PNNL-18119
WTP-RPT-169, Rev 0

U.S. DEPARTMENT OF
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Characterization, Leaching, and Filtration Testing for Tributyl Phosphate (TBP, Group 7) Actual Waste Sample Composites

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March 2009

Pacific Northwest
NATIONAL LABORATORY

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Test Specification: 24590-PTF-TSP-RT-06-003, Rev. 1
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Test Plan: TP-RPP-WTP-467, Rev. 1
Test Exceptions: None
R&T Focus Area: Pretreatment
Test Scoping Statement: None

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Richland, Washington 99352

COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-PTF-TSP-RT-06-003, Rev. 1 and Test Plans TP-RPP-WTP-467, Rev. 1 7/31/07. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved: Gordon H. Beeman 3/9/09

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

Date

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Abbreviation/Acronym List

AEA	alpha energy analysis
ASO	Analytical Support Organization
ASR	Analytical Service Request
ASTM	American Society for Testing and Materials
AV	axial velocity
BBI	Best Basis Inventory
BET	(Brunauer, Emmett, and Teller) surface area analysis technique
BNI	Bechtel National, Incorporated
BS	blank spike
CC	corrected concentration
CCD	charge coupled device
CCN	corporate correspondence number (BNI)
CS	centrifuged solids
CUF	crossflow ultrafiltration testing apparatus (containing 2 ft cell unit filter)
DACS	data acquisition collection system
DI	deionized (water)
DOE	U.S. Department of Energy
ED	electron diffraction
EDS	energy-dispersive spectroscopy
EELS	electron energy-loss spectroscopy
EFRT	External Flowsheet Review Team
fps	feet per second
EQL	estimated quantitation limit
FTIR	Fourier transform infrared
GEA	gamma energy analysis
HAADF	High Angle Annular Dark-Field Detector
HDPE	high-density polypropylene
HF	hydrofluoric acid
HLRF	High-Level Radiochemistry Facility
*HLW	high-level waste
IC	ion chromatography
ICDD	International Centre for Diffraction Data
ICP-OES	inductively coupled plasma-optical emission spectroscopy
ICSD	Inorganic Crystal Structure Database
KOH	potassium hydroxide
KPA	kinetic phosphorescence analysis
LAW	low activity waste
LCS	laboratory control sample

LEPS	Low-Energy Photon Spectroscopy
MDL	minimum detection limit
MRQ	minimum reportable quantity
MS	matrix spike
M&TE	measuring and test equipment
NIST	National Institute of Science and Technology
OES	optical emission spectroscopy
ORP	Office of River Protection
PB	preparation blank
PNNL	Pacific Northwest National Laboratory
PSD	particle-size distribution
PTF	Pretreatment Facility
psid	pounds per square inch differential
psig	pounds per square inch gauge
QA	quality assurance
QAM	Quality Assurance Manual
QAPjP	quality assurance project plan
QARD	Quality Assurance Requirements and Descriptions
QC	quality control
REDOX	reduction-oxidation
RPD	relative percent difference
RPL	Radiochemical Processing Laboratory
RPP-WTP	River Protection Project – Waste Treatment Plant Support Program
RSD	relative standard deviation
R&T	research and technology
SAL	Shielded Analytical Laboratory
SEM	scanning electron microscopy
TBP	tributyl phosphate
TEM	transmission electron microscopy
TIC	total inorganic carbon
TMP	transmembrane pressure
TOC	total organic carbon
TRU	transuranics
SBMS	Standards Based Management System
SEM	scanning electron microscopy
STEM	scanning transmission electron microscopy
TEM/ED	transmission electron microscopy
TP	test plan
TWINS	Tank-Waste Information Network System
UDS	undissolved solids

UFP	ultrafiltration process
WCS	wet centrifuged solids
WTP	Waste Treatment and Immobilization Plant
XRD	X-ray diffraction

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Testing Summary

A testing program evaluating actual tank waste was developed in response to Task 4 from the M-12 External Flowsheet Review Team (EFRT) issue response plan. The bulk water-insoluble solid wastes that are anticipated to be delivered to the Waste Treatment and Immobilization Plant (WTP) were identified according to type such that the actual waste testing could be targeted to the relevant categories. Eight broad waste groupings were defined. Samples available from the 222S archive were identified and obtained for testing. The actual waste-testing program included homogenizing the samples by group, characterizing the solids and aqueous phases, and performing parametric leaching tests.

The tributyl phosphate sludge (TBP, Group 7) is the subject of this report. The Group 7 waste was anticipated to be high in phosphorus as well as aluminum in the form of gibbsite. Both are believed to exist in sufficient quantities in the Group 7 waste to address leaching behavior. Thus, the focus of the Group 7 testing was on the removal of both P and Al. The waste-type definition, archived sample conditions, homogenization activities, characterization (physical, chemical, radioisotope, and crystal habit), and caustic leaching behavior as functions of time, temperature, and hydroxide concentration are discussed in this report. Testing was conducted according to TP-RPP-WTP-467.

Objectives

The test objectives are summarized in Table S.1 along with a discussion of how the objectives were met. Several objectives (in gray shading lighter than header shading) did not specifically apply to the scope provided in this report; they will be reported in companion reports as indicated in the controlling test plan.

Table S.1. Test Objectives for Test Plan TP-RPP-WTP-467

Test Objective	Objective Met? (Y/N)	Discussion
1) Determine the physical and chemical characteristics (summarized in Section 6.2.2 of the test plan, TP RPP-WTP-467, Rev. 1) relevant to leaching and ultrafiltration behaviors of actual waste samples required for the validation of simulants.	Y	The following characterizations were conducted on the washed solids for Group 7: • solids chemical composition • mineral composition • particle-size distribution • crystal habit and morphology • slurry density • slurry rheology, flow curve, and shear strength • settling rate, fraction of settled solids, fraction of centrifuged solids. The results are presented in Section 3.
2) Determine the dissolution rate of aluminum in the actual waste samples, present predominantly as gibbsite, as a function of temperature and free-hydroxide concentration and over a range of sodium concentrations of interest to the caustic-leaching process.	Y	A significant portion of the Al in the Group 7 waste was present in the form of gibbsite. The behavior of this component during caustic leaching could be reasonably discerned. These results are discussed in Sections 4 and 5.

Table S.1 (Contd)

Test Objective	Objective Met? (Y/N)	Discussion
3) Determine the dissolution rate of aluminum in the actual waste samples, present predominantly as boehmite, as a function of temperature and free-hydroxide concentration and over a range of sodium concentrations of interest to the caustic-leaching process.	NA	Group 7 was not expected to contain significant quantities of boehmite, and characterization found this to be the case.
4) Determine the dissolution rate of chromium and the extent of dissolution of plutonium and other safety-related constituents (U, Fe, Mn, Ni, and Zn) in the actual waste samples as functions of temperature and over a range of NaOH concentrations of interest for oxidative leaching. (The $NaMnO_4$ dosage will be predetermined for the oxidation of the chromium in the waste solids.)	NA	Oxidative leaching was not an objective of the Group 7 testing because it was not anticipated to be a high-Cr waste.
5) Determine the dissolution/reaction rate of phosphates in the actual waste samples as a function of temperature and over a range of NaOH concentrations of interest for the caustic leaching process as well as the extent of dissolution during post-leaching wash.	Y	Group 7 contained a significant amount of P. The P behavior for the Group 7 composite during caustic leaching was characterized as a function of time, temperature, and free-hydroxide concentration. The P removal results can be found in Sections 3, 4, and 5.
6) Determine the ultrafiltration flux before and after caustic and oxidative leaching over the operating range of solids concentrations during the leaching processes at 25°C when sufficient actual waste sample is available for testing the filtration behavior.	Y	Ultrafiltration (CUF) testing was performed on the Group 7 solids. The CUF testing was performed before leaching using slurries with both low- and high-solids contents. The high-solids slurry was obtained by blending wastes from AY-102 with the Group 7 slurry. Further CUF testing was performed after caustic leaching. During these tests, the ultrafiltration flux was determined as a function of transmembrane pressure and axial velocity. The CUF tests were conducted at ambient temperature. There was no oxidative leach performed on this waste type; therefore, there was no CUF testing done on post oxidative-leach materials. All the CUF testing results are discussed in Section 5.

Table S.1 (Contd)

Test Objective	Objective Met? (Y/N)	Discussion
7) Scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) will be used to determine the primary mineral forms present for Al, Cr, and P and provide information to enable the correlation of these mineral forms to dissolution behavior.	Y	SEM, TEM, EDS, and XRD were performed on the washed Group 7 solids both before and after caustic leaching. TEM was not performed on the post leach CUF samples because of high dose rates after adding AY-102 tank waste. The solids characterization results are distributed throughout the report at the specific relevant sections.

Test Exceptions

No test exceptions applied to this work.

Results and Performance Against Success Criteria

The test plan delineated several success criteria, which are listed in Table S.2. Selected criteria were relevant to the test scope included in this report; the other criteria that are outside of the reported scope are shaded.

Table S.2. Results and Performance Against Success Criteria for TP-RPP-WTP-467

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
1) A summary (letter report format) of the available information (including published literature) is provided on the characteristics (both known characteristics and those needed to be determined) relevant to leaching and filtration behaviors of the tank farm waste groupings identified for testing.	Letter report number RPP-WTP-07-705 (GJ Lumetta and RT Hallen, WTP-RPT-151, *Review of Caustic Leaching Testing With Hanford Tank Waste Sludges*), which addressed this success criterion, was delivered to BNI-WTP on 1/24/2007.
2) The physical and chemical characteristics for each of the actual waste-sample composites selected for testing are provided (including a format in conformance with the presentation protocols [24590-WTP-GPG-RTD-001]). The relevant physical and chemical characteristics are elaborated in Test Conditions, Section 6.0, of the test plan, TP RPP-WTP-467, Rev. 1.	All physical and chemical characterization testing as defined in the test plan was completed. This included extensive physical and chemical characterization of the homogenized slurry materials and extensive chemical characterization of selected leach solids. The analytical results for each test group are reported in the appropriate report sections. TEM was not performed on the post-leach CUF samples because of high dose rates after adding AY-102 tank waste.
3) The dissolution rate and the extent of dissolution of aluminum present predominantly as gibbsite in actual waste solids are determined as a function of temperature, free-hydroxide, and sodium concentrations. The associated uncertainties in test	The dissolution of the gibbsite fraction of the Group 7 washed solids was evaluated by measuring the Al in the leaching solution as a function of time (0, 1, 2, 4, 8, and 24 h). The effects of free-hydroxide concentration and temperature were assessed. Testing was conducted at

Table S.2 (Contd)

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
results are provided.	three free-hydroxide concentrations (0.25, 1, and 3 M) and at three temperatures (40, 60, and 80°C). One test condition (3 M free hydroxide at 40°C) was conducted in triplicate to assess overall test precision. The dissolution of the gibbsite fraction of the Group 7 solids was slow at 40°C, with a large rise in the amount dissolved occurring between 8 and 24 hours. A steady state was reached at 60°C in 1 and 3 M NaOH after 4 hours and at 80°C in 1 and 3 M NaOH after 2 hours. The steady-state Al concentrations in these experiments represented 80 to 90% Al dissolution, suggesting that 10 to 20% of the Al in the Group 7 solids was present as a caustic-insoluble aluminum compound, perhaps zeolite as identified by XRD. Detailed results are presented in Section 4.0.
4) The dissolution rate and the extent of dissolution of aluminum present predominantly as boehmite in actual waste solids are determined as a function of temperature, free-hydroxide, and sodium concentrations. The associated uncertainties in test results are provided.	Not applicable. The Group 7 sample did not have significant amounts of boehmite.
5) The dissolution rate and the extent of dissolution of chromium in the actual waste solids are determined as a function of temperature and over a range of NaOH concentrations of interest to oxidative leaching. The $NaMnO_4$ dosage will be predetermined for the oxidation of the chromium in the waste solids. The associated uncertainties in the test results are provided.	Not applicable. The Group 7 sample did not have significant amounts of chromium.
6) The dissolution rate and the extent of dissolution of phosphates in the actual waste solids are determined as a function of temperature and NaOH concentration along with the uncertainty in these estimates.	Phosphorus removal from the Group 7 washed solids was evaluated by measuring the P in the leaching solution as a function of time (0, 1, 2, 4, 8, and 24 h). The effects of free-hydroxide concentration and temperature were assessed. Testing was conducted at three free-hydroxide concentrations (0.25, 1, and 3 M) and at three temperatures (40, 60, and 80°C). One test condition (3 M free hydroxide at 40°C) was conducted in triplicate to assess overall test precision. The P removal from the Group 7 solids was rapid, with steady state reached within 1 h under all conditions examined. Approximately 85 to 95% of the P was removed at all conditions examined. Detailed results are presented in Section 4.0.
7) The ultrafiltration flux before and after caustic and, as applicable, oxidative leaching (reconcentration,	The following variables were examined for the Group 7 waste slurry where the focus was measuring the filter

Table S.2 (Contd)

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
if sufficient solids are available) over the operating range of solids concentrations with the actual waste samples at 25^{o}C is defined when available sample size is adequate for the testing.	flux before and after leaching at 25°C: • Transmembrane pressure • Axial velocity • Undissolved solids concentration • Differences due to changes in the slurry during caustic leaching and rinses of waste solids. The results of this testing are summarized in Section 5.
8) Determination of the primary mineral forms present for Al, Cr, and P and a qualitative correlation of the dissolution behavior of these waste elements to the mineral forms identified.	As mainly determined by XRD, the Group 7 solids contained gibbsite, $Al(OH)_3$; threadgoldite, $Al(UO_2)_2(PO_4)_2(OH)(H_2O)_8$; zeolite, $NaAlSiO_4(H_2O)_{1.1}$; sodium iron phosphate, $Na_7(FeP_2O_7)_4PO_4$; and lepidocrocite, FeO(OH). The Al removal behavior during caustic leaching can be correlated with this observation, assuming that 60 to 70% of the Al is gibbsite, and the remaining is an insoluble Al compound, perhaps zeolite. The only P-containing compound identified by XRD in the caustic-leached and washed solids was nabaphite, $NaBa(PO_4)(H_2O)_9$. It is also likely that part of the undissolved P exists as the sodium iron phosphate that was identified in the unleached solids. Because of the low concentrations of Cr found in this waste grouping, Cr mineral forms were not identified.

Quality Requirements

Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy (DOE) by Battelle under Contract DE-AC05-76RL01830. PNNL implements a Quality Assurance Program that is based upon the requirements as defined in DOE Order 414.1C, “Quality Assurance,” and 10 CFR 830, “Energy/Nuclear Safety Management,” Subpart A—“Quality Assurance Requirements.” PNNL has chosen to implement the requirements of DOE Order 414.1C and 10 CFR 830, Subpart A by integrating them into the laboratory’s management systems and daily operating processes. The procedures necessary to implement the requirements are documented through the laboratory’s Standards-Based Management System (SBMS).

PNNL implemented the RPP-WTP quality requirements by performing work in accordance with the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Plan (*RPP-WTP-QA-001, QAP*)*. Work was performed to the quality requirements of NQA-1-1989 Part I, “Basic and Supplementary Requirements,” NQA-2a-1990, Part 2.7, and DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions (QARD)*. These quality requirements were implemented through the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Manual* (RPP-WTP-QA-003, QAM). The analytical requirements were implemented through RPP-WTP’s Statement of Work (RPP-WTP-QA-005) with the Radiochemical Processing Laboratory (RPL) Analytical Service Operations (ASO).

A matrix that cross-references the NQA-1, NQA-2a, and QARD requirements with the procedures for RPP-WTP work was provided in the test plan TP-RPP-WTP-467. It included justification for those requirements not implemented.

Experiments that were not method-specific were performed in accordance with RPP-WTP's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration and Control of Measuring and Testing Equipment" so that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

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

R&T Test Conditions

The R&T test conditions, as defined in the BNI Test Specification,(a) are summarized in Table S.3.

(a) PS Sundar. Nov. 2006. *Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes*. 24590-PTF-TSP-RT-06-003, Rev. 1.

Table S.3. R&T Test Conditions

List R&T Test Conditions	Were Test Conditions Followed?
1) Selection of actual wastes for testing: the waste samples selected for testing will be from the groupings identified in the resolution of Issue M4.	Yes. One of the eight waste groupings identified in resolution to Issue M4 were tested: Group 7 (tributyl phosphate, TBP).
2) Physical and chemical characterization properties shall be stated and carried out according to the Guideline document 24590-WTP-GPG-RTD-001.	Yes. Physical characterizations, including specific gravity (density), settling rate, rheology, volume-percent settled solids, and volume-percent centrifuged solids were determined for both test groups according to the requirements document. Chemical characterization was conducted on the supernatant (water used to dissolve and slurry the solids into a workable homogenized composite) on the solids rinsed with three contacts of 1:1 volume ratios of 0.01 M NaOH and on the rinse solution composite.
3) Actual determinations of waste leach kinetics will be carried out in well-mixed conditions. A test matrix will be forwarded to the research and technology (R&T) M12 Issue manager for concurrence before testing. Residual leached and washed solids will be characterized.	Yes. Test matrices for the Group 7 waste sample were forwarded to, and approved by, the R&T M12 Issue Manager (BNI). The actual test conditions are given in Section 4.0 and were compliant with the test matrices.
4) Testing for filtration behavior will be performed.	Yes. Cross-flow filtration testing was performed on the Group 7 solids. CUF testing matrices were applied to a low-solids slurry, a high-solids slurry, and post-caustic leaching. Rheology and particle-size distribution measurements were made before and after the various process steps.

Simulant Use

The bulk of the testing used actual Hanford tank wastes. However, due to the limitations in the quantity of supernate present, a simulant of the Group 7 supernate fraction was prepared and used to dilute the feed to allow testing at lower solids concentrations.

Discrepancies and Follow-on Tests

TEM, BET, and particle size measurements were not performed on CUF samples after the addition of AY-102. Dose rates of samples pulled from the hot cells afterwards were too high to be handled for theses analyses which are prepared in radiological fume hoods. Procedures were in place to prepare XRD and SEM slides in the hot cells so these measurements were able to be performed.

1.0 Introduction

This is one in a series of reports that define the characterization, parametric leaching, and filtration testing of actual Hanford tank wastes in support of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) pretreatment process development and demonstration. The tests reported here were conducted according to TP-RPP-WTP-467(a) and were written in response to Bechtel National, Incorporated (BNI) Test Specification 24590-PTF-TSP-RT-06-003 Rev. 1.(b) This report focuses on the tributyl phosphate (TBP) tank waste, which is referred to as Group 7 in this report.

1.1 Tank Waste Pretreatment Operations at the WTP

Figure 1.1 provides a schematic illustration of the primary functions to be performed in the WTP. Initially, the low-activity waste (LAW) liquid stream will be removed from the high-level waste (HLW) solids phase by ultrafiltration in the Pretreatment Facility (PTF). The concentrated HLW solids will be pretreated using caustic and, in some cases, oxidative leaching processes to dissolve and remove materials (aluminum, chromium, phosphates, and sulfates) that would otherwise limit HLW loading in the immobilized waste glass. The current plant design calls for the pretreatment leaching processes to be carried out in the ultrafiltration feed vessels. During pretreatment, the concentrated HLW solids will be caustic leached, washed, and in the case of high Cr wastes, oxidatively leached and washed once more. The caustic leaching will be conducted to solubilize the aluminum, phosphorus, and sulfur in the HLW solids; the oxidative leaching will be conducted to oxidize the chromium [from Cr(III) to Cr(VI)] using a sodium permanganate ($NaMnO_4$) solution and dissolve the chromate in a mild caustic solution. The HLW solids will be re-concentrated after each leach and wash operation in the ultrafilter.

The current design of the PTF was based on aluminum dissolution results from earlier small, bench-scale, caustic-leaching tests that were supplied to BNI by the U.S. Department of Energy's (DOE's) Office of River Protection (ORP). Only a limited number of small bench-scale oxidative leaching tests using two selected actual waste tank samples (SX-101 and SY-102) with the preferred oxidant $NaMnO_4$ were carried out to estimate the oxidant dosage and the efficacy of the oxidative leaching process (Rapko et al. 2004; Rapko et al. 2005), but a number of previous studies demonstrated the technical feasibility of the oxidative leaching process (Rapko 1998; Lumetta and Rapko 1999; Rapko and Vienna 2002; Rapko et al. 2002). The testing with actual radioactive wastes has been generally limited to small-scale testing (typically 1 to 10 g) because of limited sample availability and personnel safety associated with sample handling.

(a) SK Fiskum, TP-RPP-WTP-467, Rev. 0, 2/2/07 and Rev. 1 7/31/07, *Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes*.

(b) PS Sundar. 2006. 24590-PTF-TSP-RT-06-003 Rev. 1, *Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes*.

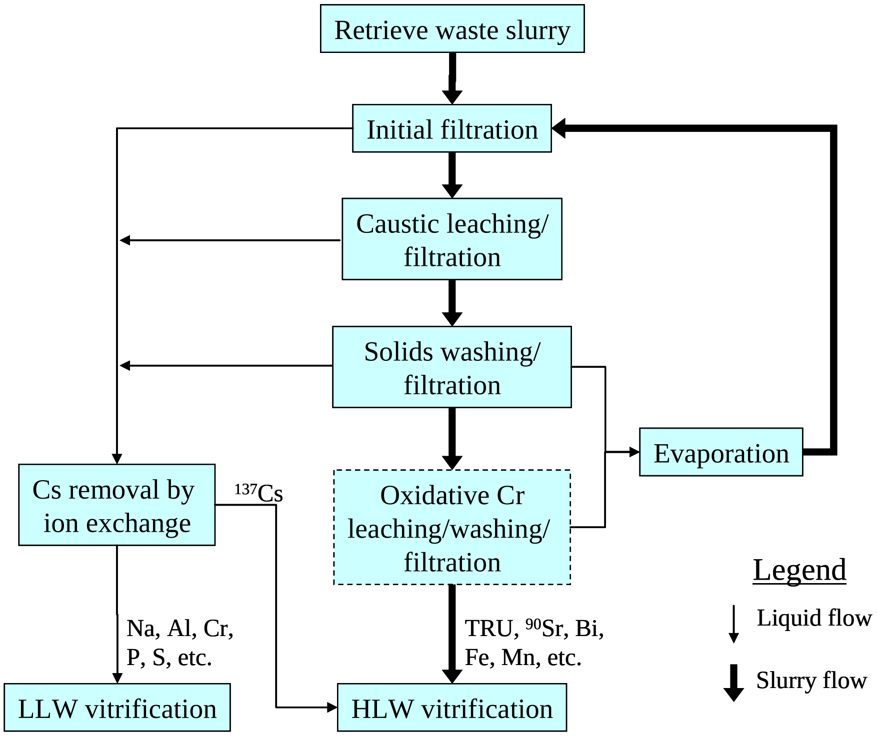

Figure 1.1. Schematic Representation of the Processes to be Performed in the PTF (Note: This is for illustrative purposes only; it is not meant to be a comprehensive view of the functions performed within the WTP.)

1.2 Issues Identified by the External Flowsheet Review Team

A team of experts from industry, national laboratories, and universities (referred to as the External Flowsheet Review Team or EFRT) was assembled by BNI in October of 2005 to conduct an in-depth review of the process flowsheet supporting the design of the WTP. The EFRT identified several issues from the critical review of the process flowsheet,(a,b) including

- Issue M4: The WTP has not demonstrated that its design is sufficiently flexible to reliably process all of the Hanford tank farm wastes at the design throughputs.
- Issue M12: Neither the caustic-leaching nor the oxidative-leaching process has been demonstrated at greater than bench scale. The small-scale experiments are capable of defining the leaching chemistry. However, they are limited in their capability to predict the effectiveness of these processes without a scale-up demonstration.

(a) WTP Doc. No. 24590-WTP-PL-ENG-06-0008, Rev 0, “Hanford Waste Treatment and Immobilization Plant (WTP) Project Response Plan for Resolution of Issues Identified by the Comprehensive Review of the WTP Flowsheet and Throughput.” L. Lucas, March 2006.

(b) WTP Project Doc. No. CCN 132846 “Comprehensive Review of the Hanford Waste Treatment Plant Flowsheet and Throughput - Assessment Conducted by an Independent Team of External Experts.” March 2006, chartered by the Hanford Waste Treatment and Immobilization Plant Project at the Direction of the U.S. Department of Energy, Office of Environmental Management, Washington DC.

- Issue M13: For wastes requiring leaching, a combination of inadequate filter flux and area will likely limit throughput to the HLW or LAW vitrification facilities.

The work scope defined in TP-RPP-WTP-467 represented the initial portion of the actual waste-testing portion of Task 4 from the M-12 EFRT issue response plan.(a) The actual tank waste testing work interfaced with responses developed to resolve EFRT Issue M4. In this case, a family of waste groupings representing the behavior of ~75% of the tank-farm inventory was developed to assist in designing subsequent tests that will assess the adequacy of the overall flowsheet design in treating the tank-farm wastes. These waste groupings were the basis for selecting actual wastes for the current scope of testing.

Additional EFRT-defined issues were identified that likely will also benefit from the actual waste testing reported herein, including:

- Issue M1: Piping that transports slurries will plug unless it is properly designed to minimize this risk. This design approach has not been followed consistently, which will lead to frequent shutdowns due to line plugging.
- Issue M2: Large, dense particles will accelerate erosive wear in mixing vessels. The effects of such particles on vessel life must be re-evaluated.
- Issue M3: Issues were identified related to mixing-system designs that will result in insufficient mixing and/or extended mixing times. These issues include a design basis that discounts the effects of large particles and of rapidly settling Newtonian slurries. There is also insufficient testing of the selected designs.
- Issue M6: Many of the process operating limits have not been defined. Further testing is required to define process limits for WTP unit operations. Without this more complete understanding of each process, it will be difficult or impossible to define a practical operating range for each unit operation.

1.3 Waste Groupings

The available information regarding tank history and tank waste characterization was analyzed. This analysis revealed eight groupings of waste tanks that represent ~75% of the inventory of those components most significant with respect to leaching in the WTP; i.e., Al, Cr, phosphate, and sulfate (Fiskum et al. 2008). Table 1.1 (Fiskum et al. 2008) provides a summary of the calculated water-insoluble quantities of each component for each major waste group studied. Table 1.2 (Fiskum et al. 2008) summarizes the selected eight waste groups along with the estimated fractions (with respect to the entire tank farm inventory) of selected components contained in each one. To support the actual waste testing, samples were obtained from the archives at the Hanford 222S Laboratory. Composites of these archived samples were made to obtain the most representative samples of each group as practical.

(a) SM Barnes, and R Voke, September 2006, 24590-WTP-PL-ENG-06-0024 Rev. 0, “Issue Response Plan for Implementation of External Flowsheet Review Team (EFRT) Recommendations - M12: Undemonstrated Leaching Process.”

Table 1.1. Water-Insoluble Component Mass (Metric Tons) Inventory as Function of Waste Type

Waste Type	Al	Cr	F	Fe	Oxalate	Phosphate	Sulfate
Total	4,871	365	226	1,252	884	1,304	149
Saltcake Category							
A	32	35	16	26	166	25	19
B	80	3	45	26	7	37	21
BY	237	46	52	41	269	145	28
R	170	11	<0.1	4	6	1	0.3
S	366	166	1	47	242	58	20
T	384	20	2	65	59	151	35
Balance of salt cake	7	1	<0.1	1	5	4	0.4
Sludge Category							
Bismuth phosphate	218	14	51	280	4	473	11
CWP	815	3	3	57	9	25	1
CWR	471	4	<0.1	17	4	2	<0.1
REDOX	1,433	23	0.1	53	25	9	1
TBP	41	1	1	92	1	228	5
FeCN	54	3	1	93	7	84	1
Balance of sludge	562	36	53	450	77	64	8

Table 1.2. Projected Distribution of Water-Insoluble Components in the Tank Waste Groupings

Group ID	Type	Al (%)	Cr (%)	F (%)	Fe (%)	Oxalate (%)	Phosphate (%)	Sulfate (%)
1	Bi Phosphate sludge	4	4	22	22	0.5	36	7
2	Bi Phosphate saltcake (BY, T)	13	18	24	8	37	23	42
3	CWP, PUREX Cladding Waste sludge	17	1	1.3	5	1	2	0.4
4	CWR, REDOX Cladding Waste sludge	10	1	<0.1	1	0.4	0.1	<0.1
5	REDOX sludge	29	6	0.1	4	3	1	0.4
6	S - Saltcake (S)	8	46	0.6	4	27	4	14
7	TBP Waste sludge	1	0.4	0.5	7	0.1	17	3
8	FeCN Waste sludge	1	1	0.4	7	1	6	1
	Balance	17	24	51	41	30	10	32

Note: The component values were rounded off; therefore, the sums may not add to exactly 100%.

1.4 Simulant Development

BNI plans to carry out process development and scale-up testing to demonstrate the design effectiveness of both the caustic- and the oxidative-leaching processes over the entire applicable range of Hanford tank farm wastes.(a) Scale-up testing will require substantial volumes of feed. Therefore, the development of simulants that mimic the chemical, leaching, and ultrafiltration behaviors over the range observed for actual waste groups is necessary to the process development and demonstration. The leaching and filtration performance data obtained from the actual waste testing will serve as benchmarks for defining the simulant characteristics and behaviors and as a basis for revising the parameters used in evaluating WTP process performance using the appropriate process models.

1.5 Testing of Group 7

The characterization, parametric leaching, and filtration/leaching testing of the TBP sludge waste (Group 7) is the subject of this report. The phosphate behavior is of particular interest, as this is the major component targeted to be removed by caustic leaching (Table 1.2). Aluminum is also of interest.

The waste-type definition, sample identification, archived sample conditions, and homogenization activities are discussed in this report. The caustic-leaching experiments and results are described for the Group 7 solids. The physical, chemical, radioisotope, and crystal morphology characterization in the waste before and after leach processing are also discussed. A single bench scale leaching and filtration test, using a crossflow filtration testing apparatus, was performed in a hot cell using the remainder of the Group 7 solids in combination with archived tank waste samples from 241-AY-102. The leaching and filtration results from this test are described and presented.

The results from these tests will refine the knowledge base of the tank waste chemical and mineralogical characteristics. Parametric leach testing will provide the leaching kinetics of gibbsite and phosphorus and support follow-on leach and filtration testing.

(a) WTP Doc. No. 24590-WTP-PL-ENG-06-0008, Rev 0, “Hanford Waste Treatment and Immobilization Plant (WTP) Project Response Plan for Resolution of Issues Identified by the Comprehensive Review of the WTP Flowsheet and Throughput.” L Lucas, March 2006.

2.0 Test-Sample Selection, Compositing, and Homogenization

This section describes the rationale for selecting TBP sludge (Group 7) test materials from the Hanford tank waste sample archive located in the 222S building of the Hanford Site. Retrieving new sample materials from the tanks was deemed to be prohibitively expensive and time intensive and therefore was not considered. Also described is the homogenization and sub-sampling of Group7 composite samples.

2.1 Tributyl Phosphate Sludge Sample Selection

TBP tank waste sludge samples with high phosphate content were targeted to construct the Group 7 composite. As part of the uranium recovery process, a solution of TBP in an organic diluent was used to extract uranium from bismuth phosphate sludges. The TBP sludge refers to the waste generated during this extraction process. The Tank-Waste Information Network System (TWINS) database(a) was queried to identify the tanks containing at least 95% of this TBP sludge as defined by the Best Basis Inventory (BBI). Only samples from 222S listed with a sludge/solid matrix were used. These tank wastes were queried in BBI(a) for the major inorganic components (phosphate, sulfate, Bi, Al, Fe, Cr, Mn, Si, and U) in the solid and sludge phases. Figure 2.1 shows the relative mass distributions of these analytes (note that major elemental and anionic contributions from Na, nitrate, nitrite, and oxalate are excluded from the data in Figure 2.1).

The decision process flowchart for selecting tank waste samples from the sample archive is summarized in Figure 2.2. The 222S archive sample inventory(b) was searched for sludge samples from the tanks identified as containing TBP waste (Figure 2.2). The samples were then cross-referenced to the TWINS database to determine if analytical data from the specific samples were available; samples identified as containing at least 95% TBP sludge were carried forward in the selection process. The final list of samples was submitted to CH2MHill personnel(c) to verify that: 1) the samples represented the TBP sludge waste stream based on the tank strata, core segment, and corresponding characterization results, and 2) the samples were not held for other activities and could be released from the archive.

(a) The TWINS database and the BBI are DOE-owned resources.

(b) Personal communication of the inventory database, file “Vials May18,” provided from P Brackenbury, Bechtel, June 2006.

(c) David Place and Bruce Higley, Process Engineers, Process Analysis Organization, CH2MHill.

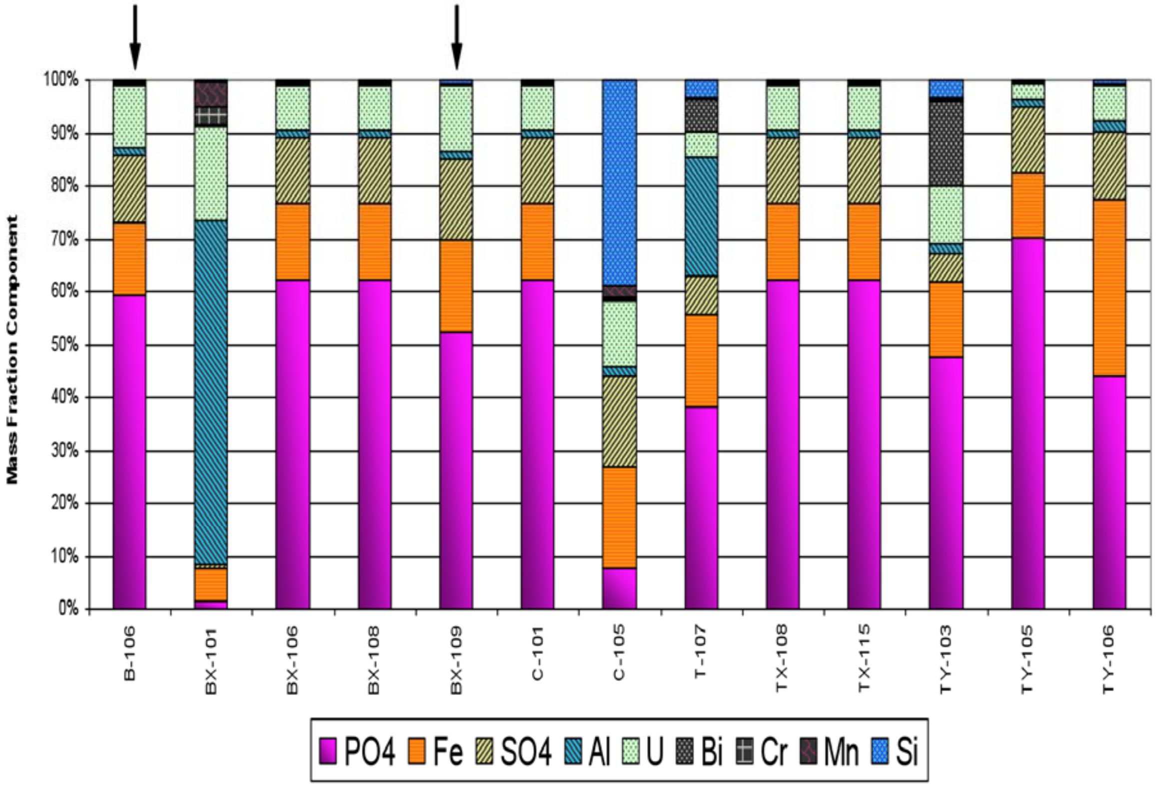

Figure 2.1. Estimated Tank Waste Composition of Selected Analytes for Group 7 Sludge Wastes in the Hanford Tank Farm (BBI Source). Note: arrows point to the tanks actually used to prepare the composite; BX-109 dominated the composite mass (see text).

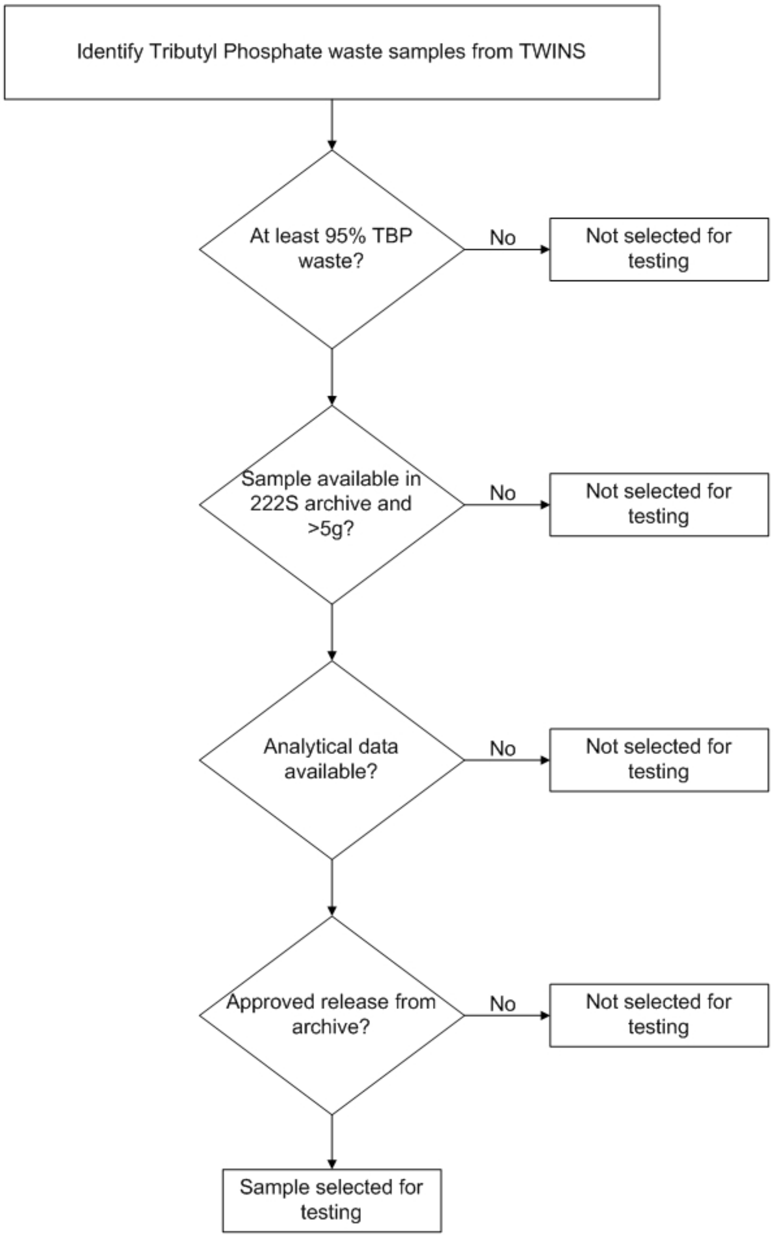

Figure 2.2. Selection Decision Process for TBP Sludge Samples

Table 2.1 summarizes the tank sources evaluated and shows whether the tank met or failed the selection criteria. Samples highlighted in bold in the table were those determined to meet all of the selection criteria.

Table 2.2 summarizes the individual samples (sample date, tank ID, sample core, and segment) from the archive that met the selection criteria. These samples had been in storage at 222-S for ~12 to 15 years. The long storage time could potentially cause the sample characteristics to be altered relative to the as-retrieved sample condition through aging and drying. But, as stated previously, obtaining fresh core samples from the Hanford waste tanks was outside the scope of the project budget and schedule. Also shown in Table 2.2 are the anticipated sample masses assumed available based on the archive inventory in ~2002. A total of 1.9 kg of TPB sludge was assumed to be available and sufficient for the complete testing scope.

The sample set was heavily represented by one tank, BX-109. The potential impact of the Group 7 composite representation primarily by BX-109 was evaluated. As seen in Figure 2.1, aside from three waste tank samples that were deemed unrepresentative of the waste type, gross deviations in the elemental compositions within the remainder of tank waste samples were relatively minor. It was concluded that BX-109 would be reasonably representative of the group.

Table 2.1. Selection of TBP Sludge Tanks

Tank	Volume TBP Sludge, kL	Total Sludge Volume, kL	Ratio TBP Sludge: Total Sludge
241-B-106	**297**	**301**	**0.987**
241-BX-101[(a)]	59	59	1
241-BX-106[(b)]	20	20	1
241-BX-108[(a)]	81	81	1
241-BX-109	**730**	**730**	**1**
241-C-101[(a)]	125	125	1
241-C-105[(c)]	50	50	1
241-T-107[(c)]	64	64	1
241-TX-108[(a)]	15	15	1
241-TX-115[(a)]	30	30	1
241-TY-103[(a)]	220	220	1
241-TY-105[(a)]	874	874	1
241-TY-106[(c)]	15	15	1

(a) Sample not listed in 222S inventory.
(b) Available samples were <20 g.
(c) Available sample material is not representative of the waste type.
Samples from bolded/shaded tanks are represented in Table 2.2

Table 2.2. Group 7, 222S TBP Samples

Date	Location	Box	Jar #	Tank	Core	Segment	Matrix	Net Weight (g)
9/3/1997	11A1B	97	13516	BX-109	85	1	Sludge	25.02
7/24/1995	11A1A	22	7424	B-106	94	2	Sludge	43.54
9/3/1997	11A1B	97	13517	BX-109	84	1	Sludge	43.64
2/6/2002	11A1B	93	19302	BX-109	84	3	Sludge	44
9/11/1997	11A1B	129	11840	BX-109	84	4	Sludge	44.7
9/4/1997	11A1B	97	13523	BX-109	84	4	Sludge	47.34
9/12/1997	11A1A	35	13473	BX-109	85	1	Sludge	48.75
9/4/1997	11A1B	97	13522	BX-109	85	4	Sludge	48.93
4/20/1995	11A1A	31	6935	BX-109	84	2	Sludge	49.03
4/20/1995	11A1A	38	6907	BX-109	84	2	Sludge	50.27
4/18/1995	11A1A	38	6927	BX-109	85	2	Sludge	50.45
7/24/1995	11A1A	56	7417	B-106	93	2	Sludge	50.49
7/26/1995	11A1B	129	7372	BX-109	84	Comp	Sludge	50.7
4/20/1995	11A1A	31	6932	BX-109	84	4	Sludge	51.65
4/20/1995	11A1A	31	6933	BX-109	84	4	Sludge	52.08
4/19/1995	11A1A	31	6931	BX-109	84	3	Sludge	52.55
4/21/1995	11A1A	34	7158	BX-109	85	4	Sludge	53.19
4/20/1995	11A1A	31	6934	BX-109	84	1	Sludge	53.25
4/18/1995	11A1A	31	6921	BX-109	85	1	Sludge	54.6
4/21/1995	11A1A	34	7154	BX-109	85	3	Sludge	54.97
4/19/1995	11A1A	31	6930	BX-109	84	3	Sludge	55.15
4/21/1995	11A1A	34	7157	BX-109	85	4	Sludge	55.51
4/18/1995	11A1A	31	6922	BX-109	85	2	Sludge	56.56
4/21/1995	11A1A	34	7153	BX-109	85	3	Sludge	57.89
3/1/1996	11A1B	104	9346	BX-109	85	3	Sludge	64.68
8/16/1999	11A2	17	16916	BX-109	85	2	Sludge	66.1
5/17/1996	11A1B	62	10116	BX-109	85	2R2	Sludge	69.5
9/3/1997	11A1B	97	13515	BX-109	84	2	Sludge	70.59
9/3/1997	11A1B	102	13092	BX-109	84	3	Sludge	72.5
8/13/1999	11A2	17	16913	B-106	93	1-2	Sludge	78.6
3/1/1996	11A1B	104	9334	BX-109	85	3	Sludge	81.74
9/26/1997	11A1B	94	13445	BX-109	85	Comp	Sludge	82.81
8/3/1995	11A2	Floor	7378	BX-109	84	Comp	Sludge	132.7
Total Sample Net Weight (g)								**1913**

2.2 Group 7 Sample Homogenization and Sub-sampling

For a detailed description of homogenization methods please refer to Appendix I.

Thirty-three archived Group 7 samples (3 from Tank B-106 and 30 from BX-109) were shipped from the 222-S laboratory. Advanced Technologies and Laboratories International (ATL) provided masses for these archived samples in the shipping letter report. Many of the samples had dried out during the time spent in archived storage. Photographs (Figure 2.3), as-received weights, and detailed sample descriptions were all recorded in TI-RPP-WTP-515. The sample material fell into the following general categories:

a. Dry powdery sample

b. Dry solid sample; added water to soak sample so it could be broken up and removed from the jar for addition to the homogenizer.

c. Semi-solid; sample was added to homogenizer without soaking sample with water first.

d. Clearly visible supernate liquid in jar.

e. Sample with visible debris (deteriorated polypropylene [blue] lids were replaced on some samples at 222S facility by heavier [green] thermoset lids—Figure 2.4.)

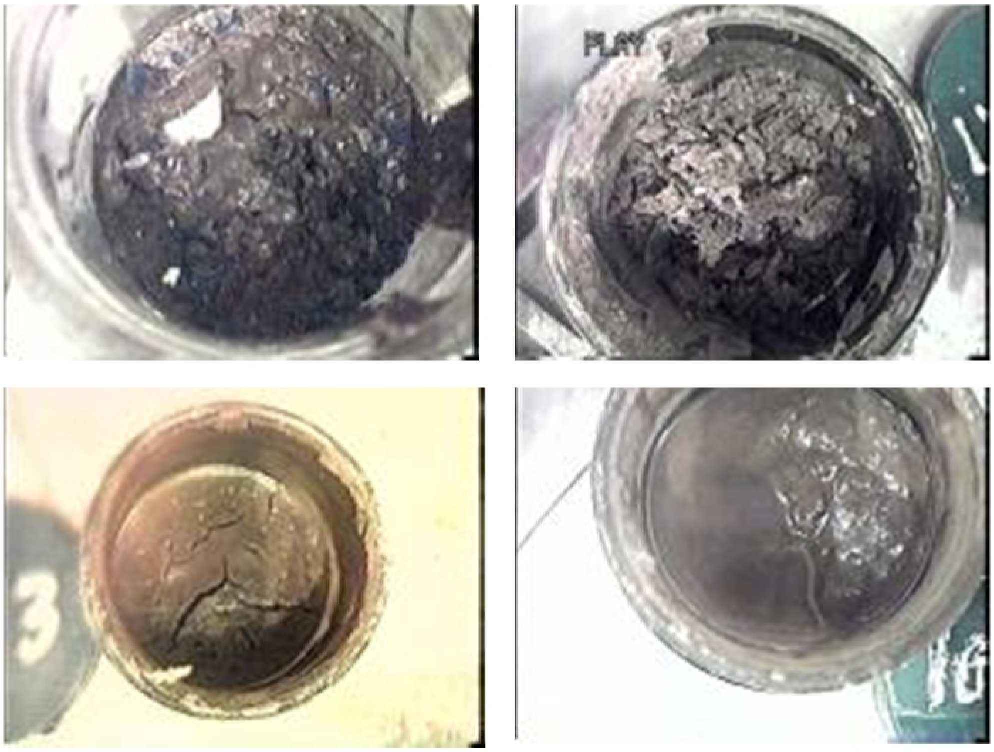

Figure 2.3. Representative Pictures of As-Received Group 7 Waste

Figure 2.4. Group 7 Sample with Visible Debris

Table 2.3 lists the individual samples added to the composite sample, along with gross mass (expected and found), the mass of the empty container, and the net mass of waste transferred to the homogenizer. Samples that appeared to be fine solids were added first and easily passed through the sieve. If foreign material, such as pieces of broken caps, were present, those were picked out with stainless steel tweezers and weighed when possible (there were very few instances of this for these samples). For wet samples, the solids were removed from the sample jar by a process of scraping and rinsing with DI water using a squirt bottle. In this fashion, nearly all residues were removed from the sample jars. These samples were originally placed in secondary containment and removed from their smaller jars into larger jars to minimize evaporative losses that sitting in the larger tank might have allowed over the several days required to empty the smaller jars.

Solids and semi-solids were forced through the sieve using DI water, rubber spatulas, and a stainless steel mashing tool that also was used in breaking up some chunks of solid materials so they could pass though the sieve. To the maximum extent possible, all sample materials were placed into the homogenizer; there was very little loss of actual sample due to splattering or spillage. Water was used conservatively during the entire process of removing the samples from the jars so as to have enough water to remove all sample residues and come close to the desired total solution added to reach the desired Na concentration.

After all of the recoverable sample materials were transferred to the homogenizer tank, the sample jars were allowed to dry, and they were then reweighed. These values were used to calculate sample recovery and actual amount of sample added to the homogenizer (Table 2.3). A few jars had significant differences between the expected gross mass and the as-found gross mass. These larger differences are probably due to loss of water from the sample over time during storage at 222S and/or sample loss in shipping. The jar lids tend to become brittle in the radiological environment over time, so some of these likely cracked, and the water evaporated. Some tare masses were based on vials with blue lids; lids had been replaced with green lids for shipping. The mass difference associated with the change in lids was ~4.6 g and this was taken into account for the samples this applied to. New lids were placed on the jars before shipping.

Table 2.3. TBP Sludge Samples (Group 7)

Hanford Tank ID	222-S ID	222S Expected Gross Mass (g)	PNNL As-found Gross Mass (g)	PNNL Jar and Lid Condition	PNNL Empty Container Mass (g)	PNNL Mass Transferred (g)
B-106	**7417**	75	74.76	Good	26.81	47.95
B-106	**7424**	63.9	64.53	Good	27.26	37.27
B-106	**16913**	121.4	124.46	Good	92.60	31.86
BX-109	**6907**	70.3	69.62	Good	29.02	40.60
BX-109	**6921**	79.8	80.24	Good	27.58	52.66
BX-109	**6922**	81.5	80.70	Good	29.75	50.95
BX-109	**6927**	66.5	66.00	Good	29.07	36.93
BX-109	**6930**	79.9	79.83	Good	30.68	49.15
BX-109	**6931**	58.9	58.36	Good	26.19	32.17
BX-109	**6932**	76.4	76.58	Good	29.51	47.07
BX-109	**6933**	76.4	76.16	Good	27.56	48.60
BX-109	**6934**	74.8	73.11	Good	27.03	46.08
BX-109	**6935**	73.9	72.30	Good	26.41	45.89
BX-109	**7153**	82.8	82.46	Good	26.71	55.75
BX-109	**7154**	80	80.52	Good	26.37	54.15
BX-109	**7157**	79.4	78.26	Good	29.62	48.64
BX-109	**7158**	76.8	73.98	Good	28.38	45.60
BX-109	**7372**	168.8	167.44	Good	134.18	33.26
BX-109	**7378**	200.1	206.48	Good	131.03	75.45
BX-109	**9334**	137.4	137.25	Good	92.37	44.88
BX-109	**9346**	133.7	133.06	Good	92.2	40.86
BX-109	**10116**	152.9	152.77	Good	95.65	57.12
BX-109	**11840**	155.3	163.76	Good	130.25	33.51
BX-109	**13092**	148.9	141.23	Good	96.92	44.31
BX-109	**13445**	144.3	145.72	Good	92.15	53.57
BX-109	**13473**	128.8	129.07	Good	90.22	38.85
BX-109	**13515**	157.2	160.20	Good	96.13	64.07
BX-109	**13516**	111.4	116.16	Good	94.79	21.37
BX-109	**13517**	129.5	134.75	Good	94.68	40.07
BX-109	**13522**	117.6	120.92	Good	94.87	26.05
BX-109	**13523**	133.8	136.35	na	95.74	40.61
BX-109	**16916**	146.2	146.01	na	92.97	53.04
BX-109	**19302**	126.9	133.46	na	92.64	40.82
Totals	---	3610.5	3636.50	---	2157.34	**1479.16**

A total of 91.8% of the received mass was recovered from the sample jars and put into the composite. The received mass was calculated by subtracting the 222S-supplied tare weights for the sample jars from the total mass measured in HLRF before transferring the sample materials. The final tank composite based on the mass balance was primarily made of BX-109 tank waste as can be seen in Figure 2.5.

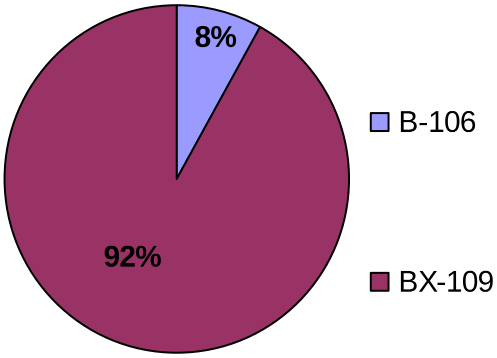

Figure 2.5. Composite Composition of Group 7 by Hanford Tank Waste

After all samples had been added to the homogenizer tank, and all equipment (spatula, sieve, mashing tool) had been rinsed free of sample, the sieve screen was removed. A total of 779.7 g of DI water was added during the compositing process. A mechanical stirrer with stainless steel impeller was lowered into the tank, the fitted lid was placed on the tank, and the material was mixed thoroughly. The temperature in the hot cell was 35°C at the start of mixing. The goal of this step was to homogenize the sample using as little force as possible. The stirrer speed was slowly increased until the solids were mobilized. The positions and arrangements for the height of the mixer relative to the support rod and impeller were predetermined during the preliminary non-radioactive testing, and the proper alignments were marked onto the impeller and support rod correctly aligned. While operating the vessel agitator, material was extracted from the collection port at the bottom of the tank and returned through the top of the vessel so that all the material was mixed well.

The total mixing time for the Group 7 composite slurry was 1 hour before sub-sampling began. Sub-sampling took 40 minutes, and the mixer continued to mix during this time. The consistency of the Group 7 composite was viscous and remained that way throughout all the subsamples. The sub-samples were removed in a specific order to pre-determined target volumes. Pre-weighed and labeled jars and centrifuge tubes were staged in collection vessels in the order provided in Table 2.4.

At the start of sub-sampling, while operating the vessel agitator, one sub-sample of sufficient size (minimum of 100 mL) was extracted through the sample valve into **TI515-G7-AR-J1** to clear material from the lowest portion of the vessel. This was then added back to the mixing vessel before sub-sampling began. The homogenized Group 7 samples settled slowly, requiring 13 days to settle completely. For compositing to be considered successful, the sample density and settled solids data standard deviation had to be less than ± 5%, and there had to be no statistically significant trend in settled solids and density variation due to subsample removal order. Figure 2.6 shows that composting was successful.

Table 2.4. Group 7 Subsample Mass Density and Settling Data

Sample ID in Order of Collection	Target Collection Volume, mL	Sample Net Wt, g	Total Slurry Volume, mL	Settled Solids Volume, mL	Gross Slurry Density	%Vol Settled Solids
TI515-G7-AR-J1	300–400	483.398	385	245	1.26	63.6
TI515-G7-AR-J2	300–400	451.141	360	225	1.25	62.5
TI515-G7-AR-J3	300–400	433.9	345	215	1.26	62.3
TI515-G7-AR-J4	300–400	458.215	365	225	1.26	61.6
TI515-G7-AR-S1	10–15	11.805	9.0	5.7	1.31	63.3
TI515-G7-AR-S2	10–15	12.094	9.4	6.0	1.29	63.8
TI515-G7-AR-S3	10–15	10.465	8.1	5.4	1.29	67.5
TI515-G7-AR-RH1	50	88.565	70	45	1.27	64.3
TI515-G7-AR-C1	25	21.831	17	11	1.28	64.7
TI515-G7-AR-C2	25	27.168	21.5	14	1.26	65.1
TI515-G7-AR-Arch1	10	22.716	20	13.0	1.14	65.0
TI515-G7-AR-P1	150	130.711	115	55	1.14	47.8

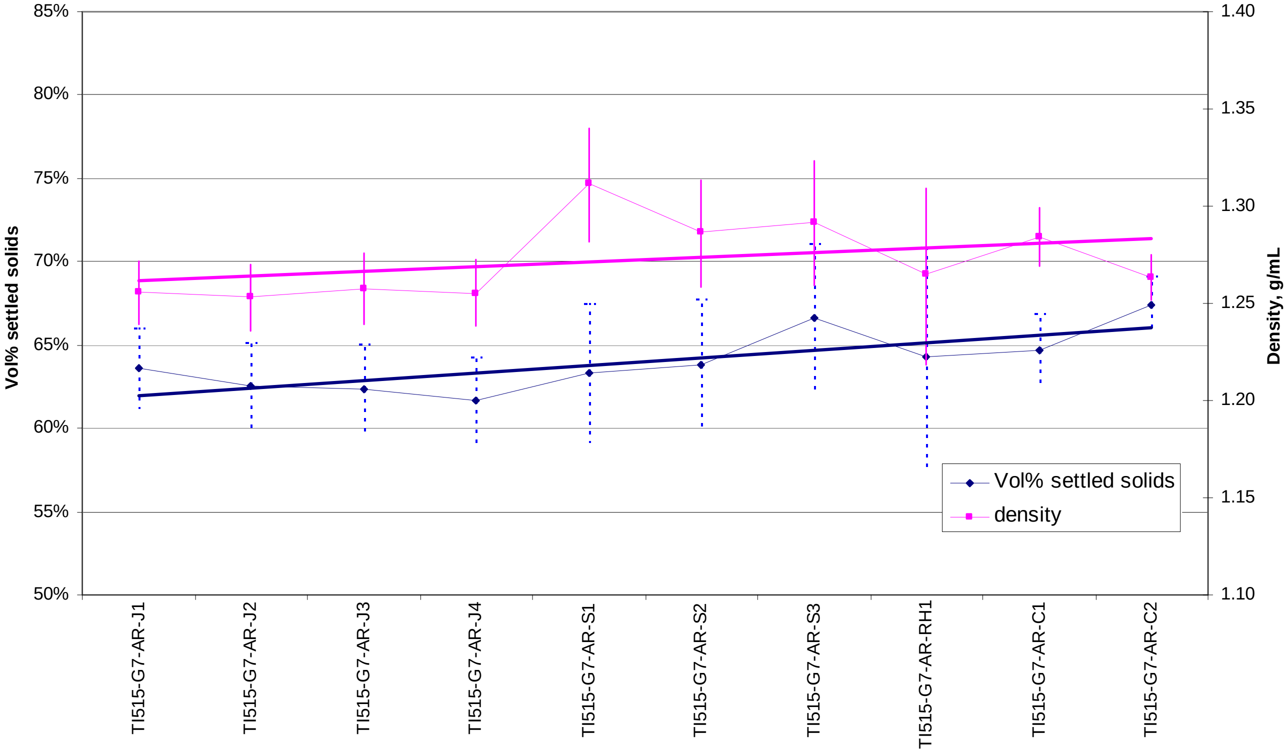

Figure 2.6. Group 7 Confirmation of Successful Material Composite Based on Density and Settled Solids

3.0 Initial Characterization Results for Tributyl Phosphate Waste Sludge Group 7

This section reports on and discusses the initial characterization results for the Group 7 tributyl phosphate (TBP) sludge slurry composite, supernatant, and washed solids. The initial characterization activities included physical-property testing and chemical analysis as shown in Figure 3.1(a) and Figure 3.2. The supernatant results represent the equilibrated aqueous phase in contact with the solids; the solids characterization results were obtained after washing with 0.01 M NaOH. Solids washing was considered crucial to better understand the nature of the solids, free of complications associated with supernatant entrainment. The solids wash solutions were separately collected in the three step-wise increments (as opposed to a total wash composite) to better evaluate the phosphate mobilization during the wash steps.

(a) The physical property testing was conducted according to TI-RPP-WTP-515, *Tributyl Phosphate Sludge Hanford Tank Waste Sample Compositing, Homogenization, and Sub-Division*, R. Swoboda, 12/5/07; the solids washing and sample handling was conducted according to TI-RPP-WTP-576, *Initial Characterization of Group 7 Tank Waste: TBP Sludge*, S Fiskum, 1/21/08.

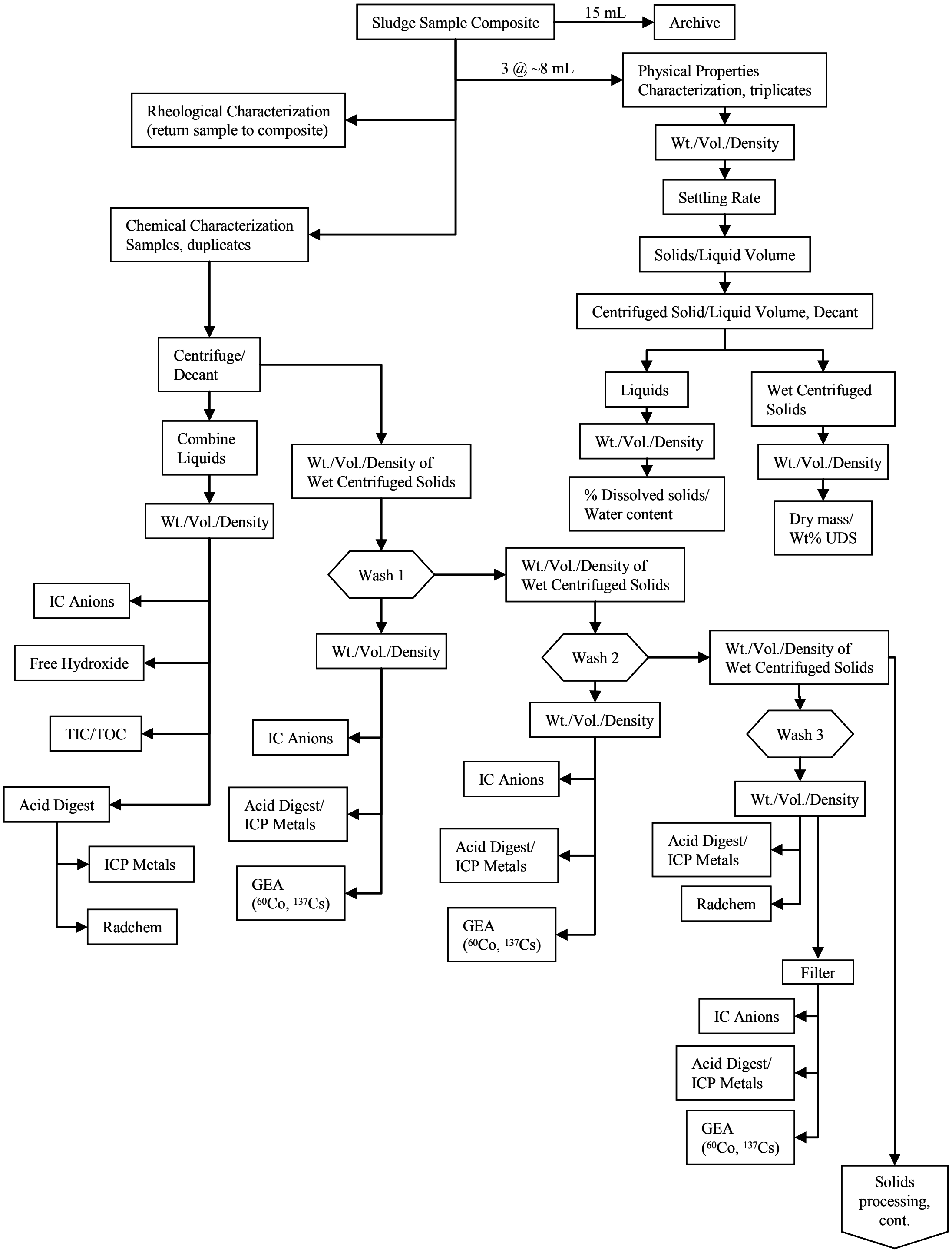

Figure 3.1. Composite Group 7 Slurry Processing and Analysis Scheme

Acronyms used in Figure 3.1:

GEA	gamma energy analysis	TIC	total inorganic carbon
IC	ion chromatography	TOC	total organic carbon
ICP	inductively coupled plasma	UDS	undissolved solids

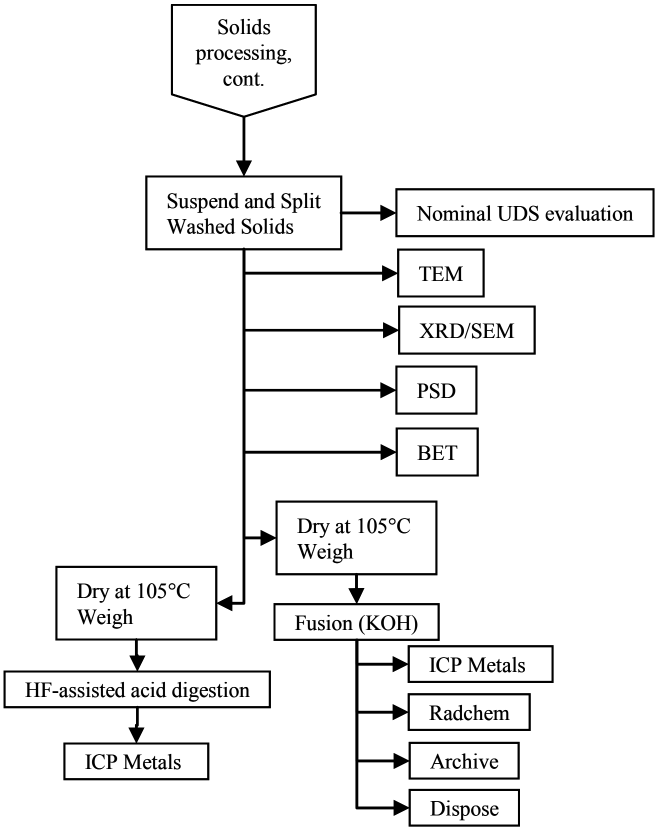

Figure 3.2. Composited Group 7 Washed Solids Processing and Analysis Scheme

Acronyms used in Figure 3.2:

BET	Brunauer, Emmett, and Teller	SEM	scanning electron microscopy
HF	Hydrofluoric Acid Digestion	TEM	transmission electron microscopy
ICP	inductively coupled plasma	UDS	undissolved solids
KOH	potassium hydroxide (fusion)	XRD	X-ray diffraction
PSD	particle-size distribution		

3.1 Physical Properties of the Composite Group 7 TBP Slurry

The settling curves of the triplicate samples of Group 7 composited solids are shown in Figure 3.3. Results are shown in two ways: 1) volume-percent settled solids as a function of time and 2) height of settled solids as a function of time. The settling curves for S2 and S3 appeared coincident whereas S1 appeared to settle slightly faster. Overall settling proceeded rather slowly, requiring nominally 50 h to reach a constant settled volume.

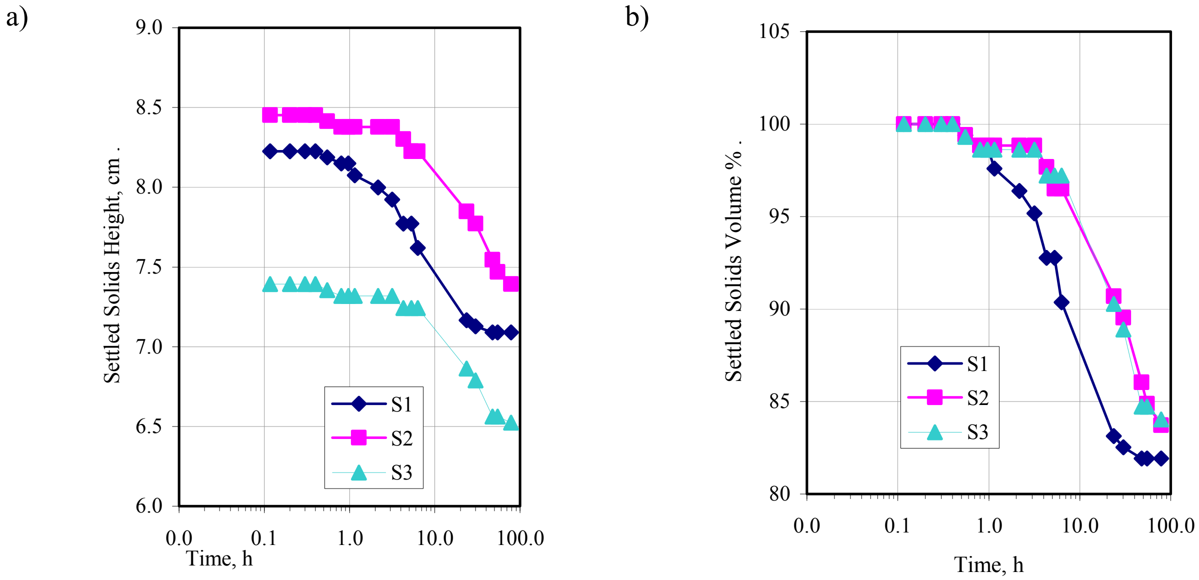

Figure 3.3. Group 7 TBP Solids Settling Test

Physical-property results for the TBP Group 7 sludge are summarized in Table 3.1 along with the propagated 1-σ errors, averages, and relative standard deviations. Good precision was obtained for the sample set. Density and vol% values associated with this testing were limited to 2 significant figures because of the small sample size (<10 mL) and volume measure uncertainty in the graduated centrifuge tubes and cylinders (~0.2 mL); the third significant figure is shown for indication only. Supernatant density was also determined to more significant figures as part of the chemical analysis processing.

Table 3.1. Physical-Property Measurements of Homogenized Group 7 TBP Slurry

Description	AR-S1	AR-S2	AR-S3	Nominal 1σ error	Avg.	RSD[a] (%)
Bulk Sample						
Sample Size (mL)	8.0	8.3	7.0	0.2	na	na
Sample Size (g)	10.975	11.523	9.704	0.003	na	na
Density (g/mL)[b]	1.37	1.40	1.39	0.036	1.38	0.90
Total Solids (wt%)	37.2	37.1	33.3	0.034	35.8	6.2
Total Undissolved Solids (wt%)	11.6	11.7	6.7	0.045	10.0	28
Settled Solids						
Density (g/mL) [b]	1.35	1.37	1.34	0.04	1.35	1.0
Vol%[b]	85.0	85.7	86.4	3.3	85.7	0.83
Wt%	86.8	87.5	88.2	3.1	87.5	0.78
Total Undissolved Solids (wt%)	13.3	13.1	7.6	0.48	11.4	28
Wet Centrifuged Solids						
Density (g/mL) [b]	1.46	1.53	1.73	0.084	1.57	8.6
Vol%[b]	43.8	42.4	45.7	2.7	44.0	3.8
Wt%	48.3	48.4	59.7	0.03	52.1	13
Total Undissolved Solids (wt%)	22.9	23.2	12.8	1.5	19.6	30
Total Solids (wt%)	45.8	45.8	36.9	0.05	42.8	12
Supernatant						
Density (g/mL) [b]	1.21	1.20	1.21	0.03	1.21	0.39
Total Dissolved Solids (wt%)	28.8	28.4	28.8	0.05	28.7	0.72
Water Content (g/g)	0.712	0.716	0.712	0.001	0.713	0.29

(a) RSD = relative standard deviation

(b) The density and vol% values are only valid to two significant figures since the volume measures were determined to two significant figures; the third significant figure is provided for indication only.

The two ~20-mL samples taken for chemical characterization were evaluated for density, wt%, and vol% centrifuged solids as part of the initial phase separation providing supplemental physical-property results. Results are summarized in Table 3.2. In this case, the wt% and vol% wet centrifuged solids were lower than the values observed with the physical-property testing samples (AR-S1, -S2, and -S3) whereas all density measures were equivalent to those observed from the physical-property testing. This is possibly due to sampling. The S3 sample appears to be outside the bounds of expected error—when S1 and S2 alone are compared to the C samples, the values are much more precise.

Table 3.2. Supplemental Physical Properties from Chemical Characterization Samples

Description	AR-C1	AR-C2	Nominal 1σ error	Avg.	RPD[a] (%)	Comparison to Table 3.1 Results
Sample Size (mL) [b]	17.0	20.5	1.0	na	na	na
Sample Size (g)	21.691	26.704	0.003	na	na	na
Bulk Density (g/mL) [b]	1.28	1.30	0.07	1.29	2.1	-6.5%
Wet Centrifuged Solids Density (g/mL)[b]	1.45	1.61	0.11	1.53	11	-2.6%
Vol% Centrifuged Solids [b]	41.2	36.6	3.4	38.9	12	-12%
Wt% Centrifuged Solids	46.665	45.270	0.004	46.0	3.0	-12%
Supernatant Density (g/mL)	1.211		0.0026	na	na	equivalent

(a) RPD = relative percent difference

(b) The density and vol% values are only valid to two significant figures since the volume measures were determined to two significant figures; the third significant figure is provided for indication only.

Bolded values indicated differences exceeding the uncertainties.

3.2 Rheology of the Composite Group 7 TBP Slurry

The rheology of select Hanford tank waste samples was characterized at the Radiochemical Processing Laboratory (RPL). Detailed rheology reports as well as rheology experimental methods can be found in Appendix F.

3.2.1 Shear Strength

The result for Group 7 initial characterization shear-strength testing is shown in Table 3.3. The single measurement for settled solids at 72 hours of settling time indicates a shear strength of 23 Pa. Because the vane immersion requirements could not be met, the measured value of 23 Pa is to be treated an order-of-magnitude estimate. .

Table 3.3. Shear Strength of Group 7 Initial Characterization Settled Solids at Ambient Hot-Cell Temperature (27.6°C)

Test Sample	Settling Time [h]	Shear Strength [Pa]
TI515-G7-AR-RH1	72	23

The degree to which the measured shear strength for Group 7 settled solids is affected by limited immersion is difficult to ascertain. It can be speculated that proximity of the top of the vane to the surface of the settled solids lowers the measured shear strength because the vane no longer has to shear settled solids above the top of the blades (i.e., the upper rotational surface). In contrast, the proximity of the vane and floor of the test container likely increases the measured value of shear strength through frictional contact and stress chain formation between vane, solid slurry particles, and the container floor.

Because of the limitations of the current test for shear strength, the value of 23 Pa measured for the shear strength of the Group 7 settled solids should be viewed with caution. The measurement is likely affected by competing effects of proximity of the vane to the surface of the settled solids and to the floor of the container and, as such, it should be treated only as an order-of-magnitude estimate.

3.2.2 Flow Curve

Figure 3.4 shows the results of flow-curve testing for the Group 7 initial characterization slurry sample. The measured flow curves indicate non-Newtonian slurry behavior, with the slurry showing finite yield stress, shearing-thinning, and significant hysteresis.

Flow-curve hysteresis is illustrated more clearly in Figure 3.5, which shows flow-curve data for the initial measurement at 25°C. As indicated by the figure, the up-ramp stress response is significantly higher than the down-ramp stress response and shows a higher degree of shear-thinning behavior. The nature of hysteresis is similar during the repeat measurement at 25°C and during the single measurement at 40°C. Although the flow-curve data at 60°C show hysteresis, the difference between the up- and down-ramp curves is significantly less than at the lower temperatures. The exact cause of hysteresis in the current measurements is difficult to ascertain from flow-curve data alone. However, because the hysteresis is characterized by a transient decrease in stress response over the course of the measurement, it can be speculated that hysteresis results from either shear-induced solids structure changes (i.e., sample thixotropy) or solids settling out of the measurement gap.

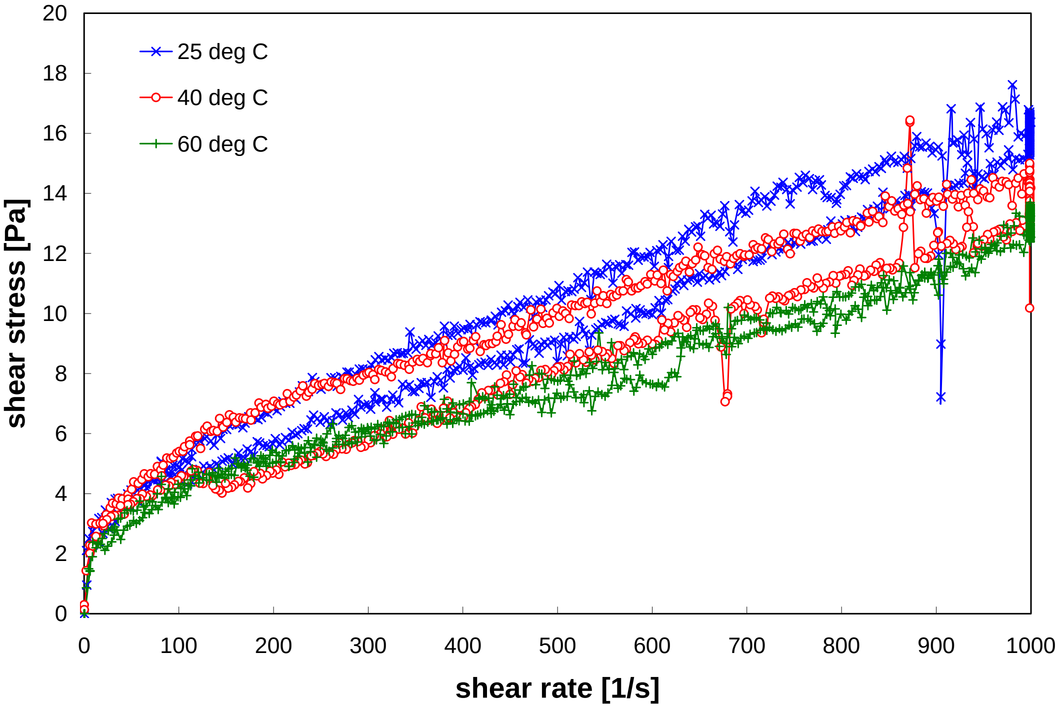

Figure 3.4. Flow Curve (shear stress versus shear rate) for the Group 7 Initial Characterization Slurry Sample at 25°C, 40°C, and 60°C. The second repeat measurement for 25°C is shown.

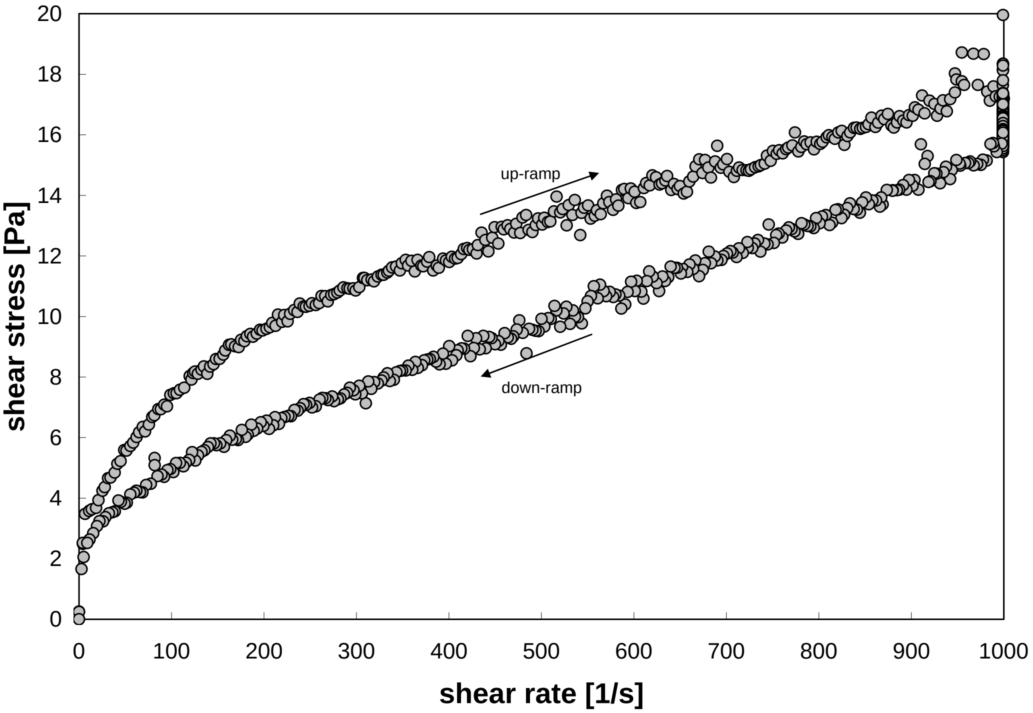

Figure 3.5. Initial Flow-Curve Measurement of the Group 7 Initial Characterization Slurry at 25°C Highlighting Significant Flow-Curve Hysteresis

Significant data overlap between the different temperature results from measurement hysteresis. As such, it is difficult to clearly determine how temperature influences the flow-curve data. Despite this difficulty, some observations can be based on rough visual inspection of the data. First, all flow-curve data indicate the slurry yield stress falls between 2 and 4 Pa. Based on a rough average of upper and lower data bounds at each temperature, it appears that the stress response of the fluid (i.e., the slurry consistency) decreases with increasing temperature.

The measured flow-curve data were fit to both Bingham-Plastic and Casson constitutive equations to obtain a quantitative description of flow behavior. Because of the significant hysteresis, it was not feasible to derive an averaged set of flow-curve parameters by fitting both up- and down-ramp flow-curve data simultaneously. Instead, flow-curve fits were limited to down-ramp data alone (shown in Figure 3.6). Up-ramp data were excluded based on the assumption that hysteresis likely results from transient breakdown of slurry structure and that the well-mixed flow behavior is most closely represented by the down-ramp flow-curve data. For Bingham-Plastic fitting analysis, data fits were restricted to a shear-rate range of 100 to 1000 s^{-1} at 25°C and 40°C and of 100 to 800 s^{-1} at 60°C. The lower bound excludes the non-linear region that occurs over 0 to 100 s^{-1} from the Bingham fitting analysis because this model cannot account for curvature. The 800 s^{-1} upper bound excludes 60°C data potentially affected by unstable flow. Unstable flow is evidenced by a sharp and unexpected increase in slope of the up-ramp data. While this slope change appears to be absent from the down-ramp data, the shear-rate limt of 800 s^{-1} is maintained as a precautionary measure.

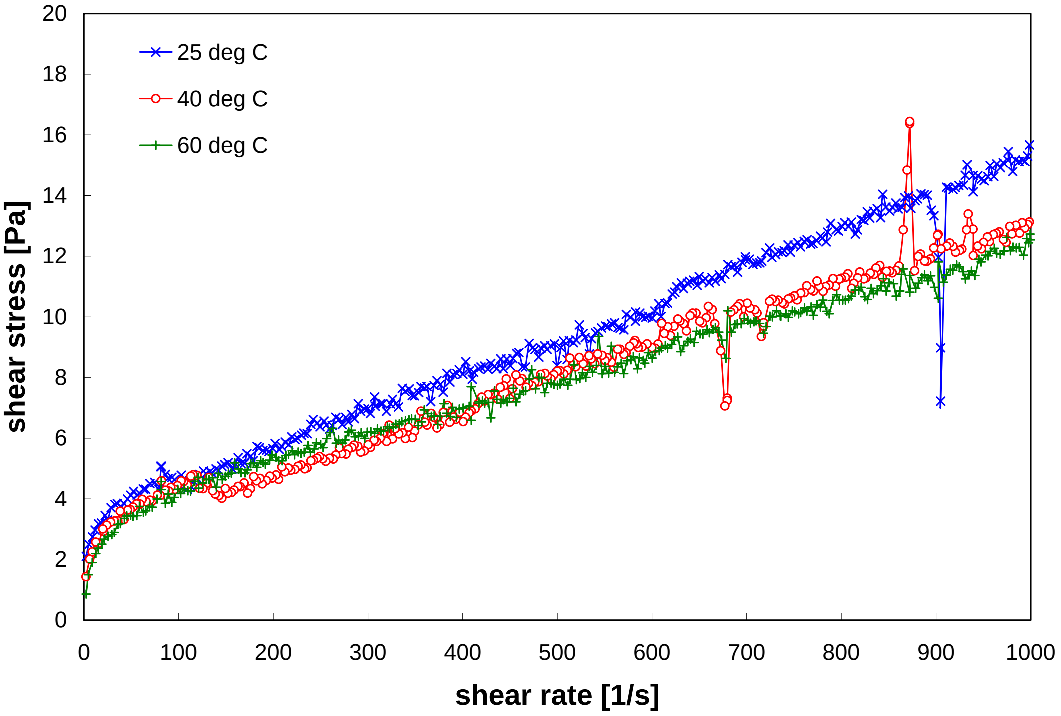

Figure 3.6. Down-Ramp Flow-Curve Data for the Group 7 Initial Characterization Slurry at 25°C, 40°C, and 60°C. The second repeat measurement for 25°C is shown.

Table 3.4 summarizes the best-fit Bingham-Plastic and Casson parameters for the Group 7 initial characterization slurry. The Bingham-Plastic parameters indicate a slurry yield stress and consistency that range from 2.8 to 4.1 Pa and 8.9 to 12 mPa·s, respectively. Likewise, the Casson model indicates a yield stress and consistency that range from 1.3 to 1.9 Pa and 4.4 to 6.6 mPa·s. The lower consistency and yield stress provided by the Casson fits is simply a result of model curvature.

The fitting results in Table 3.4 do not provide much insight into how slurry yield stress and consistency behave as a function of temperature. Although Bingham-Plastic yield stress varies over a significant range of 2.8 to 4.1 Pa, its variation does not track with temperature. Yield-stress reproducibility is poor, as indicated by the significant difference of 0.8 Pa in initial and repeat measurements at 25°C (4.1 and 3.3 Pa, respectively). Similar yield stress issues are observed with the Casson fits.

Slurry consistency does not vary significantly for the repeat measurements at 25°C and the measurement 40°C. Bingham-Plastic and Casson consistencies range from 11 to 12 and 6.0 to 6.6 mPa·s, respectively. Because both ranges cover less than the expected limit of instrument accuracy of 10%, it is unlikely that there is variation between slurry consistency at 25°C and 40°C. On the other hand, Bingham-Plastic consistency drops from 11 to 8.9 mPa·s as slurry temperature is raised from 40°C to 60°C. Although this is a significant decrease, it is difficult to state that this decrease would continue at higher temperatures with confidence given the variation in the yield-stress results. Overall, the fitting results do not indicate strong temperature trends because it is difficult to distinguish measurement-to-measurement variation from changes induced by increased temperature. It is speculated that the significant flow-curve hysteresis is the source of measurement-to-measurement variation.

Table 3.4. Results of Fitting Analysis for Rheology of the Group 7 Initial Characterization Slurry. All model parameters are based on down-ramp data only.

Model	Temperature [°C]	Range	Yield Stress [Pa]	Viscosity [mPa·s]	R
Bingham-Plastic (Flow Curve)	25 (1 of 2)	100-1000 s^{-1}	4.1	11	1.00
	25 (2 of 2)	100-1000 s^{-1}	3.3	12	0.98
	40	100-1000 s^{-1}	2.8	11	0.98
	60	100-800 s^{-1}	3.5	8.9	0.99
Casson (Flow Curve)	25 (1 of 2)	0-1000 s^{-1}	1.9	6.3	1.00
	25 (2 of 2)	0-1000 s^{-1}	1.6	6.6	0.98
	40	0-1000 s^{-1}	1.3	6.0	0.98
	60	0-800 s^{-1}	1.8	4.4	0.99

3.3 Chemical and Radiochemical Composition of the Group 7 Slurry

One of the two characterization samples is shown in Figure 3.7 following centrifuging. The centrifuged solids appeared generally uniform from top to bottom and were colored dark brown-red with a pale yellow supernatant. The supernatant density was determined to be 1.211 g/mL (T = 27°C) based on the average masses of four 1-mL volume deliveries.

Figure 3.7. Centrifuged Solids from Chemical Characterization Sample of Group 7 TBP Sludge

The specific washing scheme for the TBP sludge is provided in Figure 3.8. The centrifuged solids (CS) volumes were estimated based on the centrifuge-tube graduations. With each successive washing step, the CS volume appeared to slightly increase; however, given the measurement uncertainty, this observation is not definitive. The hydroxide concentration in the final washing solution was ~0.01 M. The final washing solution appeared to cause a dispersion of a small amount of material. The supernatant and sequential wash solutions are shown in Figure 3.9 to illustrate the dispersion. The solids suspension was attributed to the low ionic strength of the final aqueous phase.

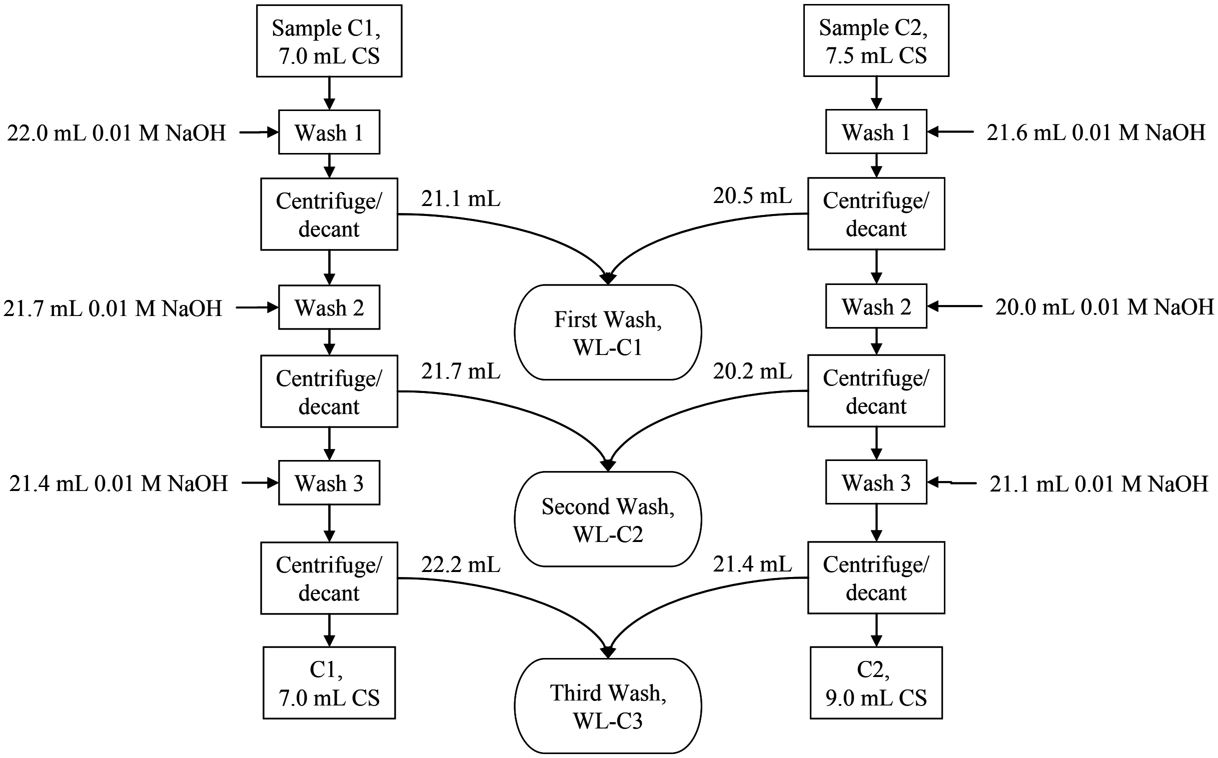

Figure 3.8. Wash Sequence of Group 7 TBP Sludge Supporting Initial Characterization

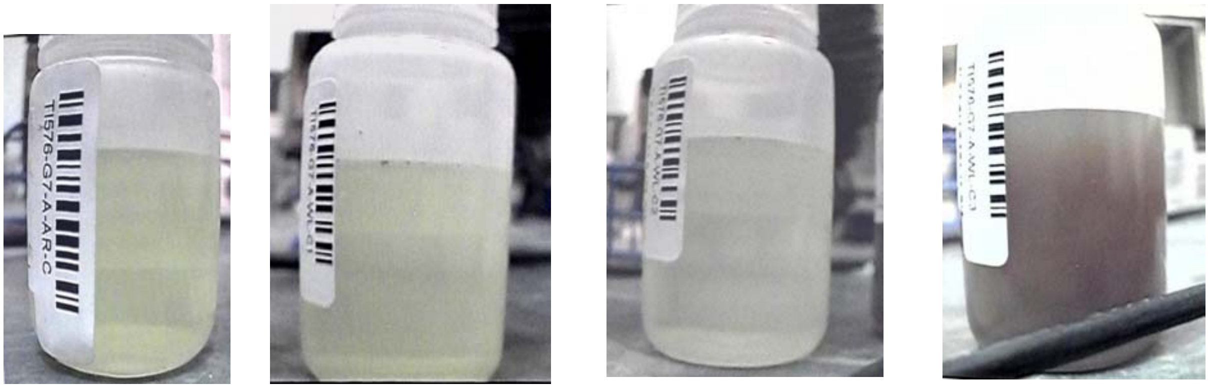
Supernatant First wash Second wash Third wash

Figure 3.9. Comparison of Group 7 TBP Sequential Wash Solutions

The effect of ionic-strength adjustment on the third wash (WL-C3) solids dispersion was tested. Small, 1-mL aliquots of the mixed composite were contacted with NaOH and $NaNO_3$ added in sufficient amounts to result in 0.2-M solutions. In both cases, the Fe floc settled within 24 h, whereas the parent material did not settle. A 5-mL aliquot was filtered through a 0.2-micrometer pore size HT Tuffryn$^{®}$ (polysuflone membrane) syringe filter (part number 4496, Gelman Sciences, Ann Arbor, MI). The filter quickly plugged from rust-colored fines indicative of $Fe(OH)_3$; the filtrate was virtually colorless. The beta-gamma activity was also greatly diminished in the filtrate relative to the starting material. Figure 3.10 shows the 24-h equilibrated result of the matrix-adjusted material, filtrate, and starting material. The filtrate was analyzed for anions, free hydroxide, and inductively coupled plasma-optical emission spectrometry (ICP-OES) metals; the unfiltered solution (with floc) was analyzed for ICP-OES metals and radionuclides.

Figure 3.10. Third Wash after Ionic Strength Adjustment and Filtration

Treatments from Left to Right: 0.2 M $NaNO_3$; 0.2 M NaOH; Filtrate; Starting Material

The average radioanalytical results for the supernatant, three wash solutions, third filtered wash solution, and washed solids are provided in Table 3.5 along with the applicable relative percent differences (RPD, measure of precision) between duplicate results. The concentrations of the gross-beta results and the sum of beta emitters, ^{137}Cs and ^{90}Sr (in secular equilibrium with ^{90}Y), were essentially equivalent (ratio close to 1.0). The reasonably good agreement between these values indicated that no other major source of beta activity was present. Similarly, the gross-alpha activity was reasonably close to the summation of alpha emitters (^{238}Pu, $^{239+240}$Pu, and detected ^{241}Am), indicating that no other significant source of alpha activity was present.

The chemical compositions of the Group 7 TBP supernatant, composite wash solution, and washed solids are provided in Table 3.6. Results for both solids preparation methods (fusion and HF-assisted acid digestion) are shown. The analysis results from the solids prepared by the HF-assisted acid digestion method were ~15% greater than the results from the fusion preparation method. This difference is just within the uncertainty stated for the preparation and analysis methods (±15%).

The supernatant salt concentrations were generally very low relative to those observed in other tank waste preparations. The free hydroxide was less than the requested analytical detection limit of 0.1 M. The supernatant was primarily sodium salts (nitrate, nitrite, sulfate, and phosphate). The anionic and cationic charge balance was evaluated for the supernatant, resulting in a 9.1% difference, well within analytical uncertainties.

Table 3.5. Radionuclide Characterization of the Group 7 TBP Sludge

	Supernatant		Wash 1	Wash 2	Filtered Wash 3	Wash 3 with Floc	Washed solids(a)	
Sample ID>	**08-01145(b)**		**08-01146**	**08-01147**	**08-01148**	**08-01149**	**08-01150**	
Analyte	**µCi/mL**	**RPD**	**µCi/mL**	**µCi/mL**	**µCi/mL**	**µCi/mL**	**µCi/g**	**RPD**
^{137}Cs	4.56E+0	1.3	7.18E-1	1.88E-1	7.66E-2	1.25E-1	3.64E+1	7.7
^{60}Co	<8.E-5	na	2.14E-5	7.22E-6	3.00E-6	<8E-5	2.11E-2	0.95
^{241}Am	<4.E-3	na	<2.E-4	<1E-4	<2E-5	<3E-4	[8.7E-2]	na
^{238}Pu	[3.9E-6]	[59]	n/a			9.68E-6	5.63E-3	3.7
$^{239+240}$Pu	1.21E-4	0.83				6.24E-4	1.95E-1	7.2
Gross alpha	<3.E-4	na				8.12E-4	3.00E-1	8.0
Gross beta	4.59E+0	1.3				1.97E+0	1.57E+3	7.0
^{90}Sr	1.00E-2	5.5				8.81E-1	7.41E+2	7.6
Alpha sum	1.24E-4	1.0				6.34E-4	2.44E-1	30
α gross/sum	na	na				1.28	1.23	na
Beta sum	4.58E+0	1.3				1.89E+0	1.52E+3	7.6
β gross/sum	1.00	na				1.04	1.03	na
Opportunistic								
^{154}Eu	<2.E-4	na	<1.E-5	<7.E-6	<9.E-6	<2.E-4	5.90E-2	19
^{155}Eu	<2.E-3	na	<2.E-4	<8.E-5	<4.E-5	<4.E-4	<5E-2	na

(a) Analyte concentrations are calculated on a dry-mass basis.
(b) This sample was not required to be run in duplicate; therefore, an RPD was not calculated.
Notes:
ASR 8108
Reference date is November 5, 2007.
na = not applicable; n/a = not analyzed

For most components, the wash solutions represented simply dilutions of the supernatant. The ratios of P, phosphate, and fluoride concentrations in the wash solutions relative to the supernatant were higher than the corresponding nitrate concentration ratio, indicating that some phosphate and fluoride were dissolved from the solids phase during washing. This indicated that water-soluble phosphate and fluoride solids were present in the unwashed solids phase. As washing progressed, the dissolved salt (electrolyte) concentrations dropped below the threshold that would limit flocculent dispersions. Concentrations of Al, Fe, and Sr were observed to increase with each wash cycle. Filtration of the third wash solution resulted in large (70×) decreases of the Fe and Sr concentrations, indicating that the colloidal particles were mostly >0.2 µm (filter pore size was 0.2 µm). In contrast, the filtrate Al concentration only decreased by 40%. Clearly, a fraction of the Al was also dissolved during the washing process.

The washed water-insoluble solids were dominated by Fe (15 wt%), Na (14 wt%), and P and U (12 wt% each) (dry mass basis).

Table 3.6. Chemical Characterization of the Group 7 TBP Sludge

	Supernatant			Wash 1	Wash 2	Wash 3	Wash 3	Washed solids(a)			
Sample ID>	08–01145			08–01146	08–01147	08–01148	08–01149	**08-01150**			
						Filtered	**with Floc**	**Fusion**		**Acid Digest**	
Analyte	**µg/mL**	**M**	**RPD**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/g**	**RPD**	**µg/g**	**RPD**
Al	<0.73	<2.7E-5	na	8.96	28.0	46.3	65.3	16,000	7.5	18,550	0.54
B	30.0	2.78E-3	5.3	9.85	3.78	1.52	1.71	[115]	[9]	<13	na
Bi	<3.65	<1.7E-5	na	<0.73	<0.74	<0.74	10.3	5,710	6.0	6,475	1.7
Cd	<0.41	<3.7E-6	na	<0.083	<0.084	<0.084	<0.083	<7.7	na	<9.2	na
Cr	57.8	1.11E-3	1.7	13.2	3.67	1.06	3.01	718	7.5	826	0.48
Fe	[1.15]	[2.1E-5]	[8.7]	[1.0]	2.20	6.08	393	140,000	7.1	156,000	2.6
K	[86]	2.19E-3	[1.9]	[15]	[3.1]	[3.1]	[2.4]	na	na	[315]	[54]
Mn	[0.16]	[2.9E-6]	[13]	[0.031]	[0.022]	[0.043]	2.28	884	7	926	0.3
Na	92,300	4.01E+0	0.22	21,300	6,380	2,480	2,560	130,500	6.9	151,500	2.0
Ni	<0.42	<7.2E-6	na	[0.080]	<0.059	<0.060	1.74	na	na	517	0.19
P	3,760	1.21E-1	1.6	994	498	519	596	107,500	6.5	123,000	0.0
S	6,260	1.95E-1	1.9	1,400	387	99.6	102	[875]	[74]	[940(c)	[77]
Si	<0.68	<2.4E-5	na	2.07	1.50	1.59	18.3	7,285	7.0	na	na
Sr	[0.050]	[5.6E-7]	[2.0]	[0.022]	0.042	0.065	4.68	3,905	6.9	4,460	2.2
U	162	6.79E-4	1.9	42.7	30.1	14.0	44.9	113,000	7.1	125,000	0.0
Zn	[0.99]	[1.5E-5]	[2.0]	[0.48]	[0.54]	[0.49]	5.53	687	8.3	856	1.3
Zr	<0.13	<1.5E-6	na	<0.027	<0.027	[0.047]	0.337	<9.3	na	[23]	[17]
U KPA	n/a							114,500	4.4	n/a	
nitrite	19,000	4.13E-1	na(b)	4,360	1,090	274	n/a				
nitrate	193,000	3.11E+0	na(b)	43,500	11,100	2,780					
phosphate	11,300	1.19E-1	na(b)	3,030	1,520	1,610					
sulfate	17,000	1.77E-1	na(b)	3,930	1,040	271					
oxalate	<5	<6E-5	na(b)	[32]	[9]	[3]					
free hydroxide	[597]	[3.5E-2]	[5.4]	[1,040]	[682]	[463]					
TOC as C	342.5	2.85E-2	4.4								

Table 3.6 (Contd)

	Supernatant			**Wash 1**	**Wash 2**	**Wash 3**	**Wash 3**	**Washed solids(a)**			
Sample ID>	08–01145			08–01146	08–01147	08–01148	08–01149	**08-01150**			
						Filtered	**with Floc**	**Fusion**		**Acid Digest**	
Analyte	**µg/mL**	**M**	**RPD**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/g**	**RPD**	**µg/g**	**RPD**
TIC as C	553	4.60E-2	6.3	n/a							
Opportunistic											
fluoride	249	1.31E-2	na(b)	298	351	243	n/a				
chloride	1310	3.70E-2	na(b)	297	74	19					
Ag	<0.256	<2.4E-6	na	<0.051	<0.052	<0.052	<0.051	[26]	[15]	[25]	[24]
As	<5.2	<7.0E-5	na	<1.0	<1.1	<1.1	<1.1	<104	na	<116	na
Ba	[0.17]	[1.2E-6]	[0.0]	0.188	[0.083]	[0.091]	2.08	289	6.9	320	0.31
Be	<0.006	<7.1E-7	na	<0.001	<0.001	<0.001	<0.001	[0.66]	[5]	[0.72]	[35]
Ca	[3.75]	[9.4E-5]	[72]	1.72	2.60	2.28	9.63	[16,000]	[13]	18,000	0.0
Ce	<1.2	<8.7E-6	na	<0.24	<0.25	<0.25	[0.31]	[115]	[9]	[130]	[15]
Co	<0.39	<6.6E-6	na	[0.063]	<0.059	<0.060	[0.079]	[25]	[4]	[27]	[11]
Cu	<0.17	<2.7E-6	na	<0.034	<0.034	<0.035	[0.17]	142	13	152	2.6
Dy	<0.35	<2.2E-6	na	<0.070	<0.071	<0.072	0.071	<7.7	na	<7.8	na
Eu	<0.13	<8.8E-7	na	<0.027	<0.027	<0.027	0.027	[3.4]	[6]	[5.3]	[30]
La	<0.34	<2.5E-6	na	<0.068	<0.069	<0.070	[0.17]	[52]	[8]	[67]	[0]
Li	4.03	5.81E-4	5.0	1.77	0.815	0.340	0.407	87.3	4.8	126	1.6
Mg	<0.28	<1.2E-5	na	[0.070]	<0.057	<0.057	7.53	3,120	7.1	4,130	0.48
Mo	6.58	6.86E-5	3.6	1.56	[0.44]	<0.13	<0.13	<19	na	[21]	[60]
Nd	<0.66	<4.6E-6	na	<0.13	<0.13	<0.13	[0.34]	179	3.9	222	4.1
Pb	<3.9	<1.9E-5	na	<0.78	<0.79	<0.79	[6.1]	2,910	6.9	3,655	0.82
Pd	<0.99	<9.3E-6	na	<0.15	<0.16	<0.16	<0.15	<17	na	<17	na
Rh	[1.77]	[1.7E-5]	[37]	<0.29	<0.30	<0.30	[0.32]	<35	na	<32	na
Ru	[2.7]	[2.7E-5]	[30]	[0.45]	<0.21	<0.21	<0.21	<18	na	<23	na
Sb	<2.4	<2.0E-5	na	<0.49	<0.49	<0.50	<0.49	<82	na	[97]	[28]
Se	<8.5	<1.1E-4	na	<1.7	<1.7	[3.5]	[3.2]	<292	na	<266	na

Table 3.6 (Contd)

	Supernatant			**Wash 1**	**Wash 2**	**Wash 3**	**Wash 3**	**Washed solids(a)**			
Sample ID>	08–01145			08–01146	08–01147	08–01148	08–01149	**08-01150**			
						Filtered	**with Floc**	**Fusion**		**Acid Digest**	
Analyte	**µg/mL**	**M**	**RPD**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/mL**	**µg/g**	**RPD**	**µg/g**	**RPD**
Sn	[4.02]	[3.4E-5]	[39]	[0.87]	[0.79]	<0.67	<0.66	<66	na	<90	na
Ta	<2.1	<1.1E-5	na	<0.41	<0.42	<0.42	<0.42	<61	na	<46	na
Te	<3.2	<2.5E-5	na	<0.63	<0.64	<0.65	<0.64	[82]	[38]	<70	na
Th	<1.2	<5.1E-6	na	<0.24	<0.24	<0.24	<0.24	<22	na	<26	na
Ti	<0.052	<1.1E-6	na	<0.010	<0.011	<0.011	0.422	371	7.0	407	0.49
Tl	[7.5]	[3.7E-5]	[35]	[1.9]	[2.5]	[1.1]	<0.93	<80	na	<164	na
V	<0.090	<1.8E-6	na	[0.062]	[0.049]	[0.058]	[0.075]	<8.5	na	<2.0	na
W	[2.79]	[1.5E-5]	[36]	<0.46	<0.47	<0.47	<0.47	<56	na	<51	na
Y	<0.054	<6.0E-7	na	<0.011	<0.011	<0.011	[0.062]	29.7	5.1	36.7	3.8

(a) Analyte concentrations are calculated on a dry-mass basis.

(b) Sample 08-01145 was analyzed in duplicate for this analytical batch with RPDs ≤1.1%.

(c) The laboratory control sample (LCS) sulfur recovery was high at 144%, indicating that the sample result might be biased high.

Notes:

ASR 8108.

Analyte uncertainties were typically within ±15%; results in brackets indicate that the analyte concentrations were greater than the minimum detection limit (MDL) and less than the estimated quantitation limit (EQL), and uncertainties were >15%.

Opportunistic analytes are reported for information only; quality control (QC) requirements did not apply to these analytes.

na = not applicable, sample was not analyzed in duplicate or the analyte was <MDL.

n/a = not analyzed, analysis was not required.

Analyte water-wash factors were calculated from the mass distribution in the combined supernatant and wash solutions relative to the total analyte mass according to Equation 3.1.

$$F_i = \frac{S_i + W_i}{S_i + W_i + UDS_i} \tag{3.1}$$

where F_i = analyte fraction removed during washing
S_i = analyte mass in supernatant fraction
W_i = analyte mass in wash solution
UDS_i = analyte mass in the undissolved solids.

The fractional distributions of selected analytes in the supernatant, combined wash, and solids phases are shown in Table 3.7 and Figure 3.11. According to TWINS data, a large portion (>90%) of the Na and S should partition to the aqueous phase. While this was the case with S for the tested Group 7 waste, the Na only partitioned 80% into the aqueous phase. Washing removed much smaller amounts of Cr (30 wt%), Al (3.4 wt%), and P (19.5 wt%). The water-wash factors obtained from the current testing were compared with the weighted mean of the water-wash factors obtained from the TWINS database. The weighting factors were calculated from the relative masses of tank wastes that were used to create the composite. The experimentally obtained Al, Na, Cr, and S wash factors agreed fairly well with the TWINS water-wash factors. The experimentally obtained P wash factor was significantly lower than the TWINS factor. Direct cross comparison of these water-wash factors with those in the TWINS database may be confounded by the sample selection process; only available TBP sludge samples in the 222S archive were selected for processing, and these had aged ~10 y.

Table 3.7. Phase Distribution of Selected Analytes in Group 7 TBP Sludge

Analyte	Supernatant wt %	Combined Wash Solution wt %	Water-Wash Factor wt %	TWINS Water-Wash Factor[a] wt %	Solids wt %
Cr	19	11	30	23.4	70
Al	<0.01	3.4	3.4	9.2	97
Na	49	31	80	91.8	20
P	9.5	10	19.5	73.7[b]	80
S	62	36	[98]	96.0[c]	[2.5]

(a) The water-wash factors represent the weighted mean of the five represented tank-waste sources from the Best Basis Inventory (BBI) in the Tank Waste Information Network System (TWINS) database (search date 10/28/08).
(b) Reported in TWINS as phosphate; phosphorous wash factor was not available.
(c) Reported in TWINS as sulfate; sulfur water wash factor was not available.
Results in brackets indicate that the analyte concentrations were >MDL and <EQL.

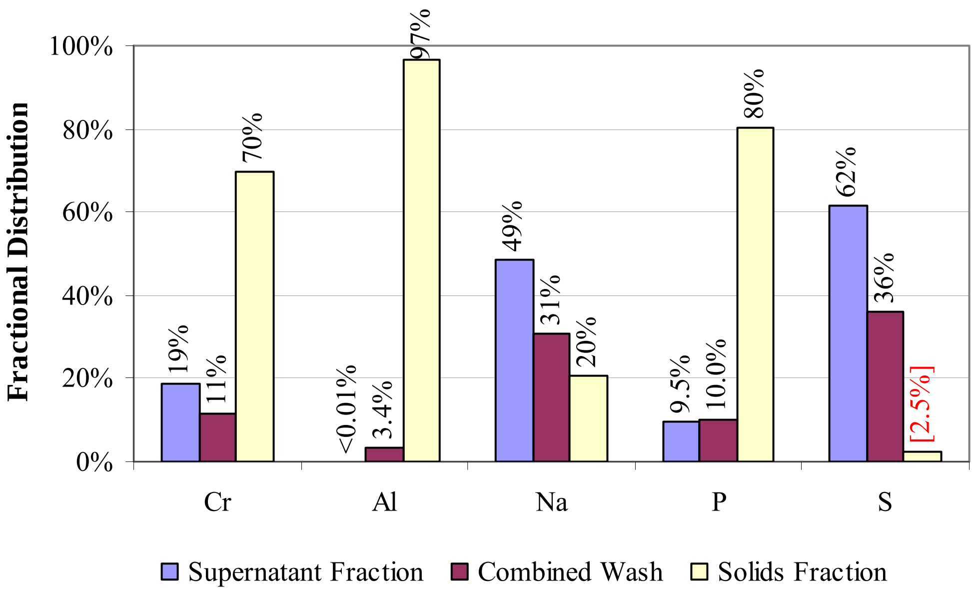

Figure 3.11. Selected Analyte Phase Distribution for Group 7 TBP Sludge

3.4 Particle Size

Figure 3.12, Figure 3.13 and Table 3.8 present the results of Group 7 initial characterization particle-size analysis as a function of test condition. Figure 3.12 and Figure 3.13 show the differential volume population distribution for the Group 7 initial characterization sample and allow a qualitative examination of the PSD behavior with respect to pump speed. Table 3.8 is a summary of the measured oversize diameter percentiles (by volume/weight) for the primary sample that present cumulative oversize diameters corresponding to the 10th, 50th, and 90th volume/weight percentiles, hereafter referred to as d(10), d(50), and d(90), respectively.

Figure 3.12 shows the PSD for the primary Group 7 initial characterization sample as a function of pump speed. The sample displayed a multi-modal distribution at all pump speeds. At 2000 RPM, the distribution ranges from 0.2 to 750 µm with peak maxima around 0.7, 7.5, 84, and 475 µm. At 3000 RPM, the distribution ranges from 0.2 to 500 µm and displays peak maxima around 0.7, 7.5, and 75 µm. At 4000 RPM, the distribution ranges from 0.2 to 200 µm and contains peak maxima around 0.7, 7.5, and 60 µm. Overall, the higher pump speeds show an increasing population of particles or agglomerates > 20 µm. The 475-µm peak seen at 2000 RPM may be an artifact of scattering signal interpretation by the Malvern software or possible flocculates in the solution that are sheared apart at higher pump speeds. The sample appears to have numerous large particles, agglomerates, or flocculates, which may result in poor reproducibility in sampling due to settling of the larger particles solids.

Figure 3.13 shows the PSD for the duplicate Group 7 initial characterization sample as a function of pump speed. This distribution shows a range of 0.2 to 150 µm with the exception of a 475-µm peak at 2000 RPM. As this 475-µm peak is observed in both the primary and duplicate sample only at 2000 RPM, it is probable that it corresponds to flocculates that are sheared apart at higher pump speeds. In the duplicate sample, a primary peak is present around 6 µm, and a shoulder exists around 0.75 µm at all pump speeds. At 4000 RPM, an additional small peak is seen around 60 µm, and at 3000 and 2000 RPM, either a small peak or a shoulder is present around 75 µm. Again, the varying distribution may indicate poor sampling due to settling of larger particles that are difficult-to-suspend.

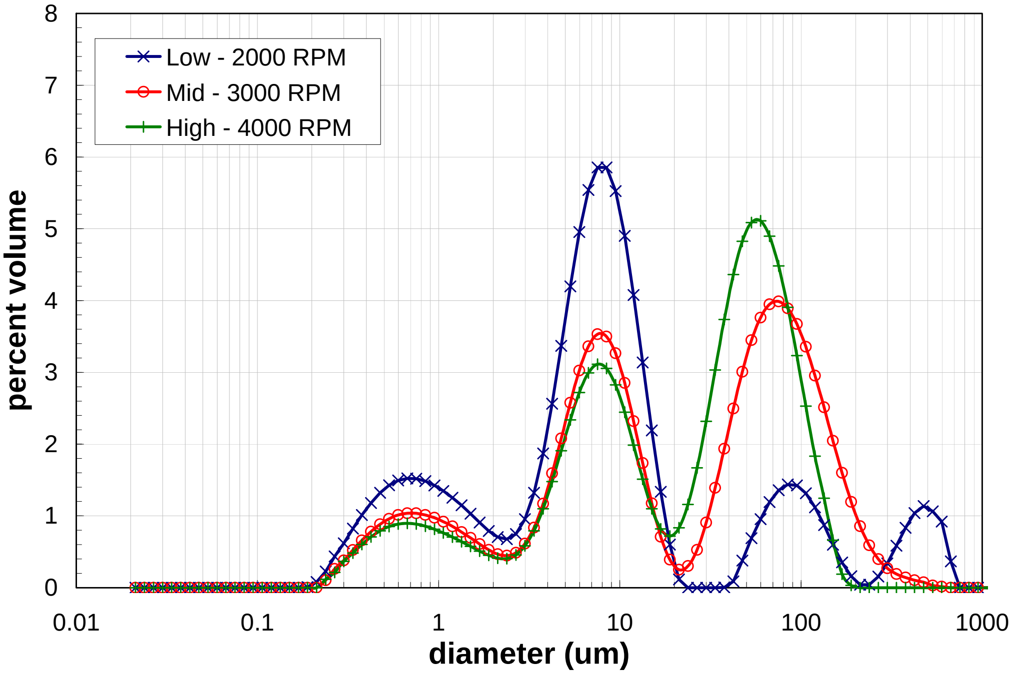

Figure 3.12. Volume Distribution Result for the Primary Group 7 Initial Characterization Sample as a Function of Pump Speed

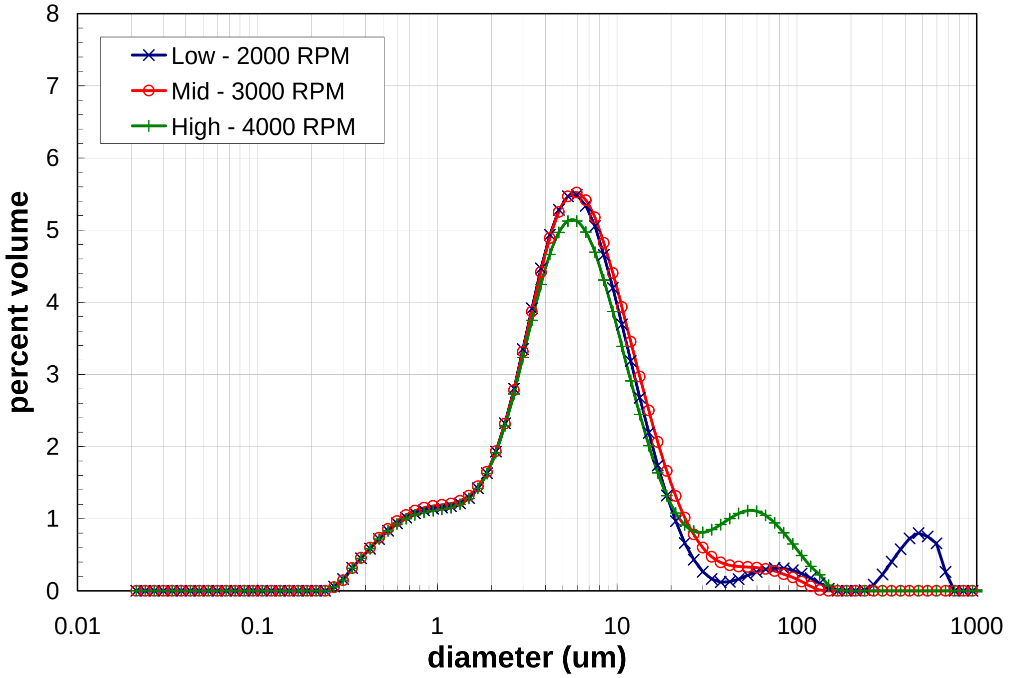

Figure 3.13. Volume Distribution Result for the Duplicate Group 7 Initial Characterization Sample as a Function of Pump Speed

Table 3.8 shows select cumulative oversize percentiles for the primary and duplicate Group 7 particle dispersions. Using the primary results as a reference, the behavior of Group 7 initial characterization particle size as a function of pump speed can be quantitatively evaluated. Specifically, the following observations can be made:

- In general, the d(10) falls between 0.70 and 1.3 µm, the d(50) between 7.4 and 31 µm, and the d(90) between 89 and 130 µm
- The listed diameter percentiles appear to be highly sensitive to changes in pump speed. Increases in pump speed appear to result in increases in the d(50). For example, increasing the pump speed from 2000 to 4000 RPM increases the mean particle diameter from 9.8 to 31 µm. This is an increase of 68%, which is above the instrument limit of accuracy (10%) and is significant and not merely random noise or measurement error.

