused by the resistance of the fluid to flow, was measured by the deflection of a torsion bar mounted between the motor and the drive shaft. This signal generated by an electronic transducer was combined with the rotational-rate information to produce shear-stress and shear-rate data. A double-gap DG41 sensor was used.

The design specifications of the RS300 included a maximum deflection of 1% of full torque with a sensitivity range of up to 0.001° for low-viscosity fluids. It had a torque range of 0.5×10^{-4} to 15 N·cm and rotational speed capability of 0.001 to 1500 rpm. This, combined with the sensor geometry, determined the optimum viscosity and shear-rate ranges available for any given measurement. The measurement head and senor combination had a manufacturer-specified optimum effective viscosity range of 1 to 10^{8} cP over a shear rate range of 0 to 1000 s^{-1}. The lower quantification limit for viscosity, over the 0 to 1000 s^{-1} shear-rate range, was approximately 0.5 cP.

4.5.2 Measurement Method

The sample (and actual AP-101 waste) viscosities were determined according to the guidance provided in 24590-WTP-GPG-RTD-001, Revision A, *Guidelines for Performing Chemical, Physical, and Rheological Properties Measurements*. Samples of the AP-101 simulant and AP-101 actual waste (Cs and Tc removed) were tested in duplicate within a week of each other on the RS300 at 25°C, 40°C, and 60°C; the simulant was also tested at 50°C.

The rheometer system was programmed to linearly increase the shear-rate from 0 to 1000 s^{-1} over 5 min, followed by a linear shear-rate decrease of 1000 to 0 s^{-1} over 5 min. These ramp-up and ramp-down cycles were performed to observe changes in flow-curve behavior. Such changes are referred to as hysteresis. Each sample was run at least twice. If data from the two runs did not compare well, the testing cycle would have been repeated until two consecutive comparable runs were obtained.

5.0 Results and Discussion

The simulant analyte concentrations were to be within ±10%, or within statistical uncertainty of the analytical method, of the expected actual AP-101 diluted process-feed analyte concentrations.[1] The uncertainties of the ICPAES and IC methods were ±15% (2-σ). Thus, the success criteria for demonstrating simulant equivalency to the actual tank waste were the measured analyte concentrations agreeing within ±15% with the waste concentration. All analytical data, traceable through the Analytical Services Request (ASR), are maintained in the Project 42365 record files.

5.1 Simulant Trial Batches

Table 5.1 shows the targeted concentrations (based on the as-received AP-101 characterization corrected for dilution [initial target composition]),[2] the measured analyte concentrations, and the percent differences from the target concentrations for each trial simulant. The percent difference was calculated according to the following equation:

$$\%\ difference = \frac{A_t - A_m}{A_t} * 100 \tag{4.1}$$

where A_t = target analyte concentration
A_m = measured analyte concentration.

Figure 5.1 and Figure 5.2 summarize the trial preparations' major metal and anionic concentrations relative to the target concentrations. This is the same information presented in Table 5.1, presented graphically.

Generally, good agreement was obtained between the targeted analyte concentrations and measured analyte concentrations in the simulants. A notable exception was Na in the second simulant where the solid NaOH used in the preparation contained an unknown amount of water. The bias that can be expected from using the solid reagent is potentially large (-22%). The high Na concentration found for the first trial batch was planned from increasing the Na concentration to boost the NO_2^- and NO_3^- concentrations. A negative bias from using the solid NaOH was not found because the solid NaOH was fresh from the manufacturer and had little exposure to moisture from the air.

The Cu and Si were lost from solution. The Cu may need a stronger complexing agent to maintain solubility in the caustic solution. Similarly, the Si may need a stronger complexing agent. The absence of Cu and Si are not expected to affect pretreatment testing.

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[1] NN Bridges. 2001. *Preparation of AP-101 Simulant Solution*. TP-RPP-WTP-078, Battelle, Pacific Northwest Division, Richland, Washington.

[2] The targeted composition was modified as additional analytical results were provided from actual AP-101DF processing.

Table 5.1. Composition of the Trial Simulants Compared to the Acceptance Criteria

Element	Target Conc. mg/L	Trial Batch 1 ASR 6259		Trial Batch 2 ASR 6314		Trial Batch 3 ASR 6359		Trial Batch 3, Aged ASR 6387		Comments
		mg/L	% Diff.	mg/L	% Diff.	mg/L	% Diff.	mg/L	% Diff.	
Al	6180	5830	-5.8	5700	-7.8	5900	-4.4	NM	NM	Acceptance criteria met.
B	14.2	**40 HB**	**181**	14.6	1.0	12.6 HB	-11	NM	NM	Acceptance criteria met in Preps 2 and 3.
Ba	0.29	<1	(a)	**[0.63]**	**114**	**[0.67]**	**128**	NM	NM	Concentration was so low that it was in the high error range near the detection limit.
Be	1.2	[1.2]	0	[1.1]	-6.1	[1.2]	2.4	NM	NM	Acceptance criteria met.
Ca	6.8	<26	(a)	**[40] HB**	**488**	**[42] HB**	**520**	NM	NM	The actual concentration was below where ICPAES can detect it. Potential impurity from feed chemicals.
Cd	1.7	[2.1]	**23**	[2.0]	13	[2.3]	**35**	NM	NM	Acceptance criteria met in Prep 2, although the concentration was so low it was in the high error range near the detection limit.
Cr	127	131	2.8	123	-3.1	120	-5.5	NM	NM	Acceptance criteria met.
Cu	1.4	<2.6	(a)	**<0.6**	(a)	**<0.5**	(a)	NM	NM	Cu may not be detected.
Fe	2.2	[2.6]	**17**	**[4.4]**	**98**	2.26 HB	2.7	NM	NM	Concentration was so low that it was in the high error range near the detection limit.
K	27,760	27,450	-1.1	24,100	-13	25,000	-11	NM	NM	Acceptance criteria met.
Li	0.3	<3.1	(a)	**[1.2]**	**300**	**[1.3]**	**330**	NM	NM	Concentration was so low that it was in the high error range near the detection limit. Potential impurity from feed chemicals.
Mo	12.9	[12.5]	-3.1	[12]	-7.5	11.9	-7.8	NM	NM	Acceptance criteria met.
Mg	NF	<10	(b)	**23.2**	(b)	**23.0**	(b)	NM	(b)	Evidence of slight contamination from 60-wt% $Al(NO_3)_3\text{-}9H_2O$.
Mn	NF	<5	(b)	**[1.3]**	(b)	**[1.3]**	(b)	NM	(b)	Evidence of slight contamination.
Na	114,950	125,500	11	**89,500**	**-22**	110,500	-3.9	NM	NM	Acceptance criteria met in Preps 1 and 3. Insufficient NaOH was added to Prep 2.
Ni	7.0	[4.2]	**-40**	[6.9]	-1.4	6.94	-0.1	NM	NM	Acceptance criteria met in Preps 2 and 3, Prep 1 had high uncertainty.
P	279	313	12	268	-3.9	287	2.9	NM	NM	Acceptance criteria met.
Pb	13	[16]	**23**	[22]	**69**	[20]	**50**	NM	NM	Concentration was so low that it was in the high error range near the detection limit.
Si	122	**<51**	(a)	**<11**	(a)	**<10**	(a)	NM	NM	Si was not detected.
Sr	NF	<1.5	(b)	**[0.60]**	(b)	**[1.0]**	(b)	NM	(b)	Potential impurity from feed chemicals.

Table 5.1 (Contd)

Element	Target Conc. mg/L	Trial Batch 1 ASR 6259		Trial Batch 2 ASR 6314		Trial Batch 3 ASR 6359		Trial Batch 3, Aged ASR 6387		Comments
		mg/L	% Diff.	mg/L	% Diff.	mg/L	% Diff.	mg/L	% Diff.	
Zn	5.0	[5.5]	10	**[10]**	**100**	**9.95 HB**	**99**	NM	NM	Concentration was so low that it was in the high error range near the detection limit. Acceptance criteria met for Prep 1.
F	53	<250	(a)	550	(c)	580	(c)	610	(c)	F, formate and acetate co-elute and F cannot be determined accurately by the IC method.
Cl	1,760	2000	14	1680	-4.6	1760	-0.1	**2035**	**15.6**	Acceptance criteria met for initial preps 1-3. Aged prep 3 slightly exceeded bound.
NO_2^-	37,260	40,050	7.5	36,900	-1.0	38,400	3.1	40,800	9.5	Acceptance criteria met.
NO_3^-	116,560	104,000	-11	118,500	1.7	114,000	-2.2	127,500	9.4	Acceptance criteria met.
PO_4^{-3}	857	**1700**	**98**[(d)]	820	-4.3	890	3.9	890	3.9	Prep 1 did not match the ICPAES value for P, which met the acceptance criteria. Acceptance criteria met in Preps 2 and 3.
SO_4^{-2}	3,580	4200	**17**	3340	-6.8	3460	-3.4	3340	-6.8	Acceptance criteria met in Preps 2 and 3. Prep 1 was 17% high.
$C_2O_4^{-2}$	1,600	**950**	**-41**	**1,100**	**-31.3**	**700**	**-56.3**	**690**	**-56.9**	Sodium oxalate measured by IC method averaged 1050 mg/L in AP-101 diluted feed. Target oxalate may be biased high.
Density g/mL	1.256	1.277	1.7	1.26	0.3	1.26	0.3	NM	NM	Acceptance criteria met.
Wt% solids	none	0.24	(b)	0.68	(b)	NM	(b)	0.20	(b)	No acceptance criteria.

Shaded and bolded values show an acceptance criteria failure.

Analytical uncertainty is estimated at ±15%. Bracketed values represent results that are within 10 times the estimated detection limit (MDL), and uncertainty is likely to exceed ±15%.

HB indicates that the preparative reagent blank showed high analyte concentration; the reported analyte value was corrected by subtracting the blank contribution.

NM indicates not measured; NF indicates not part of formulation.

(a) Percent difference could not be calculated because analyte was not detected.

(b) Percent difference could not be calculated because analyte was not part of the formulation.

(c) Fluoride, acetate and formate co-elute in the F IC peak. F concentration is an upper bound.

(d) PO_4 analysis is probably an analytical error; the total P result by ICP met the target concentration.

