PNNL-18048
WTP-RPT-181, Rev 0

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

Filtration and Leach Testing for PUREX Cladding Sludge and REDOX Cladding Sludge Actual Waste Sample Composites

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March 2009

Pacific Northwest
NATIONAL LABORATORY

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Pacific Northwest National Laboratory
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 Plan 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, Manager
WTP R&T Support Project

3/2/09
Date

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Acronyms and Abbreviations

ASO	Analytical Service Operations
ASR	Analytical Services Request
AV	axial velocity
BET	Brunauer, Emmett, and Teller (a method for measuring surface areas)
BNI	Bechtel National, Inc.
CWP	Cladding Waste, PUREX
CWR	Cladding Waste, REDOX
CUF	cross-flow ultrafiltration testing system
DACS	data-acquisition collection system
DI	deionized (water)
DOE	U.S. Department of Energy
EDS	Energy Dispersive Spectroscopy
EFRT	External Flowsheet Review Team
fps	feet per second
GEA	gamma energy analysis
GPM	gallons per minute
HDPE	high-density polyethylene
HLW	high-level waste
IC	ion chromatography
ICP	inductively coupled plasma
KOH	potassium hydroxide
KPA	kinetic phosphorescence analysis
LAW	low-activity waste
LRB	laboratory record book
MDL	minimum detection limit
M&TE	measuring and test equipment
OES	optical emission spectroscopy
ORP	Office of River Protection
PSD	particle-size distribution
psid	pounds per square inch differential
psig	pounds per square inch gauge
PNNL	Pacific Northwest National Laboratory
PTF	Pretreatment Facility
PUREX	Plutonium-uranium extraction
QAM	Quality Assurance Manual
QARD	Quality Assurance Requirements and Descriptions

REDOX	reduction-oxidation
RPL	Radiochemical Processing Laboratory
RPP-WTP	River Protection Project-Waste Treatment Plant Support Program
R&T	Research and Technology
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TMP	transmembrane pressure
TRU	transuranic
UDS	undissolved solids
UFP1	Ultrafiltration Feed Process Vessel 1
UFP2	Ultrafiltration Feed Process Vessel 2
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.[1] The test program was subdivided into logical increments. The bulk water-insoluble solid wastes that are anticipated to be delivered to the Hanford Waste Treatment and Immobilization Plant (WTP) were identified according to type such that the actual waste testing could be targeted to the relevant categories. Under test plan TP-RPP-WTP-467 (Fiskum 2007), eight broad waste groupings were defined. Samples available from the 222S archive were identified and obtained for testing. Under this test plan, a waste testing program was implemented that included:

- Homogenizing the archive samples by group as defined in the test plan.
- Characterizing the homogenized sample groups.
- Performing parametric leaching testing on each group for compounds of interest.
- Performing bench-top filtration/leaching tests in the hot cell for each group to simulate filtration and leaching activities if they occurred in the UFP2 vessel of the WTP Pretreatment Facility.

This report focuses on a filtration/leaching test performed using two of the eight waste composite samples. The sample groups examined in this report were the plutonium-uranium extraction (PUREX) cladding waste sludge (Group 3, or CWP) and reduction-oxidation (REDOX) cladding waste sludge (Group 4, or CWR). Both the Group 3 and 4 waste composites were anticipated to be high in gibbsite, thus requiring caustic leaching. PNNL-18054 (WTP-RPT-167) (Snow et al. 2008) describes the homogenization, characterization, and parametric leaching activities before benchtop filtration/leaching testing of these two waste groups. Characterization and initial parametric data in that report were used to plan a single filtration/leaching test using a blend of both wastes.

Th test focused on filtration testing of the waste and caustic leaching for aluminum, in the form of gibbsite, and its impact on filtration. The initial sample was diluted with a liquid simulant to simulate the receiving concentration of retrieved tank waste into the UFP2 vessel (< 10 wt% undissolved solids). Filtration testing was performed on the dilute waste sample and dewatered to a higher solids concentration. Filtration testing was then performed on the concentrated slurry. Afterwards, the slurry was caustic leached to remove aluminum present in the undissolved solid present in the waste. The leach was planned to simulate leaching conditions in the UFP2 vessel. During the leach, slurry supernate samples were collected to measure the dissolution rate of aluminum in the waste. After the slurry cooled down from the elevated leach temperature, the leach liquor was dewatered from the solids. The remaining slurry was rinsed and dewatered with caustic solutions to remove a majority of the dissolved aluminum from the leached slurry. The concentration of sodium hydroxide in the rinse solutions was high enough to maintain the solubility of the aluminum in the dewatered rinse solutions after dilution of the slurry supernate. Filtration tests were performed on the final slurry to compare to filtration performance before and after caustic leaching.

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[1] Barnes SM and R Voke. 2006. Issue Response Plan for Implementation of External Flowsheet Review Team (EFRT) Recommendations - M12: Undemonstrated Leaching Process. 24590 WTP-PL-ENG-06-0024, Rev. 0, Bechtel National Inc., Richland, Washington.

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

Test Objective	Objective Met? (Y/N)	Discussion
Determine the physical and chemical characteristics (summarized in Section 6.2.2 of the test plan) relevant to leaching and ultrafiltration behaviors of actual waste samples required to validate simulants.	Y	Initial characterization of the Group 3 and 4 samples was summarized in WTP-RT-167 and referenced as needed in this report. Characterization of the blended composite tested in this report was performed at various stages throughout the test.
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	Initial parametric testing of Group 3 and Group 4 for Al dissolution as gibbsite is summarized in WTP-RPT-167. Batch caustic leaching of a blend of both Group 3and 4 wastes was performed during the filtration/leaching test described in this report.
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.	Y	Initial parametric testing of REDOX sludge waste (Group 5) for Al dissolution as boehmite is summarized in PNNL-17368 (WTP-RPT-157) (Fiskum et al. 2008). Batch leaching of Group 5 for Al dissolution during two filtration/leaching tests was summarized in PNNL-17965 (WTP-RPT-172) (Shimskey et al. 2009). One of the tests leached the Group 5 in combination with S-Saltcake waste (Group 6).

Table S.1. (Cont'd)

Test Objective	Objective Met? (Y/N)	Discussion
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 NaMnO4 dosage will be predetermined for the oxidation of the chromium in the waste solids.)	Y	Initial parametric testing using S-Saltcake waste (Group 6) for Cr dissolution is summarized in WTP-RPT-157. Subsequent parametric testing using Bismuth Phosphate Saltcake waste (Group 2) for Cr was also performed as described in PNNL-17992 (WTP-RPT-166)(Lumetta et al. 2008). Batch leaching of Cr occurred during the filtration testing described in reports WTP-RPT-172 and WTP-RPT-166.
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	Initial parametric testing of the Bismuth Phosphate Sludge (Group 1) and Bismuth Phosphate Saltcake (Group 2) for phosphate dissolution by caustic leaching is summarized in WTP-RPT-166. Batch leaching of a blend of the Group 1 and 2 wastes was performed during a bench scale filtration/leaching test. The leaching results of this test are also summarized in WPT-RPT-166.
Determine 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/N	Ultrafiltration flux was determined using Group 3 and Group 4 wastes over a range of solids concentrations during waste feed dewatering, and at the maximum concentration achievable in the test equipment during post-caustic leach dewatering and washing. The quantity of undissolved solids (UDS) solids available for test was limited to the UDS mass of the samples available for the Group 3 and Group 4 wastes. To increase the UDS slurry, the Group 3 and Group 4 slurry samples were combined to obtain a UDS mass high enough to approach a final UDS concentration of 20 wt%. Filter testing of the blended slurry was performed at 10 wt%. This slurry was latered dewatered to a UDS concentration of 19 wt%. However, suspension of UDS solids were an issue during testing, requiring the overhead mixer in the slurry reservoir vessel to operate at high speeds. This resulted in a vortex to form in the vessel at lower slurry volumes which allowed the circulation pump to suck air into the chamber and cavitate. To improve pumping efficiency to achieve pressure and axial velocities for filter tests, the slurry volume was increased by the addition of filtered supernate. However, this resulted in decreasing the UDS concentration to 14 wt%, limiting the range of UDS concentrations tested.

Table S.1. (Cont'd)

Test Objective	Objective Met? (Y/N)	Discussion
		The solids concentrations during the post-caustic leach dewatering and the post-caustic leach wash were only 2.9 wt% UDS and 2 wt% UDS respectively. Because characterization results of both the Group 3 and Group 4 showed a majority of material to be gibbsite which would likely all dissolve, the final UDS concentrations were expected. Filter testing was performed prior to washing to provide filter data at a low UDS concentration (< 5wt%) with a high sodium concentration (7.8 M), However, the quantity of solids in the slurry after leaching was not significant enough to evaluate UDS concentration impacts for dewatering operations that occurred afterwords. Variables examined were: transmembrane pressure axial velocity undissolved solids concentration (prior to leaching) differences due to changes in the slurry during leaching and rinsing of waste solids.
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	Initial characterization of the material in both the Group 3 and 4 composite waste samples is summarized in WTP-RPT-167. Additional crystal imaging was performed on washed leached material resulting from the filtration/leaching test described in this report.

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

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
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 (J. G. Lumetta and R. T. Hallen, WTP-RPT-151, *Review of Caustic Leaching Testing With Hanford Tank Waste Sludges*), which addressed this success criterion, was delivered to WTP on 1/24/2007.
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.	All physical and chemical characterization testing as defined in the test plan was completed and summarized in project report WTP-RPT-167 for the Group 3, and Group 4 composites.
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 results are provided.	Initial parametric testing of the Group 3 and Group 4 waste for Al dissolution as gibbsite is summarized in WTP-RPT-167[9]. A single caustic leach test was performed during the filtration/leaching test of the Group 3/4 waste slurry. Al conversion and kinetic data for this single test are summarized in this report.
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.	Parametric testing of the Group 5 waste for Al dissolution as boehmite from caustic leaching is summarized in WTP-RPT-157. Caustic leaching testing of Group 5 material, blended with Group 6, is summarized in WTP-RPT-172 as well.
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.	Parametric testing of the Group 6 and Group 2 waste for Cr dissolution is summarized in WTP-RPT-157 and WTP-RPT-166.
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.	Phosphate dissolution was examined as an aspect of the caustic leaching by parametric testing of the Group 1 and Group 2 filtration/leaching test summarized in WTP-RPT-166.

Table S.2. (Cont'd)

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
The ultrafiltration flux before and after caustic and, as applicable, oxidative leaching (re-concentration, if sufficient solids are available) over the operating range of solids concentrations with the actual waste samples at 25°C is defined when the available sample size is adequate for the testing.	The following variables were examined for combined Group 3/Group 4 waste slurry where the focus was measuring the filter flux before and after leaching at 25°C: transmembrane pressure axial velocity undissolved solid concentration differences due to changes in the slurry during leaching and rinses of waste solids. The results of this testing are summarized in Section 3.
The primary mineral forms present for Al, Cr, and P are determined, and a qualitative correlation of the dissolution behavior of these waste elements to the mineral forms is identified.	Initial characterization of the material in both the Group 3 and 4 composite waste samples is summarized in WTP-RPT-167. Additional crystal imaging was performed on leached material resulting from the Group 3/4 filtration/leaching test. Results are summarized in this report.

Quality Requirements

Pacific Northwest National Laboratory (PNNL) implements a Quality Assurance Program that is based on the requirements defined in the U.S. Department of Energy (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.

Pacific Northwest National Laboratory implemented the River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) quality requirements by performing work in accordance with the 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 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 TP-RPP-WTP-467. It includes 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.

Research and Technology Test Conditions

The Research and Technology (R&T) test conditions, as defined in the Test Specification[1], are summarized in Table S.3.

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. Two of the eight waste groupings identified in resolution to Issue M4 were tested: Group 3, PUREX Cladding Waste Sludge, and Group 4, REDOX Cladding Waste Sludge.
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), 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) and on the slurry as a whole.
3) Actual determinations of waste leach kinetics will be carried out in well-mixed conditions. A test matrix will be forwarded to the R&T M12 Issue manager for concurrence before testing. Residual leached and washed solids will be characterized.	Yes. Test matrices for the Group 3 and Group 4 for caustic leaching of gibbsite present were forwarded to and approved by the R&T M12 Issue Manager. Conditions for the batch caustic leach for filtration/leaching test described in this report were also forwarded for approval as well.
4) Testing for filtration behavior will be performed.	Yes. Single leaching/filtration test was performed using both the Group 3 and Group 4 material. Filtration behavior before and after caustic leaching was examined.

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[1] Sundar PS. 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, Bechtel National, Inc., Richland, Washington.

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 4 supernate fraction was prepared and used to dilute the feed to allow testing at lower solids concentrations.

Discrepancies and Follow-on Tests

The testing reported here includes a test discrepancy, which is described in Table S.4.

Table S.4. Test Discrepancies Listed and Described

Test Discrepancies	Description
Low-solids filtration test occurred at a higher concentration then planned due to attempts to clear a solid plug in the circulation line of the filtration/leaching apparatus.	The settling rate of the Group 3 and Group 4 waste composite were very rapid, causing a plug in the suction line in the pump to form during homogenization activities. To unplug the line, air was pulsed backwards through the pump to loosen the plug. However, this caused supernate from the slurry reservoir to enter an overflow container attached to the reservoir. Once the line was unplugged and the circulation pump was started, the initial filtration test was initiated. It was not until the test was completed and dewatering testing was to begin that the overflow container was found to have captured close to a liter of slurry supernate. While the undissolved concentration of the slurry during the matrix test was higher than expected, this appeared not to have a significant impact.

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 Waste Treatment and Immobilization Plant (WTP) pretreatment process development and demonstration. The tests reported here were conducted according to Pacific Northwest Laboratory (PNNL) Test Plan TP-RPP-WTP-467 (Fiskum 2007) written in response to Bechtel National, Incorporated (BNI), Test Specification 24590-PTF-TSP-RT-06-003 Rev. 1.[1] This report focuses on filtration and chemical leaching testing performed using two composite waste samples representing uranium-plutonium extraction (PUREX) cladding waste sludge and reduction-oxidation (REDOX) cladding waste sludge. Filtration testing was performed on the dilute waste sample and dewatered to a higher solids concentration. Filtration testing was then performed on the concentrated slurry. Afterwards, the slurry was caustic leached to remove aluminum present in the undissolved solid present in the waste. The leach was planned to simulate leaching conditions in the UFP2 vessel.

1.1 Tank Waste Pretreatment Operations at the WTP

Figure 1.1 is 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 BNI 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 is based on aluminum dissolution results from earlier small, bench-scale, caustic leaching tests that were supplied to BNI by the DOE's Office of River Protection (ORP). 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). However, only a limited number of small bench-scale oxidative leaching tests using two selected actual waste tank samples from tanks 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). 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.

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[1] Sundar PS. 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, Bechtel National, Inc., Richland, Washington.

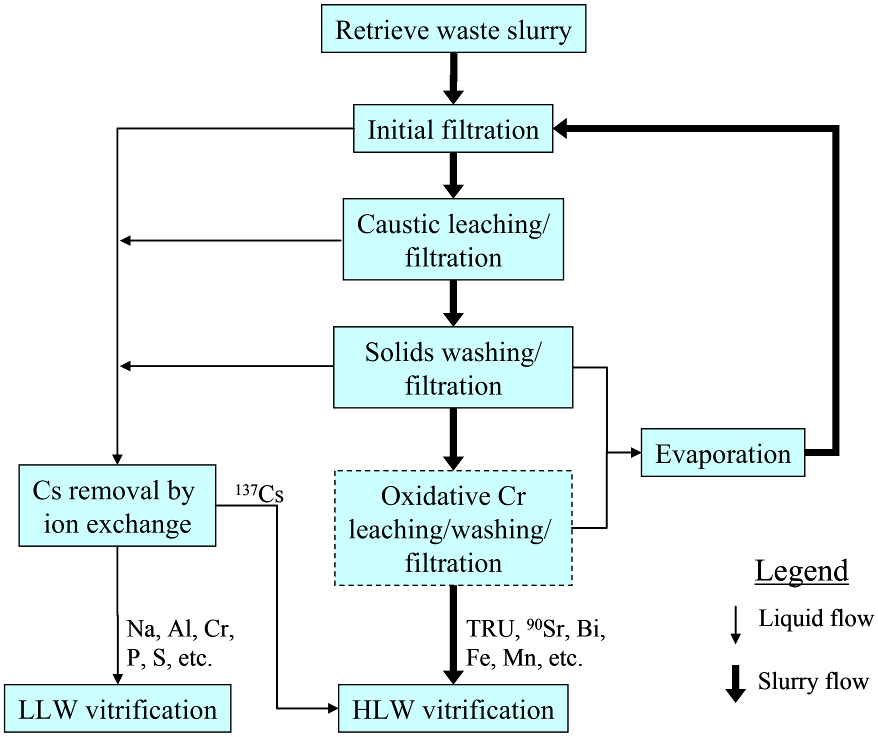

Figure 1.1. Schematic Representation of the Key Processes to be Performed in the PTF
Note: For illustrative purposes only; it is not meant to be a comprehensive view of the functions performed within the WTP.

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 [EFRT]) was assembled by BNI in October 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[1] including:

- Issue M4: The WTP has not demonstrated that its design is sufficiently flexible to reliably process all of the Hanford tank farm waste 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.

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[1] Lucas L. 2006. 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. 24590-WTP-PL-ENG-06-0008, Rev 0., Bechtel National, Inc., Richland, Washington.
WTP. 2006. Comprehensive Review of the Hanford Waste Treatment Plant Flowsheet and Throughput - Assessment Conducted by an Independent Team of External Experts. CCN 132846, 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, District of Columbia.

- 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 EFRT M12 issue response plan.[1] 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 approximately 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 waste. These waste groupings were the basis for selecting actual waste 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 approximately 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 provides a summary of the calculated water-insoluble quantities of each component for each major waste group studied. Table 1.2 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.

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[1] Barnes and Voke

Table 1.1. Water-Insoluble Component Mass 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
Units of mass in table are in metric tons.							

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

Bechtel National, Inc. 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.[1] 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 for 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 Groups 3 and 4

The Group 3 and Group 4 composite waste groups were homogenized from archive samples and characterized as described in PNNL-18054 (WTP-RPT-167), "Characterization and Leach Testing for PUREX Cladding Waste Sludge (Group 3) and REDOX Cladding Waste Sludge (Group 4) Actual Waste Sample Composites (Snow et al. 2009)." Insoluble aluminum found in these tank waste samples were largely composed of gibbsite, with additional minor phases that include, but are not limited to, sodium aluminosilicate and cancrinite. To understand the difference between boehmite and gibbsite dissolution, parametric leaching tests were performed on both the Group 3 and Group 4 waste composites once characterization was completed. The caustic leaching behavior of both Group 3 and Group 4 with specific reference to gibbsite leaching behavior as functions of time, temperature, and hydroxide concentration are provided in report WTP-RPT-167 as well.

The subject of this report is focused on the subsequent filtration/leaching test that occurred using the remaining inventory of the Group 3 and 4 waste composites after the activities described in WTP-RPT-167. The waste type definition, sample identification, and sample conditions are discussed throughout the report. Filtration of the composite wastes was examined at different aspects of the pre-treatment process (waste dewatering, caustic leaching, and washing) and how changes in the waste slurry (e.g., rheology) have impacts on the process. The physical, chemical, radioisotope, and crystal morphology characterization in the waste after leach processing are discussed and compared to previous testing. Filtration behavior is examined throughout the testing.

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[1] Lucas

2.0 Experimental Methods and Analyses

This section describes the experimental equipment and analyses used to perform the filtration and leaching tests on the Group 5 and Group 6/5 composite waste samples.

2.1 Filtration/Leaching Apparatus

The testing apparatus was a bench top system mounted on a skid that allowed up to 4 liters of a waste solution to be circulated through a tubular filter. This apparatus can measure filter feed flow rates, filtrate flow rates, system pressures, and temperatures simultaneously. The testing apparatus used a heat exchanger on the main flow loop to cool the feed solution during filtration operations and had a heater on the main holding tank to perform leaching at elevated temperatures.

2.1.1 Cell Unit Filter

The WTP PTF plans to use cross-flow ultrafiltration to separate the LAW liquid streams from the HLW slurry streams. 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 were supplied by the Mott Corporation[1], using the same specifications[2] for the filters being purchased for the WTP PTF. The filters are made of 316 stainless steel and have a nominal filter pore diameter of 0.1μm. The dimensions of the filter element used in this test are shown in Figure 2.1. These dimensions produce 0.26 ft^2 of filter surface area.

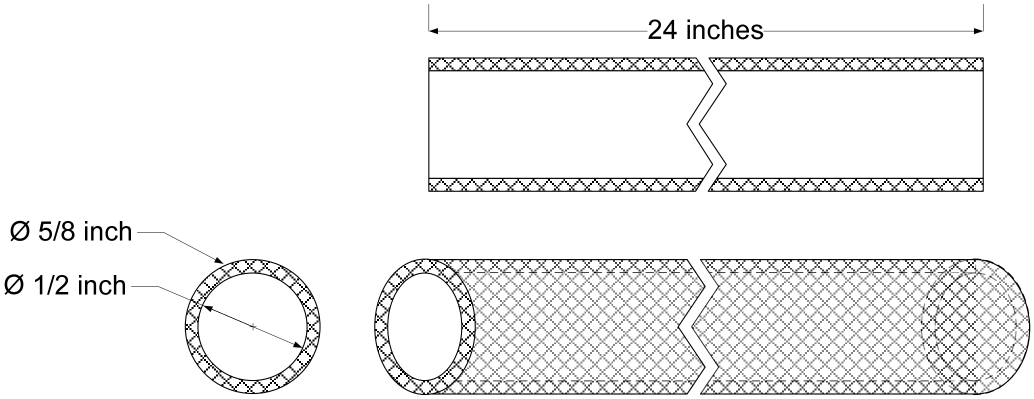

Figure 2.1. Filter Element Diagrams

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[1] Mott Corporation, 84 Spring Lane, Farmington, CT 06032.
[2] Specification WTP-070110, written by JGH Geeting, for PNNL Purchase Order 38825, February 2, 2007.

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[1] VCO®) were also placed on the inlet and outlet filter feed tube connections for easy installation on the filtration/leaching skid. Figure 2.2 and Figure 2.3 show the filter assembly.

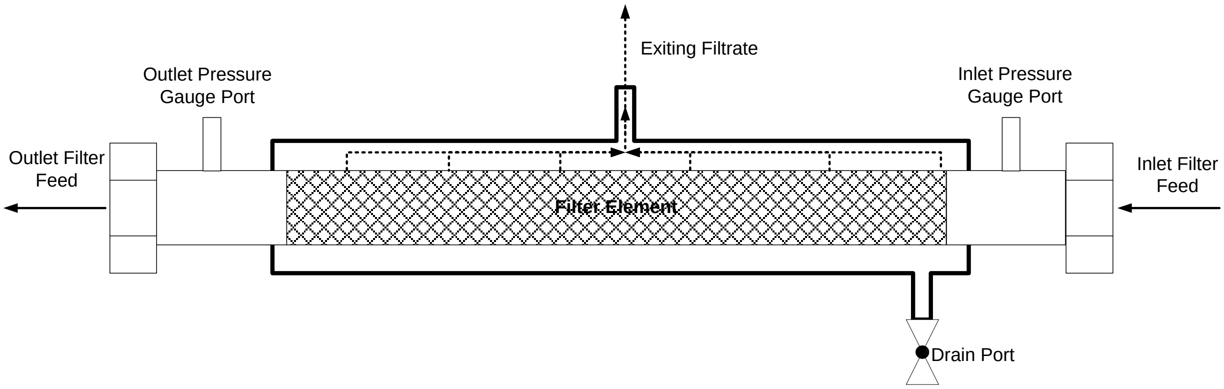

Figure 2.2. Filter Assembly Sketch (*Not to Scale*)

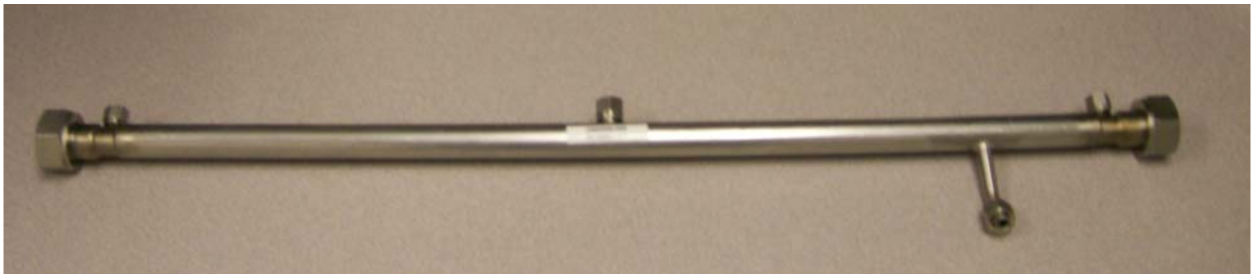

Figure 2.3. Filter Assembly

2.1.2 Cross-flow Ultrafiltration/Leaching Apparatus

The filter described in the section above was installed in a bench top testing apparatus that circulated the test waste slurries through the inside of the filter and diverted the filter permeate to a collection bottle or recycled it back into the slurry reservoir. Figure 2.4 shows a piping diagram of the testing apparatus. Figure 2.5 and Figure 2.6 are photographs of the system after assembly and installation into a hot cell in the Shield Analytical Laboratory where the testing was conducted. The testing apparatus was commonly referred to as the cross-flow, ultrafiltration testing apparatus (CUF).

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[1] Swagelok Company, 31400 Aurora Road, Solon, Ohio 44139

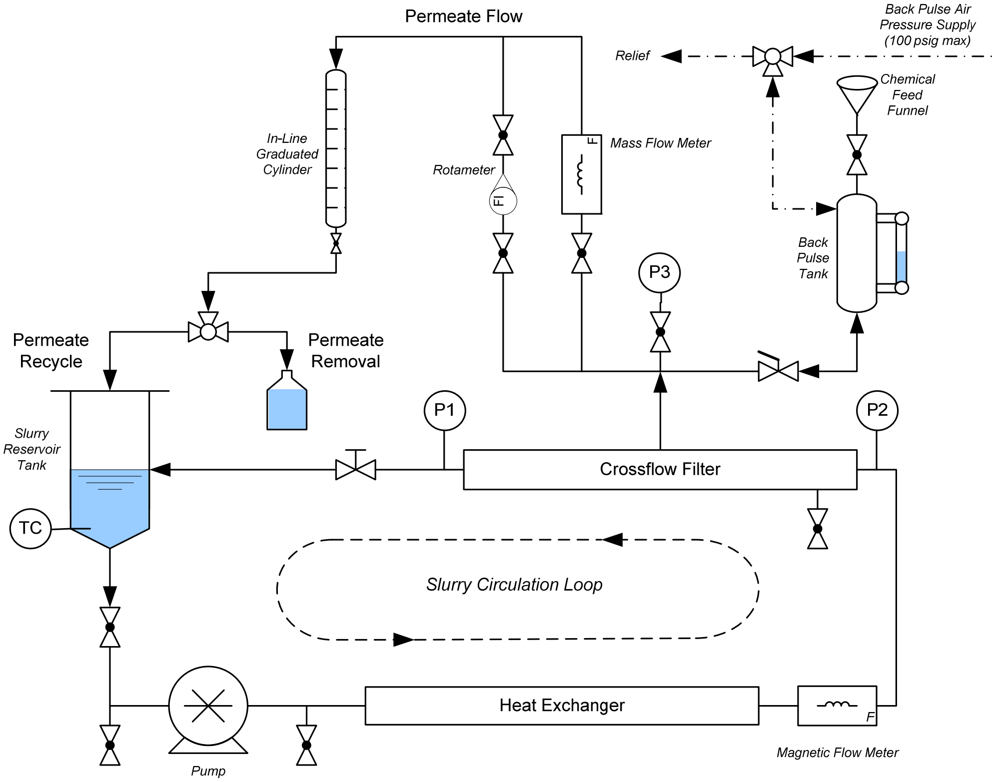

Figure 2.4. CUF Testing Apparatus Piping Diagram

Figure 2.5. CUF Testing Apparatus before Hot Cell Installation

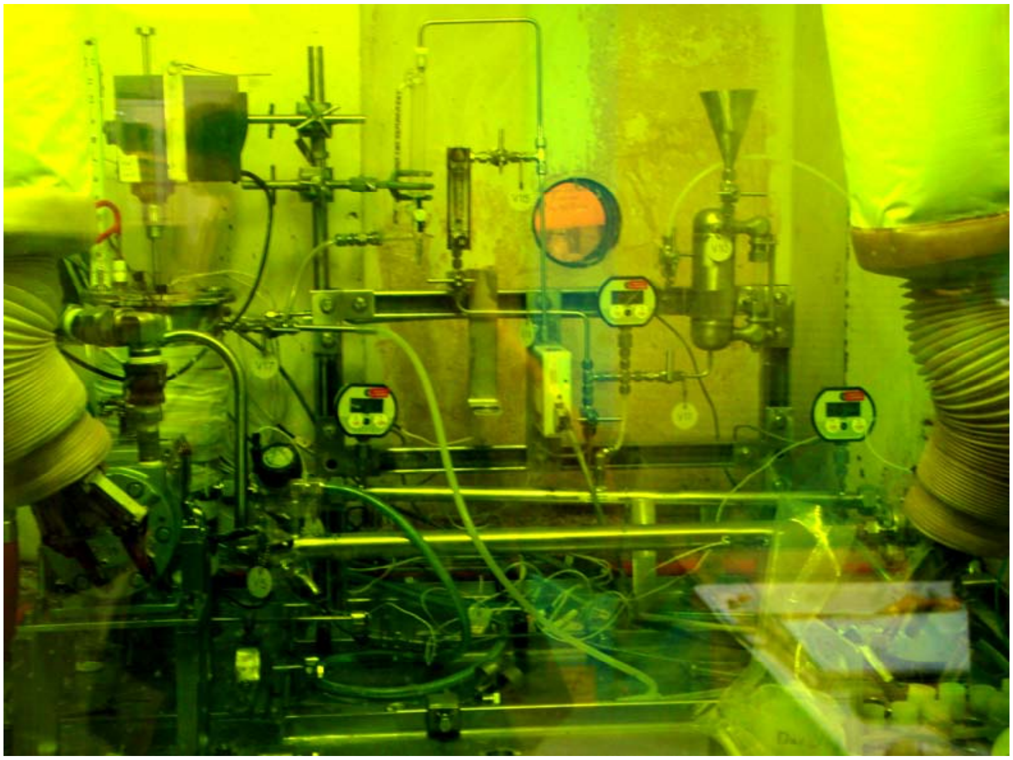

Figure 2.6. Testing Apparatus Installed in Shielded Analytical Laboratory Cell

The CUF 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. The filter element and heat exchanger were installed on a continuous slope (1/8" incline for every 12") to allow the slurry to be drained out near the discharge of the pump.

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.

2.1.3 Instrumentation and Data Acquisition System

Because the system was operated in a hot cell, the design goals of the testing apparatus were to minimize the quantity of manual measurements of the process 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[1]. This system relayed the analog data to a LabView data collection program operating on a desktop computer system using Windows XP, 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 program was verified by Software Test Plan RPP-WTP-QA-010 and all reportable data was measured on calibrated instrumentation, including the external DACS board. Figure 2.7 shows a diagram of the electronic sensors attached to the DACS, and Figure 2.8 displays the screen windows from the data collection program.

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[1] National Instruments Corporation, 11500 N Mopac Expwy, Austin, TX 78759-3504

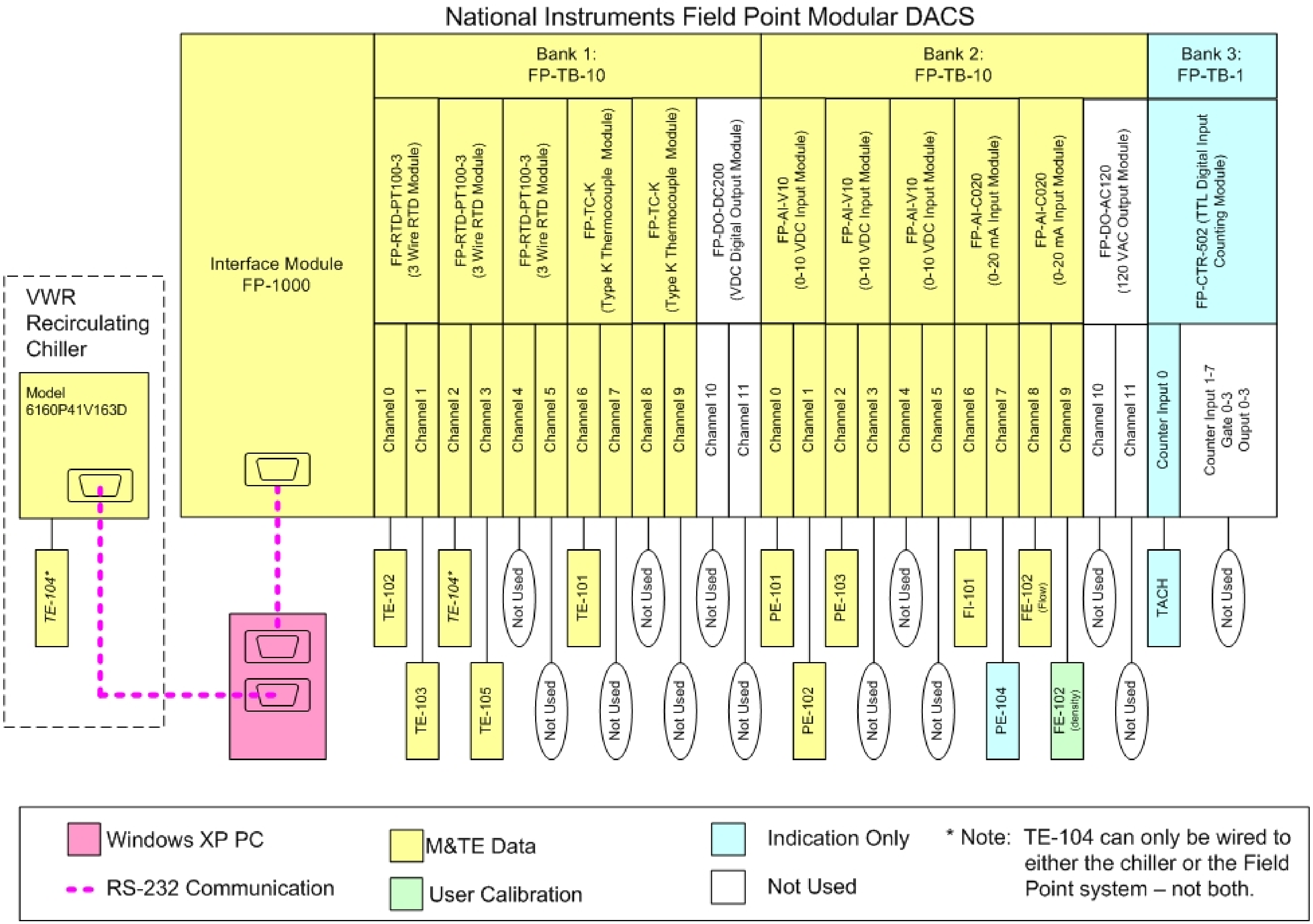

Figure 2.7. Diagram of DACS System

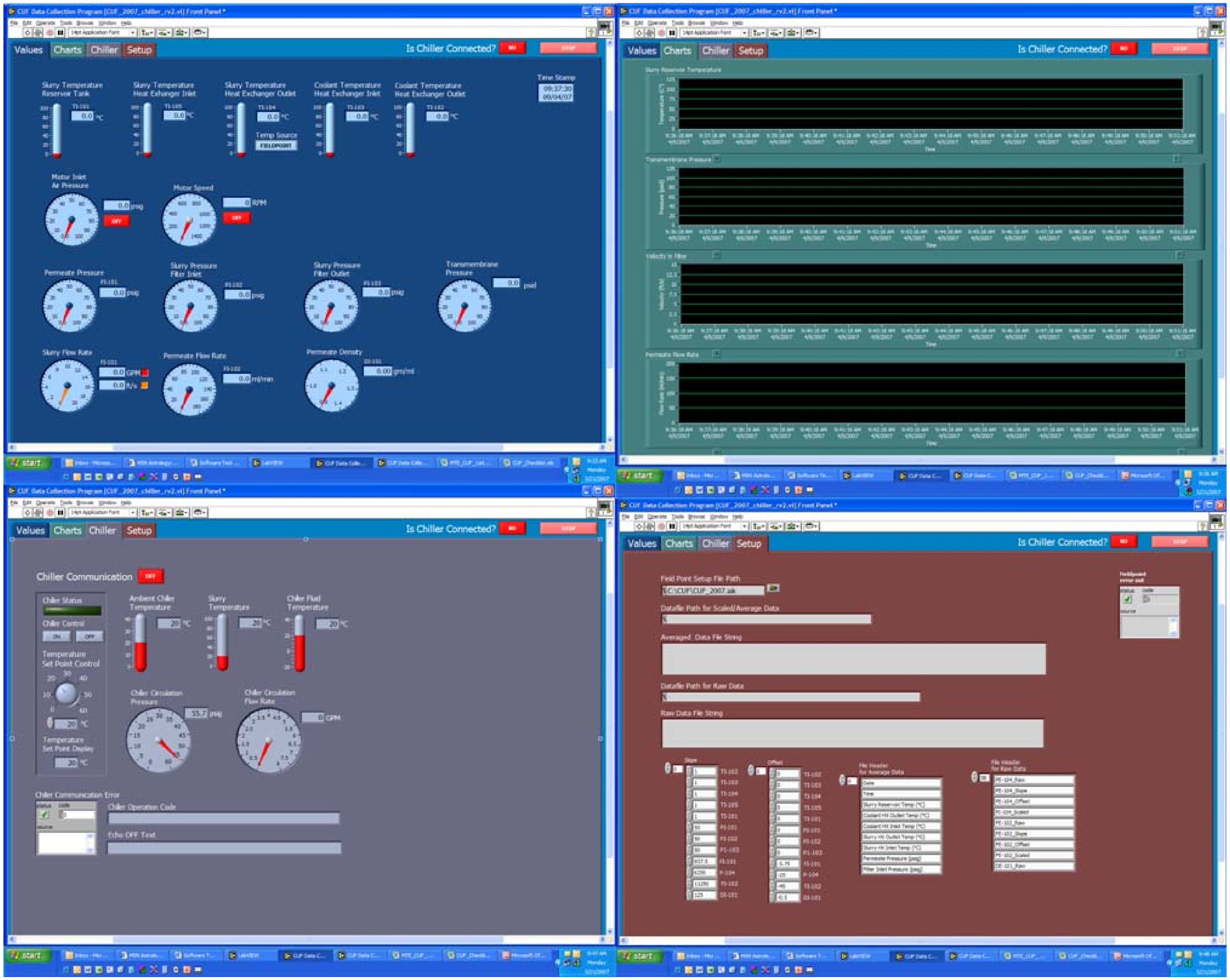

Figure 2.8. Digital Images of DACS Display Windows

2.1.4 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. 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 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, 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 inch 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 placed into a 5-mL syringe with the plunger removed and a 0.45 μm filter installed on the discharge. Once the slurry sample was in the syringe, the plunger was replaced. Pressure was applied to the plunger to force permeate through the filter on the syringe tip into a 20 mL sample vial. Figure 2.9 is a picture of a syringe, with a filter installed on, used for this operation.

Figure 2.9. Syringe with 0.45 μm Filter Installed

2.1.5 Baseline Testing of Filter

The CUF slurry and permeate piping was initially cleaned with a laboratory detergent (Alconox[1] at 1:100 dilution) to remove cutting oils and soils from the fabrication process of the testing equipment. Afterwards, the system was rinsed with deionized (DI) water several times until the rinse solution appeared clear. The filter flux was then measured with a solution of 0.01 M NaOH to verify the cleanliness of the filter, called the clean water flux. Testing was performed at 10, 15, and 20 TMP at an axial velocity of 11 feet per second (fps). 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 match a 0.35M SrCO3 slurry used in 2002 for baseline testing of a similar Mott filter, as described in WPT-RPT-043, “Filtration, Washing, and Caustic Leaching of Hanford Tank AZ-101 sludge (Geeting et al. 2002).” The prepared slurry was placed into the CUF and operated with the permeate recycling back into the slurry reservoir. Filtration tests were performed at 10, 20, and 30 TMP using an axial velocity of 11 fps. A single back pulse was performed between each test condition. Afterwards, the slurry was removed and then rinsed out with approximately 10 liters of DI water. After the system was rinsed, the clean water flux was measured again, using a solution of 0.01M NaOH, to verify that the filter was clean before testing with HLW slurries. The same filtration test conditions used in the previous clean water flux tests were used again.

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[1] Alconox, Inc., 30 Glenn Street, Suite 309, White Plains, New York 10603

The results of the baseline filter flux testing are shown in Figure 2.10, which correlate well with flux data measured in WTP-RPT-043, Section 2.3. The measured decrease at the start and end of each test condition indicate that some level of fine particulates were present in the CUF piping that impact the filter flux over time. However, the final clean water flux for the filter was demonstrated to be quite higher than the predicted flux for the waste slurries to be tested (e.g., 0.04 gpm/ft^2 for dewatering operations).

Permeate from filtration of the strontium carbonate slurry showed no solids present. The density of filter permeate was measured at 1.12 g/mL by the mass flow meter. A sample of filter permeate was taken, and its density was measured as 1.11 g/mL using a calibrated balance and a 50-mL volumetric flask. While the density could be measured, the volumetric flow of permeate was beyond the range of the mass flow meter for all three tests. After a density check, permeate flow was diverted through the CUF rotometer. For the $SrCO_3$ flux measurements, the flow was slow enough to verify the flow with the in-line volumetric cylinder to measure the permeate flow.

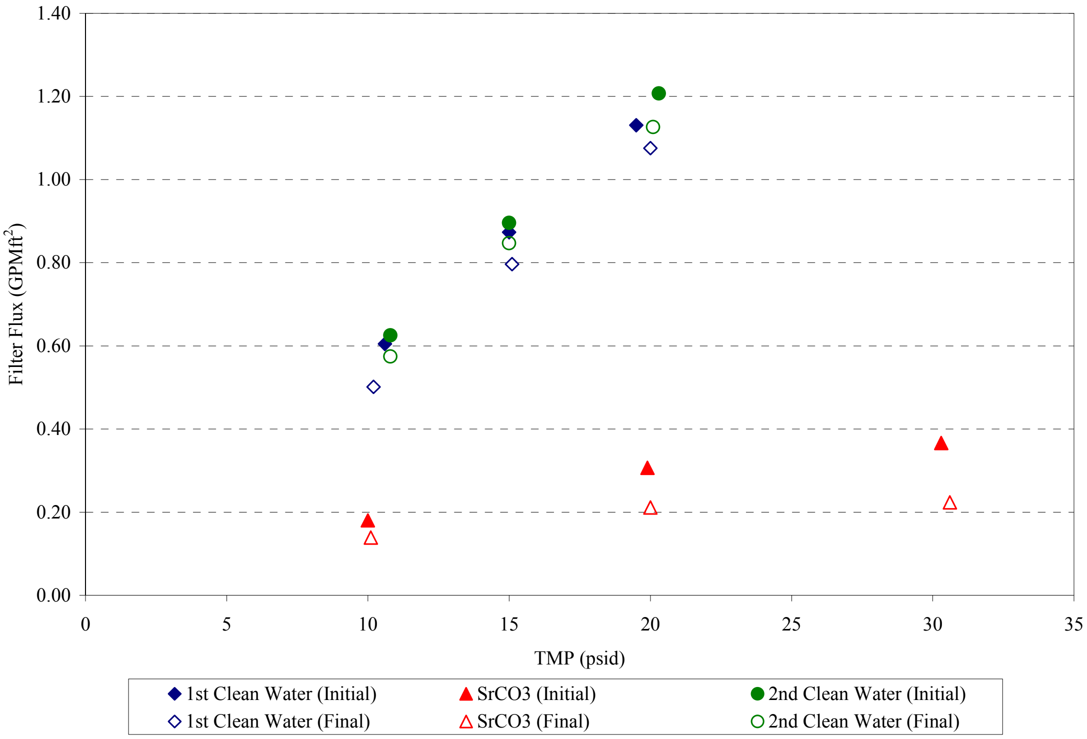


Figure 2.10. Initial Clean Water/$SrCO_3$ Flux Measurements of Filter Prior to Hot Cell Installation
Note: Data shown above taken from user calibrated rotometer and not NQA-1 Calibrated Device.

2.2 Filtration Data Analysis

2.2.1 Filtration Terms and Equations

Filtration examined in this report as a filter flux is defined as:

$$J = \frac{Q_{permeate}}{A_{filter}} \tag{2.1}$$

where J is the filter flux (gpm/ft^2), $Q_{permeate}$ is the volumetric permeate flow (gpm), and A_{filter} is the filtration surface area (ft^2).

In this study, the filter area is assumed as the inside area of the filter element, which is defined as:

$$A_{filter} = \pi D_{i_{filter}} L_{filter} \tag{2.2}$$

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 of the permeate temperature deviation from 25°C. In WTP-RPT-043, the corrected permeate flow rate at a given temperature T (°C) is defined as:

$$\begin{aligned} Q_{25\,^\circ C} &= Q_T e^{2500\left[\frac{1}{T+273}-\frac{1}{298}\right]} \\ J_{25\,^\circ C} &= J_T e^{2500\left[\frac{1}{T+273}-\frac{1}{298}\right]} \end{aligned} \tag{2.3}$$

The pressure drop across the filter is commonly called TMP. It was calculated in this test as:

$$TMP = \Delta P_m = \frac{(P_{inlet} + P_{outlet})}{2} - P_{permeate} \tag{2.4}$$

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 measurement of TMP is psid, which is pounds per square inch, differential.

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 the filter:

$$AV = \frac{Q_{slurry}}{S_a} = \frac{Q_{slurry}}{\frac{\pi}{4} D_{i_{filter}}^{\;2}} \tag{2.5}$$

where S_a is the cross sectional area of the axial flow, and Q_{slurry} is the volumetric slurry flow rate in the axial direction.

The Darcy equation describes filter flux as:

$$J = \frac{\Delta P_m}{\mu_{permeate} R_m} \tag{2.6}$$

where ΔP_m is the pressure drop across filter membrane, $\mu_{permeate}$ is the viscosity of the permeate, and R_m is the overall resistance of the filter membrane.

The overall filter resistance term is considered a more complicated term that is a sum of the resistance of the actual filter, the resistance of the filter cake that forms on the surface of the filter, and the resistance due to fouling of the filter. For dilute slurries and when turbulent flow conditions exist, the filter resistance is usually constant, the transmembrane pressure and permeate viscosity are the controlling operational parameters. During dewatering, the slurry's flow properties change, and the filter cake resistance becomes more significant. When this occurs, the Darcy equation does not truly apply anymore, as the cake resistance changes with axial velocity and slurry concentration. Eventually, the slurry can only be dewatered to a maximum UDS concentration limit at a given TMP. This limit is known as the gel concentration. As a waste slurry's solid concentration approaches the gel concentration, the filter flux can be described as

$$J = k \cdot \ln\left[\frac{C_s}{C_g}\right] \tag{2.7}$$

where C_s is the slurry UDS concentration, C_g is the slurry gel concentration at a given TMP, and k is a constant, for a given TMP and AV (note that k is a negative value).

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.

2.2.2 Filtration Test Matrix

To understand the impact of the transmembrane pressure and axial velocity on the filter flux of 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 2.1.5, the waste slurry was circulated through the filtration testing apparatus while the slurry permeate leaving the filter was recycled back to the slurry reservoir. By recycling permeate in this way, the UDS concentration of the slurry remained constant. Using a TMP of 40 psid and an AV of 13 ft/s as the baseline condition, testing conditions were varied to demonstrate how the flux varies as TMP and AV change from the center condition. Table 2.1 and Figure 2.11 outline the target conditions for the testing performed.

