

# ***Composition and Simulation of Tank WM-180 Sodium-Bearing Waste at the Idaho Nuclear Technology and Engineering Center***

*J. D. Christian*

*April 2001*



*Idaho National Engineering and Environmental Laboratory  
Bechtel BWXT Idaho, LLC*

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**Jerry D. Christian**

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**Idaho National Engineering and Environmental Laboratory  
Idaho Falls, Idaho 83415**

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## **ABSTRACT**

The 1-million liters of sodium-bearing waste in the WM-180 tank at the Idaho Nuclear Technology and Engineering Center has been concentrated and will be the first to be processed, at its current composition, by vitrification to prepare the radioactive waste for disposition. The waste has been sampled and analyzed for cations, anions, and radionuclides in the liquid and in the small amount of solids that were entrained with the liquid during sampling. The analytical results have been evaluated and a non-radioactive simulant composition and preparation procedure developed and demonstrated to result in a clear solution. The evaluation and results are reported here. This simulant is suitable for performing laboratory and pilot-scale tests in order to develop the vitrification technology.

The solids entrained from the tank with the liquid sample amount to 0.06% of the dissolved solids in the liquid. While their elemental and radionuclide composition was determined, qualitative characterization using x-ray diffraction was not possible. Because of the interest in the properties of solids that may be in the bottom of the WM-180 tank, for tank closure activities, thermodynamic modeling was performed of potential precipitates that may be in equilibrium with the solution. The results were used to derive a possible chemical composition of the solids.

# CONTENTS

ABSTRACT.....	iii
1. BACKGROUND AND INTRODUCTION .....	1
2. SAMPLING, ANALYSIS, AND DATA REDUCTION .....	1
2.1 Sampling.....	1
2.2 Liquid Analysis .....	3
2.3 Solids Analysis .....	5
2.4 Data Reduction .....	9
2.4.1 Liquid .....	9
2.4.2 Solids.....	11
2.4.3 Radionuclides.....	13
3. THERMODYNAMIC AND SOLIDS MODELING .....	17
4. SIMULANT PREPARATION .....	21
4.1 Composition Matrix .....	21
4.1.1 Solution Composition.....	21
4.1.2 Electronic Spreadsheet for Solution Makeup.....	24
4.2 Reagents .....	24
4.2.1 Selection of Reagents .....	24
4.2.2 Notes on and Preparation of Specific Reagents .....	25
4.2.3 Radionuclide Standins.....	26
4.2.4 Solids.....	28
4.3 Makeup Procedures .....	29
5. EXPERIMENTAL MAKEUP RESULTS.....	33
6. REFERENCES .....	34

## FIGURES

1. WM-180 Sample Solids Particle Size Distribution.....	8
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## TABLES

1. WM-180 Liquid Sample Analytical Results.....	3
2. WM-180 Solids Sample Analytical Results.....	6
3. WM-180 Liquid Analytical Results Corrected for NCC-102 Heel and NCD-123 Contamination .....	9
4. WM-180 Solids Analytical Results Corrected for Interstitial Liquid Salts .....	11
5. WM-180 Liquid Radionuclide Analytical Results Corrected for NCC-102 Heel and NCD-123 Contamination .....	14
6. Design Basis Fuel Element (DBFE) Total Elemental Masses Relative to Individual Radionuclides .....	15
7. WM-180 Solids Radionuclide Results Corrected for Interstitial Liquid Radionuclides.....	17
8. Estimated Solids Mass Balance Composition.....	20
9. WM-180 Simulant Solution Composition .....	21
10. Properties of Transuranic Cations and Alternative Potential Standins in Glass .....	27

# Composition and Simulation of Tank WM-180 Sodium-Bearing Waste at the Idaho Nuclear Technology and Engineering Center

## 1. BACKGROUND AND INTRODUCTION

The U.S. Department of Energy has committed to the State of Idaho to cease use of the tank farm at the Idaho Nuclear Technology and Engineering Center (INTEC) of the Idaho National Engineering and Environmental Laboratory (INEEL) by 2012. Approximately 4.6 million liters (1.2 million gallons) of radioactive sodium-bearing waste (SBW) is currently contained in the tank farm, distributed over a number of the eleven 1.1 million liter (300,000 gallon) tanks. Sodium-bearing waste is the remaining high-activity liquid waste at the INTEC that must be removed from the underground storage tanks and stabilized into a solid form. It was generated from sodium carbonate scrubbing of the tributyl phosphate extractant used in the separations process, from the second and third cycles of spent nuclear fuel processing, and from decontamination of HLW facilities. That in the WM-180 tank, 1.0 million liters (276,000 gallons) has been concentrated. It will be removed without further change and processed for stabilization and preparation for disposition. The waste in the other tanks, and any future newly-generated liquid waste (NGLW), will be concentrated using the High-Level Liquid Waste Evaporator (HLLWE) and returned to the tank farm prior to processing for final stabilization and disposal. Therefore, the contents of WM-180, as well as being at the final composition for processing, is somewhat representative of future waste compositions in the other tanks after concentration. Furthermore, the contents of WM-180 will be the first removed for processing.

The Department of Energy is currently planning to directly vitrify the liquid wastes into a qualified glass that could be accepted for disposal at the proposed Yucca Mountain repository for spent nuclear fuel and high-level waste. In preparing to process the wastes, laboratory and pilot plant development tests must be performed on liquid compositions that are as nearly identical as possible to the actual tank liquid composition. The tests are for the purpose of developing glass frit formulations and operating procedures, for characterizing the glass and off-gas from the process, and for designing and testing an off-gas treatment system. The WM-180 tank has been sampled and analyzed for elemental cation, anion, and radionuclide concentrations. Initial laboratory and pilot plant process development studies must utilize non-radioactive solutions. Therefore, a non-radioactive simulant formulation has been developed. The basis of and the procedures for preparing the simulant solution are described in this report.

## 2. SAMPLING, ANALYSIS, AND DATA REDUCTION

### 2.1 Sampling

The sampling procedure and analyses are described in detail by Garn.<sup>1</sup> An aliquot of WM-180 solution was transferred to the New Waste Calcining Facility (NWCF) blend-and-hold tank NCC-102 for sampling. Prior to the transfer, the NCC-102 tank contained a 45 gallon heel of 1.6 M  $\text{Al}(\text{NO}_3)_3$ , 1.0 M  $\text{Ca}(\text{NO}_3)_2$  solution (cold feed for the NWCF) that was rinsed with 940 gallons of  $5.5 \pm 0.5$  M  $\text{HNO}_3$  and emptied down to the 45 gallon heel level. The estimated 45 gallon heel composition to which the WM-180 sample content was added was, therefore, estimated to be 5.25 M  $\text{H}^+$ , 0.073 M  $\text{Al}^{3+}$ , 0.046 M  $\text{Ca}^{2+}$ , and 5.56 M  $\text{NO}_3^-$ . Just before the WM-180 transfer took place, approximately 110 gallons of solution from tank NCD-123 (associated with filter leach operations) drained into NCC-102, adding to the 45 gallon rinsed heel. The composition of this solution was 1.6 M  $\text{H}^+$ , 0.027 M  $\text{Al}^{3+}$ ,  $1.82 \times 10^{-4}$  M  $\text{Hg}^{2+}$ ,  $1.54 \times 10^{-6}$  M  $\text{UO}_2^{2+}$ , 0.00260 M  $\text{Cl}^-$ , 0.0268 M  $\text{F}^-$ , 0.00159 M  $\text{SO}_4^{2-}$ ,  $2.95 \times 10^3$  dps/mL  $^{134}\text{Cs}$ ,  $2.16 \times 10^6$

dps/mL  $^{137}\text{Cs}$ ,  $2.43 \times 10^3$  dps/mL  $^{154}\text{Eu}$ , and gross beta activity  $7.37 \times 10^6$  dps/mL. The gross beta activity may be considered to be comprised of  $^{90}\text{Sr}$ ,  $^{90}\text{Y}$ , and  $^{137}\text{Cs}$ . Subtracting the measured  $^{137}\text{Cs}$  activity and dividing the result by two (to account for the fact that the activities of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  are equal) results in a calculated activity of  $^{90}\text{Sr}$  of  $2.10 \times 10^6$  dps/mL. Nitrate was not reported; for charge balance, it is calculated to be  $1.649 \text{ M NO}_3^-$ . The NCD-123 tank contents had previously been transferred to tank WM-187; this transfer uses a line common with the WM-180-to-NCC-102 transfer. It is considered that the 110 gallon drain back cleared that transfer line before the transfer of the WM-180 sample.

Finally, the WM-180 aliquot was steam jetted to NCC-102. The volume received at NCC-102 was 2600 gallons. This included any steam jet dilution, which would have introduced a dilution factor of 1.05 to 1.10. Since this is representative of the dilution of wastes removed from the tank farm for processing, because that will involve steam jetting, the analyzed composition of this 2600 gallon sample is considered to be representative of the solution that will be processed and no correction is made for the steam jet dilution.

WM-180 likely has a few inches of solids on the bottom of the tank, perhaps comparable to what WM-182 has been observed to have by camera inspection (4 inches). The jet leg from which the sample was drawn extends to approximately 3 inches from the bottom of the tank. The liquid, itself, may contain a very small concentration of fine, suspended solids. Therefore, when the liquid sample was drawn, a small amount of suspended and entrained solids was taken with it.

The contents of NCC-102 were well mixed prior to sampling. Therefore, the analyzed composition was corrected as follows.

$$\text{WM-180 Composition (jet-diluted)} = (2755 \times \text{Analytical Result} - 45 \times \text{Heel Composition} - 110 \times \text{NCD-123 Composition}) / 2600 \quad (1)$$

Two types of samples were obtained from NCC-102. A "mixed" or "agitated" sample was taken while the solution in NCC-102 was air sparged. Therefore, any suspended and entrained solids that were transferred from WM-180 with the liquid would have been collected in the analytical sample. They may be expected to generally represent (with some variability) solids that will be in the melter feed stream (prior to any deliberate removal of solids) for the case of not combining the tank bottom solids with the liquid. The second, "settled", sample was taken after the air sparge in NCC-102 had been off for 24 hours to allow any settleable solids to settle and not be sampled. Any solids associated with that sample would be suspended in a fairly "quiescent" state and may generally represent the suspended portion of solids in WM-180 that was withdrawn with the liquid. It was assumed that all solids collected in the samples were WM-180 solids and not solids potentially contributed by the NCD-123 drain back.

The two liquid samples were collected in 1-liter polyethylene bottles and measured 958 and 1020 mLs, respectively, for the mixed and settled samples. Prior to taking aliquots for liquid analysis, these were allowed to settle approximately two weeks. Visual observation indicated that after 2 to 3 days, the solids had quantitatively settled to the bottom of the bottles. After the two week settling period, aliquots of the liquid portions of the samples were placed in a Horiba Instruments Model LA-300 PSD light scattering particle size analyzer that has a 0.1 to 600  $\mu\text{m}$  measurement range. The instrument detected no measurable suspended solids. Therefore, analytical results for the liquid aliquots drawn off the top of the settled samples represent dissolved salts.

## 2.2 Liquid Analysis

The two solution samples were analyzed separately. The results were very similar and were averaged. Metal ions, anions, and radioactive constituents were analyzed. Analysis were done after diluting the aliquots by a factor of 101 in order to perform the analysis outside the shielded Remote Analytical Laboratory hot cell. Metals except sodium and potassium were analyzed using the Inductively Coupled Plasma (ICP) method. Sodium and potassium were analyzed using Flame Atomic Emission Spectroscopy (FLAES). Anions were analyzed using Ion Chromatography (IC). The radioactive constituents were analyzed using gamma scan detection for gamma-emitting isotopes, alpha counting for alpha emitters that were separated using separations columns, and radiochemical specific methods for technetium-99, iodine, tritium, and total strontium.

Results of the liquid sample analyses [uncorrected for the NCC-102 heel and NCD-123 drain-back effects, see Equation (1)] are given in Table 1. Some results include standard deviation errors associated with the analytical method. Errors for ICP and FLAES metal analyses are not reported, but are generally less than  $\pm 5\%$ .<sup>3</sup>

**Table 1.** WM-180 Liquid Sample Analytical Results.<sup>a</sup>

	Agitated solution during sampling	Solution settled 24 hours prior to sampling
ANALYTE	SAMPLE 0BN22	SAMPLE 0BO68
<b>TOTAL COMPOSITION AND PHYSICAL PROPERTIES</b>		
ACID	1.096E+00 +- 8.2E-02 Normal Acid	1.101E+00 +- 8.2E-02 Normal Acid
UDS	0.234 g (solids)/L	0.088 g (solids)/L
TDS	374420 mg (solids)/ L	358720 mg (solids)/ L
SPGR	1.257E+00 +- 1.1E-02 @ 25/4	1.24916E+00 +- 3.9E-04 @ 25/4
<b>METALS<sup>b</sup></b>		
ALUMINUM	1.68373E+07 ug/L	1.70954E+07 ug/L
ANTIMONY	Not Detected: IDL= 7325.621 ug/L	Not Detected: IDL= 7325.621 ug/L
ARSENIC	3.58966E+04 ug/L	3.47281E+04 ug/L
BARIIUM	7.14273E+03 ug/L	7.3053E+03 ug/L
BERYLLIUM	7.11225E+01 ug/L	6.09622E+01 ug/L
BORON	1.25684E+05 ug/L	1.24566E+05 ug/L
CADMIUM	8.12321E+04 ug/L	7.87631E+04 ug/L
CALCIUM	1.84271E+06 ug/L	1.79109E+06 ug/L
CERIUM	6.51279E+03 ug/L	5.99461E+03 ug/L
CESIUM	< 0.970 ug/mL	<0.970 ug/mL
CHROMIUM	1.63074E+05 ug/L	1.65716E+05 ug/L
COBALT	8.4331E+02 ug/L	1.30053E+03 ug/L
COPPER	4.24906E+04 ug/L	4.1058E+04 ug/L
GADOLINIUM	2.70164E+04 ug/L	2.55736E+04 ug/L
IRON	1.15621E+06 ug/L	1.12937E+06 ug/L
LEAD	2.50555E+05 ug/L	2.6041E+05 ug/L
LITHIUM	Not Detected: IDL= 1.8887 ug/ml	2.5553E+00 ug/ml
MAGNESIUM	2.74736E+05 ug/L	2.76971E+05 ug/L