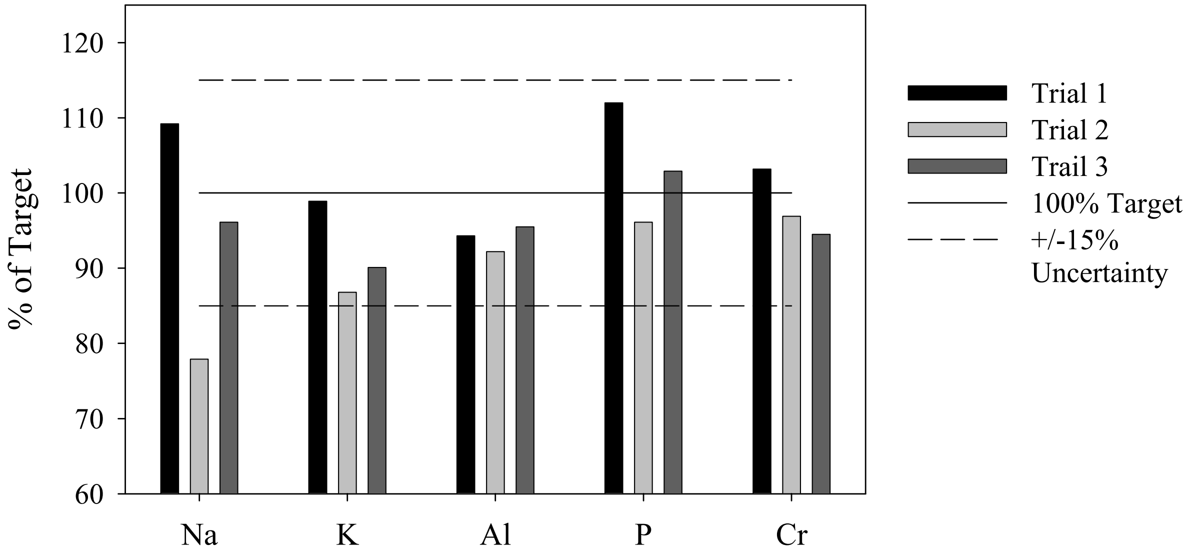

Figure 5.1. Relative Metal Analyte Concentrations of Simulant Preparation Trials

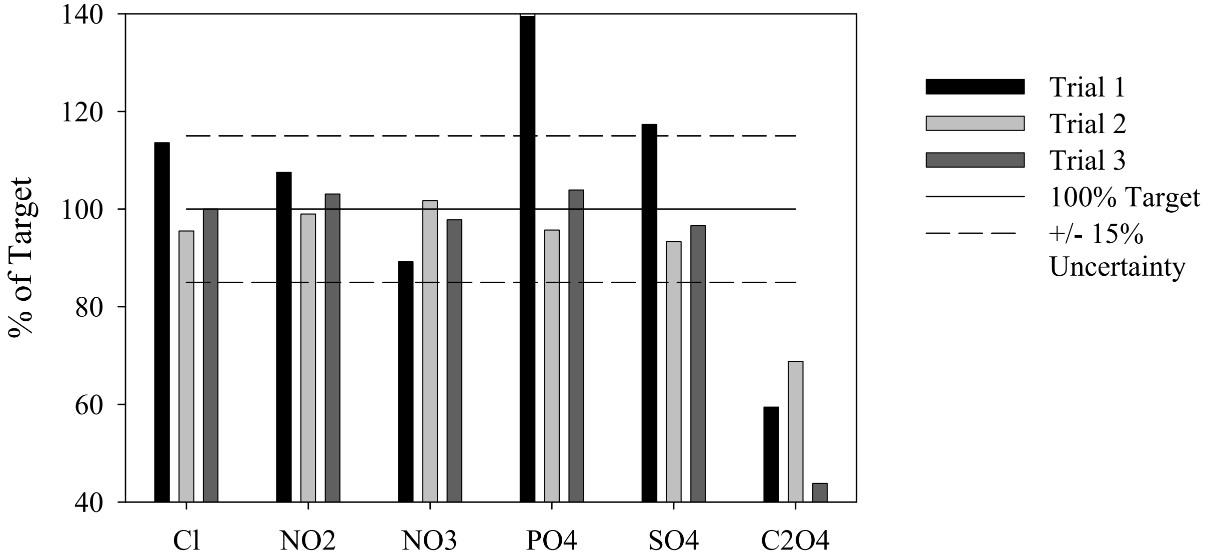

Figure 5.2. Relative Anionic Analyte Concentrations of Simulant Preparation Trials

Additional metals, not part of the formulation, measured in the trials included Mg, Mn, and Sr. Increased analyte concentrations included Ca, Li, and Ba. These analytes were probably present in one or more of the feed components as trace impurities. The concentration increases were at trace levels and were not expected to cause a change in process performance.

The F^- analysis is shown in Table 4.1 for information only. The IC method results in co-elution of fluoride, acetate, and formate. The integrated F^- peak, with the potential contaminants, is lower in apparent concentration than that found in the waste. It is possible that the F^- concentration is higher than estimated. A specific interference-free analysis for F^- should be conducted on the actual AP-101 waste to determine the correct F^- concentration.

The IC analysis of each trial simulant showed low oxalate recovery. Some of the added oxalate was lost to the solids phase as sodium oxalate (as verified by XRD), indicating that the simulant was saturated with respect to oxalate. The oxalate concentration, 1600 µg/mL, in the AP-101 diluted feed was determined by a specific organic anion analysis technique. Oxalate analysis of the same AP-101 diluted feed using the inorganic ion chromatography method resulted in an average concentration of 1050 µg/mL (66% recovery). The target oxalate concentration should be adjusted to 1050 µg/mL to compare the AP-101 oxalate results with the analytical method (inorganic ion chromatography) that was used for the simulant anion measurement.

The XRD analysis of the first trial simulant of filtered undissolved solids identified one major phase of $Na_2C_2O_4$, two minor phases including $CaCO_3$ and $NaNO_3$, and two minor unidentified peaks. Dissolution of the solids in dilute nitric acid resulted in significant effervescence, indicative of significant carbonate composition.

Each of the trial simulants was stable with respect to additional solids formation; after filtration and storage at room temperature for 2 weeks, no additional solids were observed in any of the simulant aliquots.

5.2 Verification of 10-L Simulant Batch

The target analytes affecting Cs ion exchange include Cs, Na, K, and OH^-. Target analytes affecting Tc ion exchange include NO_3^-, and to a lesser extent NO_2^-, and OH^-. Viscosity and density are important parameters for large scale processing. The simulant verification requires matching of target species[1] concentrations to within 10% or statistical uncertainty of the actual waste characterization data. Because the uncertainty of the analytical methods were generally ±15% (2-σ), target analytes were to be within ±15% of the actual waste composition.

5.2.1 Composition

Table 5.2 presents analytical results showing the initial composition (shortly after reagents were mixed) and the composition after a 3-week aging period of the 10-L simulant preparation. Also shown are the target compositions and the percent differences. The analytical report summaries with quality control results for the 10-L preparation analyses are provided in Appendix A.

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[1] Specific Cs measurement by ICP-MS was not included in the test plan characterization requirements. Cs concentration is assumed based on solubility of Cs and preparation mass measurement.

Table 5.2. Measured Composition of 10-L AP-101 Simulant Batch

			Initial composition		**Aged composition**	
	Targeted	**Targeted**	**ASR 6431**		**ASR 6461**	
Analyte	**M**	**mg/L**	**Average mg/L**	**% different from target**	**Average mg/L**	**% different from target**
Al	2.59E-1	6980	6515	-6.7	6905	-1.2
B	1.32E-3	14.2	32.7	130	[15]	[5.2]
Ba	2.11E-6	0.29	[0.64]	[121]	[0.57]	[92]
Be	1.30E-4	1.2	< 5	NA	< 5	NA
Ca	1.71E-4	6.8	**[17.2](a) HB**	**[153]**	**[35](a) HB**	**[415]**
Cd	1.58E-5	1.7	[1.9]	[12]	[1.9]	[4.1]
Cr	2.92E-3	150	**109**	**-28**	**119**	**-22**
Cs	4.51E-5	5.99	(b)	NA	(b)	NA
Cu	2.23E-5	1.4	**< 1.1**	**NA**	**< 1.1**	**NA**
Fe	3.98E-5	2.2	[6.9] HB	[214]	[3.9] HB	[76]
K	7.10E-1	27,740	24,700	-11	25,650	-7.6
Li	4.32E-5	0.30	< 1.3	NA	< 1.3	NA
Mg	NF	NF	**[23] HB(c)**	**NA**	**[23] HB(c)**	**NA**
Mo	1.34E-4	12.9	[12.5]	[-3.1]	[13.5]	[5.0]
Na	5.00E+0	115,000	109,500	-4.8	111,000	-3.4
Ni	1.20E-4	7.0	[8.1]	[16]	[4.1]	[-43]
P	1.24E-2	384	398	3.6	414	7.8
Pb	6.44E-5	13	[16.5]	[27]	[15]	[12.4]
Rb	4.13E-5	3.5	(b)	NM	(b)	NM
Si	4.34E-3	122	[120]	[-1.6]	**<27**	**>-78**
Sr	NF	NF	**[0.75](d)**	**NA**	**[0.81]**	**NA**
W	1.38E-4	25	< 22	NA	<27	NA
Zn	7.62E-5	5.0	[12] HB	[140]	[11.5] HB	[115]
F^-(e)	2.8E-3	53	<130	NA	<125	NA
Cl^-	4.09E-2	1450	1450	0.0	1360	-6.2
NO_2^-	7.07E-1	32,500	34,650	6.6	**38,000**	**17**
NO_3^-	1.68E+0	104,160	106,000	1.8	102,800	-1.3
PO_4^{-3}	1.24E-2	1180	**1550(i)**	**32**	**1550**	**32**
SO_4^{-2}	3.73E-2	3580	3800	6.1	3840	7.3
$C_2O_4^{-2}$	1.78E-2	1600	**890**	**-44**	**830**	**-48**
OH^-	1.94 E+0	33,000	1.90 M	2.1	1.90 M	2.1
CO_3^{-2}	4.46E-1	5350	0.47 M(f)	5.4	0.47 M(f)	5.4
TIC-F(g)	4.46E-1	5350	**4340**	**-19**	NM	NM
TIC-P(g)	4.46E-1	5350	5767	7.8	NM	NM
TOC-F(g)	1.09 E-1	1310	**1667**	**27**	NM	NM
TOC-P(g)	1.09 E-1	1310	**1033 (h)**	**-21**	NM	NM
Density g/mL		1.256	1.26	0.7	1.256	0.0

(**Table 5.2** notes)

Analytical uncertainty is estimated at ±15%. Bracketed values represent results within 10 times the estimated detection limit (MDL), and uncertainty is likely to exceed ±15%.
HB indicates that the analytical blank concentration was >5% of the analyte concentration.
Shaded and bolded values indicate that the analyte concentration exceeded the target by greater than the associated uncertainty.
NM = not measured; NA = not applicable; NF = not part of formulation.
(a) The Ca concentration was adjusted by subtracting the preparative blank concentration.
(b) Cs and Rb were not measured by ICP-AES.
(c) The preparative blanks resulted in 5.9 mg/L and 2.0 mg/L Mg for ASRs 6431 and 6461, respectively.
(d) The duplicate measured <0.78 mg/L.
(e) Fluoride results should be considered the upper bound concentration. Significant peak distortion of the F peak suggests the presence of co-eluting anion(s), possibly formate or acetate.
(f) Based on the third inflection point by acid titration.
(g) For TOC and TIC: P = by hot persulfate method; F = by furnace method/TIC by difference (TIC = TC-TOC), units are in mg C/L.
(h) The minimum required quantity for accurate quantitation is 1500 mg C/L.
(i) The total P determined by ICPAES meets the acceptance criteria. The PO_4^{-3} concentrations determined by IC had high variation.

Good comparisons between major targeted analyte concentrations and measured analyte concentrations were obtained. Major constituents, present at >0.1 M, included Na, Al, NO_3^-, NO_2^-, OH^-, and CO_3^{-2}, and these agreed with the target composition to within 10%, easily meeting the acceptance criteria of ±15%. The K concentration targeted at 0.259 M was 11% low, but also met the acceptance criteria.

Minor elements with concentrations <0.1 M and >0.01 M included formate, acetate, P/PO_4^{-3}, Cl^-, SO_4^{-2}, and $C_2O_4^{-2}$. Formate and acetate concentrations in the simulant were not measured. The P, Cl^-, and SO_4^{-2} agreed with the target concentration to within 6%. The $C_2O_4^{-2}$ measured low relative to the target. However, the inorganic IC oxalate analysis results of the actual waste averaged 1050 μg/mL. This compared better with the measured 890 μg/mL with a -15% difference. The high PO_4^{-3} measured by IC appeared to be due to an analytical problem. The actual AP-101 diluted-feed PO_4^{-3} results exhibited high scatter (Table 3.1), most probably associated with its low concentration in the high nitrate and nitrite matrix. The total P determined by ICPAES showed little scatter in the actual waste analyses and was given more credibility for evaluating P concentration.

The minor to trace components were present at <0.01 M and >0.001 M and included B, Cr, and Si. The Cr resulted in a 20% low bias. This was attributed to analytical error because greater accuracy is credited to the mass of Na_2CrO_4 added. Furthermore, the Cr concentration measured in the three simulant preparations met the target at 125 μg/mL. The CrO_4^{2-} chemistry was expected to behave no differently in the 10-L scale-up batch.

The trace-level constituents included Ba, Be, Ca, Cd, Cs, Cu, Fe, Li, Mo, Ni, Pb, Rb, W, and Zn. These analyte concentrations were below the estimated quantitation limit (EQL), or below the IDL. The Cs and Rb concentrations were not measured by ICP-MS. At their low concentrations, Cs and Rb stability in this matrix was not an issue, and accuracy was assumed according to added mass. For the trace-level analytes detectable by ICPAES, the associated analytical error exceeded ±15%. Generally, these analytes agreed within a factor of 2 of the target concentrations; all agreed within a factor of 3.

Trace contamination from reagents is indicated based on the high Ca and Ba results and the presence of Mg and Sr. Impurities in the reagents may contribute to higher trace-analyte compositions. The Ca analytical preparative blank for ASR 6431 (24.3 µg/mL) was >50% of the measured analyte value (42 µg/mL). The net Ca concentration (17.2 µg/mL) had a high uncertainty largely because of the uncertainty of the blank. The second Ca determination for ASR 6461 was similarly affected in that the Ca analytical preparative blank (6.7 mg/L) constituted a significant fraction of the 42 mg/L measured (net Ca calculated to be 42 mg/L – 6.7 mg/L = 35 mg/L). Thus even accounting for the preparative blank problems, the Ca concentration exceeded that which was added. The preparative blanks also contained some Mg, but at much lower levels than found in the simulant. The Ba concentration also exceeded the formulation indicating Ba may be present in another reagent source. However, the measured Ba concentration was virtually at the detection limit of 0.5 mg/L. Strontium was also measured in the simulant. Because Sr and Mg were not added as part of the formulation, Mg and Sr must have been present as trace impurities in a major added component, probably the 60 wt% $Al(NO_3)_3$-$9H_2O$ solution.[1]

The results of this simulant preparation indicate the impurity levels to be manageable, possibly affecting the trace analyte concentration up to a factor of three. These trace impurities are not expected to adversely affect Cs or Tc ion exchange behavior. The major competitor to Cs ion exchange is K and other Group 1 metals. Strontium, Ba, Ca, and Mg represent the Group 2 metals and no documented interferences attributed to these analytes have been published. Both Ba and Ca have been found in small amounts in the Cs eluate indicating some potential for exchange onto the SL-644 resin (Fiskum et al. 2002). Because SL-639 removes the $NaTcO_4$ ion pair, the cation impurities are not expected to cause any disturbance to the Tc ion exchange processing.

