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May 2003

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Battelle—Pacific Northwest Division Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by 24590-WTP-TSP-RT-01-015, Rev. 0 and TP-RPP-WTP-143. 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

Summary

Objectives

Battelle—Pacific Northwest Division (PNWD) is contracted to Bechtel National Inc. (BNI) on the River Protection Project – Waste Treatment Plant (RPP-WTP) project to perform research and development activities. Large storage tanks will be used in the WTP to receive Hanford tank waste. However, heels from the previous waste transfer are likely to be present, resulting in the mixing of tank wastes from different sources. In addition, various liquid-process solutions will be generated by WTP operations, resulting in the potential mixing of these solutions with the tank wastes as well. This investigation is intended as a survey seeking to evaluate potential impacts from the mixing of these disparate waste streams.

This investigation was conducted according to the test plan prepared by Rapko (2002) in response to the test requirements (Sherwood 2001) designed to address issues noted by Barnes et al. (2002) in Section 5.7 of Bechtel's Research and Technology Plan and test scoping statement B-84. Objectives as noted in the test requirements were to perform, analyze the data from, and report on the following tests:

- Combine actual Hanford tank supernatants and recycle solutions involving:
 - minor amounts of one supernatant with a major amount of a second supernatant
 - the system described above with a solution derived from water washing or caustic leaching of the actual tank solids or an appropriate simulant/substitute
 - the system described immediately above with an offgas simulant (Vitreous State Laboratory-High Level Waste-Submerged Bed Scrubber condensate) from high-level waste (HLW) vitrification.
- Measure the initial technetium K_d with SuperLig® 639 for each mixed solution.^(a)
- Measure the initial viscosity for each mixed solution.
- Monitor each mixed solution visually for at least 1 week to detect any changes.
- Measure the final technetium K_d with SuperLig® 639 for each mixed solution.
- Measure the final viscosity for each mixed solution.
- Monitor any changes in the solution by multi-nuclear magnetic resonance (NMR) spectroscopy.
- Isolate and characterize any significant amounts of precipitated solids.

Conduct of Testing

Various Hanford tank supernatants and process solutions expected from unit operations in the RPP-WTP were combined. The solutions examined, as well as the relative phase ratios present in the mixed

⁽a) K_d measures the efficiency with which the SuperLig® 639 ion-exchange resin removes ⁹⁹Tc from the solution: $K_d = (C_i/C_f - 1)V/(mF)$; C_i and C_f are initial and final ⁹⁹Tc solution concentrations, respectively; V is the volume of the liquid sample; m is the as-received resin mass; and F = m/M where M is the dried resin mass.

solutions, are summarized in Table S.1 below. The combined materials were examined for changes, both initially and after a contact time of at least 1 week, in solution viscosity, precipitate formation, and pertechnetate concentration. The latter was evaluated indirectly by looking for changes in the Tc K_d following batch contacts with SuperLig® 639 and directly by looking for changes in the solution's pertechnetate concentration by ⁹⁹Tc NMR spectroscopy. In addition, the speciation of phosphorus and aluminum-containing compounds was examined in the mixed process solutions by ³¹P and ²⁷Al NMR spectroscopy.

The identity of precipitated solids was evaluated by powder X-ray diffraction analysis (for crystalline phases), by inductively coupled plasma-atomic emission spectroscopy to identify metals, and by ion chromatography to identify anions. Calculations were performed using the Environmental Simulation Program (ESP) model to compare with observed solids formation and with the identification of isolated solids.

				VSL HLW SBS
Test	AP-101	AZ-101	AZ-101 Caustic Leachate	Simulant
1	10	90	0	0
2	10	80	10	0
3	10	70	10	10
				VSL HLW SBS
	AZ-102	AN-102	AN-102 Sr/TRU Wash	Simulant
4	10	90	0	0
5	10	80	10	0
6	10	70	10	10
				VSL HLW SBS
	AN-102	AN-104	C-104 Solids Wash	Simulant
7	10	90	0	0
8	10	80	10	0
9	10	70	10	10

Table S.1. Phase Ratios Used in Process Heels Test Modeling by ESP

Results and Performance Against Objectives

A summary of key findings is given below:

• To evaluate the changes in the technetium oxidation state upon mixing of process solutions, the amount of pertechnetate in each mixed process solution was evaluated indirectly by the mixed process solution's response to batch contacts with SuperLig® 639 and directly by ⁹⁹Tc NMR spectroscopy. Both methods indicate that minimal to no detectable changes in pertechnetate concentration occur as a function of time (all systems were studied for a minimum of 1 week and up to 3 months after mixing). However, changes in the pertechnetate line shape as a function of time were observed, which indicates that some time-dependent changes in the chemical environment are occurring, although the nature of the changes is unknown. Rigorous quantification of the absolute pertechnetate concentration in solution by either method was not performed, primarily because of the number of interacting variables that influence the batch contact in the case of the SuperLig® 639

contacts or, in the case of the ⁹⁹Tc NMR studies, because of the small but measurable impact of the test solution's overall ionic strength on the NMR spectrometer's response to a given concentration of pertechnetate.

Phosphorus-31 and aluminum-27 NMR spectroscopy were performed on the mixed process solutions following their examination by technetium-99 NMR. The speciation of phosphorus and aluminum was straightforward, with phosphate being the major phosphorus-containing species, and a single component in a tetrahedral environment, probably sodium tetrahydoxyaluminate, being the sole aluminum-containing species.

• Solids formation was evaluated during each of the three independent measurements for any given combination of process solutions to determine whether solids are formed when the process solutions are mixed. In addition, the ESP model was used to evaluate whether solids formation could be expected.

In general, the ESP modeling results suggest that the tank supernatants themselves are often saturated to oversaturated in aluminum, and occasionally saturated to oversaturated in components such as fluoride and oxalate. Perturbation, then, by solutions that would tend to decrease the amount of soluble aluminum still further, such as solutions with low amounts of hydroxide, will exacerbate the problem and may well initiate aluminum precipitation. However, the saturation of process solutions in fluoride may be due to the reporting of and use in the ESP model of a maximum possible fluoride concentration.

Only in Tests 8 & 9 were sufficient solids isolated for analysis. Consistent with the overall trends predicted by ESP modeling, the precipitates observed in Tests 8 and 9 were found to contain substantial amounts of aluminum and fluoride. Of the crystalline phases identified in the precipitated solids from Tests 8 and 9, fluorophosphate and fluorosulfate salts were identified, together with such ubiquitous components as sodium nitrate, nitrite, and carbonate, which are likely derived from evaporation of the solid's interstitial liquid during preparation and analysis of the solids.

Viscosity measurements made on the process solutions and their mixtures indicate that the individual process solutions as well as the mixtures show normal Newtonian behavior. In general, the presence of the more dilute (and usually less viscous) process solutions derived from sludge washing and leaching, as well as the Vitreous State Laboratory-High Level Waste-Submerged Bed Scrubber (VSL-HLW-SBS) simulant, led to decreases in the mixed solution's viscosity. No significant time-dependent changes were observed. One interesting feature is that the mixing of AN-102/AN-104 supernatants gave solutions with viscosities greater than those found with either individual tank supernatant; this may be a reflection of small amounts of precipitates (possibly colloidal in nature) being generated by mixing these process solutions. If so, the precipitates would have been generated immediately upon mixing, with little additional change occurring over the following week. Such behavior would be in contrast to the observations made during other testing with these process solutions where precipitates were indeed found, but only upon prolonged standing and not with the mixing of AN-102/AN-104 supernatants themselves (Test 7). The magnitude of the viscosity in the 10 percent AN-102/90 percent AN-104 supernatant combination (almost doubling the measured viscosity of the AN-104 supernatant itself) is noteworthy.

Quality Requirements

Battelle—Pacific Northwest Division (PNWD) implemented the RPP-WTP quality requirements in a quality assurance (QA) project plan (QAPjP) as approved by the RPP-WTP QA organization. This work was conducted to the quality requirements in NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7, as instituted through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP). The analytical requirements are implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs*.

PNWD addressed data-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 that the reported work satisfied the Test Plan objectives. The review procedure is part of PNWD's WTPSP QA Manual.

Issues

In selected combinations of test solutions, precipitates were observed. In addition, ESP modeling indicated many other solutions to be saturated to oversaturated in selected components. If the modeling is correct, slow precipitation of solids, even after the filtration step in the WTP, may occur, with potential impacts to downstream operations such as ion-exchange. Furthermore, this precipitation of solids may lead to an increase in the amount of material reporting to HLW vitrification. Alternatively, the poor agreement between the ESP modeling conclusion and the observation of the mixed process solution may reveal limitations in the predictive capability of the ESP model or the analytical results.

Acronyms

BNI	Bechtel National Inc.
DOE	U.S. Department of Energy
EDTA	ethylenediaminetetraacetic acid
ESP	Environmental Simulation Program
HLW	high-level waste
IC	ion chromatography
ICDD	International Centre for Diffraction Data
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
LAW	low-activity waste
LSC	liquid scintillation counting
NIST	National Institute for Standards and Technology
NMR	nuclear magnetic resonance (spectroscopy)
ORP	Office of River Protection
PNWD	Battelle—Pacific Northwest Division
QA	quality assurance
QAPjP	Quality Assurance Project Plan
R&D	research and development
RPL	Radiochemical Processing Laboratory
RPP-WTP	River Protection Project – Waste Treatment Plant
SAL	Shielded Analytical Laboratory
SBS	submerged bed scrubber
SD	standard deviation
SRTC	Savannah River Technology Center
TRU	transuranic

VSL-HLW-SBS	Vitreous State Laboratory-High-Level Waste-Submerged Bed Scrubber (simulant)
WTP	Waste Treatment Plant
WTPSP	Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual
XRD	X-ray diffraction

Contents

Sum	mmary	iii
Acr	ronyms	vii
Con	ntents	ix
1.0	Introduction	1.1
	1.1 Objectives	1.6
	1.2 Purpose	1.6
	1.3 Quality Assurance	
2.0	Experimental	2.1
	2 1 General	2.1
	2.2. Aspects of the Experimental Design	2.1
	2.2 Aspects of the Experimental Design	2.2
	2.5 Solution Sources	
	2.4 Experimental Procedure: Technetium Batch K_d Measurements with SuperL	ig® 6392.6
	2.5 Experimental Procedure: Precipitated Solids Analyses	2.7
	2.6 Experimental Procedure: Viscosity Measurements	2.7
	2.7 ESP Modeling Procedure	
	2.7.1 Method	
	2.7.3 Mixing Processes	2.10
	2.8 NMR Procedure	2.11
	2.8.1 General	2.11
	2.8.2 Sample Preparation	2.12
3.0	Results	
	3.1 Solids Formation	3.1
	3.2 Technetium Batch Contacts with SuperLig® 639	
	3.3 Viscosity Measurements	
	3.4 ESP Modeling	

	3.5 NMR Studies	
	3.5.1 ⁹⁹ Tc NMR	
	3.5.2 ²⁷ Al and ³¹ P NMR	
4.0	Conclusions	4.1
5.0	References	

Figures

Figure 2.1.	Outline of Process Heels Mixing	2.2
Figure 2.2.	Testing Matrix for Process Heels Mixture Study	2.3
Figure 2.3.	NMR Sample Apparatus	.2.12
Figure 3.1.	XRD of Precipitated Solids (Test 8)	3.3
Figure 3.2. Super	Summary of Tc Equilibrium Batch-Contact Distribution Measurements with Lig® 639	3.5
Figure 3.3.	Newtonian Viscosity Measurement of Individual and Mixed Process Solutions at 25°C.	3.7
Figure 3.4.	AZ-101 and AP-101 Heel Mixing Test Analysis	3.9
Figure 3.5.	AN-102 and AZ-102 Heel Mixing Test Analysis	.3.10
Figure 3.6.	AN-104 and AN-102 Heel Mixing Test Analysis	.3.11
Figure 3.7.	Plot of NMR ⁹⁹ Tc Signal Response Versus Pertechnetate Concentration	.3.15
Figure 3.8.	Plot of NMR ⁹⁹ Tc Signals in AZ-101 and AN-102 Supernatants	.3.17
Figure 3.9.	Sample of Integral Changes Over Time	.3.19
Figure 3.10 Funct	9. Summary of Relative Intensity Changes in AP-101/AZ-101 Tests as a ion of Time	.3.19
Figure 3.11 Funct	. Summary of Relative Intensity Changes in AZ-102/AN-102 Tests as a ion of Time	.3.20
Figure 3.12 Funct	. Summary of Relative Intensity Changes in AN-102/AN-104 Tests as a ion of Time	.3.20

Tables

Table S.1. Phase Ratios Used in Process Heels Test Modeling by ESP	iv
Table 1.1. Low-Activity Waste Feed Staging Sequence (Kirkbride et al. 2002)	1.2
Table 1.2. Active Mixing Tests Performed by SRTC (Table 3 in Hassan et al. 2000)	1.5
Table 2.1. Observed Components from ICP-AES and IC Analysis of AN-102 Sr/TRU Solid	s Wash 2.5
Table 2.2. Measured Process Solution Densities	2.6
Table 2.3. Molar Conversion Summary	2.11
Table 2.4. Calculated Versus Activity Based 99Tc Concentrations in Dilute Aqueous Standard Solutions	2.13
Table 3.1. Solids Formation in Process and Mixed Process Solutions	
Table 3.2. Major Components in Test 8 Solids as Determined by ICP-AES and IC	
Table 3.3. Tc Equilibrium Batch Contact Distribution Values	
Table 3.4. Summary of Newtonian Viscosity Measurement with Individual and Mixed Proce Solutions at 25°C	ess 3.6
Table 3.5. Data Used in Viscosity Prediction Calculations	
Table 3.6. ⁹⁹ Tc NMR Response to Standard Aqueous Pertechnetate Solutions (receiver gain	= 150)3.15
Table 3.7. 99 Tc NMR Signal Response to Solution Ionic Strength Changes in a 1 mM Aque Ammonium Pertechnetate Solution	ous
Table 3.8. Summary of ⁹⁹ Tc NMR Results with Process Solutions	
Table 3.9. Summary of ²⁷ Al and ³¹ P Chemical Shift and Line Width Measurements	

1.0 Introduction

The U.S. Department of Energy (DOE) plans to vitrify the large amount of waste at the Hanford Site in Washington State. The vitrified high-level waste (HLW) will be permanently disposed of in an offsite depository, and the vitrified low-activity waste (LAW) will be disposed of onsite.