**Table 1.** WM-180 Liquid Sample Analytical Results<sup>a</sup> (continued).

	Agitated solution during sampling	Solution settled 24 hours prior to sampling
ANALYTE	SAMPLE 0BN22	SAMPLE 0BO68
<b>METALS<sup>b</sup> (continued)</b>		
MANGANESE	7.30889E+05 ug/L	7.30889E+05 ug/L
MERCURY	3.66E+02 +- 5.4E+01 ug/ml	4.00E+02 +- 5.4E+01 ug/ml
MOLYBDENUM	1.91218E+04 ug/L	1.57587E+04 ug/L
NICKEL	8.16893E+04 ug/L	8.12829E+04 ug/L
NIOBIUM	Not Detected: IDL= 1361.489 ug/L	Not Detected: IDL= 1361.489 ug/L
PALLADIUM	Not Detected: IDL= 2357.204 ug/L	Not Detected: IDL= 2357.204 ug/L
PHOSPHOROUS	4.06848E+02 ug/ml	3.94294E+02 ug/ml
POTASSIUM <sup>c</sup>	7.13E+03 ug/mL	7.36E+03 ug/mL
RUTHENIUM	5.88285E+03 ug/L	1.79026E+04 ug/L
SELENIUM	Not Detected: IDL= 10891.91 ug/L	Not Detected: IDL= 10891.91 ug/L
SILICON	Not Detected: IDL= 7.9992 ug/ml	Not Detected: IDL= 7.9992 ug/ml
SILVER	Not Detected: IDL= 538.4992 ug/L	Not Detected: IDL= 538.4992 ug/L
SODIUM <sup>c</sup>	4.37E+04 ug/mL	4.56E+04 ug/mL
STRONTIUM	1.06176E+04 ug/L	9.09352E+03 ug/L
SULFUR	2.10201E+03 ug/ml	2.12645E+03 ug/ml
THALLIUM	Not Detected: IDL= 7.8881 ug/ml	Not Detected: IDL= 7.8881 ug/ml
TIN <sup>d</sup>	Not Detected: IDL= 4602.644 ug/L	Not Detected: IDL= 4602.644 ug/L
TITANIUM	2.5553E+00 ug/ml	2.6664E+00 ug/ml
URANIUM	7.74423E+04 ug/L	7.3622E+04 ug/L
VANADIUM	Not Detected: IDL= 44390.17 ug/L	Not Detected: IDL= 436.8956 ug/L
ZINC	6.57172E+04 ug/L	6.37969E+04 ug/L
ZIRCONIUM	5.61868E+03 ug/L	5.27323E+03 ug/L
<b>ANIONS</b>		
CHLORIDE	1.012E+03 +- 2.6E+01 ug/mL	1.002E+03 +- 2.5E+01 ug/mL
FLUORIDE	8.8E+02 +- 2.9E+02 ug/mL	8.6E+02 +- 2.9E+02 ug/mL
NITRATE	4.948E+00 +- 6.5E-02 Molar	4.691E+00 +- 6.5E-02 Molar
PHOSPHATE	1.92689E+02 mg/L	3.54626E+02 mg/L
SULFATE	4.89E+03 +- 2.1E+02 ug/mL	4.91E+03 +- 2.1E+02 ug/mL
<b>RADIOACTIVE CONSTITUENTS</b>		
AM241	3.22E+03 +- 3.6E+02 d/s/ml	2.90E+03 +- 2.8E+02 d/s/ml
CO60	2.05E+02 +- 2.5E+01 d/s/ml	2.18E+02 +- 2.9E+01 d/s/ml
CS134	4.43E+02 +- 4.7E+01 d/s/ml	4.07E+02 +- 4.6E+01 d/s/ml
CS137	1.08E+06 +- 1.2E+05 d/s/ml	1.147E+06 +- 7.4E+04 d/s/ml
EU154	2.36E+03 +- 3.1E+02 d/s/ml	2.18E+03 +- 2.4E+02 d/s/ml
I129	8.86E-01+-1.47E-01d/s/ml	-7.04E+00+-14.37E+00 d/s/ml <sup>e</sup>
NP237	1.65E+01 +- 1.1E+00 d/s/ml	1.66E+01 +- 1.0E+00 d/s/ml

**Table 1.** WM-180 Liquid Sample Analytical Results<sup>a</sup> (continued).

	Agitated solution during sampling	Solution settled 24 hours prior to sampling
ANALYTE	SAMPLE 0BN22	SAMPLE 0BO68
<b>RADIOACTIVE CONSTITUENTS (continued)</b>		
PU238	2.17E+04 +- 1.9E+03 d/s/ml	2.29E+04 +- 2.0E+03 d/s/ml
PU239	3.22E+03 +- 2.9E+02 d/s/ml	3.36E+03 +- 3.1E+02 d/s/ml
TOTAL SR	2.28E+01 +- 2.0E+00 uCi/ml	8.37E+00 +- 7.2E-01 uCi/ml
TC99	3.05E+02+-5.91E-02 d/s/ml	3.89E+02+-5.71E-02 d/s/ml
TRITIUM	2.05E-02 +- 5.4E-03 uCi/ml	2.23E-02 +- 5.7E-03 uCi/ml
U234	4.03E+01+-8.02E+00 d/s/ml	3.89E+01+-7.73E+00 d/s/ml
U235	1.16E+00+-5.38E-01 d/s/ml	1.76E+00+-6.97E-01 d/s/ml
U236	2.26E+00+-8.20E-01 d/s/ml	2.06E+00+-7.50E-01 d/s/ml
U238	9.08E-01+-4.37E-01 d/s/ml	8.24E-01+-3.96E-01 d/s/ml

<sup>a</sup> No attempt has been made to adjust significant figures.

<sup>b</sup> Except where noted, metal results were determined by ICP instrumentation to "within 5%," per the ICP analyst.

<sup>c</sup> Sodium and potassium results were obtained using atomic absorption spectroscopy. No error is reported.

<sup>d</sup> Any tin would come from Zircaloy, which has a w/w Sn/Zr ratio of 0.01479 (atom ratio 0.01137). Therefore, the probable concentrations are: Sample 0BN22 = 83.1 µg/L; Sample 0bO68 = 78.0 µg/L, well below the detection limit. These values may be used as the basis for simulant makeup.

<sup>e</sup> The I-129 result for the Settled Sample was  $-7.04 \pm 14.37$  d/s/mL. It is considered to be zero here and averaged with the Mixed Sample result.

## 2.3 Solids Analysis

The solids were separated from the liquid samples for analysis as follows. Following settling in the 1-liter polyethylene bottles for two weeks, the clear liquid (which contained no solids as determined by the Horiba particle size analyzer) was carefully decanted to near the surface of the settled solids. The bottoms were then agitated and transferred to separate centrifuge tubes for the "agitated" and "settled" liquid aliquot samples from NCC-102. After centrifuging, the supernate above the solids was poured off. Each tared centrifuge tube was weighed at this point; the weights were 311 and 123 mg for the "agitated" and "settled" samples, respectively. The samples were then air dried for eight days and reweighed, yielding results of 295 and 118 mg. Because of the small quantities of solids, they were combined for analysis by transferring them to a crucible. Small losses during transfer were recorded (10 and 7 mg) for corrections to be applied to the results. The combined solids were then heated to 180°C for four hours and reweighed. The weight loss was 95 mg, assumed to be waters of hydration. By apportioning the final dry weight of 301 mg according to the ratio of the original air-dried solids weights, correcting for transfer losses, and dividing each result by the respective sample liquid volume, the result of 0.234 g UDS/L and 0.088 g UDS/L is obtained for the agitated and settled sample, respectively.

This technique, which did not involve washing the solids (either as centrifuged or filtered solids), measures all solids in equilibrium with the original solution, including any precipitates as well material that was introduced into the tank as undissolved material. Any washing might have partially dissolved precipitates; this was avoided.

A small correction is applied to these results to account for the small amount of dissolved salts that were precipitated onto the solids when the residual liquid solution was evaporated from the solids. If one considers that the weight loss during air drying was entirely due to interstitial water in the centrifuged solids, and assumes an oven-dried particle density of 2.0 g/cc, void fractions of 12.5 and 10.0% are calculated for the two samples, with a weighted average of 11.8% estimated. (Significant figures are only

good to 1 or 2 places.) The total dissolved solids (TDS) in the solution (see Section D, Data Reduction) is about 367 g/L. The 12% void solution in the solids corresponds to dissolved salts of approximately 4.1 % of the total mass of weighed oven-dried solids, based on particle density of 2.0 g/cc. Therefore, the corrected UDS concentrations are 0.225g/L and 0.085 g/L. For hydrated (air dried) solids, the corrected concentrations are 0.296 and 0.111 g/L for the agitated and settled sample, respectively. Since the correction is small, and because the contribution of UDS to the overall waste composition is very small (about 0.06% for the agitated sample and 0.02% for the settled sample) the approximations used in the estimates are adequate.

The water lost during oven drying (24 wt%) is consistent with what one would expect for waters of hydration of potential species (see analytical results). The weight % H<sub>2</sub>O in some hydrated species is as follows. Potential precipitates: K<sub>3</sub>H<sub>6</sub>Al<sub>5</sub>(PO<sub>4</sub>)<sub>8</sub>•18H<sub>2</sub>O, 24.2 wt% H<sub>2</sub>O; Al<sub>2</sub>(SO<sub>4</sub>)•18H<sub>2</sub>O, 48.7% H<sub>2</sub>O; Al(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O, 43.2% H<sub>2</sub>O. Potential undissolved process solids: SiO<sub>2</sub>•H<sub>2</sub>O, 23.1 wt% H<sub>2</sub>O. Since a substantial potential component, NaNO<sub>3</sub>, is not hydrated, the mix with some higher percentages of water is reasonable. See Section 3 Thermodynamic and Solids Modeling for further discussion on potential precipitates and projected water content.

The solids were analyzed after applying three fusion methods on the furnace-dried solids. Lithium tetraborate fusion was used in the determination of most metals and radioisotopes. Sodium hydroxide fusion was used in the determination of lithium, boron, and all anions requested except phosphate. Sodium carbonate fusion was used for phosphate analysis. Sodium carbonate is more aggressive towards breaking down difficult phosphate complexes.

The fused samples were dissolved in nitric acid or water. The resultant solutions were analyzed using the same analytical instrumentation as was used for the liquid samples, described previously.

The analytical results for the solids (uncorrected for salts from liquid evaporated in the interstices) are presented in Table 2. The same comments for errors from the liquid analyses apply. The ion chromatography method for determining anions does not have a database to provide bias corrections and, thus, no uncertainties are reported.

**Table 2.** WM-180 Solids Sample Analytical Results.<sup>a</sup>

ANALYTE	0BN23
<b>PHYSICAL PROPERTIES</b>	
avg. PSD	10 micrometers
<b>METALS<sup>b</sup></b>	
ALUMINUM	5.9619E+00 wt%
ANTIMONY	4.09524E-03 wt%
ARSENIC	Not Detected: IDL= 0.000952381 wt%
BARIUM	3.42857E-03 wt%
BERYLLIUM	Not Detected: IDL= 0.0001904762 wt%
BORON	Not Detected: IDL= 0.052 wt%
CADMIUM	1.82857E-02 wt%
CALCIUM	4.42667E-01 wt%
CERIUM	4.38095E-03 wt%
CESIUM	5.24E-02 Wt%

ANALYTE	0BN23
<b>ANIONS<sup>d</sup></b>	
CHLORIDE	9.08777E-01 mg/g
FLUORIDE	1.22383E-0.01 mg/g
NITRATE	4.54667E+02 mg/g
PHOSPHATE	6.5085E+01 mg/g
SULFATE	9.22348E+00 mg/g
<b>RADIOACTIVE CONSTITUENTS</b>	
AM241	1.18E+04 +- 1.1E+03 d/s/g
CO60	1.33E+03 +- 2.6E+02 d/s/g
CS134	9.70E+03 +- 8.0E+02 d/s/g
CS137	9.72E+06 +- 6.3E+05 d/s/g
EU154	1.60E+04 +- 1.3E+03 d/s/g
I129	-6.92E+01+-9.57E+01 d/s/g

**Table 2.** WM-180 Solids Sample Analytical Results<sup>a</sup> (continued).

ANALYTE	0BN23	ANALYTE	0BN23
METALS <sup>b</sup>		RADIOACTIVE CONSTITUENTS	
CHROMIUM	6.92381E-02 wt%	NP237	1.26+E02+/-1.2E+01 d/s/g
COBALT	Not Detected: IDL= 0.00152381 wt%	PU238	3.24E+06 +/- 3.2E+05 d/s/g
COPPER	1.39048E-02 wt%	PU239	4.83E+05 +/- 4.9E+04 d/s/g
GADOLINIUM	8.38095E-03 wt%	Sb125	1.246E+05 +/- 9.5E+03 d/s/g
IRON	2.02E+00 wt%	TOTAL SR	2.31E+06 +/- 2.0E+05 d/s/g
LEAD	5.40952E-02 wt%	TC99	8.96E+02 +/- 7.88E-02 d/s/g
LITHIUM	Not Detected: IDL= 0.016 wt%	U234	1.66E+02+/-4.22E+01 d/s/g
MAGNESIUM	1.4019E-01 wt%	U235	3.42E+00+/-5.38E+00 d/s/g
MANGANESE	1.6181E-01 wt%	U236	6.43E+00+/-8.53E+00 d/s/g
MERCURY	Not Detected: MDL=8930.458 mg/kg	U238	1.46E+00+/-2.35E+00 d/s/g
MOLYBDENUM	3.57143E-02 wt%		
NICKEL	2.81905E-02 wt%		
NIOBIUM	Not Detected: IDL= 1.004 wt%		
PALLADIUM	Not Detected: IDL= 0.076 wt%		
PHOSPHOROUS	5.436E+00 wt%		
POTASSIUM <sup>c</sup>	1.52 wt%		
RUTHENIUM	3.6E-02 wt%		
SELENIUM	Not Detected: IDL= 0.128 wt%		
SILICON	2.092E+00 wt%		
SILVER	4.95238E-03 wt%		
SODIUM <sup>c</sup>	8.12 wt%		
STRONTIUM	2.28571E-03 wt%		
SULFUR	5.19905E-01 wt%		
THALLIUM	Not Detected: IDL= 0.136 wt%		
TIN	2.12E-01 wt%		
TITANIUM	9.59048E-02 wt%		
URANIUM	3.53333E-02 wt%		
VANADIUM	Not Detected: IDL= 0.001333333 wt%		
ZINC	2.0E-02 wt%		
ZIRCONIUM	2.79714E+00 wt%		

<sup>a</sup> Solids were combined from the mixed and settled samples for sample 0BN23. No attempt has been made to adjust significant figures.

