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(a) Author (Print/Sign): Huber, Heinz J. <i>Heinz J. Huber</i>		Date: 06/13/13	
(b) Reviewer (Optional, Print/Sign):			
Herting, D.L. <i>Daniel Herting</i>		Date: 06/14/13	
Cary Seidel <i>Cary M Seidel</i>		Date: 6/14/13	
Duncan, James - See electronic approval page 2 of 2		Date: _____	
Ramsey, William - See electronic approval page 2 of 2		Date: _____	
(c) Responsible Manager (Print/Sign): Seidel, Cary M. <i>Cary M Seidel</i>		Date: 06/14/13	
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Electronically Approved by:

UserName: Duncan, James (h0079048)
Title: APD Chemist
Date: Tuesday, 18 June 2013, 09:18 AM Pacific Time
Meaning: Approved by the author or delegate
=====

UserName: Herting, Daniel (h0004821)
Title: APD Chemist
Date: Tuesday, 18 June 2013, 10:26 AM Pacific Time
Meaning: Additional approval obtained
=====

UserName: Ramsey, William (h9535491)
Title:
Date: Tuesday, 18 June 2013, 02:20 PM Pacific Time
Meaning: Approved by the customer or delegate
=====

UserName: Seidel, Cary (h0009079)
Title: APD Manager
Date: Tuesday, 18 June 2013, 02:45 PM Pacific Time
Meaning: Approved by the Group Manager or delegate
=====

Laboratory Report on Performance Evaluation of Key Constituents during Pre-Treatment of High-Level Waste Direct Feed

Heinz J. Huber

Washington River Protection Solutions

Richland, WA 99352

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Abstract: The analytical capabilities of the 222-S Laboratory are tested against the requirements for an optional start up scenario of the Waste Treatment and Immobilization Plant on the Hanford Site. In this case, washed and in-tank leached sludge would be sent directly to the High Level Melter, bypassing Pre-treatment. The sludge samples would need to be analyzed for certain key constituents in terms identifying melter-related issues and adjustment needs. The analyses on original tank waste as well as on washed and leached material were performed using five sludge samples from tanks 241-AY-102, 241-AZ-102, 241-AN-106, 241-AW-105, and 241-SY-102. Additionally, solid phase characterization was applied to determine the changes in mineralogy throughout the pre-treatment steps.

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H. J. Huber

Washington River Protection Solutions LLC

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List of Terms

Abbreviations

A.D.	Acid digest
AFA	Automated feature analysis
AN-106	Tank 241-AN-106
AP-101	Tank 241-AP-101
ATL	Advanced Technologies and Laboratories International, Inc.
AW-105	Tank 241-AW-105
AY-102	Tank 241-AY-102
AZ-102	Tank 241-AZ-102
b.d.l.	Below detection limit
BBI	Best basis inventory
BSE	Backscatter electron
CL	Caustic leachate
CPS	Caustic and permanganate treated solids
CS	Caustic treated solids
DF	Direct feed
DOE	Department of Energy
EDS	Energy dispersive spectrometer
EM	Environmental Management
F.D.	Fusion digest

HLW	High-level waste
HTWOS	Hanford Tank Waste Operations Simulator
IC	Ion chromatography
ICP-AES	Inductively coupled plasma source atomic emission spectrometry
ICP-MS	Inductively coupled plasma source mass spectrometry
LAW	Low-activity waste
MDL	Minimum detection limit
n	Refractive index
OC	Original composite
OC-A	Original composite with acid digest for RCRA metals analysis
OC-F	Original composite with fusion digest for RCRA metals analysis
PL	Permanganate leach liquid
PLM	Polarized light microscopy
PSD	Particle size distribution
PUREX	Plutonium-Uranium Extraction
RCRA	Resource Conservation and Recovery Act
REE	Rare Earth Elements
RPD	Relative Percent Difference
SEI	Secondary electron image
SEM	Scanning electron microscope
SY-102	Tank 241-SY-102
TCS	Theoretical caustic leached solids
TGA	Thermogravimetric analysis
TIC/TOC	Total inorganic carbon/total organic carbon
TWINS	Tank Waste Information Network System
TWS	Theoretical water leached solids
WL	Water leach liquid
WRPS	Washington River Protection Solutions LLC
WS	Water leached solids
WTP	Waste Treatment and Immobilization Plant
XRD	X-ray Diffraction

Units

g	gram
hr	hour
M	molar (mol/L)
m	meter
mL	milliliter
wt%	weight percent
mmol	millimoles
µg/g	microgram per gram
µg/mL	microgram per milliliter
µm	micrometer

1.0 INTRODUCTION

The U. S. Department of Energy (DOE) Hanford tank farms contain approximately 56 million gallons of wastes, most of which originated during the reprocessing of spent nuclear fuel to produce plutonium for defense purposes. According to the Tri-Party Agreement, *Hanford Federal Facility Agreement and Consent Order* (Ecology et al., 1989), DOE will separate the tank waste into a high-level waste (HLW) fraction and a low-activity waste (LAW) fraction; both of these fractions are to be vitrified for immobilization in the Hanford Waste Treatment and Immobilization Plant (WTP). Extensive pre-treatment including leaching with water, caustic, and an oxidative agent, ion exchange, and filtration is necessary to adjust the two feed streams for further processing.

A potential alternative path to be used primarily for plant start-up involves direct waste delivery from the Tank Farms to the HLW vitrification facility of WTP, bypassing the pre-treatment facility. This concept is currently referred to as Direct Feed (DF) HLW. As described in detail within the engineering study RPP-RPT-53225, *Preconceptual Engineering Study for Direct Feed High-Level Waste*, a three-tier approach has been proposed: Stage 1 would include only water washing in tank with decanting as the method of separation, Stages 2 and 3 would provide for caustic leach and oxidative strike operations in purpose-built processing tanks. As the Tank Farm operation contractor, Washington River Protection Solutions LLC (WRPS) has the responsibility to provide the feed to the WTP, be it in the form of untreated tank waste to the Pretreatment Facility, or by supplying the treated material direct feed option.

A key requirement for providing direct feed to the WTP melter is to better understand the chemical behavior of the feed during retrieval and pre-processing in the Tank Farm. To allow for preliminary modeling of process control and process mass flow, several key constituents need to be evaluated during the pre-treatment steps. Key constituents include the mass drivers chromium, iron, aluminum, zirconium, nickel, and silicon and the so-called species of concern, such as chloride, fluoride, sulfate, phosphate, and bismuth.

In the compilation report on sludge washing tests of actual Hanford tank waste performed throughout the late 1990s at the Pacific Northwest Laboratory, Los Alamos National Laboratory, and Oak Ridge National Laboratory (DOE/EM-0520, *Sludge Washing*), the focus was on the leachability of Al, Cr, and P under various conditions¹. Correspondingly, a recent evaluation of the HLW feed (RPP-RPT-50309, *Evaluation of Tank Waste Feed for the WTP HLW Mission: Basis for Integration of Waste Feed Delivery and Blending with Optimization of Waste Throughput*) discussed the impact of eight of the components (Fe, Al, Zr, Cr, Ni, Bi, P, and S) within the Hanford Tank Waste Operations Simulator (HTWOS) System Plan.

The current HTWOS model assumes the presence of certain constituents and their reactions in the tank waste and models the necessary pre-treatment of the waste prior to transfer to WTP.

¹ The samples involved in these studies were from tanks 241-B-101, 241-BX-110, 241-BX-112, 241-C-102, and 241-S-101. None of these tanks are likely candidates for a DF HLW operation.

This model relies on the wash and leach factors to predict the estimated leachability during washing and caustic leaching in WTP Pretreatment. The actual extent of dissolution for various species of concern in the DF HLW stream is still not completely understood. This is due to lack of chemical and mineralogical analyses, uncertainties within the existing analyses (known and unknown), and the general problem of obtaining a representative sample of a million gallon tank containing stratified solids. Additionally, laboratory analytical protocols restrict the sample sizes due to the high dose rates.

The intent of this laboratory study using actual archived tank sludge was to better understand the process chemistry for the DF HLW and to evaluate the current analytical capabilities of the 222-S Laboratory, including the ability to analyze archived sample material. Composites of solid material were prepared for five tanks: 241-AY-102 (AY-102), 241-AW-105 (AW-105), 241-AN-106 (AN-106), 241-AZ-102 (AZ-102), and 241-SY-102 (SY-102). The composite samples were prepared and treated as presented in Figure 1.

Figure 1. Flowchart of the Analytical Approach.

Details of the sample selection, composition, leaching, and analytical methods and results are provided in the next sections. Sections 4.1 to 4.5 discuss the results for each of the tank composites. The results of the mineralogical analyses are presented in Attachment A; Attachment B contains the results of the chemical analyses as provided by ATL. An overview of which analyses were performed for each of the tank samples is provided in Attachment C as “Sample Breakdown Diagrams”. Attachment D contains a detailed listing of the masses involved during testing.

One objective of the tests was to evaluate current analytical protocols against process control requirements. This included the use of “routine” analytical procedures, e.g., the use of a nitric acid digest followed by inductively coupled plasma source atomic emission spectrometry

(ICP-AES) for Resource Conservation and Recovery Act (RCRA) metals analyses. For comparison, a fusion digest with potassium hydroxide was performed followed by ICP-AES, and the data are compared in Section 3.0.

The second objective of the tests was to identify the chemical phases and phase changes associated with key constituents during DF HLW unit operations. Solid phase analyses of the samples before and after washing and caustic leaching are helpful in evaluating the potential concerns associated with some species such as halides and sulfur-bearing phases.

The tertiary goal was a better understanding and evaluation of the Tank Farms and WTP baseline flowsheet model predictions. The approach within the direct feed initiative is to bypass the pretreatment facility for the first ~5 years of operation using in-tank settle-decant as the solid-liquid separation in the tanks. Since this method does not split the two streams into a solid-free and a solid-bearing substream as sharply as micro- or ultrafiltration does, modeling the waste feed will be more challenging. The results of this study will feed into the HTWOS successor model for future improvements. The tests were designed to best achieve these goals, all the while using sufficient material for potential future solidification experiments on the leached residual solids.

2.0 SAMPLES AND ANALYTICAL TECHNIQUES

2.1 Sample Selection and Composite Preparation

The selection criteria for the tanks used in this study were:

- 1) WTP commissioning waste (AY-102)
- 2) Potential for early processing within first 5 to 7 years (AZ-102)
- 3) Potential for minimal pre-treatment (AW-105)

The two other tanks were added to identify the analytical quality for high oxalate amounts (AN-106) and SY-102 was chosen as a potential candidate in the 200-West tank farm area.

The major contributors of the chosen tanks to the overall tank inventory based on the Best Basis Inventory (BBI) are shown in Table 1, displaying the difference in chemistry for the five selected tanks. AY-102 is a high aluminum tank with the largest amount of iron and sodium. AZ-102 has the highest sulfate content and is (beside AZ-101) the highest activity tank within the tank farms, which in turn causes serious issues for sample handling. AN-106 contains the largest amount of bismuth, phosphorus, and aluminum, which tend to form Fe-Bi-P and Na-Al-P phases. AW-105 has the highest amount of zirconium and fluoride; SY-102 contains the largest amount of chromium.

Table 1. Total Inventory of Select Species Based on Best-Basis Inventory Database.

Inventory (kg)	AY-102	AZ-102	AW-105	AN-106	SY-102
Mass Drivers					
Aluminum	73,600	54,400	3,730	98,000	52,600
Chromium	2,030	2,830	1,180	1,940	20,900
Iron	83,700	36,100	3,040	51,700	10,700
Nickel	2,330	2,460	221	8,870	332
Silicon	8,880	1,890	2,540	29,200	6,490
Sodium	459,000	362,000	149,000	272,000	202,000
Zirconium	78	4,560	97,600	5,070	92
Elements of Concern					
Bismuth	83	121	194	17,400	2,830
Chloride	4,790	6,030	646	2,850	4,210
Fluoride	5,650	2,250	64,900	9,980	1,430
Phosphate	12,600	7,790	3,210	121,000	21,700
Sulfate	13,600	38,300	3,020	26,100	6,150
Total Mass	4,530,000	4,450,000	1,890,000	3,160,000	2,640,000

Within the chosen tanks the individual composites for each tank were prepared from multiple jars from the tank waste archive in the 11A hot cell annex of the 222-S Laboratory. The jars were selected based upon sample amount, mode and location of retrieval (drill samples were

preferred over grab samples), and the year of retrieval. Samples from more recent sampling campaigns are preferred due to two reasons: First, older samples have a higher chance of complete dryness, which causes problems with rehydration. Rehydrated samples do not necessarily have the same mineralogy as the original sludge, e.g., due to the precipitation of water-insoluble solids from the interstitial liquid. Rehydration also causes problems due to the very fine particles that form during precipitation; flightiness of the material during handling is a serious issue for hood work, and the precipitated smaller particles distort the actual settling times. Second, older samples have a much higher tendency to form non-waste related minerals by caustic silicon leaching from the glass of the jars (e.g., formation of Cancrinite, a Na-Ca-Al-silicate).

The total amount of solids available was 214.35 g for AY-102, 187.58 g for AZ-102, 187.71 g for AW-105, 259.80 g for AN-106, and 159.95 g for SY-102. A detailed list of the jars, original mass, and actual retrievable mass is included in Attachment C. The optical appearance of the archived sludge samples varied from light to dark brown. Some of the jars were completely dried and contained either hard chunks or crumbly cakes of material. Hard chunks were ground using a mortar and pestle, whereas the cakes fell apart during transfer into the composite jar. Some material had the consistency of sludge that is best described as muddy clay.

For AY-102 and AZ-102, all jars used in the composite contained very dry material. Water was added to leach residual material from the emptied jars and to reduce flightiness of the composite. This water addition had some influence on the water soluble species in the glass jars. Since most of those species precipitated from drying interstitial liquid in the original sludge, the basic assumption that the material that re-dissolved during water addition was never present as solid phase in the original material is deemed reasonable. The AW-105 and SY-102 sludge material was sufficiently moist and all the material needed was available in a single jar, respectively; therefore the original jars were used and the content was transferred directly into clear glass jars for dissolution work. The AN-106 composite contained material from several jars and was pourable with a “muddy” consistency with no standing water.

Subsamples of 1-5 g from the total amount of solids were submitted to the 222-S analytical contractor Advanced Technologies and Laboratories International, Inc. (ATL) for chemical analyses, and another subsample was used for solid phase characterization. These composite samples are referred to as OCs, “original composites,” in the remainder of this report.

The composites were transferred to the 1E-2 Hot Cell, and about 150 g of the material was transferred into clear, tall glass jars labeled “x-T”; with “x” being “A” for AY-102, “B” for AZ-102, “C” for AW-105, “D” for AN-106, and “E” for SY-102. This was necessary since the glassware holding the composites was significantly darkened from radiation damage within a matter of weeks. Table 2 below shows the masses of material transferred; for details on the individual contributions, amounts of water added, etc., see Tables C-1 to C-5 in Appendix C.

In Figure 2, the preparation of the dissolution jar C-T is shown. The sludge material was sampled in 2008, and no rehydration was performed. In the left image, the original container from the archive with the jar number 20646 can be seen as well as the spatula which was used to transfer the material. In the right image, the plastic consistency of AW-105 is visible.

Table 2. Summary of Sample Masses in Dissolution Jars.

Tank	Number of jars combined	Rehydrated	Hot Cell ID	Mass in Dissolution Jar (g)
AY-102	6	Yes	A-T	156.02
AZ-102	4	Yes	B-T	154.45
AW-105	1	No	C-T	187.71
AN-106	2	No	D-T	150.10
SY-102	1	No	E-T	159.95

Figure 2. Preparation of Jar C-T (Tank 241-AW-105) in Hot Cell 1E-2.

The clear glass jars offer visual inspection possibilities to identify standing liquids, and the jars are tall and lean enough to allow for shaking of the whole material during dissolution using the manipulator arms. Transferring amounts of ~150 g of material into 50 mL centrifuge cones would have caused significant loss of material during transfer. The rather large amount of starting sludge was necessary to have sufficient post-dissolution material for future solidification experiments².

2.2 Chemical and Mineralogical Analyses of Untreated Sludge Samples

Table 3 shows the analytes requested by the customer; any additional analyses, i.e., elements that are analyzed due to the analytical protocol were provided as so-called “opportunistic values” and

² In 2000 and 2001, AZ-102 sludge was pretreated according to the pretreatment facility flowsheet and subsequently vitrified. The studies were reported in PNWD-3045 (BNFL-RPT-038), *Characterization, Washing, Leaching and Filtration of AZ-102 Sludge* and in PNNL-13452 (WTP-RPT-006), *Vitrification and Product Testing of C-104 and AZ-102 Pretreated Sludge Mixed with Flowsheet Quantities of Secondary Wastes*.

are not included in this report. Only in case of SY-102, ICP-MS analysis of transuranic species was performed.

Table 3. Techniques and Procedures for Chemical Analyses.

Analytes	Solids Digest Method	Analytical Techniques	ATL Procedure Number (Rev.)
Al, Bi, Ca, Cr, Fe, K, Mn, Na, Ni, P, Pb, Si, Sr, U, Th, Zr	Acid digest	--	LA-505-163 (H-0)
	Fusion digest	--	LA-549-141 (M-1a)
	--	ICP-AES	LA-505-171 (H-0)
			LA-505-174 (A-0)
Cl ⁻ , C ₂ O ₄ ²⁻ , F ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , NO ₂ ⁻	Water digest	--	LA-504-101 (M-0)
		IC-Anions	LA-533-166 (A-0/B-1)
OH ⁻	--	Titration	LA-211-102 (J-0)
TIC / TOC	Persulfate digest	Coulometry	LA-342-100 (L-0A)
Wt% water	--	TGA	LA-514-115 (G-0)
Am, Pu, Np, Th, Pa, and U isotopes	Acid digest	--	LA-505-163 (H-0)
	--	ICP-MS	LA-506-102 (G-0)

TIC/TOC= Total inorganic carbon / total organic carbon

IC = Ion chromatography

TGA = Thermogravimetric analysis

ICP-MS = Inductively coupled plasma source mass spectrometry

The procedure numbers are included to allow for specific comparison on the actual analytical protocols involved. These analyses are routine work and are commonly used for tank waste characterization. All chemical analyses were performed by the 222-S subcontractor ATL.

Solid phase characterization was performed on additional subsamples using four different techniques: Scanning electron microscopy (SEM), X-ray diffraction (XRD), polarized light microscopy (PLM), and particle size distribution (PSD) analysis. These analyses were performed by WRPS personnel from the Special Analytical Services and Process Chemistry groups.

Scanning electron microscopy analyses were conducted using an Aspex³ Personal Scanning Electron Microscope, Model II, with a Noran light element energy dispersive spectrometer (EDS) for chemical analysis in accordance with ATS-LT-161-100, 222-S *Laboratory Sample Preparation and Operating Procedure for Scanning Electron Microscopes*. The instrument was operated at an accelerating voltage of 20 kV, and the samples were mounted at a working distance of 18 to 20 mm. Samples were prepared either from dry powder or as smear slides.

³ Aspex is a registered trademark of ASPEX Instruments, Delmont, Pennsylvania.

Images were taken either as backscattered electron (BSE) images or secondary electron images (SEI).

X-ray diffraction analyses were performed in accordance with procedure ATS-LT-507-101, *222-S Laboratory X-Ray Diffractometry (XRD)* using a Rigaku®⁴ MiniFlex X-Ray Diffractometer. For sample preparation, a fraction of the sample material was individually placed in the well of a quartz zero-background slide, compressed with the plane of a glass slide, fixed with collodion binder and allowed to dry. For test information and specifics, refer to laboratory notebook HNF-N-105-1, pages 119-121.

