



U.S. DEPARTMENT OF
ENERGY

PNNL-17593

Prepared for the U.S. Department of Energy
Under Contract DE-AC05-76RL01830

Hanford Tank 241-S-112 Residual Waste Composition and Leach Test Data

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August 2008



Pacific Northwest
NATIONAL LABORATORY

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

As directed by Congress, the U.S. Department of Energy (DOE) established the Office of River Protection in 1998 to manage DOE's largest, most complex environmental cleanup project - retrieval of radioactive waste from Hanford Site tanks for treatment and eventual disposal. Sixty percent by volume of the nation's high-level radioactive waste is stored at the Hanford Site in aging, deteriorating tanks. If not cleaned up, this waste is a threat to the nearby Columbia River and the Pacific Northwest.

CH2M HILL Hanford Group, Inc. is the DOE Office of River Protection's prime contractor responsible for the storage, retrieval, and disposal of Hanford Site tank waste. As part of this effort, CH2M HILL Hanford Group, Inc. contracted with Pacific Northwest National Laboratory (PNNL) to conduct testing for selected key contaminants present in residual waste remaining in the single-shell tank 241-S-112 (S-112).

This report presents the results of laboratory characterization, testing, and analysis of two samples (designated 20406 and 20407) of residual waste collected from tank S-112 after final waste retrieval. These studies were completed to characterize the residual waste and assess the leachability of contaminants from the solids. This is the first report from this PNNL project to describe the composition and leach test data for residual waste from a salt cake tank. All previous PNNL reports describing contaminant release models, and characterization and testing results for residual waste in single-shell tanks were based on samples from sludge tanks.^{1,2}

X-ray diffraction (XRD) results for sample 20407 indicate that the primary crystalline phase in the residual waste is gibbsite [Al(OH)₃] and comprises more than ~90 wt% of the solid material. Scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) results are consistent with the XRD results, indicating the primary solid phase is Al-O(±H±C) with a composition that is 39 wt% Al and 60 wt% O (consistent with the composition of gibbsite). The SEM/EDS results also indicate that the gibbsite particles are likely coated with an Al-Na-O(±H±C) solid. The phase composition of this encrustation could not be established with certainty but appears to have a composition of 29 wt% Na, 18 wt% Al, and 52 wt% O. Results of geochemical modeling indicate dawsonite [NaAlCO₃(OH)₂] was near equilibrium with 1-month double-deionized water extracts, which suggests this phase may be an

¹Cantrell KJ, KM Krupka, WJ Deutsch, MJ Lindberg, HT Schaefer, KN Geiszler and BW Arey. 2008. *Hanford Tank 241-C-103 Residual Waste Contaminant Release Models and Supporting Data*. PNNL-16738, Pacific Northwest National Laboratory, Richland, Washington.

²Deutsch WJ, KM Krupka MJ Lindberg, KJ Cantrell, CF Brown, and HT Schaefer. 2006. *Hanford Tanks 241-C-106: Impact of Cement Reactions on Release of Contaminant from Residual Waste*. PNNL-15544, Pacific Northwest National Laboratory, Richland, Washington.

Deutsch WJ, KM Krupka MJ Lindberg, KJ Cantrell, CF Brown, and HT Schaefer. 2007a. *Hanford Tanks 241-C-106: Residual Waste Contaminant Release Model and Supporting Data*. PNNL-15187, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Deutsch WJ, KM Krupka, MJ Lindberg, KJ Cantrell, CF Brown, and HT Schaefer. 2007b. *Hanford Tanks 241-C-203 and 241-C-204: Residual Waste Contaminant Release Model and Supporting Data*. PNNL-14903, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Deutsch WJ, KM Krupka MJ Lindberg, KJ Cantrell, CF Brown, SV Mattigod, HT Schaefer, and BW Arey. 2007c. *Hanford Tanks 241-C-202 and 241-C-203 Residual Waste Contaminant Release Models and Supporting Data*. PNNL-16229, Pacific Northwest National Laboratory, Richland, Washington.

important component of this encrustation. The SEM/EDS analysis also revealed the presence of Fe oxides, a Ca-Cr-O phase, a Pb-Cl±O phase, and possibly one or more silicate phases, but particles with these compositions were very rare in the tank S-112 residual waste.

Results of the Tier 1 analysis of the bulk composition of tank S-112 samples indicate that Al is the largest, single metal component of the waste (7.1 to 8.4 wt% for the two samples). Other major metal components (Na, Fe, Cr, and Si) occurred at lower concentrations, ranging from 4.7 to 5.2%, 0.21 to 0.24%, 0.17 to 0.18%, and 0.10 to 0.14%, respectively, for the two samples. Based on these results and assuming Al occurs primarily as gibbsite, this Al phase would account for 21 to 24 wt% of the residual waste. The residual waste compositions determined in this study were generally consistent with those determined by the 222-S Laboratory, except for the concentrations determined for Al.³ The average Al concentration determined from the 222-S Laboratory results was 29.1 wt% (dry wt basis). If all Al occurred as gibbsite, this would account for 84% of the mass of the residual waste. This result is more consistent with PNNL's XRD and SEM/EDS results compared to those from the bulk composition analyses. Based on these comparisons, PNNL's Al concentrations for the unleached (as received) bulk solid appear to be underestimated. The reason for this discrepancy has not been determined to date. Our initial assessment indicates that some Al may have precipitated as fine particulates that were filtered out subsequent to the microwave acid digestion.

Chromium was the most concentrated contaminant of concern in the tank S-112 residual waste samples, occurring at 1,690 to 1,750 µg/g-dry waste. The other important contaminants, ⁹⁹Tc and ²³⁸U, were measured in the residual waste at concentrations that ranged from 0.46 to 0.48 µg/g and 17 to 36 µg/g, respectively.

Some solution analyses were conducted on supernatant from as-received sample 20406 and on leachates from sample 20407 extracted by a 1-month single-contact leach test with double deionized water at a water-to-waste ratio of 100:1. The percentages of ⁹⁹Tc, ²³⁸U, and Cr that were extractable in the 1-month single-contact leachates were 17%, 0.65%, and 10.7%, respectively, relative to the measured concentrations in the unleached bulk solid. Significant percentages of other metals in the extract leachates include Al (9.3%), Ca (81%), and Na (87%) relative to the bulk waste composition. Concentrations of all major anions determined by ion chromatography were below the detection limit, indicating that hydroxide and carbonate were the major anions in the water leachates.

Calculations were made to estimate a hypothetical pore water composition that would occur if all the dissolved components measured in the sample 20407 1-month single-contact leach tests were initially dissolved in the entrained pore water. These concentrations were compared with concentrations measured for the supernatant solution present in sample 20406. These results indicate the majority of the ⁹⁹Tc, Al, and Na in the 1-month double-deionized water extracts come from dilution of residual supernatant in the waste sample. In the case of ²³⁸U, it appears dilution of pore fluid results in precipitation of most of the ²³⁸U. This may have occurred as a result of diminished hydrolysis and carbonate complexation upon dilution (Le Chatelier's principle). For Ca, researchers determined that nearly all Ca in the extracts came

³ Parker DL and WB Barton. 2007. *Retrieval Data Report for Single-Shell Tank 241-S-112*. RPP-RPT-35112, CH2M HILL Hanford Group, Inc., Richland, Washington.

from dissolution of a Ca-containing solid phase. For Cr, calculations indicate approximately half of the Cr in the leachants came from the pore fluid, and a nearly equal quantity came from dissolution from a solid phase.

Acknowledgments

The authors wish to acknowledge M. Connelly and J. G. Kristofzski at CH2M HILL Hanford Group, Inc. (Richland, Washington) for providing project funding and technical guidance. We greatly appreciate the technical reviews provided by F. M. Mann and J. N. Appel (both from CH2M HILL Hanford Group, Inc.), and W. J. Deutsch (PNNL). The authors would also like to thank S. R. Baum, E. T. Clayton, and I. V. Kutnyakov (all from PNNL) for completing the chemical analyses of the solution samples from our studies. We are particularly grateful to H. E. Matthews (PNNL) for completing the editorial review and K. R. Neiderhiser (PNNL) for final word processing of this technical report.

Acronyms and Abbreviations

ASTM	American Society for Testing and Materials
BSE	backscattered electron
CCV	continuing calibration verification
CFR	<i>Code of Federal Regulations</i>
DDI	double-deionized (water)
DOE	U.S. Department of Energy
Dup (or dup)	duplicate
EDS	energy dispersive spectrometry
EPA	U.S. Environmental Protection Agency
EQL	estimated quantification limit
GWB	Geochemist's Workbench ^{®1}
HASQARD	Hanford Analytical Services Quality Assurance Requirements Document
IC	ion chromatography (chromatograph)
ICDD	International Center for Diffraction Data
ICP-MS	inductively coupled plasma-mass spectrometry (spectrometer)
ICP-OES	inductively coupled plasma-optical emission spectroscopy (same as ICP-AES)
JCPDS	Joint Committee on Powder Diffraction Standards
NIST	National Institute of Standards and Technology
PDF [™]	powder diffraction file
pH	measure of the acidity of a solution, where pH is the negative of the logarithm of the activity of H ⁺ in solution
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
redox	reduction-oxidation (process)
RWL	remote water lance
S-112	single-shell tank 241-S-112 (Hanford Site)
SEM	scanning electron microscopy (or microscope)
SI	saturation index
SRM	standard reference material
SST	single-shell tank
XRD	x-ray powder diffractometry analysis (commonly called x-ray diffraction)

¹ The Geochemist's Workbench is a registered trademark of the University of Illinois.

Units of Measure

θ	angle of incidence (Bragg angle)
$^{\circ}\text{C}$	temperature in degrees Celsius [$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$]
cm	centimeter
ft	foot
g	gram
gallon	gallon
in.	inch
L	liter
μ	micro (prefix, 10^{-6})
μCi	microCurie
μg	microgram
μm	micrometer
M	molarity, mol/L
mL	milliliter
mM	molarity, millimol/L
rpm	revolution per minute
I/I_0	relative intensity of an x-ray powder diffractometry analysis peak to the most intense peak
λ	wavelength
wt%	weight percent

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1.0 Introduction

CH2M HILL Hanford Group, Inc. is the U.S. Department of Energy (DOE) Office of River Protection's prime contractor responsible for the storage, retrieval, and disposal of Hanford Site tank waste. As part of this effort, CH2M HILL Hanford Group, Inc. contracted with Pacific Northwest National Laboratory (PNNL) to conduct testing for selected key contaminants present in residual waste remaining in the single-shell tank 241-S-112 (S-112) after final waste retrieval. Tank S-112 is located at the Hanford Site in Richland, Washington.

This report describes results of testing and analyses conducted on residual waste in single-shell tank (SST) 241-S-112 (S-112). These tests were completed to characterize the residual waste and assess the leachability of contaminants from residual solid waste. This is the first report from this PNNL project to describe the composition and leach test data for residual waste from a salt-cake tank. All previous PNNL reports (Cantrell et al. 2008; Deutsch et al. 2006, 2007a, 2007b, 2007c) describing characterization and testing results and contaminant release models for residual waste in SSTs were based on samples from sludge tanks.

PNNL uses a tiered approach to the characterization and testing of the tank residual waste. Initial (Tier 1) laboratory tests include determination of the inventory of contaminants and bulk constituents of the residual waste and quantification of the concentrations of water-leachable contaminants and other waste components, and x-ray diffraction (XRD). Tier 2 analyses are designed based upon the results of the Tier 1 tests, priorities, and available resources. Tier 2 tests typically consist of scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) analyses of the solids to identify reactive phases. In some cases, additional studies or analyses may include solubility tests, selective extractions, and application of synchrotron-based x-ray techniques and Mössbauer spectroscopy.

1.1 Work Scope

A set of Tier 1 laboratory tests were conducted to characterize the residual waste and identify some water-leachable constituents. The Tier 1 tests and analyses consisted of acid digestion of the as-received waste sample to measure elemental concentrations in the solid and analyses of leachates from a 1-month, single-contact water leach of contaminants from the residual waste to estimate soluble concentrations of ^{99}Tc , ^{238}U , major metals, and anions. In addition, bulk XRD and SEM/EDS analyses were completed on the as-received tank S-112 residual waste. The XRD analysis was conducted to identify crystalline mineral phases present in the residual waste. For this tank S-112 study, the only Tier 2 analysis completed was SEM/EDS. Results of the SEM/EDS analyses provided information on the morphologies and compositions of solid particles in the as-received residual waste samples.

1.2 S-100 Series Tank Description

Tank S-112 is one of 12 SSTs located at the 241-S Tank Farm in the 200 West Area of the Hanford Site (Figure 1.1). The tank is 22.9 m (75 ft) in diameter with a design capacity of 758,000 gal (101,330 ft³). The tank is constructed of 1.25-ft-thick reinforced concrete with a 1.25-ft-thick concrete

top. The tank is lined with 3/8-in.-thick carbon steel at the bottom and 5/16-in.-thick plates at the sides that transition to 0.25-in.-thick plates. Figure 1.2 presents a generalized profile view of a 100-series tank such as SST S-112 (Parker and Barton 2007).