The Office of River Protection (ORP) Hanford Waste Treatment Plant (WTP) consists of three primary facilities: a pretreatment facility and two facilities for LAW and HLW vitrification (Barnes et al. 2002; Lee et al. 2002). The pretreatment facility takes waste from the Hanford tank farms as feed and separates it into two treated waste streams: a low activity, liquid waste stream stripped of most solids and radioisotopes and an HLW slurry containing most of the solids and radioisotopes. Solids and radioisotopes are to be removed from the waste feed by a selective Sr/transuranic element (TRU) precipitation and/or filtration process, which is followed by ion exchange processes for removing the bulk of the Cs (and possibly Tc), respectively. The effluent from the ion exchange treatment forms the LAW stream. The slurry of filtered solids and two ion exchange eluate streams that contain the abovementioned radioisotopes are blended to produce the HLW stream. The operation of all three facilities will produce recycle streams that route to the pretreatment facility for either processing with the waste feed or being eliminated from the WTP.

As noted above, the pretreatment process for the Hanford WTP will provide LAW and HLW streams for vitrification as low and high activity glass, respectively (Barnes et al. 2002; Lee et al. 2002). Pretreatment includes sludge leaching and washing, filtration, precipitation, and ion exchange processes designed to remove entrained solids, cesium, TRUs, technetium, and strontium. Vitrification operations at the WTP will generate submerged bed scrubber (SBS) solutions and other liquid wastes as recycle streams. These streams will be returned to the WTP pretreatment facility where they will be combined with other recycle streams and waste feed. Other waste-processing operations, such as ion exchange and filtration, in the pretreatment facility also generate recycle streams. In addition, heels remaining in process tanks after a campaign will be mixed with waste from the following campaign as well as with recycle streams. Therefore, pretreatment processes must be capable of accommodating a variety of waste streams mixing together.

Table 1.1 shows the first part of LAW feed staging (Kirkbride et al. 2002). Supernate from Tank 241-AP- $101^{(a)}$ is the first batch; it is Envelope A LAW. The second batch is a mixture of the waste in Tank AZ-101; this is Envelope B LAW. This mixture, upon transfer to waste-receipt vessels, could see heels from the first batch, AP-101 supernate; Envelope A heels could therefore mix with Envelope B waste feed: *feed* + *heels* equals a mixing of Envelope B waste with Envelope A waste. The third batch is a mixture of the waste in Tank AZ-102, another Envelope B LAW. This mixture could see heels from the second batch, LAW from Tank AZ-101; so in this case, Envelope B heels could mix with Envelope B waste feed: B + B. The fourth batch is supernate from Tank AN-102. This batch could mix with an LAW heel from Tank AZ-102 processed in the third batch; this would be a mixture of an Envelope B heel with Envelope C supernate: C + B. The fifth batch is also supernate from Tank AN-102: C + C. The sixth batch is a solution containing material from Tank AN-104. This batch could mix with heels of

⁽a) All Hanford tank names begin with the signature prefix 241. This signature prefix will be dropped henceforth in this report.

Tank AN-102 supernate, producing mixtures of Envelope C heels with Envelope A solution: A + C. The seventh batch is also from Tank AN-104: A + A.

Wastes with identical envelope designations are generally considered to be of similar composition. For this reason, the mixing of waste of differing envelopes is more likely to generate a mixed solution significantly different than either of the component waste types. The work described in this report is based on the assumption that these more significantly perturbed systems are most likely to induce physical and chemical changes; therefore, examination of those batches that mix differing envelopes is the focus of this study. Mixed batches that meet this criterion are flagged in Table 1.1.

Envelope	Source Tank	Waste Type	Staging Tank	Batch	Feed + Heels Envelope Mix
А	AP-101	Supernate	self	1	none
	AZ-101	Supernate/	self	2	B+A ✓
D		Sludge			
D	AZ-102	Supernate/	self	3	B + B
		Sludge			
С	AN-102	Supernata	self	4	C + B ✓
		Supernate	self	5	C + C
•	AN 104	Supernate/	self	6	A + C ✓
А	AIN-104	Solids	AN-101	7	A + A
С	AN-107	Supernate	self	8	C + A
✓ denotes mixtures investigated in this report.					

 Table 1.1. Low-Activity Waste Feed Staging Sequence (Kirkbride et al. 2002)

Typical concerns associated with mixing waste streams are the formation of precipitates through the introduction of incompatible components (Hassan et al. 2000 and references therein), but the formation of gels (with associated changes in viscosity) or gases and excessive heat production could also pose problems. Any mixing of process streams may alter the pH with respect to the individual component streams, and by this means, should the individual streams contain pH-sensitive species at close to saturation levels, induce the formation of solid precipitates. Furthermore, LAW Envelope C waste contains molar concentrations of total organic carbon and may therefore have the capacity to induce precipitation by altering metal oxidation states as well as generating poorly soluble salts not likely to be present in solutions containing the relatively low concentrations of organic species found in the Envelope A or B supernatants. Solids are undesirable in WTP pretreatment and vitrification processes because they might adversely affect the performance of filters and ion exchange resins and because they might increase the amount of non-radioactive material sent to HLW vitrification.

Another concern involves potential changes in radionuclide speciation by mixing process solutions. Technetium-99 (⁹⁹Tc) has been identified as being present as pertechnetate and in non-pertechnetate forms in Hanford tank supernatants; this isotope must be in its highest oxidation state (i.e., as pertechnetate) to be effectively removed from solution by ion exchange (Hamm et al. 2000 and references therein). In Envelope A tanks, technetium is largely present in the form of pertechnetate (TcO_4^-), but is largely in non-pertechnetate forms in Envelope C tanks. It is conceivable that the agent responsible for generating non-pertechnetate species in the Envelope C stream may convert pertechnetate derived from the Envelope A stream into a non-extractable (i.e., lower oxidation state non-pertechnetate) species

(Pikaev et al. 1996) upon mixing of these envelopes of tank supernatants. This would reduce the effectiveness of technetium removal during the downstream ion exchange treatment and so ultimately increase technetium concentrations in LAW glass. Technetium oxidation-state changes in alkaline solutions have been noted both in analytical studies (Shuh et al. 2000; Schroeder et al. 2000) and in experiments with actual tank waste (Blanchard et al. 1997).

Recent studies have begun to evaluate the consequences of mixing process solutions. The Savannah River Technology Center (SRTC) examined the mixing of five Hanford tank supernatant simulants (AN-104, Envelope A; AW-101, Envelope A; AZ-101, Envelope B; AZ-102, Envelope B; and AN-107, Envelope C) and two caustic leachate simulants (AZ-102 and C-106) (Kaplan et al. 2000; Kaplan et al. 2001). Some tests involved dilution of the previously mentioned tank supernatant simulants with dilute (0.01 M) sodium hydroxide up to 100 volume percent while monitoring solids formation and turbidity for up to approximately 2 months. Several features were observed. First, a slight initial increase in turbidity was found generally as the solutions were diluted with 0.01 M NaOH; the increased turbidity decreased as the extent of dilution increased. Second, there appears to be a time dependence on solution turbidity; solutions that became turbid became increasingly turbid the longer (weeks to months) these solutions were examined. Finally, the magnitude of the turbidity increase for the AN-107 supernatant simulant was much greater than that observed for the other examined systems. Solids were isolated for the pure AN-107 supernatant simulant after 2 months, but powder X-ray diffraction analysis (XRD) revealed only sodium nitrate, sodium nitrite, and a form of sodium carbonate, $Na_3H(CO_3)_2 - 2H_2O$. At least the first two of these constituents are likely to have been formed upon drying of the mother liquor attached to the unwashed analyzed solids.

Combinations of Hanford tank supernatant simulants also were mixed in varying ratios and examined in a similar fashion to the dilution studies described above (Kaplan et al. 2000; Kaplan et al. 2001). The simulant combinations examined were AZ-101 (Envelope B) with AN-107 (Envelope C) and AN-104 (Envelope A) with AN-107 (Envelope C). The 50:50 AN-107:AZ-101 mixture and the 90:10 AN-107:AZ-101 mixture both showed increases in turbidity for the first week after contact. The solids from the 50:50 mixture were amorphous but were primarily composed of iron and manganese. Crystalline phases in the 90:10 combination were determined by XRD to be the phases observed with AN-107 alone, i.e., sodium nitrate, sodium nitrite, and a form of sodium carbonate, Na₃H(CO₃)₂ – 2H₂O, as well as an aluminum phase, NaAl(CO₃)(OH)₂.

A series of Hanford tank supernatant simulants, AN-107 (Envelope C), AN-104 (Envelope A), AW-101 (Envelope A), and AZ-102 (Envelope B), were diluted to approximately 5 M in sodium (except for AZ-102, which was kept at its original approximately 2.5 M Na concentration). Although the diluted solutions themselves showed no change in turbidity as a function of time, the combinations of about 1 part diluted AN-107 supernatant simulant with either about 10 parts diluted AN-104, AW-101, or AZ-102 supernatant simulant, respectively, led in all cases to a steady and marked increase in the mixed solution's turbidity. The composition of isolated solids was not identified.

The mixing of a caustic leachate simulant with Hanford tank supernatant simulants was explored. The mixing of various ratios of AW-101 supernatant simulant with C-106 caustic-leachate simulant, of AN-104 supernatant simulant with C-106 caustic-leachate simulant, of AZ-101 supernatant simulant with AZ-102 caustic-leachate simulant, and of AZ-102 supernatant simulant with AZ-102 caustic-leachate simulant gave no increase in turbidity upon standing. However, the mixing of AN-107 supernatant

simulant with C-106 caustic-leachate simulant resulted again in marked increases in solution turbidity. Although the caustic leachate simulant itself showed no turbidity as a function of time, mixing with AN-107 supernatant simulant generated significant turbidity. The extent of turbidity of the AN-107 supernatant simulant decreased slightly compared to a 90 percent AN-107 supernatant simulant: 10 percent C-106 caustic leachate simulant; the presence of further increases in the proportion of the C-106 caustic leachate simulant present gave enhanced turbidity over the AN-107 supernatant simulant itself. In addition, XRD analysis of the filtered solids from the 50:50 AN-107 supernatant simulant: C-106 caustic leachate simulant identified sodium nitrate, sodium nitrite, a sodium aluminum silicate hydrate, Na_{12.8}Al_{7.2}Si_{16.8}O₄₈(H₂O)₆, and sodium carbonate hydrogen peroxide, Na₂CO₃(H₂O₂)_{1.5}. The sodium nitrate and nitrite are likely derived from the drying of interstitial liquid rather than from the precipitated solids themselves.

Finally, the impact of adjusting the Hanford tank supernatant simulants AN-107, AN-104, AW-101, AZ-101, and AZ-102 to pH regimes between 10 and 14.5 was studied (Kaplan et al. 2001). For AN-107, marked increases in the solution's turbidity were observed only at the lower pH conditions. Isolation of the precipitated solid from the pH 10 solution and examination by XRD identified $Na_3H(CO_3)_2 - 2H_2O$, a sodium aluminum silicate, $Na_6(AlSiO_4)_6$, and the ubiquitous sodium nitrate and nitrite. At pH 14.5, only $Na_2CO_3 - H_2O$, sodium nitrate, and sodium nitrite were identified.

Similar to AN-107, the AN-104 supernatant simulant only showed increases in solution turbidity at the lower pH regions studied. However, in general, these systems become more turbid as a function of time. For the pH 10 system, an initial increase in turbidity over the first 2 weeks was followed by a gradual decrease in solution turbidity, although these low pH systems remained more turbid than the high pH systems. XRD analysis of the pH 10 system identified gibbsite, Al(OH)₃, Na₂CO₃ – H₂O, sodium nitrate and sodium nitrite. Again, the turbidity of the pH-adjusted AW-101 solutions increased as the pH of the system was decreased. XRD analysis revealed gibbsite, sodium nitrate, sodium nitrite, and two sodium aluminum silicate hydrates, Na₉₆Al₉₆Si₉₆O₃₈₄(H₂O)₂₁₆ and Na₂Al₂Si_{2.71}O_{9.42}(H₂O)_{4.39}. The AZ-101 and AZ-102 pH-adjusted simulants showed a similar pattern to the low pH AN-104 system, with an initial rapid increase of turbidity followed by either a gradual decrease in turbidity (AZ-101) or no further change in turbidity (AZ-102). XRD analysis of the pH 10 solutions showed the presence of gibbsite, sodium nitrate and sodium nitrite (AZ-101) or gibbsite, sodium nitrate, sodium nitrite, and a sodium aluminum silicate, Na_{1.84}Al₂Si_{2.88}O_{9.68}.