Polarized light microscopy analyses were performed according to the current revisions of procedure ATS-LT-519-107, *222-S Laboratory Polarized Light Microscopy*, using a Nikon®⁵ Eclipse E600 polarizing microscope. Samples were prepared on glass slides using refractive index (n) oil of 1.55. For specific information on each sample and image taken, see laboratory notebook HNF-N-395-1, pages 101-105 and 107-110. PLM images are shown with and without the first order red modifier (which causes the background of the images to appear in magenta).

Particle size distribution analyses were performed using the Horiba®⁶ LA-910 Laser Scattering Particle Size Distribution Analyzer following the method described in the test plan WRPS-1202158, *Test Plan for Particle Size Distribution Measurements for the Performance Evaluation of Key Constituents during Pre-Treatment of High Level Waste Direct Feed*. The samples were used as provided with no further treatment; each sample was subjected to a duplicate set of three measurement runs with increasing dispersive forces to identify agglomerates that fall apart upon sonication.

Each technique provides unique insights to the mineralogy of the sludges. SEM in combination with EDS provides excellent information on the morphology and chemistry of individual particles, but is rather limited in sample size. XRD determines the mineral identification information on a bulk sample, but needs at least amounts of 5-10% for each phase to provide an adequate signal. PLM shows the optical characteristics of select minerals, but does not provide any chemical information. However, it does provide an overview of the distribution of phases and the particle sizes. Specifically, PLM can distinguish among phases that provide the same EDS spectrum, such as carbonates and oxalates. PSD is limited to only the fraction with <660 µm diameter; this is the maximum particle size the instrument can handle. For the larger-diameter fraction, sieving tests would be appropriate and recommended.

The detailed results of each of the solid phase analyses are listed in Attachment A. Particle size distribution results are summarized in this report, while the detailed PSD results for each run, such as undersized percentage histograms, were published separately as interoffice memorandum WRPS-1205133, *Test Plan Results for Particle Size Distribution Measurements on High-Level Waste Samples*.

⁴ Rigaku is a registered trademark of Rigaku USA, The Woodlands, Texas.

⁵ Nikon is a registered trademark of Nikon Corporation, Tokyo, Japan.

⁶ Horiba is a registered trademark of Horiba, Ltd. Corporation Japan, Kyoto, Japan.

2.3 Treatment

Treatment included inhibited water washing, concentrated caustic leaching, and oxidative strikes. How each sample was treated is displayed in Figure 3; each of the steps is described in detail in the paragraphs below. The dashed lines indicate knowledge transfers, e.g., the aluminum content from the solids analyses determined the amount of caustic used in caustic leaching. One exception to the flow diagram is AY-102, for which the water leached sample was analyzed additionally to the final leach residuals. The duration of each leaching step was originally based on the times used in the engineering study RPP-RPT-53225 (see, e.g., Figure 3-34) and was adjusted to fit the actual needs and abilities (see Table 4 footnote).

Figure 3. Flow Diagram for Individual Sample Testing.

2.3.1 Inhibited Water Washing

To determine the amount of inhibited water needed for water leaching, two 50-mL centrifuge cones were prepared for each tank. About 8 g of sludge was transferred into the cones, which were then filled with inhibited water to the 40-mL line, and the mass was recorded (see Figure 4). The cones were placed on a rotisserie (see Figure 5), then decanted and reweighed.

These steps were repeated until the solids amount seemed stable. The amount of water needed was a good indicator of the actual amount needed in the dissolution jars. However, two things need to be noted: the centrifuge cones settled “perfectly” during centrifuging, and the dissolution was optimized by constant movement on the rotisserie. The centrifuge times required after the first water addition varied between 4 minutes (for AY-102 and AZ-102), 20 minutes (AN-106 and SY-102), and 30 minutes (AW-105). The next leaching steps required much longer centrifuge times of up to 3 hours to produce a visually clear decantate.

Figure 4. Preparation of Cone C-1 for Water Dissolution Pre-Testing.

Figure 5. Samples on Rotisserie for Water Dissolution Pre-Testing.

The dissolution jars were filled to about $\frac{3}{4}$ of the total height to avoid spilling during handling with the manipulators, especially during the decanting step. Figure 6 shows three of the jars after the first water addition – the different jars have distinctly different colors.

The differences in settling behavior are also clearly demonstrated. While A-T (AY-102) shows a distinct aqueous top layer, B-T (AZ-102) starts to show a separation at the top, and C-T (AW-105) shows no signs of any segregation; all three bottles were handled about 2 minutes

before the picture was taken. This also reflected in the necessary time between shaking the jars and being able to start decanting. In case of AW-105, at least two days of non-disturbance were necessary to have a decantable amount of liquid at the top. Since in many cases this top material was not clear, it was decanted into centrifuge cones, the solids centrifuged, and the mass added to the undissolved solids in the dissolution jar.

Figure 6. Jars A-T (Tank 241-AY-102), B-T (Tank 241-AZ-102), and C-T (Tank 241-AW-105) after First Water Addition.

After the top liquid was decanted, fresh inhibited water was added and the jars were shaken and left to settle. The jars were shaken at least twice daily for several minutes to ensure proper mixing of the liquid and solid fractions. The amount of water added and the dissolution durations are shown in Table 4 below.

Table 4. Water Leach Test Characteristics.

Tank Hot Cell ID	AY-102 A-T	AZ-102 B-T	AW-105 C-T	AN-106 D-T	SY-102 E-T
Starting composite mass (g)	156.02	154.45	187.71	150.10	159.95
Water Leach					
Inhibited water addition (g)	269.93	211.61	201.58	198.85	200.22
Duration first water leach (hrs)	48	24	24	336*	216*
Residual material mass (g)	260.36	239.63	317.06	227.26	274.92
Inhibited water addition (g)	213.01	201.85	172.21	205.37	201.07
Duration second water leach (hrs)	576*	576*	576*	168	120
Residual material mass (g)	244.89	204.75	262.70	244.80	271.72
Inhibited water addition (g)	206.03	198.30	203.68	208.25	-
Duration third water leach (hrs)	312	312	312	120	-
Residual material mass (g)	253.78	214.22	269.40	231.04	-
Total leaching duration (hrs)	936	912	912	624	336
Total inhibited water addition (g)	688.97	611.76	577.47	612.47	401.29

*Long leaching due to facility outages, room restrictions, and lack of resources (technician).

The difference between “residual material mass” after the first leaching and “starting sample mass” indicates the amount of water that rehydrated the solids; this is also reflected in the wt% water measurements, and in the amount of un-retrievable material due to the settling behavior. Usually decanting was stopped when the onset of solids was visible. In case of a graded increase, the top liquid was collected in centrifuge jars, the solids centrifuged, and the mass added to the solids.

2.3.2 Caustic Leaching

After the water washing step, a caustic leach was performed on some of the samples (see Figure 2). The amount of caustic to be added was determined by the amount of aluminum in the sample. The proposed approach of using an automated feature analysis (AFA⁷) on the SEM in combination with the chemical analysis to identify the amount of gibbsite could not be followed since the AFA was unavailable at the time of testing. Therefore, the amount of caustic added was based on the assumption that all aluminum is present as gibbsite. Caustic dissolution of gibbsite theoretically requires an equimolar addition per mole gibbsite, but dissolution work on gibbsite-bearing post-retrieval solids have shown that the optimum dissolution conditions are the use of 19.4 M caustic in a ratio of $\text{OH}^-/\text{Al} = \sim 3:1$ M (see RPP-RPT-54652, *Gibbsite Dissolution Studies Summary and Analysis*). This ratio also provides sufficient hydroxide to dissolve dawsonite, which was found to be another major aluminum-bearing phase in some of the tanks; for a detailed discussion, see Section 4.2 (Tank 241-AZ-102). Based on the density measured for the caustic addition, the actual molarity of the solution was 17.0 M. No reason for the dilution from 19.4 to 17.0 could be verified. After caustic addition and mixing, a water washing step was performed to remove the water-soluble sodium aluminate; for details on amounts and durations, see Table 5.

Table 5. Caustic Leach and Permanganate Strike Test Characteristics.

Tank Hot Cell ID	AY-102 A-T	AZ-102 B-T	AW-105 C-T	AN-106 D-T	SY-102 E-T
Caustic Leach					
Starting material mass (g)	253.78	214.22	see Table 4	231.04	271.72
Caustic addition (17.0 M) (g)	177.82	106.61		112.8	85.64
Duration caustic leach (hrs)	144	144		144	144
Water addition (g)	250.57	94.59		163.27	127.81
Water leach duration (hrs)	168	72		72	216
Residual mass (g)	259.51	253.25		265.77	253.61
Oxidative Leach					
Permanganate addition (1M) (g)	19.95	--			145.84
Permanganate duration (hrs)	144				144
Water addition (g)	98.97				104.44
Water leach duration (hrs)	2				2
Residual mass (g)	245.26				406.96
Duration of final settling (days)	77	92	98	89	77
Final Mass (g)	210.32	195.36	234.43	213.04	383.81

⁷ AFA is a registered trademark of ASPEX Corporation, Delmont, Pennsylvania.

The impact of the inhibited water washing and caustic leaching on the sodium budget is shown in Table 6. These numbers need to be taken into account when comparing the sodium results for the individual tanks, e.g., for AY-102 in Table 11.

Table 6. Impact of Leaching on Overall Sodium Content.

	NaOH conc.		Na addition per treatment step (mol)				
	0.01M	17.0 M	AY-102	AZ-102	AW-105	AN-106	SY-102
Water Leach	Yes	No	0.01	0.01	0.01	0.01	0.00
Caustic Leach	Yes	Yes	2.05	1.23	-	1.30	0.99
Post-Permanganate	Yes	No	0.00	-	-	-	0.00
Summary (mol Na)			2.06	1.24	0.01	1.31	0.99
Summary (mol Na per kg leached sludge)			9.77	6.31	0.02	6.13	2.58

2.3.3 Oxidative Strike

Two tanks were chosen for the permanganate strike to oxidize the residual material: AY-102 and SY-102. Permanganate was added as 1 molar solution equimolar to the concentration of Cr in the original composite, since the analyses of the water and caustic leached solids were unavailable at the time of the oxidative strike. A water leach step removed the water soluble salts. Table 5 (bottom part) displays the amounts and durations of reagent and water addition.

2.4 Post-Treatment Analyses and Storage

The remaining material was subsampled twice in the amount of 2 g each for chemical and mineralogical analyses, respectively. The techniques and analytes were the same as for the original composite. The results of the chemical analyses are shown in Tables B1 to B5, and the combined results are discussed in the sections below.

The leached solids were stored in the leaching vessels (A-T, etc.). After 2 to 3 months, the solids settled enough for a final liquid decanting step (see Table 5). The residual solids will be transferred to the 11A archive.

2.5 Deviations from the Test Plan

Two deviations were necessary during testing:

- (1) Since the electron microscope had irresolvable technical issues, the AFA could not be used as a means to identify the amount of gibbsite in the original composites (and leached solids). There was no substitution possible within the timeframe of the project. The impact on the mineralogical identification is major, since SEM could only be used

qualitatively, rather than being a (semi) quantitative technique. The SEM has been replaced by a new model with the AFA capability.

- (2) The test plan calls out for a three-tiered approach to determine the extent of water solubility of the different sludges. This approach could not be followed, due to the large difference in sludge characteristics. Some of the material was only partially dehydrated, such as AW-105, which had a muddy consistency that did not allow for precise milligram addition of material into centrifuge cones using the hot cell manipulators. Others, such as AY-102 were entirely dried out and needed to be rehydrated for safe handling purposes. This rehydration did not produce the “peanut butter texture” common for tank sludges and interfered with the chemistry in an unknown way. In particular, phases that precipitated from the original interstitial liquid may not re-dissolve with water.

Therefore, only two 50 mL cones were filled with solid material with water added to the 40 mL mark. The cones were shaken, centrifuged, and weighed. The process (water addition, shaking etc.) was repeated until the mass was considered stable. The total water amount needed was then adjusted to the actual sample mass in the leaching jars (i.e., A-T, B-T, etc.) and added in increments that filled the jar to about 1 inch below the top. The impact of this change is minimal on the overall dissolution, since the total volume of solids and water required overwhelmed the amount of addable water due to jar size limitations. Jars wider than 70 mm cannot be handled with the manipulator fingers.

3.0 EVALUATION OF ANALYSES

A four tiered approach is used in this chapter. First, the analytical results of the original composite are compared to the archived results in the Tank Waste Information Network System (TWINS) database. Then the results are subjected to the wash and leach factors as determined in the BBI, and the resulting theoretical amounts are compared to the measured composition of the leached solids. The third part focuses on a comparison between acid digest and KOH fusion digest techniques to determine the RCRA metals concentrations with ICP-AES. Since both digests have benefits and drawbacks for different elements, a simple answer on a “better” approach cannot be identified. Lastly, an approach to close the mass balance is added.

3.1 Comparison of Analytical Results to TWINS Database

The amounts of the mass drivers and elements of concern are compiled in Table 7 as mol/kg sludge. The TWINS contents were derived from the online database, only considering solid analyses with no Quality Assurance (QA) flagging and samples that were analyzed prior to the sample date of the material used in the original composites. Larger differences are found for AZ-102 aluminum, AW-105 fluoride, and AN-106 aluminum and iron; AY-102 and SY-102 have relatively well matching results. Among these differences the fluoride content in AW-105 is perhaps of the highest importance due to the potential formation of highly refractive Zr-oxyfluoride. The fluoride content of the original composite is 7 times higher than the TWINS projected content. However, a closer look into the TWINS data reveals a huge variability of the fluoride content within the individual analyses. Within two segments of the same Core 322, the fluoride content varied between 0.26 and 1.04 mol/kg. The reported results from 2006 are 4,926 µg/g and 19,799 µg/g with the two segments being taken from approximately 3 inches below the sludge liquid interface (higher number) and at the bottom of the sludge (lower number) (see RPP-RPT-44625, *Derivation of Best-Basis Inventory for Tank 241-AW-105 as of January 1, 2012*). The highest fluoride content within AW-105 was 114,600 µg/g (i.e., 6.03 mol/kg) reported in HNF-SD-WM-DP-250, *Tank 241-AW-105, Cores 195 and 196 Analytical Results for the Final Report, Rev.0A*, for a sample from Core 195, Segment 8, in 1997.

The difference in aluminum for AZ-102 can be explained by the history of the tank samples. This tank is highly stratified following removal of the supernate in 1986 prior to the addition of the main component of the current sludge, which comes from plutonium-uranium extraction (PUREX) operations (P3 sludge). This sludge is characterized by relatively low amounts of aluminum and high amounts of iron. The remnants of the earlier operation however (the so-called bottom heel) is made of high aluminum sludge. In Table 7, the AZ-102 column named “TWINS” contains averages over the sampling events in 2004 (Core 313) and 2005 (Core 317). As described in RPP-RPT-44049, *Derivation of Best-Basis Inventory for Tank 241-AZ-102 as of October 1, 2012*, Core 313 only contained material from the bottom part of the tank, whereas Core 317 mostly covered material above. The bottom part of the sludge layer is made of heel material which precipitated in the early years of operation (1976 – 1986). The material is particularly high in aluminum, i.e., about 10-fold higher compared to the main contributor, which is high-level PUREX waste between 1986 and 1990 (so-called P3). The column “Bottom” in Table 7 refers to the bottom heel and is an average of Cores 313 (2004) and 317, Segment 19

lower half (2005), and “Post ‘86” is the average of all other segments within the 2005 sampling of Core 317.

Table 7. Comparison to Tank Waste Information Network System Projected Contents.

[mol/kg]	AY-102		AZ-102				AW-105	
	Sample	TWINS	Sample	TWINS	Bottom	Post ‘86	Sample	TWINS
Mass Drivers								
Aluminum	3.20	1.46	2.72	0.66	1.72	0.21	0.14	0.20
Chromium	0.06	0.03	0.05	0.03	0.04	0.02	0.04	0.06
Iron	2.40	1.78	2.10	1.45	1.45	1.65	0.09	0.13
Nickel	0.08	0.05	0.09	0.09	0.02	0.12	0.01	0.01
Silicon	1.01	0.42	0.22	0.11	0.09	0.08	0.01	0.07
Zirconium	0.004	0.005	0.14	0.07	0.06	0.07	1.13	1.42
<i>Zr/Al ratio</i>	<i>0.001</i>	<i>0.003</i>	<i>0.05</i>	<i>0.10</i>	<i>0.03</i>	<i>0.36</i>	<i>8.12</i>	<i>7.06</i>
Elements of Concern								
Bismuth	--	0.00	0.00	0.00	0.00	0.00	--	0.00
Fluoride	0.01	0.00	0.30	0.04	0.04	0.04	4.37	0.65
Chloride	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01
Sulfate	0.01	0.01	0.14	0.12	0.10	0.11	0.04	0.01
Phosphate	0.06	0.03	0.01	0.02	0.02	0.02	--	0.01

[mol/kg]	AN-106		SY-102	
	Sample	TWINS	Sample	TWINS
Mass Drivers				
Aluminum	2.00	0.41	1.59	1.38
Chromium	0.01	0.01	0.99	0.41
Iron	1.46	0.23	0.05	0.25
Nickel	0.07	0.00	0.01	0.01
Silicon	0.06	0.10	0.04	0.06
Zirconium	0.02	0.001	0.001	0.001
<i>Zr/Al ratio</i>	<i>0.01</i>	<i>0.003</i>	<i>0.001</i>	<i>0.001</i>
Elements of Concern				
Bismuth	0.08	0.07	0.00	0.02
Fluoride	0.35	0.31	--	0.04
Chloride	0.01	0.01	0.10	0.07
Sulfate	0.04	0.03	0.02	0.03
Phosphate	0.18	0.31	0.02	0.10

The sample material was originally intended to include both sludges, but during composite preparation, only material from the bottom heel was added to the composite for various reasons. These included sample availability, amount of sample per jar, and flightiness of material. The jars with the largest individual amounts were chosen, hydrated, and combined. This led to a composite sample with a composition that is not representative for the majority of the tank. The sample matches the bottom heel insofar the ratio of sample to heel for the insoluble metals (such as Al, Fe, Si, and Zr) ranges between 1.3 and 2.5, suggesting the difference is just in the water content. The post-86 sample however, shows a significant under abundance in aluminum compared to the sample.

3.2 Comparison of Wash and Leach Factors and Actual Results

Table 8 provides an insight into the complexity and validity of the so-called wash and leach factors⁸ of the BBI. The factors were applied to the original composite results and are compared to the analyzed leached material. For each tank, the theoretical amount after leaching is shown first, followed by the analytical result. In case two leaching steps were performed but no interim solid sample was taken, both theoretical values are shown (see, e.g., AZ-102, TWS [theoretical water leached solids] and TCS [theoretical caustic leached solids]). For details on the calculation, see the bottom of the table. In general, the theoretical values match the actual analyses quite well. The largest discrepancies were found for silicon. This is not surprising in the light of the adjustments described in the next paragraph.

Table 8. Comparison of Theoretical and Analytical Amounts Retained in Solids.
(2 sheets)

[mmol]	AY-102				AZ-102			AW-105	
	TWS	WS	TCS	CPS	TWS	TCS	CS	TWS	WS
Mass Drivers									
Aluminum	444	418	180	151	352 ^F	128 ^F	222 ^F	23	14.4
Chromium	8.0	5.7	5.3	4.1	3.6	1.5	3.4	2.0 ^F	1.7 ^F
Iron	338	292	338	249	278	278	256	15 ^F	8.3 ^F
Nickel	12	9.8	-	8.8	12	-	15	0.4	0.3
Silicon	139 ^F	14.1 ^F	109 ^F	15.9 ^F	27 ^F	10 ^F	13 ^F	7.6 ^F	2.4
Zirconium	0.5 ^F	0.7 ^F	-	0.6	19 ^F	-	17 ^F	198 ^F	90
Elements of Concern									
Bismuth	-	0.0	-	0.0	0.0	0.0	0.0	-	-
Fluoride	0.5	-	-	-	10	-	1.0	126	39
Chloride	0.1	-	-	-	0.0	-	-	0.0	0.4
Sulfate	0.8	0.2	0.4	0.2	1.4	0.0	0.2	0.2	0.6
Sulfur	2.0	2.0	0.9	1.0	1.8	0.0	0.3	0.1	0.2
Phosphate	5.7	1.5	1.4	1.2	1.5	0.7	-	-	-
Phosphorus	16	7.7	3.9	4.6	7.9	3.8	1.1	1.9	2.6

⁸ Within the BBI, the “wash factor is the fraction of a waste constituent removed from the solid phase of a waste to the liquid phase by washing with water,” while the “leach factor is the fraction of a waste constituent removed from the washed solid phase of a waste to a liquid phase through leach processing.”