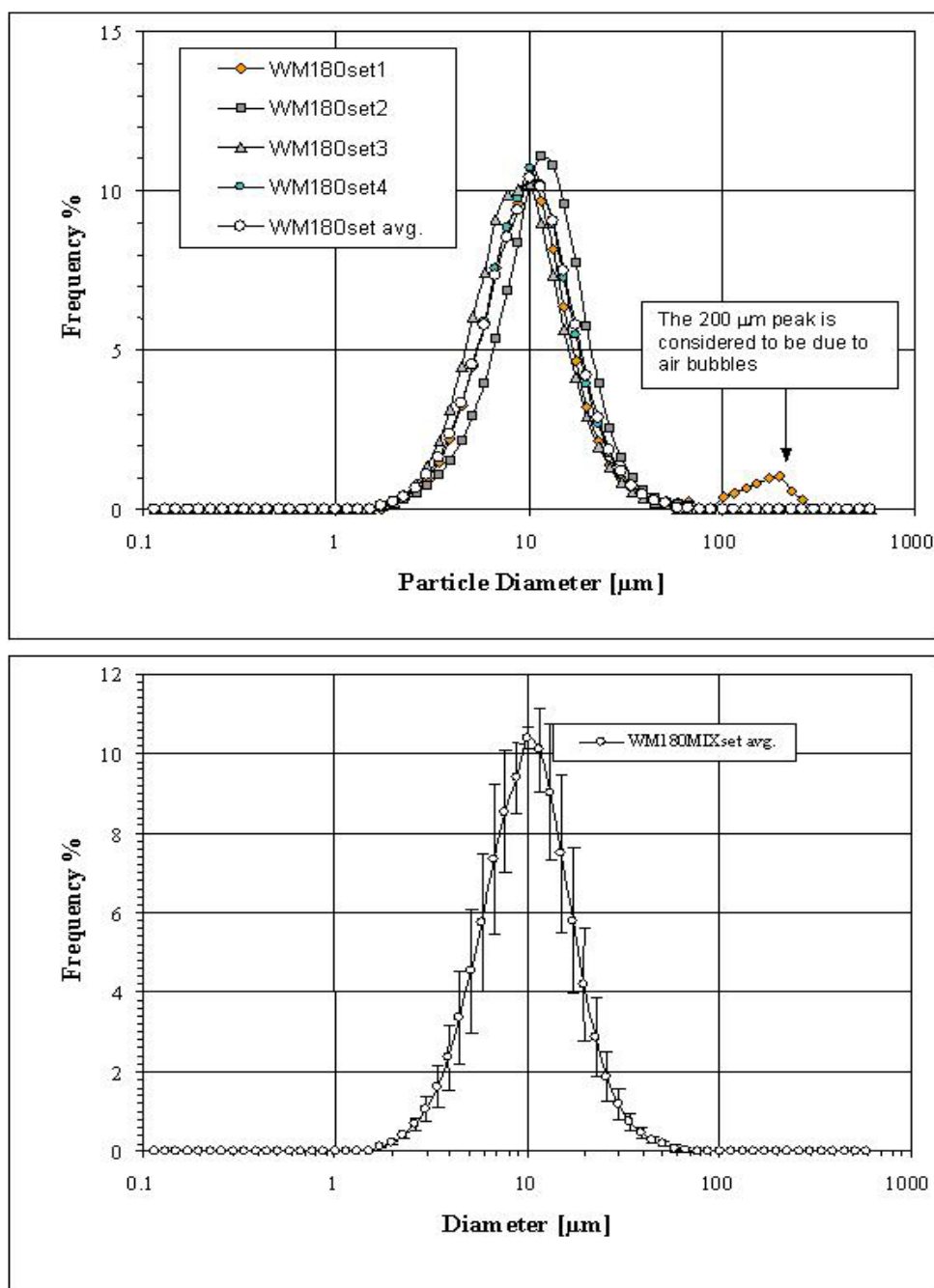
<sup>b</sup> Except where noted, metal results were determined by ICP instrumentation to "within 5%," per the ICP analyst.

<sup>c</sup> Sodium and potassium results were obtained using atomic absorption spectroscopy. No error is reported.

<sup>d</sup> Error values were not reported for anion results.

An attempt was made to obtain an X-ray diffraction (XRD) pattern for the solids. However, there were no discernable peaks. The analyst interpretation is that either there were insufficient solids to obtain a detectable response or the solids were amorphous.

The settled solids from the "agitated" sample were analyzed for particle size distribution using a Horiba LA-300 laser scattering particle size distribution (PSD) analyzer.<sup>2</sup> The particle diameters were normally distributed between 0.2 and 65  $\mu\text{m}$ , with the center of the distribution at 10  $\mu\text{m}$ . The results are depicted in Figure 1.



**Figure 1.** WM-180 Sample Solids Particle Size Distribution.

## 2.4 Data Reduction

### 2.4.1 Liquid

The sulfur and phosphorous results obtained by ICP analysis show greater concentrations than the sulfate and phosphate concentrations obtained by ion chromatographic analyses. The precision between samples is also better for the ICP results, which are considered to be more accurate. Because it is important to represent the total concentrations of these elements in the glass, the ICP results are used to establish the sulfate and phosphate simulant makeup compositions. For phosphorous, the glass form will be  $P_2O_5$ , regardless of its initial solution form. Some might, for example, be present as tri-n-butyl phosphate and as di-butyl phosphate, as well as inorganic phosphate.

The sum of cation and anion mass concentrations, exclusive of the volatile  $HNO_3$ , in the average result of the two raw liquid sample analyses is 314.3 g/L. When  $NO_3^-$  is increased by 0.29 molar to achieve charge balance – see next paragraph (a 6.0% increase in  $NO_3^-$ ), the calculated Total Dissolved Solids (TDS) on an anhydrous basis is 332.2 g/L. The measured TDS in the two samples, obtained by evaporating the solutions to dryness and heating for one hour at 180°C, cooling in a dessicator, and weighing) was 374.4 and 358.7 g/L for the agitated and settled samples, respectively. The average is  $366.6 \pm 7.9$  g/L. Thus, the elemental analyses (corrected to a charge balance) yielded a  $90.6 \pm 2.0$  % mass balance.

The average data from Table 1 for solution cation and anion compositions are corrected for the NCC-102 heel and NCD-123 drain-back [see Equation (1)] in Table 3. As expected, a complete charge balance is not quite obtained when comparing cation and anion results. Therefore, to achieve a charge balance,  $NO_3^-$  is allowed to float when preparing a simulant composition. This results in a 4.7% increase in the nitrate concentration of the corrected composition. This is not unreasonable. Nitrate analysis by ion chromatography may typically be low by that amount. Given the maximum potential standard deviations in individual cation and anion analyses, this agreement is quite remarkable.

**Table 3.** WM-180 Liquid Analytical Results Corrected for NCC-102 Heel and NCD-123 Contamination.

Uncorrected Analytical Results Metals - Average of Mixed & Settled Samples					Heel Composition	NCD-123 Analytical Results		Corrected WM-180 Results
Analyte	Units	Value	Atomic Wt	Molar	Molar	µg/mL	Molar	Molar
TDS	g/L	366.57			0.377 g/L	0.231 g/L		387.81 g/L
Sp.Gr.@25/4		1.2531			1.19 sp. gr.	1.05706		1.2625 sp.gr.
Acid, Normal	Molar	1.099E+00		1.101	5.25		1.60	1.008E+00
Aluminum	ug/L	1.70E+07	26.981538	0.628207332	0.073		0.027	6.633E-01
Antimony	ug/L	< 7.33E+03	121.757	6.01659E-05				6.375E-05
Arsenic	ug/L	3.53E+04	74.9216	0.000471159				4.992E-04
Barium	ug/L	7.23E+03	137.327	5.26116E-05				5.575E-05
Beryllium	ug/L	6.61E+01	9.0122	7.32897E-06				7.766E-06
Boron	ug/L	1.26E+05	10.811	0.011608547				1.230E-02
Cadmium	ug/L	8.00E+04	112.411	0.000711674				7.541E-04
Calcium	ug/L	1.82E+06	40.0780	0.045286691	0.046			4.719E-02

**Table 3.** WM-180 Liquid Analytical Results Corrected for NCC-102 Heel and NCD-123 Contamination (continued).

Uncorrected Analytical Results Metals - Average of Mixed & Settled Samples					Heel Composition	NCD-123 Analytical Results		Corrected WM-180 Results
Analyte	Units	Value	Atomic Wt	Molar	Molar	µg/mL	Molar	Molar
Cerium	ug/L	6.25E+03	140.1160	4.46059E-05				4.727E-05
Cesium	ug/L <	9.70E+02	132.9054	7.29842E-06				7.734E-06
Chromium	ug/L	1.65E+05	51.9961	0.003163699				3.352E-03
Cobalt	ug/L	1.07E+03	58.9332	1.81816E-05				1.927E-05
Copper	ug/L	4.18E+04	63.546	0.000657791				6.970E-04
Gadolinium	ug/L	2.63E+04	157.25	0.00016725				1.772E-04
Iron	ug/L	1.15E+06	55.845	0.020503178				2.173E-02
Lead	ug/L	2.56E+05	207.2	0.001233108				1.307E-03
Lithium	ug/L	2.22E+03	6.941	0.00032022				3.393E-04
Magnesium	ug/L	2.76E+05	24.305	0.011355688				1.203E-02
Manganese	ug/L	7.31E+05	54.9380	0.013305897				1.410E-02
Mercury	ug/L	3.83E+05	200.590	0.001909367		36.6	0.000182462	2.015E-03
Molybdenum	ug/L	1.75E+04	95.94	0.000181885				1.927E-04
Nickel	ug/L	8.15E+04	58.6934	0.001388572				1.471E-03
Niobium	ug/L <	1.36E+03	92.9064	1.46544E-05				1.553E-05
Palladium	ug/L <	2.36E+03	106.4200	2.215E-05				2.347E-05
Phosphorous	ug/L	4.01E+05	30.9738	0.012931913				1.370E-02
Potassium	ug/L	7.25E+06	39.0983	0.185302174				1.963E-01
Ruthenium	ug/L	1.19E+04	101.07	0.000117641				1.247E-04
Selenium	ug/L <	1.09E+04	78.96	0.000137943				1.462E-04
Silicon	ug/L <	8.00E+00	28.0855	2.84816E-07				3.018E-07
Silver	ug/L <	5.38E+02	107.8680	4.9922E-06				5.290E-06
Sodium	ug/L	4.47E+07	22.98977	1.94216819				2.058E+00
Strontium	ug/L	9.85E+03	87.62	0.000112417				1.191E-04
Sulfur	ug/L	2.11E+06	32.066	0.065926527				6.986E-02
Thallium	ug/L <	7.89E+03	204.383	3.85942E-05				4.090E-05
Tin	ug/L <	4.60E+03	118.71	3.87718E-05				4.108E-05
Titanium	ug/L	2.61E+03	47.867	5.45438E-05				5.780E-05
Uranium	ug/L	7.55E+04	237.534	0.000317849		0.3665	1.54294E-06	3.367E-04
Vanadium	ug/L <	4.44E+04	50.9415	0.000871396				9.233E-04
Zinc	ug/L	6.48E+04	65.39	0.000990213				1.049E-03
Zirconium	ug/L	5.45E+03	91.224	5.96882E-05				6.325E-05

**Table 3.** WM-180 Liquid Analytical Results Corrected for NCC-102 Heel and NCD-123 Contamination (continued).

Uncorrected Analytical Results Anions - Average of Mixed & Settled Samples					Heel Composition	NCD-123 Analytical Results		Corrected WM-180 Results
Analyte	Units	Value	Atomic Wt	Molar	Molar	µg/mL	Molar	Molar
Chloride	ug/mL	1.007E+03	35.4527	0.028404043		92	0.002595007	2.999E-02
Fluoride	ug/mL	8.700E+02	18.998403	0.045793322		510	0.026844361	4.739E-02
Nitrate	M	4.8195	62.00494	4.8195	5.56			5.011E+00
Phosphate <sup>a</sup>	mg/L	1228.161405	94.971362	0.012931913				1.370E-02
Sulfate	ug/mL	4.900E+03	96.0636	0.051007874			0.00159	5.398E-02
Sulfate corrected to S <sup>b</sup>		6333.139475	96.0636	0.065926527			0.00159	6.979E-02
Iodide(estd)	M	0.0159	126.90447	1.26E-04				1.299E-04

<sup>a</sup> Based on ICP total phosphorous expressed as phosphate.

<sup>b</sup> Based on ICP total S expressed as sulfate; see text.

## 2.4.2 Solids

The data from Table 2 for solids cation and anion composition are corrected for interstitial solution salts in Table 4. A mass balance of 80.3 percent is obtained when adding the weight percents of cations and anions for the oven-dried solids. Additional mass can come from oxides that may be present in addition to the salts. See Section 3, Thermodynamic and Solids Modeling, for more discussion.

**Table 4.** WM-180 Solids Analytical Results Corrected for Interstitial Liquid Salts.

METALS <sup>a</sup>				
	Corrected Wt %	g-atoms/100 g solids	Valence	Charge
Aluminum	5.846	0.2167	+3	+0.6501
Antimony	0.0040	3.32E-5	+3	+1.0E-4
Arsenic	<7.11E-4	<9.49E-6	+3	<+2.8E-5
Barium	0.0034	2.46E-5	+2	+4.9E-5
Beryllium	<1.90E-4	2.11E-5	+2	+4.2E-5
Boron	<0.0511	<0.00473	+3	<+0.0142
Cadmium	0.0177	1.57E-4	+2	+3.16E-4
Calcium	0.4303	0.0107	+2	+0.0215
Cerium	0.0043	3.10E-5	+3	+9.3E-5
Cesium	0.0524	3.94E-4	+1	+3.92E-4
Chromium	0.0681	0.00131	+3	+0.00393
Cobalt	<0.0015	<2.57E-5	+3	<+7.7E-5
Copper	0.0136	2.14E-4	+2	+4.29E-4
Gadolinium	0.0081	5.17E-5	+3	+1.55E-4
Iron	2.012	0.0360	+3	+0.1081



**Table 4.** WM-180 Solids Analytical Results Corrected for Interstitial Liquid Salts (continued).

METALS <sup>a</sup> (continued)				
	Corrected Wt %	g-atoms/100 g solids	Valence	Charge
Lead	0.0524	2.53E-4	+2	+5.05E-4
Lithium	<0.0160	<0.00231	+1	<+0.00230
Magnesium	0.1383	0.00569	+2	+0.0114
Manganese	0.1568	0.00285	+3	+0.00857
Mercury	<0.8904	<0.00444	+2	<+0.00888
Molybdenum	0.0356	3.71E-4	+6	+0.00223
Nickel	0.0276	4.71E-4	+2	+9.42E-4
Niobium	<1.004	<0.0108	+5	<+0.0540
Palladium	<0.0760	<7.14E-4	+2	<+0.00143
Phosphorous	5.433	0.1754		
Potassium	1.471	0.0376	+1	+0.0376
Ruthenium	0.0359	3.55E-4	+3	+0.00107
Selenium	<0.1279	<0.00162	+4	<+0.00648
Silicon	2.092	0.0745	+4	+0.2979
Silver	0.0049	4.58E-5	+1	+4.58E-5
Sodium	7.816	0.3400	+1	+0.3400
Strontium	0.0022	2.53E-5	+2	+5.06E-5
Sulfur	0.5055	0.0158		
Thallium	<0.1359	<6.65E-4	+3	<+0.00200
Tin	0.2120	0.00179	+4	<+0.00714
Titanium	0.0959	0.00200	+4	+0.00801
Uranium	0.0348	1.46E-4	+4	+5.85E-4
Vanadium	<0.0010	<2.02E-5	+5	+1.01E-4
Zinc	0.0196	2.99E-4	+2	+5.98E-4
Zirconium	2.797	0.0307	+4	+0.1226

Sum Cation Wt%:<sup>b</sup>

23.45 without S and P

Sum of Cation Charges:<sup>b</sup> +1.62425.78 including S and P in excess of anion  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  from I.C.