Aging had some effect. All major constituent concentrations were essentially unchanged, with the possible exception of NO_2^-. The reported NO_2^- concentration resulted in a 10% increase; the corresponding NO_3^- concentration resulted in a 3% decrease. Both of these changes were within the uncertainty of the analysis methods (±15%); however, it is possible that the solution was reducing in nature, causing the NO_3^- to reduce to the NO_2^-. The Si concentration dropped with aging from 120 µg/mL to <27 µg/mL, perhaps because of insufficient F as a complexant. The B concentration appeared to drop as well.

The undissolved solids (UDS) remaining, after all reagents were combined and brought to volume, comprised 0.33 wt% (dry basis at 95°C). The UDS content was 0.28 wt% after a 3-week aging period. At 0.28-wt% solids, the total solids content in the 10-L preparation was calculated to be 35.2 g. The XRD spectrum of the UDS is shown in Figure 5.3. Most of the sample (60 wt%) was composed of amorphous solids, 20-wt% sodium oxalate, 8-wt% $NaNO_3$, 4- to 6-wt% $Na_3H(CO_3)_2$, and 4- to 6-wt% $NaNO_2$.

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[1] Mg first appeared when 60-wt% $Al(NO_3)_3$-$9H_2O$ solution was used as a feed component.

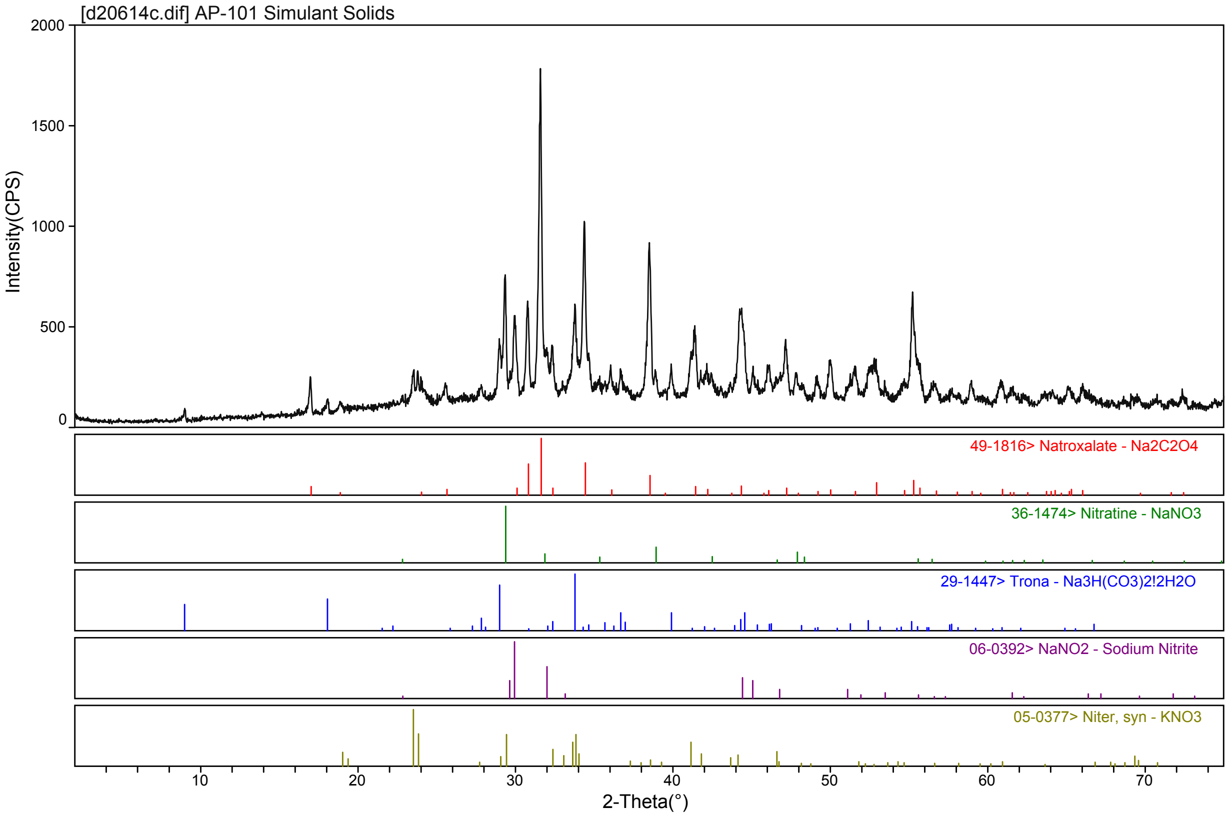

Figure 5.3. XRD Spectrum of Aged Solids from the AP-101 10-L Preparation

Oxalate has a limited solubility in water of approximately 9 wt%. However, with other ions present in solution, the solubility was expected to decrease further. As prepared, the $Na_2C_2O_4$ would have comprised 0.19 wt% of the AP-101 simulant. The supernatant analysis indicated that 17 g of the $Na_2C_2O_4$ were in solution, corresponding to saturation at 0.14 wt%. By difference, the precipitate should consist of 6.8 g $Na_2C_2O_4$ (equivalent to 19 wt% of the calculated total dried solids).

5.2.2 Rheology

Analysis with the RS300 indicated that the AP-101 simulant and AP-101 actual waste were both Newtonian in nature. No hysteresis was observed. A duplicate sample also resulted in comparable data. The AP-101 actual waste and the simulant were identical in rheological behaviors within the error of the method. The viscosity curves for both the simulant and actual waste at various temperatures are shown in Figure 5.4, Figure 5.5, and Figure 5.6.

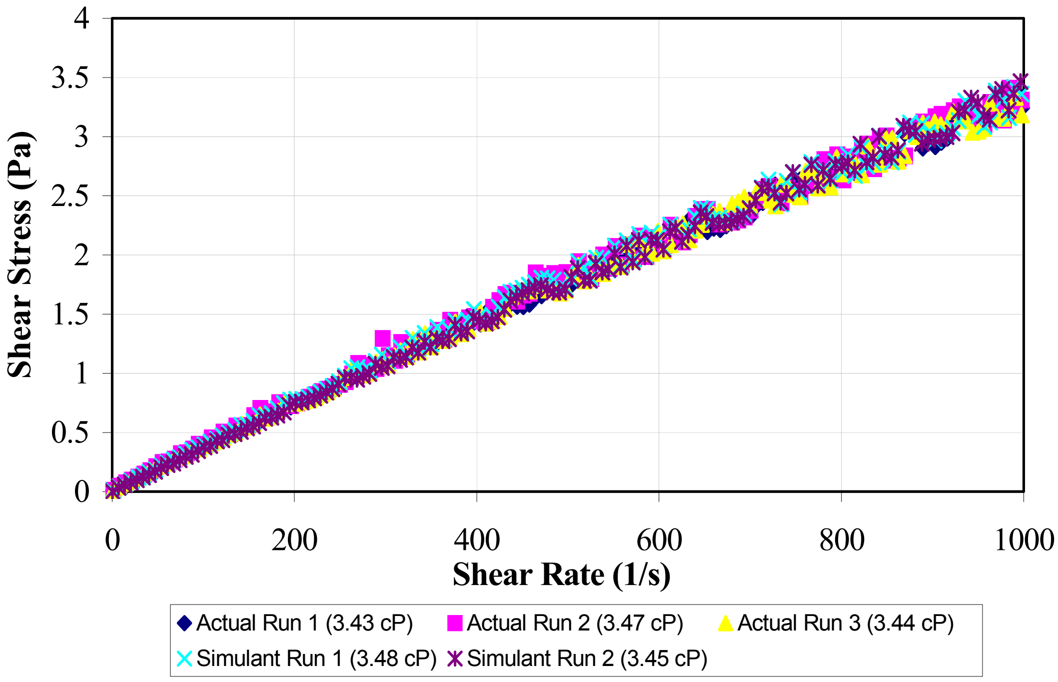

Figure 5.4. AP-101 Simulant and AP-101 Actual Waste Viscosity Determined by the Haake RS300 at 25°C

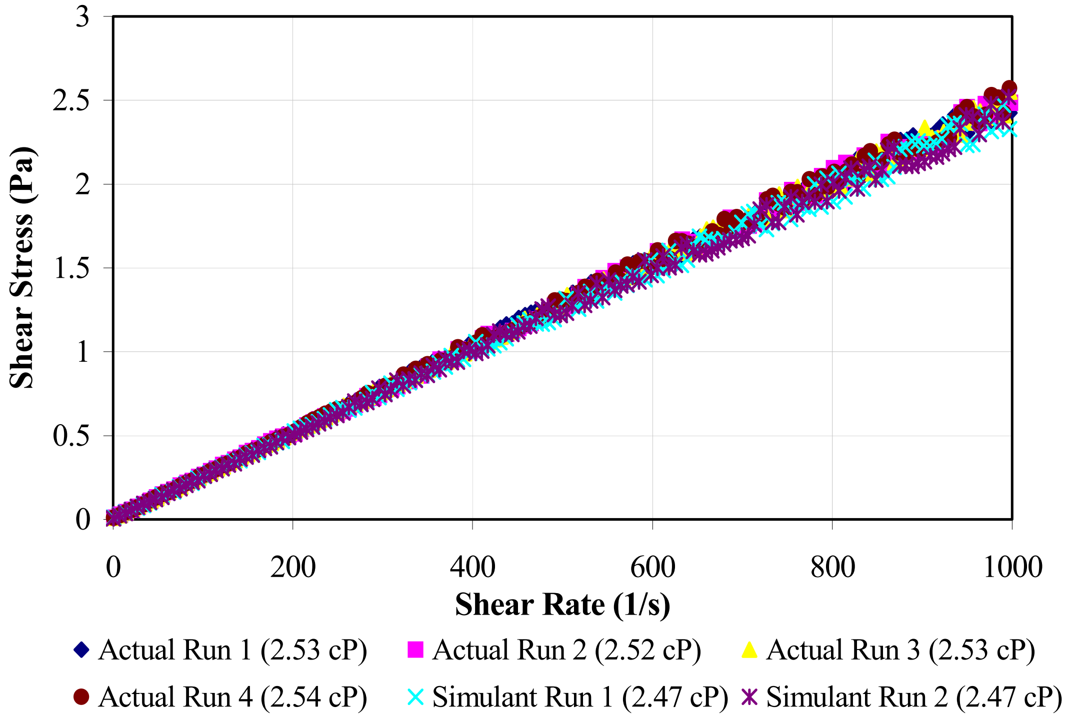

Figure 5.5. AP-101 Simulant and AP-101 Actual Waste Viscosity Determined by the Haake RS300 at 40°C