Table 8. Comparison of Theoretical and Analytical Amounts Retained in Solids. (2 sheets)

[mmol]	AN-106			SY-102		
	TWS	TCS	CS	TWS	TCS	CPS
Mass Drivers						
Aluminum	157	49	52	112	42	33
Chromium	0.6	0.3	0.2	72	41	24
Iron	92	90	39	5.4	5.3	1.8
Nickel	5.7	-	2.6	1.0	-	0.3
Silicon	49 ^F	31 ^F	13 ^F	8.6 ^F	5.9 ^F	5.9 ^F
Zirconium	1.5 ^F	-	1.8	0.1	-	0.0
Elements of Concern						
Bismuth	4.8	4.8	2.2	0.2	0.2	0.1
Fluoride	13	-	3.2	-	-	-
Chloride	0.0	-	-	0.0	-	0.5
Sulfate	0.1	0.0	0.3	0.0	0.0	0.2
Sulfur	0.1	0.0	0.3	0.0	0.0	0.1
Phosphate	7.5	1.6	1.2	0.7	0.1	0.4
Phosphorus	19	3.9	2.0	1.6	0.2	0.3

TWS = theoretical amount retained in water leached residual solids = original composite * (1- wash factor)

TCS = theoretical amount retained in caustic leached residual solids =

= [original composite * (1- wash factor)] * (1- leach factor) * (1- wash factor)

CPS = caustic and permanganate leached solids;

CS = caustic leached solids;

WS = only water leached solids

F ... fusion digest result or equivalently adjusted values (see Footnote 9, page 29)

In cases the fusion digest result was used instead of the acid digest, a superscript “F” is added to the value. In case of the theoretical values this implies that the fusion digest result was used as the base for the calculation. In case of an actual leached residual solids result it implies that the acid digest result was adjusted by the ratio of the equivalent original composite fusion over acid digest results (see Footnote 9, page 29). Especially for silicon, the key issue with the dissolution of silicon-bearing material is that silicates are rather resistant to dissolution in nitric acid.

However, the current protocol requires only the notification and recording of residual solids after solids digests, but no follow-up in terms of re-digest or solid phase characterization. This in turn requires adjusting the leached solids analyses. In a best-available approach the assumption was used, that all acid digest analyses had the same relative amount of non dissolvable residuals, so the ratio of fusion over acid digest from the original composite could be applied.

3.3 Comparison of Acid Digest and KOH Fusion Digest Results

One of the issues with chemical analyses of solids using ICP-AES or ICP-MS is the digestion step. In an effort to evaluate the differences between the two most commonly used digest methods, acid digest using nitric acid and the KOH fusion digest⁹, they were both applied to the

⁹ A microwave assisted acid digest method would be procedurally available at 222-S, however it is rarely used.

original composites followed by ICP-AES analysis. In Table 9, a compilation of the results shows the biggest differences, and Table 10 contains the relative percent differences (RPDs) of duplicate analyses for fusion and acid digest. All numbers in these two tables were directly copied from the results spreadsheet provided by ATL. The underlined values in Table 9 show the cases where the fusion digest results were used.

Table 9. Comparison of Fusion and Acid Digest Dissolution.

[µg/g]	AY-102			AZ-102			AW-105		
	F.D.	A.D.	F / A	F.D.	A.D.	F / A	F.D.	A.D.	F / A
Aluminum	84,200	86,300	1.0	<u>73,500</u>	62,300	1.2	7,330	3,750	2.0
Bismuth	<567	28.2		<589	46.7		<570	<11.5	
Calcium	<7,560	3,610		<7,860	3,480		<7,600	3,110	
Chromium	2,820	3,010	0.9	2,690	2,530	1.1	2,300	1,420	1.6
Iron	129,000	134,000	1.0	109,000	117,000	0.9	8,120	4,690	1.6
Manganese	31,000	31,500	1.0	3,230	3,550	0.9	9,580	6,190	1.5
Sodium	117,000	96,700	1.2	<u>137,000</u>	118,000	1.2	219,000	137,000	1.6
Phosphorus	4,630	4,800	1.0	2,350	1,970	1.2	2,290	1,700	1.3
Lead	7,210	7,460	1.0	1,680	1,720	1.0	<570	148	
Sulfur	542	791	0.7	6,580	5,900	1.1	510	452	1.1
Silicon	<u>28,400</u>	2,710	10.5	<u>6,190</u>	991	6.2	<u>2,590</u>	306	8.5
Strontium	319	285	1.1	210	230	0.9	<190	19.8	
Thorium	715	856	0.8	511	656	0.8	<475	<9.59	
Uranium	<1,890	1,190		9,810	8,360	1.2	29,500	17,800	1.7
Zirconium	<u>328</u>	83.4	3.9	13,300	13,000	1.0	<u>168,000</u>	103,000	1.6
Average ratios (excl. Si, Zr)			1.0				1.0		

[µg/g]	AN-106			SY-102		
	F.D.	A.D.		F.D.	A.D.	
Aluminum	74,900	53,900	1.4	42,800	39,400	1.1
Bismuth	16,800	12,500	1.3	691	472	1.5
Calcium	<8,210	684		<7,920	918	
Chromium	820	539	1.5	51,400	46,500	1.1
Iron	81,700	64,800	1.3	5,030	3,030	1.7
Manganese	3,910	3,080	1.3	963	842	1.1
Sodium	<u>90,200</u>	65,100	1.4	162,000	148,000	1.1
Phosphorus	14,000	10,500	1.3	2,120	1,550	1.4
Lead	5,580	4,270	1.3	1,040	944	1.1
Sulfur	1,900	1,610	1.2	<495	863	
Silicon	<u>17,200</u>	1,770	9.7	<u>2,810</u>	1,040	2.7
Strontium	<205	121		<198	13.5	
Thorium	697	436	1.6	<495	64.9	
Uranium	4,490	3,060	1.5	<1,980	644	
Zirconium	<u>1,740</u>	616	2.8	<99.0	83.4	
Average ratios (excl. Si, Zr)			1.4			1.3

F.D. ... Fusion digest; A.D. ... Acid digest; Underlined ... Fusion digest result used.

Potassium and nickel were not reported for the fusion digest, since KOH and KNO₃ are reagents used as digestion media, and the fusion is performed in a nickel crucible. Most of the analytical results are in fairly good agreement.

Figure 7 displays the plot of fusion versus acid digest for all metals analyses up to 50,000 µg/g. The general trend of most metals is rather narrow band with a slope of 0.9, meaning that the acid digest results are about 10% lower than the fusion digest results. This is calculated from the average of the acid/fusion ratios, excluding zirconium and silicon. Zirconium seems to tend towards lower relative results for small amounts whereas silicon is in general under represented by acid digest results. As mentioned before, this is largely due to the existence of residual solids from undigested silicates.

Figure 7. Plot of Fusion Digest Results Versus Acid Digest Results For All Original Composite Metals Analyses.

The RPD for duplicate analyses are shown in Table 10 as well as the associated qualifiers from ATL's Quality Control/Quality Assurance. One sample was chosen per batch to be duplicated and spiked.

Four things are rather remarkable:

- (1) The RPD for silicon analyses is >10%, independent of the digest method.
- (2) The spike recovery for the fusion digest method is very good as opposed to the acid digest.
- (3) The chromium results had a fairly reasonable RPD of 5.85%. However, the spike recovery was 581%, which indicates that the results are reproducible but incorrect. Aluminum showed a very good RPD of 0.9% difference, but a spike recovery of 312%; again, no qualifier was applied.
- (4) The acid digest phosphorus analysis with an RPD of 97.9% but a spike recovery of -25.5% did not get marked with a qualifier.

Table 10. Comparison of Fusion and Acid Digest Dissolution ICP-AES Metals Analyses by ATL.

	AW-105 Fusion Digest			SY-102 Acid Digest		
	RPD [rel. %]	Spk Rec [rel. %]	Qualifier	RPD [rel. %]	Spk Rec [rel. %]	Qualifier
Aluminum	1.00	99.9	B	0.927	312	-
Bismuth	n/a	93.4	U	4.26	97.1	-
Calcium	n/a	96.8	U	0.932	106	J
Chromium	1.14	94.8	-	5.85	581	-
Iron	5.34	93.7	J	2.53	108	-
Potassium	n.d.	-	-	0.474	82.6	-
Manganese	2.83	95.6		0.615	103	-
Sodium	1.81	95.6	E	1.12	134	-
Nickel	n.d.	-	-	0.844	104	-
Phosphorus	1.57	94.1	J	97.9	-25.5	-
Lead	n/a	99.7	U	2.19	102	-
Sulfur	n/a	94.6	U	0.899	98.2	B
Silicon	27.7	95.0	BJ	13.4	104	Bae
Strontium	n/a	93.2	U	9.86	102	J
Thorium	n/a	92.9	U	10.8	101	-
Uranium	0.0229	93.6	-	0.519	99.3	Y
Zirconium	3.70	94.7	-	1.48	95.1	-

RPD = relative percent difference

Spk Rec = spike recovery

n.d. = not determined

n/a = at least one "<" result

For a full list of qualifiers and explanations, see ATS-GD-1028, *Flagging Data in LIMS*.

B = blank exceeds minimum criteria

U = amount below minimum detection limit (MDL)

J = result considered estimate

e = serial dilution result has >10% difference

a = percent recovery of control sample outside range

Y = required qualifying comments

3.4 Mass Recovery, Charge Balance, and Theoretical Mineralogical Composition

Table 11 comprises the so-called mass recovery percentages. These values provide a means to evaluate the closure of a mass balance by rationing the sum of leachates and residual material over the original composition. The numbers vary highly, with some being consistently low (e.g., chromium, silicon) and others being very small to very large (e.g., nickel, zirconium). The low concentrations can be attributed to the superior performance of the fusion digest technique on the original composite, as well as on losses due to non-analytical issues, e.g., the presence and composition of interstitial liquid in the sludge. Other issues that interfere with these numbers are the influence of evaporated and rehydrated solids and inhomogeneity within the solids during sampling.

An explanation for the low recovery in SY-102 is attempted in the chapter on this tank, however, no distinct answer was found.

Table 11. Mass Recovery.

(%)	AY-102	AZ-102	AW-105	AN-106	SY-102
Aluminum	77%	91%	92%	62%	49%
Chromium	70%	75%	57%	70%	44%
Iron	74%	92%	55%	41%	33%
Nickel	75%	129%	107%	45%	31%
Silicon	14%	48%	64%	30%	70%
Zirconium	144%	90%	44%	117%	34%
Bismuth	--	18%	--	45%	47%
Fluoride	97%	55%	60%	95%	--
Chloride	82%	71%	131%	67%	106%
Sulfate	80%	63%	75%	78%	101%
Phosphate	212%	204%	--	76%	190%

Formula: Recovery (%) = [(sum of leachates) + residual solids]*100/original composite; all amounts used in mmole; see tables in individual chapters 4.x.

To evaluate the quality of liquid analyses applied to the leachate samples, a charge balance was calculated for each sample as shown in Table 12. Metals were treated as cations, except for aluminum, which was attributed to the anions as aluminate $[\text{Al}(\text{OH})_4^-]$. Phosphorus and sulfur were excluded since phosphate and sulfate were measured using IC. Most of the leachate samples are in excellent balance, however, the lack of TIC/TOC analyses for some of the interim leachate samples artificially enhances the differences.

Table 12. Charge Balance for Leachate Samples.

Tank	[mol/L]	WL	CL	PL
AY-102	Sum positive charges	0.99	4.75	2.35
	Sum negative charges	1.25	4.52*	2.18
AZ-102	Sum positive charges	1.18	4.59	-
	Sum negative charges	0.59*	4.77	-
AW-105	Sum positive charges	1.32	-	-
	Sum negative charges	1.43	-	-
AN-106	Sum positive charges	0.66	3.55	-
	Sum negative charges	0.51*	3.62	-
SY-102	Sum positive charges	2.57	3.45	2.28
	Sum negative charges	2.23*	3.46*	1.56

As a means to evaluate the chemical analyses and the mineralogical findings, a recalculation effort was started to identify the relative percentages of minerals. This effort is following the

same logic that is commonly used for mass balances by attributing a certain mineralogical composition to an element. However, in this case a more sophisticated approach was taken to identify the distribution of some elements within several contributing phases, e.g., aluminum within gibbsite (aluminum hydroxide), boehmite (aluminum oxyhydroxide), and dawsonite (sodium aluminum carbonate). In some instances this distribution was not identifiable, for example in cases where both sodium carbonate (thermonatrite) and dawsonite were present. In this case special assumptions were necessary. The starting point in all cases was the minerals identified by solid phase characterization. These minerals were “used up” by their “essential elements,” e.g., silicon was 100% attributed to cancrinite. In Table 13 below, a compilation of the mineral compositions and of the respective molecular masses are shown. The amount of sodium left after all the identified minerals were calculated was used to calculate all identified anion contents and displayed as “other phases.” In case more sodium was left it was attributed to sodium hydroxide with a mass of 40. The results and details on the distribution of elements within the minerals are presented for each tank in the individual chapters.

Table 13. Mineral Compositions Used in Recalculations.

Mineral	Formula	Molecular Mass	Essential Analyte
Boehmite	AlO(OH)	60	Al
Cancrinite	Na ₆ Ca ₂ Al ₆ Si ₆ O ₂₄ (CO ₃) ₂ x 2H ₂ O	1088	Si
Clarkeite	Na(UO ₂)O(OH) x H ₂ O	344	U
Dawsonite	NaAlCO ₃ (OH) ₂	144	Al, TIC
Fe-Mn-oxide	(Fe,Mn) ₂ O ₃	variable	Fe, Mn
Gibbsite	Al(OH) ₃	78	Al
Hematite	Fe ₂ O ₃	160	Fe
Iron hydroxide	Fe(OH) ₃	107	Fe
Kogarkoite	Na ₃ SO ₄ F	184	S
Natrophosphate	Na ₇ (PO ₄) ₂ F x 19H ₂ O	712	F, P
Nitratine	NaNO ₃	85	NO ₃
Sodium carbonate	Na ₂ CO ₃	78	TIC
Sodium formate	NaHCOO	68	Formate
Sodium nitrite	NaNO ₂	69	NO ₂
Sodium oxalate	Na ₂ C ₂ O ₄	134	Oxalate
Sodium phosphate	Na ₃ PO ₄ x 12H ₂ O	380	P
Sodium sulfate	Na ₂ SO ₄	142	S
Sodium zirconium oxide	Na _{0.08} Zr _{0.92} O _{1.88}	116	Zr
Thermonatrite	Na ₂ CO ₃ x H ₂ O	124	TIC
Villaumite	NaF	42	F
Zirconium oxyhydroxide	ZrO(OH)	124	Zr

4.0 RESULTS BY TANK

4.1 Tank 241-AY-102

This tank was chosen as the commissioning tank for the WTP and has been extensively studied. According to PNNL-20646, *Hanford Waste Physical and Rheological Properties: Data and Gaps*, the waste contains only BL type sludge, i.e., low-level waste from B-plants' strontium and cesium recovery operations between 1967 and 1976. However, based on its history as described in RPP-RPT-44630, *Derivation of Best-Basis Inventory for Tank 241-AY-102 as of July 1, 2012*, tank AY-102 solids contain mostly mixed waste types from the sluicing of tank 241-C-106 in 1998 and some B Plant sludge.

In 2006 the supernate was transferred to AN-106, and AY-102 was refilled with supernate from tank 241-AP-101 (AP-101) in 2007. One potential impact this transfer could have is the precipitation of potassium salts onto the sludge layer (see LAB-RPT-12-00010, *Solid Phase Characterization of Tank 241-AY-102 Annulus Space Particulate*) due to the high potassium content of the aforementioned AP-101 supernate. The sludge samples chosen are from 2005 prior to this transfer (see Appendix A, Table A4). The samples were water leached, caustic leached, and a permanganate strike was applied.

Table 13 shows the amounts of the key constituents within the original composite and subsequent leachate samples and solid samples. When comparing the solid analyses, the caustic leach reduced the amount of aluminum by 2/3, and that of iron and nickel were reduced by 1/4. The results of the liquid analysis show a significant issue with the iron and nickel analyses. Each of the leachates had below detection limit (b.d.l.) results; however, the amount removed should be well within the analytical abilities.

Zirconium shows the problems with the small sample sizes for the analyses: while the water leached solids content plus the water leachate content add up to the original content within 15 rel%, the caustic leach step caused a virtual increase of the amount of zirconium. This could be attributed to the analysis of one larger zirconium-bearing crystallite that can cause a serious outlier.

The amount of chromium did not reduce during the oxidative leach, but rather was mostly removed with the water leach. Based on the data below, about 14 mol% ($[0.47 \text{ mmole WL} + 0.67 \text{ mmole CL}] / 8.15 \text{ mmole OC} = 0.14$) of chromium in the original composite was water-leachable, thus in the $\text{Cr}^{\text{VI}+}$ state. This amount can be attributed to chromium in the original interstitial liquid, which, while the sample dried in the archive and the water soluble chromium precipitated, still stayed oxidized. Comparatively, the amount of oxidized chromium after the permanganate addition is only 5 mol% ($0.40 \text{ mmole PL} / 8.15 \text{ mmole OC} = 0.05$).

The majority of the nitrites are removed during water leaching and only minor changes are visible for the permanganate leach. Additionally, the ratio of nitrate to nitrite does not change from the water leached solids to the caustic and permanganate leached solids. This excludes the possible explanation that nitrites are competing with chromium for oxidation.

As mentioned earlier, the silicon analyses pose a specific challenge. The amounts in Table 14 are based on the fusion digest results for the OC and are equivalently adjusted for the leached samples (WS and CPS)¹⁰. However, the results of the liquid analyses are still one to two orders of magnitude too small to close the mass balance. No resolution of this discrepancy was found.

Table 14. Amounts Retained and Released During Leaching for Tank 241-AY-102.

Solid (mmole) Leachate (mmole)	OC	WL	WS	CL	PL	CPS	TR (ratio)
Aluminum	450	0.01	418	163	32.8	151	1.7
Chromium	8.15	0.47	5.65	0.67	0.40	4.13	1.6
Iron	338	b.d.l.	292	b.d.l.	b.d.l.	249	1.4
Nickel	11.8	b.d.l.	9.83	b.d.l.	b.d.l.	8.77	1.3
Silicon	<i>142</i>	0.12	<i>14.1</i>	3.59	0.51	<i>15.9</i>	0.6
Zirconium	<i>0.51</i>	0.12	<i>0.68</i>	0.01	b.d.l.	0.60	0.6
Bismuth	b.d.l.	b.d.l.	0.01	b.d.l.	b.d.l.	0.02	--
Fluoride	1.35	0.54	b.d.l.	0.66	0.11	b.d.l.	--
Chloride	0.32	0.06	b.d.l.	0.16	0.04	b.d.l.	--
Sulfate	1.43	0.83	0.22	0.13	0.02	0.16	2.8
Sulfur	3.47	0.86	1.97	0.16	b.d.l.	0.98	2.5
Phosphate	7.81	2.65	1.53	10.1	2.66	1.19	-6.4
Phosphorus	21.8	2.46	7.67	9.71	2.42	4.64	1.6
Sodium	592	167	260	1,762*	309	301	1.4
Zr/Al	0.001		0.002			0.004	
Ni/Cr	1.4		1.7			2.1	
Nitrite	20.1	10.9	0.58	1.68	0.25	0.33	22
Nitrate	2.32	1.01	0.80	0.29	0.09	0.48	2
Nitrate/Nitrite	0.1	0.1	1.4	0.2	0.3	1.4	

OC ...original composite; WL ... water leachate; WS ... water leached solids; CL ... caustic leachate; PL ... permanganate leachate; CPS ... Caustic permanganate leached solids; TR (ratio) ... theoretical residuals relative to CPS; TR = (OC-WL- CL- PL)/CPS; *italics* ... fusion digest result.