**Table 4.** WM-180 Solids Analytical Results Corrected for Interstitial Liquid Salts (continued).

ANIONS				
	Corrected Wt %	g-atoms/100 g solids	Valence	Charge
Chloride	0.0909	0.00256	-1	-0.00256
Fluoride	0.0033	1.76E-4	-1	-1.76E-4
Nitrate	43.43	0.7004	-1	-0.7004
Phosphate	6.500 (16.659) <sup>c</sup>	0.0684 (0.1754) <sup>c</sup>	-3	-0.5262 <sup>c</sup>
Sulfate	0.8889 (1.514) <sup>c</sup>	0.00925 (0.0158) <sup>c</sup>	-2	-0.0185 <sup>c</sup>

Sum Anion Wt%: 50.91 (61.70)<sup>c</sup> Sum of Anion Charges: -1.261<sup>c</sup>

Mass balance:<sup>b</sup> 76.7% using  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  by I.C. and ICP total S and P in excess of  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ .

85.2% using cations without S and P and  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  values equivalent to ICP analyses.  
Balance will be oxygen in individual compounds, such as oxides.

Charge balance:<sup>b</sup> +0.697 based on  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  values from I.C. analysis.

+0.363 based on  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  values equivalent to ICP analyses.

Balance will be due to oxygen, such as in oxides.

<sup>a</sup> Includes phosphorous and sulfur.

<sup>b</sup> Excluding species below detection limit.

<sup>c</sup> Based on ICP results for total element S or P

### 2.4.3 Radionuclides

The average radionuclide data in Table 1 for the liquid samples are corrected for the NCC-102 heel and NCD-123 drain-back [see Equation (1)] in Table 5. The results of activity are converted to estimated total elemental molarities as follows. The Fluorinel Design Basis Fuel Element (DBFE) is representative of the average of naval fuels processed at INTEC. The fission and actinide product isotopic compositions for the DBFE have been calculated for fuel that has been out of the reactor for two years.<sup>3</sup> Those associated with the analyzed radionuclide isotopes were tabulated and decayed to 10 and 15 years out of reactor, expressed as masses. The ratio of the sum of the mass of all isotopes of an element to that of the analyzed isotope was then calculated. The results of this tabulation are in Table 6. This factor was used to multiply the mass of the analyzed isotope (derived from its activity) to total mass of the element. The period of 15 years out of reactor was chosen as being representative of the waste that will be processed.

The final results corrected for heels and converted to total elemental molar concentration are given in the last column of Table 5. The total of the individually determined uranium isotopes is  $3.97 \times 10^{-4}$  molar, compared with the elemental uranium analysis result of  $3.37 \times 10^{-4}$  molar. However, the average standard deviation in the isotopic determinations is 47% and the average difference in individual isotope results between the settled and agitated samples is 16%. This compares to approximately 5% estimated standard deviation for the elemental measurement, and the elemental measurement result is used for the simulant composition.

Similar considerations were made for the solids radionuclide results. In this case, the element/radionuclide factor was applied to the analytical results for the isotopes corrected for salts from interstitial solution when the solids were dried. Results are in Table 7.

**Table 5.** WM-180 Liquid Radionuclide Analytical Results Corrected for NCC-102 Heel and NCD-123 Contamination.<sup>a</sup>

Sample Radioactive Constituent					NCD-123 Anal Results	Corrected WM-180 Results		Spec. Activ. g/Ci	Isotope Wt	Corrected Average Values		Calculated Total Element at 15 Yrs Out of Reactor, Molar
		Mixed	Settled	Average		Original Units	Ci/L			Molar	g/L	
Am-241	dps/mL	3.22E+03	2.90E+03	3.06E+03		3.24E+03	8.76E-05	0.291721	241.056823	1.06E-07	2.56E-05	1.077E-07
Co-60	dps/mL	2.05E+02	2.18E+02	2.12E+02		2.24E+02	6.06E-06	0.000959	59.9332	9.69E-11	5.81E-09	9.692E-11
Cs-134	dps/mL	4.43E+02	4.07E+02	4.25E+02	2.95E+03	3.26E+02	8.80E-06	0.0007734	134.9051	5.04E-11	6.80E-09	
Cs-137	dps/mL	1.08E+06	1.15E+06	1.11E+06	2.16E+06	1.09E+06	2.94E-02	0.011552	137.9051	2.46E-06	3.40E-04	7.884E-06
Ba-Total (Calcd)	Molar				Not analyzed. Estimated from Cs decay using ORIGEN II.							9.477E-07
Eu-154	dps/mL	2.36E+03	2.18E+03	2.27E+03	2.43E+03	2.30E+03	6.22E-05	0.003853	153.9209	1.56E-09	2.40E-07	3.123E-08
I-129	dps/mL	8.86E-01	0	4.43E-01		4.69E-01	1.27E-08	5733	128.904989	5.64E-07	7.27E-05	6.368E-07
Np-237	dps/mL	1.65E+01	1.66E+01	1.66E+01		1.75E+01	4.74E-07	1419	237.04803	2.84E-06	6.73E-04	2.837E-06
Pu-238	dps/mL	2.17E+04	2.29E+04	2.23E+04		2.36E+04	6.39E-04	0.058415	238.0495	1.57E-07	3.73E-05	1.343E-06
Pu-239	dps/mL	3.22E+03	3.36E+03	3.29E+03		3.49E+03	9.42E-05	16.119	239.05216	6.35E-06	1.52E-03	8.857E-06
Strontium(total) <sup>b</sup>	uCi/mL	2.28E+01	8.37E+00	1.56E+01	7.04E+01	1.35E+01	1.35E-02	0.007065688	89.9056	1.06E-06	9.56E-05	2.044E-06
Tc-99	dps/mL	3.05E+02	3.89E+02	3.47E+02		3.68E+02	9.94E-06	58.92	98.9064	5.92E-06	5.86E-04	5.920E-06
Tritium	uCi/mL	2.05E-02	2.32E-02	2.19E-02		2.32E-02	2.32E-05	0.000103417	3.01605	2.15E-14	6.47E-14	2.146E-14
U-234	dps/mL	40.3	38.9	3.96E+01		4.20E+01	1.13E-06	160.4	234.0409	7.77E-07	1.82E-04	3.971E-04 <sup>c</sup>
U-235	dps/mL	1.16	1.76	1.46E+00		1.55E+00	4.18E-08	462800	235.04393	8.23E-05	1.94E-02	
U-236	dps/mL	2.26	2.06	2.16E+00		2.29E+00	6.19E-08	1.55E+04	236.04573	4.05E-06	9.56E-04	
U-238	dps/mL	0.908	0.824	8.66E-01		9.18E-01	2.48E-08	2.98E+06	238.0508	3.10E-04	7.38E-02	
Zr-95	dps/mL			0.00E+00		0.00E+00	0.00E+00	4.66E-05	94.9079	Shouldn't be any at 15 yrs.		
Gross beta	dps/mL				7.37E+06 <sup>d</sup>							

<sup>a</sup> Corrected WM-180 Composition = (2755\*Analytical Result - 45\*Heel Composition - 110\*NCD-123 Composition)/2600. There is no NCC-102 heel component for radioactive constituents. Its effect is one of dilution.

<sup>b</sup> The only radioactive fission product strontium in aged waste is Sr-90.

<sup>c</sup> NCD-123 uranium result = 1.55E-6 M; contributes (110/2600)\*1.55E-6 = 6.6E-8 M to WM-180 sample results – negligible. The total elemental result of 3.97E-4 molar obtained from summing the uranium isotopes compares with the uranium elemental analysis of 3.37E-4 molar.

<sup>d</sup> Gross beta is the sum of <sup>90</sup>Sr, <sup>90</sup>Y, and <sup>137</sup>Cs. Normally, there are about equal numbers of curies of each.<sup>25</sup> But, if one has the value for <sup>137</sup>Cs and can subtract it out (as we have here), the remaining beta activity is 50% <sup>90</sup>Sr and 50% <sup>90</sup>Y. Therefore, <sup>90</sup>Sr activity in NCD-123 is calculated to be 7.04E+01 μ/mL.

**Table 6.** Design Basis Fuel Element (DBFE) Total Elemental Masses Relative to Individual Radionuclides. Isotopes in bold were analyzed in WM-180 waste samples.

Isotope	$t_{1/2}$ , yr	DBFE grams at n years out-of-reactor			Total elemental mass/Isotope mass		
		n = 2 yrs <sup>a</sup>	n = 10 yrs	n = 15 yrs	n = 2 yrs	n = 10 yrs	n = 15 yrs
<b>Am-241</b>	432.7	0.656	2.032	2.647	1.064	1.021	1.016
Am-242m	141	0.00446	0.00430	0.00420			
Am-243	7370	0.0376	0.0376	0.0376			
Co-57	0.7441						
<b>Co-60</b>	5.271						
Cs-133	stable	423	423	423			
<b>Cs-134<sup>b</sup></b>	2.065	8.93	0.607	0.113	115.8	1581	8176
Cs-135	2.3E+06	212	212	212			
<b>Cs-137</b>	30.17	390	324.2	288.8	2.651	2.961	3.199
Ba-134	stable		8.232	8.817			
Ba-137	stable	24.0	89.82	125.2			
Ba-137m	3.552 min	6.17E-05	4.96E-05	4.42E-05			
Ba-tot/Cs-tot w/w		0.02321	0.1022	0.1451			
Eu-150	36	—					
Eu-151	stable	0.313	0.313	0.313			
Eu-152	13.48	0.0533	0.0355	0.0275			
Eu-153	stable	21.4	21.4	21.4			
<b>Eu-154</b>	8.59	3.26	1.711	1.143	7.740	13.75	20.05
Eu-155	4.71	0.207	0.0677	0.0336			
I-127	stable	8.36	8.36	8.36			
<b>I-129</b>	1.57E+07	65.0	65.0	65.0	1.129	1.129	1.129
Np-235	1.085	—					
Np-236	1.55E+05	0	0				
<b>Np-237</b>	2.14E+06	96.8	96.82	96.84	1	1	1
Pu-236	2.87	3.69E-05	5.28E-06	1.57E-06			
<b>Pu-238</b>	87.7	9.72	9.13	8.88	8.127	8.434	8.572

**Table 6.** Design Basis Fuel Element (DBFE) Total Elemental Masses Relative to Individual Radionuclides (continued).

Isotope	$t_{1/2}$ , yr	DBFE grams at n years out-of-reactor			Total elemental mass/Isotope mass		
		n = 2 yrs <sup>a</sup>	n = 10 yrs	n = 15 yrs	n = 2 yrs	n = 10 yrs	n = 15 yrs
<b>Pu-239</b>	2.410E+04	54.6	54.6	54.6	1.447	1.410	1.394
Pu-240	6560	9.61	9.60	9.60			
Pu-241	14.4	4.36	2.97	2.33			
Pu-242	3.75E+05	0.706	0.706	0.706			
Pu-244	8.0E+07	—					
Sr-86	stable	0.0267	0.0267	0.0267			
Sr-87	stable	7.43E-06	7.43E-06	7.43E-06			
Sr-88	stable	161	161	161			
Sr-89	0.1383	—					
<b>Sr-90</b>	29.1	238	197	175	1.677	1.819	1.922
Tc-97	2.6E+06	—					
Tc-98	4.2E+06	—					
<b>Tc-99</b>	2.13E+05	302	302	302	1	1	1
Zr-90	stable	27.9	69.2	91.3			
Zr-91	stable	272	272	272			
Zr-92	stable	285	285	285			
Zr-93	1.58E+06	307	307	307			
Zr-94	stable	310	310	310			
Zr-95 <sup>c</sup>	0.1753	0.00640	1.17E-16	3.04E-25	2.37E+05	1.33E+19	5.20E+27
Zr-96	stable	312	312	312			
<b>Sb-123</b>	stable	1.08	1.08	1.08	3.32	18.20	61.00
Sb-125	2.758	0.465	0.0628	0.0180			
Te-122	stable	0.0167	0.0167	0.0167			
Te-125	stable	0.893	1.2943	1.3398			
Te-125m	0.1588	0.0113	0	0			
Te-tot/Sb-tot w/w atoms/atoms					0.596 0.591	1.147 1.127	1.235 1.216

<sup>a</sup> Tabulated for DBFE.

<sup>b</sup> Half-life is too short to be useful.

<sup>c</sup> At 1.2E-16 g/DBFE at 10 yrs out-of reactor, there should not be any <sup>95</sup>Zr detected in the sample.

**Table 7.** WM-180 Solids Radionuclide Results Corrected for Interstitial Liquid Radionuclides.

RADIOACTIVE CONTITUENTS		
	Corrected Ci/g solids	Corrected wt %, <sup>a</sup> g element/100 g solids
Am-241	3.13E-7	9.27E-6
Co-60	3.55E-8	3.41E-9
Cs-134	2.59E-7	
Cs-137	2.61E-4	9.64E-4
Eu-154	4.30E-7	3.32E-6
I-129	0	0
Np-237	3.37E-9	4.79E-4
Pu-238	8.75E-5	4.38E-3
Pu-239	1.30E-5	2.93E-2
Sb-125	3.37E-6	1.94E-5
Total Sr	6.16E-5	8.36E-5
Tc-99	2.35E-8	1.39E-4
U-234	4.31E-9	
U-235	8.88E-11	
U-236	1.67E-10	
U-238	3.79E-11	1.52E-2

<sup>a</sup> Total elemental equivalent.

### 3. THERMODYNAMIC AND SOLIDS MODELING

The solids in the WM-180 tank samples may have originated as insoluble solids in process solutions added and/or as precipitates that formed as different solutions were added together in the tanks or as solution nearly saturated in a slightly soluble salt cooled. While cation and anion compositions were determined for the collected solids, unfortunately, qualitative information in the form of x-ray diffraction patterns could not be obtained. Thus, the specific compounds cannot be directly identified. Two approaches are taken to evaluate the possible chemical species. The first is to model the approximate thermodynamic stability of the solution composition with respect to possible precipitating compounds. The second is to attempt a mass balance calculation for the solids composition by assuming various potential compounds.

To determine whether any identifiable salts may be near or at saturation in the WM-180 solution, the equilibrium composition was modeled with available thermodynamic data in the HSC Chemistry for Windows<sup>®</sup> database.<sup>4</sup> This database includes entries for more than 15,000 substances with data from 823 sources that include many major compilations. Aqueous solution calculations using this (or any free energy minimization software) are only approximate without the input of reliable activity coefficients. While the software has the capability for such input, it does not have a compilation of activity coefficient functions. Calculations without activity coefficients tend to underpredict solubilities in multielectrolyte systems, i.e., may predict precipitate formation at smaller aqueous component concentrations than corresponds to saturation. The presence of diverse salts will generally increase the solubility of precipitates due to the shielding of the dissociated ionic species, decreasing their activities. This effect

can be more than a factor of two. Nevertheless, solution stability calculations can be useful in attempting to understand whether a potential precipitating species is far from or near saturation.