Tank S-112 went into service in 1952 and was declared inactive in 1976 (Parker and Barton 2007). During its service life, the tank was used to store waste from many sources, including waste from the reduction-oxidation (redox) process, evaporator bottoms, and recycling streams from the 242-S Evaporator-Crystallizer. The Hanford Defined Waste (HDW) model (Agnew 1997) indicates that tank S-112 received two waste types: a sludge waste R1 (redox) and a salt-cake waste (S1-SltCk). From 1952 through the first quarter of 1957, the tank received redox first cycle waste via cascade overflow. In 1974 and 1975, the tank received 242-S Evaporator bottoms and recycle supernatants. The tank was removed from service in the second quarter of 1976, declared inactive during the third quarter of 1976, primary stabilized in 1979, and partially isolated in December 1982.

Waste retrieval of tank S-112 occurred in two phases. The first phase of the tank S-112 retrieval demonstration used salt-cake dissolution and modified sluicing to meet the *Hanford Federal Facility Agreement and Consent Order* Milestone M-45-03C (Ecology et al. 1996). Phase I occurred from September 26, 2003, through May 17, 2005. This first retrieval phase reached its waste retrieval capacity limit with an estimated 31,000 gal (4,144 ft³) of waste remaining (approximately 95%). This remaining volume was later revised to 28,465 gal (3,805 ft³) when it was discovered the tank bottom was higher than originally estimated (Parker and Barton 2007).

In the second phase of tank S-112 waste retrieval, the remote water lance (RWL) was installed to retrieve the remaining hard heel. Use of this device was followed by two 25% caustic (NaOH) additions, enhanced sluicing operations, and finally a 50-wt % caustic addition. After final retrieval, the total residual waste volume in tank S-112 was estimated to be 2,390 gal (319 ft³) (Parker and Barton 2007).

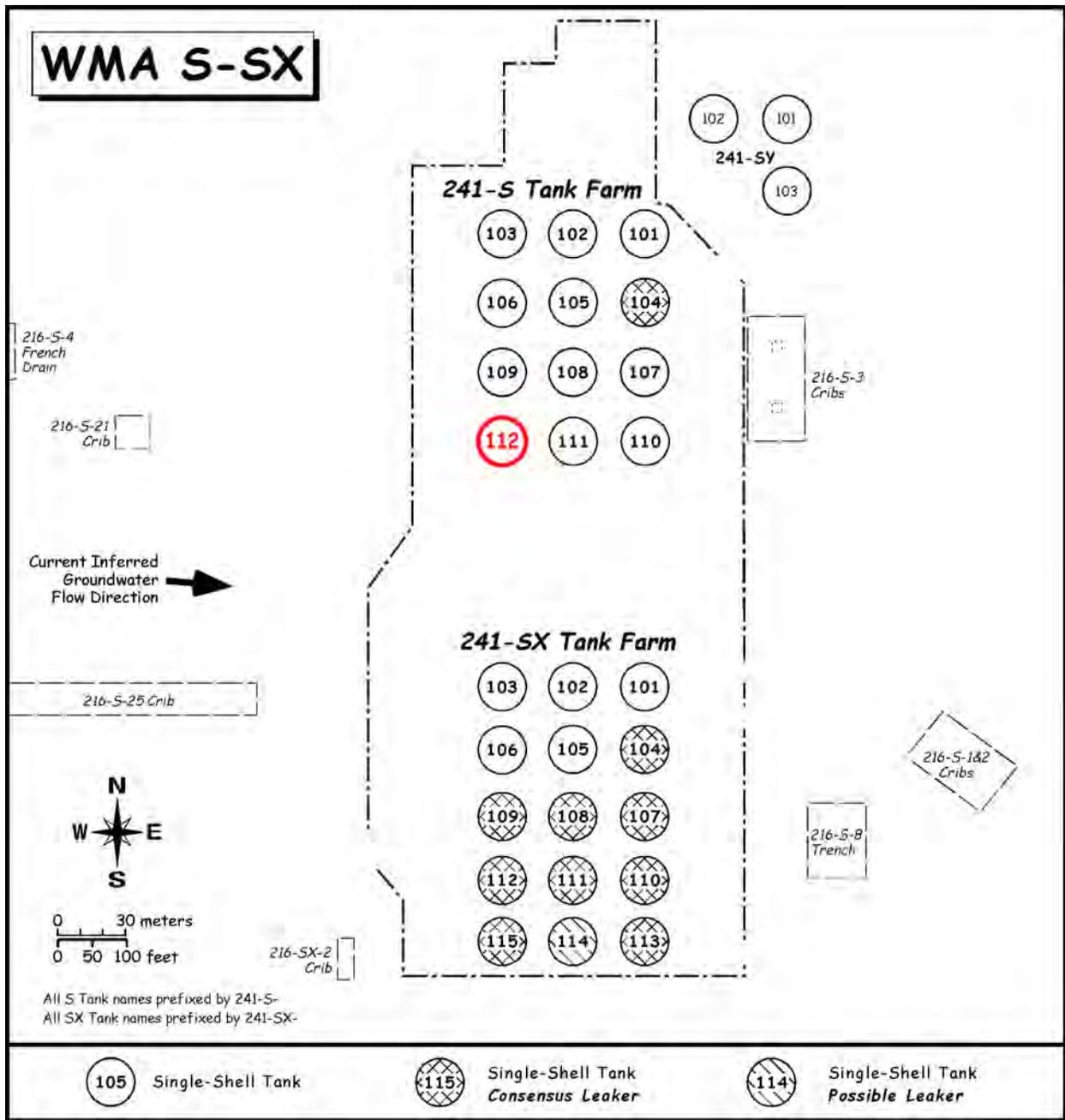


Figure 1.1. Hanford S and SX Tank Farms

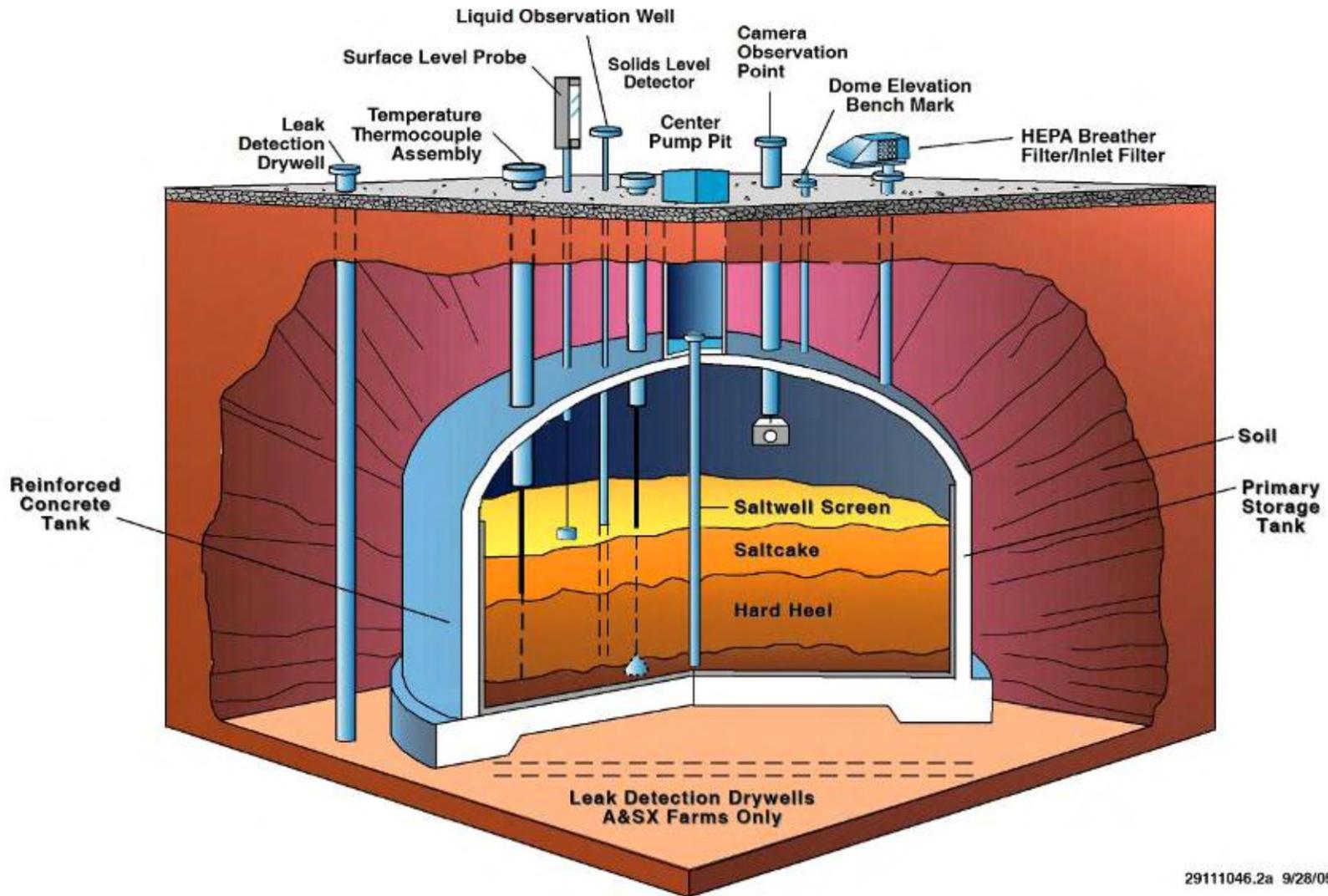


Figure 1.2. Generalized Profile View of a 100-Series Tank Such as Tank S-112 (Parker and Barton 2007)

2.0 Materials and Laboratory Test Methods

This section describes residual waste samples provided to PNNL and the analytical methods and various tests used to characterize the material and measure contaminant release.

2.1 Tank S-112 Residual Waste Samples

Residual waste samples from tank S-112 were collected by CH2M HILL Hanford Group, Inc. during post-retrieval activities in June 2006. The material from tank S-112 (samples 20406 and 20407) was provided to PNNL on June 7, 2007 (Table 2.1). Figure 2.1 and 2.2 show as-received samples 20406, and 20407, respectively.

Table 2.1. Tank S-112 Samples Provided to PNNL by 222-S Laboratory

Sample Number	Jar Size (mL)	Labcore Number	Net Weight of Sample Received (g)
20406	125	S07T006451	60
20407	125	S07T006452	60

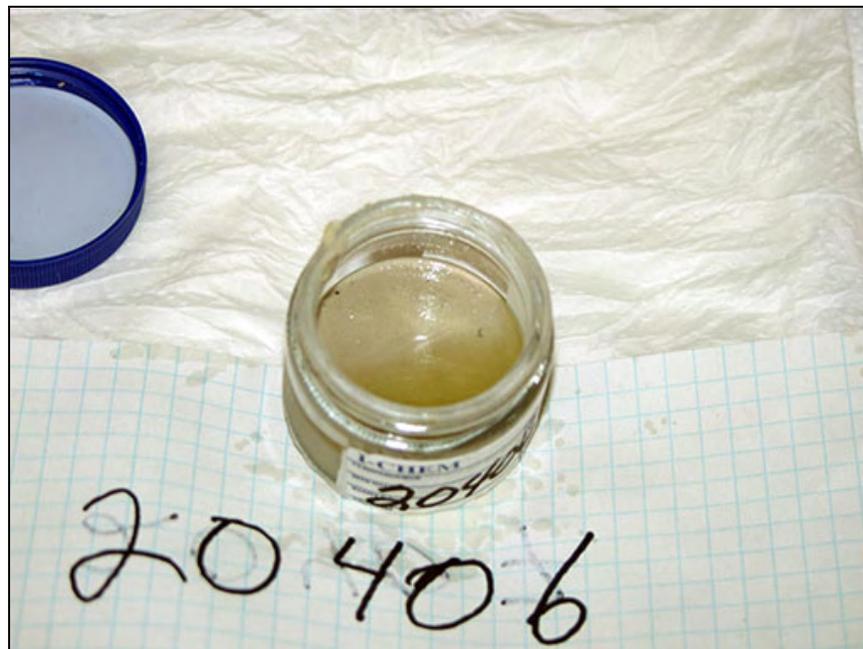


Figure 2.1. Tank S-112 Residual Waste (Sample 20406)



Figure 2.2. Tank S-112 Residual Waste (Sample 20407)

2.2 Tier 1 Tests

Tier 1 tests used in this study are described in this section. Studies of tank waste samples are generally completed using a tiered approach similar to the one developed for investigating contaminant fate and transport issues associated with past SST leaks in the vadose zone (e.g., Brown et al. 2007). Such an approach allows for initial (Tier 1) screening of samples using relatively inexpensive analytical techniques. This is followed by data analysis to determine the need for further testing (Tier 2). The only Tier 2 analysis method used on tank S-112 residual waste was SEM/EDS.

All laboratory activities were conducted in accordance with the requirements of Title 10, *Code of Federal Regulations*, Part 830.120, “Quality Assurance” (10 CFR 830.120), and the *Hanford Analytical Services Quality Assurance Requirements Documents* (HASQARD) (DOE-RL 2007). These requirements were implemented using PNNL’s online quality assurance (QA) plan, “Conducting Analytical Work in Support of Regulatory Programs.” PNNL’s QA plan is based on the requirements of DOE Order 414.1A as described in PNNL’s Standards-Based Management System, the HASQARD relevant elements of NQA-1, as well as recognized industry standards (e.g., U.S. Environmental Protection Agency [EPA], American Society for Testing and Materials [ASTM], and American National Standards Institute).