* 2,050 mmol of sodium were added as sodium hydroxide during caustic leach (see Table 6). This amount is taken into account in the calculation of the TR as a sodium addition to the balance.

In Table 15 the mineralogical composition identified by solid phase techniques is shown. In previous sludge analyses of AY-102, the presence of Gibbsite, Hematite, Goethite, Dawsonite, and sodium diuranate (see RPP-RPT-46618, *Hanford Waste Mineralogy Reference Report*) was

¹⁰ Example of “equivalent adjustment” for silicon in water leached solids (WS) – for data, see table in Attachment B and Table 9:

$$\text{Ratio (OC fusion digest) / (OC acid digest)} = 28400 \mu\text{g/g} / 2710 \mu\text{g/g} = 10.48$$

$$\text{WS adjusted} = 248 \mu\text{g/g (WS acid digest)} * 10.48 = 2599 \mu\text{g/g.}$$

$$\Rightarrow \text{Converted to molality: WS adjusted} = [(2599 \mu\text{g/g}) / (28.09 \text{ g/mol})] / 1000 = 0.0925 \text{ mol/kg} = 9.25 * 10^{-5} \text{ mol/g.}$$

$$\Rightarrow \text{Net amount of solids in jar: WS} = [9.25 * 10^{-5} \text{ mol/g} * 253.78 \text{ g (mass of WS)}] * \{[100 - 40 \text{ (wt\% water)}] / 100\} \\ = 1.41 * 10^{-2} \text{ mol} = 14.1 \text{ mmol.}$$

This assumes that the same fraction of silicon did not get analyzed with the acid digest for the OC, WS and CPS.

determined. In this study, XRD has identified Dawsonite, Hematite, Gibbsite, and Cancrinite in the archived original composite. SEM confirmed these phases and found traces of a Na-U-rich phase (presumably Clarkeite). The material was too fine grained for any PLM identification.

Table 15. Mineralogy of Tank 241-AY-102 Sludge Based on Solid Phase Characterization.

	Minerals / Phases
OC	Dawsonite, Cancrinite, Hematite (all >25%), Gibbsite (~20%); Dawsonite had the largest individual crystals (SEM); Ag-Br-rich phase (SEM trace), Fe-Mn-rich phase (SEM)
WS	Hematite (~40%), Cancrinite (~25%), Gibbsite (~20%), Dawsonite (<20%); Ag-rich phase (SEM trace), Fe-Mn-rich phase (SEM)
CPS	Cancrinite (~40%), Hematite (~30%), Gibbsite (~25%); Ag-rich particle (SEM), Fe-Mn-rich phase (SEM)

OC ...original composite; WS ... water leached solids; CPS ... Caustic permanganate leached solids;

Table 16 shows the theoretical mass distribution of microscopically observed and/or X-ray-diffraction detected minerals, “other phases,”¹¹ and weight percent water¹². The numbers were derived from the chemical composition by using the identified minerals from the solid phase characterization.

Table 16. Tank 241-AY-102 Sludge Composition Based on Chemical Analyses.

[weight percent]	OC	WS	CPS
Observed minerals	71.9	43.5	31.9
Other phases	5.9	5.0	8.6
Water	9.8	40.0	41.6
Sum	87.5	88.5	82.2

The distribution within the observed minerals was calculated and the results are shown in Table 17. This effort was based on the minerals identified and the concentrations of the elements forming these minerals. For some of the phases, the amount was clearly attributed, e.g., the amount of Fe-Mn-oxide was determined by the amount of iron and manganese in the composite. For other phases, such as Gibbsite, Dawsonite, and Cancrinite, which all contain aluminum as a central element, the distinction was more evolved.

The major phases in the original composite are a mixed Fe-Mn-oxide with Hematite structure making up around 33 wt% and Dawsonite making up 39 wt%. The derivation of the mineral distribution within the Al-Na-CO₃-system was approached with the assumption that Cancrinite

¹¹ “Other phases” comprise phases that are considered present as pure sodium salts, but were not identified by solid phase characterization techniques. These included sodium nitrate, sodium nitrite, and sodium carbonate. Any amount of sodium that was not “consumed” by any measured anion was attributed to NaOH. Neither of these phases is expected to be present as precipitated solids, but rather in the interstitial liquid and/or in non decanted liquid.

¹² The measurement by TGA does not specifically identify water as the phase that is driven off during heating. Therefore, this number should be more accurately called “weight percent of material volatilizing below 100 °C”.

consumed all silicon, the remaining carbonate determined the amount of Dawsonite, and then the remaining aluminum determined the amount of Gibbsite. This led to a distribution of Cancrinite being present at 26 wt%, Gibbsite as a minor phase (~3 wt%), and Clarkeite even less (0.2 wt%).

Table 17. Mineralogy of Tank 241-AY-102 Sludge Based on Chemical Composition.

Mineral	[mmoles in jar]			[wt%] within minerals		
	OC	WS	CPS	OC	WS	CPS
Fe-Mn-oxide	209	178	153	33	42	62
Gibbsite	35	346	114	2.7	41	23
Dawsonite	273	57.9	21.4	39	13	7.9
Cancrinite	24	2.35	2.64	26	3.9	7.3
Clarkeite	0.7	0.6	0.2	0.2	0.3	0.2
Other phases	158	184	259	-	-	-

OC ...original composite; WS ... water leached solids; CPS ... Caustic permanganate leached solids

A major assumption within these calculations is the minimum water content after water leaching. The reported value of 21.8 wt% is considered incorrect, based (1) on the comments in the analytical worksheet calling the sample “Dry clumpy Black Dry Mud” – the material that was loaded out of the hot cell was sludge with standing liquid on top –, (2) on the water content after caustic leaching (41.6 wt%), and (3) on the average weight percent solids from TWINS (53.9 wt%). As a minimum water content, 40 wt% was used in the calculations.

The calculated mineralogy and the amounts determined by XRD posed an interpretive challenge for Cancrinite. Cancrinite is identified as one of the major phases by XRD within all three samples (OC, WS, and CPS), but based on the silicon analysis from the acid digest it would only be present in trace amounts. This led to the use of fusion digest results for the OC and equivalently adjusted values for the WS and CPS for these calculations. Even then, based on the chemical analysis, Cancrinite formed only a minor phase (<10%) within the water leached and caustic leached solids.

The mixed Fe-Mn-oxides need a more detailed explanation on their structure. The XRD pattern showed only signs of Hematite (Fe_2O_3). Manganese can, in general, replace iron in hematite up to a certain degree without changing the lattice structure. Mineralogical studies on Mn-replacement for Fe in hematite structures found a maximum of 5 mol% (see *Effect of manganese on the transformation of ferrihydrite into goethite and jacobite in alkaline media*, Cornell and Giovanoli, 1987), i.e., $\text{Fe}_{1.9}\text{Mn}_{0.1}\text{O}_3$, while the cubic mineral Bixbyite of the general formula $(\text{Mn}_{1-x}\text{Fe}_x)_2\text{O}_3$ was identified with x up to 0.63 (see *Structures of α - Mn_2O_3 , $(\text{Mn}_{0.983}\text{Fe}_{0.017})_2\text{O}_3$ and $(\text{Mn}_{0.37}\text{Fe}_{0.63})_2\text{O}_3$ and relation to magnetic ordering*, Geller, 1971). Bixbyite was not identified in the AY-102 XRD pattern.

The EDS spectra for the hematite in the composite sample showed a significant portion of manganese present, but due to the very fine-grained nature of the composite sample in this study, no clear evidence for mineral formation could be obtained via SEM. Based on the chemical composition, about 20% of the iron could be replaced by manganese in the average AY-102

original composite, comparable to the previously identified composition of $\text{Fe}_{1.75}\text{Mn}_{0.25}\text{O}_3$ described in 7S110-DLH-03-007, *Caustic Demand Test Results, Tank 241-AY-102 Sludge*, Table 9. This would indicate that either the cubic mineral Bixbyite formed co-existing with hematite but in too low concentration to be detected by XRD, or that Hematite formed with some manganese incorporated, and the remaining manganese and iron formed amorphous Fe-Mn-rich material.

The latter is likely the case from the appearance under the SEM and from observations in Cornell and Giovanoli, 1987, where it was found that after replacing up to 5 mol% of iron by manganese, the remaining manganese would precipitate onto the hematite as an “unidentified form.” In terms of Moh’s hardness, the differences between the two minerals are minor (5-6 for Hematite, 6.0-6.5 for Bixbyite according to Anthony et al., 2013, *Handbook of Mineralogy*).

All three leaching operations were performed on this sample to show the impact of each operation step on the key constituents and on the mineral phases.

The mixed Fe-Mn-oxides were slightly reduced in their amount during leaching (in actual numbers of mmole), but this is more likely attributable to the loss of fine grained solids during decanting rather than actual dissolution, since the leachates have Fe and Mn contents below detection limit.

Gibbsite significantly increases from the OC to the water leached WS. This is primarily explainable with the disproportion of Dawsonite, which produced water insoluble Gibbsite and water soluble Thermonatrite (Na-carbonate). The newly formed gibbsite in turn will then dissolve together with the original gibbsite to water soluble sodium aluminate. The following equations are part of the detailed discussion on dawsonite dissolution in Hanford tank environments by Reynolds et al. (2012). The amount of free hydroxide present in the original sample and the added hydroxide from the inhibited water seem to have been sufficient for the first reaction to happen during the water leach:

The caustic leach then reduced the amount of Gibbsite by 2/3. The amount of dawsonite was reduced by ~80% by the water leach and again ~50% by the caustic leach. Solid phase characterization identified dawsonite as the largest crystals in the original composite with laths of 10 x 2 micron. This is in accordance with earlier sample analyses (see *Evidence for dawsonite in Hanford high-level nuclear waste tanks*, Reynolds et al., 2012). XRD identified dawsonite in the water leached solids, but could not detect it in the caustic leached samples, while SEM did not confirm dawsonite in either leach sample.

One of the aspects of concern for the direct feed of this sludge to the HLW melter is mineral associations of chromium and nickel. If chromium is oxidized (i.e., Cr[VI]), it is highly soluble and washed out of the HLW stream. However, in the reduced form (Cr[III]) it can form the

highly insoluble Cr-Ni-spinels¹³ with the composition NiCr_2O_4 , which are thermodynamically preferred at melting temperatures and are one of the major limitations for waste loading during glass production. The amount of retained chromium after all leaches is 54 mol% of the OC, while 75 mol% of nickel is retained. Although no Ni-Cr-bearing particle was found in the sludge sample, the OC, WS, and CPS samples have a nickel over chromium molar ratio of 1.4, 1.7, and 2.1, respectively, indicating a high probability for these spinels to form in the melter.

¹³ Spinel is a mineral with the general structure $\text{A(II)B}_2\text{(III)O}_4$ – the most common combination in nature is MgAl_2O_4 ; no spinel analysis could be confirmed to date in actual Hanford tank sludges.

4.2 Tank 241-AZ-102

Tank AZ-102 received PUREX waste and B plant waste; in particular, it was one of the receiving tanks for high level PUREX waste between 1986 and 1988 of the so-called P3 sludge and for a clean-out run of the PUREX plant in 1990 (RPP-RPT-44049). The samples described in Table A2 are from core sampling events in 2004 and 2005. As described earlier in Section 3.0, paragraph 3, the samples were not representative for the average sludge of the tank. The material included in the original composite was entirely¹⁴ from the bottom heel of material introduced before 1986.

AZ-102 (and tank 241-AZ-101) is of particular interest for vitrification due to its high sulfur content. Sulfur has a relatively low upper limit of <1 wt% to be incorporated into the glass. For higher concentrations in the feed it can form sodium sulfate, which is highly water soluble and has the effect of extracting cesium and strontium (for an overview on sulfur in borosilicate melts see, e.g., *Additive Testing for Improved Sulfur Retention: Preliminary Report*, Amoroso and Fox, 2011, pages A4 to A6, for specific details on solubilities, see *Sulfur chemistry in a borosilicate melt. Pt. 1: Redox equilibria and solubility*, Schreiber et al., 1987). This would have a particularly negative impact for a direct feed option without ion exchange in pre-treatment.

The sample was water and caustic leached. Table 18 compiles the amounts of the key constituents within the original composite and subsequent leachate samples and solid samples; the analytical results for all elements are in Attachment B. About 30-50% of the aluminum and chromium are leached while iron and zirconium are entirely retained. Fluoride, which is a major contributor within the anions, gets entirely dissolved during the two leaching steps, indicating that the highly refractory zirconium oxyfluoride¹⁵ is not present in these samples.

**Table 18. Amount of Constituents Retained and Released during Leaching.
(2 sheets)**

Solid (mmole)	OC			CS	TR
Leachate (mmole)		WL	CL		(ratio)
Aluminum	361	b.d.l.	106	222	1.1
Chromium	6.45	0.76	0.70	3.36	1.5
Iron	278	b.d.l.	b.d.l.	256	1.1
Nickel	11.7	b.d.l.	b.d.l.	15.1	0.8
Silicon	29.2	0.05	1.14	12.9	2.2
Zirconium	19.3	0.24	0.00	17.1	1.1
Bismuth	0.03	b.d.l.	b.d.l.	0.01	5.5
Fluoride	39.4	6.57	14.0	1.03	18
Chloride	0.21	0.09	0.06	b.d.l.	

¹⁴ It is not possible to determine whether the current sample jar of Core 317, Segment 19, contains the lower half or the upper half of the segment. This sample was subsampled for several studies prior and was repackaged at least once.

¹⁵ See Section 4.3 on issues during DF-HLW operations due to this phase.

Table 18. Amount of Constituents Retained and Released during Leaching.
(2 sheets)

Solid (mmole) Leachate (mmole)	OC	WL	CL	CS	TR (ratio)
Sulfate	18.6	10.6	1.01	0.16	45
Sulfur	24.4	10.4	3.09	0.32	35
Phosphate	1.60	0.19	1.10	b.d.l.	
Phosphorus	8.43	0.21	3.10	1.12	4.6
Sodium	790	171	761 *	198	5.5
Zr/Al	0.06	-	-	0.09	
Ni/Cr	1.8	-	-	4.5	

OC ...original composite; WL ... water leachate; WS ... water leached solids; CL ... caustic leachate; CS ... Caustic leached solids; TR (ratio) = (OC-WL- CL)/CS ... theoretical residuals

* 1,230 mmol of sodium were added as sodium hydroxide during caustic leach (see Table 6). This amount is taken into account in the calculation of the TR as a sodium addition to the balance.

Tables 19, 20, and 21 show the sludge composition based on recalculated chemical analyses and actual mineralogical analyses.

Table 19. Tank 241-AZ-102 Sludge Composition Based on Chemical Analyses.

[weight percent]	OC	CS
Observed minerals	55.0	43.2
Other phases	21.0	1.7
Water	14.2	40.0
Total sum	90.2	84.8

As is the case of AY-102, a major assumption necessary was the water content of the caustic leached solids. The analysis reported a value of 10.82%, with a duplicate of 9.787 %. However, the sample description was “dry brown flakey dirt”. Since this material was taken from the jar with freshly leached material and standing liquid, this description indicates that the material in the 20-mL vial dried out during storage; the material was analyzed 36 days after load-out from the hot cell. The average TWINS percent solids content in earlier analyzed sludges of AZ-102 is 44.6 wt%. The assumed minimum water content was 40 wt%.

Table 20. Mineralogy of Tank 241-AZ-102 Sludge Based on Solid Phase Characterization.

	Minerals / Phases
OC	Dawsonite (~40%), Gibbsite (>10%), Hematite, Boehmite (minor), Clarkeite (trace); Zr-rich phase, Na-S-F-rich phase, Na-Ca-REE-rich phase (all SEM traces)
CS	Dawsonite (~75%); Hematite, Gibbsite, Boehmite (all minor), Clarkeite (trace); Zr-rich phase, Zr/U-rich, and REE-rich phase (all SEM traces)

OC ...original composite; CS ... Caustic leached solids

Dawsonite, Gibbsite, Boehmite, Hematite and Clarkeite were found in the XRD pattern and confirmed by SEM/EDS. However, the zirconium-rich phase is either mostly non-crystalline or a non-identified phase. This phase, which was only found in the EDS spectra but not confirmed by XRD, was defined as $\text{ZrO}(\text{OH})_2$ for calculation purposes. As mentioned above, zirconium oxyfluoride was ruled out by the high solubility of fluoride during the water leach.

The iron-bearing phase hematite was the second most abundant phase based on the chemistry, but was only present as a minor phase (<10 rel%) within the XRD spectrum. Therefore the rest (~70 %) seems to be present as non-crystalline Fe-oxide/hydroxides.

Kogarkoite (sodium sulfate fluoride) was identified as the only sulfur-bearing mineral by SEM but is undetected in the XRD spectrum due to its small contribution. This phase contributed about 4 mol% to the original composite and gets nearly entirely removed by water leaching (compare WL and CL in Table 16).

Table 21. Mineralogy of Tank 241-AZ-102 Sludge Based on Chemical Composition.

Mineral	[mmoles in jar]		[wt%] within minerals	
	OC	CS	OC	CS
Dawsonite	238	147	47	42
Hematite	139	128	30	40
Gibbsite	76	35	7.4	4.8
Kogarkoite	19	0.2	4.7	0.1
Zr-oxyhydroxide	19	17	3.7	4.8
Boehmite	47	40	4.6	5.5
Clarkeite	4.7	4.1	2.2	2.8
other phases	345	46.6	-	-

Sodium nitrite was identified by XRD but not confirmed by SEM and is considered an artifact from sample preparation. The sample was too fine grained for PLM to identify any phases. Since sodium nitrite is a major contributor to the supernate/interstitial liquid, a possible interpretation could be that it precipitated during XRD sample preparation on the slide.

To address the amount of Dawsonite in the mass balance, an assumption needed to be made regarding the aluminum dissolution. The assumption is that the ratio of aluminum-carbonate-rich to aluminum-rich phases stays the same throughout the dissolution. This is per-se incorrect, however, it was found to be a necessary approach due to the high abundance of TIC and because neither TIC nor aluminum could be exactly attributed to one phase.

In addition, the ratio of gibbsite to boehmite from the XRD spectra was used as an indicator¹⁶. Boehmite dissolves in caustic to:

¹⁶ These ratios were provided for information only, not reported numbers and are based on the relative intensities of the XRD lines. No quantification or even semi-quantitative analysis was performed. Gibbsite / Boehmite = 13/8 (as molar ratio) in OC and 7/12 in CS. Gibbsite in OC = 13/21 = 62%. Gibbsite in CS = 7/15 = 47%.

However, the kinetics of this dissolution are significantly slower than for gibbsite. This makes the aforementioned assumption seem reasonable insofar as the calculated dissolution of boehmite would be <15% (from 47 to 40 mmole), which would be expected for the leaching conditions.

For comparison, by taking into account the amount of gibbsite produced by the dawsonite dissolution, an actual gibbsite dissolution rate of 79% is achieved¹⁷.