In addition, SRTC examined mixing actual Hanford tank supernatants from Envelopes A, B, and C as well as with various process solutions (Hassan et al. 2000); their testing is summarized in Table 1.2. The ⁹⁹Tc distribution values of the mixed solutions with SuperLig® 639 were measured. No precipitates were noted upon mixing, and the conclusions of the report were that little further change occurs beyond that of the initial mixing and that the observed initial changes should have minimal facility impact.

PNWD has examined the mixing of actual tank supernates from Hanford Tanks AN-107 and AW-101 with actual wash and leach solutions generated from Tanks C-104 and AN-107 solids (Lumetta et al. 2001). Similar results were observed in that perturbation of the AN-107 solution tended to generate additional solids whereas perturbation of all other supernatants produced little, if any, observable adverse changes. The ⁹⁹Tc distribution values of the mixed solutions with SuperLig® 639 were measured. The isolated solids from the AN-107-containing solutions appeared to be composed primarily of Al, B, Fe,

Mn, and Si, and mixing induced no unexpected changes in the ⁹⁹Tc distribution values measured by batch contact of the mixed solutions with SuperLig® 639.

	Mixing Ratios	Mixture	
Mixture	(mL/mL)	Age	Treatment
Envelope A diluted with	30/3	< 4 hours	4-hr-old mixture in 24-hr contact with
Envelope B			SL-639
Envelope A diluted with	30/3	14 days	14-day-old mixture in 24-hr contact with
Envelope B			SL-639
Envelope A diluted with	30/3	< 4 hours	4-hr-old mixture contacted with SL-639
Envelope C			
Envelope A diluted with	30/3	14 days	14-day-old mixture in 24-hr contact with
Envelope C			SL-639
Envelope B diluted with	30/3	< 4 hours	4-hr-old mixture in 24-hr contact with
Envelope C			SL-639
Envelope B diluted with	30/3	14 days	14-day-old mixture in 24-hr contact with
Envelope C			SL-639
Envelope C after Cs-IX	N/A	< 1 day	< 1 day after contact with Cs-IX, a 24-hr
processing			contact with SL-639
Envelope C after Cs-IX	N/A	14 days	14-days after contact with Cs-IX, a 24-hr
processing			contact with SL-639
Envelope B after Cs-IX	N/A	14 days	14-days after contact with Cs-IX, a 24-hr
processing			contact with SL-639
Sr and TRU ppt. wash/	2/20	1–14 days	Mixture observed for 14 days
Envelope C filtrate			
Sr and TRU ppt. wash/	10/10	1–14 days	Mixture observed for 14 days
Envelope C filtrate			

Table 1.2. Active Mixing Tests Performed by SRTC (Table 3 in Hassan et al. 2000)

The Pretreatment Integration Program is currently investigating three types of stream blending in the Pretreatment Facility: (1) Incoming waste feed from the tank farms that mixes with heels remaining in receipt vessels from a prior waste-feed batch of a different waste type, with and without a minor contribution from recycle streams. For example, Envelope B waste feed mixing into Feed Receipt Vessels containing heels of Envelope A remaining from a prior batch. (2) Various Pretreatment and Vitrification Facility recycle streams enter the Plant Wash Vessels, which transfers the mixture to the (Waste Feed) Evaporator Feed Vessels along with an effluent stream from the Ultrafiltration Process. (3) Solids separated from the waste-feed stream by the Ultrafiltration Process are combined with radioisotope-rich (cesium and technetium) eluate streams from these two ion exchange processes to make up the HLW product sent to the HLW Vitrification Facility. The first of these is the focus of this report. The other two areas are under investigation at the Savannah River Technology Center in South Carolina.

1.1 Objectives

The objectives of the work described in this report are to perform, analyze the data from, and report on the following tests:

- Combine actual Hanford tank supernatants and recycle solutions. These will involve
 - minor amounts of one supernatant with a major amount of a second supernatant
 - the system described above with a solution derived from water washing or caustic leaching of the actual tank solids or an appropriate simulant/substitute
 - the system described immediately above with an offgas simulant (Vitreous State Laboratory HLW submerged bed scrubber condensate) from HLW vitrification.
- Measure the initial technetium K_d with SuperLig® 639 for each mixed solution.^(a)
- Measure the initial viscosity for each mixed solution.
- Visually monitor each mixed solution for at least 1 week to detect any changes.
- Measure the final technetium K_d with SuperLig® 639 for each mixed solution.
- Measure the final viscosity for each mixed solution.
- Monitor any changes in the solution by multi-nuclear NMR spectroscopy.
- Isolate and characterize any significant amounts of precipitated solids.

1.2 Purpose

This report documents testing, results, and analysis associated with the mixing of actual Hanford tank supernatants and process solutions. The report is intended to aid the River Protection Project – Waste Treatment Plant (RPP-WTP) project by performing a survey of the effects of combining mixtures of markedly different compositions to see if conditions likely to cause a process upset are generated either immediately or upon contact over a period of days to weeks.

1.3 Quality Assurance

Battelle—Pacific Northwest Division (PNWD) implemented the RPP-WTP quality requirements in a quality assurance (QA) project plan (QAPjP) as approved by the RPP-WTP QA organization. This work was conducted to the quality requirements in NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7, as instituted through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP). The analytical requirements are implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs*.

⁽a) K_d measures the efficiency with which the SuperLig® 639 ion-exchange resin removes ⁹⁹Tc from the solution: $K_d = (C_i/C_f - 1)V/(mF)$; C_i and C_f are initial and final ⁹⁹Tc solution concentrations, respectively; V is the volume of the liquid sample; m is the as-received resin mass; and F = m/M where M is the dried resin mass.

PNWD addressed data-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 that the reported work satisfied the Test Plan objectives. The review procedure is part of PNWD's WTPSP QA Manual.

2.0 Experimental

This section describes the sources and the processes for developing the process solutions used in these tests. It also describes the experimental procedures used for technetium batch K_d measurements, precipitated solids analyses, viscosity measurements, ESP modeling, and the NMR procedure.

2.1 General

SuperLig® 639 (Lot # 0102227CTC-9-23) was purchased from IBC Advanced Technologies, Inc., American Fork, Utah.^(a) All chemicals were of reagent grade unless otherwise noted. Water was deionized before use unless otherwise indicated. Concentrations of prepared sodium hydroxide solutions were analyzed by acid titrations using the National Institute for Standards and Technology (NIST) procedure SRM 84j. Metal concentrations were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), anion concentrations by ion chromatography (IC), and technetium concentrations by inductively coupled plasma-mass spectrometry (ICP-MS). Crystalline solid phases were identified by powder XRD as described below.

2.2 Aspects of the Experimental Design

Figure 2.1 describes the general experimental outline, and Figure 2.2 describes the process solutions and the relative proportions (by volume) used in the testing. As outlined in Figure 2.1, several independent sets of measurements needed to be performed at approximately the same time. It was deemed too demanding to try and synchronize all of the measurements; for this reason, multiple subsamples of the process solutions were made so that, for each type of measurement, the samples could be combined in identical proportions and measurements made independently after similar elapsed times had occurred.

Three types of tests were performed for each set of mixed process solutions. One type of test involved technetium equilibrium batch contacts of the mixed process solutions with SuperLig® 639, which, as noted above, is selective for technetium when present as pertechnetate. The assumption here is that if marked changes in the values of the technetium equilibrium batch contacts were observed as a function of time, this would reflect changes in technetium speciation. This test then provides an indirect indicator of the pertechnetate concentrations in solution; its virtue lies in the relative simplicity of the measurement.

The total volume of mixed process solutions in the batch-contact tests varied from test to test, depending on the amount of various process solutions available for testing; a total of 35-mL was used for Tests 5 and 6, and a total volume of 50-mL was used for all other tests. The other measurements required less solution. The total volume of mixed process solutions used for the solution viscosity measurements was approximately 20-mL, and the total volume of mixed process solutions used for batch-contact testing were greater than with the other tests, particular attention was paid during those experiments to identifying and isolating any precipitated solids.

⁽a) RL Bruening. 2000. "Improvement of Superlig® 639 Capacity and Density." Letter Report from IBC Advanced Technologies, Inc. to British Nuclear Fuels, Limited.



Figure 2.1. Outline of Process Heels Mixing

2.3 Solution Sources

The sources of the tank supernatants and process solutions used in these tests were as follows:

AP-101: see Urie et al. (2000).

AZ-101: see Urie et al. (2002b). Additional material shipped to PNWD from the 222-S Laboratory (06/02) was contained in three bottles: Jar # AZ-00-64, Jar # AZ-00-66, and Jar # 18927.

AZ-102: see Fiskum (2002).

AN-102: see Urie et al. (2002a) for the initial tank supernatant. This material was initially about 50 volume percent solids and 50 volume percent supernatant. It was centrifuged in the Shielded Analytical Laboratory (SAL) hot cells at about 2500 rpm for approximately 0.5 hours. The supernatant was then decanted off. To simulate the actual September 2001 addition of 26.5 kgal of 50 weight percent NaOH to the approximately 920 kgal of material in Hanford Tank AN-102, 4.2-mL of 50 weight percent NaOH (Aldrich Chemical Corporation) was added to 150-mL of the AN-102 supernatant, and the bottle was shaken overnight to mix well the added NaOH before use.

Test Number	Heel in Waste Feed Receipt Vessel	Feed Stream into Waste Feed Receipt Vessel	aste Recycle Streams into Waste Feed el Receipt Vessel	
	241-AP-101 Supernatant	241-AZ-101 Supernatant	241-AZ-101 Caustic Leachate	VSL HLW SBS Condensate
1	10%	90%		
2	10%	80%	10%	
3	10%	70%	10%	10%
	241-AZ-102 Supernatant	241-AN-102 Supernatant	241-AN-102 Sr/TRU ppt.	VSL HLW SBS Condensate
4	10%	90%		
5	10%	80%	10%	
6	10%	70%	10%	10%
	241-AN-102 Supernatant	241-AN-104 Supernatant	241-C-104 Alkaline Wash	VSL HLW SBS Condensate
7	10%	90%		
8	10%	80%	10%	
9	10%	70%	10%	10%

Figure 2.2. Testing Matrix for Process Heels Mixture Study

AN-104: Jar # 18325, received from the 222-S Laboratory on 6-17-2002. See Herting (1998) for analytical information for this tank supernatant.

AZ-101 Caustic Leachate Solution: see Geeting et al. (2002).

C-104 wash solution: see Brooks (2000). The feed staging sequence (Kirkbride 2002) indicates that solids from C-104 will be mixed in the staging tanks at the same time as AN-104 feed. Since AN-104 has little to no solids, any generated wash/leach process solutions will be derived from contact with the remaining C-104 solids. For this reason, the process solution derived from an alkaline wash of C-104 solids was needed.

Vitreous State Laboratory-High-Level Waste-Submerged Bed Scrubber (VSL-HLW-SBS) simulant: Received courtesy of Bond Calloway, SRTC. The following analytical information for this simulant was supplied by SRTC: Solution pH: 2.9 to 3.6 (depending on the analysis source). Major Components (parts per million [ppm]): Boron 95, Sodium 73, Selenium 37, Calcium 18, Lithium 14, Strontium 14, Potassium 10. Percent total solids = 0.25 percent. Percent Insoluble Solids ≤ 0.1 percent.

AN-102 Sr/TRU precipitation wash solution: based on the procedure described in Hallen (2002). Approximately 112-mL of the AN-102 material from Jar # 18944 was transferred into two centrifuge bottles and diluted with 0.01 M NaOH until a total volume of 171-mL in each bottle was obtained. The

solution's hydroxide concentration was then increased by 0.3 M by adding 5.3-mL of 10 M NaOH into each of the two suspensions. The bottles were then capped and shaken manually to agitate the contents. At this point, most of the solids appeared to have dissolved. A 2.5-mL aliquot was removed, filtered through a 0.2-µm Nylon® syringe filter, and set aside for analysis. At this point, 5.25-mL of an aqueous 1 M strontium nitrate solution were added to each bottle. Again, the bottles were capped and manually shaken to mix the contents. Next, 5.25 mL of a 1 M aqueous sodium permanganate solution were added to each bottle. The bottles were capped and manually shaken to mix the contents. Next, the capped bottles were placed in a rotary shaker and shaken at 200 rpm overnight at 26°C. The bottles then were centrifuged at 2500 rpm for about 10 minutes, leaving about 15 mL of centrifuged solids in each bottle. The supernatant was removed by decantation, and a 5-mL aliquot of this supernatant was taken, filtered through a 0.2-µm Nylon® syringe filter, and set aside for analysis.

A volume of 0.01 M NaOH equal to the volume of centrifuge solids was placed in each bottle, the bottles were capped and vigorously shaken manually to re-suspend the centrifuged solids, and the bottles were then placed in the rotary shaker and shaken at 200 rpm for 0.5 hours. The bottles were again centrifuged, and the supernatant was removed by decanting. This was repeated twice more, and the decanted solutions were all collected in one container. A small but visible amount of solids was also transferred by this procedure, so the system was filtered again through a 0.2-µm Nylon® filter before testing. Aliquots of the filtered wash solution were removed and either placed in 0.5 M nitric acid for analysis by ICP-AES or in deionized water for analysis by IC.

The component concentrations from the C-104 wash solution and the wash of the solids from the Sr/TRU treatment of AN-102 results were directly measured by IC and ICP-AES. These measured component concentrations are shown in Table 2.1.