2.2.1 Residual Waste Composition by Acid Digestion

Bulk compositions of residual waste solids were determined using EPA SW-846 Method 3052 (EPA 1996a) with substitutions. The substitutions to EPA SW-846 Method 3052 consist of 1) decreasing the concentrated nitric acid (HNO_3) volume from 9 mL to 5 mL and 2) increasing the double-deionized (DDI) water volume from the recommended volume of 0 to 5 mL up to 10 mL. This method was used to measure metals concentrations and a limited number of nonmetals (e.g., P and S) in the residual waste. This method is not appropriate for the anion concentrations (e.g., NO_3 , Cl, F, and BO_3) because of the

addition of acids used in the procedure and analyses. The anion compositions were measured separately in solutions obtained by water leaching of the solids (see Section 2.2.5).

The basic acid-digestion procedure is described in EPA SW-846 Method 3052 (EPA 1996a). In this procedure, 300 mg of the sample is placed in a Teflon[®] microwave digestion vessel; 10-mL water, 5-mL 16 M HNO₃, 2-mL 12 M HCl, and 1-mL 29 M HF are added to the sample; and the vessel is sealed and placed in a microwave-assisted digestion system.¹ The samples are treated at the EPA-recommended temperatures and times. The sample is then allowed to cool, and 0.45 g of boric acid (H₃BO₃) is added to the digestate and shaken by hand. Samples are filtered through a 0.45-µm pore-size syringe filter prior to analysis. There were no visible solids when the digestions were complete.

Table 2.2 lists the digestion factors (wet solid-to-solution ratios) for residual waste samples 20406 and 20407 used for the EPA acid digestions. These factors were calculated from the wet weight of waste material divided by the volume of extracting solution. The digestion factors were then multiplied by the percentage solids, as determined from moisture content analysis, to convert to a dry weight basis. The dissolved metal concentrations of the filtered solutions were then analyzed by a combination of methods, including inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES). These analytical methods are described in Lindberg and Deutsch (2003).

Table 2.2. Digestion Factors for Residual Waste Solids Used for the EPA Acid Digestion Treatment

Sample Number	Dry Weight Corrected Digestion Factor (g/L)
20406	8.83
20406 Dup ^(a)	7.64
20407	9.30
20407 Dup	8.27
Dup = Duplicate sample.	

2.2.2 Moisture Content

The moisture contents of the tank waste samples were measured to calculate dry weight concentrations for constituents in the waste. Dry weight concentrations provide a consistent measurement unit for comparison purposes that eliminates the effect of variable water content on sample concentrations.

Gravimetric water content of the waste material was determined using the ASTM procedure D2216-98, *Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass* (ASTM 1998), with the following minor exceptions: 1) the volume of sample recommended was decreased due to radiological concerns; and 2) the sample was dried at a lower oven temperature, 105°C, for a longer period of time to prevent dehydration of the solids.

Residual waste samples were placed in tared containers, weighed, and dried in an oven until a constant weight was achieved, usually 24 to 48 hours. The container was then removed from the oven,

¹ Teflon is a registered trademark of E.I. du Pont de Nemours and Company.

sealed, cooled, and weighed. All measurements were performed using a calibrated balance. The gravimetric water content is computed as the percentage change in waste sample weight before and after oven drying (i.e., $[(\text{wet weight} - \text{dry weight})/\text{dry weight}]$).

2.2.3 Single-Contact Residual Waste Extraction Tests and Analysis of Residual Supernatant

Water-soluble inorganic constituents were determined using a DDI water extraction method. The extract was prepared by adding 30 mL of DDI water to a quantity of residual waste ranging from 0.200 to 0.600 g contained in a 50-mL polypropylene centrifuge tube. The centrifuge tube was sealed, briefly shaken by hand, and then placed on a mechanical orbital shaker for 1 month. After being shaken for the predetermined time, the tube was placed in a centrifuge and spun at 4,000 revolutions per minute (rpm) for 20 minutes. The supernatant was carefully decanted and filtered through 0.45- μm pore-size membrane. More details can be found in ASTM procedure D3987-85 *Standard Test Method for Shake Extraction of Solid Waste with Water* (ASTM 1999).

In addition to these single-contact extraction tests, supernatant from sample 20406 was analyzed for dissolved constituents. Besides providing composition information about the residual supernatant that may still remain in the tank, the composition of the supernatant provides a baseline for comparing the leachate compositions from the DDI water extraction tests.

2.2.4 pH

The pH of the solutions was measured using EPA SW-846 Method 9040C (EPA 2004) with a modification. The modification consists of using a solid-state pH electrode instead of the recommended glass electrode.

2.2.5 Anion Analysis

Anion analysis was performed using an ion chromatograph (IC) following the technical procedure AGG-IC-001 (Lindberg 2004).² Chloride, NO_2 , Br, NO_3 , SO_4 , and PO_4 were separated on a Dionex AS17 column with a gradient elution technique from 1-mM to 35-mM NaOH and measured using a conductivity detector. This methodology is a substitution for EPA SW-846 Method 9056A (EPA 2007), with the exception of using gradient elution with NaOH instead of the recommended isocratic elution with a HCO_3 buffer.

2.2.6 Cations and Trace Metals

Major cation analysis (including Al, Si, Ca, Mg, Na, K, Fe, and Mn) was performed by ICP-OES following PNNL-AGG-ICP-AES (Baum 2008).³ Selected trace metals analysis (^{99}Tc and U isotopes) was performed by ICP-MS following PNNL-AGG-415 (Clayton 2008).⁴

² Lindberg MJ. 2004. *Determinations by Ion Chromatography (IC)*. AGG-IC-001 (Rev. 0). Unpublished PNNL technical procedure, Pacific Northwest National Laboratory, Richland, Washington.

³ Baum SR. 2008. *Inductively Coupled Plasma -Optical Emission Spectrometry (ICP-OES) Analysis*. PNNL-AGG-ICP-AES (Rev. 2). Unpublished PNNL technical procedure, Pacific Northwest National Laboratory, Richland, Washington.

For both ICP-OES and ICP-MS, high-purity calibration standards were used to generate calibration curves and to verify continuing calibration during the analysis. Dilutions of 10 and 5 times were made for each sample and analyzed to investigate and correct for matrix interferences.

2.2.7 Alkalinity

The sample alkalinity was measured by standard titration. A volume of standardized sulfuric acid was added to the sample to an endpoint of pH 4.5 to measure total alkalinity. Alkalinity is reported in terms of an equivalent mass of CaCO_3 . The alkalinity procedure follows Standard Method 2320 B, “Alkalinity by Titration” (Clesceri et al. 1998).

2.3 X-Ray Powder Diffractometry

Standard bulk powder XRD techniques were used to identify crystalline phases present in two as-received tank S-112 residual waste subsamples, designated as 20407 and 20407 duplicate (dup).

Because the residual waste samples were highly radioactive dispersible powders, it was necessary to prepare the XRD mounts of these samples inside a fume hood regulated for handling radioactive materials. Residual waste samples were prepared for XRD analysis by placing milligram quantities of each sample into a mixture of water and collodion solution. The collodion solution consists of 2% nitrocellulose dissolved in amyl acetate and is an x-ray amorphous, viscous binder commonly used to make random powder mounts for XRD when only a limited amount of sample is available. A trace quantity of reference-material corundum powder ($\alpha\text{-Al}_2\text{O}_3$, alumina) (National Institute of Standards and Technology Standard Reference Material [NIST SRM] 676 [NIST 2005]) was added to each sample slurry as internal 2θ standard to correct for any observed peak shifts caused by slight misalignments of the mounted samples.

A pipette was used to transfer sample slurry onto a circular platform (1 cm [0.39 in.] in diameter) that was placed on top of the post located on the base inside a disposable XRD-specimen holder (Figure 2.3). This specimen holder was designed specifically for safe handling of dispersible powders containing highly radioactive or hazardous materials (Strachan et al. 2003). After the samples were allowed to air-dry overnight, the holder was assembled and a piece of Kapton[®] film was placed between the cap and the retainer.⁵ The holder was sealed with wicking glue and removed from the fume hood.

Each sample was analyzed using a Scintag XRD unit equipped with a Peltier thermoelectrically cooled detector and a copper x-ray tube. The diffractometer was operated at 45 kV and 40 mA. Individual scans were obtained from 2 to $65^\circ 2\theta$ with a step size of 0.02° and dwell time of 2 seconds. Scans were collected electronically and processed using the Jade[®] XRD pattern-processing software.⁶

⁴ Clayton ET. 2008. *Inductively Coupled Plasma Mass Spectrophotometry (ICP-MS) Analysis*. PNNL-AGG-415 (Rev. 2). Unpublished PNNL technical procedure, Pacific Northwest National Laboratory, Richland, Washington.

⁵ Kapton is a registered trademark of E.I. du Pont de Nemours and Company.

⁶ Jade is a registered trademark of Materials Data Inc.

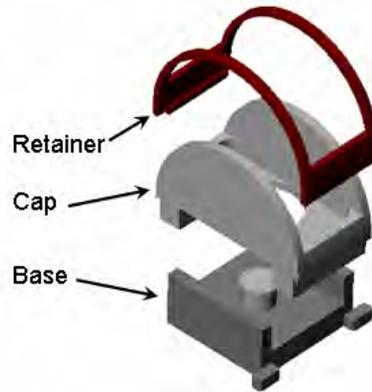


Figure 2.3. Exploded Schematic View of the XRD Sample Holder (Kapton[®] film not shown) (see Strachan et al. 2003)

A sample consisting of only a dry film of the collodion solution was previously prepared and analyzed by XRD (Krupka et al. 2004) so that its contribution relative to the background signals of the XRD patterns for the residual waste samples could be quantified. The resulting XRD pattern for the collodion solution film is shown in Figure 2.4. The most obvious feature of this diffraction pattern is the broad peak positioned between 10° and $30^\circ 2\theta$. The symmetry of this peak is characteristic of those resulting from the XRD of amorphous (noncrystalline) material. Although subtracting the collodion background from residual waste XRD patterns allows for better phase matching, this process may eliminate minor reflections and inconspicuous pattern features. Therefore, each as-measured XRD pattern was examined before and after background subtraction to ensure that the integrity of the pattern was maintained. For background subtraction, the Jade software provides the user with control over the selection of background-subtraction points. This process allows a better fit to 2θ regions under broad reflections, such as those resulting from amorphous materials. On average, 30 to 40 background points were selected from each XRD pattern, and a cubic-spline curve was then fit through each set of points. Adjustments to this curve were made by selecting additional background points in regions of a pattern that were difficult to fit. Once a well-matched curve was fitted to a pattern, the background was subtracted from each as-measured XRD pattern, resulting in a smooth tracing.

Identification of the mineral phases in XRD patterns was based on a comparison of the patterns measured for the residual waste samples with the mineral powder diffraction files (PDF[™]) published by the Joint Committee on Powder Diffraction Standards (JCPDS) International Center for Diffraction Data (ICDD). As a general rule, a crystalline phase must be present at greater than ~5 to 10 wt% of the total sample mass (greater than 1 wt% under optimum conditions) to be readily detected by XRD. In general, the measured peak intensities depend on several factors, including the combined mass of each crystalline phase in the sample. Because of the physical characteristics of these residual waste samples, such as high radioactivity, high dispersibility, and variable moisture content, the mass of residual waste combined with the collodion solution for each XRD mount could not be controlled or easily determined. Dissimilarities in mineral segregation (settling) resulting from the different densities of minerals mixed with the collodion solution and associated effects on relative peak intensities also influence the overall pattern intensity. The combined effect of these factors could have some effect on the characteristic mineral peak intensities, which precluded quantitative comparisons of peak intensities for equivalent reflections in background-subtracted XRD patterns for different residual waste samples.

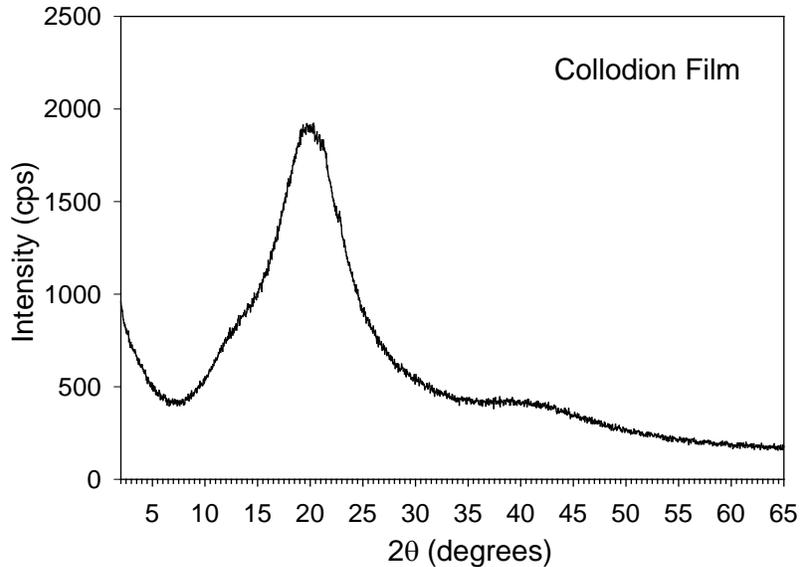


Figure 2.4. XRD Pattern for Collodion Film Measured in the Absence of Any Residual Waste Material (from Krupka et al. 2004)

2.4 Scanning Electron Microscopy/Energy Dispersive Spectrometry Analysis

Analyses by SEM/EDS were completed to characterize the morphologies and compositions of solid phases present in two as-received tank S-112 residual waste samples, designated as 20407 and 20407 dup. Two mounts were prepared for the sample to compensate for the possibility that a less-than-optimum mount of the sample might occur, thus improving the likelihood of obtaining representative SEM images of each sample. The mounts used for SEM/EDS consisted of double-sided carbon (C) tape attached to standard Al-mounting stubs. For each mount, small aliquots of each residual waste sample were placed on the exposed upper surface of the C tape using a micro spatula. Each mount was then coated with C using a vacuum sputter-coater to improve the conductivity of the samples and, thus, the quality of the SEM images and EDS signals.