Table 2.1. Filtration Test Matrix Operating Conditions

Test number	Minimum Duration (hours)	Target TMP (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

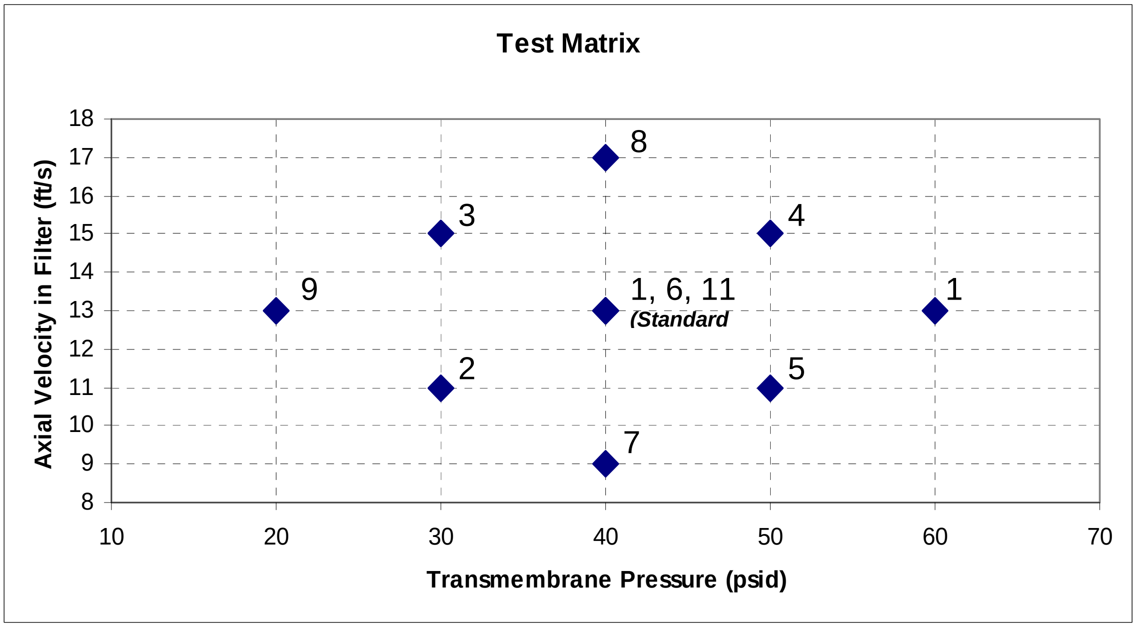


Figure 2.11. Filtration Test Matrix Chart

Each filtration condition was maintained for at least an hour while permeate was recycled back to the slurry reservoir tank. Before test conditions were changed, a back pulse on the filter was performed to provide the same starting conditions for each test. Typically, the back pulse occurred after the slurry pressure was below 20 psig and with the back pulse chamber pressurized to 80 psig. The initial test performed at the baseline condition was performed for a minimum of 3 hours to observe how the filter flux varied with time to track possible fouling due to the waste. When the slurry is at low concentrations, the system is expected to be controlled by the transmembrane pressure (Equation 2.6), 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.

2.2.3 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 2.12. As discussed earlier, the filter flux is initially expected to follow Equation 2.6 for low solids concentrations, which will appear as a horizontal line on the chart when the TMP is held constant. But as the slurry begins to concentrate, the filtration behavior of the slurry is expected to change and begin to follow Equation 2.7. With graphic analysis, the transition in filtration behavior can be understood. The analysis also predicts the slurry's gel UDS concentration. This value can be compared to the measured centrifuge UDS of the slurry, which has been indicated as a good method of estimating the gel concentration (Peterson et al. 2007).

2.2.4 Effects of Rheology and Particle Size

During testing operations, rheology and particle-size samples are taken 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 impacts the cross flow behavior of the filter directly and the formation of filter cake. Particle size also can have an impact by affecting the gel concentration of the slurry and possibly impacting the filter 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 in changing the particle size of the slurry.

This effort has focused on obtaining filtration data under typical processing conditions but has not attempted to develop correlations between physical parameters, such as particle size and filtration rate.

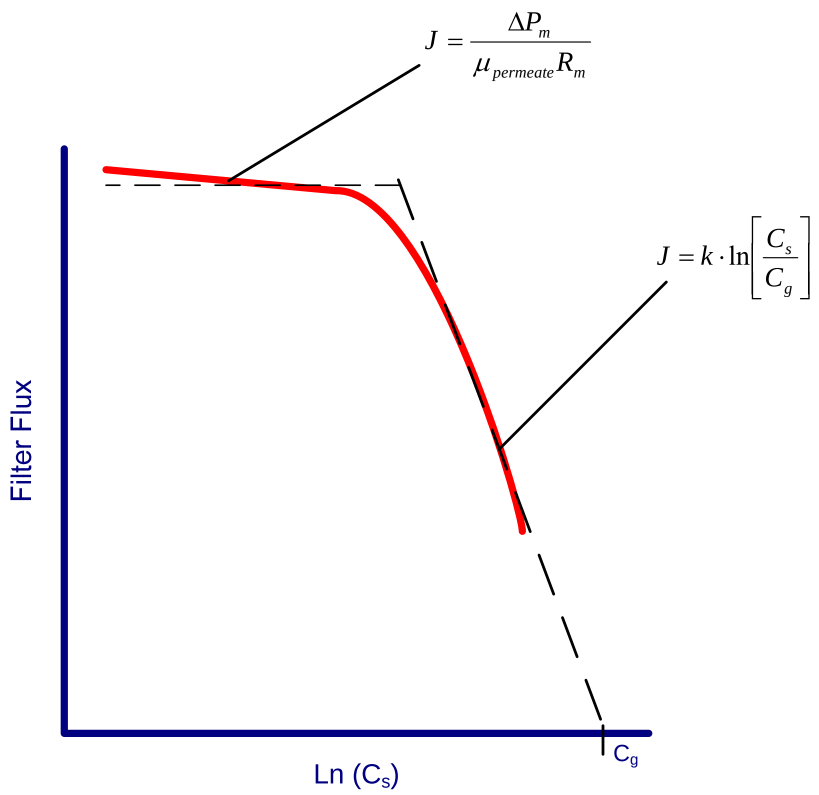


Figure 2.12. Example of a Dewatering Curve at a Constant TMP and AV

2.3 Chemical Data Analysis

During the test, the mass of material added to and removed from the testing apparatus is always being measured to perform an overall mass balance of the slurry during the test. Two main goals are to be achieved from this analysis—verification that transuranic (TRU) material stays in the HLW stream, and calculation estimates of the chemical leach factors of glass-limiting compounds of interest, in this case, aluminum and chromium.

2.3.1 Validation of Filtration Separation of TRU Material

The main goal of the chemical and physical separation processes tested in this report was to demonstrate the effectiveness of removing load-limiting glass compounds (e.g., aluminum and chromium) from the HLW stream while not introducing TRU material into the LAW waste stream. During filtration, it was 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 µm. During leaching, it was also important to verify that TRU compounds were not chemically dissolved during operations designed only to remove glass-limiting compounds for the LAW stream. This was performed by conducting radiochemical analysis on permeate and slurry samples throughout the test to verify that the permeate streams contain minimal TRU compounds and that a mass balance on the system shows that almost all the TRU stays in the HLW slurry stream.

2.3.2 Chemical Leach Factors for Caustic and Oxidative Leaching

The chemical leach factor is defined as the percentage difference in mass of a solid component in the waste after chemical leaching.

$$f_i = 1 - \frac{m_i^{final}}{m_i^{initial}} \tag{2.8}$$

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 physical property measurement of the solid fraction of the slurry. Using chemical analytical data and mass measurements of additions and removals of waste slurry, samples, and dewatered permeate, changes to the elemental changes to the solids and liquid fraction of the slurry can be calculated at each stage of the test, as well as leach factor.
- Perform a mass balance of the slurry before and after leaching using insoluble components such as 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:

$$f_i = 1 - \left(\frac{x_i^{final}}{x_i^{initial}} \right) \left(\frac{x_j^{initial}}{x_j^{final}} \right) \tag{2.9}$$

- Perform a mass balance of the liquid supernate before and after leaching to measure the change of mass in the solids to calculate leach factor.

2.3.3 Physical Examination of Final Leach Material

The chemical characterization and physical morphology are examined after leaching to understand the crystal structure of the solids in the remaining slurry. While most of the analyses used are qualitative, they can show:

- If particles are crystalline, agglomerates, or amorphous.
- If TRU and glass-limiting compounds (like aluminum) are blends of different phases or single compounds.
- What is the crystal phase of remaining glass-limiting compound (e.g., boehmite/gibbsite for aluminum).

3.0 CUF Testing and Results

This section describes the filtration/leaching tests performed for the PUREX/REDOX cladding waste sludge composites referred to as the Group 3 and 4 waste samples performed under test instruction TI-RPP-WTP-601 (Shimskey 2008) and subsequent results. The UDS inventory of either slurry was not enough to generate a 20 wt% slurry in the CUF by itself, and therefore the slurries were blended. This blending of wastes was approved by BNI in concurrence letter WTP/RPP-MOA-PNNL-00172 (see Appendix D).

3.1 Test Plan

Figure 3.1 outlines the testing that was performed and is reported in this section. The goals of this test were to:

- Evaluate the filtration of the REDOX sludge waste composite.
- Evaluate the effectiveness of caustic leaching on aluminum present in the blended waste.
- Evaluate the filtration of the washed leached solids.

Note: These tests are of relatively short duration and therefore do not provide any significant insight into the expected lifetime of the filter elements.

The first half of the testing was to perform filtration studies on a blend of the Group 3 and 4 waste sample composites to understand its filtration and dewatering behavior, as outlined in the first column of Figure 3.1. Initially, 490 mL of the Group 3 composite (approximately 600 g at 28.8 wt% UDS) was mixed with 540 mL of Group 4 composite (approximately 700 g at 29 wt% UDS) inside the CUF slurry reservoir. Next, 2.88L of a simulant supernate was added to dilute the blended slurry to 9 wt% UDS. The simulant was a synthetic solution that corresponded in composition to the liquid fraction in the Group 4 waste. The composition of the simulant consisted of the following:

- The anionic composition of simulant was based on the Group 4 supernate composition.
- The metal composition of the simulant was composed only of sodium and potassium. Concentration of other metallic elements in the Group 3 and Group 4 supernate were considered insignificant.
- The free hydroxide level of the simulant was made 0.3M. The measured free hydroxide concentration of the Group 4 supernate was 0.1M, while the concentration of the Group 3 supernate was 0.3M.
- The final sodium concentration was 3.0M, compared to 2.85M for the Group 4 supernate and 3.15M for the Group 3 supernate.

Once the slurry was homogenized in the slurry reservoir tank, it was circulated through the slurry recirculation loop with filter permeate recycling back to the slurry reservoir. A test matrix was performed as described in Section 2.2.2 to determine the filtration behavior of the waste at a low UDS concentration (≤ 10 wt%). After completion of the test matrix, the waste sample was dewatered to the minimum operating volume in the slurry recirculation loop. To improve pump efficiency for filter testing, permeate was then returned to the slurry until the final volume of the slurry was approximately 2 L. The target UDS concentration inside the slurry loop was 20 wt% UDS after the dilution. At this point, another test matrix was performed to evaluate the change in the filtration behavior after concentrating the waste slurry. Finally, the slurry was sampled for characterization and parametric leaching studies prior to caustic leaching.

The second half of the testing was to evaluate the caustic leaching behavior of the Group 3-4 waste slurry at predicted leaching conditions of the WTP pretreatment UFP2 vessel, as outlined in the right column of Figure 3.1. 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 approximately 3.8 liters with a final sodium concentration of 8.4M, and free hydroxide concentration of 5.3M. The caustic addition was based on:

- An estimation that approximately 94 grams of aluminum was present in the 390 grams of undissolved solids remaining after sampling.
- A 90% leach factor of aluminum (as gibbsite) present in the solids was assumed, and that hydroxide is consumed during dissolution at a 1:1 mole ratio to aluminum.
- Knowing the volume of the leach solution, the predicted aluminum concentration in slurry supernate was calculated.
- The final hydroxide concentration required to prevent aluminum from precipitating out of the leach supernate after cooling was calculated using an empirical equation developed by Misra (reported by Huixin Li et al. 2005) to predict Al solubility as a function of the free hydroxide concentration. The final molar ratio of free hydroxide to aluminum was predicted to be approximately 7:1.
- The mass of NaOH required for the leach was then calculated as the mass of hydroxide consumed during dissolution of aluminum plus the mass of hydroxide needed in the leach supernate to maintain Al solubility after cooling. This mass was to be added as a 19M NaOH solution.
- Once the volume of dewatered slurry and 19M 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. So, the 19M NaOH addition and water addition for steam condensate were combined into one solution. The final solution became 1.8 liters of 14M NaOH.

This caustic solution was used to flush additional solids in the CUF piping prior to isolating the slurry reservoir tank for leaching operations. After flushing, the CUF slurry piping with the caustic addition, the drained slurry, supernate, and caustic addition solution was added to the isolated slurry reservoir tank with the overhead mixer operating. The system was heated to 100°C over a 5.3 hour interval. The slurry was then maintained at 100°C for 12 hours, during which the slurry supernate was sampled periodically to evaluate the aluminum dissolution rate. Afterwards, the slurry was allowed to cool to room temperature over a 12 hour interval. At this point, the leached slurry was allowed to enter the piping of the CUF, and it was dewatered to minimum operating volume of the circulation pump. Three equal-volume caustic wash solutions (1.2 liters) were then added to the leached slurry. To prevent aluminum from precipitating during washing, addition 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:

- 1.78 M for the first rinse solution
- 0.78 M NaOH for the second rinse solution

- 0.30 M NaOH for the third rinse solution

After 20-30 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 solid 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 A, B, C, D, and G.

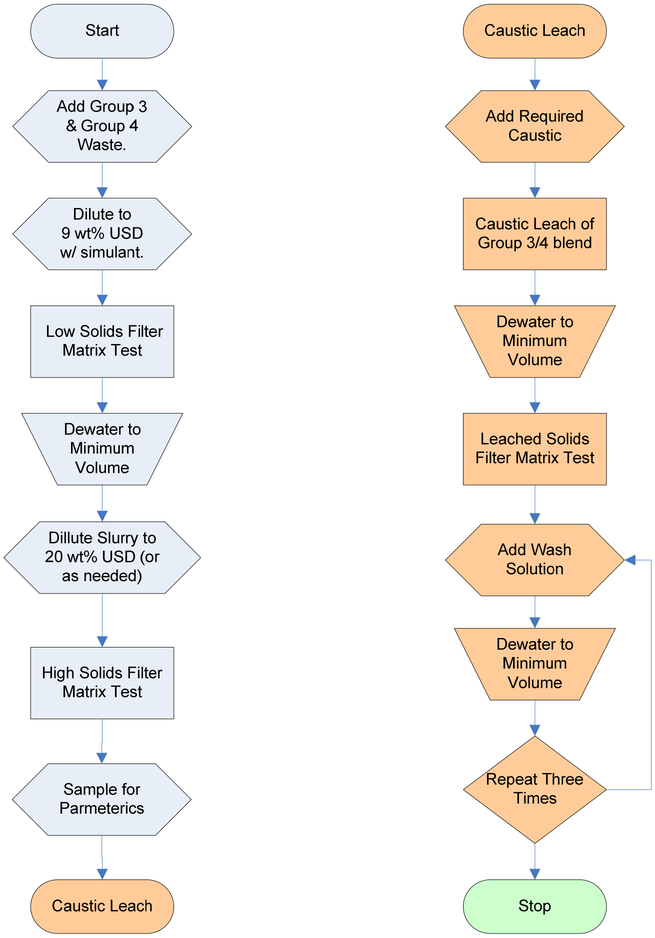


Figure 3.1. Group 3/4 Testing Flowchart

3.2 Initial Clean Water Flux Measurements

Three waste slurry tests (Shimskey et al. 2009, Lumetta et al. 2009) were performed using the same filter prior to this test. After draining the slurry from the CUF after each test, the system was cleaned using a 2M nitric acid solution for one hour. Once the solution was drained from the CUF and rinsed free of acid (verified using pH paper), the CUF was filled with 0.01M NaOH and clean water measurements were performed at varying TMP and an AV of 11 ft/s. The clean water flux results are shown in Figure 3.2 below. Clean water flux measurements taken after nitric cleaning the system after the Group 1/2 CUF test indicated that the filter could benefit from further cleaning. A cleaning solution of 0.5 M oxalic acid was chosen to clean the CUF because it had been proven to be effective in cleaning the filter system used for simulant development when dealing with iron rich simulants. After circulating the solution in the CUF for an hour and rinsing it free of acid, the clean water flux was measured again using a solution of 0.01M NaOH, shown in Figure 3.2. Initial results from that cleaning showed the clean water filter flux increased close to the original clean water flux measured.

After cleaning was completed for the Group 1/2 CUF test, the filter was left in standby (filled with a solution of 0.01M NaOH) for one week prior to the start of the Group 3/4 CUF Test . Before material from the Group 3 and 4 waste slurries were introduced to the CUF for filtration testing, the clean water flux was measured again (Figure 3.3). Initial measurements of the clean water filter flux showed it to be similar to the original clean water flux shown in Figure 2.10. However, the clean water flux decayed over the fifteen minutes it was measured to a value approximately 5 times lower. The results indicate that some form of particulate was now present in the slurry loop of the CUF that quickly deposited on the filter surface, reducing the clean water flux measurement. However, back pulsing between test conditions appeared to initially restore the filter flux indicating that this was not a depth fouling problem with the filter. With the final clean water flux being significantly higher (>0.1 GPM/ft^2) than the expected measured flux during this test (0.01-0.05 GPM/ft^2), the condition of the filter was deemed acceptable for testing.

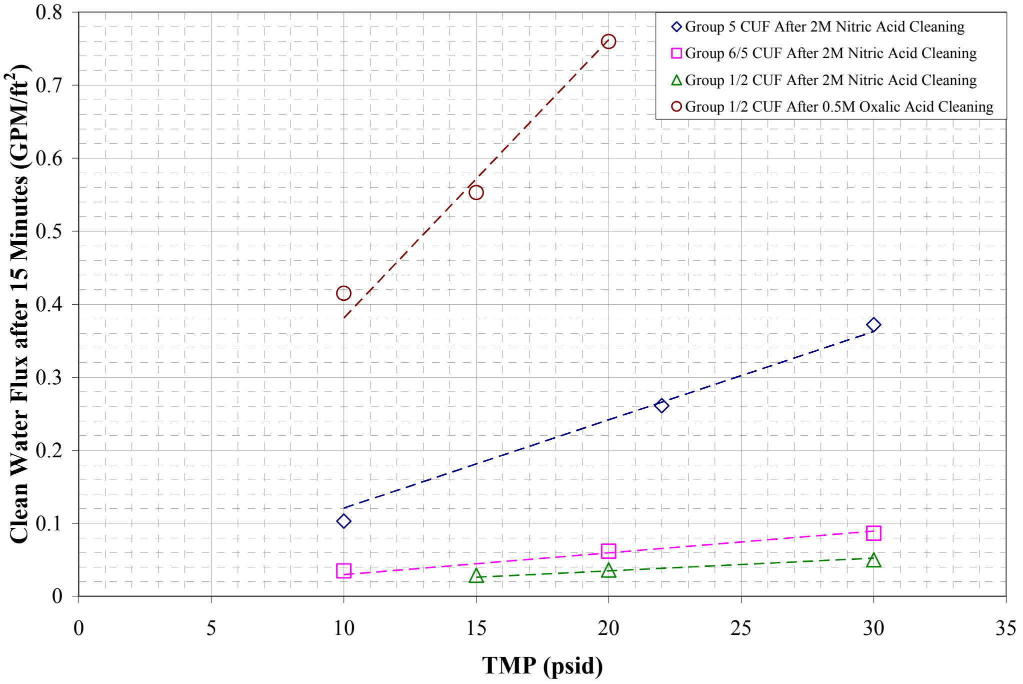


Figure 3.2. Cleaning Water Flux Measurements after Cleaning Operations from Previous Tests

Note: Data shown above taken from user calibrated rotometer and not NQA-1 Calibrated Device.

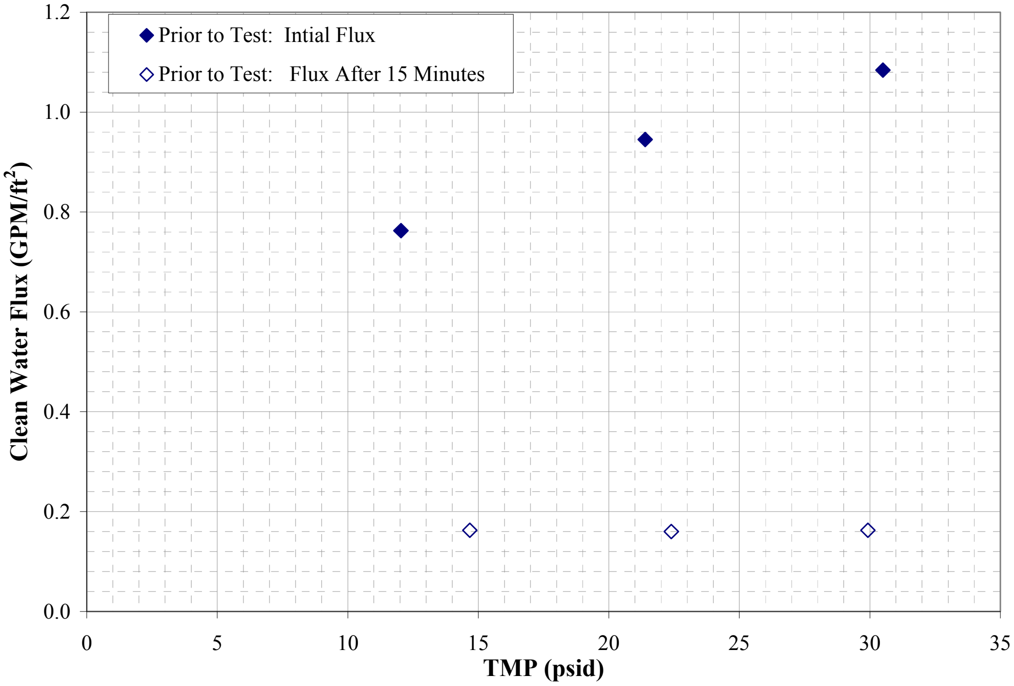


Figure 3.3. Clean Water Flux Measurements Prior to Add Group 3 and Group 4 Waste
Note: Data shown above taken from user calibrated rotometer and not NQA-1 Calibrated Device.

3.3 Blending Group 3 and 4 Wastes with Simulant Supernate

This section discusses the operations of introducing feed material into the CUF. The activities described are:

- Initial additions of simulant supernate and Group 3 and Group 4 simulant waste slurry added to the CUF reservoir prior to recirculating the slurry through the CUF slurry loop.
- The plugging of the circulation pump inlet, why it occurred, and how the circulation of the slurry was initiated.
- Characterization of the slurry prior to filtration testing.

3.3.1 Waste Slurry and Simulant Supernate Additions

Figure 3.4 below outlines the activities and materials added to the CUF to produce the Low Solids Slurry. The initial characterization (Table 3.1) found that both waste types had similar concentrations of metals, with the most significant differences being S, Zn, and Zr. The most abundant metal in these waste types is Al, found mostly as gibbsite, and virtually all insoluble. There is also a high concentration of Na. Based on this information, the simulant was made up to represent the concentration of sodium and the respective anions that were found in the waste characterization (Table 3.2). The makeup of the simulant ultimately had a higher concentration of free hydroxide than the slurry and increased the concentration upon addition. It was determined that caustic leaching was needed due to the high concentration of gibbsite in the waste.

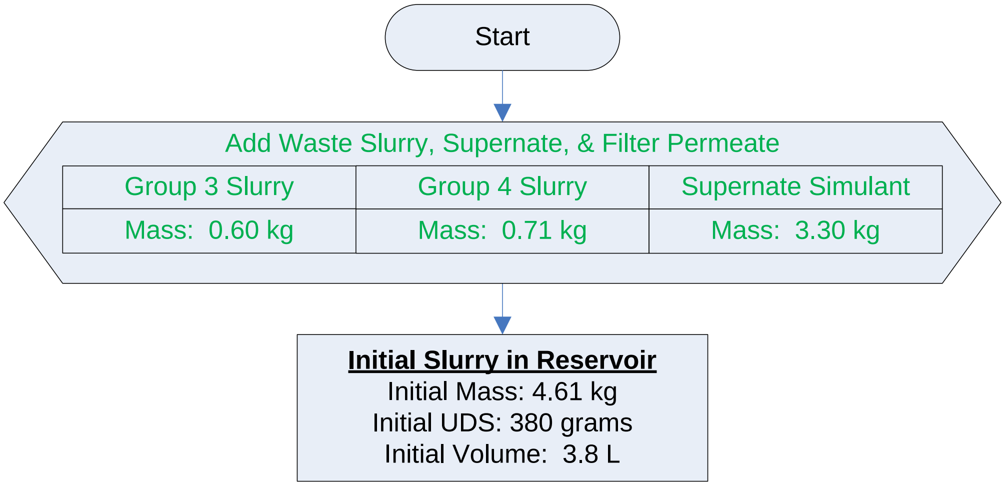


Figure 3.4. Group 3/4 Initial Slurry Preparation

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.1. Group 3 and 4 Waste Composite Additions to Slurry Reservoir

	Group 3 PUREX Cladding Waste Sludge		**Group 4 REDOX Cladding Waste Sludge**		**Total**
Solids	Wt%	g	Wt%	g	g
Total Mass Added		598		710	1308
Undissolved Solids in Slurry	28.8%	172	29.7%	211	383
Dissolved Solids in Supernate	17.9%	76	17.1%	85	161
Metals	mg/g (wet basis)	mg	mg/g (wet basis)	mg	mg
Al	9.1E+01	54,500	9.5E+01	67,700	122,200
B	8.4E-03	5	1.2E-01	86	91
Bi	2.2E-01	130	3.8E-01	270	400
Cr	2.7E-01	160	6.8E-01	480	640
Fe	4.3E+00	2,550	1.6E+00	1,130	3,680
Mn	2.9E-01	180	5.1E-01	360	540
Na	6.1E+01	36,400	5.3E+01	37,700	74,100
P	7.1E+00	4,200	7.1E+00	5,000	9,300
S	5.0E+00	2,980	5.2E-01	370	3,340
Si	2.6E+00	1,550	1.8E+00	1,270	2,820
Zn	5.6E-02	30	2.4E-01	170	200
Zr	2.4E+00	1,420	3.8E-02	30	1,450
Total U	2.8E+00	1,680	1.1E+00	750	2,430
Radiochemical Isotopes	µCi/g (wet basis)	µCi	µCi/g (wet basis)	µCi	µCi
Pu-239+240	2.7E+02	162	5.2E+01	40	200
Pu-238	3.0E+01	18	8.0E+00	6	24
Gross Alpha	5.9E+02	350	2.5E+02	180	530
Am-241	2.9E+02	172	2.1E+02	150	320
Eu-154	8.3E+01	49	6.5E+01	50	100
Eu-155	3.3E+01	20	2.2E+01	20	40
Co-60	1.5E+01	9	5.7E+00	4	13
Cs-137	4.2E+04	25,000	1.5E+04	10,400	35,400
Sr-90	8.0E+04	47,700	1.0E+04	7,500	55,200
Gross Beta	1.9E+05	112,000	3.6E+04	26,000	138,000

Table 3.2. Simulant Addition to Group 3/4 Waste

	Simulant Addition (2.9L)		Actual Slurry Waste (1.3kg)		% slurry due to simulant
Cations	mg	mg/ml	mg	mg/g (wet basis)	wt%
Na	190,000	66,000	74,000	57	72%
Anions	mg	mg/ml	mg	mg/g (wet basis)	wt%
OH	13,000	4,500	5,000	4	72%
C_2O_4	10,000	3,400	2,300	2	81%
NO_2	27,000	9,000	16,200	12	63%
NO_3	260,000	90,000	120,000	92	68%
PO_4	32,000	11,000	9,400	7	77%

3.3.2 Pump Plugging and Recovery Operations

Additions of the Group 3, Group 4, and simulant to the slurry reservoir were made over the course of a 2-3 hour time period. During waste addition to the slurry reservoir (with the lid removed), the overhead mixer was kept turned off to prevent splashing waste out of the reservoir. Once the additions were completed, the lid was placed on the slurry reservoir and the agitator turned on. After thirty minutes of mixing, the valves isolating the circulation pump from the slurry reservoir were opened. Shortly afterwards, the pump was turned on, but it quickly stalled. After some troubling shooting, it became evident that the suction line to the circulation pump was plugged with solids from the slurry (Figure 3.5).

After the pump had seized from the plug of solids that formed in the suction to the pump, further examination of the waste characteristics for the Group 3 and 4 waste composites were conducted since this problem had not occurred with any other waste tested. Examination of the Group 3 and Group 4 characterization data (summarized in WPT-PRT-167) found several physical characteristics of the waste that attributed to this problem. Settling rate data of both the CWP and CWR found that the settling rate of the slurries was unusually fast. Over 80% of the waste solids appeared to have settled by the first hour into the test, eventually reaching the final settled volume 1-2 hours later (Figure 3.6). The fast settling rate was attributed to the viscosity of the slurry supernate being relatively low (2-3 mPa-s @ 25°C) and the large quantity of particles in the waste that were > 10 μm in size (Figure 3.7 and Figure 3.8). Another interesting phenomenon was observed during rheology testing. While the flow curves of the concentrated slurries behaved as Newtonian during flow conditions, the shear strengths of settled solids in each slurry (after a 72 hour settling time) were very high, ranging from 100 to 700 Pa (Table 3.4). It was estimated that the measured shear stress measurements were low because both measurements were performed with the rotary vane of the instrument only half immersed into the sample. Overall, the measurement showed that once these waste samples settled, re-suspension of solids was going to be difficult.

The evidence suggested that in the absence of agitation, the solids in both waste composites rapidly settle into a compact slurry with extremely high shear strength. The shear strength of the settled slurry at the bottom of the slurry reservoir was more than sufficient to cause a plug in the suction line of the pump. In summary:

- Over the 2-3 hour period that Group 3 and Group 4 waste samples were added to the CUF, undissolved solids in the slurry samples settled into the bottom of the CUF slurry reservoir and into the suction line of the pump.

- Even with the agitator running afterwards, the high shear stress of the settled slurry resisted re-suspension at the heel of the tank and entrance to the suction line of the pump.
- Once the positive displacement pump began to pull the concentrated slurry into the suction line of the pump, it most likely concentrated the slurry even further until a plug formed.

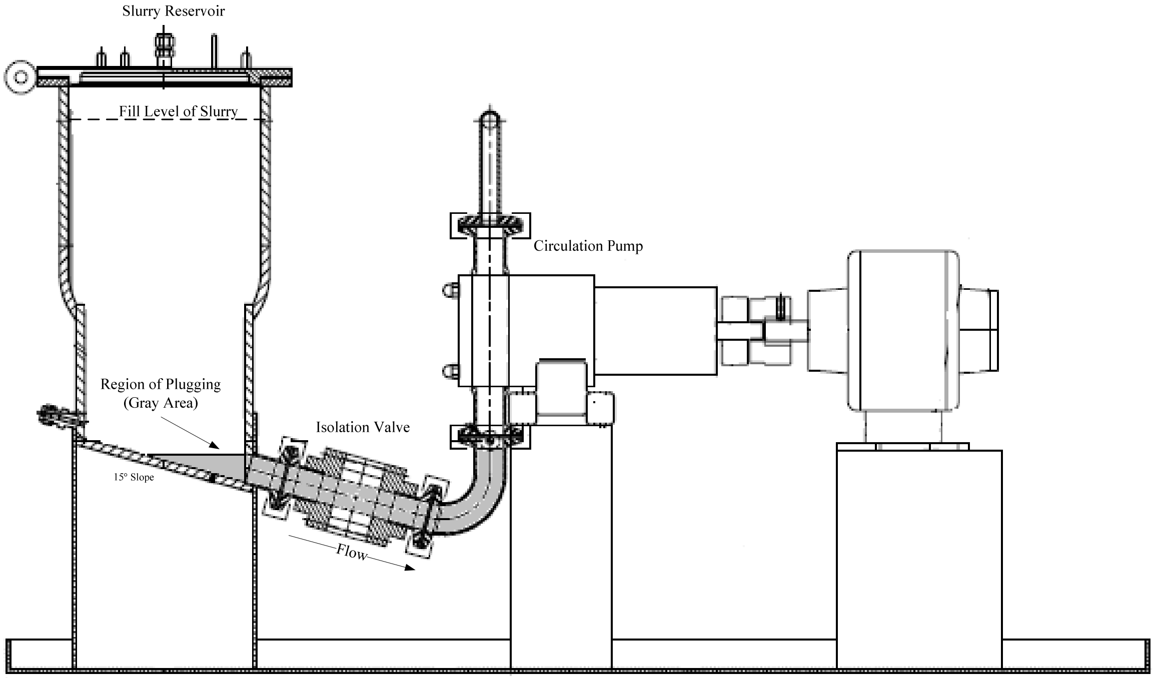


Figure 3.5. Drawing of Plugged Region of CUF Apparatus

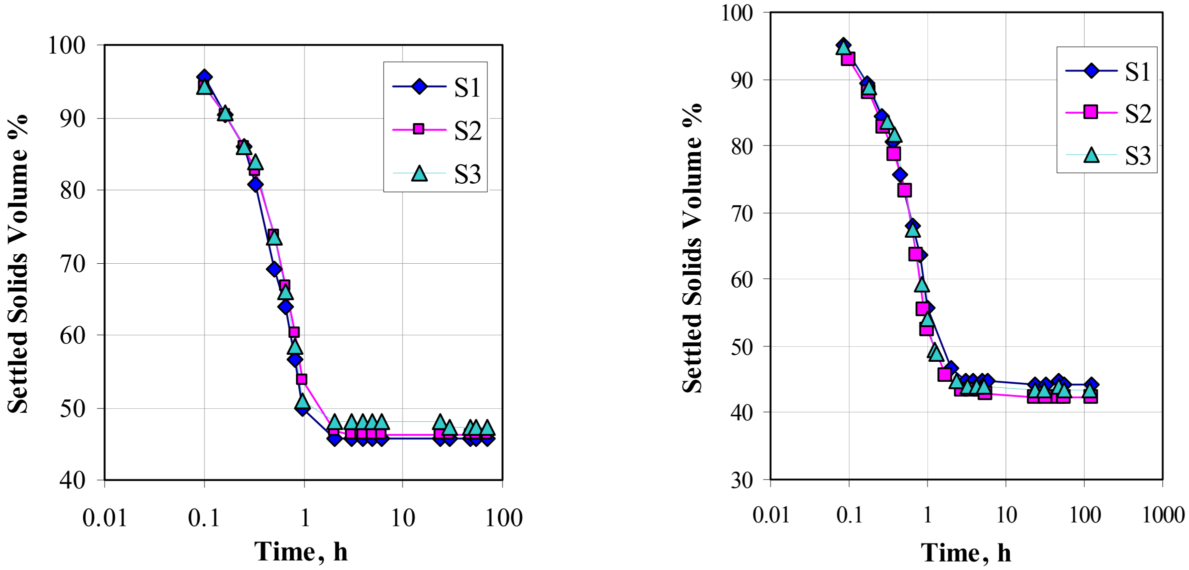


Figure 3.6. Settling Test Results for the Group 3 (left) and Group 4 (right)

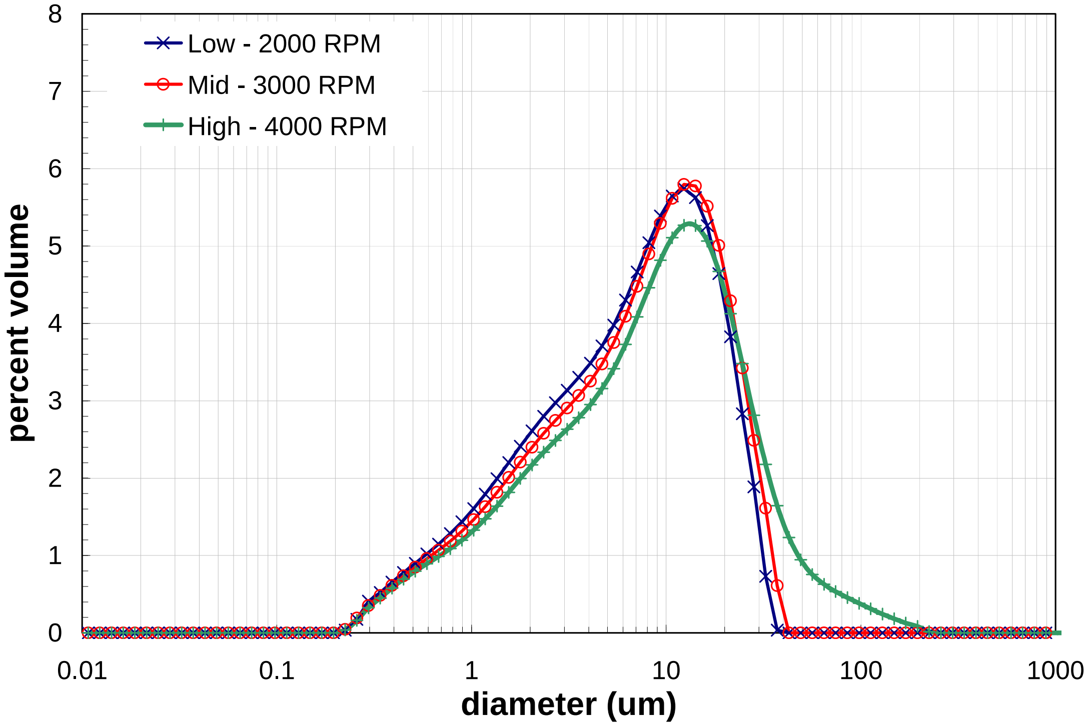


Figure 3.7. Group 3 (CWP) Particle Size Distribution, Pump Speed as a Variable

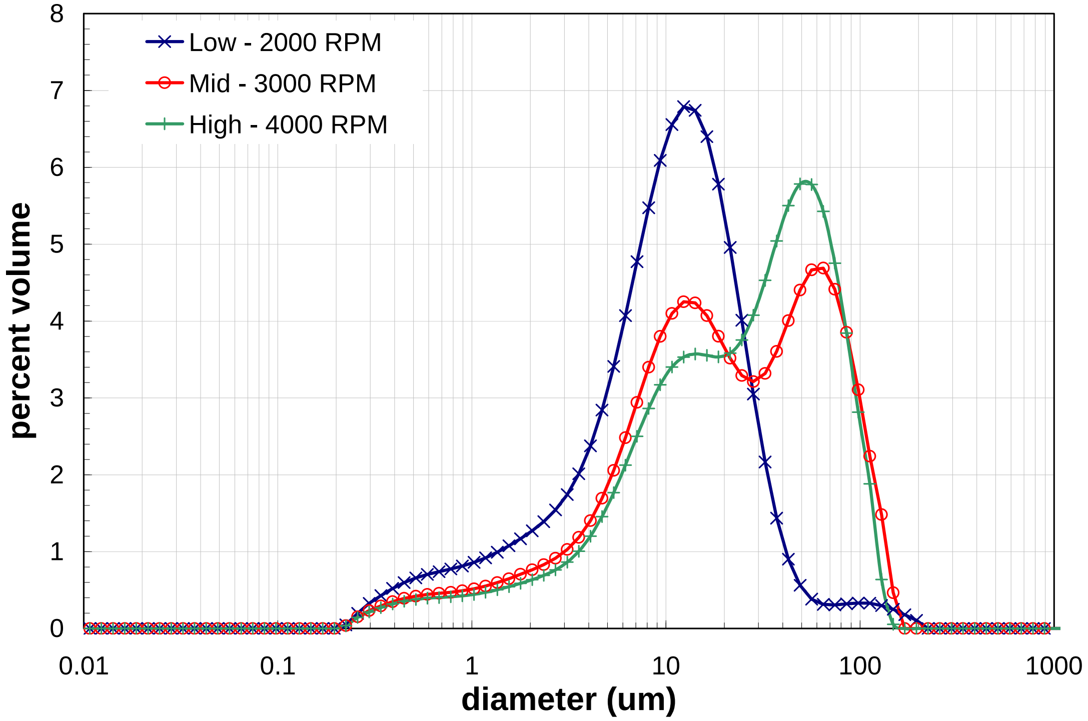


Figure 3.8. Group 4 (CWR) Particle Size Distribution, Pump Speed as a Variable

Table 3.3. PSD Comparison of Group 3 and Group 4 Composite Wastes

Waste Sample	d[10]	d[50]	d[90]
Group 3 (CWP)	1.0-1.3 μm	5.5-8.8 μm	14-30 μm
Group 4 (CWR)	1.4-3.9 μm	7.9-26 μm	17-83 μm

Table 3.4. Shear Strength Measurements of Group 3 and Group 4 Settled Slurries

Sample IDr	Location of Vane in Sample Cup	Shear Strength* [Pa]
Group 3		
TI513-G3-AR-J1	Center	700 Pa
Group 4		
TI514-G4-AR-RH1	Center	100 Pa
	Radial (Near Wall)	290-340 Pa

* Value corresponds to test where only half vane immersion is achieved. Actually shear strengths are likely ~2 times the table value.

Initially, attempts to back pulse the plug loose with air were made over an eight hour period. While air eventually could flow through the pump inlet to the slurry reservoir, this did not loosen the plug sufficiently to allow the pump to operate. This method also lead to another problem. The use of air to loosen the plug caused slurry and supernate to over flow into a capture vessel at the back of the system (Figure 3.9). The overflow capture system was designed to prevent fluid inside the reservoir from overflowing onto the cell floor. However, it was located on the back side of the vessel, where a 1 liter bottle was positioned to capture escaped solids/liquids. After the dewatering operation was completed and the high-solids matrix test was started, this bottle was discovered full of diluted slurry. The overflow bottle was estimated to contain about 500 mL of the initial slurry and about 500 mL of supernate from the settled slurry and was not returned to the testing apparatus.

After this method was abandoned, the pump was then operated in reverse (requiring air supply lines to the air motor inside the cell to be swapped). The goal of this operation was to pull supernate from the slurry reservoir and to force it into and through the plug of settled solids at the pump inlet. This method proved to be successful. The pump was allowed to operate backwards for an hour, pumping the slurry through the slurry circulation loop and slurry reservoir, to re-suspended solids that settled in the circulation piping. The agitator in the slurry reservoir was running to ensure that the solid in the tank bottom remained suspended. The direction of the pump was then switched and the test was resumed.

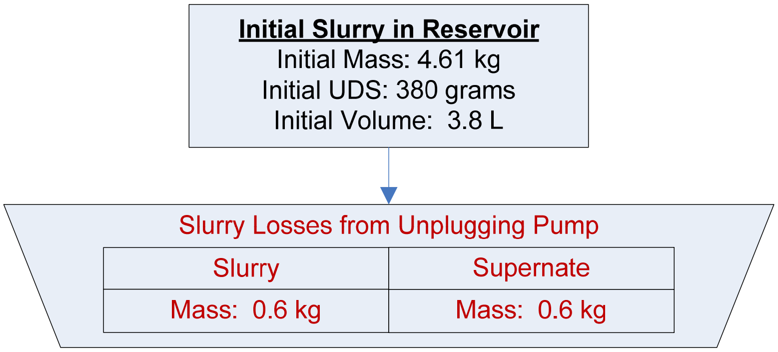


Figure 3.9. Group 3/4 Slurry and Supernate Loss during Unplugging Activities
Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

3.3.3 Low Solids Slurry Characterization

Once the slurry started to circulate through the slurry piping successfully, samples of the initial slurry were taken for physical and chemical characterization (Figure 3.10**)**. Due to concerns of settling of solids, samples of the slurry were taken from the circulation drain valve while the pump was running to get the most representative sample inside the slurry recirculation loop. During the efforts to unplug the pump, it is estimated that 500 mL of slurry and 500 mL of supernate were lost. The loss of specific analytes due to this is outlined in Table 3.5. The losses are anywhere from 13%-26% depending on the solubility of the analyte.

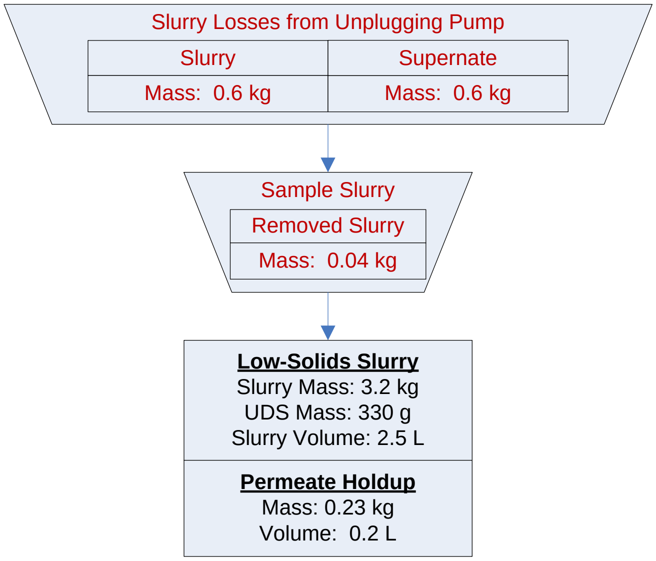


Figure 3.10. Group 3/4 CUF Low-Solids Slurry Initial Sampling
Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.5. Losses due to Pump Plugging

Radiochemical Isotopes	% loss	Metals	% loss
Pu-239+240	13%	Al	14%
Pu-238	13%	B	22%
Gross Alpha	13%	Bi	13%
Am-241	13%	Cr	18%
Eu-154	13%	Fe	13%
Eu-155	13%	Mn	13%
Co-60	15%	Na	26%
Cs-137	22%	P	22%
Sr-90	13%	S	24%
Gross Beta	15%	Si	13%
		Zn	13%
		Zr	13%
		Total uranium	14%

After the slurry and permeate piping were filled, the circulating slurry was sampled for characterization. Physical property measurements were performed on two samples collected in 10 - 15 mL glass centrifuge tubes that were allowed to settle for a minimum of 24 hours and then centrifuged for a minimum of 1 hour at 1000 G. The average results from the two samples are detailed in Table 3.6. The definition of each term in the table is:

- Slurry density: The measured density of the sampled circulating slurry using the net weight of the sample and the volume of the sample collected.
- Supernate density: The measured density of the decanted slurry supernate after centrifuging the sample at 1000 G for a minimum of 1 hour.
- Settled Solids: The solid volume fraction of the slurry after gravity settling for a minimum of 24 hours.
- Centrifuged UDS: The weight percent of UDS present in the centrifuged solids fraction of the slurry after decanting the supernatant liquid.
- Total Solids (TS): The TS fraction of the slurry. The water fraction of the slurry is calculated from substracting TS from 1.
- UDS: The UDS fraction of the slurry
- Dissolved Solids (DS): The DS fraction of the supernate. This is not the same as the DS of the slurry, which is equal to the difference between the TS and UDS measurements of the slurry.

The measured UDS concentration (6 wt%) was lower than predicted (0.33 kg ÷3.2 kg ≅ 10 wt%), indicating that a significant fraction of the undissolved solids were still not suspended. The slurry would be later sampled again to verify this (Section 3.4.2). The chemical composition of the slurry is shown in Table 3.7 and opportunistic analytes of the supernate in Table 3.8.