Comparing these results to previous AZ-102 sludge washing tests, like the one reported in BNFL-RPT-038, *Characterization, Washing, Leaching and Filtration of AZ-102 Sludge*, shows equal results. The test conditions were significantly different, with 8 hours of caustic leaching using 3 M caustic at 85 °C in a recirculation loop of a crossflow filtration unit. The remaining amount of aluminum was 36% (52% this study), chromium was 42% (49% this study), and iron was 99% (99% this study). This indicates that the longer leaching times and the higher temperature were outbalanced by the lower molarity (3M as opposed to 19M) of the caustic solution.

The presence of dawsonite in these samples is an interesting aspect. As Reynolds et al., 2012, laid out, core samples taken in 2002 contained Dawsonite. No Dawsonite was found in 2003 after caustic addition for chemistry control in AZ-102, but aluminum and TIC dissolved equimolar upon hydroxide addition during caustic demand testing. The samples in this study were cored in 2004 and 2005 and show a very clear presence of Dawsonite. Since the samples used in this study are all from the lowermost part of the tank, it indicates that Dawsonite in these regions might not have been dissolved during the caustic addition.

¹⁷ 76 mmoles (Gibbsite in OC) + [238 mmoles (Dawsonite in OC) – 147 mmoles (Dawsonite in CS)] = 167 mmoles dissolvable gibbsite. Reduction from 167 mmoles to 35 mmoles in CS = 35/167 = 0.21.

4.3 Tank 241-AW-105

Tank AW-105 is considered a prime candidate for DF-HLW without the need for caustic leaching. This tank has a very low aluminum content and high zirconium content which leads to a molar Zr/Al ratio of ~8; Tank 241-AW-103 has a molar Zr/Al ratio of ~3, while all other tanks at Hanford have a ratio of <0.1. The main contributors to the AW-105 inventory were zirconium cladding waste (so-called CWZr2) and dilute, non-complexed PUREX waste according to the BBI report RPP-RPT-44625, R1, *Derivation of Best-Basis Inventory for Tank 241-AW-105 as of January 1, 2012*.

According to the BBI database, fluoride has a wash factor of 0.74, which indicates a rather high amount of water insoluble fluorine species. This poses a potential materials compatibility concern for the high level feed. If the fluoride is located primarily in a highly refractory phase such as zirconium oxy fluoride, it can have a severe negative impact on some melter components life-cycle (e.g., bubblers) and overall performance.

The sample material was used directly with no hydration. Only minor drying happened lowering the water content to 41 wt%; the BBI water content for AW-105 is between 59 and 64 wt%. Based on the amounts shown in Table 22 in combination with the theoretical amounts from Table 8, the water leach was more effective than predicted. Aluminum was leached by 40% ($9.2/15.3 = 0.6$) and sodium and fluoride by 84 % ($108/658 = 0.16$) and 92 % ($39.4/483 = 0.08$), respectively.

The fluoride TR ratio of 6 implies that the actual leaching is more in the range of 50% [$(483-248)/483 = 0.49$] with the remaining fluoride not being detectable using the standard IC analysis with water leach preparation. Zirconium was released by 28% ($147/203 = 0.72$), however, most likely this occurred by decanting of unsettled material rather than by actual leaching, based on the minute amount of zirconium in the water leachate. AW-105 contained the material that settled the slowest during testing; e.g., in order to obtain a clear water leachate sample for analysis, the slurry had to be centrifuged for 1.5 hours.

Table 22. Amount of Constituents Retained and Released during Leaching. (2 sheets)

Solids [mmole] Liquid [mmole]	OC	WL	WS	TR (Ratio)
Aluminum	15.3	7.66	9.19	0.8
Chromium	4.88	0.13	2.67	1.8
Iron	16.0	0.00	8.76	1.8
Nickel	0.71	0.48	0.28	0.8
Silicon	10.2	4.10	2.42	2.5
Zirconium	203	0.06	147	1.4
Bismuth	b.d.l.	b.d.l.	b.d.l.	
Fluoride	483	248	39.4	6.0
Chloride	2.26	2.58	0.37	-0.9

Table 22. Amount of Constituents Retained and Released during Leaching. (2 sheets)

Solids [mmole] Liquid [mmole]	OC	WL	WS	TR (Ratio)
Sulfate	3.92	2.31	0.63	2.5
Sulfur	1.56	2.33	0.24	-3.2
Phosphate	b.d.l.	b.d.l.	b.d.l.	
Phosphorus	6.06	2.75	2.56	1.3
Sodium	658	494	108	1.6
Zr/Al	13.3	-	16.0	
Ni/Cr	0.1	-	0.1	

OC ...original composite; WL ... water leachate; WS ... water leached solids; TR = (OC-WL)/WS

As shown in Table 8, AW-105 had the most systematic difference between fusion and acid digest results. All of the fusion digest results were higher between 1.2 and 1.6 times (average 1.4) except for silicon (9.7x) and zirconium (2.8x). This indicates a general error during sample preparation such as a dilution factor rather than incomplete dissolution. However, looking through the available notes did not indicate such an error.

Tables 23 and 24 compare and contrast the re-calculated and the identified mineral composition of the sludge and the final leached sample.

Table 23. Tank 241-AW-105 Sludge Composition Based on Chemical Analyses.

[weight percent]	OC	WS
Observed minerals	47.3	22.5
Other constituents	12.3	11.0
Water	41.2	68.7
Total sum	100.8	102.2

Solid phase characterization determined the major contributor among the observed minerals as Villiaumite, the mineral form of sodium fluoride; no other fluoride-bearing phase could be identified.

Table 24. Mineralogy of Tank 241-AW-105 Sludge Based on Solid Phase Characterization.

	Minerals / Phases
OC	Villiaumite (>90%), Sodium zirconium oxide, Clarkeite (both <5%)
WS	Villiaumite (~6%), Gibbsite (>20%), Sodium zirconium oxide (>10%), Clarkeite (<5%)

OC ...original composite; WS ... water leached solids

The crystalline form of the zirconium phase was defined as sodium zirconium oxide. This zirconium phase is not truly a mineral, but rather an XRD reference material that fits to the XRD

spectrum and as well as the SEM observation of sodium being omnipresent with zirconium. Its formula is $\text{Na}_{0.08}\text{Zr}_{0.92}\text{O}_{1.88}$ with a structure close to baddeleyite (pure ZrO_2) and is not to be mistaken with the commercially available sodium zirconium oxide Na_2ZrO_3 ; thus a better referral to the phase found in this sludge would be sodium-bearing zirconium oxide. In addition, most of the zirconium bearing material is either non- or poorly crystalline (see below).

Gibbsite is not identifiable in the original XRD spectrum due to the overpowering amount of Villiaumite, however, in the water leached sample, the aluminum species is identified and thus assumed to be present in the original composite. An alternative explanation would be that Dawsonite is present in the original composite and disproportioned into gibbsite and sodium carbonate during the water leach, of which the latter would be washed out. No proof could be found for either interpretation.

Within the calculated mineral distribution of Table 25, the dominance of Villiaumite is apparent. This is in accordance with the optical appearance and the XRD results. On the other hand, the Na-Zr-oxides seem to be poorly crystallized since they were barely identifiable with the XRD, but rather prominent according to the recalculation from the chemical analysis. On the SEM and PLM images, the crystals were very prominent in the original composite with 50-micron long laths (see Figure 8, and Section A-7). These crystals were water soluble under the leaching conditions; none could be identified in the water leached solids.

Table 25. Mineralogy of Tank 241-AW-105 Sludge Based on Chemical Composition.

Mineral	[mmoles in jar]		[wt%] within minerals	
	OC	WS	OC	WS
Villiaumite	483	39	39	10
NaZr-oxide	221	98	49	69
Clarkeite	13	7	9	15
Gibbsite	24	14	4	7
other phases	491	119	-	-

Figure 8. Electron (left) and Optical (right) Microscopy Images and EDS Spectrum (middle) of the Na-Zr-bearing Lath Shaped Phase.

One of the possible zirconium-bearing phases was the highly refractory zirconium oxyfluoride (ZrOF_2). This phase could not be identified by XRD nor do the EDS-spectra show a fluoride peak. Additionally, the amount of fluoride in the post-leach sample is insufficient to accommodate more than 15% of the available zirconium even when neglecting the presence of the identified Villiaumite remnants¹⁸. However, whether or not any amorphous (or barely crystallized) Zr-O-F associations exist cannot be answered.

Water leaching caused some of the Villiaumite crystals to remain structurally intact with deep fractures on the surface. Figure 10 illustrates the comparison between original composite crystals which show nearly perfect structure and the water leached solids in both SEM and PLM images. This shows that the water leach of these large crystals was incomplete, and more vigorous mixing could likely have resulted in an even higher reduction in fluoride in the residual sludge.

Figure 9. Change of Villiaumite Appearance during Treatment: Original Composite (left) and Post-leaching (middle and right).

Among the “other phases,” sodium oxalate was positively identified only by PLM and could be attributed to 7 mmol (i.e., 2 wt% of total solids) based on the chemical composition. As iron-bearing mineral, a Fe-Mn-bearing hydroxide was chosen and would account for 29 mmol (6 wt%); no iron bearing phase was identified in either XRD or SEM (PLM cannot identify opaque minerals). The hydroxide form was chosen over the hematite composition based on reports of iron hydroxide from earlier studies as summarized in RPP-RPT-46618, *Hanford Waste Mineralogy Reference Report*.

¹⁸ $39.4(\text{fluoride content in WS in mmole}) \times \frac{1}{2} = 19.7 \text{ mole ZrOF}_2 \text{ possible; amount of Zr} = 147 \text{ mmole; } 19.7/147 = 0.13.$

4.4 Tank 241-AN-106

This tank did not get designated as a specific waste type due to the mixture of waste types prior to 2003 based on the BBI report on AN-106 (RPP-RPT-43992, *Derivation of Best Basis Inventory for Tank 241-AN-106 as of November 07, 2012*). From 2003 to 2012, it was the receiving tank for several C-farm retrievals (tanks 241-C-103, 241-C-106, 241-C-107, 241-C-108, 241-C-109, 241-C-110, 241-C-201, 241-C-202, 241-C-203, and 241-C-204) which caused a significant increase in sludge solids and overall change in sludge composition. In particular, retrieval of tank C-106 was performed using oxalic acid which introduced abundant amounts of oxalates when the retrieval slurry was neutralized in tank AN-106. The samples in this study were taken in 2004 and 2005, after the C-106 transfer.

The treatment was equivalent to the treatment of AZ-102, including water washing, caustic leach, and final water leach to remove any components that turned into water soluble species, such as sodium aluminate. The treatment was rather effective; as shown in Table 26, the amount of aluminum is reduced to $\sim 1/3$ ($51.5/163 = 0.32$), chromium, iron, silicon, and bismuth are reduced to $\sim 1/2$, while zirconium increased slightly. In the fusion digest analysis, the amount of zirconium in the original composite increased to $1740 \mu\text{g/g}$ as opposed to $616 \mu\text{g/g}$, however, it is still less than the amount detected in the leached sample ($2280 \mu\text{g/g}$). It could not be identified whether this is solely attributable to sample heterogeneity or a general analytical issue. For all metals (except silicon and zirconium) the fusion digest reported values between 1.3 and 1.6 times higher than the acid digest (silicon 10x, zirconium 3x).

However, the results have serious accuracy issues. As shown in the last column in Table 26, the theoretical leached solids ratio is consistently in the range of 2 to 4, meaning that the calculated amounts based on the original composite and the leachate results, are significantly higher than the reported caustic leached solids results for all key constituents. Assuming that the problem lies within the solid analyses rather than the liquid analyses, leaves several reasons, including analytical errors, sampling errors, and weighing errors.

Since the difference is across all of the metals analyzed, a systematic difference is more likely. One rather “simple” solution is presented in the last column of Table 26, entitled CS adjusted. The adjustment was to reduce the water content within the sample analyzed (as opposed to the actual sample which might very well have had 66 wt% water) to about 30 wt% water. In this case the theoretical and actual results are strikingly overlapping for all of the metals analyzed (see TR adjusted ratios). This shows one of the key issues with the comparison of actual solids within a slurry; the dependency on accurate determination of the water content. While the TGA method reports weight percent of volatile material at $\sim 100^\circ\text{C}$ it does not distinguish between different sources. Additionally, as seen with the original composite analyses of AY-102 and AZ-102, a completely dried out sample was analyzed and reported with a comment, but not rerun using a more appropriate subsample.

Based on the chemical composition, the sludge composition was reconstructed as shown in Table 27 by using the identified mineral phases from Table 28. The observed mineralogy is rather simple – Gibbsite and Hematite dominate the sample, with minor contributions of sodium

oxalate and Clarkeite. This is in good agreement with the chemical compositions and depletions shown in Table 26.

Table 26. Amount of Constituents Retained and Released during Leaching.

Solid [mmoles] Liquid [mmoles]	OC	WL	CL	CS	TR (ratio)	CS adjusted	TR adjusted
Aluminum	163	1.35	47.3	51.5	2.2	109	1.0
Chromium	0.84	0.12	0.23	0.24	2.0	0.50	1.0
Iron	94.4	0.04	0.04	38.7	2.4	81.9	1.2
Nickel	5.75	0.01	b.d.l.	2.59	2.2	5.49	1.0
Silicon	49.8	0.02	2.09	13.1	3.7	27.7	1.7
Zirconium	1.55	0.00	0.01	1.81	0.9	3.83	0.4
Bismuth	4.87	b.d.l.	0.02	2.17	2.2	4.59	1.1
Fluoride	28.3	8.07	15.5	3.21	1.5	6.79	0.7
Chloride	0.96	0.39	0.26	b.d.l.	--	0.00	--
Sulfate	3.49	1.47	0.95	0.30	3.6	0.63	1.7
Sulfur	4.09	1.59	1.03	0.28	5.2	0.59	2.5
Phosphate	14.7	5.04	4.91	1.21	3.9	2.57	1.9
Phosphorus	36.8	4.91	4.75	2.00	14	4.22	4.2
Sodium	319	77.4	845*	240	2.9	509	1.4
Zr/Al	0.01	-	-	0.04		0.04	
Ni/Cr	6.8	-	-	10.9		10.9	

OC ...original composite; WL ... water leachate; WS ... water leached solids; CL ... caustic leachate; CS ... Caustic leached solids; TR (ratio) = (OC-WL- CL)/CS ... theoretical residuals; CS-adjusted ... CS, but an assumed water content of 28 wt%; TR adjusted ... calculated as TR, but using CS-adjusted.

* 1,300 mmol of sodium were added as sodium hydroxide during caustic leach (see Table 6). This amount is taken into account in the calculation of the TR as a sodium addition to the balance.

Table 27. Tank 241-AN-106 Sludge Composition Based on Chemical Analyses.

[weight percent]	OC	CS
Observed minerals	41.2	12.5
Other phases	12.3	12.5
Water	45.8	66.0
Sum	99.4	91.0

Table 28. Mineralogy of Tank 241-AN-106 Sludge Based on Solid Phase Characterization.

	Minerals / Phases
OC	Gibbsite, Hematite (both <40%), Sodium nitrite (<30%); Thermonatrite possible, Cancrinite (SEM only) and Natrophosphate (SEM, PLM);
CS	Thermonatrite (>50%), Hematite (~20%), Gibbsite, Sodium oxalate (both >10%), Clarkeite (<5%)

OC ...original composite; CS ... Caustic leached solids;

The recalculated mineralogy in Table 29 identified the two key components, but also found phases that were not directly observed with XRD, such as Natrophosphate and Thermonatrite in the original composite (both > 10%). SEM identified possible Thermonatrite, Natrophosphate was found by SEM and confirmed by PLM. Cancrinite was calculated with the fusion digest result using the same rational as for AY-102 (see Section 4.1). Sodium nitrite was considered an artifact that precipitated on the XRD stub drying preparation rather than being present as a solid. Neither SEM nor PLM found evidence of nitrites.

Table 29. Mineralogy of Tank 241-AN-106 Sludge Based on Chemical Composition.

Mineral	[mmoles in jar]		[wt%] within minerals	
	OC	CS	OC	CS
Gibbsite	113	38	26	33
Hematite	47	19	22	34
Thermonatrite	21	0.0	7.7	0.0
Cancrinite	8.3	2.2	27	26
Natrophosphate	7.4	0.6	16	4.8
Clarkeite	1.0	0.4	1.1	1.6
Other Na-salts	171	222	-	-

Two phases that were identified by SEM but not by XRD are lath-shaped and are made of Na-Al-P and Na-Bi-Fe-P. These needles or laths are quite prominent; however, since the crystal structure is unidentified to date, these phases could not be included in the recalculation effort, and all of the aluminum was attributed to Gibbsite. Figure 11 shows examples of the morphology and chemistry of the two kinds of laths – for more details see Section A-8. Neither of these crystals could be found in the post-treated sample.

Figure 10. Phosphorus-bearing Lath-Shaped Crystalline Material in Tank 241-AN-106.

These Na-Al-P-bearing phases were identified in several recent tank waste analyses. An ongoing study focuses on the formation of these phases within tank farm conditions (see WRPS-1300252, *Test Plan and Procedure for Aluminum Phosphate Testing*).

4.5 Tank 241-SY-102

Tank SY-102 contains primarily transuranic waste solids (so-called Z sludge) from the Plutonium Finishing Plant (see RPP-RPT-44643, *Derivation of Best-Basis Inventory for Tank 241-SY-102 as of January 1, 2012*). Other solids sources are related to retrieval transfers from tanks 241-S-102 and 241-S-112.

In terms of chemical composition, this tank has about a tenfold amount of chromium compared to the other tank samples, about double the amount of phosphates, and roughly five times the amount of total organic carbon (17,600 µg/g for OC). This leads to very different tank chemistry compared to the other samples.

For the sample composite only material that was not used in the current plutonium particle assessment was available. Therefore the amount of plutonium and associated elements is significantly reduced compared to the average TWINS values and also compared to the amounts identified in said study (see LAB-RPT-12-00006, R.1, *Characterization of Plutonium-Bearing Waste in the High-Level Waste Storage Tanks 241-SY-102, 241-TX-118, and 241-AZ-101 and the Plutonium Finishing Plant Z-9 Crib*).

The samples were water leached, caustic leached, and water leached again; permanganate was added and a final water leach was performed. The results of the key constituents are presented in Table 30; the complete analyses are shown in Attachment B.

Table 30. Amount of Constituents Retained and Released during Leaching.
(2 sheets)

Solids [mmole] Liquids [mmole]	OC	WL	CL	PL	CPS	TR (ratio)
Aluminum	145	6.75	23.8	7.90	33.3	3.2
Chromium	89.0	1.31	0.96	12.4	24.2	3.1
Iron	5.40	b.d.l.	b.d.l.	b.d.l.	1.77	3.0
Nickel	0.99	0.01	b.d.l.	0.00	0.30	3.3
Silicon	10.0	0.26	0.63	0.19	5.93	1.5
Zirconium	0.09	b.d.l.	b.d.l.	b.d.l.	0.03	3.0
Bismuth	0.22	b.d.l.	b.d.l.	b.d.l.	0.11	2.1
Fluoride	b.d.l.	0.32	0.27	0.07	b.d.l.	
Chloride	9.71	5.64	3.37	0.76	0.55	-0.1
Sulfate	2.17	1.13	0.70	0.16	0.21	0.9
Sulfur	2.68	1.51	0.89	0.17	0.15	0.7
Phosphate	2.19	1.84	1.54	0.36	0.41	-3.8
Phosphorus	4.98	1.77	1.60	0.38	0.32	3.9
Sodium	640	221	637*	173	207	2.9
Zr/Al	0.001	-	-	-	0.001	
Ni/Cr	0.01	-	-	-	0.01	

Table 30. Amount of Constituents Retained and Released during Leaching.
(2 sheets)

Solids [mmole]	OC				CPS	TR
Liquids [mmole]		WL	CL	PL		(ratio)
Nitrite	347	52.1	32.5	7.25	20	13
Nitrate	153	64.5	40.8	8.85	9	5
Nitrate/Nitrite	0.44	1.24	1.25	1.22	0.44	3.2

OC ...original composite; WL ... water leachate; CL ... caustic leachate; PL ... permanganate leachate; CPS ... Caustic permanganate leached solids;

* 990 mmol of sodium were added as sodium hydroxide during caustic leaching. This amount is taken into account in the calculation of the TR as a sodium addition to the balance.