Table 3.8. Particle-Size Analysis Percentile Results from Primary Group 7 Initial Characterization Sample

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	n/a	1.0	19	130
1	3000	n/a	1.1	5.5	17
2	4000	n/a	1.3	31	89
2	4000	n/a	1.2	5.8	35
3	2000	n/a	0.87	9.8	120
3	2000	n/a	1.2	5.9	66
4	2000	n/a	0.70	7.4	110
4	2000	n/a	1.2	5.5	19

3.5 Surface Area

Duplicate samples (0.176 g and 0.158 g) tested for surface area resulted in 66.1 ± 0.14 m^2/g. The overall experimental uncertainty was estimated to be ±5%.

3.6 Crystal Form and Habit

XRD sample analysis was carried out by PNNL's Radiochemical Science and Engineering Group. The XRD instrument used was the Scintag PAD V X-ray Diffractometer. Phase identification was done with the JADE search match routines (version 6.0, Materials Data Inc.) with comparison to the International Centre for Diffraction Data (ICDD) database PDF-2 release 1999, which includes the Inorganic Crystal Structure Database (ICSD) (maintained by Fachinformationszentrum [FIZ], Karlsruhe, Germany). In general, the patterns contain a very large number of peaks along with significant peak overlapping in areas (Figure 3.14). The phases identified were not good matches to the measured XRD patterns, indicating that the pattern contains phases that are likely somewhat different than the patterns available in the database. Phases identified were:

- Rutile, TiO_2 (internal standard)
- Zeolite, $NaAlSiO_4(H_2O)_{1.1}$

- Threadgoldite, $Al(UO_2)_2(PO_4)_2(OH)(H_2O)_8$
- Sodium Iron Phosphate, $Na_7(FeP_2O_7)_4PO_4$
- Lepidocrocite, $FeO(OH)$
- Humboldtine, $C_2FeO_4 \cdot 2H_2O$
- Iron (III) phosphate oxide, Fe_2PO_5
- Dioxouranium(VI) bis(dihydrogenphosphate(I)) hydrate, $(UO_2)(H_2PO_2)_2(H_2O)$
- Sodium Uranyl Phosphate, $Na_6(UO_2)_2(PO_4)_4$
- Gibbsite, $Al(OH)_3$.

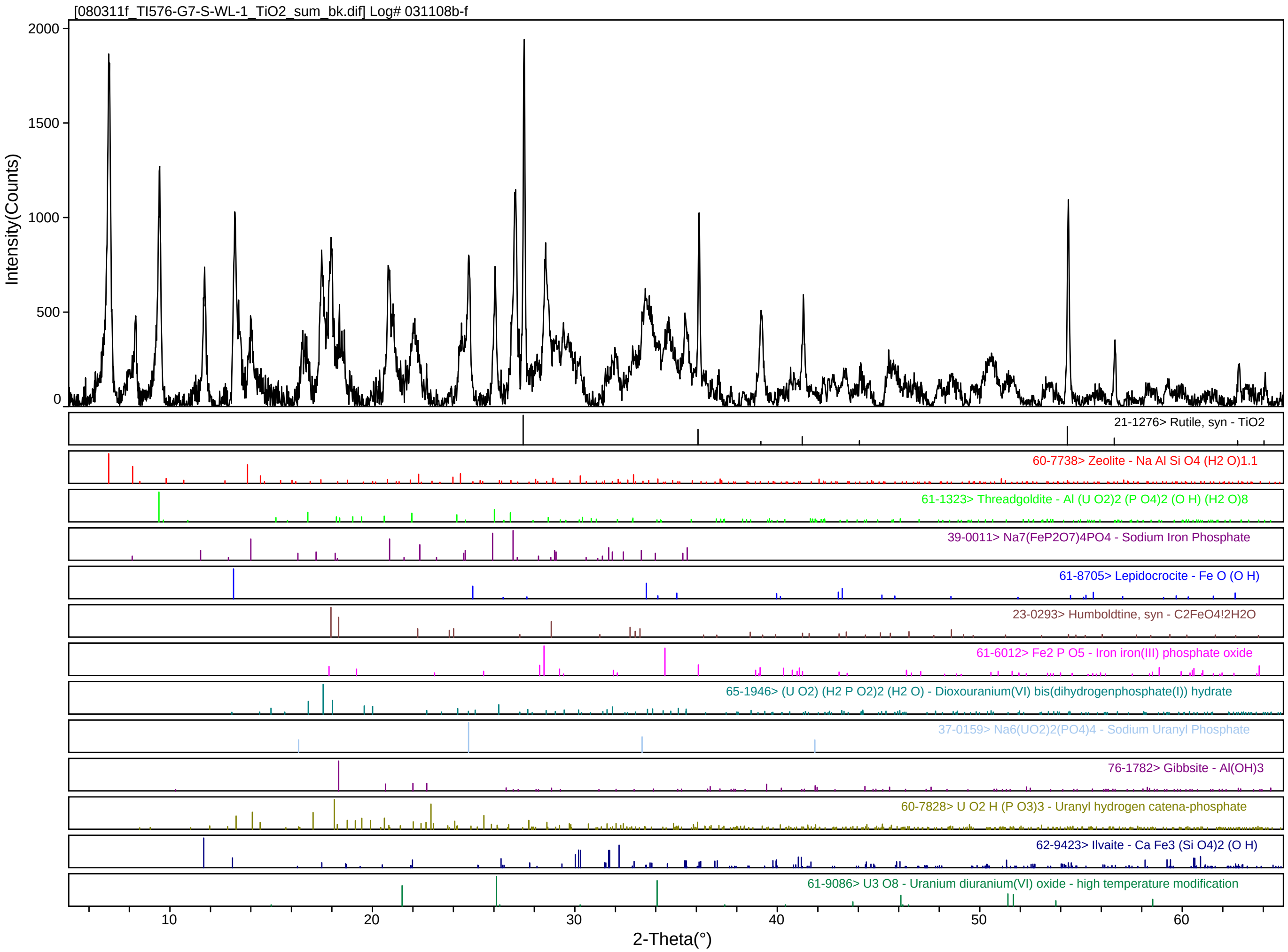

Figure 3.14. XRD Pattern of Washed Group 7 TBP Sludge with Rutile (TiO_2) Internal Standard Background-Subtracted Pattern with Stick-Figure Peak Identification

Several SEM images of the washed Group 7 solids are shown in Figure 3.15 through Figure 3.18. The washed TBP sludge particles tended to agglomerate. A significant population of platy particles appeared to agglomerate in a spherical structure (see Figure 3.16 and Figure 3.17a) with a complex chemical composition including O, Na, Al, P, Ca, and Fe. Spot 2 in Figure 3.17b shows a relatively large, platy structure with flat faces in the *xyz* planes of similar composition, except it contains U. Possible gibbsite-like structures appear in Figure 3.17b, spots 1 and 5, and Figure 3.18 Spot 3 with only Al and O identified by energy-dispersive spectroscopy (EDS) examination.

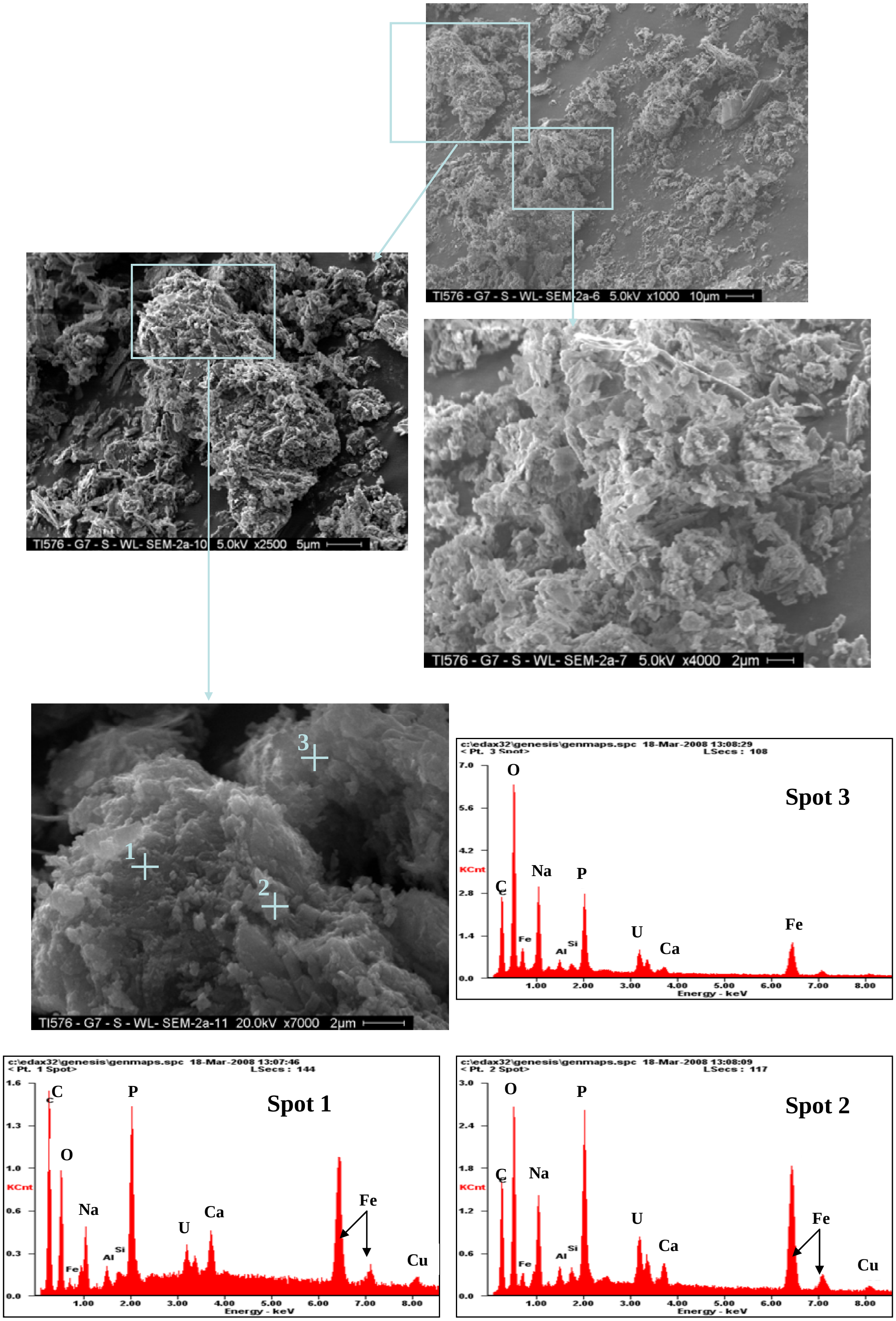

Figure 3.15. SEM Images of Washed Group 7 TBP Sludge with EDS Evaluation

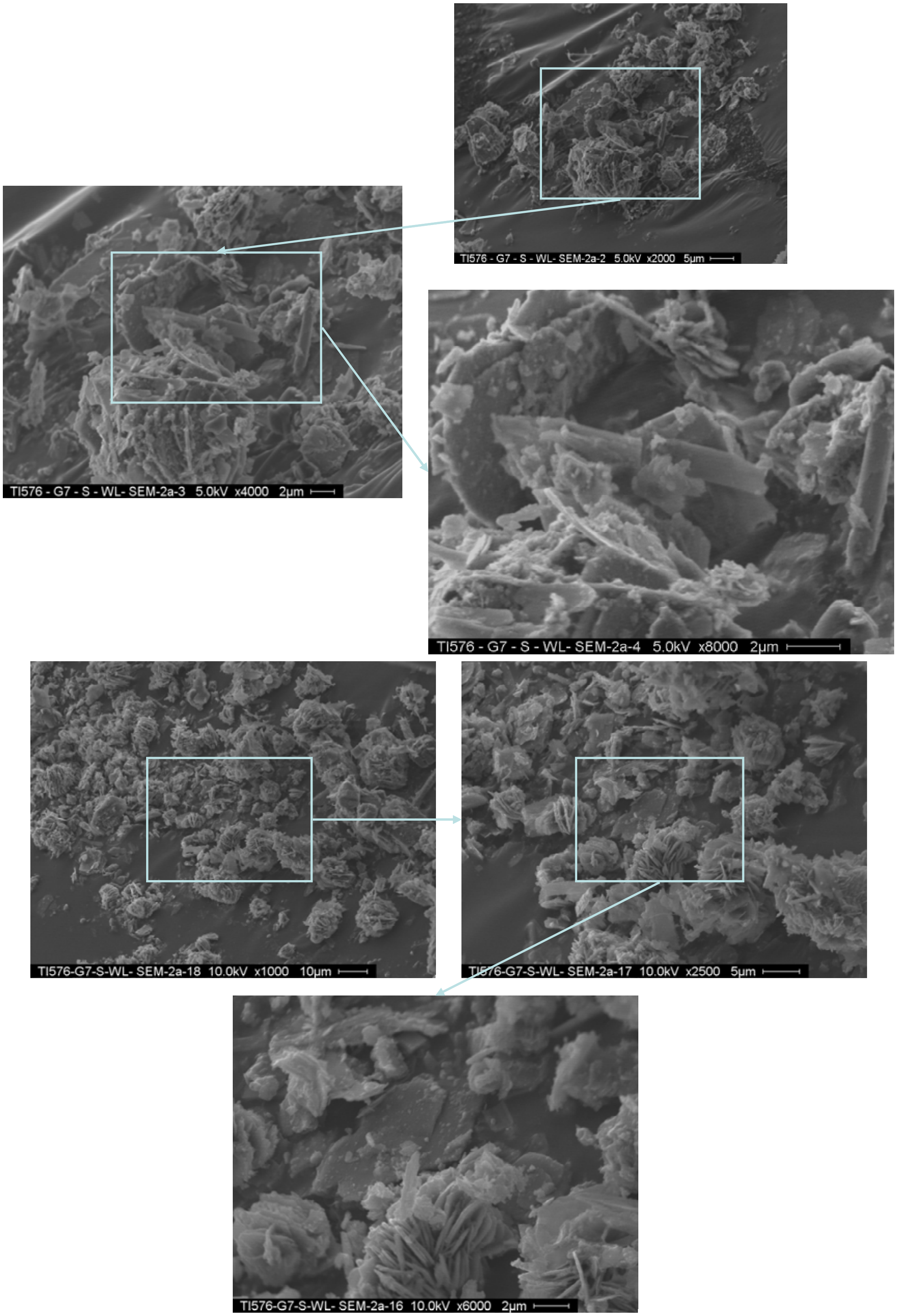

Figure 3.16. SEM Images of Washed Group 7 TBP Sludge

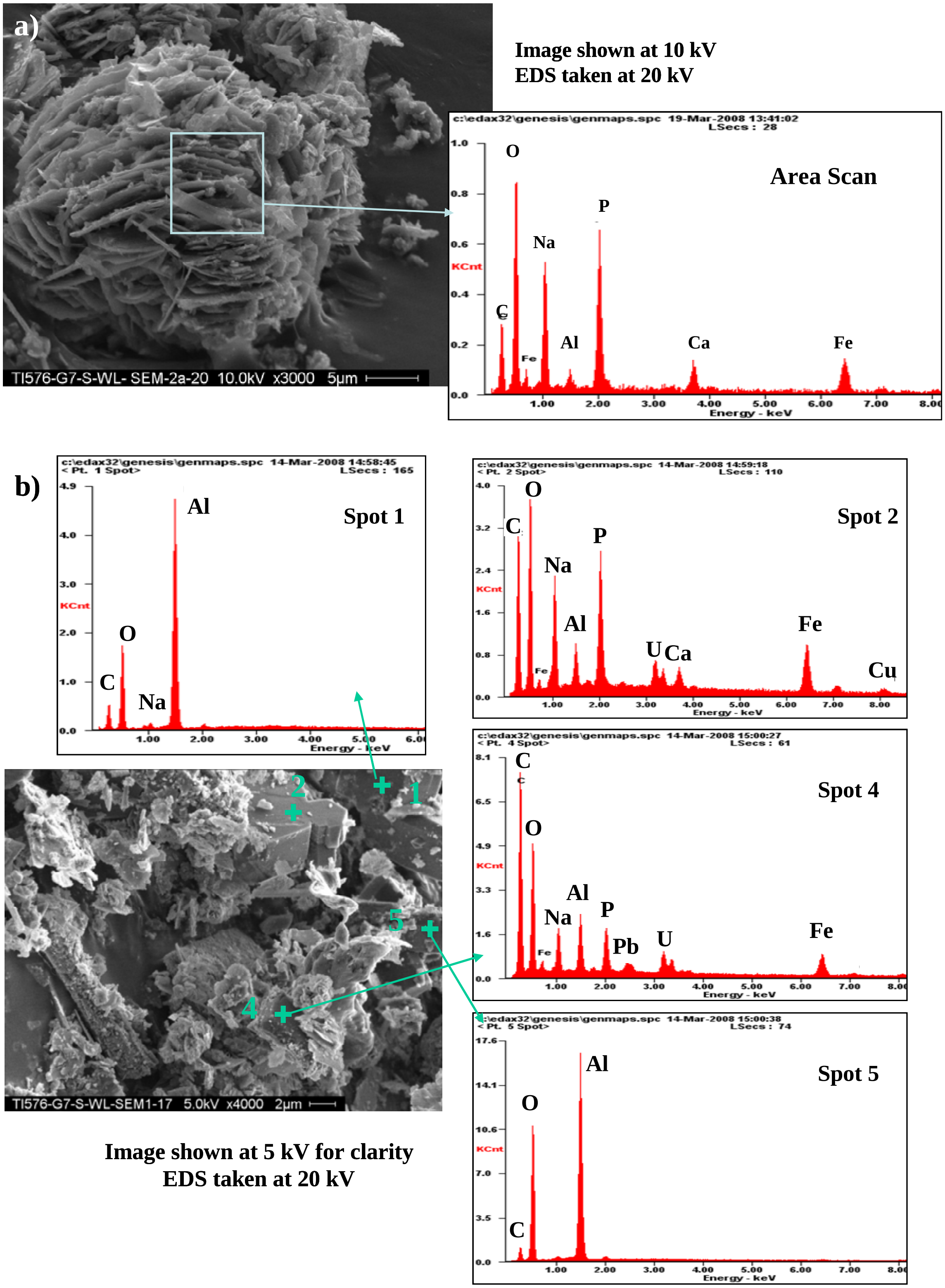

Image shown at 10 kV
EDS taken at 20 kV

Image shown at 5 kV for clarity
EDS taken at 20 kV

Figure 3.17. SEM Images with EDS Evaluation of Group 7 TBP Washed Sludge

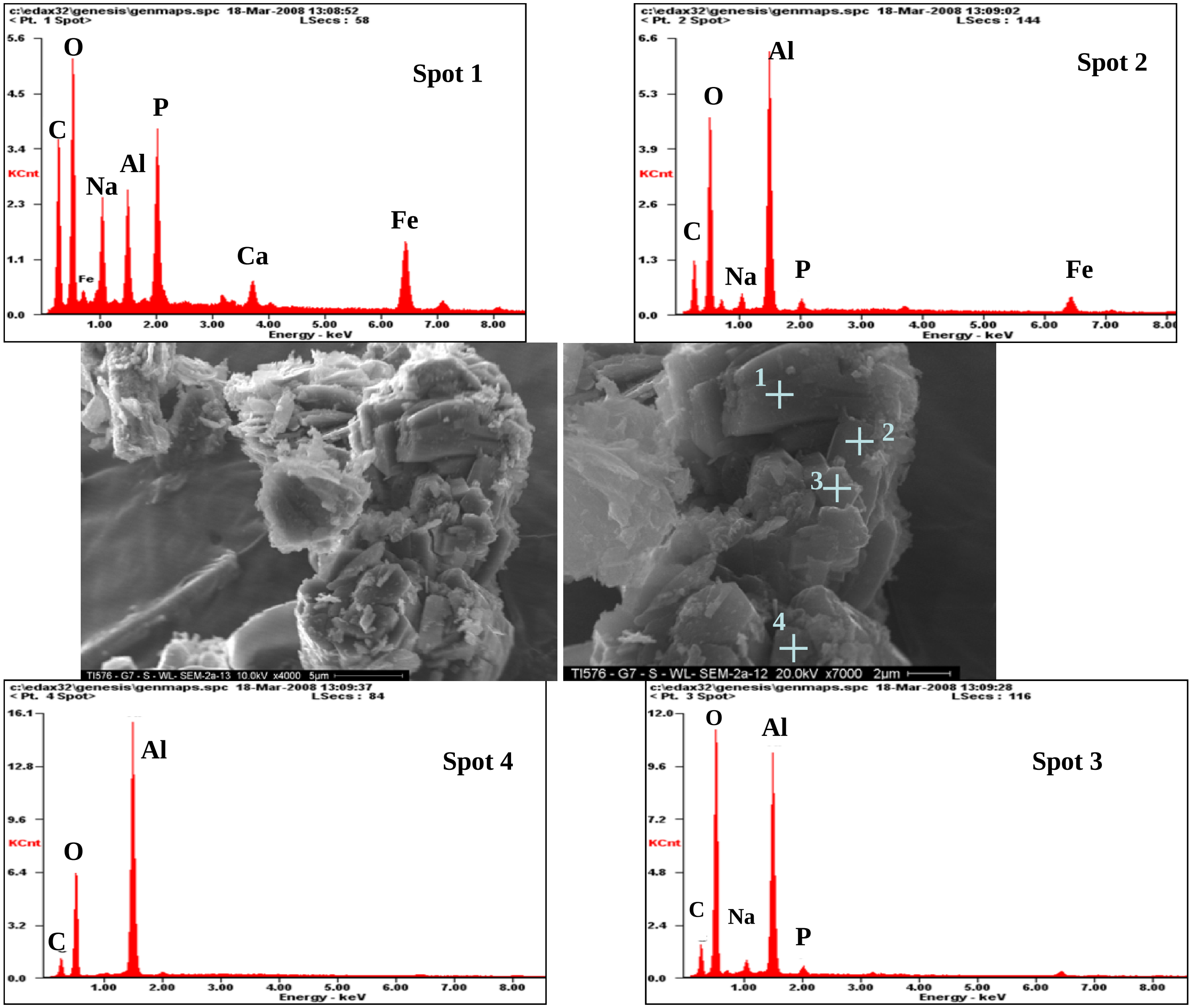

Figure 3.18. SEM Imaging of Washed Group 7 TBP Sludge with EDS Analysis

TEM images were obtained and the dominant surface area phase in the G7 sample was an iron calcium phosphate (see Figure 3.19). This phase occurred as a finely divided phase that was attached tenaciously to larger crystals that were iron and uranium rich. Large iron bearing particles were also found (see Figure 3.20). In Table 3.9, the compositional analysis of this phase is described. The major elements were Na, Fe, and P.

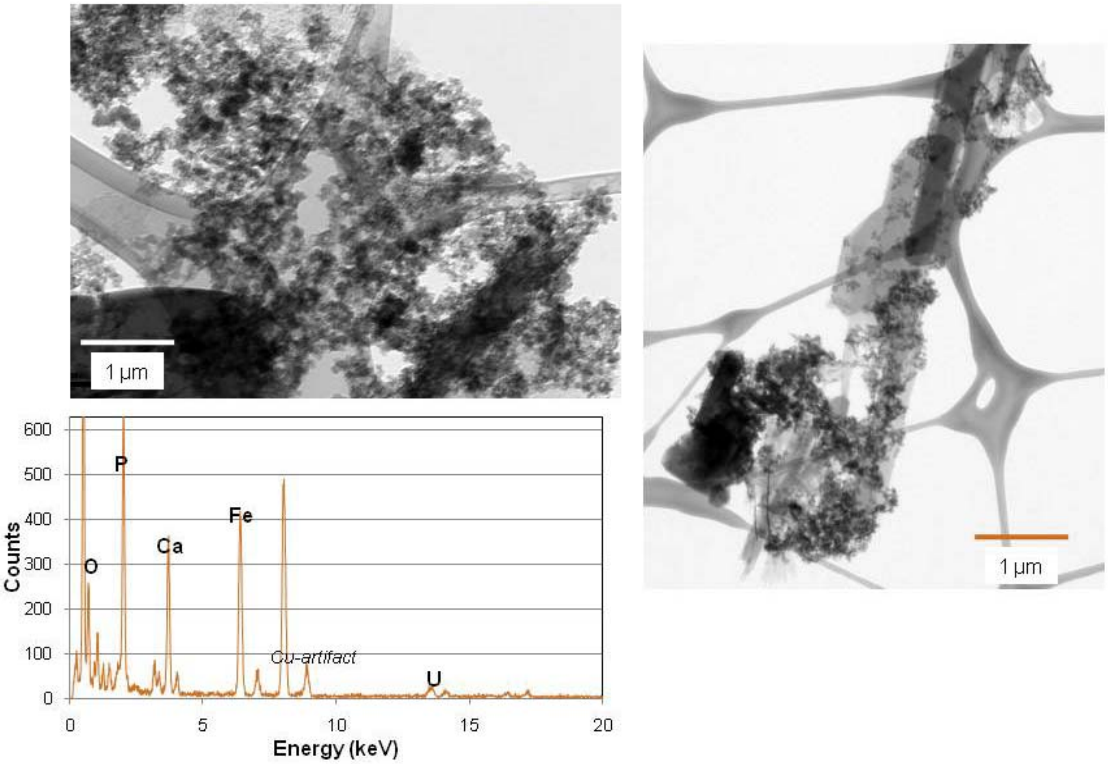

Figure 3.19. TEM Analysis of an Iron Calcium Phosphate Phase and EDS Analysis of the Phase

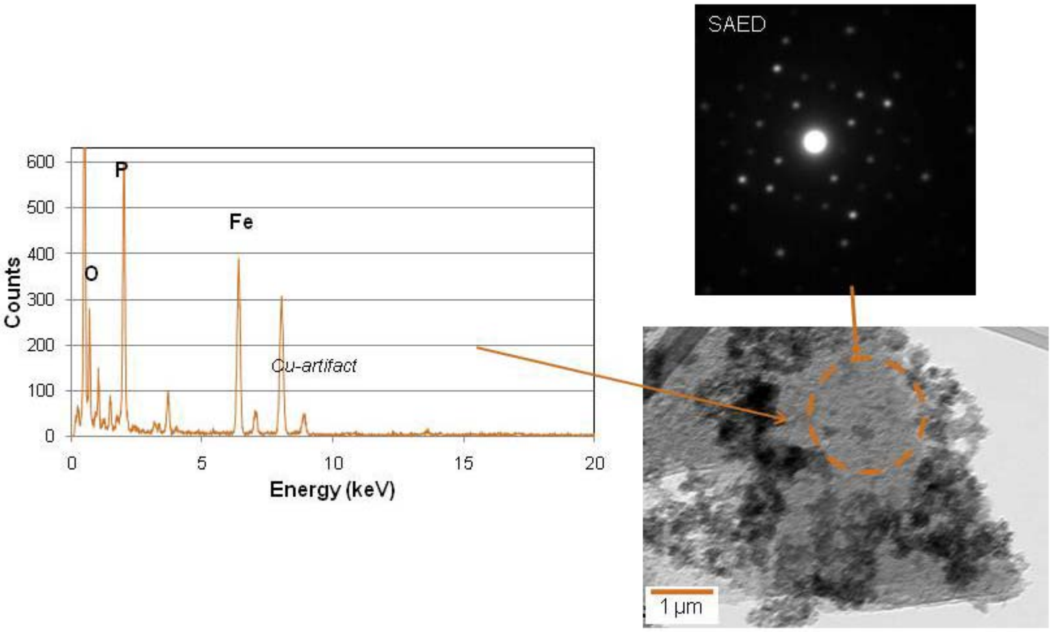

Figure 3.20 EDS analysis of an iron phosphate phase, electron diffraction of the phase and a TEM image.

The compositional analysis of the phase (Table 3.9) indicates, assuming that the phase is a phosphate, that the formula is $NaFe_{2\text{-}3}(PO_4)_{4\text{-}5}$. The iron phosphates, kidwellite $[Na(Fe^{3+},Cu)_{9+x}(PO_4)_6(OH)_{11}{\bullet}3(H_2O)]$ and cyrilovite $[NaFe^{3+}{}_3(PO_4)_2(OH)_4{\bullet}2(H_2O)]$, have been reported in nature in occurrence with autunites and other uranyl phosphates. Natrodufrenite $[Na(Fe^{3+}, Fe^{2+})(Fe^{3+}, Al)_5(PO_4)_4(O)_6{\bullet}2(H_2O)]$ and ercitite $[Na(Mn^{3+},Fe^{3+})(PO_4)(OH)_2{\bullet}(H_2O)]$ are formed under low-temperature hydrothermal conditions that can be similar to the environments found in the Hanford sludges. For example, cancrinite and the uranyl phosphates are known to form in laboratory tests under low-temperature and high-pH hydrothermal conditions. The best match in terms of diffraction, formation conditions, and composition is ercitite.

Table 3.9. EDS Analysis of Iron Phosphate Phase

Element	Weight %	Atomic %	Uncertainty %
Na(K)	6.55	10.99	0.185
Mg(K)	1.48	2.36	0.106
Al(K)	3.85	5.51	0.141
P(K)	38.04	47.38	0.419
Ca(K)	5.54	5.33	0.175
Fe(K)	38.65	26.70	0.462
Sr(K)	2.75	1.21	0.172
U(L)	3.14	0.51	0.538

Large crystals of a uranium phosphate were common in the sample. The particles were several micrometers in length and up to 1 to 2 µm across. The particles were electron transparent, suggesting that they were <50 to 100 nm thick (consistent with the PSD measurements). A few small precipitates were found on the surface of the acicular (needlelike; mineral growth in long and slender crystals) crystals. An

EDS probe was used to determine the exact composition of the phase. Sodium was visible but would be removed rapidly by condensing down the probe even slightly. Electron diffraction on the platy axis revealed a well-formed slightly distorted rectangular lattice (Figure 3.21). The crystal went amorphous under the electron beam after a few minutes of intense irradiation. Figure 3.21 shows a clear diffraction pattern of the phase, Figure 3.22a is a rotational average of the diffraction pattern, and Figure 3.22b is an EDS analysis of the phase. Based on the ease of amorphization, the composition, and the shape of the crystal, it was clear that the phase was a uranyl phosphate. There are many varieties of uranyl phosphates in nature; autunite and meta-autunite are the most common. At least three uranyl phosphate phases were suggested by the XRD analysis (see above). Figure 3.23 shows a prime example of a large single crystal of uranyl phosphate in the Group 7 sludge.

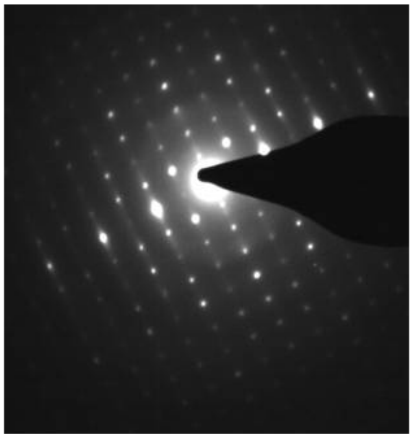

Figure 3.21. Electron Diffraction Pattern of U(VI) Phase in G7-S-WL

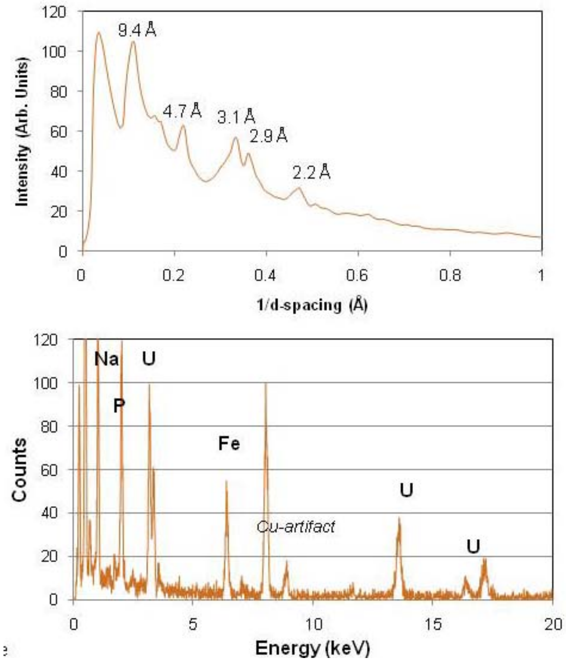

Figure 3.22. (a) Rotational Average Spectrum from Diffraction Pattern and (b) Compositional Analysis of U(VI) Phase

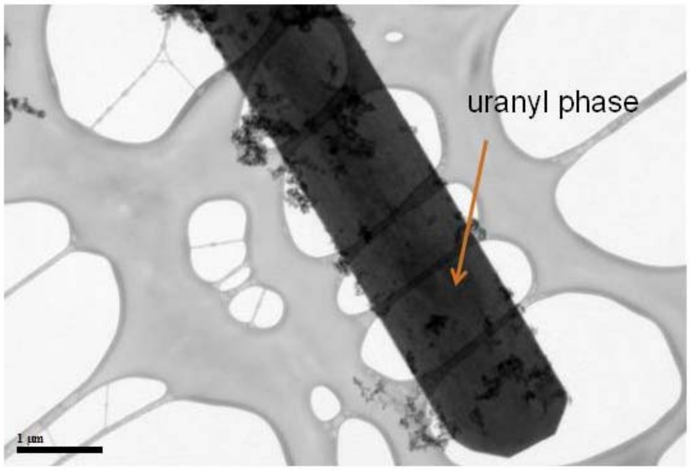

Figure 3.23. TEM Image of Large Sodium Uranyl Phosphate Phase in G7 Tank Sludge

4.0 Group 7 Tributyl Phosphate Sludge Batch Parametric Leaching

This section reports on and discusses the parametric leach testing and leaching results for the Group 7 TBP sludge slurry composite.

4.1 Group 7 Tributyl Phosphate Sludge Batch Parametric Leaching: Experimental

Parametric caustic leaching tests were performed on the Group 7 TBP sludge sample to determine the behavior of aluminum and phosphate during leaching at different conditions. The composite Group 7 sample material was rinsed with 0.01 M NaOH, subdivided, and subjected to a parametric test matrix for caustic leach testing as discussed in the following sections.

4.1.1 Initial Washing of the Group 7 Solids

The Group 7 composite sample was mixed with an overhead stirrer fitted with a bladed stainless steel impeller. A 98.4-g aliquot was removed with a large transfer pipette and transferred to a 200-mL centrifuge bottle. At a concentration of 0.123 g dry water-insoluble solids per gram of slurry, the 98.4-g slurry contained 12.1 g of water-insoluble solids. The slurry aliquot was centrifuged at ~2500 RPM (1200 G) for 15 min, and then the supernatant liquid was removed. The volume of centrifuged solids was estimated to be ~15 mL based on volume graduations on the sample bottle. Approximately 45 mL (3× the centrifuged solids volume) of 0.01 M NaOH was added to wash the solids. The slurry was placed on a vortex mixer to loosen the solids and then shaken for 15 minutes on a shaker table. The slurry was centrifuged at ~1200 G for 15 min, and then the supernatant liquid was removed. The washing steps were repeated twice for a total of three washes. The third wash was centrifuged for 65 minutes because the wash liquid had floating solids. After 65 minutes, there were still floating solids, so 0.5 mL of 19 M NaOH was added. The slurry was mixed gently and centrifuged for an additional 15 minutes at ~1200 G. At this point, the solution was clear and nearly colorless.

The washed solids were thinned by adding 80.6 g of deionized (DI) water to conduct the sample subdivision. While mixing this slurry with an overhead mixer, the sample bottle was knocked over. Approximately $^{2}/_{3}$ of the sample was lost, leaving 31.4 g of slurry. Since the sample had been mixing for ~10 minutes before the sample loss, it was assumed that the sample was reasonably well mixed, and it was calculated that the 31.4 g of slurry contained ~3.5 g of UDS.

To make up for the lost sample, a new 73.3-g aliquot of the sample was removed with a large transfer pipette and transferred to a 200-mL centrifuge bottle. At a concentration of 0.123 g dry water-insoluble solids per gram of slurry, the 73.3-g slurry contained 9.0 g of water-insoluble solids. The slurry aliquot was centrifuged at ~2500 RPM (1200 G) for 15 min, and then the supernatant liquid was removed. The solids were washed in the same manner as described above. Again, floating solids were observed during the third wash that did not settle after centrifuging for 75 minutes. In this case, approximately 5 g of the wash solution was left on the solids.

4.1.2 Division of the Washed Group 7 Solids

To conduct a successful sample subdivision, the two bottles containing washed centrifuged solids needed to be combined, and the total sample needed to be thinned. DI water (~50 mL) was added to the solids in the first wash vessel. The slurry was mixed by shaking by hand and the contents transferred to the second wash vessel. At this point, the first vessel was clean. Then DI water was added to the 100-mL mark on the second wash vessel, for a total of about 84 g of DI water in the solids.

An overhead mixer equipped with a three-bladed stainless steel impeller was used to homogenize the thinned slurry. Ten ~9.4-g slurry samples were transferred to 125-mL high-density polyethylene (HDPE) bottles with a large disposable polyethylene pipette. Each sample contained ~1 g UDS. The samples were removed from the hot cell for follow-on processing at the fume-hood workstation.

One additional sample (623-G7-WL-Solids) containing approximately 10.0 g of slurry was transferred to a 60-mL HDPE bottle. A portion of this sample was submitted for a KOH fusion and the following subsequent analyses: ICP-OES metals, GEA, Pu, total alpha, total beta, ^{90}Sr, and U by kinetic phosphorescence analysis (KPA). These analyses were performed to establish the starting composition of the washed solids.

4.1.3 Caustic Leaching of the Washed Group 7 Solids

The leaching test matrix for each of the 10 samples is summarized in Table 4.1. The test matrix evaluated the effects of free-hydroxide concentration (0.25 to 3 M NaOH) and temperature (40 to 80°C) on gibbsite and phosphorus leaching kinetics.

Table 4.1. Group 7 Caustic Leaching Conditions

	Free OH, M		**Na, M**		**Temperature, °C[(b)]**
Bottle ID	**Target**	**Measured[(a)]**	**Target**	**Measured[(a)]**	
G7-40-1	1	1.02	1	1.10	40
G7-40-3a	3	3.12	3	3.21	40
G7-40-3b	3	3.00	3	3.04	40
G7-40-3c	3	3.19	3	3.17	40
G7-60-0.25	0.25	0.24	0.25	0.28	60
G7-60-1	1	1.01	1	1.01	60
G7-60-3	3	3.02	3	3.00	60
G7-80-0.25	0.25	0.25	0.25	0.30	80
G7-80-1	1	1.05	1	1.04	80
G7-80-3	3	3.05	3	2.95	80

(a) The measured analyte concentrations represent the concentration obtained after a 24-h contact time.
(b) The temperature uncertainty was ±2.5°C.
Note: All analyte concentrations were measured at ambient (~21°C) temperature.
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The NaOH concentration in each leaching mixture was adjusted to support the test matrix. Sodium hydroxide was added to each aliquot of the washed solids slurry. For the four samples run at 40°C, 19 M sodium hydroxide was used and added in the following amounts: 5.3 mL to yield 1 M NaOH, and 15.8

mL to yield 3 M NaOH. For the samples run at 60 and 80°C, 10 M sodium hydroxide was used and added in the following amounts: 2.5 mL to yield 0.25 M NaOH, 10.0 mL to yield 1 M NaOH, and 30.0 mL to yield 3 M NaOH. The leaching mixtures were then diluted to a final volume of 100 mL (with an estimated uncertainty of 2 mL) with DI water. (The 100-mL volume had been pre-marked on each sample bottle.) The contact time with the concentrated NaOH was brief (<5 min). The sample bottles were weighed after each addition of reagents (NaOH and water). Each leaching vessel was closed with a cap equipped with a tube condenser. The condenser was used to eliminate pressurization and minimize water loss while at the same time minimizing the spread of contamination.

The sample slurries were transferred to a temperature-controlled shaker table. The temperature was controlled with an aluminum heating block (J-KEM Scientific, Inc.) equipped with a Type T thermocouple. The temperature of the sample solution was not monitored during this process. The heating block was supported on a J-KEM BTS-3500 digital bench-top shaker (Figure 4.1). The shaking speed was digitally controlled to 200 RPM; based on visual inspection, the solids were well suspended in solution. The samples were grouped according to the leaching temperature, and one group was leach-tested at a time. The heating block was pre-heated to the appropriate temperature before leach testing.

Figure 4.1. Aluminum Heating Block and Shaker Table Used in Parametric Leaching Tests

The leaching mixtures were shaken at temperature for 24 hours, and solution samples were withdrawn at 0 (taken before insertion into heating block), 1, 2, 4, 8, and 24 hours. At each sampling time, the shaker was stopped, and the solids were allowed to settle for ~5 to 10 min, resulting in sufficient clarification of the aqueous portion to support sampling without removing any solids. Approximately 1.5 mL of the clarified leachate solution was withdrawn with a transfer pipette and filtered through a 0.45-μm pore size nylon syringe filter; the syringe filter and the syringe had been pre-heated in an oven to the sample temperature (40, 60, or 80°C) before filtering in an effort to minimize temperature changes impacting the sample. One 0.5-mL sample of filtered solution was acidified with 15 mL of 0.3 M HNO_3 for analysis by ICP-OES; another 0.5-mL sample of filtered solution was removed for analysis by IC. The remaining filtered solution was returned to the leaching vessel, and the leaching process was continued. The new liquid level was marked after each sample was taken. Evaporation was minimal during the course of the experiment, but when evaporation was observed, DI water was added to restore the volume to the previously marked liquid level. After 24 hours, additional leachate samples were taken to determine the free-hydroxide ion concentration and gamma-emitting isotopes by GEA.

After the final samples were taken at temperature, the slurries were removed from the mixing/heating block and cooled to ambient (~22^{o}C) temperature. The slurries were centrifuged, and the leachate was decanted.(a)

The equilibrium concentration values for free hydroxide and sodium are shown in Table 4.1 and were based on results from the samples taken at 24 hours.

4.1.4 Washing of Caustic Leached Group 7 Solids for Analysis

The solids from the triplicate samples (G7-40-3a, -3b, and -3c, leached at 40°C in 3 M NaOH, and each consisting of ~2.4 g centrifuged slurry) were prepared for characterization as shown in Figure 4.2. One of the solids samples was slurried in ~15 mL of 0.01 M NaOH and divided between the remaining two solids samples. The leaching bottle was then rinsed with 10 mL of 0.01 M NaOH, and the wash was split between the remaining two solids samples. The solids were mixed on a shaker table for 15 minutes. The slurry was centrifuged for 5 min and the supernatant removed. Dilute sodium hydroxide solution (0.01 M; 15 mL) was added to each of the solids, the compacted solids were broken up with a disposable pipette, and the two slurry samples were mixed on a shaker table for 15 minutes. The two slurry samples were centrifuged for 5 min and the supernatant removed. The wash steps were repeated once more for a total of three washes. Additional 0.01 M NaOH was used to move the solids from one of the bottles to combine all solids in one bottle. The sample was centrifuged for 5 min and the supernatant removed. After the final wash, the solids were slurried in ~2 mL of DI water and sub-divided for analysis by PSD, XRD, TEM, SEM, a surface area measurement with BET, and a KOH fusion with subsequent analysis for ICP-OES metals, GEA, Pu, total alpha, total beta, ^{90}Sr, and U by KPA.

(a) The contact dose rates of the leached solids were too high to safely conduct transfer to volume-graduated centrifuge tubes to assess the volume of centrifuged solids.

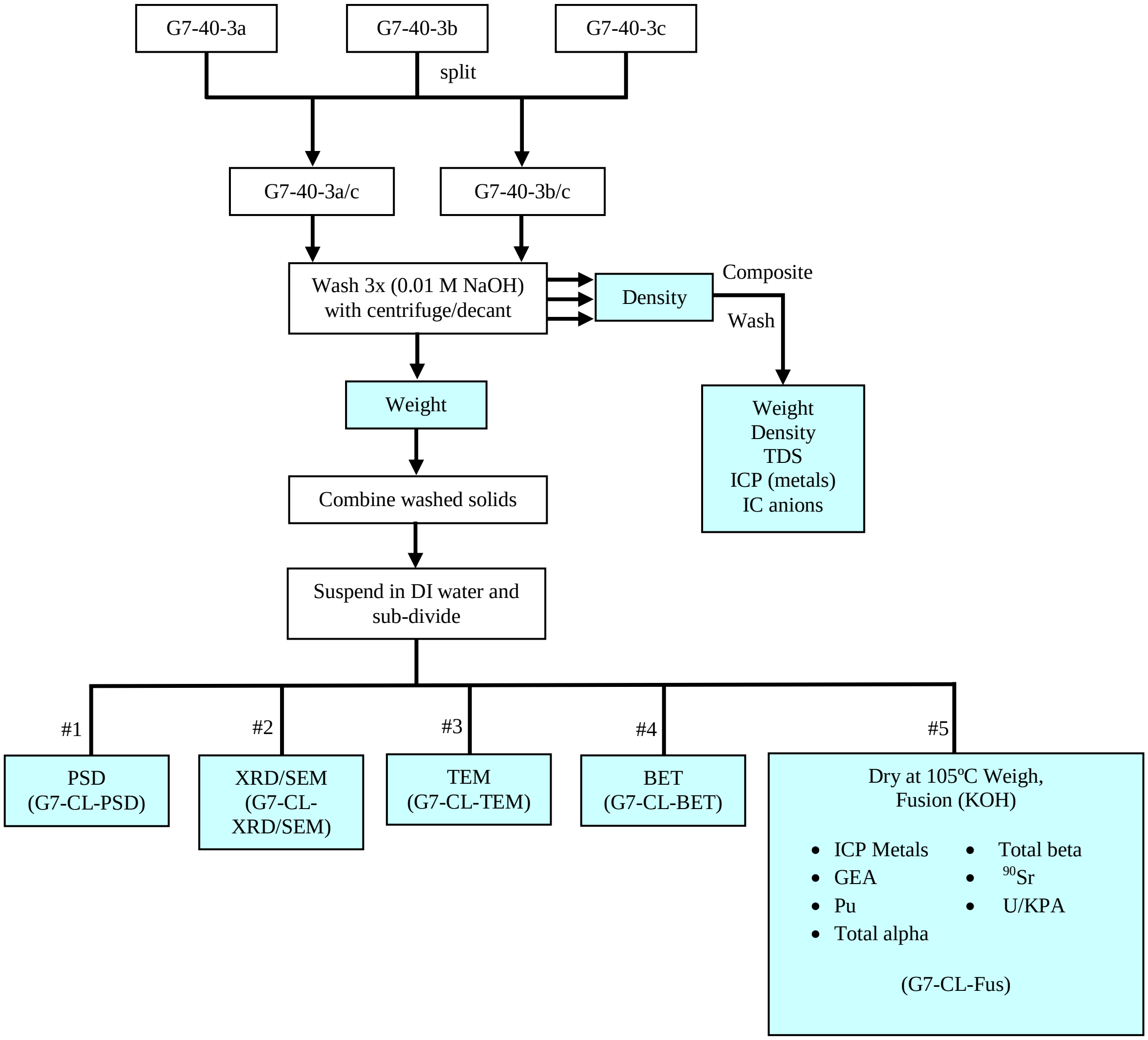

Figure 4.2. Washing, Subdivision, and Analysis Scheme for the Group 7 Caustic-Leached Solids

4.2 Group 7 Tributyl Phosphate Sludge Parametric Caustic-Leaching Test Results

The Group 7 waste was anticipated to be high in phosphorus as well as aluminum in the form of gibbsite. Therefore, the parametric leach testing of this waste sample was directed toward understanding gibbsite and phosphorus dissolution in the actual tank waste to understand and subsequently match the dissolution properties to a simulant material. The parametric leaching results and residual solids composition are discussed in the following sections. Data for the figures in this section can be found in Appendix G.

4.2.1 Time, Temperature, and Hydroxide Effects on Aluminum Dissolution from the Group 7 Solids

The rate and extent of Al removal from the washed Group 7 solids were investigated as a function of time, temperature, and free-hydroxide concentration. As indicated in Section 3, the aluminum appears to be a mix of gibbsite and an aluminum-bearing phosphate phase. The aluminum leaching data at 40, 60, and 80°C at varying free-hydroxide concentrations are plotted in Figure 4.3 through Figure 4.5, respectively. A measure of experimental precision is shown by the triplicate tests conducted at 3 M free hydroxide and at 40°C in Figure 4.3. The scatter in the data was within the analytical characterization uncertainty of ±15%.

At the higher temperatures (60 and 80°C), aluminum dissolution reached a steady-state value. At 40°C, the amount of Al dissolved continued increasing throughout the entire sampling period. At 60°C, the Al dissolution reached a steady-state value between 4 and 8 hours, except in the case of 1 M NaOH, which had a significant rise in the Al concentration between 8 and 24 hours, and reached nearly the same final Al concentration as the sample in 3 M NaOH. The sample in 0.25 M NaOH only reached ~60% dissolved Al, much less than the values obtained in 1 and 3 M NaOH. At 80°C, for the two highest hydroxide concentrations, steady-state was reached between 2 and 4 hours. Between 80 and 90% of the Al was dissolved at the higher temperatures, suggesting that a small amount of a caustic-insoluble Al compound was present, perhaps zeolite as identified by XRD.

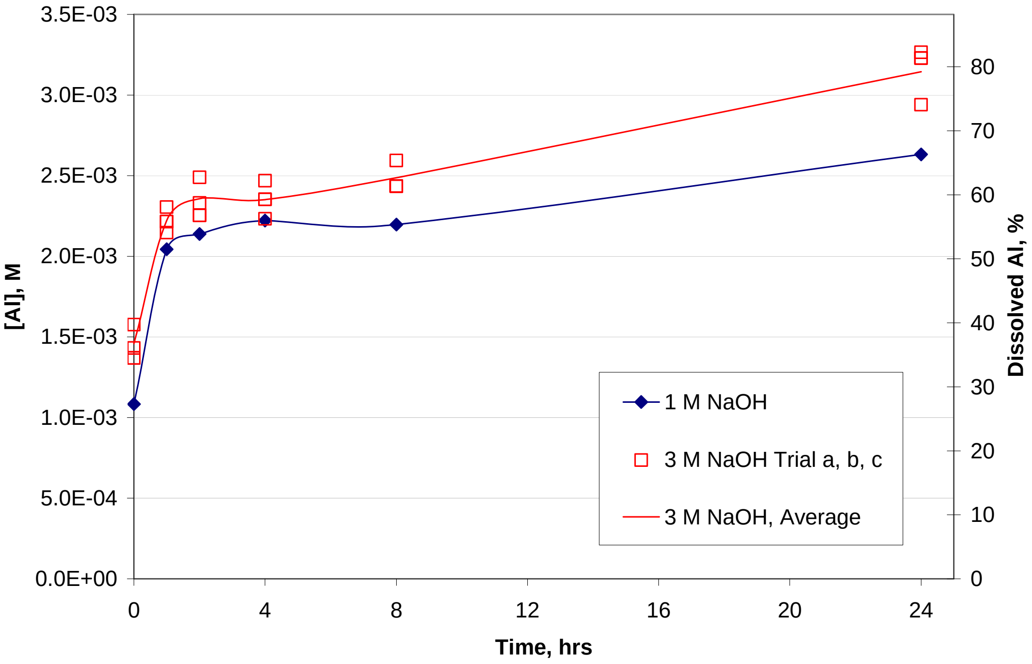

Figure 4.3. Aluminum Concentration and Percent Removed Versus Time at 40°C for Leaching of the Group 7 Washed Solids in 1 and 3 M NaOH

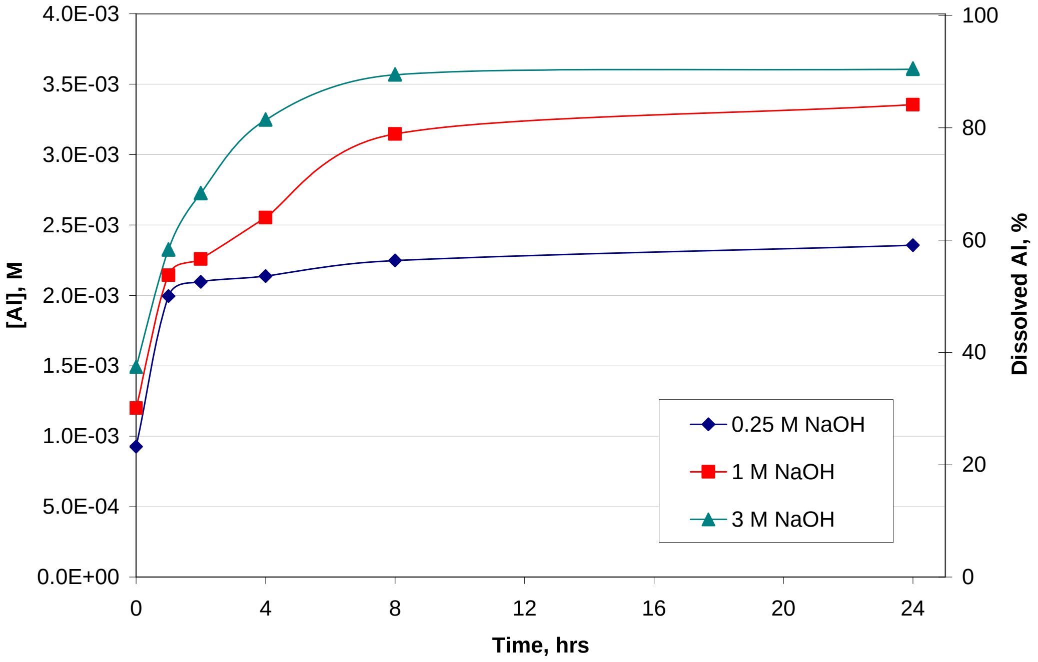

Figure 4.4. Aluminum Concentration and Percent Removed Versus Time at 60°C for Leaching of the Group 7 Washed Solids in 0.25, 1, and 3 M NaOH

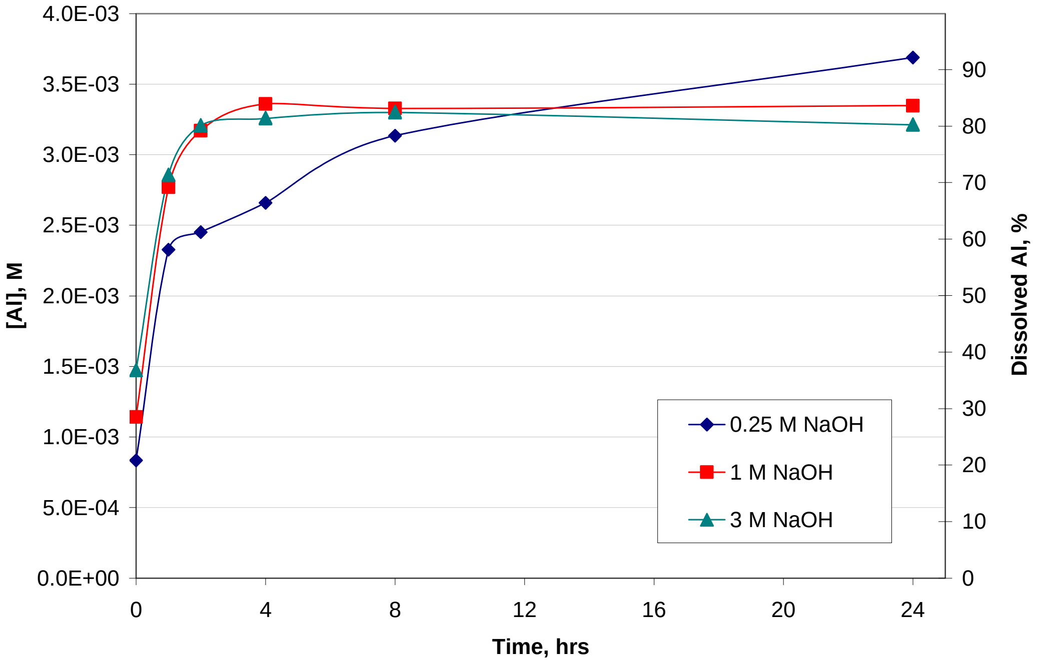

Figure 4.5. Aluminum Concentration and Percent Removed Versus Time at 80°C for Leaching of the Group 7 Washed Solids in 0.25, 1, and 3 M NaOH

The same data are re-plotted in Figure 4.6 through Figure 4.8 to show the effect of temperature at constant free-hydroxide concentrations of 0.25, 1, and 3 M NaOH, respectively.

The temperature had a large effect on the gibbsite dissolution rate at lower hydroxide concentrations. In 0.25 M NaOH, the reaction at 60°C was slower and much less Al was removed than at 80°C, reaching ~60 and 90% Al dissolution, respectively. In 1 M NaOH, approximately the same Al dissolution was achieved at the two higher temperatures, with the dissolution at 40°C being ~20% less. In 3 M NaOH, the samples at all three temperatures reached nearly the same final value (~80 to 90%). Note that during all of these tests, there appeared to be two forms of aluminum dissolving. In all these tests, roughly 50% of the aluminum dissolved rapidly. This initial dissolution was likely due to the dissolution of an aluminum phosphate phase. Subsequently, an additional 30 to 40% of the aluminum (likely gibbsite) dissolved with extended time. As expected, the data are consistent with faster dissolution at higher temperatures and hydroxide concentrations.

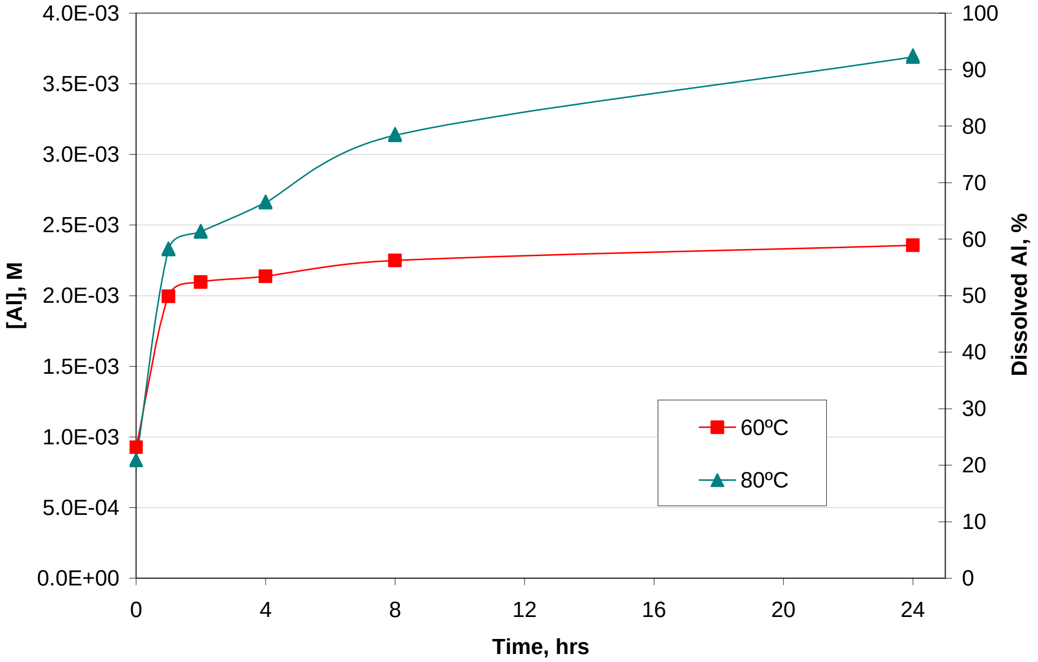

Figure 4.6. Aluminum Concentration and Percent Dissolved in 0.25 M NaOH

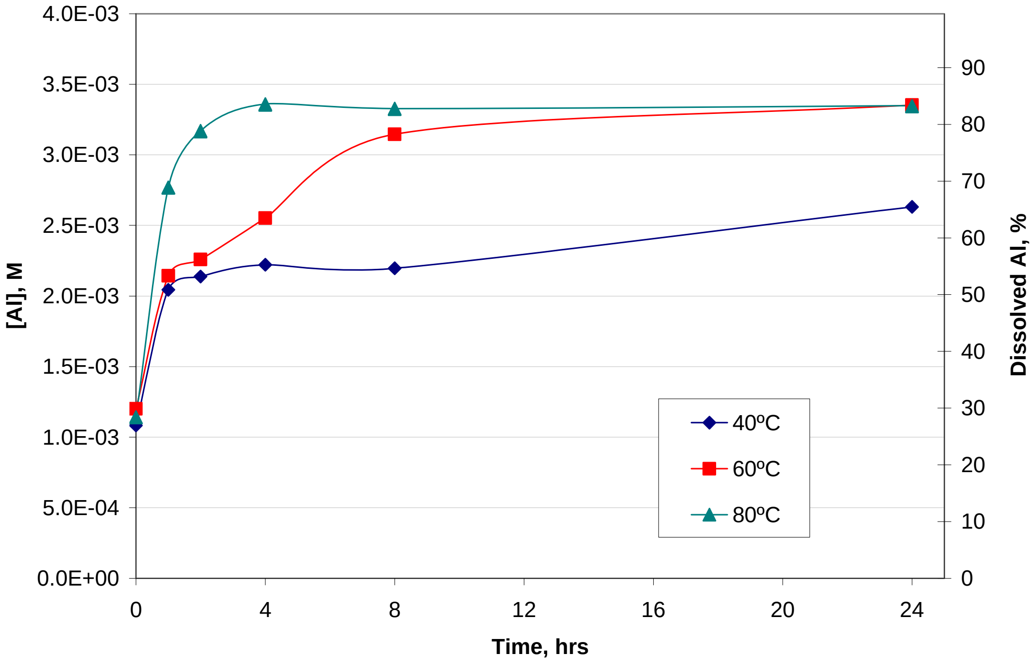

Figure 4.7. Aluminum Concentration and Percent Dissolved in 1 M NaOH

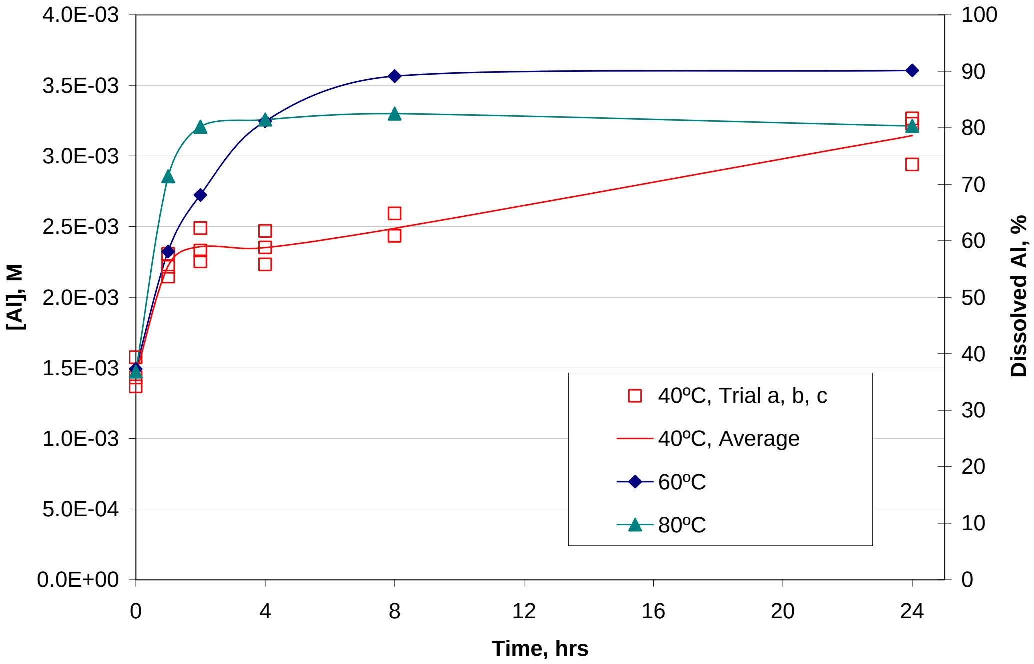

Figure 4.8. Aluminum Concentration and Percent Dissolved in 3 M NaOH

4.2.2 Time, Temperature, and Hydroxide Effects on Phosphorus Dissolution from the Group 7 Solids

The rate and extent of P removal from the washed Group 7 solids were investigated as a function of time, temperature, and free-hydroxide concentration. The phosphorus leaching data at 40, 60, and 80°C at varying free-hydroxide concentrations are plotted in Figure 4.9 through Figure 4.11, respectively. A measure of experimental precision is shown by the triplicate tests conducted at 3 M free hydroxide and at 40°C in Figure 4.9. The scatter in the data was within the analytical characterization uncertainty of ±15%.

Under all conditions, there was rapid transfer of P to the liquid phase. Even before heating was applied (i.e., at t = 0), ~50 to 80% of the P was removed from the solid phase. In this respect, the P behavior was similar to what was observed for the bismuth phosphate sludge (Lumetta et al. 2008). The amount of P removed before the application of heat was dependent on the hydroxide concentration, with ~52% of the P removed in 0.25 M NaOH, 61 to 69% of the P removed in 1 M NaOH, and 71 to 82% of the P removed in 3 M NaOH. For all temperatures at all hydroxide concentrations, a steady-state value of P dissolution was reached in the first hour, with nearly complete P dissolution obtained for all conditions (85 to 95%). Hydroxide concentration had virtually no effect on the P dissolution once heating was applied. Within the experimental uncertainty, the same amount of P was dissolved in samples run in 0.25 M NaOH as in samples run in 3 M NaOH.

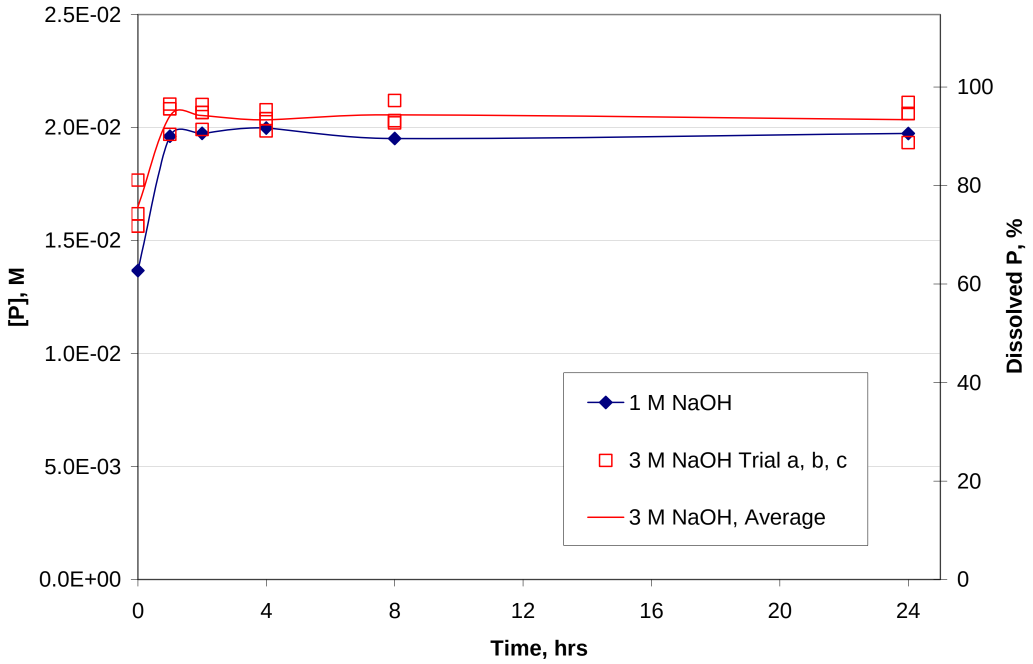

Figure 4.9. Phosphorus Concentration and Percent Removed Versus Time at 40°C for Leaching of the Group 7 Washed Solids in 1 and 3 M NaOH

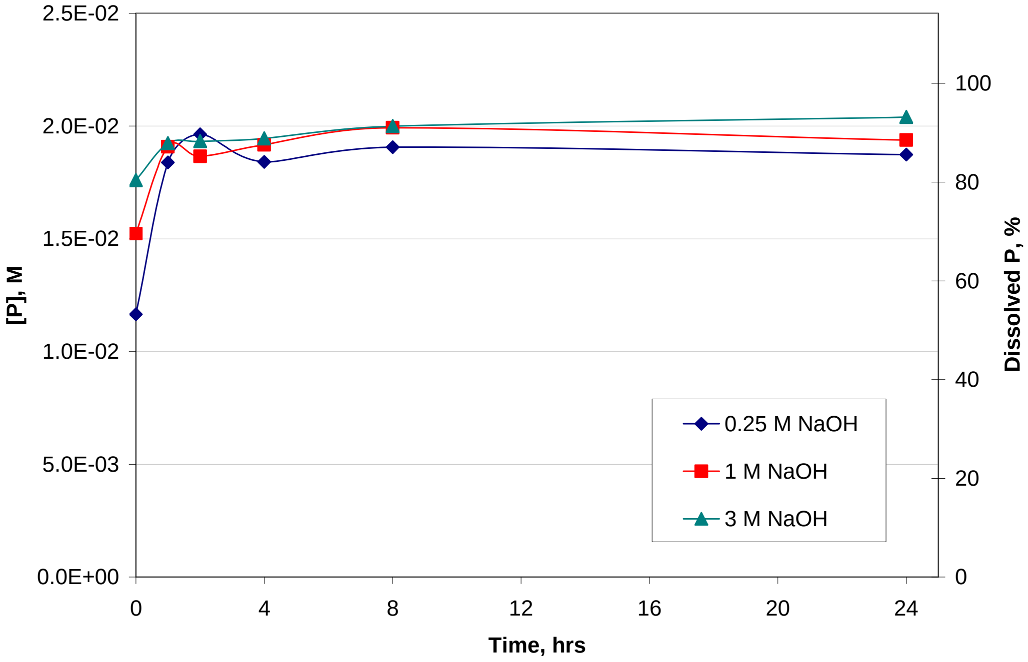

Figure 4.10. Phosphorus Concentration and Percent Removed Versus Time at 60°C for Leaching of the Group 7 Washed Solids in 0.25, 1, and 3 M NaOH

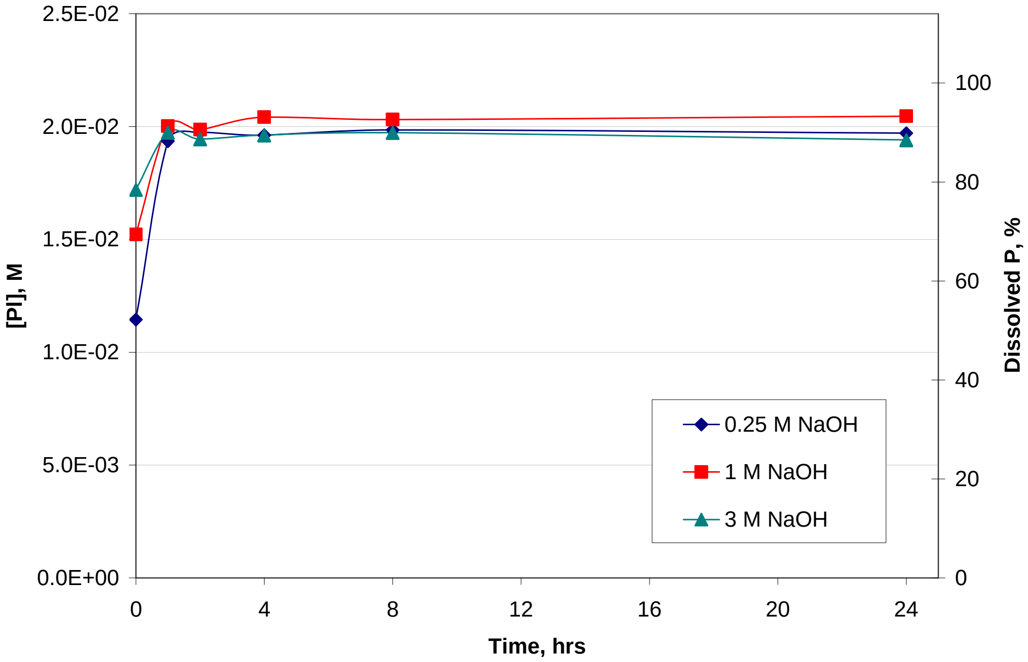

Figure 4.11. Phosphorus Concentration and Percent Removed Versus Time at 80°C for Leaching of the Group 7 Washed Solids in 0.25, 1, and 3 M NaOH

The same data are re-plotted in Figure 4.12 through Figure 4.14 to show the effect of temperature at constant free-hydroxide concentrations of 0.25, 1, and 3 M NaOH, respectively. The temperature had little influence on the P leaching kinetics. Rapid P removal was observed in all cases, typically with a steady-state value being achieved within 1 hour.

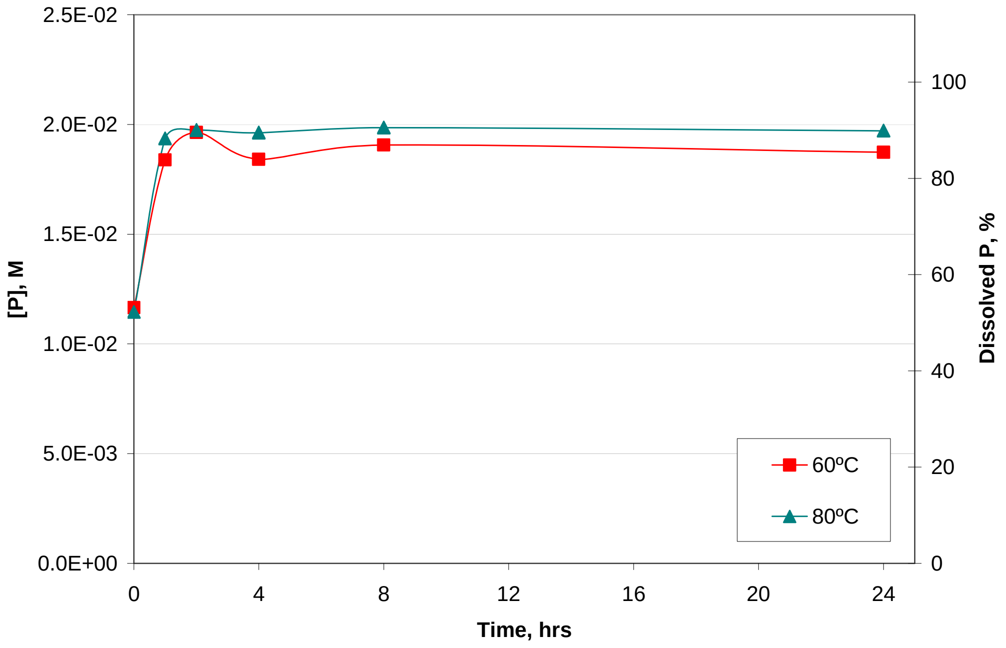

Figure 4.12. Phosphorus Concentration and Percent Removed in 0.25 M NaOH

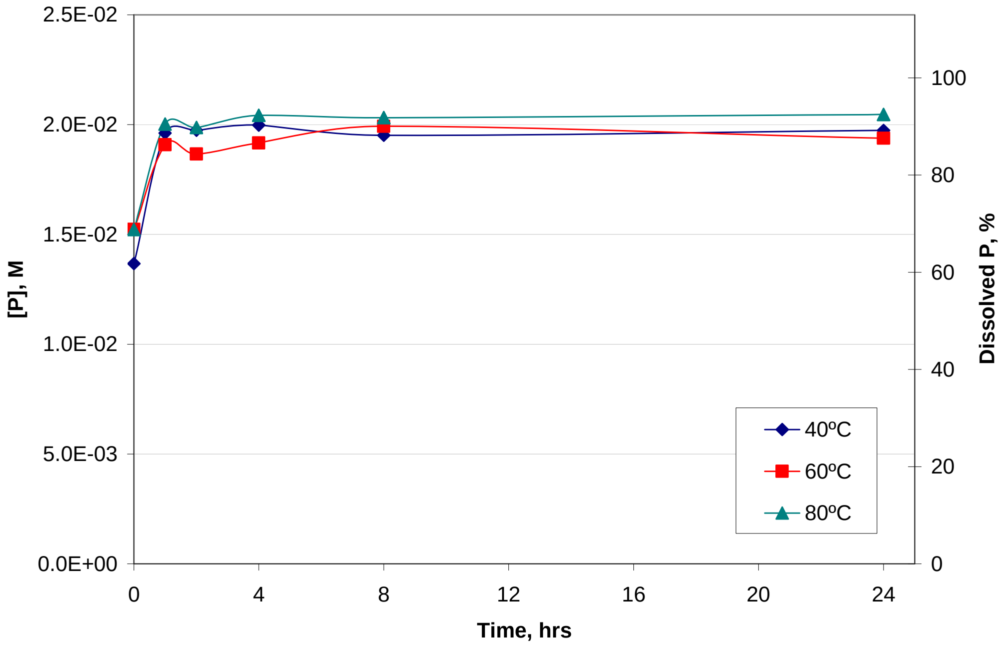

Figure 4.13. Phosphorus Concentration and Percent Removed in 1 M NaOH

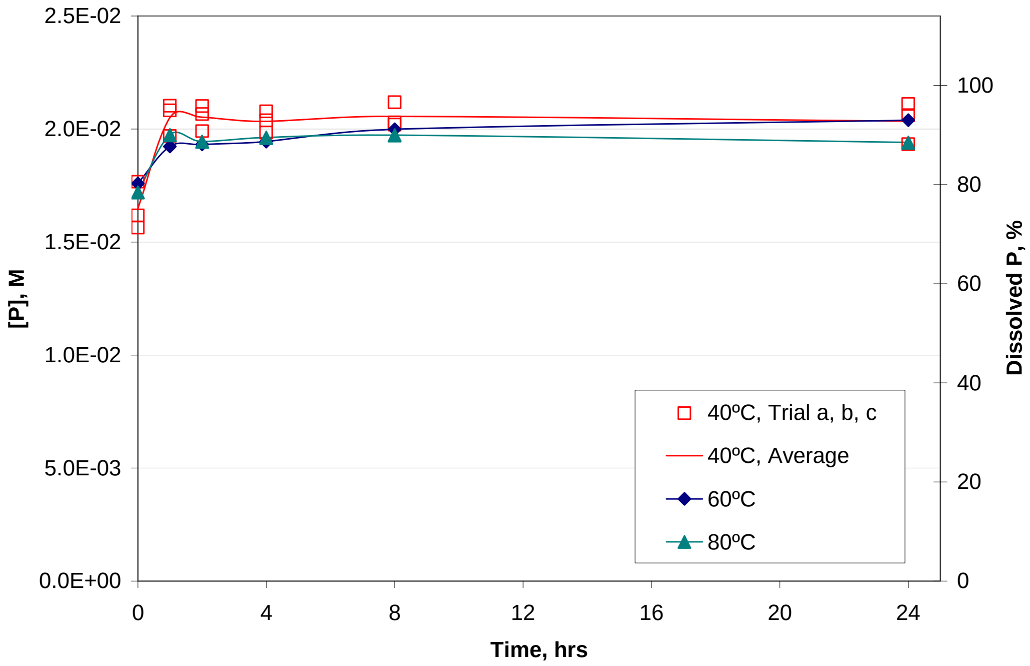

Figure 4.14. Phosphorus Concentration and Percent Removed in 3 M NaOH

4.2.3 Time, Temperature, and Hydroxide Effects on Uranium Dissolution from the Group 7 Solids

Figure 4.15 and Figure 4.16 show the effect of NaOH concentration and temperature on the behavior of uranium under caustic-leaching conditions. Under all conditions, there was an initial rapid transfer of U to the liquid phase. Before heating was applied (i.e., at t = 0), 50 to 100% of the U was observed to be in the liquid phase. As heat was applied, the uranium re-precipitated, leaving only 12 to 20% in solution.

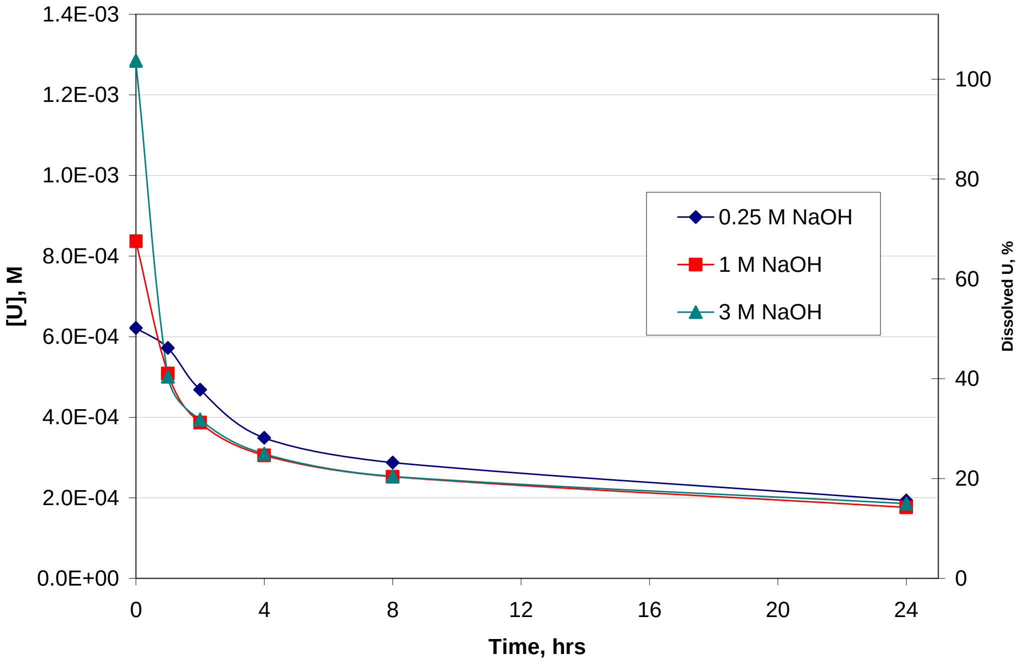

Figure 4.15. Uranium Concentration and Percent Removed Versus Time at 60°C for Leaching of the Group 7 Washed Solids in 0.25, 1, and 3 M NaOH

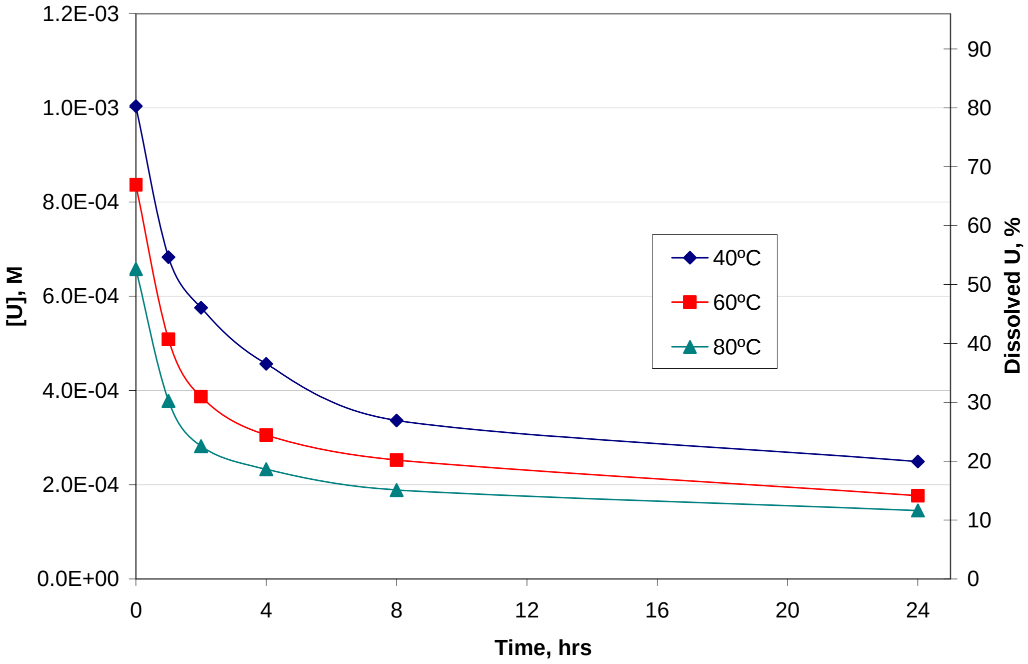

Figure 4.16. Uranium Concentration and Percent Removed in 1 M NaOH

4.2.4 Anions, Silicon, Cr, and Iron Leaching Behavior

The concentrations of Cr, Fe, and Si were measured by ICP-OES. The anionic compositions were also assessed at each sampling period. The Cr concentrations were generally low (on the order of 10^{-5} M), but appear to generally increase with increasing leaching time. The Fe, Si, and anion data were generally above the EQL. The Fe, Si, and anion concentrations (fluoride, nitrite, nitrate, and sulfate) in the leachate did not significantly change during the leach testing. The results are summarized in Appendix G.

4.2.5 Assessment of Final Leaching Conditions

A summary of the final (24-h) leaching solution chemistry and physical parameters is shown in Table 4.2. The final free-hydroxide and sodium concentrations were at the targeted values within the uncertainty of the analytical methods (±15%). The calculated percentage of phosphorus that was removed at each leaching condition is also shown. Appendix G provides a compilation of the concentrations of Al, Cr, Fe, Na, P, Si, U, fluoride, nitrite, nitrate, phosphate, and sulfate in the final leaching solutions. The GEA results for ^{60}Co and ^{241}Am were <MDL; the GEA results are also provided in Appendix G.

Table 4.2. Group 7 TBP Sludge Leaching Final (24 hr) Aqueous Phase Conditions

Temp., °C	Density, g/mL	Free OH, M	Na, M	Al, M	P, M	Wt % P Removed
40	1.05	1.02	1.10	2.63E-03	1.97E-02	89.0
40 trial a	1.14	3.12	3.21	3.27E-03	2.11E-02	87.7
40 trial b	1.14	3.00	3.04	2.94E-03	1.93E-02	88.3
40 trial c	1.14	3.19	3.17	3.23E-03	2.06E-02	94.6
60	1.02	0.24	0.28	2.36E-03	1.87E-02	85.5
60	1.05	1.01	1.01	3.35E-03	1.94E-02	88.5
60	1.13	3.02	3.00	3.61E-03	2.04E-02	93.3
80	1.02	0.25	0.30	3.69E-03	1.97E-02	90.0
80	1.05	1.05	1.04	3.35E-03	2.05E-02	92.5
80	1.13	3.05	2.95	3.21E-03	1.94E-02	88.4
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4.2.6 Comparison of Initial and Caustic-Leached and Washed Solids Properties

The Group 7 solids that had been caustic leached at 40°C in 3 M NaOH for 24 hours were combined and washed in preparation for analysis. The wash solution composition and the washed solids chemical, radiochemical, particle size, and crystal habit are discussed.

4.2.6.1 Leached-Solids Wash Solution

After the third washing of the caustic-leached Group 7 solids, the wet centrifuged solids mass was 4.5 g. The densities of the three sequential wash solutions were 1.023 g/mL, 1.003 g/mL, and 1.003 g/mL, respectively. The composite wash-solution (126.8 mL volume) density, ICP metals, and anion composition are shown in Table 4.3.

The analysis of the wash solution by ICP-OES for metal content indicated the presence of primarily Na, Al, and Si. There was no evidence of additional dissolution of these species during the washing process.

Table 4.3. Group 7 Solids Wash Solution Composition and Density

Analyte	µg/mL	Analyte	µg/mL	Density Measurement	g/mL
Al	5.45	Si	<0.85	Density	1.007
Cr	[0.28]	nitrate	[5.10]		
Na	3,665	phosphate	126		
P	[39.4]	sulfate	[7.40]		

4.2.6.2 Chemical and Radiochemical Composition

The initial composition of washed solids (before caustic leaching) is provided in Table 4.4 along with selected results from the initial characterization study. The solids composition after leaching in 3 M NaOH at 40°C for 24 hours and washing is also shown in Table 4.4. Both the initial solids for characterization and the "before leaching" material had been extensively washed, i.e., little or no salt entrainment was expected (except for NaOH from the washing liquid). The composition of the initial characterization sample was generally consistent with that for the "before leaching" material.

Table 4.4. Group 7 TBP Sludge Leached Solids Composition and Leach Factors (Dry Mass Basis)

Analyte	Avg. Initial Charac. µg/g (ASR 8108)	Avg. Before Leaching, µg/g (ASR 8144)	Avg. After Leaching, µg/g (ASR 8144)	Observed Leach Factor
Al	16,000	15,100	[6,550]	0.79
B	[115]	<33.7	<31.452	--
Bi	5,710	7,095	13,950	--
Cd	<7.7	[43]	[66]	0.25
Fe	140,000	165,500	331,000	--
Mn	884	990	1,975	--
Na	130,500	150,000	[32,500]	0.89
P	107,500	124,000	18,400	0.93
S	[875]	<1,353	<1347.953	--
Si	7,285	9,680	[8,250]	0.58
Sr	3,905	4,670	9,165	--
U	113,000	125,500	217,500	0.15
Zn	687	905	749	0.59
Zr	<9.3	[30]	[120]	--
U KPA	114,500	134,157	227,641	0.17
^{60}Co	2.11E-2	1.65E-02	4.65E-02	--
^{90}Sr	7.41E+2	9.36E+02	1863.46	--
^{137}Cs	3.64E+1	4.83E+01	1.10E+00	0.99
^{154}Eu	5.90E-2	7.07E-02	1.40E-01	0.03
^{155}Eu	<5E-2	7.58E-02	8.89E-02	0.42
^{238}Pu	5.63E-3	4.49E-03	1.09E-02	--

Table 4.4 (contd)

Analyte	Avg. Initial Charac. µg/g (ASR 8108)	Avg. Before Leaching, µg/g (ASR 8144)	Avg. After Leaching, µg/g (ASR 8144)	Observed Leach Factor
$^{239+240}$Pu	1.95E-1	2.51E-01	5.00E-01	--
^{241}Am	8.68E-2	< 1.E-1	2.32E-01	--
total alpha	3.00E-1	4.57E-01	1.04E+00	--
total beta	1.57E+3	1.95E+03	3.72E+03	--
Opportunistic				
Ag	[26]	<5.922	<6.127	--
As	<104	<153.968	<159.304	--
Ba	289	358	726	--
Be	[0.66]	[0.38]	[0.39]	0.50
Ca	[16,000]	[18,000]	[37,000]	--
Ce	[115]	[93]	[235]	--
Co	[25]	[30]	[60]	--
Cr	718	829	1,370	0.19
Cu	142	287	315	0.46
Dy	<7.7	<11.449	<11.686	--
Eu	[3.4]	<1.461	[2.5]	--
K	na	na	na	na
La	[52]	[88]	181	--
Li	87.3	113	135	0.41
Mg	3,120	3,630	7,030	0.05
Mo	<19	<28.425	<29.410	--
Nd	179	[103]	[170]	0.19
Pb	2,910	3,505	6,425	0.10
Pd	<17	<25.267	<26.142	--
Rh	<35	<51.323	<53.101	--
Ru	<18	[120]	[210]	0.14
Sb	<82	<122.385	<126.626	--
Se	<292	<434.269	<449.318	--
Sn	<66	<98.698	<102.118	--
Ta	<61	<78.958	<81.694	--
Te	[82]	<102.645	<106.202	--
Th	<22	[215]	519	--
Ti	371	379	849	--
Tl	<80	<118.437	<122.541	--
V	<8.5	[22]	[16]	0.64
W	<56	<82.906	<85.779	--
Y	29.7	32.8	64.4	0.04

Radionuclide reference date for ASR 8108: November 5, 2007.

Radionuclide reference date for ASR 8144: April 9, 2008.

As a comparison, two methods of determining the percent leached were performed. Method 1 used the concentration of the analytes in the final leachate solutions and the concentration in the final leached solids. Method 2 used the concentrations in the initial and final solids and the "concentration factor" method.

For the first method, the mass of residual solids in each of the three samples treated at 40°C in 3 M NaOH was first determined. These three solids samples were combined, washed, and then slurried in water. A sample of this slurry was dried to determine the wt% UDS. The total mass of solids was determined from the slurry mass and wt% UDS. This number was then divided by three to obtain the average mass of dried solids in each of the three samples of leached solids. This mass was then multiplied by the concentration of each component in the final solids to determine the mass (in µg) of the component in each leached sample. The leach factor was then calculated by dividing the mass of the component in the leachate solution (W_L) by the total mass of the component in each sample, calculated from the mass of each in the final solids and leachate solution (sum of W_L and weight in the final samples [W_{FS}]) as shown in Equation 4.1.

$$LF_{triplicate\_samples} = \left(\frac{W_L}{W_L + W_{FS}} \right) \tag{4.1}$$

The average leach factor from the three samples was calculated. The average of the concentration of each component in the final leachates from the triplicate runs was divided by the average leach factor of the triplicate samples to obtain an average corrected concentration (CC) that corresponds to the concentration that would be obtained if 100% of the sample had dissolved. The weight of each component in the leachate solutions is divided by the average corrected concentration to determine the leach factors as shown in Equation 4.2.

$$LF_1 = \left(\frac{W_L}{CC} \right) \tag{4.2}$$

The second method is the same that was previously reported in Fiskum et al. (2008). The analysis of the leachate solutions showed that Bi, Fe, Mn, Sr, ^{154}Eu, ^{241}Am, ^{90}Sr, $^{239+240}$Pu, and ^{238}Pu were not dissolved by caustic leaching. The relative concentration factor (CF) of these analytes averaged 2.04 in the final leached solids, based on the ratio of the analyte concentrations after leaching to the analyte concentrations before leaching. This term was used to determine the specific analyte leach factors according to Equation 4.3:

$$LF_2 = 1 - \left(\frac{C_L}{C_W \times 2.04} \right) \tag{4.3}$$

where LF_2 is the caustic-leach factor, C_L is the leached analyte concentration, and C_W is the washed analyte concentration.

Results from the two methods are given in Table 4.5. For most of the samples, the CF method gave larger values of fraction removed, on the order of 10 to 15% higher values. All values of percent leached plotted in this section and shown in Table 4.2 and Table 4.4 were calculated using method two, the “CF” method.

Extended (24-hr) leach times did not mobilize Sr, Mn, or Pu to the aqueous phase. Consistent with previous leaching tests with Hanford sludge solids, most (99%) of the ^{137}Cs was dissolved and would be routed to the LAW PTF.

Approximately 47% of the metals mass dissolved with a 24-hr leach time. As shown in Figure 4.17, in this case, iron and uranium were the predominant residual metals, and iron would be expected to become the limiting component of the HLW glass loading.

Table 4.5. Group 7 TBP Sludge Aluminum and Phosphorus Leach Factors

Temp., °C	**Free OH, M**	**Na, M**	**Fraction Removed Based on final solids/leachate solution (Method 1)**		**Fraction Removed Based on initial/final solids (“concentration factor” method; Method 2)**	
			Al	**P**	**Al**	**P**
40	1.02	1.10	0.55	0.83	0.65	0.89
40 trial a	3.12	3.21	0.84	0.93	0.75	0.88
40 trial b	3.00	3.04	0.83	0.93	0.74	0.88
40 trial c	3.19	3.17	0.84	0.93	0.81	0.95
60	0.24	0.28	0.50	0.80	0.59	0.86
60	1.01	1.01	0.71	0.82	0.84	0.88
60	3.02	3.00	0.76	0.87	0.91	0.93
80	0.25	0.30	0.78	0.84	0.93	0.90
80	1.05	1.04	0.70	0.86	0.83	0.93
80	3.05	2.95	0.67	0.82	0.80	0.88

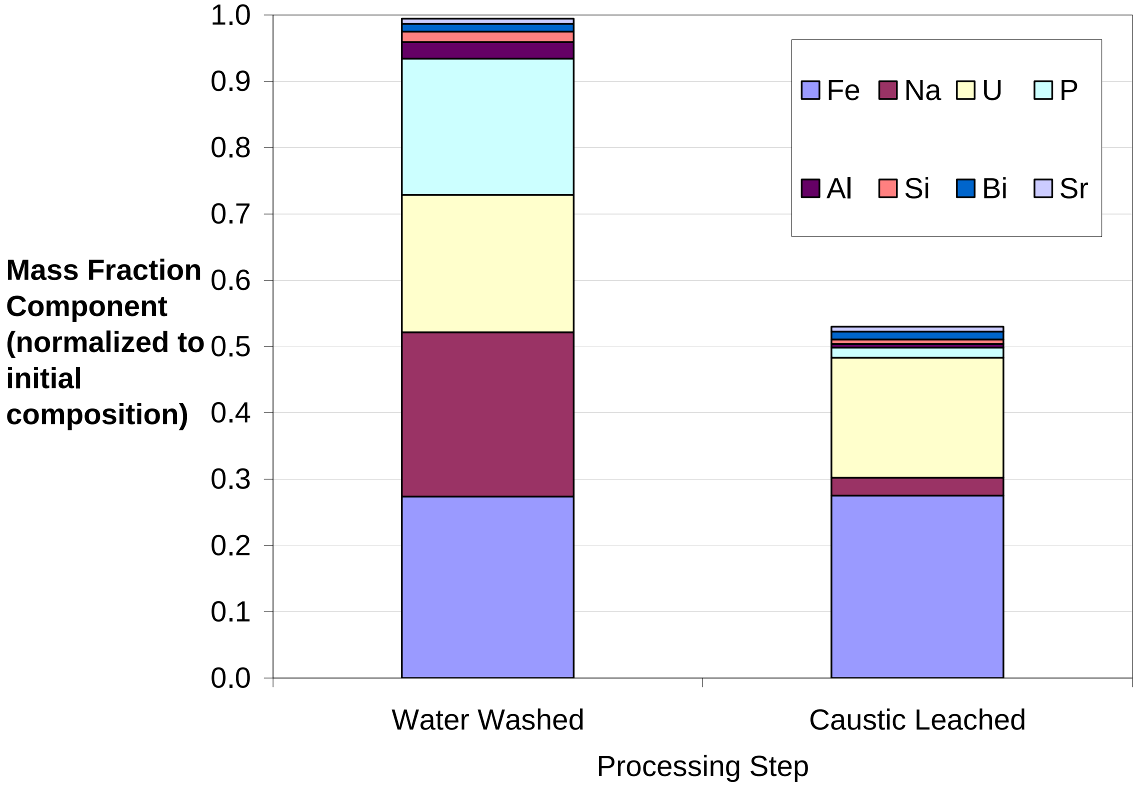


Figure 4.17. Group 7 TBP Sludge Reduction in Solid Mass with Water Washing and Caustic Leaching

4.2.6.3 Particle-Size Distribution

PSD measurements were performed on a sample of the caustic-leached solids (sample ID 623-G7-CL-PSD). Table 4.6 gives a summary of the measured oversize diameter percentiles (by volume/weight) for this sample as a function of test condition. Here, the d(10) ranges from 0.57 to 0.72 µm, the d(50) ranges from 2.1 to 2.9 µm, and the d(90) ranges from 10 to 93 µm. More extensive percentile results are provided in Appendix E.

Figure 4.18 shows the PSD for the Group 7 caustic-leached sample as a function of pump speed. All of the pump speeds show a multi-modal distribution with peak maxima around 1.2 and 8 µm. At 2000 RPM, the range is 0.24 to 20 µm, although at higher pump speeds, a broader range exists. At 3000 RPM, the range is 0.24 to 300, µm and an additional peak is seen around 135 µm. At 4000 RPM, the range is 0.24 to 200 µm, and again an additional peak is observed, although its maximum is around 70 µm. This larger diameter peak most likely indicates the presence of larger particles or agglomerates that are suspended by faster pump speeds. As this peak shifts to smaller particle diameters at 4000 RPM, this may also indicate shear-induced breakage of agglomerates, which would account for the relative increase in the 4- to 10-µm peak observed.

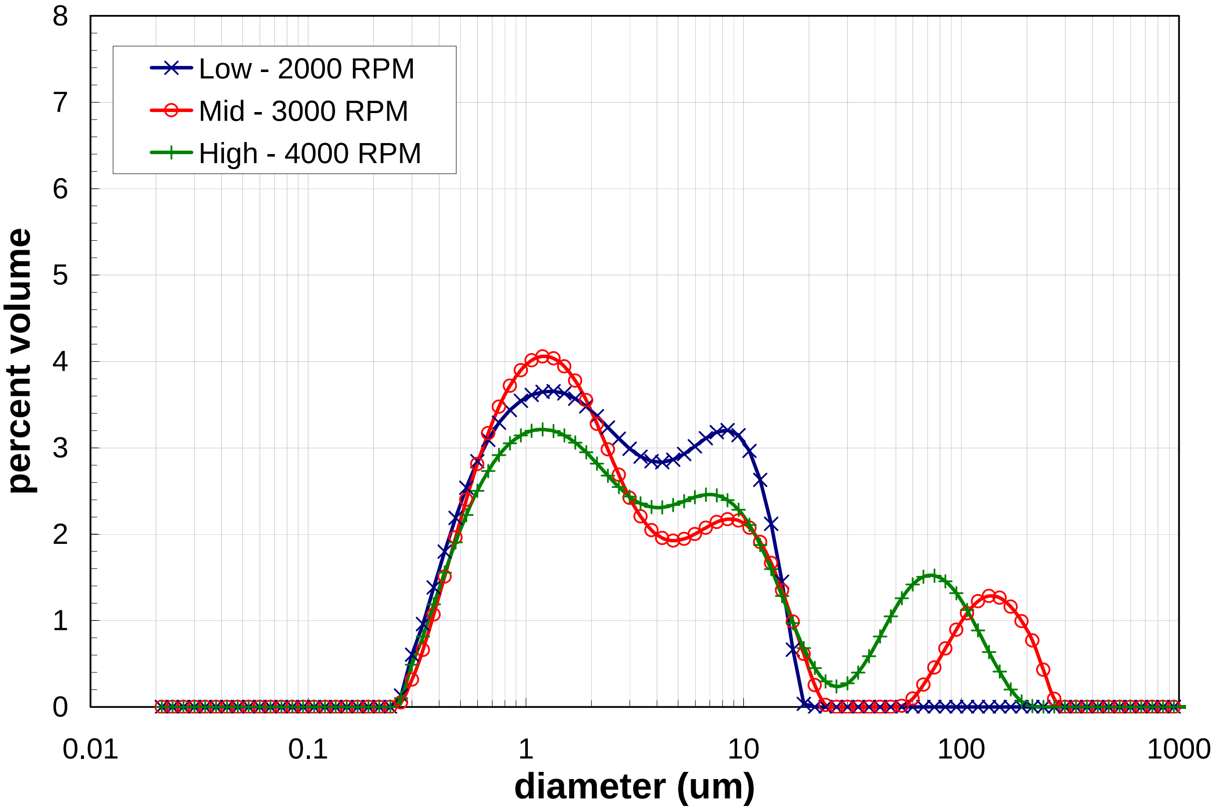


Figure 4.18. Volume Distribution Result for the Group 7 Caustic-Leached Sample as a Function of Pump Speed

Table 4.6 shows select cumulative oversize percentiles for the Group 7 caustic-leached sample particle dispersion. Using these results as a reference, the behavior of Group 7 caustic-leached particle size as a function of pump speed can be quantitatively evaluated. Specifically, the following observations can be made:

- In general, the d(10) falls between 0.57 and 0.72 µm, the d(50) between 2.1 and 2.9 µm, and the d(90) between 10 and 93 µm.
- The listed diameter percentiles appear to be sensitive to changes in pump speeds. Increases in flow rate appear to result in increases in the mean diameter [i.e., the d(50)]. For an increase from 3000 to 4000 RPM, the mean particle diameter increases from 2.1 to 2.9 µm. This is an increase of ~38% and is significant relative to the accuracy of the instrument.

Table 4.6. Particle-Size Analysis Percentile Results from the Group 7 Caustic-Leached Sample

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	n/a	0.61	2.1	78
2	4000	n/a	0.61	2.9	59
3	2000	n/a	0.72	2.7	93
4	2000	n/a	0.57	2.2	10

The particle-size analysis of the caustic-leached Group 7 sample displays multi-modal PSDs ranging from 0.24 to 300 µm. Higher pump speeds result in an additional peak consisting of particles >20 µm. This may indicate the presence of larger difficult-to-suspend particles, which may result in irreproducible sampling due to settling.

The influence of caustic-leaching and washing on the Group 7 (TBP sludge) solids can be evaluated by comparing PSDs for the source material (i.e., for initial characterization sample TI576-G7-S-WL-PSD) to the caustic-leached and washed Group 7 parametric testing PSD sample (623-G7-CL-PSD). The PSD measurement for the primary initial characterization sample is used for this comparison. Comparison of the percentiles and distributions of the initial sample (presented in Section 3.4) and the caustic-leached sample can highlight the effects of chemical treatment on the Group 7 waste PSD. Caution must be used when directly comparing PSDs, however, because these PSDs include both primary particles and particle agglomerates. The structure of the agglomerates fractions depends on 1) physical conditions such as the analyzer pump speed and 2) chemical conditions such as particle interaction potentials and sample history.

One expected outcome of caustic leaching is a decrease in particle size as a result of solids dissolution. However, removing the leachable solid species may reveal the size distribution of particles only minimally represented in the initial sample. In addition, changes in the dominant particle-surface chemistry can yield increased particle agglomeration, which in turn results in increases in the apparent particle size. In addition to chemical effects, the mechanical force needed to pump the dispersion can also shear particle agglomerates (as well as influence the volume of agglomerates suspended). As such, the apparent PSD of a material may also vary with pump speed. Comparisons will be made at measurement condition 1 (3000 RPM).

Table 4.7 and Figure 4.19 show changes that occur to the Group 7 solids PSD as a result of caustic-leaching and washing. Figure 4.19 shows that both the initial characterization and parametric testing (caustic-leached) samples are tri-modal with peak maxima located around similar particle diameters. The most noticeable difference is the shift to lower particle diameters after caustic-leaching and washing. The reduction in particle size is likely a result of either dissolution of material from the particle surface or agglomerate breakage.

Table 4.7. Cumulative Undersize Percentiles Showing the Influence of Caustic-Leaching and Washing on the PSD of Group 7 (TBP sludge) Solids at Measurement Condition 1 (3000 RPM)

Sample	d(10) [µm]	d(50) [µm]	d(90) [µm]
Group 7 Initial Characterization (TI576-G7-S-WL-PSD-1)	1.0	19	130
Group 7 Parametric Testing (TI623-G7-CL-PSD)	0.61	2.1	78

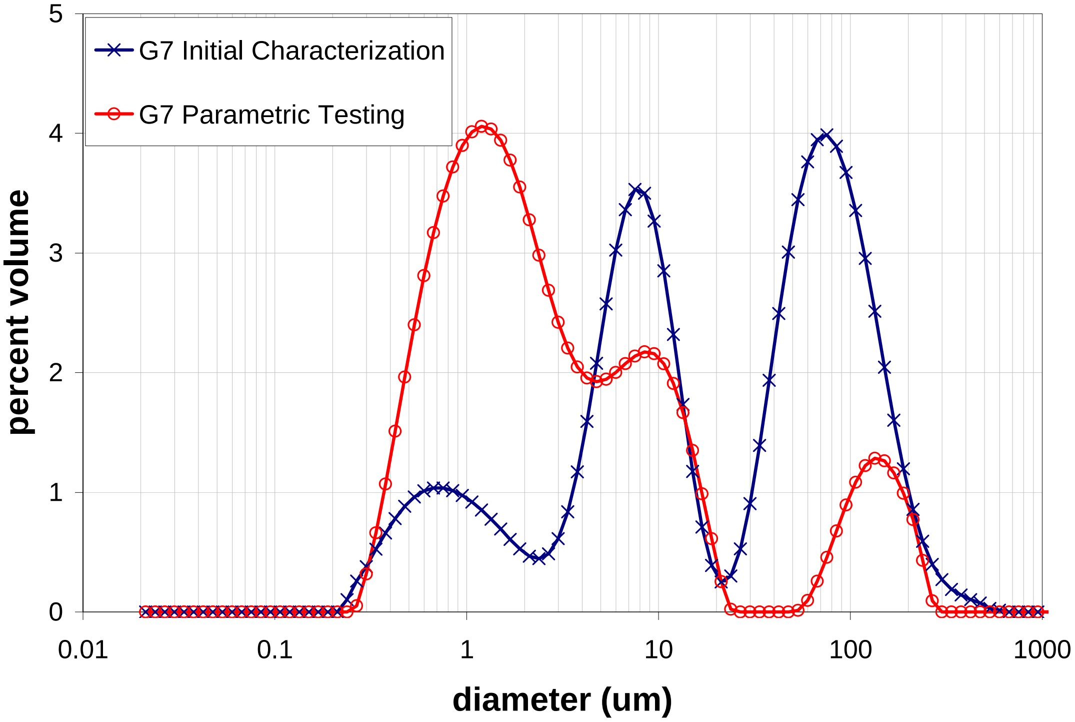


Figure 4.19. Influence of Caustic-Leaching and Washing on Group 7 (TBP sludge) Solids PSD. PSDs were taken at measurement condition 1 (3000 RPM).

4.2.6.4 Crystal Form and Habit

The following sections summarize the mineral-phase evaluation of the leached and washed solids.

4.2.6.4.1 XRD

The XRD pattern of the leached and washed solids (sample ID 585-G7-CL-XRD) is provided in Figure 4.20a; the background-subtracted XRD pattern with stick-figure phase identification is shown in Figure 4.20b.

Rutile, TiO_2, was used as an internal standard for 2-theta calibration. Identification was done on 2-theta calibrated data. This material is predominantly amorphous as indicated by the very broad peak system from about 12 to 37 degrees 2-theta. Sodium uranium oxide hydrate [$Na_2U_2O_7 \cdot 6H_2O$] was a good fit to all peaks but one in the pattern. The peak at 25.4° 2-theta has a significant intensity mismatch. Becquerelite [$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$] and nabaphite [$NaBa(PO_4)(H_2O)_9$] are good fits to the data. Clarkeite [$Na(UO_2)O(OH)$] is a good fit to the broad peaks at ~15°, 27°, and 36° 2-theta in the pattern. Broad peaks indicate that this phase has an extremely small crystallite size (~ 10 nm). Calcium nitrate [$Ca(NO_3)_2$] is a possible fit to minor peaks unaccounted for in the pattern, although it is unlikely that calcium nitrate was present in the washed sample, as it is water-soluble.

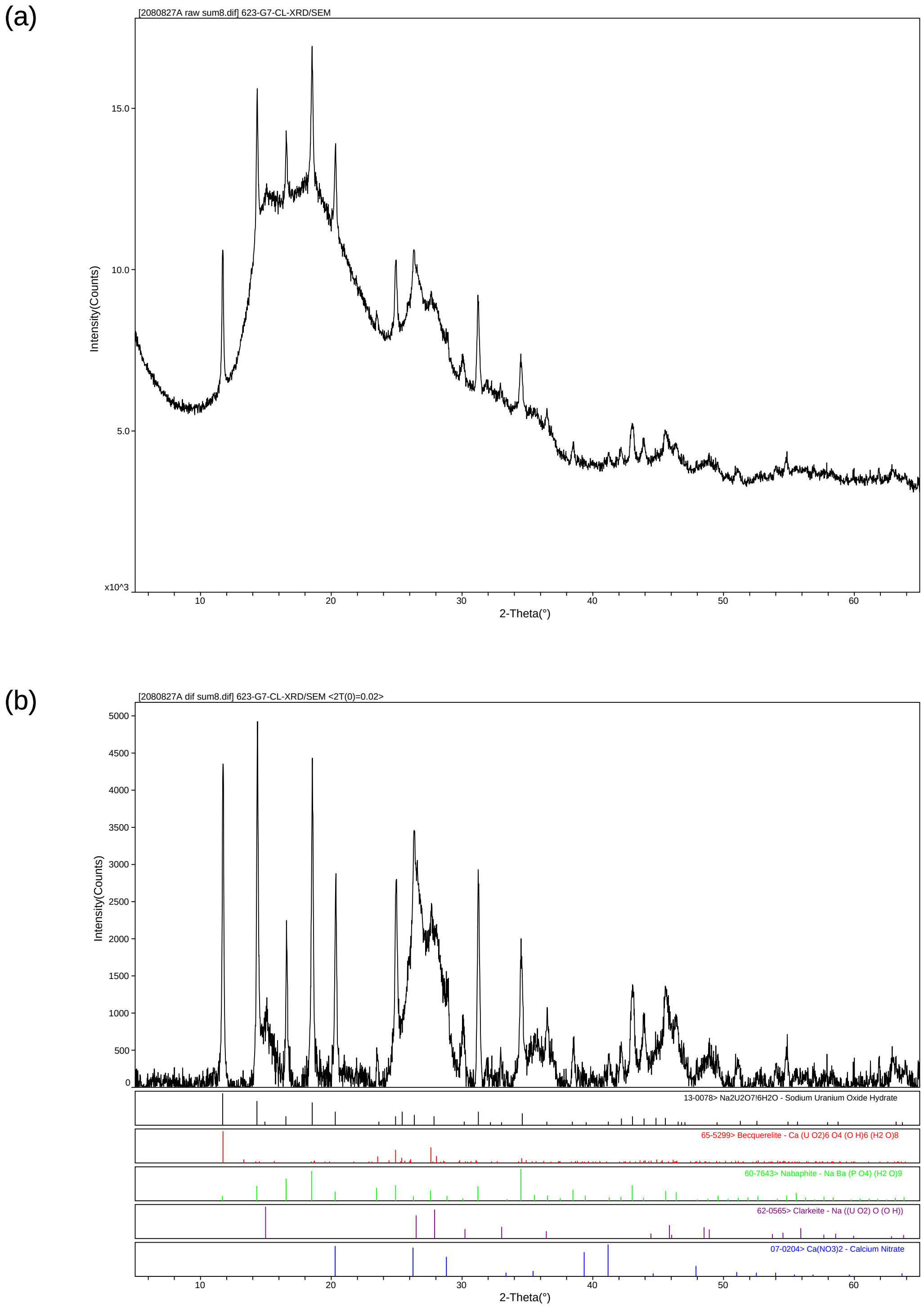


Figure 4.20. XRD Pattern of Caustic-Leached Group 7 TBP Sludge with Rutile (TiO_2) Internal Standard (a) Raw Data and (b) Background-Subtracted with Stick-Figure Peak Identification

4.2.6.4.2 SEM and TEM

Several SEM images are shown in Figure 4.21. Particles seen in these images are typically on the order of 10 to 40 µm.

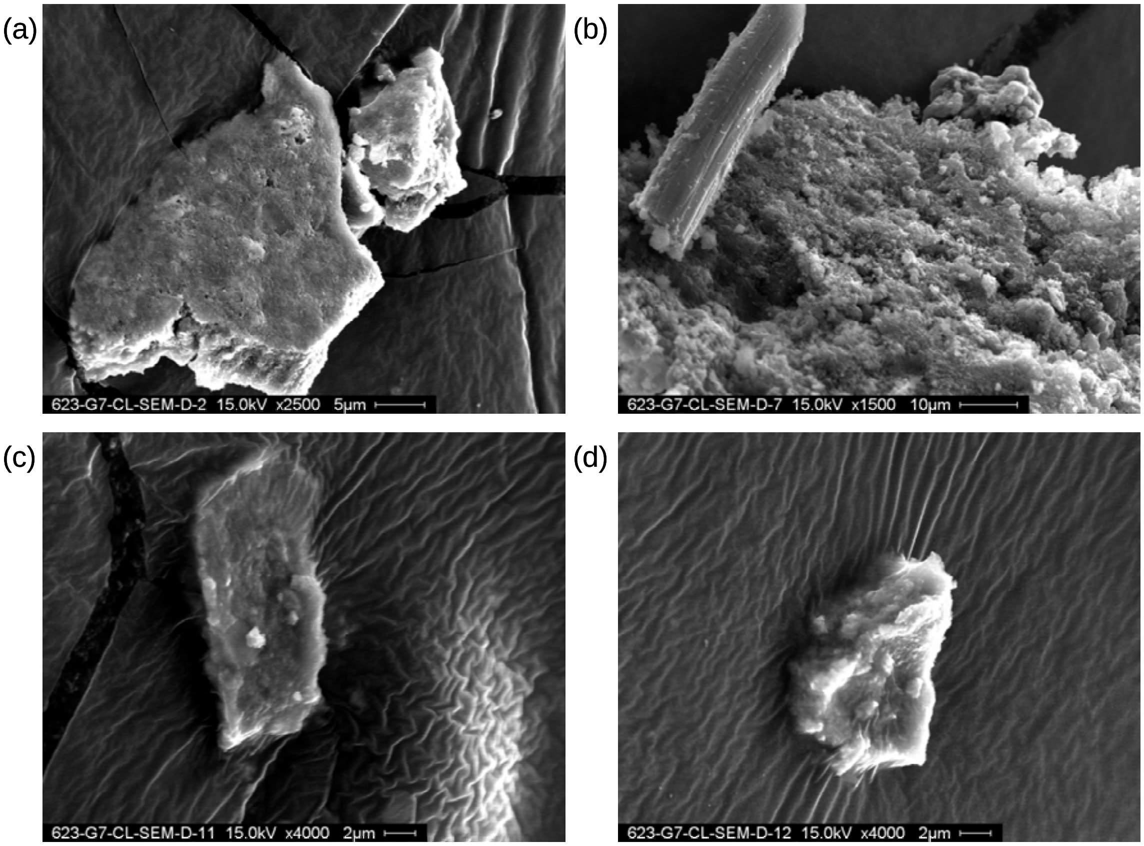


Figure 4.21. SEM Images of Group 7 TBP Sludge Caustic Leached and Washed Solids (a) 15 kV, 2500×; (b) 15 kV, 1500×; (c) 15 kV, 4000×; (d) 15 kV, 4000×

Figure 4.22 shows an SEM image along with EDS spectra of two particles. The elemental analysis shows a large amount of oxygen and carbon, which is an artifact of the sample preparation (carbon is sputtered onto the sample to eliminate problems with charging). If this is removed, and the other constituents are normalized, the weight percentages shown in Table 4.8 for each analysis are obtained. The particle at spot 3 in Figure 4.21 consists mainly of Fe as well as a small amount of U. The particle at spot 4 in Figure 4.21 is more representative of the average of the 17 spots that were examined by SEM EDS, showing high amounts of Fe, fairly high amounts of U, and smaller concentrations of other analytes. This is in agreement with the ICP results from the residual solids, which showed that the residual solids are 33% Fe and 21.8% U.