A JEOL JSM-840 SEM was used for high-resolution imaging of micrometer/submicrometer-size particles in the residual waste samples. The EDS system provided qualitative elemental analysis for scanned areas of particles. The SEM is equipped with an INCA Energy EDS System⁷ to automate the collection of EDS spectra over multi-micrometer-size areas of an SEM-imaged sample. The EDS software was calibrated to a copper reference standard mounted on a specimen holder. Operating conditions consisted of 20 keV for SEM imaging and 20-keV 100 live seconds⁸ for the EDS analyses. The EDS analyses are limited to elements with atomic weights heavier than boron (B). Compositions

⁷Oxford Instruments, Concord, Massachusetts.

⁸Live time is when (real time less dead time) the EDS system is available to detect incoming x-ray photons. Dead time is the portion of the total analyzing time that is actually spent processing or measuring x-rays. While each x-ray pulse is being measured, the system cannot measure another x-ray that may enter the detector and is, therefore, referred to as “dead.”

determined by EDS are qualitative and have large uncertainties resulting from alignment artifacts caused by the variable sample and detector configurations that exist when different particles are imaged by SEM.

Photomicrographs of high-resolution backscattered electron (BSE) images were obtained as digital images and stored in electronic format. To help identify particles that contain elements with large atomic numbers, such as Tc, the SEM was operated in the BSE mode. Backscattered electron emission intensity is a function of the element's atomic number – the larger the atomic number, the brighter the signal.

Each SEM mount was examined by the SEM to identify those particles and surface features that were typical or unusual for the sample. During this examination, a SEM micrograph was first recorded at low magnification for a representative area of the mount to provide a general perspective of the sizes, types, and distributions of particles that comprise each SEM mount. Additional SEM micrographs were then recorded of particles at greater magnifications to provide a more detailed representation of the particles' characteristics, and selected points on these particles were then analyzed by EDS.

3.0 Laboratory Results

This section provides results of tests conducted on residual waste samples 20406 and 20407 from tank S-112. Section 3.1 includes a description of the residual waste composition obtained from acid digestion methods. The results of the residual waste leach test and analysis of the residual waste supernatant in sample 20406 are described in Section 3.2. Residual waste characterization data generated by using XRD and SEM/EDS are discussed in Sections 3.3 and 3.4, respectively.

3.1 Residual Waste Composition

An important component of contaminant release-rate calculations is an accurate measurement of the total concentrations of the contaminants in the source material. As described in Section 2.2.1, the total metals and radionuclide concentrations of the residual wastes were measured using an acid digestion method. The results of these analyses are described in this section. The anionic (nonmetal) composition of the residual waste was estimated by water extraction as part of the Tier 1 analyses (Section 2.2.5). Tier 1 anion results are discussed in Section 3.2.

Table 3.1 lists the moisture content ($(\{\text{wet wt} - \text{dry wt}\} / \text{dry wt}) \times 100\%$) of the tank S-112 residual waste samples used for the EPA acid digestions. These values are used with the digestion factors (Table 2.2) to convert the solution analyses of the extracts from the treatments to dry weight solid concentrations. The moisture contents of the residual waste samples ranged from 25.0 to 30.5%. Note that in the case of sample 20406, the moisture content was made on a sample from which free liquid was drained as it was collected from the sample container with a spatula.

Table 3.1. Moisture Contents of Tank S-112 Residual Waste Samples

Sample Number	Moisture Content
20406	30.5%
20407	25.0%

Concentrations listed in parentheses in the following tables are defined as less than the estimated quantification limit (EQL) but greater than a zero instrument signal (concentration of zero). These values are reported for informational purposes only. They may reflect actual concentrations that are real but have larger associated uncertainties than values above the EQL or may reflect values that were calculated from the instrument's background signal and are not representative of actual residual waste composition. The EQL of an element is determined by analyzing a suite of continuing calibration verification (CCV) standards at the beginning and end of each analytical run. The lowest CCV standard that is within $\pm 10\%$ of its certified value is multiplied by the dilution factor for the sample to determine the EQL for the element for the particular analytical run. The EQL may vary with each analysis, depending on sample matrix, dilution factors, and instrument performance. Concentrations listed as less-than (<) values in the tables refer to instrument measurements that are less than zero. In these instances, the reported analyte concentration is assigned a value of "<EQL" using the EQL value appropriate for that particular analyte and set of analytical conditions.

The following discussion of element concentrations of the residual waste is organized in terms of the analytical method used to measure concentrations in the solution extract. These methods were ICP-OES, ICP-MS, and IC. For the tables, the solution concentrations have been converted from a mass-per-liter basis to a dry, residual solid-mass basis.

The results of elemental analyses by ICP-OES are listed in Table 3.2 through Table 3.4. Boron values from acid digestion are not reported because boric acid was used in the digestion process. Among the suite of 30 elements that were analyzed, 23 elements were present above the instrumental detection limits in all samples. These elements included Al, As, Ba, Bi, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Si, Sb, Sr, Ti, Zn, and Zr. Average concentrations of the elements that were present in measurable concentrations are listed in Table 3.5.

Comparison of the elemental compositions from the ICP-OES analyses of the two residual waste samples (Table 3.5) indicates that the two samples are generally quite similar, with all elemental concentrations being well within $\pm 20\%$ of the average for the two samples. Aluminum is clearly the dominant metal component, with an average concentration of 7.7 wt% (for the two samples). Other significant components include Na, Fe, Cr, and Si, with average concentrations of 4.9, 2.3, 1.7, and 1.2 wt%, respectively.

The concentrations of ^{99}Tc and ^{238}U measured by ICP-MS are listed in Table 3.6. The average ^{99}Tc concentrations determined by acid digestion for the two samples 20406 and 20407 were 0.476 and 0.472 $\mu\text{g/g}$ waste, respectively. The average ^{238}U concentrations determined by acid digestion for the two samples 20406 and 20407 were 28.8 and 18.7 $\mu\text{g/g}$ waste, respectively.

3.1.1 Comparison of Analytical Results S-112 Residual Waste with 222-S Results

The ICP-OES and ICP-MS results reported here are compared with those determined by the 222-S Laboratory (Parker and Barton 2007) in Table 3.7. The 222-S Laboratory results in Table 3.7 were corrected to a dry weight basis for the comparison. Differences between elemental concentrations can be expected as a result of heterogeneity of the different samples analyzed by the two laboratories. For most elements, the ICP-OES and ICP-MS results reported above the EQL were reasonably consistent with those determined by the 222-S Laboratory (Parker and Barton 2007) (Cr, Fe, Mn, Ti, ^{99}Tc , and ^{238}U). For several elements (Ca, Cu, Pb, Sb, Ti, Zr), meaningful comparisons cannot be made because results from one of the laboratories were below their quantification limit. Significantly higher concentrations of Si and Zn were determined here relative to the results of the 222-S Laboratory. It is believed that the microwave digestion procedure, similar to EPA SW-846 Method 3052 (EPA 1996a) is a more effective digestion for these elements than EPA SW-846 Method 3050B (EPA 1996b) performed by the 222-S Laboratory. Al concentrations reported here were considerably less than concentrations measured at the 222-S Laboratory. The average Al concentration determined by the 222-S Laboratory was 291,000 $\mu\text{g/g}$ dry waste, while the average concentration reported here was 77,200 $\mu\text{g/g}$ dry waste. If it is assumed that the 222-S Laboratory result for Al is correct and all the Al occurs as gibbsite, then gibbsite would account for 84% of the mass of the residual waste. This result is more consistent with the XRD and SEM/EDS results (see Sections 3.3 and 3.4) than those from the bulk composition analyses reported here. Based on these comparisons, the Al concentrations for the unleached (as-received) bulk sludge appear to be underestimated. The reason for this discrepancy is being evaluated. Our preliminary assumption is that the method similar to EPA SW-846 Method 3052 (EPA 1996a) may result in the formation of fine particulate Al precipitates in samples with very high concentrations of Al that were filtered out by a 0.45- μm filter. There is also the potential for Al to adsorb to surfaces of the reaction vessel after the digestion.

Table 3.2. Residual Waste Composition Measured by ICP-OES (Al through Cu)

Sample Number	Al	As	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu
	µg/g Dry Waste									
EPA Acid Digestion										
20406	8.18E+04	(5.48E+01)	1.22E+01	(3.52E-01)	(3.90E+00)	(4.77E+01)	(1.31E+00)	<5.66E+00	1.79E+03	2.08E+01
20406 Dup	8.59E+04	(5.09E+01)	1.37E+01	(9.80E-02)	(1.67E+00)	(6.01E+01)	(1.07E+00)	<6.55E+00	1.71E+03	1.96E+01
20407	7.82E+04	(4.94E+01)	1.12E+01	(5.01E-02)	(3.61E+00)	(3.71E+01)	(1.07E+00)	<5.38E+00	1.68E+03	1.63E+01
20407 Dup	6.27E+04	(2.13E+01)	1.33E+01	<3.02E+00	(1.99E+00)	8.25E+01	(1.45E+00)	<6.04E+00	1.69E+03	1.57E+01
20406 Avg	8.39E+04	(5.28E+01)	1.29E+01	(2.25E-01)	(2.79E+00)	(5.39E+01)	(1.19E+00)	<6.10E+00	1.75E+03	2.02E+01
20407 Avg	7.05E+04	(3.54E+01)	1.23E+01	(1.54E+00)	(2.80E+00)	5.98E+01	(1.26E+00)	<5.71E+00	1.69E+03	1.60E+01
Avg = Average. Dup = Duplicate. EQL = Estimated quantification limit. Concentrations listed in parentheses were <EQL.										

Table 3.3. Residual Waste Composition Measured by ICP-OES (Fe through Pb)

Sample Number	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb
	µg/g Dry Waste									
EPA Acid Digestion										
20406	1.99E+03	(6.84E+01)	(6.13E+00)	(2.32E+00)	1.37E+01	(6.04E+00)	5.20E+04	(9.28E+00)	(4.15E+01)	(8.96E+00)
20406 Dup	2.24E+03	(8.17E+01)	(6.90E+00)	(4.57E+00)	1.45E+01	(3.41E+00)	5.13E+04	(8.42E+00)	(5.21E+01)	(5.05E+00)
20407	2.30E+03	(5.93E+01)	(6.63E+00)	(3.69E+00)	1.34E+01	(2.85E+00)	4.57E+04	(8.33E+00)	(4.51E+01)	(5.53E+00)
20407 Dup	2.57E+03	(6.63E+01)	(4.16E+00)	(8.71E+00)	1.58E+01	<1.21E+01	4.74E+04	(1.00E+01)	(3.10E+01)	(8.88E+00)
20406 Avg	2.11E+03	(7.50E+01)	(6.51E+00)	(3.45E+00)	1.41E+01	(4.73E+00)	5.17E+04	(8.85E+00)	(4.68E+01)	(7.00E+00)
20407 Avg	2.43E+03	(6.28E+01)	(5.40E+00)	(6.20E+00)	1.46E+01	(7.47E+00)	4.66E+04	(9.17E+00)	(3.80E+01)	(7.21E+00)
Avg = Average. Dup = Duplicate. EQL = Estimated quantification limit. Concentrations listed in parentheses were <EQL.										

Table 3.4. Residual Waste Composition Measured by ICP-OES (S through Zr)

Sample Number	S	Sb	Se	Si	Sr	Ti	Tl	V	Zn	Zr
	µg/g Dry Waste									
EPA Acid Digestion										
20406	(5.89E+00)	4.75E+01	<1.13E+03	1.56E+03	(4.03E+00)	1.59E+01	(1.31E+01)	<1.42E+01	5.01E+01	4.82E+00
20406 Dup	<2.62E+02	5.55E+01	<1.31E+03	1.24E+03	(4.67E+00)	1.07E+01	<1.31E+02	<1.64E+01	5.01E+01	4.81E+00
20407	<2.15E+02	3.81E+01	<1.08E+03	9.72E+02	(2.97E+00)	9.81E+00	(1.39E+01)	(7.36E-02)	4.64E+01	3.95E+00
20407 Dup	<2.42E+02	4.60E+01	<1.21E+03	1.11E+03	(4.42E+00)	8.59E+00	(1.32E+01)	<1.51E+01	4.57E+01	4.02E+00
20406 Avg	(1.34E+02)	5.15E+01	<1.22E+03	1.40E+03	(4.35E+00)	1.33E+01	(7.20E+01)	<1.53E+01	5.01E+01	4.81E+00
20407 Avg	<2.28E+02	4.20E+01	<1.14E+03	1.04E+03	(3.70E+00)	9.20E+00	(1.35E+01)	(7.59E+00)	4.61E+01	3.98E+00
Avg = Average. Dup = Duplicate. EQL = Estimated quantification limit. Concentrations listed in parentheses were <EQL.										