One very apparent result is the discrepancy between the theoretical residual (OC-WL-CL-PL) and the actual residual composition shown in the last column of Table 30. All metal cations are off by a factor of 2 to 3, while the anions are underrepresented. Comparing the fusion versus acid digest results of the original composite shows a general trend towards higher numbers for the fusion digest between 1.1 and 1.7 times the acid digest results. Multiplying the acid digest results of the CPS with an average factor of 1.25 (average of the fusion over acid digest results for OC) slightly reduces the TR ratio, but does not resolve the issue. Again, as with AN-106, reducing the water content within the calculation of the mmols in the solids from the measured 76.1 wt% to about 40 wt% would resolve this problem. However, there is no indication on the TGA spectra for such a serious error. One possible explanation could be that the sample for the ICP-AES was left to dry while the other samples were taken before with the appropriate moisture content.

Table 31. Tank 241-SY-102 Sludge Composition Based on Chemical Analyses.

[weight percent]	OC	CPS
Observed minerals	34.3	13.6
Other phases	28.4	5.4
Water	37.8	76.1
Total sum	100.5	95.1

One of the largest contributors (after sodium and aluminum), chromium, was not identified as a crystalline phase (see Table 32), and thus was added as the fictional CrOOH phase. This phase is assumed insofar that no analysis has shown its existence but it is chemically feasible that it could form in the tank environment. What has been found are fine-grained (<2 μm) amorphous Na-Al-Cr-rich particles and some rare (only) chromium-rich material. Since these identifications were done by SEM-EDS, no crystal structures were identified. Additionally, previous analyses found associations of aluminum with chromium to be present in the SY-102 sludge (see RPP-RPT-46618).

Table 32. Mineralogy of Tank 241-SY-102 Sludge Based on Solid Phase Characterization.

	Minerals / Phases
OC	Sodium oxalate (>30%), Sodium phosphate dodecahydrate (>25%), Sodium nitrate (>20%), Sodium nitrite (>10%), Gibbsite (<10%); Dawsonite and Clarkeite traces (SEM only)
CPS	Sodium oxalate (~80%), Gibbsite (~20%); Cancrinite (SEM only)

OC ...original composite; CPS ... Caustic permanganate leached solids

The mineralogy based on the chemical composition with the input of the actually identified mineral phases is shown in Table 33. The prime contributor is sodium oxalate, together with Gibbsite and Thermonatrite (sodium carbonate monohydrate). Dawsonite appeared as laths as large as 20- μ m long but was not included in the recalculation since it was unidentified in the leached sample, and the ratio of aluminum-bearing versus “pure” sodium carbonate could not be determined. This is one example where AFA could have provided essential information. In the leached sample, thermonatrite was not identified by either technique, but was included to address the carbonate amount. Nitratine (sodium nitrate) is included in the table, since it was identified by SEM and XRD as a solid phase of the OC.

Table 33. Mineralogy of Tank 241-SY-102 Sludge Based on Chemical Composition.

Mineral	[moles in jar]		[wt%] within minerals	
	OC	CPS	OC	CPS
Gibbsite	135	27	30	16
Natroxalate	119	45	46	46
Nitratine	113	6.5	0	0.0
Thermonatrite	32	25	13	28
Na-phosphate	5.0	0.3	5.4	0.9
Cancrinite	1.7	1.0	5.2	8.3
other phases	196	53	-	-

The combined leaching steps lead to a significant reduction of the key constituents, in many cases even more than projected using the wash and leach factors. Except for zirconium and bismuth, all constituents were reduced by >65% (dry based molar ratio). As opposed to the sample of AY-102, where the oxidation step using permanganate had little to no influence, the permanganate leaching step had the desired effect of oxidizing chromium to a water leachable species (compare chromium in WL, CL, and PL in Table 28). However, as mentioned above, the numbers for chromium do not add up in the way that CPS plus all leachates should be equal or close to OC.

The extent of chromium leaching was comparable to studies focused on optimizing oxidative leaching for the WTP pretreatment using sludge simulants as reported in PNNL-16794 (WTP-RPT-164), *Process Development for Permanganate Addition during Oxidative Leaching of Hanford Tank Sludge Simulants*. The PNNL study reported a dissolution rate of ~85% with optimized agitation conditions for several hours. The study reported herein achieved about

~73% ¹⁹ using the less effective mixing technique (shaking) but higher caustic concentrations (17.0 M) and a 1:1 ratio of manganese over chromium.

¹⁹ 24.2 mmole in CPS (non adjusted) / 89.0 mmole in OC = 0.27.

5.0 RECOMMENDATIONS

In order to achieve a reasonable analytical data package with the currently available instrumentation, the following adjustments are recommended:

- (1) For RCRA metals analyses, both KOH fusion digest and acid digest should be performed. The alternative of the microwave-assisted acid digest should be considered and evaluated for the specific needs of HLW feed. All protocols are in place as analytical procedures.
- (2) X-ray diffraction analyses should be performed in a quantitative mode. This would allow for quantitative information on the crystalline material with comparable results. Minor method development to incorporate standardization and revisions of the current analytical protocol would be necessary.
- (3) The AFA on the SEM should become a standard analytical device. This would provide vital information on the mineralogy of the samples, especially on amorphous material and low crystalline material. Minor revisions to the current standard analytical protocol would be necessary.
- (4) The water content needs to be measured more accurately. One option would be to compare a recently developed technique of using a moisture content analyzer with the currently used thermogravimetric analyses. The moisture content method was applied in a recent study on 241-C-109 hard heel samples and showed very promising results. Minor method development and revisions of current analytical protocols would be necessary.
- (5) Sample sizes should be depending on the activity level of the sample. The reason for the very small samples lies in the high activity level of some of the samples. However, the sample sizes currently used for chemical analyses seem insufficient. This is especially true for solids digests, where minerals of up to several hundreds of micrometer diameter can have a serious impact on how representative a microgram sample is for the rest of the jar, and on a grander scheme, for the whole tank material. The recommendation would be to have a protocol in place which defines the maximum size of material based on the α , γ , and $\beta+\gamma$ emissions. Method development and revisions of the current analytical protocols would be necessary. An alternative approach would be to require duplicate or triplicate digests for sludge samples using the current protocol.

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7.0 REFERENCES

- 7S110-DLH-03-007, 2003, "Caustic Demand Test Results, Tank 241-AY-102 Sludge," (interoffice memorandum from D. L. Herting, G. A. Cooke, and W. R. Warrant to K. G. Carothers, October 17), CH2MHILL Hanford Group, Inc., Richland, Washington.
- Anthony J. W., R. A. Bideaux, K. W. Bladh, and M. C. Nichols, Eds., *Handbook of Mineralogy*, Mineralogical Society of America, Chantilly, Virginia, <http://www.handbookofmineralogy.org/>.
- ATS-GD-1028, *Flagging Data in LIMS*, Rev. 8, Washington River Protection Solutions LLC, Richland, Washington.
- ATS-LT-161-100, "222-S Laboratory Sample Preparation and Operating Procedure for Scanning Electron Microscopes," Washington River Protection Solutions LLC, Richland, Washington.
- ATS-LT-507-101, "222-S Laboratory X-Ray Diffractometry (XRD)," Washington River Protection Solutions LLC, Richland, Washington.
- ATS-LT-519-107, "222-S Laboratory Polarized Light Microscopy," Washington River Protection Solutions LLC, Richland, Washington.
- BNFL-RPT-038, (PNWD-3045), 2000, *Characterization, Washing, Leaching, and Filtration of AZ-102 Sludge*, Rev. 0, Batelle, Richland, Washington.
- Cornell R. M. and R. Giovanoli, 1987, "Effect of manganese on the transformation of ferrihydrite into goethite and jacobsonite in alkaline media", *Clays and Clay Minerals*, Vol. 35, pp. 11-20.
- DOE/EM-0520, 2000, *Sludge Washing*, US Department of Energy, Office of Environmental Management, Office of Science and Technology, Washington DC.
- Ecology, EPA, and DOE, 1989, Hanford Federal Facility Agreement and Consent Order – Tri-Party Agreement, as amended, State of Washington Department of Ecology, U. S. Environmental Protection Agency, and U. S. Department of Energy, Olympia, Washington.
- Geller S., 1971, "Structures of α - Mn_2O_3 , $(\text{Mn}_{0.983}\text{Fe}_{0.017})_2\text{O}_3$ and $(\text{Mn}_{0.37}\text{Fe}_{0.63})_2\text{O}_3$ and relation to magnetic ordering," *Acta Crystallographica* Section B27, Vol. 27, Part 4, pp. 821–828.
- HNF-SD-WM-DP-250, 1997, *Tank 241-AW-105, Cores 195 and 196 Analytical Results for the Final Report*, Rev.0A, Waste Management of Hanford Corp., Inc., Richland, Washington.
- LA-211-102, "Determination of Free OH-/H+ using Metrohm Titrando," Rev. J-0, Advanced Technologies and Laboratories International, Inc., Richland, Washington.

- LA-212-106, "pH Determination of Aqueous Samples," Rev. I-0, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-342-100, "Determination of Carbon by Hot Persulfate Oxidation and Coulometric Detection," Rev. L-0A, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-504-101, "Water Leach Sample Preparation," Rev. M-0, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-505-163, "Acid Digestion of Sediments, Sludges, or Soil Samples for Spectroscopic Analysis of Metals," Rev. H-0, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-505-171, "Metals Analysis of IH Samples by Inductively Coupled Plasma Atomic Emission Spectrometry for ICP-JY," Rev. H-0, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-505-174, "Inductively Coupled Plasma (ICP) Emission Spectrometric Method for the Thermo Scientific iCAP 6500," Rev. A-0, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-506-102, "Determination of Trace Elements and Radionuclides using the PQ EXCELL Inductively Coupled Plasma –Mass Spectrometer," Rev. G-0, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-514-115, "Thermal Stability and Percent Weight Loss using the TA DSC and TGA," Rev. G-0, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-533-166, "Ion Chromatographic Analysis of Anions and Small Organic Acids on DIONEX Model ICS 3000," Rev. A-0/B-1, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LA-549-141, "Fusion by Alkali Metal Hydroxide," Rev. M-1a, Advanced Technologies and Laboratories International, Inc., Richland, Washington.
- LAB-PLN-12-00006, 2012, *Test Plan for the Performance Evaluation of Key Constituents during Pre-Treatment of High Level Waste Direct Feed*, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.
- LAB-RPT-12-00006, 2013, *Characterization of Plutonium-Bearing Waste in the High-Level Waste Storage Tanks 241-SY-102, 241-TX-118, and 241-AZ-101 and the Plutonium Finishing Plant Z-9 Crib*, Rev. 1, Washington River Protection Solutions LLC, Richland, Washington.
- LAB-RPT-12-00010, 2013, *Solid Phase Characterization of Tank 241-AY-102 Annulus Space Particulate*, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.

- PNNL-13452 (WTP-RPT-006), 2001, *Vitrification and Product Testing of C-104 and AZ-102 Pretreated Sludge Mixed with Flowsheet Quantities of Secondary Wastes*, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.
- PNNL-20646 (EMSP-RPT-006), 2011, *Hanford Waste Physical and Rheological Properties: Data and Gaps*, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.
- PNWD-3045 (BNFL-RPT-038), 2000, *Characterization, Washing, Leaching, and Filtration of AZ-102 Sludge*, Rev. 0, Batelle, Richland, Washington.
- Reynolds J. G., G. A. Cooke, D. L. Herting, and R. W. Warrant, 2012, "Evidence for dawsonite in Hanford high-level nuclear waste tanks," *Journal of Hazardous Materials*, Vol. 209-210, pp. 186-192.
- RPP-RPT-43992, 2013, *Derivation of Best Basis Inventory for Tank 241-AN-106 as of November 07, 2012*, Rev. 6, Washington River Protection Solutions LLC, Richland, Washington.
- RPP-RPT-44049, 2013, *Derivation of Best-Basis Inventory for Tank 241-AZ-102 as of October 1, 2012*, Rev. 6, Washington River Protection Solutions LLC, Richland, Washington.
- RPP-RPT-44625, 2012, *Derivation of Best-Basis Inventory for Tank 241-AW-105 as of January 1, 2012*, Rev. 1, Washington River Protection Solutions LLC, Richland, Washington.
- RPP-RPT-44630, 2012, *Derivation of Best-Basis Inventory for Tank 241-AY-102 as of July 1, 2012*, Rev. 4, Washington River Protection Solutions LLC, Richland, Washington.
- RPP-RPT-44643, 2012, *Derivation of Best-Basis Inventory for Tank 241-SY-102 as of January 1, 2012*, Rev. 2, Washington River Protection Solutions, LLC, Richland, Washington.
- RPP-RPT-46618, 2011, *Hanford Waste Mineralogy Reference Report*, Rev. 2, Washington River Protection Solutions LLC, Richland, Washington.
- RPP-RPT-50309, 2011, *Evaluation of Tank Waste Feed for the WTP HLW Mission: Basis for Integration of Waste Feed Delivery and Blending with Optimization of Waste Throughput*, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.
- RPP-RPT-53225, 2012, *Preconceptual Engineering Study for Direct Feed High-Level Waste*, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.
- RPP-RPT-54652, 2013, *Gibbsite Dissolution Studies Summary and Analysis*, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.
- Schreiber H. D., S. J. Kouzak, P. G. Leonhard, and K. K. McManus, 1987, "Sulfur Chemistry in a Borosilicate Melt. Part I. REDOX Equilibria and Solubility", *Glastechnische Berichte* Vol. 60, pp. 389-398.

SRNL-STI-2011-00524, 2011, *Additive Testing for Improved Sulfur Retention: Preliminary Report*, Rev 0, Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, Aiken, South Carolina.

WRPS-1202158, 2012, “Test Plan for Particle Size Distribution Measurements for the Performance Evaluation of Key Constituents during Pre-Treatment of High Level Waste Direct Feed,” (interoffice memorandum from R. B. Mabrouki to C. M. Seidel, May 31), Washington River Protection Solutions LLC, Richland, Washington.

WRPS-1205133, 2012, “Test Plan Results for Particle Size Distribution Measurements on High-Level Waste Samples,” (interoffice memorandum from R. B. Mabrouki to C. M. Seidel, November 30), Washington River Protection Solutions LLC, Richland, Washington.

WRPS-1300252, 2013, “Test Plan and Procedure for Aluminum Phosphate Testing,” (interoffice memorandum from D. L. Herting to J. G. Reynolds, January 28), Washington River Protection Solutions LLC, Richland, Washington.

ATTACHMENT A

SOLID PHASE CHARACTERIZATION

A-1. Particle Size Distribution.

Table A-1. Summary of Mean Diameter Ranges of Particles from Particle Size Distribution Measurements.

Tank	Sample	Sample number	Mean Ø (µm)
AY-102	OC	S12R000268	7.7 - 85.0 (525.8)
	WS	S12R000348	8.4 – 37.9 (174.8)
	CPS	S12R000275	4.8 – 6.6
AZ-102	OC	S12R000233	2.2 – 5.3 (83.9)
	CS	S12R000239	1.0 – 1.4
AW-105	OC	S12R000245	2.7 – 8.7
	WS	S12R000251	1.4 – 3.9
AN-106	OC	S12R000256	4.5 – 6.9
	CS	S12R000262	3.5 – 4.9
SY-102	OC	S12R000281	3.3 – 3.6
	CPS	S12R000288	3.1 – 5.0 (14.3)

This table compiles the range of mean diameters for each sample within the six measurement runs. Each measurement run had an increasing level of shear on the particle. If one run among the six showed an outlier, that number is added in parenthesis. For details on the technique, settings, and the individual results of the different runs, see the report WRPS-1205133.

A-2. Tank 241-AY-102 (Original Composite)

Sample number S12R000268.

X-ray Diffraction

Sample appeared to be a dry reddish-brown fine powder, and once dried, appeared to be homogeneous reddish-brown fine solids.

Major phases: Dawsonite, Hematite, Gibbsite, and Cancrinite.

Chemical Name	Mineral	Formula	Rel. Amount
Sodium Calcium Aluminum Silicate Carbonate	Cancrinite	$\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$	~30%
Iron Oxide	Hematite	Fe_2O_3	>25%
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	>20%
Sodium Aluminum Carbonate Hydroxide	Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$	~20%

Polarized Light Microscopy

Sample is dark brown, dry, very fine grained and prepared in 1.55 refractory index oil; consists of mostly opaque material with some Gibbsite.

40x, uncrossed polars

60x, crossed polars, Red I compensator

Scanning Electron Microscopy

Sample was prepared from dry powder by crushing lightly and lifting particulate onto adhesive carbon tab.

General area EDS shows dominance of Fe, Al, and Na, with Si, Mn, and P as minor elements and traces of Pb and Ca.

Very fine-grained material. Largest crystals are laths of Dawsonite about 10 μm by 2 μm. Dawsonite (Na/Al-rich), Gibbsite (Al-rich), Hematite (Fe-Mn-rich), and Cancrinite (Na/Al/Si-rich) all confirmed. Found Clarkeite (Na/U-rich) and patches of Na-rich that could be Thermonatrite. Ag/Br-phase seen in SEM.

A-3. Tank 241-AY-102 (Water Leached)

Sample number S12R000348.

X-ray Diffraction

Sample appeared to be a damp, dark, reddish-brown fine solid, and once dried appeared to be homogeneous reddish-brown fine solids.

Major phases: Hematite, Gibbsite, Cancrinite, and Dawsonite.

Chemical Name	Mineral	Formula	Rel. Amount
Iron Oxide	Hematite	Fe_2O_3	~40
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	>20
Sodium Calcium Aluminum Silicate Carbonate	Cancrinite	$\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$	>20
Sodium Aluminum Carbonate Hydroxide	Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$	<20

Polarized Light Microscopy

Sample is reddish very fine grained, mounted in 1.55 refractory index oil; consists of mostly opaque material with occasional Gibbsite and unidentifiable birefringent phase.

20x, crossed polars, Red I compensator

10x, uncrossed polars

Scanning Electron Microscopy

The general area EDS shows no changes in overall chemistry; the peaks have about the same relative ratios.

Confirmed the existence of Cancrinite (Na/Al/Si rich), Hematite (Fe-Mn-rich), and Gibbsite (Al-rich) as main phases. The Ag-rich phase was found in one particle with a reduced amount of Br and associated Hg.

A-4. Tank 241-AY-102 (Water Caustic Permanganate Leached)

Sample number S12R000275.

X-ray Diffraction

Sample S12R000275 (AY-102-PS-1) appeared to be a wet, reddish-brown fine sludge, and once dried appeared to be homogeneous reddish-brown fine solid.

Major phases: Hematite, Gibbsite, and Cancrinite.

Chemical Name	Mineral	Formula	Rel. Amount
Sodium Calcium Aluminum Silicate Carbonate	Cancrinite	$\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$	>40
Iron Oxide	Hematite	Fe_2O_3	>30
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	<30

Polarized Light Microscopy

Reddish sample mounted in 1.55 refractory index oil, very fine grained, about 75% of the opaques are made of scale and amber-colored material. Few birefringent fragments are visible, some of which could be identified as Gibbsite.

60x, crossed polars, Red I compensator

40x, uncrossed polars

Scanning Electron Microscopy

In the general area EDS spectrum, a slight reduction in Hematite in relationship to Cancrinite can be seen, consistent with the reduced relative amounts seen in the XRD.

One Ag-rich particle was found.