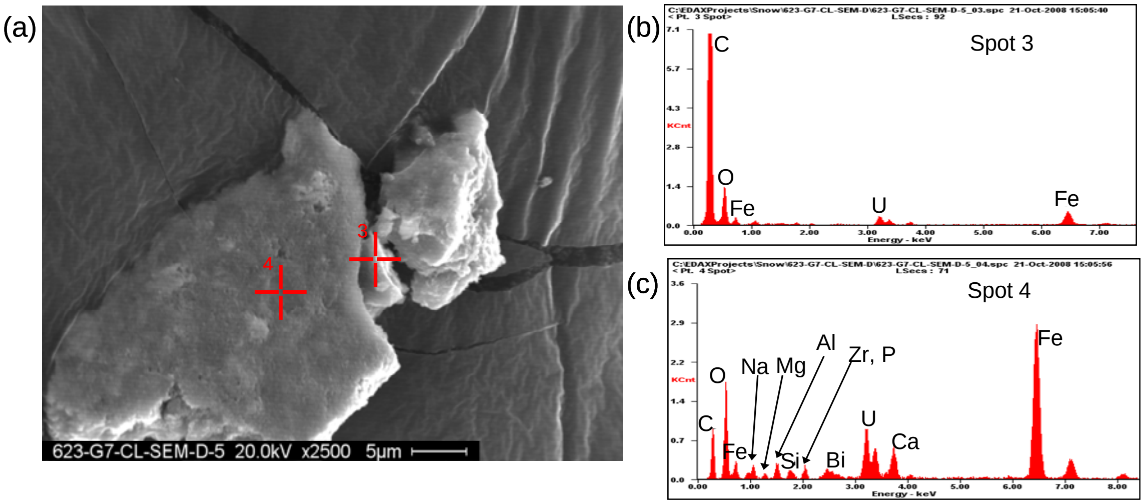


Figure 4.22. SEM Image of Group 7 TBP Sludge Caustic Leached and Washed Solids with EDS Spectra (a) SEM Image; (b) EDS Spectra of Spot 3; (c) EDS Spectra of Spot 4

Table 4.8. Normalized Weight Percents for Various Analytes Found by EDS of SEM Images for Figure 4.22

Element	Normalized Weight Percent	
	Spot 3	Spot 4
Fe	95.5	65.5
Cu	0	6.85
Na	0	1.86
Mg	0	3.84
Al	0	1.72
Si	0	1.63
P	0	0.35
Zr	0	3.40
Bi	0	12.67
U	4.1	2.21

As discussed in section 4.1.3, there was an apparent initial dissolution of the uranium compounds followed by a re-precipitation. Examination of the caustic-leached solids by TEM showed that the uranium phosphate phases in the caustic-leached sample were considerably smaller than those observed in the initial characterization sample. Figure 4.23 shows two TEM images of agglomerate phases in the caustic-leached and washed solids, as well as an EDS and selected area electron diffraction (SAED) analysis of the uranium phosphorus phase; any evidence of crystallinity in the phases was absent, and there was clear evidence that the original uranium phosphate phase dissolved and the uranium phase re-precipitated. This can be seen by comparing the uranium phases seen in Figure 4.23 to the sodium uranyl phosphate crystals in the initial characterization sample as seen in Figure 3.23.

In nature, uranyl phosphates and the often isostructural uranyl arsenates constitute nearly 70 of the known 200 U(VI) mineral phases. The autunite group have the general composition $A(UO_2PO_4)_2.nH_2O$ where A is typically a divalent cation, and n represents the hydration number. The structure of autunite results in perfect (001) basal cleavage. In the sludge sample, the individual crystals were several microns in length but electron transparent along the c-axis. The caustic-leaching process dissolved these large crystals; however, uranium phosphates were still present. Sandino and Bruno (1992) demonstrated that uranyl phosphate complexation dominates when the total concentration ratio $[PO_4^{3-}]_T/[CO_3^{2-}]_T$ is >0.1 between pH 6 and 9. Hence, although treatment conditions permitted the dissolution of the uranyl phosphate, it is likely that the phase re-preciptiated.

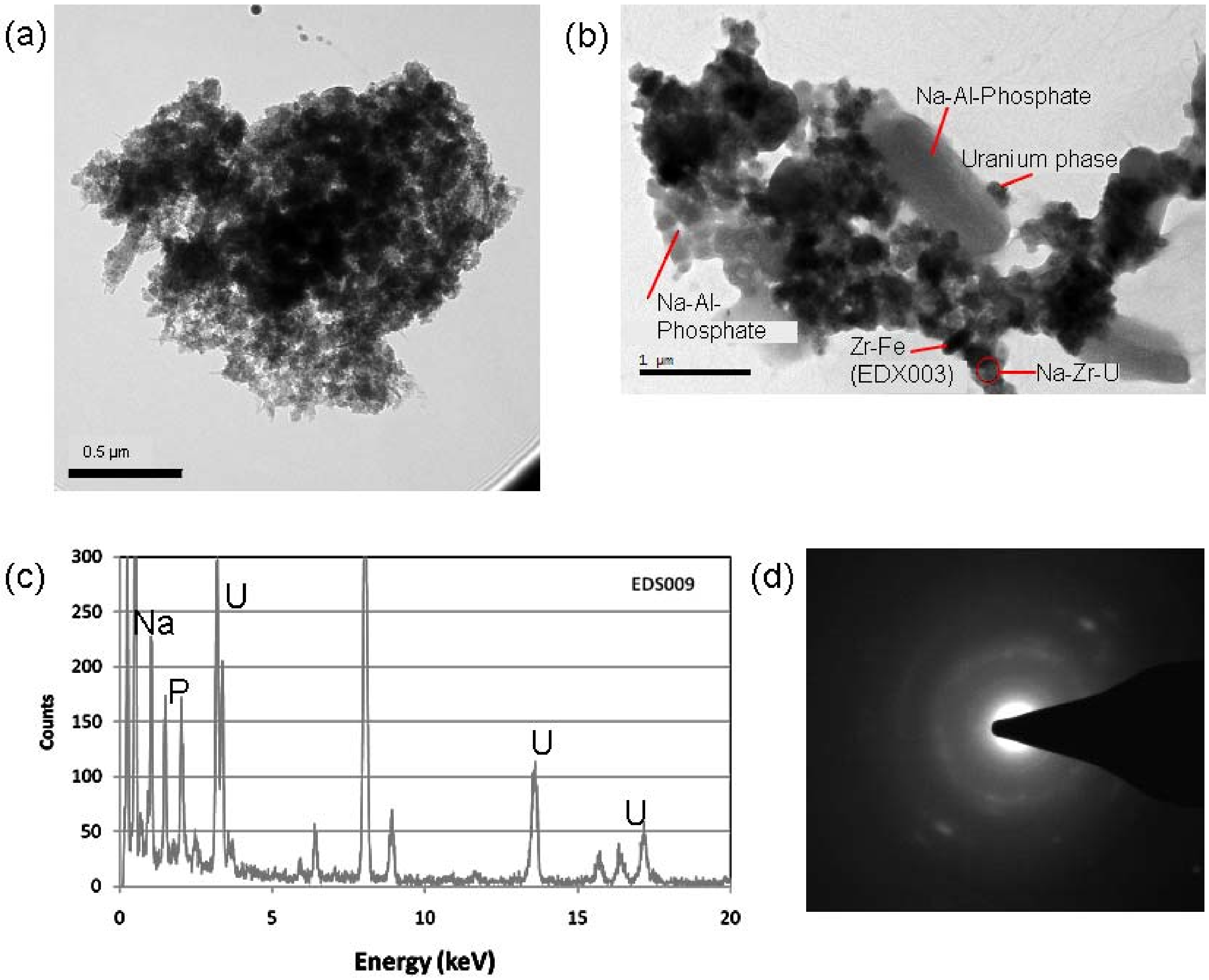


Figure 4.23. TEM Image of Group 7 TBP Sludge Caustic Leached and Washed Solids (a) TEM Image of an Agglomerate; (b) TEM Image Showing Various Phases; (c) EDS Analysis of a Uranium Phosphorus Phase in the Agglomerate Shown in (a); (d) SAED Image of the Uranium Phosphorus Phase

A crystalline sodium alumino-phosphate was also found in the sample, as seen in Figure 4.23b. The EDS and SAED analysis of this crystal is given in Figure 4.24.

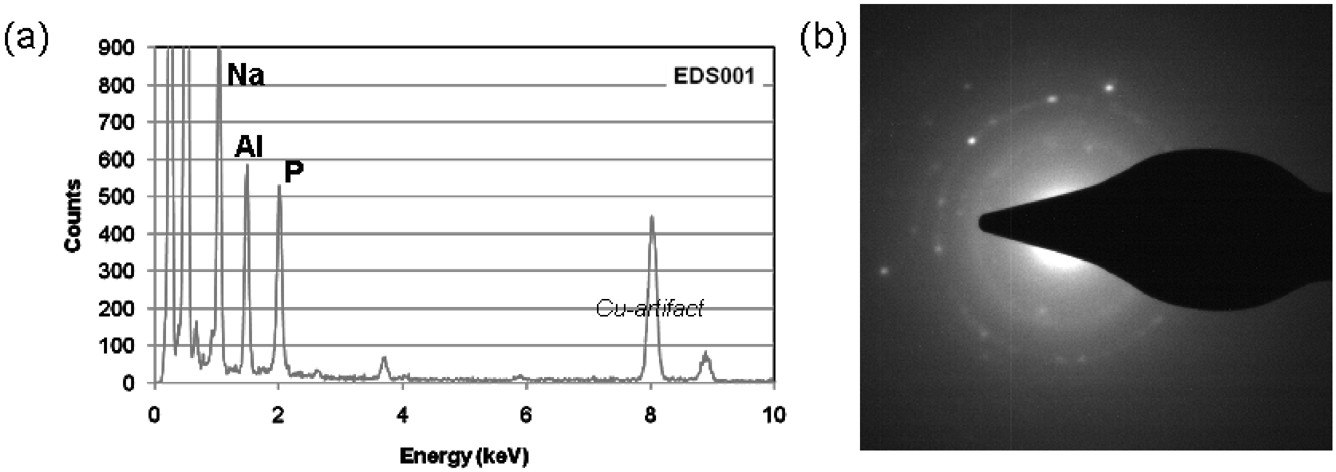


Figure 4.24. TEM Analysis of a Sodium Aluminum Phosphate Phase in the Group 7 TBP Sludge Caustic Leached and Washed Solids (a) EDS Analysis; (b) SAED Image

Iron phases were also seen. Figure 4.25 shows STEM-HAADF and TEM images as well as an EDS analysis of an iron phase. Figure 4.26 shows a large iron particle; the electron diffraction of this particle was consistent with hematite. This particle was exceptionally large compared to the other phases observed in this sample.

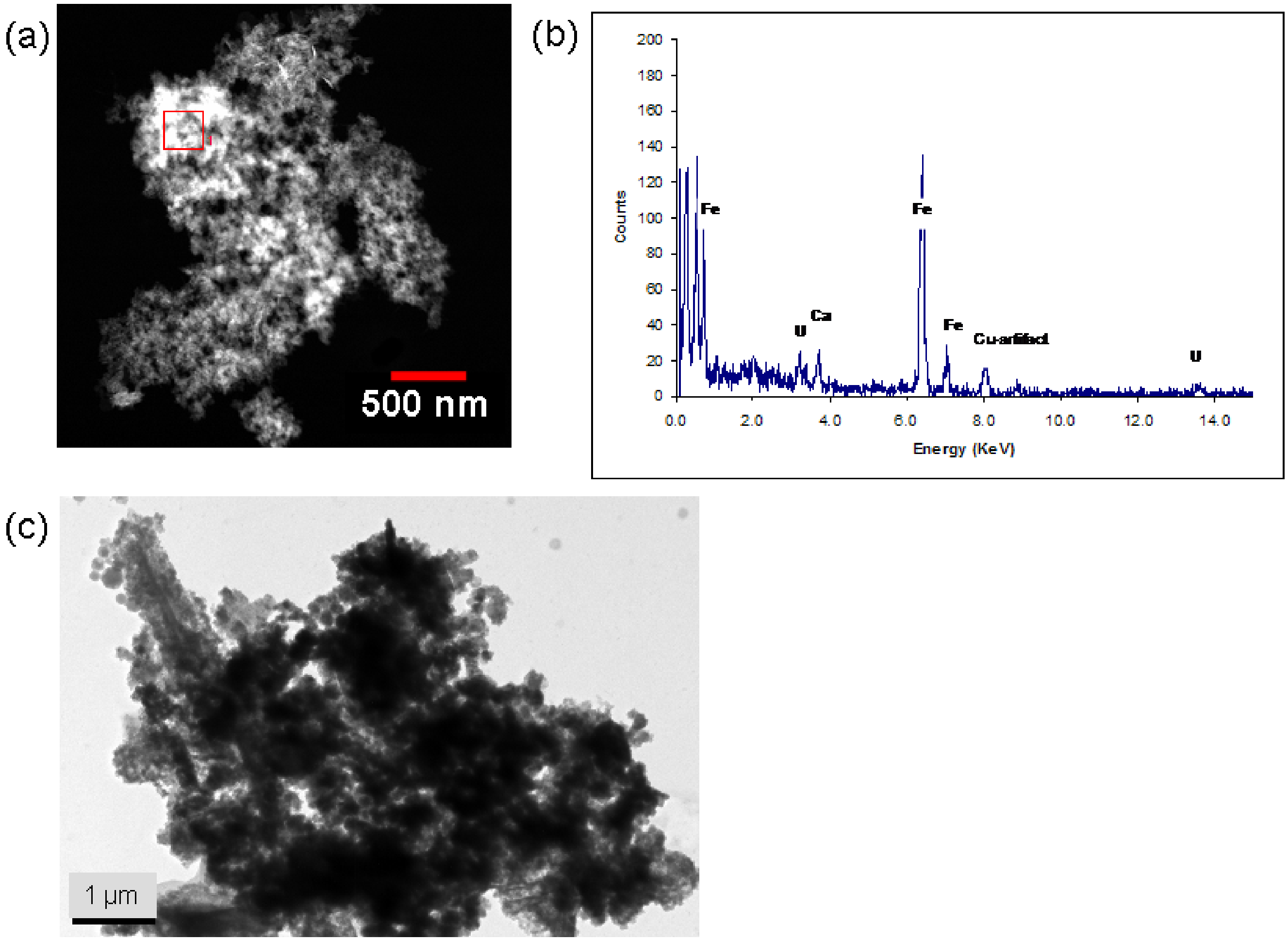


Figure 4.25. TEM Images and Analysis of an Iron Phase in the Group 7 TBP Sludge Caustic Leached and Washed Solids (a) STEM-HAADF Image of a Particle; (b) EDS Analysis of an Iron Phase; (c) TEM Image of the Agglomerate

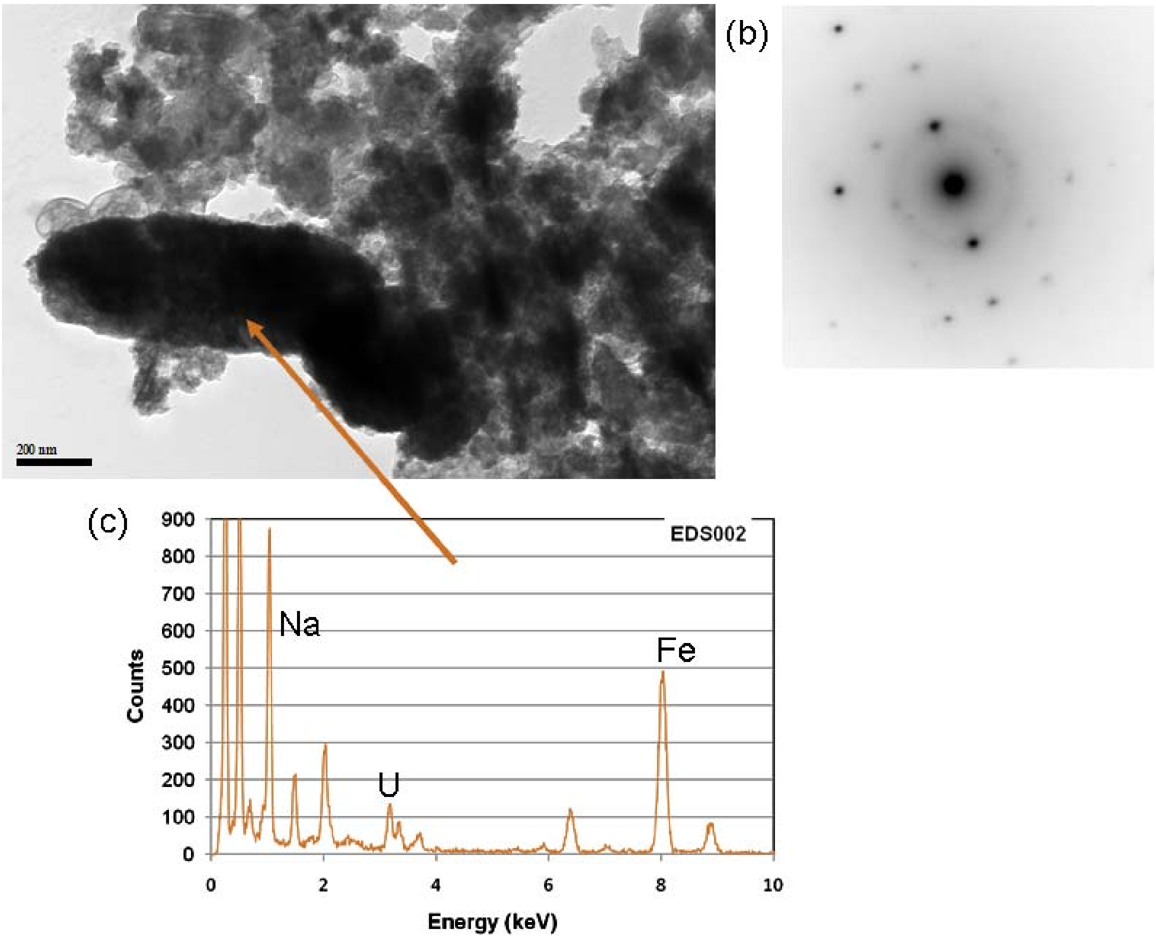


Figure 4.26. Iron Oxide Phase Surrounded by Uranium-Bearing Particles in the Group 7 TBP Sludge Caustic-Leached and Washed Solids. (a) TEM Image; (b) SAED Image; (c) EDS Analysis

Various other phases were also found in the samples as shown in Figure 4.27.

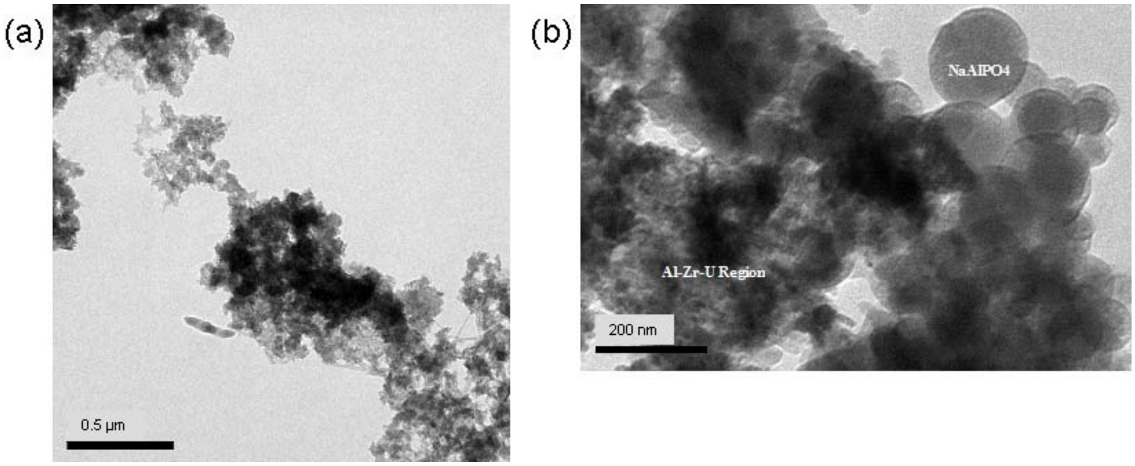


Figure 4.27. TEM Images of Particles in the Group 7 TBP Sludge Caustic-Leached and Washed Solids. (a) TEM Image of an Agglomerate Phase; (b) TEM Image Showing Regions Rich in Sodium, Aluminum, and Phosphorus, and Al-Bearing Phases

4.2.6.5 Surface Area by BET

A BET measurement was conducted on the caustic leached and washed solids, resulting in a surface area of 248 m^2/g. This shows an increase in relative surface area following caustic leaching from the value of 66 m^2/g found for the initial washed solids.

5.0 CUF Testing and Results

This section describes the filtration/leaching tests performed using the CUF for the TBP waste sludge composite referred to as the Group 7 waste sample performed under TI-RPP-WTP-624[a] and subsequent results. The UDS inventory of the Group 7 waste slurry was not enough to generate 20-wt% slurry in the CUF by itself, and therefore the slurry was blended with archive samples from HLW Tank 241-AY-102. This blending of wastes was approved by BNI in response to letter request WTP/RPP-MOA-PNNL-00216.

5.1 Test Plan

Figure 5.1 outlines the testing that was performed, which is reported in this section. The goals of this test were to:

- Evaluate the filtration of the TBP sludge waste composite
- Blend with samples from Tank 241-AY-102 and evaluate the change in filtration
- Evaluate the effectiveness of caustic leaching on removing aluminum from the blended waste
- Evaluate the filtration of the washed leached solids.

The first half of the testing was to perform filtration studies on the Group 7 waste sample and understand its dewatering behavior, as outlined in the first column of Figure 5.1. The waste was to be initially evaluated at a target UDS concentration of 4 wt%, which is the expected solids concentration entering the WTP-Pretreatment UFP2 vessel. To accomplish this, approximately 1.4 L of Group 7 composite material (measured at 10 wt% UDS) was diluted with 2.0 L of a simulated supernate solution (based on the Group 7 slurry supernate composition) to a final volume of 3.5 L. Once the slurry was homogenized, a test matrix was performed as described in Appendix H to determine the filtration behavior of the waste at a low UDS concentration. After completion of the test matrix, the waste sample was dewatered to the minimum operating volume in the slurry recirculation loop at a predicted concentration of 13 wt% UDS.

The target concentration for the dewatering of waste slurry was 20 wt% UDS. However, this required approximately 300 grams of solid to be present in the initial slurry sample, and only 180 grams was present. As done in previous testing, another waste sample was added to the waste at this point to increase the mass of solids. Archived samples from Tank 241-AY-102 were selected to be added to the slurry to increase the solids mass. These archived samples were considered a neutral category waste, which did not fix any of the specific waste groups, but could be added to supplement any of the waste groups for CUF testing. Examination of the composition of the AY-102 from past studies performed at Savannah River (Coleman, 2003) and PNNL (Krupka 2004) showed the following similarities and differences in the wastes:

(a) Conducted according to TI-RPP-WTP-624, *HLW Filtration and Caustic Leaching of Group 7 / AY-102 Composite Waste*, R Shimskey, April, 2008.

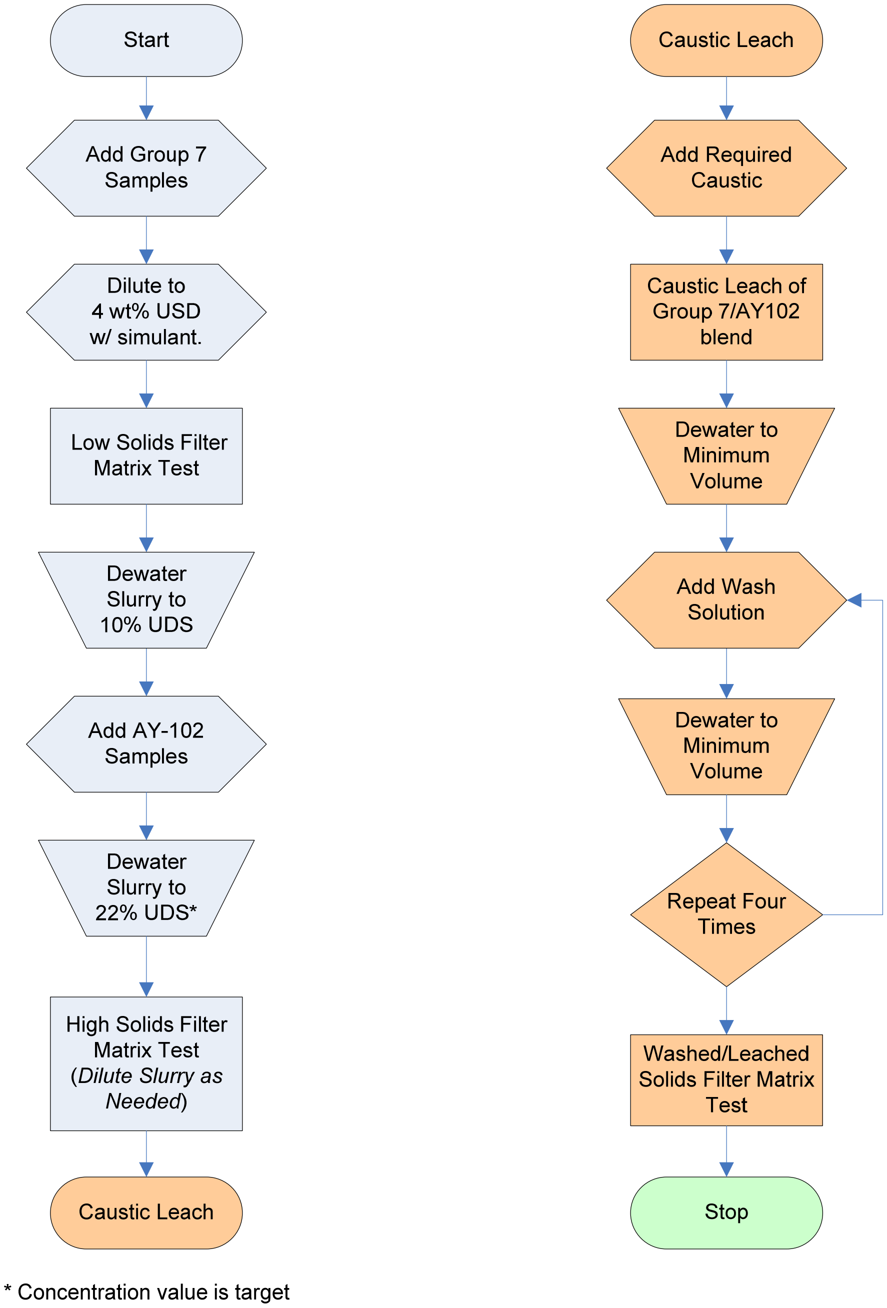


Figure 5.1. Group 7 / AY-102 Testing Flowchart

- Both the Group 7 composite and the AY-102 archive tank sample contained insoluble aluminum (in the form of gibbsite), which had the potential to be removed by caustic leaching. However, a majority of the aluminum inventory came from AY-102.
- The quantity of phosphorus in the AY102 was not significant, so a majority of the phosphorus present in the composite waste was to be from Group 7.
- Both wastes contained similar quantities of iron.

- The TRU inventory in the AY-102 samples was greater than 100 times higher than that present in the Group 7 waste.

The AY-102 slurry was added to the CUF and diluted with additional supernate to maintain the slurry UDS concentration at ~11 wt%. After the slurry was homogenized again, it was dewatered to minimum volume and target UDS concentration. At this point, another test matrix was performed to evaluate the change in the filtration behavior after concentrating the waste slurry.

The second half of the testing was to evaluate the caustic-leaching behavior of the Group 7/AY-102 blended waste slurry, as outlined in the right column of Figure 5.1. After completing the high-solids-concentration filtration test matrix, the sample was drained from the CUF piping and placed back into the slurry reservoir after isolating the tank from the filtration piping. At this point, a known volume and concentration of NaOH was blended with the concentrated slurry to increase the leach volume to 3.4 liters. The caustic addition was based on the following preparations:

- Approximately 20 grams of aluminum was present in the combined slurry—4 grams from the 180 grams of insoluble Group 7 solids and 16 g from the 220 grams of insoluble 241-AY-102 solids.
- A leach factor of 100% for the 20 grams of aluminum present was used to verify that the final free-hydroxide concentration was high enough to maintain Al solubility(a) after the leach solution cooled to room temperature. The final molar ratio of free hydroxide to aluminum was predicted to be 10 to 1.
- After calculating the free-hydroxide concentration needed to maintain Al solubility after cooling, the required addition of NaOH was calculated. This mass was to be added as a 19-M NaOH solution.
- Once the volume of dewatered slurry and 19 M NaOH was known, the volume of water to be added to the leach solution representing the leach volume increase due to condensation from heating via steam injection was calculated.
- Because this was a hot-cell operation, only one solution addition was desired. Therefore, the 19-M NaOH addition and water addition for steam condensate were combined into one solution. The final solution became 1.4 liters of 5.3 M NaOH.
- The expected sodium concentration during the leach was planned to be 4.5 M while the final free-hydroxide concentration was 2.7 M.
- The consumption of hydroxide by phosphorus was considered to be negligible for this test

This caustic solution was used to rinse additional solids in the CUF piping before isolating the slurry reservoir tank for leaching operations. After rinsing the CUF slurry piping with the caustic addition, the drained slurry, supernate, and caustic addition solution were added to the isolated slurry reservoir tank with the overhead mixer operating. Because leaching for phosphorus and aluminum in the form of gibbsite does not require leaching beyond 60°C, the process for the leach deviated from the historic baseline conditions as follows:

- The leach slurry was heated from 25°C to 60°C (+5°/-10°C) over a 2.5-hour period.
- The leach slurry temperature was held at 60°C for 8 hours.

(a) Solubility of aluminum and hydroxide taken from data reported by Huixin Li, et al., in *The Influence of Al(III) Supersaturation and NaOH Concentration on the Rate of Crystallization of* $Al(OH)_3$ *Precursor Particles From Sodium Aluminate Solutions*, Journal of Colloid and Interface Science (2005, Vol. 286, pg. 511-519).

- The leach slurry was cooled to 25°C over 5.6 hours.

During the 8-h leaching period, the slurry was sampled and filtered to measure changes in the supernate composition to track the dissolution rate of aluminum and phosphorus. After the leaching slurry had cooled to ambient temperature, it was dewatered to the minimum operating volume of the circulation pump. Four equal-volume caustic wash solutions (1.2 liters) were then added to the leached slurry. To prevent aluminum from precipitating during washing, additional caustic was added to each wash solution to prevent the free-hydroxide concentration from falling too low to maintain aluminum solubility. The concentration of NaOH in each wash was:

- 0.5 M for the first rinse solution
- 0.1 M for the second rinse solution
- 0.05 M for the third rinse solution
- 0.01 M for the fourth rinse solution.

After 20 to 30 minutes of mixing the slurry with each rinse solution, the slurry was dewatered. A final test matrix was performed on the washed leached slurry to compare with the filter behavior of the pre-leached slurry.

During testing, slurry and supernate samples were periodically collected to track the solids content in the waste slurry and to track the chemical composition of the slurry to perform mass balance calculations to evaluate the effectiveness of the process in separating LAW waste components from the HLW components in the waste sample. Details of the analyses performed and planning for this test scheme can be found in Appendices H.

5.2 Low-Solids Slurry Characterization

Figure 5.2 and Table 5.1 outline the activities and materials added to the CUF to produce the low-solids slurry. Initially, 1.79 kg of the TBP sludge (at 10 wt% UDS) was added to the slurry reservoir. These waste samples were taken from the Group 7 characterization/homogenization study (described in Section 3). To dilute the waste slurry to ~4 wt% UDS for the low-solids matrix test, 2.42 kg of a simulant supernate was added to the reservoir and blended with the actual waste samples. The composition of the simulant (shown in Table 5.2) was based on results of supernate characterization performed on the homogenized Group 7 waste (see Section 3).

Once the actual waste samples and simulant were blended in the slurry reservoir tank, the slurry was circulated through the CUF with permeate from the ultra filter recycling back to the slurry reservoir. The hold-up of slurry supernate in the filter and permeate loop was ~200 mL. Slurry samples were collected for chemical and physical characterization inside the slurry circulation loop. These samples were inadvertently destroyed during replacement of a broken pump, so no physical-property data are available for the initial slurry. The chemical and radiological composition of the waste slurry is summarized in Table 5.3 and the supernate opportunistic composition in Table 5.4. The composition is based on the characterization of the starting material, the known composition of the simulant added, and changes due to slurry sampling. Results are expressed as the total amount of components in the CUF slurry (mass balance) and include the supernate present in the permeate loop.

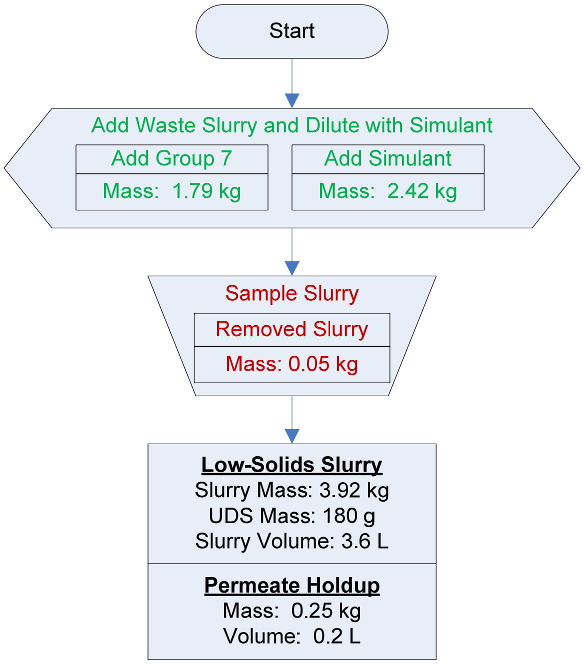


Figure 5.2. Process Flow Diagram of Creating Low-Solids Slurry

Table 5.1. Mass Balance Overview of Group 7 Low-Solids Slurry

Step	Change in Mass (g)	Total Mass (g)	Estimated Solid Mass (g)	Slurry Circulating Mass (g)	Estimated Slurry UDS (wt%)
Add Group 7 Slurry	+1790	1790	180		
Add Simulated Supernate	+2420	4210	180		
Initial Slurry	0	4210	180	3970	4.3
Slurry Sample Loss/ Low-Solids Slurry	-50	4160	180	3920	4.3

Table 5.2. Simulant Addition to Group 7 Composite

	Simulant Addition (2.00 L)		Actual Slurry Waste & Simulant (4.21 kg)		% slurry due to simulant
Cations	**mg/L**	**mg**	**mg/g**	**mg**	**wt%**
Na	99,000	198,000	83.2	350,000	57
Metals					
Al	0	0	0.94	3,980	0
Cr	0	0	0.06	250	0
P	3,720	7,430	9,300	39,100	19
Anions					
C_2O_4	0	0	0.02	63.3	0
NO_2	18,400	36,800	14.5	60,800	60
NO_3	180,000	359,000	143	603,000	60
SO_4	17,300	34,500	13.4	56,300	61
PO_4	11,400	22,800	9.86	41,500	55

Table 5.3. Low-Solids Inventory and Composition (including permeate hold-up)

	Slurry[a]	Liquid Fraction[b]		Solids Fraction[c]	
Mass (kg)	4.17	3.99		0.18	
Wt% of Slurry	100%	95.7%		4.3%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	3.9E+00	5.0E-01	1.6E+02	3.4E+00	1.9E+04
B	7.2E-02	6.6E-02	2.0E+01	6.4E-03	3.6E+01
Bi	1.3E+00	< 1.E-2	< 4.E+0	1.3E+00	7.6E+03
Ca	3.7E+00	3.2E-02	1.0E+01	3.7E+00	2.1E+04
Cd	1.1E-03	4.7E-03	1.5E+00	n/a[d]	n/a[d]
Cr	2.4E-01	7.6E-02	2.3E+01	1.7E-01	9.5E+02
Fe	3.3E+01	2.1E-03	6.6E-01	3.3E+01	1.9E+05
K	1.7E-01	4.4E-01	1.4E+02	n/a[d]	n/a[d]
Mn	2.0E-01	5.3E-04	1.7E-01	2.0E-01	1.1E+03
Na	3.5E+02	3.0E+02	9.2E+04	5.0E+01	2.8E+05
Ni	1.2E-01	< 9.E-4	< 3.E-1	1.2E-01	6.5E+02
P	3.9E+01	1.5E+01	4.5E+03	2.4E+01	1.4E+05
S	1.9E+01	1.9E+01	5.9E+03	3.2E-01	1.8E+03
Si	1.6E+00	< 2.E-3	< 7.E-1	1.6E+00	9.2E+03
Sr	9.2E-01	3.5E-04	1.1E-01	9.2E-01	5.2E+03
Zn	1.8E-01	3.2E-03	1.0E+00	1.8E-01	9.9E+02
Zr	5.6E-03	5.2E-04	1.6E-01	5.0E-03	2.8E+01
U	2.6E+01	4.4E-01	1.4E+02	2.6E+01	1.5E+05

Table 5.3 (Contd)

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	4.17	3.99		0.18	
Wt% of Slurry	100%	95.7%		4.3%	
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	μCi	**μCi**	**μCi /ml**	**μCi**	**μCi /g**
Co-60	4.6E+00	< 2.E-1	< 7.E-5	4.6E+00	2.6E-02
Cs-137	1.3E+04	9.9E+03	3.1E+00	3.3E+03	1.8E+01
Eu-152	n/a(e)	< 9.E-1	< 3.E-4	n/a(d)	n/a(d)
Eu-154	1.3E+01	< 6.E-1	< 2.E-4	1.3E+01	7.3E-02
Eu-155	n/a(e)	< 5.E+0	< 2.E-3	< 9.E+0(f)	< 5.E-2(f)
Am-241	1.9E+01	< 8.E+0	< 3.E-3	1.9E+01	1.1E-01
Gross Alpha	6.7E+01	< 9.E-1	< 3.E-4	6.7E+01	3.8E-01
Gross Beta	3.5E+05	9.8E+03	3.0E+00	3.4E+05	1.9E+03
Sr-90	1.6E+05	5.4E+01	1.7E-02	1.6E+05	9.2E+02
Pu-239+240	4.4E+01	1.3E-01	4.1E-05	4.4E+01	2.5E-01
Pu-238	1.2E+00	< 4.E-3	< 1.E-6	1.2E+00	7.0E-03
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	μg/ml	**[M]**	**g**	**μg/g**	**g**
F	2.6E+02	1.4E-02	1.4E+00	1.3E+02	2.4E-02
Cl	5.7E+02	1.6E-02	6.0E-01	n/a(d)	n/a(d)
C_2O_4	< 3.E+1	< 3.E-4	6.3E-02	2.6E+03	4.6E-01
NO_2	1.8E+04	4.0E-01	6.0E+01	1.9E+04	3.4E+00
NO_3	1.8E+05	2.9E+00	6.0E+02	1.5E+05	2.7E+01
SO_4	1.7E+04	1.7E-01	5.6E+01	1.6E+04	2.8E+00
PO_4	1.3E+04	1.4E-01	4.1E+01	4.5E+04	8.0E+00
OH	2.4E+03	1.4E-01	1.4E+01		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-169, Section 3). Loss of mass from sampling was incorporated.
(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI624-G7-A (ASO ID 08-02059) and the predicted mass of supernate in the system.
(c) Solids Fraction mass components were calculated from the difference between the slurry component mass and liquid component mass fraction.
(d) Values (based on supernate) were calculated to be less than zero.
(e) Not enough component information to calculate a slurry value for Group 7. Later addition of AY-102 solids introduced component.
(f) Based on initial characterization values for group 7 (WTP-RPT-169, Section 3).

Particle-size measurements were performed on the slurry sample taken before the filtration testing. Table 5.5 shows select cumulative undersize percentiles for the low-solids slurry. Here the d(10) ranges between 28 and 38 μm, the d(50) between 81 and 240 μm, and the d(90) between 150 and 510 μm. With regard to pump-speed effects, the d(50) and d(90) percentiles show a significant increase in size at 4000 RPM, indicating the presence of large, difficult-to-suspend particles.

Figure 5.3 shows the PSD for the Group 7 low-solids matrix as a function of pump speed. The sample shows a broad bi-modal distribution. At 2000 RPM, the distribution ranges from 1 to 500 μm with peak maxima at 190 and 30 μm. At 3000 RPM, the range is from 0.3 to 300 μm with peak maxima at 90 and 12 μm. At 4000 RPM, the distribution ranges from 0.6 to 750 μm with peak maxima at 330 and 50 μm.

As the pump speed increases from 3000 to 4000 RPM, there are more large particles or agglomerates that may be difficult-to-suspend; this may account for the extended range at 4000 RPM. These particles suspended at 4000 RPM may be slow settling relative to the measurement time and may contribute to the larger particle diameters at 2000 RPM in comparison with the distribution at 3000 RPM. Overall, the distribution shows that the majority of particles and/or agglomerates are >20 µm, and their distribution is dependent upon pump speed.

Table 5.4. Group 7 Low-Solids Supernate Opportunistic Composition

Opportunistic Analytes	**Supernate Measured[(a)] μg/mL**
Ag	<2.6E-1
As	<6.3E+0
Ba	[0.17]
Be	<6.3E-3
Ca	[10.0]
Ce	<1.2E+0
Co	<2.9E-1
Cu	<1.7E-1
Dy	<3.5E-1
Eu	<1.3E-1
La	<3.4E-1
Li	3.76
Mg	<2.8E-1
Mo	[2.9]
Nd	<2.1E+0
Pb	<3.9E+0
Pd	<7.7E-1
Rh	[1.8]
Ru	[1.1]
Sb	<2.4E+0
Se	[14]
Sn	<3.3E+0
Ta	<2.1E+0
Te	<3.2E+0
Th	<1.2E+0
Ti	<5.2E-2
Tl	<4.6E+0
V	[0.35]
W	[3.15]
Y	<5.3E-2

(a) Supernatant measured from, ASR 8176, sample TI624-G7-A (RPL ID 08-02059); reference date November 5, 2007.

Analyte uncertainties were typically within ±15%; results in brackets indicate that the analyte concentrations were greater than the method detection limit (MDL) and less than the estimated quantitation limit (EQL), and uncertainties were >15%.

Opportunistic analytes are reported for information only; quality control (QC) requirements did not apply to these analytes.

Table 5.5. Particle Size Analysis Percentile Results for Group 7 Low-Solids Matrix

Measurement Condition	Pump Speed	Sonication	d(10) [μm]	d(50) [μm]	d(90) [μm]
1	3000	n/a	28	81	150
2	4000	n/a	38	240	510
3	2000	n/a	38	190	350
4	2000	n/a	31	170	290

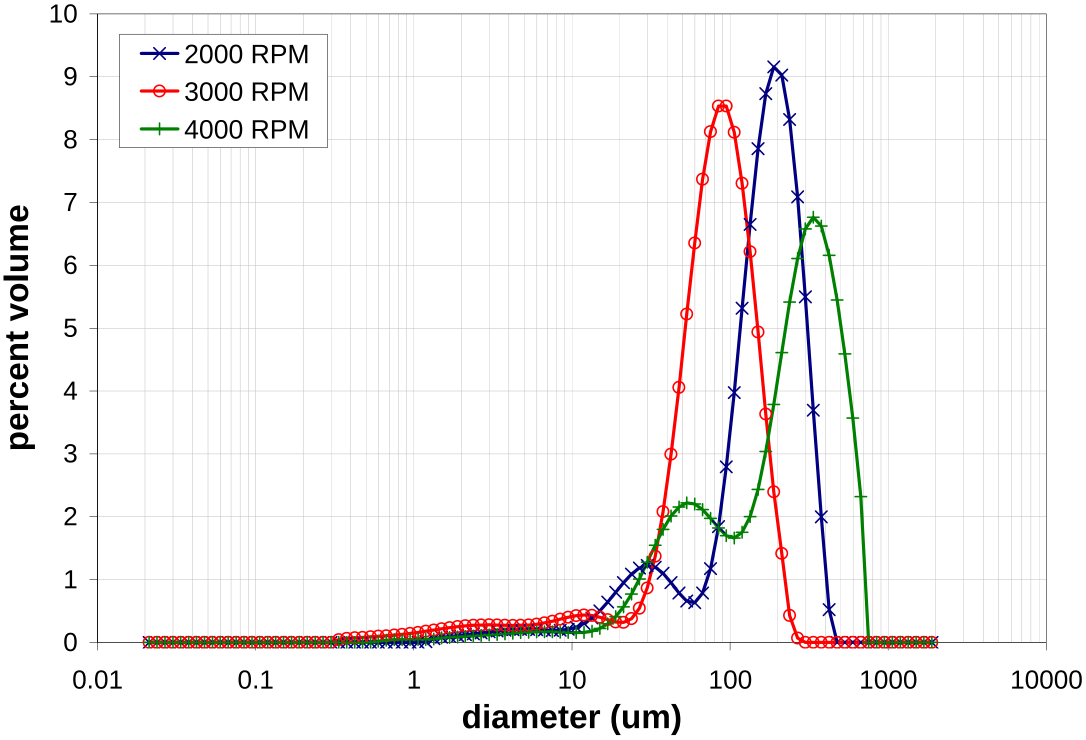


Figure 5.3. PSD of CUF Group 7 Low-Solids Slurry as a Function of Pump Speed

Table 5.6 and Figure 5.4 show the influence of circulation in the CUF on the PSD of Group 7 waste solids. Here, select cumulative undersize percentiles and the PSD for the initial characterization are compared to low-solids matrix slurry. Both samples show a similar PSD range of 0.2 to 400 μm with a primary peak maximum between 70 to 90 μm. The major difference observed in the low-solids matrix slurry is a large shift in the population to the primary peak diameter. This shift may likely be due to transient effects, such as shear-induced agglomeration or flocculation occurring in the PSD analyzer, resulting in a significant relative increase in 20- to 300-μm particles. This shift may also indicate a variation in composition because of sampling difficulties due to large difficult-to-suspend particles. These larger particles also present a complication since they are near the upper limit of the instrument's particle suspension capability and cannot be suspended reliably. The impact of poor suspension on the measured volume particles in this size range is difficult to quantify, as it depends on the settling rate of particles in the instrument flow cell. In addition, preparation and analysis steps for CUF PSD samples typically involve dilution and resuspension. As such, there is significant potential for dissolution, reprecipitation, and ripening.

Table 5.6. Cumulative Undersize Percentiles Showing the Influence of Circulation in the CUF on Group 7 PSD at Measurement Condition 1 to 3000 RPM

Sample	d(10) [μm]	d(50) [μm]	d(90) [μm]
Group 7 Initial Characterization (TI576-G7-S-WL-PSD-1)	1.0	19	130
Group 7 Low Solids Matrix Slurry (TI624-G7-3-PSD)	28	81	150

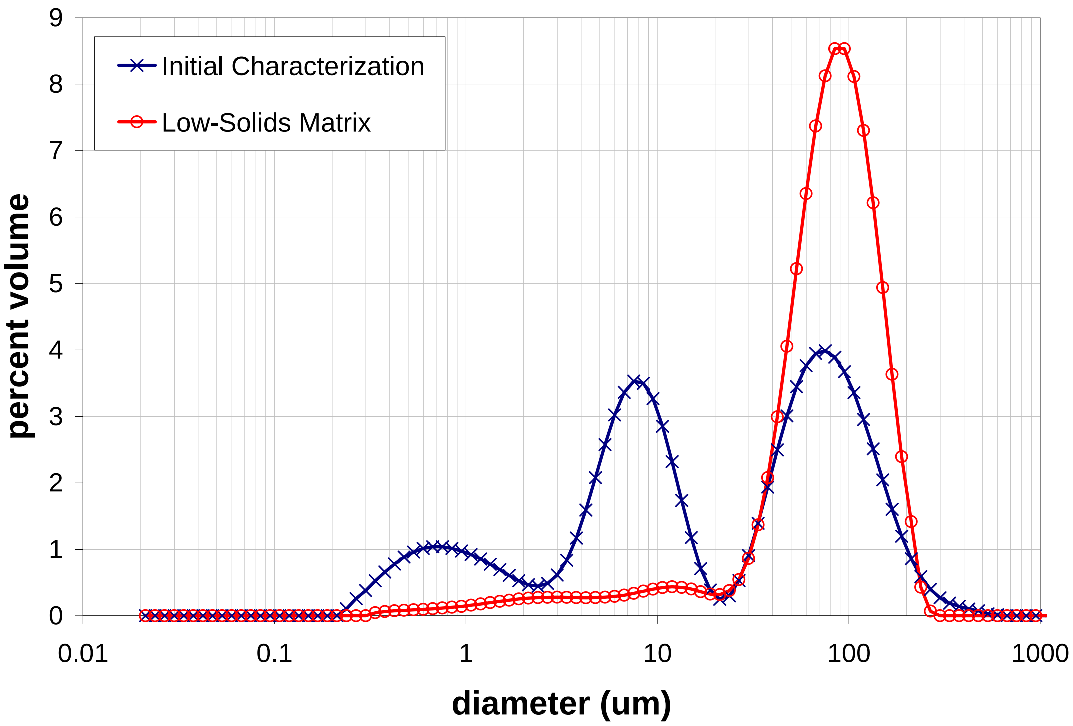


Figure 5.4. Influence of Circulation in the CUF for Group 7. All PSDs were taken at measurement condition 1 to 3000 RPM.

Rheology measurements of the low-solids slurry were taken before the filtration test as well. Figure 5.5 shows the results of flow-curve testing for the low-solids slurry. The measured flow curves indicate non-Newtonian slurry behavior, with the slurry showing finite yield stress, shearing-thinning, and possible hysteresis. The exact cause of possible hysteresis in the current measurements is difficult to ascertain from flow-curve data alone. However, because the hysteresis is characterized by a transient decrease in stress response over the course of the measurement, it can be speculated that hysteresis results from either shear-induced solids structure changes (i.e., sample thixotropy) or solids settling out of the measurement gap.

Flow-curve data at 25°C, 40°C, and 60°C were fit to both Bingham-Plastic and Casson models. Table 5.7 summarizes the best-fit model parameters for the low-solids slurry. Since the data were not influenced by Taylor vortex formation, the full range of shear rates (0 to 500 s^{-1}) is employed in the Casson fitting analysis. Bingham-Plastic analysis cannot account for slurry shear thinning, and as a result, its fitting analysis is limited to 100 to 500 s^{-1} to avoid bias introduced by slurry shear thinning at low shear rates.

Both models provide reasonable fits of the data, although the Casson model provides a better description of the flow curve (especially over 0 to 100 s^{-1}).

Apparent viscosities at 33, 100, 500, and 1000 s^{-1} were derived from each measurement. For each temperature, the 33, 100, and 500 s^{-1} reference viscosities were determined from the average of both up-ramp and down-ramp flow-curve data. The apparent viscosity at 1000 s^{-1} is derived from the averaging of all apparent viscosity measurements during constant rotation at 1000 s^{-1}. As a point of comparison, apparent viscosities were also calculated using the Bingham-Plastic and Casson fitting parameters in Table 5.7. The results of these analyses are provided in Table 5.8.

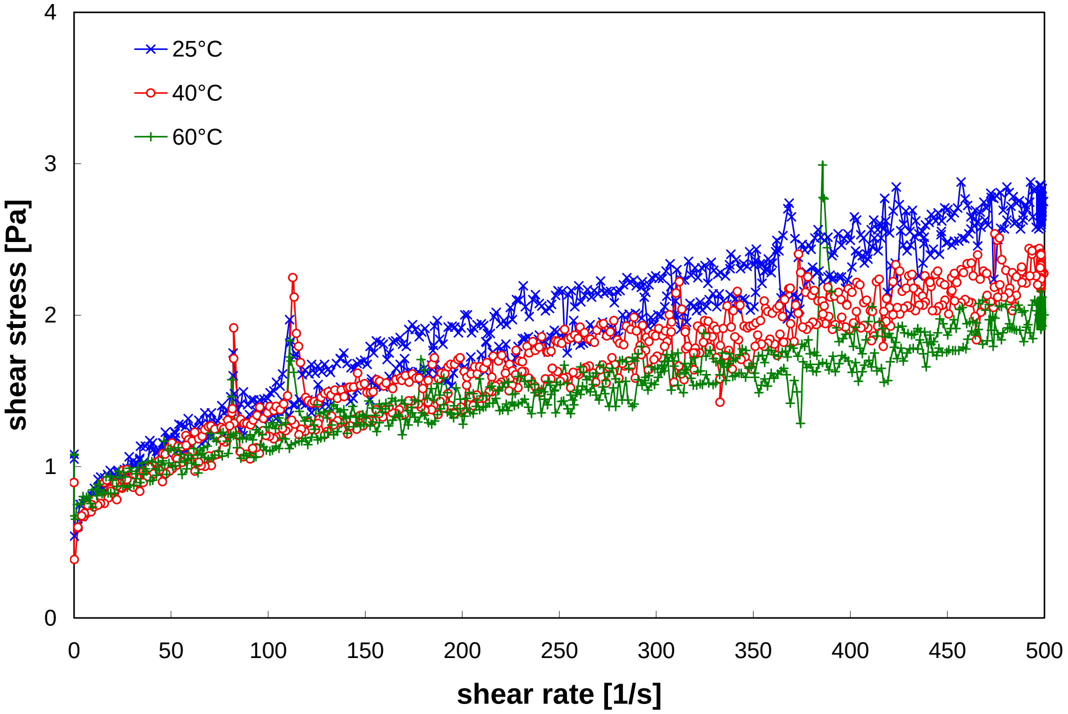


Figure 5.5. Flow Curves for Group 7 CUF Low Solids Slurry

Table 5.7. Results of Fitting Analysis for Group 7 CUF Low Solids Matrix

Model	Temperature [°C]	Range	Yield Stress [Pa]	Consistency [mPa·s]	R
Bingham-Plastic	25 (1 of 2)	100–500 s^{-1}	1.3	3.1	0.96
	25 (2 of 2)	100–500 s^{-1}	1.2	3.1	0.97
	40	100–500 s^{-1}	1.1	2.4	0.94
	60	100–500 s^{-1}	1.0	1.9	0.92
Casson	25 (1 of 2)	0–500 s^{-1}	0.7	1.3	0.98
	25 (2 of 2)	0–500 s^{-1}	0.7	1.4	0.98
	40	0–500 s^{-1}	0.7	1.0	0.97
	60	0–500 s^{-1}	0.7	0.7	0.95

Table 5.8. Select Apparent Viscosities for the Low Solids Slurry

Source	Temperature [°C]	Apparent Viscosity [mPa·s]			
		@ 33 s^{-1}	@ 100 s^{-1}	@ 500 s^{-1}	@ 1000 s^{-1}
Measured	25 (1 of 2)	34	15	6.6	n/a*
	25 (2 of 2)	31	14	5.5	n/a*
	40	27	13	4.2	n/a*
	60	29	12	4.4	n/a*
Bingham-Plastic	25 (1 of 2)	41	16	5.6	4.3
	25 (2 of 2)	39	15	5.5	4.3
	40	35	13	4.6	3.5
	60	33	12	4.0	3.0
Casson	25 (1 of 2)	35	15	5.6	4.0
	25 (2 of 2)	32	14	5.4	4.0
	40	29	13	4.5	3.2
	60	29	12	4.0	2.7

5.3 Filter-Flux Test Matrix and Initial Dewater

This section describes the filtration testing performed using the Group 7 composite and AY-102 tank sample before leaching, as shown in the left column of Figure 5.1. The following tests were performed.

- Filtration testing of the composite Group 7 waste slurry at a low-solids concentration as described in Appendix H. Testing compares the effects of transmembrane pressure (TMP), axial velocity (AV), and operation time on filter flux.
- Dewatering of the waste slurry to a higher UDS concentration using a constant TMP and AV to understand the impact of solids concentration on filtration performance, and to provide data that can be compared to previous testing of other wastes.
- Adding the AY-102 archive tank waste samples to the Group 7 (TBP) sample in the system to achieve the high solids concentration of about 20 wt% in the dewatered slurry.
- Dewatering the blended waste using a constant TMP and AV to compare to dewatering of the Group 7 before the AY-102 addition and increase the UDS concentration to ~20 wt%.
- Filtration testing of the slurry at a high-solids concentration. Like before, testing compares the effects of TMP, AV, and operation time on filter flux.

5.3.1 Low-Solids Test Matrix

After all the slurry samples were collected, and the rheology sample was returned to the CUF, the low-solids matrix test was performed. The average filter flux and process parameter for each filtration test in the matrix is reported in Table 5.9. The measured filter flux over the course of the test matrix is shown in Figure 5.6 where t = 0 is defined as the starting point of the test matrix. The average TMP and AV from each test condition are plotted against the target values for each test in Figure 5.7.

The average filter flux from each test condition (Table 5.9) was plotted against TMP, AV, and the median operational time of the test condition to qualitatively gauge their impact. The filter flux was found to be directly proportional to the TMP (Figure 5.8). The plot for AV (Figure 5.9) contains a large amount of scatter and does not show a significant relationship between the filter flux and the AV. The plot for filter flux over time (Figure 5.10) has a slightly downward but significant trend. Comparing test conditions 1 and 11 at the standard conditions (TMP = 40 psid, AV = 13 ft/s) demonstrates that the filter flux drops from 0.028 to 0.018 GPM/ft^2 which is a 36% decrease over the course of the 16-hour test. This indicates that the filter membrane was fouling and that filter resistance was not at steady state during this test.

The effects of TMP, AV, and relative processing time on filter flux was quantified by modeling of the data using a least-squares-fit method. Process time reflects the average time for the given process conditions since the start of testing. This variable is intended to assess the fouling of the filter that occurs through the duration of testing. A linear-fit equation with an R^2 correlation of 0.98 was developed using TMP and processing time as variables (Figure 5.11). The model also showed that processing time had a measureable negative effect on flux, demonstrating that filter resistance was slightly increasing over time by some fouling mechanism occurring with the waste. Axial velocity was shown to have no significant impact on the filter flux from this analysis.

Use of this model was limited to comparing TMP and AV impacts on filter flux during this test and how filter behavior changed later. During development of the linear model, a positive offset was created. Therefore, the model does not predict a zero filter flux when the TMP is zero, demonstrating that the input to these models must be bound by the range of TMP used in this filter test, shown in Table 5.9. The use of the model should also be limited to when the test matrix occurred because the filter resistance was not at steady state, and the parameters developed in these models would be expected to change past the 16-hour period that this model predicts.

Table 5.9. Average Operating Conditions and Permeate Flux for Low-Solids Matrix Test

Design Test Condition	Median Operation Time of Test[(a)] (hr:mm)	Slurry Temp[(b)] (°C)	TMP[(c)] (psid)	Axial Velocity (ft/s)	Permeate Flowrate (mL/min)	Corrected Permeate Flux (GPM/ft^2)	Axial Pressure Drop[(c)] (psid/ft)
1	1:41	23.5	41.0	13.1	26.3	0.028	2.0
2	3:48	23.4	31.1	11.0	20.0	0.021	1.7
3	5:02	23.7	31.0	14.9	18.3	0.019	2.3
4	6:25	23.5	49.8	15.2	24.8	0.026	2.4
5	7:43	24.2	50.4	11.0	25.5	0.026	1.8
6	8:54	24.4	41.2	13.0	19.9	0.020	2.0
7	10:12	24.2	40.8	8.8	20.1	0.021	1.5
8	11:36	24.6	40.4	17.1	17.8	0.018	2.6
9	12:52	24.5	22.3	12.9	10.2	0.010	1.9
10	14:06	24.8	62.5	13.2	26.6	0.027	2.0
11	15:11	24.4	40.9	12.8	17.6	0.018	1.9

(a) Median operation time refers to the midpoint in processing time of the specific filtration test condition relative to the start time of the test (T = 0). Time periods between test conditions were excluded.
(b) Thermocouple accuracy ± 2°C.
(c) Pressure transducer accuracy ± 1 psig.

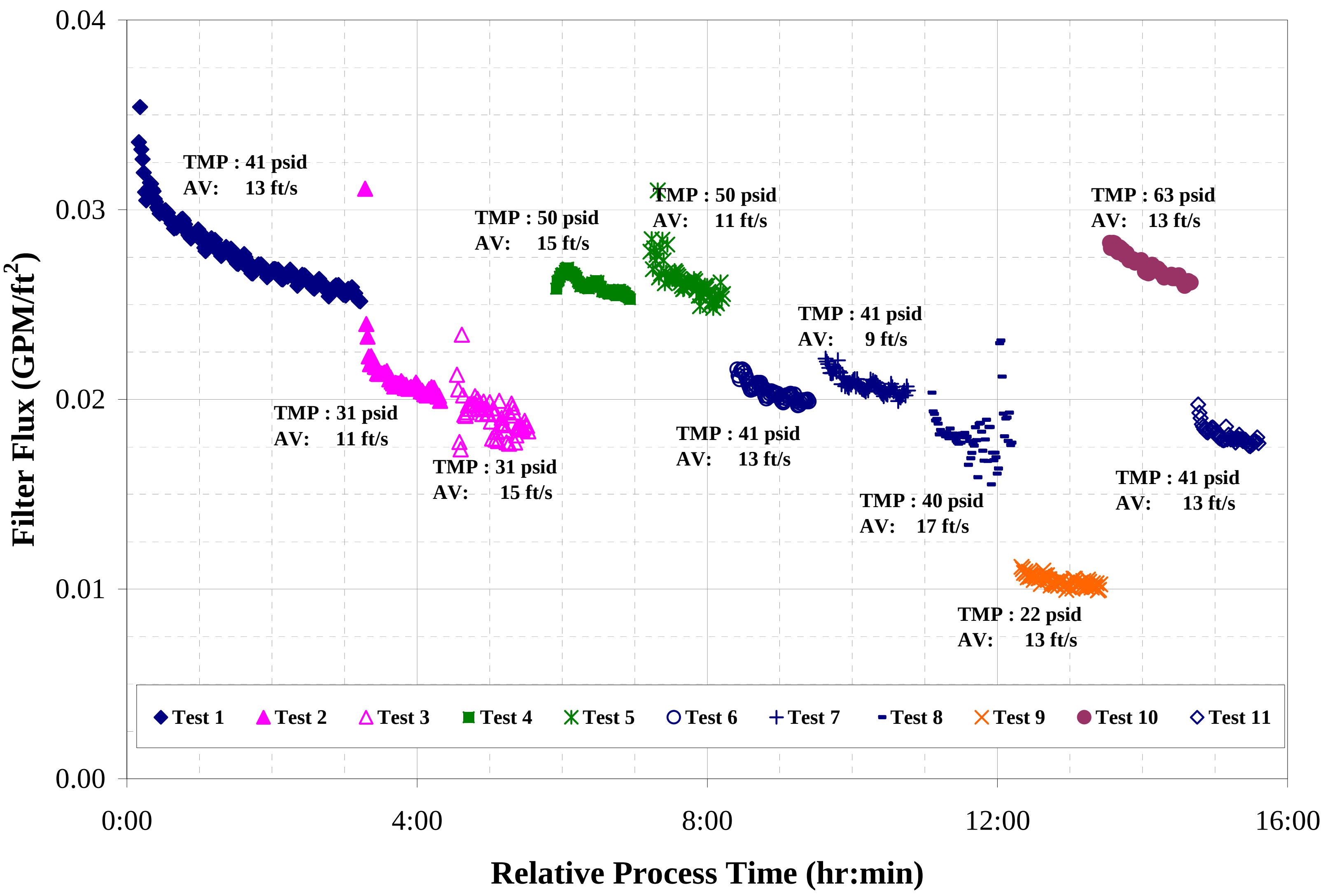


Figure 5.6. Filter-Flux Data for Low-Solids Matrix (Predicted UDS concentration of 4 wt%)

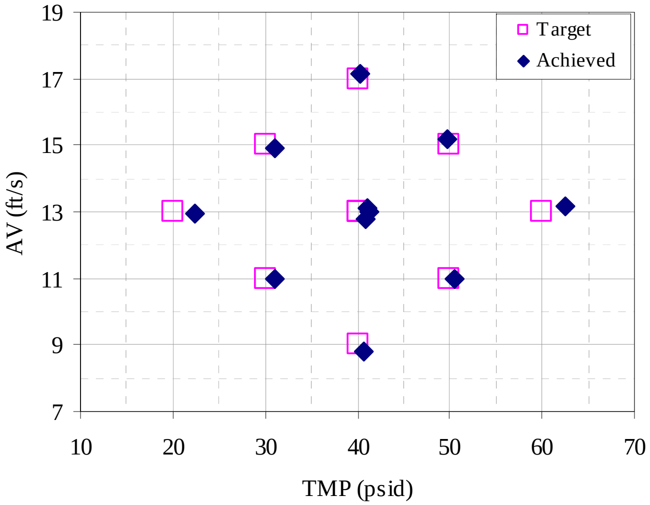


Figure 5.7. Filter Test Matrix for Group 7 Lows-Solids

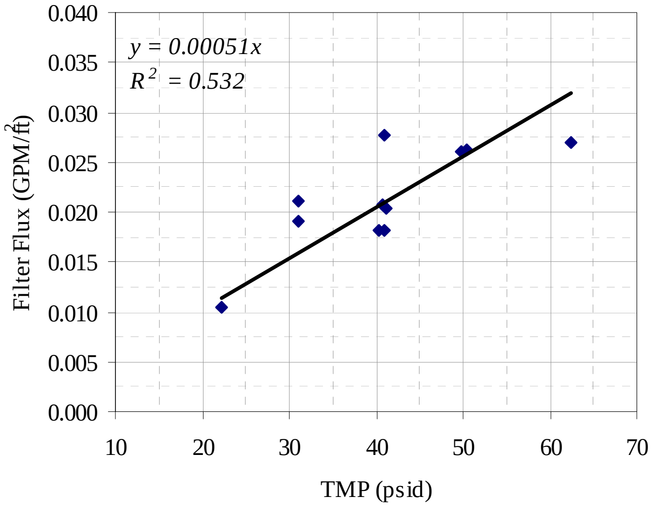


Figure 5.8. Flux vs. TMP for Group 7 Low-Solids

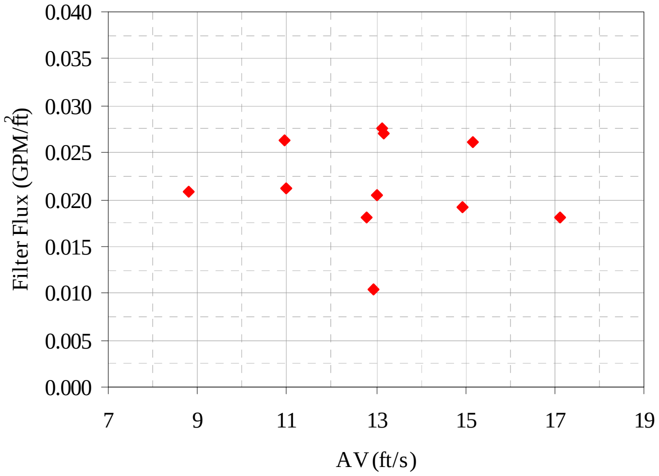


Figure 5.9. Flux vs. AV for Group 7 Low-Solids

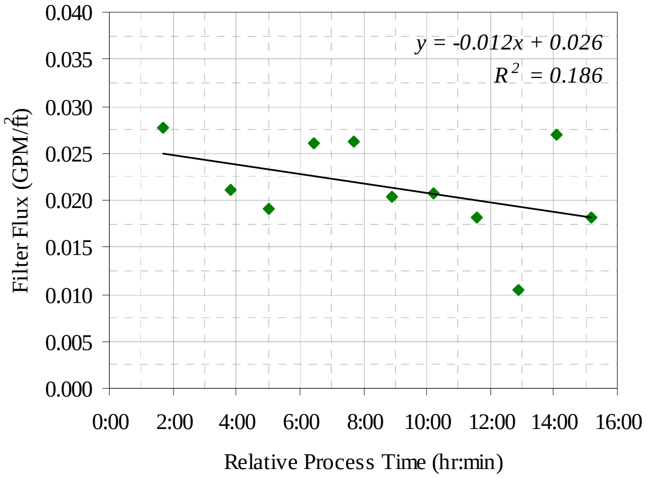
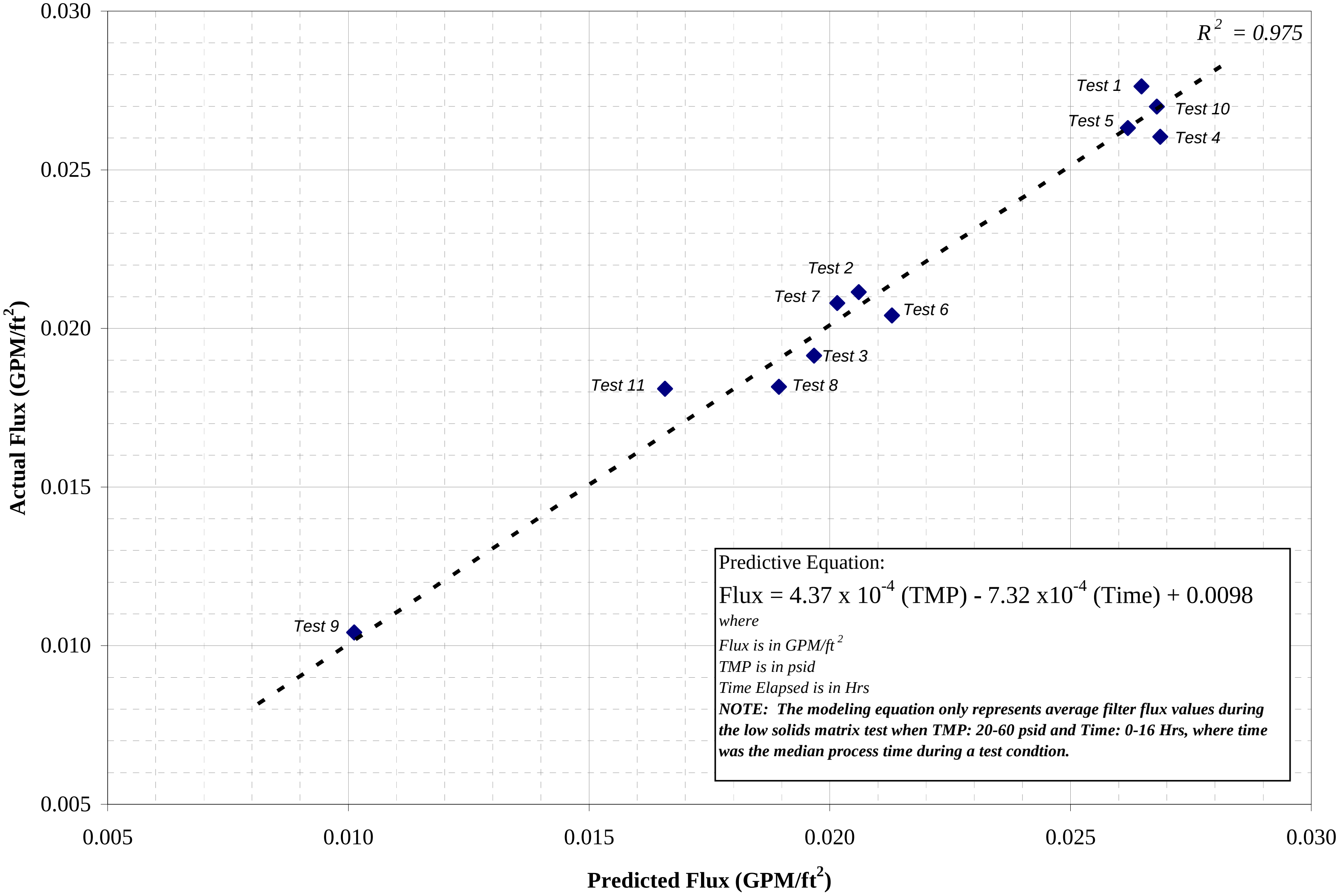


Figure 5.10. Flux vs. Median Process Time of Test Condition for Group 7 Low-Solids



Predictive Equation:

Flux = 4.37 x 10^{-4} (TMP) - 7.32 x10^{-4} (Time) + 0.0098

where

Flux is in GPM/ft^2

TMP is in psid

Time Elapsed is in Hrs

NOTE: The modeling equation only represents average filter flux values during the low solids matrix test when TMP: 20-60 psid and Time: 0-16 Hrs, where time was the median process time during a test condtion.

Figure 5.11. Correlation Calculations of Average Flux as Function of TMP and Time (Predicted UDS of 4 wt%)

5.3.2 Group 7 Dewatering

The Group 7 sample was dewatered after the low-solids test to a target UDS of 13 wt%. An overview of the test activities and mass balance is shown in Figure 5.12 and Table 5.10. Filter-flux results are charted against relative processing time in Figure 5.13. Approximately 2 L of filtered supernate was removed from the slurry over the course of 110 minutes, increasing the slurry UDS concentration to 12 wt% inside the CUF slurry circulation loop. Over the course of the dewatering, the filter flux rate decreased from 0.019 to 0.017 GPM/ft^2. A spike in the filter flux was observed from 25 to 30 minutes into the dewatering. Examining axial-velocity data during this time shows noticeable variation, indicating a problem with the pump, such as cavitation. Despite the increase in the filter flux measured, the TMP decreased from 42 to 40 psid, and the AV decreased from 13.0 to 12.5 ft/s. After 15 minutes, the TMP and AV returned to the original settings without any adjustments. If air bubbles were entrained into the slurry, this would explain the variation seen in the filter permeate flow and changes in the pumping behavior during this time frame. Examination of the raw data over this time range revealed that the variability in the averaged flux data is due to highly erratic readings from the mass flowmeter. Such readings are indicative of air bubbles periodically passing through the meter.

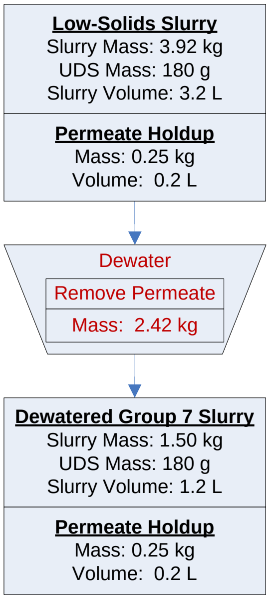


Figure 5.12. Process Flow for Dewatering Group 8 Slurry

Table 5.10. Mass Balance Overview of Dewatering

Step	Change in Mass (g)	Total Mass (g)	Estimated Solid Mass (g)	Slurry Circulating Mass (g)	Estimated Slurry UDS (wt%)
Low-Solids Slurry		4160	180	3920	4.3 wt%
Dewatered Slurry	-2420	1750	180	1500	12 wt%

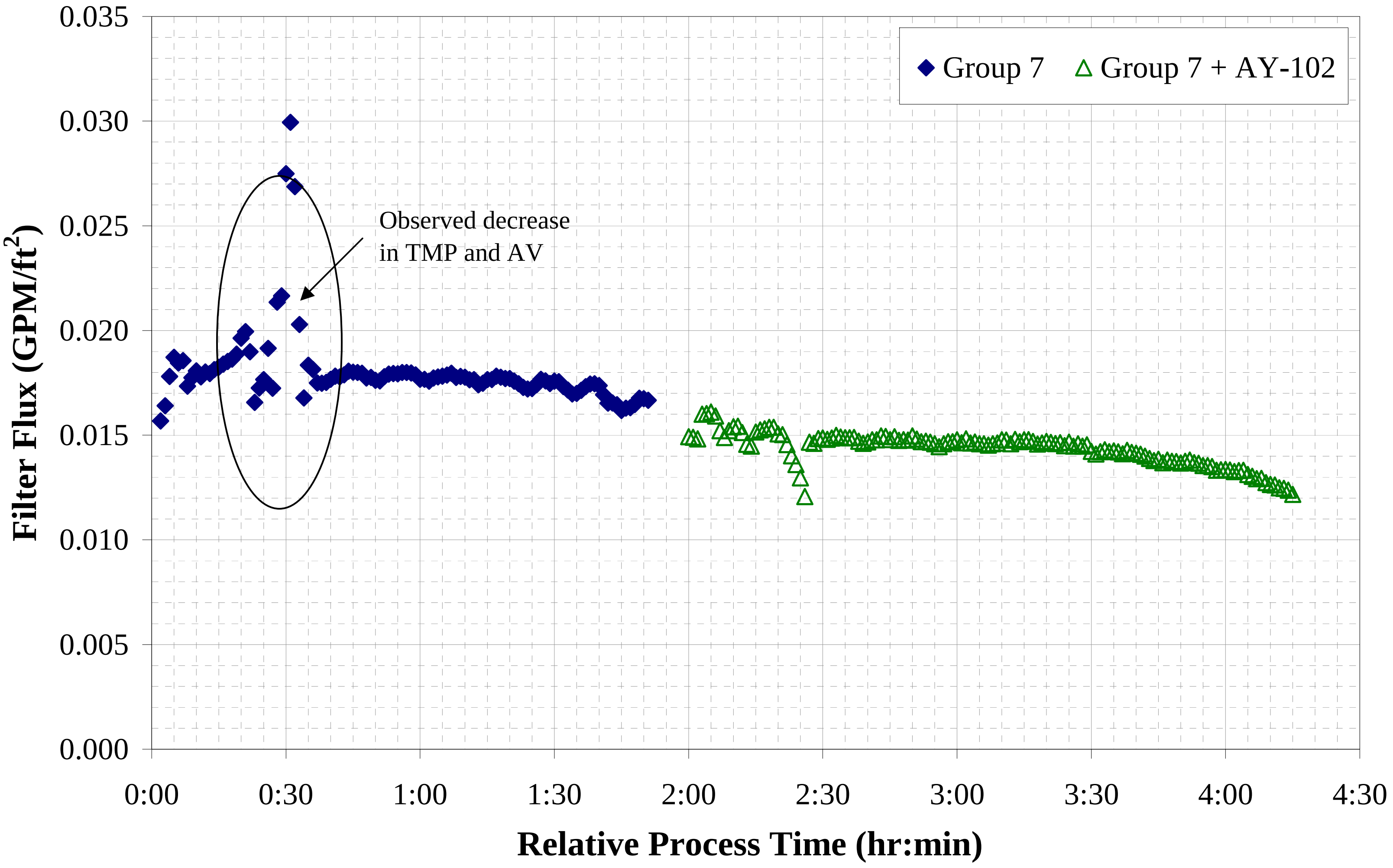


Figure 5.13. Dewatering of Group 7 (4 to 12 wt% UDS) and the Blended Waste (12 to 26 wt% UDS)

5.3.3 Adding AY-102 and Pump Failure

AY-102 was added to the Group 7 sample in the system after the low solids filtration matrix test was completed to boost the solids content of the sample, as discussed in Sec. 5.1. Physical-property measurements performed on the combined slurry are shown in Table 5.11. The mass balance for the addition is shown in Figure 5.14 and Table 5.12.

After the samples of the AY102 were added to the CUF, the pump froze before the blended waste sample could be dewatered. Despite initial success in cleaning and restarting the pump, it soon froze again, and the main seal failed. The pump head was removed, and a magnetic stir bar was discovered inside, most likely from adding one of the AY-102 samples. The system was drained, the pump replaced, and the sample returned to the system. Permeate collected in the previous step was used during cleaning operations to recover a majority of the slurry solids.

When the slurry was returned, the mass of the returned slurry was measured to account for losses that occurred from the pump failure and draining of the slurry out of the CUF. Physical-property measurements indicated that initial estimates of the UDS concentration of the archived AY-102 slurry were lower than believed. Despite the losses created from the pump failure, the inventory of solids in the CUF at this point was believed to be 460 grams at this point in the process, based on the final results of physical-property testing (Table 5.11). The waste solids ratio between AY-102 to Group 7 was estimated as 2:1.

Table 5.11. Physical Properties of the Blended Group 7/AY102 Slurry Before Dewatering

Slurry Density (g/mL)	1.28
Supernate Density (g/mL)	1.24
Settled Solids (Vol %)	48%
Centrifuged UDS (Wt %)	55%
Total Solids (Wt %)	33%
Dissolved Solids (Wt%)	24%
UDS (Wt%)	12%

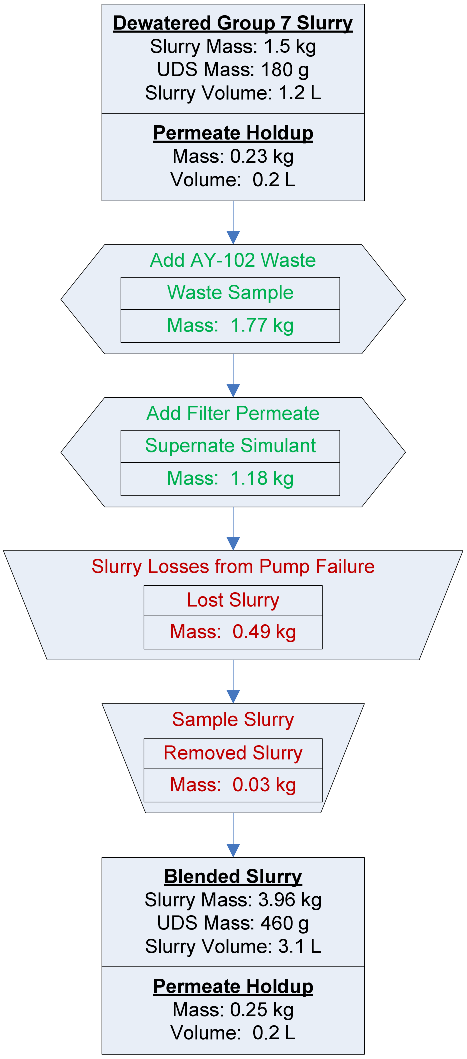


Figure 5.14. Process Flow of AY-102 Addition and Losses Created by Pump Failure

Table 5.12. Mass Balance Overview of Dewatering, AY-102 Addition

Step	Change in Mass (g)	Total Mass (g)	Estimated Solid Mass (g)	Slurry Circulating Mass (g)	Estimated Slurry UDS (wt%)	Measured Slurry UDS (wt%)
Initial dewatering (Incl. Sample)		1750	180	1500	12 wt%	
Add AY-102	+1770	3520		3270		
Add permeate	+1180	4700		4450		
Mass Loss from Leakage and Transfers	-460	4240		3990		
Sampling	-30	4210	***460***	3960		11.6 wt%

5.3.4 Dewatering Group 7/AY-102 Slurry

The blend slurry was dewatered to a UDS concentration of 26 wt%. An overview of the mass balance is shown in Figure 5.15 and Table 5.13. The measured filter flux is compared to the initial dewatering of the Group 7 waste in Figure 5.13. Comparing the flux before and after the AY102 test shows that the measured flux at the end of the Group 7 dewatering was similar to the start of the blended slurry dewatering. Over the course of 2 hours, the flux ranged from 0.016 to 0.012 GPM/ft^2, and 1.8 L of permeate was collected. Overall, the flux was stable over most of the duration of the dewatering operations. The exception to this occurred about 20 minutes into dewatering of the blended slurry, when the pump speed decreased by by ~10% unexpectedly for about five minutes. During this time, the TMP decreased from 40 psid to 33 psid, which correlated to a decrease in the permeate flow. Without any adjustments, the pump speed returned to normal after five minutes, and dewatering continued at the standard conditions. Physical-property measurements of the slurry afterwards showed that the centrifuge UDS concentration of the blended slurry was 55 to 58 wt%. This indicates that the slurry was capable of being dewatered perhaps even higher than 26 wt% before the slurry UDS concentration began to limit filter flux. The filter flux began to decrease slightly during the last 30 minutes, indicating that the slurry was beginning to approach a region where the UDS concentration, and not transmembrane pressure, was the dominant filtration parameter.

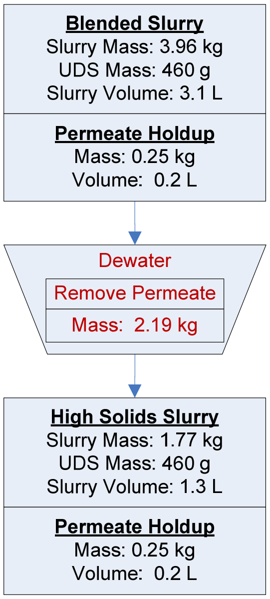


Figure 5.15. Process Flow for Dewatering the Blended Waste Slurry (Group 7/AY-102)

Table 5.13. Mass Balance Overview for the Dewatering of the Blended Slurry to 26 wt%

Step	Change in Mass (g)	Total Mass (g)	Estimated Solid Mass (g)	Slurry Circulating Mass (g)	Estimated Slurry UDS (wt%)	Measured Slurry UDS (wt%)
Blended Slurry		4210	460	3960		11.6 wt%
Dewatered Slurry (High-Solids Slurry)	-2190	2020	460	1770	26 wt%	26 wt%

5.3.5 High-Solids Matrix

After dewatering, the high-solids matrix test was started. Figure 5.16 displays the complete permeate flux data for each step with respect to the relative processing time. The average filter flux ranged from 0.007 to 0.015 GPM/ft^2, with a value near 0.012 GPM/ft^2 for the standard filtration condition of TMP=40 psid and AV=13 ft/s. Table 5.14 contains the average operating conditions and filter flux for each step of the high-solids matrix. The average TMP and AV from each test condition are plotted against the target values for each test in Figure 5.17.

The average filter flux from each test condition was plotted against TMP, AV, and the median operational time of the test condition to qualitatively gauge their impact, as shown in Figure 5.18 through Figure 5.20. The median operation time for the test condition was used to assess if fouling of the filter was significant during the test, which would shift the results of the test matrix. Filter flux was found to be directly proportional to TMP (Figure 5.18), with a R^2 correlation of 0.64. The plot for AV (Figure 5.19) also showed that filter flux was proportional to AV. While the R^2 correlation for the trend in Figure 5.19 was only 0.049, it still suggests some dependence of the flux on the AV. The plot for filter flux over time (Figure 5.20) does not show a significant relationship. Comparing test conditions 1, 6, and 11 at the standard conditions (TMP = 40 psid, AV = 13 ft/s) demonstrates little difference in the average filter flux.

Modeling the data using a least-squares-fit method was then used to quantify the effects of TMP, AV, and relative processing time on filter flux. Process time reflects the average time for the given process conditions since the start of testing. This variable is intended to assess the fouling of the filter that occurs through the duration of testing. While the individual correlations of AV and TMP to flux were not very good, a linear fit equation combining both TMP and AV effects was developed with an R^2 correlation of 0.89 (Figure 5.21). This indicates that after dewatering, the slurry filtration behavior was influenced by both the filter medium resistance and the filter cake resistance. As seen from Figure 5.20, the process time was found not to have any significant impact. As seen in previous testing, fouling effects over time tend to decay over time, reaching a steady-state condition.

The use of this model was limited to comparing TMP and AV impacts on filter flux during this test and how the filter behavior changed after dewatering. During development of the linear model, a negative offset was created. Therefore, the model does not predict a zero filter flux when the TMP is zero, demonstrating that the input to these models must be bound by the range of TMP used in this filter test, shown in Table 5.14. The use of the model should also be limited to when the test matrix occurred. While changes in the filter resistance appeared to be not significant over the course of this test, a 16-hour filter matrix test cannot predict fouling influences impacting long-term operations of the CUF.

Table 5.14. Average Operating Conditions and Permeate Flux for High-Solids Matrix Test

Design Test Condition	Median Operation Time of Test[a] (hr:mm)	Slurry Temp[b] (°C)	TMP[c] (psid)	Axial Velocity (ft/s)	Permeate Flowrate (mL/min)	Corrected Permeate Flux (GPM/ft^2)	Axial Pressure Drop[c] (psid/ft)
1	1:42	23.0	39.8	12.9	10.8	0.012	2.2
2	3:59	22.7	30.2	11.0	9.2	0.010	1.8
3	5:16	23.9	29.9	15.1	9.4	0.010	2.3
4	6:37	29.7	50.7	14.2	17.1	0.015	2.4
5	7:48	23.0	50.7	11.0	11.6	0.012	1.9
6	9:01	24.6	40.5	13.1	12.3	0.013	2.1
7	10:15	22.3	40.1	8.9	8.5	0.009	1.8
8	11:36	27.0	41.0	14.3	12.9	0.012	2.3
9	12:50	24.4	21.6	13.3	6.7	0.007	2.0
10	14:12	28.2	61.9	12.5	16.1	0.015	2.2
11	15:41	26.1	39.8	12.9	11.3	0.011	2.1

(a) Median operation time refers to the midpoint in processing time of the specific filtration test condition relative to the start time of the test (T = 0). Time periods between test conditions were excluded.
(b) Thermocouple accuracy ± 2°C.
(c) Pressure transducer accuracy ± 1 psig.

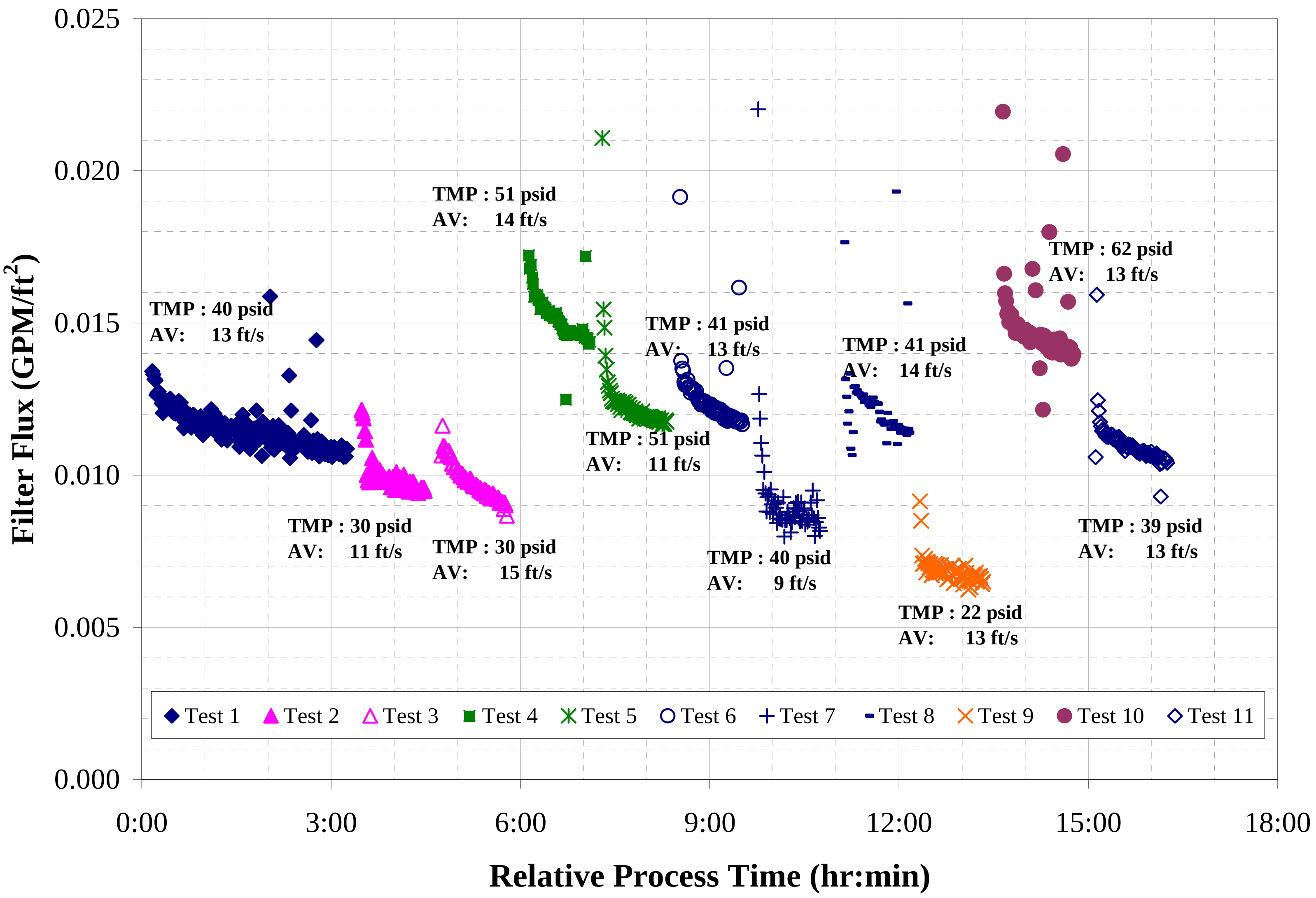


Figure 5.16. Filter-Flux Data for Group 7-AY102 High-Solids Matrix (Measured as 26 wt% UDS)

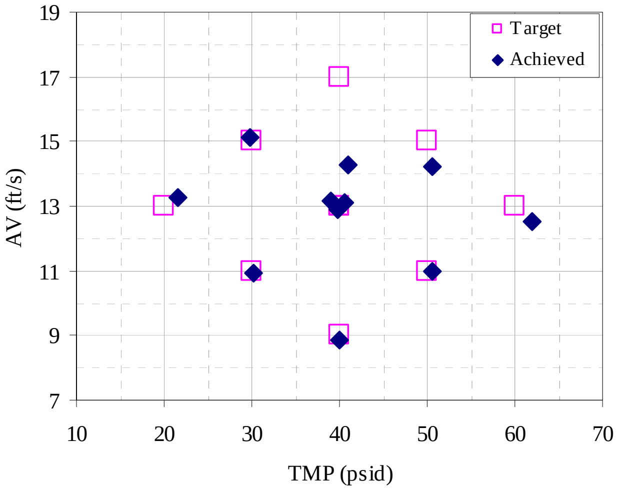


Figure 5.17. Filter Test Matrix for Group 7-AY102 High-Solids

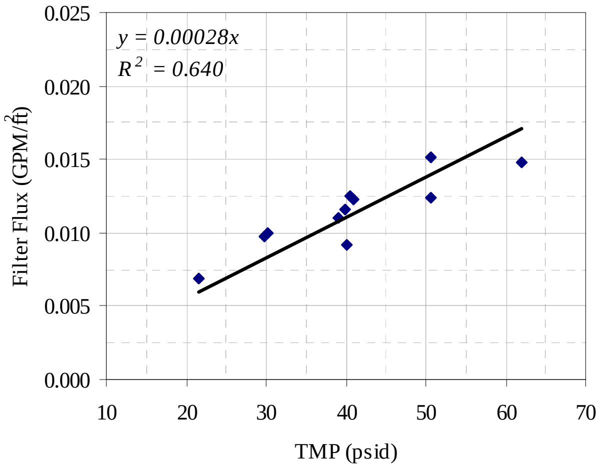


Figure 5.18. Flux vs. TMP for Group 7-AY102 High-Solids

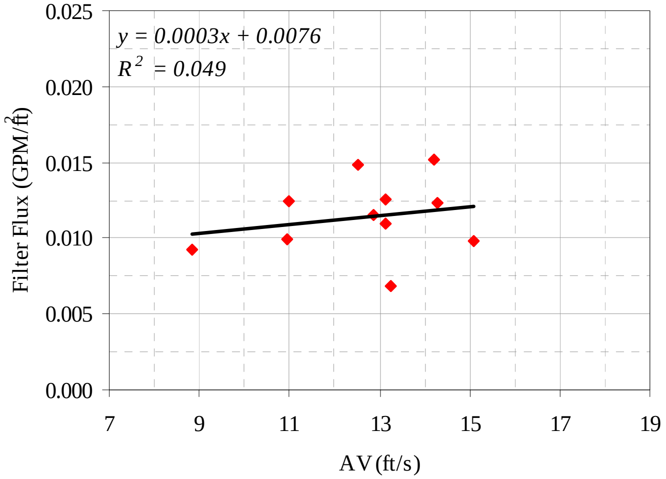


Figure 5.19. Flux vs. AV for Group 7-AY102 High-Solids

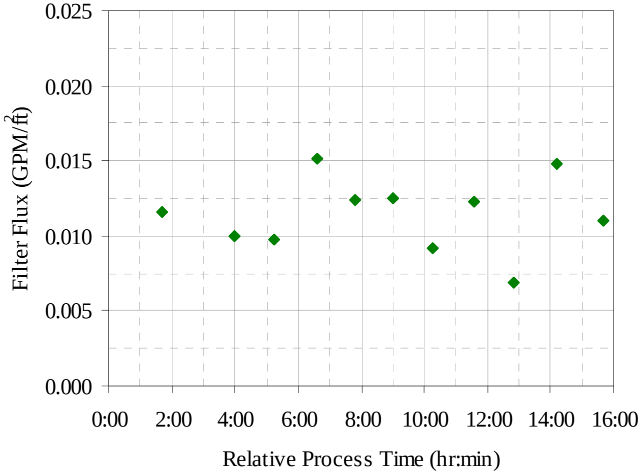
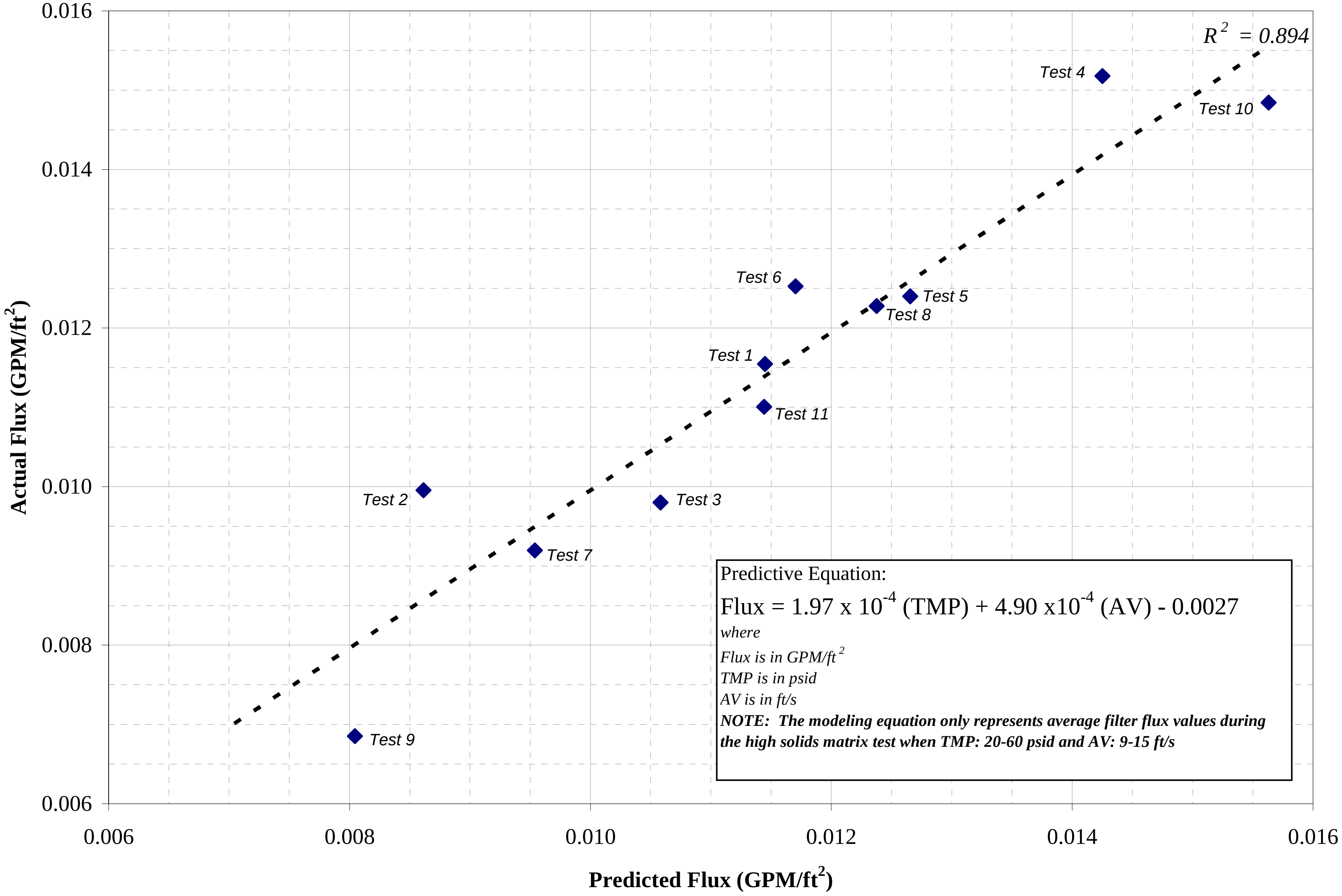


Figure 5.20. Flux vs. Median Process Time of Test for Group 7-AY102 High-Solids



Predictive Equation:

Flux = 1.97 x 10^{-4} (TMP) + 4.90 x10^{-4} (AV) - 0.0027

where

Flux is in GPM/ft^2

TMP is in psid

AV is in ft/s

NOTE: The modeling equation only represents average filter flux values during the high solids matrix test when TMP: 20-60 psid and AV: 9-15 ft/s

Figure 5.21. Least Squares Fit to High-Solids Matrix Test Results to Linear Model (Measured UDS of 26 wt%)

5.4 Pre-Leached Slurry Characterization

5.4.1 Physical-Property and Chemical-Characterization Measurements

At the completion of the high-solids test matrix, the slurry in the recirculation loop was sampled for physical and chemical analysis (Figure 5.22). Results from the physical-property measurements of the slurry samples are shown in Table 5.15, which correlate with the predicted concentration calculated from Table 5.13. The high-solids slurry wet-composition (including permeate hold-up) before caustic leaching is shown in Table 5.16. The slurry composition in terms of supernate and solid composition is provided in Table 5.17.

Comparing the low-solids slurry to the high solids slurry shows that adding the AY-102 sample resulted in significant increases in all radionuclides and in Al, Cr, Fe, Mn, Si, and C_2O_4. These species were presumably high in the AY-102 sample, and since they are usually found in the solids (with the exception of ^{137}Cs), they would not be reduced by the dewatering step. Al added from the AY-102 sample was expected to be in the form of gibbsite, dawsonite, and cancrinite [Krupka 2004]. The exception, ^{137}Cs, shows unusual behavior. The majority of the ^{137}Cs in the Group 7 slurry before adding the AY-102 sample was found in the supernate (75%). Only 7% was found in the supernate after the AY-102 addition, suggesting that the AY-102 solids contain an insoluble Cs species.

The following species typically found in the supernatant were observed to decrease after AY-102 addition and dewatering: Na, P, and all anions other than C_2O_4. Uranium, though normally found in the solids, was also observed to decrease after AY-102 addition and dewatering. In the Group 7 slurry, before adding the AY-102 sample, 2% of the total U mass was found in the supernate. After AY-102 addition, 46% was found in the supernate after dewatering. The dewatering operation removed 39 wt% of the U inventory of the slurry because of the large fraction of uranium that became soluble after the addition was made. An increase in the P concentration in the supernate was also observed, which was unexpected because the AY102 supernate had a lower P concentration than the Group 7 slurry [Coleman, 2003]. This indicated that some P in the insoluble solids (such as phosphate) dissolved into the slurry supernate.,

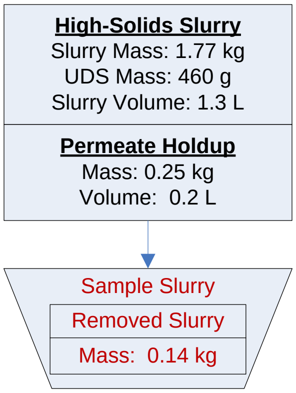


Figure 5.22. Process Flow Through the High-Solids Matrix

Table 5.15. High-Solids Slurry Physical-Property Measurements (inside slurry loop)

Slurry Density (g/mL)	1.45
Supernate Density (g/mL)	1.35
Settled Solids (Vol %)	95%
Centrifuged UDS (Wt %)	58%
Total Solids (Wt %)	44%
Dissolved Solids (Wt%)	24%
UDS (Wt%)	26%

Table 5.16. High-Solids Slurry Inventory and Composition

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	2.02	1.57		0.46	
Wt% of Slurry	100%	77.4%		22.6%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	3.3E+01	1.3E-02	1.1E+01	3.3E+01	7.2E+04
B	2.9E-02	2.4E-02	2.1E+01	5.5E-03	1.2E+01
Bi	8.3E-01	< 4.E-3	< 4.E+0	8.3E-01	1.8E+03
Ca	4.7E+00	1.9E-02	1.6E+01	4.7E+00	1.0E+04
Cd	9.8E-02	1.5E-03	1.3E+00	9.7E-02	2.1E+02
Cr	1.3E+00	5.2E-02	4.5E+01	1.3E+00	2.7E+03
Fe	7.2E+01	2.1E-03	1.8E+00	7.2E+01	1.6E+05
K	4.4E-01	3.5E-01	3.0E+02	8.5E-02	1.9E+02
Mn	1.1E+01	2.5E-04	2.2E-01	1.1E+01	2.3E+04
Na	1.4E+02	1.0E+02	8.6E+04	4.0E+01	8.6E+04
Ni	1.8E+00	< 3.E-4	< 3.E-1	1.8E+00	4.0E+03
P	1.9E+01	5.7E+00	5.0E+03	1.3E+01	2.9E+04
S	5.4E+00	5.1E+00	4.4E+03	2.9E-01	6.3E+02
Si	1.8E+01	2.0E-03	1.7E+00	1.8E+01	3.9E+04
Sr	7.1E-01	2.4E-04	2.1E-01	7.1E-01	1.5E+03
Zn	2.0E-01	1.0E-03	8.8E-01	2.0E-01	4.4E+02
Zr	1.7E+00	1.5E-03	1.3E+00	1.7E+00	3.7E+03
U	1.1E+01	4.4E+00	3.8E+03	6.1E+00	1.3E+04
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	7.8E+01	7.6E-01	6.6E-04	7.7E+01	1.7E-01
Cs-137	1.7E+05	1.1E+04	9.5E+00	1.6E+05	3.6E+02
Eu-152	1.0E+02	< 5.E-1	< 4.E-4	1.0E+02	2.3E-01
Eu-154	2.6E+03	< 4.E-1	< 3.E-4	2.6E+03	5.6E+00
Eu-155	1.2E+03	< 4.E+0	< 3.E-3	1.2E+03	2.5E+00
Am-241	4.2E+03	< 4.E+0	< 3.E-3	4.2E+03	9.3E+00
Gross Alpha	6.2E+03	2.4E+01	2.0E-02	6.2E+03	1.3E+01
Gross Beta	7.2E+06	1.1E+04	9.5E+00	7.2E+06	1.6E+04
Sr-90	3.7E+06	3.3E+02	2.8E-01	3.7E+06	8.1E+03

Table 5.16 (Contd)

Pu-239+240	1.6E+03	2.6E+01	2.2E-02	1.5E+03	3.4E+00
Pu-238	2.5E+02	3.7E+00	3.2E-03	2.5E+02	5.4E-01
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	µg/ml	**[M]**	**g**	**µg/g**	**g**
F	4.4E+02	2.3E-02	5.0E-01	1.3E+02	6.1E-02
Cl	4.6E+02	1.3E-02	5.3E-01	0.0E+00	0.0E+00
C_2O_4	1.7E+03	2.0E-02	2.0E+00	2.6E+03	1.2E+00
NO_2	1.4E+04	3.1E-01	1.6E+01	1.9E+04	8.6E+00
NO_3	1.2E+05	2.0E+00	1.4E+02	1.5E+05	7.0E+01
SO_4	1.2E+04	1.3E-01	1.4E+01	1.6E+04	7.3E+00
PO_4	1.5E+04	1.6E-01	1.7E+01	4.5E+04	2.1E+01
OH	1.9E+03	1.1E-01	2.2E+00		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-169, Section 3). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI624-G7-B (ASO ID 08-02060) and the predicted mass of supernate in the system.

(c) Solids Fraction mass components were calculated from the difference between the slurry component mass and liquid component mass fraction.

Table 5.17. Group 7/AY102 High-Solids Slurry Composition Based on ICP-OES/Radionuclide Characterization

ICP-OES Analytes	**Dry Slurry[a] (μg/g)**	**Supernate[b] (μg/mL)**	**Dry Solids[c] (μg/g)**
Al	42,000	11	72,000
B	[23]	20.5	--
Bi	1,040	--	1,800
Cd	113	[1.3]	190
Cr	1,630	44.7	2,700
Fe	91,200	[1.8]	156,000
Mn	13,500	[0.220]	23,000
Na	153,000	86,000	60,000
Ni	2,440	--	4,200
P	22,500	4,960	27,000
S	5,320	4,390	--
Sr	892	0.205	1,500
U	12,400	3,840	12,000
Zn	270	[.88]	460
Zr	2,280	[1.3]	3,900
Ag	*67.6*	*10.9*	*90*
Ba	*580.0*	*[.19]*	*990*
Be	*0.787*	*[.0064]*	*1.3*
Ca	*6,330*	*16.1*	*11,000*
Ce	*633*	--	*1,100*
Cu	*209*	--	*360*
La	*725*	--	*1,200*
Li	*87*	*3.65*	*140*
Mg	*1,690*	--	*2,900*
Mo	*[17]*	*[5.0]*	*[20]*
Nd	*1,060*	--	*1,800*
Pb	*3,930*	*[5.2]*	*6,700*
Ru	*217*	*[9.6]*	*350*
Th	*486*	--	*830*
Ti	*199*	--	*340*
V	*16.9*	*[0.590]*	*30*
W	*232*	*[12]*	*370*
Y	*94.0*	*[0.069]*	*160*
Si	23,200	[1.7]	40,000
Radionuclides	Dry Slurry (μCi/g)	Supernate (μCi/mL)	Dry Solids (μCi/g)
^{60}Co	1.01E-1	6.56E-4	1.7E-1
^{137}Cs	2.25E+2	9.51E+0	3.6E+2
^{154}Eu	3.37E+0	< 3.E-4	5.8E+0
^{155}Eu	1.49E+0	< 3.E-3	2.5E+0
^{241}Am	5.49E+0	< 3.E-3	9.4E+0
^{90}Sr	4.83E+3	2.83E-1	8.3E+3
$^{239/240}$Pu	1.99E+0	2.22E-2	3.3E+0
^{238}Pu	3.32E-1	3.21E-3	5.6E-1

(a) Test sample TI624-G7-6, ASO ID 08-2074
(b) Test sample TI624-G7-B, ASO ID 08-2060
(c) Calculated using results from TI624-G7-6 and TI624-G7-B.

Analyte uncertainties were typically within ±15%; results in brackets indicate that the analyte concentrations were greater than the method detection limit (MDL) and less than the estimated quantitation limit (EQL), and uncertainties were >15%. Opportunistic analytes (in italics) ware reported for information only; quality control (QC) requirements did not apply to these analytes.

5.4.2 Rheology of the AY-102 Slurry and High-Solids Slurry

Rheology measurements were done on the AY-102 source material before introduction into the CUF. Figure 5.23 shows the results of flow-curve testing for the AY-102 slurry sample. The results of the measurement indicate that the flow behavior is Newtonian. Flow-curve data show a linear stress response over shear rates from zero up to 400 or 500 s^{-1}. At higher shear rates (generally 500 s^{-1} and above), flow-curve data show an increase in the slope of the stress response curve. This increase is likely a result of Taylor vortex formation onset (i.e., unstable/turbulent flow), which renders the affected data unusable.

The flow curves are relatively free of hysteresis. Specifically, the up- and down-ramp data generally agree with the instrument limits of accuracy (~0.5 Pa). Any difference can easily be attributed to rotor inertial effects. The lack of hysteresis suggests that the measurements are not significantly affected by shearing or settling of the sample. It should be noted that lack of hysteresis does not necessarily mean that these effects are absent because any changes could have taken place during the shearing step or before analysis took place.

Given the ±0.4 Pa typical stress variation in measurement data, the best description of the current flow behavior that can be concluded based on the current measurement data is Newtonian. As such, Newtonian viscosity was derived for each flow-curve measurement. Data believed to be influenced by Taylor vortex formation are excluded from the fits. The shear-rate range for all fits is limited to the ranges specified in Table 5.18. Rotor inertial effects and measurement noise sometimes caused down-ramp stress data to fall below zero.

Table 5.18 summarizes the best-fit Newtonian parameters for the AY-102 slurry. The results indicate a Newtonian viscosity that generally falls between 1.8 and 4.1 mPa·s, depending on temperature. Increased temperature yields a decrease in the slurry viscosity, likely as a result of suspending phase viscosity decrease. The initial and replicate viscosity measurements at 25°C show agreement with a discrepancy of ~5%, which is below the accuracy level of the measurement.

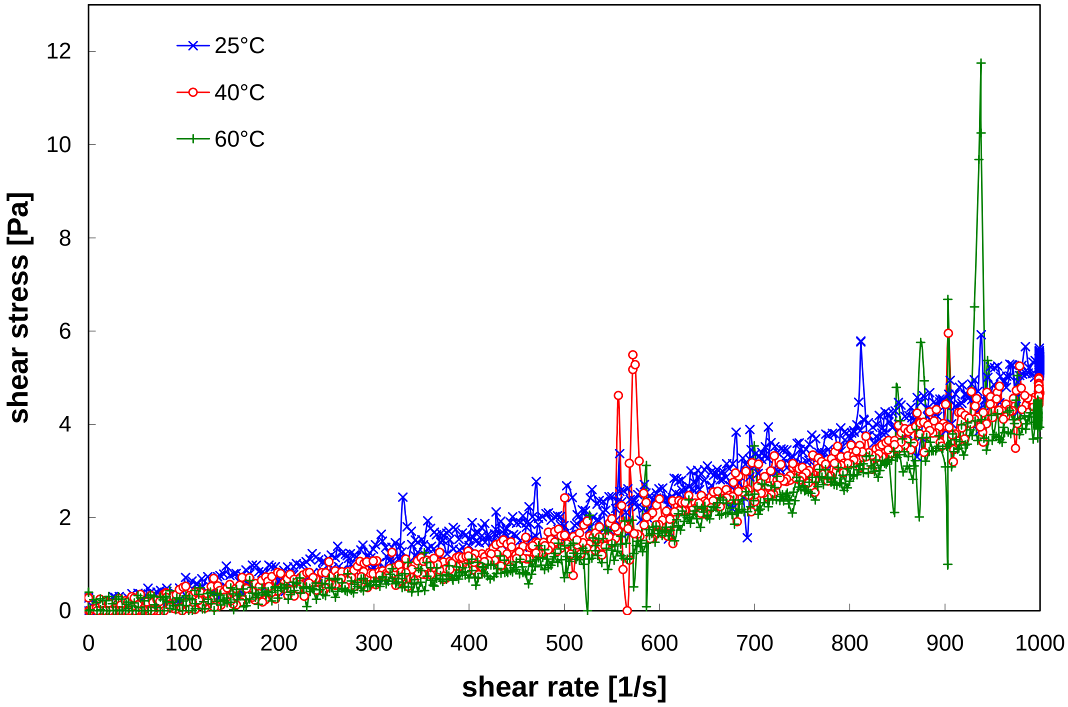


Figure 5.23. Flow Curves for the AY-102 Slurry

Table 5.18. Results of Fitting Analysis for AY-102 Slurry

Model	Temperature [°C]	Range	Viscosity [mPa·s]	R
Newtonian (Flow Curve)	25 (1 of 2)	0–500 s^{-1}	3.9	0.96
	25 (2 of 2)	0–500 s^{-1} (a)	4.1	0.96
	40	0–400 s^{-1} (a)	2.7	0.95
	60	0–400 s^{-1} (a)	1.8	0.85
(a) Based on fit of up-ramp data only.				

Figure 5.24 shows the results of flow-curve testing for the high-solids slurry. The flow behavior is non-Newtonian. Flow-curve data indicate that the dewatered slurry has a finite yield stress of approximately 3 to 5 Pa and that the slurry is shear thinning. Flow-curve hysteresis is minor and can be attributed to rotor inertial effects alone. The lack of hysteresis suggests that the internal structure of the slurry (such as particle agglomerates) is stable with respect to shear or that any changes in structure occur quickly and are complete at the end of the 3-minute shearing step performed immediately before flow-curve measurement. With regard to data anomalies, the curves are free of any slope discontinuities that could be associated with Taylor vortex formation.

Flow-curve data at 25°C, 40°C, and 60°C were fit to both Bingham-Plastic and Casson models. Table 5.19 summarizes the best-fit model parameters for the high-solids slurry. Since the data were not influenced by Taylor vortex formation, the full range of shear rates (0 to 1000 s^{-1}) is employed in the Casson fitting analysis. Bingham-Plastic analysis cannot account for slurry shear thinning, and as a result, its fitting analysis is limited to 100 to 1000 s^{-1} to avoid bias introduced by slurry shear thinning at low shear rates. Both models provide reasonable fits of the data, although the Casson model provides a better description of the flow curve (especially over 0 to 100 s^{-1}). On the other hand, although the Bingham-Plastic cannot capture slurry shear thinning below 100 s^{-1}, it better captures the flow-curve linearity at higher shear rates.