Table 3.5. Average Compositions for Tank S-112 Residual Waste Samples 20406 and 20407 Measured by ICP-OES

Element	20406	20407
	µg/g Dry Waste	
Al	83,900	70,500
Ba	12.9	12.3
Ca	(53.9)	(59.8)
Cr	1,750	1,690
Cu	20.2	16.0
Fe	2,110	2,430
Mn	14.1	14.6
Na	51,700	46,600
Sb	51.5	42.0
Si	1,400	1,040
Ti	13.3	9.20
Zn	50.1	46.1
Zr	4.81	3.98
Concentrations listed in parentheses were <EQL. EQL = Estimated quantification limit.		

Table 3.6. Concentrations of ⁹⁹Tc and ²³⁸U Measured in Tank S-112 Residual Waste by ICP-MS

Sample Number	⁹⁹ Tc	²³⁸ U
	µg/g Dry Waste	
EPA Acid Digestion		
20406	0.479	35.5
20406 Dup	0.473	22.1
20407	0.483	20.4
20407 Dup	0.460	17.0
20406 Avg	0.476	28.8
20407 Avg	0.472	18.7
Avg = Average. Dup = Duplicate.		

Table 3.7. Comparisons of Average Compositions for Tank S-112 Residual Waste Samples 20406 and 20407 Measured by ICP-OES with Results from 222-S Laboratory

Element	20406	20407	222-S
	µg/g Dry Waste		
Al	83,900	70,500	291,000
Ca	(53.9)	(59.8)	512
Cr	1,750	1,690	1,438
Cu	20.2	16.0	(7.03)
Fe	2,110	2,430	1,477
Mn	14.1	14.6	14.8
Na	51,700	46,600	59,200
Pb	(7.0)	(7.2)	83.2
Sb	51.5	42.0	(84.2)
Si	1,400	1,040	71.9
Ti	13.3	9.20	(7.36)
Zn	50.1	46.1	16.4
Zr	4.81	3.98	(6.92)
⁹⁹ Tc	0.476	0.472	0.641
²³⁸ U	28.8	18.7	15.3
Concentrations listed in parentheses were <EQL. EQL = Estimated quantification limit.			

3.2 Double-Deionized Water-Leach Tests and Supernatant Composition

Data obtained from the water-leach tests on residual waste subsamples 20407 and 20407 dup are presented in this section. Because sample 20406 contained supernatant, the water-leach test was not conducted on this sample. Concentrations of dissolved constituents in the supernatant were determined in place of the extract concentrations for sample 20406. The single-contact, water-leach tests were run in duplicate with an equilibration time of 1 month. Double-deionized water was used as the leachant. Concentrations of the constituents in the water extracts tabulated in this section are expressed in units of microCurie or microgram per gram of dry residual waste.

3.2.1 Residual Waste to Double-Deionized Water Ratios: Single-Contact Double-Deionized Water Extracts

In the single-contact DDI water extractions, 30 ml of DDI water was contacted with about 0.3 g of moist residual waste. The moisture content of these 20407 residual waste subsamples was 25.0% by mass (Table 3.1). The dry residual waste masses calculated from moisture content measurements were used to compute the dry residual waste to DDI water ratios (Table 3.8). These ratios ranged from about 7.64 to 9.85 g/L.

Table 3.8. Residual Waste to Double-Deionized Water Ratios Used in Leach Tests

Sample Number	Waste to DDI Water Ratio (g/L)
20407	7.64
20407 Dup	9.85
Dup = Duplicate.	

3.2.2 Water Extract pH and Alkalinity – Supernatant and Single-Contact Double-Deionized Water Extracts

The alkalinities and pH values measured in duplicate samples of the 20406 supernatant and the 1-month DDI water extract for 20407 are listed in Table 3.9. The average pH and alkalinity values for the 20406 supernatant (>12 and 370,000 mg/L, respectively) are significantly higher than those of the water extracts for sample 20407 (10.80 and 902 mg/L, respectively). Because a ratio of water to solid of approximately 100 mL/g was used in the water-leach tests, these results suggest that the alkalinity components leached from sample 20407 were likely derived from residual solution entrained in the sample.

Table 3.9. The pH and Alkalinity Values for Supernatant (20406) and Single-Contact Water Extract (20407)

Sample Number	pH	Total Alkalinity (as CaCO ₃) at pH 4.5 Endpoint (mg/L)
20406 (supernatant)	>12	380,000
20406 Dup (supernatant)	>12	361,000
20407 (1-month DDI water extract)	10.81	783
20407 Dup (1-month DDI water extract)	10.78	1,020
Dup = Duplicate.		

3.2.3 Dissolved Concentrations of ⁹⁹Tc and ²³⁸U – Supernatant and Single-Contact Water Extracts

The radionuclides ⁹⁹Tc and ²³⁸U pose a long-term environmental risk because of their long half-lives and high mobility in the dissolved state. Dissolved concentrations of ⁹⁹Tc and ²³⁸U determined in the 20406 supernatants and 20407 1-month DDI water extracts are shown in Table 3.10. In addition to these concentrations, pore water concentrations of ⁹⁹Tc and ²³⁸U were calculated from the 20407 water extract measurements under the assumption that all dissolved constituents came from entrained pore water that was diluted by the water added for the DDI water extractions. Comparison of these pore water values for ⁹⁹Tc with the 20406 supernatant results indicates the calculated pore water concentrations are somewhat higher than those of the supernatant. This suggests the majority of the ⁹⁹Tc in the DDI water extracts came from the pore water. Concentrations of ²³⁸U in the supernatant are much higher than the calculated pore water concentrations. This result suggests that a major portion of the ²³⁸U in the pore water precipitated during the 1-month DDI water extraction. This could occur as a result of a decrease in complexation of dissolved U as the concentrations of dissolved hydroxide and carbonate (major complexing agents of uranyl ions) were diluted by the DDI.

Table 3.10. Dissolved ^{99}Tc and ^{238}U Concentrations in Supernatant (20406), DDI Water Extracts (20407), and Calculated Pore Water (20407) from Tank S-112 Residual Waste Samples

Sample Number	^{99}Tc	^{238}U	^{99}Tc	^{238}U
	$\mu\text{g/L}$		$\mu\text{Ci/L}$	
20406 (supernatant)	160	2,310	2.71	7.76E-4
20406 Dup (supernatant)	136	2,070	2.31	6.96E-4
20407 (1-month DDI water extract)	0.550	0.740	0.00935	2.49E-7
20407 Dup (1-month DDI water extract)	0.850	1.43	0.0145	4.80E-7
20407 (calculated pore water)	177	238	3.00	7.99E-5
20407 Dup (calculated pore water)	273	459	4.64	1.54E-4

3.2.4 Extractable ^{99}Tc and ^{238}U – Single-Contact Water Extracts

The DDI extractable concentrations of ^{99}Tc and ^{238}U per gram of dry waste after 1 month of contact for sample 20407 are listed in Table 3.11. The average concentration of ^{99}Tc extracted from the single-contact extracts from sample 20407 was fairly low (0.079 $\mu\text{g/g}$ waste). When compared to the total ^{99}Tc in the residual waste as measured by acid digestion (Table 3.6), the average water leachable concentration represents about 17% of the ^{99}Tc in the residual wastes (Table 3.11).

Table 3.11. Concentrations and Average Water-Leachable Percentages of ^{99}Tc and ^{238}U Extracted from Tank S-112 Residual Waste Sample 20407 Using Single-Contact Water-Leach Tests

Sample Number	^{99}Tc	^{238}U	^{99}Tc	^{238}U	^{99}Tc	^{238}U
	$\mu\text{g/g Dry Waste}$		$\mu\text{Ci/g Dry Waste}$		Percent Water Leachable (%)	
20407	0.0719	0.0968	1.22E-03	3.25E-08		
20407 Dup	0.0863	0.145	1.47E-03	4.88E-08		
20407 Average	0.0791	0.121	1.34E-03	4.06E-08	16.8%	0.65%

The concentration of ^{238}U extracted from the tank S-112 residual waste with DDI was relatively low. The average extractable ^{238}U concentration for sample 20407 was 0.12 $\mu\text{g/g}$ waste. The percentages calculated using the acid digestion concentrations for the total values indicate that 0.65% ^{238}U leached from the residual waste (Table 3.11). These low percentages, especially when compared to those for Na and Ca (discussed in Section 3.2.4), indicate that ^{238}U and possibly ^{99}Tc are present in the as-received residual waste in solid forms with relatively low solubilities or slow dissolution rates.

3.2.5 Dissolved Concentrations of Metals – Supernatant and Single-Contact Water Extracts

Concentrations of several metals, such as Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sr, Ti, Tl, V, Zn, and Zr in the DDI water extracts, were measured by ICP-OES. Among these, only four metals (Al, Ca, Cr, and Na) were present in concentrations above the EQL (Table 3.12). Dissolved concentrations of Al, Ca, Cr, and Na determined in the 20406 supernatants

and 20407 water extracts are shown in Table 3.12. In addition to these concentrations, pore water concentrations calculated from the 20407 water extract measurements were made assuming that all the dissolved metals came from pore water entrained in the sample, which was diluted by the water added for the DDI water extractions. Comparison of the concentrations of the 20407 calculated pore water concentrations for Al and Na with the 20406 supernatant are quite similar, indicating that dissolved Al and Na in the 20407 DDI water extracts were likely derived from diluted pore water in the sample. The calculated 20407 pore water concentrations of Ca are over 200 times that of the supernatant, indicating that essentially all the Ca in the 20407 DDI water extracts was derived from dissolution of a solid phase in the as-received waste sample. The calculated 20407 pore water concentrations of Cr are nearly twice that of the supernatant, indicating that approximately half the Cr in the 20407 DDI water extracts was derived from the pore fluid and half from dissolution of a solid in the sample.

Table 3.12. Dissolved Metal Concentrations in Supernatant (20406), Double-Deionized Water Extracts (20407), and Calculated Pore Water (20407) from Tank S-112 Residual Waste Samples

Sample Number	Al	Ca	Cr	Na
	µg/L			
20406 (supernatant)	2.16E+07	(5.15E+02)	2.81E+05	1.59E+08
20406 Dup (supernatant)	2.16E+07	(3.00E+02)	2.80E+05	1.54E+08
20407 (1-month DDI water extract)	4.90E+04	4.14E+02	1.37E+03	3.08E+05
20407 Dup (1-month DDI water extract)	6.64E+04	4.23E+02	1.79E+03	4.05E+05
20407 (calculated pore water)	1.57E+07	1.33E+05	4.41E+05	9.88E+07
20407 Dup (calculated pore water)	2.13E+07	1.36E+05	5.74E+05	1.30E+08
Dup = Duplicate. Concentrations listed in parentheses were <EQL.				

3.2.6 Extractable Metal Concentrations – Single-Contact Double-Deionized Water Extracts

Table 3.13 lists concentrations of extractable metals that were measured at concentrations about the EQL (Al, Ca, Cr, and Na) in the DDI water extracts after 1 month of contact with residual waste sample 20407 as determined on a per gram of dry waste basis. The most highly leachable element was Na followed by Al, Cr, and Ca. Percentages of total metals that were DDI water extractable are also listed in Table 3.13. These results indicate that Na and Ca are both highly extractable, while Al and Cr are moderately extractable.

Table 3.13. Concentrations and Average Water-Leachable Percentages of Metals in Single-Contact Water Extractions from Tank S-112 Residual Waste Sample 20407

Sample Number	Al	Ca	Cr	Na
	µg/g Dry Waste			
20407	6.41E+03	5.42E+01	1.80E+02	4.02E+04
20407 Dup	6.74E+03	4.29E+01	1.81E+02	4.11E+04
20407 Average	6.58E+03	4.85E+01	1.81E+02	4.07E+04
Percent Water Leachable (%)				
20407 Average	9.3	81.2	10.7	87.4
Dup = Duplicate.				

3.2.7 Extractable Anion Concentrations – Single-Contact Water Extracts

Concentrations of anions extractable per gram of dry waste that were present in the DDI water extracts after 1-month contact were measured by IC (Table 3.14). All anions determined by this IC method were below their detection limits; this indicates the major anions in the leachates were hydroxide and carbonate.

Table 3.14. Average Extractable Anion Concentrations Determined from Single-Contact Double-Deionized Water Extractions from Tank S-112 Residual Waste Sample 20407

Sample Number	F	Cl	NO ₂	NO ₃	SO ₄	PO ₄
	µg/g Dry Waste					
20407 1 Month	<2.62E+02	<6.54E+02	<1.31E+03	<1.31E+03	<1.96E+03	<1.96E+03
20407 1 Month Dup	<2.03E+02	<5.07E+02	<1.01E+03	<1.01E+03	<1.52E+03	<1.52E+03
Dup = Duplicate.						

3.3 X-Ray Diffraction Results

Bulk XRD patterns were measured on two as-received tank S-112 residual waste subsamples (designated 20407 and 20407 dup). The XRD mounts were prepared as described in Section 2.3. The XRD sample mounts of tank S-112 residual waste included the addition of a trace quantity of reference-material corundum powder (α -Al₂O₃, alumina) (NIST SRM 676 [NIST 2005]) as an internal 2 θ standard for each XRD pattern. Identification of the mineral phases in XRD patterns was based on a comparison of the XRD patterns measured for the residual waste samples with the mineral PDFs™ published by the JCPDS ICDD.