Clarkeite (Na/U-rich) appeared in several particles.

A-5. Tank 241-AZ-102 (Original Composite)

Sample number S12R000233.

X-ray Diffraction

Sample appeared to be a dry, reddish-brown fine powder, and once dried appeared to be homogeneous reddish-brown fine solids.

Major phases: Dawsonite, Gibbsite, and Sodium Nitrite.

Minor phases: Hematite, Boehmite.

Trace phase: Clarkeite.

Chemical Name	Mineral	Formula	Rel. amount
Sodium Aluminum Carbonate Hydroxide	Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$	~40%
Sodium Nitrite	--	NaNO_2	>25%
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	>10%
Iron Oxide	Hematite	Fe_2O_3	<10%
Aluminum Oxide Hydroxide	Boehmite	$\text{AlO}(\text{OH})$	<10%
Sodium Uranium Oxide Hydroxide Hydrate	Clarkeite	$\text{Na}((\text{UO}_2)\text{O})(\text{OH})\cdot(\text{H}_2\text{O})$	<5%

Polarized Light Microscopy

Sample is dark brown, dry, and prepared in 1.55 refractory index oil. Phases are too fine grained for identification, some opaques.

40x, uncrossed polars

40x, crossed polars, Red I compensator

Scanning Electron Microscopy

Sample was prepared from dry powder by crushing lightly and lifting particulate onto adhesive carbon tab.

General area EDS shows primary Al-, Na-, and Fe-bearing phases with traces of Zr, U, and K.

All the crystallites are very fine-grained <5 micron). Dawsonite (Na/Al-rich), Hematite (Fe-rich), Gibbsite/Boehmite (Al-rich), Clarkeite (Na/U-rich) confirmed. Found a Na/Ca-rich (containing REE) phase that might be consistent with Gregoryite. Also found possible Cancrinite (Na/Al/Si-rich), Zr-rich, Na/F-rich, and possible Kogarkoite (Na/S/F-rich). SEM could not confirm particle types with chemistry consistent with sodium nitrite, Trona, and Weddellite.

A-6. Tank-241-AZ-102 (Water Caustic Leached)

Sample number S12R000239.

X-ray Diffraction

Sample appeared to be a dry, reddish-brown fine powder, and once dried appeared to be homogeneous reddish-brown fine solids.

Major phases: Dawsonite

Minor phases: Hematite, Gibbsite, Boehmite

Trace phase: Clarkeite

Chemical Name	Mineral	Formula	Rel. Amount
Sodium Aluminum Carbonate Hydroxide	Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$	~75%
Iron Oxide	Hematite	Fe_2O_3	<10%
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	<10%
Aluminum Oxide Hydroxide	Boehmite	$\text{AlO}(\text{OH})$	<10%
Sodium Uranium Oxide Hydroxide Hydrate	Clarkeite	$\text{Na}((\text{UO}_2)\text{O})(\text{OH})\cdot(\text{H}_2\text{O})$	<5%

Polarized Light Microscopy

Sample is very fine grained, flighty, mounted in 1.55 refractive index oil; some opaque clusters, most particles < 5 μm .

60x, uncrossed polars

40x, crossed polars, Red I compensator

Scanning Electron Microscopy

The general area EDS shows the presence of Al-, Fe-, and Zr-bearing phases.

Dawsonite, Hematite, and Gibbsite are confirmed, although Gibbsite is rare and appears partially dissolved.

Clarkeite was confirmed; several Zr- and Zr/U-rich particles and one REE-rich Al/P particle were found.

A-7. Tank 241-AW-105 (Original Composite)

Sample number S12R000245.

X-ray Diffraction

Sample appeared to be a wet, dark reddish-brown fine sludge, and once dried appeared to be homogeneous reddish-brown fine solids.

Major phase: Villiaumite.

Traces of sodium zirconium oxide and Clarkeite .

Chemical Name	Mineral	Formula	Rel. Amount
Sodium Fluoride	Villiaumite	NaF	>90%
Sodium Zirconium Oxide	-	Na _{0.08} Zr _{0.92} O _{1.88}	<5%
Sodium Uranium Oxide Hydroxide Hydrate	Clarkeite	Na((UO ₂)O)(OH) (H ₂ O)	<5%

Polarized Light Microscopy

Sample is light brown, slightly moist, and prepared in 1.55 refractory index oil. The phase appearing as triangular dipyramid about 20 to 30 microns wide could be Villiaumite; some sodium oxalate and sodium aluminate needles are identifiable. Large laths of up to 50 microns with high birefringence.

20x, uncrossed polars

40x, uncrossed polars

10x, crossed polars, Red I compensator

40x, crossed polars, Red I compensator

Scanning Electron Microscopy

Slurry sample was prepared by smearing onto polycarbonate filter and applying vacuum to wick liquid and dissolved solids away.

The general area EDS shows predominant Zr- and Na-bearing phases with minor amounts of Al, Si, Mn, and Fe.

Villiaumite (Na-F) occurs as moderate sized (5-20 microns) crystals usually in the form of dipyrramids.

A Na/Zr-rich phase is the next most common. It occurs in both crystalline and amorphous forms. The crystals are often lathlike.

A single blade-like crystal of a Na-rich phase (sodium oxalate?) was also observed.

A-8. Tank 241-AW-105 (Water Leached)

Sample number S12R000251.

X-ray Diffraction

Sample appeared to be a wet, dark reddish-brown fine sludge, and once dried appeared to be homogeneous reddish-brown fine solids.

Major phase: Villiaumite, Gibbsite

Minor phase: Sodium zirconium oxide

Trace phase: Clarkeite

Chemical Name	Mineral	Formula	Rel. Amount
Sodium Fluoride	Villiaumite	NaF	~60%
Aluminum Hydroxide	Gibbsite	Al(OH) ₃	>20%
Sodium Zirconium Oxide	-	Na _{0.08} Zr _{0.92} O _{1.88}	>10%
Sodium Uranium Oxide Hydroxide Hydrate	Clarkeite	Na((UO ₂)O)(OH)·(H ₂ O)	<5%

Polarized Light Microscopy

Sample contains mostly opaques, which are agglomerates of fine-grained, non-scale material appearing to have the shape of the original Na-fluoride, some Gibbsite fragments, and minor anisotropic fragments.

60x, crossed polars, Red I compensator

10x, uncrossed polars

Scanning Electron Microscopy

The general area EDS shows Zr as the major element; however, the Zr-bearing phase could not be found as the original laths but rather as amorphous spots.

Some villiaumite crystals remained with signs of dissolution.

A-9. Tank 241-AN-106 (Original Composite)

Sample number S12R000256.

X-ray Diffraction

Sample appeared to be a wet, dark reddish-brown fine sludge, and once dried appeared to be homogeneous reddish-brown fine solids.

Major phases: Gibbsite, Hematite, and sodium nitrite (precipitated from liquid).

Chemical Name	Mineral	Formula	Rel. Amount
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	<40%
Iron Oxide	Hematite	Fe_2O_3	<40%
Sodium Nitrite	--	NaNO_2	<30%

Polarized Light Microscopy

Sample is dark brown, slightly moist, and prepared in 1.55 refractory index oil. Mostly Gibbsite (very fine), minor natrophosphate with some opaques and sodium oxalate needles.

40x, uncrossed polars

40x, crossed polars, Red I compensator

Scanning Electron Microscopy

Slurry sample was prepared by smearing onto polycarbonate filter and applying vacuum to wick liquid and dissolved solids away.

General area EDS shows primarily Al- and Na-rich phases with Fe, Si, and P as minor contributors. Some Bi, Mn, and U are present.

Gibbsite (Al-rich) occurs as small characteristic hexagonal plates (ca. 5-15 microns). Hematite (Fe-rich) also confirmed. Small patch of Na-rich radial blades have morphology consistent with Thermonatrite. Cancrinite (Na/Al/Si-rich) and partially dissolved Natrophosphate (Na/P/F-rich) also seen.

Two different lath or needle-like crystalline phases are present. One is a Na/Al/P-rich phase and the other is a Na/P/Bi/Fe-rich phase that is quite prominent in the backscatter image; the three images and spectra below show representative examples.

A-10. Tank 241-AN-106 (Water Caustic Leach)

Sample number S12R000262.

X-ray Diffraction

Sample appeared to be a very wet, dark reddish-brown fine sludge, and once dried appeared to be homogeneous reddish-brown fine solids.

Major phases: Hematite and Thermonatrite.

Minor phases: Gibbsite and Natroxalate.

Trace phase: Clarkeite.

Chemical Name	Mineral	Formula	Rel. Amount
Sodium Carbonate	Thermonatrite	$\text{Na}_2\text{CO}_3 \cdot (\text{H}_2\text{O})$	>50%
Iron Oxide	Hematite	Fe_2O_3	~20%
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	>10%
Sodium Oxalate	Natroxalate	$\text{Na}_2\text{C}_2\text{O}_4$	>10%
Sodium Uranium Oxide Hydroxide Hydrate	Clarkeite	$\text{Na}((\text{UO}_2)\text{O})(\text{OH}) \cdot (\text{H}_2\text{O})$	<5%

Polarized Light Microscopy

Sample is very fine grained, some small ~10 μm opaques and traces of needles (2 kinds) remaining.

40x, crossed polars+, Red I compensator

20x, uncrossed polars

Scanning Electron Microscopy

General area EDS shows dominance of Na, Al, and Fe in samples.

Cancrinite, Gibbsite, and Clarkeite confirmed from XRD. No P-bearing needles (such as Na-Al-P or Na-P-Bi-Fe) from original sample were found. Gibbsite appears in most cases in proximity to Cancrinite (see balls in image below).

Hematite in conjunction with Al-Bi-bearing material is confirmed.

A-11. Tank 241-SY-102 (Original Composite)

Sample number S12R000281.

X-ray Diffraction

Sample appeared to be a wet, dark brown fine sludge, and once dried appeared to be homogeneous whitish-gray fine solids.

Major phases: Natroxalate, sodium phosphate, and Nitratine (precipitated from liquid).

Minor phases: Gibbsite and sodium nitrite (precipitated from liquid).

Chemical Name	Mineral	Formula	Rel. Amount
Sodium Oxalate	Natroxalate	$\text{Na}_2\text{C}_2\text{O}_4$	>30%
Sodium Phosphate Dodecahydrate	--	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	>25%
Sodium Nitrate	Nitratine	NaNO_3	>20%
Sodium Nitrite	--	NaNO_2	>10%
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	<10%

Polarized Light Microscopy

Sample is slightly moist, very dark brown, and prepared in 1.55 refractory index oil. Mixture of carbonates and oxalate needles; major amounts of amber particles, some opaques.

40x, uncrossed polars

20x, crossed polars, Red I compensator

Scanning Electron Microscopy

Sample slurry was prepared by smearing onto polycarbonate filter and applying vacuum to wick liquid and dissolved solids away.

General area EDS shows Na, Al, and Cr as major elements with traces of Si, Cl, K, Ca, and Fe.

Nitratine (Na/O/N-rich), Gibbsite (Al-rich), and Natroxalate confirmed. Gibbsite occurs as small (<10 μm) rectangular rhombohedrons. Dawsonite occurs as thin laths up to 20 microns by 4 microns that are easily damaged by the beam and traces of Clarkeite (Na/U-rich). There is a fine-grained, amorphous Na/Al/Cr-rich phase that includes some rare Cr-rich particles.

A Na/Cl-rich phase is observed that is only rarely seen in tank waste.

Thermonatrite occurs as large efflorescent patches on the SEM specimen.

A-12. Tank 241-SY-102 (Water Caustic Permanganate Leached)

Sample number S12R000288.

X-ray Diffraction

Sample appeared to be a wet, dark brown fine sludge, and once dried appeared to be homogeneous gray fine solids.

Major phases: Natroxalate, Gibbsite.

Chemical Name	Mineral	Formula	Rel. Amount
Sodium Oxalate	Natroxalate	$\text{Na}_2\text{C}_2\text{O}_4$	~80%
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	~20%

Polarized Light Microscopy

Sample was very fine grained, was mounted in its own liquor; contains mostly needles of two kinds (~50+%), ~20% anisotropic fragments, and rest are amber colored opaques. The small needles are 5-15 μm long, ~1 μm wide, and have the optical properties of Natroxalate. The larger needles are also optically (-), but less birefringent and are 40-70 μm long and 3-10 μm wide.

20x, uncrossed polars

60x, crossed polars, Red I compensator

Scanning Electron Microscopy

Confirmed the presence of Gibbsite, but no sodium oxalate found. Neither Bismuth nor plutonium particulate was found²⁰.

Cancrinite (below) and a Cr-rich phase (next image) were found.

²⁰ SY-102 material containing plutonium particulate was specifically chosen for a study on said particles as reported in LAB-RPT-12-00006, R1. The remaining material was depleted in plutonium and bismuth and did not show specific particles.

Attachment B

**Chemical Analyses Provided by Advanced Technologies and Laboratories International,
Inc.**

Tank 241-AY-102	OC-A	OC-F	WS	CPS	WL	CL	PL
	[µg/g]	[µg/g]	[µg/g]	[µg/g]	[µg/mL]	[µg/mL]	[µg/mL]
Aluminum	86,300	84,200	74,100	33,200	1.87	11,800	6,650
Bismuth	28.2	<567	19.8	31.3	<1.50	<6.00	<6.00
Calcium	3,610	<7,560	2,730	2,880	<20.0	<80.0	<80.0
Chromium	3,010	2,820	1,930	1,750	143	93.8	155
Iron	13,4000	129,000	107,000	113,000	<2.50	<10.0	<10.0
Potassium	262	n/a	<31.9	691	87.6	57.8	832
Manganese	31,500	31,000	22,900	25,900	<0.250	<1.00	<1.00
Sodium	96,700	117,000	39,300	56,300	22,300	109,000	53,400
Nickel	4,900	n/a	3,790	4,190	<0.250	<1.00	<1.00
Phosphorus	4,800	4,630	1,560	1,170	442	809	563
Lead	7,460	7,210	5,860	6,480	<1.50	14.2	<6.00
Sulfur	791	542	414	257	161	14.2	<5.00
Silicon	2,710	28,400	248	346	19.3	271	
Strontium	285	319	212	231	<0.500	<2.00	<2.00
Thorium	856	715	642	711	23.2	<5.00	<5.00
Uranium	1,190	<1,890	928	448	358	22.8	<20.0
Zirconium	83.4	328	103	444	65	1.61	<1.00
Fluoride	182		<2.88	<2.83	59.7	33.6	16
Glycolate	<21.0		<16.8	<16.5	<1.87	<1.87	<1.87
Acetate	971		<10.8	<10.6	495	41.4	<1.21
Formate	172		155	154	64	31.4	17.2
Chloride	79.9		<17.9	<28.2	12.5	15.3	10.5
Nitrite	6,560		174	125	2,900	208	87.8
Sulfate	979		141	128	462	33.3	16.5
Oxalate	968		61.5	93.5	626	26.5	29
Bromide	<130		95.6	<102	<11.6	45.3	24
Nitrate	1,020		325	241	364	49	41
Phosphate	5,270		954	917	1,460	2,570	1,900
TIC	27,300		4,930	2,610	6,310	n/a	1,570
TOC	2,120		899	747	873	n/a	78.2
Percent water	9.77		21.3	41.6	n/a	n/a	n/a
Hydroxide	n/a		n/a	n/a	n/a	67,900	27,200
pH	n/a		n/a	n/a	10	n/a	n/a

	xxx	xxx	xxx	xxx	xxx	xxx
Sample numbers	269	349	276	272	273	274
S12R000xxx	270	350	277			
	271	351	278			

OC-A Original composite with acid digest for RCRA metals analysis

OC-F Original composite with fusion digest for RCRA metals analysis

WS Water leached solids

CS Caustic leached solids

CPS Caustic and permanganate treated solids

WL Water leach liquid

CL Caustic leach liquid

PL Permanganate leach liquid

RPP-RPT-53688 R0
Attachment B

Tank 241-AZ-102	OC-A	OC-F	CS	WL	CL
	[µg/g]	[µg/g]	[µg/g]	[µg/mL]	[µg/mL]
Aluminum	62,300	73,500	43,400	<1.50	17,200
Bismuth	46.7	<589	9.66	<1.50	<6.00
Calcium	3,480	<7,860	3,410	<20.0	<80.0
Chromium	2,530	2,690	1,490	261	219
Iron	117,000	109,000	122,000	<2.50	<10.0
Potassium	4,290	n/a	418	1,080	456
Manganese	3,550	3,230	2,860	<0.250	<1.00
Sodium	118,000	137,000	33,400	25,900	105,000
Nickel	5,190	n/a	7,560	<0.250	<1.00
Phosphorus	1,970	2,350	296	43.2	576
Lead	1,720	1,680	1,510	<1.50	<6.00
Sulfur	5,900	6,580	86.2	2,200	212
Silicon	991	6,190	494	9.61	193
Strontium	230	210	261	<0.500	<2.00
Thorium	656	511	537	<1.25	<5.00
Uranium	8,360	9,810	8,420	1,050	<20.0
Zirconium	13,000	13,300	13,024	146	1.14
Fluoride	5,650		167	822	1,600
Glycolate	<21.3		<20.6	<7.50	<9.37
Acetate	1130		149	475	60.1
Formate	208		189	122	<4.67
Chloride	57.1		<22.0	21.6	12.6
Nitrite	40,000		203	15,300	1,300
Sulfate	13,500		128	6,720	580
Oxalate	3,810		<57.3	1,290	95.6
Bromide	876		142	363	130
Nitrate	7,070		351	2,780	579
Phosphate	1,150		<36.8	120	1,760
TIC	34,000		15,000	n/a	10,500
TOC	2,130		456	n/a	521
Percent water	13.2		10.3	n/a	n/a
Hydroxide	n/a		n/a	n/a	36,600
pH	n/a		n/a	9.85	n/a

	xxx	xxx	xxx	xxx
Sample numbers	233	240	237	238
S12R000xxx	234	241		
	235	242		

OC-A Original composite with acid digest for RCRA metals analysis
OC-F Original composite with fusion digest for RCRA metals analysis
WS Water leached solids WL Water leach liquid
CS Caustic treated solids CL Caustic leach liquid

Tank 241-AW-105	OC-A	OC-F	WS	WL
	[µg/g]	[µg/g]	[µg/g]	[µg/mL]
Aluminum	3,750	7,330	3,380	531
Bismuth	<11.5	<570	<21.7	<1.50
Calcium	3,110	<7,600	3,060	<20.0
Chromium	1,420	2,300	1,170	17.5
Iron	4,930	8,120	4,050	<2.50
Potassium	4,690	n/a	1,900	1660
Manganese	6,190	9,580	5,750	1.38
Sodium	137,000	219,000	33,700	29,200
Nickel	379	n/a	221	72.9
Phosphorus	1,700	2,290	1,080	219
Lead	148	<570	163	<1.50
Sulfur	452	510	107	192
Silicon	306	2,590	926	296
Strontium	19.8	<190	18.8	<0.500
Thorium	<9.59	<475	<18.1	<1.25
Uranium	17,800	29,500	14,600	8.18
Zirconium	103,000	168,000	112,000	14.8
Fluoride	83,100		10,200	12,100
Glycolate	<528		<86.7	<46.8
Acetate	<924		<55.9	<30.2
Formate	3,330		851	888
Chloride	725		181	235
Nitrite	11,200		2,950	4,450
Sulfate	3,410		825	571
Oxalate	5,240		1,340	1,380
Bromide	<495		<537	384
Nitrate	20,800		5,580	8,530
Phosphate	<660		<155	<83.5
TIC	5,170		2,120	1,360
TOC	8,250		4,730	2,010
Percent water	41.2		65.1	n/a
Hydroxide	n/a		n/a	2,030
pH	n/a		n/a	n/a

	xxx	xxx	xxx
Sample numbers	246	251	250
S12R000xxx	247	253	
	248	254	

OC-A Original composite with acid digest for RCRA metals analysis
OC-F Original composite with fusion digest for RCRA metals analysis
WS Water leached solids
WL Water leach liquid