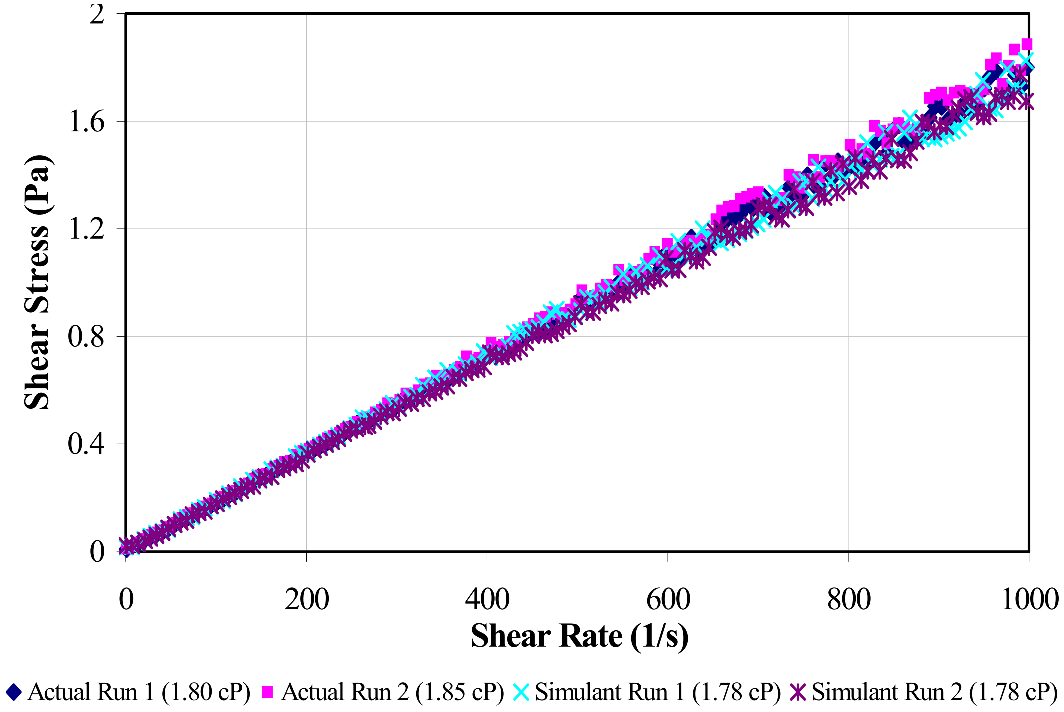

Figure 5.6. AP-101 Simulant and AP-101 Actual Waste Viscosity Determined by the Haake RS300, 60°C

A comparison of the viscosity data between the actual AP-101 waste and the AP-101 simulant analyzed on the same rheometer at similar conditions resulted in a very high correlation between the waste and the simulant from a rheological standpoint. Similar conditions include sodium concentration (4.9 M for actual; 4.8M for simulant), temperature (25°C, 40°C, and 60°C for both samples), and instrument (Haake RS300 with DG41 sensor for both samples). The rheograms of the waste and the simulant appear to be linear with the relationship going through the origin. This indicates Newtonian behavior. The viscosity variations between the actual AP-101waste and the AP-101 simulant at the three temperatures tested were less than 5% with variations of 0.1cP or less. The comparative data are summarized in Table 5.3. The average viscosity of the actual AP-101 waste at 25°C was 3.4 cP, and the average viscosity of the AP-101 simulant was 3.5 cP. The average viscosity of both the actual waste and simulant were 2.5 cP and 1.8 cP at 40°C and 60°C, respectively.

The Andrade Correlation (Munson et al. 1990) (Perry et al. 1984) is a mathematical relationship often used when evaluating the relationship between the increasing temperature and decreasing viscosity of liquids. It is not accurate for high-temperature fluids (T/T_c>0.75; where T_c is the critical temperature of the fluid).

The Andrade Correlation is defined as:

$$\ln \eta = A + B/T \tag{4.1}$$

where: A and B = constants associated with a specific fluid
T = temperature (K)
η = viscosity (cP)

Table 5.3. Newtonian Comparison of AP-101 Simulant and Actual Supernate

	Temperature		**Pretreated AP-101DF Supernate 4.9 M Na**		**AP-101 Simulant 4.8 M Na**	
Run	**C**	**K**	**Viscosity (cP)**	**R^2**	**Viscosity (cP)**	**R^2**
1	25	298	3.4	0.993	3.5	0.990
2	25	298	3.5	0.990	3.5	0.996
3	25	298	3.4	0.992	NM	NA
Average	**25**	**298**	**3.4**	**NA**	**3.5**	**NA**
1	40	313	2.5	0.998	2.5	0.996
2	40	313	2.5	0.998	2.5	0.996
3	40	313	2.5	0.998	NM	NA
4	40	313	2.5	0.998	NM	NA
Average	**40**	**313**	**2.5**	**NA**	**2.5**	**NA**
1	50	323	NM	NA	2.1	0.995
2	50	323	NM	NA	2.1	0.996
Average	**50**	**323**	**NA**	**NA**	**2.1**	**NA**
1	60	333	1.8	0.998	1.8	0.996
2	60	333	1.9	0.998	1.8	0.998
Average	**60**	**333**	**1.8**	**NA**	**1.8**	**NA**

NA = not applicable; NM = not measured
(a) Both the simulant and actual waste supernatant were measured with Haake RS300 rheometer

The close correlation of the AP-101 simulant with the actual AP-101 waste is in Figure 5.7. This indicates that, for the purposes of rheological behavior over the measured temperature range, the simulant and wastes are almost identical with a 95% confidence (F- test, Snedecor and Cochran 1980). This application of the Andrade Correlation also allows for the reasonable interpolation of the viscosity for both the waste and the simulant at temperatures other than those actually measured.

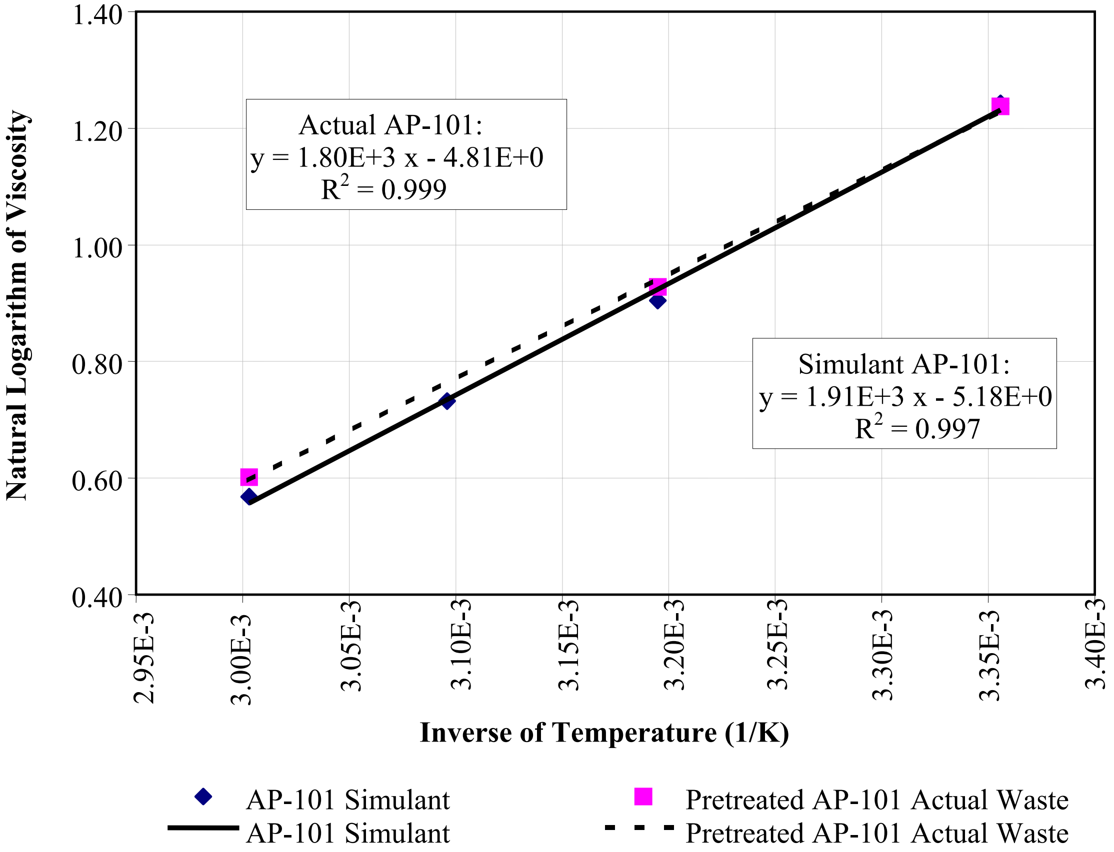

Figure 5.7. Andrade Correlation of AP-101 Simulant and AP-101 Actual Waste (Pretreated)

6.0 Conclusions

The AP-101 simulant was created for use in pretreatment Cs and Tc ion exchange studies. It is intended to be applicable for Cs and pertechnetate/perrhenate (as added) ion exchange studies in AP-101 tank waste matrix. It may also be applicable to the processing fate of hazardous constituents inclusive of Cd, Cr, Ni, and Pb. The close match in rheological behavior of the simulant and actual waste also makes it a good candidate as a rheological simulant.

To the extent that the actual Hanford tank waste AP-101 diluted feed composition is known, the AP-101 simulant preparation closely mimics the major and minor cationic and anionic constituents. This simulant has been verified according to the verification criteria delineated in the test plan. Simulant verification parameters from *Simulant Definition and Verification Methodology*[1] were evaluated with respect to chemical composition, physical properties, and rheological properties; process performance testing is scheduled in fiscal year 2003 under Technical Scoping Statement B-42 and B-43 of the *Research and Technology Plan*.

- The major (Na, K, OH^-, NO_3^-, NO_2^-, and CO_3^{2-}) and minor (P, Cl^-, and SO_4^{2-}) AP-101 simulant analytes agreed with actual AP-101 diluted feed analytes within 11%. The aged NO_2^- concentration was 10% higher than the initial concentration, and was 17% higher than the target concentration.
- The minor and trace constituents (oxalate and Cr) concentrations were low. Both the oxalate[2] and Cr[3] target concentration values, however, were probably too high.
- Greater variability of the trace constituents was found. Some analyte concentrations approached a factor of three higher than the targeted analyte concentration. The variability of the trace analyte recoveries was probably driven by the purity of added reagents and the inherent variability of measuring low concentrations in a high-ionic-strength solution.
- Analytes added to the simulant but not detected included Si and Cu.
- Impurities (probably originating from chemical additions) included Ca, Ba, Mg, and Sr.
- Specifically not included in the simulant were the hazardous constituents As, CN, Sb, and Tl.[4]
- Specifically not included in the simulant were U (45 μg/mL) and other radioisotopes because most simulant applications are non-radioactive.
- The viscosity of the AP-101 simulant was virtually identical to that of the pretreated (Cs and Tc removed) actual waste AP-101 diluted feed.

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[1] P. S. Townson, 24590-WTP-RPT-TE-01-003, Rev. 0.

[2] It appears likely that the oxalate target concentration, based on an organic IC method, was biased high; the inorganic IC method consistently resulted in a lower oxalate concentration in AP-101 diluted feed, more consistent with what was obtained experimentally on the simulant.

[3] The Cr concentration was targeted at the highest found concentration (150 μg/mL) in the actual waste; the average of the other three measurements was 130 μg/mL or 14% lower than the target.

[4] The simulant is not necessarily valid for environmental/regulatory assessment for organics, CN, Hg, Ag, Tl, Sb, As, Cu, Se, and V. These constituents can be "spiked" into the simulant to support environmental needs, but that may invalidate the simulant for the initial functions for which it has been verified.

A few uncertainties about the AP-101 diluted feed composition remain. Neither the F^- nor organic constituent identification and concentrations in the actual waste are well defined. However, these uncertainties are not expected to cause performance variability for pretreatment and vitrification activities. Nevertheless, the incomplete organic constituent reconstruction *may* have an effect on the minor and/or trace cation solubilities and behavior.

7.0 References

Burgeson IE, DL Blanchard Jr., and JR Deschane. 2002. *Small Column Testing of SuperLig$^{®}$ 639 for Removing ^{99}Tc from Hanford Tank Waste Envelope A (Tank 241-AP-101)*, WTP-RPT-030, Battelle Pacific Northwest Division, Richland, WA.

Fiskum SK, PR Bredt, JA Campbell, OT Farmer, LR Greenwood, EA Hoppe, GJ Lumetta, GM Mong, RT Ratner, CZ Soderquist, MJ Steele, RG Swoboda, MW Urie, and JJ Wagner. 2000. *Inorganic, Radioisotopic, and Organic Analysis of 241-AP-101 Tank Waste*, PNNL-13354 (formerly PNWD-3046), WTP-RPT-009, Rev. 1, Pacific Northwest National Laboratory, Richland WA.

Fiskum SK, ST Arm, DL Blanchard, and BM Rapko. 2002. *Small Column Ion Exchange Testing of Superlig® 644 for Removal of ^{137}Cs from Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A),* WTP-RPT-016, Battelle, Pacific Northwest Division, Richland, WA.

Goheen SC, PR Bredt, OT Farmer, III, SK Fiskum, KA Gaither, LR Greenwood, LK Jagoda, AP Poloski, RD Scheele, CZ Soderquist, RG Swoboda, MP Thomas, MW Urie, and JJ Wagner. 2002. *Chemical Analysis and Physical Property Testing of Diluted 241-AP-101 Tank Waste*, WTP-RPT-022, Battelle, Pacific Northwest Division, Richland, WA.