Table 3.6. Physical Property Measurements of the Low Solids Slurry (Slurry Circulation Loop)

Slurry Density (g/ml)	1.21
Supernate Density (g/ml)	1.16
Settled Solids (Vol %)	15%
Centrifuged Undissolved Solids (Wt %)	40%
Total Solids of the Slurry (Wt %)	25%
Dissolved Solids of the Supernate (Wt%)	20%
Undissolved Solids of the Slurry (Wt%)	6%

Table 3.7. Low Solids Slurry Inventory and Composition (Including Permeate Hold-up)

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	3.38	3.05		0.33	
Wt% of Slurry	100%	90.3%		9.7%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	1.0E+02	3.8E+00	1.4E+03	1.0E+02	3.1E+05
B	7.0E-02	4.4E-02	1.7E+01	2.6E-02	7.9E+01
Bi	3.4E-01	< 1.E-2	< 4.E+0	3.4E-01	1.0E+03
Cr	5.2E-01	1.5E-01	5.8E+01	3.7E-01	1.1E+03
Fe	3.2E+00	4.5E-03	1.7E+00	3.1E+00	9.6E+03
Mn	4.6E-01	2.1E-04	7.8E-02	4.6E-01	1.4E+03
Na	1.9E+02	1.8E+02	6.8E+04	8.7E+00	2.6E+04
P	1.5E+01	9.4E+00	3.6E+03	5.7E+00	1.7E+04
S	2.5E+00	1.9E+00	7.3E+02	5.8E-01	1.8E+03
Si	2.4E+00	5.1E-02	1.9E+01	2.4E+00	7.2E+03
Zn	1.7E-01	3.4E-03	1.3E+00	1.7E-01	5.1E+02
Zr	1.2E+00	< 4.E-4	< 1.E-1	1.2E+00	3.8E+03
U	2.1E+00	8.2E-02	3.1E+01	2.0E+00	6.0E+03
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	1.1E+01	1.5E+00	5.5E-04	9.2E+00	2.8E-02
Cs-137	2.7E+04	1.6E+04	6.0E+00	1.2E+04	3.5E+01
Eu-154	8.2E+01	< 8.E-1	< 3.E-4	8.2E+01	2.5E-01
Eu-155	3.0E+01	< 5.E+0	< 2.E-3	3.0E+01	9.2E-02
Am-241	2.8E+02	< 2.E+0	< 9.E-4	2.8E+02	8.4E-01
Gross Alpha	4.5E+02	3.0E+00	1.1E-03	4.5E+02	1.4E+00
Gross Beta	1.1E+05	1.6E+04	6.1E+00	9.9E+04	3.0E+02
Sr-90	4.7E+04	3.8E+02	1.4E-01	4.7E+04	1.4E+02
Pu-239+240	1.7E+02	1.6E+00	6.0E-04	1.7E+02	5.1E-01
Pu-238	2.0E+01	1.6E-01	5.9E-05	2.0E+01	6.1E-02
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	µg/ml	**[M]**	**g**	**µg/g**	**g**
F	4.7E+02	2.5E-02	1.2E+00	2.8E+03	9.3E-01
C_2O_4	3.4E+03	3.8E-02	8.9E+00	8.8E+03	2.9E+00
NO_2	1.2E+04	2.6E-01	3.1E+01	2.6E+04	8.4E+00
NO_3	1.0E+05	1.7E+00	2.8E+02	2.3E+05	7.6E+01
SO_4	< 8.E+0	< 8.E-5	6.1E+00	4.7E+03	1.6E+00
PO_4	1.1E+04	1.2E-01	3.0E+01	4.2E+04	1.4E+01
OH	4.9E+03	2.9E-01	1.3E+01		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-167). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI601-G4-A (ASO ID 08-01365) 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. Leached Solid Fraction were calculated using analytical results from characterization data (WTP-RPT-167).

Table 3.8. Group 3/4 Low-Solids Supernate Opportunistic Composition

Opportunistic Analytes	Supernate Measured[(a)] μg/mL
Ag	<2.6E-1
As	<5.2E+0
Ba	[0.25]
Be	<6.3E-3
Ca	[7.4]
Ce	<1.2E+0
Co	[0.35]
Cu	[0.27]
Dy	<3.5E-1
Eu	<1.3E-1
La	<3.4E-1
Li	[0.46]
Mg	<2.8E-1
Mo	[2.5]
Nd	<6.6E-1
Pb	[38]
Pd	<7.7E-1
Rh	<1.5E+0
Ru	[1.2]
Sb	<2.4E+0
Se	<8.5E+0
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	1.46
W	[5.5]
Y	<5.4E-2

(a) Supernatant measured from, ASR 8125, sample TI601-G4-A (RPL ID 08-01365); 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.

Slurry samples were taken prior to the filtration testing and analyzed for particle size. Figure 3.11 shows the PSD for Group 3/4 low solids matrix sample as a function of pump speed before sonication. The distribution of particles ranges from 0.2 to 40 µm with the range extending to 200 µm at 4000 RPM. The peak maxima are around 9 µm and all three conditions are continuous and uni-modal, although there is a small shoulder near 0.4 µm and at 4000 RPM there is also a shoulder around 70 µm. Changes with respect to the flow rate are minor with the exception of some suspension of larger particle diameters at 4000 RPM. This is expected as higher pump speeds are capable of suspending larger particles and particle agglomerates.

Figure 3.12 shows the particle size distribution as a function of sonication and indicates that the effects of sonication are minimal on the Group 3/4 low solids matrix sample. During sonication the distribution remains uni-modal and continuous with a peak maximum around 9 µm. After sonication, a small increase is seen in particles of approximately 50 µm, which may be a result of agglomerate formation or more likely is noise or a spurious flocculate.

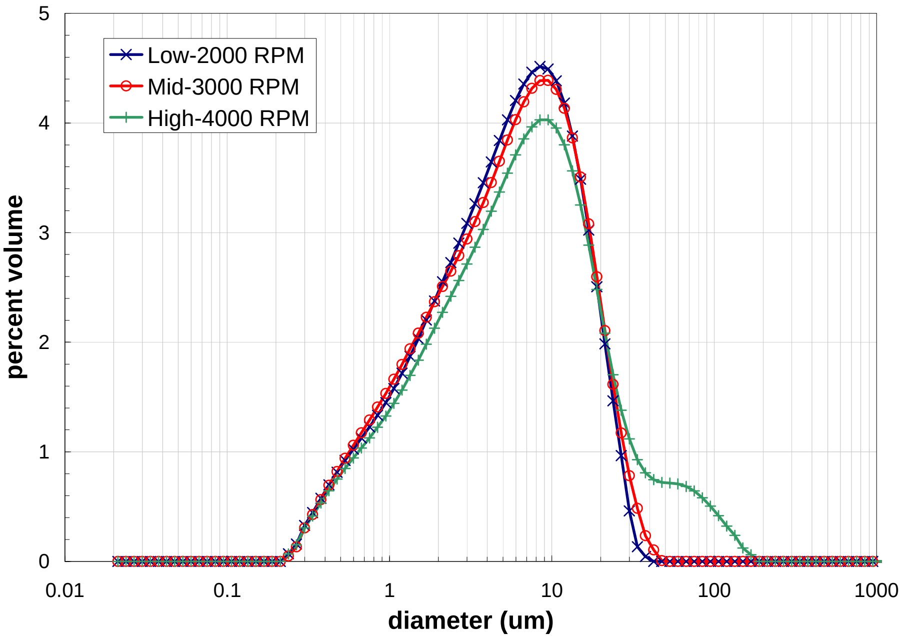


Figure 3.11. PSD of CUF Group 3/4 Low-Solids Slurry as a Function of Pump Speed

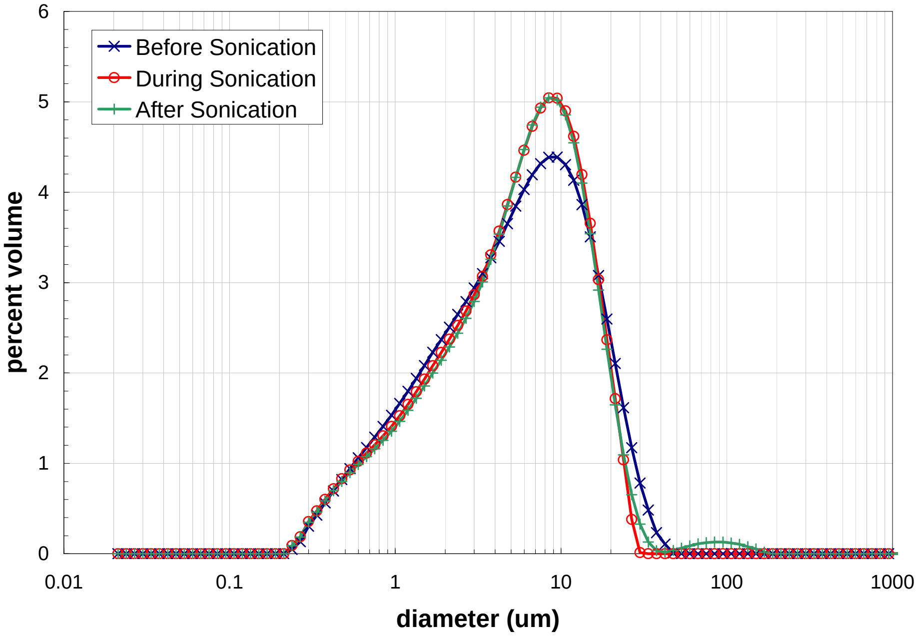


Figure 3.12. PSD of CUF Group 3/4 Low-Solids Slurry as a Function of Sonication

A sample for rheology measurements of the low solids slurry was obtained before extensive CUF processing (i.e., shearing) of the Group 3/4 slurry, and as such, is considered an "unsheared" sample. Table 3.9 summarizes the best-fit Newtonian viscosities for the low solids, unsheared slurry. Results confirm that viscosity shows a decrease with increasing temperature. At 25°C, both initial and replicate flow curves yield a viscosity of 2.0 mPa-s. Viscosity decreases to 1.6 mPa-s and 0.9 mPa-s at 40°C and 60°C, respectively. Measurement noise affects the quality of the fit as indicated by the low R values of 0.57 to 0.85. Finally, the change in viscosity with increasing temperature is near the limit of measurement accuracy (±0.5mPa-s). From 25°C to 40°C, shows an insignificant 0.4 mPa-s decrease. The change in viscosity from 40°C and 60°C of 0.7 mPa-s is near the limit of significance.

Figure 3.13 shows the results of flow curve testing for the low solids, unsheared slurry. The flow curves indicate that the slurries are Newtonian, having a linear slope up to approximately 450 to 550 s^{-1}. At shear rates higher than 550 s^{-1}, an increase in the flow curve slopes is observed and suggests the formation of Taylor vortices. As such, flow curve data beyond 450 s^{-1} are likely influenced by flow instabilities and, as such, are not useable for determination of slurry viscosity. Given that the total range of shear stress over shear rates between 0 to 450 s^{-1} is only 1.0 to 1.5 Pa, it is likely that the noise is substantial for the current measurements because the viscosity of the test slurry is approaching the measuring system's limit of accuracy of ±0.5 mPa-s.

Table 3.9. Results of Fitting Analysis for Group 3/4 CUF Low Solids Matrix

Model	Temperature [°C]	Range	Viscosity [mPa·s]	R
Newtonian	25 (1 of 2)	0-400 s^{-1}	2.0	0.75
	25 (2 of 2)	0-400 s^{-1}	2.0	0.85
	40	0-400 s^{-1}	1.6	0.79
	60	0-400 s^{-1}	0.9	0.57
R is the correlation coefficient.				

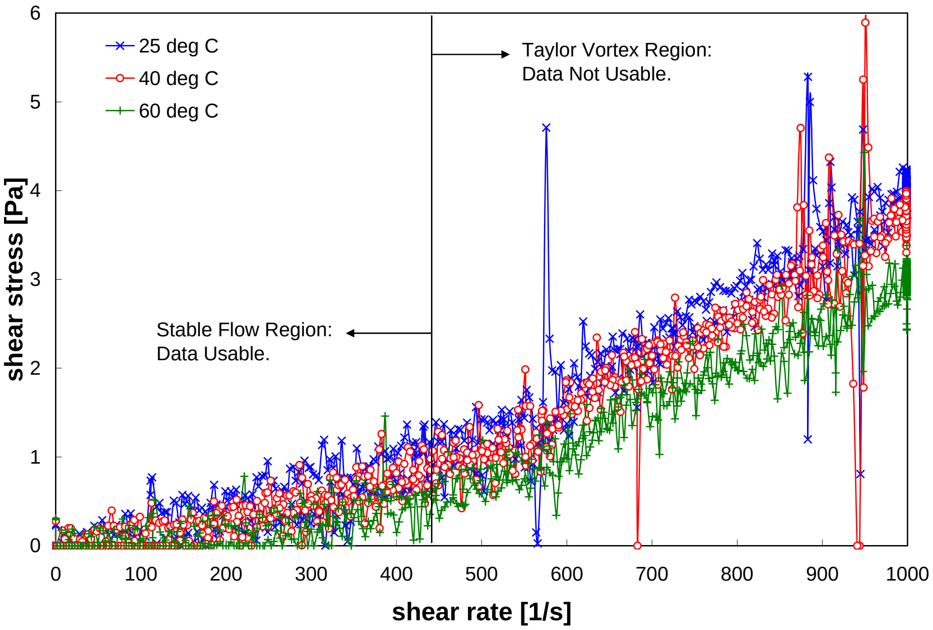


Figure 3.13. Flow Curves for Group 3/4 CUF Low Solids Slurry

3.4 Filter Flux Test Matrix and Initial Dewater

This section describes the filtration testing performed using the Group 3/4 composite before leaching, as shown in the left column (colored blue) of Figure 3.1. The following tests were performed:

- Filtration testing of the composite Group 3/4 waste slurry at a low solids concentration as described in Section 2.2. Testing compares the effects of transmembrane pressure, axial velocity, and operation time on filter flux.
- Re-sampling the low-solids slurry after testing for physical characterization.
- Dewatering of the waste slurry to a higher UDS concentration using a constant TMP and AV to understand the impact of how solids concentration impacts filtration and compare to previous testing of other wastes.

- Filtration testing of the slurry at a high solids concentration as described in Section 2.2. , Testing compares the effects of transmembrane pressure, axial velocity, and operation time on filter flux.

3.4.1 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 3.10. The complete permeate flux data with respect to time are displayed in Figure 3.14 and Figure 3.15. At the start of the test, it was apparent that the suction line to the circulation pump was not completely cleared. Use of a positive displacement pump allowed target TMP parameters to be consistently met. However, reduction of pumping efficiency, such as a plug in the suction line, reduces the range of AV that can be achieved for applying higher back pressure on the pump. For the initial test condition, the maximum AV achieved at a TMP of 40 psid was 9 ft/s. Difficulties persisted for the next four test conditions, with axial velocities reaching only 7 ft/s - 10 ft/s. At this point, an easier test condition was tried to help clear the line. Using a TMP of only 20 psid, the pump was able to achieve an axial velocity of 13 ft/s, which helped improve the pump performance afterwards. Two of the initial five test conditions were retested at the end of the testing to increase the number of tests to 13. Figure 3.16 plots the actual TMP and AV of each test condition against the target values for comparison. Overall, the test matrix was skewed with the achievable AV decreasing with increases in TMP.

The average filter flux from each test condition (Table 3.10) was plotted against TMP and AV to compare their individual impact on filter flux (Figure 3.17 and Figure 3.18). Figure 3.17 demonstrated that filter flux was directly proportional to TMP, with a R^2 correlation factor of 0.85. The plot for AV shows a slight negative trend, but the scatter between points is too great to decipher a significant relationship (Figure 3.18). The results indicate that the filtration behavior of the slurry at this concentration could be explained by Darcy's Law (Equation 2.6) where TMP effects are dominant.

To evaluate if filter flux was changing significantly during the course of the test, the filter flux from each test condition was also plotted against the mean operational time of the test condition. The plot for filter flux over time (Figure 3.19) demonstrated a negative trend over the course of the test. The significance of the impact was not large when compared to TMP, with a R2 correlation constant of 0.01. However, a 28% reduction in flux was found between the initial test condition (0.032 GPM/ft^2) and the final test condition (0.023 GPM/ft^2) after approximately 20 more hours of operation, indicating that a filter decay mechanism was at work that was increasing filter resistance.

Modeling of the data using a least square fit method was then used to quantify the effects of TMP. AV, and the median operation time of the matrix test time on filter flux. A linear fit equation with a R^2 correlation of 0.91 was developed using TMP and processing time as variables (Figure 3.20). As demonstrated in Figure 3.17, filter flux was found to be direct proportional to TMP. The model also included the negative impact that processing time was found to have on filter flux. The model showed that 27.3 hours of processing the waste slurry was equivalent to a 10 psid decrease in the filter flux.

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 this model must be bound by the range of TMP used in this filter test, shown in Table 3.10. 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 21 hour period that this model predicts.

Table 3.10. Average Operating Conditions and Filter Flux for Low Solids Matrix Test

Design Test Condition	Median Operation Time of Test[(a)] (hr)	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	2.73	25.3	42.1	8.8	32.3	0.032	1.21
2	5.61	25.2	29.9	9.9	21.1	0.021	1.28
3	6.85	25.1	35.7	6.7	24.7	0.025	1.01
4	7.98	25.1	40.4	7.0	27.6	0.028	1.02
5	10.11	24.7	50.8	8.4	32.5	0.033	1.27
6	12.05	24.8	20.4	12.7	13.9	0.014	1.56
7	13.56	25.1	60.9	9.3	50.0	0.050	1.42
8	14.85	25.0	41.1	12.0	31.5	0.032	1.60
9	16.20	24.8	30.8	13.5	20.5	0.021	1.79
10	17.40	25.4	31.1	14.7	18.9	0.019	1.93
11	18.60	25.3	50.2	12.4	33.3	0.033	1.64
12	19.87	25.6	39.5	13.9	21.9	0.022	1.82
13	21.09	24.9	40.3	12.9	22.8	0.023	1.66

(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.

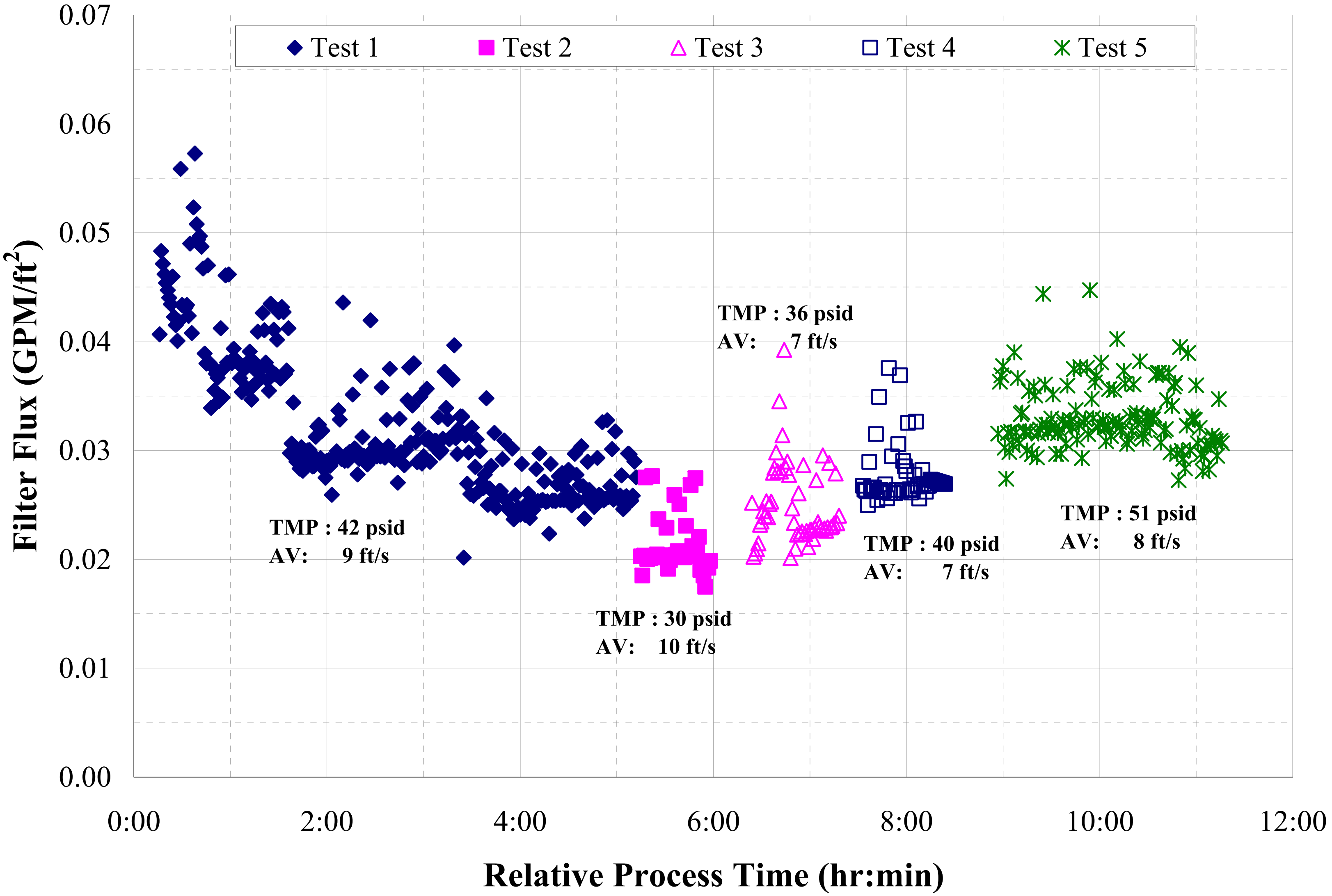


Figure 3.14. Group 3/4 Filter Flux Data for Low Solids Matrix (First Five Conditions)

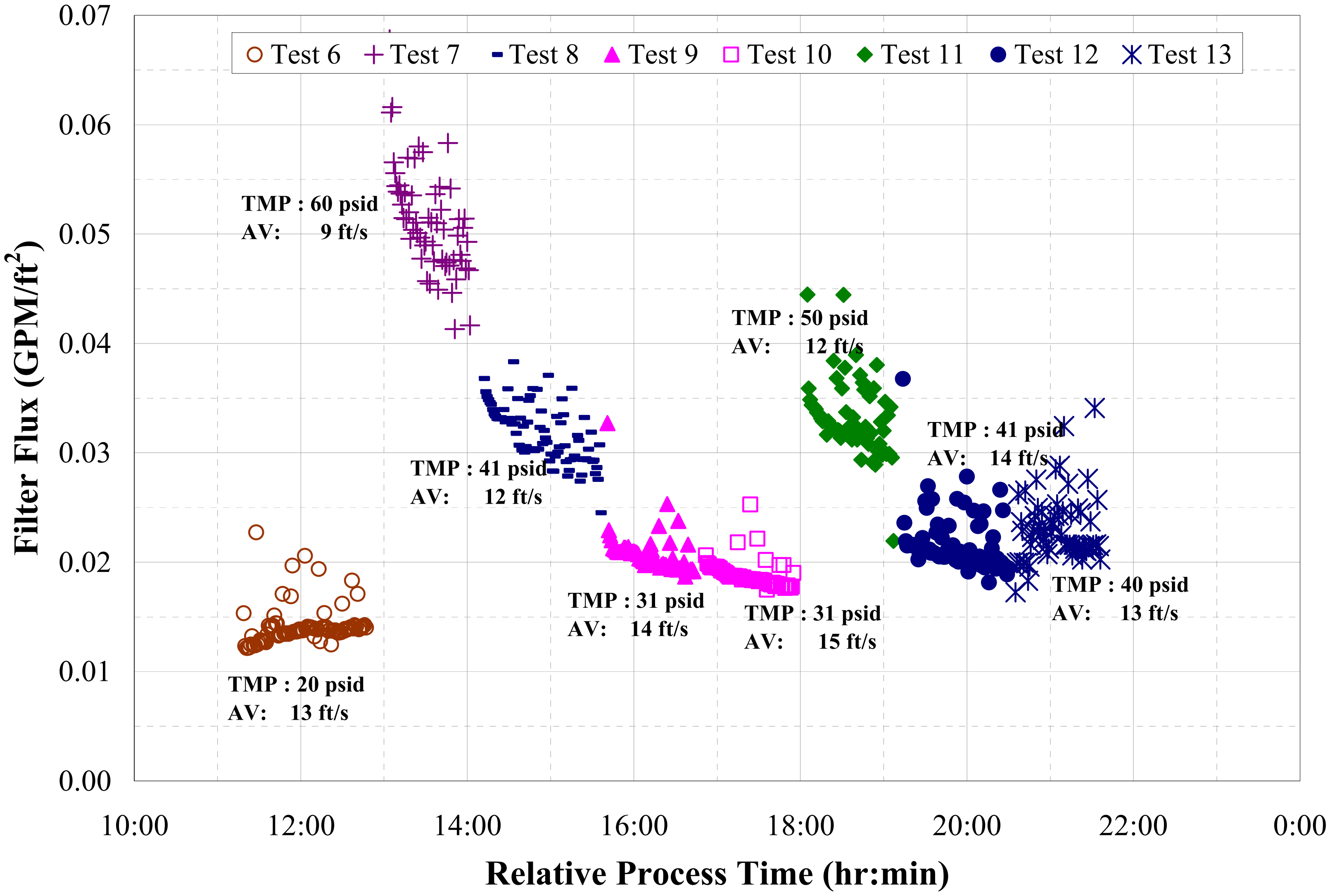


Figure 3.15. Group 3/4 Filter Flux Data for Low Solids Matrix (Last Eight Conditions)

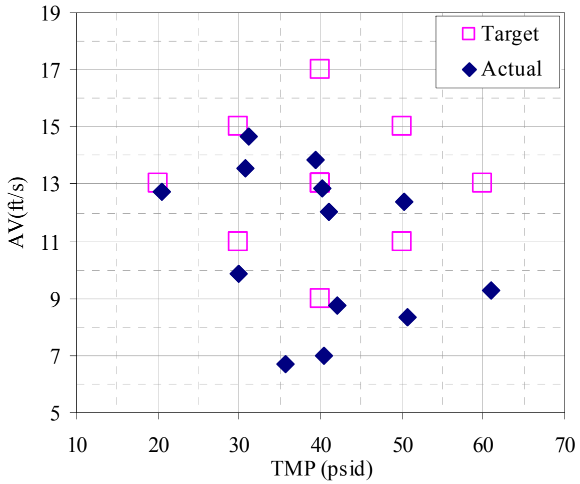


Figure 3.16. Group 3/4 Filter Test Matrix for Low-Solids

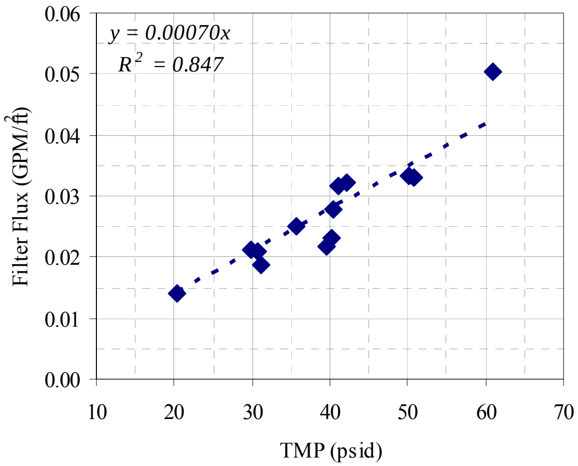


Figure 3.17. Group 3/4 Flux vs. TMP for Low-Solids

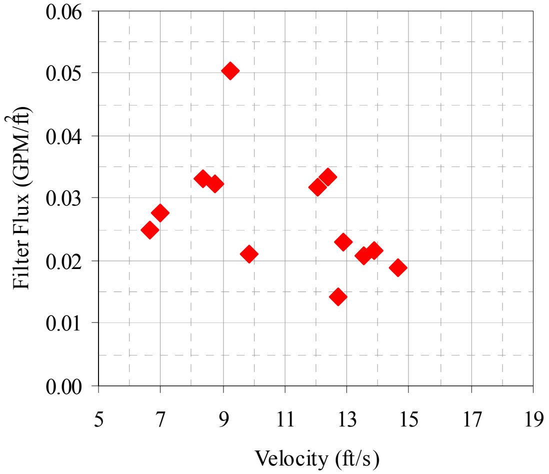


Figure 3.18. Group 3/4 Flux vs. AV for Low-Solids

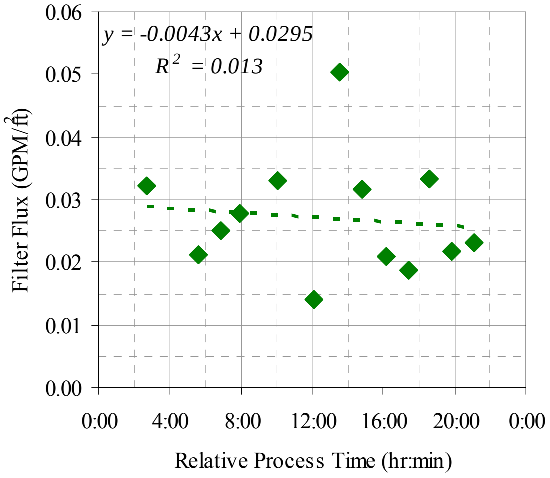
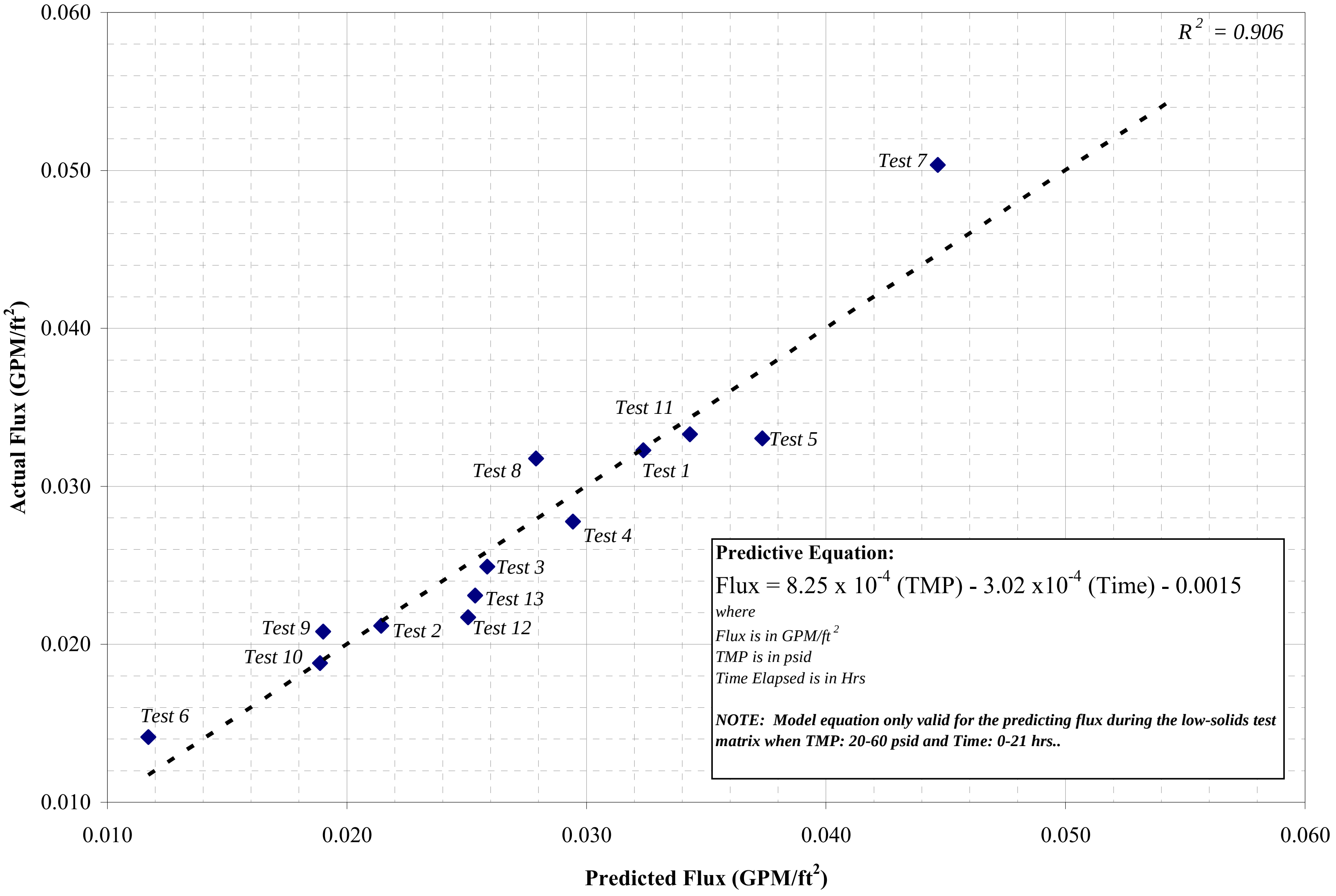


Figure 3.19. Group 3/4 Flux vs. Time for Leached-Solids



Predictive Equation:

Flux = 8.25 x 10^{-4} (TMP) - 3.02 x10^{-4} (Time) - 0.0015

where

Flux is in GPM/ft^2

TMP is in psid

Time Elapsed is in Hrs

NOTE: Model equation only valid for the predicting flux during the low-solids test matrix when TMP: 20-60 psid and Time: 0-21 hrs..

Figure 3.20. Group 3/4 Linear Correlation of Average Flux During Low Solids Matrix Test as Function of TMP and Median Operational Time of Test Conditions

3.4.2 Physical Characterization of Slurry after Low Solids Matrix

Once the low solids matrix was completed (Figure 3.21), the re-circulating slurry was re-sampled (from the loop drain valve) for physical characterization (Table 3.11). Measurements of the UDS concentration (11 wt%) were closer to the predicted UDS concentration (0.33kg ÷3.2 kg ≅ 10 wt%), indicating that most of the solids in the slurry were now completely suspended inside the slurry recirculation loop.

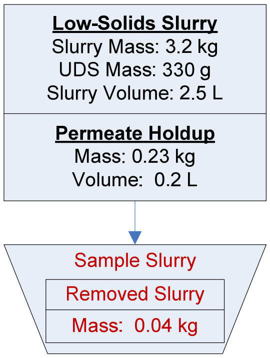


Figure 3.21. Group 3/4 Low Solids Slurry Preparation and Sampling

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.11. Physical Property Measurements of the Final Low Solids Slurry (Inside Slurry Circulation Loop)

Slurry Density (g/ml)	1.24
Supernate Density (g/ml)	1.15
Settled Solids (Vol %)	40%
Centrifuged Undissolved Solids (Wt %)	50%
Total Solids of the Slurry (Wt %)	29%
Dissolved Solids of the Supernate (Wt%)	20%
Undissolved Solids of the Slurry (Wt%)	11%

A slurry sample was taken after the low solids matrix test for particle size distribution measurements of a sheared sample to track particle size changes in the slurry. Figure 3.22 shows the PSD for the Group 3/4 sheared, low solids matrix sample as a function of pump speed before sonication. At 2000 RPM, the PSD is uni-modal with the peak around 5 µm. Particle sizes range from 0.2 µm - 30 µm, and a weak shoulder is present around 0.4 µm. At higher pump speeds the range increases up to 200 µm and the peak maximum shifts to around 8 µm. This is expected as higher pump speeds are capable of suspending larger particles and particle agglomerates that may settle out at lower pump speeds.

Figure 3.23 shows the particle size distribution as a result of applied sonication. This figure indicates particles > 30 µm may be mostly agglomerates that are disrupted during sonication. The 100 µm peak present before sonication does not exist during or after sonication. The relative peak maxima are shifted to larger volumes as a result of the agglomerate disruption. Similarities between the during and after sonication distribution suggest that the changes that occur during sonication are irreversible over the time frame of the post-sonication particle size analyses.

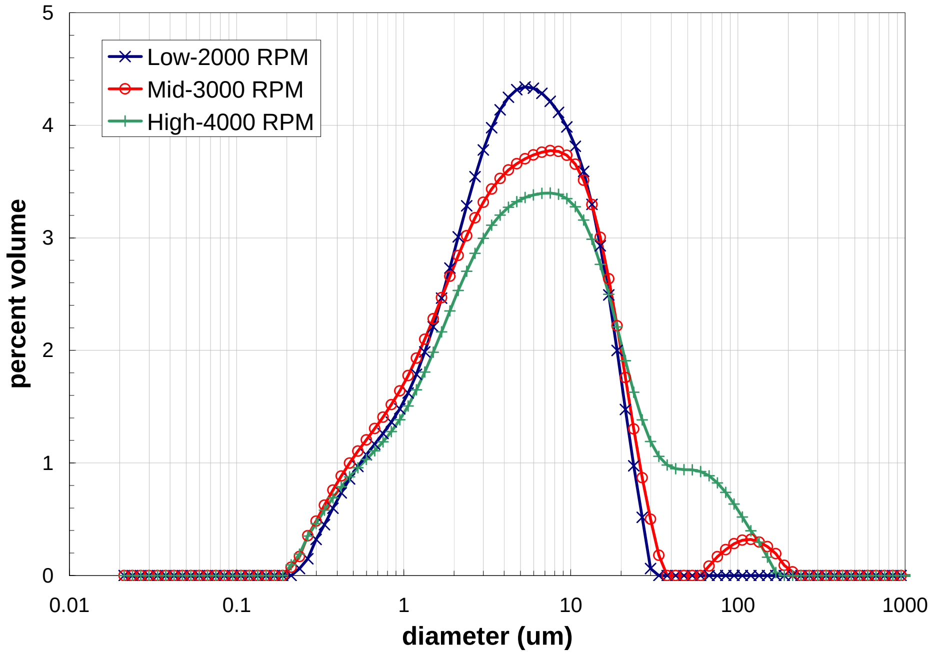


Figure 3.22. PSD of CUF Group 3/4 Low-Solids Slurry as a Function of Pump Speed

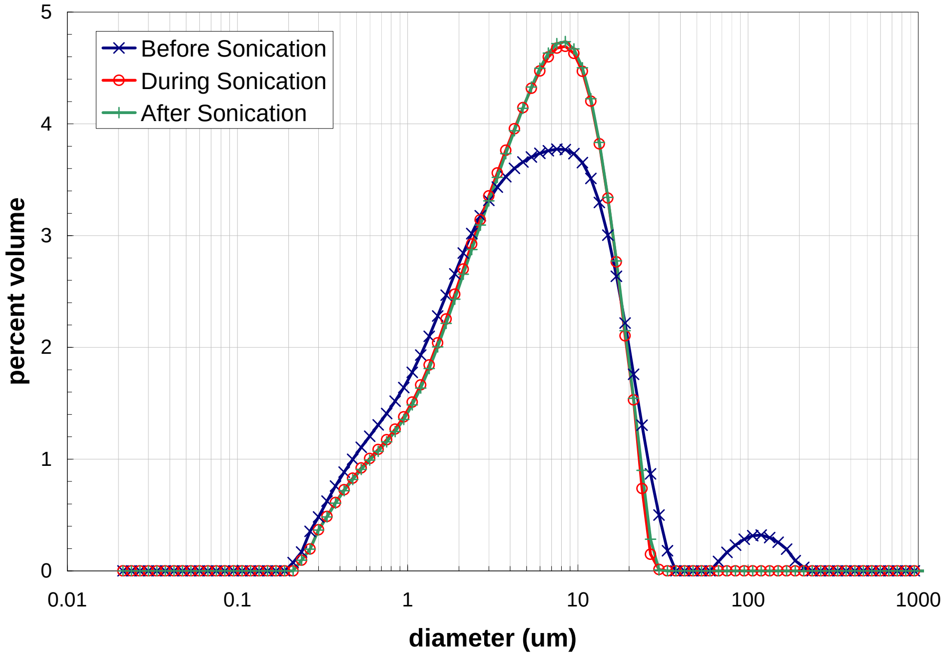


Figure 3.23. PSD of CUF Group 3/4 Low-Solids Slurry as a Function of Sonication

3.4.3 Dewatering of Group 3/4 Low-Solids Slurry

After completing the low solids filtration matrix test, the slurry was to be dewatered to a UDS concentration of approximately 20 wt%. An overview of the test activities and mass balance are shown in Figure 3.24 and Table 3.12. The dewatering occurred over a two hour interval where approximately 1.3 L of permeate was collected. During the two hours, the average filter flux was measured as 0.02 GPM/ft^2, as shown in Figure 3.25. Increasing the UDS concentration of the slurry to 19 wt% did not lead to a significant decrease (> 10%) in the slurry filter flux, which would demonstrate a filter cake dominant filtration regime.

However, a 10% decrease in the filter flux was observed over the two hour span of the test. This change was similar to the decreases observed during the low solids matrix tests (Section 3.4.1). Analysis of filter flux matrix testing results showed that filter flux was slowly decreasing with time, and was likely due to irreversible fouling of the filter. Examination of the filtration parameters showed changes in the filtration TMP and AV were likely responsible for the observed decrease in the filter flux. Figure 3.25 plots the percent change of TMP and AV from the target values over the course of the filtration. The plot demonstrates that decreases in TMP (and AV to an extent) corresponded to decreases to filter flux.

The decrease in the operational TMP and AV during dewatering was cause by the limitation of the system to pump the slurry at lower volume. As the volume decreased, the pumping efficiency of the slurry decreased due to the circulation pump pulling air into the pump. Because of solid suspension issues inside the slurry reservoir, the over head mixer was operating at a high speed to avoid plugging the inlet. This created vortexing at the center of the slurry that allowed air entrainment and reduced pump efficiency. The decrease in pumping efficiency are not believed to be caused by changes in the slurry rheology. Axial pressure drop across the filter did not exceed 2 psid/ft^2 (Accuracy of pressure instrumentation was ± 1 psig.) over the course of the dewatering.

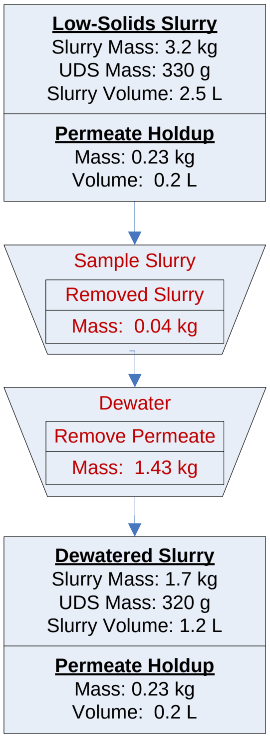


Figure 3.24. Group 3/4 Dewatering of Low Solids Slurry

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.12. Group 3/4 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%)	Measured Slurry UDS (wt%)
Low-Solids Slurry (after sampling)	----	3,330	320	3,100	10.3%	11%
Dewatered Slurry	-1,430	1,900	320	1,670	19.2%	

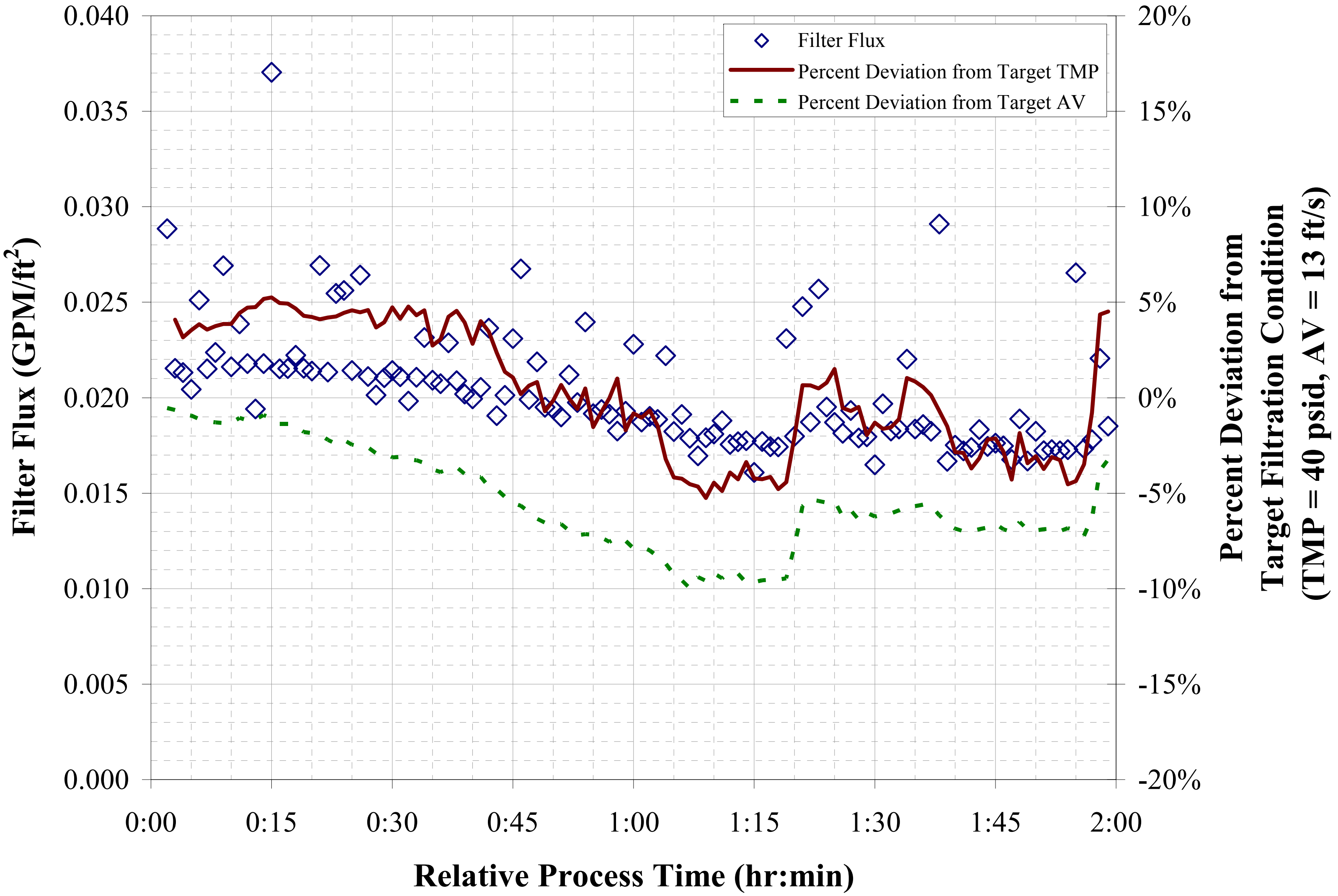


Figure 3.25. Dewatering of Group 3/4 Low-Solids Waste Slurry

3.4.4 High Solids Matrix

The high solids test matrix was performed after returning approximately 0.5L of permeate back to the CUF to increase the circulating volume of slurry to 2.1 liters (Figure 3.26). This was done to improve pumping efficiency by reducing air entrainment at the pump inlet, as experienced during the dewatering of the slurry. It prevented pump cavitation and achieved high axial velocities. The addition changed the estimated UDS concentration of the slurry from 19 wt% to 14 wt% (Table 3.13). The slurry was later sampled for physical properties and measured the UDS concentration as 13 wt% UDS (Section 3.5).

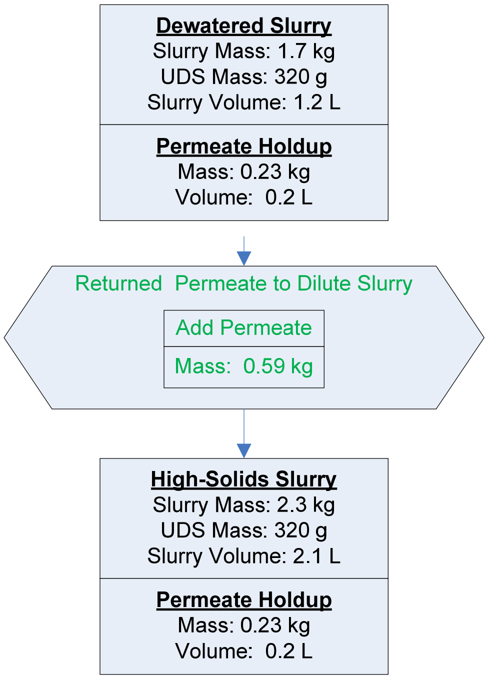


Figure 3.26. Group 3/4 High Solid Slurry

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.13. Mass Balance Summary of Diluting Dewatering Slurry for High Solids Matrix Test

Step	Change in Mass (g)	Total Mass (g)	Estimated Solid Mass (g)	Slurry Circulating Mass (g)	Estimated Slurry UDS (wt%)	Measured Slurry UDS (wt%)
Dewatered Permeate	----	1,900	320	1,670	19.2%	
Measured High Solids UDS	+590	2490	320	2260	14.2%	13%

Once the slurry was diluted to the test operating volume, the high solids test matrix was performed as outlined in Section 2.2.2. Table 3.14 summarizes the results of that testing while the filter flux results graphed over time are displayed in Figure 3.27. The average TMP and AV from each test condition is plotted against the target values in Figure 3.28. Despite efforts to improve the pump efficiency, the upper range of AV conditions (≥ 15 ft/s) was not achieved for the upper TMP range (≥ 40 psid) for the test matrix. It was likely that the overhead mixer speed needed to be decreased to reduce vortexing of the slurry. However, the risk of plugging the inlet of the pump was deemed too great to change the mixer speed.