Tank 241-AN-106	OC-A	OC-F	CS	WL	CL
	[µg/g]	[µg/g]	[µg/g]	[µg/mL]	[µg/mL]
Aluminum	53,900	74,900	19,200	309	5,330
Bismuth	12,500	16,800	6,250	<1.50	21.4
Calcium	684	<8,210	343	<20.0	<80.0
Chromium	539	820	171	54.6	50.4
Iron	64,800	81,700	29,800	16.8	11.9
Potassium	398	n/a	121	64.8	94.4
Manganese	3,080	3,910	1,420	<0.250	<1.00
Sodium	65,100	90,200	76,300	15,100	81,200
Nickel	4,150	n/a	2,100	7.16	<1.00
Phosphorus	10,500	14,000	853	1,290	615
Lead	4,270	5,580	2,140	<1.50	110
Sulfur	1,610	1,900	124	431	138
Silicon	1,770	17,200	521	3.77	245
Strontium	121	<205	57.6	1.29	<2.00
Thorium	436	697	210	<1.25	<5.00
Uranium	3,060	4,490	1,420	93	27.2
Zirconium	616	1,740	2,280	1.77	3.46
Fluoride	6,610		841	1,300	1,230
Glycolate	<37.9		<22.9	<4.68	<4.68
Acetate	179		<14.7	40.1	<3.02
Formate	<18.9		189	<2.34	<2.34
Chloride	419		<39.0	117	38.4
Nitrite	19,100		1,100	5,930	1,480
Sulfate	4,120		396	1,200	383
Oxalate	895		118	260	72.5
Bromide	<235		<142	<29.0	<29.0
Nitrate	29,600		1,470	9,040	1,990
Phosphate	17,200		1,590	4,060	1,950
TIC	5,520		478	n/a	421
TOC	301		<114	n/a	69.1
Percent water	45.8		66	n/a	n/a
Hydroxide	n/a		n/a	<41.7	53,500
pH	n/a		n/a	n/a	n/a

	xxx	xxx	xxx	xxx
Sample numbers	257	263	260	261
S12R000xxx	258	264		
	259	265		

OC-A	Original composite with acid digest for RCRA metals analysis
OC-F	Original composite with fusion digest for RCRA metals analysis
WS	Water leached solids WL Water leach liquid
CS	Caustic leached solids CL Caustic leach liquid

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Attachment B

Tank 241-SY-102	OC-A	OC-F	CPS	WL	CL	PL
	[µg/g]	[µg/g]	[µg/g]	[µg/mL]	[µg/mL]	[µg/mL]
Aluminum	39,400	42,800	9,800	2,060	3,450	2,200
Bismuth	472	691	243	<3.00	<6.00	<6.00
Calcium	918	<7,920	310	<40.0	<80.0	<80.0
Chromium	46,500	51,400	13,700	768	268	6,650
Iron	3,030	5,030	1,080	<5.00	<10.0	<10.0
Potassium	1,420	n/a	3,710	803	236	4,510
Manganese	842	963	6,420	<0.500	<1.00	<1.00
Sodium	148,000	162,000	51,900	57,500	78,800	41,000
Nickel	582	n/a	189	5.59	<1.00	1.82
Phosphorus	1,550	2,120	107	620	266	120
Lead	944	1,040	311	<3.00	23.4	6.86
Sulfur	863	<495	51.5	548	154	56.5
Silicon	1,040	2,810	672	84.1	94.8	56.4
Strontium	13.5	<198	<3.89	<1.00	<2.00	<2.00
Thorium	64.9	<495	28.9	<2.50	<5.00	<5.00
Uranium	644	<1,980	213	<10.0	<20.0	<20.0
Zirconium	83.4	<99.0	30.6	<0.500	<1.00	<1.00
Fluoride	<30.0		<3.69	69.4	27.3	12.9
Glycolate	<175		<21.5	<18.7	<4.68	<3.75
Acetate	1,020		166	357	101	48.8
Formate	2,660		323	1,190	335	152
Chloride	3,460		212	2,260	643	278
Nitrite	41,900		2570	27,100	7,510	3,440
Sulfate	2,100		220	1,230	363	158
Oxalate	105,000		43,100	2,200	1,110	4,300
Bromide	<1.080		<133	162	43.8	40.3
Nitrate	70,600		4360	45,200	12,700	5,660
Phosphate	2,090		424	1,980	789	351
TIC	3,890		3,300	n/a	n/a	946
TOC	17,600		6,400	n/a	n/a	726
Percent water	37.8		76.1	n/a	n/a	n/a
Hydroxide	n/a		n/a	10,600	49,200	18,200
pH	n/a		n/a	n/a	n/a	n/a
Neptunium-237	<2.17		<2.07	n/a	n/a	n/a
Thorium-232	82.1		26.7	n/a	n/a	n/a
Uranium-233	<4.34		<4.13	n/a	n/a	n/a
Uranium-234	<0.108		<0.103	n/a	n/a	n/a
Uranium-235	5.68		1.38	n/a	n/a	n/a
Uranium-236	<0.0868		<0.0826	n/a	n/a	n/a
Uranium-238	785		256	n/a	n/a	n/a

	xxx	xxx	xxx	xxx	xxx
Sample numbers	282	289	285	286	287
S12R000xxx	283	290			
	284 / 510	291 / 511			

OC-A / F	Original composite with acid / fusion digest for RCRA metals analysis
CPSCaustic and permanganate treated solids	WL Water leach liquid
CL Caustic leach liquid	PL Permanganate leach liquid

ATTACHMENT C

SAMPLE BREAKDOWN DIAGRAMS AND ARCHIVE SAMPLE DESCRIPTION

Customer: Research
Project: Direct Feed HLW
Group 20120689
Due: TBD

AY-102

Customer: Research
Project: Direct Feed HLW
Group 20120686
Due: TBD

Customer: Research
Project: Direct Feed HLW
Group 20120687
Due: TBD

AW-105

Customer: Research
Project: Direct Feed HLW
Group 20120685
Due: TBD

Customer: Research
Project: Direct Feed HLW
Group 20120688
Due: TBD

SY-102

Table C1. Samples Used for Tank 241-AY-102 Composite and Subsequent Mass Changes.

Laboratory ID	Tank	Core	Segt	Jar – Vial Nr.	Size (ml)	Net Wt [#] (g)	Retrievable Amount (g)
S05T000275	AY-102	315	16	15522	125	52.7	44.22
S05T000269	AY-102	315	16	19521	60	20.2	18.34
S05T000266	AY-102	315	17	19523	60	18	18.12
S05T000270	AY-102	315	17	19533	60	19.6	19.42
S05T000953	AY-102	319	1	19725	60	19.5	12.23
S05T000952	AY-102	319	1	19839	125	82.7	76.51
Sum amount dry solids							188.84
Amount dry solids after grinding							187.25
Amount wet solids*							214.35
Amount transferred into jar ‘Recon “A”’ for rehydration							199.09
Amount after rehydration							359.69
Amount of slurry transferred into “A-T” for leach test							338.59
Amount of wet solids in “A-T” **							156.02

[#] As recorded in 11A Sample Archive.

^{*} The water was used to empty the jars and to assure a reduced amount of flightiness during analysis.

^{**} The slurry transferred into A-T contained a substantial amount of standing liquid. In the leaching calculations, this amount of water is integrated in the water leach; it is part of the leachate that was decanted and then used for chemical analyses.

Table C2. Samples Used for Tank 241-AZ-102 Composite and Subsequent Mass Changes.

Laboratory ID	Tank	Core	Segt	Jar – Vial Nr.	Size (ml)	Net Wt [#] (g)	Retrievable Amount (g)
S04T000269	AZ-102	313	19R3	19715	60	20.5	13.07
S05T000762	AZ-102	317	19	19834	125	54.4	46.34
S04T000308	AZ-102	313	19	19890	60	39.6	32.23
S04T000232	AZ-102	313	19R2	20217*	250	109.4	96.63*
Sum amount dry solids (chunks)							188.27*
Amount of ground dry solids							157.45
Amount wet solids							187.58
Amount of wet solids transferred to “B-T”							154.45

[#] As recorded in 11A Sample Archive.

^{*} Contained 30g of broken lid pieces of blue plastic; separated with tweezers.

Table C3. Sample Used for Tank 241-AW-105 Composite.

Laboratory ID	Tank	Core	Segt	Jar – Vial Nr.	Size (ml)	Net Wt [#] (g)	Retrievable Amount (g)
S08T009981	AW-105	322	8R1	20504	250	245.1	N.A.
Amount of wet solids transferred to “C-T” *							187.71

[#] As recorded in 11A Sample Archive.

^{*} Sludge was moist enough to be transferred; no water addition prior to leach.

Table C4. Samples Used for Tank 241-AN-106 Composite.

Laboratory ID	Tank	Grab Sample Identification	Jar – Vial Nr.	Size (ml)	Net Wt [#] (g)	Retrievable Amount (g)
S11T016339	AN-106	6AN-11-05	20163	125	119.7	108.11
S11T016368	AN-106	6AN-11-06	20160	250	170.8	155.20
Amount of wet composite						259.80
Amount of wet solids transferred to “D-T” *						150.10

[#] As recorded in 11A Sample Archive.

* Sludge was moist enough to be transferred; no water addition prior to leach.

Table C5. Samples to be Used for Tank 241-SY-102 Composite.

Laboratory ID	Tank	Core	Segt	Jar – Vial Nr.	Size (ml)	Net Wt [#] (g)	Retrievable Amount (g)
S01T001865	SY-102	285	16	17028	250	265.1	N.A.
Amount of wet solids transferred to “E-T” *							159.95

[#] As recorded in 11A Sample Archive.

* Sludge was moist enough to be transferred; no water addition prior to leach.

ATTACHMENT D

SAMPLE MASSES DURING TESTING

Tank	AY-102	AZ-102	AW-105	AN-106	SY-102
Hot Cell ID	A-T	B-T	C-T	D-T	E-T
Start Date	27-Jun	28-Jun	28-Jun	12-Jul	24-Jul
Jar number	20648	20646	20504	20683	17028
Sample point	Solids	Solids	Solids	Solids	Solids
Jar ID	A-T	B-T	C-T	D-T	E-T
Tare weight Jar (g)	298.05	299.78	296.41	359.37	358.42
Step 1: Add sludge sample					
Mass of Jar (g)	454.07	454.23	484.12	509.47	518.37
[Mass of Jar (g) Step 1] - [Tare weight Jar (g)] = Sample mass (g)	454.07	454.23	484.12	509.47	518.37
	-298.05	-299.78	-296.41	-359.37	-358.42
	156.02	154.45	187.71	150.10	159.95
Step 2: Add inhibited water					
Mass of Jar (g)	724.00	665.84	685.70	708.32	718.59
[Mass of Jar (g) Step 2] - [Mass of Jar (g) Step 1] = Amount water added (g)	724.00	665.84	685.70	708.32	718.59
	-454.07	-454.23	-484.12	-509.47	-518.37
	269.93	211.61	201.58	198.85	200.22
Step 3: Decant liquid					
Date	29-Jun	29-Jun	29-Jun	26-Jul	2-Aug
Mass of Jar (g)	558.41	539.41	613.47	586.63	633.34
[Mass of Jar (g) Step 3] - [Tare weight Jar (g)] = Sample mass (g)	558.41	539.41	613.47	586.63	633.34
	-298.05	-299.78	-296.41	-359.37	-358.42
	260.36	239.63	317.06	227.26	274.92
[Sample mass (g) Step 3] - [Sample mass (g) Step 1] = Dissolution delta (g)	260.36	239.63	317.06	227.26	274.92
	-156.02	-154.45	-187.71	-150.10	-159.95
	104.34	85.18	129.35	77.16	114.97
100*[Dissolution delta (g)] / [Sample mass (g) Step 1] = Dissolution delta (wt% original)					
	66.88	55.15	68.91	51.41	71.88
Step 4: Add inhibited water					
Mass of Jar (g)	771.42	741.26	785.68	792.00	834.41
[Mass of Jar (g) Step 4] - [Mass of Jar (g) Step 3]	771.42	741.26	785.68	792.00	834.41
	-558.41	-539.41	-613.47	-586.63	-633.34

Tank	AY-102	AZ-102	AW-105	AN-106	SY-102
Hot Cell ID	A-T	B-T	C-T	D-T	E-T
= Amount water added (g)	213.01	201.85	172.21	205.37	201.07

Step 5: Decant liquid				
Date	23-Jul	23-Jul	23-Jul	2-Aug
Mass of Jar (g)	542.94	504.53	559.11	604.17
[Mass of Jar (g) Step 5] -	542.94	504.53	559.11	604.17
[Tare weight Jar (g)]	-298.05	-299.78	-296.41	-359.37
= Sample mass (g)	244.89	204.75	262.70	244.80

Date	25-Jul	25-Jul	25-Jul
Mass of Jar (g) - reweighed	542.81	504.10	558.90

Step 6: Add inhibited water				
Mass of Jar (g)	748.84	702.40	762.58	812.42
[Mass of Jar (g) Step 6] -	748.84	702.40	762.58	812.42
[Mass of Jar (g) Step 5]	-542.81	-504.10	-558.90	-604.17
= Amount water added (g)	206.03	198.30	203.68	208.25

[Amount water added (g) Step 2] +	269.93	211.61	201.58	198.85	200.22
[Amount water added (g) Step 4] +	213.01	201.85	172.21	205.37	201.07
[Amount water added (g) Step 6]	206.03	198.30	203.68	208.25	--
= Sum of water added (g)	688.97	611.76	577.47	612.47	401.29

<i>Sample point</i>	<i>Sol & Liq</i>	<i>Liquid</i>	<i>Sol & Liq</i>	<i>Liquid</i>	<i>Liquid</i>
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Step 7a: Decant liquid					
Date	7-Aug	7-Aug	7-Aug	7-Aug	7-Aug
Mass of Jar (g)	560.88	522.93	565.81	617.72	655.74
[Mass of Jar (g) Step 7] -	560.88	522.93	565.81	617.72	655.74
[Tare weight Jar (g)]	-298.05	-299.78	-296.41	-359.37	-358.42
= Sample mass (g)	262.83	223.15	269.40	258.35	297.32

Step 7b: Calculate mass of standing liquid					
[Height of standing liquid in jar (mm)] * [Jar radius (=33 mm)]^2 * π = Volume of standing liquid (mm³)	5	3	n.d.	5	n.d.
	* 3421	* 3421		* 3421	
	17106	10264		17106	

[Sample mass (g) Step 7a] -	262.83	223.15	258.35
[Volume of standing liquid (g)] / 1000	-17.11	-10.26	-17.11
= Calculated residual sample mass (g)	245.72	212.88	241.24

Tank	AY-102	AZ-102	AW-105	AN-106	SY-102
Hot Cell ID	A-T	B-T	C-T	D-T	E-T

Step 7c: Decant standing liquid
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Mass of Jar (g)	551.83	514.00	590.41	630.14
[Mass of Jar (g) Step 7c] - [Tare weight of jar (g)]	551.83	514.00	590.41	630.14
= Residual sample mass (g)	-298.05	-299.78	-359.37	-358.42
	253.78	214.22	231.04	271.72

Step 8: Add concentrated caustic solution
--

Mass of Jar (g)	729.65	620.61	703.21	715.78
Caustic addition (mL) - goal in brackets	121 (122)	72 (76)	76 (75)	58 (67)
[Mass of Jar (g) Step 8] - [Mass of Jar (g) Step 7c]	729.65	620.61	703.21	715.78
= Amount of caustic added (g)	-551.83	-514.00	-590.41	-630.14
	177.82	106.61	112.80	85.64
<i>Density of caustic</i>	1.47	1.48	1.48	1.48

Comment: average density of 1.48 indicates a molarity of 17.0 according to the Handbook of Chemistry and Physics, at 25°C. According to the DOW chemicals MSDS, at 30 °C, a 46% solution has a specific gravity of 1.481, which is equivalent to 17.0 mol/L. 46 wt% with 40g/mol => 46g/100g/ 40g/mol = 46/40 mol/g = 1.15 mol/100g = 11.5 mol/kg = 11.5mol/(1.481^-1 L) = 17.0 mol/L.

Step 9: Add inhibited water

Date	13-Aug	13-Aug	13-Aug	13-Aug
Mass of Jar (g)	897.67	715.20	866.48	843.59
Water target (mL)	242	144	152	120
[Mass of Jar (g) Step 9] - [Mass of Jar (g) Step 8]	897.67	715.20	866.48	843.59
= Amount of water added (g)	-729.65	-620.61	-703.21	-715.78
	168.02	94.59	163.27	127.81

Step 10: Decant liquid

Date	16-Aug	16-Aug	16-Aug	16-Aug
Mass of Jar (g)	589.20	553.03	625.14	739.32
[Mass of Jar (g) Step 10] - [Tare weight Jar (g)]	589.20	553.03	625.14	739.32
= Sample mass (g)	-298.05	-299.78	-359.37	-358.42
	291.15	253.25	265.77	380.90

Sample point

Sol/Liq

Sol/Liq

Liquid

Tank	AY-102	AZ-102	AW-105	AN-106	SY-102
Hot Cell ID	A-T	B-T	C-T	D-T	E-T
Step 11: Add inhibited water					

Mass of Jar (g) **671.75**

<i>[Mass of Jar (g) Step 11] -</i>	671.75			
<i>[Mass of Jar (g) Step 10]</i>	-589.20			
= Amount of water added (g)	82.55			

[Amount of water added (g) Step 9] +	168.02	94.59		163.27	127.81
[Amount of water added (g) Step 11]	82.55	0.00		0.00	0.00
= Total amount of water added	250.57	94.59		163.27	127.81

Step 12: Decant liquid					
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Date **20-Aug** **22-Aug**

Mass of Jar (g) **557.56** **612.03**

[Mass of Jar (g) Step 12 or 10] -	557.56	553.03		625.14	612.03
[Tare weight Jar (g)]	-298.05	-299.78		-359.37	-358.42
= Sample mass (g)	259.51	253.25		265.77	253.61

Sample point *Liquid*

Step 13: Add 1 M permanganate solution					
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Date **22-Aug** **22-Aug**

Mass of Jar (g) **577.51** **757.87**

<i>[Mass of Jar (g) Step 13] -</i>	577.51			757.87
<i>[Mass of Jar (g) Step 12]</i>	-557.56			-612.03
= Amount of permanganate added (g)	19.95			145.84

Step 14: Add inhibited water					
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Date **28-Aug** **28-Aug**

Mass of Jar (g) **676.48** **862.31**

<i>[Mass of Jar (g) Step 14] -</i>	676.48			862.31
<i>[Mass of Jar (g) Step 13]</i>	-577.51			-757.87
= Amount of water added (g)	98.97			104.44

Step 15: Decant liquid					
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Mass of Jar (g) **543.31** **765.38**

[Mass of Jar (g) Step 15] -	543.31			765.38
[Tare weight Jar (g)]	-298.05			-358.42
= Sample mass (g)	245.26			406.96

Sample point *Sol/Liq* *Sol/Liq*

Tank	AY-102	AZ-102	AW-105	AN-106	SY-102
Hot Cell ID	A-T	B-T	C-T	D-T	E-T
Step 16: Decant liquid					
Date	13-Nov	16-Nov	13-Nov	13-Nov	13-Nov
Mass of Jar (g)	508.37	495.14	530.84	572.41	742.23
[Mass of Jar (g) Step 16] - [Tare weight Jar (g)] = Final Sample mass (g)	508.37	495.14	530.84	572.41	742.23
	-298.05	-299.78	-296.41	-359.37	-358.42
	210.32	195.36	234.43	213.04	383.81

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		Date 06/11/2013

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