The calculations are also only as good as the comprehensiveness of solid species thermodynamic data. If a potentially precipitating species is not present in the database, it cannot, of course, be predicted to form.

The solution composition in Table 3 was inputted to the HSC program and the equilibrium composition was calculated at 25°C.\* In addition to the HSC database, the Gibbs energy of formation tabulated by Steele et al.<sup>5</sup> for  $\text{NaNO}_3 \bullet \text{Na}_2\text{SO}_4 \bullet 2\text{H}_2\text{O}$  was inputted for the calculations. Also, data available from INEEL<sup>6,7</sup> for aqueous fluoride species that include HF, aluminum fluorides, calcium fluoride, and boron fluorides were incorporated.

In principle, since the input composition was the analyzed solution composition, a stable solution should have been predicted, but see discussion in previous paragraphs. The results indicated that the phosphate in the solution should have quantitatively precipitated as  $\text{Ca}(\text{OH})_2 \bullet \text{Ca}_3(\text{PO}_4)_2$ . Additionally, approximately 68% of the sulfate in solution should have precipitated as  $\text{Al}_2(\text{SO}_4)_3 \bullet 6\text{H}_2\text{O}$ , 73% of the potassium as  $\text{KNO}_3$ , and 15% of the chloride as  $\text{K}_2\text{AlCl}_6$ . This would correlate to 24.4 g precipitate/L in the tank [14.5 g/L  $\text{KNO}_3$ , 7.1 g/L  $\text{Al}_2(\text{SO}_4)_3 \bullet 6\text{H}_2\text{O}$ , 2.6 g/L  $\text{Ca}(\text{OH})_2 \bullet \text{Ca}_3(\text{PO}_4)_2$ , 0.2 g/L  $\text{K}_2\text{AlCl}_6$ ]. For the 276,000 gallon (1,045,000 L) of solution in the 50-foot (1,520-cm) diameter WM-180, this would correspond to a solids depth of approximately 6.7 inches (17 cm), assuming a particle density of  $2.0 \text{ g cm}^{-3}$  and a settled bulk solids void fraction of 0.6. This calculation, of course, is only hypothetical, since these ions are, in fact, analyzed as being in solution. If, in fact, precipitates have formed, one cannot quantitatively estimate how much is present without knowledge of the solution composition prior to the precipitation. Also little can be said about how many undissolved (as opposed to precipitated) process solids may actually be present but not associated with the solution composition.

The  $\text{Ca}(\text{OH})_2 \bullet \text{Ca}_3(\text{PO}_4)_2$  thermodynamic data are rated “Class 3” by HSC, which is very uncertain. It is a curious result that the basic calcium form would form in an acidic solution [ $\text{Ca}(\text{OH})_2$ , while in the HSC calculation, did not form]. If one deletes this species, then another precipitate,  $\text{K}_3\text{H}_6\text{Al}_5(\text{PO}_4)_8 \bullet 18\text{H}_2\text{O}$ ,\* is predicted to remove all the phosphate from solution. The total mass of solids and solids depth calculated remain virtually unchanged.

Since the phosphate is in solution by analysis, the degree of saturation is not clearly known. The species indicated above are potential components of the solids in WM-180. Phosphate is the limiting constituent of the predicted phosphate precipitates. All others are present at excess concentrations.

Regarding the solids phosphate, the calcium is stoichiometrically deficient, only 14% of that required to be associated with phosphate as  $\text{Ca}(\text{OH})_2 \bullet \text{Ca}_3(\text{PO}_4)_2$ . Thus, we consider that

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\* The concentrations in the WM-180 tank are approximately 5 to 10% greater because these analytical results were obtained after jet dilution occurred upon transfer from the tank to the NWCF for sampling. However, they are appropriate for modeling the analyzed solution in contact with the entrained solids.

\* Two sets of thermodynamic parameters are available for this species. They are: J. A. Dean, **Lange's Handbook of Chemistry** Thermodynamic Properties, McGraw-Hill, New York, 1985,  $\Delta H_f^\circ = -4,464.4 \text{ kcal mol}^{-1}$ ,  $S^\circ = 835.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ; M. Kh. Karapetyants, **Chemical Thermodynamics**, MIR Publishers, Moscow, p. 690, 1978,  $\Delta H_f^\circ = -4523.0 \text{ kcal mol}^{-1}$ ,  $S^\circ = 335.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$  (full references given in HSC). Because of the greater entropy, the former predicts greater stability for the solid, but either one predicts precipitation of the species.

$\text{K}_3\text{H}_6\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$  is present in the sampled solids, as well as  $\text{Ca}(\text{OH})_2 \cdot \text{Ca}_3(\text{PO}_4)_2$  in calculating the mass balance.

If all the phosphate in the analyzed solids were in the form of  $\text{Ca}(\text{OH})_2 \cdot \text{Ca}_3(\text{PO}_4)_2$  (consuming all the calcium) plus  $\text{K}_3\text{H}_6\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$ , it would account for 9.1 wt % of all the solids on an anhydrous basis. If the phosphate is based on the phosphorous ICP analysis (which is 2.56 times as much for the solids on a molar basis than phosphate from ion chromatography analysis), some  $\text{AlPO}_4$  and  $\text{FePO}_4$  would have to be added to take up the balance of phosphate, since the calcium and potassium would be insufficient. These four phosphate species would then account for 22% of the dried solids mass. This will be adopted for the phosphate content. When adding in the sulfate calculated as  $\text{Al}_2(\text{SO}_4)_3$ , again on an anhydrous basis, the total calculated mass balance for the dried solids becomes 24% based on ICP results for sulfur and phosphorous expressed as sulfate and phosphate. Clearly, other components are the major constituents of the solids.

Another consideration of the observed solids is to assume potential undissolved oxide solids in addition to the salts associated with the analyzed anions. First, a discussion of the balance of anions is needed. The primary anion is nitrate. Its mole ratio to the sum of cations times their valences (i.e., stoichiometric ratio) is 0.525 and, thus, a majority of the cations must be expressed as nitrate-containing compounds.

Even if the percent voids measured in the solids is increased by a factor of 6 (to make them more consistent with typical void fractions), in order to calculate solution nitrates that were left behind upon drying, the nitrate would still have a stoichiometric ratio of 0.40. The other possibility is that additional solution above the level of the solids was present prior to drying. Again, that might increase the liquid correction to the extent that it would reduce the nitrate stoichiometric ratio in the solids to 0.20 or 0.25. All of this conjecture is also inconsistent with the weight loss upon drying, i.e., it would have had to be much greater than observed.

While HSC does not predict nitrate precipitates, its database contains  $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , but not  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The NBS tabulation<sup>8</sup> lists the standard enthalpy of formation for  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  of  $-897.95 \text{ kcal mol}^{-1}$ , which is  $216.68 \text{ kcal mol}^{-1}$  more negative than for  $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . While no entropy is given, the nonahydrate is likely more stable than the hexahydrate and could form a precipitate. Indeed, the CRC Handbook lists its solubility at  $25^\circ\text{C}$  as 1.70 molal ( $K_{\text{SP}} = 2.88$ ). The product of  $\text{Al}^{3+}$  and  $\text{NO}_3^-$  molal concentrations in the WM-180 solution is 4.79; even if one assumes all the sodium has precipitated nitrate, the remaining nitrate results in a product of 2.91. Therefore, it is probable that aluminum nitrate has precipitated.

The mystery is why so much sodium is found in the solids; sodium molar content is one-half that of nitrate.  $\text{NaNO}_3$  is questionable as a precipitate. The HSC calculation indicates a solubility product at  $25^\circ\text{C}$  of 9.88. The product of  $\text{Na}^+$  and  $\text{NO}_3^-$  molalities in solution is 14.9, which would suggest saturation in the absence of other nitrate salts. However, the CRC Handbook lists  $\text{NaNO}_3$  solubility at  $25^\circ\text{C}$  as 10.8 molal,  $K_{\text{SP}} = 117$ .\*

It should be noted that the HSC calculated solubility in the solution mixture of  $\text{NaNO}_3$  is right at the limit of the measured solution concentration. Any small increase would result in predicted precipitation. Therefore,  $\text{NaNO}_3$  could be in equilibrium with the solution as a precipitate of unknown

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\* The solubility product derived from the solubility is for pure salt in water. The presence of other diverse ions in solution will affect the solubility, but, generally, they would tend to enhance the solubility.



quantity and account for much of the observed solids. It is necessary to adopt this assumption in order to achieve a cation balance against the nitrate.

There may be an unidentified binary or ternary nitrate salt that has limited solubility. While such a salt might also include phosphate or sulfate, it is not likely, because their relative molar amounts are much less than that of nitrate.

The remaining calculation is to assume that cations not associated with phosphate, nitrate, or sulfate are largely oxides, i.e., undissolved material from process solutions. Taking into consideration the above analysis and evaluations, a possible chemical speciation for the solids collected with the WM-180 liquid sample is provided in Table 8. There is a slight imbalance of charge (cations and anions plus oxide) that is accommodated by allowing the phosphate to float (decrease) slightly. The final total phosphorous value is 0.129 moles/100 g solids, compared with 0.175 from the ICP analysis and 0.068 from ion chromatography analysis of phosphate. The mass balance from the composition is 87%.

**Table 8.** Estimated Solids Mass Balance Composition (see text).<sup>a</sup>

Constituent	Moles/100 g dried solids	Wt% of dried solids
NaNO <sub>3</sub>	0.3400	28.90
Al(NO <sub>3</sub> ) <sub>3</sub> <sup>b</sup>	0.1202	25.60
K <sub>3</sub> H <sub>6</sub> Al <sub>5</sub> (PO <sub>4</sub> ) <sub>8</sub> <sup>b</sup>	0.0125	12.77
FePO <sub>4</sub>	0.0360	5.43
SiO <sub>2</sub>	0.0745	4.48
ZrO <sub>2</sub>	0.0303	3.74
AlPO <sub>4</sub>	0.0233	2.85
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> <sup>c</sup>	0.00525	1.80
Ca(OH) <sub>2</sub> •Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	0.00268	1.03
SnO <sub>2</sub>	0.00179	0.269
Ag <sub>2</sub> O	2.29E-5	0.00532
Sb <sub>2</sub> O <sub>3</sub>	1.66E-5	0.00484
TOTAL MASS BALANCE		86.87

<sup>a</sup> Major components and those elements unique to the solids, not detected in liquid. Expressed as the anhydrous equivalent of the actual salt. Total H<sub>2</sub>O content of hydrated species indicated would correspond to 27 wt% H<sub>2</sub>O; this compares favorably with 25 wt% loss during oven drying of the air-dried solids.

<sup>b</sup> Would be present as hydrate in contact with solution: Al(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O; K<sub>3</sub>H<sub>6</sub>Al<sub>5</sub>(PO<sub>4</sub>)<sub>8</sub>•18H<sub>2</sub>O.

<sup>c</sup> Possibly present as hydrate in contact with solution: Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•18H<sub>2</sub>O.

## 4. SIMULANT PREPARATION

### 4.1 Composition Matrix

#### 4.1.1 Solution Composition

The solution composition is compiled in Table 9. The table includes makeup reagents and quantities to prepare 1 liter of synthetic solution that represents the WM-180 composition when steam-jetted to a feed makeup tank. The selection and preparation of reagents is discussed in Section 4.2 below. The table includes species that are below detection limits, specified at the detection limit level. Generally, it is recommended that these not be included in the makeup solution as it is likely that they are, in fact, not present at significant levels. They are included in the matrix only for the cases where a process may be potentially sensitive to the constituent and the researcher may wish to test its effects at the detection limit. Otherwise, those elements that are below detection limit should not be included.

**Table 9.** WM-180 Simulant Solution Composition.

Analyte	Amt of Reagent for		Mol Wt	Units	Form and Notes	Reagent	Moles/L
1	Liter(s)	Units	or Conc'n				
METALS – BULK ELEMENTAL ANALYSIS							
Sp. Gr 4/25						Specific Gravity:	1.2625
Aluminum	3.015E-01	Liter	2.2	M Al <sup>3+</sup>	Solution	Al(NO3)3*9H2O	6.633E-01
Arsenic	4.936E-02	g	197.8414	g/mol		As2O3	2.495E-04
Arsenic	0.000E+00	g	389.7985	g/mol	Alternate Arsenic acid	H5As3O10 <sup>a</sup>	0.000E+00
Barium	1.457E-02	g	261.3398	g/mol		Ba(NO3)2	5.575E-05
Beryllium	3.651E-04	g	47.00898	g/mol		BeF2	7.766E-06
Boron	7.605E-01	g	61.83302	g/mol		H3BO3	1.230E-02
Cadmium	2.326E-01	g	308.48092	g/mol		Cd(NO3)2*4H2O	7.541E-04
Calcium	1.114E+01	g	236.14892	g/mol		Ca(NO3)2*4H2O	4.719E-02
Cerium	2.053E-02	g	434.22638	g/mol		Ce(NO3)3*6H2O	4.727E-05
Chromium	1.100E+00	g	328.0871	g/mol		Cr(NO3)3*5H2O	3.352E-03
Cobalt	5.608E-03	g	291.03468	g/mol		Co(NO3)2*6H2O	1.927E-05
Copper	1.684E-01	g	241.60164	g/mol		Cu(NO3)2*3H2O	6.970E-04
Gadolinium	7.679E-02	g	433.3411	g/mol		Gd(NO3)3*5H2O	1.772E-04
Iron	8.779E+00	g	403.99922	g/mol		Fe(NO3)3*9H2O	2.173E-02
Lead	4.329E-01	g	331.2098	g/mol		Pb(NO3)2	1.307E-03
Lithium	2.339E-02	g	68.9459	g/mol		LiNO3	3.393E-04
Magnesium	3.085E+00	g	256.40648	g/mol		Mg(NO3)2*6H2O	1.203E-02
Manganese	5.046E+00	g solution	178.9478	g/mol	AlfaAesar50% soln	Mn(NO3)2	1.410E-02
Mercury	6.904E-01	g	342.61508	g/mol		Hg(NO3)2*H2O	2.015E-03
Molybdenum	1.927E-03	Liter	0.1	M MoO2(NO3)2 <sup>b</sup>	Soln: see prep notes	Mo in HNO3	1.927E-04
Nickel	4.278E-01	g	290.79488	g/mol		Ni(NO3)2*6H2O	1.471E-03
Potassium	1.983E+01	g	101.1032	g/mol		KNO3	1.962E-01
Ruthenium	2.587E-02	g	207.4281	g/mol		RuCl3	1.247E-04
Ruthenium	0.000E+00	Liter	1.48E-01	molar solution	Alternate: Solution of	Ru(NO)(NO3)3 <sup>c</sup>	0.000E+00
Ruthenium	0.000E+00	g	237.434	g/mol	2 <sup>nd</sup> Alternate for Ru	Ru(NO)Cl3 <sup>d</sup>	0.000E+00
Sodium	1.749E+02	g	84.99467	g/mol		NaNO3	2.058E+00
Strontium	2.521E-02	g	211.6298	g/mol		Sr(NO3)2	1.191E-04