The average filter flux from each test condition (Table 3.14) was plotted against TMP, and AV, as shown in Figure 3.29 and Figure 3.30. As with the low solids slurry, filter flux was found to be directly proportional to TMP while being independent to AV for the range tested. Filter flux was also plotted against the mean operational time for each test condition (Figure 3.31) to evaluate changes in filter resistance during the test. A statistically significant trend could not be found in Figure 3.31. While the scatter between points on the plot was too great to deciphered a significant relationship, comparison of the filter flux from the initial test condition (0.018 GPM/ft^2) to the final test condition (0.014 GPM/ft^2) demonstrated a 22% decrease in filter flux over the course of the test,

Modeling of the data using a least square fit method was then used to quantify the effects of TMP, AV, and processing time on filter flux. A linear fit equation with a R^2 correlation of 0.97 was developed using TMP and processing time as variables (Figure 3.32). Much like Figure 3.29, the model demonstrated that filter flux was significantly impacted by changes in the TMP. The model also showed that processing time had a similar negative effect on flux seen in the low solids matrix test and during the slurry dewatering operations. The model demonstrated the ratio of the TMP and time coefficients in the model (2.7:1) to be the same ratio seen in the low solid model. However, the change in the slurry concentration between the two test matrixes was relatively small, so this result was not unexpected.

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 3.14. 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 14 hour period that this model predicts.

Table 3.14. Average Operating Conditions and Permeate Flux for High Solids Matrix Test

Design Test Condition	Median Operation Time of Test[a] (hr)	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	1.73	25.2	41.4	12.9	17.6	0.018	1.70
2	4.01	25.1	30.5	10.9	13.2	0.013	1.46
3	5.21	26.0	30.4	14.8	12.4	0.012	1.96
4	6.32	26.0	49.4	12.6	22.8	0.022	1.78
5	7.38	25.1	48.8	11.1	23.3	0.023	1.73
6	8.43	25.3	40.6	12.9	17.0	0.017	1.86
7	9.53	25.1	39.3	8.9	17.2	0.017	1.33
8	10.63	25.7	40.1	13.5	16.0	0.016	1.93
9	11.85	25.1	20.5	13.1	6.7	0.007	1.66
10	13.13	25.4	58.4	11.3	26.5	0.026	1.77
11	14.31	25.3	40.1	12.9	14.4	0.014	1.71

(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.

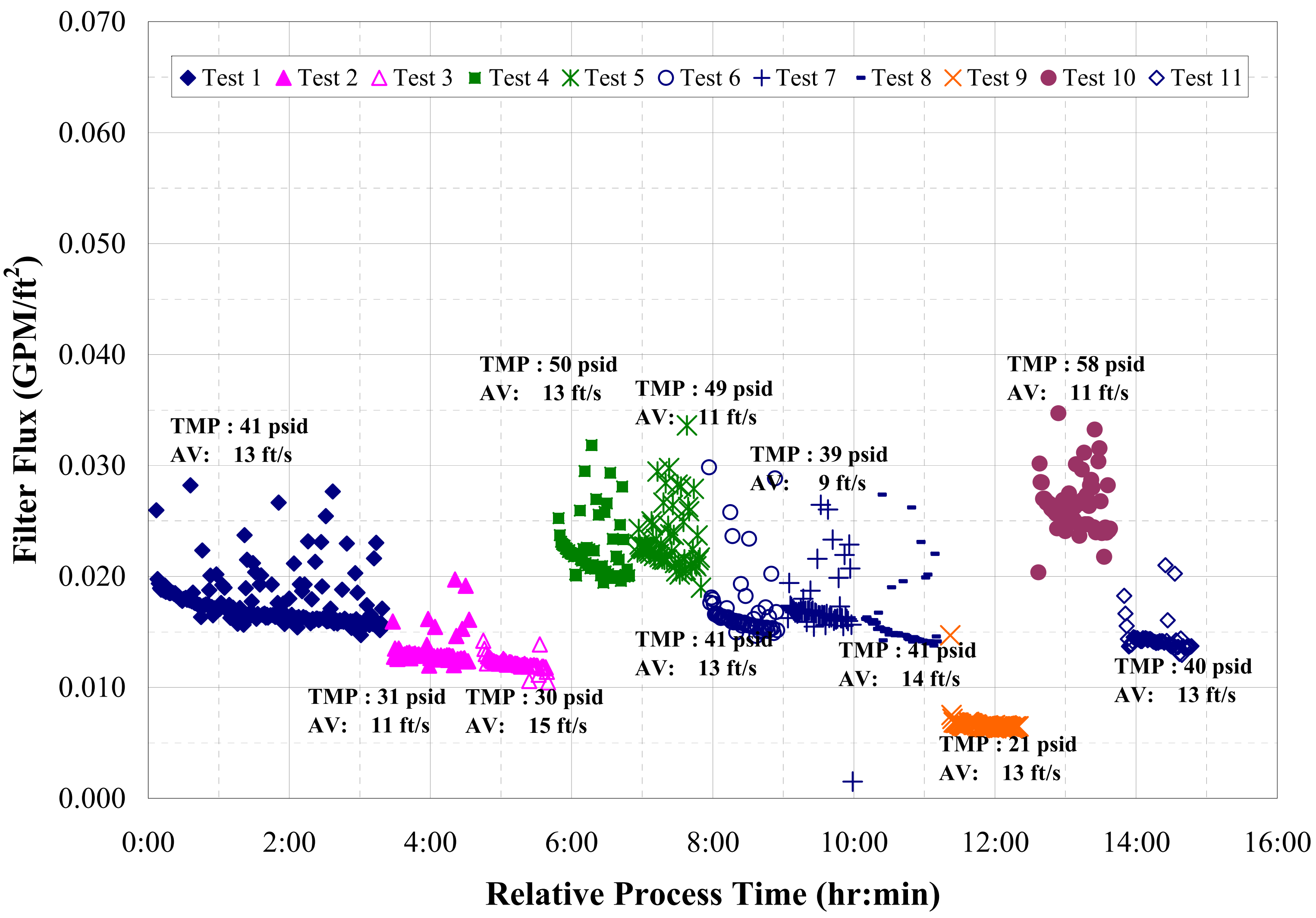


Figure 3.27. Group 3/4 Filter Flux Data for High Solid Matrix

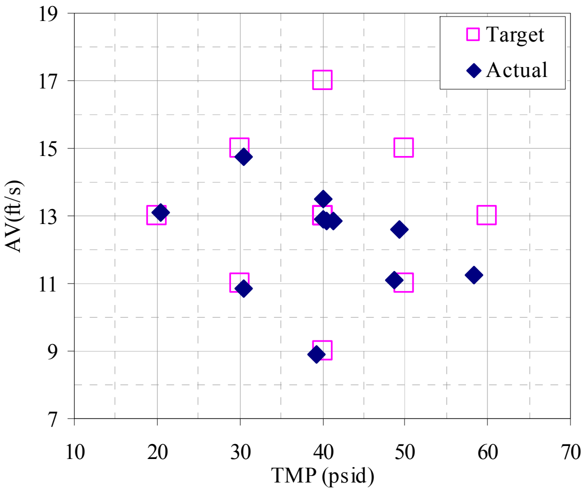


Figure 3.28. Group 3/4 Filter Test Matrix for High-Solids

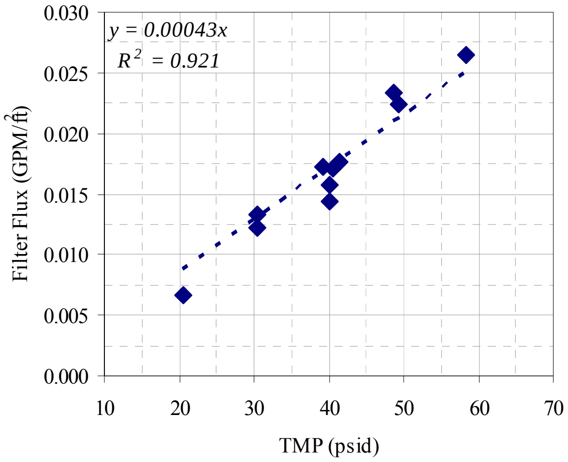


Figure 3.29. Group 3/4 Flux vs. TMP for High-Solids

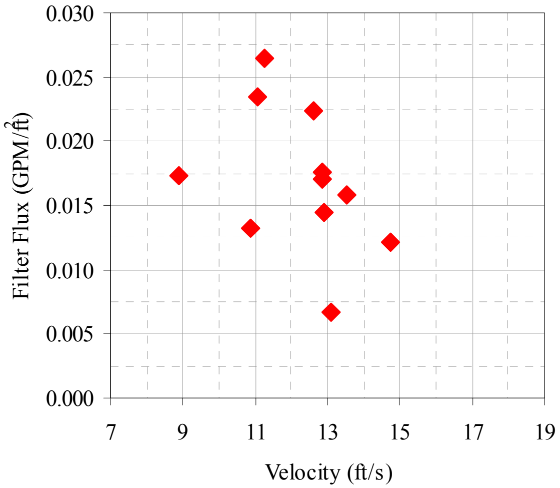


Figure 3.30. Group 3/4 Flux vs. AV for High-Solids

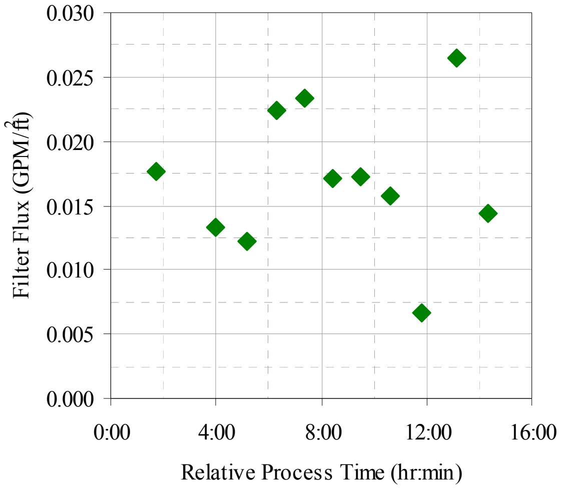
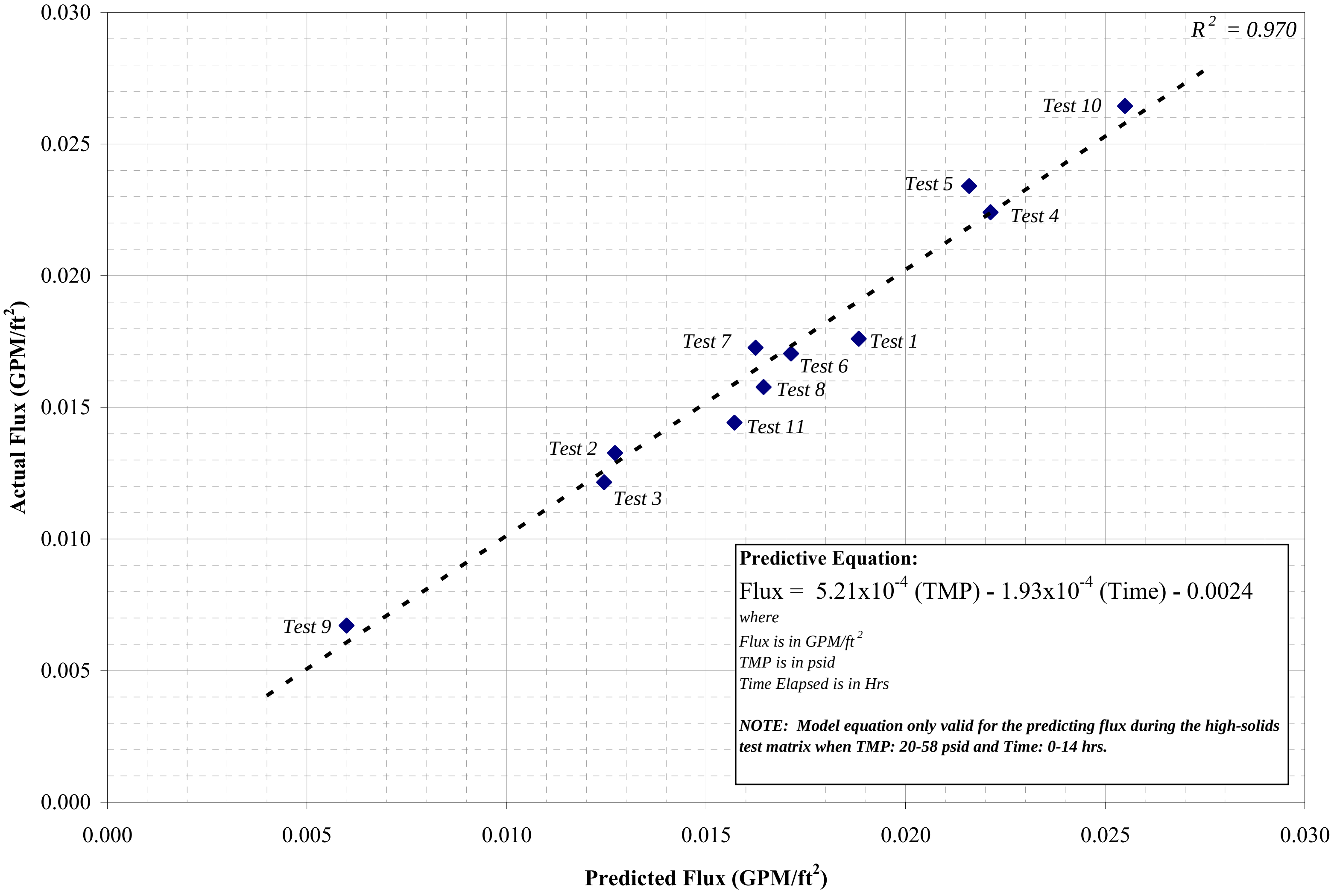


Figure 3.31. Group 3/4 Flux vs. Time for High-Solids



Predictive Equation:

Flux = 5.21×10^{-4} (TMP) - 1.93×10^{-4} (Time) - 0.0024

where

Flux is in GPM/ft^2

TMP is in psid

Time Elapsed is in Hrs

NOTE: Model equation only valid for the predicting flux during the high-solids test matrix when TMP: 20-58 psid and Time: 0-14 hrs.

Figure 3.32. Group 3/4 Linear Correlation of Average Flux During High Solids Matrix Test as Function of TMP and Median Operational Time of Test Conditions

3.5 High Solids Slurry Characterization

At the completion of the high solids test matrix, the slurry in the recirculation loop was sampled for physical and chemical analysis (Figure 3.33). Physical property measurements of the slurry samples are shown below in Table 3.15. The high solids slurry composition (including permeate hold-up) prior to caustic leaching is shown in Table 3.16 and an alternate composition calculation using slurry data is shown in Table 3.17. This slurry calculation method was used to calculate leach factors that can be compared to leach factors obtained using supernate analysis.

Comparison of the low solids slurry to the high solids slurry shows that the dewatering of the slurry caused an expected decrease in the total mass inventory of supernate anions present in the slurry. This anion decrease reduced the total slurry P (dewatered as PO_4), S (dewatered as SO_4), as well as Na and soluble Cs-137. Aside from the Cs, the radionuclides remained with the slurry in the solids.

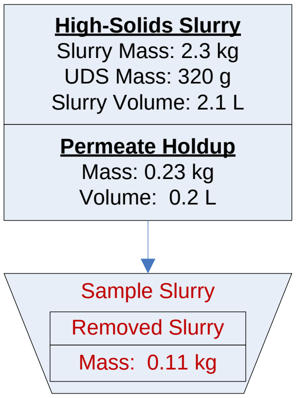


Figure 3.33. Group 3/4 Sampling of High Solids Matrix

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.15. Physical Property Measurements of the Group 3/4 High Solids Slurry (Inside Slurry Recirculation Loop)

Slurry Density (g/ml)	1.26
Supernate Density (g/ml)	1.16
Settled Solids (Vol %)	55%
Centrifuged Undissolved Solids (Wt %)	42%
Total Solids of the Slurry (Wt %)	31%
Dissolved Solids of the Supernate (Wt%)	21%
Undissolved Solids of the Slurry (Wt%)	13%

Table 3.16. Group 3/4 High Solids Slurry Inventory and Composition

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	2.49	2.17		0.32	
Wt% of Slurry	100%	87.0%		13.0%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	1.0E+02	2.7E+00	1.4E+03	9.9E+01	3.1E+05
B	5.6E-02	3.1E-02	1.7E+01	2.6E-02	7.9E+01
Bi	3.4E-01	< 7.E-3	< 4.E+0	3.4E-01	1.0E+03
Cr	4.7E-01	1.1E-01	5.8E+01	3.7E-01	1.1E+03
Fe	3.1E+00	3.2E-03	1.7E+00	3.1E+00	9.6E+03
Mn	4.5E-01	1.5E-04	7.8E-02	4.5E-01	1.4E+03
Na	1.4E+02	1.3E+02	6.8E+04	9.0E+00	2.8E+04
P	1.2E+01	6.6E+00	3.6E+03	5.6E+00	1.7E+04
S	1.9E+00	1.4E+00	7.3E+02	5.8E-01	1.8E+03
Si	2.4E+00	3.6E-02	1.9E+01	2.3E+00	7.2E+03
Zn	1.7E-01	2.4E-03	1.3E+00	1.7E-01	5.1E+02
Zr	1.2E+00	< 3.E-4	< 1.E-1	1.2E+00	3.8E+03
U	2.0E+00	5.8E-02	3.1E+01	2.0E+00	6.0E+03
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	1.0E+01	1.0E+00	5.5E-04	9.0E+00	2.8E-02
Cs-137	2.3E+04	1.1E+04	6.0E+00	1.1E+04	3.5E+01
Eu-154	8.1E+01	< 6.E-1	< 3.E-4	8.1E+01	2.5E-01
Eu-155	3.0E+01	< 3.E+0	< 2.E-3	3.0E+01	9.2E-02
Am-241	2.7E+02	< 2.E+0	< 9.E-4	2.7E+02	8.4E-01
Gross Alpha	4.5E+02	2.2E+00	1.1E-03	4.4E+02	1.4E+00
Gross Beta	1.1E+05	1.1E+04	6.1E+00	9.8E+04	3.0E+02
Sr-90	4.6E+04	2.7E+02	1.4E-01	4.6E+04	1.4E+02
Pu-239+240	1.7E+02	1.1E+00	6.0E-04	1.7E+02	5.1E-01
Pu-238	2.0E+01	1.1E-01	5.9E-05	2.0E+01	6.1E-02
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	µg/ml	**[M]**	**g**	**µg/g**	**g**
F	4.7E+02	2.5E-02	8.9E-01	2.8E+03	9.2E-01
C_2O_4	3.4E+03	3.8E-02	6.3E+00	8.8E+03	2.8E+00
NO_2	1.2E+04	2.6E-01	2.2E+01	2.6E+04	8.3E+00
NO_3	1.0E+05	1.7E+00	2.0E+02	2.3E+05	7.4E+01
SO_4	< 8.E+0	< 8.E-5	4.3E+00	4.7E+03	1.5E+00
PO_4	1.1E+04	1.2E-01	2.1E+01	4.2E+04	1.3E+01
OH	4.9E+03	2.9E-01	9.2E+00		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-167). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI601-G4-A (ASO ID 08-01365) 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. Leached Solid Fraction were calculated using analytical results from water leach sample TI601-G4-6, (ASO ID 08-01381).

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

Table 3.17. Group 3/4 High-Solids Slurry Composition Based on ICP-OES/Radionuclide Characterization

Slurry Prep Method	ICP-OES Analytes	Dry Slurry[(a)]	Supernate[(b)] (µg/mL)	Dry Solids[(c)] (µg/g)
HF Assisted Acid Digestion, and KOH Fusion	Al	133,750	1,440	352,322
	B	188	16.5	408
	Bi	794	<3.7E+0	2,119
	Cd	[9.05]	[2.2]	[11.3]
	Cr	696	58.1	1,532
	Fe	5,848	[1.7]	15,769
	K	727	436	-639
	Mn	568	[0.078]	1,533
	Na	182,000	68,100	85,043
	Ni	372	8.32	953
	P	13,100	3,550	14,181
	S	2,035	728	1,150
	Si	[5500.0]	19.2	[14726.62]
	Sr	27.0	[0.068]	72.5
	U	3,798	[31]	10,062
	Zn	281	[1.3]	751
	Zr	2,018	<1.3E-1	5,443
	Ag	[4.05]	<2.6E-1	[9.4]
	As	200.00	<5.2E+0	508.42
	Ba	30.9	[0.25]	81.9
	Be	1.043	<6.3E-3	2.776
	Ca	549	[7.4]	1,437
	Ce	[25]	<1.2E+0	[59]
	Co	[5.5]	[0.35]	[12.75]
	Cu	48.3	[0.27]	128.8
	La	[17]	<3.4E-1	[45]
	Li	[14]	[0.46]	[34]
	Mg	176	<2.8E-1	473
	Mo	[20]	[2.5]	[39]
	Nd	[34]	<6.6E-1	[87]
	Pb	1,198	[38]	3,005
	Ru	[11]	[1.2]	[23]
	Th	[74]	<1.2E+0	[191]
	Ti	32.6	<5.2E-2	87.6
	Tl	140.00	<4.6E+0	350.15
	V	12.5	1.46	25.1
	W	[28]	[5.5]	[41]
	Y	[4.3]	<5.4E-2	[11.28]

Table 3.17 (Cont'd)

Slurry Prep Method	ICP-OES Analytes	Dry Slurry[a]	Supernate[b] (µg/mL)	Dry Solids[c] (µg/g)
KOH Fusion	Co-60	1.29E-2	5.54E-4	3.16E-2
	Cs-137	2.58E+1	5.99E+0	3.38E+1
	Eu-154	1.07E-1	< 3.E-4	2.87E-1
	Eu-155	4.69E-2	< 2.E-3	< 1.E-1
	Am-241	3.70E-1	< 9.E-4	9.94E-1
	Sr-90	6.05E+1	1.43E-1	1.62E+2
	Pu-239/240	2.16E-1	5.97E-4	5.78E-1
	Pu-238	1.96E-2	5.91E-5	5.25E-2

(a) Test sample TI601-G4-A, ASO ID 08-01365
(b) Test sample TI601-G4-6, ASO ID 08-01381
(c) Calculated using results from TI601-G4-A and TI601-G4-6
Note: Analytes in italics were measured opportunistically. Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

Samples were taken for PSD measurements of the high solids slurry. Figure 3.34 shows the PSD for the Group 3/4 high-solids matrix sample as a function of pump speed before sonication. The particle size distribution ranges from 0.2 µm - 200 µm with a peak centered around 5 µm and a weak shoulder around 0.5 µm. There is also a shoulder or separate peak at diameters > 40 µm. These particles have an increasing population as the pump speed increases. This is expected as higher pump speeds are capable of suspending larger particles and particle agglomerates that may settle out at lower pump speeds.

Figure 3.35 shows the particle size distribution as a result of applied sonication. Sonication shifts the range from 0.2 µm - 200 µm to 0.2 µm - 30 µm, eliminating the secondary peak centered around 120 µm. The primary peak is shifted from 5 µm to 7 µm, which is likely a result of the disruption of >30 µm agglomerates. Agglomerate recovery is observed after sonication, as the range extends to 200 µm, although the peak population remains centered around 7 µm.

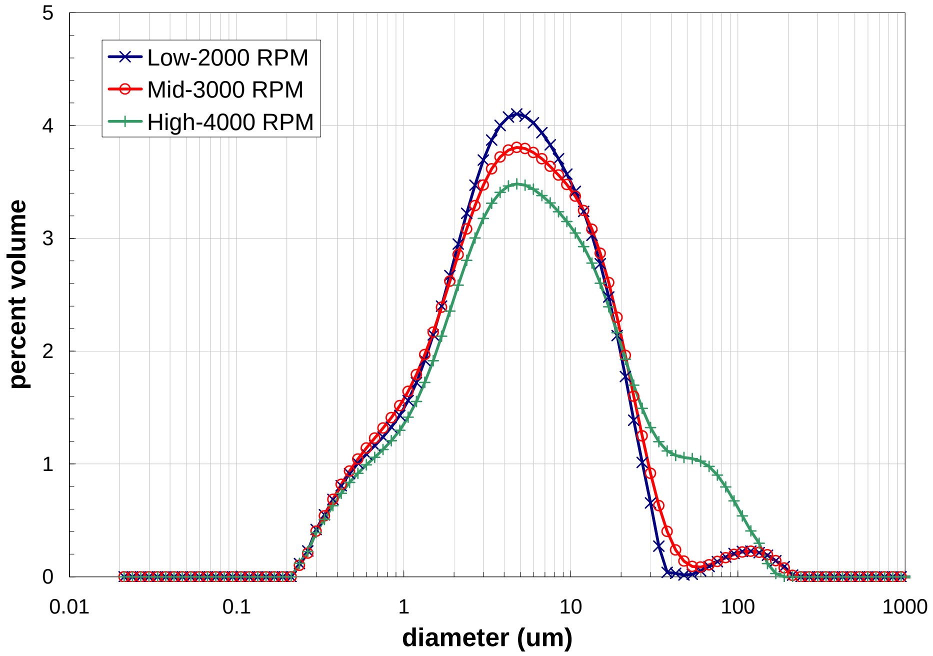


Figure 3.34. PSD of CUF 3/4 High Solids Matrix as a Function of Pump Speed

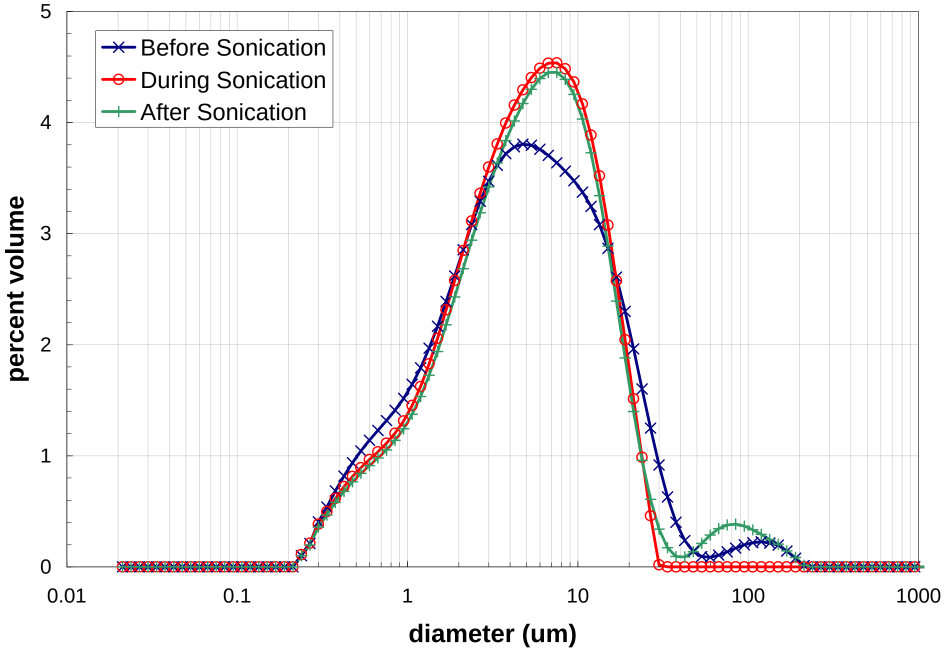


Figure 3.35. PSD of CUF 3/4 High Solids Matrix as a Function of Sonication

The flow curves for the high solids matrix are similar to those for the source material. Figure 3.36 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 2 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 three minute shearing step performed immediately before flow curve measurement.

Flow curve data indicate that slurry rheology tends to become weaker at higher temperatures. Although changes in the slurry yield stress are small and difficult to determine given the ±0.5 Pa limit of instrument accuracy, the slope of the flow curve data does appears to decrease with increasing temperature (indicating a lower slurry consistency at high temperature). The stress response of the slurry at 25°C and 40°C is similar such that there is some overlap between the two data sets as a result of measurement noise. Overall, the majority of 40°C flow curve data fall below those at 25°C. Flow curve data at 60°C show a significantly reduced stress response relative to the lower test temperatures. The decrease in slope and reduced stress response are consistent with a reduction in rheology at higher temperatures.

Table 3.16 summarizes the best fit Bingham-Plastic and Casson parameters for the high solids slurry. Both models provide reasonable fits with the data. While the Casson model provides a better description of the flow curve (especially over 0-100 s^{-1}), it tends to overstate shear thinning at shear rates beyond 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.

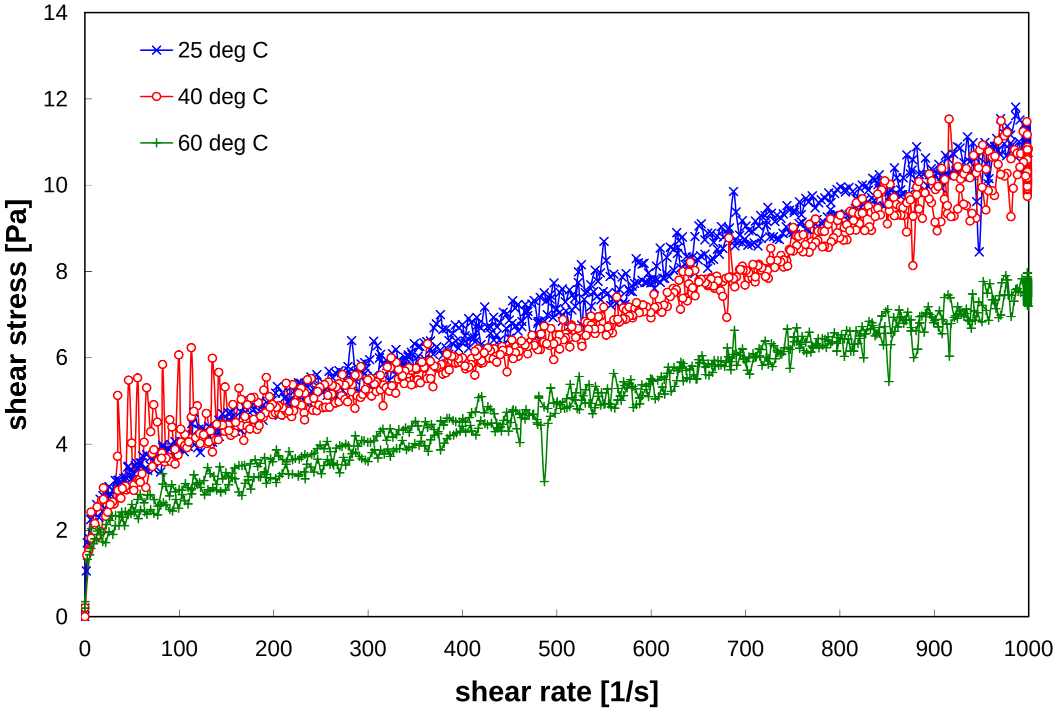


Figure 3.36. Flow Curves for Group 3/4 CUF High Solids Slurry

Table 3.18. Results of Fitting Analysis for the Group 3/4 CUF High Solids Matrix

Model	Temperature [°C]	Range	Yield Stress [Pa]	Consistency [mPa·s]	R
Bingham-Plastic	25 (1 of 2)	100-1000 s^{-1}	3.1	7.1	1.00
	25 (2 of 2)	100-1000 s^{-1}	3.4	7.6	0.99
	40	100-1000 s^{-1}	3.2	7.0	0.99
	60	100-1000 s^{-1}	2.3	5.2	0.99
Casson	25 (1 of 2)	0-1000 s^{-1}	1.5	3.8	1.00
	25 (2 of 2)	0-1000 s^{-1}	1.7	4.0	0.99
	40	0-1000 s^{-1}	1.7	3.5	0.98
	60	0-1000 s^{-1}	1.2	2.7	0.99

3.6 Caustic Leaching/Washing

After completing the filtration, sampling, and rheological testing of the high solids slurry, the slurry was drained from the system and prepared for caustic leaching (Figure 3.37.). 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 drained and recovered from the system, the slurry reservoir was isolated from the slurry loop. At this point, all the recovered slurry, permeates, and caustic solutions were placed into the reservoir for caustic leaching, as outlined in the right column of Figure 3.1. It is estimated that 0.16 kg of material loss occurred due to transfer operations. This estimate came from measuring the mass of slurry, permeate, and caustic recovered from the CUF and the mass added back to the slurry reservoir. This difference was 0.16 kg. The activities involved in this process were:

- Batch caustic leaching of the slurry for removing aluminum from undissolved solids in the slurry.
- Dewatering a majority of the leached slurry supernate from the slurry solids.
- Perform a filtration matrix test using the dewatered leached slurry, as described in Section 2.2.2.
- Batch washing of the caustic-leached slurry and dewatering of the diluted supernate afterwards. Three total wash solutions were added to the slurry to remove aluminum from the slurry.

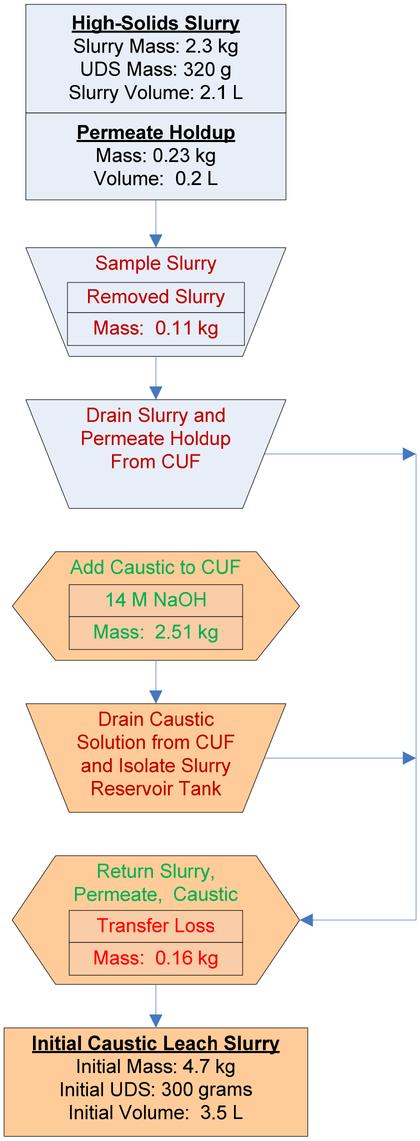


Figure 3.37. Group 3/4 Preparation for the Caustic Leach

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

3.6.1 Caustic Batch Leaching Results

After the slurry, permeate, and caustic was placed in the slurry reservoir, the lid for the slurry reservoir was placed on the tank and the overhead mixer was started (Figure 3.38). The heat controller was then started to ramp the slurry temperature to 100°C (-10°C /+5°C) over a 5.3 hour period. After the heat ramp was completed, this temperature was held for eight hours, and then cooled at a controlled rate to the hot cell ambient temperature over a 12 hour period.

Slurry samples were collected during the batch leach, and filtered for supernate ICP analysis (Table 3.19). The slurry was sampled twice during the heat ramp and at the 0, 4, and 8 hour points during the leach. Analysis of the filtered supernate indicated that by the end of the heat ramp the apex of gibbsite dissolution had occurred; 94% of the solid aluminum had leached into solution (Figure 3.39). Similar to the parametric testing (WTP-RPT-167) that saw marked increases in dissolution at 80°C, the CUF leach showed the bulk of the dissolution happening somewhere between 40°C - 70°C. Figure 3.40 shows the concentrations of the major analytes during the evolution of the heat ramp and caustic leach.

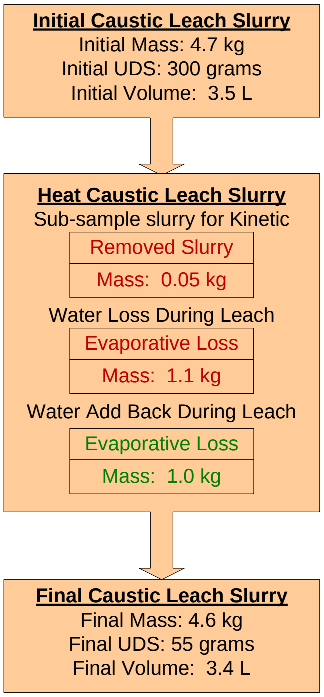


Figure 3.38. Group 3/4 Caustic Leach

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

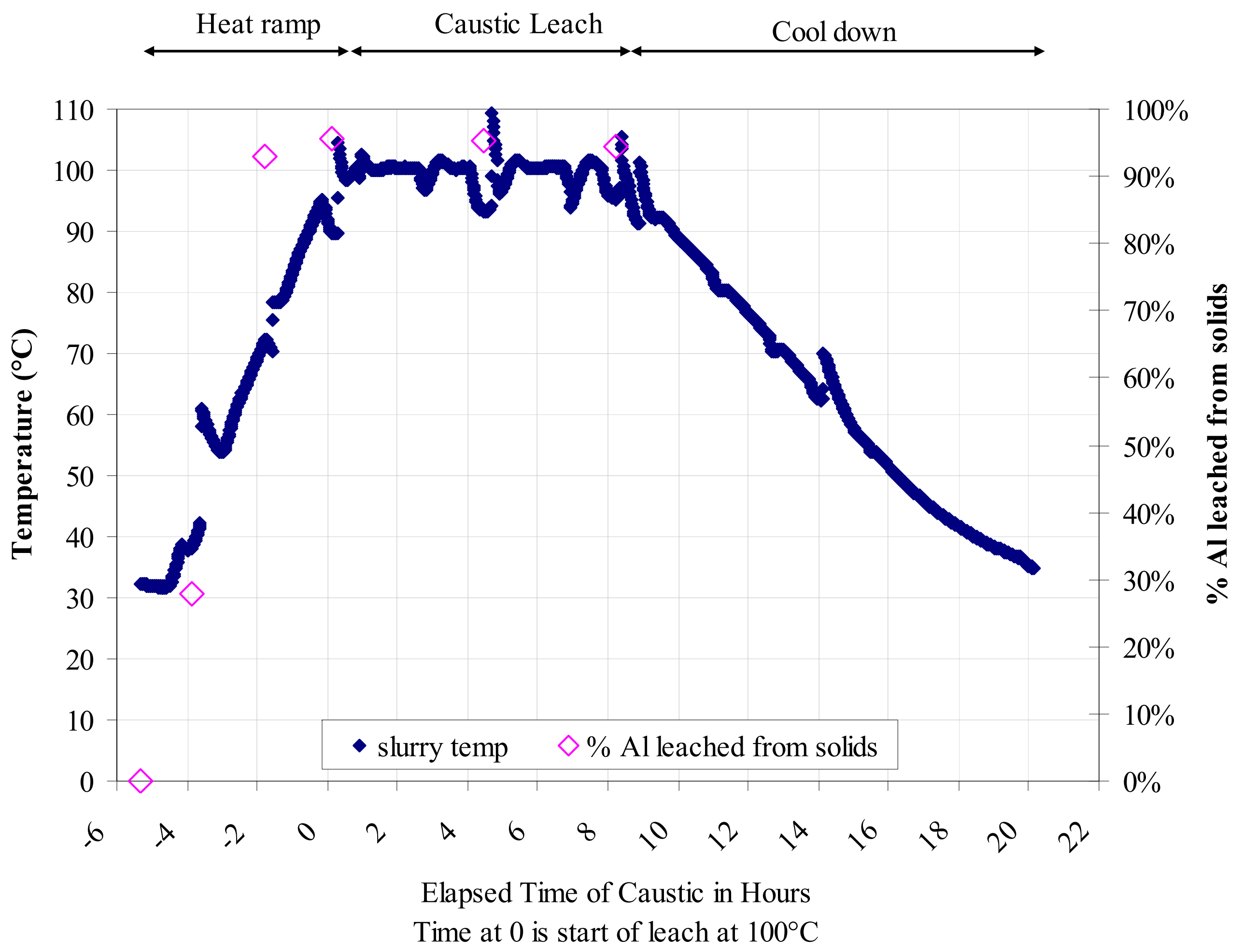


Figure 3.39. Group 3/4 Temperature Profile/Aluminum Leach Factor during Caustic Leaching

Table 3.19. Concentration of Major Analyte Components of Filtered Caustic Leach Samples, Corrected for Sample Evaporation

	start of heat up[(a)] (32°C)	1 hour heat up[(b)] (38°C)	3 hour heat up[(c)] (72°C)	0 hour leach[(d)] (90°C)	4 hour leach[(e)] (93°C)	8 hour leach[(f)] (95°C)
	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml
Al	6.5E+02	7.8E+03	2.4E+04	2.5E+04	2.5E+04	2.5E+04
B	7.5E+00	1.2E+01	< 3.E+0	8.8E+00	1.8E+01	1.8E+01
Bi	< 2.E+0	2.6E+01	3.6E+01	6.2E+01	5.2E+01	6.6E+01
Cr	2.6E+01	4.2E+01	4.9E+01	5.5E+01	6.0E+01	6.4E+01
Fe	7.7E-01	3.7E+01	4.9E+01	5.7E+01	4.7E+01	6.6E+01
K	2.0E+02	5.7E+02	4.6E+02	5.1E+02	4.7E+02	4.8E+02
Mn	3.5E-02	5.5E+00	1.3E+01	1.8E+01	1.1E+01	1.9E+01
Na	3.1E+04	1.8E+05	1.8E+05	1.8E+05	1.8E+05	1.8E+05
P	1.6E+03	5.1E+02	1.8E+03	5.5E+02	1.3E+03	2.0E+03
S	3.3E+02	3.8E+02	4.0E+02	3.6E+02	4.0E+02	4.0E+02
Si	8.7E+00	6.5E+01	9.4E+01	1.2E+02	9.3E+01	8.5E+01
U	1.4E+01	1.7E+01	< 2.E+1	2.2E+01	< 2.E+1	2.1E+01
Zn	5.9E-01	1.5E+01	4.0E+01	4.2E+01	4.4E+01	4.4E+01
Zr	6.1E-02	4.2E+00	1.1E+01	8.3E+00	1.1E+01	1.1E+01
	[M]	[M]	[M]	[M]	[M]	[M]
OH	0.13	6.6	5.3	5.6	5.7	6.0

(a) Predicted concentrations from mixing caustic addition (14M) with slurry supernate. Composition of supernate based on sample TI601-G4-A, ASO ID 08-01365.

(b) Composition based on sample TI601-G4-C1, ASO ID 08-01369. Values divided by 1.02 to account for evaporative loss of sample.

(c) Composition based on sample TI601-G4-C2, ASO ID 08-01370. Values divided by 1.10 to account for evaporative loss of sample.

(d) Composition based on sample TI601-G4-C3, ASO ID 08-01371. Values divided by 1.06 to account for evaporative loss of sample.

(e) Composition based on sample TI601-G4-C4, ASO ID 08-01372. Values divided by 1.16 to account for evaporative loss of sample.

(f) Composition based on sample TI601-G4-C5, ASO ID 08-01373. Values divided by 1.07 to account for evaporative loss of sample.

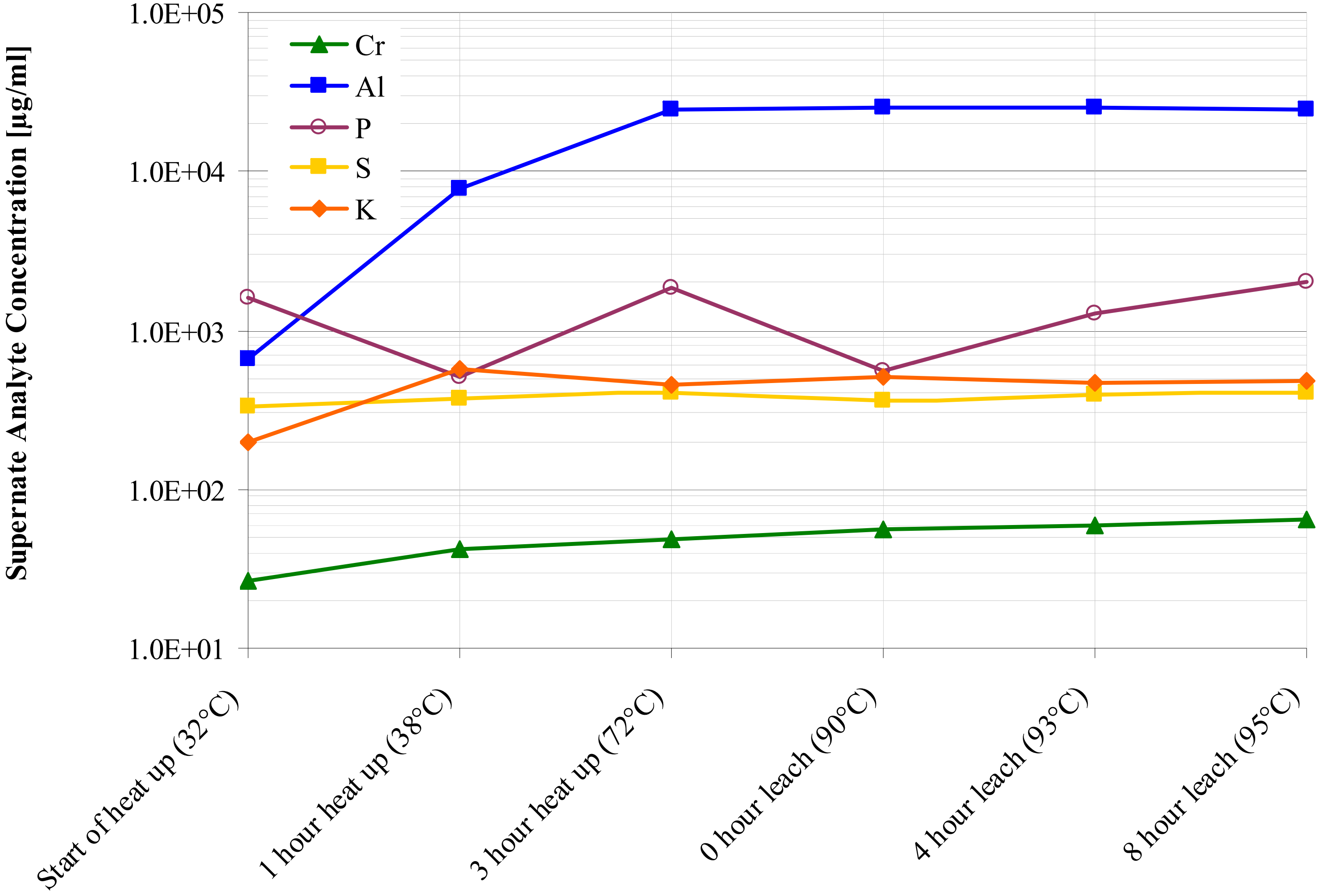


Figure 3.40. Concentration of Al, Cr, P, S and K during Caustic Leach of Group 3/4 Slurry

3.6.2 Caustic Leach Dewatering

After the cool down period of the batch leach was complete, the valves isolating the slurry reservoir from the slurry recirculation loop were opened. The circulation pump was then turned on allowing slurry to recirculate through the filter and allowing permeate to exit the filter and recycle back to the slurry reservoir. Once the density, measured by the permeate mass flow meter was stable and the temperature of the slurry was at 25°C, the back-pulse chamber was filled with permeate, and two back pulses were performed on the filter.

At this point, filter permeate was directed away from the slurry reservoir and captured in a sample container to dewater the caustic leached slurry (Figure 3.41). The dewatering occurred at the standard operating conditions (TMP = 40 psid, AV = 13 ft/s) over a three hour period. Approximately 1.9 liters of slurry supernate was removed. Figure 3.42 is a plot of the filter flux for the dewatering step. The permeate flux decreased from 0.015 GPM/ft^2 to 0.008 GPM/ft^2. The lower flux value was due to the higher density and viscosity of the caustic leaching solution (see Table 3.20). The results indicate that viscosity effects may dominate for this waste type.