Apparent viscosities at 33, 100, 500, and 1000 s^{-1} were derived from each measurement. For each temperature, the 33, 100, and 500 s^{-1} reference viscosities were determined from the average both up-ramp and down-ramp flow-curve data. The apparent viscosity at 1000 s^{-1} is derived from the average of all apparent viscosity measurements during constant rotation at 1000 s^{-1}. As a point of comparison, apparent viscosities were also calculated using the Bingham-Plastic and Casson fitting parameters in Table 5.19. The results of these analyses are provided in Table 5.20.

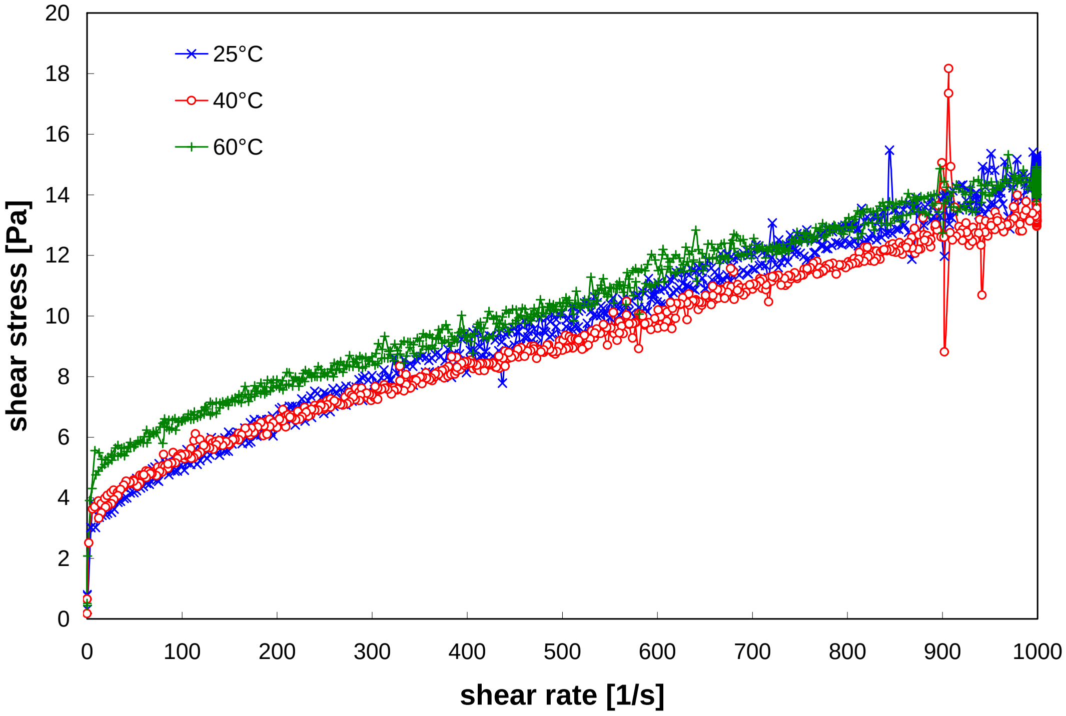


Figure 5.24. Flow Curves for the CUF High Solids Slurry

Table 5.19. Results of Fitting Analysis for the CUF High Solids Rheology Matrix

Model	Temperature [°C]	Range	Yield Stress [Pa]	Consistency [mPa·s]	R
Bingham-Plastic	25 (1 of 2)	100–1000 s^{-1}	5.2	10	0.98
	25 (2 of 2)	100–1000 s^{-1}	4.6	10	0.99
	40	100–1000 s^{-1}	4.8	8.6	0.99
	60	100–1000 s^{-1}	6.1	8.3	0.99
Casson	25 (1 of 2)	0–1000 s^{-1}	2.6	5.3	0.98
	25 (2 of 2)	0–1000 s^{-1}	2.3	5.2	0.99
	40	0–1000 s^{-1}	2.6	4.1	0.99
	60	0–1000 s^{-1}	3.7	3.4	0.99

Table 5.20. Select Apparent Viscosities for the High-Solids Slurry

Source	Temperature [°C]	Apparent Viscosity [mPa·s]			
		@ 33 s^{-1}	@ 100 s^{-1}	@ 500 s^{-1}	@ 1000 s^{-1}
Measured	25 (1 of 2)	130	54	21	15
	25 (2 of 2)	120	52	19	15
	40	130	54	18	13
	60	170	66	20	14
Bingham-Plastic	25 (1 of 2)	170	62	21	15
	25 (2 of 2)	150	56	19	15
	40	160	57	18	13
	60	190	70	21	14
Casson	25 (1 of 2)	130	55	21	15
	25 (2 of 2)	110	50	20	15
	40	120	51	19	13
	60	160	64	21	14

5.5 Caustic Leaching/Washing

After completing the filtration and rheological testing of the high-solids slurry, the slurry was drained from the system and prepared for caustic leaching, as outlined in Figure 5.25. The slurry loop was rinsed using part of the caustic addition for the leach and additional permeate that was remaining in the back-pulse chamber. After the slurry and caustic additions were recovered from the system, the slurry reservoir was isolated from the slurry loop. At these points, all the recovered slurry, permeate, and caustic solutions were placed into the reservoir for caustic leaching, as outlined in the right column of Figure 5.1. It is estimated that 0.1 kg of material was lost due to transfer operations.
The activities involved in this process were:

- Batch caustic leaching of the slurry for removing aluminum, and phosphorus from UDS in the slurry.
- Dewatering the leached slurry.
- Batch washing of the caustic-leached slurry and dewatering of the diluted supernate afterwards. Five total wash solutions were added to the slurry to remove aluminum and phosphrous from the slurry.

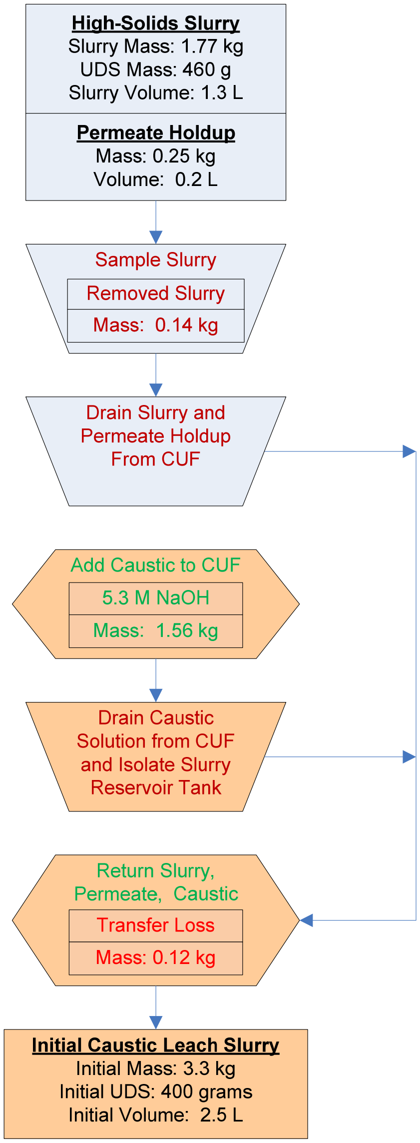


Figure 5.25. Process Flow for Caustic-Leach Preparation

5.5.1 Caustic Batch Leaching Results

After the slurry, permeate, and caustic were placed in the slurry reservoir, the lid for the slurry reservoir was placed on the tank, and the over-head mixer was started (Figure 5.26). The heat controller was then started to begin elevating the slurry temperature to 60°C (-10/+5°C) over a 2.5-hour period. After the heat ramp was completed, the temperature controller maintained the slurry temperature at 60°C for 8 hours, and then the slurry was allowed to cool to the hot-cell ambient temperature over another 5.6-hour period (Figure 5.27). As seen in previous testing, the slurry temperature was slightly higher than the cell ambient temperature at the end of the cooling ramp (slurry temperature ~35°C versus the cell ambient temperature ~30°). The slurry temperature was later decreased to 25°C once it was circulated through the slurry loop heat exchanger before dewatering. The mixer was turned off during sampling operations to prevent contact issues with the pipette. Afterwards, it was observed that temperature spikes in the slurry were occurring after the mixer was turned back on. Because the thermocouple controlling the heat controller is at the bottom of the tank while the heating jacket is on the side walls, it is believed that the controller was applying heat to the tank because the thermocouple would drop in temperature after the mixer was turned off. While one of the temperature spikes exceeded 10°C, the duration of the temperature spikes are less than 10 minutes. The level of the leach solution was periodically checked during the leaching process. Unlike previous testing that was performed at 100°C, no significant change in the leach slurry volume was observed.

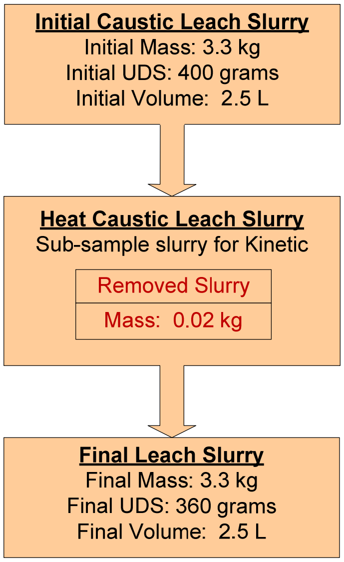


Figure 5.26. Process Flow for the Caustic Leach

The slurry was sampled once during the heat ramp and four times during the 8-hour soak at 60°C (Table 5.21). ICP analysis of the supernate filtered from these samples shows that although only 57 wt% of the solid aluminum dissolved, most of the dissolution occurred during the temperature ramp (Figure 5.27). Nineteen percent of the Al had dissolved in 3 hours into the temperature ramp when the slurry was 37°C. This represents 34 wt% of the total solid aluminum that would dissolve by the end of the leach. Forty-one weight percent of the Al had dissolved when the slurry reached the target leach temperature, 60°C. This represents 72 wt% of the total solids that would dissolve. After 2 hours at the target leaching temperature, the dissolution was effectively complete, with 56 wt% dissolved. The rapid reaction rate observed was indicative of gibbsite dissolution, while the extent of reaction implied that a significant fraction of aluminum was present in an insoluble form, like cancrinite. Figure 5.28 shows the concentrations of the major analytes during the evolution of the heat ramp and caustic leach.
The Al and Cr concentrations increase rapidly and level off. Phosphorus, potassium, and sulfur concentrations remain steady throughout the leach. Interestingly, the uranium concentration in the supernate decreases by a factor of 100 during the leach.

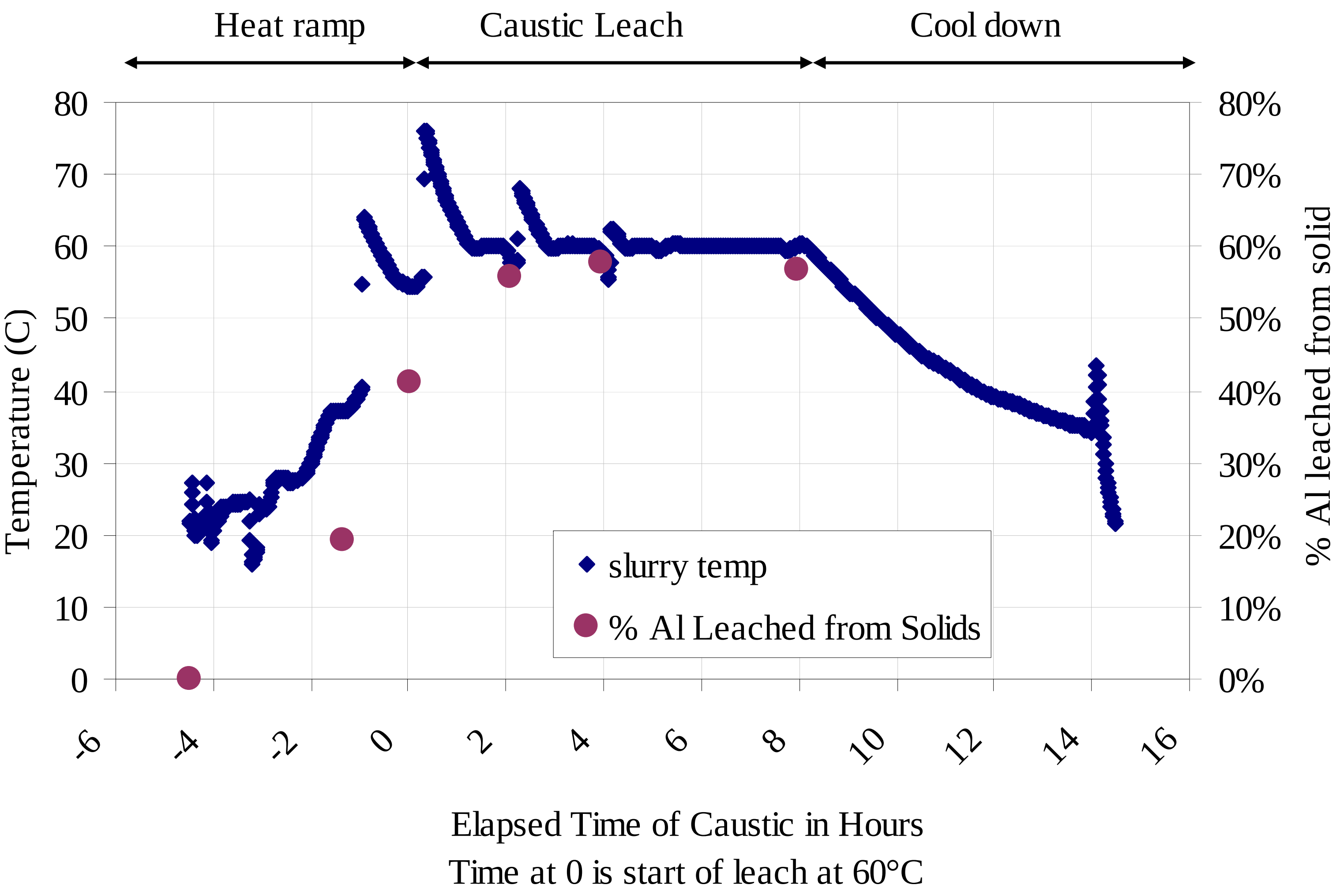


Figure 5.27. Temperature Profile/Aluminum Leach Factor During Caustic Leaching

Table 5.21. Concentration of Major Analyte Components of Filtered Caustic Leach Samples, Corrected for Sample Evaporation

	Start of heat up[a] (22°C)	3 hour heat up[b] (37°C)	0 hour leach[c] (55°C)	2 hour leach[d] (58°C)	4 hour leach[e] (59°C)	8 hour leach[f] (60°C)
	µg/ml	**µg/ml**	**µg/ml**	**µg/ml**	**µg/ml**	**µg/ml**
Al	5.5E+00	2.5E+03	5.2E+03	7.2E+03	7.4E+03	7.3E+03
B	9.9E+00	1.0E+01	1.1E+01	1.2E+01	1.1E+01	1.1E+01
Bi	< 2.E+0	< 4.E+0	< 4.E+0	< 4.E+0	< 4.E+0	3.2E+00
Ca	7.8E+00	4.4E+00	4.7E+00	5.0E+00	1.4E+01	1.9E+00
Cd	6.3E-01	1.4E+00	1.4E+00	1.4E+00	1.5E+00	1.2E+00
Cr	2.2E+01	5.7E+01	8.3E+01	1.0E+02	1.1E+02	1.1E+02
Fe	8.7E-01	2.5E+01	3.7E+01	3.3E+01	8.1E+01	5.9E+00
K	1.5E+02	2.7E+02	2.9E+02	2.7E+02	2.7E+02	2.8E+02
Mn	1.1E-01	2.8E+00	4.6E+00	4.4E+00	1.2E+01	3.1E-01
Na	4.2E+04	1.1E+05	1.1E+05	1.1E+05	1.1E+05	1.1E+05
Ni	< 1.E-1	4.9E-01	6.3E-01	5.3E-01	2.0E+00	< 2.E-1
P	2.4E+03	1.5E+03	1.7E+03	1.6E+03	1.5E+03	1.1E+03
S	2.1E+03	2.3E+03	2.3E+03	2.4E+03	2.3E+03	2.2E+03
Si	8.2E-01	1.3E+02	1.1E+02	7.5E+01	7.3E+01	6.0E+01
Sr	9.9E-02	2.4E-01	3.5E-01	3.4E-01	7.7E-01	6.4E-02
U	1.9E+03	1.5E+02	8.1E+01	5.0E+01	4.7E+01	2.8E+01
Zn	4.2E-01	1.8E+01	1.9E+01	1.7E+01	1.6E+01	1.3E+01
Zr	6.3E-01	4.4E-01	7.7E-01	5.7E-01	1.4E+00	< 1.E-1
	[M]	**[M]**	**[M]**	**[M]**	**[M]**	**[M]**
OH	0.05	2.6	2.4	2.4	2.2	1.9

(a) Predicted concentrations from mixing caustic addition (5.3M) with slurry supernate. Composition of supernate based on sample TI624-G7-A, ASO ID 08-02059.
(b) Composition based on sample TI624-G7-C1, ASO ID 08-02064. Values divided by 1.02 to account for evaporative loss of sample.
(c) Composition based on sample TI624-G7-C2, ASO ID 08-02065. Values divided by 1.03 to account for evaporative loss of sample.
(d) Composition based on sample TI624-G7-C3, ASO ID 08-02066. Values divided by 0.99 to account for evaporative loss of sample.
(e) Composition based on sample TI624-G7-C4, ASO ID 08-02067. Values divided by 0.97 to account for evaporative loss of sample.
(f) Composition based on sample TI624-G7-C5, ASO ID 08-02068. Values divided by 0.82 to account for evaporative loss of sample.

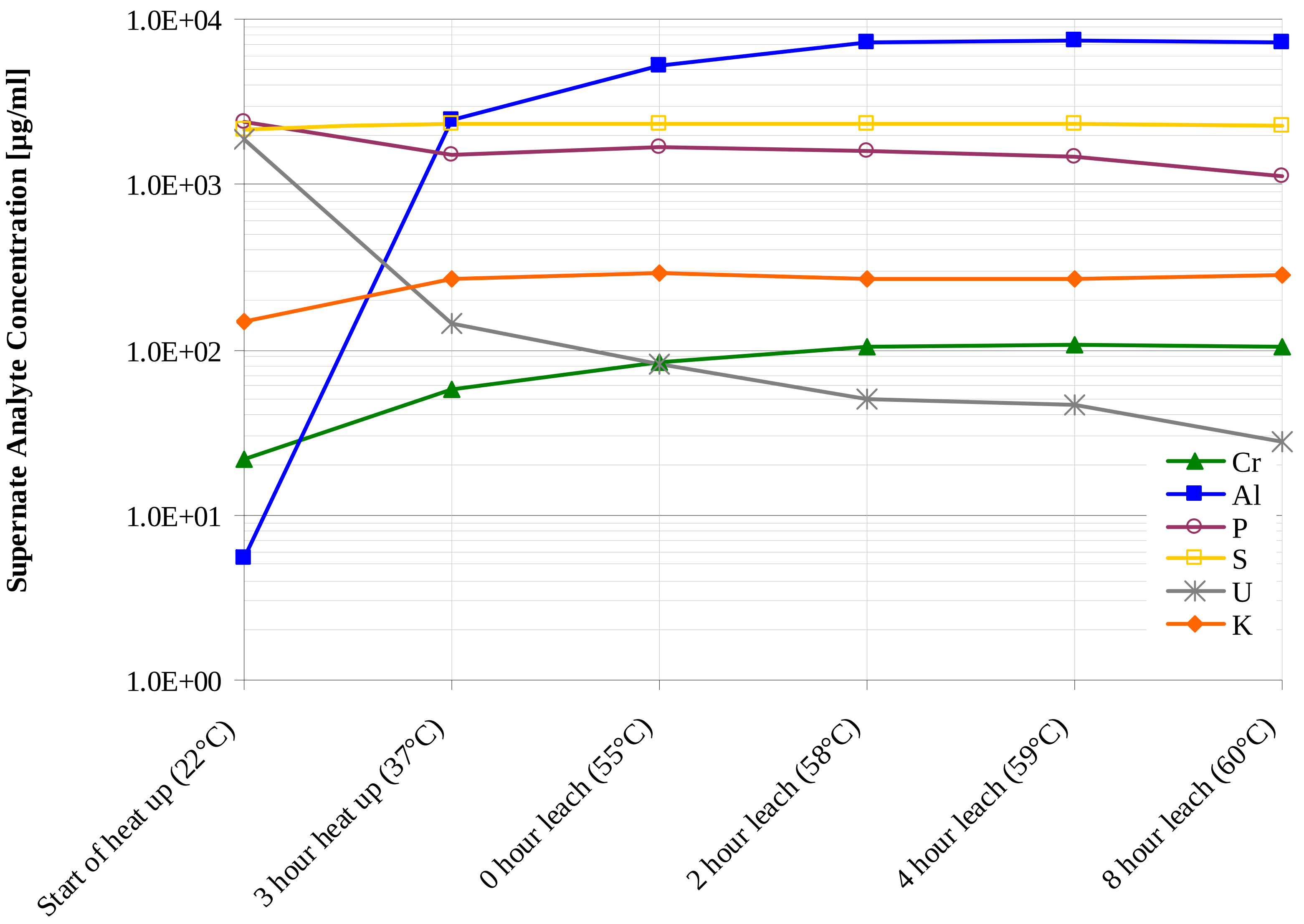


Figure 5.28. Concentration of Al, Cr, P, S, U and K during Caustic Leach of Group 3/4 Slurry

5.5.2 Caustic-Leach Dewatering

After the temperature controller's cooling ramp cycle was completed, the slurry was allowed to circulate through the slurry reservoir loop and cooled to 25°C before dewatering. It was allowed to circulate at this temperature for about 30 minutes to verify that the slurry supernate was at thermal equilibrium. Afterwards, the slurry was dewatered at standard conditions (Figure 5.29). The caustic-leached slurry was dewatered from a total system volume of ~2.5 L to ~1.7 L over 2 hours. The slurry would have been dewatered further, but the systems-level measuring device was malfunctioning, and so initial estimates of the slurry volume were incorrect. A total of 1.04 kg of permeate was collected during the dewatering step. Figure 5.30 is a plot of the permeate flux for the dewatering step. The permeate flux decreased from 0.007 to 0.006 GPM/ft^2 over the first 60 minutes, but then stayed relatively constant afterwards. While the flux is lower when compared to the slurry before caustic leaching, it resulted from increases in the sodium and free-hydroxide concentration in the slurry supernate from the caustic addition, which caused an increase in the supernate viscosity (see Table 5.22). The magnitude of change in the filter flux is in proportion to the change in the supernate viscosity, as predicted by the Darcy equation.

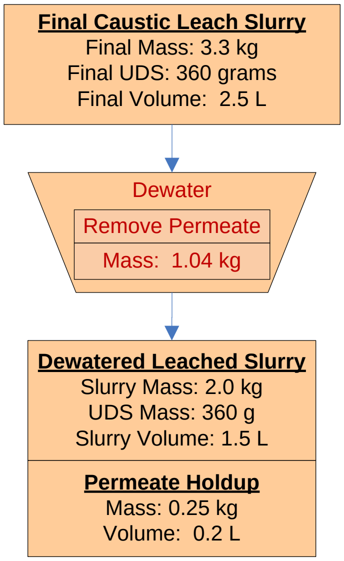


Figure 5.29. Process Flow of Dewatering Caustic Leached Slurry

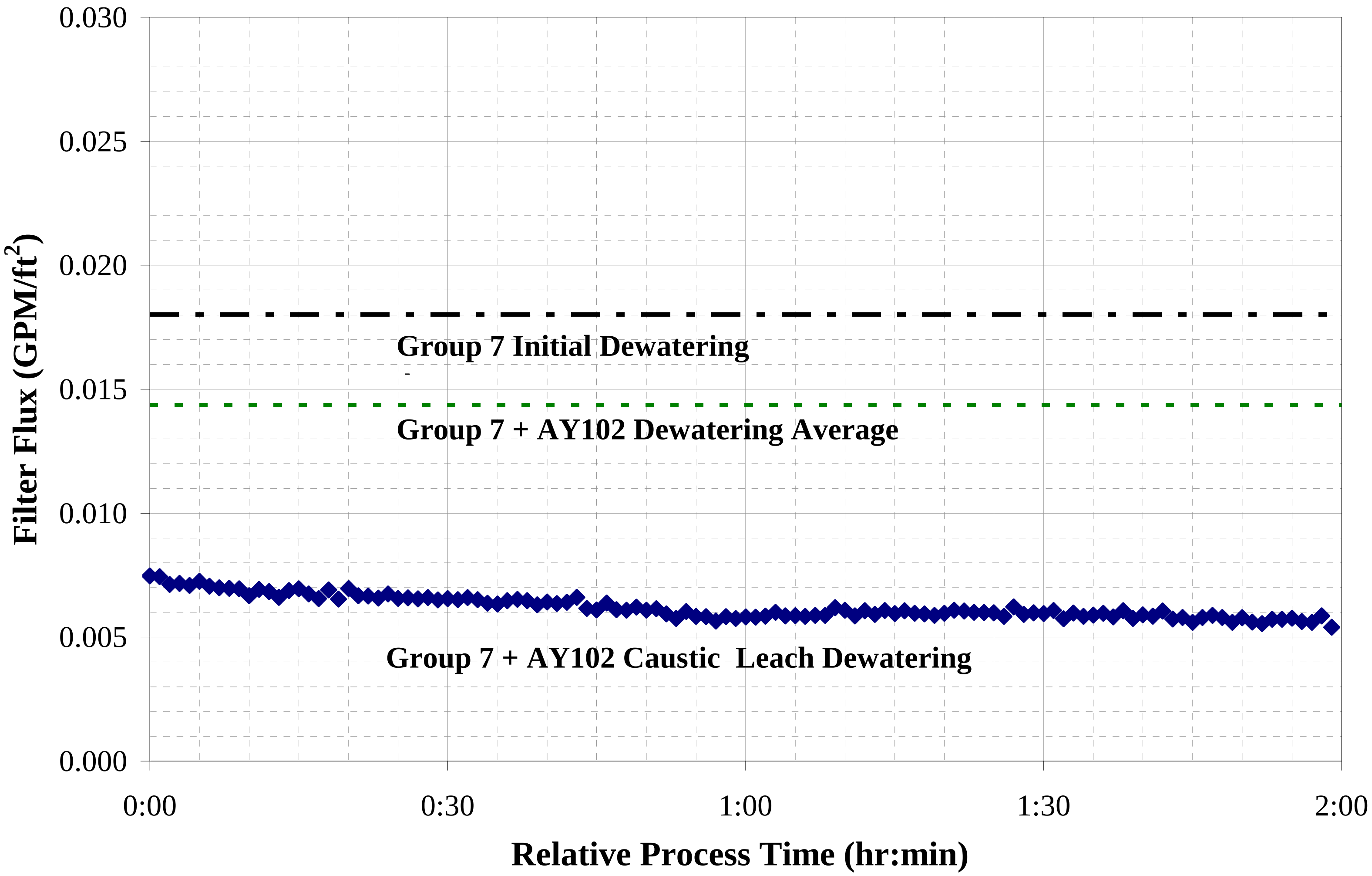


Figure 5.30. Dewatering Leached Blended Slurry (Group 7/AY102) at Standard Conditions

Table 5.22. Comparison of Slurry Supernate Attributes to Filter Flux

Supernate Sample	Viscosity at 25°C (mPa·s)	[Na] (M)	[OH] (M)	[Al] (M)	Nominal Flux at Standard Conditions (GPM/ft^2)
High-Solids Slurry	1.8	3.74	0.11	4.2E-4	0.014
Leach Permeate	3.1	4.70	2.26	2.7E-1	0.006

5.5.3 Dewatered Leached Slurry Physical Characterization

After dewatering the leached slurry, the slurry was sampled for physical and chemical analysis (Figure 5.31). The results of physical-property measurements of the leached, dewatered material are shown in Table 5.23. The total slurry composition, based on mass balance calculations resulting from the removed mass of the dewatered leach permeate, is shown in Table 5.24. The composition of both the slurry and supernate at this point is shown in Table 5.25. Using chemical characterization data of the high solids slurry in Table 5.25, solid leach factors were calculated for each of the analytes listed, using iron and zirconium as baseline components (i.e., assuming these components do not dissolved during caustic leaching) to predict concentration factors.

As predicted by the filtered supernate analysis, the solids leach factor for aluminum was found to be about 50%. The leach factor for phosphorus was calculated to be a negative value, which indicates that increases in the sodium concentration precipitated phosphate initially present in the un-leached slurry supernate and is suppressing the release of water-soluble phosphate present in the solids at this point in the process. The leach factor for this analyte was re-examined after washing (Section 5.5.4, Section 5.6), and much higher values were found after the sodium in the supernate was decreased. These observations would be consistent with the formation of solid $Na_3PO_4 \cdot 12H_2O$ at high sodium concentration, which becomes readily soluble as the Na concentration decreases during washing.

Before leaching, a large portion of uranium was found to be soluble in the slurry supernate. Leaching decreased the concentration of U in the slurry from 3,800 μg/mL to 50 μg/mL. It is predicted that the increase in the hydroxide concentration caused this portion in the slurry to precipitate as a hydroxide or oxide. The solids leach factor calculated for this term was found to be -0.8, which also indicates an increase in the solids uranium content of the slurry. While cesium shows a decrease in the overall inventory, this was due to removal of cesium in the aqueous phase of the supernate. Examining the leach factors shows that a majority of the cesium is present in the solids phase and is not removed by caustic leaching, much like the transuranic elements.

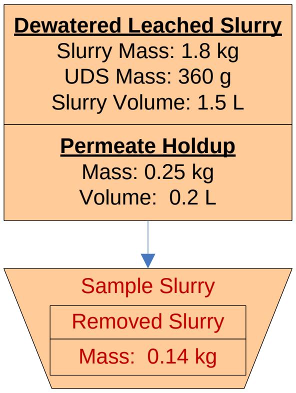


Figure 5.31. Sampling of Dewatered Caustic Leached Slurry

Table 5.23. Dewatered Caustic Leached Slurry Physical-Property Measurements (inside circulation loop)

Slurry Density (g/mL)	1.46
Supernate Density (g/mL)	1.33
Settled Solids (Vol %)	95%
Centrifuged UDS (Wt %)	43%
Total Solids (Wt %)	35%
Dissolved Solids (Wt%)	19%
UDS (Wt%)	20%

Table 5.24. Group 7 Caustic leached, Dewatered Slurry Inventory and Composition

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	2.12	1.79		0.33	
Wt% of Slurry	100%	84.3%		15.7%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	2.2E+01	1.1E+01	7.4E+03	1.1E+01	3.4E+04
B	1.0E-02	2.5E-02	1.8E+01	n/a(d)	n/a(d)
Bi	6.8E-01	< 5.E-3	< 4.E+0	6.8E-01	2.1E+03
Ca	3.9E+00	4.1E-03	2.9E+00	3.9E+00	1.2E+04
Cd	8.0E-02	2.0E-03	1.4E+00	7.8E-02	2.4E+02
Cr	9.9E-01	1.6E-01	1.1E+02	8.3E-01	2.5E+03
Fe	6.0E+01	8.9E-03	6.2E+00	6.0E+01	1.8E+05
K	1.2E-01	4.1E-01	2.9E+02	n/a(d)	n/a(d)
Mn	8.7E+00	2.1E-04	1.5E-01	8.7E+00	2.6E+04
Na	1.8E+02	1.5E+02	1.1E+05	2.8E+01	8.4E+04
Ni	1.5E+00	< 4.E-4	< 3.E-1	1.5E+00	4.5E+03
P	1.5E+01	2.1E+00	1.5E+03	1.2E+01	3.7E+04
S	2.7E+00	3.3E+00	2.3E+03	n/a(d)	n/a(d)
Si	1.5E+01	7.2E-02	5.0E+01	1.5E+01	4.5E+04
Sr	5.8E-01	1.6E-05	1.1E-02	5.8E-01	1.8E+03

Table 5.24 (Contd)

	Slurry(a)	Liquid Fraction(b)		Solids Fraction(c)	
Mass (kg)	2.12	1.79		0.33	
Wt% of Slurry	100%	84.3%		15.7%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Zn	1.6E-01	1.8E-02	1.2E+01	1.4E-01	4.2E+02
Zr	1.4E+00	4.4E-04	3.1E-01	1.4E+00	4.2E+03
U	8.7E+00	7.4E-02	5.2E+01	8.6E+00	2.6E+04
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	6.5E+01	3.6E-01	2.5E-04	6.4E+01	1.9E-01
Cs-137	1.4E+05	1.7E+04	1.2E+01	1.2E+05	3.6E+02
Eu-152	8.7E+01	< 4.E-1	< 3.E-4	8.7E+01	2.6E-01
Eu-154	2.1E+03	< 3.E-1	< 2.E-4	2.1E+03	6.5E+00
Eu-155	9.7E+02	< 5.E+0	< 3.E-3	9.7E+02	2.9E+00
Am-241	3.5E+03	< 1.E+1	< 9.E-3	3.5E+03	1.1E+01
Gross Alpha	5.2E+03	2.5E+00	1.7E-03	5.2E+03	1.6E+01
Gross Beta	6.0E+06	1.4E+04	9.9E+00	6.0E+06	1.8E+04
Sr-90	3.1E+06	3.4E+00	2.4E-03	3.1E+06	9.5E+03
Pu-239+240	1.3E+03	3.2E+00	2.3E-03	1.3E+03	4.0E+00
Pu-238	2.1E+02	4.4E-01	3.1E-04	2.1E+02	6.2E-01
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	µg/ml	**[M]**	**g**	**µg/g**	**g**
F	1.7E+02	8.9E-03	2.6E-01	5.7E+02	2.0E-01
Cl	1.6E+03	4.5E-02	2.4E+00	2.7E+03	9.3E-01
C_2O_4	9.0E+02	1.0E-02	1.4E+00	2.6E+03	9.0E-01
NO_2	7.6E+03	1.6E-01	1.1E+01	1.4E+04	5.1E+00
NO_3	6.5E+04	1.0E+00	9.8E+01	1.1E+05	4.0E+01
SO_4	6.5E+03	6.8E-02	9.8E+00	1.2E+04	4.2E+00
PO_4	4.6E+03	4.9E-02	7.0E+00	6.6E+04	2.3E+01
OH	3.8E+04	2.3E+00	5.8E+01		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-169, Section 3). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI624-G7-D (ASO ID 08-02061) and the predicted mass of supernate in the system.

(c) Solids Fraction mass components were calculated from the difference between the slurry component mass and liquid component mass fraction.

(d) Values (based on supernate) were calculated to be less than zero.

Table 5.25. Dewatered Leached Slurry Composition and Solid Leach Factor Calculations

Slurry Prep Method	**Analyte**	**Dry Slurry(a) (µg/g)**	**Supernate(b) (µg/mL)**	**Dry Solids(c) (µg/g)**	**Solids Leach Factor(d)**
HF Assisted Digestion Concentration Factor of 1.20 based on Fe/Zr	Al	36,800	7,370	42,000	0.51
	B	[23]	17.5	-[12]	-0.14
	Bi	1,240	--	2,200	-0.02
	Cd	132	[1.4]	230	0.01
	Cr	1,750	110	2,700	0.15
	Fe	107,000	6.24	190,000	
	Mn	15,800	[0.15]	28,000	0.00
	Na	249,000	108,000	110,000	-0.58
	Ni	2,900	--	5,100	-0.01
	P	25,300	[1500]	40,000	-0.24
	S	4,480	2,310	940	1.64
	Sr	1050.0	[0.011]	1,800	0.00
	U	15,100	51.70	26,000	-0.80
	Zn	313	12.3	510	0.07
	Zr	2,670	[.31]	4,700	
	Ag	***47.0***	***5.34***	***66***	*0.39*
	Ba	***680***	***[0.16]***	***1,200***	*0.00*
	Be	***[0.94]***	***[0.022]***	***[1.6]***	*0.01*
	Ca	***7,390***	***[2.9]***	***13,000***	*0.00*
	Ce	***751***	***--***	***1,300***	*-0.01*
	Cu	***247***	***[1.1]***	***430***	*0.00*
	La	***862***	***--***	***1,500***	*-0.01*
	Li	***98.9***	***1.84***	***170***	*0.01*
	Mg	***1,990***	***--***	***3,500***	*0.00*
	Mo	***[19]***	***[2.7]***	***[25]***	*-0.21*
	Nd	***1,280***	***--***	***2,200***	*-0.03*
	Pb	***4,590***	***[5.7]***	***8,000***	*0.00*
	Ru	***243***	***[6.0]***	***410***	*0.03*
	Th	***579***	***--***	***1,000***	*-0.02*
	Ti	***234.0***	***--***	***410***	*0.00*
	V	***19.30***	***0.980***	***31***	*0.07*
	W	***273***	***[15]***	***430***	*0.02*
	Y	***111***	***--***	***190***	*-0.01*
KOH Fusion Concentration Factor of 0.67 based on Fe	Fe	64,600	6.24	110,000	
	Si	[16,300]	50.0	[28,000]	-0.06
	Radionuclide	**Dry Slurry (µCi/g)**	**Supernate (µCi/mL)**	**Dry Solids (µCi/g)**	
	^{60}Co	8.28E-2	2.49E-4	1.4E-1	-0.24
	^{137}Cs	1.81E+2	1.17E+1	2.8E+2	-0.15
	^{154}Eu	1.05E-1	<3.E-4	1.8E-1	-0.22
	^{155}Eu	2.72E+0	< 2.E-4	4.8E+0	-0.14
	^{241}Am	1.12E+0	< 3.E-3	2.0E+0	-0.34
	^{90}Sr	4.86E+0	< 9.E-3	8.5E+0	0.06
	$^{239+240}$Pu	3.00E+3	2.40E-3	5.3E+3	-0.09
	^{238}Pu	1.41E+0	2.27E-3	2.5E+0	-0.34

(a) Test sample TI624-G7-9, ASO ID 08-2075
(b) Test sample TI624-G8-D, ASO ID 08-2061
(c) Calculated using results in from TI624-G7-9 and TI624-G7-D.
(d) Calculated using the concentration factor in the first column and by using the solid concentrations value calculated in Table 5.17 as the initial concentration.

Analyte uncertainties were typically within ±15%; results in brackets indicate that the analyte concentrations were greater than the method detection limit (MDL) and less than the estimated quantitation limit (EQL), and uncertainties were >15%. Opportunistic analytes are in italics.

The slurry was also sub-sampled for rheological measurement. Figure 5.32 shows the results of flow-curve testing for the leached dewatered slurry. The flow behavior is non-Newtonian. Flow-curve data indicate that the dewatered slurry has a finite yield stress of approximately 1 to 3 Pa and that the slurry is shear thinning. Flow-curve hysteresis is minor and can be attributed to rotor inertial effects alone. The lack of hysteresis suggests that the internal structure of the slurry (such as particle agglomerates) is stable with respect to shear or that any changes in structure occur quickly and are complete at the end of the 3-minute shearing step performed immediately before flow-curve measurement. With regard to data anomalies, the curves are free of any slope discontinuities that could be associated with Taylor vortex formation.

Flow-curve data at 25°C, 40°C, and 60°C were fit to both Bingham-Plastic and Casson models. Table 5.26 summarizes the best-fit model parameters for the leached dewatered slurry. Since the data were not influenced by Taylor vortex formation, the full range of shear rates (0 to 1000 s^{-1}) is employed in the Casson fitting analysis. Bingham-Plastic analysis cannot account for slurry shear thinning, and as a result, its fitting analysis is limited to 100 to 1000 s^{-1} to avoid bias introduced by slurry shear thinning at low-shear rates. Both models provide reasonable fits of the data.

Apparent viscosities at 33, 100, 500, and 1000 s^{-1} were derived from each measurement. For each temperature, the 33, 100, and 500 s^{-1} reference viscosities were determined from the average of both up-ramp and down-ramp flow-curve data. The apparent viscosity at 1000 s^{-1} is derived from the averaging of all apparent viscosity measurements during constant rotation at 1000 s^{-1}. As a point of comparison, apparent viscosities were also calculated using the Bingham-Plastic and Casson fitting parameters in Table 5.26. The results of these analyses are provided in Table 5.27.

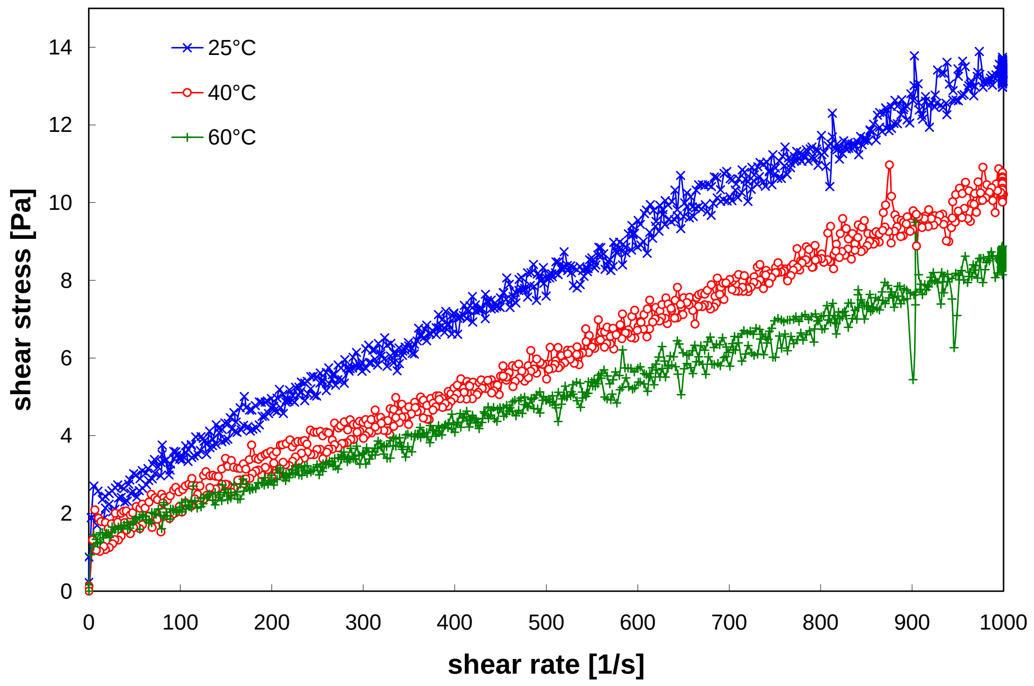


Figure 5.32. Flow Curves for Group 8 CUF Leached Dewatered Slurry

Table 5.26. Results of Fitting Analysis for the Group 7 CUF Leached Dewatered Slurry

Model	Temperature [°C]	Range	Yield Stress [Pa]	Consistency [mPa·s]	R
Bingham-Plastic	25 (1 of 2)	100–1000 s^{-1}	2.5	11	1.00
	25 (2 of 2)	100–1000 s^{-1}	2.6	11	1.00
	40	100–1000 s^{-1}	1.5	8.9	1.00
	60	100–1000 s^{-1}	1.4	7.1	0.99
Casson	25 (1 of 2)	0–1000 s^{-1}	0.83	7.4	1.00
	25 (2 of 2)	0–1000 s^{-1}	1.0	7.2	1.00
	40	0–1000 s^{-1}	0.45	6.5	1.00
	60	0–1000 s^{-1}	0.45	5.0	0.99

Table 5.27. Select Apparent Viscosities for the Leached Dewatered Slurry

Source	Temperature [°C]	Apparent Viscosity [mPa·s]			
		@ 33 s^{-1}	@ 100 s^{-1}	@ 500 s^{-1}	@ 1000 s^{-1}
Measured	25 (1 of 2)	59	31	16	13
	25 (2 of 2)	78	34	16	13
	40	48	23	11	10
	60	49	22	9.8	8.6
Bingham-Plastic	25 (1 of 2)	87	36	16	13
	25 (2 of 2)	90	37	16	13
	40	55	24	12	10
	60	49	21	10	8.5
Casson	25 (1 of 2)	60	31	16	13
	25 (2 of 2)	65	33	16	13
	40	39	22	12	10
	60	35	19	10	8.4

5.5.4 Caustic Batch Rinsing Results

After slurry sampling, the slurry was washed four times with decreasing concentrations of sodium hydroxide, as shown in Figure 5.33. The volume of each wash solution was 1.2 liters, approximately the same volume of supernate present in the system after dewatering from caustic leaching. After each solution was added, the slurry was re-circulated in the CUF for ~ 30 minutes while filter permeate was recycled back to the slurry reservoir. The slurry was then dewatered at standard conditions to return the slurry back to its original volume. To prevent damage to the pump, the final dewatering was stopped at 1 liter because cavitation was occurring. Grab samples of the filtered permeate were collected half-way between each dewatering step to assess the composition of the filtrate. The results were used to predict the slurry inventory and composition at each wash step, shown in Table 5.28 through Table 5.31. The measured concentration of free hydroxide, radionuclides, and opportunistic ICP-OES analytes for each filtered wash solution is provided in Table 5.32.

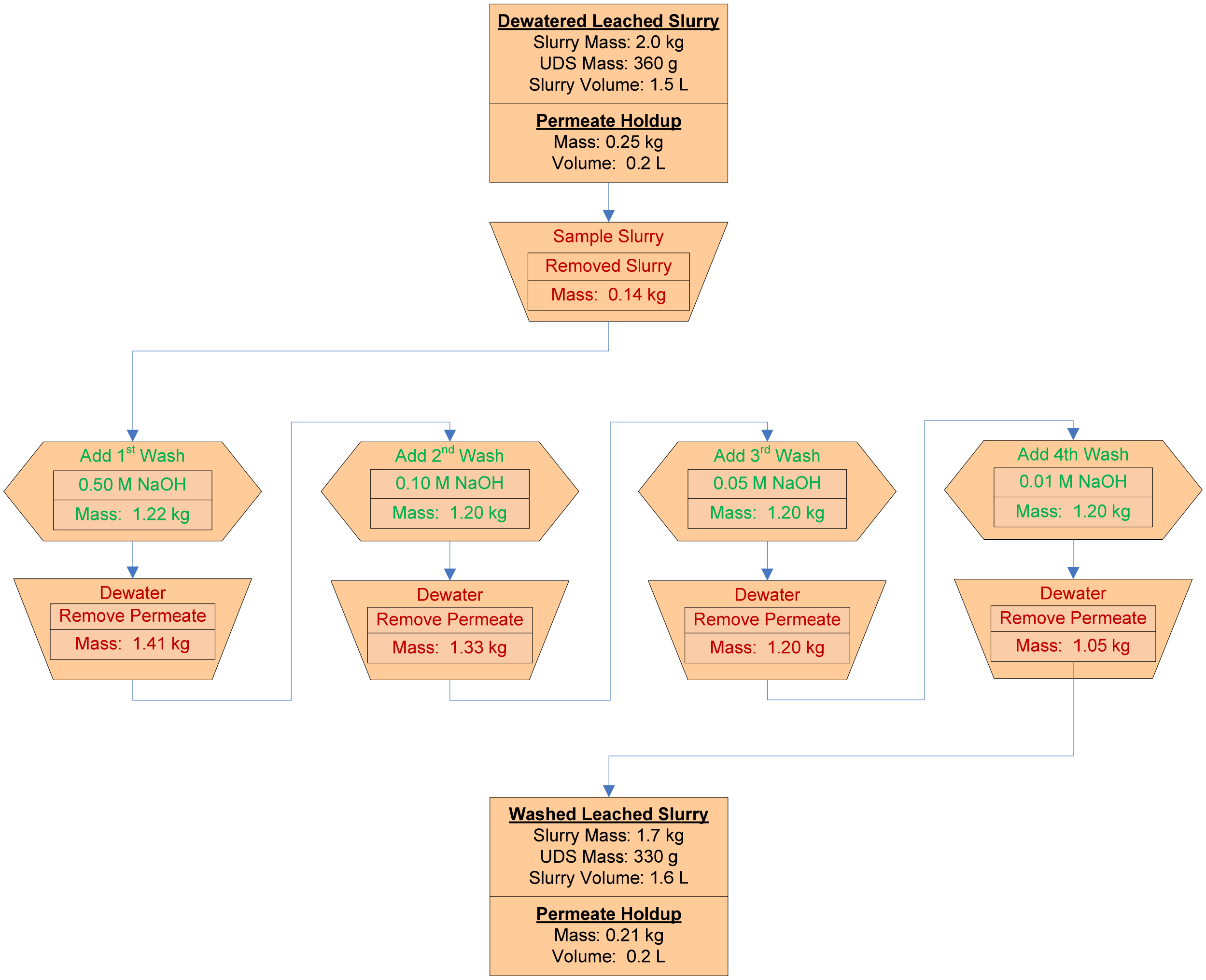


Figure 5.33. Process Flow of Batch Washing Operations

Table 5.28. Group 7/AY-102 Caustic leached Slurry Inventory and Composition after the First Wash

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	1.92	1.60		0.32	
Wt% of Slurry	100%	83.3%		16.7%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	1.7E+01	5.5E+00	4.0E+03	1.1E+01	3.6E+04
B	2.2E-03	8.8E-03	6.4E+00	n/a(d)	n/a(d)
Bi	6.8E-01	< 5.E-3	< 4.E+0	6.8E-01	2.1E+03
Ca	3.9E+00	3.7E-03	2.7E+00	3.9E+00	1.2E+04
Cd	7.9E-02	1.7E-03	1.2E+00	7.7E-02	2.4E+02
Cr	9.1E-01	8.4E-02	6.1E+01	8.3E-01	2.6E+03
Fe	6.0E+01	2.9E-03	2.1E+00	6.0E+01	1.9E+05
K	2.0E-01	2.0E-01	1.4E+02	n/a(d)	n/a(d)
Mn	8.7E+00	1.7E-04	1.2E-01	8.7E+00	2.7E+04
Na	1.1E+02	9.3E+01	6.8E+04	2.1E+01	6.7E+04
Ni	1.5E+00	< 4.E-4	< 3.E-1	1.5E+00	4.6E+03
P	1.1E+01	3.6E+00	2.6E+03	7.8E+00	2.4E+04
S	1.2E+00	1.7E+00	1.2E+03	n/a(d)	n/a(d)
Si	1.5E+01	4.0E-02	2.9E+01	1.5E+01	4.6E+04
Sr	5.8E-01	< 1.E-5	< 1.E-2	5.8E-01	1.8E+03
Zn	1.5E-01	6.7E-03	4.9E+00	1.4E-01	4.5E+02
Zr	1.4E+00	4.4E-04	3.2E-01	1.4E+00	4.3E+03
U	8.7E+00	5.6E-02	4.1E+01	8.6E+00	2.7E+04
Anions	**Liquid Fraction**				
	µg/ml	**[M]**	**g**		
OH	2.5E+04	1.5E+00	3.5E+01		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-169, Section 3). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI624-G4-E (ASO ID 08-02069) and the predicted mass of supernate in the system.

(c) Solids Fraction mass components were calculated from the difference between the slurry component mass and liquid component mass fraction.

(d) Values (based on supernate) were calculated to be less than zero.

Table 5.29. Group 7/AY-102 Caustic leached Slurry Inventory and Composition after the Second Wash

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	1.79	1.49		0.30	
Wt% of Slurry	100%	83.3%		16.7%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	1.5E+01	2.5E+00	1.9E+03	1.2E+01	4.1E+04
B	4.4E-03	4.4E-03	3.3E+00	n/a(d)	n/a(d)
Bi	6.8E-01	< 5.E-3	< 4.E+0	6.8E-01	2.3E+03
Ca	3.9E+00	3.2E-03	2.4E+00	3.9E+00	1.3E+04
Cd	7.7E-02	1.6E-03	1.2E+00	7.6E-02	2.5E+02
Cr	8.8E-01	3.8E-02	2.9E+01	8.4E-01	2.8E+03
Fe	6.0E+01	1.8E-03	1.3E+00	6.0E+01	2.0E+05
K	1.0E-01	1.0E-01	7.4E+01	n/a(d)	n/a(d)
Mn	8.7E+00	9.6E-05	7.1E-02	8.7E+00	2.9E+04
Na	7.2E+01	5.0E+01	3.7E+04	2.3E+01	7.5E+04
Ni	1.5E+00	< 4.E-4	< 3.E-1	1.5E+00	4.9E+03
P	7.5E+00	4.3E+00	3.2E+03	3.2E+00	1.1E+04
S	5.0E-01	7.6E-01	5.7E+02	n/a(d)	n/a(d)
Si	1.5E+01	2.0E-02	1.5E+01	1.5E+01	4.9E+04
Sr	5.8E-01	1.5E-05	1.1E-02	5.8E-01	1.9E+03
Zn	1.5E-01	2.6E-03	1.9E+00	1.4E-01	4.8E+02
Zr	1.4E+00	2.2E-04	1.6E-01	1.4E+00	4.6E+03
U	8.6E+00	3.6E-02	2.7E+01	8.6E+00	2.9E+04
Anions	**Liquid Fraction**				
	µg/ml	**[M]**	**g**		
OH	1.3E+04	7.7E-01	1.8E+01		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-169, Section 3). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI624-G4-F (ASO ID 08-02070) and the predicted mass of supernate in the system.

(c) Solids Fraction mass components were calculated from the difference between the slurry component mass and liquid component mass fraction.

(d) Values (based on supernate) were calculated to be less than zero.

Table 5.30. Group 7/AY-102 Caustic leached Slurry Inventory and Composition after the Third Wash

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	1.74	1.44		0.30	
Wt% of Slurry	100%	82.8%		17.2%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	1.4E+01	1.2E+00	8.7E+02	1.3E+01	4.2E+04
B	-3.5E-03	2.0E-03	1.5E+00	n/a(d)	n/a(d)
Bi	6.8E-01	3.2E-03	2.4E+00	6.8E-01	2.3E+03
Ca	3.9E+00	1.3E-03	9.5E-01	3.9E+00	1.3E+04
Cd	7.7E-02	3.5E-04	2.6E-01	7.7E-02	2.6E+02
Cr	8.6E-01	1.9E-02	1.4E+01	8.4E-01	2.8E+03
Fe	6.0E+01	5.0E-04	3.7E-01	6.0E+01	2.0E+05
K	-2.0E-01	6.6E-02	4.9E+01	n/a(d)	n/a(d)
Mn	8.7E+00	5.4E-05	4.0E-02	8.7E+00	2.9E+04
Na	5.3E+01	2.4E+01	1.8E+04	2.9E+01	9.8E+04
Ni	1.5E+00	< 8.E-5	< 6.E-2	1.5E+00	4.9E+03
P	5.8E+00	2.0E+00	1.5E+03	3.8E+00	1.3E+04
S	1.9E-01	3.6E-01	2.7E+02	n/a(d)	n/a(d)
Si	1.5E+01	1.6E-02	1.2E+01	1.5E+01	4.9E+04
Sr	5.8E-01	6.6E-06	4.9E-03	5.8E-01	1.9E+03
Zn	1.5E-01	8.8E-04	6.5E-01	1.5E-01	4.9E+02
Zr	1.4E+00	4.6E-05	3.4E-02	1.4E+00	4.6E+03
U	8.6E+00	2.2E-02	1.7E+01	8.6E+00	2.9E+04
Anions	**Liquid Fraction**				
	µg/ml	**[M]**	**g**		
OH	6.6E+03	3.9E-01	8.9E+00		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-169, Section 3). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI624-G4-G (ASO ID 08-02071) and the predicted mass of supernate in the system.

(c) Solids Fraction mass components were calculated from the difference between the slurry component mass and liquid component mass fraction.

(d) Values (based on supernate) were calculated to be less than zero.

Table 5.31. Group 7/AY-102 Caustic leached Slurry Inventory and Composition after the Fourth Wash

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	2.34	2.04		0.30	
Wt% of Slurry	100%	87.2%		12.8%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	1.3E+01	8.6E-01	4.4E+02	1.3E+01	4.2E+04
B	2.9E-03	2.9E-03	1.5E+00	n/a(d)	n/a(d)
Bi	6.8E-01	5.3E-03	2.7E+00	6.7E-01	2.2E+03
Ca	3.9E+00	2.2E-03	1.1E+00	3.9E+00	1.3E+04
Cd	7.7E-02	5.1E-04	2.6E-01	7.6E-02	2.5E+02
Cr	8.6E-01	1.4E-02	7.0E+00	8.5E-01	2.8E+03
Fe	6.0E+01	7.3E-04	3.7E-01	6.0E+01	2.0E+05
K	6.4E-02	6.4E-02	3.3E+01	n/a(d)	n/a(d)
Mn	8.7E+00	6.1E-05	3.1E-02	8.7E+00	2.9E+04
Na	4.8E+01	1.7E+01	8.8E+03	3.1E+01	1.0E+05
Ni	1.5E+00	< 1.E-4	< 6.E-2	1.5E+00	4.9E+03
P	5.4E+00	1.4E+00	7.3E+02	4.0E+00	1.3E+04
S	1.2E-01	2.5E-01	1.3E+02	n/a(d)	n/a(d)
Si	1.5E+01	1.6E-02	8.4E+00	1.5E+01	4.9E+04
Sr	5.8E-01	8.2E-06	4.2E-03	5.8E-01	1.9E+03
Zn	1.5E-01	1.6E-03	7.9E-01	1.4E-01	4.8E+02
Zr	1.4E+00	< 5.E-5	< 3.E-2	1.4E+00	4.6E+03
U	8.6E+00	2.2E-02	1.1E+01	8.6E+00	2.9E+04
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	6.5E+01	< 1.E-1	< 7.E-5	6.5E+01	2.2E-01
Cs-137	1.2E+05	1.3E+03	6.8E-01	1.2E+05	4.1E+02
Eu-152	8.7E+01	< 5.E-1	< 3.E-4	8.7E+01	2.9E-01
Eu-154	2.1E+03	< 3.E-1	< 2.E-4	2.1E+03	7.1E+00
Eu-155	9.7E+02	< 2.E+0	< 8.E-4	9.7E+02	3.2E+00
Am-241	3.5E+03	< 3.E+0	< 2.E-3	3.5E+03	1.2E+01
Gross Alpha	5.2E+03	1.2E+00	6.1E-04	5.2E+03	1.7E+01
Gross Beta	6.0E+06	1.4E+03	7.1E-01	6.0E+06	2.0E+04
Sr-90	3.1E+06	2.5E+00	1.3E-03	3.1E+06	1.0E+04
Pu-239+240	1.3E+03	7.0E-01	3.6E-04	1.3E+03	4.4E+00
Pu-238	2.1E+02	9.3E-02	4.7E-05	2.1E+02	6.9E-01
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	µg/ml	**[M]**	**g**	**µg/g**	**g**
F	2.0E+01	1.1E-03	3.9E-02	3.8E+02	1.1E-01
Cl	1.1E+02	3.0E-03	2.1E-01	1.9E+03	5.7E-01
C_2O_4	5.3E+01	6.0E-04	1.0E-01	1.6E+03	4.7E-01
NO_2	4.1E+02	9.0E-03	8.1E-01	1.3E+04	3.9E+00
NO_3	3.5E+03	5.7E-02	6.9E+00	7.0E+04	2.1E+01
SO_4	3.6E+02	3.8E-03	7.1E-01	7.7E+03	2.3E+00

Table 5.31 (Contd)

	Slurry(a)	Liquid Fraction(b)		Solids Fraction(c)	
Mass (kg)	2.34	2.04		0.30	
Wt% of Slurry	100%	87.2%		12.8%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
PO_4	2.2E+03	2.4E-02	4.3E+00	3.5E+04	1.0E+01
OH	3.1E+03	1.8E-01	6.2E+00		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-169, Section 3). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI624-G7-H (ASO ID 08-02062) and the predicted mass of supernate in the system.

(c) Solids Fraction mass components were calculated from the difference between the slurry component mass and liquid component mass fraction.

(d) Values (based on supernate) were calculated to be less than zero.

Table 5.32. Caustic Wash Solutions Radionuclide and Opportunistic Compositions

	Wash 1	**Wash 2**	**Wash 3**	**Wash 4**	**Composite Wash**
ASO Sample ID	**08-02069**	**08-01370**	**08-01371**	**08-02062**	**08-02063**
Density$^{(a)}$, g/mL>	**1.17**	**1.11**	**1.07**	**1.04**	**NA**
Analyte					
free OH, M	1.48 M	0.77 M	0.39 M	0.19 M	0.72 M
Opportunistic Analytes					
Analyte	**μg/mL**	**μg/mL**	**μg/mL**		**μg/mL**
Ag	2.92	[1.3]	0.685	[0.32]	1.45
As	<6.4E+0	<6.4E+0	<1.3E+0	<1.3E+0	<1.3E+0
Ba	[0.094]	[0.053]	[0.032]	[0.024]	[0.071]
Be	[0.012]	<6.4E-3	[0.0016]	<1.3E-3	[0.0029]
Ca	[2.7]	[2.4]	[0.95]	[1.1]	[0.87]
Ce	<1.2E+0	<1.2E+0	<2.5E-1	<2.5E-1	<2.5E-1
Co	<2.9E-1	<3.0E-1	<5.9E-2	<5.9E-2	<6.0E-2
Cu	[0.59]	<1.7E-1	[0.039]	<3.5E-2	[0.15]
Dy	<3.5E-1	<3.6E-1	<7.2E-2	<7.2E-2	<7.3E-2
Eu	<1.3E-1	<1.4E-1	<2.7E-2	<2.7E-2	<2.8E-2
La	<3.4E-1	<3.5E-1	<6.9E-2	<6.9E-2	<7.0E-2
Li	[1.4]	[1.2]	0.733	0.571	0.959
Mg	<2.8E-1	<2.8E-1	<5.7E-2	<5.7E-2	<5.8E-2
Mo	[1.4]	[1.1]	[0.30]	[0.17]	[0.71]
Nd	<2.1E+0	<2.1E+0	<4.2E-1	<4.2E-1	<4.3E-1
Pb	<3.9E+0	<4.0E+0	[0.98]	[1.5]	[2.0]
Pd	<7.7E-1	<7.8E-1	<1.6E-1	<1.6E-1	<1.6E-1
Rh	<1.5E+0	<1.5E+0	<3.0E-1	<3.0E-1	[0.37]
Ru	[2.9]	[1.9]	[0.67]	[0.34]	[1.4]
Sb	<2.4E+0	<2.5E+0	[0.50]	<4.9E-1	<5.0E-1
Se	[15]	<8.7E+0	[2.5]	<1.7E+0	[2.6]
Sn	<3.3E+0	[5.6]	[2.3]	[1.2]	[2.7]
Ta	<2.1E+0	<2.1E+0	<4.2E-1	<4.2E-1	<4.3E-1
Te	<3.2E+0	<3.2E+0	<6.4E-1	<6.4E-1	<6.5E-1
Th	<1.2E+0	<1.2E+0	<2.4E-1	<2.4E-1	<2.5E-1
Ti	<5.3E-2	<5.3E-2	<1.1E-2	[0.013]	<1.1E-2
Tl	<4.7E+0	<4.7E+0	<9.4E-1	<9.4E-1	<9.6E-1
V	0.953	[0.71]	0.274	0.189	0.496
W	[9.4]	[4.5]	[1.8]	[1.2]	4.02
Y	<5.4E-2	<5.4E-2	<1.1E-2	<1.1E-2	<1.1E-2
Analyte	**μCi/mL**	**μCi/mL**	**μCi/mL**	**μCi/mL**	**μCi/mL**
^{137}Cs				6.81E-1	3.02E+0
^{60}Co				< 7.E-5	< 8.E-5
^{241}Am				< 2.E-3	< 3.E-3

Table 5.32 (Contd)

	Wash 1	**Wash 2**	**Wash 3**	**Wash 4**	**Composite Wash**
ASO Sample ID	**08-02069**	**08-01370**	**08-01371**	**08-02062**	**08-02063**
Density[(a)], g/mL>	**1.17**	**1.11**	**1.07**	**1.04**	**NA**
Analyte					
^{90}Sr				1.26E-3	2.32E-3
^{238}Pu				4.74E-5	1.65E-4
$^{239+240}$Pu				3.56E-4	1.23E-3
Gross alpha				6.07E-4	9.05E-4
Gross beta				7.12E-1	3.17E+0
^{154}Eu				< 8.E-4	< 2.E-3

(a) Density values were obtained from the mass flow meter, which had not been calibrated to NQA-1 standards; they are reported for information only.

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Analyte uncertainties were typically within ±15%; results in brackets indicate that the analyte concentrations were greater than the method detection limit (MDL) and less than the estimated quantitation limit (EQL), and uncertainties were >15%.
Opportunistic analytes are reported for information only; QC requirements did not apply to these analytes.

Adding the AY-102 sample to the Group 7 sample considerably increased the Al inventory, with virtually all Al in the solids (Figure 5.34). The caustic leach removed 57 wt% of the Al from the insoluble solids. The addition of AY-102 also increased the quantity of insoluble Cr in the waste slurry (Figure 5.35). Caustic leaching dissolved 16 wt% of the Cr in the insoluble solids present in the composite waste.

Soluble phosphorus accounts for 38 wt% of the original Group 7 slurry P content (Figure 5.36) and can be directly attributed to phosphates. It is believed that the portion of the P that appears as solid in the slurry is either a result of gelling (WTP-RPT-173 [Lumetta 2008]) or PO_4 entrainment in solids. The phosphorus content of the AY102 slurry was relatively low (Coleman 2003), so the addition was not expected to contribute to the total inventory of the blended slurry. After adding the AY-102 sample, 41% of the insoluble P present in the blended slurry dissolved into the slurry supernate. Since the phosphate concentration in the AY-102 supernate was lower that that of the Group 7 supernate, a portion of the phosphate present in the Group 7 insoluble solids dissolved until the phosphate concentration in the supernate was in equilibrium with the solid phase. Interestingly, a significant increase in the U concentration in the supernate occurred at the same time of this event.

Washing the solids removes a large portion of the remaining P as phosphate after caustic leaching. The high caustic during the leaching and the washing precipitates the phosphate, leading to the irregular behavior noted in Figure 5.36. At the start of the leach, it appeared that some phosphorus precipitated after adding caustic. Once the slurry was heated, it re-dissolved, but precipitated back during the leach cool down and stayed as a solid during the leach dewatering step. It would take additional washing to remove this portion of the phosphate out of the slurry. By the end of the test, 43 wt% of the original insoluble P had been dissolved by the AY-102 addition and by caustic leaching and washing. When looking at the caustic-leached slurry, washing removed 46 wt% of the remaining inventory at that point (Figure 5.37). Dewatering and washing of the leach slurry removed the Al and Cr in the aqueous phase of the slurry after caustic leaching. By the end of the fourth wash, 50 wt% of Al and 15 wt% of the Cr present in the leached slurry was removed.

The concentration of phosphorus in the supernate tracks inversely with the sodium concentration, suggesting the precipitation of $Na_3PO_4 \cdot 12H_2O$ at high sodium concentrations. As the concentration of all species drops with the washes, the phosphate initially rises as the precipitate is re-dissolved and then drops as almost all of the soluble P is removed by the washes (Figure 5.38). The aluminum concentration in the supernate mimics that of the Na and free-hydroxide concentrations, reflecting dissolution at high hydroxide, which is removed by the washes. This is consistent with gibbsite behavior.

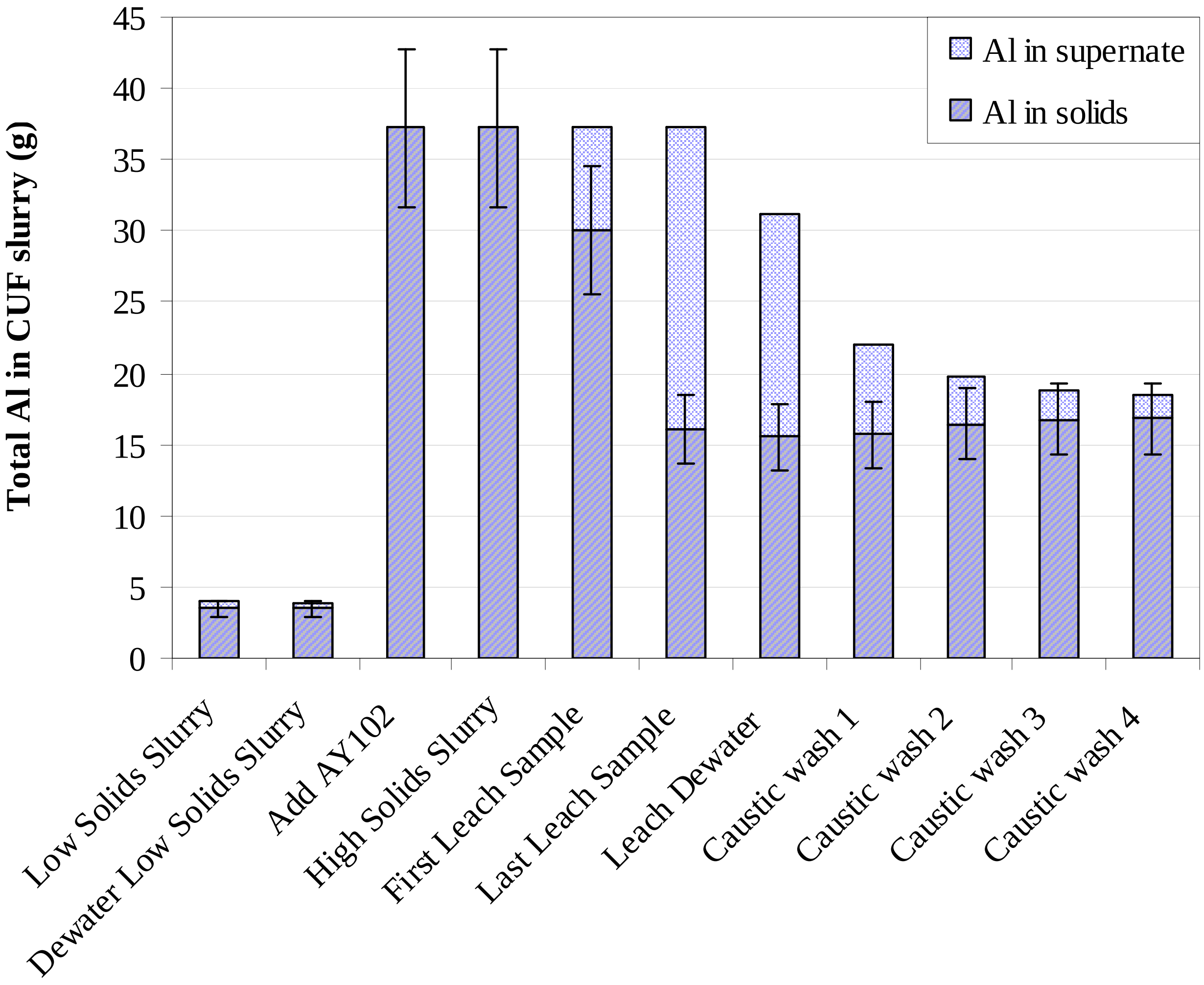


Figure 5.34. Total Aluminum in Group 7/AY-102 CUF Slurry

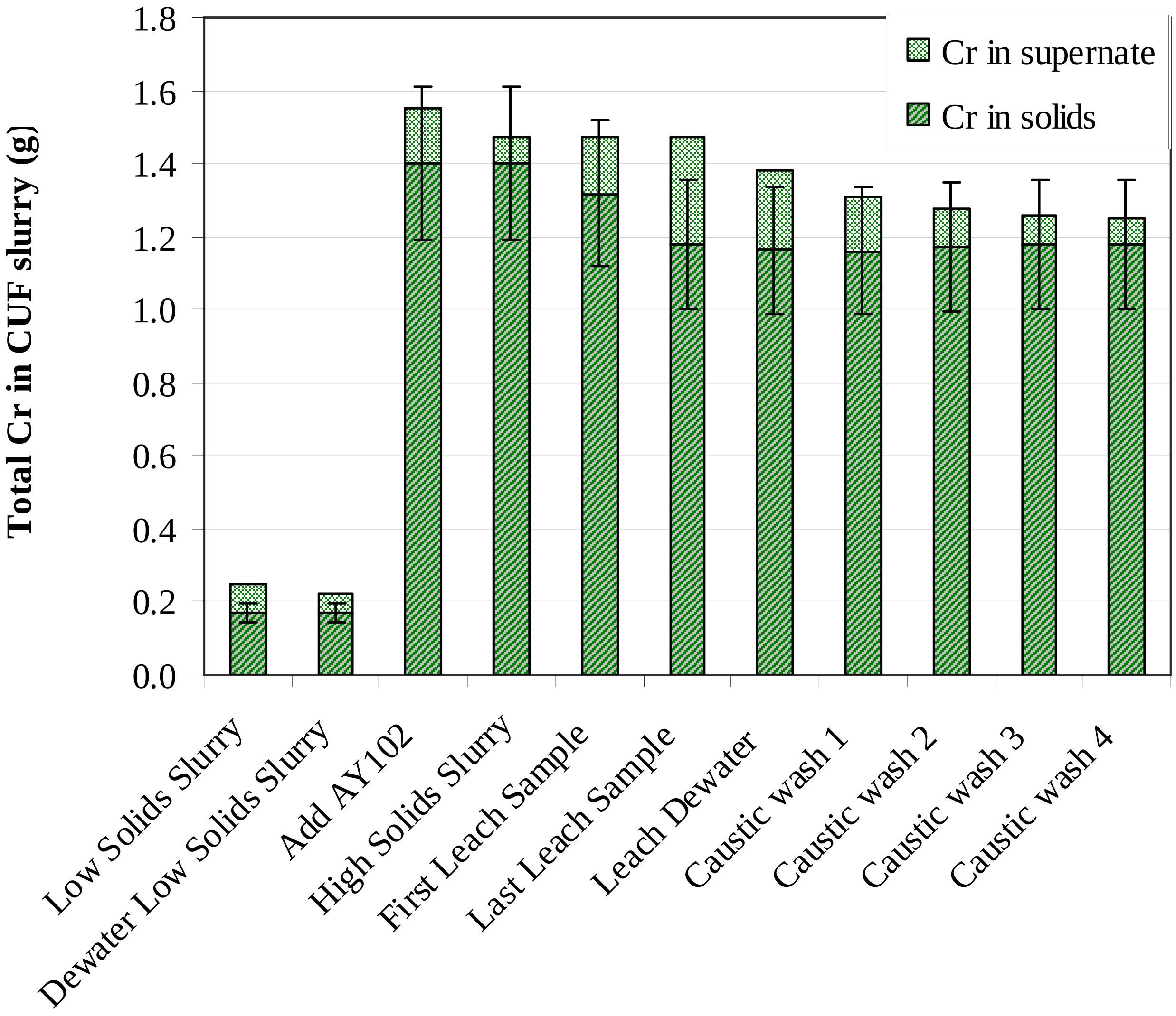


Figure 5.35. Total Chromium in Group 7/AY-102 CUF Slurry

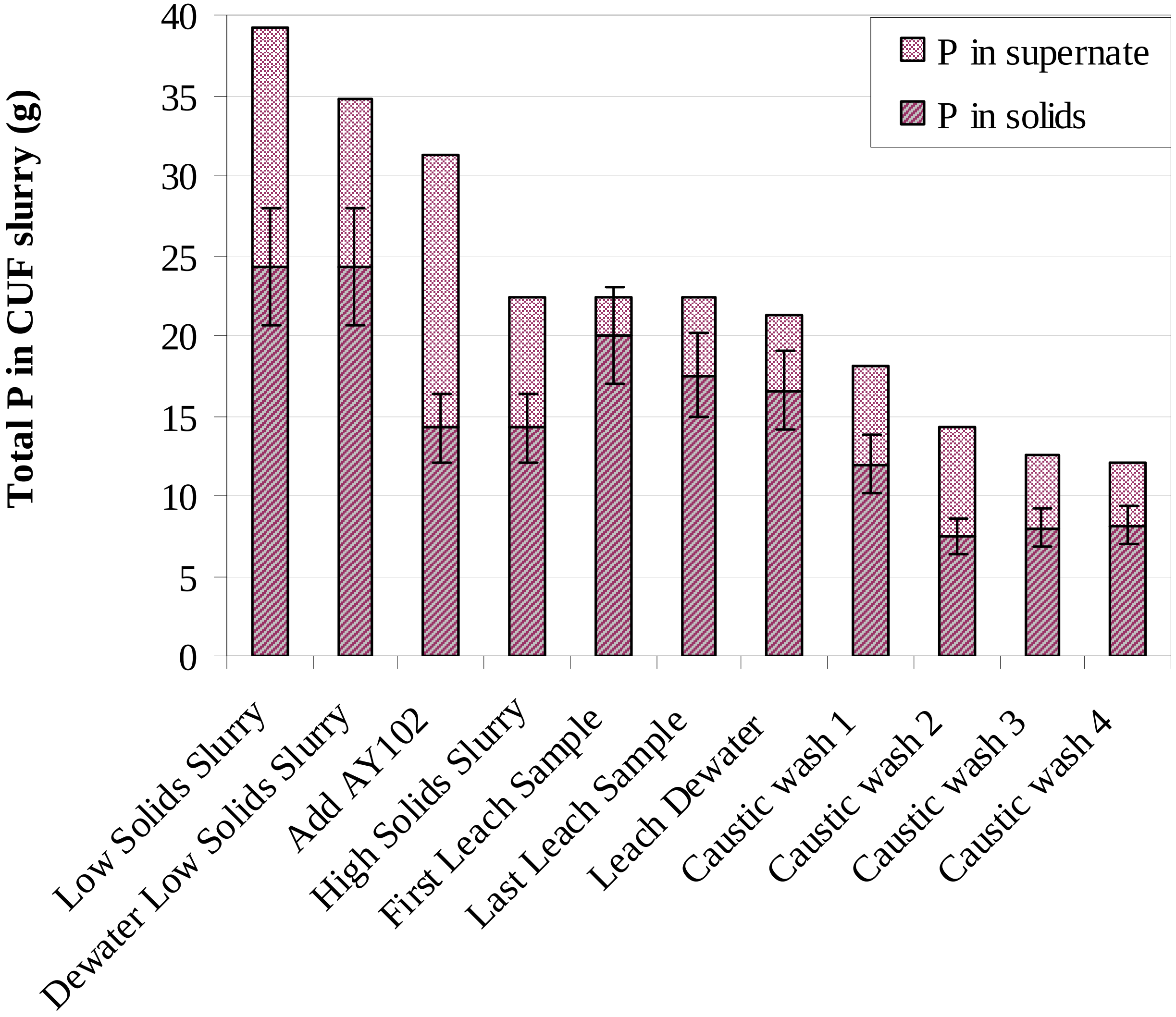


Figure 5.36. Total Phosphorus in Group 7/AY-102 CUF Slurry

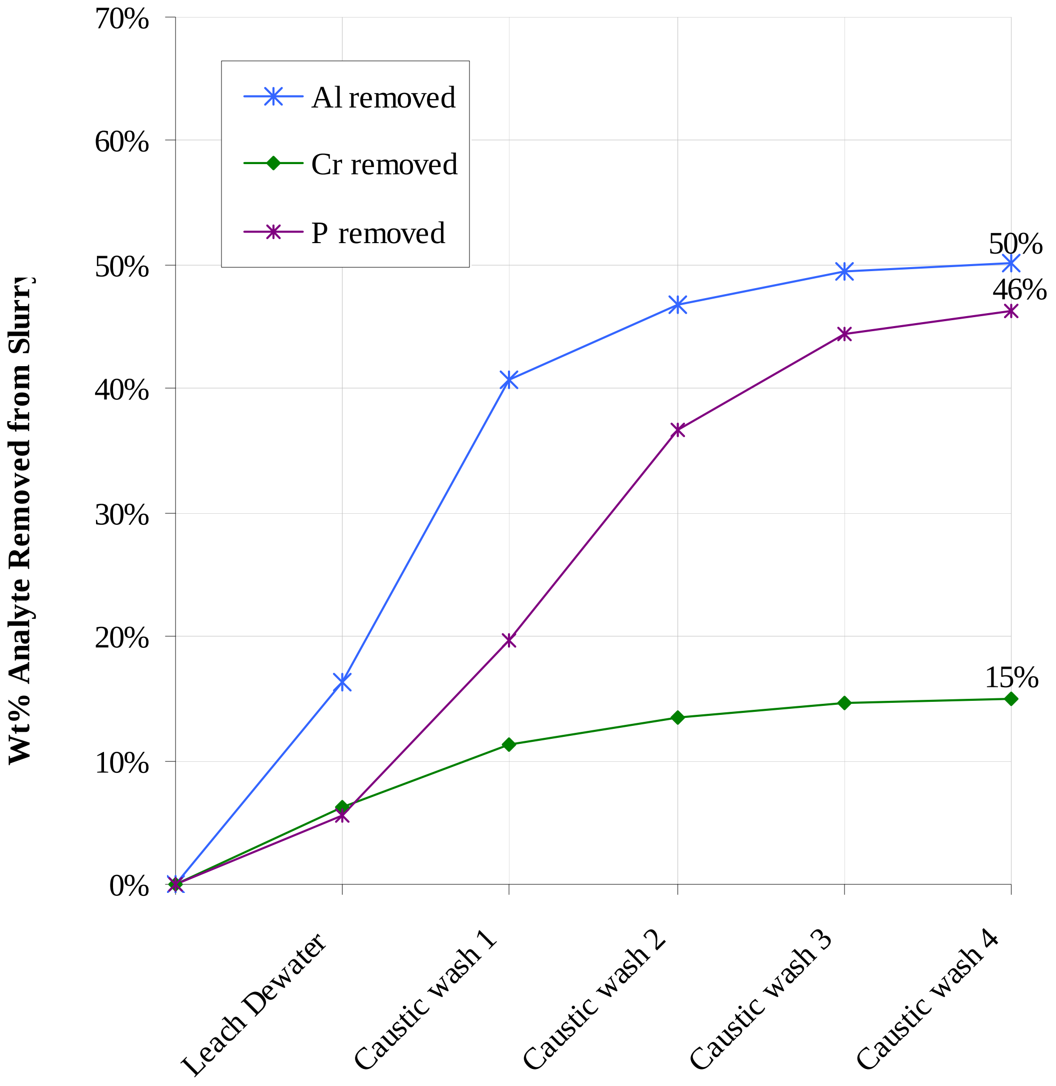


Figure 5.37. Al, Cr and P removed from Dewatering and Washing the Group 7/AY-102 CUF Slurry After Caustic Leaching

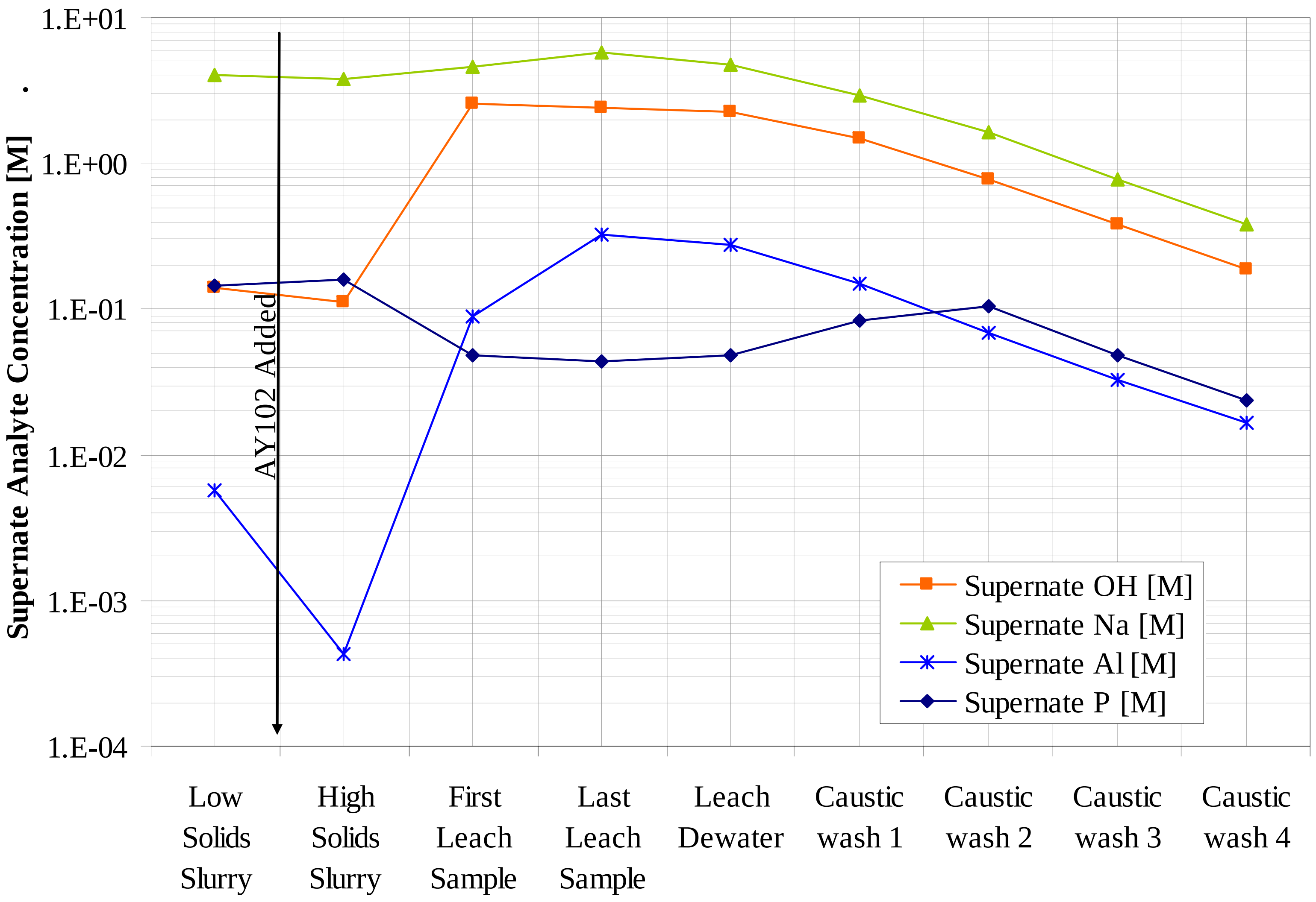


Figure 5.38. Free OH, Na, Al, and P Molarity in Group 7/AY-102 CUF Slurry

5.5.5 Dewatering Caustic-Wash Solutions

The filter flux results from dewatering the slurry after each wash solution are shown in Figure 5.39 and Table 5.33. Each wash volume was filtered from the slurry in 103, 69, 57, and 48 minutes sequentially. Comparing the average filter flux from each dewatering operation to the ionic composition of the supernate shows how diluting the supernate improves filter flux by reducing supernate viscosity.

Decreases in the flux for the last two washes resulted from decreases in TMP and axial velocity during the dewatering step. As the slurry volume was reduced, pump cavitation increased, also resulting in more scatter in the permeate flow data presented in Figure 5.39. The final TMP for the last two washes decreased from 40 psid to 30 psid, while the axial velocity decreased from 13 ft/s to 11 ft/s.

Table 5.33. Comparison of Washed Slurry Supernate Attributes to Filter Flux

Process Step	Wash Volume (L)	Wash addition [NaOH} M	Dewatered Supernate			Average Filter Flux (GPM/ft^2)
			[Na] M	[OH] M	[Al] M	
Wash 1 Dewater	1.20	0.50	2.9	1.5	0.15	0.012
Wash 2 Dewater	1.20	0.10	1.6	0.77	0.069	0.018
Wash 3 Dewater	1.20	0.05	0.77	0.39	0.032	0.023
Wash 4 Dewater	1.20	0.01	0.38	0.18	0.016	0.024
Blended Slurry Dewater			3.7	0.11	4.6E-4	0.014
Leached Slurry Dewater			4.7	2.3	0.27	0.006

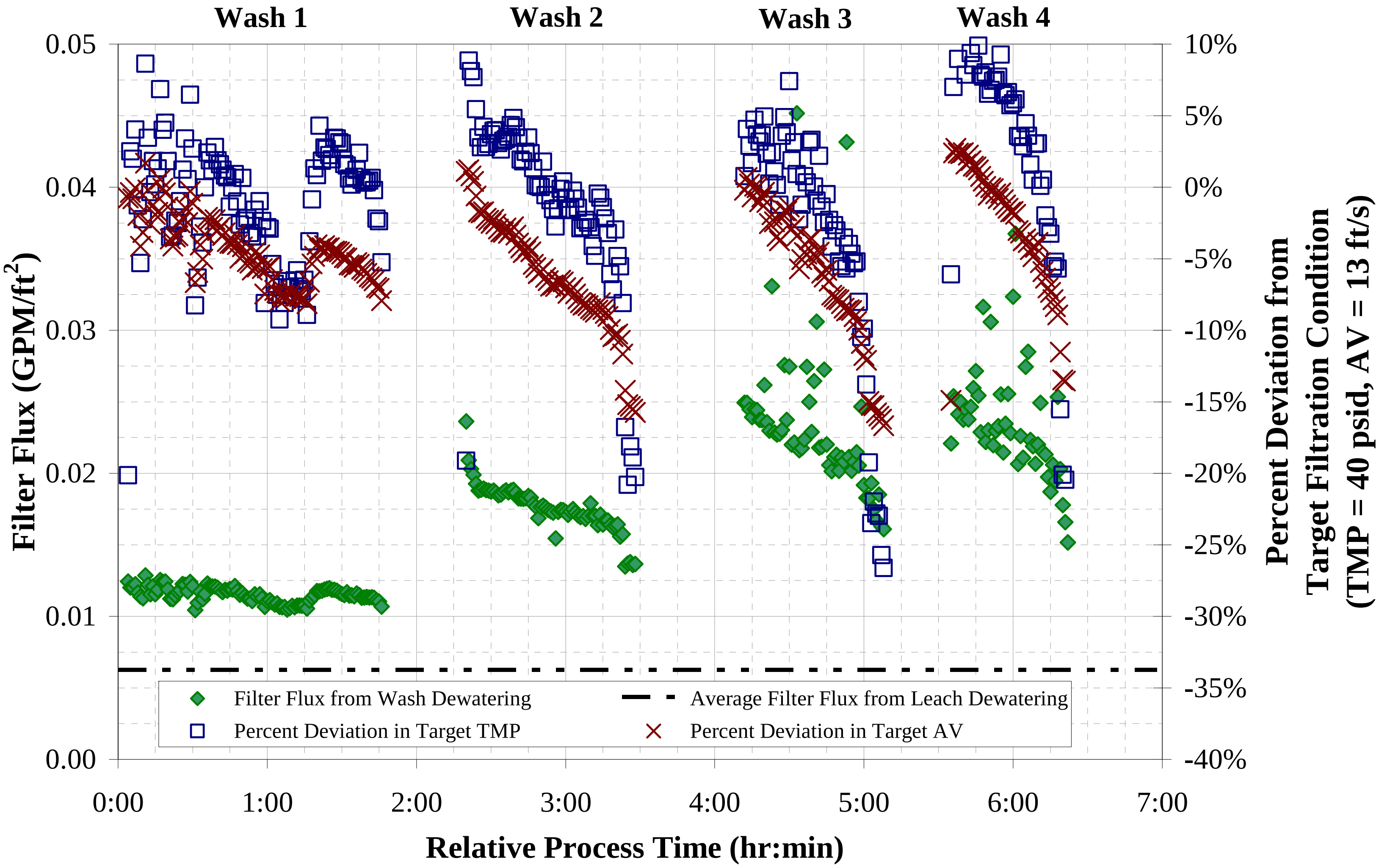


Figure 5.39. Filter Flux During Caustic Wash Steps and Comparison to Leach Dewatering Average Flux

5.6 Final Filter Flux Test Matrix

As discussed earlier (Section 5.5.5), dewatering the final wash solution from the slurry decreased the volume of the slurry to a point where the pump began to cavitate and entrain air into the slurry. This resulted in a loss of pumping efficiency, making it impossible to reach the desired velocities and pressures needed for the test matrix. It was decided that the best course of action was to return permeate from the last dewatering step back to the slurry. Once ~0.4 L of the filtered supernate was returned, the cavitation stopped, and the pumping efficiency improved (Figure 5.40).

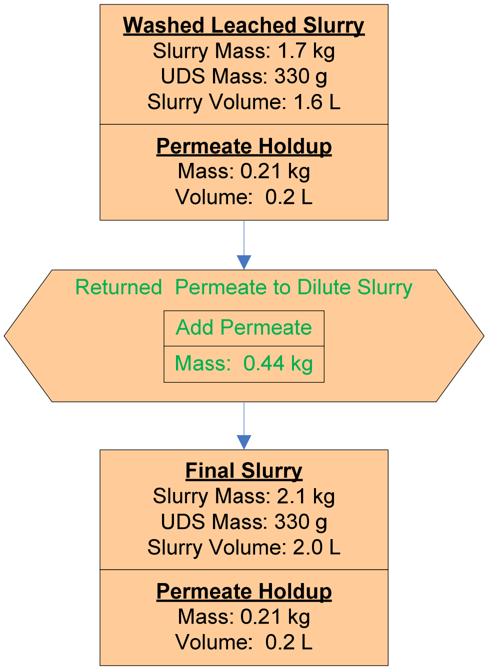


Figure 5.40. Process Flow for Final Filter Slurry

The filter-flux results from the test matrix are shown in Figure 5.41. Cavitation was still an issue, even after adding the permeate. This caused variations in the measured permeate flow rate. Also, the target axial velocity could not be met for test conditions 4 and 8, as shown in Table 5.34 and Figure 5.42. The average filter flux and process conditions achieved during the matrix test ranged from 0.014 to 0.036 GPM/ft^2. The average filter flux at the standard condition (TMP=40 psid and AV=13 ft/s) stayed relatively constant, varying between 0.024 and 0.025 GPM/ft^2.

The average filter flux from each test condition (Table 5.34) was plotted against TMP, AV, and the median operational time of the test condition to qualitatively gauge their impact, as shown in Figure 5.43 through Figure 5.45. As with the low-solids slurry, filter flux was found to be directly proportional to the TMP (Figure 5.43), while AV showed little impact (Figure 5.44). As in the high-solids slurry, no impact from the processing time (Figure 5.45) was found either.

Modeling the data using a least-squares-fit method was then used to quantify the effects of TMP, AV, and processing time on filter flux. Process time reflects the average time for the given process conditions since the start of testing. This variable is intended to assess the fouling of the filter that occurs through the duration of testing. A linear-fit equation with an R^2 correlation of 0.97 was developed using only TMP (Figure 5.46). The modeling confirmed the results shown in Figure 5.44 and Figure 5.45, which showed no relationship between AV and process time with filter flux for the slurry at this concentration (measured at 14 wt% in Section 5.7). As Figure 5.43 demonstrated, the TMP significantly impacted filter flux and was proportional to filter flux as predicted by the Darcy equation. Centrifuge UDS measurements of this slurry were taken afterwards (Section 5.7), which is considered a good estimate of the gel concentration of the slurry. The value measured was 52 wt%, which indicates that the slurry UDS concentration needed to be much higher before the axial velocity began to have any impacts. Diluting the slurry to perform the test could have impacted these results.

The use of this model was limited to comparing TMP and AV impacts on filter flux during this test and how the filter behavior changed after caustic leaching and washing. During development of the linear model, a negative offset was created. Therefore, the model does not predict a zero filter flux when the TMP is zero, demonstrating that the input to these models must be bound by the range of TMP used in this filter test, shown in Table 5.34. The use of the model should also be limited to when the test matrix occurred because the filter resistance was not at steady state, and the parameters developed in these models would be expected to change past the 16-hour period that this model predicts.

Table 5.34. Average Flux Values for Rinsed Leached Group 7 Solids

Design Test Condition	Median Operation Time of Test[(a)] (hr:mm)	Slurry Temp[(b)] (°C)	TMP[(c)] (psid)	Axial Velocity (ft/s)	Permeate Flowrate (mL/min)	Corrected Permeate Flux (GPM/ft^2)	Axial Pressure Drop[(c)] (psid/ft)
1	1:31	25.3	40.5	13.1	24.8	0.025	1.5
2	3:37	25.1	31.6	10.9	17.9	0.018	1.2
3	4:40	25.1	31.7	15.0	17.8	0.018	1.5
4	6:32	25.2	47.9	13.9	27.8	0.028	1.5
5	7:48	25.1	51.7	11.3	29.1	0.029	1.2
6	9:08	25.1	40.2	13.1	24.0	0.024	1.3
7	10:26	25.0	41.1	9.1	25.8	0.026	1.0
8	11:42	25.2	41.0	14.2	24.3	0.024	1.5
9	12:50	25.2	20.1	13.0	13.6	0.014	1.3
10	14:01	26.6	60.1	12.8	37.4	0.036	1.6
11	15:12	25.2	40.5	13.3	23.6	0.024	1.4

(a) Median operation time refers to the midpoint in processing time of the specific filtration test condition relative to the start time of the test (T = 0). Time periods between test conditions were excluded.
(b) Thermocouple accuracy ± 2°C.
(c) Pressure transducer accuracy ± 1 psig.

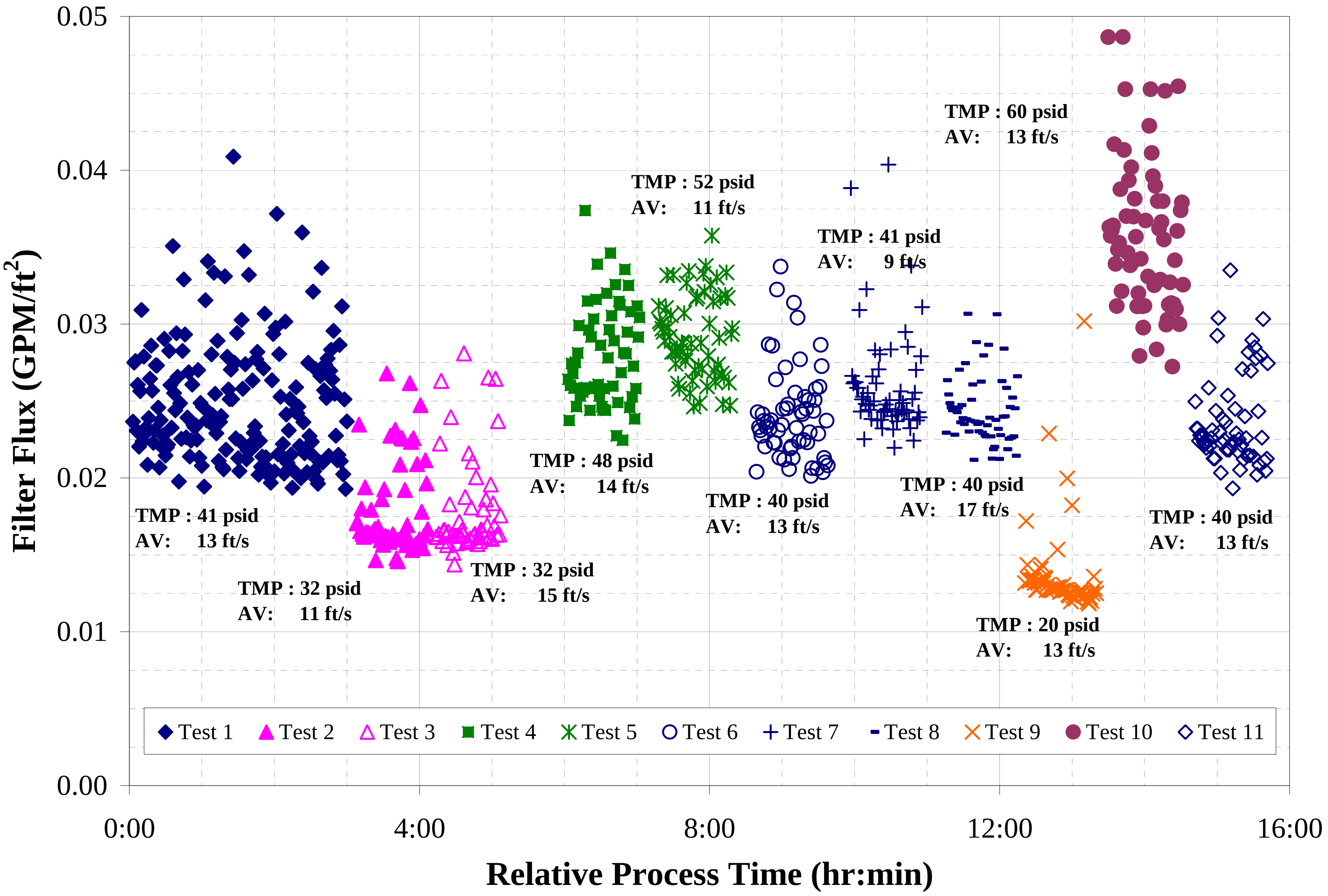


Figure 5.41. Filter Flux for the Washed Leached Filter Test Matrix (Measured UDS of 14 wt%)

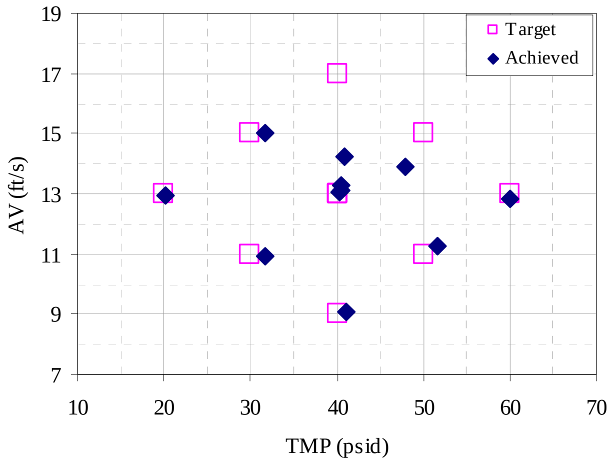


Figure 5.42. Filter Test Matrix for Group 7-AY102 Leached-Solids

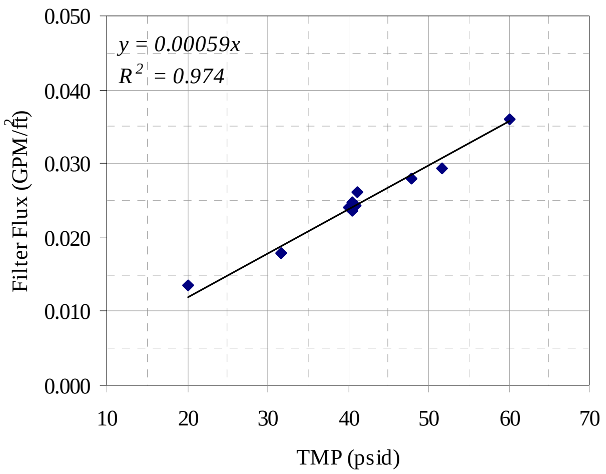


Figure 5.43. Flux vs. TMP for Group 7-AY102 Leached-Solids

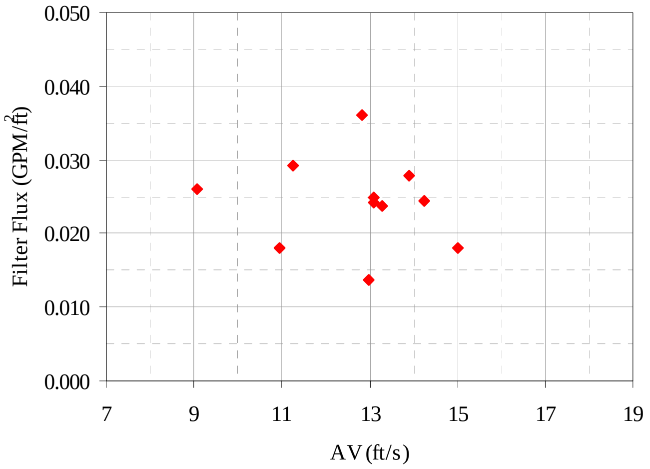


Figure 5.44. Flux vs. AV for Group 7-AY102 Leached-Solids

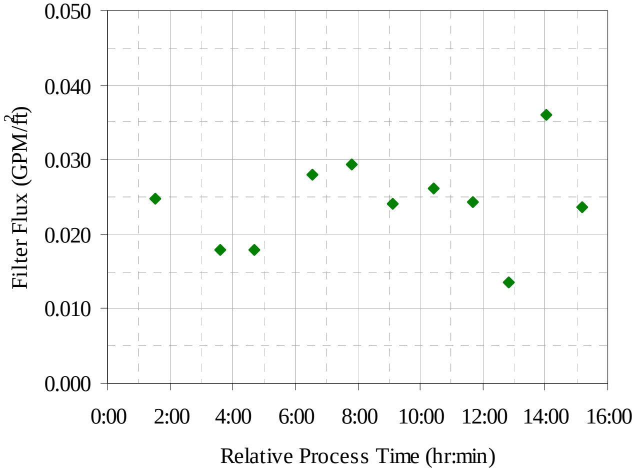


Figure 5.45. Flux vs. Median Process Time of Test for Group 7-AY102 Leached-Solids

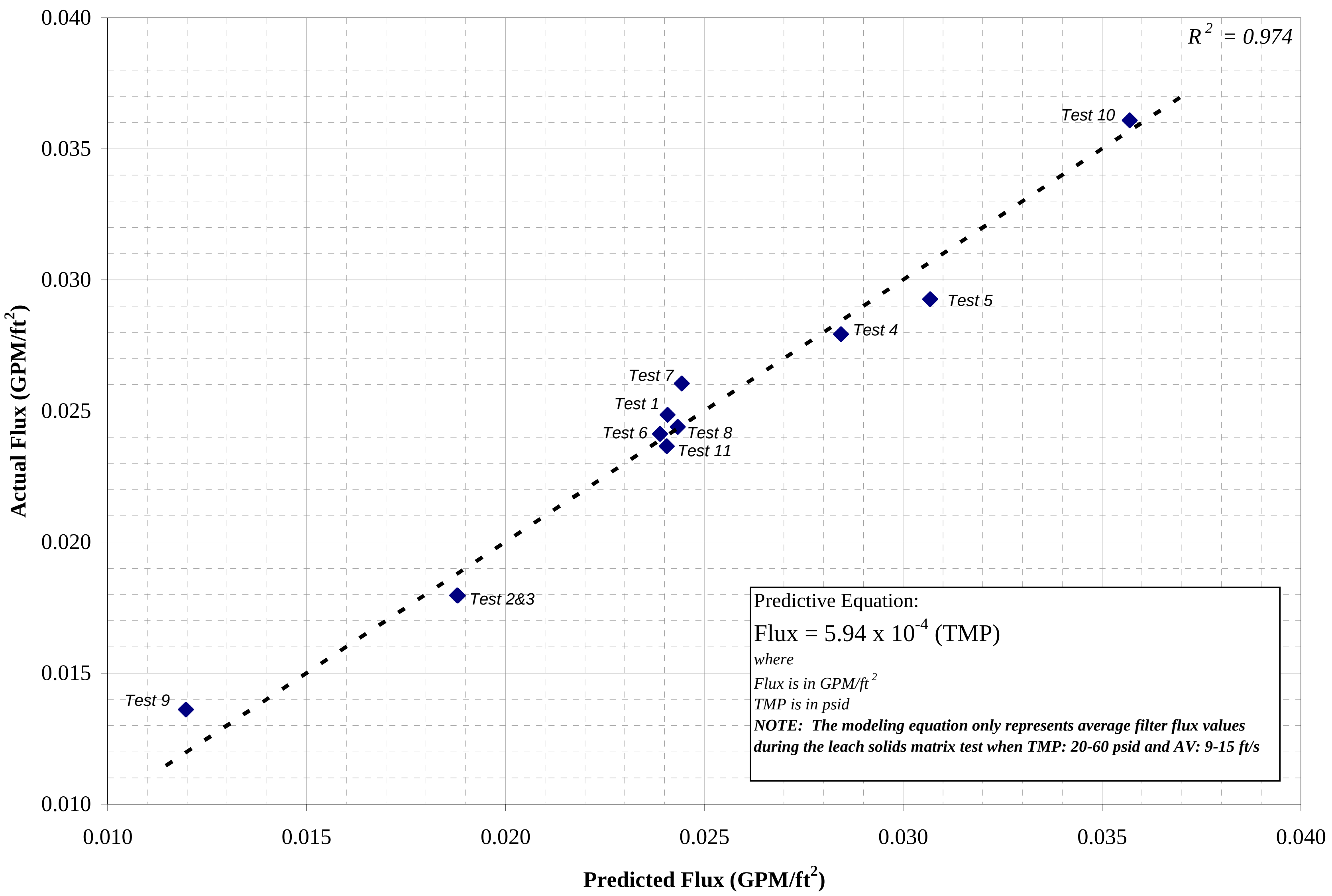


Figure 5.46. Least-Squares-Fit of Leached Solid Test Matrix Results with Linear Model (Measured UDS of 14 wt%)

5.7 Leached-Material Characterization

After leaching and washing operations, the slurry was sampled and drained from the CUF. Physical and chemical analyses were performed on the samples collected, and the remaining slurry was saved as an archive sample to be used later. Physical-property measurements shown in Table 5.35 found the UDS concentration to be 14 wt%, which compared well to the predicted concentrations of 16 wt% (0.33 kg/2.1 kg). The final predicted composition of the slurry is shown in Table 5.36. The data in this table are the result of mass-balance calculations performed on the slurry using supernate ICP-OES/IC/radionuclides data and measured mass changes to the slurry. The measured composition of the slurry by ICP-OES/radionuclide analysis is found in Table 5.37. The slurry composition is broken down to supernate and solid concentrations. The solids compositions were then used to calculate solids leach factors for the analytes listed using data generated in Table 5.17.

Overall, leach factors calculated after the caustic leach (Table 5.25) compared well with those calculated for those after washing (Table 5.37). The radiochemical isotopes measured in the slurry all have calculated negative leach factors, indicating that they do not leave the HLW stream. Mass-balance calculations showed no significant quantities of the measured isotopes in the permeate removed, with the exception of cesium, which was already partially present in a soluble phase. Figure 5.47 shows the remaining fraction of each isotope measured in the slurry by mass-balance calculations. After correcting for sample losses, the chart showed that almost all of the material stayed in the slurry. Some cesium was removed during dewatering operations, but 88% still remained in the slurry. After caustic leaching was performed, the majority uranium present remained in the solid phase.

The biggest discrepancy in the leach-factor data was with phosphorus, which now showed a calculated leach factor of 0.63 instead of -0.24. As discussed early, the caustic leach was expected to suppress the release of phosphorus as soluble phosphate because of increases in the sodium concentration. As discussed in Section 5.5.4, phosphorus does not dissolve until slurry washing decreases the Na concentration (Figure 5.38). Figure 5.48 shows the quantity of anions released at different parts of the test. While the mass of released nitrate and nitrite concentrations decreased after washing, significant quantities of phosphate were still being released. This supports the ICP data, which indicates that phosphorus removal occurs later in the process and not during the caustic-leach dewatering.

Table 5.35. Final Leached and Washed Slurry Physical-Property Measurements

Slurry Density (g/mL)	1.19
Supernate Density (g/mL)	1.05
Settled Solids (Vol %)	81%
Centrifuged UDS (Wt %)	52%
Total Solids (Wt %)	19%
Dissolved Solids (Wt%)	10%
UDS (Wt%)	14%

Table 5.36. Final Leached, Washed Dewatered Slurry Composition (Including Permeate Hold-up)

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	2.32	2.02		0.30	
Wt% of Slurry	100%	87.2%		12.8%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	1.3E+01	8.4E-01	4.4E+02	1.2E+01	4.2E+04
B	2.9E-03	2.9E-03	1.5E+00	n/a(d)	n/a(d)
Bi	6.7E-01	5.2E-03	2.7E+00	6.7E-01	2.2E+03
Ca	3.8E+00	2.1E-03	1.1E+00	3.8E+00	1.3E+04
Cd	7.6E-02	5.0E-04	2.6E-01	7.5E-02	2.5E+02
Cr	8.5E-01	1.3E-02	7.0E+00	8.3E-01	2.8E+03
Fe	5.9E+01	7.1E-04	3.7E-01	5.9E+01	2.0E+05
K	6.3E-02	6.3E-02	3.3E+01	n/a(d)	n/a(d)
Mn	8.6E+00	5.9E-05	3.1E-02	8.6E+00	2.9E+04
Na	4.8E+01	1.7E+01	8.8E+03	3.1E+01	1.0E+05
Ni	1.5E+00	< 1.E-4	< 6.E-2	1.5E+00	4.9E+03
P	5.3E+00	1.4E+00	7.3E+02	3.9E+00	1.3E+04
S	1.1E-01	2.5E-01	1.3E+02	n/a(d)	n/a(d)
Si	1.5E+01	1.6E-02	8.4E+00	1.5E+01	4.9E+04
Sr	5.8E-01	8.1E-06	4.2E-03	5.8E-01	1.9E+03
Zn	1.4E-01	1.5E-03	7.9E-01	1.4E-01	4.8E+02
Zr	1.4E+00	< 5.E-5	< 3.E-2	1.4E+00	4.6E+03
U	8.5E+00	2.1E-02	1.1E+01	8.5E+00	2.9E+04
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	6.4E+01	< 1.E-1	< 7.E-5	6.4E+01	2.2E-01
Cs-137	1.2E+05	1.3E+03	6.8E-01	1.2E+05	4.0E+02
Eu-152	8.7E+01	< 5.E-1	< 3.E-4	8.7E+01	2.9E-01
Eu-154	2.1E+03	< 3.E-1	< 2.E-4	2.1E+03	7.1E+00
Eu-155	9.6E+02	< 2.E+0	< 8.E-4	9.6E+02	3.2E+00
Am-241	3.5E+03	< 3.E+0	< 2.E-3	3.5E+03	1.2E+01
Gross Alpha	5.1E+03	1.2E+00	6.1E-04	5.1E+03	1.7E+01
Gross Beta	5.9E+06	1.4E+03	7.1E-01	5.9E+06	2.0E+04
Sr-90	3.1E+06	2.4E+00	1.3E-03	3.1E+06	1.0E+04
Pu-239+240	1.3E+03	6.8E-01	3.6E-04	1.3E+03	4.4E+00
Pu-238	2.0E+02	9.1E-02	4.7E-05	2.0E+02	6.8E-01
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	µg/ml	**[M]**	**g**	**µg/g**	**g**
F	2.0E+01	1.1E-03	3.9E-02	3.8E+02	1.1E-01
Cl	1.1E+02	3.0E-03	2.1E-01	1.9E+03	5.7E-01
C_2O_4	5.3E+01	6.0E-04	1.0E-01	1.6E+03	4.6E-01
NO_2	4.1E+02	9.0E-03	8.0E-01	1.3E+04	3.9E+00
NO_3	3.5E+03	5.7E-02	6.9E+00	7.0E+04	2.1E+01
SO_4	3.6E+02	3.8E-03	7.1E-01	7.7E+03	2.3E+00

Table 5.36 (Contd)

	Slurry[(a)]	**Liquid Fraction**[(b)]		**Solids Fraction**[(c)]	
Mass (kg)	2.32	2.02		0.30	
Wt% of Slurry	100%	87.2%		12.8%	
PO_4	2.2E+03	2.4E-02	4.3E+00	3.5E+04	1.0E+01
OH	3.1E+03	1.8E-01	6.1E+00		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-169, Section 3). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI624-G7-H (ASO ID 08-02062) and the predicted mass of supernate in the system.

(c) Solids Fraction mass components were calculated from the difference between the slurry component mass and liquid component mass fraction.

(d) Values (based on supernate) were calculated to be less than zero.

Table 5.37. Washed Caustic-Leached Slurry Composition and Solid-Leach-Factor Calculations

Slurry Prep Method	**Analyte**	**Dry Slurry(a) (µg/g)**	**Supernate(b) (µg/mL)**	**Dry Solids(c) (µg/g)**	**Solid Leach Factor(d)**	
					Before washing	**After washing**
HF Assisted Digestion Concentration Factor of 1.43 based on Fe/Zr	Al	41,900	440	53,000	0.51	0.48
	B	[22]	[1.5]	[21]	-0.14	2.64
	Bi	1,910	[2.7]	2,500	-0.02	0.00
	Cd	213	[0.26]	2300	0.01	-0.04
	Cr	2,500	7.00	3,300	0.15	0.14
	Fe	168,000	[0.37]	220,000		
	Mn	24,700	[0.031]	33,000	0.00	0.00
	Na	110,000	8,800	96,000	-0.58	-0.12
	Ni	4,450	--	5,900	-0.01	0.00
	P	13,700	726	14,000	-0.24	0.63
	S	[1,600]	129	[1,400]	1.64	[1.80]
	Sr	1,610	[0.0042]	2,200	0.00	0.01
	U	22,900	11.1	31,000	-0.80	-0.75
	Zn	456	[0.79]	6600	0.07	0.08
	Zr	4,140	--	5,500		
	Ag	***183***	***[.32]***	***240***	*0.39*	*-0.89*
	Ba	***1,050***	***0.02***	***1,400***	*0.00*	*0.01*
	Be	***1.5***	***--***	***2.0***	*0.01*	*-0.05*
	Ca	***11,400***	***[1.1]***	***15,000***	*0.00*	*0.01*
	Ce	***1,150***	***--***	***1,500***	*-0.01*	*0.01*
	Cu	***383***	***--***	***510***	*0.00*	*0.00*
	La	***1320***	***--***	***1,800***	*-0.01*	*0.00*
	Li	***149***	***0.571***	***200***	*0.01*	*0.02*
	Mg	***3,060***	***--***	***4,100***	*0.00*	*0.01*
	Mo	***[22]***	***[0.17]***	***[28]***	*-0.21*	*-0.15*
	Nd	***1,990***	***--***	***2,700***	*-0.03*	*-0.03*
	Pb	***7,150***	***[1.5]***	***9,500***	*0.00*	*0.00*
	Ru	***234***	***[0.34]***	***310***	*0.03*	*0.38*
	Th	***875***	***--***	***1,200***	*-0.02*	*0.02*
	Ti	***370***	***[0.013]***	***490***	*0.00*	*-0.02*
	V	***25.1***	***0.189***	***30***	*0.07*	*0.18*
	W	***365***	***[1.2]***	***480***	*0.02*	*0.09*
	Y	***169***	***--***	***230***	*-0.01*	*0.02*
KOH Fusion Concentration Factor of 1.42 based on Fe	Fe	178,000	[0.37]	240,000		
	Si	39,900	8.35	53,000	0.05	-0.06
	Radionuclide	**Dry Slurry (µCi/g)**	**Supernate (µCi/mL)**	**Dry Solids (µCi/g)**		
	^{60}Co	2.05E-1	< 7.E-5	2.7E-1	-0.24	-0.12
	^{137}Cs	3.85E+2	6.81E-1	5.1E+2	-0.15	0.01
	^{154}Eu	6.63E+0	< 2.E-4	8.8E+0	-0.22	-0.08
	^{155}Eu	3.25E+0	< 8.E-4	4.3E+0	-0.14	-0.20
	^{241}Am	1.03E+1	< 2.E-3	1.4E+1	-0.34	-0.03
	^{90}Sr	8.75E+3	1.26E-3	1.2E+4	0.06	0.00
	$^{239+240}$Pu	3.93E+0	3.56E-4	5.2E+0	-0.09	-0.11
	^{238}Pu	6.73E-1	4.74E-5	9.0E-1	-0.34	-0.13

(a) Test sample TI624-G7-12, ASO ID 08-2076

(b) Test sample TI624-G8-H, ASO ID 08-2062

(c) Calculated using results in from TI624-G7-12 and TI624-G7-H.