**Table 9.** WM-180 Simulant Solution Composition (continued).

Analyte	Amt of Reagent for		Mol Wt				
	1 Liter(s)	Units	or Conc'n	Units	Form and Notes	Reagent	Moles/L
<b>METALS – BULK ELEMENTAL ANALYSIS</b>							
Titanium	1.096E-02	g	189.6908	g/mol		TiCl4	5.780E-05
Uranium	1.687E-01	g	502.12928	g/mol		UO2(NO3)2*6H2O	3.360E-04
Zinc	3.121E-01	g	297.49148	g/mol		Zn(NO3)2*6H2O	1.049E-03
Zinc	0.000E+00	g	136.2954	g/mol	Alternate: ZnCl2	ZnCl2 <sup>e</sup>	0.000E+00
Zirconium	1.325E-03	Liter	0.05	M ZrF4 in 9.8M HF <sup>f</sup>	Soln:see prep notes	ZrF4	6.625E-05
<b>ANION ANALYSES</b>							
Chloride	2.449E-03	Liter	12	molar solution		HCl	2.938E-02
Fluoride	1.131E-03	Liter	28.9	molar solution		HF <sup>g</sup>	3.268E-02
Fluoride	0.00000	g	48	wt% HBF4 solution	Alternate for F	HBF4 <sup>g</sup>	-5.963E-19
Iodide	2.156E-02	g	166.0028	g/mol		KI	1.299E-04
Nitrate	4.650E-02	Liter	15.4	molar solution		HNO3	7.160E-01
Phosphate	9.384E-04	Liter	14.6	molar solution		H3PO4	1.370E-02
Sulfate	3.877E-03	Liter	18	molar solution		H2SO4	6.979E-02
<b>RADIONUCLIDE ANALYSES AND SIMULANTS.<sup>h</sup></b>							
TOTAL ELEMENTAL CONCENTRATION CALCULATED FROM RADIONUCLIDE ANALYSES.							
Cesium	1.507E-03	g	194.91035	g/mol		CsNO3	7.734E-06
Cesium	1.302E-03	g	168.3582	g/mol	Alternate: CsCl	CsCl	7.734E-06
Europium	1.393E-05	g	446.0705	g/mol		Eu(NO3)3*6H2O	3.123E-08
Rhenium <sup>i</sup>	1.102E-03	Liter	0.00537	M Re, 0.814MHNO3	Aqueous solution of	Re in 5% HNO3	5.920E-06
Neodymium <sup>j</sup>	4.721E-05	g	438.346			Nd(NO3)3*6H2O	1.077E-07
Thorium <sup>k</sup>	2.055E-03	Liter	0.00431	M Th, 0.814MHNO3	Aqueous solution of	Th(NO3)4 in 5% HNO3	8.857E-06
<b>ELEMENTS LOOKED FOR BUT NOT DETECTED<sup>l</sup></b>							
CONCENTRATIONS GIVEN ARE DETECTION LIMITS EXCEPT WHEN INDICATED AS A CALCULATED LIMIT THAT IS LESS THAN THE DETECTION LIMIT. IF ANY OF THESE IS NOT ADDED, ENTER ZERO IN ITS RESPECTIVE CELL IN ROW 70 TO ELIMINATE THE SMALL EFFECT ON CALCULATED ANION CONCENTRATIONS. NOTE VALUE DELETED FOR FUTURE.							
Antimony	1.454E-02	g	228.115			SbCl3	6.375E-05
Niobium (Calcd)	1.443E-03	Liter	0.01076	M Nb, 0.998 M HF	Aqueous solution of	NbCl5 in 2% HF	1.553E-05
Palladium	2.938E-02	g solution	8.5	wt% Pd=7.99E-4 mol/g solution. Solution		Pd(NO3)2	2.347E-05
Selenium	1.155E-02	Liter	0.01266	M Se, 0.814MHNO3	Aqueous solution of	Se in 5% HNO3	1.462E-04
Silicon	8.475E-06	Liter	0.03561	M Si, 0.814MHNO3	Aqueous solution of	Si in 5% HNO3	3.018E-07
Silver	8.986E-04	g	169.873			AgNO3	5.290E-06
Thallium	8.359E-03	Liter	0.004893	M Tl, 0.814MHNO3	Aqueous solution of	Tl in 5% HNO3	4.090E-05
Tin (Calcd) <sup>m</sup>	0.000E+00	g	156.7068			SnF2	0.000E+00
Vanadium	4.704E-02	Liter	0.01963	M V, 0.814MHNO3	Aqueous solution of	V in 5% HNO3	9.233E-04

**Table 9. WM-180 Simulant Solution Composition (continued).**

**FOOTNOTES. Comments include references to spreadsheet use for modifying inputs.**

- <sup>a</sup> If using  $\text{H}_5\text{As}_3\text{O}_{10}$  instead of  $\text{As}_2\text{O}_3$ , delete the value in column L for  $\text{As}_2\text{O}_3$  (cell L10), and enter it in the row for  $\text{H}_5\text{As}_3\text{O}_{10}$  (cell L11) as = L70. The spreadsheet will automatically adjust the reagent additions.
- <sup>b</sup> 0.100 M  $\text{MoO}_2(\text{NO}_3)_2$  in 6.8M  $\text{HNO}_3$ . See prep notes in simulant letter.
- <sup>c</sup> If using  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  solution instead of  $\text{RuCl}_3$ , delete the value in column AK for  $\text{RuCl}_3$  (cell AK31) and enter it in the row for  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  (cell AK32) as =AK70 (the total Ru). Enter the Ru molar concentration of the reagent in cell D32. If the solution contains excess  $\text{HNO}_3$ , enter its molar concentration in cell H82. The spreadsheet will automatically adjust the  $\text{HCl}$  and  $\text{HNO}_3$  additions. Note: If you later go back to  $\text{RuCl}_3$  or  $\text{Ru}(\text{NO})\text{Cl}_3$ , reenter 1E9 in cell D34 and 0 in cell H86). RuNO(NO<sub>3</sub>)<sub>3</sub> solution excess HNO<sub>3</sub> molar concentration: 3
- <sup>d</sup> If using  $\text{Ru}(\text{NO})\text{Cl}_3$  instead of  $\text{RuCl}_3$ , delete the value in column AK for  $\text{RuCl}_3$  (Cell AK31) and enter it in the row for  $\text{Ru}(\text{NO})\text{Cl}_3$  (cell AK33) as = AK70 (the total Ru).
- <sup>e</sup> If using  $\text{ZnCl}_2$  instead of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , delete the value in column AV for  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (cell AV38) and enter it in the row for  $\text{ZnCl}_2$  (cell AV39) as = AV70 (the total zinc). The spreadsheet will automatically calculate mass to add and adjust the other nitrate and chloride balances. Initial HF molarity used for Zr dissolution (total fluoride): 10.00
- <sup>f</sup> If using  $\text{ZrF}_4$  solutions of different  $\text{ZrF}_4$  and HF concentration, enter the new Zr molarity in cell D40. Enter the initial HF concentration into which the Zr was dissolved in cell H90. The new residual HF concentration will be automatically calculated as  $[\text{HF}]_0 - 4 \cdot [\text{Zr}]$  in cell I40. If the solution also contains  $\text{HNO}_3$ , enter its concentration in cell H92. If it contains boric acid, enter the boron concentration in cell H94. HNO<sub>3</sub> molarity in the Zr solution: 0.3 Boron molarity in Zr solution: 0
- <sup>g</sup> If using  $\text{HBF}_4$  solution instead of HF, enter 0 in cell BA43. Enter the wt %  $\text{HBF}_4$  reagent in cell D44 if different from the default 48%. This will recalculate the amount of  $\text{H}_3\text{BO}_3$  to add, line 14. Later, if you return to the use of HF reagent instead of  $\text{HBF}_4$  set cell BA43 = BA71. This will automatically set  $\text{HBF}_4$  to 0 and adjust HF and  $\text{H}_3\text{BO}_3$  appropriately.
- <sup>h</sup> Isotopes and total elemental composition of the following radionuclides are included in and bracketed by the bulk chemical analysis and makeup reagents: Ba, Ce, Co, Gd, I, Mo, Ru, Zr, Sr. Cerium is normally used as a standin for plutonium. Its concentration in the bulk reagents encompasses the plutonium content. Uranium, if added for the bulk uranium content, brackets and may serve as a standin for neptunium.
- <sup>i</sup> Rhenium is a standin for Tc-99.
- <sup>j</sup> Neodymium is a standin for Am(III).
- <sup>k</sup> Thorium is a standin for Pu(IV). The Pu speciation at 100°C is estimated to be 70% Pu(III), 30% Pu(IV). In glass, it will be 100% Pu(IV). IF ONE CANNOT WORK WITH THORIUM, THE CE(IV) FROM CERIUM ADDED FOR THE BULK ANALYZED REAGENTS IS ADEQUATE AND AT SUFFICIENT CONCENTRATION FOR A STANDIN FOR PLUTONIUM. If thorium is NOT added, enter 0 in cell AS70 to eliminate the small effect on calculated nitrate. If you later add thorium, reenter 8.857E-6 in cell AS70.
- <sup>l</sup> Cesium was analyzed for in bulk elemental analyses and not detected at 7.343E-6 M. Calculated total cesium from Cs-137 radiochemical analysis is 7.884E-6 M. The detection limit value is used here for the estimate of cesium and it is included with the radionuclides, above.

Individual researchers may also choose not to include other reagents, for example hazardous substances that are restricted in the laboratory setting.

Sulfate is a key component for consideration in vitrification. It's presence at significant concentrations (i.e., the present concentration for the WM-180 waste) can result in a separate phase formation during vitrification and it poses challenges for the frit formulation. At substantially smaller concentrations, these difficulties can go away. It is important to note here that the WM-180 concentration

of sulfate (either based on the ion chromatography analysis or the ICP analysis of total S) brackets all other waste tank sulfate concentrations, both present and projected from waste concentration operations. Thus, this formulation is a "worst case" for testing sulfate effects and developing vitrification procedures to accommodate it.

#### 4.1.2 Electronic Spreadsheet for Solution Makeup

An Excel spreadsheet of the solution makeup matrix is included on a 3-1/2 inch floppy diskette provided with this report. The spreadsheet is also available as an e-mail attachment from [cdj@inel.gov](mailto:cdj@inel.gov), [jerry@srv.net](mailto:jerry@srv.net), or [alolson@inel.gov](mailto:alolson@inel.gov). The spreadsheet has provisions for the user to input the volume of simulant makeup (in liters) and it will then calculate the quantities of specified reagents needed. The user can choose to eliminate specific components. When this is done, the effect on overall composition must be accounted for and adjusted where necessary. The spreadsheet will enable this to be done by simply entering zero for the molar concentration of the ion being eliminated. This is the blue number in row 70 at the bottom of the spreadsheet, which is the entry value of the analytical result. The spreadsheet will automatically adjust other reagent concentrations to retain the appropriate mass balances. This spreadsheet also provides the user the capability to change the input waste composition; it will then calculate the simulant makeup composition. Thus, for future waste compositions from other tanks or tank waste management scenarios, the spreadsheet can be used to determine the simulant makeup composition.

It is recommended that a copy of the spreadsheet be made and saved under another name before modifying it for a specific use. In this way, the original data and functional form will be preserved.

## 4.2 Reagents

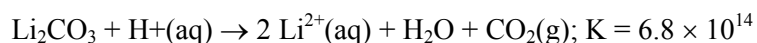
### 4.2.1 Selection of Reagents

In settling on the reagents to use and the makeup procedures, experience was drawn from prior simulant makeups by L. G. Olson and S. H. Hinckley,<sup>9</sup> stock chemicals specified by C. M. Barnes for 1999 SBW glass makeup,<sup>10</sup> and D. R. Peterman's SBW simulant makeup procedures of Feb 21, 2000.<sup>11</sup> For some components, modifications were made to assure correct speciation and dissolution, e.g., for zirconium, molybdenum, and ruthenium as discussed in the notes below.

The contribution of the solids to the overall melter feed composition is trivial and are not considered in the general simulant composition. Except for silicon and traces of antimony, silver, tin, and cesium, they contain the same elemental components as the liquid and the total mass of solids, relative to total dissolved solids in the liquid, is 0.06%. See further discussion in the section on solids below.

In listing reagent chemicals to use in the simulant makeup, available forms were determined from the Alfa AESAR catalog. In a few instances, the spreadsheet accommodates the use of alternative reagents for a component.

Most of the reagents used for the simulant preparation are nitrate salts. For those that are present at very small concentrations, one may judiciously substitute alternative salts. For example  $\text{Li}_2\text{CO}_3$  has been substituted for  $\text{LiNO}_3$  on a molar basis. Since the concentration of  $\text{Li}^{2+}$  is only  $3.39 \times 10^{-4}$  molar, the reaction has negligible effect on the  $\text{H}^+$  and  $\text{NO}_3^-$  concentrations.



#### 4.2.2 Notes on and Preparation of Specific Reagents

1. Arsenic. Thermodynamic calculations (HSC) indicate that arsenic will exist in solution as As(III) in the form of the associated aqueous species  $\text{HAsO}_2$  and  $\text{H}_3\text{AsO}_3$ . Therefore, As(III) hydrolyzes to produce 3  $\text{H}^+$  and the effect on charge remains +3. The available form of arsenic acid is  $\text{H}_5\text{As}_3\text{O}_{10}$ , which is As(V). The trichloride and trifluoride are liquids and could be weighed for adding to the waste simulant solution. According to the CRC Handbook,  $\text{As}_2\text{O}_3$  is soluble in water to 0.046 molar and in HCl; the kinetics of dissolution is not known. Dissolution in  $\text{H}_2\text{O}$  would produce  $\text{HAsO}_2/\text{H}_3\text{AsO}_3$ . Arsenic acid, if used, ought to adjust the valence in the solution.

The INEEL chemical inventory database lists only arsenic oxide. Therefore, the makeup is based on its use. If other reagents as described above are available, they may be substituted with appropriate adjustments to anions or (in the case of arsenic acid)  $\text{H}^+$  (the effect on acid is sufficiently small to be ignored, however). If  $\text{As}_2\text{O}_3$  dissolves with difficulty in  $\text{H}_2\text{O}$ , heat the solution. When it is added to the acid simulant, the dissolution will likely be completed.