Kurath DE, DL Blanchard, Jr., JR Bontha. 2002. *Small Column Ion Exchange Testing of Superlig 644 for Removal of 137Cs from Hanford Tank Waste Envelope C (Tank 241-AN-107)*, PNWD-3039, Battelle, Pacific Northwest National Laboratory, Richland, WA.

Munson BR, DF Young, TH Okiishi. 1990. *Fundamentals of Fluid Mechanics*, Wiley, NY.

Perry RH and DW Green. 1984. *Perry's Chemical Engineering Handbook*, 6th Edition, McGraw Hill, New York, NY.

Snedecor GW and WG Cochran. 1980. *Statistical Methods*, 7th Edition, The Iowa State University Press, Ames, IO.

Smith, GL. 2002. *Desk Instruction: R&T Simulant Development, Approval, Validation, and Documentation.* River Protection Project – Waste Treatment Plant, Bechtel National, Inc., Richland, WA.

Townson PS. 2001. *Simulant Definition and Verification Methodology*, 24590-WTP-RPT-TE-01-003, Rev. 0, River Protection Project Waste Treatment Plant, Richland, WA.

Appendix A

Analytical Quality Control

Appendix A: Analytical Quality Control

A.1 ICPAES Quality Control

The AP-101 diluted feed acid-digested samples required 5-fold dilutions to quantify all analytes of interest according to PNL-ALO-211, *Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry*. The detected analytes at or above the estimated quantitation limit (EQL) (equivalent to ten times the method detection limit [MDL]) were reported with an uncertainty of ±15% (2-σ). As the MDL was approached, uncertainty increased to 100%.

Quality control for the ICPAES analysis consisted of sample duplicates, process blanks (PBs), matrix spikes (MSs), laboratory control sample (LCS)/blank spike (BS), post spikes, serial dilutions, calibration verification check standards, interference check standards, and linear range check standards. Matrix spike recovery, LCS (or BS) recovery, and precision (based on duplicate analyses) quality control (QC) acceptance criteria were defined by the Test Specification. These QC criteria were evaluated in detail and are summarized in Tables A.1 and A.2.

Analytes of interest, other than Na, with concentrations greater than the EQL had relative percent differences (RPDs) within the acceptance criteria of <15%. The RPD for the duplicate Na analysis is within the acceptance criteria of <3.5%.

Calcium was the only analyte of interest measured in the PB above the acceptance criteria (i.e., <EQL or <5% of sample concentration). Calcium was measured at a level of ~24 µg/mL, which was above the EQL for the particular analysis run. Calcium measured in the two samples, however, was below the EQL level of ~40 µg/mL due to an additional 5-fold instrument dilution. Given the higher inherent uncertainties in the measured calcium contents in the samples, therefore, it is possible that most if not all of the observed calcium is from background levels in the reagents.

For the LCS/BS, all analytes of interest were recovered within the acceptance criteria of 80% to 120%. All matrix-spiked analytes of interest (spiked at greater than 20% of the sample concentration) were recovered within acceptance criteria of 80% to 120%. The spikes for Al, Cr, K, Na, and P could not be recovered since the spikes were less than 20% of the analyte concentration in the sample. All analytes of interest, measured above the EQL, were recovered within the acceptance criteria of 75% to 125% in the post-spike samples. Serial dilution was required to evaluate matrix-interference effects. All analytes of interest measured above the EQL were within the acceptance criteria of ±10%.

Table A.1. ICP-AES Analysis QC Results for AP-101 Simulant 10-L Batch

Analyte	MDL mg/L	Prep Blank mg/L	ASR 6431 02-2408 Average mg/L	Data Flag	RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Acceptance Criteria					*15*	*80-120*	*75-125*	*75-125*	*75-125*	*<±10*
Test Spec Analytes										
Al	2.7	[4.4]	6515		5	105	n/r	105	NA	4.4
B	2.2	–	32.7		10	93	71	100	NA	NA
Ba	0.5	–	[0.64]	J	(a)	103	97	96	NA	NA
Ca	11	24.3	[42]	J	(a)	107	109	102	NA	NA
Cd	0.7	–	[1.9]	J	(a)	110	(b)	103	NA	NA
Cr	0.9	–	109		5	107	n/r	101	NA	5.7
Cu	1.1	[1.4]	–	U	(a)	107	(b)	101	NA	NA
Fe	1.1	[0.71]	[6.9]	J	(a)	107	103	100	NA	NA
K	88	–	24,700		5	105	n/r	103	NA	6.3
Mg	4.4	[5.9]	[23]	J	(a)	109	109	104	NA	NA
Mo	2.2	–	[12.5]	J	(a)	(b)	(b)	99	NA	NA
Na	6.6	137	109,500		1(c)	102	n/r	n/r	NA	3.5
Ni	1.3	[0.43]	[8.1]	J	(a)	107	101	104	NA	NA
P	4.4	–	398		4	110	n/r	102	NA	1.8
Pb	4.4	–	[16.5]	J	(a)	116	(b)	109	NA	NA
Si	22	–	[120]	J	(a)	(b)	(b)	107	NA	NA
Zn	2.2	[1.2]	[12]	J	(a)	106	(b)	101	NA	NA
Other Opportunistic Analytes										
Ag	1.1	–	–	U	(a)	106	(b)	98	NA	NA
As	11	–	–	U	(a)	109	(b)	101	NA	NA
Be	0.5	–	–	U	(a)	106	(b)	100	NA	NA
Bi	4.4	–	–	U	(a)	106	103	99	NA	NA
Ce	8.8	–	–	U	(a)	(b)	(b)	NA	97	NA
Co	2.2	–	–	U	(a)	108	(b)	101	NA	NA
Dy	1.1	–	–	U	(a)	(b)	(b)	NA	96	NA
Eu	4.4	–	–	U	(a)	(b)	(b)	NA	96	NA
La	2.2	–	–	U	(a)	(b)	(b)	NA	97	NA
Li	1.3	–	–	U	(a)	101	102	96	NA	NA
Mn	2.2	–	–	U	(a)	111	(b)	104	NA	NA
Nd	4.4	–	–	U	(a)	(b)	(b)	NA	97	NA
Pd	33	–	–	U	(a)	(b)	(b)	NA	81	NA
Rh	13	–	–	U	(a)	(b)	(b)	NA	94	NA
Ru	49	–	–	U	(a)	(b)	(b)	NA	NA	NA
Sb	22	–	–	U	(a)	(b)	(b)	100	NA	NA
Se	11	–	–	U	(a)	110	(b)	102	NA	NA
Sn	66	–	–	U	(a)	(b)	(b)	NA	NA	NA
Sr	0.7	–	[0.75]	J	(a)	106	(b)	98	NA	NA
Te	66	–	–	U	(a)	(b)	(b)	NA	NA	NA

Table A.1 (Contd)

Analyte	MDL mg/L	Prep Blank mg/L	ASR 6431 02-2408 Average mg/L	Data Flag	RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Th	44	–	–	U	(a)	(b)	(b)	NA	97	NA
Ti	1.1	–	–	U	(a)	(b)	(b)	94	NA	NA
Tl	22	–	–	U	(a)	105	(b)	97	NA	NA
U	88	–	–	U	(a)	(b)	(b)	NA	98	NA
V	2.2	–	–	U	(a)	102	(b)	96	NA	NA
W	22	–	–	U	(a)	(b)	(b)	NA	NA	NA
Y	2.2	–	–	U	(a)	104	(b)	98	NA	NA
Zr	2.2	–	–	U	(a)	(b)	(b)	99	NA	NA

"—" indicates analyte result was less than the detection limit.
J = Estimated value. Value is above MDL but below EQL.
U = undetected, value is less than the MDL.
n/r = not recovered (spike concentration <20% of sample concentration); NA = not applicable
(a) RPD only calculated when both the sample and duplicate results are greater than the EQL.
(b) Analyte was not present in the spike solution.
(c) Target RPD for Na was 3.5%

Table A.2. ICP-AES Analysis QC Results for AP-101 Simulant Aged 10-L Batch

Analyte	MDL mg/L	Prep Blank mg/L	ASR 6461 02-2682 Average mg/L	Data Flag	RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Acceptance Criteria					*15*	*80-120*	*75-125*	*75-125*	*75-125*	*<±10*
Test Spec Analytes										
Al	2.7	[2.2]	6905		4.5	107	n/r	n/r	NA	1.3
B	2.2	–	[15]	J	(a)	76	88	98	NA	NA
Ba	0.5	–	[0.57]	J	(a)	106	93	93	NA	NA
Ca	11	[6.7]	[42]	J	(a)	114	104	101	NA	NA
Cd	0.7	–	[1.9]	J	(a)	116	(b)	101	NA	NA
Cr	0.9	–	119		4.0	113	n/r	101	NA	2.0
Cu	1.1	[1.8]	–	U	(a)	108	(b)	96	NA	NA
Fe	1.1	[0.53]	[4.5]	J	(a)	112	101	99	NA	NA
K	88	[26]	25,650		5.0	101	n/r	n/r	NA	1.6
Mg	4.4	[2.0]	[23]	J	(a)	118	107	105	NA	NA
Mo	2.2	–	[14]	J	(a)	(b)	(b)	100	NA	NA
Na	6.6	24	111,000		2.1(c)	102	n/r	n/r	NA	2.1
Ni	1.3	–	[4.1]	J	(a)	112	(b)	96	NA	NA
P	4.4	–	414		4.7	113	n/r	101	NA	-1.4
Pb	4.4	–	[15]	J	(a)	120	(b)	103	NA	NA
Si	22	–	–	U	(a)	(b)	(b)	105	NA	NA
Zn	2.2	[0.79]	[12]	J	(a)	128	(b)	104	NA	NA

Table A.2 (Contd)

Analyte	MDL mg/L	Prep Blank mg/L	ASR 6461 02-2682 Average mg/L	Data Flag	RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Other Analytes										
Ag	1.1	–	–	U	(a)	111	(b)	97	NA	NA
As	11	–	–	U	(a)	111	(b)	106	NA	NA
Be	0.5	–	–	U	(a)	112	(b)	107	NA	NA
Bi	4.4	–	–	U	(a)	105	101	98	NA	NA
Ce	8.8	–	–	U	(a)	(b)	(b)	NA	97	NA
Co	2.2	–	–	U	(a)	117	(b)	102	NA	NA
Dy	1.1	–	–	U	(a)	(b)	(b)	NA	100	NA
Eu	4.4	–	–	U	(a)	(b)	(b)	NA	98	NA
La	2.2	–	–	U	(a)	(b)	(b)	NA	98	NA
Li	1.3	–	–	U	(a)	103	97	91	NA	NA
Mn	2.2	–	–	U	(a)	116	(b)	106	NA	NA
Nd	4.4	–	–	U	(a)	(b)	(b)	NA	98	NA
Pd	33	–	–	U	(a)	(b)	(b)	NA	83	NA
Rh	13	–	–	U	(a)	(b)	(b)	NA	92	NA
Ru	49	–	–	U	(a)	(b)	(b)	NA	NA	NA
Sb	22	–	–	U	(a)	(b)	(b)	103	NA	NA
Se	11	–	–	U	(a)	106	(b)	105	NA	NA
Sn	66	–	–	U	(a)	(b)	(b)	NA	NA	NA
Sr	0.7	–	[0.81]	J	(a)	109	(b)	96	NA	NA
Te	66	–	–	U	(a)	(b)	(b)	NA	NA	NA
Th	44	–	–	U	(a)	(b)	(b)	NA	100	NA
Ti	1.1	–	–	U	(a)	(b)	(b)	93	NA	NA
Tl	22	–	–	U	(a)	112	(b)	98	NA	NA
U	88	–	–	U	(a)	(b)	(b)	NA	97	NA
V	2.2	–	–	U	(a)	106	(b)	96	NA	NA
W	22	–	–	U	(a)	(b)	(b)	NA	NA	NA
Y	2.2	–	–	U	(a)	110	(b)	99	NA	NA
Zr	2.2	–	–	U	(a)	(b)	(b)	99	NA	NA

"—" indicates analyte result was less than the detection limit.
J = Estimated value, value is above MDL but below EQL.
U = undetected, value is less than the MDL
n/r = not recovered (spike concentration <20% of sample concentration); NA = not applicable.
(a) RPD only calculated when both the sample and duplicate results are greater than the EQL.
(b) Analyte was not present in the spike solution.
(c) Target RPD for Na was 3.5%

A.2 IC Quality Control

Inorganic anion analysis was conducted according to method PNL-ALO-212, *Determination of Inorganic Anions by Ion Chromatography*. The IC method was used to evaluate the anions of interest in the AP-101 simulant. The samples were prepared for IC anion analysis by dilution at 1000-fold to

10,000-fold to assure that the anions were measured within the calibration range. Column overloading prohibited analysis of the sample at dilutions less than 1000-fold.