(d) Calculated using the concentration factor in the first column and by using the solid concentrations value calculated in Table 5.13 as the initial concentration.

Analyte uncertainties were typically within ±15%; results in brackets indicate that the analyte concentrations were greater than the method detection limit (MDL) and less than the estimated quantitation limit (EQL), and uncertainties were >15%. Opportunistic analytes are in italics.

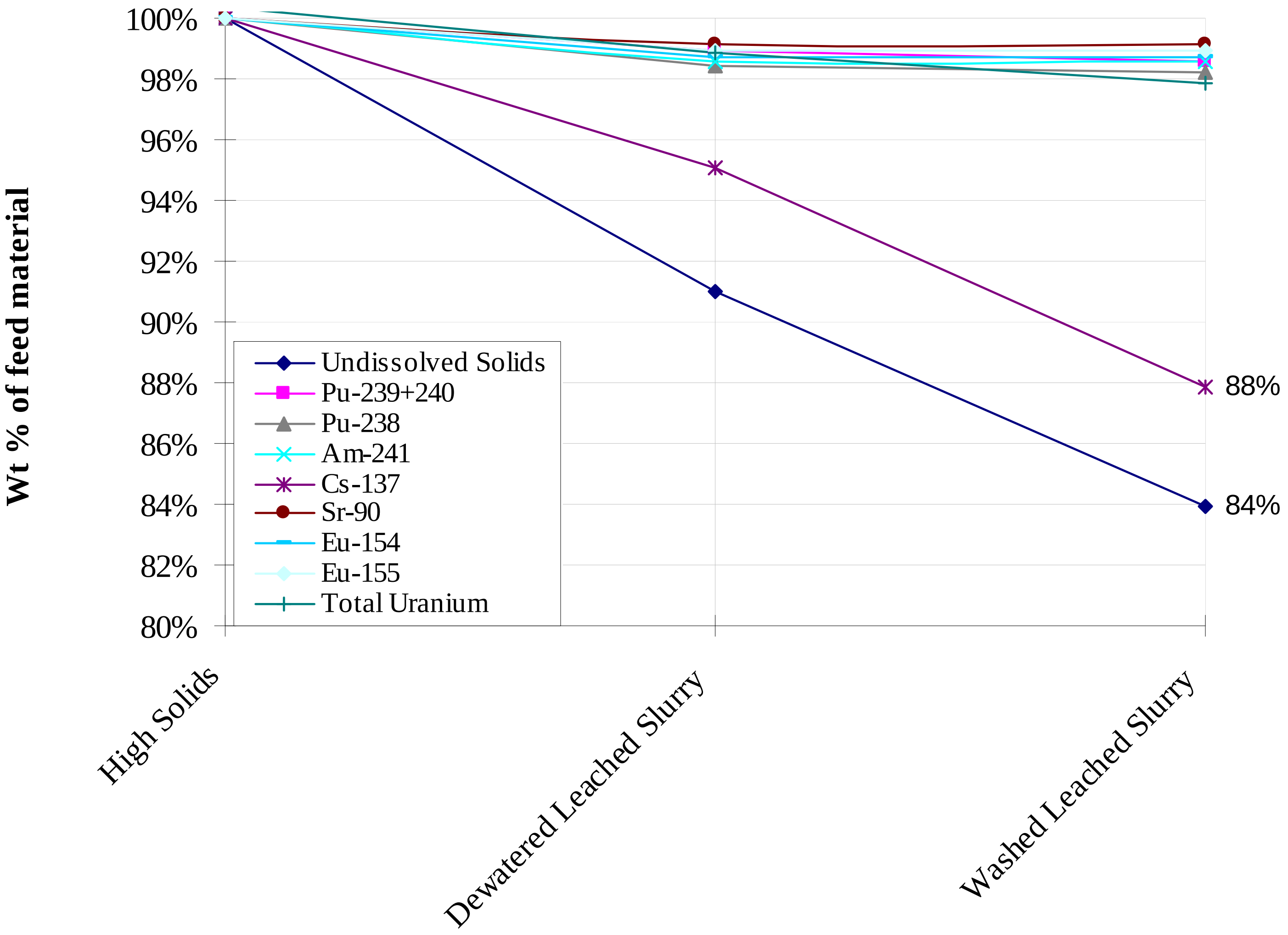


Figure 5.47. Radionuclides/Total Solids in Group 7/AY-102 CUF Slurry, Adjusted for Sampling

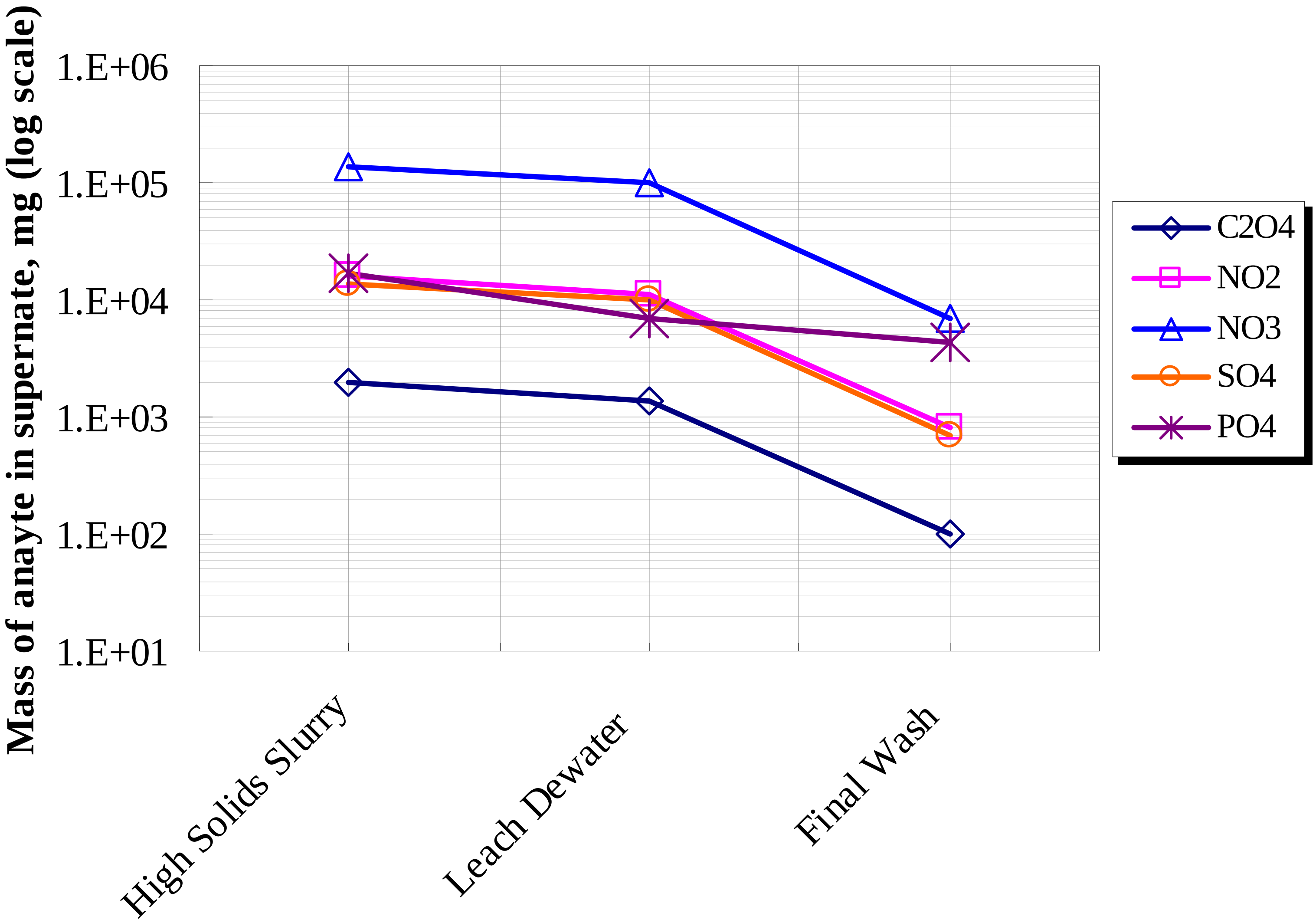


Figure 5.48. Anions in the Group 7/AY-102 Slurry Supernate

The leached and washed solids were examined by XRD analysis. The identified phases, ranked by relative peak intensities, are given below (Figure 5.49). All of the phases identified in the sample are at very low concentration, which in general equates to less certainty of the identified phases. It is possible that there are additional phases present in the sample, but due to the small amount of sample that could be used (driven by the high radioactivity), minor phases are not visible in the scan. Gibbsite was observed as a significant phase of aluminum in the AY-102 waste sample [Krupka 2004]. The absence of gibbsite in the XRD scans from the leached slurry sample indicated that aluminum in this phase was completely dissolved..

- Hematite, Fe_2O_3
- Cancrinite, $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \cdot 2H2O$
- Collinsite, Fairfieldite group, $MgCa_2(PO_4)_2(H_2O)_2$
- Hydroxyapatite, $Ca_5(PO_4)_3(OH)$

SEM images and subsequent EDS analysis (Figure 5.50 and Figure 5.51) are consistent with the XRD results because phases rich in Fe, Si, Ca, Al, Mg were all identified.

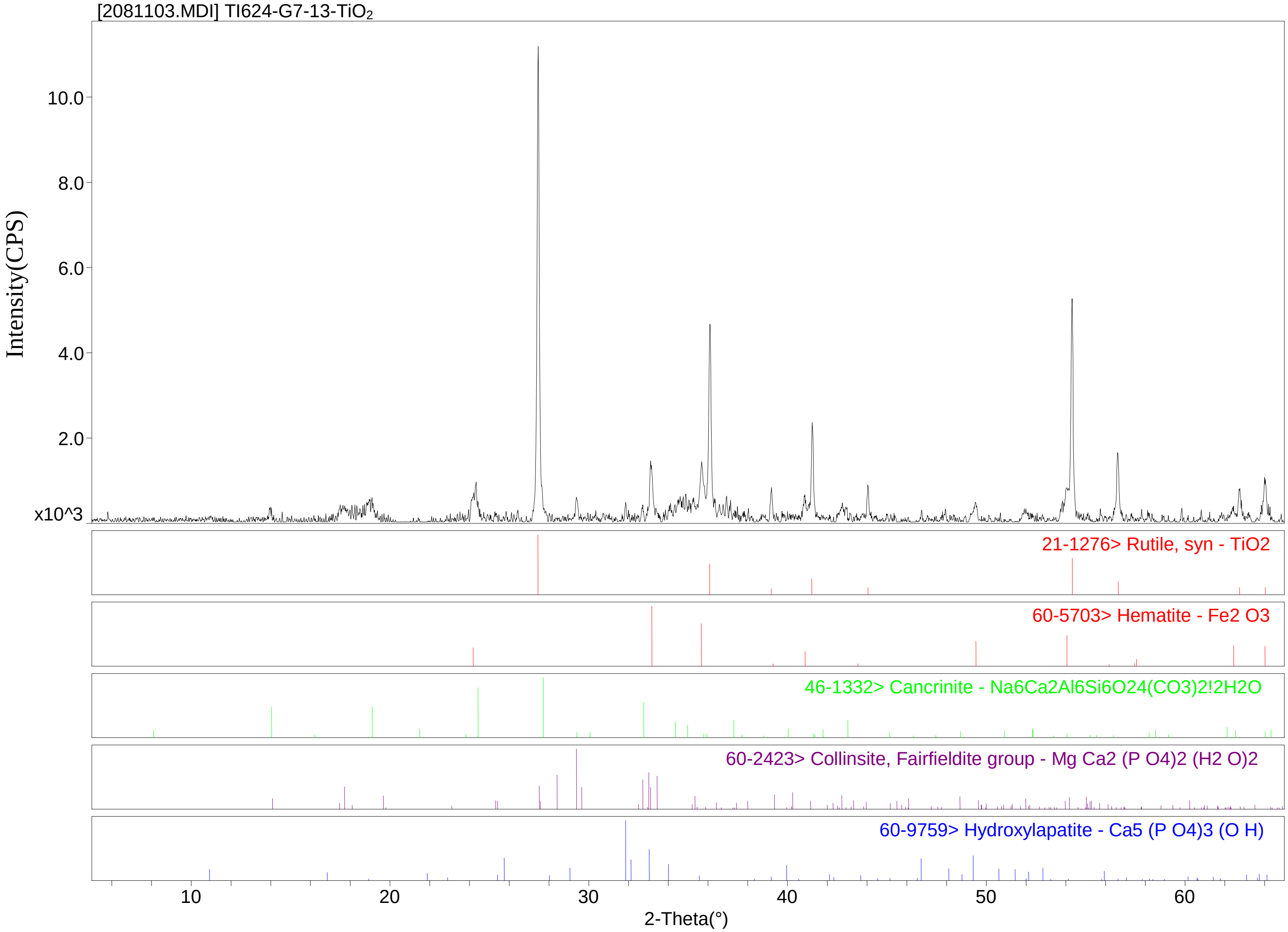
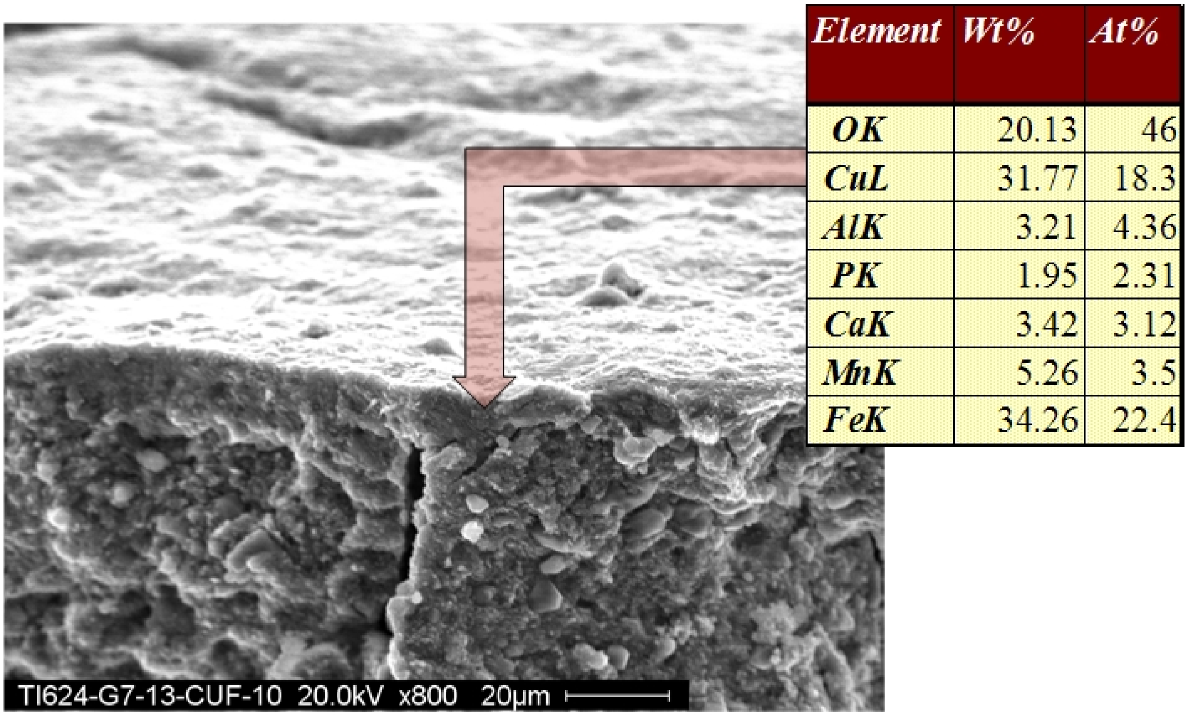
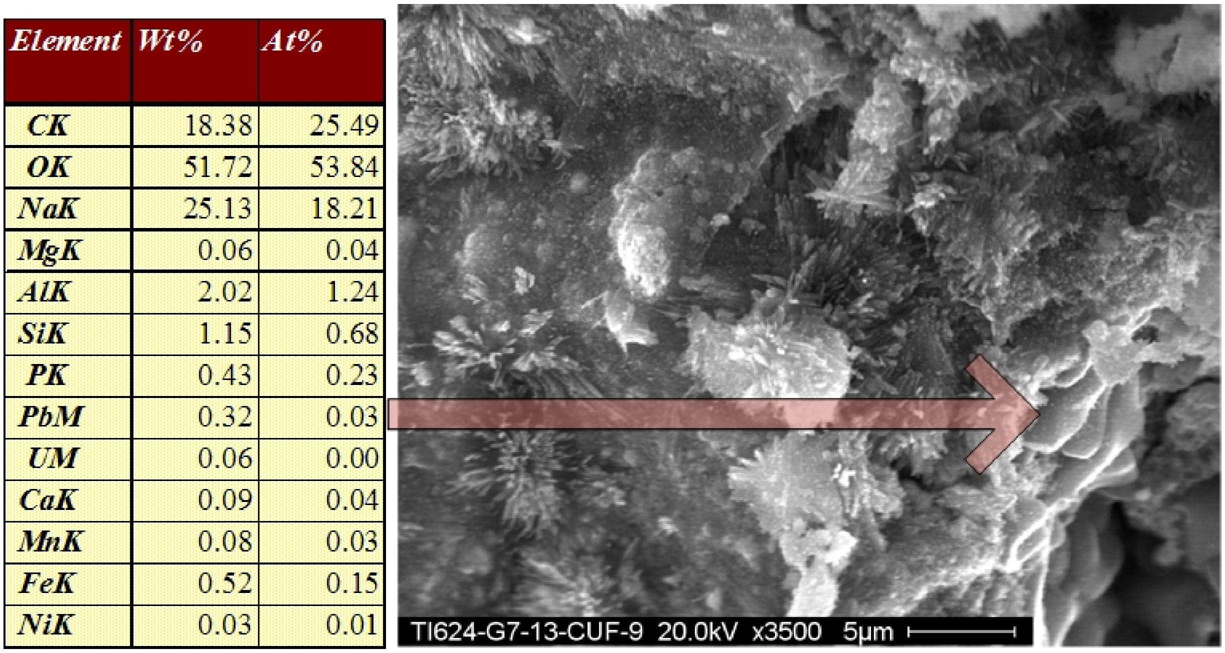


Figure 5.49. XRD Scan Result for the Leached and Washed Solids from the CUF Experiments



Element	Wt%	At%
OK	20.13	46
CuL	31.77	18.3
AlK	3.21	4.36
PK	1.95	2.31
CaK	3.42	3.12
MnK	5.26	3.5
FeK	34.26	22.4

Figure 5.50. SEM of Leached and Washed Particle



Element	Wt%	At%
CK	18.38	25.49
OK	51.72	53.84
NaK	25.13	18.21
MgK	0.06	0.04
AlK	2.02	1.24
SiK	1.15	0.68
PK	0.43	0.23
PbM	0.32	0.03
UM	0.06	0.00
CaK	0.09	0.04
MnK	0.08	0.03
FeK	0.52	0.15
NiK	0.03	0.01

Figure 5.51. SEM 2 of Leached and Washed Particle

Rheology measurements were performed on the leached and washed slurry. Figure 5.52 shows the results of flow-curve testing. The results of the measurement indicate that the flow behavior is weakly non-Newtonian. The yield stress is low (~0.5 Pa) and near or at the instrument limit of detection. After the yield stress is exceeded, the flow-curve data show a linear stress response over shear rates from zero up to 500 s^{-1}. At higher shear rates (generally 500 s^{-1} and above), flow-curve data show an increase in the slope of the stress response curve. This increase is likely a result of Taylor vortex formation onset (i.e., unstable/turbulent flow), which renders the affected data unusable.

Flow-curve data at 25°C, 40°C, and 60°C were fit to both Bingham-Plastic and Casson models. The instrument uncertainty matched the nominal value measured, and establishing the Bingham-plastic nature of the specimen is questionable. Table 5.38 summarizes the best-fit model parameters for the leached washed slurry. Since the data were influenced by Taylor vortex formation, only the range of shear rates, 0 to 500 s^{-1}, is employed in the Casson fitting analysis. Bingham-Plastic analysis cannot account for slurry shear thinning, and as a result, its fitting analysis is limited to 100 to 500 s^{-1} to avoid bias introduced by slurry shear thinning at low shear rates. Both models provide reasonable fits of the data up to the limit of fitting analysis (i.e., 500 s^{-1}). Beyond 500 s^{-1}, the model and data diverge as a result of Taylor vortex formation.

Apparent viscosities at 33, 100, 500, and 1000 s^{-1} were derived from each measurement. For each temperature, the 33, 100, and 500 s^{-1} reference viscosities were determined from the average of both up-ramp and down-ramp flow-curve data. The apparent viscosity at 1000 s^{-1} is derived from the averaging of all apparent viscosity measurements during constant rotation at 1000 s^{-1}. As a point of comparison, apparent viscosities were also calculated using the Bingham-Plastic and Casson fitting parameters in Table 5.38. The results of these analyses are provided in Table 5.39.

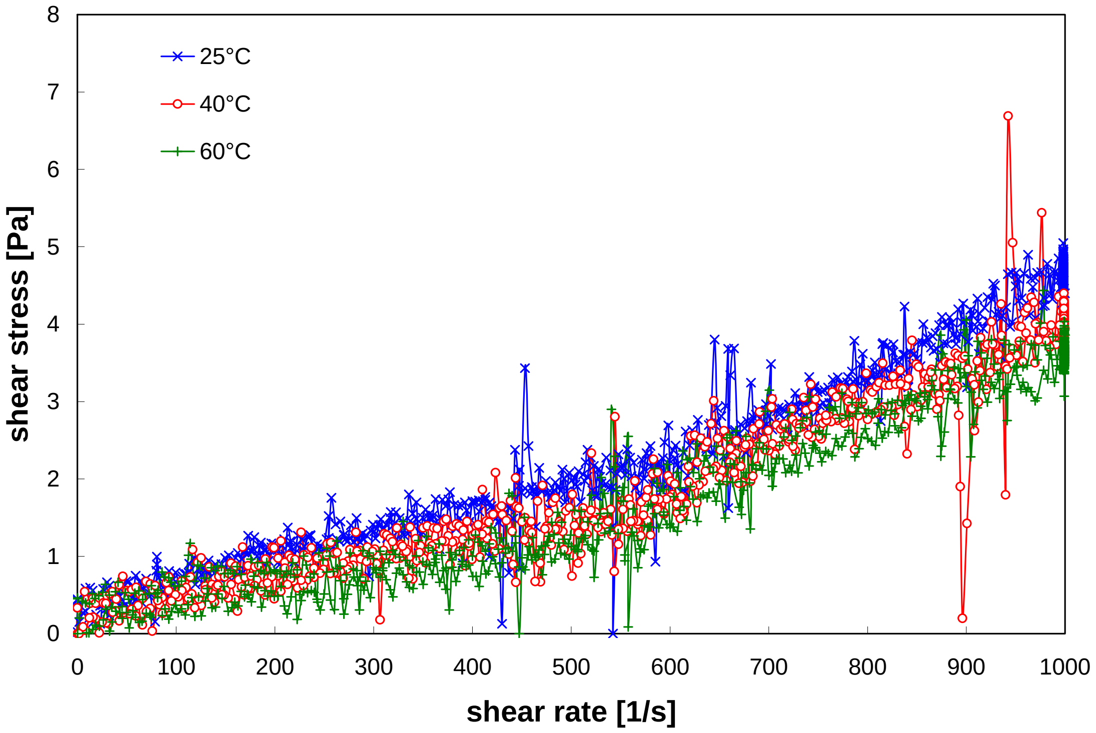


Figure 5.52. Flow Curves for the Group 7 Leached, Washed Slurry

Table 5.38. Results of Fitting Analysis for the Group 7 Leached, Washed Slurry

Model	Temperature [°C]	Range	Yield Stress [Pa]	Consistency [mPa·s]	R
Bingham-Plastic	25 (1 of 2)	100–400 s^{-1}	0.5	3.1	0.85
	25 (2 of 2)	100–400 s^{-1}	0.5	2.8	0.84
	40	100–400 s^{-1}	0.3	2.3	0.73
	60	100–400 s^{-1}	0.4	1.4	0.46
Casson	25 (1 of 2)	0–400 s^{-1}	0.1	2.1	0.93
	25 (2 of 2)	0–400 s^{-1}	0.2	1.7	0.92
	40	0–400 s^{-1}	0.1	1.4	0.84
	60	0–400 s^{-1}	0.2	0.7	0.67

Table 5.39. Select Apparent Viscosities for the Leached Washed Slurry

Source	Temperature [°C]	Apparent Viscosity [mPa·s]			
		@ 33 s^{-1}	@ 100 s^{-1}	@ 500 s^{-1}	@ 1000 s^{-1}
Measured	25 (1 of 2)	12	5.1	n/a[(a)]	n/a[(a)]
	25 (2 of 2)	13	7.2	3.8	4.7
	40	10	5.0	2.5	4.1
	60	7.6	4.8	2.4	3.6
Bingham-Plastic	25 (1 of 2)	17	7.7	4.0	3.5
	25 (2 of 2)	18	7.7	3.8	3.3
	40	12	5.5	3.0	2.6
	60	13	5.2	2.1	1.7
Casson	25 (1 of 2)	13	7.0	4.0	3.4
	25 (2 of 2)	14	7.3	3.7	3.0
	40	9.9	5.4	2.9	2.4
	60	10	4.9	2.1	1.6

(a) Measured apparent viscosity not available as a result of suspected Taylor vortexing.

Table 5.40 compares the rheology at different points during the test. The Group 7 source material is non-Newtonian with a yield stress of 3.3 Pa and a consistency of 12 mPa·s at 25°C and has an UDS concentration of ~10 wt%. In comparison, the Group 7 slurry low-solids matrix is also non-Newtonian with a yield stress of 1.2 Pa and a consistency of 3.1 mPa·s at 25°C. The lower mixture viscosity relative to the source material is consistent with the lower UDS concentration of the dilute CUF slurry (~5 wt%). As expected, the solids concentration appears to have a significant influence on both Group 7 slurry yield stress and consistency.

The concentrated Group 7/AY-102 mixed slurry shows significant non-Newtonian rheology. It has a yield stress of 4.6 Pa and a consistency of 10 mPa·s. The source materials for this mixed Group 7/AY-102 slurry include the low solids Group 7 CUF slurry and the archive AY-102 slurry. The concentrated mixed slurry shows increased yield stress and consistency relative to both of these materials. Part of this increase is a result of increased UDS concentration in the mixed slurry. Dewatering and solids addition increases the slurry solids concentration from ~5 wt% to ~26 wt%. An increased solids concentration will likely yield increased slurry yield stress and consistency. However, because of adding AY-102 solids, the increase in slurry rheology that occurs solely as a result of increased solids concentration cannot be quantified.

Relative to the source Group 7 material, the mixed Group 7/AY-102 shows similar rheology. Despite having almost twice the UDS concentration of the source material, the mixed CUF slurry has a lower consistency (10 mPa·s for the mixed slurry versus 12 mPa·s for the source slurry) and a somewhat higher yield stress (4.6 Pa for the mixed slurry versus 3.3 Pa for the source slurry). It can be speculated that the similarity of the mixed and source slurry rheologies, despite their dissimilar concentrations, derives from weakening the mixed slurry yield stress and consistency either as a result of mixing with AY-102 slurry (which is Newtonian) or as a result of prolonged shear in the CUF. Unfortunately, without additional information on how quickly Group 7 slurry rheology changes with respect to solids concentration, it is difficult to make conclusions about the slurry behavior with certainty.

Before leaching, the slurry shows non-Newtonian behavior with a yield stress of 4.6 Pa and a consistency of 10 mPa·s. After leaching, the slurry is also non-Newtonian and exhibits a lowered yield stress of 2.6 Pa and a similar viscosity of 11 mPa·s, relative to the pre-leach slurry. The lowered yield stress can be attributed in part to the lowered UDS concentration of the leached slurry (20 wt% for the post-leach slurry versus 26 wt% for the pre-leach slurry). Changes in particle chemistry as a result of leaching may also contribute to the lower yield stress. With regard to consistency, the similarity between the pre- and post-leach samples is unexpected given the difference in both dissolved solids and UDS concentrations. The leached slurry shows significantly lower dissolved solids and UDS concentrations, and on this basis, would be expected to show lower consistency. The fact that the post-leach slurry shows similar consistency suggests that changes in particle surface chemistry and interactions are influencing slurry rheology.

The results indicate that washing effects a significant reduction in viscosity. Before washing, the slurry is non-Newtonian with a yield stress of 2.6 Pa and a consistency of 11 mPa·s at 25°C. After washing, the slurry is borderline Newtonian (i.e., has a yield stress near ~0.5 Pa) with a consistency of 2.8 mPa·s at 25°C. The reduction in UDS from ~20 wt% to ~14 wt% likely contributed to the reduction. Another factor is a reduction in the dissolved-solids content of the slurry. Washing of the Group 7 slurry employed dilute sodium hydroxide solutions and reduced dissolved solids from ~19 wt% to ~6 wt%. It is certain that this reduction in dissolved solids content also contributes to the observed reduction in viscosity.

Table 5.40. Rheology at Different Points During the CUF Testing

Description	Total Solids	Dissolved Solids	Undissolved Solids	Rheology	Yield Stress [Pa]	Consistency [mPa·s]
Group 7 Source	~36-wt%	~29-wt%	~10-wt%	Non-Newtonian(a)	3.3	12
AY-102 Sample	n/a	n/a	~20-wt%	Newtonian	n/a	4.1
Group 7 CUF Low-Solids Matrix	n/a	n/a	~5-wt%	Non-Newtonian(a)	1.2	3.1
Concentrated Group 7 Mixture	~44-wt%	~24-wt%	~26-wt%	Non-Newtonian(a)	4.6	10
Caustic-Leached / Dewatered	~35-wt%	~19-wt%	~20-wt%	Non-Newtonian(a)	2.6	11
Caustic-Leached / Dewatered / Washed	~19-wt%	~6-wt%	~14-wt%	Non-Newtonian(a)	0.5	2.8

(a) Non-Newtonian properties reported are Bingham-Plastic model parameters.

6.0 Summary and Conclusions

A scope of work[(a)] was developed to perform caustic and oxidative leaching bench-scale tests of actual Hanford tank waste samples to address Task 4 of the M-12 External Flowsheet Review Team (EFRT) response plan.[(b)] Supporting this response, eight groupings of actual waste had been developed encompassing a large fraction of the high-level waste (HLW) types present at the Hanford Site. Each waste grouping was developed to specifically address a Waste Treatment and Immobilization Plant (WTP) processing challenge. Together, the eight waste groupings represented ~75% of the HLW mass expected to be processed through the WTP.

The waste group tested and discussed in this report is Tributyl Phosphate (Group 7, TBP). This waste type was of interest because of its high phosphate content. Aluminum in the form of gibbsite [$Al(OH)_3$] was also expected in lesser quantities. The work focused on understanding the behavior of these elements during caustic leaching. Because of its relatively low chromium content, no oxidative leaching tests were performed on the Group 7 sample.

Materials representative of Group 7 were retrieved from archived samples of Tanks BX-109 and B-106 at the 222S Laboratory, although the sample composite used was dominated by the BX-109 waste. Samples were shipped to the hot cells at the Radiochemical Processing Laboratory (RPL), transferred to a compositing vessel with water, homogenized, and then subdivided. The composited material was characterized for physical properties, chemical composition, and crystal habit of the insoluble solids. The Group 7 sludge was subjected to parametric caustic-leach testing to evaluate phosphate and aluminum leaching kinetics for this waste type. The remaining composite material was tested in a bench top filtration/leaching apparatus, commonly called the CUF, in the hot cells where ultrafiltration and caustic leaching conditions that were expected to be conducted at the WTP pre-treatment facility were simulated. The filtration testing was conducted in a parametric test sequence to understand filter-flux dependency on axial velocity and trans-membrane pressure both before caustic leaching (low and high solids content) and after leaching and washing (high solids content.). The CUF system was capable of filtering HLW slurry using a cross-flow ultrafilter (2 ft long with a 0.5 inch ID) rated for 0.1-µm-diameter particles. Caustic leaching and solids washing in conjunction with filtration were performed in the apparatus; the effectiveness of maintaining transuranic material in the HLW process stream (slurry side of the CUF) was evaluated.

The following objectives of the test plan were accomplished:

- Physical and chemical characterization (settling rate, particle-size distribution [PSD], rheology, concentrations of metal, anions, and radionuclides, and crystal habit and morphology using X-ray Diffraction [XRD], scanning electron microscopy [SEM], and transmission electron microscopy [TEM]).

(a) SK Fiskum, TP-RPP-WTP-467, Rev. 0, 2/2/07 and Rev. 1 7/31/07, Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes.

(b) WTP Doc. No. 24590-WTP-PL-ENG-06-0008, Rev 0, “Hanford Waste Treatment and Immobilization Plant (WTP) Project Response Plan for Resolution of Issues Identified by the Comprehensive Review of the WTP Flowsheet and Throughput.” L Lucas, March 2006.

- Parametric filtration testing at 4 wt% UDS and 26 wt% UDS before caustic leaching was performed and at 14 wt% UDS after caustic leaching and washing.
- Caustic leaching at 60°C for 8 h in a 2.6-M free-hydroxide matrix while periodically sampling the aqueous fraction to evaluate Al and P dissolution as a function of time.
- Final characterization of the caustic leached and washed solids including PSD, concentrations of metal, anions, and radionuclides, and crystal habit and morphology.

6.1 Characterization

The major analyte concentrations of the Group 7 supernatant before processing are shown in Table 6.1 and Table 6.2.

Table 6.1. Initial Radionuclide Content in Group 7

Process	**Initial Composition**			
Phase>	**Supernatant**		**Washed solids**	
Analyte	**µCi/mL**	**RPD**	**µCi/g**	**RPD**
^{137}Cs	4.56E+0	1.3	3.64E+1	7.7
^{60}Co	<8.E-5	na	2.11E-2	0.95
^{241}Am	<4.E-3	na	[8.7E-2]	na
^{238}Pu	[3.9E-6]	[59]	5.63E-3	3.7
$^{239+240}$Pu	1.21E-4	0.83	1.95E-1	7.2
Gross alpha	<3.E-4	na	3.00E-1	8.0
Gross beta	4.59E+0	1.3	1.57E+3	7.0
^{90}Sr	1.00E-2	5.5	7.41E+2	7.6
^{154}Eu	<2.E-4	na	5.90E-2	19
^{155}Eu	<2.E-3	na	<5E-2	na

Table 6.2. Initial ICP Metals Content in Group 7

Process	Initial Composition		Washed Solids			
Phase>	**Supernatant**		**Fusion**		**acid digest**	
Analyte	**μg/mL**	**RPD**	**μg/g**	**RPD**	**μg/g**	**RPD**
Al	<0.73	na	16,000	7.5	18,550	0.54
B	30.0	5.3	[115]	[9]	<13	na
Bi	<3.65	na	5,710	6.0	6,475	1.7
Cd	<0.41	na	<7.7	na	<9.2	na
Cr	57.8	1.7	718	7.5	826	0.48
Fe	[1.15]	[8.7]	140,000	7.1	156,000	2.6
K	[86]	[1.9]	na	na	[315]	[54]
Mn	[0.16]	[13]	884	7	926	0.3
Na	92,300	0.22	130,500	6.9	151,500	2.0
Ni	<0.42	na	na	na	517	0.19
P	3,760	1.6	107,500	6.5	123,000	0.0
S	6,260	1.9	[875]	[74]	[940]	[77]
Si	<0.68	na	7,285	7.0	na	na
Sr	[0.050]	[2.0]	3,905	6.9	4,460	2.2
U	162	1.9	113,000	7.1	125,000	0.0
Zn	[0.99]	[2.0]	687	8.3	856	1.3
Zr	<0.13	na	<9.3	na	[23]	[17]
U KPA	Na	na	114,500	4.4		

XRD analysis was done on the initial washed solids. In general, the patterns contain a very large number of peaks along with significant peak overlapping in areas. Phases identified were:

- Zeolite, $NaAlSiO_4(H_2O)_{1.1}$
- Threadgoldite, $Al(UO_2)_2(PO_4)_2(OH)(H_2O)_8$
- Sodium Iron Phosphate, $Na_7(FeP_2O_7)_4PO_4$
- Lepidocrocite, $FeO(OH)$
- Humboldtine, $C_2FeO_4{\cdot}2H_2O$
- Iron (III) phosphate oxide, Fe_2PO_5
- Dioxouranium(VI) bis(dihydrogenphosphate(I)) hydrate, $(UO_2)(H_2PO_2)_2(H_2O)$
- Sodium Uranyl Phosphate, $Na_6(UO_2)_2(PO_4)_4$
- Gibbsite, $Al(OH)_3$.

Washing data from the initial characterization shows 96 wt% of the aluminum, 68 wt% of the chromium, and 82 wt% of the phosphorus are water insoluble. Particle size and rheology measurements were also done on the washed solids, and results are summarized in Table 6.3 with the filtration results.

Table 6.3. Summary of Group 7 Filtration Results

Filtration Step	Property	Results
Initial Characterization of Group 7 **(Section 3.0)**	Material Description	TBP tank waste sludge
	UDS	10.0 wt%
	Slurry Rheology @ 25°C @ 40°C @ 60°C	Newtonian Viscosity: 6.3-12 mPa·s @ 25°C 6.0-11 mPa·s @ 40°C 4.4-8.9 mPa·s @ 60°C
	PSD *(3000 RPM pump speed)*	d(10): 1.0-1.1 μm d(50): 5.5-19 μm d(90): 17-130 μm
Low Solids Filtration Testing **(Section 5.2)** *Baseline Conditions* *TMP: 40 psid* *AV: 13 ft/s*	Material Description	Group 7 diluted w/ simulant supernatant and circulated in CUF
	UDS	Predicted to be 4 wt%
	Slurry Rheology @ 25°C @ 40°C @ 60°C	Newtonian Viscosity: 1.3-3.1 mPa·s @ 25°C 1.0-2.4 mPa·s @ 40°C 0.7-1.9 mPa·s @ 60°C
	PSD *(3000 RPM pump speed)*	d(10): 28 μm d(50): 81 μm d(90): 150 μm
	Baseline Filter Flux	0.028 GPM/ft^2
	Controlling Parameter	Proportional to TMP Secondary negative effects from Time
Dewatering of Group 7 Waste Prior to Leaching **(Section 5.3)** *Filtration Conditions* *TMP: 40 psid* *AV: 13 ft/s*	Initial Flux	0.018 GPM/ft^2
	Final Flux	0.016 GPM/ft^2
	Final UDS	Predicted at 12 wt%
	Behavior	TMP controlling
	Supernate Composition	[Na]: 4.0 [OH]: 0.14 [Al]: 0.006
Dewatering of Blend Slurry (Group 7 /AY102) **Prior to Leaching** **(Section 5.3)** *Filtration Conditions* *TMP: 40 psid* *AV: 13 ft/s*	Initial Flux	0.016 GPM/ft^2
	Final Flux	0.012 GPM/ft^2
	Final UDS	Measured at 26 wt%
	Behavior	TMP controlling
	Supernate Composition	[Na]: 3.7 M [OH]: 0.12 M [Al]: 11 μg/mL

Table 6.3 (Contd)

Filtration Step	Property	Results
High Solids Filtration Testing (Section 5.3) *Baseline Conditions* *TMP: 40 psid* *AV: 13ft/s*	Material Description	Added AY102 to Group 7 slurry, dewatered and circulated in CUF
	UDS	Measured at 26 wt%
	Slurry Rheology @ 25°C to 60°C	non-Newtonian Shear Stress range: 0.1 to 0.5 Pa Consistency range: 3.4 to 10 mPa·s
	PSD *(3000 RPM pump speed)*	Could not be run because of dose concerns
	Baseline Filter Flux	0.012 GPM/ft^2
	Controlling Parameter	Proportional to TMP and AV
Caustic Leach Dewater (Section 5.5) *Filtration Conditions* *TMP: 40 psid* *AV: 13 ft/s*	Initial Flux	0.007 GPM/ft^2
	Final Filter Flux	0.006 GPM/ft^2
	Final UDS	Measured at 20 wt%
	Behavior	TMP controlling
	Supernate Composition	[Na]: 4.7 M [OH]: 2.3 M [Al]: 0.27 M
Caustic Wash 1 (Section 5.5) *Filtration Conditions* *TMP: 40 psid* *AV: 13ft/s*	Wash Solution	0.5 M NaOH
	Supernate Composition	[Na]: 2.9 M [OH]: 1.5 M [Al]: 0.15 M
	Filter Flux	0.012 – 0.011 GPM/ft^2
Caustic Wash 2 (Section 5.5) *Filtration Conditions* *TMP: 40 psid* *AV: 13ft/s*	Wash Solution	0.1 M NaOH
	Supernate Composition	[Na]: 1.6 M [OH]: 0.77 M [Al]: 0.069 M
	Filter Flux	0.024 – 0.014 GPM/ft^2
Caustic Wash 3 (Section 5.5) *Filtration Conditions* *TMP: 40 psid* *AV: 13ft/s*	Wash Solution	0.05 M NaOH
	Supernate Composition	[Na]: 0.77 M [OH]: 0.39 M [Al]: 0.032 M
	Filter Flux	0.025 – 0.016 GPM/ft^2
Caustic Wash 4 (Section 5.5) *Filtration Conditions* *TMP: 40 psid* *AV: 13ft/s*	Wash Solution	0.01 M NaOH
	Supernate Composition	[Na]: 0.38 M [OH]: 0.18 M [Al]: 0.0016 M
	Filter Flux	0.022 – 0.015 GPM/ft^2
Washed Caustic Leached Slurry (Section 5.6-5.7)	UDS	14 wt%
	PSD *(3000 RPM pump speed)*	Could not be run because of dose concerns
	Rheology @ 25°C to 60°C	Weakly non-Newtonian Yield Stress range: 0.1 to 0.5 Pa Consistency range: 0.7 to 3.1 mPa·s

6.2 Parametric Leaching Results

The Group 7 TBP sludge was subjected to parametric caustic-leach testing to understand phosphorus and aluminum dissolution characteristics and to support the development of a suitable simulant material for this type of waste (although simulant development was outside the scope of the work reported here). Leaching was conducted in a 1:100 solids-mass to solution-volume ratio under varying hydroxide concentrations (0.25, 1, and 3 M) and varying temperature (40, 60, and 80°C). Periodic sampling (0 to 24 h) and analysis was conducted to determine the reaction behavior at each leaching condition. The composition of the caustic-leached solids and the leach factors for select analytes are given in Table 6.4. The following are the key conclusions from this work.

- Under all caustic-leaching conditions examined, phosphorus removal from the Group 7 solids was rapid and nearly complete (85 to 95% dissolution was obtained). Even before the application of heat, ~50 to 80% of the P was removed from the solid phase. The removal of P before the application of heat was dependent on the hydroxide concentration, with ~52%, 61 to 69%, and 71 to 82% of the P removed in 0.25, 1, and 3 M NaOH, respectively. This is in contrast to the results seen in the CUF, where the leach factor for phosphorus after caustic-leaching was calculated to be a negative value. The difference is because in the CUF, the leachate solutions were likely near the phosphate solubility, whereas in the parametric tests, the greater dilution volume resulted in lower phosphate concentrations.
- For all temperatures and all hydroxide concentrations, a steady-state value of P dissolution was reached in the first hour. Hydroxide concentration and temperature had little effect on the P dissolution.
- A steady-state value of Al dissolution was obtained for the higher temperatures (60 and 80°C), but at 40°C, the amount of Al dissolved continued increasing throughout the entire sampling period.
- Dissolution of Al at lower temperatures and hydroxide concentrations (40°C in and 1 M NaOH and 60°C in 0.25 M NaOH) was lower than for other conditions, reaching only 59 to 65% dissolution.
- Between 80 and 90% of the Al was dissolved at the higher temperatures, suggesting that a small amount of a caustic-insoluble Al compound was present, perhaps zeolite, as identified by XRD.
- Both temperature and hydroxide concentration had a large effect on the gibbsite dissolution rate at the lower temperatures and lower hydroxide concentrations.
- Under all conditions, there was a rapid dissolution of uranium. Before heating was applied, 50 to 100% of the U was removed from the solid phase. The amount of U removed before the application of heat was dependent on the hydroxide concentration, with much more U dissolution seen in 3 M NaOH than in 0.25 M NaOH. As heat was applied, the uranium re-precipitated, leaving 12 to 20% in solution. Examination by TEM suggests that crystals of a uranyl phosphate phase were present in the initial solids. These appeared to have dissolved and then re-precipitated as smaller uranyl phosphate phases during the caustic-leaching process.
- 59 to 93% of the Al present in the washed Group 7 solids is readily dissolved in caustic media (during a 24-hour caustic-leach).

- 86 to 95% of the P present in the washed Group 7 solids is readily dissolved in caustic media (during a 24-hour caustic-leach).
- Iron would likely be the component constraining waste loading in the HLW glass for the Group 7 solids remaining after leaching in 3 M NaOH at 40°C for 24 hours.
- The PSD for the leached Group 7 solids shows that both the initial solids and the caustic-leached and washed solids have tri-modal particle sizes, with peak maxima located around similar particle diameters. With caustic leaching and washing, there is a shift of these populations of particles to lower particle diameters, from ~75 and 7.5 µm before leaching to ~8.5 and 1.3 µm after caustic-leaching.
- The reduction in particle size is likely a result of either dissolution of material from the particle surface or agglomerate breakage, but it is not entirely clear which is the case.

Table 6.4. Composition of Caustic-Leached Group 7 Solids with Leach Factors of Selected Analytes (3 M NaOH, 40°C, 24 h)

Analyte	**Leached Solids, µg/g$^{(a)}$**	**Fraction Leached**	**Analyte**	**Leached Solids, µCi/g$^{(a)}$**	**Fraction Leached**
Al	[6,550]	0.79	^{60}Co	4.65E-02	--
B	<31.452	--	^{90}Sr	1863.46	--
Bi	13,950	--	^{137}Cs	1.10E+00	0.99
Cd	[66]	0.25	$^{239+240}$Pu	5.00E-01	--
Cr	1,370	0.19	^{241}Am	2.32E-01	--
Fe	331,000	--	No data		
Mn	1,975	--			
Na	[32,500]	0.89			
P	18,400	0.93			
S	<1347.953	--			
Si	[8,250]	0.58			
Sr	9,165	--			
Zn	749	0.59			
U (KPA)	227,641	0.17			

(a) Dry-mass basis of washed solids.

Analyte uncertainties were typically within ±15% (2-σ); results in brackets indicate that the analyte concentrations were less than the minimum detection limit (MDL) and greater than the estimated quantitation limit (EQL), and uncertainties were >15%.

Radionuclide reference date: April 9, 2008.

"--" calculation could not be made from one or more "less-than" values.

6.3 Filtration Behavior

The parametric filtration test evaluated Group 7 with 4.3 wt% UDS before caustic leaching. This slurry was blended with archived tank samples from AY-102 and dewatered to 26 wt% UDS, and another parametric filtration test was performed. Filtration tests were conducted on 20 wt% UDS after caustic leaching and 14 wt% UDS blended after washing the slurry. The filtration results are summarized in Table 6.3 along with relevant slurry parameters such as rheology and PSD. The following general observations were made:

- Despite the slurry supernate viscosity being relatively low (1 to 2 cP), the filter flux for the blended cladding waste slurry was relatively low (0.012 to 0.018 GPM/ft^2). The supernate viscosity of the REDOX sludge was similar, but had high filter flux (0.06 GPM/ft^2).
- Increases in transmembrane pressure (TMP) correlated to proportional increases in the filter flux throughout the test.
- Axial velocity appeared to have an impact on filtration at the concentrations tested when the slurry UDS concentration exceeded 20 wt%.
- The filter flux showed some decay over time on the onset of testing. However, after 2 days of operations, this effect became less pronounced.
- Changes to the permeate viscosity from caustic leaching to washing operations significantly changed the filter flux more than changes in the UDS concentration of the slurry up to 20 wt%. The estimated gel concentration of the slurry was >50 wt% based on centrifugal UDS measurements, indicating that the slurry could be concentrated a great deal before the UDS concentration impacted filtration.

6.4 Leaching Behavior During CUF Testing

The Group 7 material was caustic leached during the CUF test. The leaching of the slurry was performed at 60°C for 8 hours at a free-hydroxide concentration of 2.4 to 2.6 M (sodium concentration was 4.6 to 4.8 M) at an initial UDS concentration of 12 wt%. The caustic leaching results of the Group 7 CUF test are summarized in Table 6.5. The following general observations were made:

- Overall kinetic dissolution of Al appeared very fast, completing before the temperature of the leach slurry reached 50°C. Previous XRD scans of AY102 [Krupka 2004] found aluminum phases of gibbsite, and cancrinite present. While gibbsite was expected to be dissolved by caustic leach, cancrinite was not. .XRD results of the leached material showed the absence of gibbsite with the major crystalline phase present being:
    - Hematite, Fe_2O_3
    - Cancrinite, $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2{\cdot}2H_2O$
    - Collinsite, Fairfieldite group, $MgCa_2(PO_4)_2(H_2O)_2$
    - Hydroxyapatite, $Ca_5(PO_4)_3(OH)$

  Therefore, all of gibbsite present in the waste slurry was dissolved during caustic leaching as expected.
- Leach factors for solid aluminum were found to be between 56 and 58 wt% from supernate and slurry ICP measurements. The extent of reaction here for aluminum indicates that 42-44 wt% of the aluminum present in the slurry solids was present in an insoluble form, such as cancrinite.
- A significant fraction (42 wt%) of phosphate in the Group 7 insoluble solids dissolved into the liquid phase of the slurry after the addition of the AY-102 waste sample. Previous studies of the composition of the AY-102 [Coleman 2003] found the supernate have a significantly lower phosphate concentration. It is likely that phosphate salts present in the Group 7 solids became soluble after the supernate was diluted from the AY-102 addition. The mechanism

causing this increase in phosphate (and uranium, see below) concentration is not known at this time.

- A significant fraction of the uranium present in the solids became soluble in the blended slurry supernate as well after the AY-102 addition at the same time that a fraction of the phosphate dissolved. As seen in the parametric testing, soluble uranium in the supernate precipitated out during caustic leaching. However, dewatering of the slurry prior to caustic leach removed 39 wt% of the uranium present in the slurry.
- Phosphate in the supernate appeared to have precipitated during the caustic leach because of the high sodium concentration in the slurry supernate after the caustic addition. This slowed the release of phosphorus from the slurry, where a majority of it was removed during the washing steps instead of the caustic dewatering step.
- Caustic leaching did not dissolve measureable quantities of transuranic isotopes from the slurry solids.
- The concentration of chromium was low (6.5E-1 mg/g) in the initial slurry. Of that, however, a solid leach factor between 25 and 27 wt% was found.
- After four volumetric washes, 9 mg sodium/g slurry was present in the interstitial liquid of the slurry (Figure 6.1). Additional rinses would likely further reduce the quantities present.

Table 6.5. Caustic Leaching Summary of Group 7 Slurry

Element	Solid Leach Factor from Total Mass Balance (Supernate Analysis), (wt%)	Solid Leach Factor Using (Slurry/Supernate Analysis), (wt%)	Total Removal from Slurry (Four Equal Volume Washes) (wt%)
Al	55	48–51	53
P	69	63	58
Cr	18	14–15	21

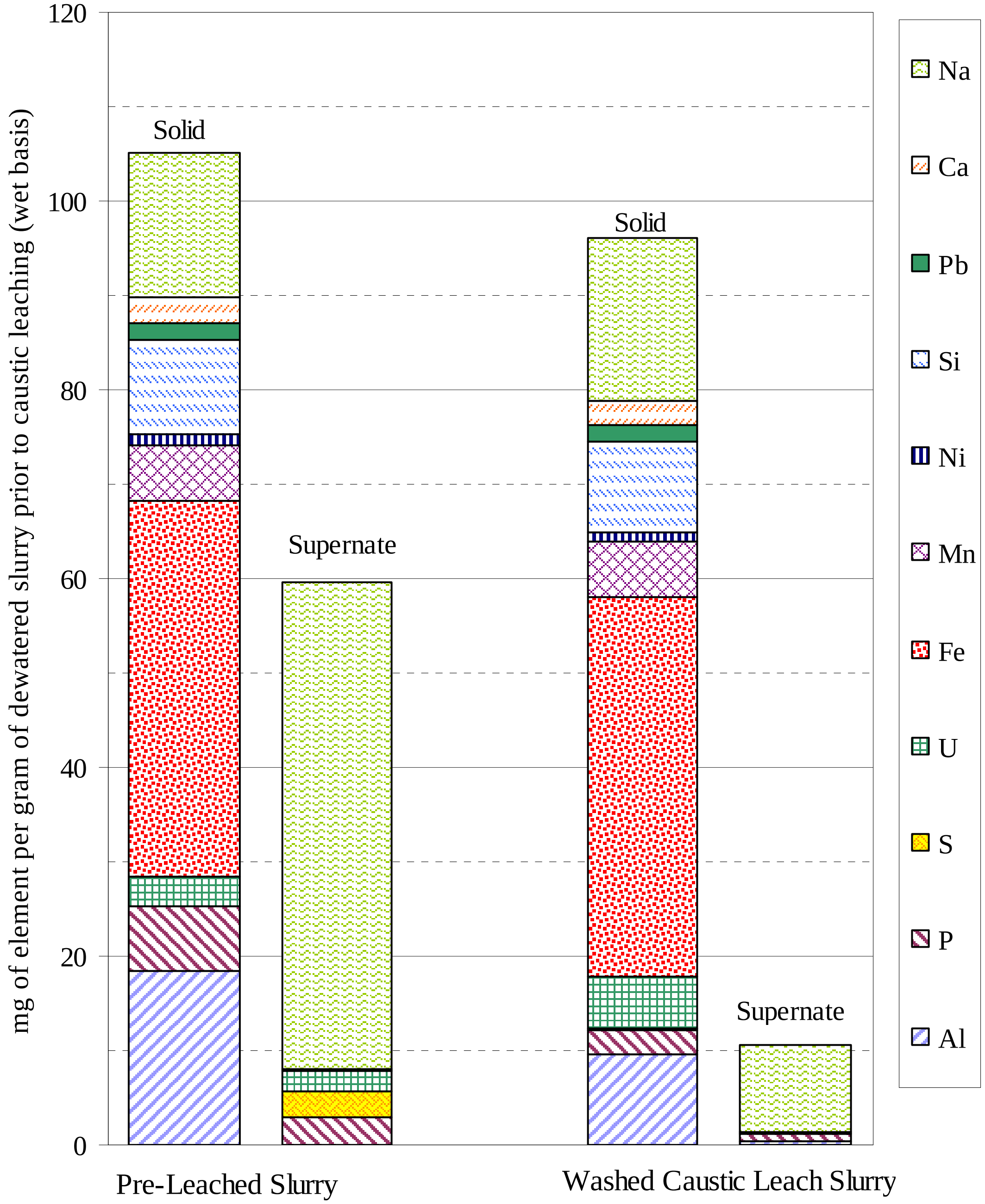


Figure 6.1. Comparison of Slurry Composition Before and After Caustic Leaching and Washing (*Basis 1 gram of dewatered slurry*)

Appendix A

Analytical Methods

Appendix A: Analytical Methods

This section describes the analytical methods used to determine the chemical and radiochemical composition of the Group 7 samples.

A.1 Sample Preparation for Chemical Characterization

The samples taken for chemical characterization were centrifuged at 1000 G for 1 hour, and then the supernatant liquids were decanted. The solids were washed with three successive additions of 0.01 M NaOH.(a) After adding each washing solution, the sample was agitated for 15 min and centrifuged 30 min at 1000 G, and then the liquid phase was removed. The three wash solutions were combined into a composite and passed through a 0.45-micron pore size nylon filter. The supernatant and wash-solution densities were determined by measuring the masses of 1-mL volume deliveries four times per sample.

More 0.01 M NaOH was added to the washed solids so that the slurry could be easily mixed with a Teflon®-coated stirbar, and the solids were suspended. Aliquots of the suspended-solids slurries were taken for chemical and radiochemical analysis, particle-size distribution (PSD), the Brunauer, Emmett, and Teller (BET) method for determining surface area, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) analyses. The washed solids slurry sample aliquots taken for chemical analysis were dried to constant mass at 105°C; the solids chemical analysis was based on the dry sample mass. The supernatant liquid and the filtered solids washing solution were provided directly to the Analytical Services Operation (ASO) for chemical characterization.

A.2 Chemical and Radioisotope Characterization

The following sections describe the procedures used to support the chemical and radiochemical characterization of the solids and aqueous samples. Aqueous samples were distributed directly to the free hydroxide, ion chromatrography (IC), and total inorganic carbon/total organic carbon (TIC/TOC) analytical workstations. The solids and liquids required a digestion step before distribution to the inductively coupled plasma-optical emission spectroscopy (ICP-OES) and radiochemistry workstations.

A.2.1 Free Hydroxide

The free-hydroxide concentration was determined by potentiometric titration with standardized HCl according to procedure RPG-CMC-228, *Determination of Hydroxyl (OH^-) and Alkalinity of Aqueous Solutions, Leachates, and Supernates and Operation of Brinkman 636 Auto-Titrator*. The free hydroxide was defined as the first inflection point on the titration curve. Quality control (QC) samples were generated at the analytical workstation and included a sample replicate determination, process blank, blank spike (BS), and matrix spike (MS).

A.2.2 Anions

Anions were determined by IC using a Dionix ICS-2500 IC system equipped with a conductivity detector according to procedure RPG-CMC-212, *Determination of Common Anions by Ion Chromatography*.

(a) Specific wash volumes are provided in the context of the results discussion.

Additional sample dilutions from 100× to 25,000× were required to accurately measure the analytes. QC samples were generated at the analytical workstation and included a sample replicate determination, process blank, BS, and MS.

A.2.3 TIC/TOC

The TIC was determined by using silver-catalyzed hot persulfate (HP) oxidation according to procedure RPG-CMC-385, *Carbon Measured in Solids, Sludge, and Liquid Matrices*. The HP wet-oxidation method was used. This method takes advantage of acid decomposition of the carbonate (TIC measure) followed by oxidation of organic carbon (TOC measure) using acidic potassium persulfate at 92 to 95^{o}C. QC samples were generated at the analytical workstation and included a sample replicate determination, process blank, BS, and MS.

A.2.4 Acid Digestion

Aqueous samples were digested with acid according to procedure PNL-ALO-128, *HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*. The acid-digested solutions were brought to a nominal 25-mL volume (resulting in a nominal 25× dilution where the initial sample size was 1-mL); absolute volumes were determined based on final solution weights and densities. As part of the analytical preparation batch, the ASO processed a digestion preparation blank (PB), a BS, and an MS. The spike solution contained a broad suite of stable elements; radionuclides were not included in the digestion preparation. Aliquots of the BS, MS, and PB, along with the sample aliquots, were delivered to the ICP-OES workstation for analysis; sample and PB aliquots were delivered to the radiochemical workstations for separations supporting specific radioisotope analysis.

A.2.5 KOH Fusion

The potassium hydroxide (KOH) fusion was conducted in the shielded analytical facility (hot cells) according to PNL-ALO-115, *Solubilization of Metals from Solids using KOH-KNO_3 Fusion*. A nominal sample size of 0.1 to 0.2 g dry solids was combined with a KOH/KNO_3 flux mixture and fused at 550^{o}C for 1 hour in a nickel crucible. The fused material was acidified with HNO_3, taken to a 100-mL volume with DI water, and then split for metals and radionuclide analysis. Samples were typically prepared in duplicate along with a fusion blank and a laboratory control sample (LCS) (SRM-2710, Montana Soil, purchased from the National Institute for Science and Technology [NIST]).

A.2.6 NaOH/Na_2O_2 Fusion

The NaOH/Na_2O_2 fusion was conducted in the shielded analytical facility (hot cells) according to PNL-ALO-114, *Solubilization of Metals from Solids using a Na_2O_2-NaOH Fusion*. A nominal sample size of 0.1 to 0.2 g dry solids was combined with a NaOH/Na_2O_2 flux mixture and fused at 550^{o}C for 1 hour in a zirconium crucible. The fused material was acidified with HNO_3, taken to a 100-mL volume with DI water, and then split for metals analysis. The sample was prepared in duplicate along with a fusion blank and an LCS (SRM-2710, Montana Soil).

A.2.7 HF-Assisted Acid Digestion

The HF-assisted acid digestion was conducted in the Sample Receiving and Preparation Laboratory according to PNL-ALO-138, *HNO_3-HF-HCl Acid Digestion of Solids for Metals Analyses Using a Dry Block Heater*. A nominal sample size of 0.1 to 0.2 g dry solids was contacted with a mixture of concentrated HF and HNO_3 and evaporated to dryness in a Teflon® reaction tube. Concentrated HCl was then added, and the sample was evaporated to dryness a second time. Additional concentrated HNO_3 and HCl were added, the reaction tube was capped tightly, and the mixture was heated in a dry-block heater at 95°C for 6.5 h. The digestate was cooled, brought to a 50-mL volume, and then split for metals analysis. The sample was prepared in duplicate along with a fusion blank and an LCS (SRM-2710, Montana Soil).

A.2.8 Metals Analysis by ICP-OES

Metals were measured by ICP-OES according to procedure RPG-CMC-211, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICPOES)*. The preparative QC samples (duplicate, PB, BS, MS) were processed along with analytical workstation QC (post digestion spike and serial dilution).

A.2.9 U (KPA)

Uranium was determined directly from samples prepared by KOH fusion with a Chem Chek Instruments KPA according to procedure RPG-CMC-4014, Rev. 1, *Uranium by Kinetic Phosphorescence Analysis*. The LCS did not contain U, so preparative QC was limited to the duplicate and PB. A post-digestion spike was conducted at the analytical workstation.

A.2.10 Gamma Energy Analysis

Gamma energy analysis was performed with direct or diluted samples that were prepared from acid digestion, fusion, or neat (see Figure 4.1). Sample counting was conducted according to procedure RPG-CMC-450, *Gamma Energy Analysis (GEA) and Low-Energy Photon Spectroscopy (LEPS)*, using high-purity germanium detectors. Extended count times (up to 20 hours) were employed as needed to achieve low detection limits. In many cases, the Compton background from the high ^{137}Cs activity (661 keV) limited the achievable detection limit of lower energy gamma emitters (e.g., ^{241}Am at 59 keV). The QC associated with the GEA analysis was composed of the sample duplicate and PB; because this is a direct analysis, no additional QC samples were required.

A.2.11 Gross Alpha and Gross Beta

Aqueous samples were prepared for gross alpha and beta determinations by acid-digestion, and the washed-solids samples were prepared by KOH/KNO_3 fusion. Prepared sample aliquots were plated directly onto stainless steel planchets according to procedure RPG-CMC-4001, *Source Preparation for Gross Alpha and Gross Beta Analysis*. The mounts prepared for gross alpha analysis were counted with Ludlum alpha scintillation counters. The gross alpha analysis tends to be confounded by the dissolved solids in the sample matrix. The solids can absorb the alpha particles, decreasing the intensity relative to the detector, which biases the results low. The sources prepared for gross beta analysis were counted with an LB4100 gas-proportional counter. In both cases, counting operations were conducted according to procedure RPG-CMC-408, Rev.1, *Total Alpha and Total Beta Analysis*. The preparative QC included the sample duplicates and the preparation blank. The BS and MS were prepared at the analytical workstation on sample dilutions.

A.2.12 Pu Isotopes: ^{238}Pu and $^{239+240}$Pu

The ^{238}Pu and $^{239+240}$Pu activities were measured from aqueous samples prepared by acid-digestion, and washed-solids samples prepared by KOH/KNO_3 fusion. Radiochemical separations were conducted according to procedure RPG-CMC-4017, *Analysis of Environmental Water Samples for Actinides and Strontium-90* (analyte purification using ion exchange); source preparation was conducted according to RPG-CMC-496, *Coprecipitation Mounting of Actinides for Alpha Spectroscopy* (co-precipitation of PuF_3 with LaF_3); and alpha counting was conducted according to RPG-CMC-422, Rev.1, *Solutions Analysis: Alpha Spectrometry*. The preparative QC included the sample duplicates and the preparation blank. The BS and MS were prepared at the analytical workstation on sample dilutions.

A.2.13 Strontium-90

The ^{90}Sr activities were measured from aqueous samples prepared by acid-digestion, and washed-solids samples were prepared by KOH/KNO_3 fusion. Radiochemical separation was conducted according to procedure RPG-CMC-476, *Strontium-90 Separation Using Eichrom Strontium Resin*; source preparation and beta counting were conducted according RPG-CMC-474, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*.

Appendix B

Physical Properties Determination and BET Methods

Appendix B: Physical Properties Determination and BET Methods

This appendix describes the experimental methods used to determine physical properties and surface area measurements.

B.1 Physical Properties

The physical-property characterization was conducted according to procedure RPL-COLLOID-02, Rev. 1, *Measurement of Physical and Rheological Properties of Solutions, Slurries and Sludges*, which is consistent with the Waste Treatment and Immobilization Plant (WTP) guidelines document.(a) Samples for physical-properties characterization were taken in triplicate near the beginning (S1), middle (S2), and end (S3) of the aliquoting activity following slurry homogenization. Samples sizes were generally between 10 and 15 mL. The samples were collected in volume-graduated, glass centrifuge tubes.

Settling studies were conducted by thoroughly agitating the samples and then allowing the solids to settle by gravity with periodic measurement of the settled-solids volume. The sample tubes were undisturbed over the 3-day settling period. Following the settling measurements, the samples were centrifuged at ~1000 G for 1 hour. The total sample volume and solids volume were recorded to assess the vol% wet centrifuged solids (WCSs). The centrifuged supernatants were decanted and transferred to tared graduated cylinders; the net solution masses and volumes were determined. The remaining WCSs were weighed in the centrifuge tubes to assess gross densities. The supernatant samples were transferred to tared glass vials. Both the supernatant fractions and the residual solids fractions (containing interstitial supernatant) were air-dried and then transferred to a 105°C oven for continued drying until constant mass was attained. The data collected were processed as described by Smith and Prindiville(a) to determine the volume and weight percent of wet solids (total, settled, and centrifuged), densities, total undissolved solids, and dissolved solids content.

B.2 Surface Area (BET)

Samples were prepared for surface-area measurements in an effort to minimize solidification into a monolith upon drying. To this end, the solids were rinsed twice with ethanol and twice again with diethyl ether according to procedure TPR-RPP-WTP-486, *Procedure for BET Sample Preparation Using Ethanol and Ethyl Ether as Drying Agents.* Each rinse was conducted in a centrifuge tube. The solids were well suspended in the rinse solution, and then the phases were separated by centrifuging and decanting. The final ethyl ether rinse was used to transfer the solids slurry to the sample cell. The diethyl ether was then evaporated at room temperature directly from the sample cell.

The sample was further dried and out-gassed using the Quantachrome Instruments Monosorb Model MS-21 (Boynton Beach, FL) outgassing station. This entailed pre-flushing nitrogen through the sample cell for ~10 min and then heating and flushing for overnight (>10 h) at 110°C.

(a) 24590-WTP-GPG-RTD-001, Rev 0, "Guidelines for Performing Chemical, Physical, and Rheological Properties Measurements," GL Smith and K Prindiville, May 2002.

The surface-area measurements were conducted according to OCRWM-BET-01, *Surface Area Measurement with a Monosorb Gas Analyzer*, which is consistent with American Society for Testing and Materials (ASTM) method D5604-96, “Test Method B” (Single-Point Surface Area by Flowing Gas Apparatus). The flow gas used in the measurement mode was composed of 30% nitrogen in helium. The system was calibrated per manufacturer instructions. The system performance was assessed using a 29.9 ± 0.75 m^2/g carbon surface area standard Lot D-6 obtained from Micromeritics (Norcross, GA).

Appendix C

Crystal Form and Habit

Appendix C: Crystal Form and Habit

This section describes the methods used to determine the crystal forms and habits of the tank-solids samples. The solids crystal characteristics were determined on small aliquots of the solids. In all cases, the solids sample fractions were allowed to air dry at room temperature in preparation for analysis. This effort was intended to minimize morphological changes that might occur upon heating. The methods applied for X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) evaluations are discussed in the following sections.

C.1 X-Ray Diffraction

The sample mounts for XRD examination were prepared from the dried solids according to procedure RPL-PIP-4, *Preparing Sealed Radioactive Samples for XRD and Other Purposes*. Specimens were pulverized to a powder with a boron carbide mortar and pestle, mixed with an internal standard (rutile, TiO_2, or alumina, Al_2O_3), and mounted on a glass slide. In some cases, the internal standard was omitted to provide better clarity of the sample diffraction pattern free from potential interference from the internal standard diffraction pattern. The XRD examination was conducted according to procedure PNNL-RPG-268, *Solids Analysis, X-Ray Diffraction Using RGD #34*. Process parameters included examining the X-ray 2-theta range from 5 to 65 degrees with a step size of 0.02 degrees and a dwell time of 20 seconds.

Phase identification was performed with JADE, Version 8.0 (Materials Data Inc., Livermore, CA) software search and peak match routines with comparison to the International Centre for Diffraction Data (ICDD) database PDF-2, Version 2.0602 (2006). The ICDD database included the Inorganic Crystal Structure Database (ICSD) maintained by Fachinformationszentrum, Karlsruhe, Germany. Phase identification incorporated chemistry restrictions based on the elements determined from chemical analysis.

C.2 Scanning Electron Microscopy

A small sample was transferred with a wooden Q-tip stem onto carbon tape supported by an aluminum pedestal mount. The sample was analyzed using the radiation-shielded Amray Model 1610T SEM according to RPL-611A-SEM, *Scanning Electron Microscope Examinations*. In selected cases, the mount was carbon-coated. Selected sample areas were evaluated by energy dispersive X-ray spectroscopy (EDS) for qualitative elemental composition.

C.3 Transmission Electron Microscopy

The TEM samples were prepared in a two-step methanol rinsing process. A small amount of the sludge slurry was mixed and transferred into methanol; a drop of the methanol slurry was transferred into a second vial containing methanol; then a drop of this second solution was deposited onto a lacey carbon TEM grid. The particles were air-dried on the lacey grid. Note that the sample drying process may induce changes in the morphology of the particle agglomerates. However, the objective of the TEM investigation was to look at the fundamental characteristics and sizes of individual particle crystallites that are not dependent on drying effects.

The TEM examinations were performed on an FEI Tecnai G2-30 (FEI Inc., Hillsboro, OR) with a field emission filament operating at 300 keV equipped with a Scanning Transmission Unit and High Angle Annular Dark-Field Detector (HAADF), EDS detector, and a Gatan Imaging Filter (GIF), model GIF2000 (Gatan Inc., Pleasanton, CA). Particle or area analysis was performed by identifying the composition with EDS and electron energy-loss spectroscopy (EELS). Images were obtained with either the scanning transmission electron microscopy (STEM) system or normal bright-field imaging. Energy-filtered images were also obtained with the image filter to produce element-specific area maps.

C.4 Electron Energy-Loss Spectroscopy

The EELS spectra were obtained with a 0.6-mm entrance aperture and an energy dispersion of 0.1 eV/channel. Low-loss spectra (including the zero loss peak) were acquired with an integration time of <0.2 s and core-loss spectra between 2 and 5 s. To reduce potential beam reduction, the acquisition time was kept as small as possible. The spectra were collected in the imaging mode of the transmission electron microscope and were corrected for dark current and channel-to-channel gain variation of the charge coupled device (CCD) detector.

The core-loss regime was energy calibrated, and the energy drift was measured while data were being acquired by collecting zero-loss spectra before or after core-loss spectra were collected. The position of the C-K (1 *s*) peak at 284 eV (arising from transitions to the π^* molecular orbital) from the TEM lacy carbon support film was used to evaluate the energy calibration and roughly check that the energy resolution was sufficient for collecting data.

Two methods were adopted for determining the chemical state of chromium in the sludge samples. In the first method, we obtained the following ratio defined as:

$$\mathrm{I-ratio} = \frac{\mathrm{I}(\mathrm{L}_3)}{\mathrm{I}(\mathrm{L}_2)} \tag{C.1}$$

L_2 and L_3 are the intensities of background-corrected Cr-absorption edges. The second method was to look at the O:Cr ratio as an indication of oxygen content. Oxygen detection with EELS is more accurate that with X-rays because the loss in energy of the primary beam is measured instead of an emitted X-ray, as in the case of EDS analyses, which can be subjected to significant attenuation.

Appendix D

Quality Assurance and Quality Control

Appendix D: Quality Assurance and Quality Control

This appendix describes the quality assurance (QA) program and quality control (QC) measures applied to the conduct of work.

D.1 Application of Waste Treatment Plant Support Program Quality Assurance Requirements

Pacific Northwest National Laboratory's (PNNL's) QA program is based on requirements defined in DOE Order 414.1C, "Quality Assurance,' and 10 CFR 830, "Energy/Nuclear Safety Management," Subpart A–Quality Assurance Requirements (a.k.a., the Quality Rule). PNNL has chosen to implement the requirements of DOE Order 414.1C and 10 CFR 830, Subpart A by integrating them into the laboratory's management systems and daily operating processes. The procedures necessary to implement the requirements are documented through PNNL's Standards-Based Management System.

PNNL implemented the River Protection Project-Waste Treatment Plant (RPP-WTP) quality requirements by performing work in accordance with the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Plan* (RPP-WTP-QA-001, QAP). Work was performed to the quality requirements of NQA-1-1989 Part I, "Basic and Supplementary Requirements," NQA-2a-1990, Part 2.7, and DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions (QARD)*. These quality requirements are implemented through the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Manual* (RPP-WTP-QA-003, QAM).

A matrix that cross-references the NQA-1, NQA-2a, and QARD requirements with PNNL's procedures for this work was given in the test plan, TP-RPP-WTP-467.[a] It included justification for those requirements not implemented. The QA requirements of DOE/RW-0333P, Rev 13, QARD and DOE Order 414.1C were not identified as a requirement for this work in the test specification.

D.2 Conduct of Experimental and Analytical Work

Experiments that were not method-specific were performed in accordance with PNNL's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration and Control of Measuring and Testing Equipment," verifying that sufficient data were taken with properly calibrated measuring and test equipment to obtain quality results.

As specified in the supporting Test Specification, 24590-PTF-TSP-RT-06-0001, Rev. 0, BNI's Quality Assurance Project Plan (QAPjP), PL-24590-QA00001, was not applicable because the work was not performed in support of environmental/regulatory testing, and the data will not be used as such.

Balances are calibrated annually by a certified contractor, QC Services, Portland, Oregon. A balance performance check was conducted each day the balance was used.

(a) SK Fiskum, TP-RPP-WTP-467, Rev. 0, 2/2/07 and Rev. 1 7/31/07, *Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes*, Pacific Northwest National Laboratory, Richland, WA.

ASO conducted analytical testing according to the Statement of Work RPP-WTP-QA-005, Rev. 2, *Analytical Support by the PNNL RPL Analytical Support Operation.* The analytical results and raw data are traceable through the project files according to the Analytical Services Request number and Radiochemical Processing Laboratory number.

D.3 Internal Data Verification and Validation

PNNL addressed internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNNL's procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and the reported work satisfied the Test Plan objectives. This review procedure is part of PNNL's RPP-WTP QAM.

Appendix E

Group 7 Particle-Size Methods and Analysis (TDP-WTP-273)

Appendix E: Group 7 Particle-Size Methods and Analysis (TDP-WTP-273)

Battelle
The Business *of* Innovation

TDP-WTP-273

Internal Distribution
Sandy Fiskum
Rick Shimskey
Lanée Snow
Amanda Casella
File/LB

Date	November 10, 2008
To	Sandy Fiskum Rick Shimskey Lanée Snow
From	Amanda Casella
Subject	Particle Size Distribution for Group 7 [Tributyl Phosphate (TBP) Sludge] Initial Characteristic, Parametric Testing and CUF Testing Samples

Acronyms and Abbreviations

AV	Axial Velocity
CA	Contamination Area
CUF	Cells Unit Filter
DI	Deionized (water)
CCP	Computational Computer Program (application)
LRB	Laboratory Record Book
NIST	National Institute of Standards and Technology
PSD	Particle Size Distribution
RI	Refractive Index
RMA	Radioactive Material Area
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project
SAL	Shielded Analytical Laboratory
TBP	Tributyl Phosphate
TMP	Transmembrane Pressure
UDS	Undissolved Solids
WTP	Waste Treatment Plant (Support Program)

1 Introduction

In fulfillment of the requirements of Test Plan TP-RPP-WTP-467 [1], the particle size distribution (PSD) of select Hanford tank waste water insoluble solids was characterized at the Radiochemical Processing Laboratory (RPL). This interim characterization report presents PSD results for Group 7 [Tributyl Phosphate (TBP) Sludge] wastes derived during initial characterization and parametric testing and processed in the Cells Unit Filter (CUF) located at the RPL's Shielded Analytical Laboratory (SAL).

2 Background

Particle size distribution (PSD) describes the size fractionation of solid species in a given powder, dispersion, or slurry sample. PSD is typically described by either cumulative or differential population fraction versus a given particle size indicator. For example, the size distribution of particles in a slurry are often described using a histogram expressing the differential volume of particles falling between two equivalent sphere diameters over a large array of equivalent sphere diameters. PSD measurements can be accomplished using a number of approaches, such as settling experiments, microscopic imaging, and light obscuration and scattering.

The particle size measurements discussed herein are carried out on a Malvern Mastersizer 2000 particle size analyzer (Malvern Instruments, Inc., Southborough, MA). This instrument operates using the principle of laser diffraction (see Figure 1). Here, a monochromatic laser (red and/or blue) is directed through a transparent cell containing a dilute dispersion of the solid particles being analyzed. On the opposite side of the flow cell is a series of ring detectors capable of detecting the intensity of laser light at various scattering angles. If the laser does not strike a particle in the flow cell, it simply passes through the cell undisturbed and strikes the central detector. When the laser interacts with a particle, it is scattered at various angles. The scattered light is picked up across a number of rings of the detector, creating a unique "scattering pattern" that can be mapped as a function of scattered light intensity versus ring detector position. Prolonged observation of the light scattered from the dispersion allows complete sampling of the particle species contained therein. Comparison of the time-averaged scattering signal against a reference "clean" cell signal generates a scattering pattern unique to that dispersion. Given the optical properties of the particulate and dispersing phases, mathematical analysis of the averaged "scattering pattern" allows determination of size fractionation species contained in the dispersion.

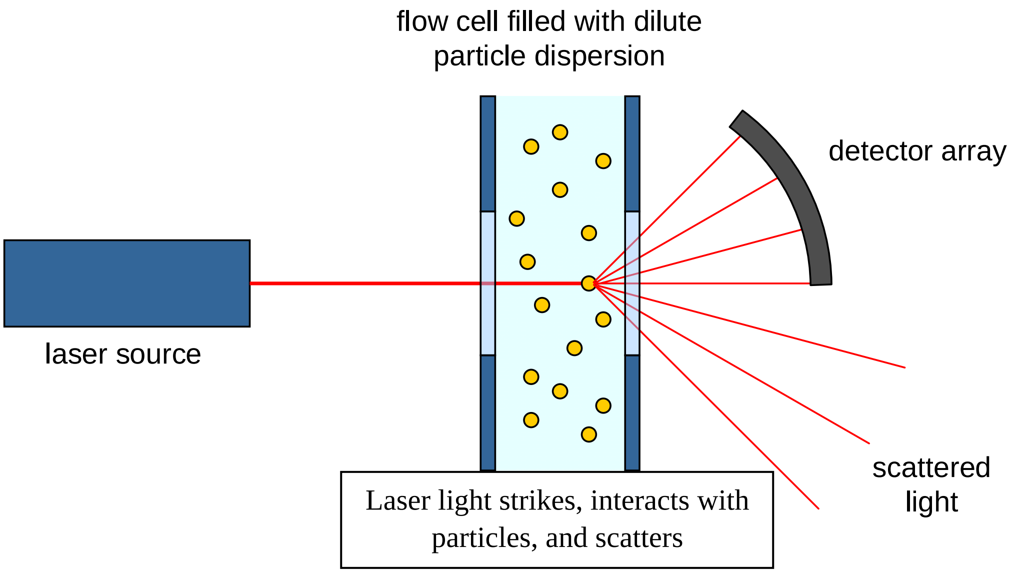


Figure 1. Schematic of a typical laser diffraction particle size analyzer.

It is important to recognize that particle size measurements by laser diffraction are intended to capture the size of a single, well-dispersed particle species. This “true” PSD captures all particles in the solid dispersion in an un-agglomerated primary particle state. Full dispersion at the primary particle level requires the correct selection of suspending phase chemistry, which is often further modified through the use of dispersing agents or surfactants, and sufficient flow to suspend all particles during analysis.

When dealing with complex dispersions such as Hanford tank waste, which contain multiple particle species and a broad distribution of sizes, finding the correct dispersing medium and measurement conditions is difficult (if not impossible), as individual particle species in the solids mixture may have contradictory suspending phase chemistry requirements. As such, particle size analysis of complex solids dispersions is generally performed to determine the “apparent” PSD as a function of processing conditions such as flow rate and sonication and suspending phase chemistry such as pH. The apparent PSD differs from the true PSD in two ways: 1) particle agglomerates exist and are treated as single particle species and 2) not all particles may be suspended at the flow conditions selected. Despite these short comings, apparent PSDs provide useful information about how the PSD of the test dispersion exists in the process from which it is derived and can highlight potential difficulties in suspending large/dense particles.

3 Samples

Group 7 particle size measurement samples were derived as part of bench-scale homogenization and leaching studies using actual tank waste. Source material for the studies included initial characterization, parametric testing, and CUF testing of Group 7 [TBP Sludge] solids. Four samples were submitted for analysis, including a primary and duplicate of the initial characterization (TI576-G7-S-WL-PSD-1 and TI576-G7-S-WL-PSD-2), a caustic-leached (i.e. parametric testing) sample (TI623-G7-CL-PSD) and a low-solids matrix sample (TI624-G7-3-PSD) before the caustic-leach in the CUF.

Group 7 CUF particle size measurement samples were derived as part of bench-scale crossflow ultrafiltration and leaching studies using actual tank waste. The Group 7 sludge samples were added to the slurry reservoir tank with simulant supernate. The combination was initially mixed in the tank then allowed to circulate through the CUF at a high flow rate for approximately an hour. Sample TI623-G7-3-PSD was taken after the initial slurry had been circulated in the CUF, although before any dewatering or leaching took place. Various transmembrane pressures (TMP) and axial velocities (AV) were examined. This slurry was then dewatered and sample AY-102 added to obtain a high-solids slurry. This mixture resulted in a break-down of the pump due to an unnoticed stir bar remaining in the slurry. The mixture in the CUF was drained from the system while the pump was repaired. After the system became operational and the slurry mixture added back to the CUF the slurry was subjected to the following operations:

1. dewatering of the waste slurry to transform the low-concentration Group 7 slurry to a high-concentration Group 7 slurry
2. full-recycle ultrafiltration of the high-concentration waste slurry at various AV and TMP
3. caustic-leaching of the waste slurry with ~5 M sodium hydroxide for 8 hours at 60°C (not including time for slurry heat-up and cool-down)
4. dewatering of the caustic-leached slurry
5. full-recycle ultrafiltration of the high-concentration caustic-leached slurry at various AV and TMP
6. washing of the caustic-leached slurry with relatively dilute sodium hydroxide solutions (includes four successive washes with increasingly dilute NaOH solutions)

For CUF particle size testing, samples were derived from various points in the ultrafiltration process outlined above. With regard to slurry samples, waste aliquots for particle size were sampled after:

- after loading and circulating the sample in the CUF (before pump break-down),
- after caustic-leaching and dewatering (i.e. after step 4)
- dewatering the initial slurry (i.e. after step 1),
- after washing the caustic-leached slurry (i.e., after step 6),

For sampling, approximately 0.5 mL of source slurry was taken. These slurry samples were subsequently diluted to ~5 mL total volume with a solution of 0.01 M NaOH in water. It should be noted that this dilution step may alter both the apparent and primary particle size distributions of solids in the sample submitted for size analysis (by either particle dissolution or change in the state of particle agglomeration). As such, the PSDs measured during analysis may not correspond directly to the size distribution that exists in the CUF at a given processing step. Due to dose concerns the only CUF sample able to be analyzed for PSD was TI624-G7-3-PSD. Table 1 provides a summary of the samples analyzed and their given sample identification number.

Table 1. Samples associated with Group 7 particle size testing.

Sample Jar ID	Description
TI576-G7-S-WL-PSD-1	Primary Group 7 Initial Characterization Sample
TI576-G7-S-WL-PSD-2	Duplicate Group 7 Initial Characterization Sample
TI623-G7-CL-PSD	Group 7 Parametric Testing Sample
TI624-G7-3-PSD	Slurry – Low-solids matrix Group 7 slurry before caustic leaching

4 Analysis

Particle size distributions for Group 7 samples were measured on the dates shown in Table 2. The analyses produced the following reportable data:

- particle diameters corresponding to the 10%, 50%, and 90% cumulative weight/volume undersize percentiles
- volume differential distributions (mass population percentage versus diameter)

Alternate analyses of the data, such as number/surface area distributions, are available on request.

Table 2. Sample analysis dates for Groups 7

Sample	Date
TI576-G7-S-WL-PSD-1	October 7, 2008
TI576-G7-S-WL-PSD-2	October 7, 2008
TI623-G7-CL-PSD	October 7, 2008
TI624-G7-3-PSD	October 16, 2008

5 Instrument

Particle size characterization was accomplished using a Mastersizer 2000 (Malvern Instruments, Inc., Southborough, MA 01772 USA) with a Hydro µP wet dispersion accessory. The Mastersizer has a nominal size measurement range of 0.02-2000 µm. The actual range is dependent on the accessory used as well as the properties of the solids being analyzed. When coupled with the Hydro µP wet dispersion accessory, the nominal measuring range is reduced to 0.02-150 µm. Although particle sizes above 150 µm can be observed with the Hydro µP, their volume/number contribution cannot be determined reliably.

The Hydro µP wet dispersion accessory consists of a 20 mL sample flow cell with a continuously variable and independent pump and ultrasound. Both flow and sonication can be controlled and changed during measurement. As such, PSD measurements can be made before, during, and after sonication, allowing determination of the influence of each on the sample’s PSD. The primary measurement functions of the Malvern analyzer are controlled through computer software. For the current measurements, Mastersizer 2000 software, Version 5.40 [Malvern Instruments, Ltd. Copyright © 1998-2007] was employed.

Table 3 provides a summary of basic information regarding the analyzer and accessory. The Malvern Mastersizer 2000 is located in the northwest contamination area (CA) fume hood in RPL Room 302. It should be noted that the dispersion unit’s sonication capability was not functioning at the time the standard or sample measurements were taken. As such, only “before sonication” data are available.

Table 3. Summary of Malvern Mastersizer 2000 instrument information.

Analyzer:	Mastersizer 2000
Measurement principle:	Laser Diffraction (Mie Scattering)
Analyzer Accessory:	Hydro µP
Serial Number:	MAL100406
Measurement Range:	0.02-2000 µm nominal (0.02-150 µm with accessory)
Type:	Flow cell system with continuously variable and independent pump and ultrasound.
Capacity:	20 mL
Pump Speed Range:	0-5000 RPM (variable)
Ultrasound Power	0-20 W (variable)
Software Version	5.40

6 Governing Test Plan, Procedure, and Test Instructions

The test plan governing the physical characterizations for these samples is River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) document number TP-RPP-WTP-467, Revision 0 [1]. Operation of the Malvern Mastersizer 2000 is governed by RPL-COLLOID-01, Revision 1 [2].

7 Instrument Performance Check

As required by RPL-COLLOID-01, the performance of the Malvern analyzer must be verified at the beginning of each series of analyses (with the period between performance checks not to exceed 90 days during use). Checks are performed using particle size standards traceable to the National Institute of Standards and Technology (NIST). Checks verify that the particle size analyzer can measure a PSD standard’s d(50), the 50% volume/weight fractile and mean particle size, to within 10% of the value specified on the manufacturer’s certificate of analysis.

For the measurements described in this report, the performance check employed a NIST traceable polydisperse particle size standard purchased from Whitehouse Scientific (Waverton, Chester, CH3 7PB, UK). Table 4 provides a summary of the standard properties. The standard is traceable back to its certificate of analysis through a unique bottle number identifier.

Table 4. Properties of the NIST standard used to verify performance of the Malvern Mastersizer 2000 and performance check results.

Size Range:	1-10 µm		
Catalogue #:	PS-192		
Bottle #	2103		
Weight:	0.10 g		
PSD Percentiles	List	Measured (µm)*	Absolute Error**
d(10):	2.88 ± 0.24 µm	2.60	n/a
d(50):	4.18 ± 0.34 µm	4.16	0.43%
d(90):	6.23 ± 0.56 µm	6.74	n/a

*As measured for the period of performance applicable for this report.

**Calculated before rounding of significant figures in List and Measured

The instrument performance check covering size analysis of samples TI576-G7-S-WL-PSD-1, TI576-G7-S-WL-PSD-2, TI623-G7-CL-PSD, and TI624-G7-3-PSD was run on October 2, 2008. Performance check results for this period were recorded to the Malvern file "2008-10Oct02-G2 Para PSD.mea".

The particle size standard was supplied as 0.10 g single shot of dry powder that was dispersed in ~0.5% sodium hexametaphosphate in water. This dispersion was subsequently sonicated for 5 minutes in a bath sonicator. Addition of sodium hexametaphosphate and subsequent sonication helps eliminate any particle agglomerates in the initial dispersion. Before measuring the performance check standard, the Hydro µP dispersion unit was filled with ~0.5% sodium hexametaphosphate in water. Next, an aliquot of the particle size standard dispersion was then sampled and loaded into the Malvern using a 5 mL plastic transfer pipette. A continuous pump speed of 2000 RPM was set to mix the flow cell contents and the PSD was measured.

The performance check size analysis employed a particle refractive index and absorption of 1.544 and 0, respectively, and a suspending phase particle refractive index of 1.33 (for water). An average of three 2000 RPM measurements of the PSD indicated a d(50) of 4.16 µm. This deviates less than 1% from the d(50) listed on the standard's certificate of analysis from Whitehouse Scientific and is also within the range provided on the certificate. As such, acceptable instrument performance was verified for the period of performance covering samples TI576-G7-S-WL-PSD-1, TI576-G7-S-WL-PSD-2, TI623-G7-CL-PSD, and TI624-G7-3-PSD.

8 Sample Handling

Group 7 samples were analyzed "as-is". No additional treatment was performed except for the mechanical agitation and re-suspension of any settled solids at the time of analysis.

9 Experimental

Particle size measurements of waste samples TI576-G7-S-WL-PSD-1, TI576-G7-S-WL-PSD-2, TI623-G7-CL-PSD, and TI624-G7-3-PSD were performed using the Malvern analyzer in RPL Room 302. All measurements were performed in 0.01 M sodium hydroxide. Before each analysis, the analyzer was drained, flushed with 20 mL of deionized (DI) water at least three times, filled with 20 mL 0.01 M sodium hydroxide solution, and brought into a measurement ready state. PSD characterization for each sample was accomplished as follows:

1. The analyzer flow cell pump was set to 3000 RPM with no sonication.
2. The material (sample) and suspending phase optical properties were set in the analyzer software (see Table 5).
3. The sample was prepared for analysis by re-suspending the settled solids. This was accomplished by repeatedly pulsing the samples with a 10 mL disposable plastic pipette until the contents were uniformly dispersed. Each pulse involved drawing off a fraction of the sample into the pipette and immediately jetting the drawn liquid back into the sample vial.
4. Immediately after re-suspension, the sample dispersion was added drop-wise to the instrument (while the pump was active) until the appropriate laser obscuration was achieved. Obscurations

ranging from 3.5 to 35% were considered acceptable. For the current analyses, an obscuration of 10-20% was targeted.

5. The sample PSD was measured under the conditions outlined in the sample test matrix (see Table 6).

Table 5. Material and suspending optical properties used for analysis of Group 7 particle size distributions.

Sample Name	Material Selected for Optical Properties	Refractive Index (RI)	Absorption
TI576-G7-S-WL-PSD-1	Boehmite	1.655	1.0
TI576-G7-S-WL-PSD-2	Boehmite	1.655	1.0
TI623-G7-CL-PSD	Boehmite	1.655	1.0
TI624-G7-3-PSD	Boehmite	1.655	1.0
Suspending Phase	Water	1.33	n/a

Table 6. Particle size analysis test matrix used for samples TI576-G7-S-WL-PSD-1, TI576-G7-S-WL-PSD-2, TI623-G7-CL-PSD, and TI624-G7-3-PSD.

Condition No.	Pump Speed (RPM)	Sonic Power	Comment
1	3000	n/a	no sonication
2	4000	n/a	no sonication
3	2000	n/a	no sonication
4	2000	n/a	no sonication

As indicated in the analysis outline above, the optical properties, such as the refractive index (RI) of the sample and suspending phase must be entered into analyzer at the time of measurement. Because the exact optical properties of the tank waste solids are unknown, the optical properties selected were those of most abundant species. Analytical results indicate Al as the major species, so optical properties for boehmite [AlO(OH)] were employed in the measurement and analysis of Group 7 samples. Use of the correct optical properties (in particular the RI) only serves to refine measured PSD (see Appendix A of TDP-WTP-271). As such, the boehmite optical properties can be used while still allowing the analysis to provide a reasonable representation of the actual waste PSD.

The size distribution of particles was measured under flow conditions without sonication. Table 6 outlines the test matrix performed for all sample measurements. For each condition, three successive 20-second measurements of PSD were taken. An average of these measurements was then generated by the analyzer software. Both individual and averaged PSDs were saved to the analyzer data file. Once measurements were complete, the flow rate for the next condition was set, the sample was given approximately 30 seconds to equilibrate, and the next set of measurements was taken. Measurements for TI576-G7-S-WL-PSD-1, TI576-G7-S-WL-PSD-2, and TI623-G7-CL-PSD were logged to the Mastersizer 2000 file “2008-10Oct07-initial char PSD.mea”. Measurements for TI624-G7-3-PSD were logged to the Mastersizer 2000 file “2008-10Oct16-G8 CUF PSD.mea”.

Analysis of the raw particle size data is performed automatically by the Mastersizer software immediately after each measurement. Analysis calculates the particle size distribution based on 1) the scattered light intensity as a function of detection angle, the particle size model selected [single narrow, multiple narrow, or broad peaks] and 2) the optical properties entered into the software at the time of measurement. For the current measurements, appropriate optical properties were selected at the time of measurement for all samples.

The particle size results for Group 7 initial characterization and parametric testing samples appear largely free of defects or data artifacts caused by air/bubble entrapment in the instrument. In the Group 7 CUF testing (TI624-G7-3-PSD) a peak is observed around 1300 µm. As particles of this size exceed the instrument's upper measuring range boundary of 150 µm, the ~1300 µm particle population may not have been properly suspended and/or reliably sampled due to their size. Likewise, size determinations between 1000-2000 µm appear to be strongly influenced by instrument electronic background, and determination of particles in this size range can sometimes result from measurement artifacts (such as a poor background reading). For these reasons, the distribution range was limited to less than 1000 µm to remove these peaks from the analysis.

10 Results and Discussion

10.1 Group 7 Initial Characterization PSD Results

Results for TI576-G7-S-WL-PSD (Group 7 Initial Characterization)

Figures 2-3 and Tables 7 and 8 present the results of Group 7 initial characterization particle size analysis as a function of test condition. Figures 2-3 show the differential volume population distribution for the Group 7 initial characterization sample and allow a qualitative examination of the PSD behavior with respect to pump speed. Table 7 is a summary of the measured oversize diameter percentiles (by volume/weight) for the primary sample, TI576-G7-S-WL-PSD-1. Table 8 presents the same results for the duplicate sample, TI576-G7-S-WL-PSD-2. Both tables present cumulative oversize diameters corresponding to the 10th, 50th, and 90th volume/weight percentiles, hereafter referred to as d(10), d(50), and d(90), respectively. More extensive percentile results are provided in section 12 of this interim report. These tables will be used to quantitatively examine reproducibility and changes in particle size.

Figure 2 shows the PSD for the primary Group 7 initial characterization sample as a function of pump speed. The sample displayed a multi-modal distribution at all pump speeds. At 2000 RPM the distribution ranges from 0.2-750 µm with peak maxima around 0.7, 7.5, 84 and 475 µm. At 3000 RPM, the distribution ranges from 0.2-500 µm and displays peak maxima around 0.7, 7.5, and 75 µm. At 4000 RPM, the distribution ranges from 0.2-200 µm and contains peak maxima around 60, 7.5, and 0.7 µm. Overall, the higher pump speeds show an increasing population of particles or agglomerates > 20 µm. The 475 µm peak seen at 2000 RPM may be an artifact of scattering signal interpretation by the Malvern software or possible flocculates in the solution which are sheared apart at higher pump speeds. The sample appears to have numerous large particles, agglomerates, or flocculates, which may result in poor sampling due to settling and/or insufficient solids.

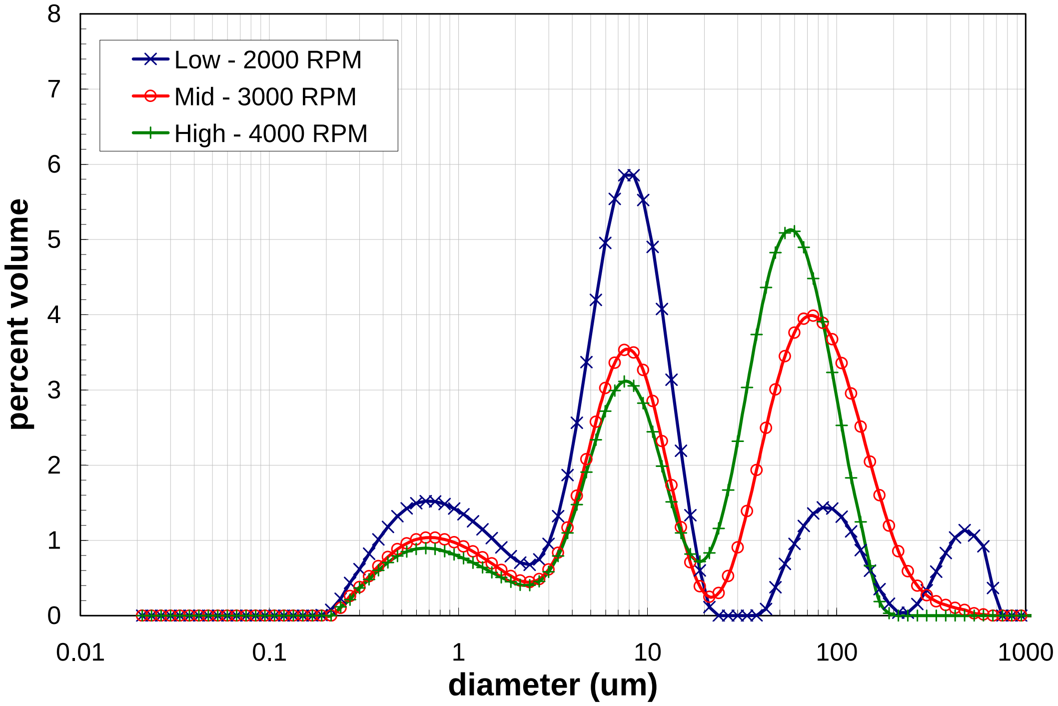


Figure 2. Volume distribution result for the primary Group 7 initial characterization sample as a function of pump speed.

Figure 3 shows the PSD for the duplicate Group 7 initial characterization sample as a function of pump speed. This distribution shows a range of 0.2-150 µm with the exception of a 475 µm peak at 2000 RPM. As this 475 µm peak is observed in both the primary and duplicate sample only at 2000 RPM it is probable that it corresponds to flocculates which are sheared apart at higher pump speeds. In the duplicate sample a primary peak is present around 6 µm and a shoulder exists around 0.75 µm at all pump speeds. At 4000 RPM an additional small peak is seen around 60 µm and at 3000 and 2000 RPM either a small peak or a shoulder is present around 75 µm.

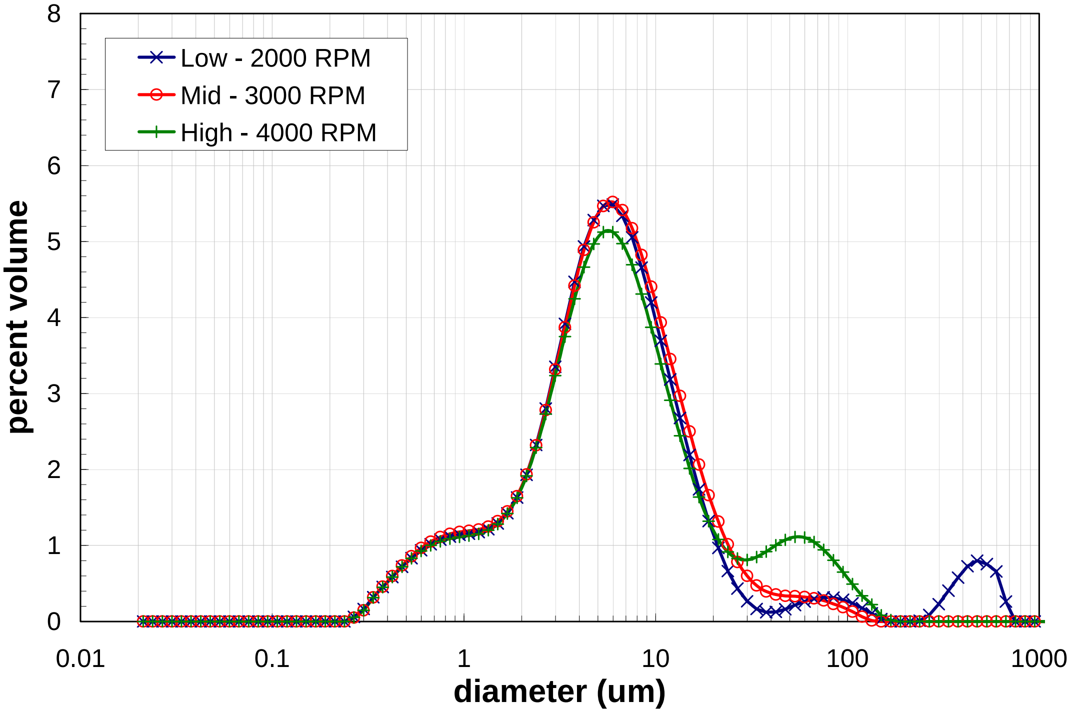


Figure 3. Volume distribution result for the duplicate Group 7 initial characterization sample as a function of pump speed.

Tables 7 and 8 show select cumulative oversize percentiles for the primary and duplicate Group 7 particle dispersions. Using the primary results as a reference, the behavior of Group 7 initial characterization particle size as a function of pump speed can be quantitatively evaluated. Specifically, the following observations can be made:

- In general, the d(10) falls between 0.70 and 1.3 µm, the d(50) between 7.4 and 31 µm, and the d(90) between 89 and 130 µm
- The listed diameter percentiles appear to be highly sensitive to changes in pump speed. Increases in pump speed appear to result in increases in the d(50). For example, a decrease between 4000 and 2000 RPM decreases the particle diameter from 31 to 9.8 µm. This is a decrease of 68%, which is above the instrument limit of accuracy (10%) and is significant and not merely random noise or measurement error.

Table 7. Particle size analysis percentile results from primary Group 7 initial characterization sample, TI576-G7-S-WL-PSD-1.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	n/a	1.0	19	130
2	4000	n/a	1.3	31	89
3	2000	n/a	0.87	9.8	120
4	2000	n/a	0.70	7.4	110

Table 8. Particle size analysis percentile results from duplicate Group 7 initial characterization sample, TI576-G7-S-WL-PSD-2.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	n/a	1.1	5.5	17
2	4000	n/a	1.2	5.8	35
3	2000	n/a	1.2	5.9	66
4	2000	n/a	1.2	5.5	19

Behavior of the duplicate sample PSD with respect to pump speed shows it favors smaller diameters for the d(50) and d(90) than that of the primary at equivalent measurement conditions. Table 9 shows the absolute relative percent difference between the d(10), d(50), and d(90) values determined for the primary and duplicate Group 7 initial characterization samples. Here, absolute relative percent difference is determined using the following equation:

$$RPD = \left| \frac{d_d(n) - d_p(n)}{d_p(n)} \right| \qquad \text{Eq. 1}$$

where $d_p(n)$ and $d_d(n)$ are the primary and duplicate cumulative oversize diameters corresponding to the n^{th} percentile. The listed RPDs indicate that there is a significant difference between samples.

Table 9. Absolute relative percent difference between primary and duplicate Group 7 initial characterization samples.

Measurement Condition	Pump Speed	Sonication	Absolute RPD		
			d(10)	d(50)	d(90)
1	3000	n/a	9.1%	71%	87%
2	4000	n/a	6.5%	81%	61%
3	2000	n/a	44%	40%	45%
4	2000	n/a	67%	25%	82%

For particle size measurements on the Malvern Mastersizer 2000, RPDs of up to 10% are generally expected given the accuracy of the instrument. The results for Group 7 initial characterization samples show RPDs that range from 9.1 to 87% depending on the measurement condition and percentile examined. Based on the large number of RPDs greater than 10% in Table 9, it is likely that there is a significant size difference in the solids species in the primary and duplicate samples.

Figure 4 shows how the differences in the primary and duplicate PSDs described in the preceding paragraphs manifest in the differential volume distributions. The peak maxima for the two samples are around similar diameters, although the population distribution between the samples is dissimilar. The increased number of > 20 µm particles in the primary sample may be a result of flocculates or aggregates. Therefore, this may indicate poor sampling due to the settling of these larger difficult-to-suspend particles, flocculates, and/or agglomerates.

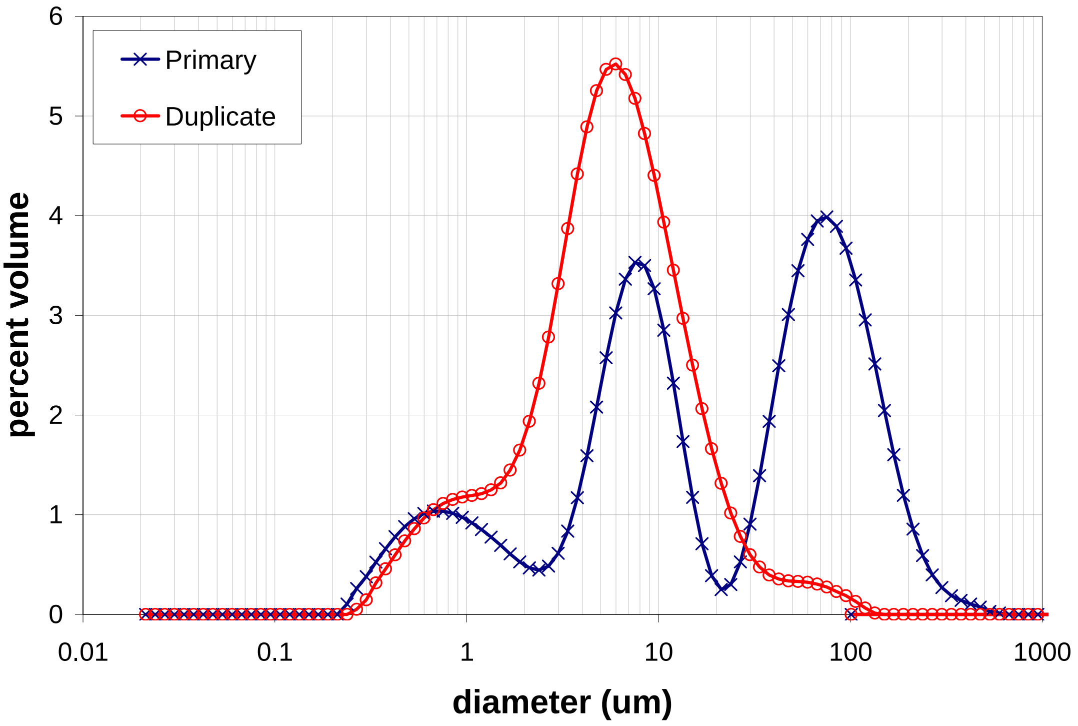


Figure 4. Comparison of primary and duplicate sample differential volume PSD of Group 7 initial characterization at 3000 RPM.

The Group 7 initial characterization particle size distribution ranged from 0.2-800 µm and was multi-modal. The primary and duplicate samples show similar peak maxima although the population distribution shows a preference to larger particle diameters, agglomerates, or flocculates in the primary sample. The varying distribution may indicate poor sampling due to settling of larger particles that are difficult-to-suspend. At the low pump speed (2000 RPM) an additional peak appears around 475 µm in both the primary and duplicate samples and is most likely due to flocculates, which are sheared at the higher pump speeds.

10.2 Group 7 Parametric Testing PSD Results

Results for TI623-G7-CL-PSD (Group 7 Parametric Testing)

Figure 5 and Table 10 present the results of Group 7 parametric testing particle size analysis as a function of test condition. Figure 5 shows the differential volume population distribution for the Group 7 parametric testing sample and allows a qualitative examination of the PSD behavior with respect to pump speed. Table 10 is a summary of the measured oversize diameter percentiles (by volume/weight) for TI623-G7-CL-PSD which presents the d(10), d(50), and d(90) results. More extensive percentile results are provided in section 12 of this interim report.

Figure 5 shows the PSD for the Group 7 parametric testing sample as a function of pump speed. All of the pump speeds show a multi-modal distribution with peak maxima around 1.2 and 8 µm. At

2000 RPM the range is 0.24-20 µm, although at higher pump speeds a broader range exists. At 3000 RPM the range is 0.24-300 µm and an additional peak is seen around 135 µm. At 4000 RPM the range is 0.24-200 µm and again an additional peak is observed, although its maximum is around 70 µm. This larger diameter peak most likely indicates the presence of larger particles or agglomerates, which are suspended by faster pump speeds. As this peak shifts to smaller particle diameters at 4000 RPM this may also indicate shear induced breakage of agglomerates, which would account for the relative increase in the 4-10 µm peak observed.

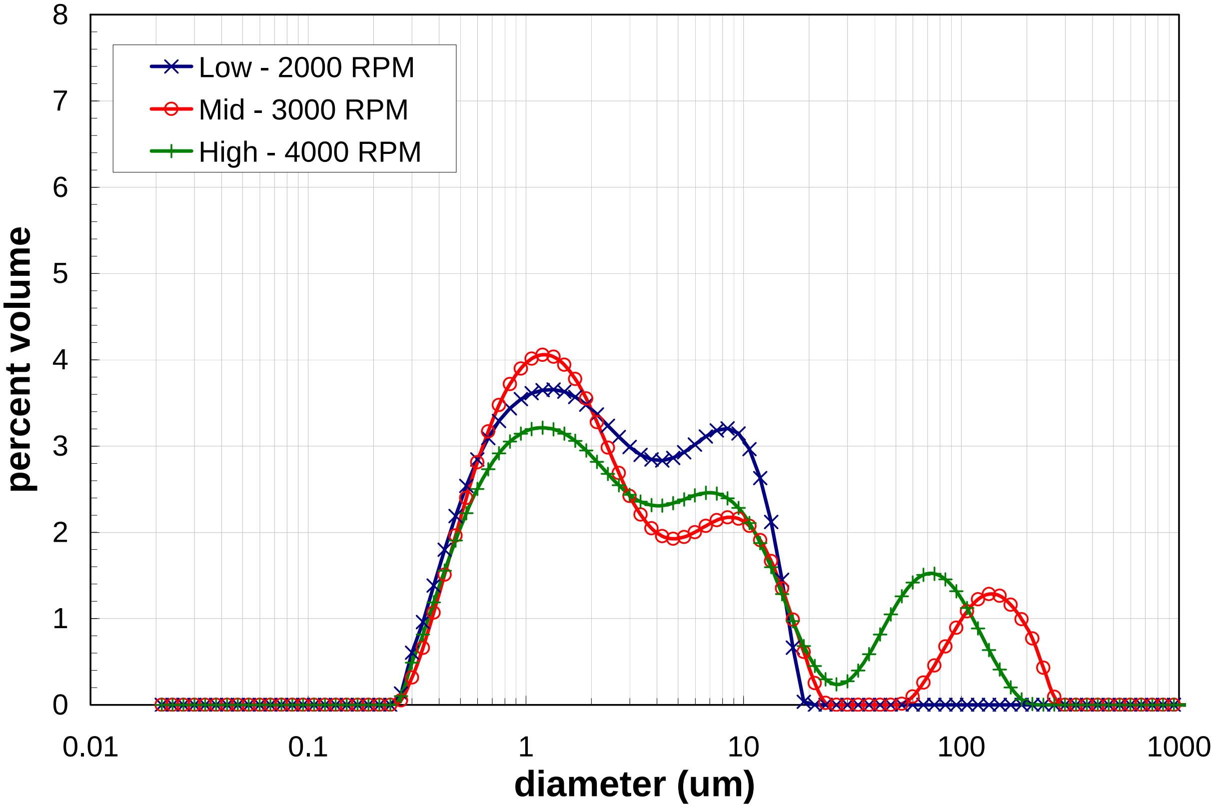


Figure 5. Volume distribution result for the Group 7 parametric testing sample as a function of pump speed.

Table 10 shows select cumulative oversize percentiles for the Group 7 parametric testing particle dispersion (TI623-G7-CL-PSD). Using these results as a reference, the behavior of Group 7 particle size as a function of pump speed can be quantitatively evaluated. Specifically, the following observations can be made:

- In general, the d(10) falls between 0.57 and 0.72 µm, the d(50) between 2.1 and 2.9 µm, and the d(90) between 10 and 93 µm
- The listed diameter percentiles appear to be sensitive to changes in pump speeds. Increases in flow rate appear to result in increases in the mean diameter [i.e., the d(50)]. For an increase from 3000 to 4000 RPM the mean particle diameter increases from 2.1 to 2.9 µm. This is an increase of ~38% and is significant relative to the accuracy of the instrument.

Table 10. Particle size analysis percentile results from Group 7 parametric testing sample, TI623-G7-CL-PSD.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	n/a	0.61	2.1	78
2	4000	n/a	0.61	2.9	59
3	2000	n/a	0.72	2.7	93
4	2000	n/a	0.57	2.2	10

The particle size analysis of parametric testing of Group 7 displays multi-modal particle size distributions ranging from 0.24-300 µm. Higher pump speeds result in an additional peak consisting of particles >20 µm. This may indicate the presence of larger difficult-to-suspend particles, which may result in poor sampling due to settling.

10.3 Influence of Chemical Treatment on Group 7

Comparison of the percentiles and distributions presented in Sections 10.1 and 10.2 of this report can highlight the effects of chemical treatment on Group 7 waste PSD. Caution must be used when directly comparing PSDs, as these PSDs include both primary particles and particle agglomerates. The structure of the agglomerates fractions depends on 1) physical conditions such as the analyzer pump speed and 2) chemical conditions such as particle interaction potentials and sample history.

One expected outcome of caustic leaching is a decrease in particle size as a result of solid dissolution. However, removal of leachable solid species may reveal the size distribution of particles only minimally represented in the initial sample. In addition, changes in the dominant particle surface chemistry can yield increased particle agglomeration, which in turn results in increases in the apparent particle size. In addition to chemical effects, the mechanical force needed to pump the dispersion can also shear particle agglomerates (as well as influence the volume of agglomerates suspended). As such, the apparent PSD of a material may also vary with pump speed. Comparisons will be made at measurement condition 1 (Table 6: 3000 RPM).

Caustic-Leaching and Washing of Group 7 Waste Solids

The influence of caustic-leaching and washing of Group 7 (Tributyl Phosphate Sludge) solids can be evaluated by comparing PSDs for the source material (i.e., for initial characterization sample TI576-G7-S-WL-PSD) to the caustic-leached and washed Group 7 parametric testing PSD sample (TI623-G7-CL-PSD). The PSD measurement for the primary initial characterization sample is used for this comparison.