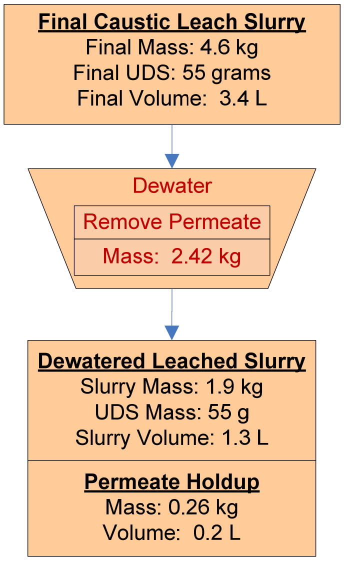


Figure 3.41. Group 3/4 Dewatering Caustic Leached Slurry

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

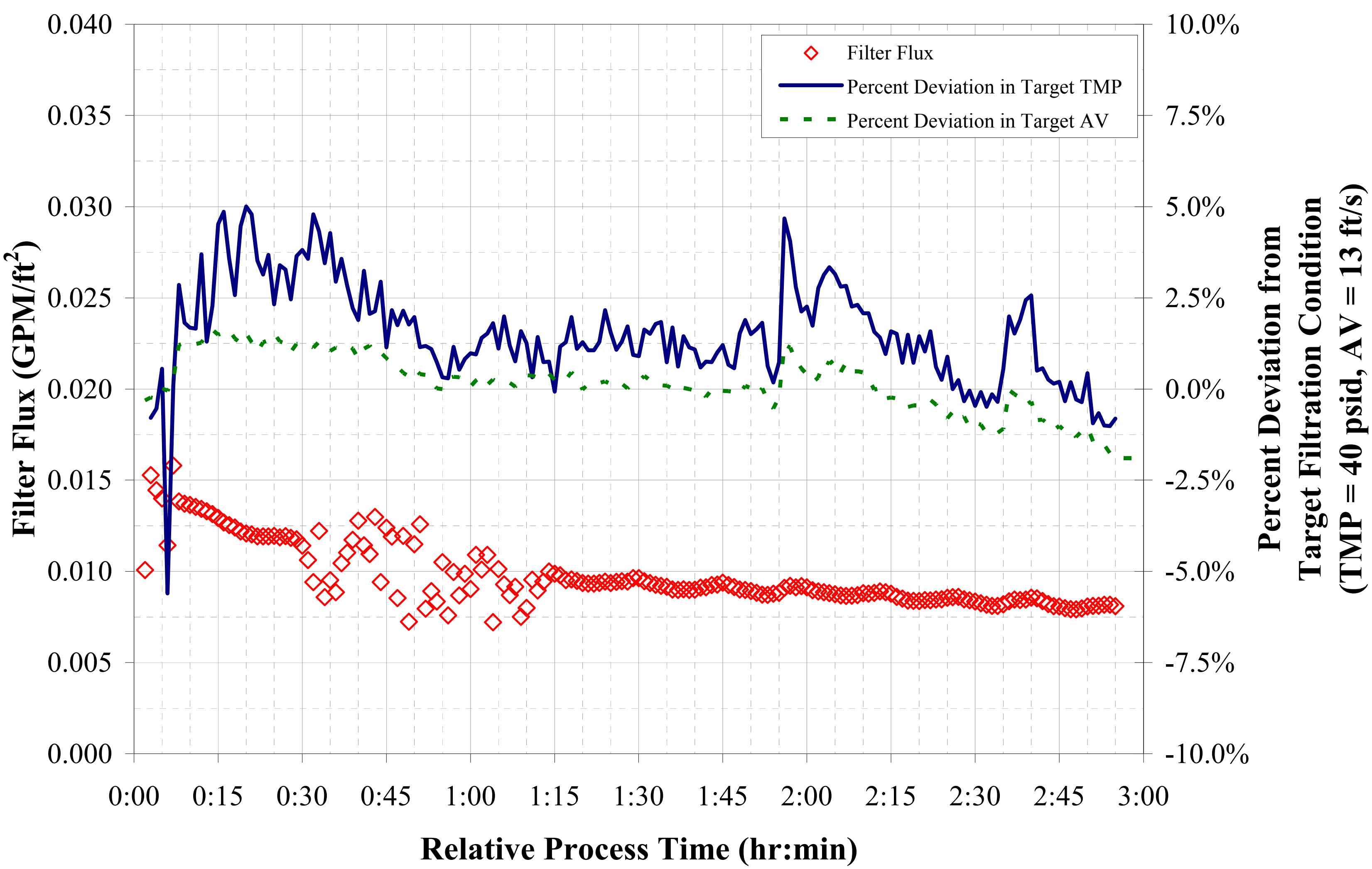


Figure 3.42. Group 3/4 Dewatering Caustic Leached Slurry at Standard Conditions

Table 3.20. Group 3/4 Comparison of Slurry Supernate Attributes to Filter Flux

Slurry Condition	Supernate Density (g/mL)	Supernate Viscosity at 25°C (mPa-s)	Filtered Supernate Composition			Nominal filter flux at standard condition (GPM/ft^2)
			[Na] (M)	[OH] (M)	[Al] (M)	
Pre-Leached Slurry (13 wt% UDS)	1.16	1.4-1.6	3.0	0.3	0.05	0.020
Leached Slurry (< 5 wt% UDS)	1.29	8.2	7.8	5.6	089	0.010

3.6.3 Leached Slurry Test Matrix

After dewatering the caustic leached slurry, a filter matrix test of 11 conditions was performed (Figure 3.43). The results of this test matrix are outlined in Table 3.21 and Figure 3.44. The flux ranged from 0.003 GPM/ft^2 to 0.009 GPM/ft^2. The filter flux at the standard condition (TMP = 40 psid and AV = 13 ft/s) decreased over the course of the test with an initial result of 0.007 GPM/ft^2 and a final flux of 0.005 GPM/ft^2.

The average filter flux from each test condition (Table 3.21) was plotted against TMP and AV, and shown in Figure 3.46 and Figure 3.47. As with the previous test matrix results, filter flux was found to be linearly proportional to the filter flux (Figure 3.46), while was found to be independent of axial velocity (Figure 3.47). The expected UDS concentration after leaching was only 3 wt%, so the results were expected.

Filter flux was also plotted against the median operational time of the test condition (Figure 3.48) observe changes in filter resistance during the test. Filter flux was found to decrease over the course of the testing, indicating that an irreversible fouling mechanism was still in effect after leaching.

Modeling of the data using a least square fit method was then used to quantify the effects of TMP, AV, and the median operational time on filter flux. A linear fit equation with a R^2 correlation of 0.90 was developed using TMP and processing time as variables (Figure 3.49). As the previous analysis indicated, filter flux was linearly proportional to TMP. However, there was still significant, but that cessing time was also now more significant. To compare to the previous test results, the ratio of the coefficients for TMP and Time was 2.7:1 for the low and high solids matrix tests. For the leach slurry, the coefficient ratio was 0.67:1. Axial velocity was once again shown not to be significant, but this is most likely due to the UDS concentration being too low for filter cake resistance to be significant (< 5 wt%).

During development of the linear model, a positive offset was created. Therefore, this model does not predict a zero filter flux when the TMP is zero. This demonstrates that the input to these models must be bound by the range of TMP used in this filter test, shown in Table 3.21. 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 15 hour period that this model predicts.

Dewatered Leached Slurry
Slurry Mass: 1.9 kg
UDS Mass: 55 g
Slurry Volume: 1.3 L

Permeate Holdup
Mass: 0.26 kg
Volume: 0.2 L

Figure 3.43. Group 3/4 Leached Slurry used for Test

Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.21. Group 3/4 Average Flux Values for the Dewatered Caustic Leached Slurry

Design Test Condition	Median Operation Time of Test[a] (hr)	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	1.84	25.0	41.8	13.0	7.2	0.0072	2.24
2	4.13	24.9	30.0	10.9	6.5	0.0066	1.76
3	5.28	25.2	30.8	15.2	7.0	0.0070	2.70
4	6.44	28.2	49.8	15.0	9.9	0.0091	2.70
5	7.56	25.0	49.6	10.8	8.1	0.0082	1.81
6	8.70	25.0	40.9	13.0	7.0	0.0070	2.18
7	9.93	24.5	40.1	8.9	6.6	0.0068	1.46
8	11.18	26.6	40.7	15.6	6.6	0.0063	2.84
9	12.38	24.5	20.2	13.1	3.3	0.0033	2.09
10	13.61	26.9	59.8	12.8	8.8	0.0084	2.19
11	14.84	24.7	39.3	13.0	5.2	0.0053	2.11

(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.

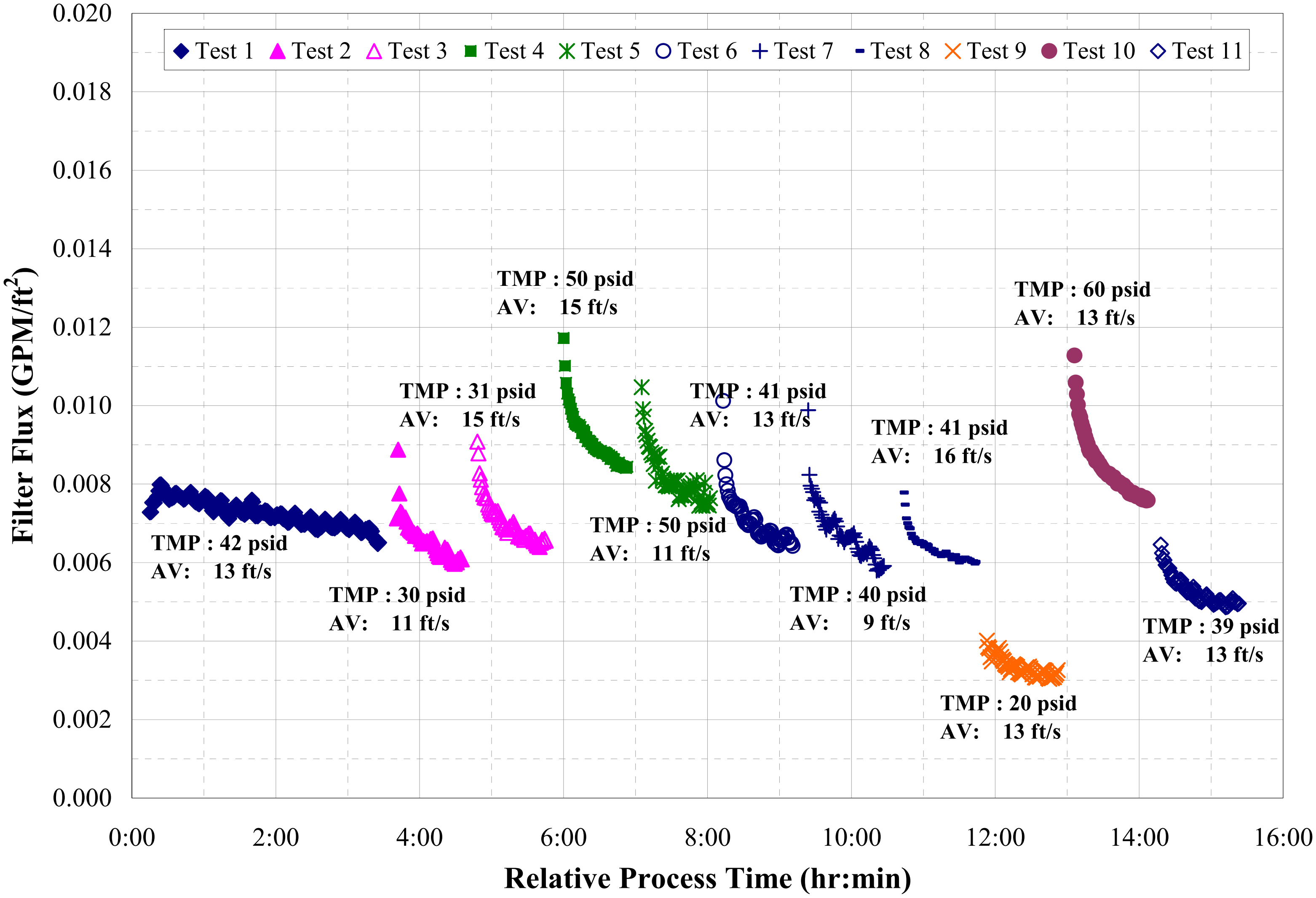


Figure 3.44. Group 3/4 Filter Matrix Results of Dewatered Caustic Leached Slurry

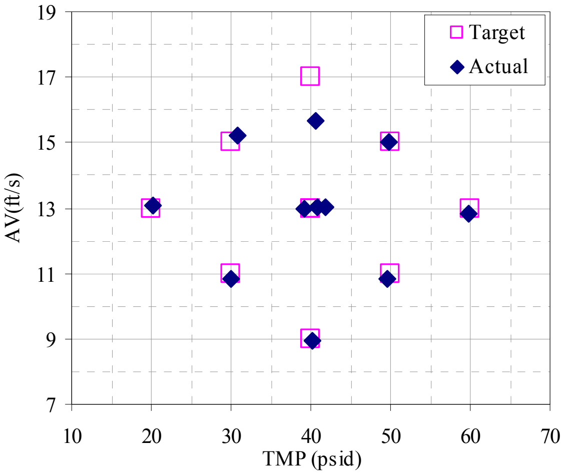


Figure 3.45. Group 3/4 Filter Test Matrix for Leached Solids

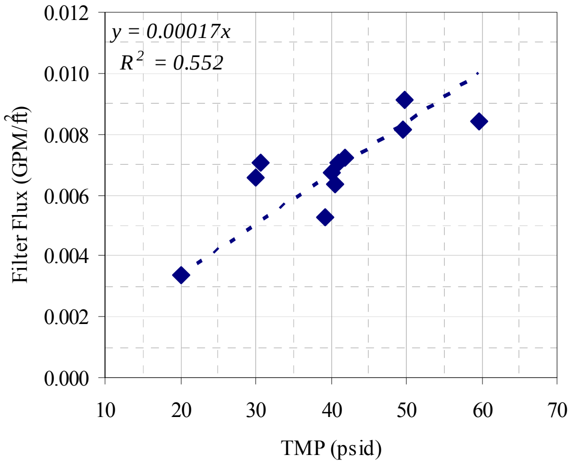


Figure 3.46. Group 3/4 Flux vs. TMP for Leached Solids

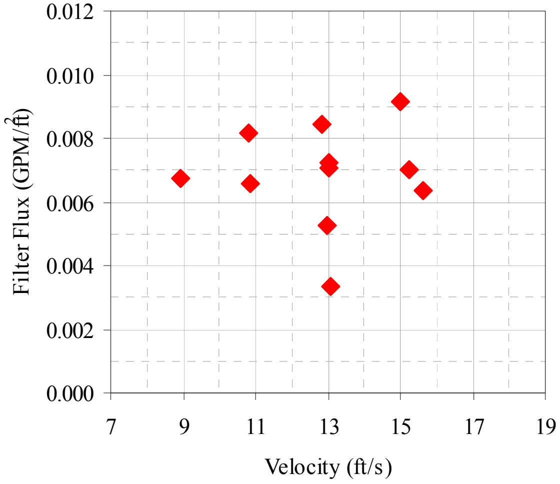


Figure 3.47. Group 3/4 Flux vs. AV for Leached Solids

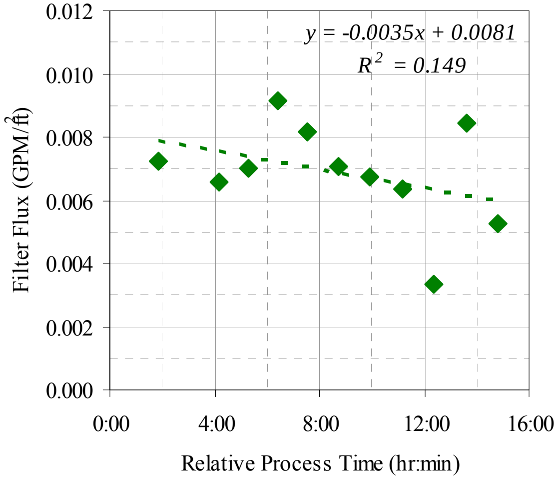


Figure 3.48. Group 3/4 Flux vs. Time for Leached Solids

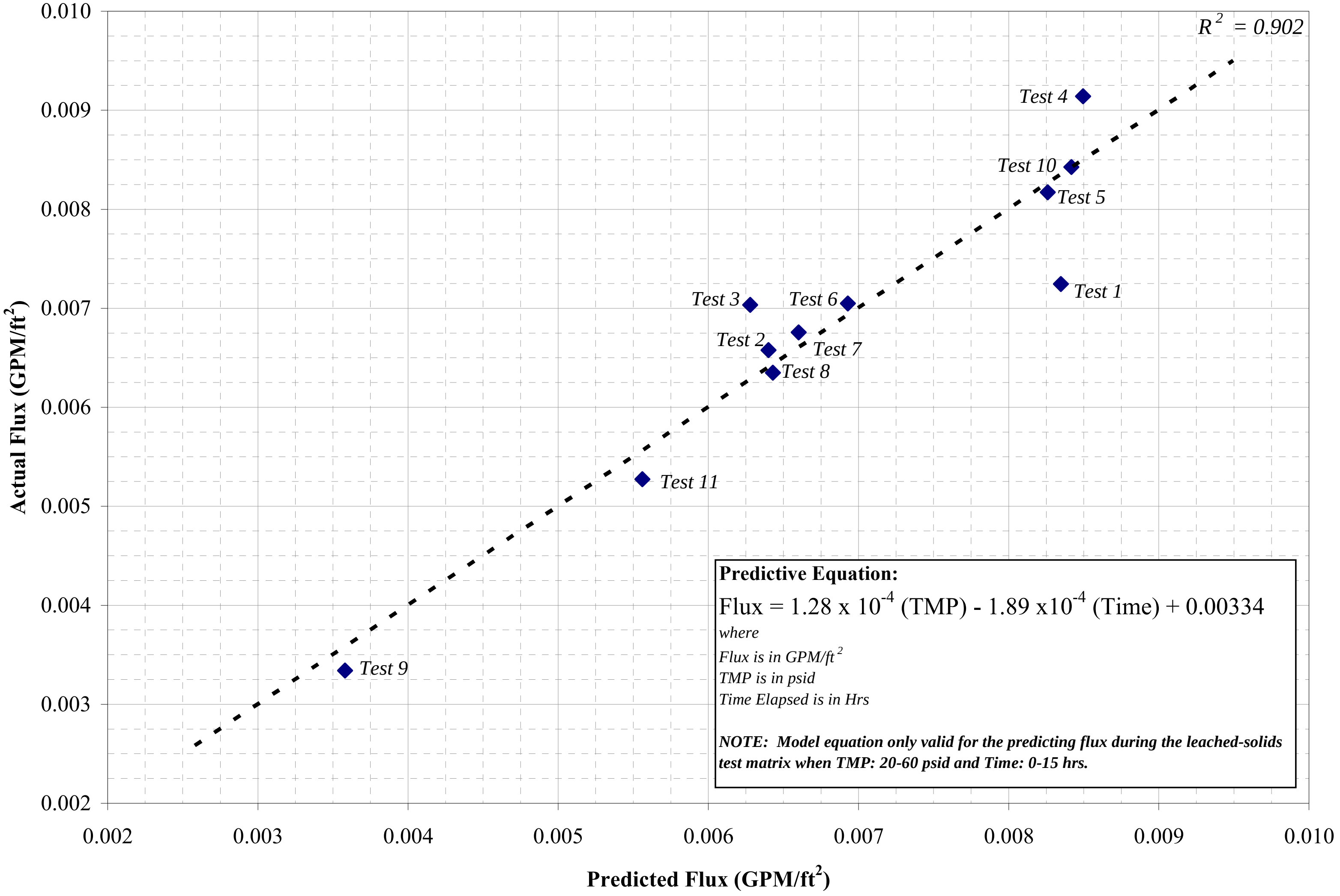


Figure 3.49. Group 3/4 Linear Correlation of Average Flux During Leached Solids Matrix Test as Function of TMP and Median Operational Time of Test Conditions

3.6.4 Dewatered Leached Slurry Physical Characterization

After dewatering the leached slurry and performing matrix testing, the slurry was sampled for physical and chemical analysis (Figure 3.50). The results of physical property measurements of the leached, dewatered material are shown in Table 3.22. The predicted solid concentration based on mass-balance data (Table 3.23) can be compared to the calculated solid concentration using the measured composition of the slurry and supernate (Table 3.24).

Leach factors were calculated for analytes measured from the slurry analysis by comparing the composition of the leach slurry in Table 3.24 to the composition of the high-solids slurry in Table 3.17, using uranium, zirconium and iron as a basis. This was used as a comparison to the leach factors obtained from the supernate calculations. Overall, only the aluminum fraction in the slurry solids significantly changed, with a calculated 0.93 leach factor. Phosphorus did not appear to have been removed from the solid phase at this point of the test. Because of the increase in the sodium concentration of the supernate from the caustic leach, insoluble phosphorus released as phosphate was believed to have re-precipitated as sodium phosphate. This theory was proven correct later, once the slurry was washed and the sodium concentration of the supernate decreased.

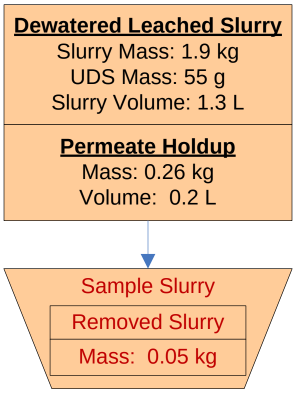


Figure 3.50. Group 3/4 Sampling of Dewatered Caustic Leached Slurry
Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.22. Physical Property Measurements of Group 3/4 Dewatered Caustic Leached Slurry (Inside Circulation Loop)

Slurry Density (g/ml)	1.35
Supernate Density (g/ml)	1.29
Settled Solids (Vol %)	28%
Centrifuged Undissolved Solids (Wt %)	10%
Total Solids of the Slurry (Wt %)	37%
Dissolved Solids of the Supernate (Wt%)	35%
Undissolved Solids of the Slurry (Wt%)	3%

Table 3.23. Group 3/4 Caustic leached, Dewatered Slurry Inventory and Composition

	Slurry(a)	Liquid Fraction(b)		Solids Fraction(c)	
Mass (kg)	2.10	2.05		0.05	
Wt% of Slurry	100%	97.4%		2.6%	
Metal	**g**	**g**	**µg/ml**	**g**	**µg/g**
Al	4.0E+01	3.8E+01	2.4E+04	1.7E+00	3.2E+04
B	6.2E-02	6.2E-02	3.9E+01	n/a(d)	n/a(d)
Bi	2.0E-01	7.8E+00	4.9E+03	n/a(d)	n/a(d)
Cr	2.6E-01	1.2E-01	7.4E+01	1.4E-01	2.7E+03
Fe	2.4E+00	3.7E-02	2.3E+01	2.4E+00	4.4E+04
Mn	3.8E-01	3.2E-04	2.0E-01	3.8E-01	7.1E+03
Na	2.9E+02	2.9E+02	1.8E+05	3.5E+00	6.4E+04
P	9.6E+00	8.6E-01	5.4E+02	8.7E+00	1.6E+05
S	8.7E-01	5.9E-01	3.7E+02	2.8E-01	5.2E+03
Si	1.6E+00	1.6E-01	1.0E+02	1.4E+00	2.6E+04
Zn	6.1E-02	6.7E-02	4.2E+01	n/a(d)	n/a(d)
Zr	1.0E+00	5.3E-03	3.3E+00	1.0E+00	1.9E+04
U	1.6E+00	< 6.E-3	< 4.E+0	1.6E+00	3.0E+04
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	8.5E+00	< 2.E-1	< 1.E-4	8.5E+00	1.6E-01
Cs-137	1.3E+04	5.1E+03	3.2E+00	8.3E+03	1.5E+02
Eu-154	6.8E+01	< 5.E-1	< 3.E-4	6.8E+01	1.3E+00
Eu-155	2.5E+01	< 3.E+0	< 2.E-3	2.5E+01	4.6E-01
Am-241	2.2E+02	< 3.E+0	< 2.E-3	2.2E+02	4.2E+00
Gross Alpha	3.7E+02	< 7.E-1	< 4.E-4	3.7E+02	6.9E+00
Gross Beta	8.6E+04	4.7E+03	2.9E+00	8.2E+04	1.5E+03
Sr-90	3.9E+04	4.6E+01	2.9E-02	3.8E+04	7.2E+02
Pu-239+240	1.4E+02	4.6E-01	2.9E-04	1.4E+02	2.6E+00
Pu-238	1.7E+01	4.8E-02	3.0E-05	1.7E+01	3.1E-01
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	µg/ml	**[M]**	**g**	**µg/g**	**g**
F	1.5E+01	7.9E-04	2.4E-02	2.0E+03	1.0E-01
C_2O_4	3.0E+01	3.4E-04	4.8E-02	6.9E+03	3.7E-01
NO_2	5.7E+03	1.2E-01	9.0E+00	1.0E+04	5.5E-01
NO_3	5.0E+04	8.1E-01	8.0E+01	9.4E+04	5.1E+00
SO_4	1.0E+03	1.1E-02	1.7E+00	1.9E+03	1.0E-01
PO_4	2.3E+03	2.4E-02	3.6E+00	2.8E+04	1.5E+00
OH	9.4E+04	5.6E+00	1.5E+02		

Table 3.23. (Cont'd)

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-167). Loss of mass from sampling was incorporated.
(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI601-G4-D3 (ASO ID 08-01366) 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. Leached Solid Fraction were calculated using analytical results from water leach sample TI601-G4-9, (ASO ID 08-01382).
(d) Values (based on supernate) were calculated to be less than zero.

Table 3.24. Group 3/4 Dewatered Leached Slurry Composition and Calculated Solids Leach Factors

Slurry Prep Method	**ICP-OES Analytes**	**Dry Slurry(a) (µg/g)**	**Supernate(b) (µg/mL)**	**Dry Solids(c) (µg/g)**	**Solids Leach Factor(d)**
HF Assisted Acid Digestion, and KOH Fusion, Concentration Factor of 5.04 based on U, Zr, and Fe	Al	52,700	24,000	117,013	0.93
	B	[116]	38.8	[657]	0.68
	Bi	[652]	[29]	[9,215]	0.14
	Cd	6.30	[1.7]	47.91	0.16
	Cr	527	73.8	5,986	0.22
	Fe	5,550	23.3	84,995	NA
	K	490.00	595	[9703.14]	-2.01
	Mn	523	[0.20]	8,067	-0.05
	Na	368,000	180,000	456,957	-0.07
	Ni	352.00	[2.1]	5372.65	-0.12
	P	8,040	542	108,379	-0.52
	S	1000.00	370	4698.91	0.19
	Si	[5,400]	101	[80,425]	-0.08
	Sr	34.3	[0.020]	528.1	-0.45
	U	3,505	<6.5E+5	54,104	NA
	Zn	[134]	42.0	[850]	0.78
	Zr	1,537	3.32	23,622	NA
	Ag	[3.4]	<4.8E+7	[52.48]	-0.11
	As	420.00	<9.7E+4	6483.26	-1.53
	Ba	29.1	[0.32]	439.1	-0.06
	Be	.40	0.176	.99	0.93
	Ca	482	<2.5E+4	7,440	-0.03
	Ce	[19]	<1.3E+7	[293]	0.01
	Co	[2.4]	[0.43]	[24.57]	0.62
	Cu	30.2	4.70	329.0	0.49
	La	[19]	<1.2E+6	[293]	-0.30
	Li	[12]	[1.4]	[142]	0.17
	Mg	150	<3.2E+5	2,315	0.03
	Mo	[20]	[3.0]	[222]	-0.13
	Nd	[28]	<4.8E+5	[424]	0.03
	Pb	691	177	5,530	0.63

Table 3.24 (Cont'd)

Slurry Prep Method	Radionuclides	Dry Slurry[(a)] (µCi/g)	Supernate[(b)] (µCi/mL)	Dry Solids[(c)] (µCi/g)	Solids Leach Factor[(d)]
HF Assisted Acid Digestion, and KOH Fusion, Concentration Factor of 5.04 based on U, Zr, and Fe	Ru	33.00	<2.9E+7	509.40	-3.49
	Th	[65]	[1.4]	[955]	0.01
	Ti	30.4	<1.8E+6	469.3	-0.06
	Tl	<6.2E+1	<7.8E+5	<9.6E+2	0.46
	V	10.4	[0.23]	154.5	-0.22
	W	[24]	[6.3]	[188]	0.10
	Y	[4.45]	<6.6E+5	[68.69]	-0.21
KOH Fusion, Concentration Factor of 5.04 based on U, Zr, and Fe	Co-60	9.95E-3	< 1.E-4	1.50E-1	0.05
	Cs-137	1.64E+1	3.20E+0	1.61E+2	0.06
	Eu-154	9.55E-2	< 3.E-4	1.47E+0	-0.02
	Eu-155	3.32E-2	< 2.E-3	< 5.E-1	0.22
	Am-241	3.63E-1	< 2.E-3	5.55E+0	-0.11
	Sr-90	5.96E+1	2.90E-2	9.20E+2	-0.13
	Pu-239/240	2.41E-1	2.90E-4	3.71E+0	-0.28
	Pu-238	2.02E-2	2.99E-5	3.11E-1	-0.18

(a) Test sample TI601-G4-D3, ASO ID 08-01366

(b) Test sample TI601-G4-9, ASO ID 08-01382

(c) Calculated using results from TI601-G4-D3 and TI601-G4-9

(d) Calculated using dry solids concentration results listed in Table 3.17

Note: Analytes in italics were measured opportunistically. Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

Particle size distribution measurements were performed on the sampled slurry. Figure 3.51 shows the PSD for the dewatered Group 3/4 after caustic leach sample as a function of pump speed before sonication. At 2000 RPM, the distribution ranges from 0.2 µm - 200 µm and is non-continuous and tri-modal. Three peaks are present with the primary peak centered around 10 µm, the secondary peak centered around 1.5 µm, and a third peak centered around 100 µm. At 3000 RPM, the distribution ranges from 0.2 µm - 30 µm and is continuous and bi-modal with the primary peak centered around 1.5 µm and the secondary peak centered around 10 µm. At 4000 RPM, the distribution ranges from 0.2 µm - 200 µm and is continuous and tri-modal with the primary peak centered around 70 µm, the secondary peak centered around 1.5 µm, and the third peak centered around 10 µm. The fraction of > 20 µm at 4000 RPM most likely indicates a significant quantity of large difficult-to-suspend particles or agglomerates. As the conditions ran at 3000, 4000, and 2000 RPM, the 100 µm peak at 2000 RPM is likely a carryover of slowly settling particles or agglomerates suspended at 4000 RPM.

Figure 3.51 shows the particle size distribution as a result of applied sonication. The range of the particles appears to remain unaffected as a result of sonication. There is a significant peak shift where the majority of the particle population moves from 1.5 µm to 12 µm. This effect may be a result of increased suspension of particles as a result of input of sonic energy, or more likely may be a result of increased disruption of larger settled particles as indicated below.

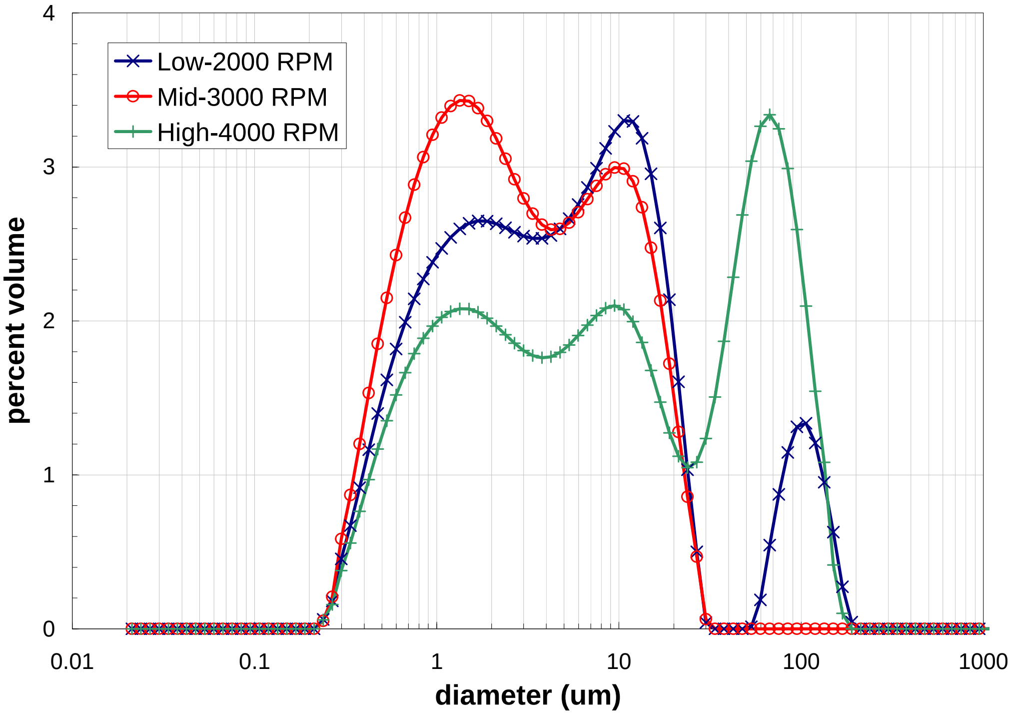


Figure 3.51. PSD of Group 3/4 CUF Leached, Dewatered Slurry as a Function of Pump Speed

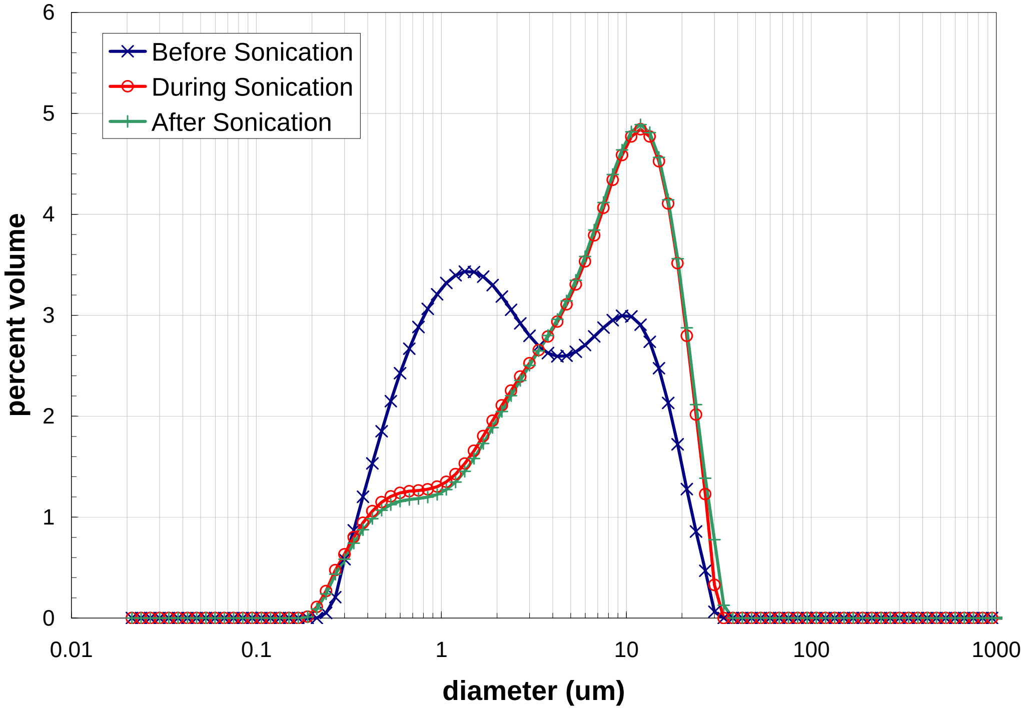


Figure 3.52. PSD of Group 3/4 CUF Leached, Dewatered Slurry as a Function of Sonication

The slurry was also sub-sampled for rheological measurement. Figure 3.53 shows the results of flow curve testing for the caustic leached, dewatered slurry. Below 500 s^{-1}, the flow curve stress data exhibit a linear response with shear rate. The low shear rate data are free of hysteresis, with exception of the 25°C flow curve, which exhibits a lower stress response during the down ramp portion of the measurement. This hysteresis is either a result of shear disruption of internal sample structure or could indicate settling of the solids material. The latter is supported by observation of a 1 mm - 2 mm layer of settled solids on the bottom of the test cup after testing.

Up ramp measurement data for 25°C and 40°C above 500 s^{-1} are not linear and show an anomalous increase between 600 and 700 s^{-1}. This increase persists into the constant rotation step but is absent on the down ramp. Such behavior is characteristic of rotor misalignment. It is speculated that in-cell vibration or vibration of the instrument as it reached 700 s^{-1} yielded the misalignment and that constant rotation at 1000 s^{-1} re-seated the rotor properly for the down ramp portion. With regard to its effect on the overall data, this anomaly only appears to affect up ramp data at shear rates above 600 s^{-1}.

In general, the flow curve data indicate that the slurry is Newtonian. The slurry exhibits a decreased stress response with increasing temperature that is consistent with reduced slurry viscosity at higher temperatures. Although the slurry is Newtonian, it shows a significant stress response at all temperatures tested. For example, the caustic leached, dewatered slurry exhibits an approximately 7 Pa shear stress at a shear rate of 500 s^{-1} at 25°C. In comparison, the stress response of the low solids slurry at 500 s-1 and 25°C is only approximately 1 Pa.

Table 3.25 summarizes the best-fit Newtonian viscosities for the caustic leached, dewatered slurry. These results indicate a viscosity of 15-16 mPa-s at 25°C that decreases to 9.5 and 5.4 mPa-s at 40 and 60°C, respectively. The initial and replicate flow curve measurements agree within the 10% accepted limit of instrument accuracy. In addition, the correlation coefficient of the fit (R) is high (0.97-0.99) suggesting good correlation between the data and model.

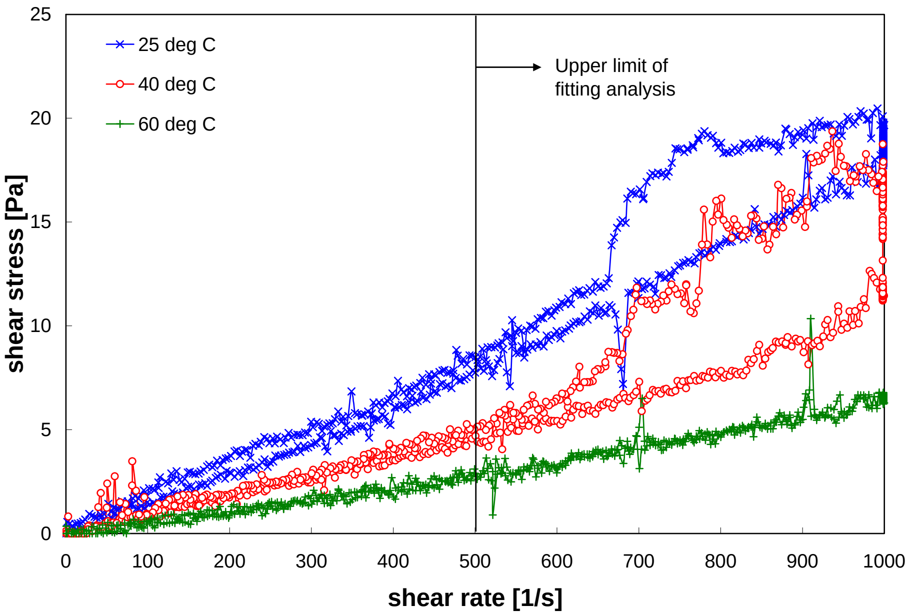


Figure 3.53. Flow curves for Group 3/4 CUF leached dewatered slurry

Table 3.25. Results of fitting analysis for the Group 3/4 CUF leached dewatered slurry

Model	Temperature [°C]	Range	Viscosity [mPa·s]	R
Newtonian	25 (1 of 2)	0-500 s^{-1}	15	0.99
	25 (2 of 2)	0-500 s^{-1}	16	0.99
	40	0-500 s^{-1}	9.5	0.97
	60	0-500 s^{-1}	5.4	0.99

3.6.5 Caustic Batch Washing Results

After slurry sampling, the slurry was washed three times with decreasing concentrations of sodium hydroxide, as shown in Figure 3.54. 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 approximately 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 due to cavitation that 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 3.26 through Table 3.28. The measured concentration of free hydroxide, radionuclides, and opportunistic ICP-OES analytes for each filtered wash solution is provided in Table 3.29.

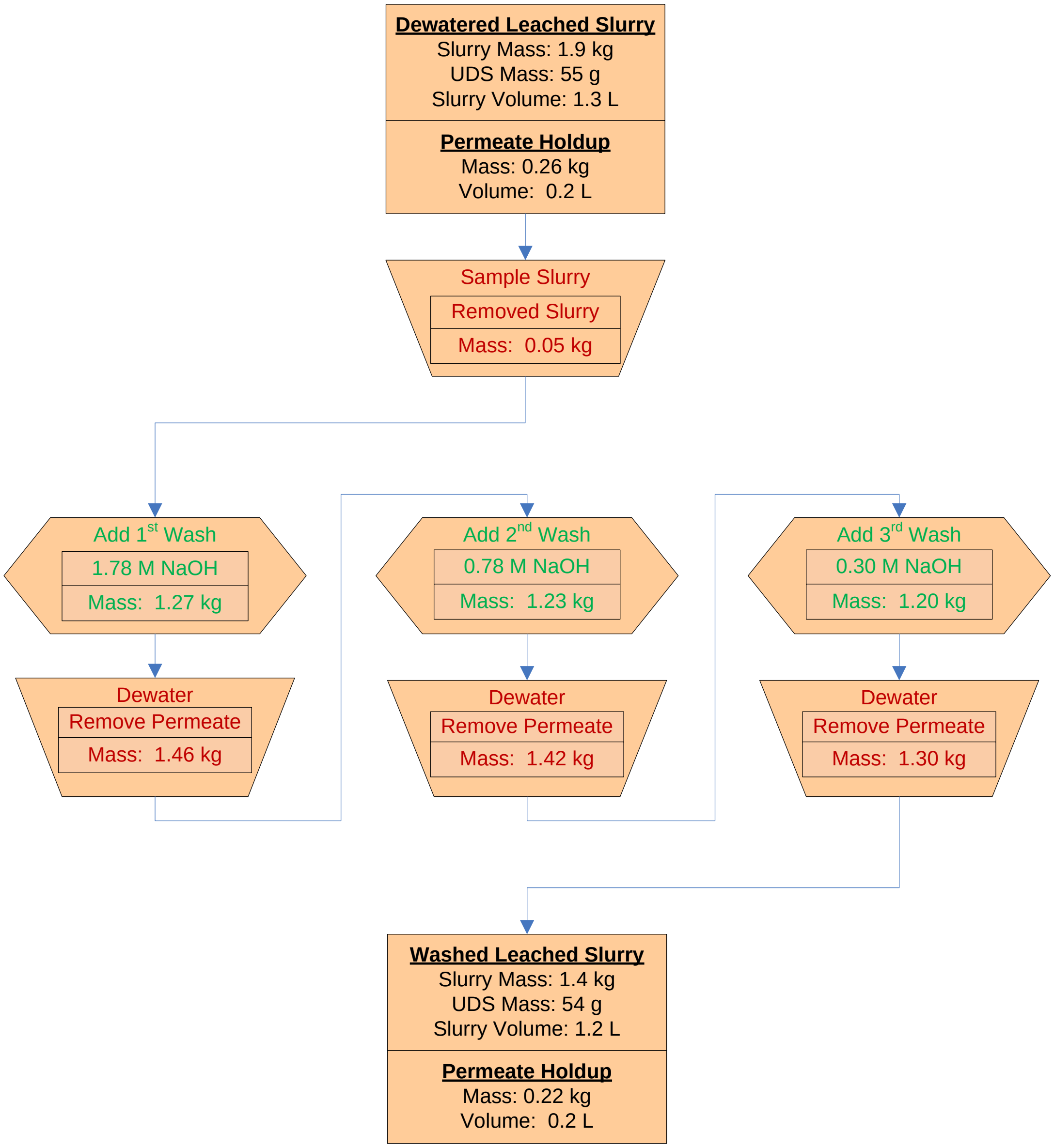


Figure 3.54. Group 3/4 Washing of Caustic Leached Slurry
Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.26. Group 3/4 Caustic leached Slurry Inventory and Composition after the First Wash

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	1.89	1.83		0.05	
Wt% of Slurry	100%	97.2%		2.8%	
Metal	g	g	µg/ml	g	µg/g
Al	2.4E+01	2.0E+01	1.3E+04	3.7E+00	6.9E+04
B	< 4.E-3	< 4.E-3	< 3.E+0	n/a(d)	n/a(d)
Bi	2.0E-01	< 3.E-2	< 2.E+1	2.0E-01	3.7E+03
Cr	2.1E-01	6.5E-02	4.4E+01	1.4E-01	2.7E+03
Fe	2.4E+00	1.4E-02	9.6E+00	2.4E+00	4.4E+04
Mn	3.8E-01	< 2.E-4	< 1.E-1	3.8E-01	7.1E+03
Na	2.0E+02	1.7E+02	1.2E+05	2.8E+01	5.1E+05
P	8.6E+00	1.2E+00	8.0E+02	7.4E+00	1.4E+05
S	6.2E-01	3.0E-01	2.0E+02	3.2E-01	6.0E+03
Si	1.5E+00	5.9E-02	4.0E+01	1.5E+00	2.7E+04
Zn	3.2E-02	3.6E-02	2.4E+01	n/a(d)	n/a(d)
Zr	1.0E+00	5.6E-03	3.8E+00	1.0E+00	1.9E+04
U	1.6E+00	< 3.E-2	< 2.E+1	1.6E+00	3.0E+04
Anions	**Liquid Fraction**				
	µg/ml	**[M]**	**g**		
OH	6.8E+04	4.0E+00	1.0E+02		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-167). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI601-G4-E (ASO ID 08-01374) 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 3.27. Group 3/4 Caustic leached Slurry Inventory and Composition after the Second Wash

	Slurry(a)	**Liquid Fraction**(b)		**Solids Fraction**(c)	
Mass (kg)	1.69	1.64		0.05	
Wt% of Slurry	100%	97.1%		2.9%	
Metal	g	g	µg/ml	g	µg/g
Al	1.5E+01	9.9E+00	7.0E+03	5.1E+00	1.0E+05
B	< 4.E-3	< 4.E-3	< 3.E+0	n/a(d)	n/a(d)
Bi	2.0E-01	< 3.E-2	< 2.E+1	2.0E-01	4.1E+03
Cr	1.8E-01	3.2E-02	2.3E+01	1.5E-01	3.0E+03
Fe	2.4E+00	5.6E-03	3.9E+00	2.4E+00	4.8E+04
Mn	3.8E-01	< 2.E-4	< 1.E-1	3.8E-01	7.7E+03
Na	1.3E+02	1.0E+02	7.2E+04	3.0E+01	6.1E+05
P	6.4E+00	2.6E+00	1.8E+03	3.8E+00	7.8E+04
S	4.7E-01	1.7E-01	1.2E+02	3.0E-01	6.2E+03
Si	1.5E+00	3.0E-02	2.1E+01	1.5E+00	3.0E+04
Zn	1.6E-02	1.9E-02	1.3E+01	n/a(d)	n/a(d)
Zr	1.0E+00	6.6E-03	4.6E+00	1.0E+00	2.0E+04
U	1.6E+00	< 3.E-2	< 2.E+1	1.6E+00	3.2E+04
Anions	**Liquid Fraction**				
	µg/ml	**[M]**	**g**		
OH	4.0E+04	2.4E+00	5.7E+01		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-167). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI601-G4-F (ASO ID 08-01375) 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 3.28. Group 3/4 Caustic leached Slurry Inventory and Composition after the Third Wash

	Slurry$^{(a)}$	**Liquid Fraction$^{(b)}$**		**Solids Fraction$^{(c)}$**	
Mass (kg)	1.60	1.56		0.04	
Wt% of Slurry	100%	97.6%		2.4%	
Metal	g	g	µg/ml	g	µg/g
Al	1.1E+01	5.4E+00	3.6E+03	5.1E+00	1.3E+05
B	6.7E-03	6.7E-03	4.5E+00	n/a$^{(d)}$	n/a$^{(d)}$
Bi	1.9E-01	8.0E-03	5.3E+00	1.9E-01	4.8E+03
Cr	1.6E-01	1.8E-02	1.2E+01	1.5E-01	3.8E+03
Fe	2.4E+00	3.3E-03	2.2E+00	2.4E+00	6.1E+04
Mn	3.8E-01	7.0E-05	4.7E-02	3.8E-01	9.7E+03
Na	7.9E+01	6.4E+01	4.2E+04	1.5E+01	4.0E+05
P	4.4E+00	2.5E+00	1.6E+03	1.9E+00	4.8E+04
S	4.1E-01	8.3E-02	5.5E+01	3.2E-01	8.3E+03
Si	1.5E+00	1.9E-02	1.3E+01	1.5E+00	3.8E+04
Zn	6.3E-03	1.1E-02	7.5E+00	n/a$^{(d)}$	n/a$^{(d)}$
Zr	1.0E+00	2.0E-03	1.3E+00	1.0E+00	2.6E+04
U	1.6E+00	6.5E-03	4.3E+00	1.6E+00	4.1E+04
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	8.5E+00	< 1.E-1	< 7.E-5	8.5E+00	2.2E-01
Cs-137	9.2E+03	6.9E+02	4.6E-01	8.5E+03	2.2E+02
Eu-154	6.8E+01	< 3.E-1	< 2.E-4	6.8E+01	1.7E+00
Eu-155	2.5E+01	< 1.E+0	< 7.E-4	2.5E+01	6.4E-01
Am-241	2.2E+02	< 2.E+0	< 1.E-3	2.2E+02	5.8E+00
Gross Alpha	3.7E+02	< 6.E-1	< 4.E-4	3.7E+02	9.5E+00
Gross Beta	8.3E+04	5.8E+02	3.8E-01	8.2E+04	2.1E+03
Sr-90	3.8E+04	8.3E+00	5.5E-03	3.8E+04	9.9E+02
Pu-239+240	1.4E+02	3.9E-02	2.6E-05	1.4E+02	3.5E+00
Pu-238	1.7E+01	3.9E-03	2.6E-06	1.7E+01	4.3E-01
Anions	**Liquid Fraction**			**Leached Solids Fraction**	
	µg/ml	**[M]**	**g**	**µg/g**	**g**
F	4.3E+02	2.2E-02	6.4E-01	2.6E+03	1.0E-01
C_2O_4	9.6E+02	1.1E-02	1.5E+00	8.6E+03	3.4E-01
NO_2	8.6E+02	1.9E-02	1.3E+00	5.6E+03	2.2E-01
NO_3	7.6E+03	1.2E-01	1.1E+01	6.1E+04	2.4E+00
SO_4	1.6E+02	1.7E-03	2.5E-01	1.1E+03	4.4E-02
PO_4	5.5E+03	5.9E-02	8.4E+00	4.1E+04	1.6E+00
OH	2.2E+04	1.3E+00	3.4E+01		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-167). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI601-G4-G (ASO ID 08-01367) 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. Leached Solid Fraction were calculated using analytical results from water leach sample TI601-G4-12, (ASO ID 08-01383).