The densities of these process solutions were measured by weighing the process solutions in a tared Type A volumetric flask. The measured process-solution densities are summarized in Table 2.2.

	C-104 Wash – Corrected AN-102 Wash – Corrected				
	for Analysis Dilutions	for Analysis Dilutions			
Analyte	(moles/L), M	(moles/L), M			
Al	3.46E-01	5.36E-02			
K	2.55E-03	5.73E-03			
Na	1.91E+00	1.14E+00			
Р	7.25E-03	5.41E-03			
Si	6.86E-03	1.24E-03			
Ag	2.65E-06				
В	9.23E-04	2.34E-03			
Ba		9.50E-07			
Be	1.01E-04				
Bi	7.60E-06				
Са		1.07E-03			
Cd	1.88E-06	5.66E-05			
Cr	8.94E-04	3.77E-04			
Cu		2.23E-05			
Fe	7.01E-06	1.03E-05			
Li	2.59E-04				
Mg	5.66E-05				
Mo	2.76E-05	5.44E-05			
Ni		7.28E-04			
Pb		1.01E-04			
Sn	4.61E-04				
Sr		7.21E-04			
U	1.51E-04				
V	1.52E-05				
W		7.69E-05			
Zn	1.01E-04	9.81E-06			
Fluoride	< 1.39E-04	3.40E-02			
Chloride	< 7.45E-05	1.17E-02			
Nitrite	2.43E-03	1.90E-01			
Br	5.59E-05	1.70E-03			
Nitrate	1.34E-03	3.33E-01			
Phosphate	3.64E-03	5.44E-03			
Sulfate	5.29E-04	1.43E-02			
Oxalate	3.00E-04	2.40E-02			
Hydroxide	Iydroxide 1.46E+00 Not analyzed				
Below detection limits					
< values are shown for F and Cl because these values were					
provided for	or the ESP modeling. The	"<" indicates the analyte			
was not observed above the instrument detection limit					

Table 2.1. Observed Components from ICP-AES and ICAnalysis of AN-102 Sr/TRU Solids Wash

	Average Density				
Process Solution	(g/mL) – Duplicate Measurements	SD Density			
SBS simulant	1.0072	0.0013			
AZ-101 caustic leach	1.1462	0.0009			
C-104 caustic leach	1.0970	0.0007			
AN-102 Sr/TRU ppt -					
Alkaline wash	1.0596	0.0026			
Test 1 soln	1.2689	0.0025			
Test 2 soln	1.2578	0.0025			
Test 3 soln	1.2433	0.0005			
Test 4 soln	1.4283	0.0061			
Test 5 soln	1.4013	0.0019			
Test 6 soln	1.3588	0.0041			
Test 7 soln	1.4912	0.0035			
Test 8 soln	1.4625	0.0003			
Test 9 soln	1.4155	0.0057			
SD = Standard Deviation					

Table 2.2. Measured Process Solution Densities

2.4 Experimental Procedure: Technetium Batch K_d Measurements with SuperLig® 639

F-factors and the SuperLig® 639 resin pre-equilibration were performed as described previously (Rapko et al. 2003). Targeted combinations of the process solutions were combined in 125-mL plastic bottles and shaken in a rotary shaker at 200 rpm for 0.5 hours to mix the contents. In duplicate, a 1-mL aliquot was removed from each 125-mL plastic bottle to determine the initial technetium concentration by ICP-MS. Meanwhile, in duplicate, 50 mg of the conditioned SuperLig® 639 resin was placed in a 20-mL glass vial. Five milliliters of the target solution were carefully layered on top of the resin to prevent splashing the resin above the liquid line. The resin-target solution mixture was then shaken at 200 rpm for 72 hours at ambient temperature. After 72 hours of shaking, the suspension was filtered through a 0.2-µm Nylon® syringe filter to separate the resin from the solution. The filtered solution was then removed to analyze the final technetium concentration.

The 125-mL bottles were allowed to stand for at least 1 week. After this time, the bottles were inspected for precipitates. If none were observed, the technetium batch-contact procedure was repeated. If precipitates were observed, the solution was decanted from the solids before the batch-contact procedure was repeated. In selected instances, the bottle's contents were allowed to stand for several additional weeks, and the technetium batch contact procedure was repeated.

2.5 Experimental Procedure: Precipitated Solids Analyses

When solids were observed in the 125-mL bottles described in the batch K_d procedure above, the solids were isolated and examined as follows. In the hot cell, the bulk of the liquid was decanted from the solids, and all residual free-standing liquid was removed with a disposable pipette. The bottle was allowed to dry in air for several days. The solids then were transferred into a tared vial. The solids-containing vial was reweighed and removed from the hot cell to a fume hood.

In the fume hood, solid samples were prepared for powder XRD measurement by slurrying the solid with an amyl acetate based, low X-ray background, glue, placing the slurry on a glass slide and drying the prepared sample before analysis. Therefore, the sample was on a thin mount, with only a few milligrams present on the glass slide. The XRD measurement was performed on a Sintag PAD V X-ray Powder diffractometer using Cu-K α radiation and a solid-state detector. Measurement parameters include operation at 45 KV and 40 ma, with 0.05 degrees/step, and a counting time of 3 sec (1 degree/min 2 θ) over a 2 θ range of 5°C to 65°C. The diffraction patterns were compared with known 2 θ /intensity data using MDI (Materials Data Inc.) JADE 6.1 software and the International Centre for Diffraction Data (ICDD) database PDF-2 (Powder Diffraction File) release 2002 to identify crystalline phases from peak positions and intensities. A semi-quantitative analysis was performed using JADE whole pattern fitting and Rietveld treatment. Because the sample was too thin for total absorption of x-rays, any assignments and quantitation must be considered tentative.

Weighed quantities of solid were dissolved in weighed amounts of 0.5 M nitric acid for analysis by ICP-AES. Weighed quantities of solid were dissolved in weighed amounts of deionized water for analysis by IC.

2.6 Experimental Procedure: Viscosity Measurements

A Haake RS300 rheometer was used. The RS300 system has been configured as a concentric cylinder rotational system. The sensor system consists of an inner cylinder that is placed inside an outer cylinder with an annular gap of known dimensions. When the inner cylinder rotates, the resulting fluid resistance to the flow is measured electronically. When this signal is combined with the rotational rate, it can be mathematically transformed into shear-stress and shear-rate data. For the samples analyzed in this report, a Haake Z41 sensor system was used.

The testing was conducted as follows. The samples were loaded into the sample container, and the shear rate was increased from 0 to 1000 L/s in 5 minutes. The sample was held at a shear rate of 1000 L/s for 1 minute. Lastly, the shear rate was decreased from 1000 to 0 L/s in 5 minutes. The test was then immediately duplicated with the same sample.

The purpose of this set of testing parameters was to identify the rheological behavior and shear sensitivity of the materials. The first ramp cycle showed newly loaded or fresh sample behavior, including breakdown of sample structure through hysteresis, if present. (Hysteresis is when the ramp-down curve is different from the ramp-up curve.) An immediate repeat allows little or no time for the sample to recover. The complete cycle repeat with the used sample shows the effects of a shear history with a short time of recovery for the sample.

A 9.8 cP (at 25°C) viscosity standard oil was used to validate the calibration of the machine. A value of 9.98 cP was measured at 25°C. Newtonian behavior was observed, with a plot of τ versus γ showing good linearity (a correlation coefficient of 0.9996) over shear rates from 0 to 1000/sec.

The nine mixtures shown in Figure 2.2 were tested with target volumes of 20-mL. The samples were mixed with a magnetic stir bar for a period of 30 minutes. A set of rheological measurements immediately followed. The samples were then allowed to equilibrate for a period between 1 to 4 weeks, followed by a second set of rheological measurements. Each set of rheological measurements was performed in duplicate at 25°C. In addition, the rheological properties of eight of the nine individual process streams presented in Figure 2.2 were measured; the remaining material, AP-101, was not available in sufficient quantities for an individual measurement.

2.7 ESP Modeling Procedure

2.7.1 Method

The mixing tests were simulated using the Environmental Simulation Program (ESP) to determine the predictive capabilities of the software and to provide insight into possible enhancements or alternatives to the mixing schemes. ESP, produced by OLI Systems, is a chemical process simulator extensively used at Hanford, other DOE sites, and by many chemical, oil, and mineral processing companies. It is designed to model the processing of concentrated aqueous solutions, organic liquids, solids, and vapors. ESP uses sophisticated thermodynamic models to predict the activity coefficients and equilibrium constants of most species and equilibrium relationships that can exist in tank wastes or during the processing of such wastes. It can be used to calculate the equilibrium or time-dependent composition of complex mixtures of solids, liquids, and gases.

ESP is composed of two main sections: simulation tools and databooks. The simulation tools include the Process module for simulating steady-state processes, the Express module for performing single- or multiple-point equilibrium calculations for a single composition, and the Water Analyzer module for inputting laboratory-element and anion analyses and reconciling charge imbalances. Databooks are databases that contain thermodynamic and physical properties of various chemical species as well as parameters for a variety of chemical and physical property models.

The main ESP databook is called PUBLIC, and it contains many thousands of general inorganic, organic, aqueous, and metallic species. Other databooks contain a more narrow collection for a specific area of application, such as geochemistry, corrosion, or complexing agents. The supplied databooks can be supplemented with "private" databooks developed by the licensee. The FELMY databook was created from the database of Andy Felmy of PNWD, which is based on the Pitzer model for the water-activity and all-activity coefficients. The details on the inclusion of the Pitzer model can be found elsewhere (Sanders et al. 2001). The Felmy database has been detailed in earlier reports (Felmy et al. 1994; Felmy 2000; Felmy and MacLean 2001). Because the Pitzer and Bromley-Zemaitis models use different equations and parameters to describe solute-interaction phenomena, they are not compatible, and a special version of ESP has been created to use it. A Bromley-based private databook called NUCLEAR has been developed by Fluor Federal Services to eliminate a thermodynamic inconsistency in PUBLIC because of using what is called the "binter" parameter and to incorporate better parameter fits for the aqueous NaNO₂

and NaNO₃ systems. Both the FELMY and NUCLEAR databooks were used and compared in simulating the mixing tests.

For the ESP simulations, analytical data were taken from the reports described below and in Section 2.3 unless otherwise indicated. Analytical data for AN-104 supernatant was taken from Herting (1998). For the AN-102 supernatant, caustic solution was added to the existing tank supernatant after the sample was analyzed, so it was modeled by accounting for the caustic addition. The supernatant caustic content was increased in September 2001 by adding 25,600 gal of 50-weight percent caustic soda solution (19 M NaOH) to 920,000 gal of AN-102 supernatant. This is equivalent to a caustic-to-supernatant volume ratio of approximately 0.028. For the simulation, then, the AN-102 feed stream was diluted with 50-weight percent caustic soda solution by this ratio before it was fed to the mixing process. The relative volumes of the process solutions mixed together for each modeling simulation are given in Figure 2.2.

2.7.2 Stream Analysis

Laboratory data containing the concentrations of analytes in ppm were entered into the ESP Water Analyzer module to prepare the input feed streams for the mixing test processes. All analyzed organic carbon was inputted as oxalate, chromium as $CrO_4^{2^-}$, and silicon as $H_3SiO_4^{-}$, and, whenever concentrations for both S and $SO_4^{2^-}$ or P and $PO_4^{3^-}$ were reported, the average would be entered as $SO_4^{2^-}$ or $PO_4^{3^-}$. The laboratory sample analysis was charge balanced by adjusting the concentration of one or more analytes based on several criteria. Whenever there was an analyzed concentration of free OH⁻ (aqueous) or a pH measurement available, the OH input was adjusted to match the measured value. The specific adjustment criteria for each water analyzer module's input data are as follows:

- AP-101—Input laboratory data were taken from the Urie Characterization Report (Urie et al. 2000). The water analyzer module's composition was reconciled by adjusting carbonate ion $(CO_3^{2^-})$.
- AZ-101—This is the same as sample AZ-A from the leaching experiments conducted by John Geeting at PNWD (Geeting 2002). The input stream from the ESP simulations of the Geeting experiments was used directly.
- AZ-101 LEACHATE—This is the same as sample AZ-G from the leaching experiments conducted by John Geeting at PNWD (Geeting 2002). The input stream from the ESP simulations of the Geeting experiments was used directly.
- AZ-102—Lab data were taken from the SRTC characterization report (Hay 2000). The water analyzer module's composition was reconciled by adjusting the OH⁻ concentration to balance the charges.
- AN-102—Input laboratory data were taken from the Urie Characterization Report (Urie et al. 2002a). The water analyzer module's composition was reconciled by adjusting Na⁺ until the analyzed free OH⁻ concentration was obtained.
- AN-104—The supernatant sample analysis from Herting was used (Herting 1998). Input OH concentration was adjusted to match the measured OH⁻.
- SIMULANT—Input laboratory data were taken from SRTC sample analysis. Reconciliation was achieved by adjusting Na⁺, NO₂⁻, and H⁺ until the analyzed pH of 3.6 was obtained.

- AN-102 WASH—Input laboratory data from Table 2.1 were used. The concentrations used for the water analyzer module's compositions were reconciled by adjusting OH until charges were balanced.
- C-104 WASH—Input laboratory data from Table 2.1 were used. The average of P and PO₄³⁻ analyses was used for PO₄³⁻ (517 mg/L), and since no TIC analysis was available, it was assumed that CO₃⁻² was about the same as PO₄³⁻ (500 mg/L). The original information for the C-104 Wash stream gave the Al concentration as "large," with no value for hydroxide ion, so it was assumed the solution was saturated with Al(OH)₃, and the charges were balanced by adjusting OH while maintaining Al saturation. This gave a predicted OH⁻ concentration of 1.7 M, slightly larger than the value of 1.5 M eventually reported.