Table 11 and Figure 6 show changes that occur to the Group 7 solids PSD as a result of caustic-leaching and washing operations. Figure 6 shows both the initial characterization and parametric testing samples are tri-modal with peak maxima located around similar particle diameters. The most noticeable difference is the shift to lower particles diameters after caustic-leaching and washing. The reduction in particle size is likely a result of either dissolution of material off of the particle surface or agglomerate breakage. As the peak maxima are similar this may indicate the particle size is 0.3-4 µm and those particles greater than this range, particularly > 20 µm may be mostly agglomerates.

Table 11. Cumulative undersize percentiles showing the influence of caustic-leaching and washing on the PSD of Group 7 (Tributyl Phosphate Sludge) solids at measurement condition 1 – 3000 RPM (see Table 6).

Sample	d(10) [µm]	d(50) [µm]	d(90) [µm]
Group 7 Initial Characterization (TI576-G7-S-WL-PSD-1)	1.0	19	130
Group 7 Parametric Testing (TI623-G7-CL-PSD)	0.61	2.1	78

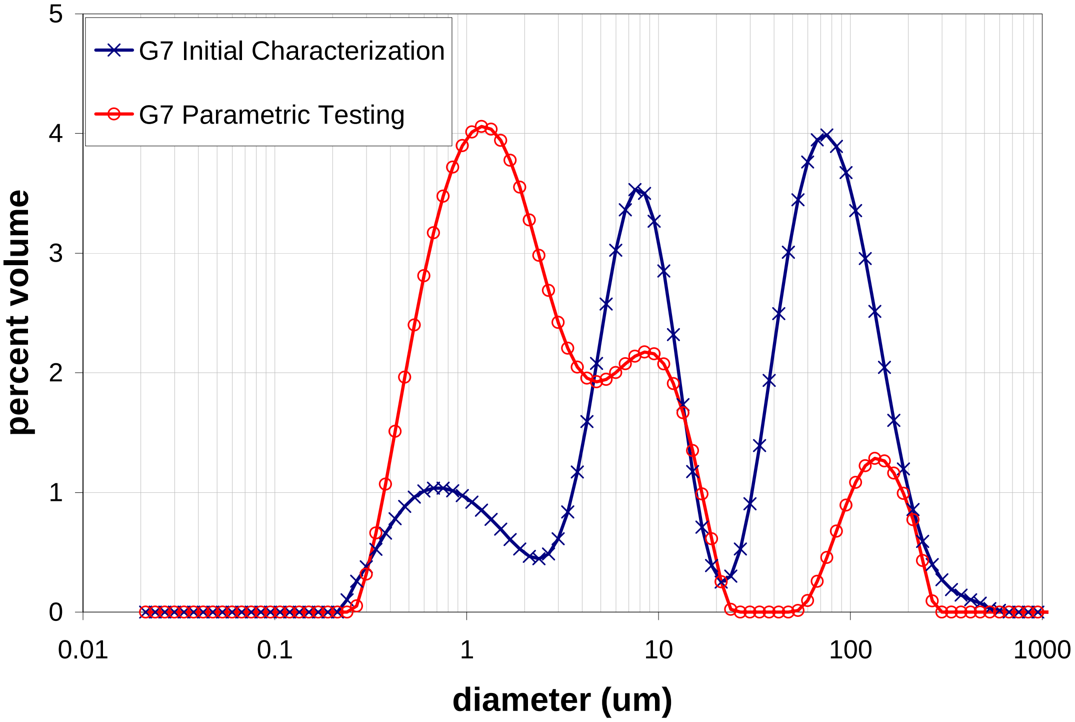


Figure 6. Influence of caustic-leaching and washing on Group 7 (Tributyl Phosphate Sludge) waste solids PSD. PSDs were taken at measurement condition 1 – 3000 RPM (see Table 6).

10.4 Group 7 CUF Testing PSD Results

The following sub-section discusses the PSD results for Group 7 CUF testing sample. A brief outline of how select cumulative oversize diameter percentiles behave as a function of test condition is given, and a graph of particle size distributions is given as a function of flow rate without sonication. The reproducibility of PSD for each sample in not assessed. In addition, the current section focuses on changes in the PSD with measurement condition. Comparison of PSDs to one another to highlight effects of CUF processing shall be examined in Section 10.5.

Results for TI624-G7-3-PSD (Low-Solids Matrix)

Sample TI624-G7-3-PSD is representative of the low-solids matrix (dilute) slurry that was initially run in the CUF system. Table 12 shows select cumulative undersize percentiles for sample TI624-G7-3-PSD, more extensive percentile results are shown in section 12. Here the d(10) ranges between 28 and 38 µm, the d(50) between 81 and 240 µm, and the d(90) between 150 and 510 µm. With regards to pump speed effects, the d(50) and d(90) percentiles show a significant increase in size at 4000 RPM, indicating the presence of large, difficult-to-suspend particles.

Table 12. Particle size analysis percentile results the Group 7 low-solids matrix sample (TI624-G7-3-PSD).

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	n/a	28	81	150
2	4000	n/a	38	240	510
3	2000	n/a	38	190	350
4	2000	n/a	31	170	290

Figure 7 shows the PSD for Group 7 low-solids matrix (TI624-G7-3-PSD) sample as a function of pump speed. The sample shows a broad bi-modal distribution. At 2000 RPM the distribution ranges from 1-500 µm with peak maxima at 190 and 30 µm. At 3000 RPM the range is from 0.3-300 µm with peak maxima at 90 and 12 µm. At 4000 RPM the distribution ranges from 0.6-750 µm with peak maxima at 330 and 50 µm. As the pump speed increases, from 3000 to 4000 RPM, there are more large particles or agglomerates that may be difficult-to-suspend, this may account for the extended range at 4000 RPM. These particles suspended at 4000 RPM may be slow settling relative to the measurement time and may contribute to the larger particle diameters at 2000 RPM in comparison with the distribution at 3000 RPM. Overall, the distribution shows the majority of particles and/or agglomerates are >20 µm and their distribution is dependent upon pump speed.

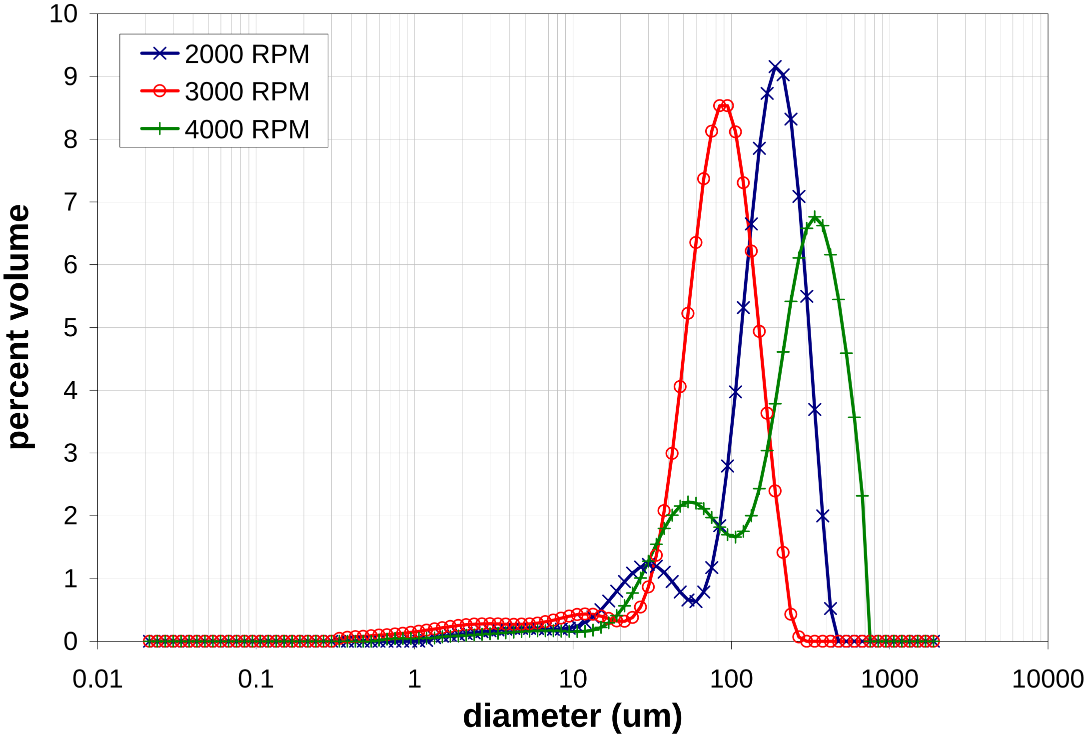


Figure 7. Volume distribution result for the Group 7 low-solids matrix (TI624-G7-3-PSD) sample as a function of pump speed.

10.5 CUF Processing Effects on Group 7 Solids

Shearing Effect on Group 7 (Low-solids matrix)

Table 13 and Figure 8 show the influence of circulation in the CUF on the PSD of Group 7 waste solids. Here, select cumulative undersize percentiles and PSD for the initial characterization (TI576-G7-S-WL-PSD-1) are compared to low-solids matrix slurry (TI624-G7-3-PSD). Both samples show a similar particle size distribution range of 0.2-400 µm with a primary peak maximum between 70-90 µm. The major difference observed in the low-solids matrix slurry is a large shift in the population to the primary peak diameter. This shift may likely be due to transient effects, such as shear induced agglomeration or flocculation resulting in a significant relative increase in 20-300 µm particles. This shift may also indicate a variation in composition as a result of sampling difficulties due to large difficult-to-suspend particles. These larger particles also present a complication, since they are near the upper limit of the instrument detection, and may not be as accurately measured.

Table 13. Cumulative undersize percentiles showing the influence of circulation in the CUF on Group 7 PSD at measurement condition 1 – 3000 RPM (see Table 6).

Sample	d(10) [µm]	d(50) [µm]	d(90) [µm]
Group 7 Initial Characterization (TI576-G7-S-WL-PSD-1)	1.0	19	130
Group 7 Low Solids Matrix Slurry (TI624-G7-3-PSD)	28	81	150

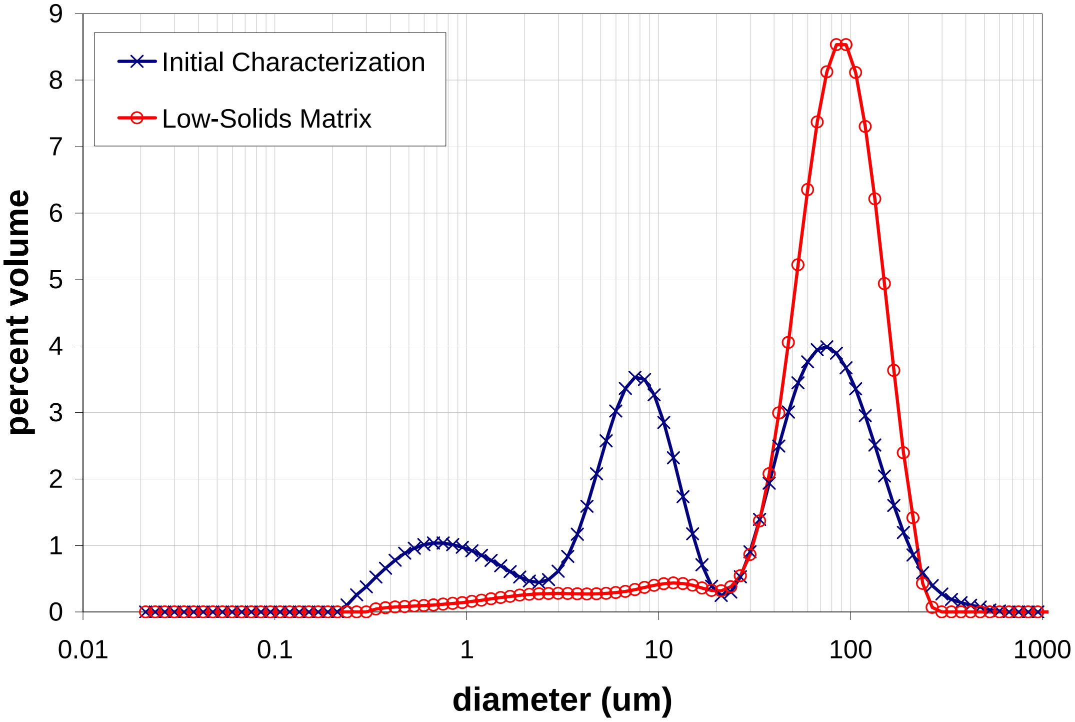


Figure 8. Influence of circulation in the CUF for Group 7. All PSDs taken at measurement condition 1 – 3000 RPM (see Table 6).

11 Records

Data records relating to Group 7 particle size distribution measurements and post-measurement analysis exist in original Malvern Mastersizer 2000 data files and Laboratory Record Books (LRBs):

- Malvern Mastersizer Files: "2008-10Oct16-G8 CUF PSD.mea", "2008-10Oct02-G2 Para PSD.mea", "2008-10Oct07-G7 initial char PSD.mea"
- LRB BNW 56933: Pages 134, 138, 139, 144, and 145
- Test Data Package: TDP-WTP-273, TDP-WTP-271, CCP-WTPSP-573, CCP-WTPSP-641, and CCP-WTPSP-651

References

1. Doc. No. TP-RPP-WTP-567, Revision 0, “Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes,” SK Fiskum, Battelle – Pacific Northwest Division, February 2007.
2. Doc. No. RPL-COLLOID-01, Revision 1, “Particle Size Analysis Using Malvern MS2000,” AP Poloski, Pacific Northwest National Laboratory, May 2007.

12 Detailed Cumulative PSD

Results: TI576-G7-S-WL-PSD (Group 7 Initial Characterization)

Table 12-1 and 12-2 present detailed cumulative oversize distributions (by volume/weight) for Group 7 initial characterization samples TI576-G7-S-WL-PSD-1 and -2, respectively. Results are reported as a function of test condition (see Table 6). This section does not provide discussion of the detailed distributions; however, a portion of these results (specifically, the 10th, 50th, and 90th diameter percentiles) are presented and discussed in other sections of this interim report.

Table 12-1. Cumulative oversize diameter distributions for the primary Group 7 initial characterization sample, TI576-G7-S-WL-PSD-1.

Test Condition	**Volume / Weight Cumulative Oversize Diameter (µm)**														
	1%	**5%**	**10%**	**20%**	**25%**	**30%**	**40%**	**50%**	**60%**	**70%**	**75%**	**80%**	**90%**	**95%**	**99%**
1 - 3000	0.34	0.59	1.0	4.6	5.8	6.9	9.7	19	49	67	77	89	130	160	270
2 - 4000	0.34	0.63	1.3	5.2	6.5	7.8	12	31	43	54	60	68	89	110	140
3 - 2000	0.31	0.53	0.87	3.6	4.8	5.8	7.6	9.8	14	60	71	83	120	170	550
4 - 2000	0.30	0.47	0.70	1.7	3.4	4.5	6.0	7.4	9.0	11	13	16	110	380	580

Table 12-2. Cumulative oversize diameter distributions for the duplicate Group 7 initial characterization sample, TI576-G7-S-WL-PSD-2.

Test Condition	**Volume / Weight Cumulative Oversize Diameter (µm)**														
	1%	**5%**	**10%**	**20%**	**25%**	**30%**	**40%**	**50%**	**60%**	**70%**	**75%**	**80%**	**90%**	**95%**	**99%**
1 - 3000	0.40	0.70	1.1	2.4	3.0	3.5	4.5	5.5	6.8	8.5	9.7	11	17	25	68
2 - 4000	0.40	0.71	1.2	2.5	3.0	3.6	4.6	5.8	7.2	9.4	11	14	35	61	100
3 - 2000	0.40	0.73	1.2	2.6	3.1	3.7	4.7	5.9	7.4	9.6	11	14	66	130	560
4 - 2000	0.40	0.70	1.2	2.5	3.0	3.5	4.5	5.5	6.8	8.6	9.9	12	19	100	560

Table 12-3 shows the absolute relative percent difference (RPD) between primary and duplicate results, which is calculated as:

$$RPD = \left| \frac{d_d(n) - d_p(n)}{d_p(n)} \right| \qquad \text{Eq. A-1}$$

where $d_p(n)$ and $d_d(n)$ are the primary and duplicate cumulative oversize diameters corresponding to the n^{th} percentile. As before, this section does not provide discussion of the RPD results; however, the RPD for the 10th, 50th, and 90th diameter percentiles are presented and discussed in other sections of this interim report.

Table 12-3. Relative percent difference between primary and duplicate Group 7 initial characterization samples (TI576-G7-S-WL-PSD -1 and -2, respectively) as a function of test condition.

Test Condition	Absolute RPD (%)														
	1%	**5%**	**10%**	**20%**	**25%**	**30%**	**40%**	**50%**	**60%**	**70%**	**75%**	**80%**	**90%**	**95%**	**99%**
1 - 3000	19%	17%	9.1%	47%	49%	50%	54%	71%	86%	87%	87%	87%	87%	85%	75%
2 - 4000	18%	12%	6.5%	52%	53%	55%	62%	81%	83%	83%	82%	80%	61%	45%	29%
3 - 2000	30%	37%	44%	28%	35%	37%	38%	40%	47%	84%	84%	83%	45%	24%	1.8%
4 - 2000	34%	49%	67%	42%	13%	22%	25%	25%	24%	23%	24%	30%	82%	74%	3.4%

Results: TI623-G7-CL-PSD (Group 7 Parametric Testing)

Table 12-4 presents detailed cumulative oversize distributions (by volume/weight) for Group 7 parametric testing samples TI623-G7-CL-PSD. Results are reported as a function of test condition (see Table 6). This section does not provide discussion of the detailed distributions; however, a portion of these results (specifically, the 10th, 50th, and 90th diameter percentiles) are presented and discussed in other sections of this interim report.

Table 12-4. Cumulative oversize diameter distributions for the primary Group 7 parametric testing sample, TI623-G7-CL-PSD.

Test Condition	Volume / Weight Cumulative Oversize Diameter (µm)														
	1%	**5%**	**10%**	**20%**	**25%**	**30%**	**40%**	**50%**	**60%**	**70%**	**75%**	**80%**	**90%**	**95%**	**99%**
1 - 3000	0.35	0.49	0.61	0.86	1.0	1.2	1.5	2.1	3.2	5.7	7.5	9.8	78	140	210
2 - 4000	0.34	0.47	0.61	0.91	1.1	1.3	1.9	2.9	4.7	7.6	9.7	13	59	87	130
3 - 2000	0.40	0.57	0.72	1.0	1.2	1.4	1.9	2.7	4.3	6.5	7.9	9.8	93	140	530
4 - 2000	0.33	0.45	0.57	0.83	0.98	1.1	1.6	2.2	3.2	4.7	5.8	6.9	10	12	15

Results: TI624-G7-3-PSD (Low-solids matrix Group 7)

Table 12-5 present detailed cumulative oversize distributions (by volume/weight) for Group 7 CUF testing sample TI624-G7-3-PSD. Results are reported as a function of test condition (see Table 6). This section does not provide discussion of the detailed distributions; however, a portion of these results (specifically, the 10th, 50th, and 90th diameter percentiles) are presented and discussed in other sections of this interim report.

Table 12-5. Cumulative oversize diameter distributions for the Group 7 CUF testing sample, TI624-G7-3-PSD.

Test Condition	Volume / Weight Cumulative Oversize Diameter (µm)														
	1%	**5%**	**10%**	**20%**	**25%**	**30%**	**40%**	**50%**	**60%**	**70%**	**75%**	**80%**	**90%**	**95%**	**99%**
1 - 3000	1.0	6.5	28	49	55	60	71	81	93	110	110	120	150	170	210
2 - 4000	3.2	24	38	65	87	120	190	240	290	350	380	410	510	580	670
3 - 2000	3.1	19	38	110	130	140	170	190	220	250	270	290	350	410	570
4 - 2000	3.3	18	31	92	110	120	150	170	190	220	230	250	290	330	380

Appendix F

Group 7 Rheology Methods and Analysis

Appendix F: Group 7 Rheology Methods and Analysis

Date:	**November 6, 2008**	Project No.:	**53019**
To:	**Sandy Fiskum**	Internal Distribution:	**Sandy Fiskum** **Richard Daniel** **File/LB**
From:	**Richard Daniel**		
Subject:	**Rheology of TBP Waste Sludge (Group 7): Initial Characterization**		

Acronyms and Abbreviations

Acronym	Definition
CCP	Computational Computer Program
CUF	Cells Unit Filter
DI	Deionized (Water)
LRB	Laboratory Record Book
NIST	National Institute of Technology
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project
SAL	Shielded Analytical Laboratory
TBP	Tributyl Phosphate
TDP	Test Data Package
UDS	Undissolved Solids (Concentration)
WTP	Waste Treatment Plant (Support Program)

1 Introduction

In fulfillment of the requirements of Test Plan TP-RPP-WTP-467 [1], the rheology of select Hanford tank waste samples was characterized at the Radiochemical Processing Laboratory (RPL). This interim characterization report presents rheology test results for a single initial characterization sample for waste processing Group 7, tributyl phosphate (TBP) waste sludge. The studies described herein will be limited to flow-curve and shear strength testing of this single waste group.

2 Background

Rheology is the science of material flow and deformation. For fluid systems, including pure liquids, mixtures of liquids, and suspensions of solids in liquids, the rheological properties of that system describe how it responds to an applied force or stress. When applied to solids, stress (below that required yield the solid material) induces a strain or finite deformation in the material. When applied to pure liquids, stress causes a continuous deformation of the substance or, in simpler terms, fluid flow. Suspensions of solids in liquids or liquid mixtures with internal structure can show a combination of both solid- and liquid-like behavior. In addition, the response of materials to force and deformation may not be constant. Changes in internal structure of materials that occur as a result of mechanical and chemical processes, such as breakage, precipitation of solids, and gelation, may alter the macroscopic flow and deformation properties. For the current study, two regions of tank waste flow behavior are considered: 1) incipient motion in settled tank waste solids and 2) non-elastic flow of tank waste slurries and supernates. Both are discussed in more detail in the following sub-sections.

Characterization of Incipient Motion – Shear Strength Testing

For settled tank waste slurry solids, a finite stress must be applied before the material will begin to flow. The stress required to transition the settled solids from elastic deformation to viscous flow is referred to as the shear strength, and its origin can be attributed to static and kinetic friction between individual particles and/or aggregates, strength of the matrix supporting the coarse fraction (i.e., the interstitial fluid), and sludge cohesion arising from interparticle adhesive forces such as van der Waals forces. The resistance of settled solids to motion can be quantified through shear strength testing.

In the current study, measurement of shear strength will be accomplished using the vane method. For the vane technique, the stress required to begin motion is determined by slowly rotating a vane immersed in the test sample's settled solids while continuously monitoring the resisting torque as a function of time. A material's static shear strength is then associated with the maximum torque measured during the transition from initial to steady-state vane rotation. A typical experimental setup for measuring shear strength with a vane is shown in Figure 1. An example torque versus time curve is shown in Figure 2.

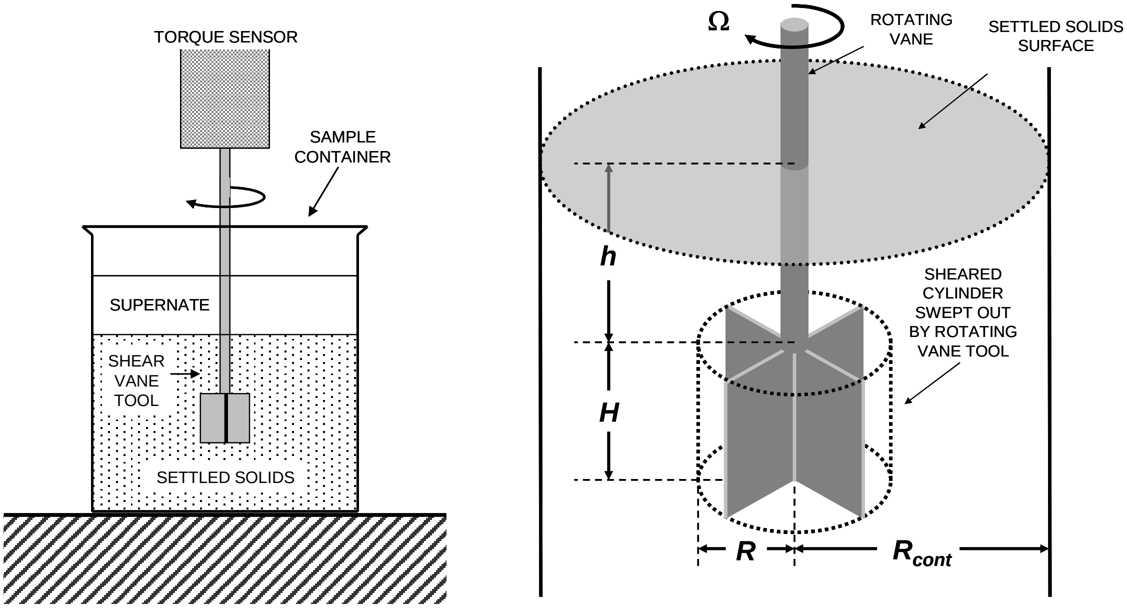


Figure 1. Typical shear strength experimental setup. A sludge / slurry sample in a container of radius R_{cont} is allowed to settle over a given period of time. A vane tool attached to a viscometer (i.e., a torque sensor) is immersed into the settled solids portion of a sludge or slurry to a depth h (relative to the top of the vane blades). The vane blades have a radius R and a height H. The vane is then slowly rotated at a constant rotational speed, Ω. The torque versus time profile is recorded and the maximum torque required to initiate rotation determined. The shear strength is then calculated from this maximum torque based on the assumption of a uniform stress distribution on the known vane tool geometry.

The maximum torque required for incipient motion is dependent on vane geometry. To account for vane geometry effects, shear strength is expressed in terms of a uniform and isotropic stress acting over the surface area of the cylinder of rotation swept out by the vane. This uniform stress (i.e., the shear strength of the material) is related to the maximal torque during incipient motion by the equation [2]:

$$\tau_{SS} = \frac{M_{max}}{4\pi R^3\left(\frac{H}{2R}+\frac{1}{3}\right)} \qquad \text{Eq. 1}$$

Here, τ_{ss} is the shear strength [N/m^2], M_{max} is the maximum torque [N·m], and R and H are the radius and height of the cylinder of rotation swept out by the vane [m]. Because the shear band observed upon slow rotation of the vane does not extend appreciably beyond the vane paddles, R and H are taken to be the dimensions of the vane itself.

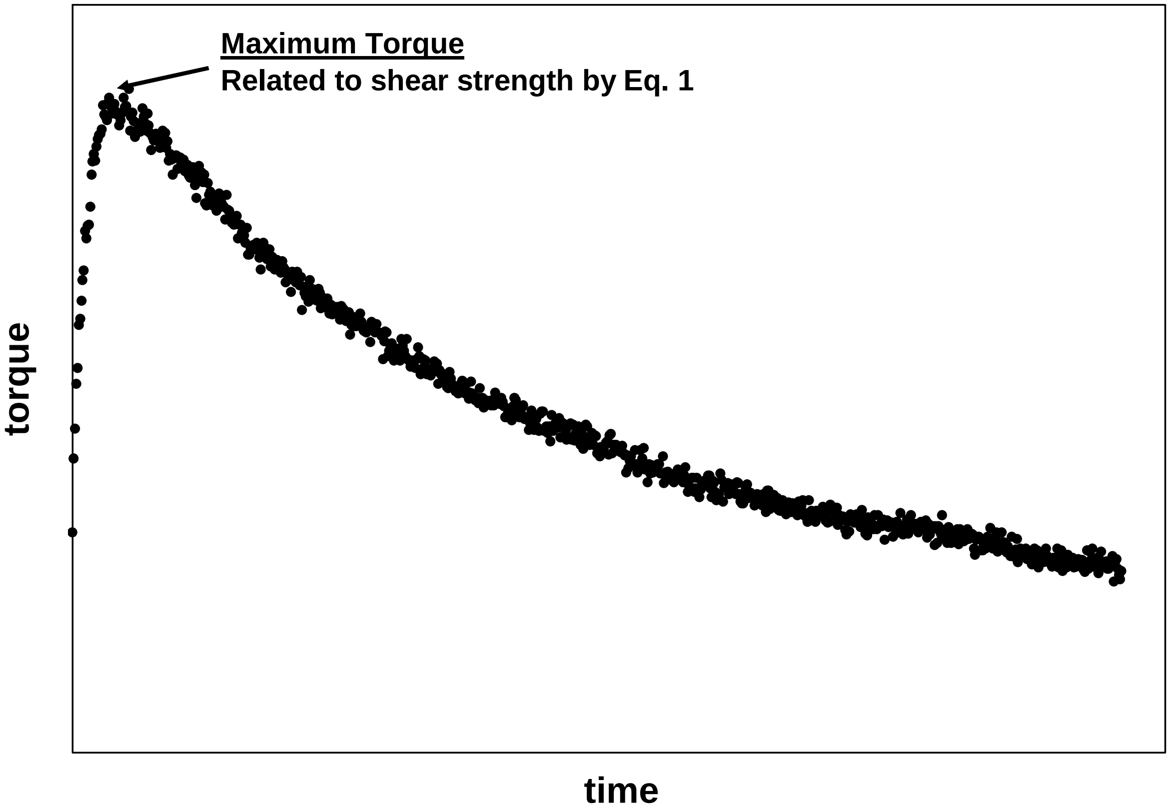


Figure 2. Example shear strength torque versus time curve. The maximum torque corresponds to the onset of motion. Here, the stress applied by vane rotation is finally sufficient to overcome frictional, cohesive, and other structural forces stabilizing the settled solids.

Proximity of the vane to the sample container inner surfaces as well as the free surface of the settled solids can impact shear strength results. As such, certain geometric constraints must be satisfied for the test to be considered independent of container geometry. These constraints are outlined in Table 1.

Table 1. Vane immersion depth and container geometry constraints for shear strength tests using the vane technique.

Constraint	Criterion	For 8×16 mm (R×H) Vane
Vane height to radius	H < 7R	H < 56 mm (Satisfied)
Container radius to vane radius	$R_{cont} > 2R$	$R_{cont} > 16$ mm
Immersion depth to vane height	h > H	h > 16 mm
Separation between bottom of vane and container floor (h_{floor})	$h_{floor} > 0.5H$	$h_{floor} > 8$ mm

Characterization of Fluid Flow – Flow Curve Testing

Non-elastic flow of tank waste slurries and supernatants is characterized with rotational viscometry. The goal of rotational viscometry is measurement of a material's flow curve, which describes the shear stress response, τ , as a function of applied shear rate, $\dot{\gamma}$ (also called the rate-of-strain). The result of a flow curve measurement is a set of τ versus $\dot{\gamma}$ measurements, which are called flow curve data. Flow curve data can be interpreted with several constitutive equations that relate viscous stress to shear-rate. Such analysis allows the flow behavior over a broad range of conditions to be described with just a few rheological descriptors such as viscosity, yield stress, consistency, and flow index.

A concentric cylinder rotational viscometer operated in controlled-rate mode will be used for flow curve testing of tank waste slurries and supernatants. These viscometers operate by placing a given volume of test sample into a measurement cup of known geometry. A cylindrical rotor attached to a torque sensor is then lowered into the sample until the slurry is even with, but does not cover, the top of the rotor. Both the radius and height of the rotor are known such that the gap distance between cup and rotor and surface area of fluid contact can be determined. In addition, the top and bottom of the rotor have recessed surfaces such that the fluid only contacts the radial surfaces of the rotor. A filled rotor-in-cup test geometry is shown in Figure 3. Determination of the fluid flow properties of the sample is made by spinning the rotor at a known rotational speed, Ω, and measuring the resisting torque, *M*, acting on the rotor. Because fluid only contacts the rotor on the radial surfaces of rotation, all of the force resisting steady-state rotation can be ascribed to shearing of the fluid in the cup-rotor gap. Assuming an isotropic fluid and cup and rotor dimensions as shown in Figure 3, the torque acting on the rotor can be directly related to the shear stress at the rotor using the equation,

$$\tau = \frac{M}{2\pi H R_I^2} \qquad \text{Eq. 2}$$

Shear stress has units of force per area [N/m²]. Calculation of the fluid shear rate at the rotor is complicated by the fact that shear rate depends on both on the measurement system geometry and the fluid rheological properties. For the simplest fluids (i.e., Newtonian fluids) the shear rate of the fluid at the rotor can be calculated given the geometry of the cup rotor shear (see Figure 3) by using the equation,

$$\dot{\gamma} = \left(\frac{2R_O^2}{R_O^2 - R_I^2} \right) \Omega \qquad \text{Eq. 3}$$

Here, shear rate has units of inverse seconds [s^{-1}]. Calculation of shear rate for materials showing more complex shear stress versus shear rate behavior (i.e., non-Newtonian fluids) requires input of flow curve parameters such as yield stress and degree of shear-thinning or shear-thickening. Because the required input parameters are typically not known prior to measurement, this requirement is typically circumvented by using a cup and rotor system with a small gap (~1 mm) such that shear rate effects introduced by fluid properties are minimized. For these systems, Eq. 3 provides an accurate determination of shear rate for non-Newtonian materials.

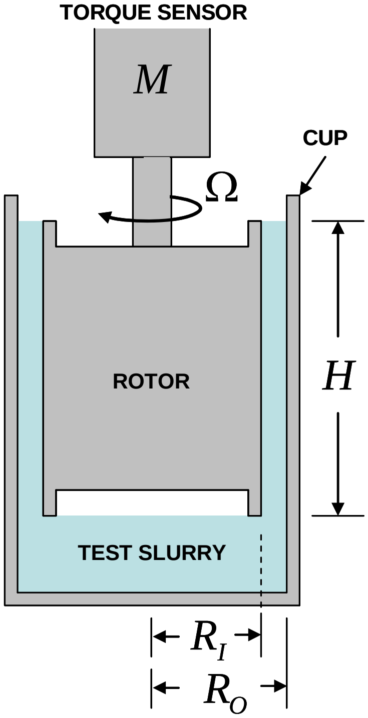


Figure 3. Rotor and cup geometry used in rotational viscometry testing.

Shear rates examined in this study will span approximately 1 to 1000 s^{-1} and are typical of the order of magnitude of shear rates experienced in pipeline flow [3]. Pipeline flows encountered in the Waste Treatment Plant may exceed the range studied herein. As such, mechanistic models of waste rheology shall be employed to fit shear stress versus shear rate data, allowing extension to shear rates beyond those studied herein.

The resistance of a fluid to flow can be described in terms of the fluid's apparent viscosity, η_{app}, which is defined as the ratio of the shear stress to shear rate:

$$\eta_{app} = \frac{\tau}{\dot{\gamma}} \qquad \text{Eq. 4}$$

Often the shear stress and viscosity vary as a function of shear rate. Since the viscosity is defined as the ratio of shear stress to shear rate, the units of the variable are Pa·s. Typically, viscosity is reported in units of centipoise (cP; where 1 cP = 1 mPa·s).

Flow curve data are usually combined plots of τ and η_{app} as a function of $\dot{\gamma}$. As stated above, flow curve data can be interpreted with several constitutive equations (i.e., flow curves), allowing characterization of that data with just a few rheological descriptors. The behavior of tank waste sludges, slurries, and supernates can be described by five common flow curve equations. These are:

- **Newtonian** – Newtonian fluids flow as a result of any applied stress and show constant viscosity over all shear conditions. The flow curve for Newtonian fluids is,

$$\tau = \eta\dot{\gamma} \qquad \text{Eq. 5}$$

where η is the Newtonian viscosity.

- **Power-Law (Ostwald)** – Power law fluids flow as a result of any applied stress and have viscosities that either increase or decrease with increasing shear rate. The are described by,

$$\tau = m\dot{\gamma}^{n} \qquad \text{Eq. 6}$$

where m is the power law consistency index and n is the power law index. Power law fluids with $n < 1$ are referred to as psuedoplastic (shear-thinning), whereas power law fluids with $n > 1$ are referred to as dilatant (shear-thickening).

- **Bingham Plastic** – Bingham plastics are fluids that show finite yield points. This stress (i.e., the yield stress) must be exceeded before these types of materials flow. Once flow is initiated, the stress response of the material is Newtonian over the rest of the shear rate range. Bingham plastics are described by,

$$\tau = \tau_o^B + k_B\dot{\gamma} \qquad \text{Eq. 7}$$

where τ_o^B is the Bingham yield index and k_B is the Bingham consistency index.

- **Herschel-Bulkley** – Fluids that behave in accordance with a Herschel-Bulkley model show a finite yield followed by power-law behavior over the rest of the shear rate range. They are described by,

$$\tau = \tau_o^H + k_H\dot{\gamma}^b \qquad \text{Eq. 8}$$

where τ_o^H is the Herschel-Bulkley yield index, k_H is the Herschel-Bulkley consistency index, and *b* is the Herschel-Bulkley power law index.

- **Casson** – Fluids that behave in accordance with a Casson model show a finite yield followed by psuedoplastic behavior. They are described by,

$$(\tau)^{0.5} = \left(\tau_o^C\right)^{0.5} + \left(k_C \dot{\gamma}\right)^{0.5} \qquad \text{Eq. 9}$$

where τ_o^C is the Casson yield index and k_C is the Casson consistency index. Although more limited in the types of flow behavior it can describe relative to the Herschel-Bulkley equation, the Casson model is popular because it is capable of accurately describing many shear-thinning fluids and because units on the parameters are more physically meaningful (e.g., the consistency is in Pa·s versus Pa·s^n for the Herschel-Bulkley model).

Power-law fluids, Bingham plastics, Herschel-Bulkley, and Casson fluids are referred to as non-Newtonian fluids. In generally, liquids without internal and/or interconnected structures (such as tank waste supernatants) are Newtonian. Sludges and slurries are typically non-Newtonian, but their exact behavior depends on the concentration of solids and suspending phase chemistry. Sufficiently dilute slurries may show Newtonian behavior.

3 Sample and Analysis

A single waste sample, Jar TI515-G7-AR-RH1, was employed for shear strength and flow curve testing of waste Group 7. This sample was derived from homogenization of tank wastes associated with processing Group 7. Flow curve testing was performed on July 31, 2008; shear strength testing was performed on October 16, 2008. Flow curve and shear strength analyses produced the following reportable data for the Group 7 initial characterization sample:

- a single measurement of settled solids shear strength after 48 to 72 hours
- flow curve data for Group 7 slurries at 25° C, 40° C, and 60° C
- best-fit Bingham-Plastic and Casson parameters at 25° C, 40° C, and 60° C

4 Instrumentation

Rheological characterization was accomplished using a Rotovisco® RV20 Measuring System equipped with an M5 measuring head and RC20 controller. These components were purchased from HAAKE Mess-Technik GmbH u. Co. (now the Thermo Electron Corporation, Madison, WI 53711). This system is installed in Cell 4 of the Shielded Analytical Laboratory (SAL) at the Radiochemical Processing Laboratory (RPL). The M5 measuring head (SN# 902398) is a "Searle" type viscometer capable of producing rotational speeds up to 500 RPM and measuring torques up to 0.049 N·m. The minimum rotational speed and torque resolution achievable by this measuring head are 0.05 RPM and 0.49 mN·m, respectively. Table 2 summarizes the M5 measuring system information.

Table 2. Summary of Haake RV20 system with M5 measuring head.

Analyzer:	Rotorvisco® RV20 Measuring System M with M5 Measuring Head.
Measurement principle:	Controlled Rate
Serial Number:	902398
Torque Sensor Range	0.49 to 49 mN·s
Rotational Rate Range	0.05 to 500 RPM

Specific measurement tools such as cup and rotor assemblies and shear vanes are attached to measure selected rheological properties. Shear strength measurements employ 8 mm ×16 mm (R × H) shear vane tool. Flow curve measurements employed an MV1 stainless steel measuring cup and rotor. The dimensions of the MV1 and vane measuring systems are listed in Table 3.

Table 3. Vane and Cup and Rotor Measuring System Dimensions.

Measuring System	Vane/Rotor Radius	Vane/Rotor Height	Cup Radius	Gap Width
Vane Tool	8 mm	16 mm	> 16 mm (a)	> 8 mm (a)
MV1	20.04 mm	60 mm	21 mm	0.96 mm
(a) Vane tests must satisfy the requirements outlined in Table 1.				

Temperature control is achieved using a combination of the standard measuring system temperature jacket and a Cole-Parmer® Polystat® Temperature-Controlled Recirculator, Model Number C-12920-00. This recirculator allows heating and cooling of recirculation fluid to the rheometer over -5° to 80º C with a stability of ±0.5° C. The temperature jacket is used only for flow curve measurements. It connects the measuring head to the measuring system, centers the cup, and provides heat transfer area between cup and recirculating fluid. The recirculating unit is located next to, but outside, the SAL Cell 4. The recirculator is connected to the water jacket through a combination of stainless steel piping (outside of cell) and flexible fiber reinforced plastic hose (inside cell). The desired temperature is set using the digital control interface on the recirculating unit. Fluid is circulated between the recirculator and jacket until the desired temperature is achieved at the jacket. Jacket temperature is monitored using a Type-K thermocouple (Omega Model TJ36-CASS-116-G-6-CC) calibrated over 0° to 100° C connected to a multichannel display unit located in the SAL Gallery. Temperature control is employed only for flow curve measurements. Shear strength measurements are carried out at ambient temperature. Details of the temperature measurement and display calibration are given in Table 4. It should be noted that only the first two channels of the temperature display were calibrated. All measurements taken herein employ channel 1.

Temperature control and measurement employed thermocouple 22887 and display 22890. For shear strength measurement of Group 7 settled solids, the ambient in-cell temperature was measured using the thermocouple attached to the Cells Unit Filter (CUF) slurry reservoir installed in SAL Cell 5 (Calibration Barcode 24072).

Table 4. Calibration information for temperature measurement and display systems.

System	Serial #	Calibration Barcode	Range Calibrated	Date Calibrated	Date Due
Type-K Thermocouple	n/a	22887	0° to 100° C (±2° C)	4/4/2008	4/4/2009
Temperature Display	6220071	22890	0° to 100° C (±2° C)	4/2/2008	4/2/2009
Type-K Thermocouple	n/a	24072	0° to 110° C (±2° C)	5/28/2008	5/28/2009

Rheometer control and data acquisition are accomplished through remote computer connection using the RheoWin Pro Job Manager Software, Version 2.96. The RheoWin software serves as a central program for obtaining, processing, and recording to disk data from the RV20-M5 Measuring System. During measurement, the software automatically converted rotor torque readings into shear stresses based on the appropriate A-factor conversion, such that

$$\tau = AM \qquad \text{Eq. 10}$$

For the cup and rotor system, the A-factor is defined by

$$A = \frac{1}{2\pi H R_I^2} \qquad \text{Eq. 11}$$

The vane tool, the A-factor is defined as:

$$A = \frac{1}{4\pi R^3 \left(\frac{H}{2R} + \frac{1}{3} \right)} \qquad \text{Eq. 12}$$

A-factors for MV1 and 8 mm × 16 mm vane sensor systems are 6570 m^{-3} and ~117,000 m^{-3}, respectively. For flow curve testing, the RheoWin software also automatically converted the rotational rate readings into shear rates based on a factory-set “M-factor”, such that:

$$\dot{\gamma} = M_R \Omega \qquad \text{Eq. 13}$$

where Ω is the rotational rate in radians per second, and M_R is the “M-factor”. The M-factor is defined as

$$M = \left(\frac{2R_O^2}{R_O^2 - R_I^2} \right) \qquad \text{Eq. 14}$$

For the MV1 sensor system, the M-factor is 22.350. The RheoWin software also allows post-measurement processing and interpretation of data. Specifically, it can be used to determine maxima points in shear strength testing and fit flow curve data to any flow curve model (i.e., Eqs. 5-9).

6 Governing Test Plan, Procedure, and Test Instructions

The test plan governing the physical characterizations for these samples is River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) document number TP-RPP-WTP-467, Revision 0 [1]. Operation of the HAAKE RV20-M5 Measurement System is governed by RPL-COLLOID-02, Revision 1 [4].

7 Experimental

The waste slurry and settled solids were tested "as-is"; that is, no sample treatment was performed prior to analysis with exception of the mechanical agitation required to disperse the waste solids in sample jar TI515-G7-AR-RH1. The sample slurry jars had been stored undisturbed, and the sludge solids had settled to the bottom of the sample jars. Immediately before flow curve testing, the solids in jar TI515-G7-AR-RH1 were dispersed uniformly by vigorously shaking the jar by remote manipulator. After shaking, the sample jar was moved to Cell 4, and a sub-sample of the slurry quickly transferred to the rheometer measuring cup to minimize the potential for settling and evaporation. Visual inspection of the slurry during and after transfer found no immediately observable solids settling. Shear strength testing was done at a later date. Before shear strength testing, settled slurry solids were again dispersed uniformly by vigorously shaking the jar by remote manipulator. The dispersion was then transferred to Cell 4 and allowed to settle for 72 hours. After this period of time, the shear strength of the settled solids was measured.

Instrument Performance Check

As required by RPL-COLLOID-02, the performance of the Haake M5 rheometer must be verified at the beginning of each series of analyses (with the period between performance checks not to exceed 30 days during use). Checks are performed using Newtonian viscosity standards certified by methods traceable to the United States National Institute of Standards and Technology (NIST). Checks verify that the Haake M5 rheometer can measure the standard's viscosity to within 10% for fluids of 10 cP or greater and to within 15% for fluids less than 10 cP at the temperature listed on the certificate of analysis.

For the measurements described in this report, the performance check employed General Purpose Silicone Fluids purchased from Brookfield Engineering Laboratories, Inc. (Middleboro, Massachusetts, USA, 02346). Silicone oils are single phase liquids and have no suspended solids. For testing, two standards were used: Brookfield Fluid 10 and Brookfield Fluid 100. Tables 5 to 6 provide a summary of each viscosity standard's properties. Standards are traceable back to their certificate of analysis through a unique lot number.

Table 5. Properties of Brookfield Fluid 10.

Fluid	10
Viscosity	9.1 cP
Temperature	25
Lot Number	021308
Expires	April 2009

Table 6. Properties of Brookfield Fluid 100.

Fluid	100
Viscosity	98.2 cP
Temperature	25
Lot Number	020108
Expires	April 2009

Performance checks consisted of temperature controlled flow curve measurements that employed the MV1 measuring cup and rotor. The instrument performance check covering the period of testing for Group 7 slurry flow curve measurement was run on July 16th, 2008; the performance check covering Group 7 settled solids shear strength measurements took place on October 7th, 2008. In both cases, execution of performance verifications was as follows:

1. The MVI rotor was installed on the M5 measuring head.
2. The temperature jacket was installed and the recirculator turned on and set to 25° C. The jacket was allowed to achieve temperature equilibrium before continuing.
3. Approximately 40 to 50 mL of viscosity fluid was added to the MV1 cup.
4. The measuring cup was installed into the water jacket by slowly raising it on a laboratory jack stand. During installation, the cup slides into the base of the water jacket where it slides over the rotor. The rotor volume displaces the test material, forcing it to fill the gap between cup and rotor. While the cup was being raised, the liquid level relative to the top of the rotor was monitored through an opening in the top of the water jacket using a small digital video camera installed in-cell. The cup was raised until the test material was observed to spill over the top of the rotor. Before continuing, an attempt was made to remove the excess viscosity standard from the top of the rotor using a plastic transfer pipette. However, 1 to 3 mL of excess test liquid could not be retrieved and remained in the upper rotor recess during flow curve measurement.
5. The viscosity standard was left undisturbed in the measuring system for 5 minutes to allow temperature equilibration.
6. The material flow curve data were measured. Rheological analysis was performed over a 15-minute period, split into three 5-minute intervals. Over the first 5 minutes, the shear rate was smoothly increased from zero to 1000 s^{-1}. For the second 5 minutes, the shear rate is held constant at 1000 s^{-1}. For the final 5-minutes, the shear rate was smoothly reduced back to zero. During this time, the resisting torque and rotational rate is continuously monitored and recorded.

After the measurement, flow curve data were automatically fit to a Newtonian model (Eq. 5) by the RheoWin software. The regressed value was saved to the measurement file and was also transcribed into the LRB. The absolute percent error, E, between the measured viscosity, η_{meas}, and that listed on the certificate of analysis, η_{list}, was calculated as:

$$E = \left| \frac{\eta_{meas} - \eta_{list}}{\eta_{list}} \right| \times 100\% \qquad \text{Eq. 15}$$

The performance check is considered acceptable if E is less than 10% for fluids with list viscosities greater than or equal to 10 cP or is less than 15% for fluids with list viscosities less than 10 cP. Before the start of any quality affecting measurements of Group 7 rheology, the RV20-M5 was verified to be in acceptable performance. Table 7 lists the results of each performance verification/check carried out in association with Group 7 Initial Characterization efforts. As indicated in the table, the RV20-M5 measuring system showed acceptable performance for all tests.

Table 7. Results of rheometer performance checks.

Fluid	Period of Performance	List Viscosity (cP)	Measured Viscosity (cP)	*E*	Acceptable
Brookfield Fluid 10	July '08	9.1	9.9	8.7%	Yes
Brookfield Fluid 100	July '08	98.2	100.9	2.7%	Yes
Brookfield Fluid 100	October '08	98.2	99.1	0.9%	Yes

Shear Strength Testing

A single measurement of shear strength was made on settled solids in sample jar TI515-G7-AR-RH1. Because the volume of settled solids in the test jar as it was provided for shear strength measurement was limited, it was not possible to satisfy the insertion depth and floor clearance constraints outlined in Table 1. After 72 hours of settling, the settled solids provided approximately 20 mm of height of settled solids for testing. To avoid contact with the floor of the sample jar, the vane was immersed until the top of the blades were just beneath the surface of the solids. Because the constraints in Table 1 were not satisfied during testing, the shear strength result reported herein is not independent of container geometry.

The settled solids in test jar TI515-G7-AR-RH1 were dispersed 72 hours before testing and allowed to settle undisturbed for the entire period between dispersion and testing. The shear strength test was performed directly in the 120 mL Qorpak sample jar in which the slurry was provided. Shear strength testing was conducted as follows:

1. A 8×16 mm (radius by height) shear vane tool was installed on the measuring head.
2. The sample jar being tested was opened and positioned on a laboratory jack stand directly beneath the measuring head/vane.
3. The lab jack was slowly raised until the maximum vane insertion depth was achieved.
4. The vane was slowly rotated at 0.3 RPM for 240 seconds. For the entire duration of rotation, the time, rotational rate, and vane torque were continuously monitored and recorded.
5. At the completion of testing, the vane was removed from the settled solids and rinsed clean of residual solids with deionzied (DI) water. The sample jar was closed and set aside.

At the end of the measurement, the software parsed the shear stress versus time data and determined and reported the maximum measured shear stress (i.e., the material's shear strength). The curve of shear stress versus time was visually inspected using the RheoWin software to verify that the appropriate stress maximum was selected. All information relevant to the measurement, including raw and calculated measurement results and sample information, are saved to disk using the RheoWin file format and a unique filename identifier. The shear strength and filename associated with that measurement, along with a basic sample identifier, are recorded in a Laboratory Record Book (LRB). A separate data file is used for each shear strength measurement. It should be noted that shear strength measurements were conducted at ambient cell temperature (27.6° C).

Flow Curve Testing

Flow curve testing for slurry sample TI515-G7-AR-RH1 employed an MV1 cup and rotor. Each flow curve measurement was accomplished as follows:

1. The MV1 rotor was installed on the measuring head.
2. The temperature jacket was installed and the recirculator turned on and set to 25° C. The jacket was allowed to achieve temperature equilibrium.
3. The test sample was transferred from its source jar into the MV1 measurement cup. Sample was added to the cup until the fluid level was above the first (i.e., lowest) cup level marker but still below the second level marker. This typically required 40 to 50 mL of sample. Gross material transfer was accomplished by pouring the sample into the test container until a rough estimate of the required sample volume was obtained. Fine level adjustments were made by adding and removing material to and from the measuring cup using a plastic transfer pipette.
4. The measuring cup was installed into the water jacket by slowly raising it on a laboratory jack stand. The cup was raised until the test material was observed to spill over the top of the rotor. Before continuing, excess material was removed from the top of the rotor (to the extent possible) using a plastic transfer pipette. In most cases, there was approximately 1-3 mL of excess material that could not be removed from the upper rotor recess.
5. A moisture barrier was wetted and installed over the opening at the top of the temperature jacket. This barrier is a stainless steel clamshell collar lined with a sponge. It serves to minimize sample evaporation by blocking openings at the top of the water jacket (where the sample is exposed to air) and by humidifying the air space above the sample.
6. The sample was left undisturbed in the measuring system for 5 minutes to allow temperature equilibration.
7. The sample was sheared for 3 minutes to break sample structure, to attempt re-suspension any settled slurry particles, and to verify that the rotor was properly centered.
8. The material flow curve data were measured. Rheological analysis was performed over a 15-minute period, split into three 5-minute intervals. Over the first 5 minutes, the shear rate was smoothly increased from zero to 1000 s^{-1}. For the second 5 minutes, the shear rate was held constant at 1000 s^{-1}. For the final 5-minutes, the shear rate was smoothly reduced back to zero. During this time, the resisting torque and rotational rate were continuously monitored and recorded.
9. The flow curve data for 25° C were saved using the RheoWin file format and a unique filename identifier. Sample information and the associated RheoWin filename were entered into the LRB.
10. The cup was raised so that fresh sludge/slurry filled the gap. Excess sludge was pipetted from the top. The moisture guard was, removed, re-wetted, and then re-installed.
11. The flow curve measurement at 25° C was repeated as per steps 7 through 9.
12. The temperature set point was set to 40° C. Once, the jacket had reached the temperature set point, the sample was allowed an additional 5 minutes to reach temperature equilibrium. The cup was raised so that fresh sludge/slurry filled the gap. Excess sludge was pipetted from the top. The moisture guard was, removed, re-wetted, and then re-installed.
13. The flow curve at 40° C was measured as per steps 7 through 9.
14. The temperature set point was set to 60° C. Once, the jacket had reached the temperature set point, the sample was allowed an additional 5 minutes to reach temperature equilibrium. The cup was raised so that fresh sludge/slurry filled the gap. Excess sludge was pipetted from the top. The moisture guard was, removed, re-wetted, and then re-installed.
15. The flow curve at 60° C was measured as per steps 7 through 9.
16. At the end of testing, the measuring cup was removed from the system. The test material was returned to its original container. The measuring system was disassembled. Any slurry or

precipitated salt solids remaining in the cup or rotor were cleaned-off using by rinsing with copious amounts of water and by wiping down the instrument with a damp cloth.

At the end of each flow curve or constant rotation measurement, all information relevant to the measurement, including raw and calculated measurement results and sample information, were saved to disk using the RheoWin file format and a unique filename identifier. The filename, temperature, start and end of temperature equilibration, and a basic sample identifier were recorded in a Laboratory Record Book (LRB). A separate data file was used for each flow curve measurement.

Post-measurement analysis and review of flow curve data were accomplished using the RheoWin Pro Data Manager software, Version 2.96. For each set of measurement data, the flow curve data was characterized by determining the best-fit parameters for the constitutive equation outlined in Section 2.0 of this report (i.e., the Newtonian, Power-Law, Bingham-Plastic, Herschel-Bulkley, and Casson flow models). This analysis utilized the least-squares data regression routine native to the RheoWin 2.96 software. Regressions typically included both up- and down-ramp portions of the flow curve, resulting in an “average” set of model parameters for the total flow curve. Model fits were often limited to specific shear rate ranges to avoid flow curve anomalies such as Taylor Vortex formation.

8 Results and Discussion

Results of Shear Strength Testing

The result for Group 7 initial characterization shear strength testing is shown in Table 8. The single measurement for sample TI515-G7-AR-RH1 settled solids at 72 hours of settling time indicates shear strength of 23 Pa. Because the vane immersion requirements could not be met, the shear strength reported for Group 7 settled solids is likely influenced by proximity of the vane to the surface of the solids and the floor of the test jar.

Table 8. Shear strength of Group 7 Initial Characterization settled solids at ambient hot-cell temperature (27.6° C)

Test Sample	Settling Time	Shear Strength [Pa]
TI515-G7-AR-RH1	72 hours	23 Pa

The degree to which the measured shear strength for Group 7 settled solids is affected by limited immersion is difficult to ascertain. It can be speculated that proximity of the top of the vane to the surface of the settled solids lowers the measured shear strength as the vane no longer has to shear settled solids above the top of the blades (i.e., the upper rotational surface). In contrast, proximity of the vane and floor of the test container likely increases the measured value of shear strength through frictional contact and stress chain formation between vane, solid slurry particles, and the container floor. Such coupling effects were observed during the measurement of Group 4 settled shear strength solids strength [5], where shear strength was made at both central and radial test locations. Because of limited space for Group 4 settled solids testing, radial test locations were run with wall-vane clearances of 1-vane radius or less. Two repeat tests at radial locations exhibited shear strengths ~3 times greater than that at the central location.

Because of the limitations of the current test for shear strength, the strength of 23 Pa measured for Group 7 settled solids should be approached with caution. The measurement is likely affected by competing effects of proximity of the vane to the surface of the settled solids and to the floor of the container and, as such, it should be treated as an order of magnitude estimate.

Results of Flow Curve Testing – Group 7 Slurry

Figure 4 shows the results of flow curve testing for the Group 7 initial characterization slurry sample, TI515-G7-AR-RH1. The measured flow curves indicate non-Newtonian slurry behavior, with the slurry showing finite yield stress, shear-thinning, and significant hysteresis.

Flow curve hysteresis is illustrated more clearly in Figure 5, which shows flow curve data for the initial measurement at 25°C. As indicated by the figure, the up-ramp stress response is significantly higher than the down-ramp stress response and shows a higher degree of shear thinning behavior. The nature of hysteresis is similar during the repeat measurement at 25°C and during the single measurement at 40°C. Although the flow curve data at 60°C show hysteresis, the difference between the up- and down-ramp curves is significantly smaller than at the lower temperatures. The exact cause of hysteresis in the current measurements is difficult to ascertain from flow curve data alone. However, because the hysteresis is characterized by a transient decrease in stress response over the course of the measurement, it can be speculated that hysteresis results from either shear-induced solids structure changes (i.e., sample thixotropy) or as a result of solids settling out of the measurement gap.

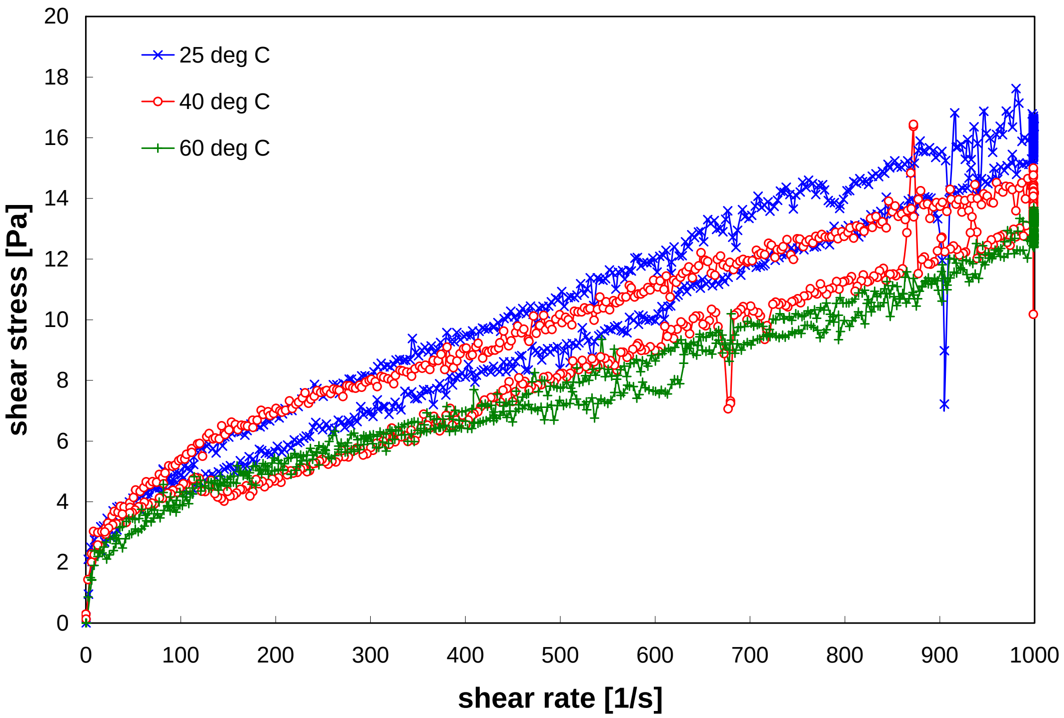


Figure 4. Flow curve (shear stress versus shear rate) for the Group 7 initial characterization slurry sample TI515-G7-AR-RH1 at 25°C, 40°C, and 60°C. The second repeat measurement for 25° C is shown.

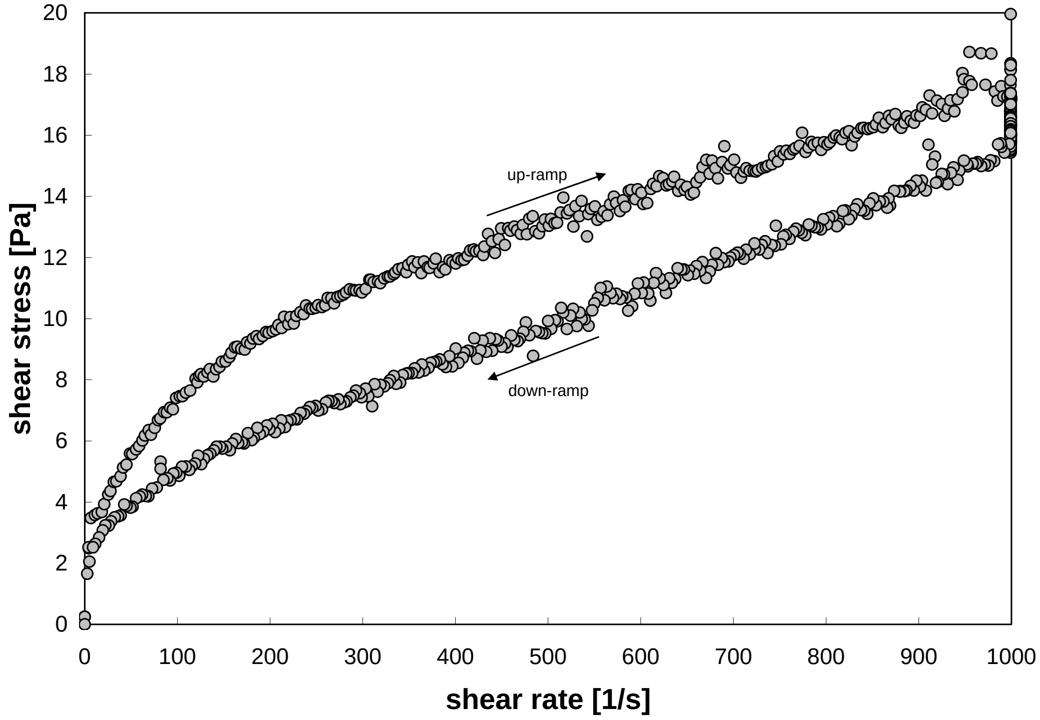


Figure 5. Initial flow curve measurement of sample TI515-G7-AR-RH1 at 25°C highlighting significant flow curve hysteresis.

Significant data overlap between the different temperature results from measurement hysteresis. As such, it is difficult to clearly determine how temperature influences the flow curve data. Despite this difficultly, some trends can be based on rough visual inspection of the data. First, all flow curve data indicate a slurry yield stress that falls between 2 and 4 Pa. Based on a rough average of upper and lower data bounds at each temperature, it appears that the stress response of the fluid (i.e., the slurry consistency) decreases with increasing temperature.

The flow curve data measured for sample TI515-G7-AR-RH1 are fit to both Bingham-Plastic and Casson constitutive equations to obtain a quantitative description of flow behavior. Because of the significant hysteresis, it is not feasible to derive an averaged set of flow curve parameters by fitting both up- and down-ramp flow curve data simultaneously. Instead, flow curve fits are limited to down-ramp data alone (shown in Figure 6). Exclusion of up-ramp data is based on the assumption that hysteresis likely results from transient break down of slurry structure, and that the well-mixed flow behavior is most closely represented by the down-ramp flow curve data. For Bingham-Plastic fitting analysis, data fits are restricted to a shear rate range of 100-1000 s^{-1} at 25°C and 40°C and of 100-800 s^{-1} at 60°C. The lower bound excludes the non-linear region that occurs over 0-100 s^{-1} from the Bingham fitting analysis as this model cannot account for curvature. The 800 s^{-1} upper bound excludes 60°C down-ramp data that exhibit a sharp and unexpected increase in slope.

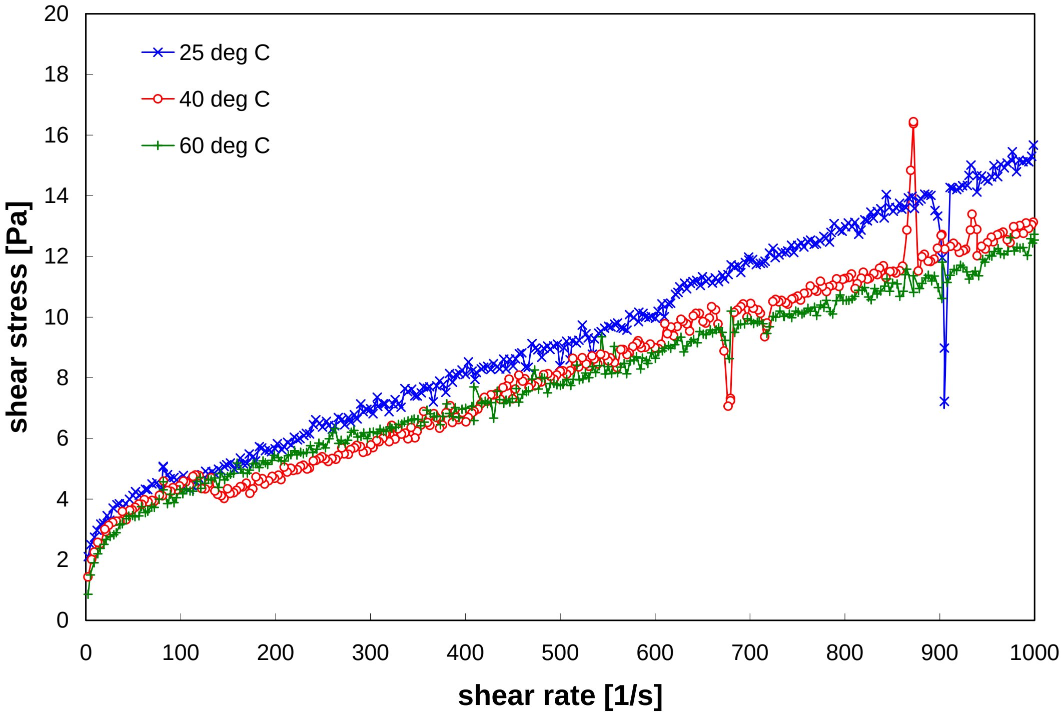


Figure 6. Down-ramp flow curve data for the Group 7 initial characterization slurry sample TI515-G7-AR-RH1 at 25°C, 40°C, and 60°C. The second repeat measurement for 25° C is shown.

Table 9 summarizes the best-fit Bingham-Plastic and Casson parameters for sample TI515-G7-AR-RH1. The Bingham-Plastic parameters indicate a slurry yield stress and consistency that range from 2.8 to 4.1 Pa and a 8.9 to 12 mPa·s, respectively. Likewise, the Casson model indicates a yield stress and consistency that range from 1.3-1.9 Pa and 4.4 to 6.6 mPa·s. As shown in Figure 7 (and also by the similarity of their correlation coefficients - R), the Casson and Bingham-Plastic models provide roughly the same fit of the data. The lower consistency and yield stress provided by the Casson fits is simply a result of model curvature.

The fitting results in Table 9 indicate do not provide much insight into how slurry yield stress and consistency behave as a function of temperature. Although Bingham-Plastic yield stress varies over a significant range 2.8-4.1 Pa, its variation does not track with temperature. Yield stress reproducibility is poor, as indicated by the significant difference of 0.8 Pa in initial and repeat measurements at 25°C (4.1 and 3.3 Pa, respectively). Similar yield stress issues are observed with the Casson fits.

Slurry consistency does not vary significantly for the repeat measurements at 25°C and the measurement 40°C. Bingham-Plastic and Casson consistencies range from 11-12 and 6.0-6.6 mPa·s, respectively. Because both ranges cover less than the expected limit of instrument accuracy of 10%, it is unlikely that the variation between slurry consistency at 25°C and 40°C is significant. On the other hand, Bingham-Plastic consistency drops from 11 to 8.9 mPa·s as slurry temperature is raised from 40°C to 60°C. Although this is a significant decrease, it is difficult to state that this decrease would continue at higher temperatures with confidence given the variation in the yield stress results. Overall, the fitting results do not indicate strong temperature trends, as it is difficult to distinguish measurement-to-measurement variation from changes induced by increased temperature. It is speculated that the significant flow curve hysteresis is the source of measurement-to-measurement variation.

Table 9. Results of fitting analysis for rheology sample TI515-G7-AR-RH1. All model parameters are based on down-ramp data only.

MODEL	TEMPERATURE [°C]	RANGE	YIELD STRESS [PA]	VISCOSITY [MPA·S]	R
Bingham-Plastic (Flow Curve)	25 (1 of 2)	100-1000 s^{-1}	4.1	11	1.00
	25 (2 of 2)	100-1000 s^{-1}	3.3	12	0.98
	40	100-1000 s^{-1}	2.8	11	0.98
	60	100-800 s^{-1}	3.5	8.9	0.99
Casson (Flow Curve)	25 (1 of 2)	0-1000 s^{-1}	1.9	6.3	1.00
	25 (2 of 2)	0-1000 s^{-1}	1.6	6.6	0.98
	40	0-1000 s^{-1}	1.3	6.0	0.98
	60	0-800 s^{-1}	1.8	4.4	0.99

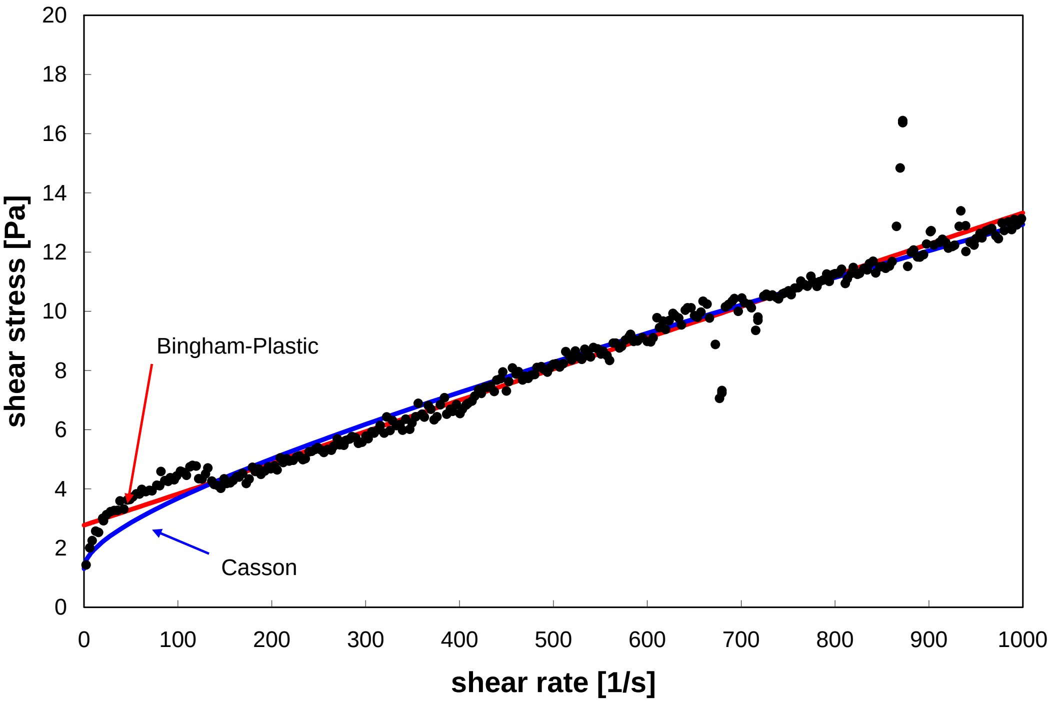


Figure 7. Example result for the fitting analysis of Group 7 initial characterization sample TI515-G7-AR-RH1. Data points (solid circles) correspond to the measurement at 40°C. The solid lines correspond to the best-fit Bingham-Plastic and Casson model calculations.

To supplement flow curve measurement and analysis, apparent viscosities for slurry sample TI515-G7-AR-RH1 were determined at 33, 100, 500, and 1000 s^{-1}. Two separate approaches were employed to determine apparent viscosity at these shear rates: 1) from actual measurement data and 2) from the flow curve fitting parameters listed in Table 9. Table 10 lists apparent viscosities determined from the actual shear versus shear rate measurement data. Here, apparent viscosities for both up- and down-ramp data, as well as an average of the two, are given for shear rates of 33, 100, 500 s^{-1}. The apparent viscosity for 1000 s^{-1} listed in Table 10 is determined by average all apparent viscosity observations made during the period of constant rotation at 1000 s^{-1}. Table 11 lists the apparent viscosities calculated using the Bingham-Plastic and Casson constitutive equations (i.e., Eqs. 7 and 9) with the apparent viscosity relationship Eq. 4. The results in Table 11 are based on fits of down-ramp data, and should match most closely with the down-ramp viscosities listed in Table 10.

Table 10. Apparent viscosities at select shear rates for sample TI515-G7-AR-RH1. Reported values are determined from flow curve measurement data.

Temperature [°C]	Section	Apparent Viscosity [mPa·s]			
		@ 33 s^{-1}	@ 100 s^{-1}	@ 500 s^{-1}	@ 1000 s^{-1}
25 (1 of 2)	up-ramp	142	74	26	n/a
	down-ramp	106	49	20	n/a
	average	124	62	23	16
25 (2 of 2)	up-ramp	94	49	22	n/a
	down-ramp	116	45	17	n/a
	average	105	47	19	16
40	up-ramp	111	54	20	n/a
	down-ramp	99	45	16	n/a
	average	105	49	18	14
60	up-ramp	82	39	15	n/a
	down-ramp	90	43	15	n/a
	average	86	41	15	13

Table 11. Apparent viscosities at select shear rates for sample TI515-G7-AR-RH1. Reported values are calculated from the flow curve fitting parameters listed in Table 9.

Source	Temperature [°C]	Apparent Viscosity [mPa·s]			
		@ 33 s^{-1}	@ 100 s^{-1}	@ 500 s^{-1}	@ 1000 s^{-1}
Bingham-Plastic	25 (1 of 2)	140	52	20	15
	25 (2 of 2)	110	45	18	15
	40	95	38	16	13
	60	110	44	16	12
Casson	25 (1 of 2)	100	47	20	15
	25 (2 of 2)	90	43	19	15
	40	76	37	17	13
	60	90	40	16	12

The results in Table 10 and 11 indicate apparent viscosities that range from ~80 to ~140 mPa·s at low shear (33 s^{-1}) but that quickly decay down to ~12 to 16 mPa·s at high shear rates (1000 s^{-1}). High apparent slurry viscosity at low shear is not surprising given the ~2 to 4 Pa yield stress of the slurry. In addition, up- and down-ramp data in Table 10 show significant difference; however, this difference is indicative of flow curve hysteresis.

In summary, flow curve analysis for Group 7 Initial Characterization slurry sample TI515-G7-AR-RH1 indicates non-Newtonian rheology. Fits of the data to a Bingham-Plastic parameters indicate a slurry yield stress and consistency that range from 2.8 to 4.1 Pa and a 8.9 to 12 mPa·s, respectively.

Similar fits using the Casson model indicate a yield stress and consistency that range from 1.3-1.9 Pa and 4.4 to 6.6 mPa·s Overall, experimental and fitting results do not indicate strong temperature trends, as it is difficult to distinguish measurement-to-measurement variation from changes induced by increased temperature. One cause for this difficulty is that the flow curve measurements are subject to significant hysteresis. Specifically, the slurry shows a transient decrease in stress response throughout the course of the measurement such that the down-ramp stress response falls below that observed during the up-ramp. This behavior is consistent slurry thixotropy or could indicate solids settling during flow curve testing.

9 Records

Data records relating to rheological characterization of Group 7 Initial Characterization samples include original Computational Computer Package (CCPs) and LRB entries. These include:

- LRB BNW 59633 – Pages 132 and 146-147
- CCP-WTPSP-616 – Group 7 initial characterization shear strength
- CCP-WTPSP-642 – Group 7 initial characterization slurry flow curves

References

1. Doc. No. TP-RPP-WTP-467, Revision 0, “Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes,” SK Fiskum, Battelle – Pacific Northwest Division, February 2007.

2. Barnes HA, and NQ Dzuy, “Rotating vane rheometry - a review,” J. Non-Newtonian Fluid Mech., 1-14 (2001).

3. Steffe JF, *Rheological Methods in Food Process Engineering*, Freeman Press, East Lansing (1996).

4. Doc. No. RPL-COLLOID-02, Revision 1, “Measurement of Physical and Rheological Properties of Solutions, Slurries and Sludges,” RC Daniel, Pacific Northwest National Laboratory, May 2007.

5. Doc. No. TDP-WTP-286, Revision 0, “Rheology of Waste Processing Group 4 (REDOX Cladding Waste Sludge): Initial Characterization,” RC Daniel, Pacific Northwest National Laboratory, October 2008.

10 Rheograms

This section contains detailed rheograms (shear stress and apparent viscosity as a function of shear) for Group 7 Initial Characterization slurry sample TI515-G7-AR-RH1. No discussion of these results is provided. They are provided for reference only.

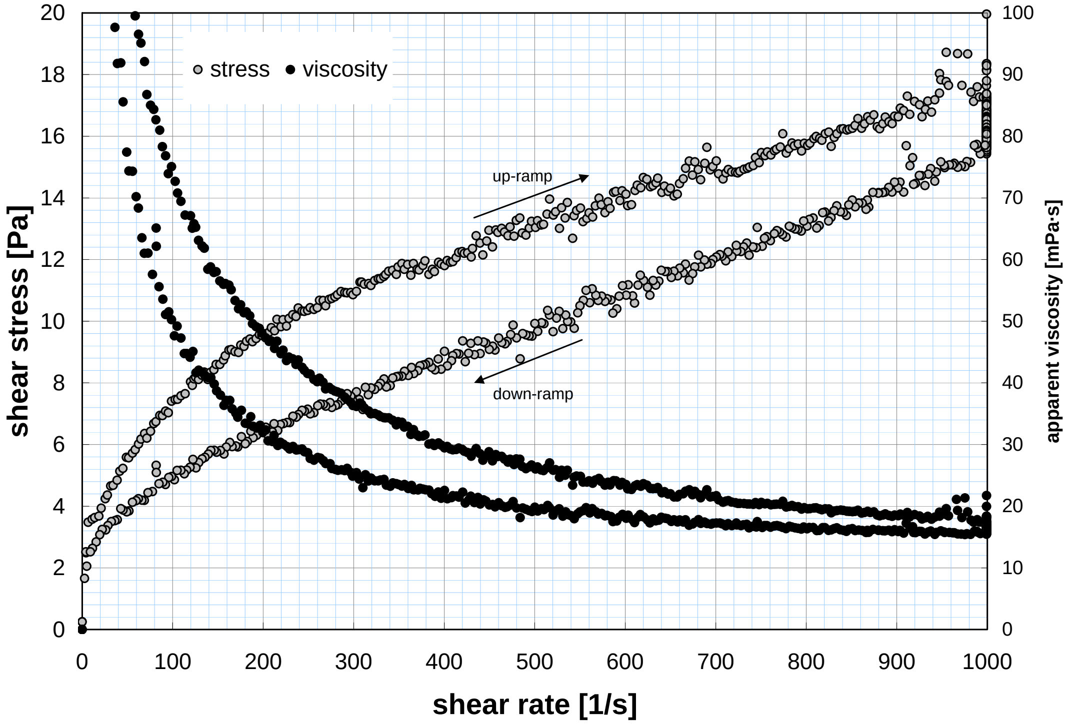


Figure 10-1. Rheogram for TI515-G7-AR-RH1 at 25°C.

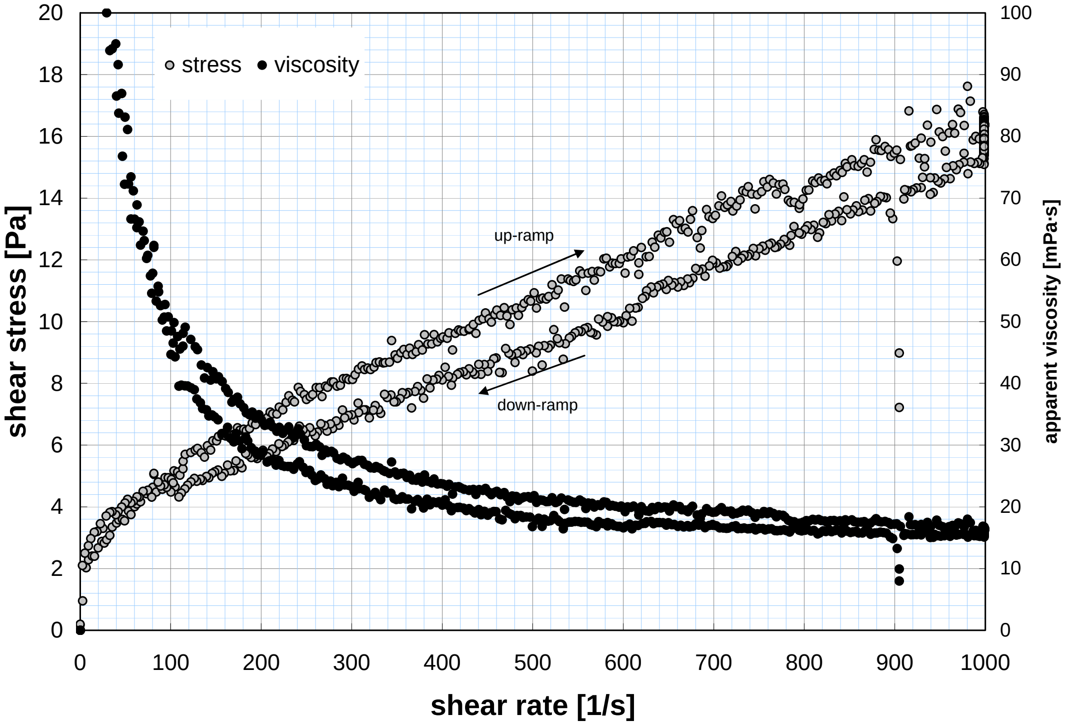


Figure 10-2. Replicate rheogram for TI515-G7-AR-RH1 at 25°C.

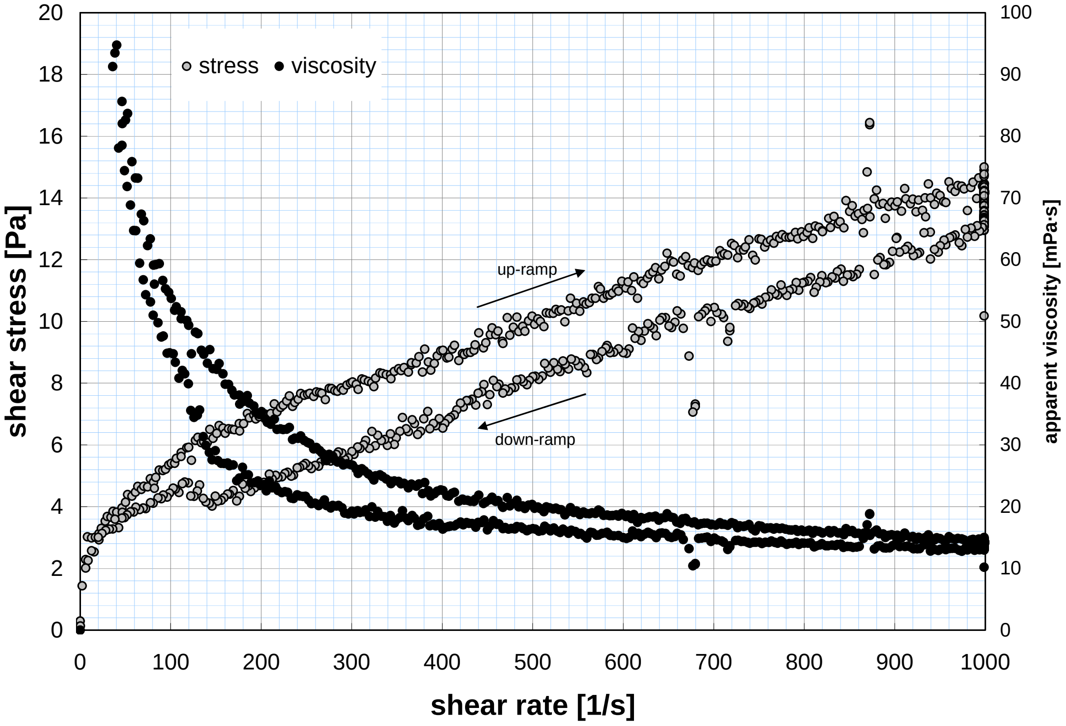


Figure 10-3. Rheogram for TI515-G7-AR-RH1 at 40°C.

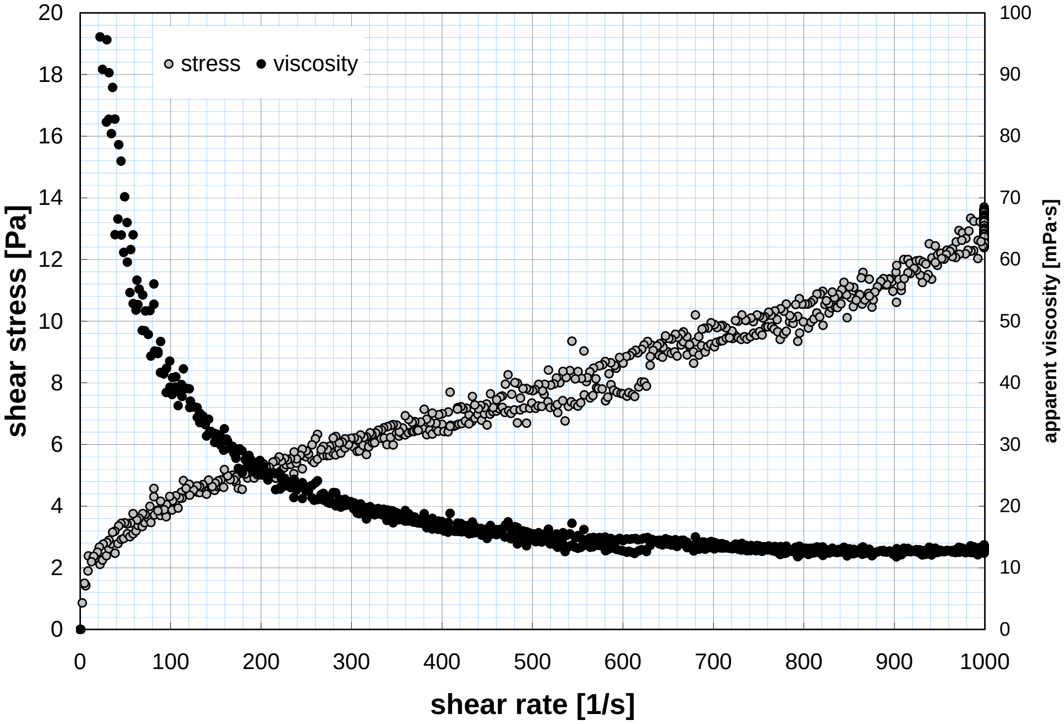


Figure 10-4. Rheogram for TI515-G7-AR-RH1 at 60°C.

Appendix G

Group 7 Analytical Results from Parametric Leaching

Appendix G: Group 7 Analytical Results from Parametric Leaching

Table G.1 provides information about analyte concentrations during leaching at various time increments at 40°C in units of µg/mL, Table G.2 at 40°C in units of M, Tables G.3 and G.4 at 60°C in units of µg/mL and M, respectively, and Tables G.5 and G.6 at 80°C in units of µg/mL and M, respectively. All data in the following tables are from CCP-WTPSP-689, Group 7 parametric leaching liquid results.

Table G.1. Analyte Concentrations as a Function of Time for Leaching at 40ºC, in µg/mL

	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; µg/mL for Metals and Anions; µCi/mL for Radionuclides					
Analyte	**0 hr**	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
1 M NaOH						
Density	1.04	1.05	1.06	1.05	1.05	1.05
Al	29.2	55.1	57.7	59.9	59.2	71.0
B	[0.411]	[0.405]	[0.376]	[0.449]	[0.355]	[1.85]
Bi	<0.948	<0.935	<0.941	<0.962	<0.711	<4.63
Cd	<0.107	<0.106	<0.107	<0.109	<0.081	<0.525
Cr	[0.272]	[0.374]	[0.408]	[0.417]	0.512	[0.679]
Fe	3.82	2.55	2.30	2.28	1.99	[2.44]
Mn	0.245	0.223	0.219	0.217	0.165	[0.210]
Na	24,045	24,454	24,426	24,552	25,120	25,219
Ni	<0.076	<0.075	<0.075	<0.077	<0.057	<0.370
P	423	607	611	619	604	611
S	<5.06	<4.98	<5.02	<5.13	<3.79	24.7
Si	5.78	21.0	23.1	24.0	23.4	21.1
Sr	0.088	[0.047]	[0.038]	[0.030]	[0.024]	[0.034]
U	239	163	137	109	80.1	59.3
Zn	2.60	3.03	2.86	2.80	2.63	[3.70]
Zr	<0.035	<0.034	<0.034	<0.035	<0.026	<0.170
Fluoride	[6.60]	[8.00]	[7.90]	[8.00]	[7.80]	[8.10]
Nitrite	[7.60]	[7.90]	[7.60]	[7.60]	[7.60]	[7.70]
Nitrate	[80.7]	84.4	81.7	83.2	82.7	83.8
Phosphate	1,370	1,950	1,870	1,890	1,880	2,020
Sulfate	9.50	[11.0]	[10.0]	[10.0]	[10.0]	[10.0]
^{60}Co	Not Measured					< 4.E-6
^{137}Cs						0.245
^{154}Eu						< 1.E-5
^{155}Eu						< 1.E-4
^{241}Am						< 1.E-4
Opportunistic Analytes						
Ag	<0.066	<0.065	[0.09]	<0.067	[0.05]	<0.324
As	<1.359	<1.340	<1.348	<1.378	<1.019	<6.637
Ba	[0.07]	[0.09]	[0.10]	[0.08]	0.14	[0.05]
Be	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]	<0.008

Table G.1 (Contd)

Analyte	**Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides**					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Ca	2.38	2.23	2.24	2.10	1.50	[5.86]
Ce	<0.316	<0.312	<0.314	<0.321	<0.237	<1.543
Co	<0.076	<0.075	<0.075	<0.077	<0.057	<0.370
Cu	0.55	0.69	0.52	0.56	0.43	[0.59]
Dy	<0.092	<0.090	<0.091	<0.093	<0.069	<0.448
Eu	<0.035	<0.034	<0.034	<0.035	<0.026	<0.170
K	[11.06]	[18.07]	[21.32]	[21.80]	24.41	<11.112
La	<0.088	<0.087	<0.088	<0.090	<0.066	<0.432
Li	[0.30]	0.40	[0.38]	0.49	0.39	[0.77]
Mg	<0.073	<0.072	<0.072	<0.074	<0.055	<0.355
Mo	<0.164	<0.162	<0.163	<0.167	<0.123	<0.803
Nd	<0.171	<0.168	<0.169	<0.173	<0.128	<0.833
Pb	<1.011	[1.25]	<1.003	<1.026	<0.758	<4.939
Pd	<0.199	<0.196	<0.198	<0.202	<0.149	<0.972
Rh	<0.379	<0.374	<0.376	<0.385	<0.284	<1.852
Ru	<0.269	<0.265	<0.267	<0.272	<0.201	[1.73]
Sb	<0.632	[0.78]	<0.627	<0.641	<0.474	<3.087
Se	<2.212	<2.181	<2.195	<2.244	<1.659	<10.804
Sn	<0.853	<0.841	<0.847	<0.865	<0.640	<4.167
Ta	<0.537	<0.530	<0.533	<0.545	<0.403	<2.624
Te	<0.822	<0.810	<0.815	<0.833	<0.616	<4.013
Th	<0.310	<0.305	<0.307	<0.314	<0.232	<1.513
Ti	[0.05]	[0.03]	[0.03]	[0.02]	[0.02]	<0.066
Tl	<1.201	<1.184	<1.192	<1.218	<0.901	<5.865
V	<0.023	[0.04]	[0.05]	[0.08]	[0.09]	[0.17]
W	<0.600	<0.592	<0.596	<0.609	<0.450	<2.932
Y	<0.014	<0.014	<0.014	<0.014	<0.010	<0.068
3 M NaOH, Trial a						
Density	1.13	1.13	1.13	1.13	1.13	1.14
Al	42.5	62.2	62.9	66.6	70.0	88.1
B	[1.61]	[1.47]	[0.762]	[1.02]	<0.740	<0.747
Bi	<4.83	<4.89	<4.76	<4.78	<4.62	<4.67
Cd	<0.547	<0.554	<0.540	<0.542	<0.524	<0.529
Cr	[0.483]	[0.554]	[0.699]	[0.605]	[0.863]	[1.28]
Fe	16.4	11.8	11.4	10.5	10.1	9.21
Mn	[0.483]	[0.391]	0.314	[0.284]	[0.253]	[0.246]
Na	74,374	73,282	72,709	73,933	72,732	73,782
Ni	<0.386	<0.391	<0.381	<0.382	<0.370	<0.374
P	547	651	651	644	656	654
S	<25.8	<26.1	<25.4	<25.5	<24.7	<24.9
Si	9.11	24.9	25.5	25.7	26.7	26.9
Sr	[0.225]	[0.121]	[0.092]	[0.080]	[0.065]	[0.056]
U	200	111	94.0	70.1	61.3	[43.6]

Table G.1 (Contd)

	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; µg/mL for Metals and Anions; µCi/mL for Radionuclides					
Analyte	**0 hr**	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Zn	[4.51]	[5.21]	5.40	[5.42]	[5.55]	[5.29]
Zr	<0.177	<0.179	<0.175	<0.175	<0.170	<0.171
Fluoride	<11.0	<11.0	<10.0	<10.0	<10.0	<10.0
Nitrite	[7.50]	[8.60]	[4.60]	[4.50]	[4.10]	[4.00]
Nitrate	94.4	98.2	60.3	60.7	61.2	59.2
Phosphate	1,620	2,010	2,020	1,750	2,030	2,050
Sulfate	[14.0]	[11.0]	[9.20]	[10.0]	[9.60]	[11.0]
^{60}Co	Not Measured					< 4.E-6
^{137}Cs						0.270
^{154}Eu						< 1.E-5
^{155}Eu						< 8.E-5
^{241}Am						< 4.E-5
Opportunistic Analytes						
Ag	<0.338	<0.342	<0.333	<0.335	<0.324	<0.327
As	<6.922	<7.002	<6.826	<6.852	<6.626	<6.693
Ba	[0.08]	[0.10]	[0.06]	[0.11]	[0.12]	[0.15]
Be	[0.01]	<0.008	[0.01]	<0.008	[0.01]	[0.02]
Ca	[5.47]	[1.79]	[2.00]	[2.68]	[1.79]	[2.83]
Ce	<1.610	<1.628	<1.588	<1.593	<1.541	<1.557
Co	<0.386	<0.391	<0.381	<0.382	<0.370	<0.374
Cu	[1.06]	[0.98]	[1.02]	[0.89]	[0.86]	[0.84]
Dy	<0.467	<0.472	<0.460	<0.462	<0.447	<0.451
Eu	<0.177	<0.179	<0.175	<0.175	<0.170	<0.171
K	<11.591	[21.82]	[22.86]	[41.43]	[43.15]	[40.47]
La	<0.451	<0.456	<0.445	<0.446	<0.431	<0.436
Li	[0.80]	[0.91]	[0.79]	[0.96]	[0.77]	[0.68]
Mg	<0.370	<0.375	<0.365	<0.366	<0.354	<0.358
Mo	<0.837	<0.847	<0.826	<0.829	<0.801	<0.809
Nd	<0.869	<0.879	<0.857	<0.860	<0.832	<0.841
Pb	<5.151	[5.54]	[5.08]	<5.099	<4.931	<4.981
Pd	<1.014	<1.026	<1.000	<1.004	<0.971	<0.981
Rh	<1.932	<1.954	<1.905	<1.912	<1.849	<1.868
Ru	<1.368	<1.384	<1.349	<1.354	<1.310	<1.323
Sb	<3.220	<3.257	<3.175	<3.187	<3.082	<3.113
Se	<11.269	<11.399	<11.113	<11.154	<10.787	<10.896
Sn	<4.347	<4.397	<4.286	<4.302	<4.161	<4.203
Ta	<2.737	<2.768	<2.699	<2.709	<2.620	<2.646
Te	<4.186	<4.234	<4.128	<4.143	<4.006	<4.047
Th	<1.578	<1.596	<1.556	<1.562	<1.510	<1.525
Ti	<0.069	<0.070	<0.068	<0.069	<0.066	<0.067
Tl	<6.117	<6.188	<6.033	<6.055	<5.856	<5.915
V	<0.119	<0.121	<0.117	<0.118	[0.12]	<0.115
W	<3.059	<3.094	<3.016	<3.027	<2.928	<2.958

Table G.1 (Contd)

Analyte	**Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides**					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Y	<0.071	<0.072	<0.070	<0.070	<0.068	<0.068
3 M NaOH, Trial b						
Density	1.12	1.13	1.13	1.13	1.13	1.14
Al	38.6	57.9	60.7	60.2	65.7	79.3
B	<0.747	<0.743	<0.759	[7.64]	[6.23]	[5.17]
Bi	<4.67	<4.64	<4.74	<4.59	<4.67	<4.56
Cd	<0.529	<0.526	<0.538	<0.520	<0.529	<0.517
Cr	[0.498]	[0.588]	[0.632]	[0.550]	[0.685]	[0.972]
Fe	15.3	11.5	11.0	10.3	10.5	8.36
Mn	[0.436]	[0.341]	[0.316]	[0.281]	[0.342]	[0.234]
Na	70,361	70,287	72,406	70,622	73,780	69,896
Ni	<0.374	<0.372	<0.379	<0.367	<0.374	<0.365
P	501	610	617	615	626	599
S	<24.9	<24.8	<25.3	<24.5	[46.7]	<24.3
Si	[8.09]	22.7	23.8	23.8	27.5	24.5
Sr	[0.215]	[0.111]	[0.095]	[0.076]	0.458	[0.049]
U	193	109	89.8	74.6	63.8	[42.5]
Zn	[4.36]	[4.64]	[4.74]	[4.89]	82.8	[5.17]
Zr	<0.171	<0.170	<0.174	<0.168	<0.171	<0.167
Fluoride	<10.0	<10.0	<10.0	<10.0	<10.0	<11.0
Nitrite	[4.20]	[4.10]	[4.00]	[4.80]	[4.30]	[6.80]
Nitrate	55.9	57.8	59.7	58.3	58.1	99.0
Phosphate	2,040	1,550	1,930	1,950	1,910	2,060
Sulfate	[8.30]	[11.0]	[9.90]	[8.70]	[9.40]	[7.30]
^{60}Co	Not Measured					< 3.E-6
^{137}Cs						0.257
^{154}Eu						< 1.E-5
^{155}Eu						< 7.E-5
^{241}Am						< 4.E-5
Opportunistic Analytes						
Ag	<0.327	<0.325	<0.332	<0.321	<0.327	<0.319
As	<6.694	<6.657	<6.798	<6.573	<6.693	<6.534
Ba	<0.042	[0.13]	[0.08]	[0.11]	3.11	[0.07]
Be	<0.008	[0.01]	[0.01]	<0.008	<0.008	<0.008
Ca	[1.84]	[1.61]	[2.50]	[1.47]	[6.23]	[3.04]
Ce	<1.557	<1.548	<1.581	<1.529	<1.557	<1.519
Co	<0.374	<0.372	<0.379	<0.367	<0.374	<0.365
Cu	[0.72]	[0.93]	[0.92]	[0.98]	[1.00]	[1.22]
Dy	<0.451	<0.449	<0.458	<0.443	<0.451	<0.441
Eu	<0.171	<0.170	<0.174	<0.168	<0.171	<0.167
K	[34.25]	[40.25]	[44.27]	<11.006	[15.57]	[30.39]
La	<0.436	<0.433	<0.443	<0.428	<0.436	<0.425
Li	[0.78]	[0.65]	[0.73]	[0.70]	[0.78]	[0.55]

Table G.1 (Contd)

	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides					
Analyte	**0 hr**	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Mg	<0.358	<0.356	<0.364	<0.352	[3.11]	<0.349
Mo	<0.809	<0.805	<0.822	<0.795	<0.809	<0.790
Nd	<0.841	<0.836	<0.854	<0.825	<0.841	<0.821
Pb	<4.981	<4.954	<5.059	<4.892	<4.981	<4.862
Pd	<0.981	<0.975	<0.996	[1.31]	<0.981	<0.957
Rh	<1.868	<1.858	<1.897	<1.834	<1.868	<1.823
Ru	<1.323	<1.316	<1.344	<1.299	[1.68]	<1.292
Sb	<3.113	<3.096	<3.162	[3.97]	<3.113	<3.039
Se	<10.897	<10.837	<11.066	<10.700	<10.896	<10.636
Sn	<4.203	<4.180	<4.268	<4.127	<4.203	<4.103
Ta	<2.646	<2.632	<2.688	<2.599	<2.646	<2.583
Te	<4.047	<4.025	<4.110	<3.974	<4.047	<3.951
Th	<1.526	<1.517	<1.549	<1.498	<1.525	<1.489
Ti	<0.067	<0.067	<0.068	<0.066	[0.12]	<0.065
Tl	<5.915	<5.883	<6.007	[6.42]	<5.915	<5.774
V	<0.115	<0.115	<0.117	<0.113	<0.115	<0.112
W	<2.958	<2.942	<3.004	<2.904	<2.957	<2.887
Y	<0.068	<0.068	<0.070	<0.067	<0.068	<0.067
3 M NaOH, Trial c						
Density	1.12	1.13	1.13	1.13	1.14	1.14
Al	36.9	59.8	60.8	63.5	65.7	87.1
B	[4.35]	[3.48]	[2.60]	[2.73]	[2.61]	[1.80]
Bi	<4.66	<4.74	<4.82	<4.88	<4.67	<4.65
Cd	<0.528	<0.537	<0.547	<0.553	<0.529	<0.527
Cr	[0.466]	[0.294]	[0.547]	[0.553]	[0.840]	[1.209]
Fe	15.2	12.2	11.4	11.3	9.99	8.86
Mn	[0.466]	[0.348]	[0.318]	[0.303]	[0.277]	[0.245]
Na	72,641	73,668	72,680	73,232	72,820	72,836
Ni	<0.373	<0.379	<0.386	<0.391	<0.373	<0.372
P	484	645	640	631	629	638
S	<24.8	<25.3	<25.7	<26.0	<24.9	<24.8
Si	[8.69]	25.3	25.0	25.3	26.0	26.4
Sr	[0.220]	[0.117]	[0.103]	[0.081]	[0.078]	[0.053]
U	201	116	97.1	78.4	60.1	[46.5]
Zn	[4.35]	[5.06]	[5.15]	[5.53]	[5.29]	[5.27]
Zr	<0.171	<0.174	<0.177	<0.179	<0.171	<0.170
Fluoride	<7.50	[7.50]	[7.50]	[8.20]	[7.50]	[7.60]
Nitrite	[7.20]	[7.40]	[7.70]	[8.90]	[7.10]	[7.20]
Nitrate	79.0	82.2	84.3	87.8	82.1	84.9
Phosphate	1,580	2,000	1,990	2,110	1,940	2,000
Sulfate	[16.0]	[10.0]	[11.0]	[11.0]	[9.90]	[10.0]

Table G.1 (Contd)

Analyte	**Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides**					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
^{60}Co	Not Measured					< 3.E-6
^{137}Cs						0.259
^{154}Eu						< 1.E-5
^{155}Eu						< 9.E-5
^{241}Am						< 2.E-4
Opportunistic Analytes						
Ag	<0.326	<0.332	<0.338	<0.342	<0.327	<0.325
As	<6.674	<6.798	<6.914	<6.998	<6.691	<6.664
Ba	<0.042	[0.06]	[0.14]	[0.23]	[0.17]	[0.07]
Be	<0.008	[0.01]	[0.01]	<0.008	[0.01]	[0.01]
Ca	[3.73]	[1.33]	[2.22]	[2.47]	[2.58]	[3.41]
Ce	<1.552	<1.581	<1.608	<1.627	<1.556	<1.550
Co	<0.373	<0.379	<0.386	<0.391	<0.373	<0.372
Cu	[0.84]	[0.98]	[0.87]	[1.14]	[1.03]	[0.93]
Dy	<0.450	<0.458	<0.466	<0.472	<0.451	<0.449
Eu	<0.171	<0.174	<0.177	<0.179	<0.171	<0.170
K	[34.15]	[41.10]	[38.59]	[39.06]	[52.90]	[49.59]
La	<0.435	<0.443	<0.450	<0.456	<0.436	<0.434
Li	[0.87]	[0.76]	[0.96]	[0.81]	[0.78]	[0.59]
Mg	<0.357	<0.364	<0.370	<0.374	<0.358	<0.356
Mo	<0.807	<0.822	<0.836	<0.846	<0.809	<0.806
Nd	<0.838	<0.854	<0.868	<0.879	<0.840	<0.837
Pb	[5.59]	<5.059	<5.145	[5.21]	<4.979	<4.959
Pd	<0.978	<0.996	<1.013	<1.025	<0.980	<0.976
Rh	<1.863	<1.897	<1.930	<1.953	<1.867	<1.860
Ru	<1.319	<1.344	<1.367	<1.383	<1.323	<1.317
Sb	<3.104	<3.162	<3.216	<3.255	<3.112	<3.099
Se	<10.865	<11.066	<11.256	<11.392	<10.892	<10.848
Sn	<4.191	<4.268	<4.341	<4.394	<4.201	<4.184
Ta	<2.639	<2.687	<2.734	<2.767	<2.645	<2.635
Te	<4.036	<4.110	<4.181	<4.231	<4.046	<4.029
Th	<1.521	<1.549	<1.576	<1.595	<1.525	<1.519
Ti	<0.067	<0.068	<0.069	<0.070	<0.067	<0.067
Tl	<5.898	<6.007	<6.110	<6.184	<5.913	<5.889
V	<0.115	<0.117	<0.119	<0.120	<0.115	<0.115
W	<2.949	<3.004	<3.055	<3.092	<2.956	<2.944
Y	<0.068	<0.070	<0.071	<0.072	<0.068	<0.068
Analyte uncertainties were typically within ±15% (2-s); results in brackets indicate that the analyte concentrations were less than the minimum detection limit (MDL) and greater than the estimated quantitation limit (EQL), and uncertainties were >15%.						

Table G.2. Analyte Concentrations as a Function of Time for Leaching at 40ºC, in M

	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; M for Metals and Anions					
Analyte	**0 hr**	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
1 M NaOH						
Density	1.04	1.05	1.06	1.05	1.05	1.05
Al	1.08E-03	2.04E-03	2.14E-03	2.22E-03	2.20E-03	2.63E-03
B	[3.80E-05]	[3.75E-05]	[3.48E-05]	[4.15E-05]	[3.29E-05]	[1.71E-04]
Bi	<4.54E-06	<4.47E-06	<4.50E-06	<4.60E-06	<3.40E-06	<2.22E-05
Cd	<9.56E-07	<9.42E-07	<9.48E-07	<9.69E-07	<7.17E-07	<4.67E-06
Cr	[5.23E-06]	[7.19E-06]	[7.84E-06]	[8.01E-06]	9.84E-06	[1.31E-05]
Fe	6.85E-05	4.56E-05	4.12E-05	4.08E-05	3.56E-05	[4.37E-05]
Mn	4.45E-06	4.05E-06	3.98E-06	3.94E-06	3.00E-06	[3.82E-06]
Na	1.05	1.06	1.06	1.07	1.09	1.10
Ni	<1.29E-06	<1.27E-06	<1.28E-06	<1.31E-06	<9.69E-07	<6.31E-06
P	1.37E-02	1.96E-02	1.97E-02	2.00E-02	1.95E-02	1.97E-02
S	<1.58E-04	<1.55E-04	<1.56E-04	<1.60E-04	<4.99E-06	<7.70E-04
Si	2.06E-04	7.48E-04	8.23E-04	8.56E-04	8.34E-04	7.53E-04
Sr	9.99E-07	[5.33E-07]	[4.29E-07]	[3.48E-07]	[2.70E-07]	[3.88E-07]
U	1.00E-03	6.83E-04	5.76E-04	4.57E-04	3.37E-04	2.49E-04
Zn	3.98E-05	4.64E-05	4.37E-05	4.29E-05	4.02E-05	[5.67E-05]
Zr	<3.81E-07	<3.76E-07	<3.78E-07	<3.87E-07	<2.86E-07	<1.86E-06
Fluoride	[3.47E-04]	[4.21E-04]	[4.16E-04]	[4.21E-04]	[4.11E-04]	[4.26E-04]
Nitrite	[1.65E-04]	[1.72E-04]	[1.65E-04]	[1.65E-04]	[1.65E-04]	[1.67E-04]
Nitrate	[1.30E-03]	[1.36E-03]	1.32E-03	1.34E-03	1.33E-03	1.35E-03
Phosphate	1.44E-02	2.05E-02	1.97E-02	1.99E-02	1.98E-02	2.13E-02
Sulfate	9.89E-05	[1.15E-04]	[1.04E-04]	[1.04E-04]	[1.04E-04]	[1.04E-04]
3 M NaOH, Trial a						
Density	1.13	1.13	1.13	1.13	1.13	1.14
Al	1.58E-03	2.31E-03	2.33E-03	2.47E-03	2.59E-03	3.27E-03
B	[1.49E-04]	[1.36E-04]	[7.05E-05]	[9.43E-05]	<6.84E-05	<6.91E-05
Bi	<2.31E-05	<2.34E-05	<2.28E-05	<2.29E-05	<2.21E-05	<2.23E-05
Cd	<4.87E-06	<4.93E-06	<4.80E-06	<4.82E-06	<4.66E-06	<4.71E-06
Cr	[9.29E-06]	[1.06E-05]	[1.34E-05]	[1.16E-05]	[1.66E-05]	[2.45E-05]
Fe	2.94E-04	2.11E-04	2.04E-04	1.88E-04	1.81E-04	1.65E-04
Mn	[8.79E-06]	[7.11E-06]	5.72E-06	[5.16E-06]	[4.60E-06]	[4.48E-06]
Na	3.24	3.19	3.16	3.22	3.16	3.21
Ni	<6.58E-06	<6.66E-06	<6.49E-06	<6.52E-06	<6.30E-06	<6.36E-06
P	1.77E-02	2.10E-02	2.10E-02	2.08E-02	2.12E-02	2.11E-02
S	<8.03E-04	<8.13E-04	<7.92E-04	<7.95E-04	<2.50E-05	<7.77E-04
Si	3.24E-04	8.88E-04	9.07E-04	9.15E-04	9.51E-04	9.59E-04
Sr	[2.57E-06]	[1.38E-06]	[1.05E-06]	[9.09E-07]	[7.39E-07]	[6.40E-07]
U	8.40E-04	4.67E-04	3.95E-04	2.95E-04	2.58E-04	[1.83E-04]
Zn	[6.89E-05]	[7.97E-05]	8.26E-05	[8.29E-05]	[8.48E-05]	[8.09E-05]
Zr	<1.94E-06	<1.96E-06	<1.91E-06	<1.92E-06	<1.86E-06	<1.88E-06
Fluoride	<5.79E-04	<5.79E-04	<5.26E-04	<5.26E-04	<5.26E-04	<5.26E-04
Nitrite	[1.63E-04]	[1.87E-04]	[1.00E-04]	[9.78E-05]	[8.91E-05]	[8.70E-05]
Nitrate	1.52E-03	1.58E-03	9.73E-04	9.79E-04	9.87E-04	9.55E-04

Table G.2 (Contd)

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; M for Metals and Anions					
	0 hr	1 hr	2 hr	4 hr	8 hr	24 hr
Phosphate	1.71E-02	2.12E-02	2.13E-02	1.84E-02	2.14E-02	2.16E-02
Sulfate	[1.46E-04]	[1.15E-04]	[9.58E-05]	[1.04E-04]	[9.99E-05]	[1.15E-04]
3 M NaOH, Trial b						
Density	1.12	1.13	1.13	1.13	1.13	1.14
Al	1.43E-03	2.15E-03	2.25E-03	2.23E-03	2.43E-03	2.94E-03
B	<6.91E-05	<6.87E-05	<7.02E-05	[7.07E-04]	[5.76E-04]	[4.78E-04]
Bi	<2.23E-05	<2.22E-05	<2.27E-05	<2.19E-05	<2.23E-05	<2.18E-05
Cd	<4.71E-06	<4.68E-06	<4.78E-06	<4.62E-06	<4.71E-06	<4.60E-06
Cr	[9.58E-06]	[1.13E-05]	[1.22E-05]	[1.06E-05]	[1.32E-05]	[1.87E-05]
Fe	2.74E-04	2.06E-04	1.96E-04	1.84E-04	1.88E-04	1.50E-04
Mn	[7.93E-06]	[6.20E-06]	[5.76E-06]	[5.12E-06]	[6.23E-06]	[4.26E-06]
Na	3.06	3.06	3.15	3.07	3.21	3.04
Ni	<6.37E-06	<6.33E-06	<6.46E-06	<6.25E-06	<6.36E-06	<6.21E-06
P	1.62E-02	1.97E-02	1.99E-02	1.98E-02	2.02E-02	1.93E-02
S	<7.77E-04	<7.73E-04	<7.89E-04	<7.63E-04	[1.46E-03]	<7.58E-04
Si	[2.88E-04]	8.08E-04	8.48E-04	8.47E-04	9.79E-04	8.72E-04
Sr	[2.45E-06]	[1.27E-06]	[1.08E-06]	[8.72E-07]	5.22E-06	[5.55E-07]
U	8.12E-04	4.58E-04	3.77E-04	3.13E-04	2.68E-04	[1.79E-04]
Zn	[6.67E-05]	[7.10E-05]	[7.25E-05]	[7.48E-05]	1.27E-03	[7.90E-05]
Zr	<1.88E-06	<1.87E-06	<1.91E-06	<1.84E-06	<1.88E-06	<1.83E-06
Fluoride	<5.26E-04	<5.26E-04	<5.26E-04	<5.26E-04	<5.26E-04	<5.79E-04
Nitrite	[9.13E-05]	[8.91E-05]	[8.70E-05]	[1.04E-04]	[9.35E-05]	[1.48E-04]
Nitrate	9.02E-04	9.32E-04	9.63E-04	9.40E-04	9.37E-04	1.60E-03
Phosphate	2.15E-02	1.63E-02	2.03E-02	2.05E-02	2.01E-02	2.17E-02
Sulfate	[8.64E-05]	[1.15E-04]	[1.03E-04]	[9.06E-05]	[9.79E-05]	[7.60E-05]
3 M NaOH, Trial c						
Density	1.12	1.13	1.13	1.13	1.14	1.14
Al	1.37E-03	2.21E-03	2.25E-03	2.35E-03	2.43E-03	3.23E-03
B	[4.02E-04]	[3.22E-04]	[2.41E-04]	[2.53E-04]	[2.42E-04]	[1.66E-04]
Bi	<2.23E-05	<2.27E-05	<2.31E-05	<2.34E-05	<2.23E-05	<2.22E-05
Cd	<4.69E-06	<4.78E-06	<4.86E-06	<4.92E-06	<4.71E-06	<4.69E-06
Cr	[8.96E-06]	[5.66E-06]	[1.05E-05]	[1.06E-05]	[1.62E-05]	[2.32E-05]
Fe	2.73E-04	2.19E-04	2.05E-04	2.02E-04	1.79E-04	1.59E-04
Mn	[8.48E-06]	[6.33E-06]	[5.80E-06]	[5.51E-06]	[5.04E-06]	[4.46E-06]
Na	3.16	3.20	3.16	3.19	3.17	3.17
Ni	<6.35E-06	<6.46E-06	<6.58E-06	<6.65E-06	<6.36E-06	<6.34E-06
P	1.56E-02	2.08E-02	2.07E-02	2.04E-02	2.03E-02	2.06E-02
S	<7.75E-04	<7.89E-04	<8.02E-04	<8.12E-04	<2.50E-05	<7.73E-04
Si	[3.09E-04]	9.01E-04	8.89E-04	9.02E-04	9.25E-04	9.40E-04
Sr	[2.52E-06]	[1.34E-06]	[1.17E-06]	[9.29E-07]	[8.88E-07]	[6.01E-07]
U	8.45E-04	4.89E-04	4.08E-04	3.30E-04	2.52E-04	[1.95E-04]
Zn	[6.65E-05]	[7.74E-05]	[7.87E-05]	[8.46E-05]	[8.09E-05]	[8.06E-05]
Zr	<1.87E-06	<1.91E-06	<1.94E-06	<1.96E-06	<1.88E-06	<1.87E-06
Fluoride	<3.95E-04	[3.95E-04]	[3.95E-04]	[4.32E-04]	[3.95E-04]	[4.00E-04]

Table G.2 (Contd)

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; M for Metals and Anions					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Nitrite	[1.57E-04]	[1.61E-04]	[1.67E-04]	[1.93E-04]	[1.54E-04]	[1.57E-04]
Nitrate	1.27E-03	1.33E-03	1.36E-03	1.42E-03	1.32E-03	1.37E-03
Phosphate	1.66E-02	2.11E-02	2.10E-02	2.22E-02	2.04E-02	2.11E-02
Sulfate	[1.67E-04]	[1.04E-04]	[1.15E-04]	[1.15E-04]	[1.03E-04]	[1.04E-04]

Analyte uncertainties were typically within ±15% (2-s); results in brackets indicate that the analyte concentrations were less than the minimum detection limit (MDL) and greater than the estimated quantitation limit (EQL), and uncertainties were >15%.