Figures 3.1 and 3.2 show the XRD patterns for subsamples 20407 and 20407 dup, respectively. In each of these figures, the top XRD pattern (designated A) and bottom XRD pattern (designated B) show, respectively, the as-measured (before background subtraction) and background-subtracted patterns for each subsample. Each XRD pattern is shown as a function of degrees 2 θ based on CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The vertical axis in each pattern represents the intensity of the XRD peaks. For comparison, the XRD patterns in Figure 3.1 are shown schematically along with the database patterns for gibbsite

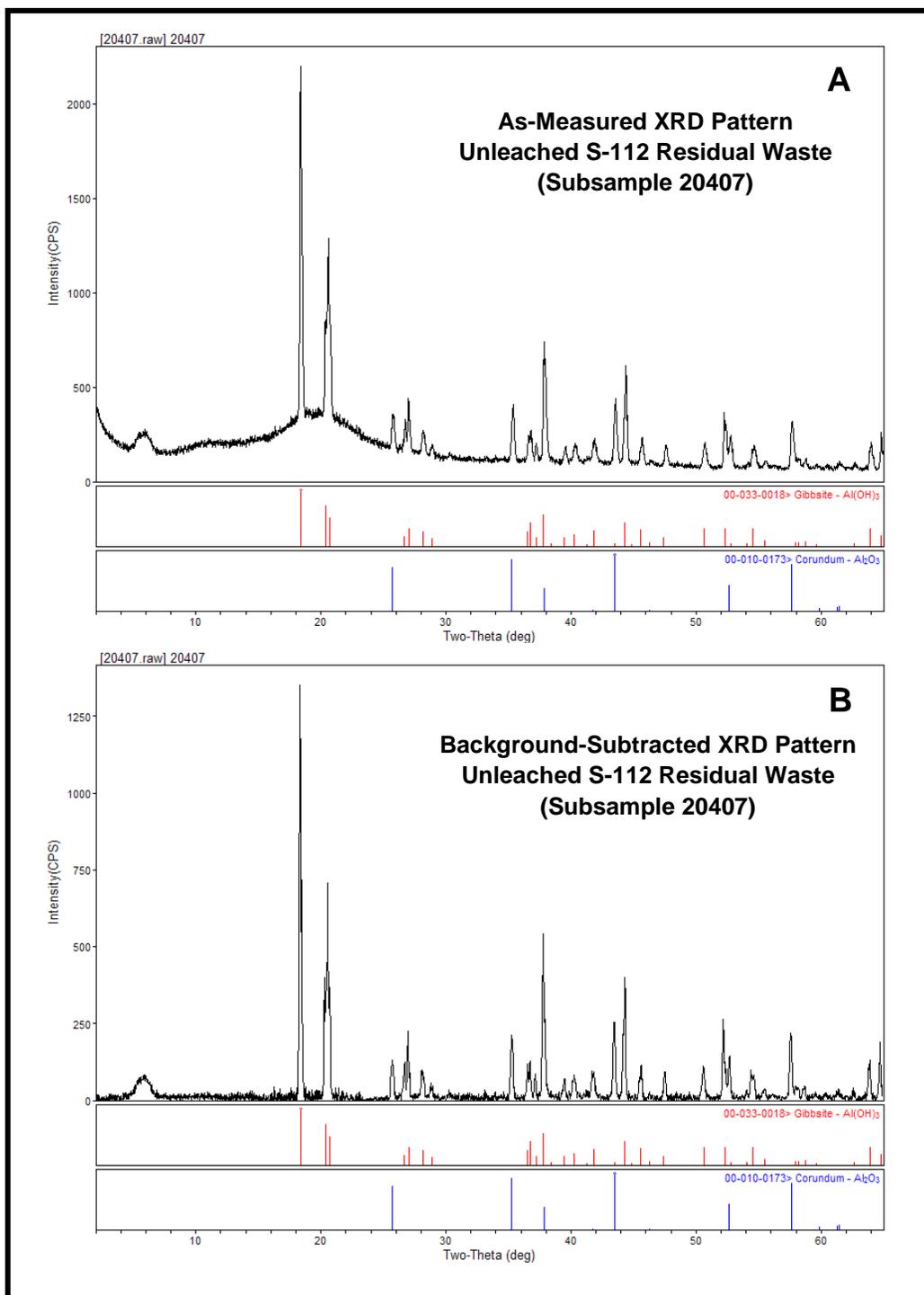


Figure 3.1. As-Measured (A) and Background-Subtracted (B) XRD Patterns for Subsample 20407 of Unleached Tank S-112 Residual Waste

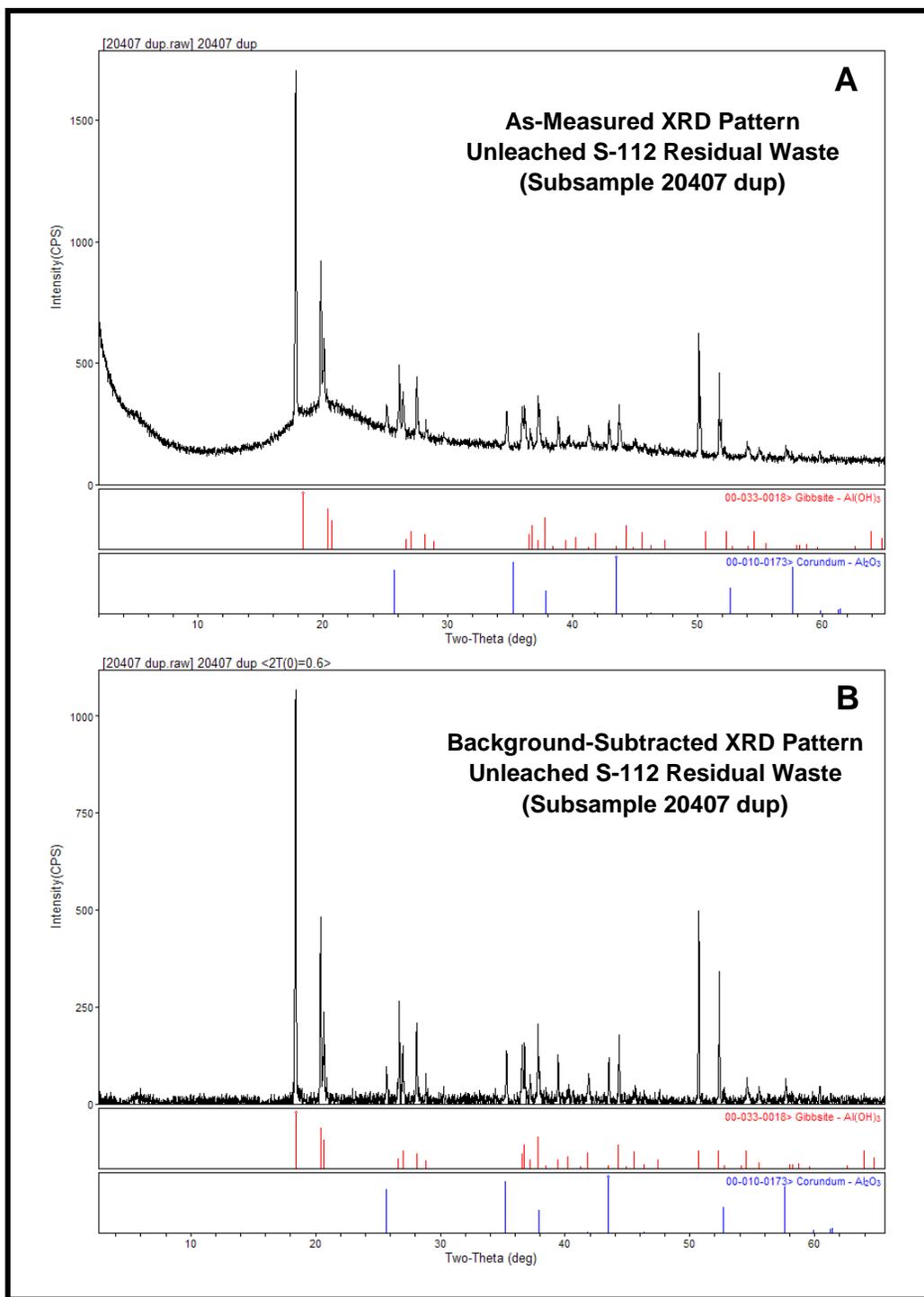


Figure 3.2. As-Measured (A) and Background-Subtracted (B) XRD Patterns for Subsample 20407 dup of Unleached Tank S-112 Residual Waste

[Al(OH)₃] (PDF #00-033-0018) and corundum (PDF #00-010-0173). In the schematic database (PDF) patterns shown in Figure 3.1, the height of each line represents the relative intensity of an XRD peak (i.e., the most intense [the highest] peak has a relative intensity of 100%).

Analysis of the XRD patterns for subsamples 20407 and 20407 dup indicate the tank S-112 waste sample 20407 consists essentially of all (more than ~90%) gibbsite. Typically, a crystalline phase must be present at greater than ~5 to 10 wt% (greater than ~1 wt% under optimum conditions) to be readily detected by bulk XRD. All reflections in the XRD patterns for subsamples 20407 and 20407 dup could be matched to peaks in the XRD database patterns for gibbsite or corundum. The absence of any unidentified reflections indicates that these samples do not contain any other crystalline phases present at greater than ~5 to 10 wt%. The two as-measured XRD patterns (e.g., see Figure 3.1A) contain a broad diffraction profile (or hump) from approximately 10 to 30°2θ. The XRD pattern for subsample 20407 (Figure 3.1) also contains a small, wide reflection at approximately 5.6°2θ. For these samples, diffraction from the nitrocellulose binder and the Kapton[®] polyimide film used in the sample holder are thought to be the main contributors to the broad diffraction profile from 10 to 30°2θ and the small reflection at 5.6°2θ, respectively.

3.4 Scanning Electron Microscopy/ Energy Dispersive Spectrometry Results

Analysis by SEM/EDS of two subsamples (designated 20407 and 20407 dup) of as-received unleached tank S-112 residual waste was completed. Sample mount preparation and SEM/EDS analyses were completed as described in Section 2.4. The Appendix contains all SEM micrographs for the two subsamples of tank S-112 residual waste and the tabulations of the elemental compositions derived from the EDS analyses of particles in these SEM-analyzed subsamples. All SEM micrographs (including those shown in this section) were collected using BSE emission to facilitate identification of particles that contain elements with large atomic numbers (i.e., the larger the atomic number, the brighter the signal contrast).

Figure 3.3 is a low-magnification micrograph that shows the morphologies, sizes, and surface textures of typical particles present in unleached tank S-112 residual waste. Analysis of the SEM micrographs, such as Figure 3.3, indicates the unleached tank S-112 residual waste is made up primarily of a single phase that likely has a coating of a second phase. Many of the typical particles have external crystal faces and exhibit hexagonal form and possibly basal cleavage (see inserts in Figure 3.3). A few particles (discussed later in this section) distinguished by their brightness and/or in a different form relative to those shown in Figure 3.3 were observed, but these trace phases were extremely rare.

Analysis of the SEM/EDS results indicate the primary phase in unleached tank S-112 residual waste is likely made up of Al, O, and possibly H and/or C, but has an encrustation on its surfaces that also contains Na. Close inspection of SEM micrographs for particles typical to Figure 3.3 indicate many (possibly most) of these particles have a multi-micrometer-thick coating on their surfaces. Examples of particles that exhibit surface features suggestive of the presence of this Na-rich coating are shown by areas circled in blue in Figure 3.4. The EDS analyses indicate most particles shown in Figure 3.3 are comprised of Al-Na-O(±H±C). However, because the SEM/EDS method is essentially a near-surface characterization technique of the top few micrometers of a probed particle (analysis depth depends on beam voltage and sample composition), the EDS analyses are therefore sensitive to the composition of any micrometer-thick surface coatings. The EDS results also indicate that Na is absent in the analyses of some particles typical to Figure 3.3 (see EDS analyses in the Appendix). The EDS spectrum (Figure 3.4)