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

Table 3.29. Caustic Wash Solutions Radionuclide and Opportunistic Compositions

	Wash 1	**Wash 2**	**Wash 3**	**Composite**
ASO Sample ID	08-01374	08-01375	08-01367	08-01368
Density$^{(a)}$, g/mL>	1.23	1.15	1.03	NA
Analyte				
free OH, M	3.99 M	2.37 M	1.31 M	2.80 M
Opportunistic Analytes				
Analyte	µg/mL	µg/mL	µg/mL	µg/mL
Ag	<1.3E+0	<1.3E+0	<2.6E-1	<2.6E-1
As	<2.6E+1	<2.6E+1	<5.3E+0	<5.3E+0
Ba	[0.54]	[0.38]	[0.13]	[0.17]
Be	[0.15]	[0.085]	[0.027]	0.0651
Ca	<3.7E+0	<3.7E+0	<7.5E-1	<7.6E-1
Ce	<6.1E+0	<6.1E+0	<1.2E+0	<1.2E+0
Co	<1.5E+0	<1.5E+0	<3.0E-1	<3.0E-1
Cu	[1.3]	<8.6E-1	[0.31]	[1.3]
Dy	<1.8E+0	<1.8E+0	<3.6E-1	<3.6E-1
Eu	<6.7E-1	<6.7E-1	<1.4E-1	<1.4E-1
La	<1.7E+0	<1.7E+0	<3.5E-1	<3.5E-1
Li	[0.61]	[0.63]	[0.71]	[0.90]
Mg	<1.4E+0	<1.4E+0	<2.8E-1	<2.8E-1
Mo	[3.3]	<3.2E+0	[0.66]	[1.2]
Nd	<3.3E+0	[4.4]	<6.7E-1	<6.7E-1
Pb	[85]	[31]	[14]	53.9
Pd	<3.8E+0	<3.9E+0	<7.8E-1	<7.8E-1
Rh	<7.3E+0	<7.3E+0	<1.5E+0	<1.5E+0
Ru	<5.2E+0	<5.2E+0	<1.1E+0	<1.1E+0
Sb	<1.2E+1	[14]	<2.5E+0	<2.5E+0
Se	<4.3E+1	<4.3E+1	<8.6E+0	<8.7E+0
Sn	<1.6E+1	<1.7E+1	[3.82]	[3.4]
Ta	<1.0E+1	<1.0E+1	<2.1E+0	<2.1E+0
Te	<1.6E+1	<1.6E+1	<3.2E+0	<3.2E+0
Th	<6.0E+0	<6.0E+0	<1.2E+0	<1.2E+0
Ti	<2.6E-1	[0.27]	[0.055]	<5.3E-2
Tl	<2.3E+1	<2.3E+1	<4.7E+0	<4.7E+0
V	[1.4]	[2.1]	1.32	0.998
W	[12]	[17]	<2.3E+0	[2.8]
Y	<2.7E-1	<2.7E-1	<5.4E-2	<5.4E-2

Table 3.29 (Cont'd)

	Wash 1	**Wash 2**	**Wash 3**	**Composite**
ASO Sample ID	08-01374	08-01375	08-01367	08-01368
Analyte	µCi/mL	µCi/mL	µCi/mL	µCi/mL
^{137}Cs			4.59E-1	1.12E+0
^{60}Co			< 7.E-5	< 7.E-5
^{241}Am			< 1.E-3	< 2.E-3
^{90}Sr			5.47E-3	1.18E-2
^{238}Pu			2.59E-6	9.27E-6
$^{239+240}$Pu			2.61E-5	9.21E-5
Gross alpha			< 4.E-4	< 4.E-4
Gross beta			3.82E-1	9.63E-1
^{154}Eu			< 2.E-4	< 2.E-4

(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.

As can be seen in Figure 3.55, the pre-leach Al composition was 98 wt% solids and, based on the initial characterization (WTP-RPT-167), can be attributed to gibbsite. The caustic leached 94 wt% of the Al from solids and, after washing the slurry, 75 wt% of the original Al was removed (Figure 3.58).

Soluble phosphorus accounts for 62 wt% of the original slurry P content and can be directly attributed to phosphates (Figure 3.56). It is believed that the portion of the P that appears as solid in the slurry is either a result of gelling (PNNL-17257 [WTP-RPT-173] [Lumetta 2008]) or PO_4 entrainment in solids. Washing the solids removes a large portion of the remaining P as phosphate. The high caustic during the leaching and the washing gels the phosphate leading to the irregular behavior noted in Figure 3.56. At the start of the leach, it appeared that some phosphorus precipitates after the addition of 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 (Figure 3.58). By the end of the test 59 wt% of the original P had been removed. This behavior was observed in the initial characterization (WTP-RPT-167) where 23 wt% (G3) and 41 wt% (G4) of the P was in the original supernate and 70 wt% (G3) and 57 wt% (G4) was removed upon washing (93 wt% (G3) and 98 wt% (G4) total removal).

The initial slurry contained 29 wt% soluble chromium (Figure 3.57). During the caustic leach, solid chromium was reduced by 49 wt%, possibly due to chromium phosphate ($CrPO_4$) leaching. The total removal of Cr in the final slurry was 53 wt%. There was no leaching of solid sulfur observed and the total removal was 72% which was >90% removal of the original soluble sulfur. This directly coincides with sulfates and the total anion removal (discussed later, Figure 3.63).

The phosphorus is difficult to characterize as soluble or solid, since when the Na concentration increases in the supernate, the phosphorus supernate concentration drops (Figure 3.59). As the Na concentration decreases, it reaches a certain point when supernate phosphorus concentration begins to increase. This is another indication of gelling, and this made it difficult to remove all the soluble P in three washes. If more washes had been performed, up to 90% of the P could have been removed. The aluminum concentration in the supernate mimics that of the Na and free hydroxide concentrations.

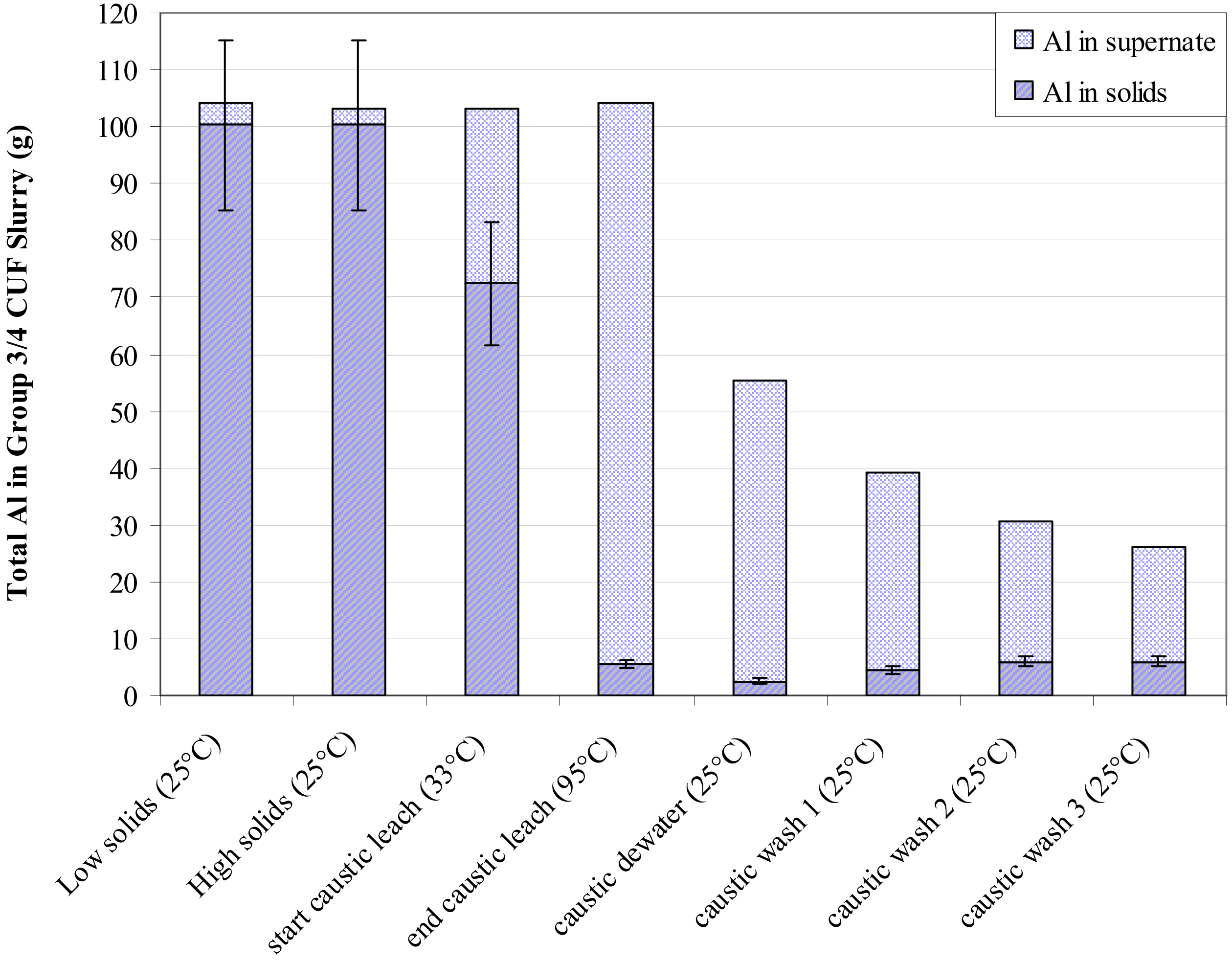


Figure 3.55. Total Aluminum in Group 3/4 CUF Slurry

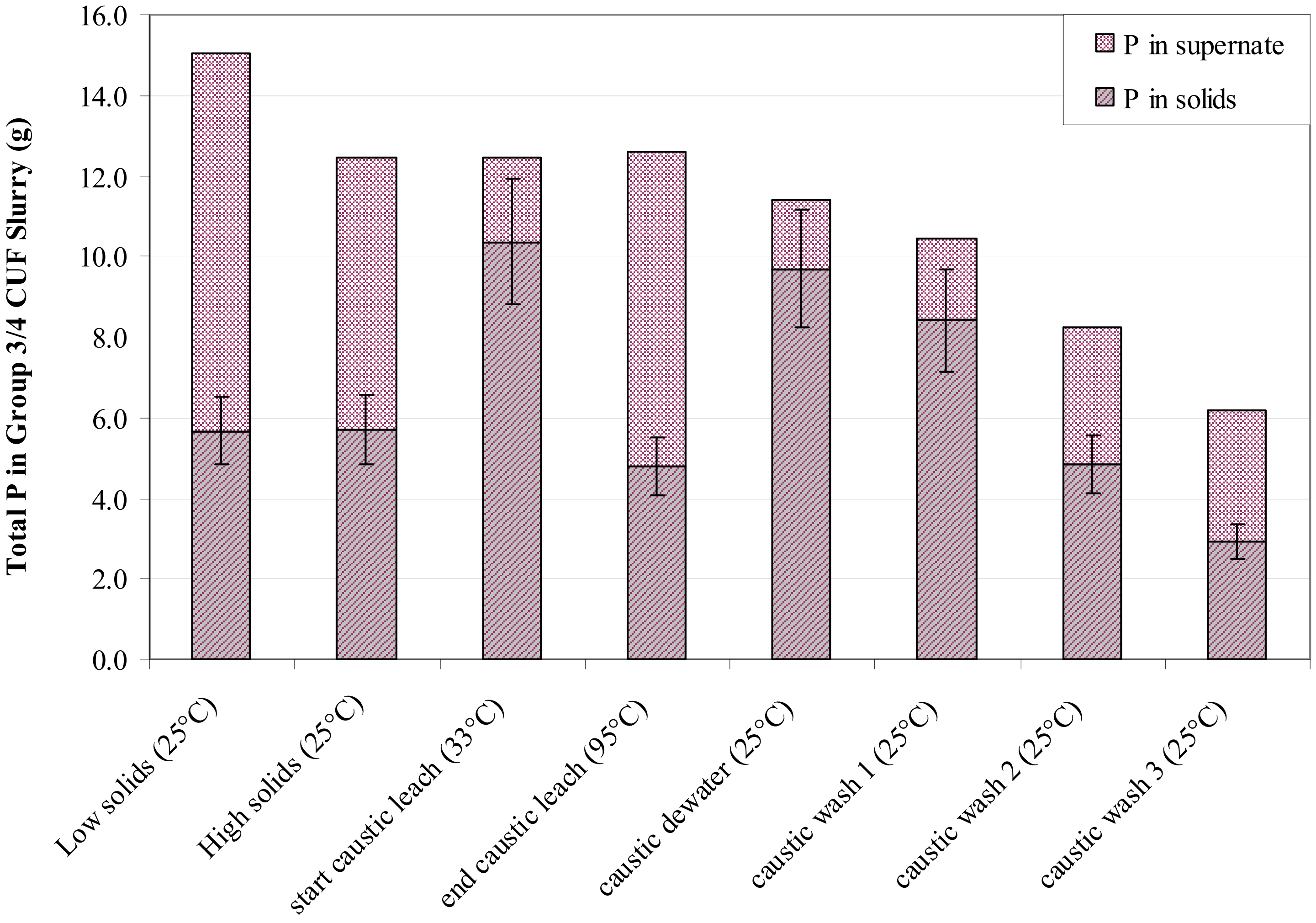


Figure 3.56. Total Phosphorus/Phosphate in Group 3/4 CUF Slurry

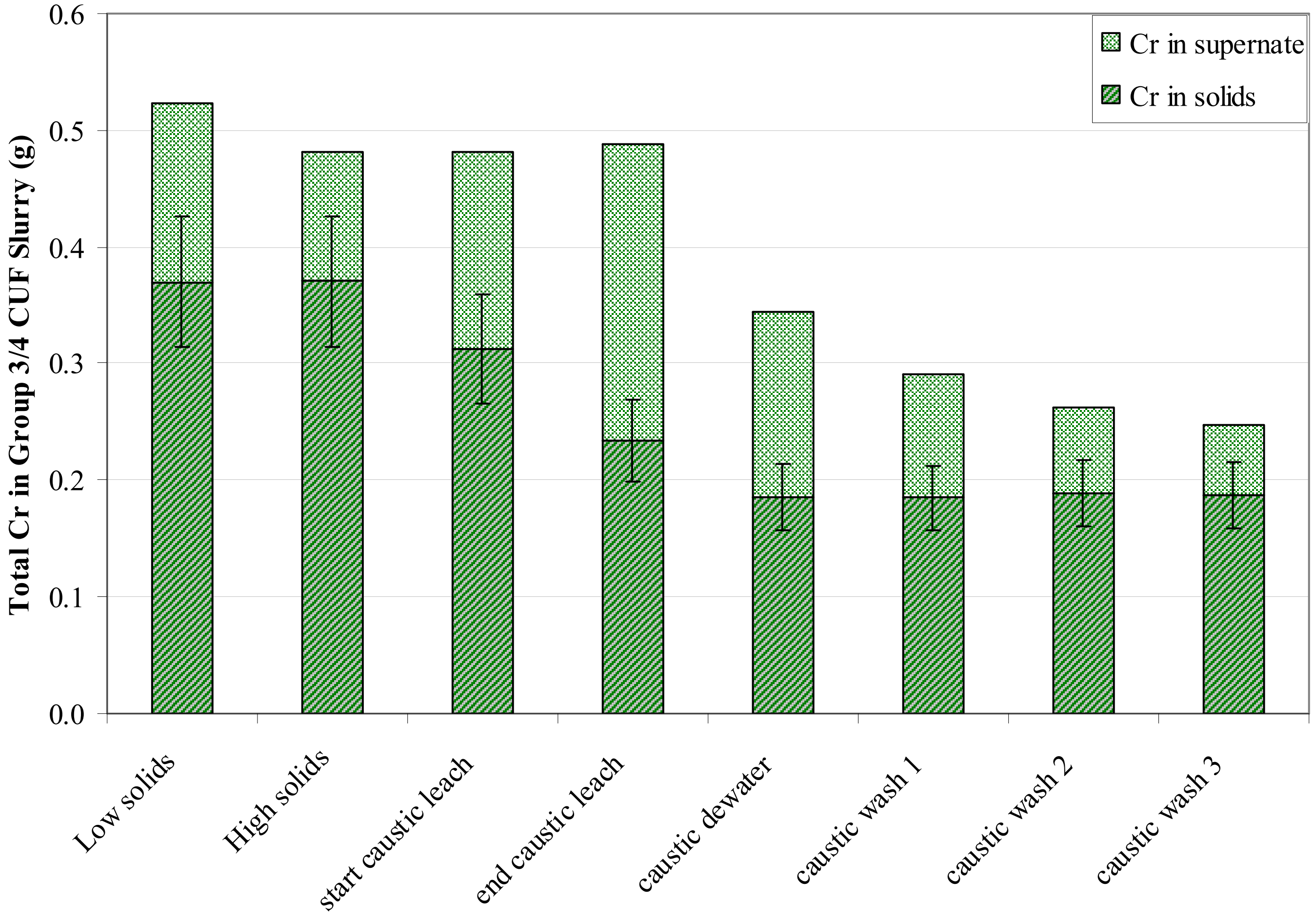


Figure 3.57. Total Chromium in Group 3/4 CUF Slurry

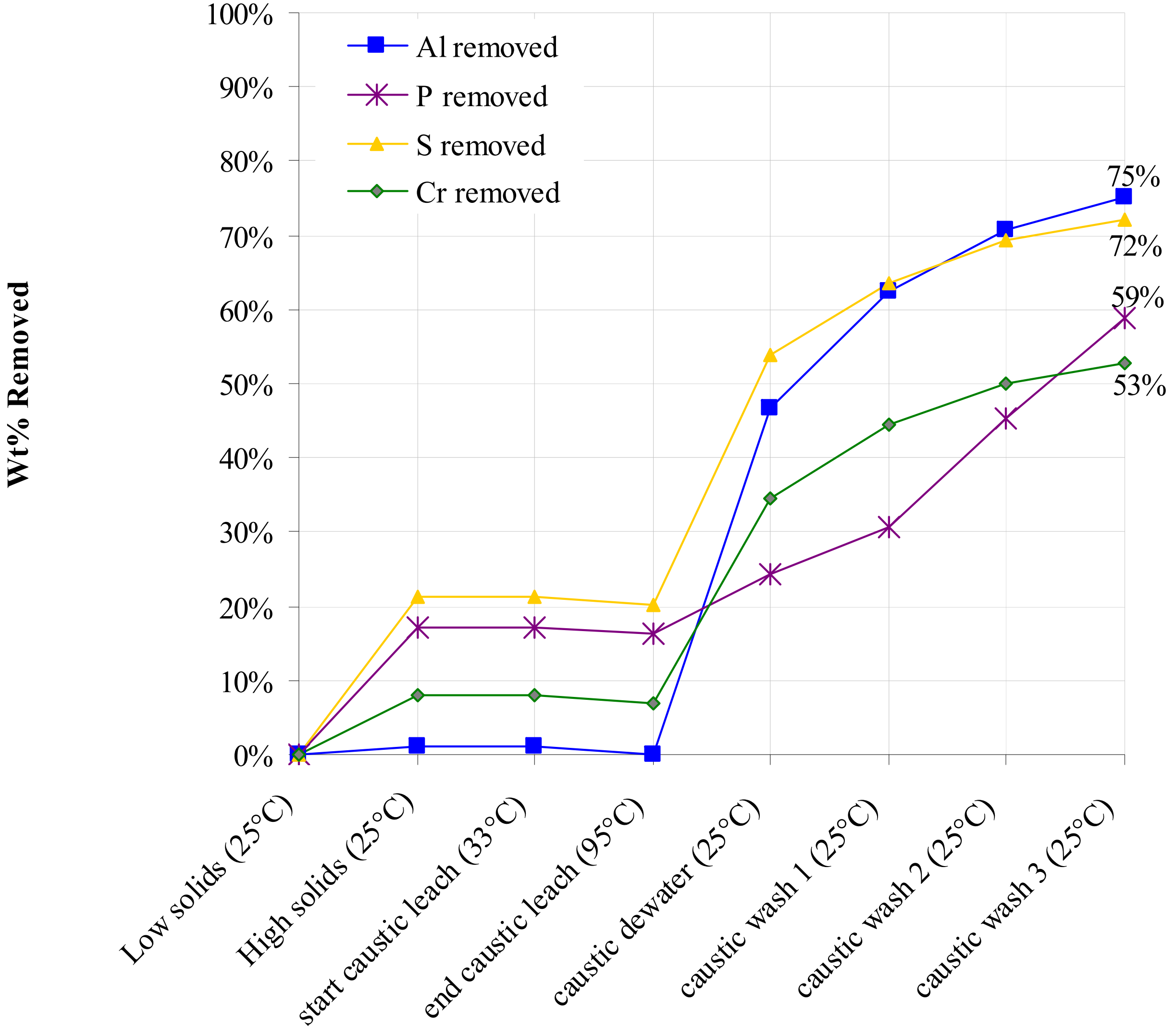


Figure 3.58. Al/Cr/P/S removed from the Group 3/4 CUF Slurry

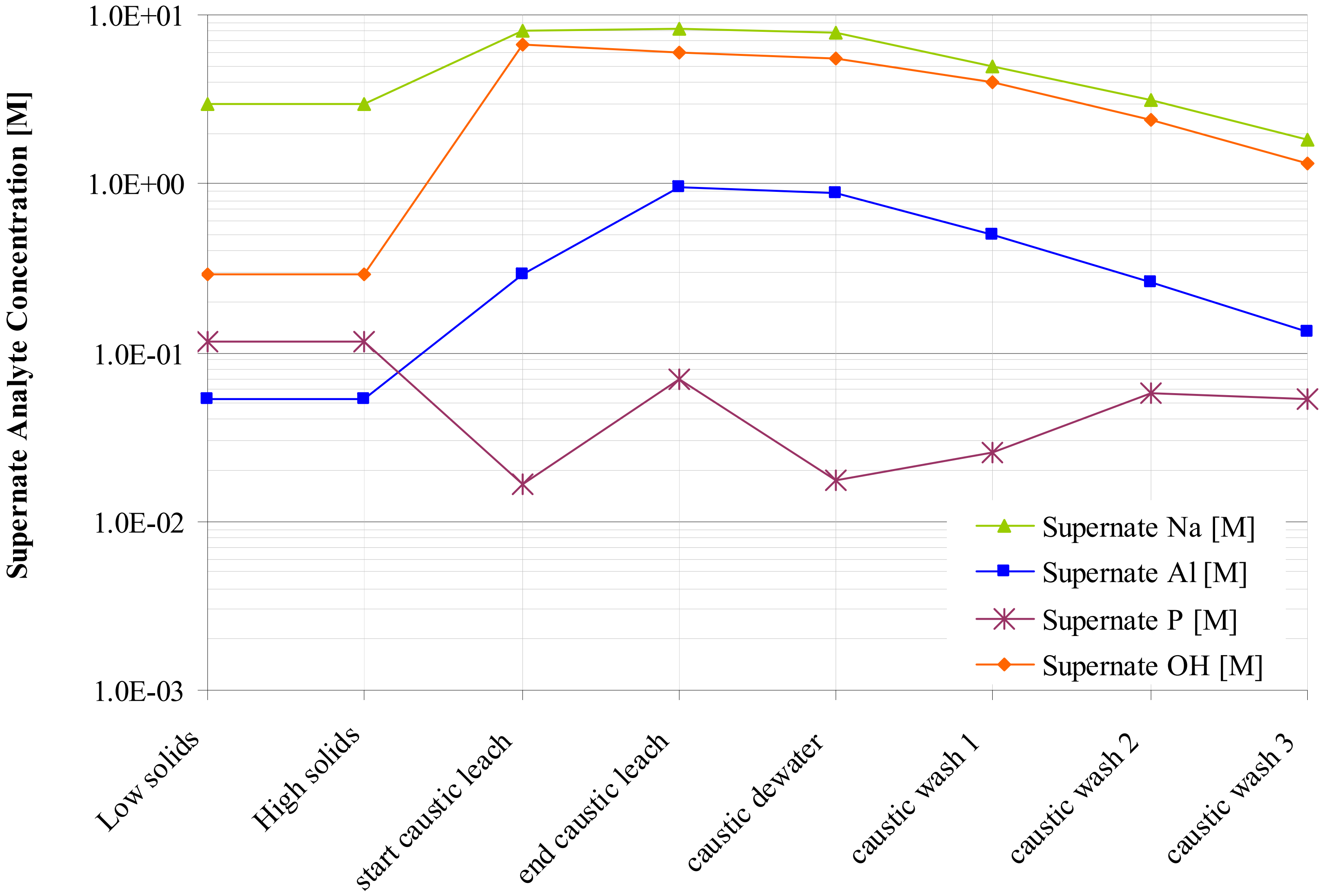


Figure 3.59. Sodium, Free Hydroxide, P and Al Molarity in Group 3/4 CUF Slurry

3.6.6 Dewatering Caustic Wash Solutions

The filter flux results from dewatering the slurry after each wash solution are shown in Figure 3.60 and Table 3.30. After each of the three washes was added, the 1.2 L wash volume was filtered from the slurry in 83, 54, and 51 minutes, sequentially. Comparison of the wash dewatering to the dewatering of the slurry before and after caustic leaching showed a correlation between filter flux and the sodium concentration of the slurry supernate. For all the dewatering operations, an increase in the filter flux was observed with a decrease in the sodium concentration of the slurry supernate.

Because the sodium concentration of waste supernate is a good measure of its viscosity, the results indicated that the change in the filter flux could be explained by the Darcy equation (Equation 2.6). The equation predicted that changes in the permeate viscosity would cause inversely proportional changes to the filter flux. This equation also indicated that the filter resistance of the slurry did not change after caustic leaching or washing, unlike results seen in other waste (e.g. REDOX sludge [Shimskey et al. 2009]). Unlike that test, it appeared that the fouling agent in the waste was not dissolved from caustic leaching or subsequent washing afterwards.

Table 3.30. Group 3/4 Comparison of Washed Slurry Supernate Attributes to Filter Flux

	Wash Volume (L)	Wash [NaOH] M	Filtered Supernate Composition			Average Filter Flux (GPM/ft^2)
			[Na] M	[OH] M	[Al] M	
Wash 1	1.20	1.78	5.0	4.0	0.50	0.015
Wash 2	1.20	0.78	3.1	2.4	0.26	0.021
Wash 3	1.20	0.30	1.8	1.3	0.13	0.027
Pre-leached Slurry			3.0	0.3	0.05	0.020
Leach Slurry			7.8	5.6	0.9	0.010

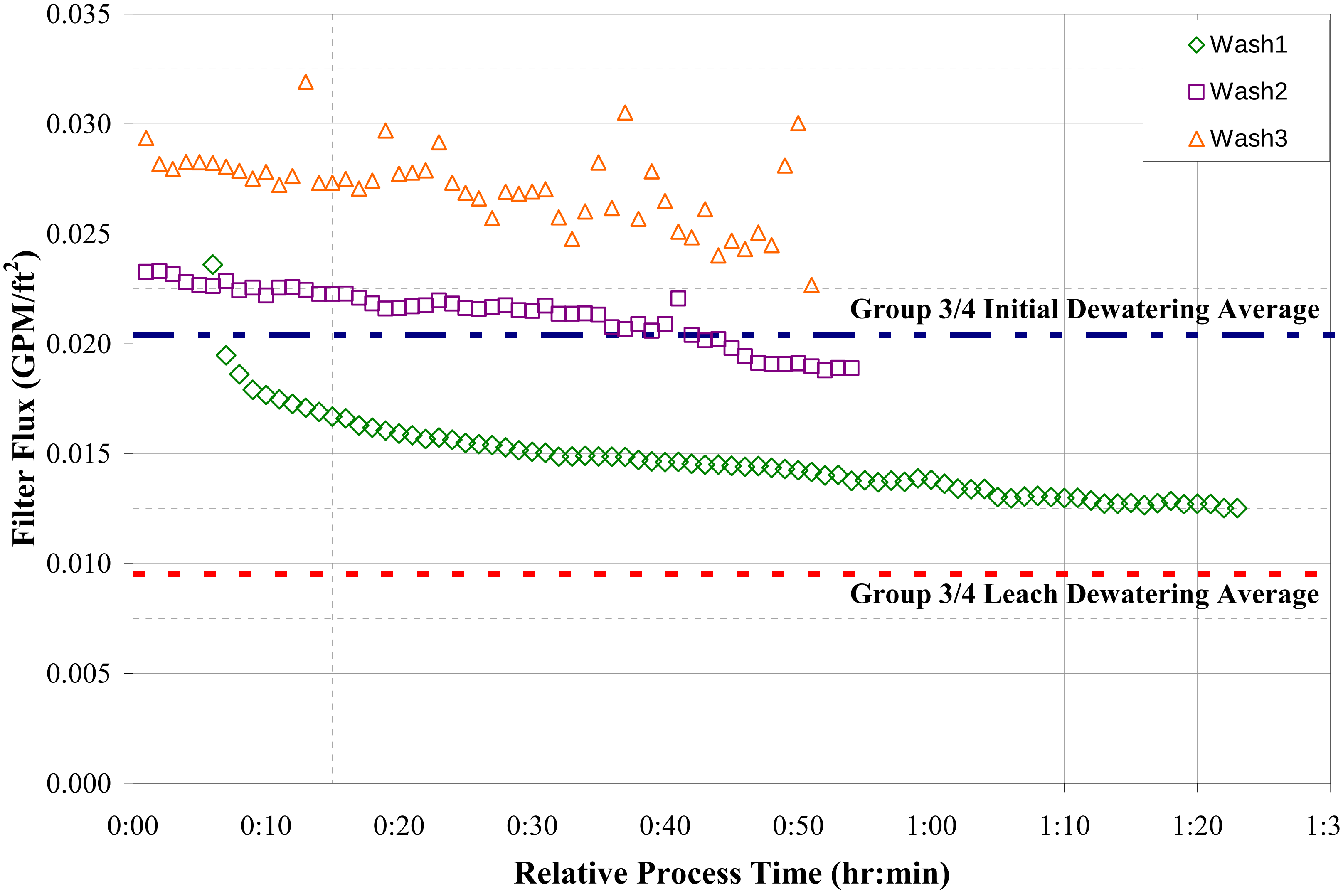


Figure 3.60. Group 3/4 CUF Dewatering of Batch Washes after Caustic Leaching

3.7 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 data for the leached and washed slurry is shown in Table 3.31. The final UDS measurement of the slurry (2 wt%) was lower than expected (0.054 kg ÷ 1.4 kg ≅ 4 wt%) which may be due to difficulties sampling. Settling of the slurry during sampling was an ongoing issue for this kind of test in the hot cells. Once a slurry aliquot was collected, transferring slurry using a pipette to a centrifuge cone was problematic. As seen previously, the solids in this slurry settled quickly (Section 3.3.2), which was attributed to large size particles suspended in a low viscosity interstitial liquid. Once the slurry's supernate viscosity decreased from washing, settling of slurry solids became more of an issue. The UDS concentration was already low because o high extent of aluminum dissolution during the leach. The lower solid fraction of solids in the slurry made it more sensitive to error caused by settling. The final composition of the slurry is shown in Table 3.32.

The results of the slurry leach factor calculation are shown below in Table 3.33. The slurry method is comparable to the supernate-mass balance method as both the Al and P are almost completely leached from solids and washed out of the slurry. Based on the slurry calculation, 6% of the americium-241 and 8% of the europium-155 was leached. The supernate-mass balance calculations (Table 3.32) have this value closer to 0%. Since no Am-241 or Eu-155 was detected in the filtered supernate, it is believed that the more accurate value is 0%. Also, the leach factors calculated here were within the error of the analytical techniques utilized (± 17% Eu-155, ±11% Am-241), and therefore should be considered insignificant.

Washed Leached Slurry
Slurry Mass: 1.4 kg
UDS Mass: 54 g
Slurry Volume: 1.2 L

Permeate Holdup
Mass: 0.22 kg
Volume: 0.2 L

Figure 3.61. Group 3/4 Final Washed Leached Slurry
Note: Mass and volume values in figure are rounded to the nearest significant digit of accuracy.

Table 3.31. Physical Property Measurements of Group 3/4 Leached and Washed Slurry (Inside Slurry Loop)

Slurry Density (g/ml)	1.15
Supernate Density (g/ml)	1.03
Settled Solids (Vol %)	6%
Centrifuged Undissolved Solids (Wt %)	18%
Total Solids of the Slurry (Wt %)	14%
Dissolved Solids of the Supernate (Wt%)	12%
Undissolved Solids of the Slurry (Wt%)	2%

Table 3.32. CUF Group 3/4 Washed Leached Slurry Inventory and Composition

	Slurry(a)	**Liquid Fraction(b)**		**Solids Fraction(c)**	
Mass (kg)	1.53	1.49		0.04	
Wt% of Slurry	100%	97.6%		2.4%	
Metal	g	g	µg/ml	g	µg/g
Al	1.0E+01	5.2E+00	3.6E+03	4.9E+00	1.3E+05
B	6.4E-03	6.4E-03	4.5E+00	n/a(d)	n/a(d)
Bi	1.7E-01	7.7E-03	5.3E+00	1.6E-01	4.3E+03
Cr	1.5E-01	1.7E-02	1.2E+01	1.3E-01	3.5E+03
Fe	2.1E+00	3.1E-03	2.2E+00	2.1E+00	5.7E+04
Mn	3.6E-01	6.7E-05	4.7E-02	3.6E-01	9.6E+03
Na	7.6E+01	6.1E+01	4.2E+04	1.5E+01	4.1E+05
P	4.2E+00	2.4E+00	1.6E+03	1.9E+00	5.0E+04
S	4.0E-01	7.9E-02	5.5E+01	3.2E-01	8.6E+03
Si	1.3E+00	1.8E-02	1.3E+01	1.3E+00	3.4E+04
Zn	4.7E-03	1.1E-02	7.5E+00	n/a(d)	n/a(d)
Zr	9.0E-01	1.9E-03	1.3E+00	9.0E-01	2.4E+04
U	1.5E+00	6.2E-03	4.3E+00	1.4E+00	3.9E+04
Radiochemical Isotopes	**Slurry**	**Liquid Fraction**		**Solid Fraction**	
	µCi	**µCi**	**µCi /ml**	**µCi**	**µCi /g**
Co-60	8.1E+00	< 1.E-1	< 7.E-5	8.1E+00	2.2E-01
Cs-137	8.8E+03	6.6E+02	4.6E-01	8.2E+03	2.2E+02
Eu-154	6.4E+01	< 3.E-1	< 2.E-4	6.4E+01	1.7E+00
Eu-155	2.3E+01	< 1.E+0	< 7.E-4	2.3E+01	6.3E-01
Am-241	2.1E+02	< 2.E+0	< 1.E-3	2.1E+02	5.7E+00
Gross Alpha	3.5E+02	< 6.E-1	< 4.E-4	3.5E+02	9.4E+00
Gross Beta	7.8E+04	5.5E+02	3.8E-01	7.7E+04	2.1E+03
Sr-90	3.6E+04	7.9E+00	5.5E-03	3.6E+04	9.7E+02
Pu-239+240	1.3E+02	3.8E-02	2.6E-05	1.3E+02	3.5E+00
Pu-238	1.6E+01	3.7E-03	2.6E-06	1.6E+01	4.2E-01

Table 3.32. (Cont'd)

Anions	Slurry(a)	Liquid Fraction(b)		Solids Fraction(c)	
	Liquid Fraction			Leached Solids Fraction	
	µg/ml	[M]	g	µg/g	g
F	4.3E+02	2.2E-02	6.1E-01	2.6E+03	9.8E-02
C_2O_4	9.6E+02	1.1E-02	1.4E+00	8.6E+03	3.2E-01
NO_2	8.6E+02	1.9E-02	1.2E+00	5.6E+03	2.1E-01
NO_3	7.6E+03	1.2E-01	1.1E+01	6.1E+04	2.3E+00
SO_4	1.6E+02	1.7E-03	2.4E-01	1.1E+03	4.2E-02
PO_4	5.5E+03	5.9E-02	8.0E+00	4.1E+04	1.5E+00
OH	2.2E+04	1.3E+00	3.2E+01		

(a) Slurry Mass components were calculated from characterization data (WTP-RPT-167). Loss of mass from sampling was incorporated.

(b) Liquid Fraction mass components were calculated using analytical results from supernate sample TI601-G4-G (ASO ID 08-01367) 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 3.33. Group 3/4 Washed Caustic Leach Slurry Composition and Overall Leach Factor Calculations Based on ICP-OES/Radiochemical Characterization

Slurry Prep Method	ICP-OES Analytes	Dry Slurry(a) (µg/g)	Supernate(b) (µg/mL)	Dry Solids(c) (µg/g)	Solids Leach Factor(d)	
					Before Wash	After Wash
HF Assisted Acid Digestion, and KOH Fusion, Concentration Factor of 7.61 based on U, Zr, and Fe	Al	57,550	3,585	149,655	0.93	0.94
	B	185	[4.45]	757	0.68	0.76
	Bi	3,175	[4.5]	15,869	0.14	0.02
	Cd	[27]	[1.25]	[87]	0.16	-0.01
	Cr	2,165	12.0	10,469	0.22	0.10
	Fe	28,350	[2.15]	143,193	NA	NA
	K	[360]	99.4	-[2,094]	-2.01	0.57
	Mn	2,385	[0.047]	12,052	-0.05	-0.03
	Na	348,500	42,000	107,105	-0.07	0.83
	Ni	1,860	[0.35]	9,386	-0.12	-0.29
	P	9,820	1,640	-14,962	-0.52	1.14
	S	[785]	[55]	[1,801]	0.19	0.79
	Si	[22900.0]	12.8	[115229.48]	-0.08	-0.03
	Sr	159	<1.0E-2	801	-0.45	-0.45
	U	15,850	[4.12]	79,941	NA	NA
	Zn	192	7.52	674	0.78	0.88
	Zr	6,263	[1.3]	31,599	NA	NA
	Ag	[21]	<2.6E-1	[104]	-0.11	-0.45
	As	320.00	<5.3E+0	1617.24	-1.53	0.58

Table 3.33. (Cont'd)

Slurry Prep Method	Radionuclides	Dry Slurry(a) (µCi/g)	Supernate(b) (µCi/mL)	Dry Solids(c) (µCi/g)	Before Wash	After Wash
HF Assisted Acid Digestion, and KOH Fusion, Concentration Factor of 7.61 based on U, Zr, and Fe	Ba	117	[0.13]	584	-0.06	0.06
	Be	[0.69]	[0.027]	[2.42]	0.93	0.89
	Ca	2,320	<7.5E-1	11,725	-0.03	-0.07
	Ce	[96]	<1.2E+0	[483]	0.01	-0.08
	Co	[34]	<3.0E-1	[172]	0.62	-0.77
	Cu	86.8	[0.31]	426.7	0.49	0.56
	La	73.9	<3.5E-1	373.5	-0.30	-0.10
	Li	25.5	[0.71]	100.9	0.17	0.61
	Mg	736	<2.8E-1	3,717	0.03	-0.03
	Mo	[65]	[0.66]	[303]	-0.13	-0.02
	Nd	120	<6.7E-1	604	0.03	0.09
	Pb	1,705	[14]	8,065	0.63	0.65
	Ru	[45]	<1.1E+0	[227]	-3.49	-0.33
	Th	305	<1.2E+0	1,539	0.01	-0.06
	Ti	138	[0.055]	693	-0.06	-0.04
	Tl	[68]	<4.7E+0	[344]	0.46	0.87
	V	23.2	1.32	65.3	-0.22	0.66
	W	[37]	<2.3E+0	[187]	0.10	0.41
	Y	16.7	<5.4E-2	84.4	-0.21	0.02
KOH Fusion, *Concentration* Factor of 7.61 based on U, Zr, and Fe	Co-60	5.03E-2	< 7.E-5	2.52E-1	0.05	-0.05
	Cs-137	4.73E+1	4.60E-1	2.21E+2	0.06	0.14
	Eu-154	4.51E-1	< 2.E-4	2.27E+0	-0.02	-0.04
	Eu-155	1.66E-1	< 7.E-4	8.14E-1	0.22	0.08
	Am-241	1.42E+0	< 1.E-3	7.13E+0	-0.11	0.06
	Sr-90	2.53E+2	5.52E-3	1.28E+3	-0.13	-0.04
	Pu-239/240	8.77E-1	2.58E-5	4.43E+0	-0.28	-0.01
	Pu-238	9.89E-2	2.63E-6	5.00E-1	-0.18	-0.25

(a) Test sample TI601-G4-G, ASO ID 08-01367
(b) Test sample TI601-G4-12, ASO ID 08-01383
(c) Calculated using results from TI601-G4-G and TI601-G4-12
(d) Calculated using dry solids concentration results listed in Table 3.17

Note: Analytes in italics were measured opportunistically. Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

The final leached and washed slurry shows significant decreases in Al, Cr, Na, P, and S from the pre-leached material. These losses are expected because of 1) the solubility of Na, PO_4, and SO_4 and 2) the leaching of solid Al and Cr. Using a mass balance calculation, initial characterization data, and supernate analysis results, the change in total solids and radionuclides present in the slurry are shown in Figure 3.62. Changes in the insoluble solids in the slurry were calculated by assuming aluminum that dissolved from the solids was all gibbsite ($Al(OH)_3$) during the caustic leach/dewatering steps and sodium phosphate (Na_3PO_4) during the caustic leach/washing of the solids. Accounting for the sampling that was done, total solids in the slurry decreased by 77 wt%, and the only significant loss of radionuclides were Cs-137 by 53 wt% and Co-60 by 4 wt%. The rest of the radionuclides stayed with the solids with only ±1% variance from the original slurry (Figure 3.62). The Co-60 was seen in the initial feed supernate, but after pre-leach dewatering the soluble Co-60 had been removed. Unlike the solid leach factor calculations (Table 3.33), no significant changes in Am-241 or Eu-155 were seen.

Anions were measured in the supernate throughout the testing with specific attention paid to the cool down period after the caustic leach (Figure 3.63). Sulfate, nitrate, and nitrite show similar declines as the slurry was dewatered and washed. Both phosphate and oxalate gradually fall out of solution during the cool down period and show a dramatic increase after the sodium concentration has decreased. As discussed previously, the phosphate begins to come out of solution as the sodium concentration decreases. Oxalate in solution follows Le Châtelier’s principal: $Na_2C_2O_{4(s)} \leftrightarrow 2Na^{+}_{(aq)} + C_2O_4{}^{2-}{}_{(aq)}$. Increased sodium concentration favors the sodium oxalate$_{(s)}$, and decreasing the sodium concentration increases oxalate$_{(aq)}$ concentration in solution. Furthermore, temperature plays a role since oxalate increases in solubility with increases in temperature; as the temperature drops, the solubility decreases, and sodium oxalate falls out of solution.

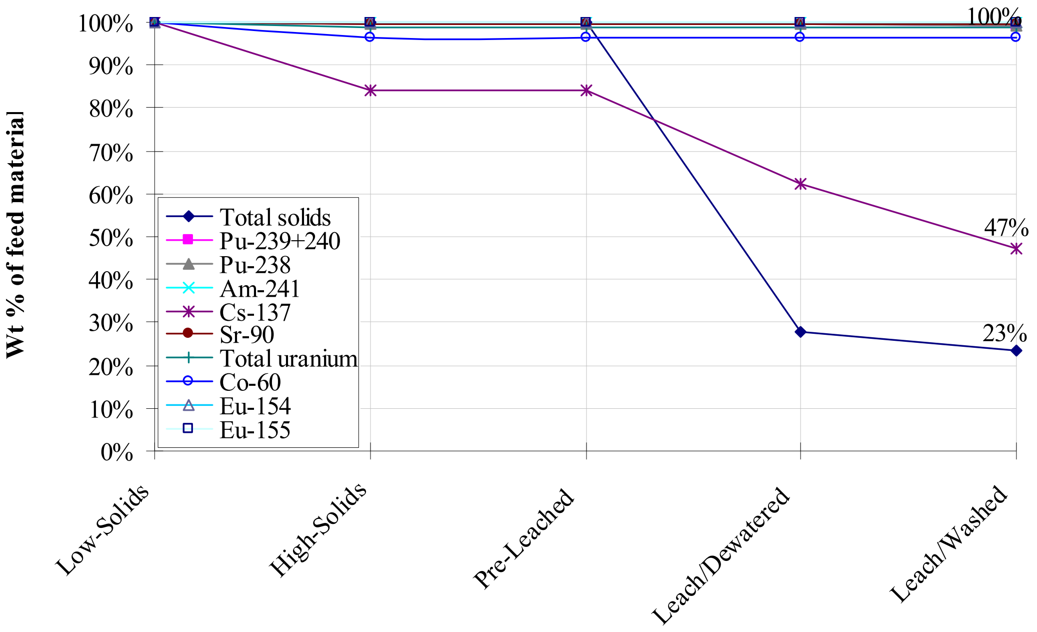


Figure 3.62. Radionuclides/Total Solids in Group 3/4 CUF Slurry, (Adjusted for Sampling)

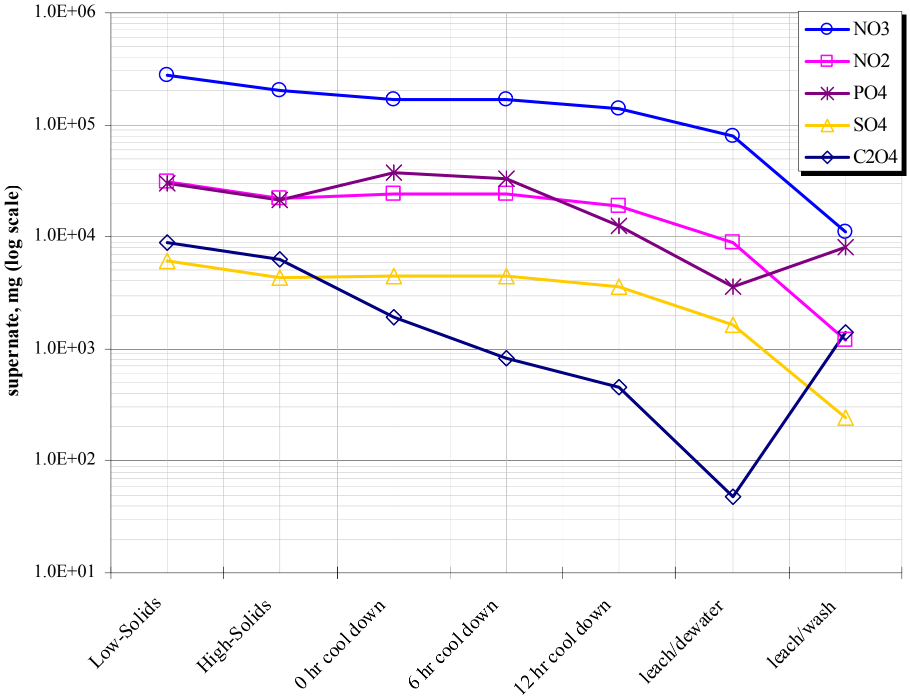


Figure 3.63. Anions in Slurry Supernate during Group 3/4 CUF Test

The leached and washed solids were dried and BET surface area and XRD analyses were performed. The BET determined the surface area to be 63 m^2/g.