After reconciliation, WaterAnalyzer samples in ionic form are distributed to molecular (neutral) species for use in a process simulation. There is a fixed tolerance criterion for element accountability that must be satisfied, and it is not adjustable by the user. When the software chooses species for this distribution, all available OLI databooks are used as sources. Some of the species used from OLI supplied databooks are not found in the FELMY databook, such as acetic acid dimer, citric acid, formic acid dimer, glycolic acid, 2, 2'-Iminobisacetic acid, ammonium hydroxide, oxalic acid, hydrobromic acid, gluconic acid, and molybdenic acid. The elements in the ions were accounted for by converting the ESP distribution species *not* in FELMY to species that *are* in FELMY. Since a few ions families are not available in FELMY, such as oxalic acid and its conjugates, the weight fraction or mole fraction of elements in the FELMY distribution are slightly different than with the OLI distribution, even though the molalities are held constant. In order to compare the FELMY and OLI results, either the water mass or the total stream mass can be keep constant. Since the former is difficult to do in practice, the total stream mass was kept constant as a close approximation.

Table 2.3 summarizes the molar conversions of compounds in the PUBLIC databook to compounds in the FELMY databook.

2.7.3 Mixing Processes

The mixing processes usually contained only one mixing block with the feed streams being the reconciled supernatants and simulant. The total masses of the feed streams were adjusted until the volume ratios summarized in Figure 2.2 were obtained. For simulations that involve AN-102, another mixing block was added to simulate the caustic-solution addition. The caustic-adjusted AN-102 then became the feed stream to the process-heels mixing block.

OLI Compound	Molecular Formula	FELMY Compounds - Moles/Mole OLI					DLI
		H_2O	NaOH	KOH	Ca(OH) ₂	Al(OH) ₃	SiO ₂
K ₂ O	K ₂ O	-1		+2			
KAl ₃ SULFAT	$KAl_3(SO_4)_2(OH)_6$	-4		+1		+3	
Al ₂ (OH) ₅ Cl	Al ₂ (OH) ₅ Cl	-1				+2	
Na ₂ SiO ₃	Na ₂ SiO ₃	-1	+2				+1
ETTRINGITE	$Ca_{6}Al_{2}(SO_{4})_{3}(OH)_{12}*26H_{2}O$	+20			+6	+2	
TRONA	$Na_3(HCO_3)(CO_3)*2H_2O$	-1	+3				
$Na_3HSO_4^2$	$Na_3(HSO_4)(SO_4)$	-3	+3				
H_6F_6	H_6F_6						
NAJAROSITE	$NaFe_3(SO_4)_2(OH)_6$	-1	+1				
HYDMAGNESITE	$Mg_5(OH)_2(CO_3)_4*4H_2O$	-4					
Fe(OH) ₃	[Fe ³⁺](OH) ₃	+1					
OLI Compound	Molecular Formula	FE	LMY C	Compo	unds - Mo	les/Mole (DLI
OLI Compound	Molecular Formula	FE H ₂ C	LMY C O ₃ H ₂ S	'ompo O ₄ HF	unds - Mo FeOOH	les/Mole (Mg(OH) ₂	DLI HCl
OLI Compound K ₂ O	Molecular Formula K ₂ O	FE H ₂ C	LMY C O ₃ H ₂ S	Compo O4 HF	unds - Mo FeOOH	les/Mole (Mg(OH) ₂	DLI HCl
OLI Compound K ₂ O KAl ₃ SULFAT	Molecular Formula K ₂ O KAl ₃ (SO ₄) ₂ (OH) ₆	FE H ₂ C	LMY C O ₃ H ₂ S +2	Compo O ₄ HF	unds - Mo FeOOH	les/Mole (Mg(OH) ₂	DLI HCI
OLI Compound K ₂ O KAl ₃ SULFAT Al ₂ (OH) ₅ Cl	Molecular Formula K ₂ O KAl ₃ (SO ₄) ₂ (OH) ₆ Al ₂ (OH) ₅ Cl	FE H ₂ C	LMY C O ₃ H ₂ S +2	Compo O ₄ HF	unds - Mo FeOOH	les/Mole (Mg(OH) ₂	DLI HCI +1
OLI Compound K ₂ O KAl ₃ SULFAT Al ₂ (OH) ₅ Cl Na ₂ SiO ₃	Molecular Formula K ₂ O KAl ₃ (SO ₄) ₂ (OH) ₆ Al ₂ (OH) ₅ Cl Na ₂ SiO ₃	FE H ₂ C	LMY C D ₃ H ₂ S +2	Compo O ₄ HF	unds - Mo FeOOH	les/Mole (Mg(OH) ₂	DLI HCI +1
OLI Compound K ₂ O KAl ₃ SULFAT Al ₂ (OH) ₅ Cl Na ₂ SiO ₃ ETTRINGITE	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	FE H ₂ C	LMY C D ₃ H ₂ S +2 +3	Compo O ₄ HF	unds - Mo FeOOH	les/Mole (Mg(OH) ₂	DLI HCI +1
OLI Compound K ₂ O KAl ₃ SULFAT Al ₂ (OH) ₅ Cl Na ₂ SiO ₃ ETTRINGITE TRONA	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	FE H ₂ C +2	LMY C O ₃ H ₂ S +2 +2	Compor O4 HF	unds - Mo FeOOH	les/Mole (Mg(OH) ₂	DLI HCI +1
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{tabular}{ c c c c c } \hline Molecular Formula \\ \hline K_2O \\ KAl_3(SO_4)_2(OH)_6 \\ Al_2(OH)_5Cl \\ Na_2SiO_3 \\ \hline Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O \\ \hline Na_3(HCO_3)(CO_3)*2H_2O \\ \hline Na_3(HSO_4)(SO_4) \\ \hline \end{tabular}$	FE H ₂ C +2	LMY C O ₃ H ₂ S +2 +3 +3 +2	20mp0 O4 HF 2	unds - Mo	les/Mole (Mg(OH) ₂	DLI HCI +1
$\begin{tabular}{ c c c c } \hline \textbf{OLI Compound} \\ \hline K_2O \\ \hline KAl_3SULFAT \\ \hline Al_2(OH)_5Cl \\ \hline Na_2SiO_3 \\ \hline ETTRINGITE \\ \hline TRONA \\ \hline Na_3HSO_4^2 \\ \hline H_6F_6 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c } \hline Molecular Formula \\ \hline K_2O \\ \hline KAl_3(SO_4)_2(OH)_6 \\ \hline Al_2(OH)_5Cl \\ \hline Na_2SiO_3 \\ \hline Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O \\ \hline Na_3(HCO_3)(CO_3)*2H_2O \\ \hline Na_3(HSO_4)(SO_4) \\ \hline H_6F_6 \\ \hline \end{tabular}$	FE H ₂ C +2	LMY C O ₃ H ₂ S +2 +2 +3 +2	Compor O4 HF 2 3 3 4 4 5 4 6 4 6	Inds - Mo	les/Mole (Mg(OH) ₂	DLI HCI +1
$\begin{tabular}{ c c c c } \hline \textbf{OLI Compound} \\ \hline K_2O \\ \hline KAl_3SULFAT \\ \hline Al_2(OH)_5Cl \\ \hline Na_2SiO_3 \\ \hline ETTRINGITE \\ \hline TRONA \\ \hline Na_3HSO_4^2 \\ \hline H_6F_6 \\ \hline NAJAROSITE \\ \hline \end{tabular}$	Molecular Formula K_2O $KA1_3(SO_4)_2(OH)_6$ $Al_2(OH)_5Cl$ Na_2SiO_3 $Ca_6Al_2(SO_4)_3(OH)_{12}$ *26H ₂ O $Na_3(HCO_3)(CO_3)$ *2H ₂ O $Na_3(HSO_4)(SO_4)$ H_6F_6 $NaFe_3(SO_4)_2(OH)_6$	FE H ₂ C +2	LMY C O ₃ H ₂ S +2 +3 +2 +2 +2	20mp0 O4 HF 2 2 3 3 2 4 4 6 2 2 4 6 2	Heooh Heooh	les/Mole (Mg(OH) ₂	DLI HCI +1
$\begin{tabular}{ c c c c } \hline \textbf{OLI Compound} \\ \hline K_2O \\ \hline KAl_3SULFAT \\ \hline Al_2(OH)_5Cl \\ \hline Na_2SiO_3 \\ \hline ETTRINGITE \\ \hline TRONA \\ \hline Na_3HSO_4{}^2 \\ \hline H_6F_6 \\ \hline NAJAROSITE \\ \hline HYDMAGNESITE \\ \hline \end{array}$	$\begin{tabular}{ c c c c c } \hline Molecular Formula \\ \hline K_2O \\ \hline KAl_3(SO_4)_2(OH)_6 \\ \hline Al_2(OH)_5Cl \\ \hline Na_2SiO_3 \\ \hline Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O \\ \hline Na_3(HCO_3)(CO_3)*2H_2O \\ \hline Na_3(HSO_4)(SO_4) \\ \hline H_6F_6 \\ \hline NaFe_3(SO_4)_2(OH)_6 \\ \hline Mg_5(OH)_2(CO_3)_4*4H_2O \\ \hline \end{tabular}$	FE H ₂ C +2 +4	LMY C O ₃ H ₂ S +2 +2 +3 +2 +2	20 mp 0 O ₄ HF 2 	Hands - Mo	Hes/Mole (Mg(OH) ₂ +5	DLI HCl +1

Table 2.3. Molar Conversion Summary

2.8 NMR Procedure

2.8.1 General

The NMR instrument used in these studies consisted of a Tecmag three-channel Discovery console and an Oxford Instruments 7.05 Tesla wide-bore superconducting magnet. In this magnet, the Larmor frequencies of the isotopes investigated in this work were as follows: $v(^{1}H) = 300.15$ MHz; $v(^{99}Tc) = 67.57$ MHz; $v(^{31}P) = 121.51$ MHz; $v(^{27}Al) = 78.21$ MHz. All experiments were performed with the same 10-mm two-channel broadband liquids probe (Nalorac). Typical 90° pulse widths were 12.5 μ s for ^{99}Tc , 7.0 μ s for ^{31}P , and 11.0 μ s for ^{27}Al . The sample temperature during NMR experiments was held at 30°C by flowing nitrogen gas thermally regulated by a Kinetics Thermal Systems temperature controller over the NMR tube.

Liquid NMR samples were contained in an 8-mm ID Teflon® sleeve sealed at the top by a Teflon® plug. The plugged sleeve was inserted in a 10-mm-OD glass NMR tube, which was then capped with a screwon top. The liquid volume for all experiments was 2.0 mL. The liquid was not removed from the Teflon® sleeve between NMR measurements during the kinetics studies.

Chemical shift scales were referenced with external standards, which, for ³¹P and ²⁷Al, were 85 percent H_3PO_4 and 0.1 M $[Al(H_2O)_6]^{3+}(aq)$, respectively (Brevard 1981). Standard solutions were prepared in perdeuterated water (D₂O) to facilitate magnet shimming; upon completion of shimming, the magnet lock channel was put in the hold mode for experiments with the process solutions, which could not be locked because of a lack of deuterated solvent. The magnetic field drift in this unlocked state was measured and found to be negligible (<0.0004 ppm/hr). Although the tank solutions could not be individually shimmed, measurements of ¹H and ³¹P linewidths suggest that the magnetic field inhomogeneity in most instances was less than 0.01 ppm.

The ⁹⁹Tc spectra presented are averages of between 2,048 and 20,480 scans. The delay between scans was selected on the basis of relaxation time measurements, which indicated optimal values of between 1 s (for standard solutions) and 200 ms for some of the tank solutions. Similar numbers of scans were acquired for ³¹P spectra, but with longer (\sim 3 s) delays.

2.8.2 Sample Preparation

These radioactive NMR samples were prepared in specialized NMR tubes as required by Radiochemical Processing Laboratory (RPL) procedure RCP-NMRPREP. Liquid samples were pipetted into a Teflon® liner in a fume hood and capped with a solid Teflon® plug. The sample was surveyed and, if no surface contamination was present, removed from the hood. A second glass sleeve was used for secondary containment of the liner as shown in Figure 2.3.

The Preparation of Aqueous ⁹⁹*Tc Standards (in D₂O):* NH₄TcO₄ was freshly prepared by oxidative dissolution of 1 g TcO₂ in 150-mL ammonium hydroxide and 50-mL hydrogen peroxide (30-weight percent aqueous solution). The solution was gently heated until the black solid completely dissolved, and the solution was clear and colorless. The solution volume was evaporated to dryness, and the salt was picked up in a minimum of deionized water with gentle heating. Slow evaporation of the solution yielded large crystallites of NH₄TcO₄. The initial solids were collected, and the solution volume was repeatedly reduced to collect the product. Two further recrystallizations were performed in a similar manner, and 1.28 g of NH₄TcO₄ (100 percent theoretical yield = 1.38 g) was ultimately collected.





Approximately 0.2 g of the solid was dried to constant weight under a heat lamp in a tared 20-mL vial. A solution 0.1022 M in ammonium pertechnetate was generated by dissolving 0.1848 g of the dried material in 10-mL D_2O in volumetric glassware.