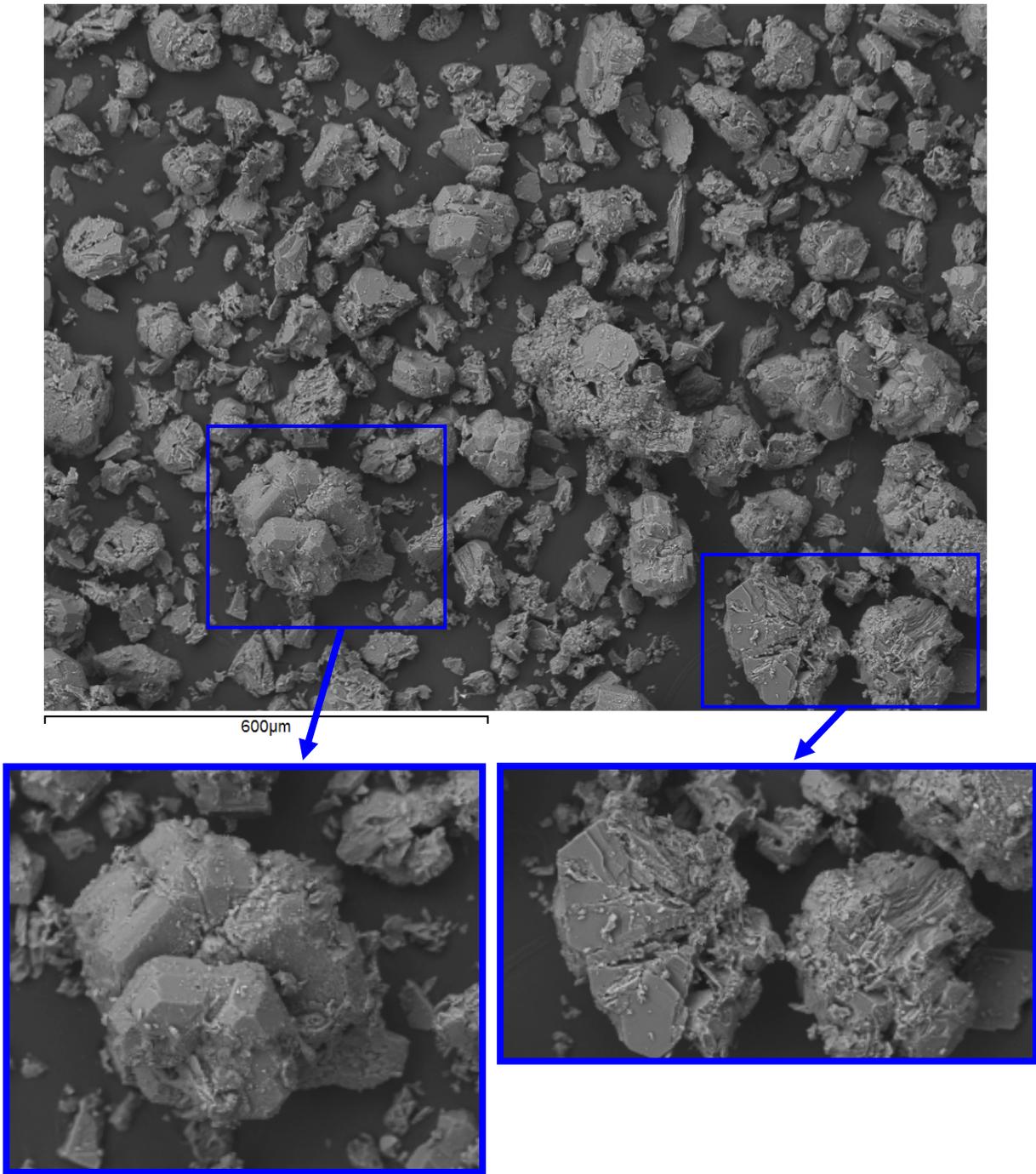


Figure 3.3. Low-Magnification Backscattered Electron SEM Images of Typical Particles in Unleached Subsample 20407 of Tank S-112 Residual Waste

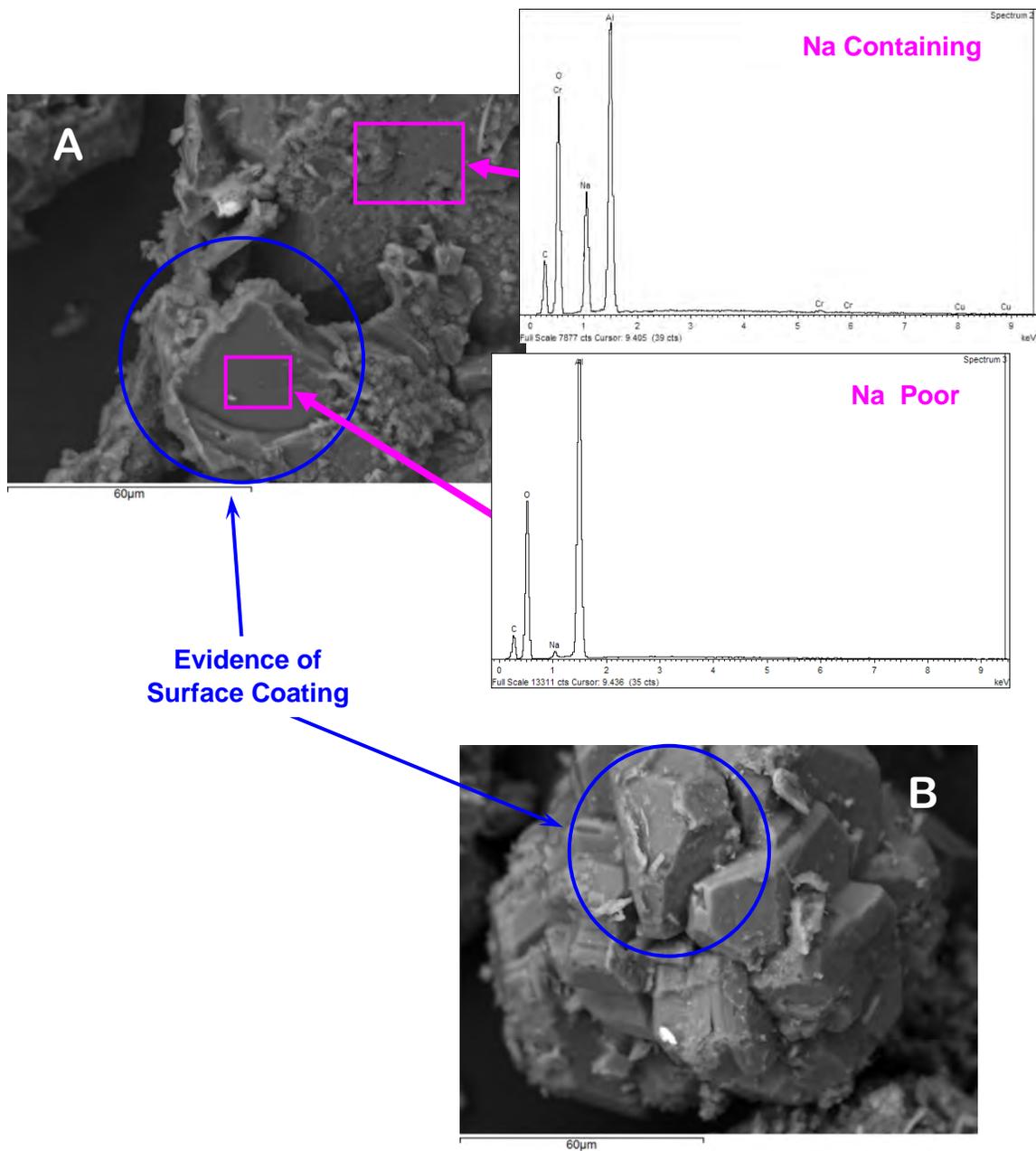


Figure 3.4. Backscattered Electron SEM Images Showing Evidence for Na-Rich Surface Coating on Typical Particles and Corresponding EDS Spectra for Na-Rich and Na-Poor Areas of Such Particles in Unleached Subsamples 20407 (A) and 20407 dup (B) of Tank S-112 Residual Waste

that shows little or no Na likely reflects the composition for surfaces of Al-O(\pm H \pm C) particles underneath this encrustation, which probably detached during sampling of the residual waste or preparation of the SEM mounts.

The conclusion based on the SEM/EDS results that the primary phase in unleached tank S-112 residual waste is composed of Al-O(\pm H \pm C) is consistent with the XRD results in Section 3.3. The XRD results indicate the crystalline solid in the bulk sample consists essentially of gibbsite [Al(OH)₃]. The EDS composition measured for the Na-poor solid shown in Figure 3.4 is 38.9 wt% Al and 60.0 wt% O, which is close to the ideal composition of gibbsite of 34.6 wt% Al, 61.5 wt% O, and 3.9 wt% H. The morphology of the majority of the particles shown in Figure 3.3 (i.e., external crystal faces, hexagonal form, and basal cleavage) is also consistent with gibbsite.

It has not been possible to identify the phase that comprises the surface coating on the gibbsite particles from the XRD and SEM/EDS analyses results. Because there were no unidentified reflections in the XRD patterns, the XRD results do not provide any information regarding the identity of this surface phase. The surface encrustation is either amorphous and thus cannot be detected by XRD, or is crystalline but present at too low a concentration to be detected by XRD. The EDS compositions measured for the Al-Na-O solid do not agree with the ideal compositions for phases such NaAlO₂ (sodium aluminate, 28.0 wt% Na, 32.9 wt% Al, and 39.00 wt% O) or dawsonite [NaAl(CO₃)(OH)₂, 16.0 wt% Na, 18.7 wt% Al, 55.6 wt% O, 8.3 wt% C, and 1.4 wt% H]. For comparison, the EDS composition for the solid having the highest measured concentration of Na is 29.4 wt% Na, 18.0 wt% Al, and 51.5 wt% O. The majority of the EDS analyses for Na-containing solids are estimated to range from approximately 5 to 20 wt% Na and 20 to 35 wt% Al.

A few particles of other compositions were observed by SEM/EDS in the unleached tank S-112 residual waste, but these phases were very rare. These phases were easily distinguished by their brightness and/or different form relative to particles typical to Figure 3.3. These phases include one or more Fe oxides shown by blue arrows in Figure 3.5; a Ca-Cr-O phase shown by the blue arrow in the SEM micrograph in Figure 3.6A; a Pb-Cl \pm O phase shown by the blue arrow in the right SEM micrograph in Figure 3.6B; possibly one or more silicate phases shown by the blue arrows in Figure 3.7; and an acicular (needle-like) phase with an unknown composition shown by the yellow arrows in Figure 3.7. The identities of the phases could not be determined based on the results of the XRD and SEM/EDS analyses. Trace concentrations of Cr and possibly Mn were associated with the few Fe oxide particles observed. The complete compositions of the Ca-Cr-O, Pb-Cl \pm O, and silicate phases are uncertain because the analyzed particles were likely aggregates that also contain Al-Na-O and/or Fe oxide solids.

Neither Tc, U, nor I was detected in any of the particles in the SEM samples of unleached tank S-112 residual waste analyzed by EDS as part of these studies.

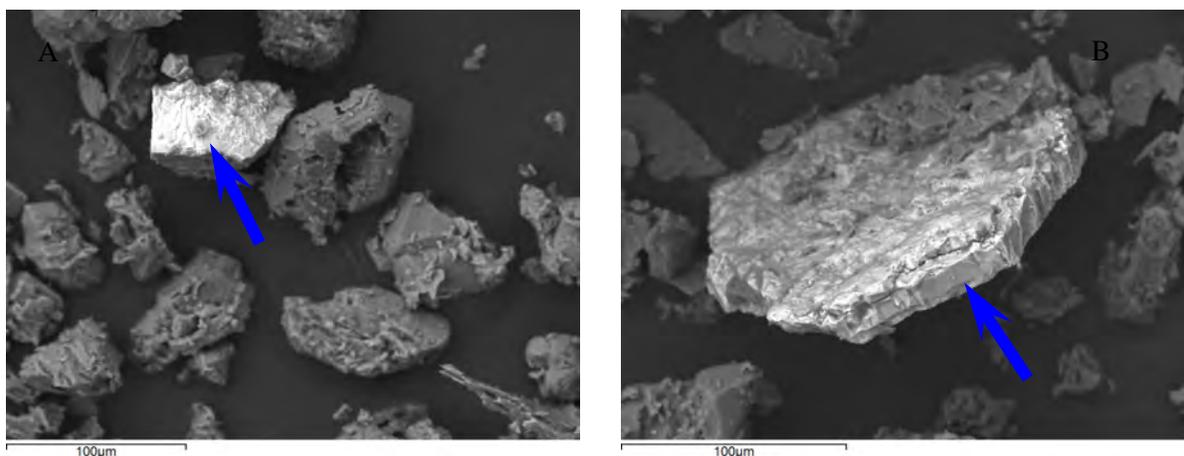


Figure 3.5. Backscattered Electron SEM Images Showing Fe Oxide Particles Present in Unleached Subsamples 20407 (A) and 20407 dup (B) of Tank S-112 Residual Waste

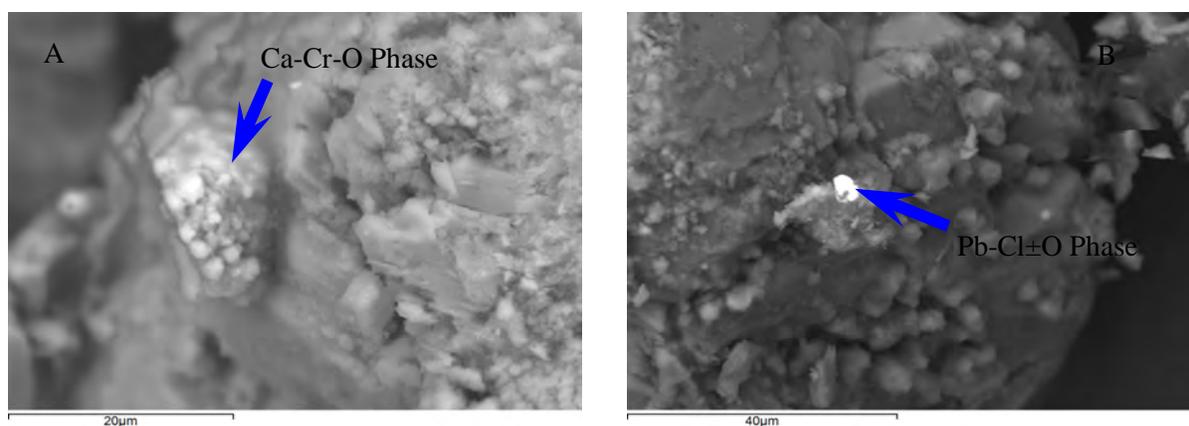


Figure 3.6. Backscattered Electron SEM Images Showing Ca-Cr-O (A) and Pb-Cl±O (B) Particles Present in Unleached Subsample 20407 dup of Tank S-112 Residual Waste. (The complete compositions of these phases are uncertain because the analyzed particles were likely aggregates that also contain Al-Na-O and/or Fe oxide solids.)