Table G.3. Analyte Concentrations as a Function of Time for Leaching at 60ºC, in µg/mL

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; µg/mL for Metals and Anions; µCi/mL for Radionuclides					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
0.25 M NaOH						
Density	1.01	1.02	1.03	1.02	1.02	1.02
Al	25.0	53.8	56.5	57.7	60.7	63.6
B	[0.844]	[0.908]	[0.789]	[0.658]	[0.739]	[0.617]
Bi	<0.938	<0.939	<0.986	<0.940	<0.964	<0.926
Cd	<0.106	[0.200]	[0.154]	<0.107	<0.109	<0.105
Cr	[0.208]	[0.344]	[0.427]	[0.407]	[0.514]	0.648
Fe	[1.14]	[1.13]	[1.18]	[1.03]	[0.931]	[0.741]
Mn	0.181	0.179	0.199	0.177	0.178	0.172
Na	6,188	6,385	6,410	6,360	6,649	6,452
Ni	<0.075	<0.075	<0.079	<0.075	<0.077	<0.074
P	361	570	608	570	591	580
S	<5.00	[6.26]	[5.92]	[6.27]	[7.07]	[6.48]
Si	3.13	16.5	20.4	19.5	19.5	18.1
Sr	[0.028]	[0.026]	[0.026]	[0.018]	[0.015]	[0.012]
U	148	136	111	83.0	68.4	46.0
Zn	[1.23]	[0.85]	[1.35]	[1.07]	[0.867]	[0.864]
Zr	<0.034	<0.034	<0.036	<0.034	<0.035	<0.034
Fluoride	[6.80]	[8.40]	[8.30]	[8.10]	[8.30]	[8.10]
Nitrite	[8.70]	[8.70]	[8.90]	[8.50]	[8.80]	[8.60]
Nitrate	87.2	90.5	93.7	90.3	93.3	91.1
Phosphate	1,170	1,830	1,890	1,800	1,880	1,830
Sulfate	[9.60]	[12.0]	[11.0]	[11.0]	[11.0]	[11.0]
^{60}Co	Not Measured					< 4.E-6
^{137}Cs						0.230
^{154}Eu						< 1.E-5
^{155}Eu						< 1.E-4
^{241}Am						< 1.E-4
Opportunistic Analytes						
Ag	<0.066	<0.066	<0.069	<0.066	<0.067	<0.065
As	<1.344	<1.346	<1.413	<1.347	<1.381	<1.327
Ba	[0.12]	[0.07]	[0.15]	[0.16]	[0.05]	[0.10]
Be	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]
Ca	[1.59]	[1.28]	[1.58]	[1.47]	[1.93]	[1.20]
Ce	<0.313	<0.313	[0.39]	<0.313	<0.321	<0.309
Co	<0.075	<0.075	<0.079	<0.075	<0.077	<0.074
Cu	[0.41]	[0.38]	0.47	[0.41]	[0.39]	[0.34]
Dy	<0.091	<0.091	<0.095	<0.091	<0.093	<0.090
Eu	<0.034	<0.034	<0.036	<0.034	<0.035	<0.034
K	<2.250	[3.13]	[4.27]	[3.76]	[3.21]	[3.70]
La	<0.088	<0.088	<0.092	<0.088	<0.090	<0.086
Li	[0.30]	0.48	0.45	0.46	0.43	0.41
Mg	<0.072	<0.072	<0.076	<0.072	<0.074	<0.071

Table G.3 (Contd)

	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides					
Analyte	**0 hr**	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Mo	<0.163	<0.163	<0.171	<0.163	<0.167	<0.161
Nd	<0.169	<0.169	<0.178	<0.169	<0.173	<0.167
Pb	<1.000	<1.002	<1.052	<1.003	<1.028	<0.988
Pd	<0.197	<0.197	<0.207	<0.197	<0.202	<0.194
Rh	<0.375	<0.376	<0.394	<0.376	<0.385	<0.370
Ru	<0.266	<0.266	[0.29]	<0.266	<0.273	<0.262
Sb	<0.625	[0.72]	[0.72]	<0.627	[0.87]	[0.62]
Se	<2.188	<2.191	<2.301	<2.193	<2.248	<2.161
Sn	<0.844	<0.845	<0.888	<0.846	<0.867	<0.833
Ta	<0.531	<0.532	<0.559	<0.533	<0.546	<0.525
Te	<0.813	<0.814	<0.855	<0.815	<0.835	<0.803
Th	<0.306	<0.307	<0.322	<0.307	<0.315	<0.303
Ti	[0.04]	[0.04]	[0.04]	[0.03]	[0.02]	[0.02]
Tl	<1.188	<1.189	<1.249	<1.191	<1.221	<1.173
V	<0.023	[0.03]	<0.024	[0.04]	[0.07]	[0.05]
W	<0.594	<0.595	<0.625	<0.595	<0.610	<0.587
Y	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014
1 M NaOH						
Density	1.03	1.06	1.05	1.05	1.05	1.05
Al	32.4	57.8	60.9	68.9	84.9	90.5
B	[0.472]	[0.601]	[0.377]	[0.475]	[0.511]	[0.404]
Bi	<0.944	<0.948	<0.942	<0.891	<1.023	<0.933
Cd	<0.107	<0.107	<0.107	<0.101	<0.116	<0.106
Cr	[0.315]	[0.474]	0.578	0.686	0.839	1.18
Fe	3.21	3.64	3.24	2.92	2.43	1.91
Mn	0.227	0.200	0.193	0.182	0.205	0.190
Na	22,206	23,076	22,742	23,242	24,273	23,260
Ni	<0.075	<0.076	<0.075	<0.071	<0.082	<0.075
P	472	591	578	594	617	600
S	[5.66]	[5.37]	[5.03]	[5.64]	[5.80]	[5.29]
Si	5.98	24.3	23.4	25.2	24.4	23.8
Sr	0.077	[0.027]	[0.027]	[0.033]	[0.026]	[0.021]
U	199	121	92.0	72.7	60.0	42.0
Zn	2.99	2.70	2.86	2.65	2.54	2.23
Zr	<0.035	<0.035	<0.035	<0.033	<0.038	<0.034
Fluoride	[8.10]	[7.20]	[7.10]	[7.20]	[7.20]	[7.40]
Nitrite	8.55	8.75	9.24	8.84	8.78	8.77
Nitrate	93.7	97.3	99.0	98.2	98.9	99.1
Phosphate	1,590	1,920	1,910	1,900	1,970	1,930
Sulfate	[10.0]	[11.0]	[11.0]	[12.0]	[11.0]	[11.0]

Table G.3 (Contd)

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; µg/mL for Metals and Anions; µCi/mL for Radionuclides					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
^{60}Co	Not Measured					< 3.E-6
^{137}Cs						0.241
^{154}Eu						< 8.E-6
^{155}Eu						< 9.E-5
^{241}Am						< 1.E-4
Opportunistic Analytes						
Ag	[0.07]	<0.066	<0.066	<0.062	<0.072	<0.065
As	<1.352	<1.359	<1.351	<1.276	<1.466	<1.337
Ba	[0.08]	[0.09]	0.53	1.01	0.80	0.62
Be	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]
Ca	[1.38]	[1.23]	[1.04]	[1.31]	[0.99]	[0.87]
Ce	<0.315	<0.316	<0.314	<0.297	<0.341	<0.311
Co	<0.075	<0.076	<0.075	<0.071	<0.082	<0.075
Cu	[0.44]	[0.41]	[0.38]	[0.39]	[0.41]	[0.37]
Dy	<0.091	<0.092	<0.091	<0.086	<0.099	<0.090
Eu	<0.035	<0.035	<0.035	<0.033	<0.038	<0.034
K	[10.69]	[14.86]	[18.53]	[20.18]	[23.18]	[22.39]
La	<0.088	<0.089	<0.088	<0.083	<0.095	<0.087
Li	[0.38]	0.42	[0.35]	0.36	[0.34]	[0.29]
Mg	<0.072	<0.073	<0.072	<0.068	<0.078	<0.072
Mo	<0.164	<0.164	<0.163	<0.154	<0.177	<0.162
Nd	<0.170	<0.171	<0.170	<0.160	<0.184	<0.168
Pb	[1.29]	<1.012	<1.005	<0.950	<1.091	<0.995
Pd	<0.198	<0.199	<0.198	<0.187	<0.215	<0.196
Rh	<0.377	<0.379	<0.377	<0.356	<0.409	<0.373
Ru	<0.267	<0.269	<0.267	<0.252	<0.290	<0.264
Sb	[1.16]	<0.632	<0.628	[0.74]	[1.16]	<0.622
Se	<2.202	<2.213	<2.199	<2.078	<2.386	<2.177
Sn	<0.849	<0.853	<0.848	<0.801	<0.920	<0.840
Ta	<0.535	<0.537	<0.534	<0.505	<0.580	<0.529
Te	<0.818	<0.822	<0.817	<0.772	<0.886	<0.809
Th	<0.308	<0.310	<0.308	<0.291	<0.334	<0.305
Ti	[0.05]	[0.04]	[0.03]	[0.03]	[0.03]	[0.02]
Tl	<1.195	<1.201	<1.194	<1.128	<1.295	<1.182
V	<0.023	[0.04]	[0.05]	[0.04]	[0.04]	[0.06]
W	<0.598	<0.601	<0.597	<0.564	<0.648	<0.591
Y	<0.014	<0.014	<0.014	<0.013	<0.015	<0.014
3 M NaOH						
Density	1.13	1.12	1.13	1.13	1.13	1.13
Al	40.2	62.7	73.5	87.6	96.2	97.3
B	[2.69]	[1.65]	[1.49]	[1.55]	[1.10]	[1.23]
Bi	<4.87	<4.68	<4.56	<4.66	<4.99	<4.74
Cd	<0.552	<0.530	<0.516	<0.528	<0.566	<0.537

Table G.3 (Contd)

Analyte	**Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides**					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Cr	[0.315]	[0.780]	[0.820]	[1.06]	[1.43]	[2.02]
Fe	16.4	14.7	13.8	12.2	10.1	7.8
Mn	[0.422]	[0.259]	[0.228]	[0.202]	[0.230]	[0.190]
Na	66,191	66,436	65,608	67,383	70,566	68,857
Ni	<0.389	<0.374	<0.364	<0.373	<0.399	[0.411]
P	545	596	598	602	619	632
S	<26.0	<25.0	<24.3	<24.8	<26.6	<25.3
Si	[5.19]	25.2	25.5	26.2	26.5	26.9
Sr	0.299	[0.087]	[0.067]	[0.059]	[0.067]	[0.060]
U	306	119	93.9	73.6	60.2	[44.2]
Zn	[4.22]	[4.68]	[5.16]	[4.66]	[4.99]	[5.05]
Zr	<0.178	<0.172	<0.167	<0.171	<0.183	<0.174
Fluoride	[6.80]	[9.20]	[7.10]	[7.40]	[8.60]	[9.60]
Nitrite	[7.50]	<5.30	[8.50]	[8.70]	[7.50]	[8.20]
Nitrate	87.1	88.0	89.3	91.0	92.0	92.0
Phosphate	1,820	1,990	1,950	1,940	1,980	1,960
Sulfate	[11.0]	<7.90	[10.0]	[11.0]	<7.90	[10.0]
^{60}Co	Not Measured					< 3.E-6
^{137}Cs						0.248
^{154}Eu						< 8.E-6
^{155}Eu						< 9.E-5
^{241}Am						< 1.E-4
Opportunistic Analytes						
Ag	<0.341	<0.328	<0.319	<0.326	<0.350	<0.332
As	<6.976	<6.706	<6.530	<6.676	<7.156	<6.791
Ba	[0.36]	[0.72]	[0.61]	[0.43]	[0.63]	1.07
Be	[0.01]	[0.01]	<0.008	<0.008	[0.01]	[0.01]
Ca	[3.57]	[2.90]	<0.926	[3.07]	[1.43]	[2.12]
Ce	<1.622	<1.560	<1.519	<1.553	<1.664	<1.579
Co	<0.389	<0.374	<0.364	<0.373	<0.399	<0.379
Cu	<0.227	[0.27]	[0.30]	[0.40]	[0.37]	[0.32]
Dy	<0.470	<0.452	<0.440	<0.450	<0.483	<0.458
Eu	<0.178	<0.172	<0.167	<0.171	<0.183	<0.174
K	[23.69]	[14.66]	[30.37]	[31.05]	[39.94]	[44.22]
La	<0.454	<0.437	<0.425	<0.435	<0.466	<0.442
Li	[0.71]	[0.75]	[0.61]	[0.84]	[0.67]	[0.47]
Mg	<0.373	<0.359	<0.349	<0.357	<0.383	<0.363
Mo	<0.844	<0.811	<0.790	<0.807	<0.865	<0.821
Nd	<0.876	<0.842	<0.820	<0.838	<0.899	<0.853
Pb	<5.191	[6.86]	[5.47]	<4.968	<5.326	<5.054
Pd	<1.022	<0.983	[1.28]	<0.978	[1.40]	<0.995
Rh	<1.947	<1.871	<1.822	<1.863	<1.997	<1.895
Ru	<1.379	[1.37]	[1.52]	[1.55]	<1.415	<1.342

Table G.3 (Contd)

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; µg/mL for Metals and Anions; µCi/mL for Radionuclides					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Sb	[4.54]	<3.119	<3.037	[3.42]	[5.99]	<3.159
Se	<11.356	<10.917	<10.631	<10.868	<11.650	<11.055
Sn	<4.380	<4.211	<4.101	<4.192	<4.494	<4.264
Ta	<2.758	<2.651	<2.582	<2.639	<2.829	<2.685
Te	<4.218	<4.055	<3.949	<4.037	<4.327	<4.106
Th	<1.590	<1.528	<1.488	<1.522	<1.631	<1.548
Ti	[0.11]	[0.10]	<0.065	<0.067	<0.072	<0.068
Tl	<6.165	<5.926	<5.771	<5.900	<6.324	<6.001
V	<0.120	<0.115	<0.112	<0.115	<0.123	<0.117
W	<3.082	<2.963	<2.886	<2.950	<3.162	<3.001
Y	<0.071	<0.069	<0.067	<0.068	<0.073	<0.069
Analyte uncertainties were typically within ±15% (2-s); results in brackets indicate that the analyte concentrations were less than the minimum detection limit (MDL) and greater than the estimated quantitation limit (EQL), and uncertainties were >15%.						

Table G.4. Analyte Concentrations as a Function of Time for Leaching at 60ºC, in M

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; M for Metals and Anions					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
0.25 M NaOH						
Density	1.01	1.02	1.03	1.02	1.02	1.02
Al	9.27E-04	2.00E-03	2.10E-03	2.14E-03	2.25E-03	2.36E-03
B	[7.81E-05]	[8.40E-05]	[7.30E-05]	[6.09E-05]	[6.83E-05]	[5.71E-05]
Bi	<4.49E-06	<4.49E-06	<4.72E-06	<4.50E-06	<4.61E-06	<4.43E-06
Cd	<9.45E-07	[1.78E-06]	[1.37E-06]	<9.48E-07	<9.72E-07	<9.34E-07
Cr	[4.00E-06]	[6.62E-06]	[8.22E-06]	[7.83E-06]	[9.88E-06]	1.25E-05
Fe	[2.04E-05]	[2.02E-05]	[2.12E-05]	[1.85E-05]	[1.67E-05]	[1.33E-05]
Mn	3.30E-06	3.26E-06	3.61E-06	3.23E-06	3.23E-06	3.14E-06
Na	0.27	0.28	0.28	0.28	0.29	0.28
Ni	<1.28E-06	<1.28E-06	<1.34E-06	<1.28E-06	<1.31E-06	<1.26E-06
P	1.17E-02	1.84E-02	1.96E-02	1.84E-02	1.91E-02	1.87E-02
S	<1.56E-04	[1.95E-04]	[1.85E-04]	[1.95E-04]	[2.20E-04]	[2.02E-04]
Si	1.11E-04	5.86E-04	7.26E-04	6.94E-04	6.94E-04	6.45E-04
Sr	[3.16E-07]	[2.96E-07]	[2.96E-07]	[2.04E-07]	[1.76E-07]	[1.34E-07]
U	6.22E-04	5.72E-04	4.68E-04	3.49E-04	2.87E-04	1.93E-04
Zn	[1.89E-05]	[1.29E-05]	[2.06E-05]	[1.63E-05]	[1.33E-05]	[1.32E-05]
Zr	<3.77E-07	<3.77E-07	<3.96E-07	<3.78E-07	<3.87E-07	<3.72E-07
Fluoride	[3.58E-04]	[4.42E-04]	[4.37E-04]	[4.26E-04]	[4.37E-04]	[4.26E-04]
Nitrite	[1.89E-04]	[1.89E-04]	[1.93E-04]	[1.85E-04]	[1.91E-04]	[1.87E-04]
Nitrate	1.41E-03	1.46E-03	1.51E-03	1.46E-03	1.50E-03	1.47E-03
Phosphate	1.23E-02	1.93E-02	1.99E-02	1.90E-02	1.98E-02	1.93E-02
Sulfate	[9.99E-05]	[1.25E-04]	[1.15E-04]	[1.15E-04]	[1.15E-04]	[1.15E-04]
1 M NaOH						
Density	1.03	1.06	1.05	1.05	1.05	1.05
Al	1.20E-03	2.14E-03	2.26E-03	2.55E-03	3.15E-03	3.35E-03
B	[4.36E-05]	[5.56E-05]	[3.49E-05]	[4.39E-05]	[4.73E-05]	[3.74E-05]
Bi	<4.52E-06	<4.54E-06	<4.51E-06	<4.26E-06	<4.89E-06	<4.46E-06
Cd	<9.51E-07	<9.56E-07	<9.50E-07	<8.98E-07	<1.03E-06	<9.41E-07
Cr	[6.05E-06]	[9.12E-06]	1.11E-05	1.32E-05	1.61E-05	2.26E-05
Fe	5.74E-05	6.51E-05	5.79E-05	5.22E-05	4.36E-05	3.42E-05
Mn	4.14E-06	3.65E-06	3.50E-06	3.32E-06	3.73E-06	3.45E-06
Na	0.97	1.00	0.99	1.01	1.06	1.01
Ni	<1.29E-06	<1.29E-06	<1.28E-06	<1.21E-06	<1.39E-06	<1.27E-06
P	1.52E-02	1.91E-02	1.87E-02	1.92E-02	1.99E-02	1.94E-02
S	[1.77E-04]	[1.68E-04]	[1.57E-04]	[1.76E-04]	[1.81E-04]	[1.65E-04]
Si	2.13E-04	8.67E-04	8.32E-04	8.96E-04	8.70E-04	8.46E-04
Sr	8.79E-07	[3.10E-07]	[3.05E-07]	[3.73E-07]	[2.92E-07]	[2.38E-07]
U	8.37E-04	5.09E-04	3.87E-04	3.06E-04	2.52E-04	1.76E-04
Zn	4.57E-05	4.12E-05	4.37E-05	4.06E-05	3.89E-05	3.41E-05
Zr	<3.79E-07	<3.81E-07	<3.79E-07	<3.58E-07	<4.11E-07	<3.75E-07
Fluoride	[4.26E-04]	[3.79E-04]	[3.74E-04]	[3.79E-04]	[3.79E-04]	[3.90E-04]
Nitrite	1.86E-04	1.90E-04	2.01E-04	1.92E-04	1.91E-04	1.91E-04
Nitrate	1.51E-03	1.57E-03	1.60E-03	1.58E-03	1.60E-03	1.60E-03

Table G.4 (Contd)

	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; M for Metals and Anions					
Analyte	**0 hr**	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Phosphate	1.67E-02	2.02E-02	2.01E-02	2.00E-02	2.07E-02	2.03E-02
Sulfate	[1.04E-04]	[1.15E-04]	[1.15E-04]	[1.25E-04]	[1.15E-04]	[1.15E-04]
3 M NaOH						
Density	1.13	1.12	1.13	1.13	1.13	1.13
Al	1.49E-03	2.32E-03	2.72E-03	3.25E-03	3.57E-03	3.61E-03
B	[2.49E-04]	[1.53E-04]	[1.38E-04]	[1.44E-04]	[1.02E-04]	[1.14E-04]
Bi	<2.33E-05	<2.24E-05	<2.18E-05	<2.23E-05	<2.39E-05	<2.27E-05
Cd	<4.91E-06	<4.72E-06	<4.59E-06	<4.70E-06	<5.03E-06	<4.78E-06
Cr	[6.05E-06]	[1.50E-05]	[1.58E-05]	[2.03E-05]	[2.75E-05]	[3.89E-05]
Fe	2.93E-04	2.63E-04	2.47E-04	2.19E-04	1.81E-04	1.40E-04
Mn	[7.68E-06]	[4.71E-06]	[4.15E-06]	[3.67E-06]	[4.18E-06]	[3.45E-06]
Na	2.88	2.89	2.85	2.93	3.07	3.00
Ni	<6.63E-06	<6.38E-06	<6.21E-06	<6.35E-06	<6.81E-06	[7.00E-06]
P	1.76E-02	1.92E-02	1.93E-02	1.94E-02	2.00E-02	2.04E-02
S	<8.10E-04	<7.78E-04	<7.58E-04	<7.75E-04	<8.31E-04	<7.88E-04
Si	[1.85E-04]	8.97E-04	9.10E-04	9.34E-04	9.45E-04	9.57E-04
Sr	0.0000	[9.97E-07]	[7.63E-07]	[6.73E-07]	[7.60E-07]	[6.85E-07]
U	1.28E-03	5.01E-04	3.94E-04	3.09E-04	2.53E-04	[1.86E-04]
Zn	[6.45E-05]	[7.16E-05]	[7.90E-05]	[7.12E-05]	[7.64E-05]	[7.73E-05]
Zr	<1.96E-06	<1.88E-06	<1.83E-06	<1.87E-06	<2.01E-06	<1.90E-06
Fluoride	[3.58E-04]	[4.84E-04]	[3.74E-04]	[3.90E-04]	[4.53E-04]	[5.05E-04]
Nitrite	[1.63E-04]	<1.15E-04	[1.85E-04]	[1.89E-04]	[1.63E-04]	[1.78E-04]
Nitrate	1.40E-03	[1.42E-03]	1.44E-03	1.47E-03	[1.48E-03]	1.48E-03
Phosphate	1.92E-02	2.10E-02	2.05E-02	2.04E-02	2.08E-02	2.06E-02
Sulfate	[1.15E-04]	<8.22E-05	[1.04E-04]	[1.15E-04]	<8.22E-05	[1.04E-04]
Analyte uncertainties were typically within ±15% (2-s); results in brackets indicate that the analyte concentrations were less than the minimum detection limit (MDL) and greater than the estimated quantitation limit (EQL), and uncertainties were >15%.						

Table G.5. Analyte Concentrations as a Function of Time for Leaching at 80ºC, in µg/mL

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; µg/mL for Metals and Anions; µCi/mL for Radionuclides					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
0.25 M NaOH						
Density	1.01	1.03	1.04	1.02	1.02	1.02
Al	22.5	62.8	66.1	71.7	84.6	99.5
B	[0.342]	[0.471]	[0.407]	[0.470]	[0.499]	[0.451]
Bi	<0.933	<0.942	<0.940	<0.940	<0.936	<0.902
Cd	<0.106	<0.107	<0.107	<0.107	<0.106	<0.102
Cr	[0.255]	0.540	0.583	0.711	0.933	1.28
Fe	[1.03]	2.02	1.72	[1.38]	[1.03]	[0.81]
Mn	0.176	0.178	0.175	0.179	0.171	0.169
Na	6,378	6,937	6,833	6,829	6,929	6,797
Ni	<0.075	<0.075	<0.075	<0.075	<0.075	<0.072
P	355	600	611	608	615	611
S	[5.91]	[5.96]	[7.52]	<5.01	[6.87]	[5.11]
Si	3.09	22.7	22.2	21.9	21.9	21.4
Sr	[0.026]	[0.019]	[0.016]	[0.014]	[0.012]	[0.014]
U	174	116	89.0	68.9	54.0	34.9
Zn	[1.24]	[0.910]	[0.815]	[0.752]	[0.968]	[0.782]
Zr	<0.034	<0.035	<0.034	<0.034	<0.034	<0.033
Fluoride	<7.50	[7.60]	[7.60]	<7.50	[7.60]	[8.20]
Nitrite	9.40	9.75	9.65	9.64	9.94	10.0
Nitrate	93.1	99.4	98.4	98.6	101	101
Phosphate	1,080	1,850	1,820	1,820	1,900	1,890
Sulfate	10.0	11.3	11.3	11.3	11.7	11.5
^{60}Co	Not Measured					< 3.E-6
^{137}Cs						0.251
^{154}Eu						< 1.E-5
^{155}Eu						< 9.E-5
^{241}Am						< 2.E-4
Opportunistic Analytes						
Ag	<0.065	<0.066	<0.066	<0.066	<0.066	<0.063
As	<1.338	<1.350	<1.348	<1.347	<1.342	<1.293
Ba	[0.06]	[0.08]	[0.04]	[0.03]	[0.16]	0.22
Be	[0.00]	[0.00]	[0.00]	[0.01]	[0.00]	[0.00]
Ca	[1.15]	[1.04]	[1.07]	[1.19]	[0.97]	[1.17]
Ce	<0.311	<0.314	<0.313	<0.313	<0.312	<0.301
Co	<0.075	<0.075	<0.075	<0.075	<0.075	<0.072
Cu	[0.37]	[0.41]	[0.38]	[0.38]	[0.41]	[0.39]
Dy	<0.090	<0.091	<0.091	<0.091	<0.091	<0.087
Eu	<0.034	<0.035	<0.034	<0.034	<0.034	<0.033
K	[5.29]	[7.22]	[6.90]	[8.14]	[3.43]	[3.91]
La	<0.087	<0.088	<0.088	<0.088	<0.087	<0.084
Li	[0.26]	0.47	0.45	0.42	0.38	[0.33]
Mg	<0.072	<0.072	<0.072	<0.072	<0.072	<0.069

Table G.5 (Contd)

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Mo	<0.162	<0.163	<0.163	<0.163	<0.162	<0.156
Nd	<0.168	<0.170	<0.169	<0.169	<0.169	<0.162
Pb	<0.996	<1.004	<1.003	<1.002	<0.999	<0.962
Pd	<0.196	<0.198	<0.197	<0.197	<0.197	<0.189
Rh	<0.373	<0.377	<0.376	<0.376	<0.375	<0.361
Ru	<0.264	<0.267	<0.266	<0.266	<0.265	<0.256
Sb	<0.622	[0.66]	[0.75]	<0.626	<0.624	<0.601
Se	<2.178	<2.197	<2.194	<2.193	<2.185	<2.105
Sn	<0.840	<0.848	<0.846	<0.846	<0.843	<0.812
Ta	<0.529	<0.534	<0.533	<0.533	<0.531	<0.511
Te	<0.809	<0.816	<0.815	<0.814	<0.811	<0.782
Th	<0.305	<0.308	<0.307	<0.307	<0.306	<0.295
Ti	[0.05]	[0.03]	[0.03]	[0.03]	[0.03]	[0.02]
Tl	<1.182	<1.193	<1.191	<1.190	<1.186	<1.143
V	<0.023	[0.08]	[0.08]	[0.07]	[0.07]	[0.08]
W	<0.591	<0.596	<0.596	<0.595	<0.593	<0.571
Y	<0.014	<0.014	<0.014	<0.014	<0.014	<0.013
1 M NaOH						
Density	1.05	1.06	1.06	1.06	1.06	1.05
Al	30.8	74.7	85.5	90.6	89.8	90.3
B	[0.325]	[0.413]	[0.369]	[0.346]	[0.316]	[0.367]
Bi	<0.996	<0.954	<0.923	<0.944	<0.949	<0.919
Cd	<0.113	<0.108	<0.105	<0.107	<0.108	<0.104
Cr	[0.249]	0.770	1.03	1.29	1.55	2.10
Fe	2.78	4.80	3.66	3.13	2.66	2.32
Mn	0.226	0.194	0.191	0.189	0.197	0.182
Na	21,745	23,792	23,663	24,077	24,002	23,882
Ni	<0.080	<0.076	<0.074	<0.076	<0.076	<0.073
P	471	620	615	633	629	634
S	[6.64]	[7.95]	[6.15]	[5.67]	[7.91]	[6.74]
Si	5.94	25.7	25.4	26.2	26.0	26.4
Sr	0.073	[0.019]	[0.016]	[0.016]	[0.015]	[0.012]
U	157	90.0	67.1	55.4	44.9	34.6
Zn	3.10	2.66	2.54	2.44	2.39	2.12
Zr	<0.037	<0.035	<0.034	<0.035	<0.035	<0.034
Fluoride	[6.80]	[8.40]	[8.60]	[8.60]	[8.60]	[8.80]
Nitrite	8.5	9.4	9.7	9.6	9.6	9.6
Nitrate	92.8	103	107	106	105	106
Phosphate	1,500	1,980	2,020	2,000	1,970	2,000
Sulfate	[10.0]	12.0	12.0	[12.0]	12.0	12.0

Table G.5 (Contd)

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
^{60}Co	Not Measured					< 3.E-6
^{137}Cs						0.262
^{154}Eu						< 1.E-5
^{155}Eu						< 9.E-5
^{241}Am						< 2.E-4
Opportunistic Analytes						
Ag	<0.070	<0.067	<0.065	<0.066	<0.066	<0.064
As	<1.428	<1.368	<1.323	<1.353	<1.360	<1.317
Ba	[0.13]	[0.08]	[0.09]	[0.15]	[0.09]	[0.07]
Be	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]
Ca	[0.76]	[0.41]	[0.52]	[0.38]	[0.54]	[0.34]
Ce	<0.332	<0.318	<0.308	<0.315	<0.316	<0.306
Co	<0.080	<0.076	<0.074	<0.076	<0.076	<0.073
Cu	[0.46]	[0.45]	0.44	[0.38]	[0.41]	[0.40]
Dy	<0.096	<0.092	<0.089	<0.091	<0.092	<0.089
Eu	<0.037	<0.035	<0.034	<0.035	<0.035	<0.034
K	[9.63]	[16.54]	[18.46]	[20.14]	[21.19]	[20.82]
La	<0.093	<0.089	<0.086	<0.088	<0.089	<0.086
Li	[0.37]	[0.30]	[0.28]	[0.28]	[0.25]	[0.22]
Mg	<0.076	<0.073	<0.071	<0.072	<0.073	<0.070
Mo	<0.173	<0.165	<0.160	<0.164	<0.164	<0.159
Nd	<0.179	<0.172	<0.166	<0.170	<0.171	<0.165
Pb	<1.062	[1.24]	[1.11]	[1.13]	<1.012	[1.04]
Pd	<0.209	[0.26]	<0.194	<0.198	<0.199	<0.193
Rh	<0.398	<0.382	<0.369	<0.378	<0.379	<0.367
Ru	<0.282	<0.270	<0.262	<0.268	<0.269	<0.260
Sb	[1.16]	<0.636	<0.615	<0.629	<0.632	[0.73]
Se	<2.324	<2.227	<2.154	<2.203	<2.214	<2.143
Sn	<0.896	<0.859	<0.831	<0.850	<0.854	<0.827
Ta	<0.564	<0.541	<0.523	<0.535	<0.538	<0.521
Te	<0.863	<0.827	<0.800	<0.818	<0.822	<0.796
Th	<0.325	<0.312	<0.302	<0.308	<0.310	<0.300
Ti	[0.04]	[0.03]	[0.02]	[0.02]	[0.02]	[0.02]
Tl	<1.262	<1.209	<1.169	<1.196	<1.202	<1.163
V	<0.025	[0.04]	[0.05]	[0.08]	[0.09]	[0.09]
W	<0.631	<0.604	<0.585	<0.598	<0.601	<0.582
Y	<0.015	<0.014	<0.014	<0.014	<0.014	<0.013
3 M NaOH						
Density	1.11	1.13	1.13	1.13	1.13	1.13
Al	39.7	77.0	86.5	87.9	89.0	86.6
B	<0.757	<0.777	[1.82]	[1.42]	[1.59]	<0.740
Bi	<4.73	<4.85	<4.63	<4.72	<4.98	<4.62
Cd	<0.536	<0.550	<0.525	<0.535	<0.565	<0.524

Table G.5 (Contd)

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Cr	[0.410]	[1.00]	[1.27]	[1.57]	[1.83]	[2.44]
Fe	13.2	18.6	14.6	11.9	10.9	9.10
Mn	[0.410]	[0.227]	[0.210]	[0.208]	[0.229]	[0.219]
Na	62,140	68,929	67,662	68,663	69,756	67,831
Ni	<0.379	<0.388	<0.371	<0.378	<0.399	<0.370
P	533	612	602	608	611	601
S	<25.2	<25.9	<24.7	<25.2	<26.6	<24.7
Si	[3.79]	24.9	26.1	26.4	26.9	26.8
Sr	[0.227]	[0.078]	[0.059]	[0.050]	[0.043]	[0.049]
U	203	90.9	65.8	53.5	[43.2]	[33.9]
Zn	[4.10]	[5.18]	[4.94]	[4.41]	[4.65]	[4.62]
Zr	<0.173	<0.178	<0.170	<0.173	<0.183	<0.170
Fluoride	[7.30]	[8.00]	[8.30]	[8.30]	[8.60]	[8.20]
Nitrite	[8.20]	[8.40]	[9.10]	[9.20]	[9.30]	[9.20]
Nitrate	81.8	94.5	93.0	97.2	94.2	94.2
Phosphate	1,660	1,890	1,940	1,940	1,970	1,910
Sulfate	[11.0]	[11.0]	[11.0]	[11.0]	[11.0]	[10.0]
^{60}Co	Not Measured					< 3.E-6
^{137}Cs						0.250
^{154}Eu						< 1.E-4
^{155}Eu						< 7.E-6
^{241}Am						< 9.E-5
Opportunistic Analytes						
Ag	<0.331	<0.340	<0.324	<0.331	<0.349	<0.324
As	<6.782	<6.958	<6.643	<6.772	<7.142	<6.629
Ba	[0.21]	[0.15]	[0.10]	[0.10]	[0.14]	[0.15]
Be	[0.01]	[0.01]	[0.01]	[0.01]	[0.02]	[0.01]
Ca	[2.68]	[1.39]	[1.67]	[1.83]	[2.16]	[2.90]
Ce	<1.577	<1.618	<1.545	<1.575	<1.661	<1.542
Co	<0.379	<0.388	<0.371	<0.378	<0.399	<0.370
Cu	[0.32]	[0.27]	[0.30]	[0.60]	[0.30]	<0.216
Dy	<0.457	<0.469	<0.448	<0.457	<0.482	<0.447
Eu	<0.173	<0.178	<0.170	<0.173	<0.183	<0.170
K	[66.24]	[64.72]	<20.391	[23.62]	[28.57]	[40.08]
La	<0.442	<0.453	<0.433	<0.441	<0.465	<0.432
Li	[0.88]	[0.68]	[0.56]	[0.50]	[0.50]	[0.34]
Mg	<0.363	<0.372	<0.355	<0.362	<0.382	<0.355
Mo	<0.820	<0.841	<0.803	<0.819	<0.864	<0.802
Nd	<0.852	<0.874	<0.834	<0.850	<0.897	<0.832
Pb	<5.047	[7.44]	[5.56]	[5.67]	[5.65]	[5.55]
Pd	<0.994	<1.019	<0.973	<0.992	[1.06]	<0.971
Rh	<1.893	<1.942	<1.854	<1.890	<1.993	<1.850
Ru	<1.341	<1.375	<1.313	<1.339	<1.412	<1.310

Table G.5 (Contd)

Analyte	**Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; μg/mL for Metals and Anions; μCi/mL for Radionuclides**					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Sb	[3.47]	<3.236	[3.09]	<3.150	[5.65]	<3.083
Se	<11.040	<11.326	<10.814	<11.024	<11.626	<10.791
Sn	<4.258	<4.369	<4.171	<4.252	<4.484	<4.162
Ta	<2.681	<2.751	<2.626	<2.677	<2.823	<2.621
Te	<4.101	<4.207	<4.016	<4.095	<4.318	<4.008
Th	<1.546	<1.586	<1.514	<1.543	<1.628	<1.511
Ti	<0.068	<0.070	<0.066	<0.068	<0.071	<0.066
Tl	<5.993	<6.149	<5.870	<5.984	<6.311	<5.858
V	<0.117	<0.120	<0.114	<0.117	<0.123	<0.114
W	<2.997	<3.074	<2.935	<2.992	<3.156	<2.929
Y	<0.069	<0.071	<0.068	<0.069	<0.073	<0.068
Analyte uncertainties were typically within ±15% (2-s); results in brackets indicate that the analyte concentrations were less than the minimum detection limit (MDL) and greater than the estimated quantitation limit (EQL), and uncertainties were >15%.						

Table G.6. Analyte Concentrations as a Function of Time for Leaching at 80ºC, in M

Analyte	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; M for Metals and Anions					
	0 hr	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
0.25 M NaOH						
Density	1.01	1.03	1.04	1.02	1.02	1.02
Al	8.35E-04	2.33E-03	2.45E-03	2.66E-03	3.13E-03	3.69E-03
B	[3.17E-05]	[4.36E-05]	[3.77E-05]	[4.35E-05]	[4.62E-05]	[4.17E-05]
Bi	<4.47E-06	<4.51E-06	<4.50E-06	<4.50E-06	<4.48E-06	<4.32E-06
Cd	<9.41E-07	<9.49E-07	<9.48E-07	<9.47E-07	<9.44E-07	<9.10E-07
Cr	[4.91E-06]	1.04E-05	1.12E-05	1.37E-05	1.79E-05	2.45E-05
Fe	[1.84E-05]	3.63E-05	3.09E-05	[2.47E-05]	[1.84E-05]	[1.45E-05]
Mn	3.20E-06	3.25E-06	3.19E-06	3.26E-06	3.11E-06	3.08E-06
Na	0.28	0.30	0.30	0.30	0.30	0.30
Ni	<1.27E-06	<1.28E-06	<1.28E-06	<1.28E-06	<1.28E-06	<1.23E-06
P	1.15E-02	1.94E-02	1.97E-02	1.96E-02	1.99E-02	1.97E-02
S	[1.84E-04]	[1.86E-04]	[2.35E-04]	<1.56E-04	[2.14E-04]	[1.59E-04]
Si	1.10E-04	8.09E-04	7.90E-04	7.78E-04	7.79E-04	7.63E-04
Sr	[3.02E-07]	[2.11E-07]	[1.79E-07]	[1.61E-07]	[1.35E-07]	[1.58E-07]
U	7.32E-04	4.89E-04	3.74E-04	2.90E-04	2.27E-04	1.47E-04
Zn	[1.90E-05]	[1.39E-05]	[1.25E-05]	[1.15E-05]	[1.48E-05]	[1.20E-05]
Zr	<3.75E-07	<3.79E-07	<3.78E-07	<3.78E-07	<3.76E-07	<3.63E-07
Fluoride	<3.95E-04	[4.00E-04]	[4.00E-04]	<3.95E-04	[4.00E-04]	[4.32E-04]
Nitrite	2.04E-04	2.12E-04	2.10E-04	2.10E-04	2.16E-04	2.16E-04
Nitrate	1.50E-03	1.60E-03	1.59E-03	1.59E-03	1.63E-03	1.63E-03
Phosphate	1.14E-02	1.95E-02	1.92E-02	1.92E-02	2.00E-02	1.99E-02
Sulfate	1.04E-04	1.18E-04	1.18E-04	1.18E-04	1.22E-04	1.20E-04
1 M NaOH						
Density	1.05	1.06	1.06	1.06	1.06	1.05
Al	1.14E-03	2.77E-03	3.17E-03	3.36E-03	3.33E-03	3.35E-03
B	[3.01E-05]	[3.83E-05]	[3.42E-05]	[3.20E-05]	[2.93E-05]	[3.40E-05]
Bi	<4.77E-06	<4.57E-06	<4.42E-06	<4.52E-06	<4.54E-06	<4.40E-06
Cd	<1.00E-06	<9.62E-07	<9.31E-07	<9.52E-07	<9.56E-07	<9.26E-07
Cr	[4.79E-06]	1.48E-05	1.98E-05	2.48E-05	2.99E-05	4.05E-05
Fe	4.98E-05	8.60E-05	6.56E-05	5.60E-05	4.76E-05	4.16E-05
Mn	4.11E-06	3.53E-06	3.48E-06	3.45E-06	3.59E-06	3.32E-06
Na	0.95	1.03	1.03	1.05	1.04	1.04
Ni	<1.36E-06	<1.30E-06	<1.26E-06	<1.29E-06	<1.29E-06	<1.25E-06
P	1.52E-02	2.00E-02	1.99E-02	2.04E-02	2.03E-02	2.05E-02
S	[2.07E-04]	[2.48E-04]	[1.92E-04]	[1.77E-04]	[2.47E-04]	[2.10E-04]
Si	2.12E-04	9.14E-04	9.06E-04	9.35E-04	9.27E-04	9.41E-04
Sr	8.37E-07	[2.18E-07]	[1.83E-07]	[1.80E-07]	[1.66E-07]	[1.40E-07]
U	6.58E-04	3.78E-04	2.82E-04	2.33E-04	1.89E-04	1.45E-04
Zn	4.75E-05	4.07E-05	3.89E-05	3.73E-05	3.66E-05	3.25E-05
Zr	<4.00E-07	<3.84E-07	<3.71E-07	<3.80E-07	<3.81E-07	<3.69E-07
Fluoride	[3.58E-04]	[4.42E-04]	[4.53E-04]	[4.53E-04]	[4.53E-04]	[4.63E-04]
Nitrite	1.85E-04	2.05E-04	2.11E-04	2.08E-04	2.08E-04	2.08E-04
Nitrate	1.50E-03	1.66E-03	1.73E-03	1.71E-03	1.69E-03	1.71E-03

Table G.6 (Contd)

	Analyte Concentration and Density at Given Time After Cooling to Ambient (~21°C) Temperature; g/mL for Density; M for Metals and Anions					
Analyte	**0 hr**	**1 hr**	**2 hr**	**4 hr**	**8 hr**	**24 hr**
Phosphate	1.58E-02	2.08E-02	2.13E-02	2.11E-02	2.07E-02	2.11E-02
Sulfate	[1.04E-04]	1.25E-04	1.25E-04	[1.25E-04]	1.25E-04	1.25E-04
3 M NaOH						
Density	1.11	1.13	1.13	1.13	1.13	1.13
Al	1.47E-03	2.85E-03	3.21E-03	3.26E-03	3.30E-03	3.21E-03
B	<7.00E-05	<7.18E-05	[1.69E-04]	[1.31E-04]	[1.47E-04]	<6.85E-05
Bi	<2.26E-05	<2.32E-05	<2.22E-05	<2.26E-05	<2.38E-05	<2.21E-05
Cd	<4.77E-06	<4.89E-06	<4.67E-06	<4.76E-06	<5.02E-06	<4.66E-06
Cr	[7.89E-06]	[1.93E-05]	[2.44E-05]	[3.03E-05]	[3.51E-05]	[4.68E-05]
Fe	2.37E-04	3.34E-04	2.62E-04	2.14E-04	1.95E-04	1.63E-04
Mn	[7.46E-06]	[4.12E-06]	[3.82E-06]	[3.78E-06]	[4.17E-06]	[3.98E-06]
Na	2.70	3.00	2.94	2.99	3.03	2.95
Ni	<6.45E-06	<6.62E-06	<6.32E-06	<6.44E-06	<6.79E-06	<6.30E-06
P	1.72E-02	1.97E-02	1.95E-02	1.96E-02	1.97E-02	1.94E-02
S	<7.87E-04	<8.08E-04	<7.71E-04	<7.86E-04	<8.29E-04	<7.69E-04
Si	[1.35E-04]	8.87E-04	9.30E-04	9.40E-04	9.58E-04	9.55E-04
Sr	[2.59E-06]	[8.86E-07]	[6.70E-07]	[5.75E-07]	[4.93E-07]	[5.63E-07]
U	8.52E-04	3.82E-04	2.77E-04	2.25E-04	[1.81E-04]	[1.43E-04]
Zn	[6.27E-05]	[7.92E-05]	[7.56E-05]	[6.74E-05]	[7.11E-05]	[7.07E-05]
Zr	<1.90E-06	<1.95E-06	<1.86E-06	<1.90E-06	<2.00E-06	<1.86E-06
Fluoride	[3.84E-04]	[4.21E-04]	[4.37E-04]	[4.37E-04]	[4.53E-04]	[4.32E-04]
Nitrite	[1.78E-04]	[1.83E-04]	[1.98E-04]	[2.00E-04]	[2.02E-04]	[2.00E-04]
Nitrate	1.32E-03	1.52E-03	1.50E-03	1.57E-03	1.52E-03	1.52E-03
Phosphate	1.75E-02	1.99E-02	2.04E-02	2.04E-02	2.07E-02	2.01E-02
Sulfate	[1.15E-04]	[1.15E-04]	[1.15E-04]	[1.15E-04]	[1.15E-04]	[1.04E-04]

Analyte uncertainties were typically within ±15% (2-s); results in brackets indicate that the analyte concentrations were less than the minimum detection limit (MDL) and greater than the estimated quantitation limit (EQL), and uncertainties were >15%.

Appendix H

CUF Filtration/Leaching Experimental Methods and Analyses

Appendix H: CUF Filtration/Leaching Experimental Methods and Analyses

This appendix describes the experimental equipment and analyses used to perform the bench top filtration and leaching tests of the Group 7 composite waste sample using the crossflow ultrafiltration testing apparatus (commonly called the CUF) described in Section 5 of this report.

H.1 Filtration/Leaching Apparatus

The testing apparatus is a bench top skid that allows up to 4-liters of a waste solution to be circulated through a tubular filter. The apparatus can simultaneously measure the filter feed flow rates, filtrate flow rates, system pressures, and temperatures. The testing skid uses a heat exchanger on the main flow loop to cool the feed solution during filtration operations, and it has a heater on the main holding tank to perform leaching at elevated temperatures.

H.1.1 Cell Unit Filter

The Waste Treatment and Immobilization Plant (WTP) Pre-Treatment Facility (PTF) plans to use cross flow ultrafiltration to separate the low-activity waste (LAW) liquid streams from the high-level waste (HLW) slurry streams through the process. The filter elements, called cell unit filters, are porous, sintered metal tubes. The filter feed flows through the inside of the filter element axially while the feed permeate passes through the tube walls radially. Filtration occurs when the pressure differential between the inside and outside walls of the filter element (known as the transmembrane pressure) is high enough to drive the slurry permeate through the tubular walls. The axial flow across the filter walls minimizes solid buildup and allows filtration to occur continuously with minimal downtime for back pulsing.

The filters purchased for this testing work were supplied by the Mott Corporation,(a) using the same specifications(b) for the filters being purchased for the WTP PTF. The filters are made of 316 stainless steel and have an effective filtration rating of 0.1 μm. The dimensions of the filter element used in this test are shown in Figure H.1.

(a) Mott Corporation, 84 Spring Lane, Farmington, CT 06032.

(b) Specification WTP-070110, written by JGH Geeting, for PNNL Purchase Order 38825, February 2, 2007.

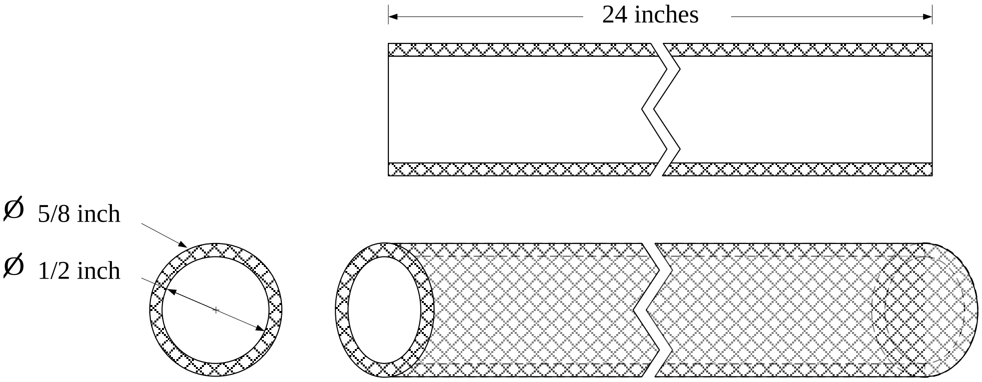


Figure H.1. Illustration of the Filter Element

The filter element was received installed in a shell-in-tube configuration with an outer tube surrounding the filter element to capture the filtrate while the inlet and the outlet of the filter (which extend past the shell and provide access to the inside diameter of the filter) were welded to steel tubing of a matching outer/inner diameter. The shell side had two $^{3}/_{8}$-inch stainless steel tubes exiting from the filter assembly, one in the center to collect filtrate from the filter, and the other near the inlet of the filter to function as a drain. Pressure ports (¼-inch stainless steel tubing) were installed on the inlet and outlet connections of the assembly to measure the pressure inside the filter. O-ring face seal fittings (Swagelok[a] VCO®) were also placed on the inlet and outlet filter feed tube connections for easy installation on the filtration/leaching skid. Figure H.2 and Figure H.3show the filter assembly.

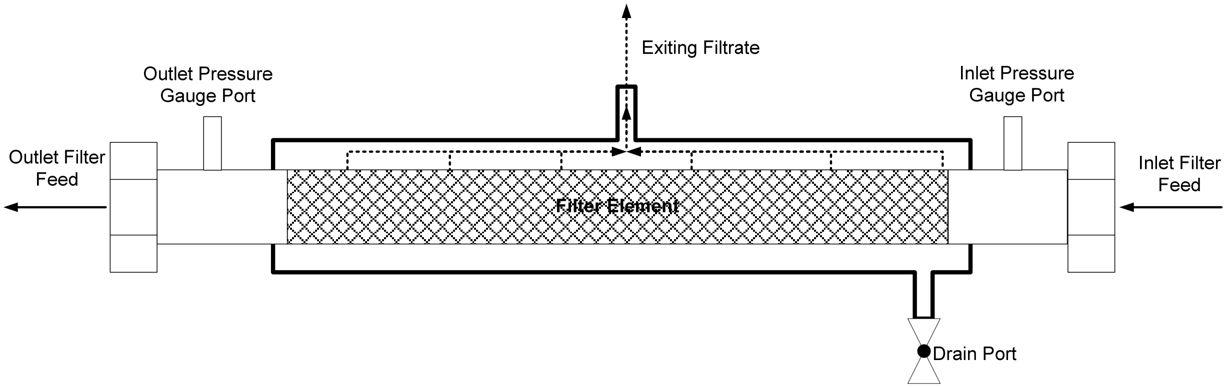


Figure H.2. Illustration of the Filter Assembly Sketch (*Not to Scale*)

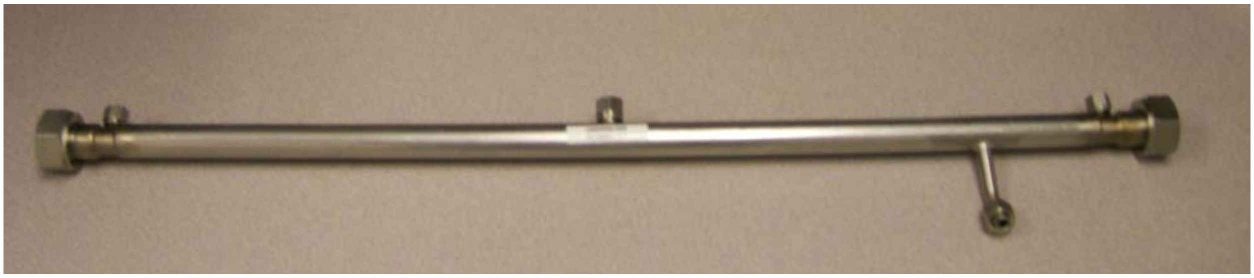


Figure H.3. Photograph of the Filter Assembly

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[a] Swagelok Company, 31400 Aurora Road, Solon, Ohio 44139

H.1.1.1 Filtration/Leaching Skid

The filter described in the section above is installed in a bench top skid that circulates the test waste slurries through the inside of the filter and diverts the filter permeate to a collection bottle or recycles it back into the slurry. Figure H.4 shows a piping diagram of the testing skid. Figure H.5 and Figure H.6 are electronic photographs of the assembled system before and after installation into a hot cell in the Shielded Analytical Laboratory where the testing was performed.

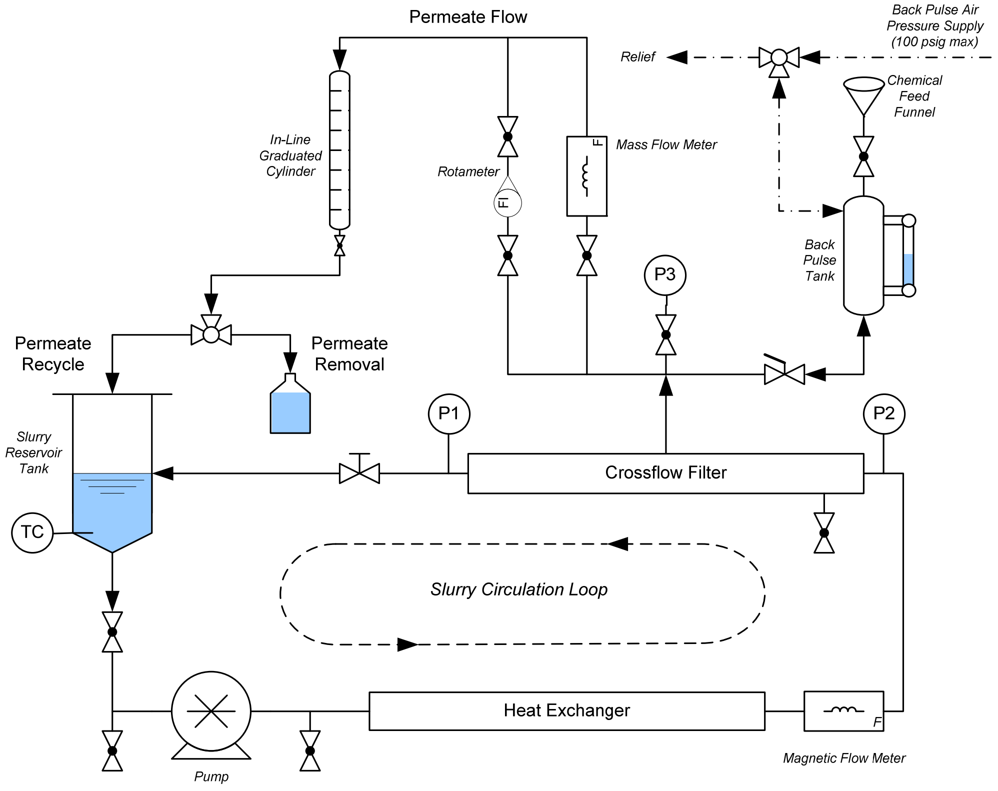

Figure H.4. Piping Diagram of CUF Skid

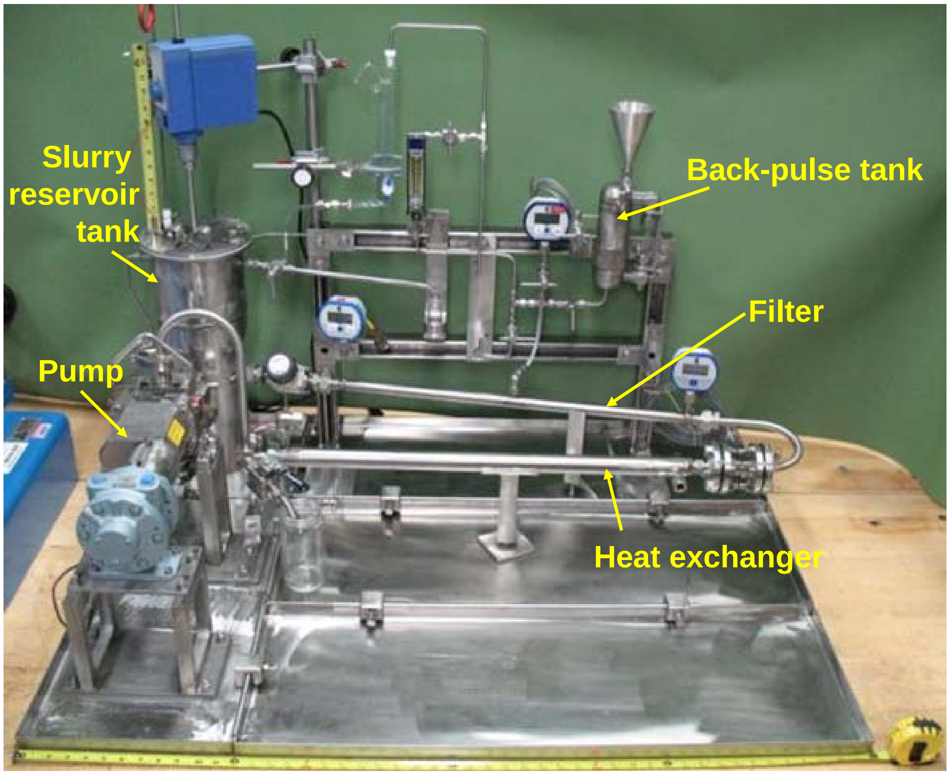

Figure H.5. Photograph of the CUF Prior to Hot Cell Installation

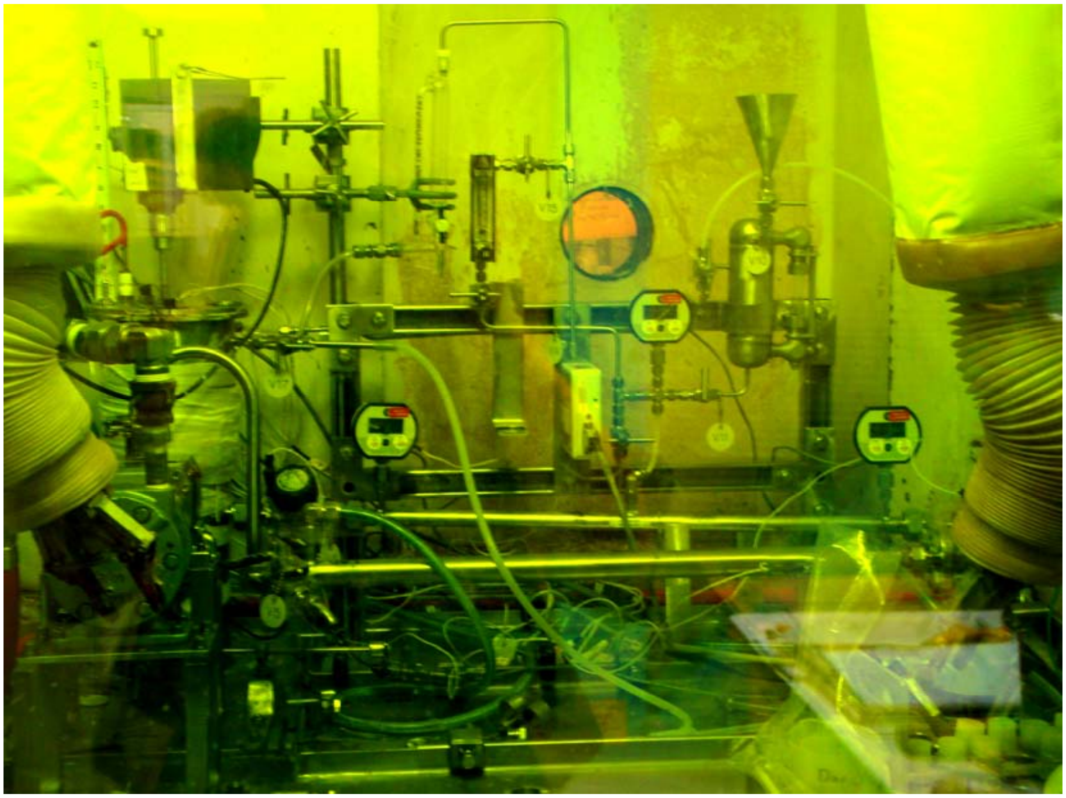

Figure H.6. Picture of the CUF Installed in Cell 5 of the Shielded Analytical Laboratory

The CUF skid has four main parts:

- Slurry reservoir tank
- Slurry recirculation loop
- Permeate flow loop
- Permeate back-pulse chamber.

The slurry reservoir was a cylindrical, stainless steel tank with a four-liter capacity. Agitation in the tank was provided with an overhead mixer using a 2-inch-diameter, three-blade, marine propeller. The bottom of the vessel was sloped at a 15° angle to allow the system to be easily drained,. Baffles were also installed on the tank wall to improve slurry mixing. Heat tape was installed around the walls of the tank for leaching at elevated temperatures. The heat tape was connected to a temperature controller that adjusted the electrical load to the heat tape based on a thermocouple input. A dual, Type-K thermocouple was installed inside the reservoir tank (extending just below the overhead mixing impeller) to measure the temperature of the slurry inside the reservoir. One of the thermocouple elements was connected to the heat tape's temperature controller and the other to a data collection system.

The slurry recirculation loop routed slurry flow from the slurry reservoir, through the filter, and back into the reservoir for filtration operations. The bottom of the slurry reservoir was connected to the suction side of the slurry recirculation pump, a positive displacement, rotary lobe pump. The pump was driven by an air motor supplied with compressed air from an external air compressor. The speed of the pump was controlled by an external air regulator controlling the pressure supplied to the air motor. An optical tachometer measured the speed of the pump by measuring the rotation speed of the connection coupling between the air motor and the pump, which had a piece of reflective tape placed on it. The pump discharge flowed through a single pass shell and tube heat exchanger used to remove excess heat from the system caused by the mechanical energy input from the mixer and pump, as well as heat generated from frictional flow.

An exterior chiller circulated chiller fluid (water/anti-freeze mixture) through the exterior shell of the heat exchanger to remove heat away from the circulating slurry on the tube side of the heat exchanger. The chiller controlled the chilling fluid temperature by monitoring the temperature of the slurry exiting the heat exchanger via a resistance temperature detector installed in the discharge line.

The slurry then flowed through a magnetic flow sensor that monitored the volumetric flow of the slurry inside the slurry recirculation loop. The sensor's output was displayed on an external panel meter that generated an analog output signal monitored by a data collection system. The data from this device was used to calculate the axial velocity (AV) inside the filter element.

The flowing slurry then entered the filter. Digital pressure gauges were installed on the inlet and outlet ports of the filter, which displayed the pressure at both locations in pounds per square inch, gauge (psig). The gauges also transmit analog output signals monitored by a data collection system. The data from these devices were used to calculate the average pressure inside the filter and the axial pressure drop across the element.

A manual pinch valve was placed on the filter's discharge. The valve was used to adjust the pressure inside the filter to drive permeate flow through the filter membrane wall. It was also connected to the slurry reservoir tank and was closed completely when the tank was isolated for leaching.

The permeate flow loop started at the center of the filter assembly where a poly-line connected the filter to a ¼-inch stainless steel pipe manifold that directed the filter permeate through a series of measurement devices. A digital pressure gauge was installed at this point to measure the pressure, in psig, on the permeate side of the filter. Like the other two digital gauges, this instrument transmitted an analog output signal to a data collection system. The transmembrane pressure (TMP) across the filter was then calculated by subtracting the pressure on the permeate side of the filter from the average pressure of the slurry inside the filter.

Flow from the filter was either diverted through a mass flow meter calibrated up to 180 mL/min or to a user calibrated rotometer that could measure flow up to 30 mL/s. The mass flow meter also measured density of the permeate flow and transmitted two analog output signals to the data collection system for the volumetric flow rate and the density. An in-line glass cylinder was installed on the discharge of both meters to take manual measurements of the permeate flow rate. Measurements were taken by closing a valve at the bottom of the cylinder, allowing permeate to fill the vessel. Liquid volume in the glass vessel was measured by markings on the outside. The permeate flow rate was calculated from observed changes in permeate volume in the cylinder over a measured time interval.

Permeate exited through a three-way valve connected to the slurry reservoir tank. This valve directed permeate either back to the slurry reservoir tank to be mixed back into the slurry or to a sampling hose used to collect permeate into sample containers.

The permeate back-pulse chamber was to the right of the permeate flow loop and connected to the filter at the same location as the permeate pressure gauge. The chamber was an approximately 500-mL steel vessel with a sight glass to track the volume inside the chamber. The vessel had three entry ports:

- ¼ inch line with a two-way toggle valve on the bottom connecting the vessel to the permeate side of the filter
- ¼ inch line with a two-way valve connecting the top of the vessel to a funnel
- ¼ inch line with a three-way valve connecting the top of the vessel to a compressed air line and vent line connected to the top of the slurry reservoir tank

The bottom line was used to direct permeate flow from the chamber to the filter. The funnel on the top of the chamber was used to introduce cleaning and rinse solutions directly to the vessel. The compressed gas line was used to pressurize the fluid in the chamber with compressed gas and to vent the chamber to atmospheric pressure.

To back-pulse the filter, the vessel was first vented to atmospheric pressure. Next, permeate was allowed to fill the chamber by opening the toggle valve. Once the chamber was half full of permeate (as seen through the sight glass), the toggle valve was closed. The three-way valve was then positioned to allow compressed gas at 80 psig to fill to the chamber and pressurize the fluid. The three-way valve was then positioned to isolate the now pressurized chamber. The slurry pressure inside the filter was then dropped below the pressure of the compressed gas line (< 20 psig). The toggle valve at the bottom of the tank was opened, allowing the pressurized permeate inside the chamber to flow backwards through the filter element. The toggle valve was closed when the permeate level was below the visible portion of the sight glass. After the back-pulse was completed, the three-way valve was positioned to vent the chamber back to atmospheric pressure.

Flow from the glass cylinder goes through a 3-way valve. This valve directs flow either back to the slurry reservoir tank to be mixed back to the slurry or to a sampling hose that is used to transfer the permeate into a sample container.

H.1.1.2 Instrumentation and Data-Acquisition System

Because the system was to be operated in a hot cell, one of the design goals of the skid was to minimize the number of manual measurements during testing and record the data in an electronic format that could be analyzed readily with other approved software. Most of the sensors on the testing apparatus transmitted analog data to an external data acquisition collection system (DACS), manufactured by National Instruments.(a) This system relayed the analog data to a LabView data-collection program operating on a desktop computer system using Windows XP (Professional), service pack 2. The software program scaled the analog data and simultaneously recorded the data electronically and displayed it on the computer's monitor. The performance of the software was verified by test plan RPP-WTP-QA-010, and all reportable data were measured on calibrated instrumentation, including the external DACS board. Figure H.7 shows a diagram of the electronic sensors attached to the DACS, and Figure H.8 displays the screen windows from the data-collection program.

(a) National Instruments Corporation, 11500 N Mopac Expwy, Austin, TX 78759-3504

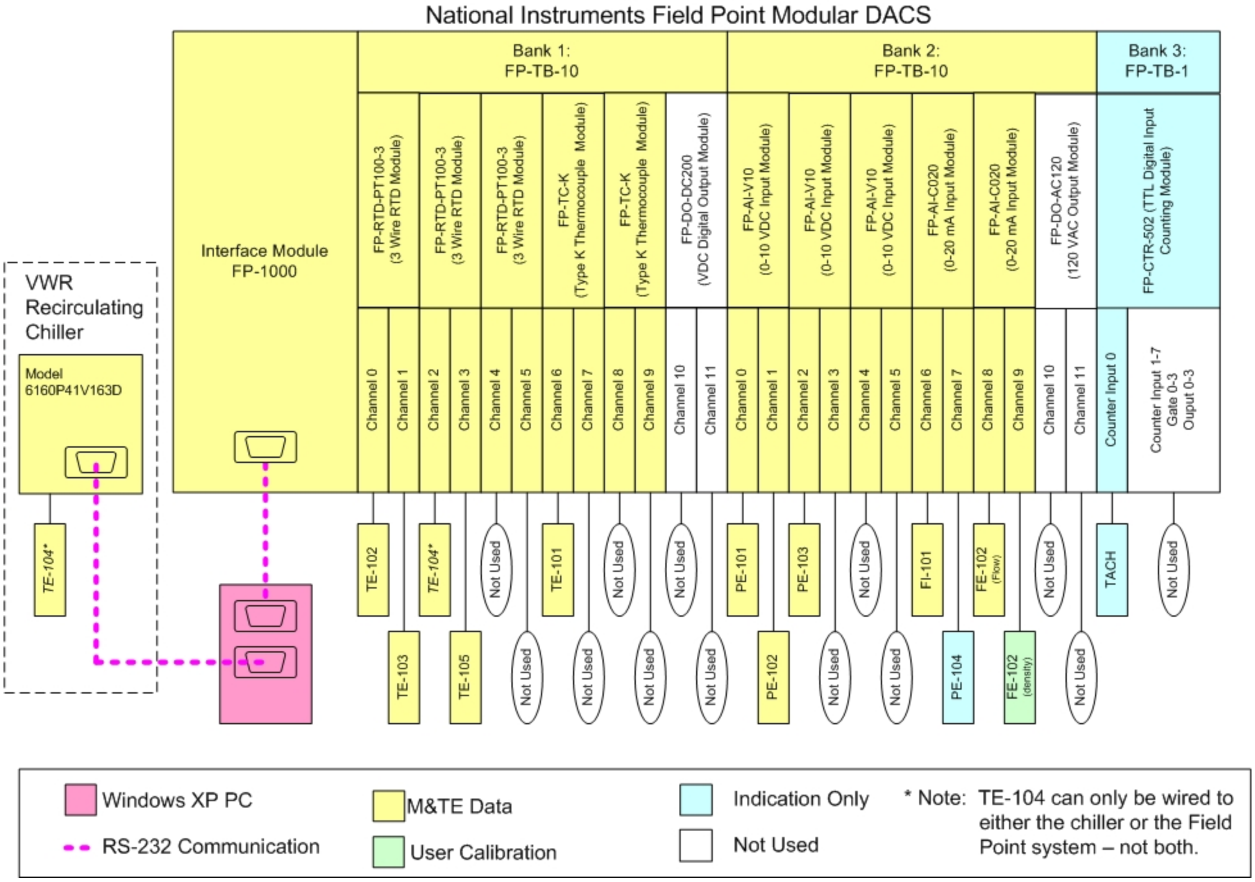

Figure H.7. Diagram of DACS System

Figure H.8. Digital Images of DACS Display Windows

H.1.1.3 CUF Operation and Sampling

The CUF was developed to operate in several different operational modes to simulate filtration and leaching processes of the WTP pretreatment system. The filtration operation occurred in a recycling or dewatering mode. During recycling operations, permeate was returned to the slurry reservoir tank. By returning permeate back into the slurry, the undissolved solids (UDS) concentration in the slurry was maintained in a steady-state condition. The CUF was operated in this mode to understand how the effects of time, pressure, and axial velocity impact the filtration of slurry while maintaining the physical properties of the slurry. During dewatering operations, permeate from the filter was diverted to a collection vessel, operating the system at a constant transmembrane pressure and axial flow rate and allowing the UDS concentration of the slurry to change. The CUF was operated in this mode to understand how the slurry's rheological and filtration properties changed as its UDS concentration changed.

Chemical leaching occurred in the slurry reservoir tank when isolated from the slurry circulation loop. Isolating the slurry reservoir tank for leaching operations required draining the slurry and permeate inside the CUF filtration piping first. Once the tank was isolated from the slurry circulation loop, the slurry and permeate were returned to the slurry reservoir tank along with the leaching agent. When the leaching operations occurred at elevated temperatures, heat tape surrounding the slurry reservoir was used to heat the vessel.

Samples were collected throughout testing to measure the physical and chemical properties of the waste slurry or permeate. Slurry samples were collected from two separate locations on the system. Small slurry samples (20 mL) were collected from the top of the slurry reservoir with the mixer operating using 18-in.-long pipettes. The tips of the pipettes were cut at an angle to allow slurry to flow into the pipette without being plugged. Larger samples (100 mL), such as for rheology measurement, were collected using the drain valve on the pump discharge while the pump is running. Permeate samples were collected during dewatering operations directly from the dewatering sample hose. However, permeate collected during leaching operations required manual filtration. A slurry sample was initially collected from the slurry reservoir using a pipette described earlier. The sample was filtered through a 0.45-μm syringe filter.

H.1.1.4 Baseline Testing of Filter

Before testing with HLW composite, the skid and the filter were initially cleaned with a laboratory cleaning solution (Alconox(a) at 1:100 dilution) and rinsed with DI water to remove cutting oils and soils from the skid fabrication process and shipping from the manufacturer. After cleaning, the filter flux was measured with a solution of 0.01M NaOH—this is referred to as the *clean water flux*. Testing was performed at 10, 15, and 20 transmembrane pressure (TMP) at an axial velocity of 11 ft/s. Each pressure condition was held for 20 minutes with a single back-pulse performed before changing the pressure. Next, a strontium carbonate ($SrCO_3$) slurry was prepared to test the filter flux with a slurry solution. As before, the $SrCO_3$ slurry was placed in the filtration skid and was operated with the permeate recycling back into the slurry reservoir. Testing was performed at 10, 20, and 30 TMP at an axial velocity of 11 ft/s. A single back-pulse was performed between each test condition. Afterwards, the slurry was removed and rinsed out with DI water (approximately 10 L). The clean water flux was again tested with a solution of 0.01 M NaOH to verify that the filter was clean before testing with HLW slurries.

The results of the baseline filter flux testing are shown in Figure H.9. Overall, the baseline flux for the filter was demonstrated to be considerably higher than the predicted flux for the waste slurries to be tested (e.g., 0.04 gpm/ft^2 for dewatering operations). No solids were evident in the permeate during filtration of the strontium carbonate slurry, and the density of the permeate was measured at 1.12 g/mL by the mass flow meter. A sample of the permeate was taken, and its density was measured as 1.11 g/mL with a calibrated balance and a 50-mL volumetric flask. While the density could be measured, the volumetric flow of the permeate was beyond the range of the mass flow meter for all three tests. After a density check, permeate flow was diverted through the skid's rotometer. For the $SrCO_3$ flux measurements, the flow was slow enough to verify the flow rate using the in-line volumetric cylinder to measure the permeate flow.

(a) Alconox, Inc., 30 Glenn Street, Suite 309, White Plains, NY 10603 USA.

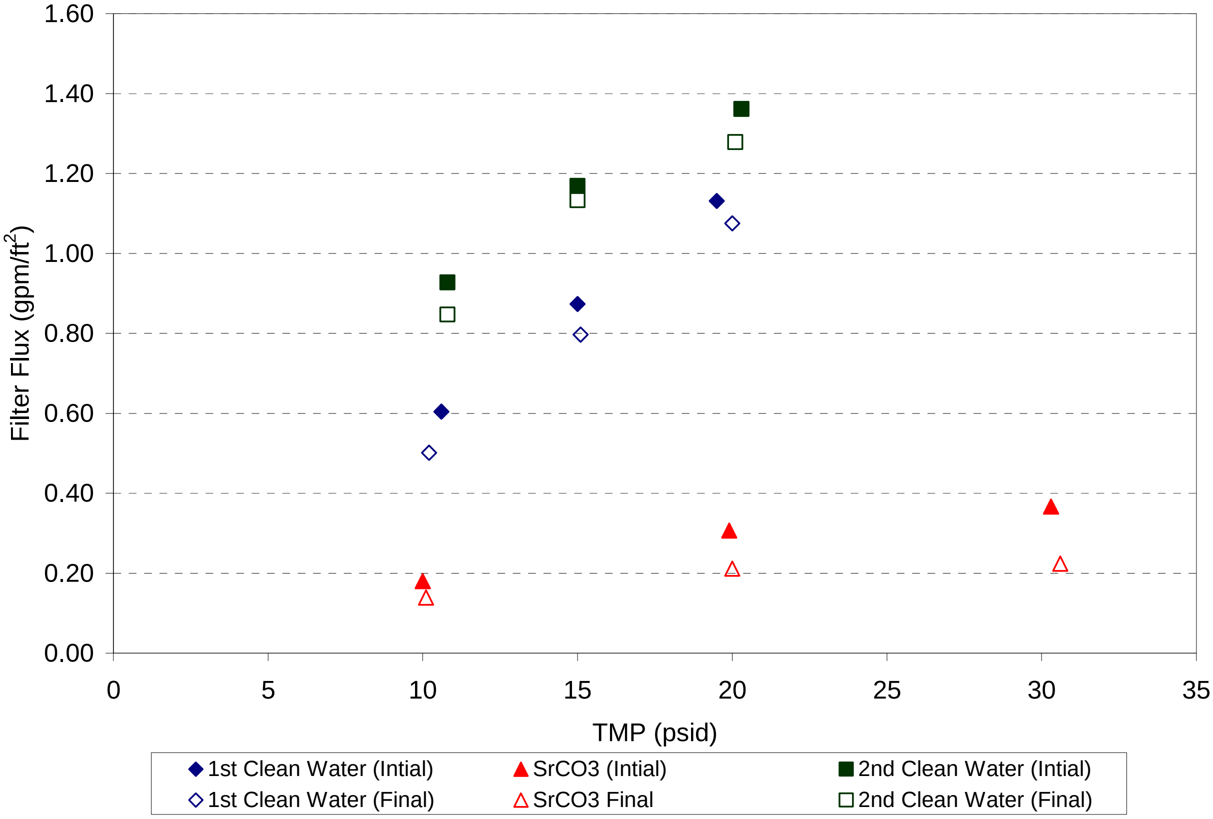

Figure H.9. Initial Clean Water/SrCO$_3$ Flux Measurements of Filter

H.1.2 Filtration Data Analysis

H.1.2.1 Filtration Terms and Equations

Filtration is examined in this report as a filter flux defined as:

$$J = \frac{Q_{permeate}}{A_{filter}} \qquad \text{(H.1)}$$

where J is the filter flux (gpm/ft^2), $Q_{permeate}$ is the volumetric permeate flow, and A_{filter} is the filtration surface area.

In this study, the filter area is assumed as the inside area of the filter element, which is defined as:

$$A_{filter} = \pi Di_{filter} L_{filter} \qquad \text{(H.2)}$$

where Di_{filter} is the filter element inside diameter, and L_{filter} is the filter element length.

The permeate volumetric flow rate is also corrected for viscosity and surface tension effects because the permeate temperature deviated from 25°C. For a temperature T, the corrected permeate flow rate and filter flux are given as:

$$Q_{25°C} = Q_T e^{2500\left[\frac{1}{T+273}-\frac{1}{298}\right]}$$
$$J_{25°C} = J_T e^{2500\left[\frac{1}{T+273}-\frac{1}{298}\right]} \quad \text{(H.3)}$$

The pressure drop across the filter (i.e., the TMP) was calculated in this test as:

$$TMP = \Delta P_m = \frac{(P_{inlet} + P_{outlet})}{2} - P_{permeate} \quad \text{(H.4)}$$

where P_{inlet} is the pressure at the filter inlet, P_{outlet} is the pressure at the filter outlet, and $P_{permeate}$ is the pressure at the permeate side of the filter. A common unit for measuring TMP is psid, which is pounds per square inch, differential.

The axial velocity inside the filter is calculated by dividing the volumetric slurry flow of the filter by the cross-section area of the inside diameter of filter:

$$AV = \frac{Q_{slurry}}{S_a} = \frac{Q_{slurry}}{\frac{\pi}{4} Di_{filter}^2} \quad \text{(H.5)}$$

where S_a is the cross sectional area of axial flow, and Q_{slurry} is the volumetric slurry flowrate in the axial direction.

The Darcy equation describes filter flux as:

$$J = \frac{\Delta P_m}{\mu_{permeate} R_m} \quad \text{(H.6)}$$

where ΔP_m is the pressure drop across the filter membrane, $\mu_{permeate}$ is the viscosity of the permeate, and R_m is the overall resistance of the filter membrane.

The filter-resistance term is considered a more complicated term, which is a sum of the resistance of the actual filter, the resistance of the filter cake that forms on the surface of the filter surface, and the resistance due to fouling of the filter. For cross-flow filtration, the overall resistance of the filter membrane for low concentrated slurries is usually constant, and turbulent flow conditions exist inside the filter. The transmembrane pressure and permeate viscosity are the controlling operational parameters. During dewatering, the slurry's flow properties change, and the filter resistance becomes more significant. When the slurry's UDS concentration begins to approach a maximum limit, known as the gel concentration, the filter flux can be described as

$$J = k \cdot \ln\left[\frac{C_s}{C_g}\right] \tag{H.7}$$

where C_s is the slurry UDS concentration, and C_g is the slurry gel concentration.

When the flux is impacted by the UDS concentration, the impact of axial velocity becomes significant as well. This is due to how the axial velocity affects the thickness of the filter cake inside the filter.

H.1.2.2 Filtration Test Matrix

To understand the impact of the transmembrane pressure and axial velocity on the filter flux of the waste slurry, a filtration test matrix was developed to understand their individual effects. Like the clean water and $SrCO_3$ slurry flux testing described in section H.1.1.4, the waste slurry is circulated through the filtration skid while the slurry permeate leaving the filter is recycled back to the slurry reservoir. By recycling permeate in this way, the UDS concentration of the slurry stays constant. Using a TMP of 40 psid and an AV of 13 ft/s as the baseline condition, the testing conditions are varied to demonstrate how the flux varies as TMP and AV change from the center condition. Table H.1 and Figure H.9 outline the conditions for the testing performed.

Each filtration condition is maintained for at least an hour while permeate is recycled back to the slurry reservoir tank. Before the test condition is changed, a back-pulse on the filter is performed to provide the same starting conditions for each test. The initial test performed at the baseline condition is performed for a minimum of 3 hours to track how the filter flux varies with time to track possible fouling due to the waste.

Table H.1. Filtration Test Matrix Operating Conditions

Test number	Minimum Duration (hours)	Target TMP[(a)] (psid)	Target AV* (fps)
1	3	40	13
2	1	30	11
3	1	30	15
4	1	50	15
5	1	50	11
6	1	40	13
7	1	40	9
8	1	40	17
9	1	20	13
10	1	60	13
11	1	40	13

(a) Actual conditions may vary based upon slurry volume and rheology. All conditions may not be obtainable.

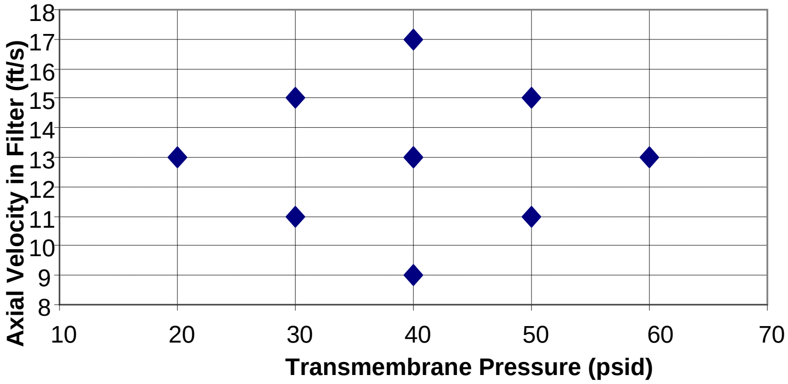

Figure H.9. Filtration Test Matrix Chart

When the slurry is at low solids concentrations, the system is expected to be controlled by the transmembrane pressure (Equation H.6), with little impact from the axial velocity. However, once the slurry is concentrated and the flow properties change, it is expected that the axial velocity will have some effect on the filtration of the system.

H.1.2.3 Dewatering Operation Analysis

During dewatering operations of the waste slurries, the transmembrane pressure and axial velocity are maintained at the baseline condition of 40 psid and 13 fps. By maintaining the operating conditions of the filtration, the only effect on filtration should be the slurry concentration. As the slurry's UDS changes, the filter flux can be monitored and graphically charted, as shown in Figure H.10. As discussed earlier, the filter flux is initially expected to follow Equation H-6 for low-solids concentrations, which will appear as a horizontal line on the chart when the TMP is held constant. However, as the slurry begins to concentrate, the filtration behavior of the slurry is expected to change and begin to follow Equation H.7. With graphic analysis, the transition in filtration behavior can be understood.

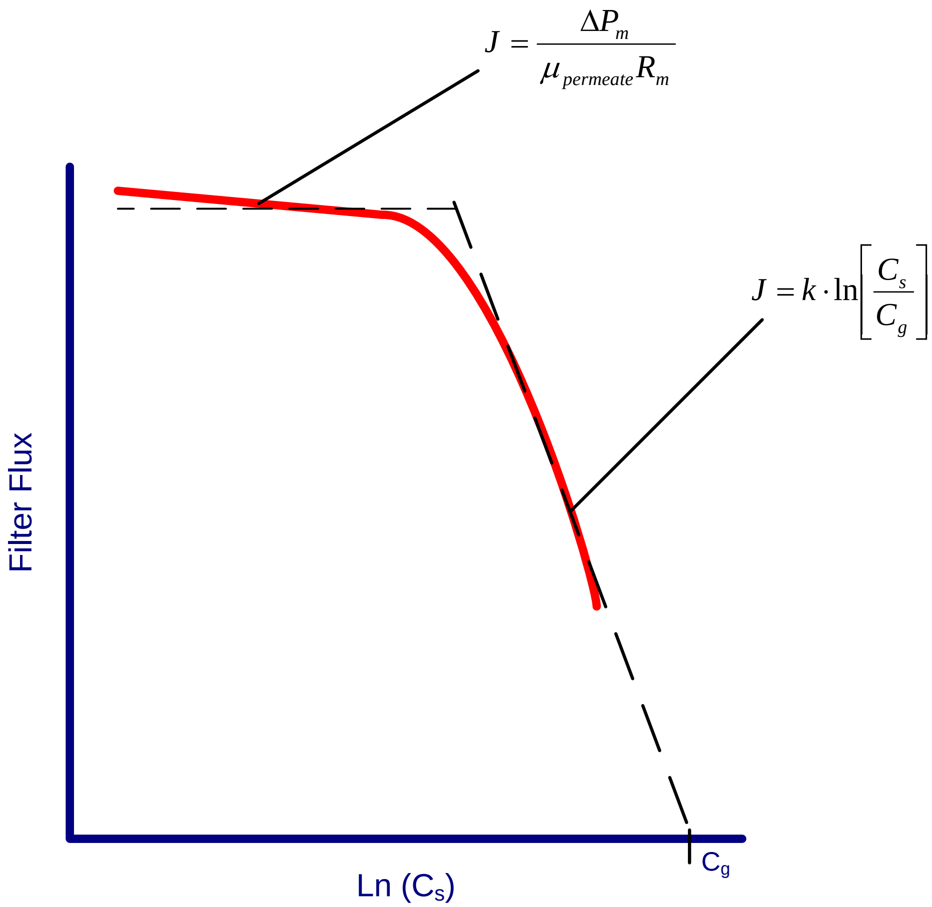

Figure H.10. Example of a Dewatering Curve

H.1.2.4 Effects of Rheology and Particle Size

During testing operations, rheology and particle-size samples are collected to characterize the solids in the slurry and their impact on flow and filtration behavior. As slurries concentrate, their flow behavior changes and becomes more viscous and less Newtonian. This directly impacts the cross-flow behavior of the filter and the formation of filter cake. The particle size also can have an impact by affecting the gel concentration of the slurry and possibly impact fouling. Because the slurries are sheared during filtration, the particle size of the slurry can change—especially if the initial solids are agglomerated. Chemical leaching has a similar impact as well.

H.1.3 Chemical Data Analysis

During the test, the mass of material placed inside the skid and removed is constantly measured to perform an overall mass balance of the slurry during the test. Two main goals are to be achieved from this analysis: 1) verification that transuranic (TRU) material stays in the HLW stream and 2) calculation of the chemical leach factors of glass-limiting compounds of interest.

H.1.3.1 Validation of Filtration Separation of TRU Material

The main goal of the chemical and physical separation processes tested in this report is to demonstrate the effectiveness of removing the glass load-limiting glass components (e.g., phosphorus) from the HLW stream while not introducing TRU material into the LAW waste stream. This is examined during filtration and leaching processes. During filtration, it is important to verify that TRU materials present in the waste slurry do not pass through the filtration media as a colloid or as a particle <0.1 mm. During leaching, it is also important to verify that TRU compounds are not chemically dissolved during operations designed only to remove glass-limiting compounds for the LAW stream. This was achieved by performing radiochemical analysis on permeate and slurry samples throughout the test to verify that the permeate streams contain minimal TRU elements and that a mass balance on the system shows that almost all the TRU stays in the HLW slurry stream.

H.1.3.2 Chemical Leach Factors for Caustic and Oxidative Leaching

In this report, the chemical leach factor is defined as the percentage difference in mass of a solid component in the waste after chemical leaching.

$$f_i = 1 - \frac{m_i^{final}}{m_i^{initial}} \tag{H.8}$$

where f_i is the leach factor for component i, $m_i^{initial}$ is the initial solid mass of component i, and m_i^{final} is the final solid mass of component i.

The following methods are used to calculate solid leach factors:

- Perform an overall elemental mass balance of the system along with a physical-property measurement of the solids fraction of the slurry. Using chemical analytical data and mass measurements of additions and removals of waste slurry, samples, and dewatered permeate, the elemental changes to the solids and liquid fractions of the slurry can be calculated at each stage of the test as well as the leach factor.
- Perform a mass balance of the slurry before and after leaching using insoluble components, such as iron and uranium, to trace the fractional change in mass. Substituting dry mass compositions for leach component *i* and inert *j* in Equation 2.8, the leach factor becomes:

$$f_i = 1 - \left(\frac{x_i^{final}}{x_i^{initial}}\right)\left(\frac{x_j^{initial}}{x_j^{final}}\right) \tag{H.9}$$

- Perform a mass balance of the liquid supernate before and after leaching to measure the change of mass in the solids to calculate the leach factor.

H.1.3.3 Physical Examination of Final Leach Material

The chemical characterization and physical morphology are examined after leaching. While most of the analyses used are qualitative, they can show:

- If particles are crystal, agglomerates, or amorphous

- Whether TRU and glass-limiting compounds (like aluminum or chromium) are blends of different phases or single compounds
- What is the crystal phase of the remaining glass-limiting compound (e.g., boehmite for aluminum).

Appendix I

Homogenization Methods

Appendix I: Homogenization Methods

The homogenization vessel and mixing system used to homogenize the Group 7 TBP sludge sample was designed and fabricated for use at Pacific Northwest National Laboratory (PNNL) in the High-Level Radiochemistry Facility (HLRF). This stainless steel equipment was specifically designed to composite tank wastes and divide them into homogeneous sub-samples. The homogenization vessel was designed to hold and effectively mix a variable volume of 1 to 5 L of waste. A set of removable baffles was designed and added to enhance mixing. Industry experience shows that the best mixing is achieved when a tank height-to-diameter ratio is 1:1. For a fixed volume batch tank, this is easy to achieve. For a variable volume tank, this presents a challenge usually solved by making the tank conical. Height restrictions and volume requirements made it unfeasible to make the entire homogenization vessel conical, so to optimize mixing, a compromise tank design was devised. The bottom of the tank with a volume capacity of ~1.5 to 2.0 L was conical. At low volumes, the mixing assistance from the baffles was less than at larger volumes. Therefore, the need to rigorously maintain the 1:1 ratio was achieved in this section of the tank. When the volumes are above 2 L, the baffles combined with a down-sweeping mixer blade were shown to be sufficient to maintain a good mixing profile in the non-conical portion of the tank. The bottom of the conical section slopes toward the side to facilitate good subdivision of the samples.

Figure I.1shows photographs of the homogenization vessel along with a schematic representation of its design. The Group 7 sample material was loaded into the vessel through a Tyler sieve mounted to the top of the vessel (see right side of Figure I.1). This was done so that no chunks of material greater than 3.2 mm in diameter were included in the composite, which was necessary for forming a uniform composite and protecting the CUF equipment during later testing. This vessel was used to composite several groups of tank samples. Extensive cleaning was done between each group with water, 0.01 M NaOH, and 0.01 M HNO_3.

Before the actual tank waste samples were homogenized, non-radioactive testing of this system with various simulants was performed to establish the best operating conditions and procedures and to verify the uniformity of the sub-samples obtained with this tank. Simulants with high yield stress values (Figure I.2) and simulants with the capability to settle rapidly (Figure I.3) were tested to verify that good mixing could be maintained and uniform sub-samples removed. Operating conditions and guidelines that resulted in a composite with homogeneous sub-samples of the most challenging simulants were then incorporated into the test instructions for the actual waste testing.

Clay simulants were prepared with high Bingham yield stresses and cohesive properties that would make them sticky. These consisted primarily of kaolin and bentonite clay mixtures. These simulants mixed well and delivered uniform samples while the homogenization vessel was tested (Figure I.2, left and center). However, they did leave a thick film of material coating the tank, mixer, and baffle surfaces (Figure I.2, right). In compositing the actual tank waste samples, solids materials with these characteristics would need to be recovered for CUF testing with extra rinses of de-ionized (DI) water after completing homogenization and sub-sampling of the bulk material.

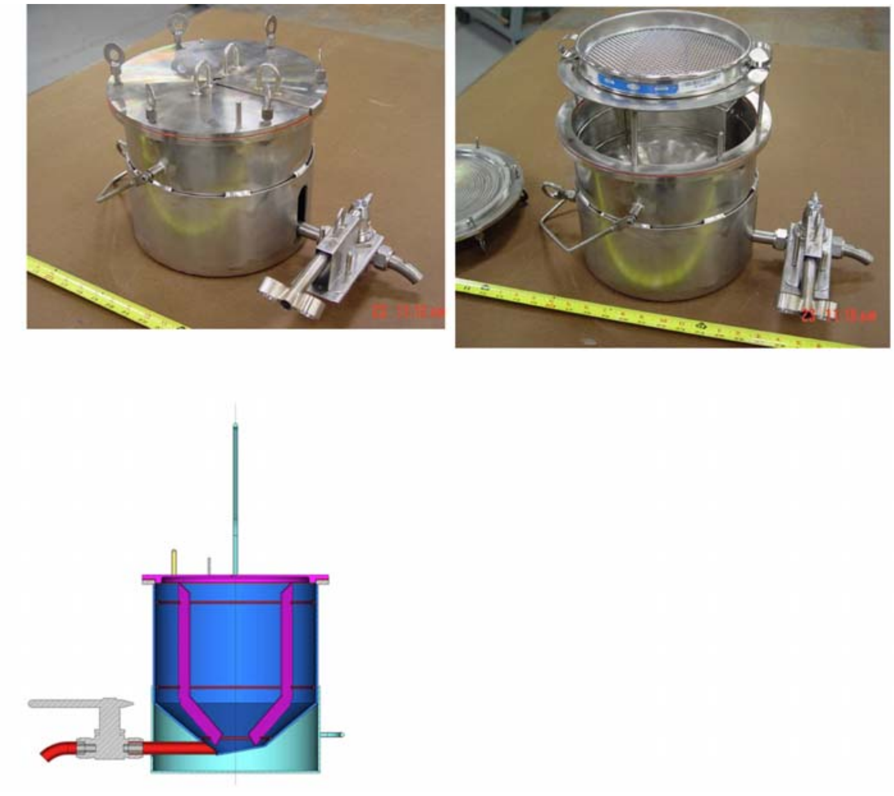

Figure I.1. Homogenization Vessel Used to Prepare and Sub-Sample the Group 7 Composite Slurry

Figure I.2. Photographs of a High Yield Stress Clay Simulant in the Homogenization Vessel Used for Group 7

Min-u-sil®-based simulants were used to test variable mixing speeds and propeller placement because of their tendency to settle swiftly when mixing is not sufficient. Figure I.3 shows that these simulant types could usually be cleanly and completely recovered from the tanks. However, the sub-samples were often non-uniform with the Min-u-sil® simulants. Figure I.4 shows an example of non-uniform settling results for sub-samples taken when the mixer speed was too low. Based on these results, a hold point was inserted into the compositing test instructions such that after 3 days of settling, the settled solids of all the composite samples would be compared and statistically analyzed to verify that good homogenization of the composite had been achieved and maintained during the sub-sampling process.

Figure I.3. Photographs of the Mixing of a Min-u-sil® Simulant that Settles Rapidly in the Homogenization Vessel Used for Group 7 (left) and the Vessel After Draining of the Material (right)

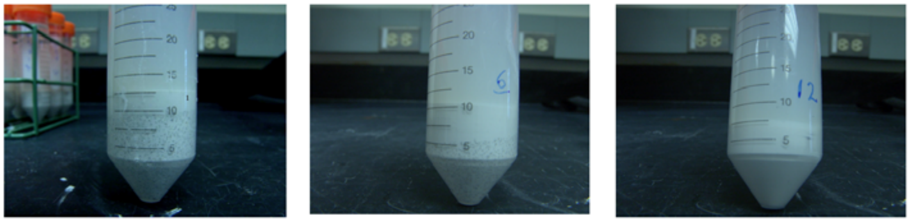

Figure I.4. Photographs of Three Different Sub-Samples Taken from the Homogenization Vessel During Non-Radioactive Testing with a Min-u-sil® Simulant. Note the different degrees of settling, which indicates in-homogeneity in the slurry.

Appendix J

Group 7/AY-102 CUF Analytical Results

Appendix J: Group 7/AY-102 CUF Analytical Results

Special Instructions for the
CUF Group 7 (TBP Sludge)/241-AY-102 Treatability Study
Analysis Requirements

A blend of two HLW samples containing liquid and sludge from Hanford waste tanks was subjected to CUF process as per TI-RPP-WTP-624. The first sample is a composite blend from tanks 241-B-106 and 241-BX, representing waste described as TBP Sludge waste (Group 7). The second waste sample was an archive tanks 241-AY101, which was similar in composition. The start date for this treatability study is April 27th, 2008. Color code: `Pastel Pink`

The processing and analysis schematic is shown by Figure 1 and Table 1. The aqueous samples are ready to directly sub-sample for analysis and acid digestion. The solid slurry samples have yet to be split into aliquots and prepped for fusion or HF-assisted acid digestion.

Two samples from ASR 8113, Group 2 CUF, will be re-sampled in cell and added to this ASR. These samples are an attempt to identify a source of contamination and will require only ICP metals. Color code: `Fluorescent Pink`

SAL Preparation/Analysis

Please record observations associated with the dissolution preparations, and record the test sample being aliquotted before and after sampling to document changes in weight since the treatability study occurred. If any residual solids remain after any of the fusion and acid digestions, note on the bench sheet (include estimated quantity, color, texture, etc.) and contact RW Shimskey or MK Edwards for further instruction prior to distribution.

Archive of SAL Fusion Preparation Samples

The fusion preparations will result in a 100-mL volume. This solution will be apportioned to the laboratory as needed to conduct work-station-specific analyses. Please prepare a 15-mL aliquot from each preparation as an archive sample. The vials need to be labeled with the following: date, ASO-ID, matrix, treatablility study, hazard, fusion prep (if applicable) and their tare, gross masses, and IDs provided to RW Shimskey or MK Edwards. The vials may be removed from the hot cells for storage. The remaining portions of the fusion preparations may be disposed of.

Quality Control

All work is to be conducted according to RPP-WTP-QA-005, Rev. 2.

Preparative or sample analysis QC includes a preparation blank, sample, sample duplicate, matrix spike, and a LCS or BS. The samples submitted for fusion are sub-aliquoted into fusion vessels in duplicate (sample, sample duplicate). If possible, the matrix spike and LCS/BS need to include all the analytes of interest to be reported for the specific analysis.

The duplicate, LCS/BS, and MS QC acceptance criteria for the aqueous phases and solid phases are provided in Table 4. The preparation blank (PB) analyte concentration shall be less than the estimated quantitation limit (EQL) or the minimum detectable activity (MDA) of the associated sample. When the PB concentration is equal to or exceeds the EQL, then the PB concentration shall not exceed 5% of the measured concentration present in the sample. Failure of the PB, and/or duplicates, and/or LCS/BS to meet the acceptance criteria requires that affected samples in the processing batch be re-prepared and re-analyzed for the failed analytes, availability of samples permitting, at ASO expense.

In the case of multi-elemental methods (IC and ICP-OES), isolated QC failure(s) may be communicated to RW Shimskey or MK Edwards for an assessment of the impact on data interpretation. If the data are acceptable, RW Shimskey or MK Edwards will indicate, in writing, that the data may be reported, and the resulting limitations on the data from the QC sample failure(s) shall be included in the final report.

When the MS fails to meet the acceptance criteria, the results shall be investigated for potential sources of error. When the sources of error cannot be identified, the failure of the MS and any resulting limitations on the data shall be included in the report.

Note that in some cases BS and MS are requested for U/KPA as well as ICP metals in solution analysis. Because the broad suite of ICP BS metals will interfere with the U KPA analysis, two MS and BS samples (one supporting each technique) will need to be prepared as part of the acid digestion.

Reporting Units

Report aqueous sample results in units of ug/mL or uCi/mL. Report solids sample results as ug/g or uCi/g; the initial dry mass of solids (as measured in each fusion crucible, preferably in the form of SAL drying bench sheets) will be provided with the ICP results. For radiochemistry, the reference date shall be February 17, 2008 for samples from TI-RPP-WTP-624.

Reporting

Please prepare the analytical data report in accordance with PNL-ASO-058, Rev. 0, Section 5.3, Comprehensive Data Report. Please be sure to include action taken with respect to any identified unexpected results and discrepancies.

The following elements may be included in the final report or be traceable to the test results (usually by entry in the LRB, Test Instruction, or data sheet) and be maintained as lifetime records:

- identification of standards used
- identification of M&TE used
- reference to the Test Plan (identified on page 1 of the ASR)
- signature and date of person who performed the test and recorded the data
- hand calculation review documentation.

Analytical results shall be reported both in hard copy and electronically. Preliminary data reports and electronic files shall be provided as soon as practical after completion of analysis. **The final ASR data report shall be provided no later than the commitment date on the ASR.**

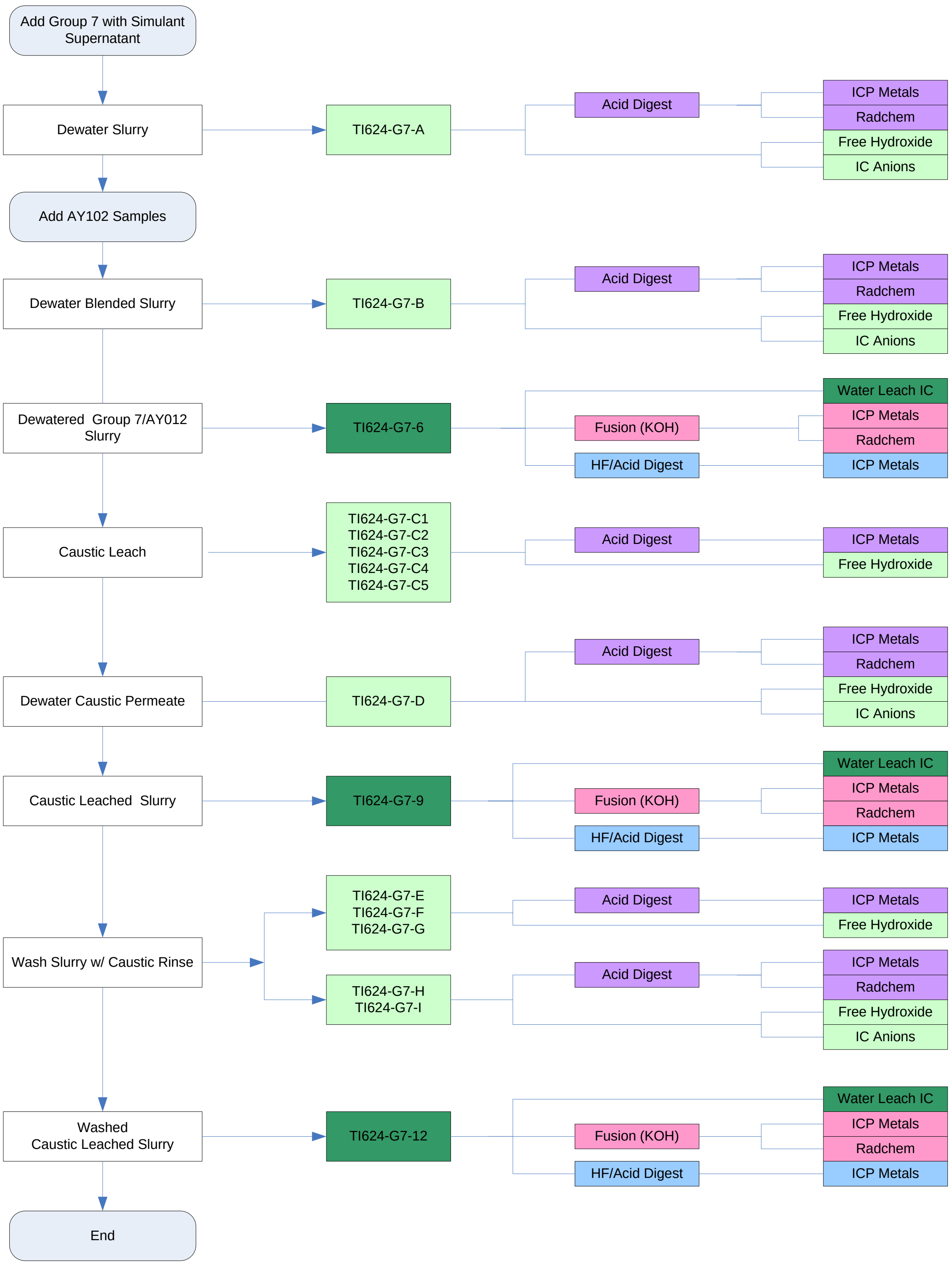

Figure 1: TI-RPP-WTP-624 Process Sampling Plan

Table 1. Cross-Reference of Process component, Sample ID, and RPL ID

Component	Sample ID	ASO ID
Group 7 Dewater filtrate	TI624-G7-A	08-02059
Group 7/AY102 Dewater filtrate	TI624-G7-B	08-02060
Dewatered Caustic Leach	TI624-G7-D	08-02061
Wash 4 Permeate	TI624-G7-H	08-02062
Composite Wash Sample	TI624-G7-I	08-02063
Caustic leach filtrate, 1 hour heat up	TI624-G7-C1	08-02064
Caustic leach filtrate, 0 hour heat up	TI624-G7-C2	08-02065
Caustic leach filtrate, 2 hour leach	TI624-G7-C3	08-02066
Caustic leach filtrate, 4 hour leach	TI624-G7-C4	08-02067
Caustic leach filtrate, 8 hour leach	TI624-G7-C5	08-02068
Wash 1 Permeate	TI624-G7-E	08-02069
Wash 2 Permeate	TI624-G7-F	08-02070
Wash 3 Permeate	TI624-G7-G	08-02071
Group 2, 3rd Oxidative wash permeate	TI572-G2-OxWash 3-1	08-02072
Group 2, 3rd Oxidative wash permeate	TI572-G2-O-1	08-02073
Dewatered Slurry	TI624-G7-6	08-02074
Caustic Leached Slurry	TI624-G7-9	08-02075
Washed Caustic Leached Slurry	TI624-G7-12	08-02076

Laboratory Analysis

The required sample analyses are shown below in Table 2.

Table 2. Filtration and Leach Testing Characterization Plan

Process Step	Analyte		
TI-RPP-WTP-624			
Dewatered slurry **(TI624-G7-6)**		HF assisted Acid digestion • ICP metals (Table 3)	
		KOH fusion • ICP metals (Table 3) • GEA • Total alpha • ^{238}Pu, $^{239+240}$Pu • U/KPA • ^{90}Sr • Total beta	
		Water Leach • Anions (Table 3)	
Dewater filtrate **(TI624-G7-A, TI624-G7-B)**		Direct distribution • Anions (Table 3) • Free hydroxide	
		Acid digestion • ICP metals (Table 3) • GEA • Total alpha • ^{238}Pu, $^{239+240}$Pu • U/KPA • ^{90}Sr • Total beta	
Time interval Caustic Leach filtrates – Kinetics **(TI624-G7-C1, TI624-G7-C2, TI624-G7-C3, TI624-G7-C4, TI624-G7-C5)**		Direct distribution • Free hydroxide	
		Acid digestion • ICP metals (Table 3)	
Caustic-leached permeate **(TI624-G7-D)**		Direct distribution • Anions (Table 3) • Free hydroxide	
		Acid digestion • ICP metals (Table 3) • GEA • Total alpha • ^{238}Pu, $^{239+240}$Pu • U/KPA • ^{90}Sr • Total beta	

Process Step	Analyte		
Caustic-leached slurry (TI624-G7-9)		HF assisted Acid digestion • ICP metals (Table 3)	
		KOH fusion • ICP metals (Table 3) • GEA • Total alpha • ^{238}Pu, $^{239+240}$Pu • U/KPA • ^{90}Sr • Total beta	
		Water Leach • Anions (Table 3)	
First and Second washes following caustic leach (TI624-G7-E, TI624-G7-F, TI624-G7-G)		Direct distribution • Free hydroxide	
		Acid digestion • ICP metals (Table 3)	
Third wash and combined wash composite following caustic leach (TI624-G7-H, TI624-G7-I)		Direct distribution • Anions (Table 3) • Free hydroxide	
		Acid digestion • ICP metals (Table 3) • GEA • Total alpha • ^{238}Pu, $^{239+240}$Pu • U/KPA • ^{90}Sr • Total beta	
Caustic-leached and washed slurry (TI624-G7-12)		HF assisted Acid digestion • ICP metals (Table 3)	
		KOH fusion • ICP metals (Table 3) • GEA • Total alpha • ^{238}Pu, $^{239+240}$Pu • U/KPA • ^{90}Sr • Total beta	
		Water Leach • Anions (Table 3)	
Group 2, 3rd Oxidative wash permeate (TI572-G2-OxWash 3-1)		Acid digestion • ICP metals (Table 3)	
Group 2, 3rd Oxidative wash permeate (TI572-G2-O-1)		Acid digestion • ICP metals (Table 3)	

All analyses are to be conducted per approved PNNL procedures or test plans with the QC defined in the QC information Section. Table 3 defines the analytes of interest, the required detection limits, and analysis methods.

Table 3. Method Detection Limits for Solids and Supernatants

Analyte	Solids	Solutions	Analysis Method
	μCi/g(a)	μCi/ml	
^{137}Cs	6.0E-02	1.0E-02	GEA
^{60}Co	3.0E-02	1.0E-02	
^{154}Eu	5.0E-03	4.0E-04	
^{155}Eu	8.0E-03	4.0E-04	
^{241}Am	3.0E-03	2.0E-03	
Pu	1.0E-03	1.0E-04	$^{239+240}$Pu and ^{238}Pu by AEA
Total alpha	1.0E-02	4.0E-03	Proportional counting
Total beta	1.0E-02	1.0E-03	Proportional counting
^{90}Sr	1.0E-02	1.0E-03	Separation and proportional counting
	μg/g	μg/ml	
Al	3.0E+02	7.5E+01	ICP-OES
B	2.0E+02	7.5E+01	
Bi	4.0E+02	3.0E+01	
Cd	7.5E+01	7.5E+01	
Cr	1.2E+02	1.5E+01	
Fe	3.0E+02	7.5E+01	
K	1.0E+03(b)	5.0E+01	
Mn	3.0E+02	1.5E+01	
Na	3.0E+03	7.5E+01	
Ni	1.6E+02(b)	3.0E+01	
P	2.0E+02	1.0E+01	
S	1.5E+03	2.0E+2	
Si	3.0E+03	7.5E+01	
Sr	3.0E+02	7.5E+01	
Zn	3.0E+02	7.5E+01	
Zr	3.0E+02	7.5E+01	
U	2.5E+03	7.5E+01	
U	6.0E+01	6.0E+01	Kinetic Phosphorescence
Fluoride	2.5E+02	1.2E+02	Ion Chromatography (water-soluble species)
Nitrite	2.5E+02	1.2E+02	
Nitrate	2.5E+02	1.2E+02	
Phosphate	2.5E+02	1.2E+02	
Sulfate	2.5E+02	1.2E+02	
Oxalate	8.0E+02	4.0E+02	
Hydroxide	NA	1E-01 M	Titration

(a) KOH fusion for solid samples.

(b) The Ni and K cannot be measured from the KOH fusion which uses a Ni crucible. The Ni and K will be assessed from a separate HF-assisted acid digestion.

Table 4. Analytical Quality Control Parameters

		Liquids			Solids		
Analyte	**Analytical Technique**	**LCS or BS % Recovery(a)**	**Matrix Spike % Recovery(b)**	**Duplicate RPD(c)**	**LCS or BS % Recovery(a)**	**Matrix or Post Spike % Recovery(b)**	**Duplicate RPD(c)**
As identified in Table 3	ICP-OES	80 - 120%	75 - 125%	<20%	80 - 120%	70 – 130%	<25%
Pu	AEA	80 - 120%	75 - 125%	<20%	80 - 120%	70 – 130%	<25%
Total alpha	Proportional counting	80 - 120%	75 - 125%	<20%	80 - 120%	70 – 130%	<25%
Total beta	Proportional counting	80 - 120%	75 - 125%	<20%	80 - 120%	70 – 130%	<25%
^{90}Sr	Proportional counting	80 - 120%	75 - 125%	<20%	80 - 120%	70 – 130%	<25%
U	KPA	80 - 120%	75 - 125%	<20%	NA(d)	NA(d)	<25%
Anions	Ion chromatography	80 - 120%	75 - 125%	<20%	80 - 120%	70 - 130%	<25%
OH^-	Potentiometric titration	80 - 120%	N/A	<20%	NA	N/A	NA
As identified in Table 3	GEA	N/A	N/A	<20%	N/A	N/A	<25%
Density	Gravimetry	N/A	N/A	<20%	N/A	N/A	<25%

N/A – not applicable

Footnotes:

(a) LCS = Laboratory Control Standard; BS = Blank Spike A laboratory control sample (LCS) or blank spike (BS) sample is used to monitor the effectiveness of the sample preparation process and is a good measure of method accuracy. Ideally, the LCS is a material similar to the sample being processed, containing the analytes of interest (e.g., standard reference material). An LCS, if available, shall be prepared with each batch of samples processed at the same time. When an appropriate LCS is not available, a BS shall be used in lieu of the LCS. A BS is distilled or deionized water or another suitable matrix spiked with the analytes of interest. It may not be possible to prepare a single BS that contains all analytes of interest (e.g., chemical incompatibility). In such cases, an agreement with the client shall be made to identify the analytes of interest used to prepare the BS, and more than one BS may be used. The BS result is expressed as percent recovery; i.e., the amount measured, divided by the known concentration, multiplied by 100.

(b) For some methods, the sample accuracy is expressed as the percent recovery of a matrix spike sample. Post spikes and analytical spikes are also included under these acceptance criteria. The spiked sample result is expressed as percent recovery; i.e., the amount measured less the amount in the sample, divided by the spike added, times 100. One matrix spike (or post spike or analytical spike) is performed per analytical batch. Samples are batched with similar matrices. For other analytes, the accuracy can be determined based on use of serial dilutions.

(c) RPD = Relative Percent Difference between the samples. Sample precision is estimated by analyzing replicates taken separately through preparation and analysis. Acceptable sample precision for liquids is usually <15% RPD if the sample result is at least 10 times the instrument detection limit. Solids RPDs are generally higher because of the difficulty associated with obtaining homogonously represented samples.

(d) The LCS used to support fusion preparations is SRM2710 (Montana soil). It contains a subset of the analyte list: Al, Ba. Ca, Cu, Fe, Mg, Mn, Na, Si, Sr, Ti, and Zn. It does not contain U.

Analytical Service Request (ASR)

ASR-FY2007-RPP-WTP Tasks Rev. 1.doc

(Information on this COVER PAGE is applicable to all samples submitted under this ASR)

Requestor --- Complete all fields on this COVER PAGE, unless specified as optional or ASR is a revision

Requestor:
Signature ____________
Print Name ____Rick Shimskey____
Phone ________376-3183________ MSIN ____P7-27__

Project Number: __________52964__________
Work Package: __________F99189__________

Matrix Type Information

- ◆ **Liquids:** X Aqueous ☐ Organic ☐ Multi-phase
- ◆ **Solids:** ☐ Soil X Sludge ☐ Sediment ☐ Glass ☐ Filter ☐ Metal ☐ Smear ☐ Organic ☐ Other
- ◆ **Other:** ☐ Solid/Liquid Mixture, Slurry ☐ Gas ☐ Biological Specimen

(If sample matrices vary, specify on Request Page)

Disposal Information

◆ **Disposition of Virgin Samples:**
Virgin samples are returned to requestor unless archiving provisions are made with receiving group!