This standard solution was diluted by volume with D_2O sequentially in volumetric glassware to obtain a set of standards of varying pertechnetate concentrations. Each standard was checked by beta liquid scintillation counting (LSC) by placing a known amount of solution into an Ultima Gold® liquid scintillation cocktail. The standard molarity values shown in Table 2.4 were used for the calibration curves described below.

Standard Molarity (M)	Expected Activity (dpm/mL)	Observed Activity (dpm/mL)	Observed Molarity (M)	Percent Difference
1.02*10 ⁻¹	3.81E+08	3.50E+08	9.40*10 ⁻²	8.0
1.02*10 ⁻²	3.81E+07	3.72E+07	9.99*10 ⁻³	2.2
1.02*10 ⁻³	3.81E+06	3.58E+06	9.62*10 ⁻⁴	5.8
1.02*10 ⁻⁴	3.81E+05	3.78E+05	1.02*10 ⁻⁴	0.6
3.03*10 ⁻⁵	1.14E+05	1.11E+05	2.98*10 ⁻⁵	2.6
1.02*10 ⁻⁵	3.81E+04	3.70E+04	9.93*10 ⁻⁶	2.7

 Table 2.4.
 Calculated Versus Activity Based ⁹⁹Tc Concentrations in Dilute Aqueous Standard Solutions

Preparation of Aqueous ⁹⁹*Tc Standards in D₂O at High Ionic Strength:* to evaluate any potential impact of ionic strength on the NMR response factor, a series of standards 1×10^{-3} M NH₄TcO₄, but at varying ionic strength, were made in D₂O using 1 M to 6 M sodium nitrate using volumetric dilutions. For example, a 6 M NaNO₃ standard was made in a 5-mL volumetric flask using the 1×10^{-2} M ⁹⁹Tc standard made above. A total of 0.5-mL of the 1×10^{-2} M NH₄TcO₄ standard and 4.16 g NaNO₃ were dissolved in D₂O, and the 5.0-mL volumetric flask was filled to the mark.

3.0 Results

This section explains the formation of solids, the technetium batch contacts with SuperLig® 639, the viscosity measurements, ESP modeling, and NMR studies.

3.1 Solids Formation

The replication of mixing solutions as a result of performing the NMR, batch-contact, and viscosity measurements independently gave multiple opportunities to examine the mixed and individual process solutions for the formation of solids. Table 3.1 summarizes the observation of solids.

Test #	Bulk Solution Study	Viscosity Study	NMR Study
1	No solids noted	No solids noted	No solids noted
2	No solids noted	No solids noted	No solids noted
3	No solids noted	No solids noted	No solids noted
4	No solids noted	No solids noted	No solids noted
5	No solids noted	No solids noted	No solids noted
6	No solids noted	No solids noted	No solids noted
7	No solids noted	Possible white	No solids noted
		colloidal material	
8	White crystalline	White crystalline	White crystalline
	precipitate (0.2718 g)	precipitate	precipitate (trace)
9	White crystalline	White crystalline	White crystalline
	precipitate (0.1234 g)	precipitate	precipitate (trace)
AP-101	Not Examined	No solids noted	Not Examined
AN-102	Not Examined	No solids noted	Not Examined
AZ-101	Not Examined	No solids noted	Not Examined
AZ-102	Not Examined	No solids noted	Not Examined
AN-104	Not Examined	White crystalline precipitate	Not Examined
		Estimated 0.5 g	

Table 3.1. Solids Formation in Process and Mixed Process Solutions

In addition, small amounts of brown solids were observed in Tests 3, 6, and 9. However, the VSL-HLW-SBS simulant itself contains a small amount of brown solids. It is likely that these solids were added directly to the test solutions rather than being generated as a result of process heels mixing. Two observations lead to this conclusion: (1) the VSL-HLW-SBS simulant solids were similar in appearance to the material found in Tests 3, 6, and 9 and (2) these brown solids were observed only for the tests in which the VSL-HLW-SBS simulant was added.

In general, similar observations were made during all examinations of any specific test condition, namely, that appreciable solids generation was observed only for Tests 8 and 9. In the case of the bulk solution studies, where the volumes of mixed solutions were the largest, enough solids precipitated during those

tests to isolate and examine the precipitated solids by ICP-AES to identify metals, by IC to identify anions, and by XRD for phase information concerning any crystalline species generated.

The XRD spectra for the precipitated solids in Tests 8 and 9 appeared identical—the highest signal-tonoise spectrum is shown in Figure 3.1. Unfortunately, the source of the major peaks at a 20 of 13 degrees and at 55 degrees was not identified. Several phases not uncommon to precipitates from tank supernatants were identified, including the ubiquitous sodium nitrate and nitrite, a form of sodium carbonate monohydrate, two fluoride-containing salts, a fluoride/phosphate double salt, $Na_7F(PO_4)_2(H_2O)_{19}$, and a fluoride/sulfate double salt, $Na_3(SO_4)F$. A semi-quantitative treatment indicates the ratios of these materials in the solid to be as follows: sodium nitrate \cong sodium carbonate monohydrate > sodium nitrite > $Na_7F(PO_4)_2(H_2O)_{19} > Na_3(SO_4)F$.

The IC and ICP-AES results (Table 3.2) are consistent with the XRD results. Because the XRD results were identical for the solids in Tests 8 and 9, only one solid was analyzed, the solid from Test 8. The major solids components, Na, P, and F, are also found in the crystalline phases from the XRD analysis. However, the ICP-AES analysis reveals that there is quite a bit more Na compared to the other metals than indicated in the XRD analysis. The IC and XRD results indicate that sodium nitrate and nitrite are present, as typically observed for solids precipitated from tank supernatants. The source of the sodium nitrate or nitrite, i.e., whether it is part of the precipitated solids or was formed by evaporation of interstitial liquid present in the solids, is unknown. However, it is likely, given the high solubility of these compounds in aqueous solution, that they are derived from their presence in the interstitial liquid before drying. However, the XRD analysis provides no insight as to the form of precipitated aluminum and potassium present in the solids, suggesting that these components are present as amorphous solids.

	Concentration	Concentration
	(µg/g ambient	(10° moles/g ambient
Analyte	air-dried solids)	air-dried solids)
Al	29000	1.07E+03
K	4800	1.23E+02
Na	272000	1.18E+04
Р	22000	7.10E+02
nitrate	137000	2.21E+03
nitrite	84000	1.83E+03
phosphate	59000	6.21E+02

 Table 3.2. Major Components in Test 8 Solids as Determined by ICP-AES and IC



Figure 3.1. XRD of Precipitated Solids (Test 8)

3:3

3.2 Technetium Batch Contacts with SuperLig® 639

As noted in the experimental section, bulk mixing tests were set up using approximately 50 mL of the mixed solutions. The process solutions were combined and shaken at 200 rpm for 0.5 hours to mix the component solutions, and 10 mL were removed for duplicate equilibrium Tc batch contacts with SuperLig® 639. The remaining solutions were set aside for at least 1 week, at which time a second sample was removed and the batch-contact measurements repeated. In selected instances, as shown in Table 3.3 and Figure 3.2, the sample was set aside for several more weeks, after which another sample was removed to measure the equilibrium Tc batch contact with SuperLig® 639. The Tc analysis was performed using ICP-MS. Experience revealed that analyzing both the initial and final measurements at the same time was needed to obtain useful results. Table 3.3 and Figure 3.2 summarize the tests performed and the initial and final measurement Tc batch-distribution coefficients.

	Time to		Time to 1 st	First Final	Time to	
	Initial K _d	Initial K _d	Final K _d	K_d	2 nd Final	2 nd Final <i>K_d</i>
Test #	(Days)	(Ave [SD])	(Days)	(Ave [SD])	K _d (Days)	(Ave [SD])
1	0	902 (51)	8	1215 (45)	94	1088 (93)
2	0	1212 (94)	8	1107 (5)	94	1339 (6)
3	0	1286 (93)	8	1016 (32)	94	1236 (83)
4	1	61 (1)	8	67 (12)	59	87 (4)
5	0	62 (4)	7	61 (6)	NM	NM
6	0	96 (7)	7	106(1)	NM	NM
7	1	667 (33)	8	818 (28)	59	663 (38)
8	0	626 (29)	8	666 (69)	NM	NM
9	0	518 (47)	8	614 (33)	NM	NM
AP-101	0	1936 (71)	NA	NA	NA	NA
AN-102	0	17 (3)	NA	NA	NA	NA
AZ-101	0	975 (6)	NA	NA	NA	NA
AZ-102	0	1347 (55)	NA	NA	NA	NA
AN-104	0	978 (159)	NA	NA	NA	NA
NM = Not M	leasured, NA :	= Not Applicable	e, SD = Standa	rd Deviation		
K_d units are 1	mL/g					

Table 3.3. Tc Equilibrium Batch Contact Distribution Values

A key observation from the Tc equilibrium batch-contact measurements is that no large, systematic changes appear to be occurring as a function of time with these mixed-process solutions. The data in the AP-101/AZ-101 systems (Tests 1-3) appear scattered, but no consistent trends can be discerned, and thus it seems likely that these measured changes are indeterminate errors rather than variations reflecting changes in Tc speciation. The AN-102/AZ-102 system (Tests 4–6), which is dominated by the speciation of Tc in the AN-102 supernatant with Tc mostly in a non-pertechnetate form, shows very low distribution values and is unchanged as a function of time. The AN-104/AN-102 system (Tests 7–9) also shows little



Cross Hatched Bars	=	Average Tc distribution values measured immediately after mixing.
Dotted Bars	=	Average Tc distribution values measured approximately 1 week after
		mixing.
Diagonally Lined Bars	=	Diagonally lined bars refer to average Tc distribution values measured 2
		3 months after mixing. One standard deviation of the average Tc

distribution values is represented in red.

to

Figure 3.2. Summary of Tc Equilibrium Batch-Contact Distribution Measurements with SuperLig® 639

change from test to test and as a function of time. It appears, qualitatively, that the observed distribution values in the mixed systems correspond to a weighed contribution of the individual components, suggestive of a static, non-interacting combination of process streams. Most of the AZ-101/AP-101 mixtures appear to have slightly enhanced distribution values compared to the pure AZ-101 component, consistent with a contribution from the much higher distribution values associated with the AP-101 solution. Similarly, the distribution values for the AN-102/AZ-102 mixtures are enhanced slightly from

the pure AN-102 system by the much higher distribution values associated with AZ-102. The AN-104/AN-102 mixtures are decreased from the distribution value found for AN-104 alone by its combination with AN-102, with its very low distribution value. It is unclear *a priori* whether a linear combination of the distribution should be expected because the observed distribution value is a function of the system's fraction of technetium as pertechnetate, the system's nitrate concentration, the system's sodium concentration, and the system's potassium concentration. Finally, a linear combination would imply ideal mixing of the two solutions with no change in technetium speciation. With these caveats, the rough correlation between the relative volumes of process solution and their proportionate K_ds to the measured K_ds appears reasonable.

3.3 Viscosity Measurements

The results of the heel mixing measurements are shown in Table 3.4 and Figure 3.3. All of the mixtures exhibited Newtonian behavior, with good linearity being observed as correlation coefficients in the plots of shear rate (in Pa) versus the shear stress (in 1/sec), which ranged from 0.984 to 1.000. However, some instrument error was observed in the Test 1 duplicate rheogram. For this reason, the reported Newtonian viscosity is based on the first measurement only. In Test 5, instrument error was observed in the ramp-up portion of the rheogram. For this reason, the Newtonian viscosity was calculated on the ramp-down portion of the rheogram. Two key behaviors are apparent: first, no significant change in viscosity was observed after the samples had been allowed to equilibrate for a period between 1 to 4 weeks; second, the viscosity of the process heel solutions uniformly appears to decrease as caustic leach and SBS simulant solutions are added.

	Initial Measurement	≥1 Week Measurement
	Average (SD) Measured	Average (SD) Measured
	Newtonian Viscosity	Newtonian Viscosity
Test #	(in cP)	(in cP)
1	4.2 ^(a)	4.5 (0.1)
2	4.1 (0.1)	3.8 (0.4)
3	3.5 (0.1)	3.3 (0.2)
4	9.6 (0.4) ^(b)	10.0 (0.4)
5	8.4 (0.3)	8.4 (0.9)
6	5.8 (0.2)	6.4 (0.1)
7	19.4 (0.3)	19.6 (0.4)
8	13.2 (1.0)	14.9 (0.3)
9	10.1 (0.2)	10.6 (0.1)
10 (AN-102)	13.6 (0.1)	NP
11 (AZ-102)	1.9 (0.0)	NP
12 (AZ-101)	2.7 (0.0)	NP
13 (AN-104)	9.3 (0.1)	NP
14 (AN-102 wash)	1.3 (0.0)	NP
15 (C-104 wash)	1.7 (0.0)	NP
16 (VSL simulant)	1.1 (0.0)	NP
17 (AZ-101 leach)	2.3 (0.0)	NP

 Table 3.4.
 Summary of Newtonian Viscosity Measurement with Individual and Mixed

 Process Solutions at 25°C

SD = Standard Deviation. (a) Single Measurement – no statistical uncertainty is therefore assigned. (b) Triplicate Measurement. NP = Not Performed (Single Component Solution).



Figure 3.3. Newtonian Viscosity Measurement of Individual and Mixed Process Solutions at 25°C

Dark blue indicates initial measurement; light blue indicates measurement after ≥ 1 week standing. See Table 3.4 and the experimental section for a description of the solution composition associated with each test #.