Quality control for the anion analysis consisted of sample duplicates, PBs, MSs, BSs, and calibration verification check standards and blanks. The QC acceptance criteria were defined by the Test Specification for the MS recovery, BS recovery, and precision (based on duplicate analyses). These QC criteria were evaluated in detail and are summarized in Tables A.3 and A.4.

The duplicate analyses met the specified QC criteria of <15% RPD for all anions detected above the MDL. A MS for the AP-101 simulant was prepared at the IC workstation, with all anions meeting the acceptance criteria of 75% to 125% recovery.

A BS and PB (i.e., IC eluant stock solution used to dilute the samples) were prepared at the IC workstation and analyzed at the same time as the samples and MS. The LCS demonstrated recoveries within the acceptance criteria of 80% to 120%, and no anions were detected above the EQL in the PB.

Table A.3. Anion Analysis QC Results of AP-101 Simulant, 10-L Batch

Analyte	**MRQ µg/mL**	**Sample EQL µg/mL**	**Prep Blank mg/L**	**ASR 6431 02-2408 Average mg/L**	**Sample Data Flag**	**RPD %**	**Lab Control (LCS/BS) % Rec.**	**Matrix Spike (MS) % Rec.**
Acceptance Criteria						*<15*	*80-120*	*75-125*
F [b]	150	130	<0.13	130	U	[a]	112	109
Cl	300	130	<0.13	1450		7	108	109
NO_2^-	3,000	2500	<0.25	34,650		3	110	112
NO_3^-	3,000	2500	<0.25	106,000		2	103	111
PO_4^{3-}	2,500	250	<0.25	1550		6	113	113
SO_4^{2-}	2,300	250	<0.25	3800		0	111	112
Oxalate	1500	250	<0.25	890		2	116	116
OH^-	7.5E+4	NR	NR	1.90 M		1	98	94
CO_3^{2-} [c]	150	NR	NR	0.47 M		3	NA	NA
TIC-F	150	150	–	4340		3 [d]	[d]	[d]
TIC-P	150	27	–	5770		2	99	106
TOC-F	1500	110	–	1700		6	103	100
TOC-P	1500	72	–	1030		10	96	104

"—" indicates analyte result was less than the detection limit.

NA = not applicable; NR = nor reported; M = moles/L

(a) RPD only calculated when both the sample and duplicate results are greater than the EQL.

(b) The fluoride results should be considered the upper-bound concentration. Significant peak distortion of the fluoride peak suggested the presence of co-eluting anion(s), possibly formate or acetate.

(c) The CO_3^{2-} result was based on titration. No carbonate BS or MS was added.

(d) TIC-F was determined by difference (TC – TOC) = TIC. The TC MS and BS recoveries were 96% and 99%, respectively. The reported RPD is for TC.

Table A.4. Anion Analysis QC Results of AP-101 Simulant, Aged 10-L Batch

Analyte	MRQ µg/mL	Sample EQL µg/mL	Prep Blank mg/L	ASR 6341 02-2408 Average mg/L	Sample Data Flag	RPD % (a)	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) % Rec.
Acceptance Criteria						*<15*	*80-120*	*75-125*
F (b)	150	125	<125	<125	U	(a)	112	107
Cl	300	125	<125	1360		3	104	103
NO_2^-	3,000	500	<500	38,000		0	104	98
NO_3^-	3,000	2500	<2,500	102,800		1	102	99
PO_4^{3-}	2,500	250	<250	1550		3	112	104
SO_4^{2-}	2,300	250	<250	3840		0	108	102
Oxalate	1500	250	<250	830		0	113	107
OH^-	7.5E+4	NR	NR	1.90 M		0	101	98
CO_3^{2-}(c)	150	NR	NR	0.47 M		1	NA	NA

"—" indicates analyte result was less than the detection limit.

NA = not applicable; NR = not reported; M = moles/L

(a) RPD only calculated when both the sample and duplicate results are greater than the EQL.

(b) The fluoride results should be considered the upper-bound concentration. Significant peak distortion of the fluoride peak suggested the presence of co-eluting anion(s), possibly formate or acetate.

(c) The CO_3^{2-} result was based on titration. No carbonate BS or MS was added.

A.3 Hydroxide Titration Quality Control

The AP-101 simulant was analyzed in triplicate for the hydroxide content following procedure PNL-ALO-228, *Determination of Hydroxyl and Alkalinity of Aqueous Solutions, Leachates & Supernates*. Direct sample aliquots were analyzed using a Brinkman 636 Auto-Titrator. A 0.1186 N NaOH solution was prepared for use as a verification standard and the matrix spiking solution, and a 0.2040 M HCl solution was prepared as the titrant.

Quality control for the OH^- analysis consisted of sample duplicates, MS, BS, and calibration verification check standards. Matrix spike recovery, BS recovery, and precision (based on duplicate analyses) QC acceptance criteria were defined by the Test Specification. These QC criteria were evaluated in detail and are summarized in Tables A.3 and A.4.

The titration curve consisted of three inflection points, which were assigned (1) the free OH concentration, (2) to the combination of carbonate and aluminate protonation, and (3) to bicarbonate protonation (this was equivalent to the carbonate concentration in solution). Weak acids such as acetate, oxalate, formate, citrate, etc. also contributed to these inflection points, but are too low in concentration relative to the carbonate and aluminate to be detected separately.

Appendix B

Rheology Results

Appendix B: Rheology Results

Quality control standard results for the Haake RS300. A Brookfield 9.8 cP viscosity standard (lot # 091901) at 25ºC measured a Newtonian viscosity of 10.0 cP (R^2 = 0.9978) at 25ºC. Deionized water at 25ºC was measured as Newtonian at 1.0 cP (R^2 =0.9946). The expected viscosity of water at 25ºC is approximately 1 cP.

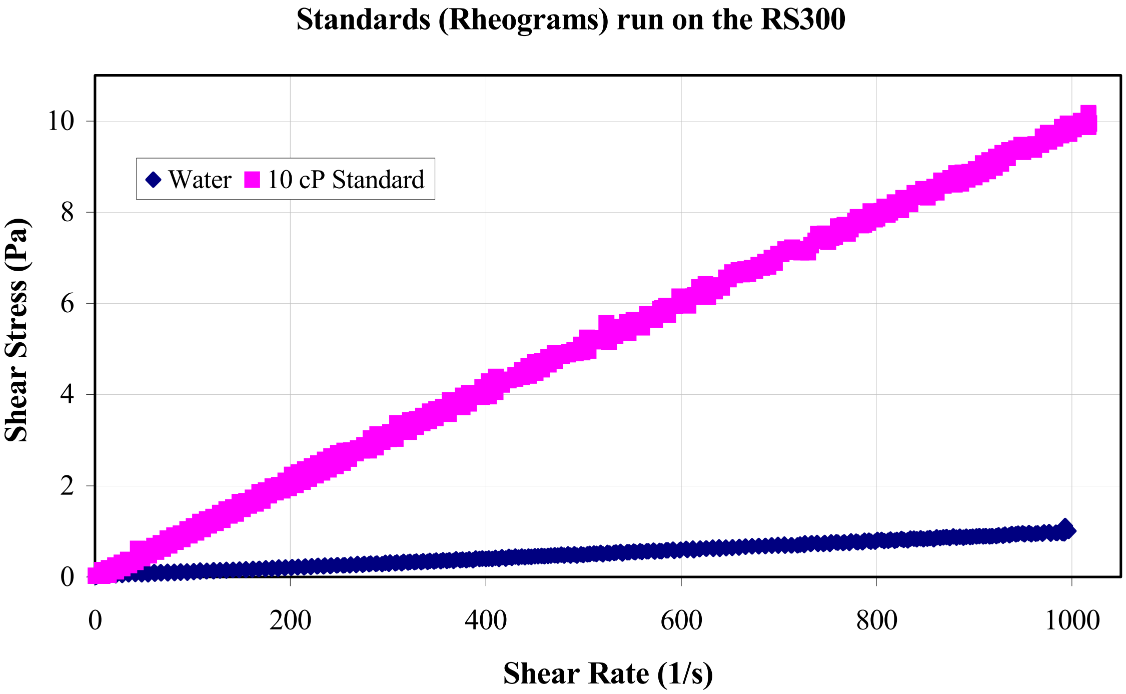

Figure B 1. Quality Control Standard Report

Appendix C

Comparison to Tank Farm Contractor Operation and Utilization Plan (TFCOUP)

Appendix C: Comparison to Tank Farm Contractor Operation and Utilization Plan (TFCOUP)

Table C.1 summarizes the comparison of the simulant recipe to the Tank Farm Contractor Operation and Utilization Plan (TFCOUP) data (Kirkbride et al., 2001). The major and minor components are bolded. Good comparability is shown for the major and minor constituents Al, K, Na, OH^-, NO_3^-, NO_2^-, and SO_4^{2-}. Analytes K, Na, OH^-, NO_3^-, and NO_2^- have been shown to affect Cs and Tc ion exchange. The achieved and target Cl concentration appeared low relative to TFCOUP. The highlighted areas show results that exceed the TFCOUP data by the ±15% threshold established for the simulant work. Of particular concern is the fluoride concentration. According to the TFCOUP data, it is a major component at 0.135 M.

Many minor constituents were added to the TFCOUP data at the detection limit for the analytical method. These analytes were omitted entirely from the simulant preparation. The detection limits are shown in the column labeled "Targeted AP-101" as less-than values. In many cases (e.g., As, Co, Sb, Tl, V) the detection limits were pushed low because ICP-MS was used for measurement. For the simulant work, ICP-AES was used for analysis. Several trace analytes were not added to the simulant that were actually measured in the simulant. These include As, Co, CN, NH_3, I, Sb, Tl, U, and Zr. The NH_3, CN, and U were given specific exclusion to the simulant per the approved test plan. The remaining elements were deemed to be at such trace quantities as not to be performance affecting for Cs and Tc ion exchange.

Table C.1 AP-101 Simulant Preparation in Comparison with TFCOUP Data

Element	Analyte in waste, not added	Targeted AP-101	Targeted AP-101	Found in simulant	Found in simulant	TFCOUP, 5 M Na	Ratio found /TFCOUP	Ratio Target /TFCOUP
	mg/L	mg/L	M	mg/L	M	M		
Ag		< 0.55	< 5.1E-6	< 1.3	< 1.2E-5	5.20E-6	< 232%	< 98%
Al		**6980**	**2.59E-1**	**6905**	**2.56E-1**	**2.30E-1**	**111.5%**	**113%**
As	1.12	< 1.1	< 1.5E-5	< 13	< 1.7E-4	1.49E-5	< 1161%	< 100%
B		14.2	1.32E-3	[15]	[1.4E-3]	1.32E-3	[105.4%]	100%
Ba		0.29	2.10E-6	[0.6]	[4.2E-6]	2.16E-6	[192%]	97%
Be		1.2	1.30E-4	< 5	< 5.5E-4	1.31E-4	< 424%	99%
Bi		< 2.2	< 1.1E-5	< 5.3	< 2.5E-5	1.06E-5	< 240%	< 101%
Ca		6.8	1.70E-4	[35]	[8.7E-4]	1.71E-4	[511%]	100%
Cd		1.7	1.60E-5	[1.9]	[1.7E-5]	1.58E-5	[106.7%]	101%
Ce		< 0.07	< 5.1E-7	< 11	< 7.9E-5	4.32E-7	< 18156%	< 117%
Cl^-		**1450**	**4.09E-2**	**1360**	**3.84E-2**	**4.97E-2**	**77.1%**	**82%**
CN	5.1	< 5.1	< 2.0E-4	NM	NM	1.95E-4	NM	< 100%
Co	0.31	< 0.3	< 5.3E-6	< 2.6	< 4.4E-5	5.20E-6	< 849%	< 102%
CO_3^{2-}		**5350**	**4.46E-1**	**0.47 M**	**4.70E-1**	**4.79E-1**	**98.2%**	**93%**
Cr		150	2.92E-3	119	2.29E-3	2.45E-3	93.5%	119%

Table C.1 (Contd)