2. Boron. Boric acid,  $\text{H}_3\text{BO}_3$ , titrates one mole of base per mole of boron:  $\text{OH}^- + \text{H}_3\text{BO}_3 \rightarrow \text{B}(\text{OH})_4^-$  or  $\text{OH}^- + \text{H}_3\text{BO}_3 \rightarrow \text{BO}_2^- + 2\text{H}_2\text{O}$ . Therefore, its presence increases the  $\text{H}^+$  concentration by boron concentration in the mass balance calculation.
3. Iodine. Iodine was not analyzed. It is estimated from values provided in the C. M. Barnes 1999 SBW average composition, relative to chloride and fluoride. In that composition, I:Cl = 0.0169 w/w; I:F = 0.01733 w/w. Applying these to the average chloride and fluoride concentrations in WM-180 mixed and settled solution results in 0.0170 and 0.0151 g I/L; the average 0.01605 g/l corresponds to  $1.26 \times 10^{-4}$  M I. This value should provide a reasonably representative concentration to use for characterizing the chemistry, flowpath, and distribution of iodine in waste processes. However, for evaluating the actual iodine concentrations in process products, one must recognize that this is an estimate, only.
4. Molybdenum. Molybdenum is amphoteric. It exists as the molybdate ion,  $\text{MoO}_4^{2-}$ , at pH > 6.5. As the solution is acidified, molybdenum makes transitions to polymeric species, e.g.,  $[\text{Mo}_7\text{O}_{24}]^{6-}$ . At pH 0.9, ( $[\text{H}^+] = 0.126$  M), the isoelectric point of molybdic acid is reached, and the neutral species  $\text{H}_2\text{MoO}_4$  precipitates. At lower pH, the molybdenyl cation,  $\text{MoO}_2^{2+}$ , forms. However, as one goes through the isoelectric point, if  $\text{H}_2\text{MoO}_4$  precipitates, experience shows that it is difficult to redissolve. Therefore, rather than dissolving molybdic acid (i.e., molybdate) into nitric acid, our approach is to prepare the molybdenyl species directly by dissolving molybdenum metal in nitric acid.

The dissolution procedure is based on experience. For a 1 L simulant recipe, prepare an excess in order to be able to measure quantities. If desired, you could scale this back to 10 mL. Dissolve 0.9593 g Mo metal in 100 mL 7 M  $\text{HNO}_3$ . If using sponge or solid metal, heat to near boiling (~95-100°C). The dissolution rate will be approximately 36 mg/cm<sup>2</sup>-min (penetration rate 0.21 cm/h). If using powdered Mo, slowly heat until you observe adequate dissolution rate. This will result in a solution of approximately 0.1 M Mo (as  $\text{MoO}_2^{2+}$ ), 6.8 M  $\text{H}^+$ , and 7 M  $\text{NO}_3^-$ . To the 1 L simulant, add 1.819 mL of this stock solution to result in 0.000182 M Mo, added  $\text{H}^+$  of 0.0124 M  $\text{H}^+$ , and added  $\text{NO}_3^-$  of 0.0127 M.

5. Ruthenium. Ruthenium exists in nitric acid solutions as complexes of nitrosyl ruthenium cation,  $\text{Ru}(\text{NO})^{3+}$ , with varying degrees of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{H}_2\text{O}$  species occupying the five coordination positions. Ideally, one would add  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  (either solution or crystalline hydrated salt). Alfa AESAR lists 1.5% w/v ruthenium nitrosyl nitrate solution (presumably 1.5 g Ru per 100 mL) and crystalline  $\text{Ru}(\text{NO})(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , 28% Ru (corresponding to  $x = 2.435$ ). Excess nitric acid for the solution is not specified. Since the INEEL chemical database lists  $\text{RuCl}_3$ , and the chloride associated with the ruthenium is less than the total chloride content of the WM-180 waste, the formulation is based on adding  $\text{RuCl}_3$ . The solution should be allowed to equilibrate for 24 hours so that the ruthenium will be converted to  $\text{Ru}(\text{NO})^{3+}$ . If one has access to the nitrosyl solution or crystal and use it, reduce the number of moles of HCl by 3 times the Ru moles and increase the nitric acid moles by 3 times the Ru moles (actually negligible in both cases). If the solution contains excess nitric acid, adjust the  $\text{HNO}_3$  addition accordingly. The specific procedure for doing so is specified in the footnote of the spreadsheet.
6. Zinc. The primary makeup is based on using  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . However,  $\text{ZnCl}_2$  may be used, if desired. If so, follow the instructions on the makeup spreadsheet so that it will adjust calculations for nitrate and chloride from other species. Specifically, enter 0 for the  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  cell in column AX (cell AX 38) and set the  $\text{ZnCl}_2$  cell in column AX (cell AX 39) equal to AX70 (the total Zn). Then, the spreadsheet will calculate the quantity of  $\text{ZnCl}_2$  to add in place of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and will adjust HCl and  $\text{HNO}_3$  additions for the change.
7. Zirconium. Note that zirconium concentration in WM-180 is very low, more than two orders of magnitude below the typical SBW concentration. The accuracy of makeup is not crucial. Zirconyl nitrate solution could be prepared from dissolving zirconyl carbonate in nitric acid. However, waters of hydration lend uncertainty. The preferred approach is to dissolve zirconium metal (or Zircaloy) in HF as follows. The quantities and concentrations are designed to be compatible with fluoride in the simulant. For the 1 L simulant, dissolve 0.456 g Zr in 100 mL 10 M HF. If using Zircaloy instead of Zr metal, the quantity to weigh is 0.466 g (Zircaloy II) or 0.465 g (Zircaloy IV). The zirconium dissolution will be exothermic and rapid. If using Zircaloy, tin will require heating overnight to effect its dissolution. The concentration of tin in the analyzed WM-180 waste was below the detection limit, but that is compatible with the quantity that would be present from the Zircaloy source of zirconium in the waste. Therefore, including it from the Zircaloy is acceptable.

This will result in a solution that is approximately 0.05 M Zr, 9.8 M  $\text{H}^+$ , and 10 M F. For the 1 L simulant, add 1.194 mL of this stock reagent to result in  $5.97 \times 10^{-5}$  M Zr, added  $\text{H}^+$  of 0.0117

### 4.2.3 Radionuclide Standins

The selection of non-radioactive substitutes for the radioactive species is based on simulating as closely as possible the phase behavior in the vitrified waste. This leads to different selections than if one were to simulate the aqueous behavior. Discussions with J. D. Vienna of PNNL led to the following selections for the transuranics.<sup>22</sup> For the transuranium elements, simulants used for standins are selected to represent the coordination number, valence, and ionic radius of the actinide in glass. Information from Vienna is summarized in Table 10. Data for the properties were taken from Shannon.<sup>12</sup>

**Table 10.** Properties of Transuranic Cations and Alternative Potential Standins in Glass.

Species	Valence	Coordination Number	Crystal Radius
<b>Am in glass</b>	<b>(III)</b>	<b>6</b>	<b>1.115</b>
Eu	(III)	6	1.086
Nd	(III)	6	1.123
Sm	(III)	6	1.098
<b>Pu in glass</b>	<b>(IV)</b>	<b>8</b>	<b>1.10</b>
Hf	(IV)	8	0.97
Th	(IV)	8	1.19
Ce	(IV)	8	1.11
Ce	(III)	8	1.283
<b>Np in glass</b>	<b>(V)</b>	<b>6</b>	<b>0.89</b>
U	(V)	6	0.90
U	(IV)	6	1.03
U	(VI)	6	0.87

#### 4.2.3.1 Americium

Both Eu(III) and Nd(III) have been used for standins for Am(III) in aqueous solutions. Choppin<sup>13</sup> suggests Eu(III). Recently, Felmy and Rai<sup>14</sup> determined that the  $\text{Nd}^{3+} - \text{Cl}^-$  Pitzer ion interaction parameters were successful in representing  $\text{Pu}^{3+} - \text{Cl}^-$  and, thus, is a suitable standin for An(III) ions. The fact that the Nd(III) ion size is closer to that of Pu(III) than is Eu(III) and that it cannot be oxidized to the (IV) state favors the use of Nd(III) as a standin for Am(III) in glass.

#### 4.2.3.2 Plutonium

Plutonium exists as Pu(IV) in glass. Hafnium provides the closest simulant for plutonium in terms of solubility in glass. However, the glass from WM-180 waste solution will be much below saturation in plutonium and solubility is not an issue. Ce(IV) is the more suitable overall simulant for Pu(IV), based on its ionic radius. However, the cerium oxidation state in glass is distributed approximately 50:50 between Ce(III) and Ce(IV).<sup>15</sup> Thorium is also a good simulant for Pu(IV) in terms of radius, and it only exists in the (IV) state. Thus, if one can work with the slightly radioactive thorium, Th(IV) is the substitute of choice for plutonium. However, if one is not able to work with thorium, cerium may be substituted by doubling its concentration over the plutonium concentration, on a molar basis. Its behavior and distribution in the glass can be used as an indicator for plutonium. The Ce(III) that forms is acceptable, given that the waste contains cerium at a molar concentration approximately 20 times the plutonium concentration, by calculation. By measurement in the WM-180 waste, the concentration ratio is 5.3. Since cerium is added already at the bulk analysis concentration, it is not necessary to add any more for plutonium substitute.

#### 4.2.3.3 Neptunium

Neptunium forms Np(V) in glass. In aqueous solutions, Np(V) is the most suitable standin for An(V) species, in general. The most suitable substitute for Np(V) in glass, otherwise, is U(V) according to Vienna. However, no U(V) oxide exists in thermodynamic databases. Those listed are  $\text{UO}$ ,  $\text{UO}_2$ ,



U<sub>4</sub>O<sub>9</sub>, U<sub>3</sub>O<sub>7</sub>, U<sub>3</sub>O<sub>8</sub>, and UO<sub>3</sub>. U(VI) has suitable properties, as well. Uranium will be converted to the prevailing stable oxide when vitrified. In air, U<sub>3</sub>O<sub>8</sub> is the stable form at glass temperature; in the presence of a reducing agent, such as FeO, it is reduced to UO<sub>2</sub>. Thus, uranium may be present as a mixture of U(+5.33) and U(+4), no matter what aqueous valence is the starting species. Therefore, uranyl nitrate in the nitric acid solution that is already present in the WM-180 waste is selected.

If one is unable to work with uranium, neptunium cannot be simulated. If uranium is, in fact, a suitable substitute, that added for the uranium content of the waste will bracket and encompass the neptunium content.

#### **4.2.3.4 Cesium and Technetium**

Rhenium is a suitable substitute for technetium-99. Their chemical features are very similar.

When radioactive waste is evaporated and vitrified, the cesium and technetium interact to form cesium pertechnetate. This both enhances cesium volatility and diminishes technetium volatility from what each would be in the absence of the other. Rimshaw and co-workers<sup>16, 17</sup> studied the volatility of technetium during the flash evaporation of high-level-liquid waste solutions as a function of temperature and found the technetium volatility to be less than 1.1% from 250 to 600°C. Halaszovich, Dix, and Merz<sup>18</sup> observed that as a drum-dried waste is heated up to 1150°C, the technetium volatilization began at 550°C and increased rapidly above 900°C. As the temperature was held at 1150°C, additional volatilization, beyond the total 60% observed as the waste was heated to that temperature did not occur. This is because the technetium is, at that point, incorporated into the glass phase in a +4 valence state. Cains and co-workers<sup>19, 20</sup> found that, at 600°C, evaporative losses of cesium were proportional to the concentration of technetium in the liquid waste, suggesting volatilization of CsTcO<sub>4</sub>. During vitrification, cesium evaporative losses without technetium present were  $1.3 \pm 1.1\%$ , but an order of magnitude higher when technetium was present.

Cesium and technetium are present at about equimolar concentrations in the WM-180 waste and, therefore, one would expect significant effects of one on the other in terms of volatilization behavior.

Because cesium-137 is of interest regarding secondary wastes from the off-gas system, pilot-scale studies measure its volatility behavior during vitrification. However, in order for it to be detected and measured in the off-gas, typically the Cs<sub>2</sub>O concentration in the glass must be at least 0.05 wt%.<sup>21</sup> For the vitrification flowsheet of the WM-180 waste, with a 30 wt% waste loading, this corresponds to a cesium concentration in the WM-180 waste feed of 0.00136 molar, which is a factor of 175 times the actual concentration (Table 9). For different waste loadings, the factor of increase is inversely proportional to the waste loading.

The cesium and rhenium (for technetium) concentrations provided in the simulant makeup procedure correspond to the actual waste composition. If an experiment is tracking the cesium in the vitrifier off gas, the cesium concentration must be increased as indicated above. When this is done, the concentration of the rhenium stand-in for technetium should be increased by the same factor, to 0.00104 molar for 30 wt% waste loading.

#### **4.2.4 Solids**

The contribution of the solids to the overall melter feed composition is trivial and generally needn't be considered for simulating the waste. Except for silicon and traces of antimony, silver, tin, and cesium, they contain the same elemental components as the liquid, and the total mass of solids, relative to total dissolved solids in the liquid, is 0.06%. If one desires to augment the simulant formulation with solids, so

far as the glass composition is concerned, the elements common to the liquid may be ignored, as they are covered within uncertainties in the liquid composition. Thus, silicon remains the main new species, along with small quantities of antimony, silver, tin, and cesium.

The quantity of undissolved solids, UDS, in the agitated liquid sample, corrected for NCC-102 and NCD-123 heel dilutions, is 0.248 g/L. When the solids composition (Table 4) is converted to an equivalent number of g-atoms element/L (molar) in the total liquid plus solids sample, the “unique” element concentrations are all less than the detection limits in the liquid, with the exception of silicon. The molar concentrations from the solids contribution are (compared with the liquid solution detection limit): Sb 8.24E-8 (<6.02E-5); Cs 9.78E-7 (<7.73E-6); Sn 4.43E-6 (3.88E-5); Si 1.85E-4 (<2.85E-7). In the case of tin, the calculated liquid concentration associated with the zirconium from Zircaloy is 7.52E-7 molar.

The silicon is likely present as SiO<sub>2</sub>. Since SiO<sub>2</sub> is a component of the frit added to the waste feed for vitrification, there is no need to add it specifically for solids contribution, since it would be negligible compared with the frit. If one were concerned about Sb or Cs in the glass, they would be added at the concentrations of the detection limits for the solution. (See discussion of radionuclides regarding cesium considerations.) Therefore, if one wanted to add any of the solids constituents to the simulated waste it would be tin at the solids level, which slightly exceeds the calculated concentration in solution. It could be added as the metal or oxide.

### 4.3 Makeup Procedures

The following is a step-by-step recipe for preparing the WM-180 simulant solution described in the Table 9 and the Excel spreadsheet that calculates the reagent quantities for 1 liter of simulant. The procedures are written for additions of water to result in a final volume. If one is preparing the simulant by weighing the solution, use the density of 1.2625 g/mL for the complete simulant to determine the final weight to achieve upon adding the final water diluent.

If you are preparing a small quantity that can be prepared in a beaker that can be stirred and heated, reagents can be inserted directly into the makeup vessel. If you are preparing a large quantity, e.g. 20 L, that utilizes a vessel that cannot be well mixed nor heated, a modification is made to enable dissolution of individual components in smaller vessels prior to adding to the makeup vessel contents.