To evaluate how well the measured viscosity data for these process-heels solutions compared with their expected behavior, we begin with the mixing rule defined below provided by Perry and Green (1997) for estimating the liquid viscosity of defined nonhydrocarbon mixtures:

$$\ln(\eta_m) = \sum_i x_i \ln(\eta_i)$$
(3.1)

where η_m is the Newtonian viscosity of the mixture, x_i is the mole fraction of component *i*, and η_i is the Newtonian viscosity of component *i*.

Perry and Green indicate that errors in using this equation average approximately 15 percent. Because this function is monotonic, the viscosity of the mixture is never predicted to exceed the supremum (i.e., the greatest upper bound) or infimum (i.e., the greatest lower bound) in the set of component viscosities.

This equation was used to calculate the viscosity of the heel mixing samples. The data presented in Table 3.5 were used in these calculations. The average molecular weight of the solutions was calculated using the measured densities for the process solutions (Table 2.2) and the analytical data for the process solutions as described in Table 2.1 and Section 2.7.2.

Component Sample	Sodium Concentration, Molarity	Density at ~ 25°C (g/mL)	Calculated Average Molecular Weight (g/mol)	Newtonian Viscosity at ~25°C (cP)
AN-102	8.00	1.42	22.3	13.6
AN-102 Sr/TRU ppt Alkaline Wash	1.14	1.06	18.5	1.3
AN-104	7.57	1.41	20.1	9.3
AP-101	5.62	1.31	20.7	4.6 ^(a)
AZ-101	4.65	1.25	19.8	2.7
AZ-101 Caustic Leach	2.64	1.15	18.5	2.3
AZ-102	2.77	1.15	19.3	1.9
C-104 Alkaline Wash	1.91	1.10	18.2	1.7
SBS Simulant	0.00633	1.01	18.0	1.1
(a) WTP-RPT-064, Rev A: LAW rheology data at 2	; interpolated from 25°C.	4.9 M, 6 M, 8	M, and 10 M Na AP	-101 pretreated

Table 3.5. Data Used in Viscosity Prediction Calculations

A comparison of the actual-to-predicted viscosities for the AZ-101/AP-101 set of heel mixing tests is shown in Figure 3.4. The actual viscosity of the mixture exceeds the 15-percent error associated with the prediction in all three tests and exceeds the greatest upper-bound value in Tests 1 and 2. This indicates that a phase change has likely occurred, resulting in a significant increase of fluid viscosity. Although no solids were visually observed during these tests, it is possible that colloid solids not visible without magnification could have formed. However, this change is not likely to be significant in any practical sense as the measured viscosities remain relatively low and never exceed the AP-101 component viscosity of 4.6 cP.

A comparison of the actual-to-predicted viscosities for the AN-102/AZ-102 set of heel mixing tests is shown in Figure 3.5. The actual viscosity of the mixture is within the 15-percent error associated with the prediction in all three tests.

A comparison of the actual-to-predicted viscosities for the AN-104/AN-102 set of heel mixing tests is shown in Figure 3.6. The actual viscosity of the mixture exceeds the 15-percent error associated with the prediction in all three tests and exceeds the greatest upper-bound value in Tests 1 and 2. This indicates that a phase change (such as colloid formation or solids precipitation) has likely occurred, resulting in increasing the fluid viscosity significantly. This is consistent with observations of a small amount of white and crystalline-appearing precipitate in the AN-104 sample itself as well solids in the Test 8 and 9 samples. In Test 7, lesser amounts of material, possibly colloidal, were observed as well. When relatively small amounts of more dilute process solutions are added to the mixture, the viscosity drops significantly.





To summarize the key observations in these viscosity measurements:

- The rheology of the AZ-101/AP-101 heel mixing samples indicates Newtonian behavior with viscosity values ranging from 3.3 to 4.5 cP at 25°C, depending on composition. These viscosities fall outside the range of predicted values, indicating possible colloid formation or solids precipitation. However, these results are not significant in practice as the measured viscosities remain relatively low and never exceed 5 cP.
- The rheology of the AN-102/AZ-102 heel mixing samples indicates Newtonian behavior with viscosity ranging from 5.8 to 10.0 cP at 25°C, depending on composition. These viscosities fall inside the range of predicted values.

The rheology of the AN-104/AN-102 heel mixing samples indicates Newtonian behavior with viscosity ranging from 10.1 to 19.6 cP at 25°C, depending on composition. These viscosities fall outside the range of predicted values, indicating possible colloid formation or solids precipitation. This agrees with visual observations of white precipitates in the AN-104/AN-102 heel mixing samples. Although a relatively high fluid viscosity approaches 20 cP for Test 1, when relatively small amounts of dilute secondary wastes are added to the mixture, the viscosity drops significantly.



Figure 3.5. AN-102 and AZ-102 Heel Mixing Test Analysis

3.4 ESP Modeling

Mixing Test 1: AP-101/AZ-101 1:9. AP-101 supernatant itself is initially very high in OH⁻ (3.2 molal) with significant amounts of fluoride. Both the NUCLEAR and FELMY databases predict that the Al in AP-101 is below the saturation concentration but that the solution is saturated with respect to fluoride. The FELMY database predicts that some fluoride should be present as NaF, whereas the NUCLEAR database predicts the double salt (NaFNa₂SO₄). The NUCLEAR database also predicts saturation with respect to sodium oxalate.

For AZ-101 supernatant, the hydroxide is much lower (~ 0.8 m), and both databases predict the presence of significant amounts of aluminum hydroxide precipitate. In fact, approximately half of the total Al in the slurry is predicted to be present in the solid phase (i.e., FELMY predicts 53 percent, NUCLEAR 47 percent). The NUCLEAR database also predicts a small amount of precipitated NaF Na₂SO₄.

Figure 3.6. AN-104 and AN-102 Heel Mixing Test Analysis

The mixed solutions acted as expected; adding the higher hydroxide from AP-101 resulted in an increase in free hydroxide from 0.8 m to about 1.0 m. This higher hydroxide dissolved some of the precipitated Al predicted for AZ-101 itself. The FELMY database predicts that 42 percent of the total Al would now be precipitated, and the NUCLEAR database predicts 34 percent. The results for F and oxalate were also expected; the initially predicted NaF in AP-101 by the FELMY database was dissolved by the AZ-101 addition. However, because the NUCLEAR database predicted some of the double salt NaFNa₂SO₄ in both wastes, this database also predicts NaFNa₂SO₄ formation in the mixture. The precipitated sodium oxalate in AP-101 predicted by the NUCLEAR database was dissolved by contact with the undersaturated AZ-101 slurry.

Mixing Test 2: AP-101/AZ-101/AZ-101 Caustic Leach (1:8:1). This mixing behavior is similar to Mixing Test 1 except for the addition of AZ-101 caustic-leach solution. The AZ-101 caustic-leach solution is higher in free hydroxide (1.9 molal) but is also higher in total aluminum: as a result, this solution also is predicted to be oversaturated with respect to aluminum hydroxides. In fact, using the FELMY database, 70 percent of the aluminum in the AZ-101 caustic-leach solution is predicted to be as a precipitate whereas 53 percent of the aluminum is predicted to be as a precipitate in the AZ-101 solution. Small amounts of the double salt NaFNa₂SO₄ and sodium oxalate are also predicted to be present using the NUCLEAR database, indicating that the solutions are near saturation with respect to fluoride, sulfate, and oxalate.

Mixing Test 3: AP-101/AZ-101/AZ-101 Caustic Leach/Simulant (1:7:1:1). This mixing behavior is similar to Mixing Test 2 except for the addition of the acidic SBS simulant. Adding acid reduces the free hydroxide and results in an even more extensive predicted aluminum hydroxide precipitation. The addition of the simulant also adds Sr to the system, which is then predicted to precipitate as SrCO₃.

Mixing Test 4: AZ-102/Caustic-Adjusted AN-102 (1:9). The AN-102 solution itself is predicted to be oversaturated with respect to several solids. Both the FELMY and NUCLEAR databases predict the precipitation of gibbsite $[Al(OH)_3]$, $Ni(OH)_2$ and $Pb(OH)_2$. The FELMY database predicts the formation of NaF and the removal of small amounts of calcium as pirssonite, $Na_2Ca(CO_3)_2$ -2H₂O. The NUCLEAR database again predicts the presence of small amounts of F and SO₄ precipitates as the double salt NaF Na₂SO₄ and the presence of calcium as hydroxyapatite, $Ca_5(OH)(PO_4)_3$. Hydroxyapatite is known to be insoluble but also very slow to form, so its actual presence in the solutions is unlikely.

The caustic adjustment to AN-102 does not change this situation much, although less aluminum is predicted to be present as precipitate. In the latter case, the FELMY database predicts that 84 percent of the aluminum should be precipitated in the original AN-102, but only 78 percent following caustic addition. The chelate concentrations are an important factor in these simulations. For example, if the amminocarboxylate complexant ethylenediaminetetraacetic acid (EDTA) were present, all of the soluble Ni is predicted to be dissolved as a Ni-EDTA complex. As a result, the tendency for metal hydroxide precipitation will be critically dependent upon the chelate concentrations.

With respect to the AZ-102 solution, the FELMY database predicts that the Al should be completely soluble. The NUCLEAR database predicts that the Al should be right at the gibbsite boundary with only a small amount of precipitate forming. The calcium is predicted to be removed by the formation of calcite $[Ca(CO_3)]$ using the FELMY database whereas it is predicted to be removed as hydroxyapatite using the NUCLEAR database. Small amounts of sodium oxalate are also predicted to form using the NUCLEAR database.

The final mixing of the caustic-adjusted AN-102 with AZ-102 really does not change the above predictions much. For example, the FELMY database still predicts the presence of gibbsite, NaF, and small amounts of Ni(OH)₂, Pb(OH)₂, and pirssonite. Indeed, 80 percent of the Al is predicted to be present as a gibbsite precipitate using the FELMY database.

Mixing Test 5: AZ-102/Caustic-Adjusted AN-102/AN-102 Wash (1:8:1). The mixing in this system is very similar to Mixing Test 4 except that a small amount of AN-102 wash solution was added. The AN-102 wash is predicted to be oversaturated with respect to aluminum hydroxides using both the FELMY and NUCLEAR databases. Therefore, adding AN-102 wash does not reduce the tendency for precipitate formation. The same final precipitates predicted in Mixing Test 4 are predicted in this mixing as well. However, the predicted precipitation of some metal hydroxides, e.g., Ni(OH)₂, is reduced somewhat owing to a dilution effect from the AN-102 wash.

Mixing Test 6: AZ-102/Caustic-Adjusted AN-102/AN-102 Wash/Simulant (1:7:1:1). The mixing of these process solutions is similar to Mixing Test 5 with the addition of a small amount of acidic SBS simulant. The addition of acidic SBS simulant has a similar effect as it did in Mixing Test 3, i.e., increases the

tendency for aluminum hydroxide precipitation and results in the predicted formation of small amounts of SrCO₃.

Mixing Test 7: Caustic-Adjusted AN-102/AN-104 (1:9). AN-104 contains a high free-hydroxide concentration (3.3 m) but also has a very high Al concentration (0.49 m). The result is that this solution is also predicted to be oversaturated with respect to aluminum hydroxides (59 percent of the Al is predicted to precipitate using the FELMY database). AN-102 has already been described previously as being oversaturated in Al. Consequently, the simulation predicts that the mixing of one oversaturated solution with another oversaturated solution results in a third oversaturated solution. The final predicted precipitates are qualitatively the same as in the caustic-adjusted AN-102.

Mixing Test 8: Caustic-Adjusted AN-102/AN-104/C-104 Wash (1:8:1). As found in the previous test simulations, with both databases ESP predicts that caustic adjusted AN-102 solution is saturated with fluoride, nickel, lead, and calcium, and oversaturated with aluminum. The three metals should not be soluble at all, so the analyses are probably in error on the high side. NUCLEAR predicts that some Na_3FSO_4 , $Na_7F(PO_4)_2$ -19H₂O, and oxalate precipitate should be present, while FELMY predicts NaF and a small amount of $Na_2Ca(CO_3)_2$ -2H₂O. The fluoride compound result is likely due to the fluoride analyses, in which the upper limit was reported because of the interference of organic anions like acetate and formate.

The AN-104 solution is predicted to be oversaturated in aluminum with both databases, but NUCLEAR also predicts that a small amount of Na₇F(PO₄)₂-19H₂O and Na₃PO₄-25NaOH-12H₂O solid should be present. With both databases, ESP predicts that about 10 percent of the aluminum should be precipitated in the C-104 Wash solution. In the mixture of all three solutions, ESP predicts with both databases the saturation in nickel, lead, and calcium, and the oversaturation with aluminum, as expected. With the NUCLEAR database, an increase in the amount of precipitated Na₇F(PO₄)₂-19H₂O and dissolution of the Na₃FSO₄ is predicted, while with FELMY, about the same amount of Na₂Ca(CO₃)₂-2H₂O as in the AN-102 solution is predicted. Overall, these results indicate that the AN-102 and AN-104 solutions are at or near saturation with fluoride, phosphate, and possibly sulfate and carbonate.

Mixing Test 9: Caustic-Adjusted AN-102/AN-104/C-104 Wash/Simulant (1:7:1:1). The results of the predictions for Test 9 are not much different than for Test 8, except that a very small amount of strontium precipitate is predicted to be both in the simulant and the final mixture. Since not much simulant solution was added, the dilution effect was minimal.