Element	Analyte in waste, not added	Targeted AP-101	Targeted AP-101	Found in simulant	Found in simulant	TFCOUP, 5 M Na	Ratio found /TFCOUP	Ratio Target /TFCOUP
	mg/L	mg/L	M	mg/L	M	M		
Cs		5.99	4.51E-5	5.99	4.51E-5	3.59E-5	125%	125%
Cu		1.4	2.20E-5	< 1	< 2.0E-5	2.25E-5	< 91%	< 98%
F^-		53	2.80E-3	< 125	< 6.6E-3	**1.35E-1**	< 5%	< 2%
Fe		2.2	4.00E-5	[3.9]	[7.0E-5]	3.96E-5	[176%]	101%
I(127)	2.27	2.27	< 1.8E-5	NM	NM	not added	not in TFCOUP	not in TFCOUP
K		**27,740**	**7.10E-1**	**25,650**	**6.56E-1**	**7.13E-1**	**92.1%**	**100%**
La		< 1.2	< 8.3E-6	< 2.6	< 1.9E-5	8.38E-6	< 223%	< 99%
Li		0.3	4.40E-5	< 1	< 1.9E-4	4.35E-5	< 431%	101%
Mg		< 2.2	< 9.2E-5	[23]	[9.5E-4]	9.07E-5	[1043%]	< 101%
Mn		< 1.2	< 2.1E-5	< 2.6	< 4.7E-5	2.10E-5	< 225%	< 100%
Mo		12.9	1.34E-4	[14]	[1.4E-4]	not added	not in TFCOUP	not in TFCOUP
Na		**115,000**	**5.00E+0**	**111,000**	**4.83E+0**	**5.00E+0**	**96.6%**	**100%**
Nd		< 2.2	< 1.5E-5	< 5.3	3.67E-5	1.54E-5	< 239%	< 100%
NH_3	1.5	< 1.5	< 8.9E-5	NM	NM	8.90E-5	< 0%	< 101%
Ni		7	1.20E-4	[4.1]	[7.0E-5]	1.20E-4	[58.2%]	100%
NO_2^-		**32,500**	**7.07E-1**	**38,000**	**8.26E-1**	**8.12E-1**	**101.7%**	**87%**
NO_3^-		**104,160**	**1.68E+0**	**102,800**	**1.66E+0**	**1.90E+0**	**87.5%**	**89%**
OH^-		**33,000**	**1.94E+0**	**1.9 M**	**1.90E+0**	**2.16E+0**	**87.9%**	**90%**
P[(a)]		**384**	**1.24E-2**	**414**	**1.34E-2**	9.52E-3	**140%**	**130%**
Pb		13	6.40E-5	[15]	[7.2E-5]	6.42E-5	[112.7%]	100%
Pd		< 16.9	< 1.6E-4	< 40.	< 3.8E-4	1.59E-4	< 236%	< 100%
PO_4^{3-}		**1180**	**1.24E-2**	**1550**	**1.63E-2**	9.52E-3	171%	130%
Pr		< 0.02	< 1.1E-7	NM	NM	1.09E-7	NM	< 98%
Rb		3.5	4.10E-5	3.5	4.10E-5	4.14E-5	99.0%	99%
Rh		< 6.8	< 6.6E-5	< 16.	< 1.6E-4	6.56E-5	< 237%	< 100%
Ru		< 24.	< 2.4E-4	< 58.	< 5.7E-4	2.46E-4	< 233%	< 96%
Sb	0.037	< 0.04	< 3.1E-7	< 26.	< 2.1E-4	2.16E-7	< 98779%	142%
Se		< 2.	< 2.6E-5	< 13.	< 1.6E-4	2.60E-5	< 634%	< 100%
Si		122	4.34E-3	< 27	< 9.6E-4	4.34E-3	< 22%	100%
SO_4^{2-}		**3580**	**3.73E-2**	**3840**	**4.00E-2**	**3.74E-2**	**107.0%**	**100%**
Sr		< 0.33	< 3.8E-6	[0.81]	[9.2E-6]	3.68E-6	[251%]	< 102%
Ta		< 0.08	< 4.4E-7	NM	NM	4.32E-7	NM	< 102%
Te		< 0.14	< 1.1E-6	< 79.	< 6.2E-4	1.09E-6	< 57040%	< 103%

Table C.1 (Contd)

Element	Analyte in waste, not added	Targeted AP-101	Targeted AP-101	Found in simulant	Found in simulant	TFCOUP, 5 M Na	Ratio found /TFCOUP	Ratio Target /TFCOUP
	mg/L	mg/L	M	mg/L	M	M		
Ti		< 0.55	< 1.2E-5	< 1.3	< 2.7E-5	1.17E-5	< 233%	< 99%
Tl	0.016	< 0.02	< 7.8E-8	< 26.	< 1.3E-4	7.84E-8	< 162310%	< 100%
TOC/F		**1310**	**1.09E-1**	**1667**	**1.39E-1**	**1.45E-1**	**95.8%**	**75%**
TOC/HP		**1310**	**1.09E-1**	**1033**	**8.61E-2**	**1.45E-1**	**59.4%**	**75%**
U	45.5	< 45	< 1.9E-4	< 110.	< 4.6E-4	2.07E-4	< 223%	< 92%
V		< 0.69	< 1.3E-5	< 2.6	< 5.1E-5	1.30E-5	< 393%	< 104%
W		25	1.40E-4	< 27	< 1.5E-4	1.39E-4	< 106%	101%
Zn		5.0	7.60E-5	[12]	[1.8E-4]	7.62E-5	[231%]	100%
Zr	1.2	< 1.2	< 1.4E-5	< 2.6	< 2.9E-5	1.36E-5	< 209%	< 100%
Formate		**1070**	**2.37E-2**	NM	NM	not added	not in TFCOUP	not in TFCOUP
Acetate		**1460**	**2.47E-2**	NM	NM	not added	not in TFCOUP	not in TFCOUP
$C_2O_4^{2-}$		**1600**	**1.78E-2**	830	9.43E-3	not added	not in TFCOUP	not in TFCOUP

Rb and Cs were not measured; the as-prepared concentrations are shown.
Bolded values indicate major and minor analytes >1E-2 M.
Gray shaded values indicate the analyte exceeded the TFCOUP concentration by > ±15%.
Bracketed results indicate the result was <EQL and errors are likely to exceed ±15%.
The "less than" values under the "Targeted AP-101" composition indicates the analyte was not added; the analyte in the actual waste was less than the given detection limit.
NM = not measured

TFCOUP data taken from HNF-SD-WM-SP-012, Rev. 3A, "Tank Farm Contractor Operation and Utilization Plan, Volume I", Kirkbride, R. A., G. K. Allen, B. A. Higley, T. M. Hohl, S. L. Lambert, R. M. Orme, D. E. Place, J. A. Seidl, R. S. Wittman, H. H. Baldwin, J. Jo, and J. N. Strode, Sept. 2001.

Appendix D

AP-101 Supernatant Simulant Preparation Procedure

Appendix D: AP-101 Supernatant Simulant Preparation Procedure

1 Simulant Designation

The AP-101 simulant mimics Envelope A AP-101 Hanford tank waste supernatant diluted to 4.9 M Na. The simulant is intended to test Cs and Tc ion exchange pretreatment processing activities. This procedure defines the preparation steps required to produce a simulant that mimics the chemical and physical properties of actual AP-101 supernatant fraction[1] diluted to 5 M Na. Of specific concern were the constituents that affect ion exchange processing parameters inclusive of Na, Cs, OH^-, NO_3^-, and K concentrations. This simulant recipe was formulated based on the actual tank waste analyses of undiluted AP-101 process feed, diluted AP-101 Cs ion exchange feed, Cs ion exchange effluent, and Tc ion exchange effluent.

2 Simulant Waste Stream Composition and Unit Operation Usage

2.1 Characterization Data Determination

The AP-101 supernatant simulant was developed to mimic the chemical and physical properties of the actual AP-101 supernatant diluted to 5 M Na. The simulant metals and anionic constituents' concentrations are to agree with actual waste concentrations within ±10%, or within analytical error of the method as determined by inductively coupled plasma atomic emission spectrometry (ICPAES) and inorganic ion chromatography (IC). Density is determined gravimetrically. Viscosity is determined as a function of temperature.

2.2 Flowsheet Operations For Which The Simulant Was Developed

The AP-101 simulant is intended to support Cs and Tc ion exchange pretreatment studies.

The close match in rheological behavior of the simulant and actual waste also makes it a good candidate as a rheological simulant.

3 Actual Simulant Preparation Procedure

3.1 Chemicals To Use

Reagent-grade salts and chemical forms were carefully selected to best mimic the actual waste composition. Cost, chemical availability, and ease of scale up were considered in choosing which chemicals to use.

The aluminum nitrate nonahydrate is added as a 60 wt% solution. Solid aluminum nitrate nonahydrate is extremely hygroscopic; storing and measuring the crystals introduces mass uncertainty

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[1] There were no entrained solids in the actual AP-101 waste material tested. Solids simulant is beyond the scope of this formulation.

from adsorbed water. The sodium hydroxide is added as a 50 wt% solution. Solid NaOH absorbs water readily from air and has been found to cause a negative Na concentration bias as much as 20%.

Most metals (Ba, Cd, Ca, Cs, Cu, Fe, Pb, Li, Ni, Zn, and Rb) are added as nitrate salts. The nitrate salts are easily available and generally very water-soluble. The transition metals usually precipitate as insoluble hydroxides in base solution, and Ca and Ba precipitate as carbonates when carbonate is present. Complexing agents (oxalate, acetate, and formate) in the simulant are used in an attempt to maintain these metals in solution. Most anions (Cl^-, F^-, PO_4^{3-}, SO_4^{2-}, NO_3^-, NO_2^-, OH^-, SiO_3^{2-}, formate, acetate, and oxalate) are added as Na salts. Again, these have high water solubility and serve to boost the Na concentration to 5 M while minimizing the acid H^+ contribution. Molybdenum is added as MoO_3, which is very soluble in base solution as the MoO_4^{2-} tetrahedron. Molybdenum oxyhalides could probably be used successfully, although they were not tested. Tungsten is also added as WO_3 and behaves similarly to MoO_3, forming the tetrahedral WO_4^{2-}. Boron is added as boric acid, H_3BO_3, existing in base solution as $B(OH)_4^-$. Carbonate is added as the Na and K salts.

The trace components As, Co, Sb, Tl, and Zn were not added to the simulant since they were present in small quantities in the actual waste and were not vital to the pretreatment testing to be performed with this simulant.

All radioactive components are deleted from this simulant composition. Radioactive Cs was replaced with non-radioactive Cs which was added at the total Cs concentration. No appropriate surrogate for U was identified; U was present in the actual waste at nominally 45 µg/mL.

If Cs load and elution profiles are needed during testing of Cs ion exchange processes, analysis by ICP-MS for ^{133}Cs or addition of ^{137}Cs tracer for GEA analysis will be required. If Tc load and elution profiles are needed, addition of pertechnetate (radioactive test) or perrhenate (non-radioactive test) will be required.

3.2 Chemical Addition Order

The organic complexing reagents (sodium acetate and sodium oxalate) are first completely dissolved in a large excess of deionized (DI) water. Full dissolution is necessary to maximize availability for subsequent cation metal complexing. All nitrate salts are then added and dissolved in solution. The specific addition order of the nitrate salts is not expected to be critical.

The Na salts of the targeted anionic species are then added to solution assuring that metasilicate (SiO_3^{2-}), CrO_4^{2-}, NO_2^-, and the carbonate salts are added after the pH adjustment with NaOH.

The specific chemical addition order is shown in Table D.1. Additional DI water will need to be added as necessary to maintain species in solution, not to exceed the final target volume. Once all chemicals are added, the mixture needs to be stirred thoroughly and allowed to cool to room temperature while stirring. Once cool, DI water is added to obtain full final volume and the solution is stirred again to achieve full mixing.

Table D.1. Chemical Addition Order and Amounts for 10-L Simulant Preparation

Compound Name	**Formula**	**Mass**
Sodium acetate	$NaCH_3CO_2$	20.29
Sodium oxalate	$Na_2C_2O_4$	23.85
Aluminum nitrate nonahydrate (60% soln)	$Al(NO_3)_3$-$9H_2O$	1617.5
Barium nitrate	$Ba(NO_3)_2$	0.0055
Beryllium oxide	BeO	0.0325
Cadmium nitrate tetrahydrate	$Cd(NO_3)_2$-$4H_2O$	0.0488
Calcium nitrate tetrahydrate	$Ca(NO_3)_2$-$4H_2O$	0.4036
Cesium nitrate	$CsNO_3$	0.0878
Rubidium nitrate	$RbNO_3$	0.0609
Copper nitrate trihydrate	$Cu(NO_3)_2$-$3H_2O$	0.0540
Iron nitrate nonahydrate	$Fe(NO_3)_3$-$9H_2O$	0.1606
Lead nitrate	$Pb(NO_3)_2$	0.2133
Lithium nitrate	$LiNO_3$	0.0298
Nickel nitrate hexahydrate	$Ni(NO_3)_2$-$6H_2O$	0.3486
Zinc nitrate hexahydrate	$Zn(NO_3)_2$-$6H_2O$	0.2266
Boric acid	H_3BO_3	0.8164
Molybdenum oxide	MoO_3	0.1930
Sodium chloride	NaCl	23.90
Sodium fluoride	NaF	1.180
Sodium dihydrogen phosphate	$Na_2H_2PO_4$	14.92
Sodium sulfate	Na_2SO_4	52.98
Sodium nitrate	$NaNO_3$	600.0
Potassium nitrate	KNO_3	200.2
Sodium hydroxide (50% soln)	NaOH	2384
Tungstic acid	H_2WO_4-H_2O	0.3201
Sodium meta-silicate	Na_2SiO_3-$9H_2O$	12.34
Sodium chromate	Na_2CrO_4	4.735
Sodium formate	HCOONa	16.14
Sodium nitrite	$NaNO_2$	487.8
Sodium carbonate	Na_2CO_3	200.3
Potassium carbonate	K_2CO_3	355.2

3.3 Precautions

- Appropriate safety apparel should be worn when working with chemicals.
- Addition of the $Al(NO_3)_3$ solution causes the simulant solution to become acidic.
- Addition of NaOH solution results in significant heat generation. The NaOH can be added slowly allowing heat to dissipate, or the mixing container can be cooled with an icebath.