The XRD analysis did not identify gibbsite, suggesting that it was almost completely leached (Figure 3.64). Corundum, Al_2O_3, was used as an internal standard for 2-theta calibration. Identification was done on the summed, 2-theta calibrated data with the background removed. The mineral phases identified were:

- Tochilinite II, $(Fe_{0.8}S_1)(Mg_{0.7}Fe_{0.3}(OH)_2)_{0.833}$ (Observed)
- Aluminum fluoride hydroxide, $AlF_{1.96}(OH)_{1.04}$ (Possible)
- Thermonatrite, $Na_2(CO_3)(H_2O)$ (Observed)
- Calcium iron aluminum oxide, $Ca_2Fe_{1.28}Al_{0.72}O_5$ (Possible)
- Cancrinite, $Na_8(AlSiO_4)_6(CO_3)(H_2O)_2$ (Observed)
- Nitratine, $Na(NO_3)$ (Observed)
- Alumophosphate zeolite, $((NH_3(C_4H_9))_2)H(Al_2P_3O_{12})$ (Possible)
- Clarkeite, $Na((UO_2)O(OH))$ (Possible)

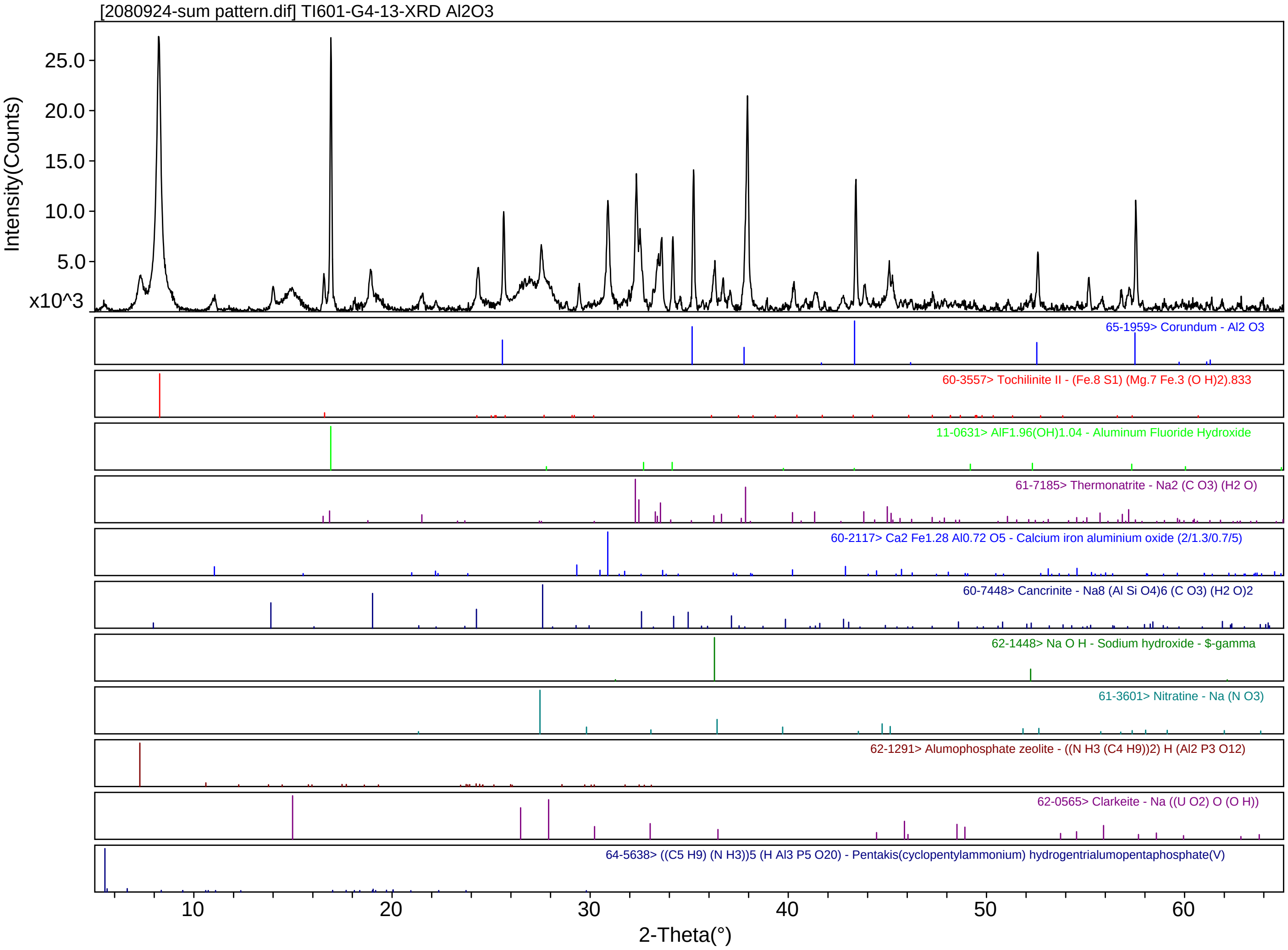
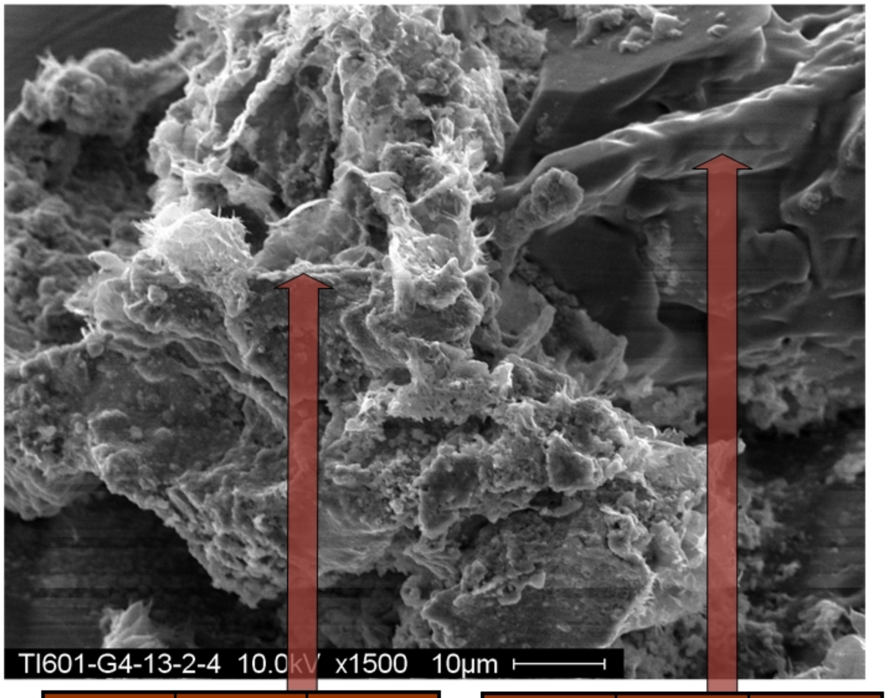


Figure 3.64. XRD Scan of Group 3/4 CUF Washed Leached Slurry Particles

SEM images were also taken of the washed, leached and dried solid material. The EDS (Figure 3.65) confirmed the presence of elements that were identified in the XRD analysis. The high quantity of carbon and oxygen seen in the EDS measurement was from the graphite coating applied to the slide and should be ignored. Closer SEM images identified small clusters (Figure 3.66) that are believed to be sodium nitrate in the slurry supernate that was dried onto the slurry solids during analysis prep. This correlates to previous discussion that three volumetric washes of the slurry was not enough to remove all of the slurry supernate.



Element	Wt%	At%
CK	39.79	63.53
OK	14.02	16.8
NaK	4.87	4.07
AlK	4.29	3.05
SiK	2.91	1.98
PK	3.55	2.2
UM	8.2	0.66
CaK	0.82	0.39
CrK	1.21	0.45
MnK	2.31	0.81
FeK	14.11	4.85
NiK	1.39	0.45
CuK	2.54	0.77

Element	Wt%	At%
CK	53.57	65.35
OK	27.53	25.21
NaK	9.04	5.76
AlK	2.1	1.14
SiK	0.54	0.28
PK	1.7	0.8
FeK	5.52	1.45

Figure 3.65. SEM and Energy Dispersive Spectroscopy (EDS) of Group 3/4 CUF Washed Leached Slurry Particles

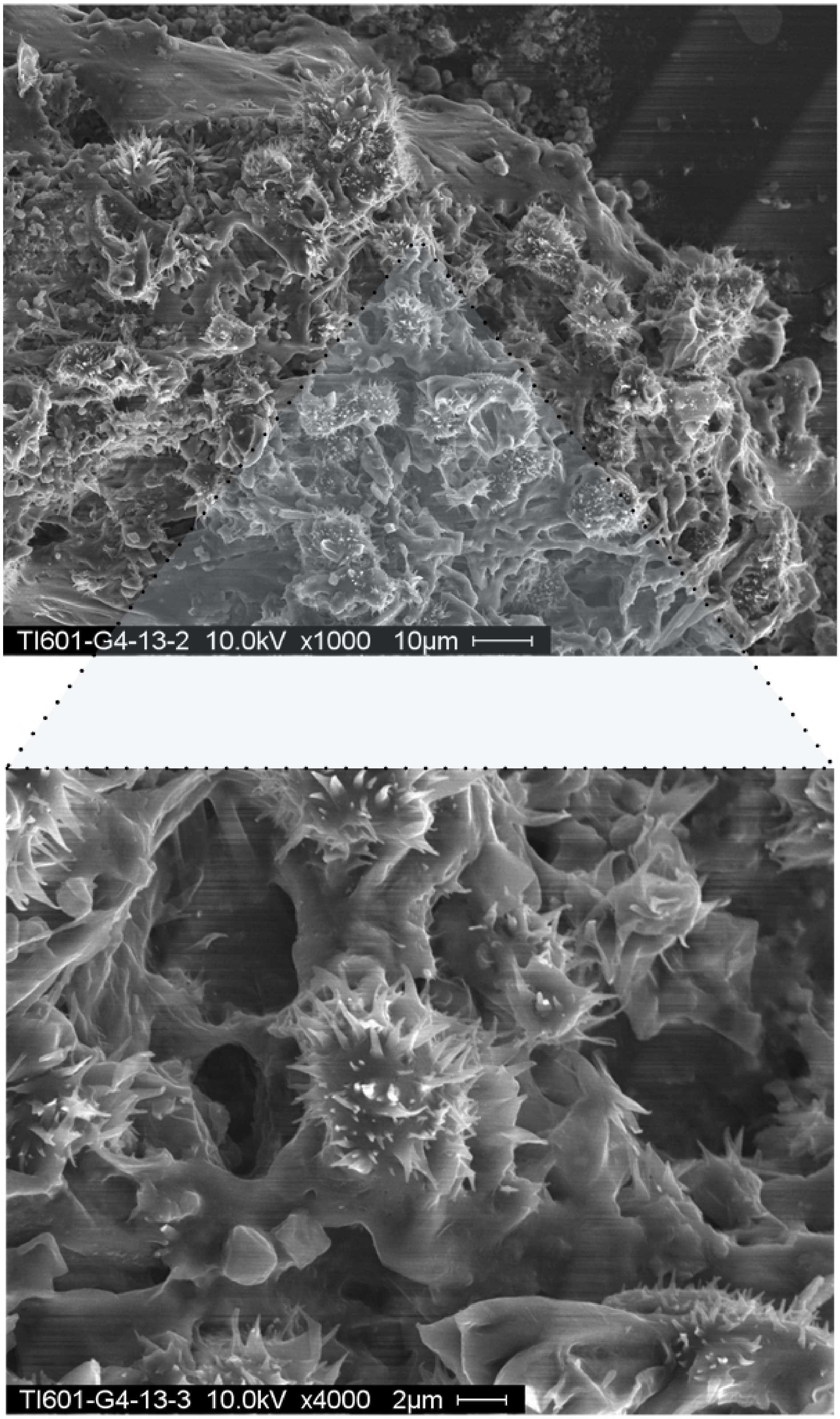


Figure 3.66. SEM Images of Group 3/4 CUF Washed Leached Slurry Particles

TEM images were also collected on the washed leached Group 3/4 slurry. Slurry samples were mixed with methanol and deposited onto a lacy carbon TEM grid after mixing. The prepared samples revealed many large particulates that were composed of several phases. Iron dominated the particles according to the EDS analysis, as shown in Figure 3.67. There was no evidence of distinct aluminum oxide, or gibbsite particles. Figure 3.68 shows a large agglomerated particle consisting of several different phases. The bright region is uranium-rich and the lighter areas contain sodium, aluminum, and silicon. There was no evidence of gibbsite in the sample. There appeared to be evidence for a sodium aluminum silicate from the sample shown in Figure 3.68, supporting XRD analysis that identified the presence of cancrinite. Analysis of other regions also supported the occurrence of a sodium aluminum silicate; however, the phases were mixed with other solids that made identification of a specific phase difficult.

Particle size measurements were taken of the final slurry sample to characterize the change in the average particle size since the start of the test. Figure 3.69 shows the PSD for the washed Group 3/4 after caustic leach sample as a function of pump speed before sonication. At 2000 RPM, the distribution is tri-modal and non-continuous with a primary peak at 1 µm, a secondary peak at 10µm and a third peak at 120 µm. At 3000 RPM, the distribution is similar to 2000 RPM although the distribution is continuous and the 11 µm - 100 µm relative contribution is larger. At 4000 RPM, the distribution remains tri-modal and continuous, although the primary peak is at 60 µm, the secondary peak is at 1 µm, and a weak peak exists at 8 µm. The strong primary peak at 4000 RPM suggests that there are numerous large difficult-to-suspend particles and/or agglomerates in the sample.

Figure 3.70 shows the particle size distribution as a result of applied sonication. During sonication, the particle size range is shifted from 0.23 µm - 200 µm to 0.2 µm - 30 µm, resulting in a tri-modal continuous distribution with peak maxima around 0.5, 2.4, and 10 µm. Sonication appears to disrupt particles around 1.2 µm, as indicated by the reduced relative fraction of particles in this size range. This peak population may be been comprised of agglomerates or may have been more susceptible to sonic induced shearing. This 1.2 µm peak reduction during sonication may also be a result of > 30 µm agglomerates preferentially reducing to particles around 0.5 µm and 2.4 µm increasing their relative population. After sonication a significant increase occurs for > 30 µm particles, indicating rapid agglomerate recovery. As the distribution for 0 µm - 30 µm particles displays similar qualities during and after sonication, the effects on the primary pre-sonication 1.2 µm peak appear to remain stable throughout the duration of the experiment.

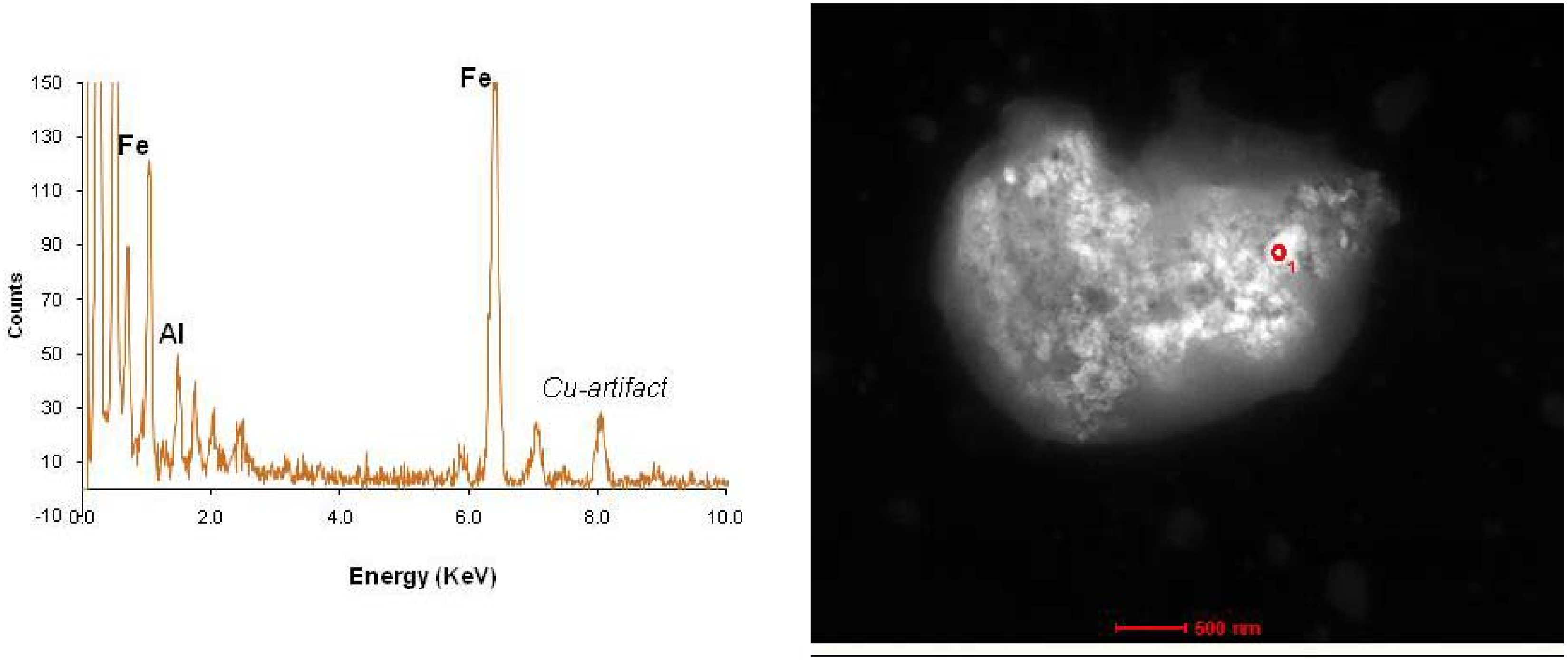


Figure 3.67. TEM Image and EDS Analysis of Iron Particle in Group 3/4 CUF Leached Slurry

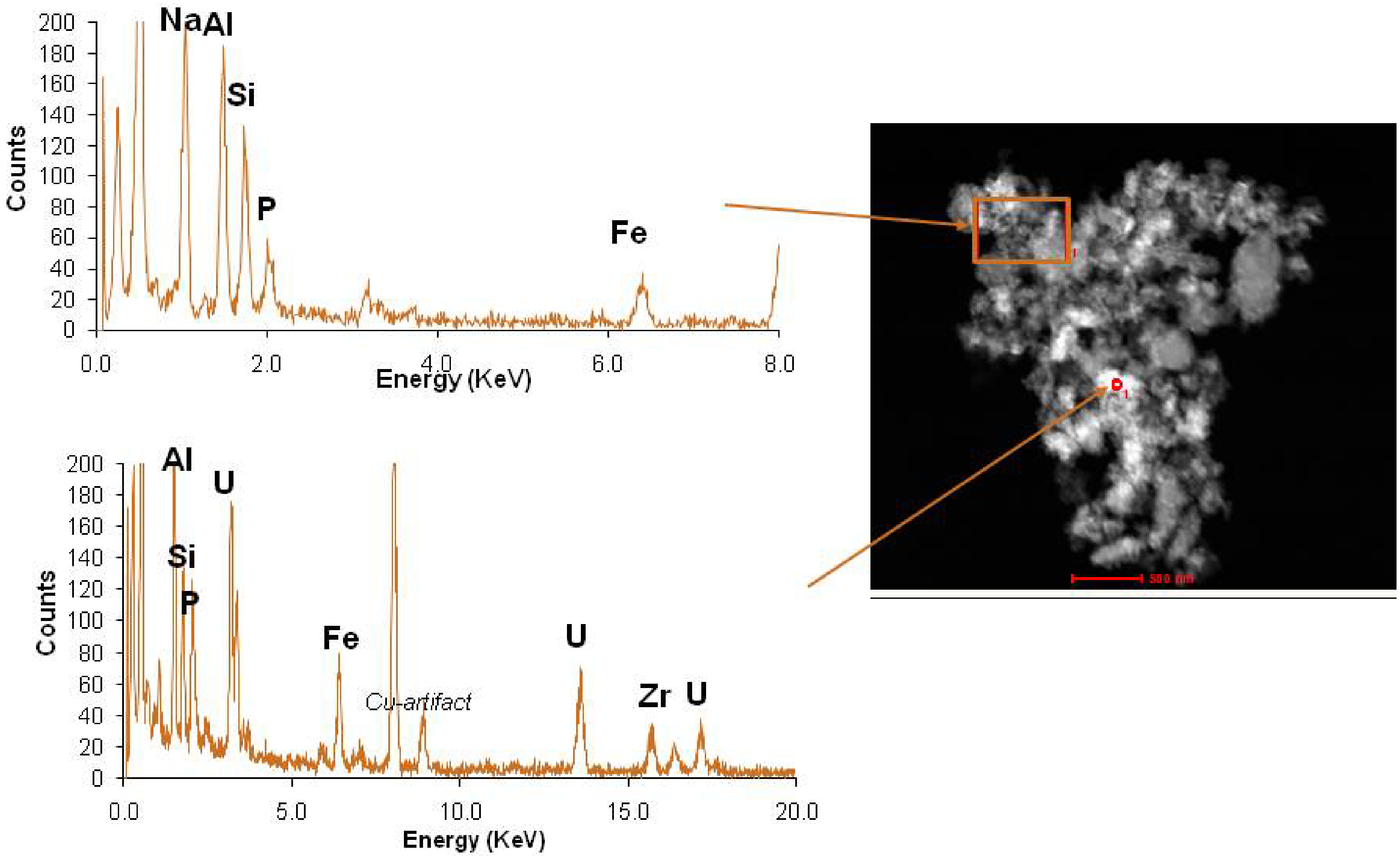


Figure 3.68. TEM Image and EDS Analysis of Particle Agglomerate Showing Aluminum, Silicon, Sodium, and Zirconium in Group 3/4 CUF Leached Slurry

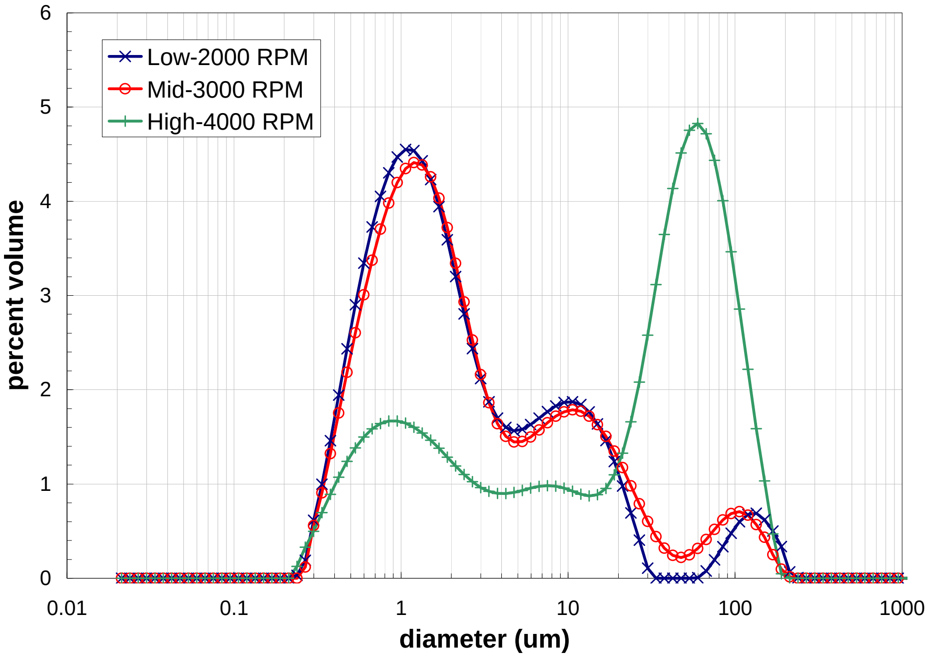


Figure 3.69. PSD Measurements of the Group 3/4 CUF Washed Leached Slurry as a Function of Pump Speed

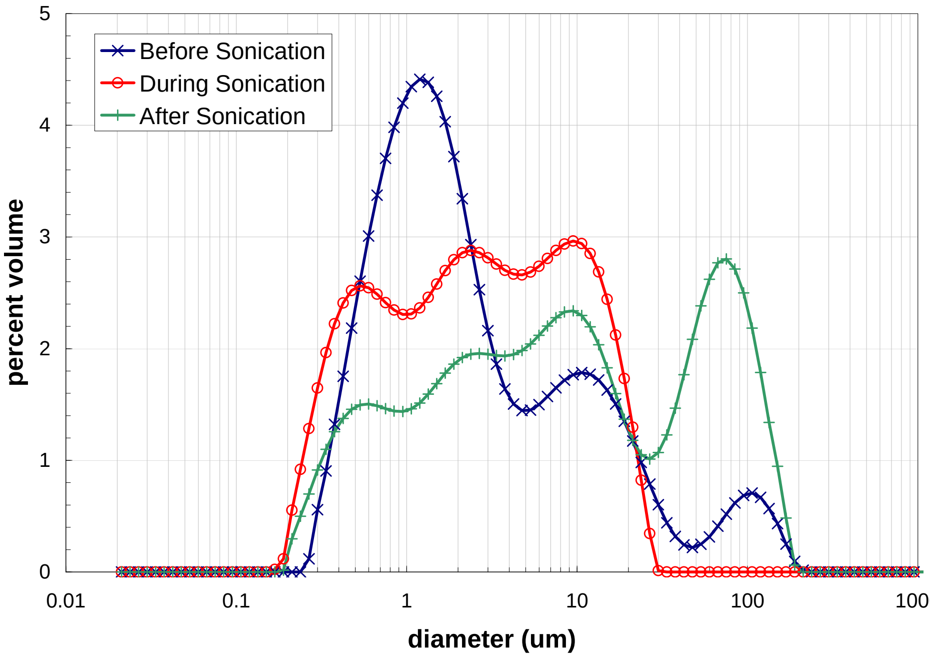


Figure 3.70. PSD Measurements of the Group 3/4 CUF Washed Leached Slurry as a Function of Sonication

Rheological measurements of the final slurry were also performed to observe changes in the slurry's shear stress and consistency after washing. Flow curve testing indicated that the slurry was Newtonian behavior and exhibited a weak stress response (i.e., a shear stress of approximately 1 Pa at 500 s^{-1} and 25°C). Because of torque corrections required for this sample, flow curve figures were not generated.

Table 3.34 summarizes the regressed Newtonian viscosities for the leached, washed slurry. The results indicate a Newtonian viscosity of 2.3 mPa-s - 2.7 mPa-s at 25°C, 1.4 mPa-s at 40°C, and 0.7 mPa-s at 60°C. The decrease in viscosity with increasing temperature is consistent with previous Group 3/4 CUF testing samples. The quality of the fit, as given by the correlation coefficient (R), decreases at higher temperatures and is indicative of the reduced stress response at higher temperature.

Table 3.34. Results of Fitting Analysis for the Group 3/4 CUF Washed Leached Slurry

Model	Temperature [°C]	Range	Viscosity [mPa·s]	R
Newtonian	25 (1 of 2)	0-500 s^{-1}	2.7	0.95
	25 (2 of 2)	0-500 s^{-1}	2.3	0.89
	40	0-300 s^{-1}	1.4	0.89
	60	0-300 s^{-1}	0.7	0.52

Table 3.35. Comparison of Group 3/4 CUF Slurry Rheology during Testing

Description	Undissolved Solids Concentration	Rheology	Yield Stress [Pa]	Consistency [mPa-s]
Group 3 Source	~29 wt%	Newtonian	n/a	3.4
Group 4 Source	~30 wt%	Newtonian	n/a	2.4
Low solids Group 3/4 Mixture	~6 wt%*	Newtonian	n/a	2.0
High solids Group 3/4 Mixture	~13 wt%	Non-Newtonian	3.4	7.6
Caustic-Leached / Dewatered Slurry	~3 wt%	Newtonian	n/a	16
Caustic-Leached / Dewatered / Washed Slurry	~2 wt%	Newtonian	n/a	2.3

* Initial measurement for slurry

3.8 Cleaning Operations and Final Clean Water Flux Measurements

After final sampling of the slurry was completed, the slurry and permeate hold-up was drained and archived for use at a later date. The inside of the slurry reservoir was then scrubbed with DI water to remove excess solids on the side of the tank walls and drain. The system was then rinsed with DI until the drained water exiting the slurry loop appeared to be clear. A solution of 0.01M NaOH was then added to the system and the clean water flux was measured, as performed in Section 3.1. The test solution was then drained afterwards for acid cleaning.

A 2M HNO_3 solution was then added to acid clean the system. The solution was allowed to circulate in the CUF through both the slurry and permeates loops for approximately one hour. At the start and end of the cleaning, three back pulses were performed on the system. The acid solution was then drained from the slurry loop and permeate loop of the CUF and rinsed with DI water twice and once with 0.01M NaOH to remove excess acid out of the system. After draining the last rinse solution, another solution of 0.01M NaOH was added to the CUF. The clean water flux of the filter was measured again. The CUF was then drained to be cleaned further.

A 0.5M solution of oxalic acid was added to further clean the filter. Like the nitric acid cleaning step, the solution was circulated through both the slurry loop and permeate loop for approximately one hour. Three back pulses were performed at the start and end of the cleaning. The solution was drained, and rinsed with DI water twice and 0.1M NaOH once to remove the excess acid. A final solution of 0.01M NaOH was then added to make a final measurement of the clean water flux of the filter.

The impact of cleaning activities in terms of clean water flux is shown in Figure 3.71 and Figure 3.72 below. Figure 3.71 compares the clean water flux of the filter after the test (post-run), after nitric cleaning (post-nitric), and after oxalic cleaning (post-oxalic). Comparison of the initial flux measurements of the system before and after nitric acid cleaning shows a slight improvement in the flux. However, the filter flux decayed dramatically with a 15 minute period, indicating that material was still inside the slurry loop which could quickly foul the filter. After oxalic acid cleaning, there was another increase in the initial filter flux measurements when comparing the initial nitric acid cleaning results to the oxalic cleaning results. But the big difference between the two cleaning cycles was that the clean water flux after oxalic acid cleaning did not decrease after 15 minutes like what occurred after nitric acid cleaning. In fact, the clean water flux looked very similar to that initial measured on the filter before testing with actual waste samples began (Figure 2.1).

Figure 3.72 compared the final clean water flux measurement of the filter prior to testing (pre-run) to the final clean water measurements after the test (post-run), and after oxalic cleaning (post-oxalic). This charts showed that the clean water flux of the filter after slurry processing was significantly lower than the clean water flux prior to testing, and that oxalic acid cleaning significantly improved clean water flux afterwards. The measured decay in the pre-run clean water flux tests was interesting when compared to the final cleaning results. As discussed in Section 3.2, the filter was place in standby with 0.1M NaOH for a week prior to the test after being oxalic clean. While oxalic acid cleaning results produced clean water flux results similar to those seen in Figure 3.71 prior to this test, the results were not repeatable a week later. This may be due to incomplete cleaning, material later being removed from the piping, or air-borne contamination from inside the hot cell having an effect. In any case, this demonstrated the sensitivity of clean water flux measurements, and how small contaminates have large impacts on filter flux.

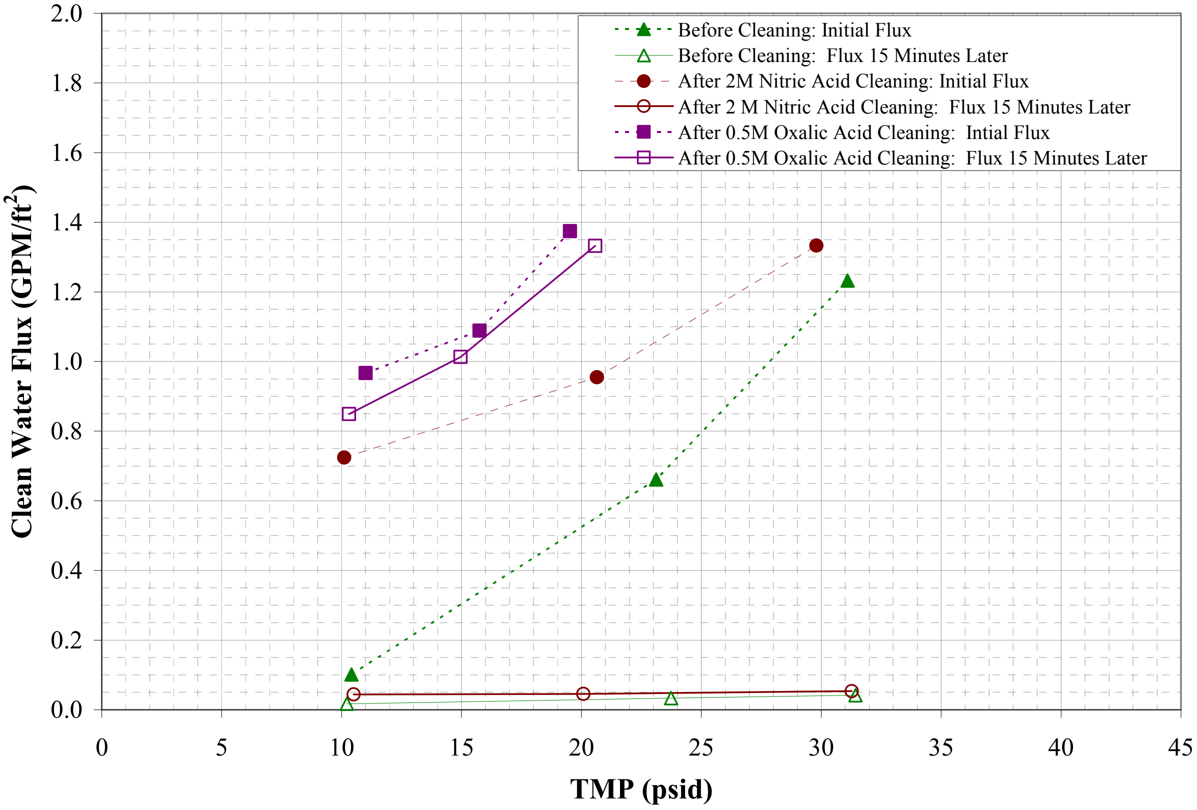


Figure 3.71. Clean Water Flux Measurements Before and After Cleaning Operation

Note: Data displayed in the figure above are from a user calibrated device, not a NQA-1 Calibrated Device.

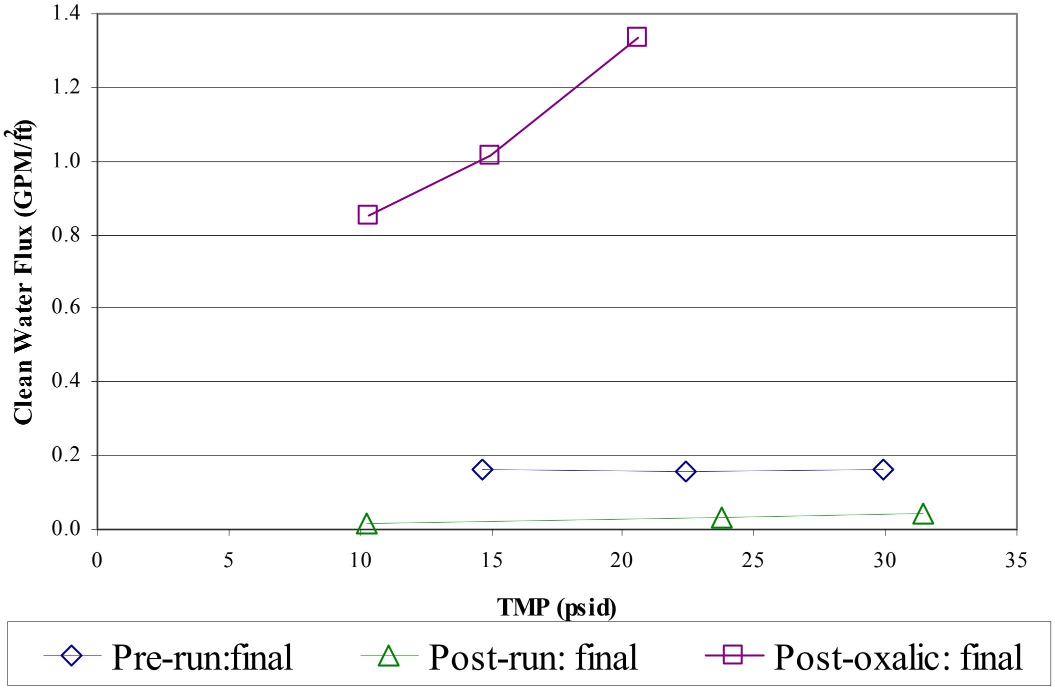


Figure 3.72. Comparison of Clean Water Flux Measurements before and after Testing
Note: Data displayed in the figure above are from a user calibrated device, not a NQA-1 Calibrated Device.

4.0 Discussions

The objectives of test plan TP-WTP-467 covered by the testing performed were to:

- Observe the filtration behavior of the Group 3/4 blended waste slurry before and after caustic leaching.
- Observe the dissolution of undissolved solids during caustic leaching and washing of the Group 3/4 waste slurry. The primary interest for leaching was for aluminum that was predominantly in the form of gibbsite in the waste slurry.
- Physically characterize the crystal behavior of the undissolved solids remaining in the Group 3/4 after caustic leaching.

4.1 Filtration Behavior

Filtration matrix testing indicated that filter flux was primarily dependent on TMP with little or no impact from AV. Comparison of the matrix test results of the pre-leached slurry showed no change in the filtration behavior when the UDS concentration was increased to 14 wt% - 15 wt%. Filtration testing of the dewatered leached slurry found similar filtration behavior to the pre-leached slurry. Because over 70 wt% of the solid mass in the slurry dissolved during the caustic leach, it was expected to behave much like the low solids slurry. While TMP was found to be the primary parameter, it was also observed that operation time had a negative effect on filter flux as well. The effect indicated that a fouling caused by the slurry was occurring that was not reversed with back pulsing. This effect became more significant after caustic leaching. This may be due to precipitation of sodium salts, but this has yet to be proven.

Dewatering operations of the pre-leached slurry to 19 wt% UDS showed only a very small decrease in the filter flux as the UDS concentration increased. While the slurry rheological flow behavior changed from Newtonian to non-Newtonian flow during dewatering to 19 wt%, the solid concentration still was not high enough to change the filtration behavior of the slurry. Examination of the physical property results indicates that the gel concentration of the slurry (predicted from the centrifuge UDS concentration) was in the proximity of 40 wt%. This result indicated that the slurry needed to be dewatered past 20 wt% UDS before effects from solid concentration and AV could become significant.

Dewatering the slurry after caustic leaching and washing showed similar dewatering behavior as well. But as discussed earlier, the dissolution of a significant fraction of the solids left the final UDS of the dewatered slurries < 5 wt%, so it was not unexpected that the flux only changed slightly over time. Changes in filter flux between all the dewatering operations could be related to the sodium concentration of the supernate (Figure 4.1). Because sodium concentration is a good measure of liquid viscosity, it showed that the filter flux was directly impacted by changes in the slurry supernate as predicted by the Darcy equation (Equation 2-6). This also indicated that filter resistance to the slurry remained fairly constant throughout the test, since transmembrane pressure was fixed at 40 psid for all dewatering operations. This indicated that irreversible fouling caused by the slurry was not dissolved by the caustic leaching or washing operations, and would require acid cleaning to restore the filter to the original condition. Initial cleaning with 2M nitric acid proved to be only partially effective. The filter was later cleaned with 0.5M oxalic acid. The effectiveness of oxalic acid implies that iron present in the slurry was likely causing the irreversible fouling of the filter.

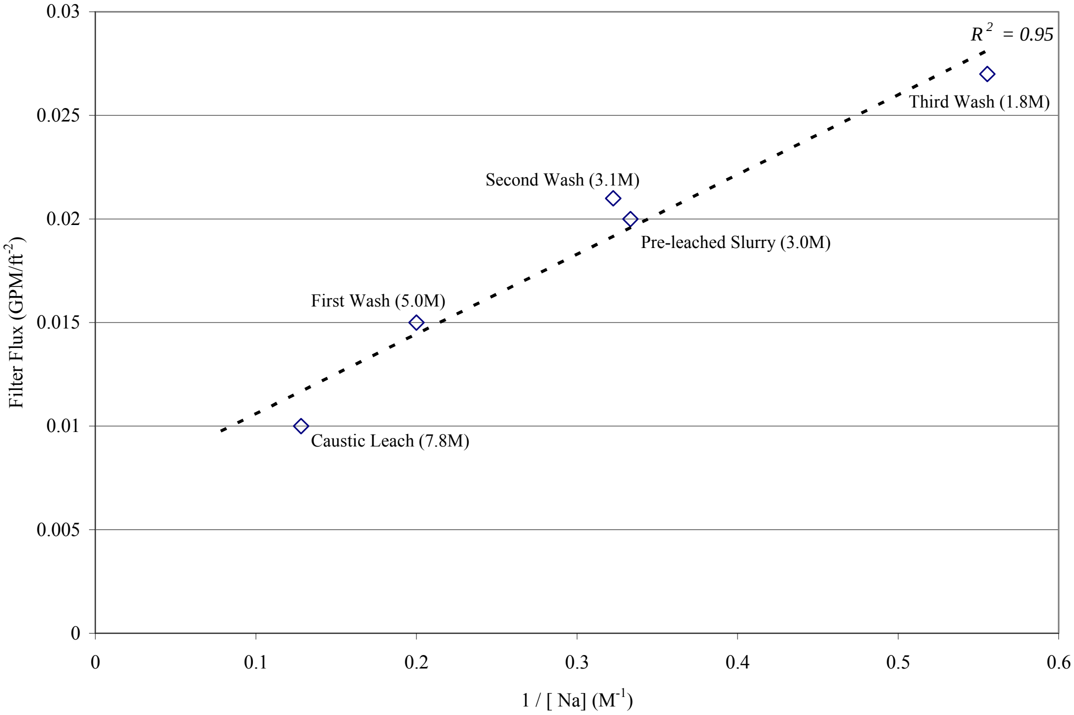


Figure 4.1. Dewatering Filter Flux versus the Inverse of the Filtrate's Sodium Concentration

4.2 Leaching Behavior

Caustic leaching of aluminum in the solid phase of the blended Group 3/4 slurry showed that aluminum dissolution was completed before reaching the planned leach temperature of 100°C, when using an initial free hydroxide concentration of 6.6M. After 3.5 hours of heating, the slurry reached a temperature of approximately 70°C, and measured aluminum dissolution was 93% (from supernate ICP analysis). After reaching 100°C 1.8 hours later, the dissolution of aluminum increased only slightly, and did not change significantly during the 8 hour leach soak. The final free hydroxide of the slurry supernate was 5.6M. The rapid dissolution and high conversion of aluminum in the waste slurry agrees with parametric leaching studies performed on the individual Group 3 and Group 4 wastes, as reported in WPT-RPT-167 Snow et al. observed a very rapid initial dissolution rate that increased with temperature and free hydroxide concentration.

Phosphorus removal was enhanced by caustic leaching, but high sodium and hydroxide concentrations used for the leach caused lower dissolution and washing effectiveness. After cooling the slurry following caustic leach, slurry and supernate results indicate that soluble phosphate in the supernate actually precipitated (-26% leach factor). Until the second wash, removal of phosphorus was hindered by its solubility in the supernate. This same behavior was also observed during the filtration and leach testing of the Group 1/2 CUF slurry PNNL-17992 (WTP-RPT-166) (Lumetta et al. 2009). The tests indicate that insoluble phosphorus was converted to phosphate from caustic leaching, but remains a solid until further washing operations later in the process. This presents processing challenges to predicting when phosphorus will be removed from the slurry and how it may behave in other operations downstream when sodium and hydroxide concentrations may be higher.

4.3 Characterization of Crystal Habits of Leached Solids

Initial characterization of the PUREX cladding waste sludge and REDOX cladding waste sludge found a majority of the undissolved solids in both wastes was gibbsite (approximately 90 wt%). After caustic leaching and washing, a significant portion of the aluminum was removed. XRD analysis found the aluminum still present to be in the insoluble form of cancrinite. Gibbsite was absent in the XRD scans and not visible in SEM images. This implied that the gibbsite present in the solids was all dissolved during the caustic leaching operation. The results showed insoluble Al to be present in the form of cancrinite, and that uranium and iron were present in crystalline oxide structures. Leaching also had a significant impact on the surface area of the leach particles, indicating that large particles of gibbsite had been dissolved. Because the slurry was only washed three times, XRD and SEM also found soluble salts present in the slurry supernate (sodium nitrate, sodium hydroxide), indicating that further washing would be beneficial. TEM imaging supported the results of SEM and XRD analyses which showed phase of iron, uranium, and sodium aluminum silicate present, as well as the absence of gibbsite.

Table 4.1. Comparison of XRD Results from Characterization Results to Group 3/4 CUF Solids

Identified Compound	**Chemical Formula**	**Identified from XRD Analysis**		
		Group 3 (CWP) Washed Solids	**Group 4 (CWR) Washed Solids**	**Group 3/4 CUF Leached Solids**
Gibbsite	$Al(OH)_3$	Observed	Observed	
Cancrinite	$Na_8(AlSiO_4)_6(CO_3)(H_2O)_2$,	Observed		Observed
Sodium aluminum silicate hydrate	$(Na_2O)_{1.31}Al_2O_3(SiO_2)_{2.01}(H_2O)_{1.65}$		Observed	
Clarkite	$Na((UO_2)O(OH))$	Possible		Observed
Sodium uranium oxide	$Na_6U_7O_{24}$		Possible	
Hemetite	$Fe_{1.67}H_{0.99}O_3$	Observed		
Tochilinite II	$(Fe_{0.8}S_1)(Mg_{0.7}Fe_{0.3}(OH)_2)_{0.833}$			Observed

Table 4.2. Comparison of BET and SEM-EDS Measurements

Waste Type	**Condition**	**BET Surface Area (m^2/g)**	**SEM EDS Elements**
Group 3 (CWP)	Washed Solids	4.4	Na, Al, Si, U, Fe, P
Group 4 (CWR)	Washed Solids	2.8	Na, Al, Si, U, Fe, Pb, Ca, Cr, Mn
Group 3/4 CUF	Washed Caustic Leached	63	Na, Al, Si, U, Fe, Ca, Cr, Mn, Ni, Cu, P

5.0 Summary and Conclusions

5.1 Summary of Testing and Objectives

To address Task 4 of the EFRT M12 response plan, a scope of work was developed to perform caustic and oxidative leaching bench scale tests of actual tank waste samples as defined in test plan TP-RPP-WTP-467. To cover as much as possible of the range of HLW types at the Hanford site, eight composite samples of waste types were assembled from archive tank samples in the 222S Laboratory and homogenized in the hot cells at the RPL. Each waste type was developed to specifically address a processing challenge. Together, the eight waste composites represented approximately 75% of the HLW mass expected to be processed through the WTP. After a composite waste group was homogenized, it was characterized for physical properties, chemical composition, and crystal habit of the insoluble solids. Parametric leaching studies were then performed on a small scale to understand the leaching kinetics of aluminum, chromium, and phosphate using planned caustic and oxidative leaching process in the PTF. Finally, the remaining waste sample was placed in a bench top filtration/leaching apparatus in the hot cells where leaching and ultrafiltration operations of the PTF were simulated to understand how leaching operations affect filtration.