Conclusions from the ESP simulation: a potential problem identified with respect to the mixing of these solutions is the tendency for aluminum hydroxide precipitation. With the exception of AP-101 supernatant and possibly AZ-102 supernatant, all other process solutions, including the AZ-101 supernatant, the AZ-101 leach solution, the AN-102 supernatant, the AN-102 caustic-adjusted supernatant, the wash solution of the AN-102 Sr/TRU precipitated solids, and the AN-104 supernatant, are predicted to be oversaturated with respect to aluminum hydroxide precipitates. Therefore, any strategy of mixing these initially Al-oversaturated solutions with other Al-oversaturated solutions simply results in another Al-oversaturated solution. Adding the acidic simulant during some of these mixings further exacerbates the problem by reducing the amount of free caustic present in the system.

However, these conclusions are not supported generally by the actual mixing experiments. ESP gave reasonable results for most species, especially in the identification of the precipitated materials as observed by ICP-AES and XRD in Tests 8 and 9, but both databases consistently predicted lower equilibrium aluminum solubility than found experimentally. The two most likely reasons are that (1) the solutions are in general supersaturated, a phenomena known to exist in alkaline solutions or (2) the models are not fully accounting for the increase in solubility with increasing salt concentration. Barney demonstrated the second phenomenon (Barney 1976), but there are still questions regarding his work, specifically with regards to equilibrium of the solids and solutions. ESP predicts increasing solubility with increasing ionic strength with either database, but not sufficiently to predict the experimental results.

It is possible that the initial solutions were in metastable equilibrium with respect to a more soluble phase of aluminum (e.g., amorphous aluminum hydroxide). It is also possible that this is the amorphous aluminum phase that formed in Tests 8 and 9 since such phases tend to have more rapid kinetics of formation than more crystalline phases such as gibbsite. However, such a situation would not eliminate the possibility of formation of the more thermodynamically stable gibbsite phase during processing, especially given the fact that gibbsite is a common phase in tank wastes. Clearly, further studies of the equilibrium and non-equilibrium chemistry of aluminum are needed to determine if the discrepancy between predictions and experiments is an equilibrium or kinetic problem.

Based on the ESP simulations, the process solution mixing that appears most compatible from a thermodynamic standpoint is that of AZ-101/AP-101. Here, the addition of the basic, low aluminum AP-101 supernatant to the oversaturated AZ-101 supernatant reduces the tendency for aluminum hydroxide precipitation.

3.5 NMR Studies

3.5.1 ⁹⁹Tc NMR

Because ⁹⁹Tc NMR measurements on Hanford waste are new, some control experiments were performed to verify that pertechnetate concentration changes indeed could be examined and monitored by this physical method. First, a series of pertechnetate standard solutions were generated in deuterated water based on volumetric dilutions of a known mass of ammonium pertechnetate. The ⁹⁹Tc NMR spectra of these samples were then examined. Figure 3.7 and Table 3.6 summarize the response factor of the instrument as a function of pertechnetate concentration. The response is linear and covers the range of pertechnetate concentrations typically found in Hanford tank supernatants.

Figure 3.7. Plot of NMR ⁹⁹Tc Signal Response Versus Pertechnetate Concentration

 Table 3.6.
 ⁹⁹Tc NMR Response to Standard Aqueous Pertechnetate Solutions (receiver gain = 150)

[TcO ₄ ⁻], M	Average Integral/Scan	95% Confidence Level
0.1	1.29E+05	NA
0.01	1.32E+04	1.40E+01
0.001	1.31E+03	5.16E+00
0.0001	1.35E+02	7.06E+00
0.00003	4.00E+01	4.17E+00
0.00001	1.38E+01	5.66E+00
NA = Not A	vailable	

A second set of experiments indicated that the solution's ionic strength has an impact on the NMR's response factor, all other experimental and instrument parameters being equal. This impact is shown in Table 3.7. However, for the purposes of this study, namely to evaluate changes in pertechnetate concentration in a given solution as a function of time, the varying response of the NMR signal to the solution's ionic strength has no impact because the ionic strength of the solution does not change during any given test as a function of time.

[NaNO ₃], M	Average Integral/Scan	95% Confidence Level
0	1.31E+03	5.16E+00
2	1.16E+03	8.29E+00
5	1.02E+03	2.01E+01

 Table 3.7.
 99 Tc NMR Signal Response to Solution Ionic Strength Changes in a 1 mM Aqueous Ammonium Pertechnetate Solution

It is possible to determine the concentration of the pertechnetate observed in solution using the signal integral integral intensities and correcting for the signal suppression caused by the high ionic strength media. However, to determine how accurately the NMR quantifies the pertechnetate in solution, an accurate pertechnetate concentration must be available. The pertechnetate content of these samples was not measured. An effort was made to use the pertechnetate and technetium concentrations available from alternate sources; however, the available data sets demonstrated a wide range of pertechnetate and total technetium concentrations, making it nearly impossible to evaluate the accuracy of the NMR quantitation.

The linewidths of the pertechnetate signal vary from supernatant to supernatant, the linewidth being narrowest in AZ-101 and broadest in AN-102. Figure 3.8 illustrates the range of observed linewidths. Understanding the source of these linewidth changes is beyond the scope of this work; however, it should be noted that the observed chemical shifts shows little to no change from that of ammonium pertechnetate itself, which provides support for the identification of the signal's source in these tank wastes as pertechnetate.

A summary of the linewidth changes and intensity changes found for the test systems as a function of time are provided in Table 3.8 and Figure 3.9 through Figure 3.12. In NMR measurements, the chemical shift is a sensitive function of the chemical environment experienced by the nucleus. The consistency of the observed chemical shift (a displacement in the absolute observed frequency in the sample from that of a reference solution) with that of pertechnetate itself in an aqueous alkaline solution supports the identification of the signals in the process solutions as pertechnetate. The intensity of this signal has been shown here to accurately reflect changes in solution pertechnetate concentration. Little change in the pertechnetate signal is observed as a function of time in all of the tests. This would suggest a relatively static system, although there is some evidence for a very small increase in pertechnetate concentration for the AN-102-containing solutions. However, the linewidths in these same AN-102-containing solutions show a marked decrease over time, especially during the first week. The linewidth in a nucleus such as pertechnetate is also very sensitive to the environment surrounding the nucleus. Therefore, the observed linewidth changes in the AN-102-containing solutions suggest that the environment experienced by pertechnetate is changing in these mixed process solutions over time. Since the linewidths of other nuclei (such as ¹H) did not change for any individual matrix as a function of time, the linewidth changes described in Table 3.8 must be associated with changes in the Tc chemical environment rather than other possibilities, such as varying homogeneities in the magnetic field. Unfortunately, the pure tank supernatants themselves were not examined to see if they too undergo such changes, so it is unknown whether these changes result from a mixing of AN-102-containing process solution or are a characteristic of the AN-102 itself

Figure 3.8. Plot of NMR ⁹⁹Tc Signals in AZ-101 and AN-102 Supernatants

Test #/Process Solution	Time (Days)	Average Integral/Scans	95% Uncertainty	$\Delta v_{1/2}$ (Hz)
1	0	8.21E+03	1.24E+02	6.8
1	6	8.53E+03	4.03E+02	5.8
1	63	8.15E+03	5.62E+01	8.8
2	0	8.11E+03	9.50E+01	5.8
2	7	8.21E+03	1.25E+02	6.3
2	59	7.72E+03	3.39E+02	5.9
3	0	6.99E+03	2.55E+02	5.9
3	6	7.18E+03	4.37E+02	6.8
3	61	6.88E+03	2.05E+02	4.9
4	0	1.43E+03	4.94E+01	46.0
4	10	1.58E+03	3.44E+01	17.1
4	78	1.65E+03	1.40E+02	15.1
5	0	1.00E+03	1.74E+02	43.9
5	29	1.07E+03	2.11E+02	14.7
6	0	9.85E+02	1.19E+02	45.9
6	22	9.86E+02	4.08E+01	10.8
7	0	4.30E+03	2.03E+02	32.7
7	7	4.39E+03	1.85E+02	26.4
7	8	4.63E+03	3.90E+02	28.8
7	62	4.28E+03	1.54E+02	28.8
8	0	3.78E+03	2.60E+02	48.8
8	37	4.10E+03	1.02E+02	22.5
9	0	2.29E+03	7.43E+01	51.8
9	30	2.47E+03	1.13E+02	15.6
AZ-101	0	1.11E+04	8.51E+01	7.3
AZ-102	0	5.55E+03	2.90E+02	3.4
AN-102	0	1.08E+03	2.05E+02	18.6
AP-101	0	1.23E+03	2.35E+01	7.8
AN-104	0	4.36E+03	6.38E+01	26.0

 Table 3.8. Summary of ⁹⁹Tc NMR Results with Process Solutions

Figure 3.9. Sample of Integral Changes Over Time

Figure 3.10. Summary of Relative Intensity Changes in AP-101/AZ-101 Tests as a Function of Time

Figure 3.11. Summary of Relative Intensity Changes in AZ-102/AN-102 Tests as a Function of Time

Figure 3.12. Summary of Relative Intensity Changes in AN-102/AN-104 Tests as a Function of Time

3.5.2 ²⁷Al and ³¹P NMR

The final test solutions were also examined by ²⁷Al and ³¹P NMR. Table 3.9 summarizes the results of these examinations. The ³¹P NMR spectra in all cases indicate that the vast majority (> 95 percent) of the phosphorus is present as phosphate, based on the multiplicity of the signal and its position (chemical shift), which is sensitive to the specific chemical environment experienced by the nuclei. The ²⁷Al NMR spectra show only one signal in all cases, although the linewidth varies somewhat from test sample to test sample (as does pertechnetate). Contact with AN-102 solution seems to correlate with an increase in the observed linewidth. This correlation is also observed in the ⁹⁹Tc NMR spectra, and it is likely that the explanation is the same. From the chemical shift of the ²⁷Al NMR signal, the environment around the Al atom is tetrahedral (Mason 1987). This is consistent with the expected presence of aluminum in these alkaline solutions as sodium tetrahydroxoaluminate, Na[Al(OH)₄], which has a tetrahedral arrangement of hydroxide anions around a central Al atom.

	³¹ P		²⁷ Al	
Sample/	Chemical Shift	Line Width	Chemical Shift	Line Width
Test #	(Hz)	(Hz)	(Hz)	(Hz)
AP-101	777	2.1	6284	31.8
AZ-101	777	3.0	6285	40
AZ-102	676	6.9	6263	17.1
AN-102	935	3.0	6250	500
AN-104	881	3.8	6256	181
C-104 wash	707	3.0	6252	20
AN-102 wash	685	3.1	6267	25
1	772	3.0	6284	35
2	770	2.8	6278	23
3	762	1.9	6281	24
4	865	3.0	6256	156
5	842	3.0	6238	172
6	816	3.2	6251	106
7	936	1.4	6245	464
8	899	1.8	6235	366
9	819	2.3	6241	221

Table 3.9. Summary of ²⁷Al and ³¹P Chemical Shift and Line Width Measurements

4.0 Conclusions

A series of tests were done on mixed process solutions either currently present in or generated from actual Hanford tank wastes (with one exception, the VSL-HLW-SBS simulant). These tests were designed as a survey to evaluate the likelihood of changes in pertechnetate concentration, the potential of solids formation, and changes in solution viscosity as a function both of the mixing of WTP process solutions and time. The evidence points to little to no change in the pertechnetate concentration in these solutions being induced by the mixing of tank supernatants and process solutions of various sources and compositions. There is evidence, based both on thermodynamic modeling and visual observation, that some of the solutions are close to saturated if not supersaturated in selected elements, and that perturbations of these solutions, such as with process solution mixing, may result in undesirable precipitation of tank materials and increases in solution viscosity.

The ESP modeling indicates that most of the tank supernatants and mixed process solutions examined in the work are saturated to oversaturated in aluminum. Indeed, only AZ-101 and AP-101 are predicted to be undersaturated with respect to Al. However, only in one of the three sets of tests performed with each combination of process solutions (the viscosity measurements) were any precipitates observed for the mixing events modeled by ESP, namely, AN-104 itself and Tests 7 through 9, the mixing of AN-102 with AN-104. This disagreement is of concern and could be due to a number of factors: uncertainties in the analytical data, a flaw in the model, or a discrepancy between the thermodynamic features predicted by the model and kinetic features of the precipitation process. In other words, the solutions indeed are supersaturated; the precipitation events predicted by the model should happen once the barriers to precipitation are removed. The latter explanation is perhaps the most disturbing—this explanation implies that a precipitation event might be induced during WTP operations. If it were to occur in the WTP receipt tanks, it would probably have little impact since the material would be filtered in the next processing step anyway-precipitation events later in processing might be more problematic. In this context, it should be noted that supersaturation of caustic solutions during the Bayer process for alumina production is well known, continues to receive study, and generally requires extensive seeding of the supersaturated solution to promote aluminum hydroxide precipitation (Herting 1984, Gerhartz et al. 1985, Watling et al. 2000, Watling 2000, Panias et al. 2001, Skoufadis et al. 2003).

ESP modeling also predicted the precipitation of fluoride salts and fluoride-containing double salts in systems where no precipitation was observed. Unlike with the Al-precipitation prediction, a likely explanation is available. The fluoride concentrations, as determined by IC, used in the ESP modeling were actually maximum possible concentrations because of the co-elution of interfering species. It is likely that actual fluoride concentrations are less; an overestimation of fluoride concentrations in the input to the ESP modeling is a probable basis for the discrepancy in this instance between prediction and experiment.

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