- During pH neutralization, significant Al solids form. Mixing may become difficult at this point. The Al solids will return to solution when pH ~10 is exceeded.

- The carbonate salts are added after the NaOH to avoid carbonate decomposition.

- The sodium formate is added after the NaOH to prevent any redox reactions from occurring. The acid form of formic acid is a fairly strong reducing agent and can react with nitric acid and other possible oxidizers.

- The sodium chromate is also added after the NaOH. In acid, the chromate converts to dichromate, which is a very strong oxidizer and can react with acetate, formate, and oxalate.

3.4 Other Considerations

- The simulant needs to be filtered through a 0.45 μm filter to remove solids.

- The simulant should be stored in a polyethylene container (or equivalent). Storage in glass may result in etching of the glass.

- The shelf life for this simulant has not been fully evaluated. However, based on appearance after six months, the simulant composition has not changed through precipitate formation.

4 Key Characteristics and Limitations of AP-101 Simulant

4.1 Key characteristics

The simulant composition is to match major, minor, and trace constituents of actual AP-101 waste diluted to 5 M Na. Of specific concern are the constituents that affect ion exchange (through SL-644 and SL-639) processing parameters and include Na, Cs, OH^-, NO_3^-, and K concentrations. Solution density and viscosity are also process-affecting (Townson, 2001). Key simulant properties for ion exchange are summarized in Table D.2.

Table D.2. Key Properties for Ion Exchange Pretreatment Simulant

Property	Cs Ion Exchange	Tc Ion Exchange
Chemical	Na, Cs, K, and pH	NO_2^-, NO_3^-, OH^-, total ionic strength
Physical	density, viscosity	density, viscosity
Rheological	viscosity	viscosity

4.2 Limitations

The simulant limitations are based primarily on chemical composition.

- Fluoride concentration was not well-defined in the actual waste. Low F concentration may adversely affect the solubility of Si.

- Organic constituent identification and concentrations in the actual waste are not well defined. Only about 50-75% of the organic constituents in the actual AP-101 were identified. The incomplete organic constituent reconstruction *may* have an effect on the minor and/or trace cation solubilities and behavior.

- Neither CN, As, or Tl were added to the formulation. Their fate during ion exchange processing will not be assessed with the current formulation and this may affect decisions with respect to environmental compliance.

- No radionuclides were added. Pu and U have been found to exchange onto SL-644, potentially consuming active sites otherwise available to Cs.

These uncertainties are not expected to cause significant performance variability for pretreatment processing activities.

5 Verification and Validation of the Simulant

Verifying simulants includes determining chemical composition, physical properties, and rheological properties in comparison with actual waste (Townson 2001 and Smith 2002). The simulant chemical composition was evaluated from two independent measurements (freshly prepared simulant and 3-week aged simulant) relative to four independent analyses of actual AP-101 tank waste diluted feed. Major, minor, and trace analyte compositions in the simulant were to match the actual waste composition to within ±10% or within the analytical uncertainty of the analysis method. Physical-property testing specifically included density, again in comparison to actual AP-101 tank waste diluted feed. The rheological properties were tested similarly to the AP-101 diluted-feed tank waste that was processed through the small-scale pretreatment unit operations (Cs and Tc ion exchange).

Simulant validation is confirmed when simulant process behavior is shown to adequately mimic actual waste process behavior (Smith 2002). The simulant Cs and Tc ion exchange performances will be evaluated relative to the actual AP-101 tank waste diluted feed in future work.

5.1 Chemical Composition

Good comparisons between major targeted analyte concentrations and measured analyte concentrations (Fiskum et al. 2002) were obtained. Major constituents, present at >0.1 M, included Na, Al, NO_3^-, NO_2^-, OH^-, and CO_3^{-2}, and these agreed with the target composition to within 10%, easily meeting the acceptance criteria.[1] The K concentration targeted at 0.259 M was 11% low, but also met the acceptance criteria.

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[1] The acceptance criteria defined in the simulant formulation task was to match the actual waste concentrations within ±10% or within analytical uncertainty of the method. The analytical uncertainty of the ICPAES and IC methods were ±15% for analytes greater than the estimated quantitation limit.

Minor elements with concentrations <0.1 M and >0.01 M included formate, acetate, P/PO_4^{-3}, Cl^-, SO_4^{-2}, and $C_2O_4^{-2}$. Formate and acetate concentrations in the simulant were not measured. The P, Cl^-, and SO_4^{-2} agreed with the target concentration to within 6%. The $C_2O_4^{-2}$ measured low relative to the target, however, subsequent testing on the actual AP-101 waste indicated the initial target was too high and the obtained oxalate concentration was on target.[1]

The minor to trace components were present at <0.01 M and >0.001 M and included B, Cr, and Si. The Cr resulted in a 20% low bias. Silicon did not stay in solution.

The trace-level constituents included Ba, Be, Ca, Cd, Cs, Cu, Fe, Li, Mo, Ni, Pb, Rb, W, and Zn. These analyte concentrations were below the EQL, or below the instrument detection limit (IDL). The Cs and Rb concentrations were not measured by ICP-MS. At their low concentrations, Cs and Rb stability in this matrix was not at issue, and accuracy was assumed according to added mass. Trace contamination from reagents is indicated based on the high Ca and Ba results and the presence of Mg and Sr. Impurities in the reagents may contribute to higher trace-analyte compositions. Because Sr and Mg were not added as part of the formulation, Mg and Sr must have been present as trace impurities in a major added component, probably the 60 wt% $Al(NO_3)_3$-$9H_2O$ solution.

Undissolved solids (UDS) were formed as a by-product of the simulant preparation. They comprised 0.33 wt% (dry basis at 95°C). Based on XRD analysis, most of the sample (60-wt%) was composed of amorphous solids, 20-wt% sodium oxalate, 8-wt% $NaNO_3$, 4- to 6-wt% $Na_3H(CO_3)_2$, and 4- to 6-wt% $NaNO_2$. After filtration, no additional solids were observed.

5.2 Charge Balancing

The anionic and cationic complexes of the targeted AP-101 simulant composition were charge-balanced; a summary of charges are shown in Table D.3.

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[1] The Cs ion exchange feed analysis for oxalate concentration resulted in 1600 mg/L. The Tc ion exchange effluent oxalate analysis resulted in 880 mg/L (Burgeson et al., 2002). The maximum oxalate concentration in the simulant preparation was nominally 890 mg/L. Oxalate was left over in the solids fraction, indicating oxalate was at its maximum solubility. This evidence indicated that the initial oxalate concentration of 1600 mg/L was probably in error.

Table D.3. Charge Balance for AP-101 Simulant

Ionic Complex	Targeted M	Molar charge	Ionic Complex	Targeted M	Molar charge
Cations					
Na^+	5.00E+0	+5.00E+0	K^+	7.10E-1	+7.10E-1
Total cationic molar charge			+5.71		
Anions					
OH^-	1.94E+0	-1.94E+0	$C_2O_4^{2-}$	1.78E-2	-3.56E-2
NO_3^-	1.68E+0	-1.68E+0	PO_4^{3-}	1.24E-2	-3.722.48E-2
CO_3^{2-}	4.46E-1	-8.92E-1	Acetate	2.47E-2	-2.47E-2
NO_2^-	7.07E-1	-7.07E-1	Formate	2.37E-2	-2.37E-2
AlO_2^-	2.59E-1	-2.59E-1	CrO_4^{2-}	2.92E-3	-5.84E-3
SO_4^{2-}	3.73E-2	-7.46E-2	F^-	2.81E-3	-2.81E-3
Cl^-	4.09E-2	-4.09E-2	(not applicable)		
Total anionic molar charge			-5.72		

Careful attention was given to the ionic form of each component added to the simulant as well as to simulant chemistry at the time the component was added. In some cases (such as AlO_2^-), the chemical form was assumed and was based on generally known aqueous chemistry. Chromate was added after pH adjustment to maintain Cr in the +6 oxidation state. Phosphorous is expected to be present in tank waste as phosphate and was thus added as phosphate.

5.3 Other Properties

The density of the AP-101 simulant should be nominally 1.256 g/mL.

6 Simulant Properties Compared to Actual Waste Properties

Excellent agreement was obtained with the actual waste and simulant densities. The measured density of the AP-101 diluted simulant was 1.256 g/mL (Fiskum et al., 2002). Density determination on the initial and three-week aged AP-101 simulant resulted in a density of 1.256 g/mL (Russell et al., 2002).

The rheograms of the waste and the simulant appear to be linear with the relationship going through the origin (Bredt et al, 2002; Russell et al., 2002). This indicates Newtonian behavior. The viscosity of the AP-101 simulant was virtually identical to that of the pretreated[1] (Cs and Tc removed) actual waste AP-101 diluted feed. The AP-101 actual waste and the simulant were identical in rheological behaviors within the error of the method. The viscosity variations between the actual AP-101waste and the AP-101 simulant at the three temperatures tested were less than 5% with variations of 0.1cP or less. The average viscosity of the actual AP-101 waste at 25°C was 3.4 cP, and the average viscosity of the AP-101 simulant was 3.5 cP. The average viscosity of both the actual waste and simulant were 2.5 cP and 1.8 cP at 40°C and 60°C, respectively.

Ion exchange testing with the AP-101 simulant to compare to the actual AP-101 waste performance has yet to be performed.

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[1] The actual waste Cs ion exchange feed was not tested for rheology.

7 Simulant Development Organization

The AP-101 diluted feed Envelope A simulant formulation was developed at Battelle, Pacific Northwest Division under the River Protection Project—Waste Treatment Plant R&T project. Two contacts for the simulant development work are:

Renee Russell	Sandra Fiskum
Mail stop: K6-24	Mail stop: P7-22
PO Box 999	PO Box 999
Battelle, PNNL	Battelle, PNNL
Richland, WA 99352	Richland, WA 99352
Phone: 509-373-6235	Phone: 509-376-7015
FAX: 509-376-3108	FAX: 509-372-2156
email: renee.russell@pnl.gov	email: sandy.fiskum@pnl.gov

8 References

Bredt, PR, AP Poloski, EC Buck, RG Swoboda. 2002. *Rheological and Physical Properties of AP-101 LAW Pretreated Waste and Melter Feed*. WTP-RPT-064. Battelle Northwest Division, Richland, WA.

Burgeson IE, DL Blanchard Jr., and JR Deschane. 2002. *Small Column Testing of SuperLig® 639 for Removing ^{99}Tc from Hanford Tank Waste Envelope A (Tank 241-AP-101)*, WTP-RPT-030, Battelle Pacific Northwest Division, Richland, WA.

Fiskum, SK, ST Arm, DL Blanchard, Fr. BM Rapko. 2002. *Small Column Ion Exchange Testing of SuperLig® 644 for Removal of ^{137}Cs from Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A)*. PNWD-3198. WTP-RPT-016. Battelle Northwest Division, Richland, WA.

Russell, RL, SK Fiskum, LK Jagoda, AP Poloski. 2002. *AP-101 Diluted Feed (Envelope A) Simulant Development Report*. WTP-RPT-057. Battelle Northwest Division, Richland, WA.

Smith, GL. 2002. *Desk Instruction: R&T Simulant Development, Approval, Validation, and Documentation.* River Protection Project – Waste Treatment Plant, Bechtel National, Inc., Richland, WA.

Townson, PS. 2001. *Simulant Definition and Verification Methodology*, 24590-WTP-RPT-TE-01-003, Rev. 0, River Protection Project Waste Treatment Plant, Richland, WA.

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Harold Sturm
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