In the procedures, all analyzed constituents are included. If, for a specified experiment, it is desired to eliminate specific reagents or to substitute different reagents, adjust accordingly. This is accomplished by entering zero for the eliminated element in the Excel Simulant Makeup Spreadsheet line for total element molar concentration, row 70. The spreadsheet will adjust the calculated quantities of reagents as necessary to reflect the change. (For most of the minor components, of course, that do not include extra acid dissolvent, effect on overall composition may be generally ignored.) It may be preferable to prepare a side stock solution of hazardous/RCRA reagents that can be added to the complete the simulant on a case-by-case experimental basis.

The following steps are for preparing 1 L of simulant in a single vessel. The quantities can be scaled to the volume actually being prepared, up to about 4 L in a glass beaker. Modifications are given, also, for preparing larger batch quantities.

The following procedure is based on the assumption that the hazardous and RCRA constituents can be handled and added without difficult controls along with the other reagents. However, an Independent Hazards Review (IHR) has not been processed. Until it has, some of the reagents cannot be included in the makeup at INTEC. The specific elements that may be affected are As, Ba, Be, Cd, Cr, Hg, Pb, and U.

An approved IHR is in place (for D. R. Peterman) that accommodates working with Ba, Cr, Hg, and Pb and it may be considered for providing an umbrella for preparations.

Likely, it will be expedient to prepare the hazardous constituent dissolutions separately by making up one or two fairly concentrated solutions of sets of them in the correct relative concentrations that can be used as stock reagent(s) to pipette in the required quantities to the rest of the simulant solution. In that way, cumbersome controls for weighing would only have to be dealt with once and subsequent simulant solution preparations would be simpler. The procedure, controls, and approvals are being developed. This includes identifying which specific reagents are affected. For example, chromium, being Cr(III), may not be the concern as if it were Cr(VI).

#### *PREPARATION OF 1 L WM-180 LIQUID SIMULANT*

1. Calibrate the makeup vessel at the target simulant volume. Either transfer an accurately measured volume of water from a volumetric flask or weigh  $1000 \times (\text{H}_2\text{O density, g/cm}^3)$  g of  $\text{H}_2\text{O}$  per liter. Assuming approximately  $20^\circ\text{C}$ , weigh 998.23 g  $\text{H}_2\text{O}$  per liter. Mark the level. Alternatively, calibrate an Erlenmeyer flask that will be used for the final dilution. This will be more accurate, since the necked-down region of the flask provides more sensitivity to volume. Or, for the 1 liter of simulant, the final dilution could be done in a volumetric flask.
2. Weigh out and place into the beaker the specified quantities of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{BeF}_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{TiCl}_4$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (or the alternate,  $\text{ZnCl}_2$ ), and KI. If necessary, break up large chunks into a powder prior to weighing.
3. Add approximately 300 mL demineralized  $\text{H}_2\text{O}$ . Stir and heat as needed to effect dissolution. This will result in a (molar) ion product of  $[\text{Na}][\text{NO}_3^-]$  of approximately 46, within the calculated solubility product at  $25^\circ\text{C}$  of 59 (from the CRC Handbook solubility), which should result in the dissolution of the limiting salt,  $\text{NaNO}_3$ . To assure that  $\text{NaNO}_3$  remains soluble, the increase in nitrate from addition of  $\text{Al}(\text{NO}_3)_3$  and  $\text{HNO}_3$  solutions will be done later only after most of the diluent water has been added.
4. In a small beaker (50 mL for a 1 L simulant), weigh in the specified amount of  $\text{H}_3\text{BO}_3$ . Add approximately 40 mL  $\text{H}_2\text{O}$ . Pipette in the specified amount of HF reagent. Stir. The HF will cause most of the boric acid to readily dissolve, forming  $\text{HBF}_4$ , though it is in slight stoichiometric deficiency. Heat gently, if needed, to effect complete dissolution of the boric acid. Transfer to the makeup vessel. Follow with a small water rinse of the small beaker to the simulant solution.
5. In a small beaker (30 mL for a 1 L simulant), weigh in the specified amount of  $\text{As}_2\text{O}_3$  (or the alternate,  $\text{H}_5\text{As}_3\text{O}_{10}$ ). Add 15 to 20 mL  $\text{H}_2\text{O}$ . Stir and heat as necessary to effect dissolution. If dissolution does not occur, add the specified volume of HCl stock solution. This should cause the arsenic to dissolve. Transfer to the makeup vessel. Follow with a small water rinse of the small beaker to the simulant solution.
6. Add the specified mass of 50 wt%  $\text{Mn}(\text{NO}_3)_2$  solution.
7. Add the specified volume of  $\text{ZrF}_4$  stock solution, prepared as instructed in Footnote 1. Stir.
8. See step 9 for comment about dilution volume at this point. Add dilution  $\text{H}_2\text{O}$  to about 500 mL per 1 L simulant. Stir.

9. Add the specified volume of  $\text{Al}(\text{NO}_3)_3$  stock solution. This will be 285.5 mL for a stock solution concentration of 2.2 M  $\text{Al}^{3+}$ . If the stock concentration is less than 2.2 M  $\text{Al}^{3+}$ , subtract the additional required volume from the 500 mL dilution volume in step 8. Stir.
10. In a separate beaker (250 mL for 1 L simulant) place 50 mL  $\text{H}_2\text{O}$ . SLOWLY add the specified volumes of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  (only if not added in step 5), and  $\text{HNO}_3$  stock solutions to the water (do not add the water to the acids – it will splatter). Stir. Slowly add this solution to the makeup vessel. Stir.
11. Add the specified volume of  $\text{MoO}_2(\text{NO}_3)_2$  stock solution that has been prepared as instructed in Footnote 2. Stir.
12. Add the specified quantity of  $\text{RuCl}_3$  (or, if using alternate  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  solution – preferred if available – , its specified volume). Stir.
13. This solution should now be at approximately 900 mL for a 1 L simulant preparation. Transfer it to a 1 L calibrated Erlenmeyer or 1 L volumetric flask. Rinse the beaker with a small volume (approximately 50 mL) of  $\text{H}_2\text{O}$  to the flask. Do not fill to the fill line at 1 liter.
14. Seal and store the flask contents until ready to use. At that time, you will add the specified volume of  $\text{H}_3\text{PO}_4$  stock solution and then add  $\text{H}_2\text{O}$  to the 1 liter fill line. Mix well. By adding the phosphoric acid just before the experiment, precipitate formation may be retarded. Phosphate precipitate may slowly form after the  $\text{H}_3\text{PO}_4$  addition.

#### *MODIFICATION OF MAKEUP PROCEDURE FOR LARGE VOLUMES*

The following modifications are based on the consideration that the primary makeup vessel cannot be adequately heated and/or stirred to effect dissolution of individual components and is a variation of the approach used by D. R. Peterman. The example is provide for preparing 20 L of simulant; it can be scaled as desired.

#### FOR 20 L SIMULANT:

1. Place 2.7 L deionized  $\text{H}_2\text{O}$  into the primary makeup vessel that is calibrated for final volume.
2. Into a 4 L beaker, weigh in the specified quantities of  $\text{NaNO}_3$  and  $\text{KNO}_3$ . If necessary, grind the salts to size-reduce large chunks.
3. Add 3.3 L  $\text{H}_2\text{O}$  to the salts in the 4 L beaker. Stir and heat as necessary to effect dissolution.
4. Transfer this solution to the primary makeup vessel. Stir.
5. Remove approximately 3 L of solution from the makeup vessel to the 4 L beaker. Add to this the specified amounts of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{BeF}_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{TiCl}_4$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (or the alternate,  $\text{ZnCl}_2$ ), and  $\text{KI}$ . If necessary, break up large chunks into a powder prior to weighing. Allow sufficient time for each salt to dissolve before adding additional salts. Stir and heat as necessary to effect dissolution.
6. Transfer this solution back into the makeup vessel. Mix well.

7. In a 1 L beaker, weigh in the specified amount of  $\text{H}_3\text{BO}_3$ . Add approximately 800 mL  $\text{H}_2\text{O}$ . Pipette in the specified amount of HF reagent. Stir. The HF will cause most of the boric acid to readily dissolve, forming  $\text{HBF}_4$ , though it is in slight stoichiometric deficiency. Heat gently, if needed, to effect complete dissolution of the boric acid. Transfer to the makeup vessel. Follow with a small water rinse of the small beaker to the simulant solution.
8. In a 600 mL to 1 L beaker, weigh in the specified amount of  $\text{As}_2\text{O}_3$  (or the alternate,  $\text{H}_5\text{As}_3\text{O}_{10}$ ). Add 300 to 400 mL  $\text{H}_2\text{O}$ . Stir and heat as necessary to effect dissolution. If dissolution does not occur, add the specified volume of HCl stock solution. This should cause the arsenic to dissolve. Transfer to the makeup vessel. Follow with a small water rinse of the small beaker to the simulant solution.
9. Add the specified mass of 50 wt%  $\text{Mn}(\text{NO}_3)_2$  solution to the makeup vessel and stir.
10. Add to the makeup vessel the specified volume of  $\text{ZrF}_4$  stock solution, prepared as instructed in Footnote 1. Stir.
11. See step 12 for comment about dilution volume at this point. Add dilution  $\text{H}_2\text{O}$  to about 10 L. Stir.
12. Add the specified volume of  $\text{Al}(\text{NO}_3)_3$  stock solution. This will be 5.71 L for a stock solution concentration of 2.2 M  $\text{Al}^{3+}$ . If the stock concentration is less than 2.2 M  $\text{Al}^{3+}$ , subtract the additional required volume from the 10 L dilution volume in step 11. Stir.
13. In a separate 4 L beaker place 1 L  $\text{H}_2\text{O}$ . SLOWLY add the specified volumes of  $\text{H}_2\text{SO}_4$ , HCl (only if not added in step 8), and  $\text{HNO}_3$  stock solutions to the water (do not add the water to the acids – it will splatter). Stir. Slowly add this solution to the makeup vessel. Stir.
14. Add the specified volume of  $\text{MoO}_2(\text{NO}_3)_2$  stock solution that has been prepared as instructed in Footnote 2. Stir.
15. Add the specified quantity of  $\text{RuCl}_3$  (or, if using alternate  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  solution – preferred if available – , its specified volume). Stir.
16. This solution should now be at approximately 18 L. Seal and store the contents until ready to use. At that time, you will add the specified volume of  $\text{H}_3\text{PO}_4$  stock solution and then add  $\text{H}_2\text{O}$  to the 20 liter fill line. Mix well. By adding the phosphoric acid just before the experiment, precipitate formation may be retarded. Phosphate precipitate may slowly form after the  $\text{H}_3\text{PO}_4$  addition.

*FOOTNOTES:*

1. Dissolve zirconium metal (or Zircaloy) in HF as follows. The quantities and concentrations are designed to be compatible with fluoride in the simulant. Dissolve 0.456 g Zr in 100 mL 10 M HF. If using Zircaloy instead of Zr metal, the quantity to weigh is 0.466 g (Zircaloy II) or 0.465 g (Zircaloy IV). The zirconium dissolution will be exothermic and rapid. If using Zircaloy, tin will require heating overnight to effect its dissolution. The concentration of tin in the analyzed WM-180 waste was below the detection limit, but that is compatible with the quantity that would be present from the Zircaloy source of zirconium in the waste. Therefore, including it from the Zircaloy is OK.
2. Preparation of stock molybdenum solution. Dissolve 0.9593 g Mo metal in 100 mL 7 M  $\text{HNO}_3$ . If using sponge or solid metal, heat to near boiling ( $\sim 95\text{-}100^\circ\text{C}$ ). Keep a watch glass over the beaker

to minimize evaporation. The dissolution rate will be approximately 36 mg/cm<sup>2</sup>-min (penetration rate 0.21 cm/h). If using powdered Mo, slowly heat until you observe adequate dissolution rate. This will result in a solution of approximately 0.1 M Mo, 6.8 M H<sup>+</sup>, and 7 M NO<sub>3</sub><sup>-</sup>. (Note: Because the solution may evaporate a bit during the heating, it may be necessary to transfer the cooled solution to a 100 mL volumetric flask, add a small amount of rinse water to the beaker, and transfer it to the volumetric flask to bring the volume to 100 mL.)

To assure that the acidity of the simulant solution is at a pH below 0.9, the isoelectric point of molybdenum, this stock solution will be added after nitric acid has been added to the simulant solution. To the 1 L simulant, add 1.819 mL of this stock solution to result in 0.000182 M Mo, added H<sup>+</sup> of 0.0124 M H<sup>+</sup>, and added NO<sub>3</sub><sup>-</sup> of 0.0127 M.

## 5. EXPERIMENTAL MAKEUP RESULTS

When preparing simulated solutions of complex makeup, often it is difficult to achieve complete solubility of all reagents or irreversible precipitates may occur. This has been the case for some past SBW simulant preparations. Attention was given in developing the current procedures to assure the preparation of a clear solution. The one component that can particularly result in a small amount of precipitate formation is phosphate, even though the composition is based on an analyzed solution composition. For that reason, the phosphoric acid reagent used for adding phosphate to the simulant solution is added as the last reagent, and then just before preparation to perform process tests on the solution. It has been found to remain stable in solution for a few days, after which small amounts of precipitate will form.

INEEL and Pacific Northwest National Laboratory (PNNL) researchers have prepared laboratory scale batches of the WM-180 simulant solution for crucible vitrification tests following the procedures described herein. PNNL researchers have prepared batches for the Research-Scale Melter (RSM) tests and batches have been prepared by INEEL researchers at Clemson University for vitrification tests in the Clemson EV-16 pilot-scale melter. The latter utilized the procedures for large batches.

Prior to phosphoric acid addition, the solutions have been stable (clear) over a long time period. After addition of phosphoric acid, they remain clear for a few days and then small amounts of precipitate form. The PNNL laboratory preparation with added phosphoric acid was stable on Friday when prepared and had small amounts of precipitate present on the following Monday.<sup>22</sup> The INEEL preparation was stable for a week after phosphoric acid addition, after which a trace of precipitates appeared.<sup>23</sup>

The precipitated phosphate solids have not been characterized. Plans have been developed to characterize them in order to gain some insight into what some solids in the HLW tank may be and the properties that may be pertinent to tank closure activities. The concentration of the precipitated solids will be determined as grams air dried, oven dried, and calcined solids per liter. This will enable stoichiometric modeling of various potential compounds vis-à-vis the source terms in solution. X-ray diffraction patterns will be obtained at each stage of treated solids. Elemental and anion analysis will be obtained. Particle characteristics will be determined (size distribution, rheological properties).

When the approximately 5 liters of molybdenum reagent was prepared for the Clemson EV-16 simulant formulation as described in the makeup procedures, a flocculent white precipitate appeared after the molybdenum metal was dissolved in nitric acid. When a sample of the solid was added to a sample of the simulant solution, it dissolved with stirring and, upon adding the slurry to the simulant solution at the makeup quantity and letting it sit overnight, all the molybdenum went into solution.<sup>24</sup> This precipitate did not form in the laboratory preparations of the molybdenum reagent.

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