If archiving, provide:
Archiving Reference Doc: ________________

◆ **Disposition of Treated Samples:**
X Dispose ☐ Return

QA/Special Requirements

◆ **QA Plan:**
X ASO-QAP-001, Rev. 6 (Equivalent to HASQARD)
X Additional QA Requirements, List Document Below:
Reference Doc Number:_RPP_WTP-QA-005, Rev. 2_

◆ **Field COC Submitted?** X No ☐ Yes

◆ **Lab COC Required?** X No ☐ Yes

◆ **Sample/Container Inspection Documentation Required?** X No ☐ Yes

◆ **Hold Time:** X No ☐ *Yes*

<u>If *Yes*, Contact ASO Lead before submitting Samples</u>
☐ Use SW 846 (PNL-ASO-071, identify analytes/methods where holding times apply)
☐ Other? Specify: ________________

◆ **Special Storage Requirements:**
X None ☐ Refrigerate ☐ Other, Specify: ____________

◆ **Data Requires ASO Quality Engineer Review?** X No ☐ Yes

Data Reporting Information

◆ **Is Work Associated with a Fee-Based Milestone?** X No ☐ Yes
If yes, milestone due date:
____

◆ **Preliminary Results Requested, As Available?** ☐ No X Yes

◆ **Data Reporting Level**
X ASO-QAP-001 (Equivalent to HASQARD).
☐ Minimum data report.
☐ Project Specific Requirements: Contact ASO Lead or List Reference Document:________________

◆ **Requested Analytical Work Completion Date:**
____
(Note: Priority rate charge for < 10 business day turn-around time)

◆ **Negotiated Commitment Date:**
____8/7/08____
(To be completed by ASO Lead)

KNP, MJS, CZS, LPD, KJC, MJS, BMO, PKB

Waste Designation Information

◆ **Sample Information Check List Attached?** X No ☐ Yes
If no, Reference Doc Attached: ________________
or, Previous ASR Number: ____8035 and 8078____________
or, Previous RPL Number: ________________

Does the Waste Designation Documentation Indicate Presence of PCBs?
X No ☐ Yes

Send Report To: ______**Rick Shimskey**______________ **MSIN** _______**P7-27**____________

______**Matt Edwards**______________ **MSIN** _______**P7-25**____________

Additional or Special Instructions _**The requirements of Statement of Work, RPP-WTP-QA-005, Rev. 2, apply to this work. Task-specific Quality Control criteria are attached. Reference Document (i.e., TP-RPP-WTP-____):____**

Receiving and Login Information *(to be completed by ASO staff)*

Date Delivered: 6/19/08
Delivered By (optional) Nicole Green
Time Delivered (optional) ________________
Group ID (optional) _RPP-WTP/Task No: [ ]
CMC Waste Sample? X No ☐ Yes

Received By: T Trang-le

ASR Number: ____**8176**________Rev.: ___**00**______

RPL Numbers: _____**08-02059 to 08-02076**______
(first and last)

ASO Work Accepted By: __KNPool__________ **Signature/Date:** __Karl N. Pool 6/25/08__

Analytical Service Request (ASR)

(REQUEST PAGE ----- Information Specific to Individual Samples)

Provide Analytes of Interest and required Detection limits - ☐ Below X Attached

ASO Staff Use Only				ASO Staff Use Only	
RPL Number	**Client Sample ID**	**Sample Description** (& Matrix, If Varies)	**Analysis Requested**	**Test**	**Library**
08-02059	TI624-G7-A	Dewater Filtrate	Direct Analyses 1) OH 2) IC-Anions Acid Digest – 128 (Prep Lab) 1) ICP/OES 2) GEA 3) Total Alpha 4) Total Beta 5) ^{238}Pu, $^{239+240}$Pu 6) ^{90}Sr 7) U/KPA (Separate BS & MS needed using U spike only)	OH IC	Lab Analyses "
08-02060	TI624-G7-B	Group 7/AY102 Dewater Filtrate		Prep-128 ICP	Lab Analyses
08-02061	TI624-G7-D	Dewatered Caustic Leach		GEA Alpha Beta	Radchem ↓
08-02062	TI624-G7-H	Wash 4 Permeate		Pu-AEA SR-90	Radchem ↓
08-02063	TI624-G7-I	Composite Wash Sample		U-KPA	Radchem
08-02064	TI624-G7-C1	Caustic Leach Filtrate – 1 hour heat	Direct Analyses 1) OH Acid Digest – 128 (Prep Lab) 1) ICP/OES	OH	Lab Analyses
08-02065	TI624-G7-C2	Caustic Leach Filtrate – 0 hour heat		Prep-128	
08-02066	TI624-G7-C3	Caustic Leach Filtrate – 2 hour heat		ICP	Lab Analyses
08-02067	TI624-G7-C4	Caustic Leach Filtrate – 4 hour heat			
08-02068	TI624-G7-C5	Caustic Leach Filtrate – 8 hour heat			
08-02069	TI624-G7-E	Wash 1 permeate			
08-02070	TI624-G7-F	Wash 2 permeate			
08-02071	TI624-G7-G	Wash 3 permeate			
08-02072	TI572-G2-OxWash 3-1	Group 2, 3rd Oxidative wash permeate – *(No OH)*			
08-02073	TI572-G2-O-1	Group 2, 3rd Oxidative wash permeate – *(No OH)*			

ASR # 8176 Rev.: 00

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ASR 8176 - Group 7 CUF ASR.doc

Analytical Service Request (ASR)

(REQUEST PAGE ----- Information Specific to Individual Samples)

Provide Analytes of Interest and required Detection limits - ☐ **Below X Attached**

ASO Staff Use Only **RPL Number**	**Client Sample ID**	**Sample Description** (& Matrix, If Varies)	**Analysis Requested**	ASO Staff Use Only **Test**	ASO Staff Use Only **Library**
08-02074	TI624-G7-6	Dewatered Slurry	KOH Fusion – 115 (SAL) 1) ICP/OES 2) GEA 3) Total Alpha 4) Total Beta 5) ^{238}Pu, $^{239+240}$Pu 6) ^{90}Sr 7) U/KPA Acid Digest – 138 (SAL) 1) ICP/OES Water Leach – 103 (SAL) 1) IC – Anions	Prep-115 ICP GEA Alpha Beta Pu-AEA Sr-90 U-KPA	Lab Analys Radchem ↓
08-02075	TI624-G7-9	Caustic Leach Slurry			
08-02076	TI624-G7-12	Washed Caustic Leached Slurry		Prep-138 ICP SAL-103 IC	Lab Analys Lab Analys

ASR # 8176 Rev.: 00

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Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report

PO Box 999, Richland, Washington 99352

Project / WP#: 52964 / F99189
ASR#: 8176
Client: R. Shimskey
Total Samples: 3 (solid)

	First	Last
RPL#:	08-02074	08-02076
Client ID:	TI624-G7-6	TI624-G7-12
Sample Preparation: PNL-ALO-115, "Solubilization of Metals from Solids using a KOH-KNO$_3$ Fusion", 7/10(SAL/ng).		

Procedure: RPG-CMC-211, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)", Rev 2.

Analyst: J. Deschane

Analysis Date (File): 07-18-2008 (C0148)

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE Number: N827583 (ICP-OES instrument)
M19445 (Mettler AT400 Balance)

7/23/08
Preparer

Review and Concur

Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report

Three samples submitted under Analytical Service Request (ASR) 8176 were analyzed by ICP-OES. The samples were prepared in the Shielded Analytical Laboratory (SAL) following RPL fusion procedure PNL-ALO-115 using a nominal 0.2 grams of sample. The samples were dried to constant mass prior to undergoing fusion and then diluted to a final volume of 100 mL.

Analytes of interest (AOIs) were specified in the ASR, and are listed in the upper section of the attached ICP-OES Data Report. The quality control (QC) results for these AOIs have been evaluated and are presented below. Analytes other than AOIs are reported in the bottom section of the report, but have not been fully evaluated for QC performance. The results are given as μg/g for each detected analyte, and have been adjusted for all laboratory processing factors and instrument dilutions.

Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure and using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte, and also used for continuing calibration verification.

Minimum Method Detection Limit (MDL) values were specified in the ASR. Except for Al, Fe, and Na, MDL levels were met for all AOIs. Because of known impurities of these analytes in the 115 fusion flux, the MDL values for these analytes have been set artificially high to account for these impurity levels. It should be noted, however, that measured levels of these analytes in the samples exceeded the requested MDL levels.

The controlling documents were ASO-QAP-001, and the client supplied RPP-WTP-QA-005, Rev. 2, and ASR 8176 Special Instructions. Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-spike, laboratory control standard (LCS), duplicate, and serial dilution were conducted during the analysis run. The LCS was prepared using a nominal 0.2 grams of SRM-2710 (Montana Soil).

<u>Preparation Blank (PB):</u>

A preparation blank (reagents only) was prepared for the fusion process. The concentrations of all AOIs were within the acceptance criteria of ≤EQL (estimated quantitation level) or less than ≤5% of the concentration in the sample.

<u>Blank Spike (BS)/Laboratory Control Sample (LCS):</u>

An LCS (Montana Soil) was prepared for the fusion process. Recovery values are listed for all analytes included in the spike that were measured at or above the EQL. The recovery values were within the acceptance criterion of 80% to 120% for all AOIs meeting the above requirement.

<u>Matrix-Spiked Sample:</u>

No matrix spike sample was provided for analysis.

Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report

Duplicate Relative Percent Difference (RPD):

A duplicate was prepared for the sample batch. RPDs are listed for all analytes that were measured at or above the EQL. Except for zirconium (~56%), the RPDs were within the client acceptance criterion of ≤25% for all AOIs meeting the above requirement. The reason for the high RPD for zirconium is suspected to be from precipitation of zirconium-phosphate resulting from the high phosphorous levels in the samples. As a result, the zirconium values for the present samples should be considered as suspect low.

Post-Spike/Analytical Spike Sample (A component):

An analytical spike (A component) was conducted for the sample batch. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. The recovery values were within the client acceptance criterion of 70% to 130% for all AOIs meeting the above requirements.

Post Spike/Analytical Spike Sample (B component):

An analytical spike (B component) was conducted for the sample batch. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. The recovery values were within the client acceptance criterion of 70% to 130% for all AOIs meeting the above requirements.

Serial dilution:

Five-fold serial dilution was conducted for the sample batch. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. Except for zirconium (~14%), the %Ds were within the acceptance criterion of ≤10% for all AOIs meeting the above requirement. The reason for the high %D for zirconium is not clear. A serial dilution test on Sample 08-02075, which had a lower zirconium content, was within the 10% criterion.

Other QC:

All other instrument-related QC tests for the AOIs passed within the appropriate acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water. Detection limits for other matrices may be determined if requested. Method detection limits (MDL) can be estimated by multiplying the IDL by the "Multiplier". The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Multiplier".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 μg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standards are validated to a precision of ±10%.
4) Absolute precision, bias and detection limits may be determined on each sample if required by the client. The maximum number of significant figures for all ICP measurements is two.

5) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	7/18/2008	7/18/2008	7/18/2008	7/18/2008	7/18/2008
		Multiplier >	1895.2	1689.2	1912.8	1785.1	2295.7
		RPL/LAB >	08-02074-115-B @5	08-02074-115-S @5	08-02074-115-D @5	08-02075-115-S @5	08-02076-115-S @5
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Prep Blank	TI624-G7-6		TI624-G7-9	TI624-G7-12
(µg/mL)	(µg/mL)	(Analyte)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
0.2900	2.900	Al	--	45,000	46,600	23,400	46,100
0.0077	0.077	B	[17]	[36]	[44]	[36]	[35]
0.0240	0.240	Bi	--	1,150	1,160	852	2,100
0.0029	0.029	Cd	[21]	136	151	108	244
0.0024	0.024	Cr	[7.2]	1,770	1,820	1,280	2,820
0.1800	1.800	Fe	--	98,000	101,000	64,600	178,000
4.0000	40.000	K	na	na	na	na	na
0.0011	0.011	Mn	[6.9]	14,500	14,800	11,200	27,100
1.9000	19.000	Na	--	168,000	165,000	174,000	111,000
0.0400	0.400	Ni	na	na	na	na	na
0.0540	0.540	P	--	25,000	25,100	17,900	12,500
0.3300	3.300	S	--	6,250	6,400	[3,100]	[1,800]
0.2300	2.300	Si	--	23,200	23,600	16,300	39,900
0.0003	0.005	Sr	[0.69]	978	987	747	1,800
0.0410	0.820	U	--	13,500	13,500	9,830	24,900
0.0032	0.064	Zn	--	267	255	211	469
0.0035	0.035	Zr (a)	--	1,550	869	86.5	258
Other Analytes							
0.0015	0.015	Ag	--	298	495	257	351
0.0390	0.390	As	--	--	--	--	--
0.0005	0.010	Ba	[1.2]	626	628	465	1,180
0.0000	0.000	Be	--	1.02	0.977	[0.75]	1.60
1.1000	11.000	Ca	--	[7,000]	[7,000]	[5,300]	[13,000]
0.0083	0.083	Ce	--	666	661	467	1,210
0.0027	0.027	Co	--	[38]	[42]	[23]	65.6
0.0020	0.020	Cu	--	250	229	183	418
0.0029	0.029	Dy	--	--	--	--	--
0.0004	0.004	Eu	--	14.3	15.8	10.6	27.2
0.0027	0.027	La	--	758	735	612	1,450
0.0019	0.019	Li	[7.0]	91.0	94.3	71.9	154
0.0052	0.052	Mg	--	1,720	1,720	1,350	3,260
0.0072	0.072	Mo	--	[21]	[21]	--	[31]
0.0062	0.062	Nd	--	1,080	1,070	889	2,070
0.0320	0.320	Pb	--	4,000	3,890	3,500	7,710
0.0064	0.064	Pd	--	--	--	--	--
0.0130	0.130	Rh	--	[29]	[30]	--	--
0.0067	0.067	Ru	--	267	251	174	453
0.0310	0.310	Sb	--	--	--	--	--
0.1100	1.100	Se	--	--	--	--	--
0.0250	0.250	Sn	--	[59]	--	--	[89]
0.0200	0.200	Ta	--	--	--	--	--
0.0260	0.260	Te	--	[140]	[180]	[120]	[320]
0.0084	0.084	Th	--	490	504	262	886
0.0005	0.005	Ti	--	214	209	156	412
0.0300	0.300	Tl	--	--	--	--	--
0.0032	0.032	V	--	[18]	[19]	[15]	[29]
0.0210	0.210	W	--	[250]	[260]	[170]	[380]
0.0003	0.003	Y	--	102	103	77.3	187

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

a) Zr values are suspect low from possible precipitation of zirconium phosphate during the fusion process.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

QC Performance 7/18/2008

Criteria >	≤ 25%	80%-120%	70%-130%	70%-130%	70%-130%	≤ 10%
QC ID >	08-02074 Dup	LCS/BS	MS (none)	08-02074 + AS-A	08-02074 + AS-B	08-02074 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	3.4	93		101		5.6
B				101		
Bi	0.6			92		
Cd	10.4			99		
Cr	3.1			99		6.3
Fe	2.7	94		104		6.4
K	na	na	na	na	na	na
Mn	2.1	98		nr		5.9
Na	2.1			94		5.6
Ni	na	na	na	na	na	na
P	0.5			108		2.5
S	2.5				98	
Si	1.8	94		94		3.3
Sr	0.9			101		5.1
U	0.3				95	7.5
Zn	4.4	97		102		
Zr (a)	56.5			119		14.1
Other Analytes						
Ag	49.7			86		9.9
As				98		
Ba	0.3	90		95		5.1
Be	4.3			98		
Ca				96		
Ce	0.8				93	
Co				99		
Cu	8.9	94		101		0.3
Dy					95	
Eu	9.5				97	
La	3.0				94	7.4
Li	3.5			95		
Mg	0.2	91		95		3.2
Mo				99		
Nd	1.6				97	22.2
Pb	2.7	93		100		4.7
Pd					89	
Rh					92	
Ru	6.3				94	
Sb				99		
Se				99		
Sn				97		
Ta				99		
Te					94	
Th	2.9				96	
Ti	2.3	87		96		3.7
Tl				92		
V				93		
W				98		
Y	1.1			95		1.2

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

a) Zr values are suspect low from possible precipitation of zirconium phosphate during the fusion process.

ASR 8176 115 Final from C0148B R. Shimskey (ASR-8176 115).XLS

Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#: 52964 / F99189
ASR#: 8176
Client: R. Shimskey
Total Samples: 15 (liquid)

	First	Last
RPL#:	08-02059	08-02073
Client ID:	TI624-G7-A	TI572-G2-O-1
Sample Preparation: RPG-CMC-128, "HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater", 6/30/08 (SRPL/ld).		

Procedure: RPG-CMC-211, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)", Rev 2.

Analyst: J. Deschane

Analysis Date (File): 07-09-2008 (C0146)

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE Number: N827583 (ICP-OES instrument)
M19445 (Mettler AT400 Balance)

7/16/08
Preparer

Ingrid Burgeson 7/17/08
Review and Concur

Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report

Fifteen samples submitted under Analytical Service Request (ASR) 8176 were analyzed by ICP-OES. The samples were prepared in the RPL Sample Receiving and Preparation Laboratory (SRPL) following Procedure RPG-CMC-128 using 1 mL of sample and diluting to a final volume of approximately 25 mL.

Analytes of interest (AOIs) were specified in the ASR, and are listed in the upper section of the attached ICP-OES Data Report. The quality control (QC) results for these AOIs have been evaluated and are presented below. Analytes other than AOIs are reported in the bottom section of the report, but have not been fully evaluated for QC performance. The results are given as µg/mL for each detected analyte, and have been adjusted for all laboratory processing factors and instrument dilutions.

Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure and using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte, and also used for continuing calibration verification.

Minimum Method Detection Limit (MDL) values were specified in the ASR. MDL levels were met for all AOIs.

The controlling documents were ASO-QAP-001, and the client supplied RPP-WTP-QA-005, Rev. 2 and ASR 8176 Special Instructions. Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-spike, blank spike, matrix spike, duplicate, and serial dilution were conducted during the analysis run. The blank spike and matrix spike were prepared using 1 mL each of BPNL-QC-1A and -2B solutions.

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the extraction process. The concentrations of all AOIs were within the acceptance criteria of ≤EQL (estimated quantitation level) or less than ≤5% of the concentration in the sample.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A blank spike was prepared for the extraction process. Recovery values are listed for all analytes included in the spike that were measured at or above the EQL. The recovery values were within the acceptance criterion of 80% to 120% for all AOIs meeting the above requirement.

Matrix-Spiked Sample:

A matrix spike was prepared for the extraction process. Recovery values are listed for all analytes included in the spike that were measured at or above the EQL. The recovery values were within the acceptance criterion of 75% to 125% for all AOIs meeting the above requirement.

Duplicate Relative Percent Difference (RPD):

A duplicate was prepared for the extraction process. RPDs are listed for all analytes that were measured at or above the EQL. The RPDs were within the acceptance criterion of ≤20% for all AOIs meeting the above requirement.

Post-Spike/Analytical Spike Sample (A component):

A post spike (A component) was conducted on one sample from the analysis batch. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. The recovery values were within the acceptance criterion of 75% to 125% for all AOIs meeting the above requirements.

Post Spike/Analytical Spike Sample (B component):

A post spike (B component) was conducted on one sample from the analysis batch. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. The recovery values were within the acceptance criterion of 75% to 125% for all AOIs meeting the above requirements.

Serial dilution:

Five-fold serial dilution was conducted on one sample from the analysis batch. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %Ds were within the acceptance criterion of ≤10% for all AOIs meeting the above requirement.

Other QC:

All other instrument-related QC tests for the AOIs passed within the appropriate acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water. Detection limits for other matrices may be determined if requested. Method detection limits (MDL) can be estimated by multiplying the IDL by the "Multiplier". The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Multiplier".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standards are validated to a precision of ±10%.
4) Absolute precision, bias and detection limits may be determined on each sample if required by the client. The maximum number of significant figures for all ICP measurements is two.
5) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	7/9/2008	7/9/2008	7/9/2008	7/9/2008	7/9/2008	7/9/2008	7/9/2008	7/9/2008
		Multiplier >	24.7	120.4	122.8	122.3	124.3	24.7	25.2	125.8
		RPL/LAB >	BLK-02059	08-02059 @5	DUP-02059 @5	08-02060 @5	08-02061 @5	08-02062	08-02063	08-02063 @5
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Prep Blank	TI624-G7-A		TI624-G7-B	TI624-G7-D	TI624-G7-H	TI624-G7-I	
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0060	0.060	Al	--	157	154	11.4	7,370	440	1,870	
0.0048	0.096	B	[1.4]	21.1	19.7	20.5	17.5	[1.5]	3.25	
0.0300	0.300	Bi	[3.5]	--	--	--	--	[2.7]	[2.9]	
0.0037	0.037	Cd	[0.30]	[1.5]	[1.4]	[1.3]	[1.4]	[0.26]	[0.26]	
0.0017	0.017	Cr	--	23.5	23.2	44.7	110	7.00	28.8	
0.0019	0.038	Fe	[0.66]	[0.62]	[0.69]	[1.8]	6.24	[0.37]	1.13	
0.0720	0.720	K	[5.1]	130	144	303	287	32.6	154	
0.0002	0.005	Mn	[0.014]	[0.17]	[0.16]	[0.22]	[0.15]	[0.031]	[0.057]	
0.0160	0.320	Na	--	91,700	91,900	86,000	108,000	8,800	over-range	37,000
0.0024	0.024	Ni	--	--	--	--	--	--	--	
0.0500	0.500	P	[1.5]	4,550	4,490	4,960	1,500	726	2,520	
0.1600	1.600	S	--	5,980	5,840	4,390	2,310	129	578	
0.0056	0.056	Si	--	--	--	[1.7]	50.0	8.35	20.1	
0.0001	0.002	Sr	[0.024]	[0.12]	[0.096]	0.205	[0.011]	[0.0042]	[0.0037]	
0.0320	0.320	U	--	135	137	3,840	51.7	11.1	24.0	
0.0028	0.056	Zn	[0.86]	[1.0]	[0.99]	[0.88]	12.3	[0.79]	2.09	
0.0011	0.011	Zr	--	[0.16]	--	[1.3]	[0.31]	--	[0.15]	
Other Analytes										
0.0021	0.021	Ag	--	--	--	10.9	5.34	[0.32]	1.45	
0.0520	0.520	As	--	--	--	--	--	--	--	
0.0003	0.005	Ba	[0.021]	[0.19]	[0.15]	[0.19]	[0.16]	[0.024]	[0.071]	
0.0001	0.001	Be	--	--	--	[0.0064]	[0.022]	--	[0.0029]	
0.0130	0.130	Ca	5.46	[16]	[4.0]	16.1	[2.9]	[1.1]	[0.87]	
0.0100	0.100	Ce	--	--	--	--	--	--	--	
0.0024	0.024	Co	--	--	--	--	--	--	--	
0.0014	0.014	Cu	--	--	--	--	[1.1]	--	[0.15]	
0.0029	0.029	Dy	--	--	--	--	--	--	--	
0.0011	0.011	Eu	--	--	--	--	--	--	--	
0.0028	0.028	La	--	--	--	--	--	--	--	
0.0006	0.012	Li	[0.063]	3.75	3.76	3.65	1.84	0.571	0.959	
0.0023	0.023	Mg	--	--	--	--	--	--	--	
0.0052	0.052	Mo	[0.14]	[2.9]	[2.9]	[5.0]	[2.7]	[0.17]	[0.71]	
0.0170	0.170	Nd	--	--	--	--	--	--	--	
0.0320	0.320	Pb	[1.8]	--	--	[5.2]	[5.7]	[1.5]	[2.0]	
0.0063	0.063	Pd	--	--	--	--	--	--	--	
0.0120	0.120	Rh	--	[1.9]	[1.7]	--	--	--	[0.37]	
0.0085	0.085	Ru	--	[1.1]	[1.1]	[9.6]	[6.0]	[0.34]	[1.4]	
0.0200	0.200	Sb	[0.57]	--	--	--	--	--	--	
0.0700	0.700	Se	[2.4]	[11]	[16]	--	[11]	--	[2.6]	
0.0270	0.270	Sn	--	--	--	--	--	[1.2]	[2.7]	
0.0170	0.170	Ta	--	--	--	--	--	--	--	
0.0260	0.260	Te	--	--	--	--	--	--	--	
0.0098	0.098	Th	--	--	--	--	--	--	--	
0.0004	0.004	Ti	--	--	--	--	--	[0.013]	--	
0.0380	0.380	Tl	--	--	--	--	--	--	--	
0.0007	0.007	V	[0.039]	[0.33]	[0.36]	[0.59]	0.980	0.189	0.496	
0.0140	0.140	W	--	[3.4]	[2.9]	[12]	[15]	[1.2]	4.02	
0.0004	0.004	Y	--	--	--	[0.069]	--	--	--	

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

Run Date >	7/9/2008	7/9/2008	7/9/2008	7/9/2008	7/9/2008	7/9/2008	7/9/2008	7/9/2008
Multiplier >	125.3	122.5	122.8	122.6	125.1	625.7	122.4	123.7
RPL/LAB >	08-02064 @5	08-02065 @5	08-02066 @5	08-02067 @5	08-02068 @5	08-02068 @25	08-02069 @5	08-02070 @5
Client ID >	TI624-G7-C1	TI624-G7-C2	TI624-G7-C3	TI624-G7-C4	TI624-G7-C5		TI624-G7-E	TI624-G7-F
(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
Al	2,430	5,100	7,220	7,580	8,820		3,990	1,860
B	[10]	[11]	[12]	[11]	13.3		[6.4]	[3.3]
Bi	--	--	--	--	[3.9]		--	--
Cd	[1.4]	[1.4]	[1.4]	[1.5]	[1.4]		[1.2]	[1.2]
Cr	55.7	80.6	101	109	128		61.1	28.5
Fe	24.7	36.1	32.2	83.4	7.13		[2.1]	[1.3]
K	263	281	259	276	345		142	[74]
Mn	2.76	4.50	4.32	12.7	[0.37]		[0.12]	[0.071]
Na	106,000	105,000	109,000	111,000	over-range	131,000	67,500	37,100
Ni	[0.48]	[0.61]	[0.52]	[2.1]	--		--	--
P	1,480	1,640	1,550	1,520	1,370		2,610	3,200
S	2,290	2,240	2,290	2,380	2,710		1,230	567
Si	129	105	72.7	74.7	72.8		29.4	14.6
Sr	0.234	0.344	0.327	0.787	[0.078]		--	[0.011]
U	143	78.6	48.3	47.8	[34]		40.7	[27]
Zn	17.2	18.1	16.5	16.2	16.1		[4.9]	[1.9]
Zr	[0.43]	[0.75]	[0.55]	1.42	--		[0.32]	[0.16]

Ag	6.35	6.20	6.26	6.85	6.81		2.92	[1.3]
As	--	--	--	--	--		--	--
Ba	[0.27]	[0.33]	[0.35]	0.839	[0.31]		[0.094]	[0.053]
Be	[0.028]	[0.042]	[0.036]	[0.034]	[0.043]		[0.012]	--
Ca	[4.3]	[4.6]	[4.9]	[14]	[2.3]		[2.7]	[2.4]
Ce	--	--	--	--	--		--	--
Co	--	--	--	--	--		--	--
Cu	[1.1]	2.04	1.83	1.94	1.84		[0.59]	--
Dy	--	--	--	--	--		--	--
Eu	--	--	--	--	--		--	--
La	[0.37]	[0.38]	--	[0.79]	--		--	--
Li	2.05	3.11	2.85	2.60	2.37		[1.4]	[1.2]
Mg	--	--	--	--	--		--	--
Mo	[2.5]	[2.8]	[2.8]	[2.7]	[2.9]		[1.4]	[1.1]
Nd	--	--	--	--	--		--	--
Pb	[12]	[12]	[9.5]	[15]	[7.3]		--	--
Pd	--	--	--	--	--		--	--
Rh	--	--	[1.6]	--	[1.5]		--	--
Ru	[5.3]	[5.3]	[5.7]	[6.5]	[6.8]		[2.9]	[1.9]
Sb	--	--	--	--	--		--	--
Se	[13]	[12]	[12]	[11]	[9.4]		[15]	--
Sn	--	--	--	--	--		--	[5.6]
Ta	--	--	--	--	--		--	--
Te	--	--	--	--	--		--	--
Th	--	--	--	--	--		--	--
Ti	--	[0.069]	--	[0.15]	--		--	--
Tl	[6.6]	--	--	--	--		--	--
V	[0.76]	[0.85]	0.922	0.933	[0.92]		0.953	[0.71]
W	[9.5]	[13]	[15]	[16]	[16]		[9.4]	[4.5]
Y	--	--	--	[0.11]	--		--	--

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

Run Date >	7/9/2008	7/9/2008	7/9/2008
Multiplier >	24.7	24.6	24.8
RPL/LAB >	08-02071	08-02072	08-02073
Client ID >	TI624-G7-G	TI572-G2-OxWash 3-1	TI572-G2-O-1
(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)
Al	871	83.5	89.7
B	[1.5]	[0.77]	[0.83]
Bi	[2.4]	[2.9]	[2.6]
Cd	[0.26]	[0.25]	[0.19]
Cr	13.9	122	131
Fe	[0.37]	0.947	[0.60]
K	48.9	[11]	[9.6]
Mn	[0.040]	[0.015]	[0.010]
Na	17,700	2,870	3,100
Ni	--	--	--
P	1,480	447	493
S	266	[27]	[31]
Si	12.0	11.5	11.8
Sr	[0.0049]	[0.0086]	[0.0052]
U	16.5	--	--
Zn	[0.65]	[0.54]	[0.57]
Zr	[0.034]	--	--
Ag	0.685	--	--
As	--	--	--
Ba	[0.032]	0.308	[0.012]
Be	[0.0016]	--	--
Ca	[0.95]	[0.64]	[0.93]
Ce	--	--	--
Co	--	--	--
Cu	[0.039]	--	--
Dy	--	--	--
Eu	--	--	--
La	--	--	--
Li	0.733	[0.15]	[0.15]
Mg	--	--	--
Mo	[0.30]	--	--
Nd	--	--	--
Pb	[0.98]	[1.5]	[1.5]
Pd	--	--	--
Rh	--	--	--
Ru	[0.67]	--	--
Sb	[0.50]	--	--
Se	[2.5]	[2.0]	[3.1]
Sn	[2.3]	--	--
Ta	--	--	--
Te	--	--	--
Th	--	--	--
Ti	--	--	--
Tl	--	--	--
V	0.274	[0.099]	[0.12]
W	[1.8]	--	--
Y	--	--	--

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

QC Performance 7/9/2008

Criteria >	≤ 20%	80%-120%	75%-125%	75%-125%	75%-125%	≤ 10%
QC ID >	08-02059 Dup	LCS/BS	08-02059 MS	08-02059 + PS-A	08-02059 + PS-B	08-02059 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	1.9	101	99	102		2.6
B	6.7	106	103	105		
Bi		88	99	94		
Cd		99	99	99		
Cr	1.3	99	99	100		3.3
Fe		98	99	100		
K	10.5	103	101	99		
Mn		101	100	101		
Na	0.3	98	nr	nr		2.8
Ni		100	102	102		
P	1.3	100	nr	100		0.9
S	2.3	99	nr		95	0.1
Si		97	100	97		
Sr		102	100	101		
U	1.5	99	98		95	
Zn		99	103	105		
Zr		103	101	101		
Other Analytes						
Ag				92		
As				96		
Ba		99	98	99		
Be		101	101	101		
Ca		104	101	99		
Ce		96	97		93	
Co				103		
Cu		101	104	105		
Dy					95	
Eu					97	
La		95	95		93	
Li	0.4	104	99	100		
Mg		100	99	100		
Mo		101	100	102		
Nd		98	97		97	
Pb		100	100	100		
Pd					92	
Rh					91	
Ru					96	
Sb				100		
Se				99		
Sn				97		
Ta				102		
Te					98	
Th		97	96		95	
Ti		101	99	99		
Tl				93		
V		95	94	96		
W		99	96	98		
Y				96		

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#: 52964 / F99189
ASR#: 8176
Client: R. Shimskey
Total Samples: 3 (solid)

	First	Last
RPL#:	08-02074	08-02076
Client ID:	TI624-G7-6	TI624-G7-12
Sample Preparation: RPG-CMC-138, "HNO_3-HF-HCl Acid Digestion of Solids for Metals Analysis Using a Dry-Block Heater", 7/11/08 (SAL/ng).		

Procedure: RPG-CMC-211, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)", Rev 2.

Analyst: J. Deschane

Analysis Date (File): 7-18-2008 (C0148)

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE Number: N827583 (ICP-OES instrument)
M19445 (Mettler AT400 Balance)

7/31/08
Preparer

C. Z. 7/31/08
Review and Concur

Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report

Three samples submitted under Analytical Service Request (ASR) 8125 were analyzed by ICP-OES. The samples were prepared following RPL procedure RPG-CMC-138 using a nominal 0.2 grams of sample and diluting to a final volume of 100 mL.

Analytes of interest (AOIs) were specified in the ASR, and are listed in the upper section of the attached ICP-OES Data Report. The quality control (QC) results for these AOIs have been evaluated and are presented below. Analytes other than AOIs are reported in the bottom section of the report, but have not been fully evaluated for QC performance. The results are given as μg/g for each detected analyte, and have been adjusted for all laboratory processing factors and instrument dilutions.

Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure and using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte, and also used for continuing calibration verification.

Minimum Method Detection Limit (MDL) values were specified in the ASR. MDL levels were met for all AOIs.

The controlling documents were ASO-QAP-001, and the client supplied RPP-WTP-QA-005, Rev. 2, and ASR-8176 Special Instructions. Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-spike, laboratory control standard (LCS), duplicate, and serial dilution were conducted during the analysis run. The LCS was prepared using a nominal 0.1 grams of SRM-2710 (Montana Soil).

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the digestion process. The concentrations of all AOIs were within the acceptance criteria of ≤EQL (estimated quantitation level) or less than ≤5% of the concentration in the sample.

Blank Spike (BS)/Laboratory Control Sample (LCS):

An LCS (Montana Soil) was prepared for the digestion process. Recovery values are listed for all analytes included in the spike that were measured at or above the EQL. The recovery values were within the acceptance criterion of 80% to 120% for all AOIs meeting the above requirement.

Matrix-Spiked Sample:

No matrix spike sample was provided for analysis.

Duplicate Relative Percent Difference (RPD):

A duplicate was prepared for the digestion process. RPDs are listed for all analytes that were measured at or above the EQL. The RPDs were within the client acceptance criterion of ≤25% for all AOIs meeting the above requirement.

Post-Spike/Analytical Spike Sample (A component):

An analytical spike (A component) was conducted for the sample batch. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. The recovery values were within the client acceptance criterion of 70% to 130% for all AOIs meeting the above requirements.

Post Spike/Analytical Spike Sample (B component):

An analytical spike (B component) was conducted for the sample batch. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. The recovery values were within the client acceptance criterion of 70% to 130% for all AOIs meeting the above requirements.

Serial dilution:

Five-fold serial dilution was conducted for the sample batch. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %Ds were within the acceptance criterion of ≤10% for all AOIs meeting the above requirement.

Other QC:

All other instrument-related QC tests for the AOIs passed within the appropriate acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water. Detection limits for other matrices may be determined if requested. Method detection limits (MDL) can be estimated by multiplying the IDL by the "Multiplier". The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Multiplier".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standards are validated to a precision of ±10%.
4) Absolute precision, bias and detection limits may be determined on each sample if required by the client. The maximum number of significant figures for all ICP measurements is two.
5) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	7/18/2008	7/18/2008	7/18/2008	7/18/2008	7/18/2008
		Multiplier >	1679.5	1377.8	1436.8	1830.8	2417.8
		RPL/LAB >	08-02074-138-B @5	08-02074-138-S @5	08-02074-138-D @5	08-02075-138-S @5	08-02076-138-S @5
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Prep Blank	TI624-G7-6		TI624-G7-9	TI624-G7-12
(µg/mL)	(µg/mL)	(Analyte)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
0.0060	0.060	Al	--	42,000	41,300	36,800	41,900
0.0048	0.096	B	--	[23]	[28]	[23]	[22]
0.0300	0.300	Bi	--	1,040	1,030	1,240	1,910
0.0037	0.037	Cd	--	113	118	132	213
0.0017	0.017	Cr	--	1,630	1,600	1,750	2,500
0.0019	0.038	Fe	[5.0]	91,200	89,900	107,000	168,000
0.0720	0.720	K	--	[550]	[430]	[550]	[260]
0.0002	0.005	Mn	[0.41]	13,500	13,300	15,800	24,700
0.0160	0.320	Na	[170]	153,000	151,000	249,000	110,000
0.0024	0.024	Ni	[7.4]	2,440	2,410	2,900	4,450
0.0500	0.500	P	--	22,500	22,100	25,300	13,700
0.1600	1.600	S	--	5,320	5,420	4,480	[1,600]
0.0056	0.056	Si	--	na	na	na	na
0.0001	0.002	Sr	--	892	877	1,050	1,610
0.0320	0.320	U	--	12,400	12,100	15,100	22,900
0.0028	0.056	Zn	[19]	270	273	313	456
0.0011	0.011	Zr	--	2,280	2,240	2,670	4,140
Other Analytes							
0.0021	0.021	Ag	--	67.6	30.6	47.0	183
0.0520	0.520	As	--	--	--	--	--
0.0003	0.005	Ba	[0.85]	580	572	680	1,050
0.0001	0.001	Be	--	0.787	0.860	[0.94]	1.50
0.0130	0.130	Ca	[22]	6,330	6,180	7,390	11,400
0.0100	0.100	Ce	--	633	632	751	1,150
0.0024	0.024	Co	--	[28]	[29]	[36]	[56]
0.0014	0.014	Cu	--	209	209	247	383
0.0029	0.029	Dy	--	--	--	--	--
0.0011	0.011	Eu	--	[14]	[13]	[17]	[24]
0.0028	0.028	La	--	725	703	862	1,320
0.0006	0.012	Li	--	87.1	85.6	98.9	149
0.0023	0.023	Mg	--	1,690	1,660	1,990	3,060
0.0052	0.052	Mo	--	[17]	[14]	[19]	[22]
0.0170	0.170	Nd	--	1,060	1,040	1,280	1,990
0.0320	0.320	Pb	--	3,930	3,840	4,590	7,150
0.0063	0.063	Pd	--	--	--	--	--
0.0120	0.120	Rh	--	--	[25]	--	[36]
0.0085	0.085	Ru	--	217	220	243	234
0.0200	0.200	Sb	--	--	--	--	--
0.0700	0.700	Se	--	--	--	--	--
0.0270	0.270	Sn	--	[39]	[56]	--	--
0.0170	0.170	Ta	--	--	--	--	[53]
0.0260	0.260	Te	--	[180]	[170]	[190]	[250]
0.0098	0.098	Th	--	486	473	579	875
0.0004	0.004	Ti	--	199	197	234	370
0.0380	0.380	Tl	--	--	--	--	--
0.0007	0.007	V	[1.3]	16.9	17.0	19.3	25.1
0.0140	0.140	W	--	232	253	273	365
0.0004	0.004	Y	--	94.0	91.7	111	169

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

QC Performance 7/18/2008

Criteria >	≤ 25%	80%-120%	70%-130%	70%-130%	70%-130%	≤ 10%
QC ID >	08-02074 Dup	LCS/BS	MS (none)	08-02074 + AS-A	08-02074 + AS-B	08-02074 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	1.8	96		101		0.5
B				104		
Bi	1.0			96		
Cd	4.4			102		
Cr	2.0			102		1.2
Fe	1.4	96		102		1.0
K				99		
Mn	1.4	100		nr		0.7
Na	1.6	87		98		1.4
Ni	1.5			101		1.0
P	1.9			102		0.7
S	1.8				99	
Si	na	na	na	na	na	na
Sr	1.7			104		0.4
U	2.0				98	0.5
Zn	1.3	99		104		
Zr	1.6			99		0.8
Other Analytes						
Ag	75.5			92		
As				98		
Ba	1.4	93		98		0.0
Be	8.8			101		
Ca	2.4	94		98		0.0
Ce	0.1				96	
Co				102		
Cu	0.2	97		100		0.1
Dy					98	
Eu					99	
La	3.0				97	1.8
Li	1.8			102		13.1
Mg	2.1	95		99		2.4
Mo				101		
Nd	2.3				99	
Pb	2.5	100		100		2.3
Pd					92	
Rh					96	
Ru	1.2				98	
Sb				101		
Se				104		
Sn				100		
Ta				101		
Te					97	
Th	2.7				98	
Ti	1.2	91		98		0.4
Tl				95		
V	1.0	96		96		
W	8.9			102		
Y	2.4			98		0.2

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

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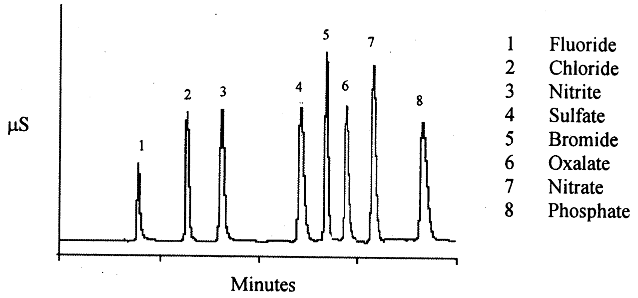
PO Box 999, Richland, Washington 99352

Common Inorganic Anions
Dionex AS18 Column; Hydroxide Gradient



Client:	R. Shimskey	***ASR #:***	8176
Project #:	52964	***# Samples:***	5 liquids
Charge Code:	F99189		

*** RPL Numbers: 08-02059 through 08-02063***
Liquid Samples Only Reported

Rev. 1 - Revised Report – Corrected RPL sample number ID's on results page.

Procedure, Analysis, System, and Records Information

Analysis Procedure	PNL-ALO-212, "Determination of Inorganic Anions by Ion Chromatography"
Prep Procedure	Bench Dilution performed in lab 400 (MJS 7/24/08 and 7/25/08)
Analyst	MJ Steele
Analysis Dates	07/25 – 26/2008
Calibration Date	5/8/08
Cal/Ver Stds Prep Date	Cal 5/8/08; Ver 7/24/08
Excel Data File	Results ASR8176 Shimskey.xls
M&TE Numbers	IC System (M&TE) N830443
	Balances: 360-06-01-031 / 1113052270
All Analysis Records	Chemical Measurement Center 98620: RIDS IC System File (IC-0168)

Prepared By   9/23/08
Date

Reviewed By   9/23/08
Date

IC Report – Rev. 1

Sample Results

See Attachment: Direct Liquid Sample Results ASR 8176

Sample Analysis/Results Discussion

Five liquid samples were submitted to the ASO for analysis under ASR 8176. The analytes of interest are fluoride, chloride, nitrite, nitrate, oxalate, sulfate and phosphate. The samples were prepared for analysis using dilutions at the bench, which included the preparation of analytical spikes and sample replicates. The dilutions were prepared in deionized water and the water was analyzed as the process dilution sample. All sample results are reported as µg/mL.

The final analysis was performed using dilutions ranging from 100x to ~10,000x to provide values within the calibration range. All results have been adjusted for all analytical dilutions. The preparation dilution blanks (water used to dilute samples at the IC workstation) are reported as analyzed, no dilution factors were applied to these samples. The estimated method detection limits (MDL) are provided, and are based on the estimated quantitation limit (EQL), which is one-tenth of the lowest calibration standard (adjusted for the dilutions used for reporting the results).

Data Limitations

None

Quality Control Discussion

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001 and the client specified special instructions, RPP-WTP-QA-005 Rev 2, which has the same specification as the QA Plan.

Processing Blanks: (Dilution) Two process dilution blanks (deionized water) were analyzed with the sample set. There were no anions detected above the method detection limit (MDL). Thus, the processing blanks met the QA Plan acceptance criteria for all analytes of interest.

Duplicate (Precision): One sample was analyzed in duplicate (08-02259). The relative percent difference (RPD) ranged from 2% to 3% for all analytes of interest. Note: the replicate RPD is not calculated for results less than the EQL.

Processing Laboratory Control/Blank Spike (LCS/BS): The routine instrument blank spike was analyzed twice with the run and had a recovery range of 95% to 118% for the analytes of interest. These recoveries meet the QA Plan acceptance criteria of 80% to 120% recovery.

Matrix Spike: (Accuracy) None prepared. Sample did not undergo sample preparation; therefore, an analytical spike was prepared and analyzed.

Post Spike: (Accuracy) One sample was prepared as an analytical spike and analyzed (08-02260). Sample 08-02260 was analyzed as a post spike using three separate dilutions. The recovery ranged from 95% to 109% for all analytes of interest, which meets the QA Plan matrix spike recovery acceptance criteria of 75% to 125%.

IC System QC Samples: Numerous calibration verification standards and calibration verification blanks were analyzed with each run day. For all data reported, the IC System QC bounding the sample analyses produced results for all analytes were within the acceptance criterion of the ASO's QA Plan (i.e., 90% to 110% recovery for verification standards and verification blank results <EQL or <5% of reported sample result).

Deviations from Procedure

None

General Comments

- The reported "Final Results" have been corrected for all dilutions performed on the sample during processing or analysis.
- The MDL is set at the concentration of the lowest calibrations standard divided by 10. The EQL is defined as the concentration of the lowest calibration standards times the sample dilution factors (processing and analysis) and assumes non-complex aqueous matrices. Matrix-specific MDLs or EQLs may be determined, if requested.
- Routine precision and bias are typically ±15% or better for non-complex aqueous samples that are free of interference.

Direct Liquid Sample Results ASR 8176 - Report Revision 1

RPL Number	Client Sample ID	F MDL µg/mL	F Result µg/mL	DF	Cl MDL µg/mL	Cl Result µg/mL	DF	NO_2 MDL µg/mL	NO_2 Result µg/mL	DF	SO_4 MDL µg/mL	SO_4 Result µg/mL	DF
08-02059	TI624-G7-A	16	257		19	572		130	18,200		190	16,700	
08-02060	TI624-G7-B	16	435		19	459		130	14,200		190	12,100	
08-02061	TI624-G7-D	16	170		19.00	1600		130	7580		38	6500	
08-02062	TI624-G7-H	3.1	20.0	J	3.7	108		5.0	412		7.6	364	
08-02063	TI624-G7-I	3.1	86		4	462		25	1850		7.6	1630	
Dilution Blank	Dilution Blank 7-24-08	0.031	0.031	U	0.037	0.037	U	0.050	0.050	U	0.076	0.076	U
Dilution Blank	Dilution Blank 7-25-08	0.031	0.031	U	0.037	0.037	U	0.050	0.050	U	0.076	0.076	U

RPL Number	Client Sample ID	C_2O_4 MDL µg/mL	C_2O_4 Result µg/mL	DF	NO_3 MDL µg/mL	NO_3 Result µg/mL	DF	PO_4 MDL µg/mL	PO_4 Result µg/mL	DF
08-02059	TI624-G7-A	25	25	U	1,000	181,000		150	13,200	
08-02060	TI624-G7-B	25	1,730		1,000	123,000		150	14,700	
08-02061	TI624-G7-D	25	899		500	64,700		30	4,630	
08-02062	TI624-G7-H	5.0	53		50	3,530		30	2,210	
08-02063	TI624-G7-I	5.0	215		250	15,700		150	7,400	
Dilution Blank	Dilution Blank 7-24-08	0.050	0.050	U	0.100	0.100	U	0.060	0.060	U
Dilution Blank	Dilution Blank 7-25-08	0.050	0.050	U	0.100	0.100	U	0.060	0.060	U

Direct Liquid Sample QC Results ASR 8176

Sample/Replicate Precision Results [(a)]

RPL Number	Sample ID	F µg/mL	RPD & %RSD	Cl µg/mL	RPD & %RSD	NO_2 µg/mL	RPD & %RSD	SO_4 µg/mL	RPD & %RSD	C_2O_4 µg/mL	RPD & %RSD	NO_3 µg/mL	RPD & %RSD	PO_4 µg/mL	RPD & %RSD
08-02059-S	Sample	257	--	572	--	18200	--	16700	--	U	--	181000	--	13200	--
	Duplicate | RPD	266	3	563	2	17800	2	16200	3	J	N/A	178000	2	13000	2

Direct Liquid Sample QC Results ASR 8176

Sample Spike Results - At IC Workstation

RPL Number	Sample ID	F µg/mL	%Rec	Cl µg/mL	%Rec	NO_2 µg/mL	%Rec	SO_4 µg/mL	%Rec	C_2O_4 µg/mL	%Rec	NO_3 µg/mL	%Rec	PO_4 µg/mL	%Rec
08-02060-S	Sample	435	--	459	--	14200	--	12100	--	1730	--	123000	--	14700	--
	AS Sample	1.52	109	1.65	99	5.22	95	16	104	4.4	107	16.7	101	5.92	96

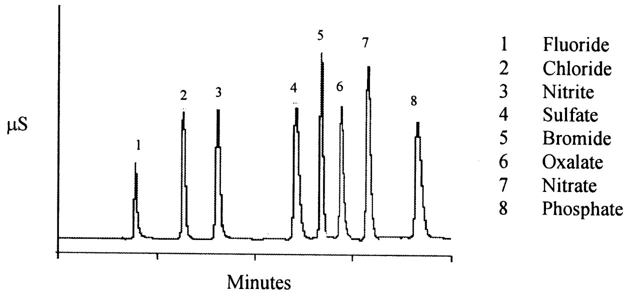
Blank Spike Results

RPL Number	Run ID	F Rec, %	Cl Rec, %	NO_2 Rec, %	SO_4 Rec, %	C_2O_4 Rec, %	NO_3 Rec, %	PO_4 Rec, %
LCS 1	7/24/2008 20:59	100	98	99	99	98	101	95
LCS 2	7/25/2008 19:03	101	99	102	101	100	118	98

AS = Analytical Spike: Spike performed at IC Workstation on liquid Sample.
LCS/BS = Laboratory Control Sample: Spike added prior to leaching solids.
RPD = Relative Percent Difference
%Rec = Percent Recovery
U = Not Detected Above Method Detection Limit
J = Detected, Result are Qualitative: Result >MDL but <EQL (estimated quantitation limit)
-- = Value Not Calculated, place holder for blank cell
▨ analytical spike recovery is outside acceptance range, an alternate analysis is also reported, which have acceptable recoveries

Battelle - Pacific Northwest National Laboratory
Analytical Support Operations – IC Report
PO Box 999, Richland, Washington 99352

Common Inorganic Anions
Dionex AS18 Column; Hydroxide Gradient



Client: R. Shimskey
ASR #: 8176
Project #: 52964
 # Samples: 3 Solids
Charge Code: F99189

*** RPL Numbers: 08-02074 through 08-02076***
Water Leached Solids Samples Only Reported

Procedure, Analysis, System, and Records Information

Analysis Procedure	PNL-ALO-212, "Determination of Inorganic Anions by Ion Chromatography"
Prep Procedure	Bench Dilution performed in lab 400 (MJS 7/24/08 and 7/25/08)
Analyst	MJ Steele
Analysis Dates	07/25 – 26/2008
Calibration Date	5/8/08
Cal/Ver Stds Prep Date	Cal 5/8/08; Ver 7/24/08
Excel Data File	Results ASR8176 Shimskey.xls
M&TE Numbers	IC System (M&TE) N830443
	Balances: 360-06-01-031 / 1113052270
All Analysis Records	Chemical Measurement Center 98620: RIDS IC System File (IC-0168)

Prepared By 08/19/08 Date

Reviewed By 8/28/08 Date

IC Report

Sample Results

See Attachment: Water Leached Solids Results ASR 8176

Sample Analysis/Results Discussion

Three solid/slurry samples were submitted to the ASO for analysis under ASR 8176. The specified analytes of are fluoride, nitrite, nitrate, sulfate, oxalate and phosphate; however, chloride has also been reported. The samples were prepared for IC analysis by drying the solids/slurry and then leaching the dry solids (from 0.3 g to 1.4 g slurry to 10 mL of deionized water), which included the preparation of a matix spike and sample duplicate. Following leaching, the samples were further diluted to bring each analyte within the calibration range. The dilutions were prepared in deionized water. Both the deionized water used to leach the solids/slurries and to make further dilutions were analyzed as a process sample. All sample results are reported as µg/g; the leach deionized water samples (referred to a the process blank, PB) has been adjusted for each sample leach factor and reported with each sample.

After screening the samples, the final analysis was performed using additional dilution factors ranging from ~20 to 2100. All sample results have been adjusted for all leaching and analytical dilution factors. The estimated method detection limits (MDL) are provided for each analyte of interest measured and the MDLs have been adjusted for all analytical dilutions. The MDLs are set at one-tenth the lowest calibration standard, which is defined as the estimated quantitation limit (EQL).

Data Limitations

None

Quality Control Discussion

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001 and the client specified special instructions, RPP-WTP-QA-005 Rev 2, which has the same specification as the QA Plan.

Dilution Blank: (Analytical Dilution) Two dilution blanks (deionized water) were analyzed with the sample set. There were no anions detected above the method detection limit (MDL). The processing blank meets the QA Plan acceptance criteria for all analytes of interest.

Process Blank: (Leach Dilution) A process blank (deionized water subjected to the same handling as the leached solid/slurry samples) was analyzed with the sample set. Only fluoride and chloride were detected in the process leach blank, but were below the EQL; thus meeting the QA Plan acceptance criteria for all analytes of interest.

Duplicate (Precision): Sample 08-02074 was analyzed in duplicate. The relative percent difference is reported for all analytes which were measured at or above the EQL. The reported RPDs ranged from 2 to 13% for all analytes of interest, which meets the Project acceptance criteria (Table 5 of ASR) of <25%.

IC Report

Processing Laboratory Control Sample/Blank Spike (LCS/BS): The leaching process LCS/blank spike was analyzed with the data set and had a recoveries ranging from 92% to 108% for the analytes of interest. These recoveries meet the Project acceptance criteria (Table 4 of ASR) of 80% to 120% recovery.

Matrix Spike: (Accuracy) A matrix spike was prepared for Sample 08-02076. However, no recoveries are reported since concentrations of all analytes of interest are greater than five times the (added) spike concentration. Post spikes were performed to evaluate accuracy.

Post Spike: (Accuracy) Multiple post spikes (i.e., standard added after leaching) were prepared for sample 08-02076 and analyzed. Sample 08-02076 was diluted by 40, 400 and 1,400 in order to obtain spikes concentrations at least 20% greater than measured sample concentration. The recovery range was from 94% to 102% for all analytes of interest, which meets the QA Plan post spike recovery acceptance criteria of 75% to 125%.

IC System QC Samples: Numerous calibration verification standards and calibration verification blanks were analyzed with each run day. For all data reported, the IC System QC bounding the sample analyses produced results for all analytes were within the acceptance criterion of the ASO's QA Plan (i.e., 90% to 110% recovery for verification standards and verification blank results <EQL or <5% of reported sample result).

Deviations from Procedure

None

General Comments

- The reported "Final Results" have been corrected for all dilutions performed on the sample during processing or analysis.
- The MDL is set at the concentration of the lowest calibrations standard divided by 10. The EQL is defined as the concentration of the lowest calibration standards times the sample dilution factors (processing and analysis) and assumes non-complex aqueous matrices. Matrix-specific MDLs or EQLs may be determined, if requested.
- Routine precision and bias are typically ±15% or better for non-complex aqueous samples that are free of interference.

ASR 8176 Attachment (Page 1 of 1)

Water Leached Solids Results -- ASR 8176

			F			Cl			NO_2			SO_4		
RPL Number	Client Sample ID	Leach Dilution	MDL µg/g	Result µg/g	DF	MDL µg/g	Result µg/g	DF	MDL µg/g	Result µg/g	DF	MDL µg/g	Result µg/g	DF
08-02074-103-S	TI624-G7-6	21.2	130	678	J	160	615	J	210	19,100		320	16,200	
08-02074-103-PB	Water Leach PB @2074 Dil.	21.2	130	545	J	160	951	J	210	210	U	320	320	U
08-02075-103-S	TI624-G7-9	7.3	45	759		54	2,980		73	14,500		110	12,000	
08-02074-103-PB	Water Leach PB @2075 Dil.	7.3	45	189	J	54	324	J	73	73	U	110	110	U
08-02076-103-S	TI624-G7-12	29.8	18	456		22	2,040		300	13,300		45	7,720	
08-02074-103-PB	Water Leach PB @2076 Dil.	29.8	18	77	J	22	133	J	300	300	U	45	45	U
			µg/mL	µg/mL	DF	µg/mL	µg/mL	DF	µg/mL	µg/mL	DF	µg/mL	µg/mL	DF
08-02074-103-PB	Water Leach Process Blank	1.0	0.031	0.130	J	0.037	0.220	J	0.050	0.050	U	0.076	0.076	U
072408 Dilution Blank	Dilution Blank 7-24 & 7-25	1.0	0.031	0.031	U	0.037	0.037	U	0.050	0.050	U	0.076	0.076	U

			C_2O_4			NO_3			PO_4		
RPL Number	Client Sample ID	Leach Dilution	MDL µg/g	Result µg/g	DF	MDL µg/g	Result µg/g	DF	MDL µg/g	Result µg/g	DF
08-02074-103-S	TI624-G7-6	21.2	210	2,820		1,500	155,000		250	45,200	
08-02074-103-PB	Water Leach PB @2074 Dil.	21.2	210	210	U	1,500	1,500	U	250	250	U
08-02075-103-S	TI624-G7-9	7.3	73	2,640		510	115,000		310	66,100	
08-02074-103-PB	Water Leach PB @2075 Dil.	7.3	73	73	U	510	510	U	310	310	U
08-02076-103-S	TI624-G7-12	29.8	30	1,580		600	70,300		360	35,200	
08-02074-103-PB	Water Leach PB @2076 Dil.	29.8	30	30	U	600	600	U	360	360	U
			µg/mL	µg/mL	DF	µg/mL	µg/mL	DF	µg/mL	µg/mL	DF
08-02074-103-PB	Water Leach Process Blank @1	1.0	0.050	0.050	U	0.10	0.10	U	0.060	0.060	U
072408 Dilution Blank	Dilution Blank 7-24 & 7-25	1.0	0.050	0.050	U	0.10	0.10	U	0.060	0.060	U

Water Leached Solids QC Results -- ASR 8176

Sample/Replicate Precision Results[(a)]

	Sample/Duplicate	F		Cl		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	Designation	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD
08-02074-103-S	Sample	J	--	J	--	19,100	--	16,200	--	2,820	--	155,000	--	45,200	--
08-02074-103-D	Duplicate	J	n/a	J	n/a	18,600	2	15,500	4	2,650	6	149,000	4	39,800	13

Sample Spike Results - Prior to Water Leach and at IC Workstation[(a)]

	Sample/Spike	F		Cl		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	Designation	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec
LCS/BS- Leached															
072508 Dilution Blank	Dilution Blank	U	--	U	--	U	--	U	--	U	--	U	--	U	--
08-02074-103-BS-IC	LCS Sample	5.1	105	6.2	105	7.7	100	11.7	101	7.6	99	13.9	103	9.5	99
072508 Dilution Blank	Dilution Blank	U	--	U	--	U	--	U	--	U	--	U	--	U	--
08-02074-103-BS-IC(20)	LCS Sample	5.1	105	6.3	108	7.7	100	12	104	7.1	92	14	104	8.9	93
Matrix Spike - Leached															
08-02076-103-S	Sample	15.3	--	68.4	--	447	--	259	--	53.1	--	2,360	--	1,180	--
08-02076-103-MS	MS Sample	24.2	n/a	94.2	n/a	588	n/a	352	n/a	88	n/a	2,930	n/a	1,440	n/a
Analytical Post Spike - After Leaching															
08-02076-103-S	Sample	15.3	--	68.4	--	447	--	259	--	53.1	--	2,360	--	1,180	--
	PS (Sample @40x Dilution)	1.32	94	2.92	101	o/r	n/a	10.1	97	3.79	99	o/r	n/a	o/r	n/a
08-02076-103-S	Sample	15.3	--	68.4	--	447	--	259	--	53.1	--	2,360	--	1,180	--
	PS (Sample @400x Dilution)	1.06	102	1.34	97	3.54	97	4.33	98	2.64	100	10.3	101	6.01	98
08-02076-103-S	Sample	15.3	--	68.4	--	447	--	259	--	53.1	--	2,360	--	1,180	--
	PS (Sample @1400x Dilution)	1.03	102	1.22	98	2.76	98	3.88	98	2.53	100	6.06	100	3.84	96

LCS Results - IC System

RPL Number	Run ID	F %Rec	Cl %Rec	NO_2 %Rec	SO_4 %Rec	C_2O_4 %Rec	NO_3 %Rec	PO_4 %Rec
LCS	7/24/2008 20:59	100	98	99	99	98	101	95
LCS	7/25/2008 19:03	101	99	102	101	100	118	98

D = Duplicate; S = Sample; DF = Data Flag; %Rec = Percent Recovery; RPD = Relative Percent Difference' o/r = over range; n/a = not applicable

LCS/BS = Laboratory Control Sample/Blank Spike: Standard processed through entire cycle ... including water leaching.

LCS = Laboratory Control Sample (Standard analyzed at IC Workstation)

MS = Matrix Spike: Sample spiked with standard solution and processed through entire cycle ... including water leaching.

PS = Analytical Post Spike: Spike performed at IC Workstation on same sample as MS prepared from.

U = Data Flag for Not Detected Above Method Detection Limit

J = Data Flag for Detected, Result are Qualitative: Result >MDL but <EQL (estimated quantitation limit)

-- = Value Not Calculated, place holder for blank cell

(a) %RPD not calculated (i.e., n/a) if either result is <EQL; %Rec not calculated (i.e., n/a) if sample or AS over-range, or spike is <25% of sample concentration

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Client: Rick Shimskey

Report Date: 7/3/2008
Analysis Date: 7/1/2008

Subject: Hydroxide Analyses for: **CUF Group 7 (TPB Sludge) / 241-AY-102 Waste Treatability Study**

ASR: **8176** Rev-0
Procedure: RPG-CMC-228-Rev 1
Sample ID. 08-02059 thru 08-02071

Direct sample aliquots of CUF Group 7 (TPB Sludge) / 241-AY-102 Waste Treatability Study samples (see above assigned RPL Sample #'s), 13 samples total were analyzed in duplicate for the base constituents content following procedure RPG-CMC-228, and using a Brinkman 636 Auto-Titrator. The titrant used was 0.1016 M HCl and the base standard, 0.1118 M NaOH was used for QC verification standards and matrix spike. -- See Chemrec_139 pdf imbedded in the result report.

The hydroxide Standard recovery was 98%, well within the allowed ± 20% recovery range. Although not required in this ASR, 2 matrix spike were analyzed with recoveries of 99% and 89%. No hydroxide was detected in the reagent blank.

The initial pH is reported on attached Report Summary along with the free hydroxide molarities at an average pH of 10 to 11. These results showed excellent Relative Percent Deviation (RPD) for the first inflection point, all <7%, well within ± 20% allowed range. A 2nd inflection point around pH 7-8, indicating final hydroxide molarity or carbonate also showed very good RPD's, well within ± 20% allowed range. All samples also indicated a third inflection point, probably bicarbonate, around pH 4-5, and again all RPD's were within ± 20% allowed range.

The best estimate of the MDL for this method is obtained from the reagent blank which did not show any inflection points and is consistent with a value of 0 within our measurement sensitivity. All samples molarities were well above the MDL (0.1M) for this analysis. The results are accepted based on the QC data meeting the acceptance criteria as specified in the ASR.

Following is the report summary, the sample results calculated from the raw data, and the record file for the standardized acid and base used. The sample fractions provided were consumed in the analysis process.

Copies of the titration curves are available upon request.

Prepared by: Date: 7/3/08
Reviewed by: Date: 7/14/08

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

ASR # 8176

WP# F99189

Hydroxide and Alkalinity Determination
Procedure: RPG-CMC-228-Rev 1

Equip # WB76843

Report Summary for ASR # -- 8176

Revision # Rev-0

Report Date: 7/3/2008
Analysis Date: 7/1/2008

				Concentration, moles / Liter					
				First Point		Second Point		Third Point	
RPG #	Client ID	Initial pH	OH conc ug/mL	Molarity	RPD	Molarity	RPD	Molarity	RPD
08-02059	TI-624-G7-A	11.53	2.40E+03	0.14		0.04		0.19	
08-02059-Dup	TI-624-G7-A	11.55	2.37E+03	0.14	1.3%	0.04	17.5%	0.18	6.6%
08-02060	TI-624-G7-B	11.43	1.97E+03	0.12		0.39		0.63	
08-02060-Dup	TI-624-G7-B	11.40	1.84E+03	0.11	6.9%	0.40	3.8%	0.63	0.0%
08-02061	TI-624-G7-D	12.38	3.90E+04	2.29		0.85		0.50	
08-02061-Dup	TI-624-G7-D	12.49	3.78E+04	2.22	3.2%	0.86	1.1%	0.50	0.6%
08-02062	TI-624-G7-H	12.20	3.05E+03	0.18		0.07		0.05	
08-02062-Dup	TI-624-G7-H	12.16	3.23E+03	0.19	5.5%	0.07	5.6%	0.05	11.8%
08-02063	TI-624-G7-I	12.40	1.21E+04	0.71		0.27		0.22	
08-02063-Dup	TI-624-G7-I	12.36	1.24E+04	0.73	2.3%	0.29	9.6%	0.20	9.8%
08-02064	TI-624-G7-C1	12.52	4.47E+04	2.63		0.51		0.39	
08-02064-Dup	TI-624-G7-C1	12.46	4.24E+04	2.50	5.2%	0.52	1.4%	0.39	0.3%
08-02065	TI-624-G7-C2	12.46	4.00E+04	2.35		0.74		0.48	
08-02065-Dup	TI-624-G7-C2	12.44	4.01E+04	2.36	0.3%	0.74	0.7%	0.44	8.0%

	µg/ml or mg/L MDL	Molarity MDL	Required RPD
OH conc (mg/L) = M (g/L) * 17,000 **free OH as specified in ASR**	1.70E+03	0.100	+/- 20%

	Initial pH		Allowed Recovery Range
Reag. Blk.1		0	
Standard 1	12.56	97.6%	+/- 20%
08-02062MS	12.47	98.6%	+/- 20%

Note: Results are presented for the first, second, and third inflection points on the titration curves, as applicable. The first inflection point is generally associated with the free hydroxide concentration. The second inflection point generally represents total hydroxide, or carbonate or a combination of aluminate and carbonate. The third inflection point is usually indicative of bicarbonate or other weak acids or possibly the continued protonation of alumina.

Analyst: 7/3/08

Reviewer: 7/14/08

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

ASR # **8176**

WP# F99189

Hydroxide and Alkalinity Determination
Procedure: RPG-CMC-228-Rev 1

Equip # WB76843

Report Summary for ASR # -- 8176

Revision # **Rev-0**

Report Date: 7/3/2008
Analysis Date: 7/1/2008

				Concentration, moles / Liter					
				First Point		Second Point		Third Point	
RPG #	Client ID	Initial pH	OH conc ug/mL	Molarity	RPD	Molarity	RPD	Molarity	RPD
08-02066	**TI-624-G7-C3**	**12.45**	3.98E+04	**2.34**		**0.84**		**0.52**	
08-02066-Dup	**TI-624-G7-C3**	**12.62**	3.94E+04	**2.32**	0.9%	**0.86**	1.6%	**0.55**	4.6%
08-02067	**TI-624-G7-C4**	**12.57**	3.88E+04	**2.28**		**0.87**		**0.51**	
08-02067-Dup	**TI-624-G7-C4**	**12.51**	3.88E+04	**2.28**	0.1%	**0.88**	0.8%	**0.52**	2.0%
08-02068	**TI-624-G7-C5**	**12.61**	4.11E+04	**2.42**		**1.10**		**0.81**	
08-02068-Dup	**TI-624-G7-C5**	**12.64**	3.92E+04	**2.30**	4.7%	**1.09**	1.0%	**0.74**	8.3%
08-02069	**TI-624-G7-E**	**12.65**	2.51E+04	**1.48**		**0.49**		**0.34**	
08-02069-Dup	**TI-624-G7-E**	**12.39**	2.53E+04	**1.49**	0.8%	**0.54**	9.6%	**0.34**	1.3%
08-02070	**TI-624-G7-F**	**12.22**	1.30E+04	**0.76**		**0.28**		**0.20**	
08-02070-Dup	**TI-624-G7-F**	**12.41**	1.32E+04	**0.78**	2.1%	**0.26**	4.5%	**0.21**	6.3%
08-02071	**TI-624-G7-G**	**12.21**	6.80E+03	**0.40**		**0.13**		**0.09**	
08-02071-Dup	**TI-624-G7-G**	**12.52**	6.35E+03	**0.37**	6.8%	**0.13**	1.5%	**0.11**	11.6%

	µg/ml or mg/L MDL	Molarity MDL	Required RPD
OH conc (mg/L) = M (g/L) * 17,000 **free OH as specified in ASR**	1.70E+03	**0.100**	+/- 20%

		Initial pH		Allowed Recovery Range
Reag. Blk.1			**0**	
Standard 1		**12.56**	**97.6%**	+/- 20%
08-02069MS	**Matrix spike**	**12.60**	**89.2%**	N/A

Note: Results are presented for the first, second, and third inflection points on the titration curves, as applicable. The first inflection point is generally associated with the free hydroxide concentration. The second inflection point generally represents total hydroxide, or carbonate or a combination of aluminate and carbonate. The third inflection point is usually indicative of bicarbonate or other weak acids or possibly the continued protonation of alumina.

Analyst: 7/3/08

Reviewer: 7/14/08

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

Procedure: **RPG-CMC-228-Rev 1** Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates

using a Brinkman 636 Auto Titrator   Equip # WB76843   Lab Loc. 525

ASR # and Rev #	**8176** Rev-0
Client:	Rick Shimskey
WP#	F99189

File: R:\radchem\hydroxide\asr **8176**
Report Date: **7/3/2008**
Analysis Date: **7/1/2008**

Spreadsheet: OH-TemplateLocked07.xls 4/1/2007

Analyst: 7/3/08

Titrant	Molarity	Chem Rec#
HCl	**0.1016**	**139**

R:\CHEMREC\C-rec_139.XLS

Std. & Spike	Molarity
NaOH	**0.1118**

RPG #	Sample ID		Dilution Factor	Sample Vol. (mL)	Sample Wt. (g)	Density g/mL	Titrator Routine #	**Diluted** Initial pH reading	**OH** **1st Equivalence** Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
08-02059	TI-624-G7-A		na	0.400	na		4	11.529	0.555	9.975	0.056	0.141	
08-02059-Dup	TI-624-G7-A	Replicate	na	0.400	na		5	11.553	0.548	9.964	0.056	0.139	1.3%
08-02060	TI-624-G7-B		na	0.300	na		6	11.432	0.342	10.694	0.035	0.116	
08-02060-Dup	TI-624-G7-B	Replicate	na	0.500	na		7,8	11.401	0.532	10.636	0.054	0.108	6.9%
08-02061	TI-624-G7-D		na	0.100	na		10	12.381	2.256	10.590	0.229	2.292	
08-02061-Dup	TI-624-G7-D	Replicate	na	0.100	na		11	12.494	2.186	10.666	0.222	2.221	3.2%
08-02062	TI-624-G7-H		na	0.400	na		12	12.195	0.707	10.605	0.072	0.180	
08-02062-Dup	TI-624-G7-H	Replicate	na	0.400	na		13	12.161	0.747	10.406	0.076	0.190	5.5%
08-02063	TI-624-G7-I		na	0.300	na		14	12.404	2.104	10.544	0.214	0.713	
08-02063-Dup	TI-624-G7-I	Replicate	na	0.200	na		15	12.357	1.436	10.556	0.146	0.729	2.3%
08-02064	TI-624-G7-C1		na	0.100	na		16	12.521	2.586	10.592	0.263	2.627	
08-02064-Dup	TI-624-G7-C1	Replicate	na	0.100	na		17	12.455	2.456	10.590	0.250	2.495	5.2%
08-02065	TI-624-G7-C2		na	0.100	na		19	12.464	2.315	10.613	0.235	2.352	
08-02065-Dup	TI-624-G7-C2	Replicate	na	0.100	na		20	12.436	2.323	10.615	0.236	2.360	0.3%
Reag. Blk.1		OH vol	OH Wt.		na		1	4.92	na			**OH % Recovery**	
Standard 1	0.1118 M NaOH	2.0	2.0107	2.000	na		2	12.563	2.149	8.873	0.2183	**97.6%**	
		OH vol	OH Wt.										
08-02062MS	+ 2mL 0.1118 M NaOH	2.0	2.0045	0.100	na		21	12.473	2.633	10.526	0.2675	87.4%	MS

Instrument Calibration

Buffer	VWR Lot #	CMS#	Expire Date
4	6350	275295	31-Dec-08
7	6325	275294	30-Nov-08
10	6303	275293	30-Nov-08

2-nd Verif	Fisher Lot #	CMS#	Expire Date
7	68198	275346	31-Mar-09

Slope
93.8%
init.pH 7 check
7.013

verif. pH reading
start 7.008
end 6.997

Performance checks using Balance # 360--01-06-037

Pipet #	Vol.	Wt.	Pipet #	Vol.	Wt.	
92501	0.100	0.1001	00545	0.0500		
		0.1000				
		0.0999				
		0.0998				
		0.1003				
	Ave	0.1000	% eror	Ave	#DIV/0!	% eror
	Std. Dev.	0.0001	0.10%	Std. Dev.	#DIV/0!	#DIV/0!

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

ASR # and 8176

File: R:\radchem\hydroxide\asr

WP# F99189

Procedure:

0

Alkalinity of Aqueous Solutions, Leachates and Supernates

using a Brinkman 636 Auto Titrator Equip # WB76843

7/3/08

Titrant	Molarity
HCl	0.1016

0

RPG #		Sample Vol. (mL)	2nd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	nillimole RPD	3rd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
08-02059	0	0.400	0.696	8.554	0.014	0.036		1.434	4.780	0.075	0.187	
08-02059-Dup	Replicat	0.400	0.716	8.094	0.017	0.043	17%	1.407	4.765	0.070	0.176	7%
08-02060	0	0.300	1.487	8.205	0.116	0.388		3.337	4.604	0.188	0.627	
08-02060-Dup	Replicat	0.500	2.514	7.945	0.201	0.403	4%	5.598	4.523	0.313	0.627	0%
08-02061	0	0.100	3.093	8.060	0.085	0.850		3.587	4.671	0.050	0.502	
08-02061-Dup	Replicat	0.100	3.032	7.995	0.086	0.860	1%	3.523	4.705	0.050	0.499	1%
08-02062	0	0.400	0.981	7.478	0.028	0.070		1.188	3.959	0.021	0.053	
08-02062-Dup	Replicat	0.400	1.006	7.302	0.026	0.066	6%	1.190	4.126	0.019	0.047	12%
08-02063	0	0.300	2.890	8.182	0.080	0.266		3.530	4.469	0.065	0.217	
08-02063-Dup	Replicat	0.200	2.013	7.336	0.059	0.293	10%	2.400	4.389	0.039	0.197	10%
08-02064	0	0.100	3.091	7.646	0.051	0.513		3.472	4.508	0.039	0.387	
08-02064-Dup	Replicat	0.100	2.968	7.412	0.052	0.520	1%	3.350	4.431	0.039	0.388	0%
08-02065	0	0.100	3.041	7.793	0.074	0.738		3.511	4.496	0.048	0.478	
08-02065-Dup	Replicat	0.100	3.054	7.507	0.074	0.743	1%	3.488	4.510	0.044	0.441	8%
						2-nd Recovered						
Standard 1		2.000	2.282	3.386	0.2319	**103.7%**						
						Total OH recovery						
08-02062MS		0.100	3.058	7.272	0.3107	**94.2%**	MS	3.358	4.271	0.3412	**98.6%**	

Matrix spike recovery is calculated as follows:
Spike = 2.00 mL 0.1023 N NaOH was added to the 0.100-mL of sample for each matrix spike.
SpikeTitrant vol. (sample @ .1mL + spike) - SampleTitrant vol. (average sample only equated to .1mL) * 0.2176 N (HCl titrant) = meq. OH
meq OH / 2.00 mL added = meq OH/mL found / 0.1023 N OH added * 100 = % recovered.

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

ASR # and Rev #	8176 Rev-0	File:	R:\radchem\hydroxide\asr **8176**
Client:	Rick Shimskey	Report Date:	**7/3/2008**
WP#	F99189	Analysis Date:	**7/1/2008**

Procedure: **RPG-CMC-228-Rev 1** Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates

using a Brinkman 636 Auto Titrator   Equip # WB76843   Lab Loc. 525

Spreadsheet: OH-TemplateLocked07.xls 4/1/2007

Analyst: 7/3/08

Titrant	Molarity	Chem Rec#
HCl	**0.1016**	**139**

R:\CHEMREC\C-rec_139.XLS

Std. & Spike	Molarity
NaOH	**0.1118**

RPG #	Sample ID		Dilution Factor	Sample Vol. (mL)	Sample Wt. (g)	Density g/mL	Titrator Routine #	Diluted Initial pH reading	OH 1st Equivalence Point Titrant Vol. (mL)	OH 1st Equivalence Point pH	Found millimoles base	Molarity base	millimole RPD
08-02066	TI-624-G7-C3		na	0.100	na		22	12.450	2.303	10.818	0.234	2.340	
08-02066-Dup	TI-624-G7-C3	Replicate	na	0.100	na		23	12.615	2.282	10.811	0.232	2.319	0.9%
08-02067	TI-624-G7-C4		na	0.100	na		24	12.568	2.249	10.787	0.228	2.285	
08-02067-Dup	TI-624-G7-C4	Replicate	na	0.100	na		25	12.507	2.246	10.773	0.228	2.282	0.1%
08-02068	TI-624-G7-C5		na	0.100	na		26	12.608	2.377	10.888	0.242	2.415	
08-02068-Dup	TI-624-G7-C5	Replicate	na	0.100	na		27	12.637	2.268	10.890	0.230	2.304	4.7%
08-02069	TI-624-G7-E		na	0.200	na		28	12.651	2.908	10.710	0.295	1.477	
08-02069-Dup	TI-624-G7-E	Replicate	na	0.100	na		29	12.390	1.465	10.755	0.149	1.488	0.8%
08-02070	TI-624-G7-F		na	0.100	na		30	12.218	0.750	10.523	0.076	0.762	
08-02070-Dup	TI-624-G7-F	Replicate	na	0.200	na		31	12.411	1.532	10.619	0.156	0.778	2.1%
08-02071	TI-624-G7-G		na	0.200	na		32	12.211	0.787	10.362	0.080	0.400	
08-02071-Dup	TI-624-G7-G	Replicate	na	0.400	na		33	12.516	1.471	10.669	0.149	0.374	6.8%
			na		na								
		Replicate	na		na								
											OH % Recovery		
Reag. Blk.1		OH vol	OH Wt.		na		1	4.92	na				
Standard 1	0.1118 M NaOH	2.0	2.0107	2.000	na		2	12.563	2.149	8.873	0.2183	**97.6%**	
		OH vol	OH Wt.										
08-02069MS	+ 2mL 0.1118 M NaOH	2.0	1.9996	0.100	na		34	12.604	3.335	10.640	0.3388	85.2%	MS

Instrument Calibration

Buffer	VWR Lot #	CMS#	Expire Date
4	6350	275295	31-Dec-08
7	6325	275294	30-Nov-08
10	6303	275293	30-Nov-08

2-nd Verif	Fisher Lot #	CMS#	Expire Date
7	68198	275346	31-Mar-09

Slope
93.8%

init.pH 7 check
7.013

verif. pH reading	
start	7.008
end	6.997

Performance checks using Balance # 360--01-06-037

Pipet #	Vol.	Wt.		Pipet #	Vol.	Wt.	
92501	0.100	0.1001		00545	0.05	0	
		0.1000			0	0	
		0.0999			0	0	
		0.0998			0	0	
		0.1003			0	0	
	Ave	0.1000	% eror	Ave		0.0000	% eror
	Std. Dev.	0.0001	0.10%	Std. Dev.		0.0000	#DIV/0!

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

ASR # and 8176

File: R:\radchem\hydroxide\asr

WP# F99189

0

Procedure:
Alkalinity of Aqueous Solutions, Leachates and Supernates
using a Brinkman 636 Auto Titrator   Equip # WB76843

7/3/08

Titrant	Molarity
HCl	0.1016

0

RPG #		Sample Vol. (mL)	2nd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	nillimole RPD	3rd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
08-02066	0	0.100	3.132	8.041	0.084	0.842		3.645	4.318	0.052	0.521	
08-02066-Dup	Replicat	0.100	3.124	7.884	0.086	0.855	2%	3.661	4.001	0.055	0.546	5%
08-02067	0	0.100	3.106	7.885	0.087	0.871		3.609	4.236	0.051	0.511	
08-02067-Dup	Replicat	0.100	3.110	7.988	0.088	0.878	1%	3.623	4.456	0.052	0.521	2%
08-02068	0	0.100	3.463	8.071	0.110	1.103		4.257	3.504	0.081	0.807	
08-02068-Dup	Replicat	0.100	3.343	8.098	0.109	1.092	1%	4.074	4.062	0.074	0.743	8%
08-02069	0	0.200	3.878	8.076	0.099	0.493		4.541	4.163	0.067	0.337	
08-02069-Dup	Replicat	0.100	1.999	7.865	0.054	0.543	10%	2.335	4.334	0.034	0.341	1%
08-02070	0	0.100	1.021	7.149	0.028	0.275		1.213	3.880	0.020	0.195	
08-02070-Dup	Replicat	0.200	2.050	7.551	0.053	0.263	5%	2.459	3.973	0.042	0.208	6%
08-02071	0	0.200	1.049	7.165	0.027	0.133		1.235	3.772	0.019	0.094	
08-02071-Dup	Replicat	0.400	1.987	7.597	0.052	0.131	2%	2.405	3.839	0.042	0.106	12%
						2-nd Recovered						
Standard 1		2.000	2.282	3.386	0.2319	**103.7%**						
						Total OH recovery						
08-02069MS		0.100	3.895	7.621	0.3957	**87.5%**	MS	4.266	4.348	0.4334	**89.2%**	

Matrix spike recovery is calculated as follows:
Spike = 2.00 mL 0.1023 N NaOH was added to the 0.100-mL of sample for each matrix spike.
SpikeTitrant vol. (sample @ .1mL + spike) - SampleTitrant vol. (average sample only equated to .1mL) * 0.2176 N (HCl titrant) = meq. OH
meq OH / 2.00 mL added = meq OH/mL found / 0.1023 N OH added * 100 = % recovered.

Battelle, Pacific Northwest National Laboratory
PO Box 999, Richland, WA 99354 USA

Filename: 08-2059 Shimskey
Rev 0
Report date: 8/8/2008

Client: R. Shimskey
Project 52964, charge code F99189
ASR 8176, 8 Samples

Prepared by: C. Soderquist 8-8-08
Concur: T Trang-le 8/11/08

Samples processed July 2008

PNL-ALO-115, Rev. 1.1, Solubilization Of Metals From Solids Using A KOH-KNO_3 Fusion
RPG-CMC-128, Rev 0, HNO_3-HCl Acid Extraction of Liquids for Metals Analysis using a Dry-Block Heater
RPG-CMC-450 Rev 1, Gamma Energy Analysis (GEA) and Low-Energy Photon Spectroscopy (LEPS)
RPG-CMC-4001 Rev 1, Source Preparation for Gross Alpha and Gross Beta Analysis
RPG-CMC-408 Rev 2, Total Alpha and Beta Analysis
RPG-CMC-476 Rev 0, Strontium-90 Separation using Eichrom Strontium Resin
RPG-CMC-474 Rev 1, Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry
RPG-CMC-4017 Rev 0, Analysis of Environmental Water Samples for Actinides and Strontium-90
RPG-CMC-496 Rev 0, Coprecipitation Mounting of Actinides for Alpha Spectroscopy
RPG-CMC-422 Rev 2, Solutions Analysis: Alpha Spectrometry
RPG-CMC-4014 Rev 1, Uranium by Kinetic Phosphorescence Analysis

M&TE:
Gamma detectors C,D,E,G, & K (gamma emitters)
Alpha spectrometry counting system (Pu-238, Pu-239+240 analysis)
Ludlum alpha counters (gross alpha)
LB4100 proportional counter (gross beta)
Perkin Elmer TriCarb model 3100 liquid scintillation spectrometer (Sr-90)
Chem Chek Instruments model KPA-11R uranium analyzer
See the M&TE summary sheet in the file for cross references to property numbers.

Reference date February 17, 2008

Sample	Lab ID
TI624-G7-A	08-2059
TI624-G7-B	08-2060
TI624-G7-D	08-2061
TI624-G7-H	08-2062
TI624-G7-I	08-2063
TI624-G7-6	08-2074
TI624-G7-9	08-2075
TI624-G7-12	08-2076

Battelle, Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename 08-2059 Shimskey
8/8/2008

Client: R. Shimskey
ASR 8176

The Samples

These samples originated in the hot cells and arrived in the analytical lab in June 2008. The samples required analysis of metals by ICPOES, hydroxide, anions, and several radionuclides. Only the radiochemistry data is reported here; the inorganic analytes are reported separately.

Sample Preparation

The aqueous samples were digested in dilute nitric acid (procedure RPG-CMC-128) in a laboratory fume hood. The solid samples were fused with potassium hydroxide (procedure PNL-ALO-115) in a hot cell.

Quality Control Results

All of the quality control results fell well within the limits prescribed by the project.

All of the requested detection limits were met except for Eu-155 and Am-241 in the aqueous samples, where the Compton background from high Cs-137 activity raised the detection limit for Eu-155 and Am-241. The hot cell blank results are small compared to the accompanying samples. All pairs of duplicates agree closely. All of the spike recoveries fell within the limits prescribed by the project, and within expected uncertainty.

Gamma Emitters (procedure RPG-CMC-450)

Gamma emitters were measured by counting aliquots of the acid digestions and potassium hydroxide fusions. All gamma emitters that were detected were reported, except for potassium-40. Eu-152 was found in the solid samples and is included on the report, even though it was not explicitely requested by the Project. Because no sample preparation or separation is done for gamma counting, no spikes are prepared.

Gross Alpha and Gross Beta (procedures RPG-CMC-4001 and -408)

To measure gross alpha, a small volume of each sample solution (the acid digestion or fusion solution) was dried onto a steel disk and counted on a Ludlum solid scintillation alpha counter.

To measure gross beta, a small volume of each sample solution was evaporated onto a planchet and counted on a gas proportional counter . Nearly all the activity is beta, not alpha, and crosstalk corrections were not necessary. Solids loading on the counting planchets was too small to affect the data.

Battelle, Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename 08-2059 Shimskey
8/8/2008

Client: R. Shimskey
ASR 8176

All but one of the aqueous samples have too little alpha to measure accurately by gross alpha counting. The sum of Pu-239+240, Pu-238, and Am-241 is a more accurate and sensitive estimate of the gross alpha activity of these samples. (Uranium contributes only a small part of the alpha activity.) Only a small amount of the fusion solution can be evaporated onto a counting disk without compromising the accuracy from mass loading.

The gross beta activity agrees reasonably well with the sum of Cs-137, Sr-90, and Y-90.

Strontium-90 (procedures RPG-CMC-476 and -474)

Strontium was chemically separated from the acid digestion preparations, then measured by liquid scintillation.

Plutonium (procedures RPG-CMC-4017, -496, and -422)

Plutonium was separated from the sample solutions by anion exchange in hydrochloric acid, then mounted for alpha spectroscopy by coprecipitation, then measured using alpha spectrometry.

Uranium (procedures RPG-CMC-4017 and -4014)

Uranium was chemically separated from the samples by anion exchange in hydrochloric acid, then measured by kinetic phosphorescence. All of the samples have easily measurable uranium, well above the blanks.

Raw aqueous sample, not the acid digestion, was used for uranium analysis. No uranium concentration is given for the acid digestion blank because the acid digestion was not used for uranium analysis.

Battelle, Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename 08-2059 Shimskey
8/8/2008

Client: R. Shimskey
ASR 8176

Procedures: RPG-CMC-128, Sample digestion in dilute nitric acid
RPG-CMC-450, Gamma counting

M&TE: Detectors C, D ,E, G, & K
Reference date Feb 17, 2008

		Measured Activity, **µci per mL** ± 1s counting error					
Sample	Lab ID	**Co-60**	**Cs-137**	**Eu-152**	**Eu-154**	**Eu-155**	**Am-241**
TI624-G7-A	08-2059	<7.E-5	**3.05E+0 ± 4%**	<3.E-4	<2.E-4	<2.E-3	<3.E-3
	08-2059 Dup	<7.E-5	**3.07E+0 ± 4%**	<3.E-4	<2.E-4	<2.E-3	<3.E-3
	RPD		1%				
TI624-G7-B	08-2060	**6.56E-4 ± 7%**	**9.51E+0 ± 3%**	<4.E-4	< 3.E-4	< 3.E-3	< 3.E-3
TI624-G7-D	08-2061	**2.49E-4 ± 10%**	**1.17E+1 ± 4%**	<3.E-4	< 2.E-4	< 3.E-3	< 9.E-3
TI624-G7-H	08-2062	< 7.E-5	**6.81E-1 ± 3%**	<3.E-4	< 2.E-4	< 8.E-4	< 2.E-3
TI624-G7-I	08-2063	< 8.E-5	**3.02E+0 ± 3%**	<3.E-4	< 2.E-4	< 2.E-3	< 3.E-3
Acid digestion blank		< 8.E-5	< 1.E-4	<4.E-4	< 2.E-4	< 2.E-4	< 1.E-4
Requested detection limit		1.0E-2	1.0E-2	--	4.0E-4	4.0E-4	2.0E-3

Battelle, Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename 08-2059 Shimskey
8/8/2008

Procedures: PNL-ALO-115, Potassium hydroxide fusion sample preparation (in hot cell)
RPG-CMC-450, Gamma counting

M&TE: Detectors C, D ,E, G, & K
Reference date Feb 17, 2008

		Measured Activity, **µci per gram** ± 1s counting error					
Sample	Lab ID	**Co-60**	**Cs-137**	**Eu-152**	**Eu-154**	**Eu-155**	**Am-241**
TI624-G7-6	08-2074	**1.01E-1 ± 3%**	**2.25E+2 ± 4%**	**1.32E-1 ± 4%**	**3.37E+0 ± 2%**	**1.49E+0 ± 3%**	**5.49E+0 ± 5%**
	08-2074 Dup	**1.04E-1 ± 3%**	**2.30E+2 ± 4%**	**1.43E-1 ± 4%**	**3.42E+0 ± 2%**	**1.57E+0 ± 3%**	**5.70E+0 ± 5%**
	RPD	3%	2%	8%	1%	5%	4%
TI624-G7-9	08-2075	**8.28E-2 ± 3%**	**1.81E+2 ± 6%**	**1.05E-1 ± 6%**	**2.72E+0 ± 2%**	**1.12E+0 ± 5%**	**4.86E+0 ± 4%**
TI624-G7-12	08-2076	**2.05E-1 ± 4%**	**3.85E+2 ± 3%**	< 7.E-2	**6.63E+0 ± 2%**	**3.25E+0 ± 8%**	**1.03E+1 ± 6%**
Hot Cell KOH fusion blank		7.80E-3 ± 7%	3.42E-1 ± 4%	< 5.E-3	< 3.E-3	< 5.E-3	< 7.E-3
Requested detection limit		3.0E-2	6.0E-2	--	5.0E-3	8.0E-3	3.0E-3

Battelle, Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename 08-2059 Shimskey
8/8/2008

Client: R. Shimskey
ASR 8176
Reference date February 17, 2008

		Measured Activity, **µCi per mL** ± 1s total uncertainty					
Sample	Lab ID	**Gross Alpha**	**Gross Beta**	**Sr-90**	**Pu-239+240**	**Pu-238**	**Total Uranium, µg/mL**
TI624-G7-A	08-2059	< 3.E-4	**2.99E+0 ± 4%**	**1.68E-2 ± 2%**	**4.18E-5 ± 5%**	< 1.E-6	**1.29E+2 ± 4%**
	08-2059 Dup	< 3.E-4	**3.07E+0 ± 4%**	**1.68E-2 ± 2%**	**4.04E-5 ± 5%**	< 1.E-6	--
	RPD	--	3%	0.1%	3%	--	--
TI624-G7-B	08-2060	**2.04E-2 ± 2%**	**9.47E+0 ± 3%**	**2.83E-1 ± 2%**	**2.22E-2 ± 2%**	**3.21E-3 ± 3%**	**3.65E+3 ± 4%**
TI624-G7-D	08-2061	**1.73E-3 ± 9%**	**9.92E+0 ± 4%**	**2.40E-3 ± 2%**	**2.27E-3 ± 2%**	**3.09E-4 ± 3%**	**4.60E+1 ± 4%**
TI624-G7-H	08-2062	**6.07E-4 ± 18%**	**7.12E-1 ± 3%**	**1.26E-3 ± 2%**	**3.56E-4 ± 2%**	**4.74E-5 ± 4%**	**8.84E+0 ± 4%**
TI624-G7-I	08-2063	**9.05E-4 ± 14%**	**3.17E+0 ± 4%**	**2.32E-3 ± 2%**	**1.23E-3 ± 2%**	**1.65E-4 ± 2%**	**1.63E+1 ± 4%**
Acid digestion blank		< 3.E-4	1.44E-2 ± 4%	< 5.E-5	2.18E-6 ± 20%	< 1.E-6	--
Requested detection limit		4.0E-3	1.0E-3	1.0E-3	1.0E-4	1.0E-4	6.0E+1
Lab blank		< 1.E-6	< 4.E-6	< 2.E-6	< 4.E-8	< 3.E-8	7.38E-2 ± 2%
Reagent spike		97%	86%	95%	95%	--	91%
Matrix spike		88%	81%	97%	91%	--	**

[Uranium matrix spike was too small for the sample uranium]

Battelle, Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename 08-2059 Shimskey
8/8/2008

Sample	Lab ID	Measured Activity, µCi per gram ± 1s total uncertainty Gross Alpha	Gross Beta	Sr-90	Pu-239+240	Pu-238	Total Uranium, µg/g
TI624-G7-6	08-2074	**8.55E+0 ± 2%**	**1.01E+4 ± 4%**	**4.83E+3 ± 2%**	**1.99E+0 ± 2%**	**3.32E-1 ± 5%**	**1.36E+4 ± 4%**
	08-2074 Dup	**7.78E+0 ± 2%**	**8.95E+3 ± 4%**	**4.96E+3 ± 2%**	**2.14E+0 ± 2%**	**3.28E-1 ± 5%**	**1.36E+4 ± 4%**
	RPD	9%	12%	3%	7%	1%	0.1%
TI624-G7-9	08-2075	**6.32E+0 ± 2%**	**7.43E+3 ± 4%**	**3.00E+3 ± 2%**	**1.41E+0 ± 3%**	**2.90E-1 ± 7%**	**9.74E+3 ± 4%**
TI624-G7-12	08-2076	**1.45E+1 ± 2%**	**1.61E+4 ± 3%**	**8.75E+3 ± 2%**	**3.93E+0 ± 2%**	**6.73E-1 ± 4%**	**2.65E+4 ± 4%**
	Hot cell KOH fusion blank	< 7.E-3	2.34E+0 ± 4%	1.14E+0 ± 1%	6.49E-4 ± 12%	7.47E-4 ± 13%	4.08E+0 ± 2%
	Requested detection limit	1.0E-2	1.0E-2	1.0E-2	1.0E-3	1.0E-3	6.0E+1
	Lab blank	< 2.E-6	< 4.E-6	< 2.E-6	< 4.E-8	< 3.E-8	7.38E-2 ± 2%
	Reagent spike	94%	89%	95%	95%	--	91%
	Matrix spike	92%	85%	97%	91%	--	**

[Uranium matrix spike was too small for the sample uranium]

ASO/CMC - Radiochemistry M&TE 5/12/2008

ID	Number of Detectors	Property #	Model or Serial #	Location	Procedures using the M&TE	PM Contract?
Dual Alpha Beta Gas Proportional Counters						
Oxford LB4100-orange	16	WD13066	L8285-O	425	Total alpha, total beta, Sr/Y-90, Tc-99	Y
Alpha Counters						
Ludlum	10	multiple	multiple	425	Total Alpha	N
AEA (Ortec)*	24	multiple	multiple	425	AEA (total alpha, Pu, Am/Cm,Np)	N
Liquid Scintillation						
Perkin Elmer TriCarb 3100 TR	1	WD48466	3100TR	425	H-3, C-14, Ni-63, Se-79, Sr-90, Tc-99, Pu-241	Y
Gamma						
HpGe*	7	see list	see list	425	GEA with 2 Ortec Nomad portables	N
LEPS (x-rays)*	2	see list	see list	425	X-ray (Fe-55, Ni-59, Nb-93m) (1 not in use)	N
Uranium						
Chemchek	1	WC47898	KPA11	525	Uranium	N
***Spectral Analysis System**						
Canberra - VAX 3000	1	WD12890	PE42AJB	425	AEA, GEA	N
Canberra - VAX 3100	1	WC38624	KA235W0225	425	AEA, GEA (Backup VAX)	N
Dell PC	1	WD49504	N/A	425	GEA	
Dell PC	1	WD49506	N/A		AEA	
Balances						
See Balance list					Calibrated annually	

Appendix K

Group 7 CUF Concurrence Letter

Appendix K: Group 7 CUF Concurrence Letter

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

April 22, 2008

Mr. Haukur R. Hazen
Bechtel National Inc.
2435 Stevens Center Place, MSIN: H4-02
Richland WA 99352

WTP/RPP-MOA-PNNL-00216

Dear Mr. Hazen:

**Subcontract NO. 24590-QL-HC9-WA49-00001 - Project 53019 (WA#2007-019)
Request Approval for Recommendation for Feed Composition, Bench-Scale Testing, and CUF Testing for Group 7**

The purpose of this letter is to seek concurrence with the recommendation for feed composition, bench-scale testing, and CUF testing as required in Section 6.4 Item 2.0 in Test Plan TP-RPP-WTP-467, *Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes*

Recommendations for Filtration, and Caustic Leaching Test Matrix in the CUF for Group 7 Sample

This test will cover the cross flow filtration and caustic leaching test for Group 7 (TBP sludge) composite tank waste slurry, blended with tank wastes samples from 241-AY-102. Accordingly, this work addresses the determination of filtration and leaching behavior at the bench-scale using the CUF system as described in TP-RPP-WTP-467. As the test plan allows, additional material may be added to a homogenized sample group for CUF testing if the total mass of the homogenized waste sample is not large enough to process by itself. Initial characterization of the Group 7 homogenized sample estimates that there are ~ 200 grams of un-dissolved solids present -- a minimum of 300 grams are required to produced a waste slurry at 20 wt% un-dissolved solids (UDS). It is proposed that archived tank waste samples from 241-AY-102 be added to the Group 7 during processing to increase the solid level of the slurry. The AY-102 samples are similar in composition and are estimated to have ~200 grams of insoluble solids in the waste samples available. While the aluminum levels in both wastes are relatively small, the insoluble fraction of phosphate present in the Group 7 waste is high enough to justify performing a caustic leach. The proposed test sequence is summarized in the scheme shown in Figure 1.

Initial Test Matrix:

The initial filtration testing, low solids test matrix shown in Table 1, will be conducted with the Group 7 homogenized sample alone diluted to an estimated 4 wt% UDS. The inventory consists of 1.3-1.4L of the waste slurry at an un-dissolved solids concentration of 10 wt%. To dilute the waste slurry to 4 wt% UDS, a supernatant simulant will be added to give a total slurry volume of ~3.5L. The supernatant simulant will be made to mimic the composition of the ~4 M Na supernatant of Group 7 waste. While the sodium concentration of the simulant is lower than prototypic concentration of 5M, it is more desirable to use a simulant based on the composition of the supernatant that is at equilibrium already with the waste. This will avoid precipitating species from the entrained supernatant and will allow for the formulation of a stable supernatant simulant. However, because the waste is caustic deficient, the free hydroxide of the simulant supernatant will be increased to 0.3M.

Dewatering:

All dewatering and filtration testing will be conducted at 25±5°C. Dewatering parameters will be conducted at the median target of the filtration testing, which is a transmembrane pressure (TMP) of 40 psi and an axial velocity (AV) of 13 ft/s.

Dewatering will be done on the initial ~4 wt% Group 7 slurry to a target of ~10 wt% UDS. Once the waste slurry is back at its original concentration, the AY-102 archive samples (1750 ml slurry @ 3.4M Na) will be added to the slurry reservoir. The AY-102 slurry samples are estimated to have the same un-dissolved solids concentration of 10 wt% UDS, so no other adjustments to the combined slurry will be made. The combined slurry (~3.2L) will then be dewatered to ~1.4 L, or to the minimum volume possible. The target solids concentration of slurry at a final volume of 1.4 L is 22 wt% UDS.

The combined dewatered supernatant will be at a sodium concentration of approximately 3.7 M Na and a free hydroxide concentration of 0.4 M. Figure 2 provides a summary of sodium molarity during dewatering for the first five years of operating the Waste Treatment Plant. Inspection of this figure indicates that 3.7 M Na is within the range of conditions expected to be seen during the initial dewatering of slurry and bounds approximately 30% of the batches.

After dewatering the combined waste slurry, a high solids filtration test matrix, shown in Table 1, will be conducted. If the slurry is unable to be pumped adequately through the system to run the test matrix , the slurry may be diluted with dewatered permeate as required.

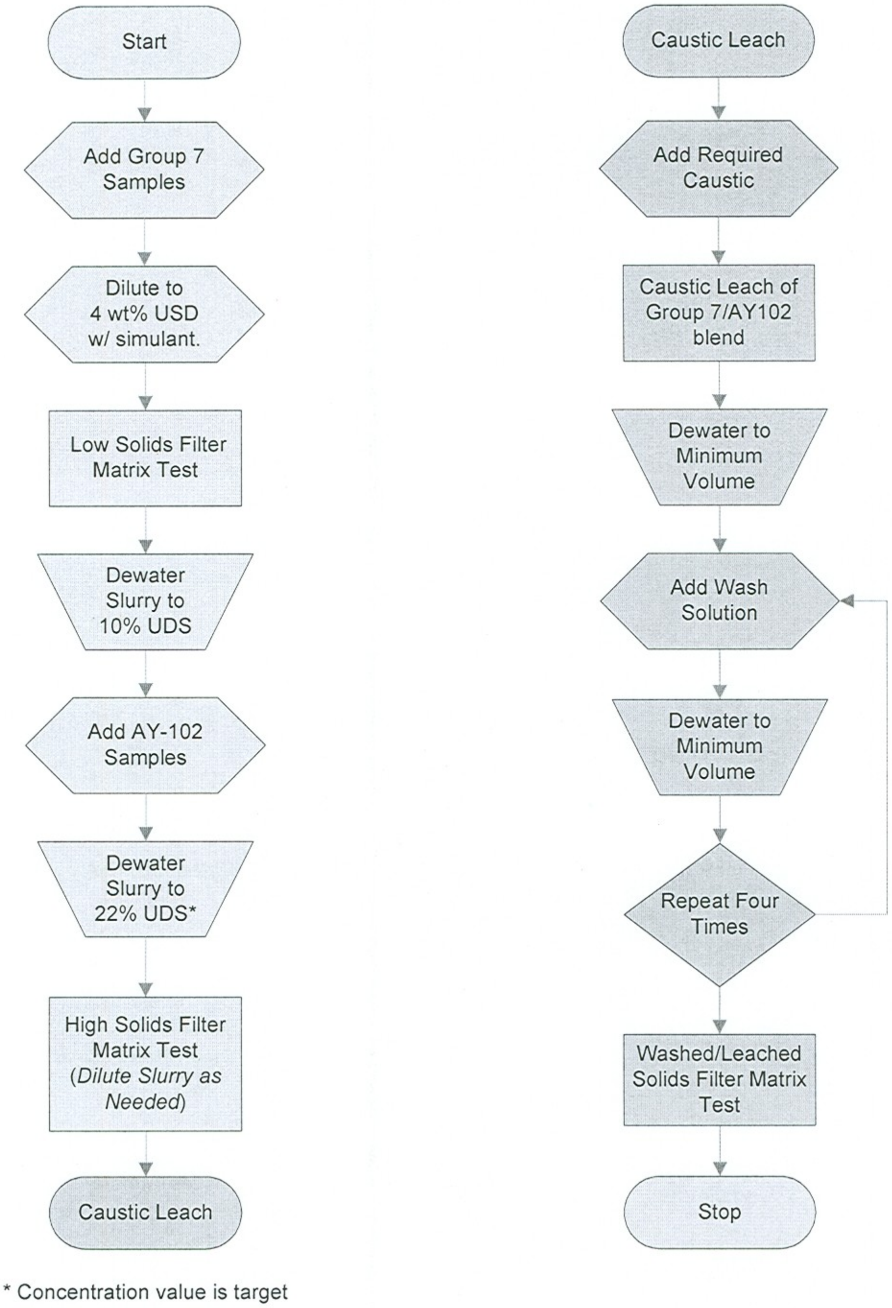

Figure 1: Proposed Test Scheme for Composite Group 7 / AY-102 CUF Test

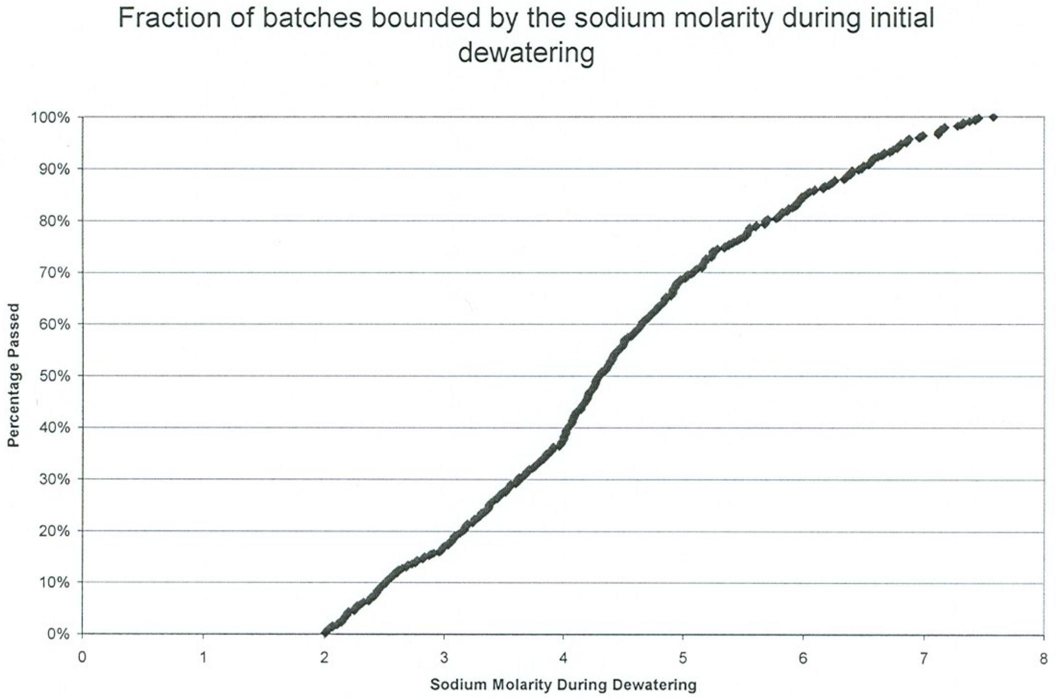

Figure 2. Projected WTP sodium molarity during initial dewatering.

Dewater Process Steps (more details provided in this section)

- First prepare the low-solids slurry by combining a supernatant simulant with the Group 7 slurry, to provide ~3.5 L of slurry at a target of ~4 wt% UDS and 4 M sodium.
- Conduct low solids filtration test matrix,

Table 1.

- Dewater to target of 10 wt% UDS or as low volume as possible to generate a dewatering data from the Group 7 waste.
- Add the archive AY-102 samples to the dewatered Group 7 waste slurry.
- Dewater to target of 22 wt% UDS or as low volume as possible to generate a detailed dewater curve.
- Conduct a high solids matrix test as shown in Table 1. (If rheology, air entrainment or temperature control does not allow operation at 22 wt%, permeate will be added back such that the test matrix could be carried out.)

Table 1. Filtration Test Matrix

Test number	Duration (hours)	Target TMP* (psi)	Target Axial Velocity* (ft/s)
1	3	40	13
2	1	30	11
3	1	30	15
4	1	50	15
5	1	50	11
6	1	40	13
7	1	40	9
8	1	40	17 (or max)
9	1	20	13
10	1	60	13
11	1	40	13

* Actual conditions may vary based upon slurry volume and rheology. All conditions may not be obtainable.

Leaching

Caustic leach conditions for the blended waste slurry are proposed below based on a slurry volume of ~1.4 L at ~22 wt% UDS, expected aluminum solid concentration, and leach factors of 100% dissolution of aluminum:

Add 1.4 L of 5.3 M NaOH (adjust as needed for Al solubility at 25°C), leach for 8 hours at 60°C, and add water as needed during the caustic leach lost by evaporation to maintain a constant volume.

The final sodium concentration is expected to be ~4.5 M. Examining Figure 3, a summary of the sodium molarity during caustic leaching for the first 5 years of WTP operation, shows that leaching at ~4.5 M sodium is at the lower end of the expected operating envelope. Because the aluminum present in the waste is relatively small (~5% aluminum in the combined solids), the required quantity of caustic to be added is lower as well. However, the main goal of the caustic leach is to dissolve the phosphate present in the Group 7 that is insoluble otherwise.

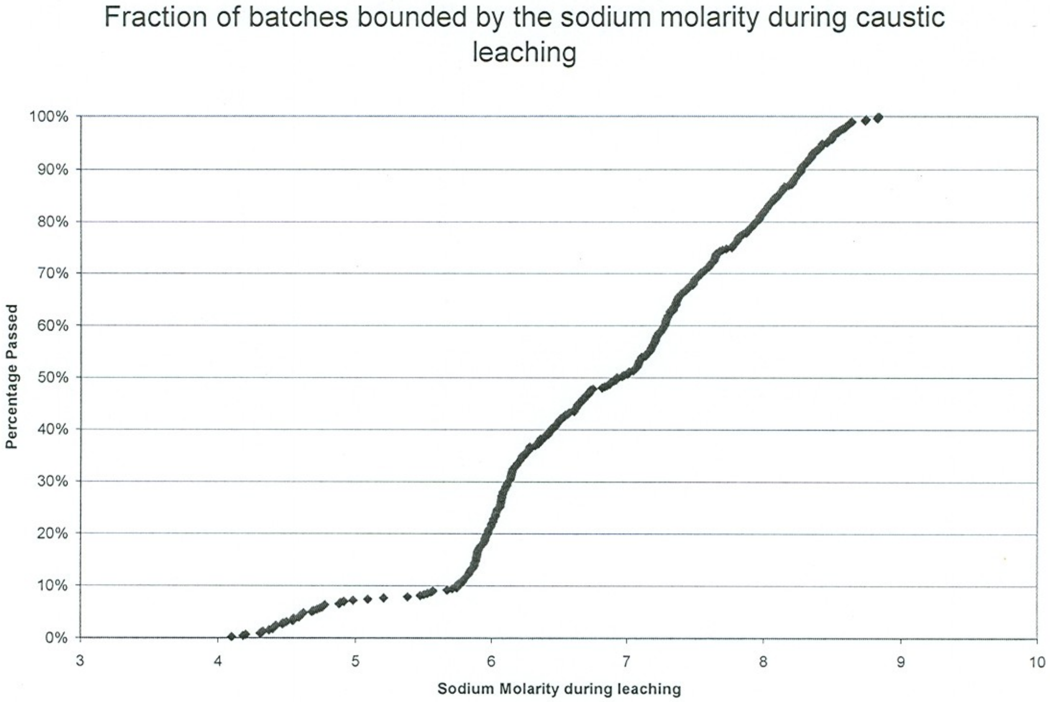

Figure 3. Projected WTP sodium molarity during caustic leaching.

Caustic Leaching Process Steps (more details provided in this section)

- Retrieve all solids from CUF and isolate in slurry feed reservoir for leaching.
- Assuming ~1.4 L of ~20 wt% UDS at 3.7 M sodium, add 1.4 L of 5.3 M NaOH. (These leaching conditions have been estimated to produce a solution saturated with Al at 25°C at the conclusion of the leaching process.)
- Based on kinetic studies of phosphate dissolution while caustic leaching, there is no need to heat the batch beyond 60°C while caustic leaching. Aluminum dissolution is not an objective for the caustic leaching of the Group 7/AY-102 waste. The process, which deviates from historic WTP baseline process conditions, is as follows:
    - Heat from 25°C to 60°C in 2.5 hours.
    - Leach for 8 h at 60 (+5/-10)°C.
    - Cool from 60°C to 25°C in 5.6 hours.

Post Caustic Leach Dewater Process Steps

- Dewater leached solids at 25°C, TMP = 40 psi, and AV = 13 ft/s.
- Dewater to a target of ~1.3 L or to minimum operating volume of CUF (~20 wt% undissolved solids assuming aluminum is all gibbsite and 100% Al dissolution).

Post Caustic Leach Washing Process Steps (if necessary)

- Four equal volume washes of the dewatered leached slurry will occur at caustic levels high enough to ensure that the solubility of Al is maintains in the leached slurry permeate and the dewatered wash solutions.
    - *Wash 1*: ~1.2 L solution of 0.5 M NaOH solution is added. Slurry is dewatered to a target of ~1.2 L or to minimum operating volume of CUF.
    - *Wash 2*: ~1.2L solution of 0.1 M NaOH solution is added. Slurry is dewatered to a target of ~1.2 L or to minimum operating volume of CUF.
    - *Wash 3*: ~1.2L solution of 0.05 M NaOH solution is added. Slurry is dewatered to a target of ~1.2 L or to minimum operating volume of CUF.
    - *Wash 4*: ~1.2L solution of 0.01 M NaOH solution is added. Slurry is dewatered to a target of ~1.2 L or to minimum operating volume of CUF.
- After the fourth rinse, perform a final filter test matrix on the washed solids, as outlined in Table 1.
- Drain slurry from CUF and retain for potential use, only dispose at the guidance of the client.
- Clean CUF and determine clean water (0.01M NaOH) flux.

Sample Plan

The sample collection and analysis plan will be implemented as defined in the test plan.

If you have any questions, please contact Reid Peterson on 376-5340.

Sincerely,

Gordon H. Beeman

Gordon H. Beeman, Manager
RPP-WTP Support Program

GHB:c^2

cc: RA Peterson (PNNL)
RW Shimskey (PNNL)
PS Sundar (BNI)
Project File/LB

From: Gilbert, Robert A (Rob) [Robert_A_Rob_Gilbert@RL.gov]
Sent: Thursday, April 03, 2008 1:34 PM
To: Barnes, Steven M; Sundar, Parameshwaran S
Cc: Peterson, Reid A
Subject: FW: Request for Approval on Group 7 Parametric Test Matrix

Steve,

ORP concurs with the Group 7 parametric test matrix. Several typos are noted in Keith's message below.

Thanks

Rob Gilbert

From: Sandroni, Keith E
Sent: Thursday, April 03, 2008 8:51 AM
To: Gilbert, Robert A (Rob)
Subject: RE: Request for Approval on Group 7 Parametric Test Matrix

Rob,

I only found minor typos in the Group 7 approval. The first paragraph of recommendations states "Group 1" when, I'm assuming, it should be group 7. Also, "volume" is misspelled in requirement 2d. I don't have any issues with the actual test matrix.

Keith

From: Gilbert, Robert A (Rob)
Sent: Wednesday, April 02, 2008 8:58 AM
To: Sandroni, Keith E
Subject: FW: Request for Approval on Group 7 Parametric Test Matrix
Importance: High

Updated matrix for review.

From: Sundar, Parameshwaran S [mailto:pssundar@bechtel.com]
Sent: Wednesday, April 02, 2008 8:55 AM
To: Gilbert, Robert A (Rob)
Cc: Barnes, Steven M; Peterson, Reid A
Subject: Request for Approval on Group 7 Parametric Test Matrix
Importance: High

ROB:

I am attaching the revised subject request for approval from PNNL for the Group 7 parametric test matrix. As you may recall we have reviewed this at yesterday's weekly meeting. The revised request incorporates the agreed to additional tests.

Please review the attached and approve, it acceptable to ORP by COB Thursday, April 3, 2008.

Regards,

SUNDAR

<<Group 7 Parametric Test Matrix Request for Approval -040208.doc>>

From: Peterson, Reid A [reid.peterson@pnl.gov]
Sent: Monday, April 28, 2008 1:27 PM
To: Sundar, Parameshwaran S
Subject: FW: Formal Concurrence Letter to BNI for Group 7 CUF Test

Attachments: Group 7 Test Concurrence Request from WTP final RAG Comments.doc
fyi

Reid

From: Gilbert, Robert A (Rob)
Sent: Monday, April 21, 2008 1:24 PM
To: Barnes, Steven M
Cc: Peterson, Reid A; Bang, Ricky
Subject: RE: Formal Concurrence Letter to BNI for Group 7 CUF Test

Steve,

ORP concurs with the subject Group 7 CUF test proposal with one change as marked in the attached file. The change does not alter the test but corrects misstatements of the test parameter basis.

Thanks

Rob Gilbert

From: Barnes, Steven M [mailto:smbarnes@bechtel.com]
Sent: Thursday, April 17, 2008 9:25 AM
To: Gilbert, Robert A (Rob)
Cc: Peterson, Reid A
Subject: FW: Formal Concurrence Letter to BNI for Group 7 CUF Test

Rob,

Please provide any comments you have on the specific tests to be performed with group 7 wastes as we have discussed in our weekly meetings.

Thank you Steve

From: Peterson, Reid A [mailto:reid.peterson@pnl.gov]
Sent: Wednesday, April 16, 2008 12:58 PM
To: Sundar, Parameshwaran S
Cc: Barnes, Steven M
Subject: FW: Formal Concurrence Letter to BNI for Group 7 CUF Test

Here is the Group 7 concurrence letter.

Reid

From: Shimskey, Rick W
Sent: Wednesday, April 16, 2008 12:56 PM

To: Charron, Chrissy E
Cc: Peterson, Reid A
Subject: Formal Concurrence Letter to BNI for Group 7 CUF Test

Chrissy,

Please format the attached word document into a formal concurrence letter to BNI.

Subcontract NO. 24590 QL HC9 WA49-00001 - Project 53019 (WA#2007-019)

Thanks,
Rick

<<Group 7 Test Concurrence Request from WTP.final.doc>>

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	R. A. Peterson	P7-22
	R. L. Russell	K6-24
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