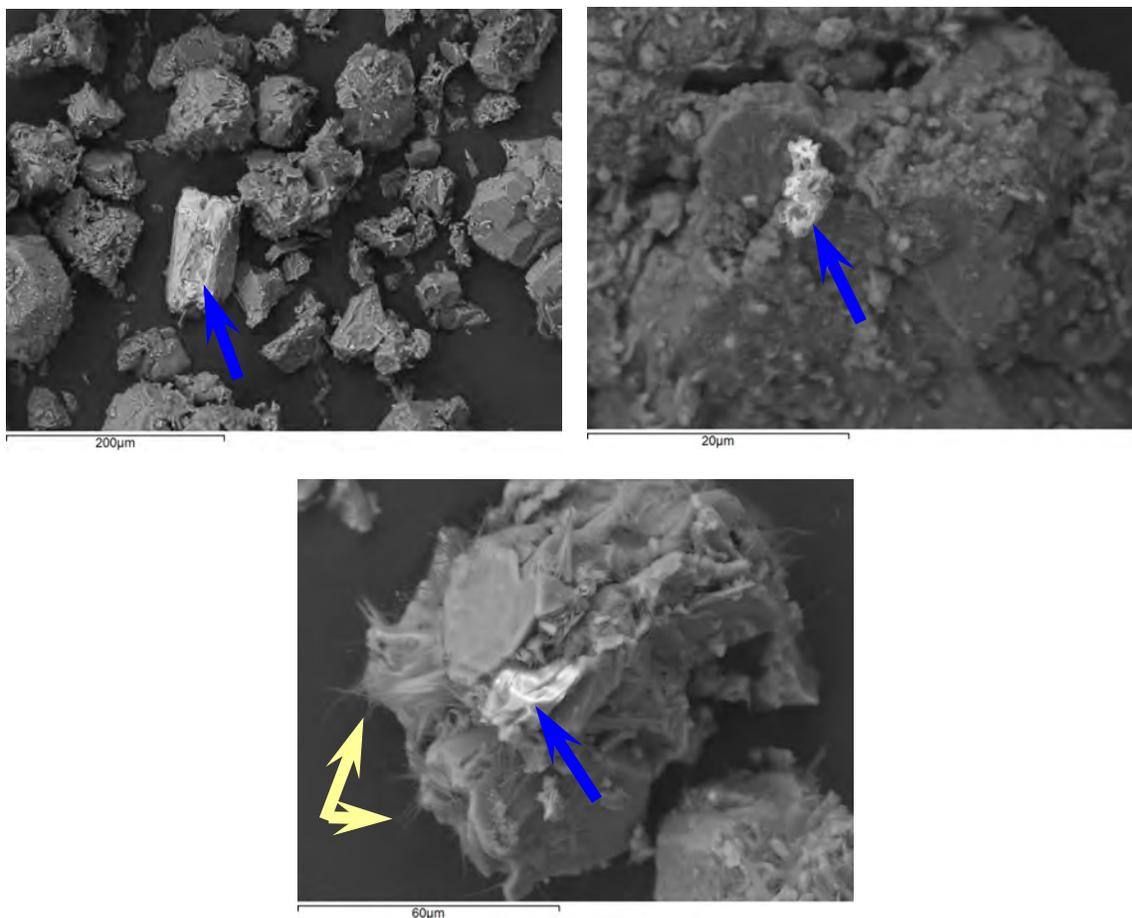


Figure 3.7. Backscattered Electron SEM Images Showing Silicate Particles (shown by blue arrows) and Needle-Like Phase (shown by yellow arrows) Present in Unleached Subsample 20407 dup of Tank S-112 Residual Waste. (The complete compositions of these phases are uncertain because the analyzed particles were likely aggregates that also contain Al-Na-O and/or Fe oxide solids.)

3.5 Geochemical Modeling

The React module of Geochemist's Workbench[®] version 7.0.3 (Bethke and Yeakel 2007) was used to calculate mineral saturation indices (SIs) based on measured compositions of leachates from the DDI 1-month, single-contact extraction tests. The SIs were computed to identify solid phases that were possibly in equilibrium with the leachate solutions. The SI is defined in Equation (3.1):

$$SI = \log (Q/K_{sp}) \quad (3.1)$$

where Q is the activity product and K_{sp} is the mineral solubility product at equilibrium at the temperature of interest. Minerals with SI values near zero (within ± 0.5 , SI values are unitless) are generally considered to be near equilibrium with the solution composition. More positive values are considered oversaturated, and more negative values are considered undersaturated with respect to the solution composition. The SIs were calculated for the 1-month single-contact extracts but not the supernatant solutions. The SI values were not determined for the supernatants because of their exceptionally high concentrations (ionic

strengths in excess of 10 M). Such SI calculations would require the use of the Pitzer ion-interaction model (Pitzer and Mayorga 1973; Pitzer 1991), which is more accurate than the Davies or Debye-Hückel activity coefficient models for modeling in high-ionic strength solutions. Although Geochemist's Workbench includes the Pitzer model, its database does not include the Pitzer parameters for Al, which are required for modeling the supernatant compositions.

The SI values for leachates from the DDI 1-month single-contact extraction tests were calculated using the thermodynamic database file thermo.com.V8.R6+.dat that is supplied with Geochemist's Workbench Version 7.0.3. The database was modified to include the stability constant for NaAlO₂ (sodium aluminate) using the Gibbs free energy of formation value taken from Wagman et al. (1982). Solubility data for čejkaite [Na₄(UO₂)(CO₃)₃] from Felmy et al. (2005), becquerelite [Ca(UO₂)₆O₄(OH)₆•8H₂O] from Rai et al. (2002), sodium diuranate hydrate [Na₂U₂O₇•xH₂O] from Yamamura et al. (1998), andersonite [Na₂Ca(UO₂)(CO₃)₃•5H₂O] and urancalcarite [Ca(UO₂)₃(CO₃)(OH)₆•3H₂O] from Chen et al. (1999), and the stability constant for the dissolved species Ca₂UO₂(CO₃)₃(aq) from Kalmykov and Choppin (2000).

Calculated SIs for relevant Al-, Na-, Ca-, Cr- and U-containing minerals based on the measured compositions of the 1-month single-contact samples with SI values greater than -3 are shown in Table 3.15. All SI values calculated for Al(oxy)hydroxides indicated that these phases were oversaturated. Calcite (CaCO₃), dawsonite [NaAlCO₃(OH)₂], and aragonite (CaCO₃) appear to be near equilibrium with the leachate. These results indicate the concentrated NaOH solutions used during the second phase of final waste retrieval from tank S-112 (Section 1.2) to dissolve the residual sludge, which is composed primarily of gibbsite (Sections 3.3 and 3.4), may have resulted in precipitation of dawsonite. Exposure of the concentrated NaOH solutions to air would result in absorption of CO₂ gas and formation of additional dissolved carbonate, which could lead to precipitation of dawsonite, and calcite or aragonite. The SEM/EDS analysis of the as-received samples indicates the gibbsite particles were coated with a Al-Na-O(±H±C) phase (Section 3.4). This coating could contain dawsonite possibly enriched with NaOH as a result of desiccation of entrained supernatant on the sample (Section 3.4). Because analysis by SEM/EDS was not conducted on solids from the DDI water extract samples, it was not possible to determine if this coating persisted through the 1-month extraction tests or if calcite or aragonite precipitated during the tests. The geochemical modeling results did not identify any Cr or U solids that were near equilibrium with the compositions of the DDI water extract samples.

Table 3.15. Calculated Saturation Indices (unitless) for Relevant Al-, Na-, Ca-, Cr-, and U-Containing Minerals Based on Compositions of Tank S-112 Double-Deionized 1-Month Single-Contact Extracts

Phase	Sample 20407	Sample 20407 Dup
	Saturation Indices (unitless)	
Diaspore [AlO(OH)]	2.10	2.26
Boehmite [AlO(OH)]	1.70	1.85
Gibbsite [Al(OH) ₃]	1.51	1.66
Calcite (CaCO ₃)	0.08	0.10
Dawsonite [NaAlCO ₃ (OH) ₂]	0.08	0.46
Aragonite (CaCO ₃)	-0.07	-0.05

4.0 Discussion

This report presents the results of testing conducted on residual waste in Hanford tank S-112 after final waste retrieval. These tests were completed to characterize the residual waste and assess the leachability of contaminants from the solids. This is the first report from this PNNL project to describe the composition and leach test data for residual waste from a salt-cake tank. All previous PNNL reports (Cantrell et al. 2008; Deutsch et al. 2006, 2007a, 2007b, 2007c) describing contaminant release models, and characterization and testing results for residual waste in SSTs were based on samples from sludge tanks.

Crystalline solids in tank S-112 waste consist of essentially all (more than ~90%) gibbsite. SEM/EDS results are consistent with the XRD results, indicating the primary phase in tank S-112 waste is comprised of Al-O(\pm H \pm C) with a composition that is 39 wt% Al and 60 wt% O (consistent with gibbsite). The SEM/EDS results also indicate the gibbsite particles appear to have a common coating of an Al-Na-O solid. The phase composition of this coating could not be established with certainty, but appeared to have been composed of 29 wt% Na, 18 wt% Al, and 52 wt% O. Geochemical modeling indicated that dawsonite [NaAlCO₃(OH)₂] was near equilibrium with the 1-month DDI water extracts. This suggests that dawsonite may be an important component of the coating. Particles with other compositions were very rare in tank S-112 residual waste. The SEM/EDS analyses identified a few particles of Fe oxides, a Ca-Cr-O phase, a Pb-Cl \pm O phase, and possibly one or more silicate phases.

Results of the Tier 1 analysis of the bulk composition of tank S-112 samples indicate Al is the largest, single metal component of the waste (7.1 to 8.4 wt% for the two samples). Other major metal components (Na, Fe, Cr, and Si) occurred at lower concentrations, ranging from 4.7 to 5.2%, 0.21 to 0.24%, 0.17 to 0.18%, and 0.10 to 0.14%, respectively, for the two samples. Based on these results and assuming the Al occurs primarily as gibbsite [Al(OH)₃], this Al phase would account for 21 to 24 wt% of the residual waste.

Residual waste compositions determined in this study for tank S-112 samples were generally consistent with those determined by the 222-S Laboratory (Parker and Barton 2007), except for the concentrations determined for Al. The average Al concentration determined from the 222-S Laboratory results was 29.1 wt% (dry wt basis). If all Al occurred as gibbsite, this would account for 84% of the residual waste mass. This result is more consistent with our XRD and SEM/EDS results than the bulk composition analyses. Based on these comparisons, the total Al concentrations appear to be underestimated. The reason for this discrepancy is being evaluated. Our initial assessment indicates that some Al may have precipitated as fine particulates that were filtered out subsequent to the microwave acid digestion.

Chromium was the most concentrated contaminant of concern in the tank S-112 residual waste samples, occurring at 1,690 to 1,750 μ g/g-dry waste. The other important contaminants ⁹⁹Tc and ²³⁸U were measured in the residual waste at concentrations that ranged from 0.46 to 0.48 μ g/g, and 17 to 36 μ g/g, respectively.

Some solution analyses were conducted on supernatant from as-received sample 20406 and on leachates from sample 20407 extracted by a 1-month single-contact leach test with DDI water at a water:waste ratio of 100:1. Leachable quantities of contaminants (⁹⁹Tc, ²³⁸U, and Cr) measured in the 1-month single-contact leachates relative to the measured concentrations in the unleached bulk solid were

17%, 0.65%, and 10.7%, respectively. Significant leachable quantities of other metals measured in the extract leachates relative to the bulk-solid composition include Al (9.3%), Ca (81%), and Na (87%). Concentrations of all major anions in the 1-month DDI water single-contact leach test were below the IC detection limit, indicating that hydroxide and carbonate were the major anions in the water leachates.

A hypothetical pore water composition was calculated assuming all the dissolved components measured in the 1-month single-contact leach test were initially dissolved in the entrained pore water. These concentrations were compared with concentrations measured in the supernatant. Results indicate the majority of the ^{99}Tc , Al, and Na in the 1-month DDI water extracts are from dilution of pore water. In the case of ^{238}U , it appears dilution of entrained pore fluid results in precipitation of most of the ^{238}U . This may have occurred as a result of diminished hydrolysis and carbonate complexation of dissolved U upon dilution (Le Chatelier's principle). For Ca, nearly all the Ca in the extracts came from dissolution of a Ca-containing solid phase. For Cr, approximately half of the Cr in the leachants came from the pore fluid, and a nearly equal quantity came from dissolution from a Cr-containing solid phase.

5.0 References

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Appendix

SEM Micrographs and EDS Results for Unleached Residual Waste from Tank S-112

Appendix

SEM Micrographs and EDS Results for Unleached Residual Waste from Tank S-112

This appendix includes the scanning electron microscope (SEM) micrographs for two subsamples (designated as 20407 and 20407 dup) of unleached residual waste from tank S-112 and element compositions derived from the energy dispersive spectroscopy (EDS) analyses of particles in these subsamples imaged by SEM. The operating conditions for the SEM and procedures used for mounting the SEM subsamples are described in Section 2.4 of the main report.

Each page in this appendix contains 1) a backscattered electron (BSE) SEM micrograph (top of each page) of particles in the two subsamples of tank S-112 unleached residual waste, and 2) the tabulated element compositions (in wt%) (bottom of each page) derived from the EDS analyses of particles identified in the top-right SEM micrograph. The micrograph at the top left of each page shows the same SEM image unobstructed by the identification numbers and locations of the EDS analyses. All SEM micrographs were collected within the BSE mode.

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