The waste groups tested and discussed in this report are the PUREX Cladding Waste (Group 3/CWP) and the REDOX Cladding Waste (Group 4/CWR) composite samples. Both waste types were of interest due to the high percentage of insoluble aluminum present in the form of gibbsite, unlike the REDOX sludge waste (Group 5) where aluminum is primarily in the form of boehmite. Both CWP and CWR wastes will require caustic leaching to remove aluminum from the HLW waste stream—so their kinetic behaviors were of interest and how gibbsite dissolution would compare to boehmite. In WTP-RPT-167, it was discussed how each of these two waste groups were homogenized, prepared for physical and chemical characterization, and what the results of parametric leaching studies were. The focus of this report was on the benchtop filtration/leaching test using the remaining Group 3 and Group 4 waste composites once the initial studies were completed.

Leaching and filtration testing was performed on a blend of the remaining Group 3 and 4 waste groups using a benchtop, filtration/leaching testing apparatus in the hot cell. The system was capable of filtering HLW slurry using a cross-flow ultrafilter (2 ft long with a 0.5 inch ID) rated nominally for 0.1 μm pore diameter. The test used a composite of both waste groups, and focused only on caustic leaching of the gibbsite present and how filtration was impacted.

The following objectives of test plan TP-WTP-467 covered in the testing performed were:

- Filtration of actual waste before and after caustic leaching was performed and compared.
- Caustic dissolution of aluminum, in the form of gibbsite, was performed using both Group 3 and Group 4 wastes. Initial characterization estimated that approximately 90 wt% of the undissolved solids present in the waste was gibbsite.
- Final characterization of the leach waste was performed using XRD, SEM, and TEM to confirm the final phases of undissolved leach solids.

5.2 Filtration Behavior

Filtration results of the Group 3/4 CUF test provided in Section 3 of this report are summarized in

Table 5.1. The following general observations were made:

- Problems were encountered while attempting to suspend the solids of the Group 3 and Group 4 waste into the circulating slurry during the test. At the onset of testing, solids in the composite slurry deposited into a low section of the circulation line, forming a plug. Characterization data of the waste composite indicated that the solids in both materials settle rapidly and a high shear strength upon settling (> 100 Pa), making re-suspension difficult.
- Despite the slurry supernate viscosity being relatively low (1 mPa-s - 2), the filter flux for the blended cladding waste slurry was relatively low (0.02 GPM/ft^2) compared to the REDOX sludge waste (0.06 GPM/ft^2). Increases in TMP caused proportional increases in the filter flux throughout the test.
- Axial velocity appeared to have little impact on filtration at the concentrations tested, and up to a pre-leached slurry UDS concentration of about 20 wt%. Physical property testing estimated that the gel concentration of the pre-leached slurry (using centrifuge UDS concentration data) was ≥ 40 wt%, which indicated that the pre-leached slurry could be dewatered to greater than 20 wt%. Because the high extent of dissolution of aluminum, the mass of solids present in the slurry after leach were too low to see significant effects from the slurry's solids concentrations.
- The filter flux showed a decay over time that was not prevented by back pulse operations equivalent to a 1 psid decrease in TMP for every 2.7 hours. The effect appeared to be a long term irreversible fouling of the filter, possibly from iron present in the waste. After leaching, the effect was more pronounced with an equivalent 1 psid decrease occurring in 0.67 hour.
- Filter flux was found to be inversely proportional to changes to the permeate viscosity that occurred from caustic leaching to washing operations, as defined by Darcy's Law (Equation 2.6).
- While some level fouling was observed during the test, the observed filter resistance appeared not to dramatically decrease or increase due to caustic leaching or washing of the slurry. This indicated that material impacting filter resistance was not dissolved from the caustic leach and remained in the slurry afterwards.
- Particle size measurements showed little change in the distribution during filtration and dewatering of the blended waste. After leaching and washing, the d[10] value for the waste decreased from 1 µm to 0.6 µm. The particle size analysis report provided from this testing is found in Appendix E.
- Rheology measurements showed that supernate viscosity and the slurry consistency and shear stress have significant impact on filtration. The rheology analysis report provided from this testing is found in Appendix F.

Table 5.1. Summary of Group 3/4 Filtration Results

Filtration Step	Property	Results
Initial Characterization of Group 3	Material Description	PUREX Cladding Waste (CWP)
	UDS	28.8 wt%
	Slurry Rheology @ 25°C-60°C	Newtonian Viscosity: 3.2-3.4 mPa-s @ 25°C 1.7 mPa-s @ 60°C
	Particle Size Distribution	d(10): 1.0-1.3 µm d(50): 5-9 µm d(90): 14-30 µm
Initial Characterization of Group 4	Material Description	REDOX Cladding Waste (CWR)
	UDS	29.7 wt%
	Slurry Rheology @ 25°C-60°C	Newtonian Viscosity: 2.3-2.4 mPa-s @ 25°C 1.1 mPa-s @ 60°C
	Particle Size Distribution	d(10): 1-4 µm d(50): 8-26 µm d(90): 17-83 µm
Low Solids Filtration Testing Baseline Conditions TMP: 40 psid AV: 13 ft/s	Material Description	Group 3/4 diluted w/ simulant supernatant and circulated in CUF
	UDS (Solid in slurry were not completely suspended at start of testing)	6 wt% (Initial) 10-11 wt% (Final)
	Slurry Rheology @ 25°C-60°C (Measured when slurry was not completely suspended)	Newtonian Viscosity: 2.0 mPa-s @ 25°C 0.9 mPa-s @ 60°C
	Particle Size	d(10): 1 µm d(50): 5-6 µm d(90): 15-16 µm
	Baseline Filter Flux	0.02-0.03 gpm/ft^2
	Controlling Parameter	Proportional to TMP

Table 5.1. (Cont'd)

Filtration Step	Property	Results
Dewatering of Waste Prior to Leaching Baseline Conditions TMP: 40 psid AV: 13 ft/s	Initial Flux	0.022 gpm/ft^2
	Final Flux	0.018 gpm/ft^2
	Final UDS	~19 wt%
	Behavior	TMP controlling Decay with time
	Supernate Composition	[Na]: 3.0M [OH]: 0.3M [Al]: 0.05M
High Solids Filtration Testing Baseline Conditions TMP: 40 psid AV: 13ft/s	Material Description	Dewatered Group 3/4 slurry diluted w/ simulant supernatant and circulated in CUF
	UDS	13-14 wt%
	Slurry Rheology @ 25°C-60°C	Non-Newtonian Shear Strength: 3.1-3.4 Pa @ 25°C 2.3 Pa @ 60°C Consistency: 7.1-7.6 mPa-s @ 25°C 5.2 mPa-s @ 60°C
	Particle Size Distribution	d(10): 1µm d(50): 5-6 µm d(90): 17 µm
	Baseline Filter Flux	0.014-0.018 gpm/ft^2
	Controlling Parameter	Proportional to TMP
Caustic Leach Dewater Baseline Condition TMP: 40 psid AV: 13 ft/s	Initial Flux	0.015 gpm/ft^2
	Final Filter Flux	0.008 gpm/ft^2
	Final UDS	3 wt%
	Behavior	TMP controlling Decay with time
	Supernate Composition	[Na]: 7.8M [OH]: 5.6M [Al]: 0.9M

Table 5.1. (Cont'd)

Filtration Step	Property	Results
Caustic Leach Filter Testing Baseline Condition TMP: 40 psid AV: 13 ft/s	Material Description	Dewatered Caustic Leached Group 3/4 Slurry
	UDS	3 wt%
	Particle Size Distribution	d(10): 0.8 µm d(50): 7 µm d(90): 18 µm
	Rheology @ 25°C-60°C	Newtonian Viscosity: 15-16 mPa-s @ 25°C 5.4 mPa-s @ 60°C
	Baseline Flux	0.005-0.007 gpm/ft^2
	Controlling Parameter	TMP controlling Decay with Time
Caustic Wash 1 Baseline Conditions TMP: 40 psid AV: 13ft/s	Wash Solution	1.78M NaOH
	Supernate Composition	[Na] : 5.0M [OH]: 4.0M [Al]: 0.50M
	Filter Flux	0.015gpm/ft^2
Caustic Wash 2 Baseline Conditions TMP: 40 psid AV: 13ft/s	Wash Solution	0.78M NaOH
	Supernate Composition	[Na] : 3.1M [OH]: 2.4M [Al]: 0.26M
	Filter Flux	0.021gpm/ft^2
Caustic Wash 3 Baseline Conditions TMP: 40 psid AV: 13ft/s	Wash Solution	0.30M NaOH
	Supernate Composition	[Na] : 1.8M [OH]: 1.3M [Al]: 0.13M
	Filter Flux	0.027gpm/ft^2
Washed Caustic Leached Slurry	UDS	2 wt%
	Particle Size Distribution	d(10): 0.6 µm d(50): 8 µm d(90): 87 µm
	Rheology @ 25°C-60°C	Newtonian Viscosity: 2.3-2.7 mPa-s @ 25°C 0.7 mPa-s @ 60°C

5.3 Leaching Behavior

Caustic leaching results of the Group 3/4 CUF test provided in Sections 3.6 of this report are summarized in Table 5.2. The following general observations were made:

- Initial characterization of the Group 3 and Group 4 solids found a majority of the aluminum solids present to be in the form of gibbsite based on XRD, SEM, and TEM imaging. After leaching was complete, the remaining slurry solids were re-examined using the same imaging techniques. In all cases, gibbsite was absent from caustic leached solids.
- Overall kinetics for dissolution of Al was fast, completing before the temperature of the leach slurry reached 100°C. The reaction appeared to be completed by the time a sample was collected when the slurry was approximately 70°C. The kinetic appeared to agree with parametric leaching results reported for Group 3 and Group 4 wastes (WTP-RPT-167).
- Leach factors for the aluminum solids were found to range from 94% - 95% based on supernate and slurry ICP measurements.
- Phosphate in the supernate appeared to have precipitated during the caustic leach due to 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 post-caustic leach washing steps instead of the dewatering step following caustic leaching.
- Caustic leaching did not dissolve measureable quantities of transuranic isotopes from the slurry solids.
- After three volumetric washes, a significant quantity of sodium, aluminum, and phosphorus was present in the interstitial liquid of the slurry (Figure 5.1). Additional rinses could further reduce the quantities present.

Table 5.2. Caustic Leaching Summary of Group 3/4 Blended Slurry

Element	Solid Leach Factor Permeate Analysis	Solid Leach Factor Slurry Analysis	Total Removal from Slurry (Three Equal Volume Washes)
Al	94 wt%	95 wt%	89 wt%
P	53 wt%	98 wt%	66 wt%
Cr	48 wt%	20-29 wt%	59 wt%

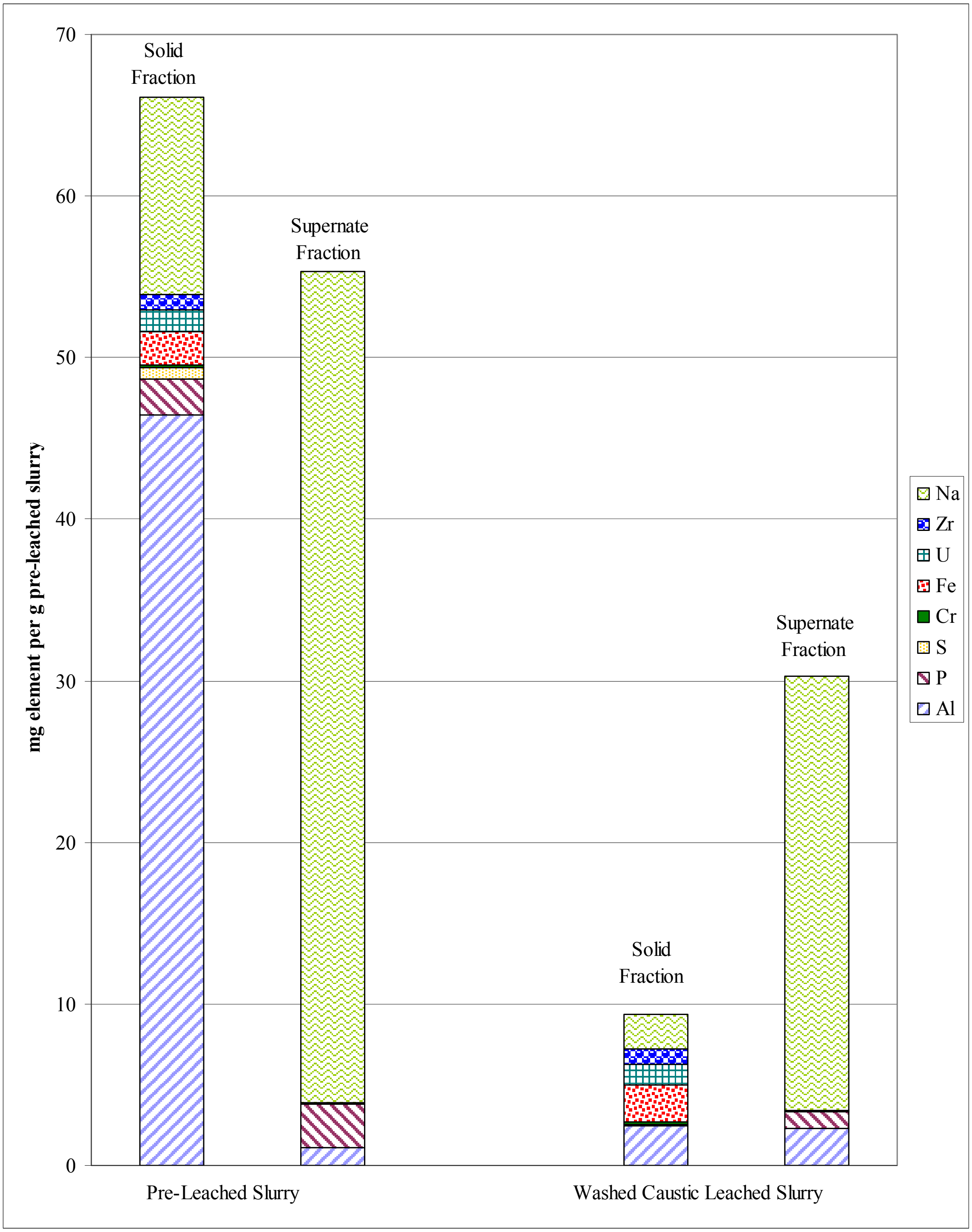


Figure 5.1. Comparison of slurry composition before and after caustic leaching and washing (Basis 1 gram of dewatered slurry)

5.4 Characterization of Crystal Habits of Solids

The results of characterization of leached material in the Group 3/4 CUF (Section 3.7) found the following:

- BET measurements of the surface area of the washed leached slurry solids were 63 m^2/g.
- SEM identified the presence of Na, Al, Si, U, Fe, Ca, Cr, Mn, Ni, Cu, and P.
- XRD did not identify the presence of gibbsite in the leach samples, confirming the chemical analysis results that indicated that a majority of aluminum was removed from caustic leaching.
- XRD identified the following phases of Al, Si, Fe, and U present in the washed leached slurry.
  - Clarkeite, $Na((UO_2)O(OH))$
  - Cancrinite, $Na_8(AlSiO_4)_6(CO_3)(H2O)_2$,
  - Tochilinite II, $(Fe_{0.8}S_1)(Mg_{0.7}Fe_{0.3}(OH)_2)_{0.833}$
  - TEM identified the presence of Na, Al, Si, U, Fe, Zr, and P. EDS supported XRD evidence that the remaining aluminum was present in the form of a sodium aluminum silicate, and not as gibbsite.

5.5 Lessons Learned

During the course of the test, several problems occurred that impacted the performance of test and have created some uncertainty about the results. However, conducting the test created additional understanding about the process that had added benefits.

Sample Settling

During loading of the samples at the start of the test, the agitator was turned off. During this time, the solids in the slurry settled rapidly to the bottom of the tank. After all the sample had been loaded, agitation was started and the pump was turned on to start recirculation. Unfortunately, the material settled quickly and had packed into the outlet from the vessel and had plugged, preventing flow. Subsequently, a great deal of effort was required to remove this plug of solids from the vessel. During subsequent tests, the agitator was started up during the slurry addition to prevent settling of the solids during this loading period. This prevented a recurrence of this problem.

Slurry Loss to Overflow

As part of the recovery from the plug that formed from slurry settling, the flow through the system was reversed while the agitator was running. This caused some material to overflow from the vessel. This material was collected in the overflow collection vessel. However, the overflow collection vessel was located behind the system and was not readily visible. Thus, the overflow was not immediately recognized and testing proceeded without the material from the overflow collection vessel. This led to a lower than planned solids inventory in the testing. It is recommended that during future tests, the overflow vessel either be located in a more readily visible location or that specific measures be taken to periodically check this vessel to ensure that material is not lost due to overflow.

High Solids Test Matrix

Prior analysis had indicated that approximately 300 grams of insoluble solids would be required to allow the system to achieve 20 wt% insoluble solids. This test, and prior tests, has indicated that 20 wt% insoluble solids can be achieved with 300 grams of insoluble solids. However, at the slurry levels present at 20 wt% with 300 grams of insoluble solids, it was not possible to reach all of the target filtration conditions. Therefore, it was necessary to increase slurry level in the vessel through the addition of some of the dewatered permeate. Thus, to achieve all of the test conditions at 20 wt%, it will be necessary for future tests to obtain greater than 300 grams of insoluble solids. Approximately 400 grams of insoluble solids or greater will likely be required.

Appendix A

Analytical Methods

Appendix A: Analytical Methods

The following sections describe 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 chromatography (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.1 Free Hydroxide

The free hydroxide was determined using 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 Anions

Anions were determined by ion chromatography 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*. 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.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 hot persulfate 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.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. The supernatant sample was processed in duplicate. 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.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°C for 1 hour in a nickel crucible. The fused material was acidified with HNO_3, taken to a 100-mL volume with deionized (DI) water, and then split for metals and radionuclide analysis. The sample was 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.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°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.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.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.9 U (KPA)

Uranium was determined directly from samples prepared by KOH fusion using 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.10 Gamma Energy Analysis

Gamma energy analysis was performed with direct or diluted samples that were prepared from acid digestion, or fusion. 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 h) 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.11 Gross Alpha and Gross Beta

The gross alpha and beta activities were measured from aqueous samples prepared by acid-digestion, and 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.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 were 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.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 Property and Rheology Measurement Methods

Appendix B: Physical Property and Rheology Methods

The following sections describe procedures used to support physical characterization of the slurry samples during bench scale filtration/leach testing to examine their impact on filtration, examine leaching behavior, and support mass balance calculations.

B.1 Physical Properties (Density, Slurry Solid Measurements)

Slurry samples were collected in tared glass graduated centrifuge cones. Slurry densities were calculated by measuring the slurry mass and the slurry volume in the cone. The vials were centrifuged at ~1000G for 1 hour. Supernatants were decanted into tared graduated cylinders. The supernatant density was calculated from the decanted mass and volume measurements. The supernatant was then placed in a tared glass vial and dried in the oven, along with the slurry solids in the centrifuge cone. Once the samples were dried to a constant mass, the mass of the centrifuge cone and the supernatant vial was measured. The collected data were processed as described by Smith and Prindiville[1] to determine the undissolved solids, dissolved solids, and centrifuge solids of the slurry.

B.2 Rheology Measurements

Rheological testing was conducted on the solids in contact with the supernatant generated as part of the homogenization process. Testing was conducted according to RPL-COLLOID-02, *Measurement of Physical and Rheological Properties of Solutions, Slurries and Sludges*. For the current study, two regions of tank waste flow behavior are considered: 1) incipient motion in settled tank waste solids (shear strength) and 2) non-elastic flow of tank waste slurries and supernates (flow curve).

B.2.1 Shear-Strength Testing

For tank waste slurries, a finite stress must be applied before the material will begin to flow. The stress required to transition the material 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, the 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 shear strength was measured 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.

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 the uniform and isotropic stress acting over the surface area of the cylinder of rotation swept out by the vane. The shear strength is related to the maximal torque during incipient motion according to Equation B.1 (Barnes and Dzuy 2001):

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[1] Smith GL and K Prindiville. May 2002. "Guidelines for Performing Chemical, Physical, and Rheological Properties Measurements," 24590-WTP-GPG-RTD-001 Rev 0, Bechtel National, Inc., Richland, Washington.

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

where, 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.

B.2.2 Flow-Curve Testing

The non-elastic flow of tank waste slurries and supernates is characterized with rotational viscometry. The typical result of such testing is a set of flow-curve data, which shows the stress response of a material to a range of applied rates-of-deformation. Specifically, flow-curve testing allows characterization of a material's shear stress, τ, and response as a function of applied shear rate, $\dot{\gamma}$. Once measured, the flow-curve data can be interpreted with several constitutive equations for the viscous stress/rate-of-strain relationship. 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 was used for flow-curve testing of tank waste slurries and supernates. Rotational 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. A single-point determination of a fluid's flow properties is made by spinning a rotor at a known rotational speed, Ω, and measuring the resisting torque, M, acting on the rotor. The torque acting on the rotor can be directly related to the shear stress at the rotor using the equation,

$$\tau = \frac{M}{2\pi H R_I^2} \tag{B.2}$$

Shear stress has units of force per area (N/m²). The rotational rate is related to the shear rate. However, calculating the fluid shear rate at the rotor is complicated by the fact that shear rate depends on both 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 by using the equation,

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

with the shear rate being units of inverse seconds (s^{-1}). Calculating the shear rate for materials showing more complex shear-stress versus shear-rate behavior (i.e., non-Newtonian fluids) requires estimates of yield stress and degree of shear-thinning or shear-thickening. As the goal of rheological testing is to determine and quantify such behavior, these values are typically not known. This requirement can be circumvented by using a cup and rotor system with a small gap (~1 mm) for fluid shear. For fluid flow in small gap cup and rotor systems, shear-rate effects introduced by fluid properties are minimized such that Equation B.3 provides an accurate determination of shear rate for non-Newtonian materials. Shear rates examined in this study spanned the range from 1 to 1000 s^{-1}.

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

$$\eta_{app} = \frac{\tau}{\dot{\gamma}} \tag{B.4}$$

For Newtonian fluids, the apparent viscosity is independent of shear rate. For non-Newtonian fluids, the apparent viscosity will vary as a function of shear rate. The units of apparent viscosity are Pa·s, although it is typically 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 four common flow-curve equations:

- **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,

  $$\tau = \eta\dot{\gamma} \tag{B.5}$$

  where η is the Newtonian viscosity.

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

  $$\tau = m\dot{\gamma}^{n} \tag{B.6}$$

  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 pseudoplastic (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. A finite 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

  $$\tau = \tau_{O}^{B} + k_{B}\dot{\gamma} \tag{B.7}$$

  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

  $$\tau = \tau_{O}^{H} + k_{H}\dot{\gamma}^{b} \tag{B.8}$$

  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.

Power-law fluids, Bingham plastics, and Herschel-Bulkley fluids are examples of non-Newtonian fluids. In general, liquids without internal and/or interconnected structures (such as tank waste supernates) 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.

B.2.3 Rheology Instrumentation

Rheological characterization was accomplished using a Rotovisco® RV20 Measuring System M equipped with an M5 measuring head sold by HAAKE Mess-Technik GmbH u. Co. (now the Thermo Electron Corporation, Madison, WI). The M5 measuring head is a "Searle" type viscometer capable of producing rotational speeds up to 500 revolutions per minute (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.

Specific measurement tools, such as cup and rotor assemblies and shear vanes, are attached to measure selected rheological properties. Shear-strength measurements employed an 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 B.1.

Table B.1. Vane and Cup and Rotor Measuring System Dimensions

MEASURING SYSTEM	VANE/ROTOR RADIUS, MM	VANE/ROTOR HEIGHT, MM	CUP RADIUS, MM	GAP WIDTH, MM
Vane Tool	8	16	> 16	> 8
MV1	20.04	60	21	0.96

The temperature was controlled with a combination of the standard measuring system M temperature jacket and a Cole-Parmer® Polystat® Temperature-Controlled Recirculator, Model Number C-12920-00. The temperature jacket provided a heat-transfer area between the cup and the recirculating fluid. The jacket temperature was monitored using a Type-K thermocouple (Omega Model TJ36-CASS-116-G-6-CC). Temperature control was employed only for flow-curve measurements. The shear strengths were measured at ambient temperature (~30°C in the hot cells).

The rheometer was controlled and data were acquired with a remote computer connection using the RheoWin Pro Job Manager Software, Version 2.96. During measurement, the software automatically collects and converts rotor torque readings into shear stresses based on Equation B.1 (for vane testing) or Equation B.2 (for flow-curve testing). Likewise, the software also automatically converts the rotational rate readings into shear rates based on Equation B.3.

B.2.4 Rheology Materials and Methods

No sample treatment was performed before analysis with the exception of the mechanical agitation required to mix and sub-sample selected waste jars.

B.2.4.1 Shear-Strength Testing

Before testing, the tank waste slurries that were provided for shear-strength testing were mixed thoroughly and subsequently allowed to settle for at least 48 to 72 h. When possible, the shear strength was measured by immersing the 8- × 16-mm vane tool to a depth of 15 mm into the settled solids. The vane was slowly rotated at 0.3 RPM for 180 s. For the entire duration of rotation, the time, rotational rate, and vane torque were continuously monitored and recorded. At the end of the measurement, shear stress versus time data were parsed, and the maximum measured shear stress (i.e., the material's shear strength) was determined.

B.2.4.2 Flow-Curve Testing

Each flow curve was measured over a 15 min period and split into three 5 min intervals. Over the first 5 min, the shear rate was smoothly increased from zero to 1000 s^{-1}. For the second 5 min, the shear rate was held constant at 1000 s^{-1}. For the final 5 min, the shear rate was smoothly reduced back to zero. During this time, the resisting torque and rotational rate were continuously monitored and recorded.

Before each test, the sample was left undisturbed in the measuring system for 5 min to allow temperature equilibration. The sample was then mixed for 3 min using the measuring system rotor to re-disperse any settled solids and to pre-shear slurries before measurement.

Flow curve tests were run at 25, 40, and 60°C. Because of limited sample volume, all three temperature tests were performed on the same sample. To combat the effects of sample evaporation, a moisture barrier was installed over the opening at the top of the temperature jacket during testing, and after each test, the cup was raised so that fresh sludge/slurry filled the measurement gap.

B.3 Particle-Size Attributes

Particle attributes, including size distribution and surface area, are discussed in the following sections.

B.3.1 Particle-Size Distribution

Particle sizes were characterized according to procedure RPL-COLLOID-01, Rev. 1, *Particle Size Analysis Using Malvern MS2000*. This procedure uses a Mastersizer 2000 (Malvern Instruments, Inc., Southborough, MA 01772) with a Hydro µP wet dispersion accessory. Malvern lists the Mastersizer particle-size measurement range as nominally 0.02 to 2000 µm. The actual PSD measurement 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 listed measuring range is reduced to 0.02 to 150 µm. The Malvern 2000 uses laser diffraction technology to define PSD.

The Hydro µP wet-dispersion accessory consisted of a 20-mL sample flow cell with a continuous variable and independent pump and ultrasound. Both flow and sonication can be controlled and altered during measurement. PSD measurements were made before, during, and after sonication, allowing the influence of each on the sample PSD to be determined. The primary measurement functions of the Malvern analyzer were controlled through Mastersizer 2000 software, Version 5.1 (Copyright© 1998-2002 Malvern Instruments, Ltd.). The optical properties applied to the test samples are summarized in Table B.2.

The PSD measurements were conducted on the washed solids in a 0.01-M NaOH dispersion solution matrix. The sample dispersion was added drop-wise to the instrument (while the pump was active) until an ~10% obscuration was reached. For all samples, less than 10 mg of solids was required to reach the desired obscuration in the 20-mL flow cell.

Table B.2. Optical Properties Applied To Test Materials

Test	Material Selected for Optical Properties	Refractive Index (RI)	Absorption
Initial Characterization			
Group 5	Boehmite[(a)]	1.655	1.0
Group 6	Boehmite[(a)]	1.655	1.0
Parametric			
Group 5	Uranium Oxide[(b)]	2.4	1.0
Group 6	Chrome Oxide[(a)]	2.5	1.0
All/Suspending Phase	Water[(a)]	1.33	n/a
(a) See reference Malvern Instruments Ltd., April 1997. (b) See reference Kaminski et al., 2005.			

The size distributions of particles were measured under varying flow conditions before, during, and after sonication. A typical test matrix is shown in Table B.3. Not all conditions were tested for some samples (e.g., initial characterization samples only employed pump speeds of 3000 RPM). For each condition, three successive 12-second measurements of PSD were taken. An average of these measurements was then generated by the analyzer software. Both individual measurement and average were saved to the analyzer data file. Once measurements were complete, the sonic power for the next condition was set, the sample was given 30 to 60 seconds to equilibrate, and the next set of measurements was taken.

Table B.3. Prototypic Particle-Size Analysis Test Matrix

Condition No.	Pump Speed (RPM)	Sonic Power	Comment
1	3000	0%	pre-sonic measurement
2	2000	0%	pre-sonic measurement
3	4000	0%	pre-sonic measurement
4	3000	25%	sonicated measurement
5	3000	50%	sonicated measurement
6	3000	75%	sonicated measurement
7	3000	0%	post-sonic measurement
8	2000	0%	post-sonic measurement
9	4000	0%	post-sonic measurement

B.3.2 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 ethyl 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 ethyl 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^{o}C.

The surface-area measurements were conducted according to OCRWM-BET-01, *Surface Area Measurement with a Monosorb Gas Analyzer,* which is consistent with 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 Instrument Corporation (Norcross, GA).

B.4 Crystal Form and Habit

The solids crystal characteristics were determined on small aliquots of the washed 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 that were applied for XRD, SEM, and TEM evaluations are discussed in the following sections.

B.4.1 X-Ray Diffraction

The sample mounts for XRD determination 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 in an effort 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 examination of 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.

B.4.2 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.

B.4.3 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 observations 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), energy dispersive X-ray detector, and a Gatan Imaging Filter (GIF), model GIF2000 (Gatan Inc., Pleasanton, CA). Particles and areas were analyzed 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.

Appendix C

Quality Assurance and Control Methods

Appendix C: Quality Assurance and Control Methods

The following sections describe the quality assurance (QA) program and quality control (QC) measures applied to the conduct of work.

C.1 Application of Waste Treatment Plant Support Program (WTPSP) QA Requirements

Pacific Northwest National Laboratory's (PNNL) 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" (the Quality Rule). Pacific Northwest National Laboratory 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.

Pacific Northwest National Laboratory 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 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.[1] It included justification for those requirements not implemented. The QA requirements of DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions* (QARD) and DOE Order 414.1C were not identified as a requirement for this work in the test specification.

C.2 Conduct of Experimental and Analytical Work

Experiments that were not method-specific were performed in accordance with PNNL procedures QA-RPP-WTP-1101, "Scientific Investigations" and QA-RPP-WTP-1201, "Calibration and Control of M&TE," verifying that sufficient data were taken with properly calibrated measuring and testing equipment (M&TE) 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.

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[1] Fiskum SK. 2007. *Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes.* TP-RPP-WTP-467, Rev. 0, and Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

The Analytical Services Operation (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 (ASR) number and RPL number.

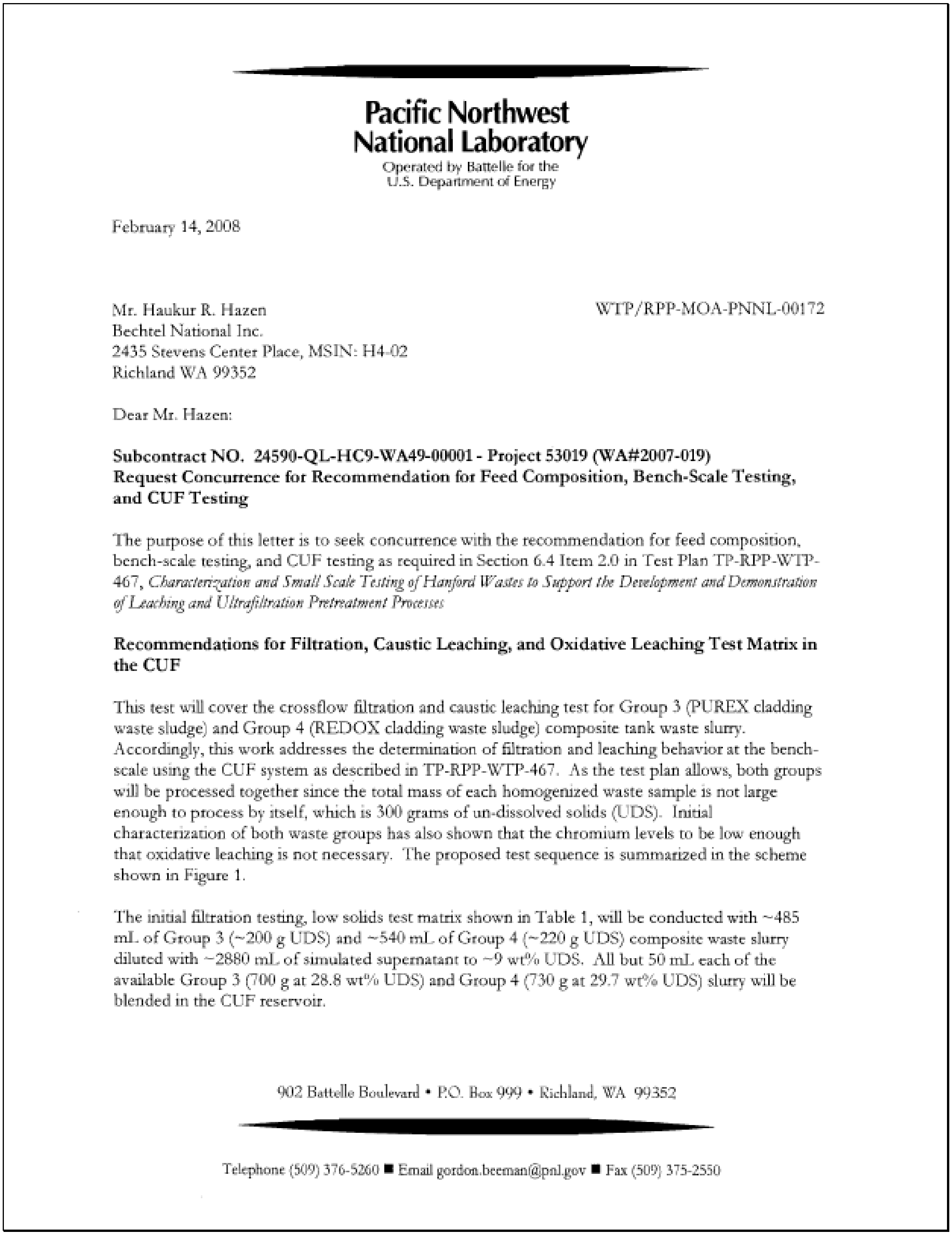
C.3 Internal Data Verification and Validation

Pacific Northwest National Laboratory addressed internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNNL 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.

Appendix D

Group 3/4 CUF Test Concurrence Letter

Appendix D: Group 3/4 CUF Test Concurrence Letter



Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

February 14, 2008

Mr. Haukur R. Hazen
Bechtel National Inc.
2435 Stevens Center Place, MSIN: H4-02
Richland WA 99352

WTP/RPP-MOA-PNNL-00172

Dear Mr. Hazen:

Subcontract NO. 24590-QL-HC9-WA49-00001 - Project 53019 (WA#2007-019)
Request Concurrence for Recommendation for Feed Composition, Bench-Scale Testing, and CUF Testing

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, Caustic Leaching, and Oxidative Leaching Test Matrix in the CUF

This test will cover the crossflow filtration and caustic leaching test for Group 3 (PUREX cladding waste sludge) and Group 4 (REDOX cladding waste sludge) composite tank waste slurry. 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, both groups will be processed together since the total mass of each homogenized waste sample is not large enough to process by itself, which is 300 grams of un-dissolved solids (UDS). Initial characterization of both waste groups has also shown that the chromium levels to be low enough that oxidative leaching is not necessary. The proposed test sequence is summarized in the scheme shown in Figure 1.

The initial filtration testing, low solids test matrix shown in Table 1, will be conducted with ~485 mL of Group 3 (~200 g UDS) and ~540 mL of Group 4 (~220 g UDS) composite waste slurry diluted with ~2880 mL of simulated supernatant to ~9 wt% UDS. All but 50 mL each of the available Group 3 (700 g at 28.8 wt% UDS) and Group 4 (730 g at 29.7 wt% UDS) slurry will be blended in the CUF reservoir.

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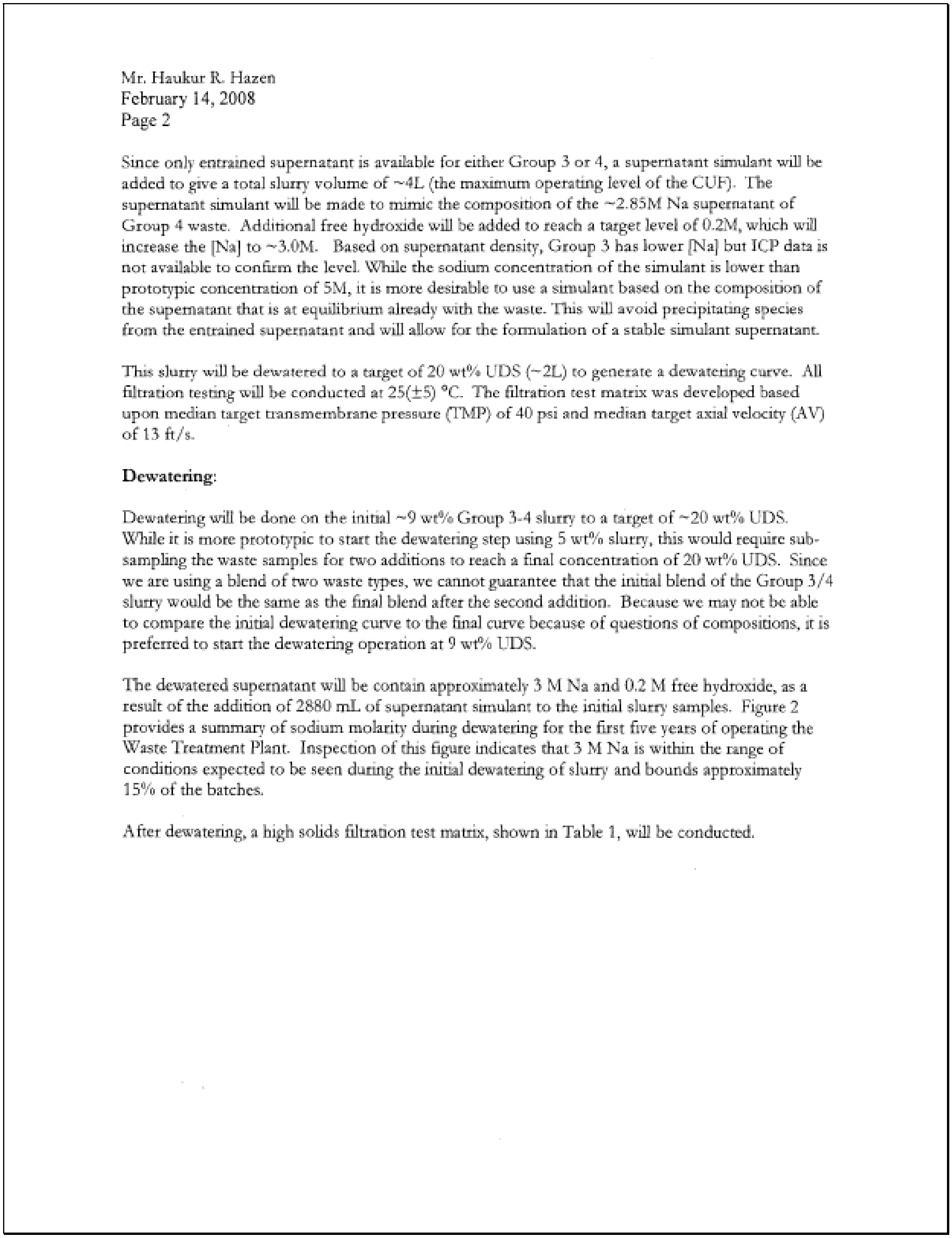

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Since only entrained supernatant is available for either Group 3 or 4, a supernatant simulant will be added to give a total slurry volume of ~4L (the maximum operating level of the CUF). The supernatant simulant will be made to mimic the composition of the ~2.85M Na supernatant of Group 4 waste. Additional free hydroxide will be added to reach a target level of 0.2M, which will increase the [Na] to ~3.0M. Based on supernatant density, Group 3 has lower [Na] but ICP data is not available to confirm the level. 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 simulant supernatant.

This slurry will be dewatered to a target of 20 wt% UDS (~2L) to generate a dewatering curve. All filtration testing will be conducted at 25(±5) °C. The filtration test matrix was developed based upon median target transmembrane pressure (TMP) of 40 psi and median target axial velocity (AV) of 13 ft/s.

Dewatering:

Dewatering will be done on the initial ~9 wt% Group 3-4 slurry to a target of ~20 wt% UDS. While it is more prototypic to start the dewatering step using 5 wt% slurry, this would require sub-sampling the waste samples for two additions to reach a final concentration of 20 wt% UDS. Since we are using a blend of two waste types, we cannot guarantee that the initial blend of the Group 3/4 slurry would be the same as the final blend after the second addition. Because we may not be able to compare the initial dewatering curve to the final curve because of questions of compositions, it is preferred to start the dewatering operation at 9 wt% UDS.

The dewatered supernatant will be contain approximately 3 M Na and 0.2 M free hydroxide, as a result of the addition of 2880 mL of supernatant simulant to the initial slurry samples. 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 M Na is within the range of conditions expected to be seen during the initial dewatering of slurry and bounds approximately 15% of the batches.

After dewatering, a high solids filtration test matrix, shown in Table 1, will be conducted.

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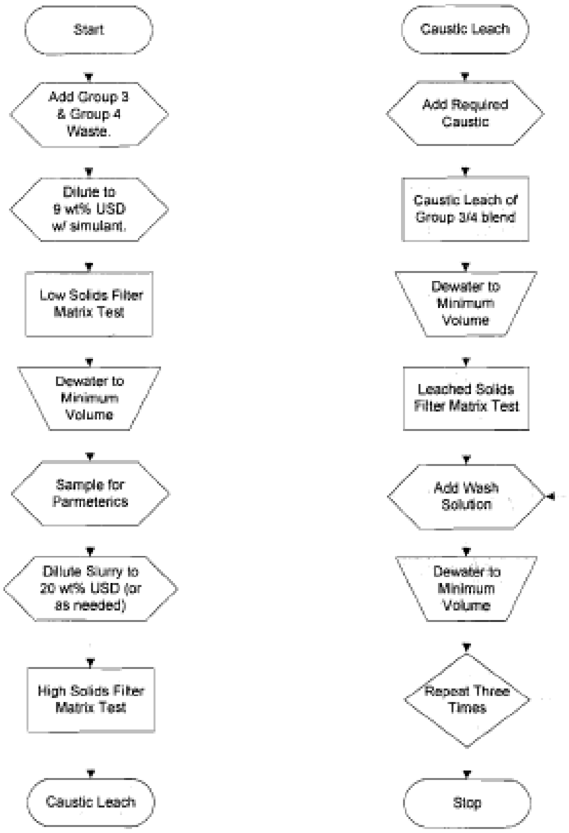
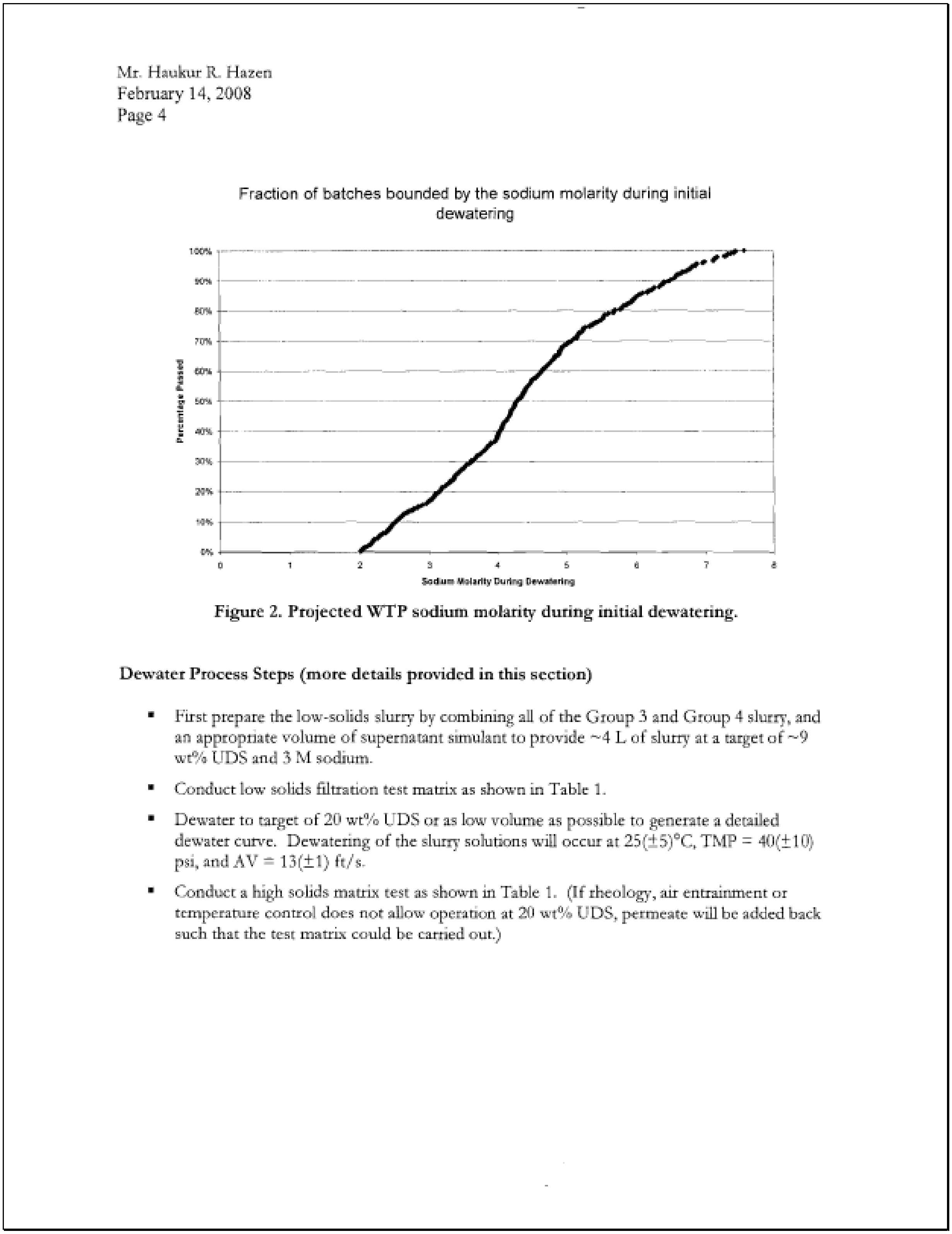


Figure 1: Proposed Test Scheme for Composite Group 3-4 CUF Test



Fraction of batches bounded by the sodium molarity during initial dewatering

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 all of the Group 3 and Group 4 slurry, and an appropriate volume of supernatant simulant to provide ~4 L of slurry at a target of ~9 wt% UDS and 3 M sodium.
- Conduct low solids filtration test matrix as shown in Table 1.
- Dewater to target of 20 wt% UDS or as low volume as possible to generate a detailed dewater curve. Dewatering of the slurry solutions will occur at 25(±5)°C, TMP = 40(±10) psi, and AV = 13(±1) ft/s.
- Conduct a high solids matrix test as shown in Table 1. (If rheology, air entrainment or temperature control does not allow operation at 20 wt% UDS, permeate will be added back such that the test matrix could be carried out.)

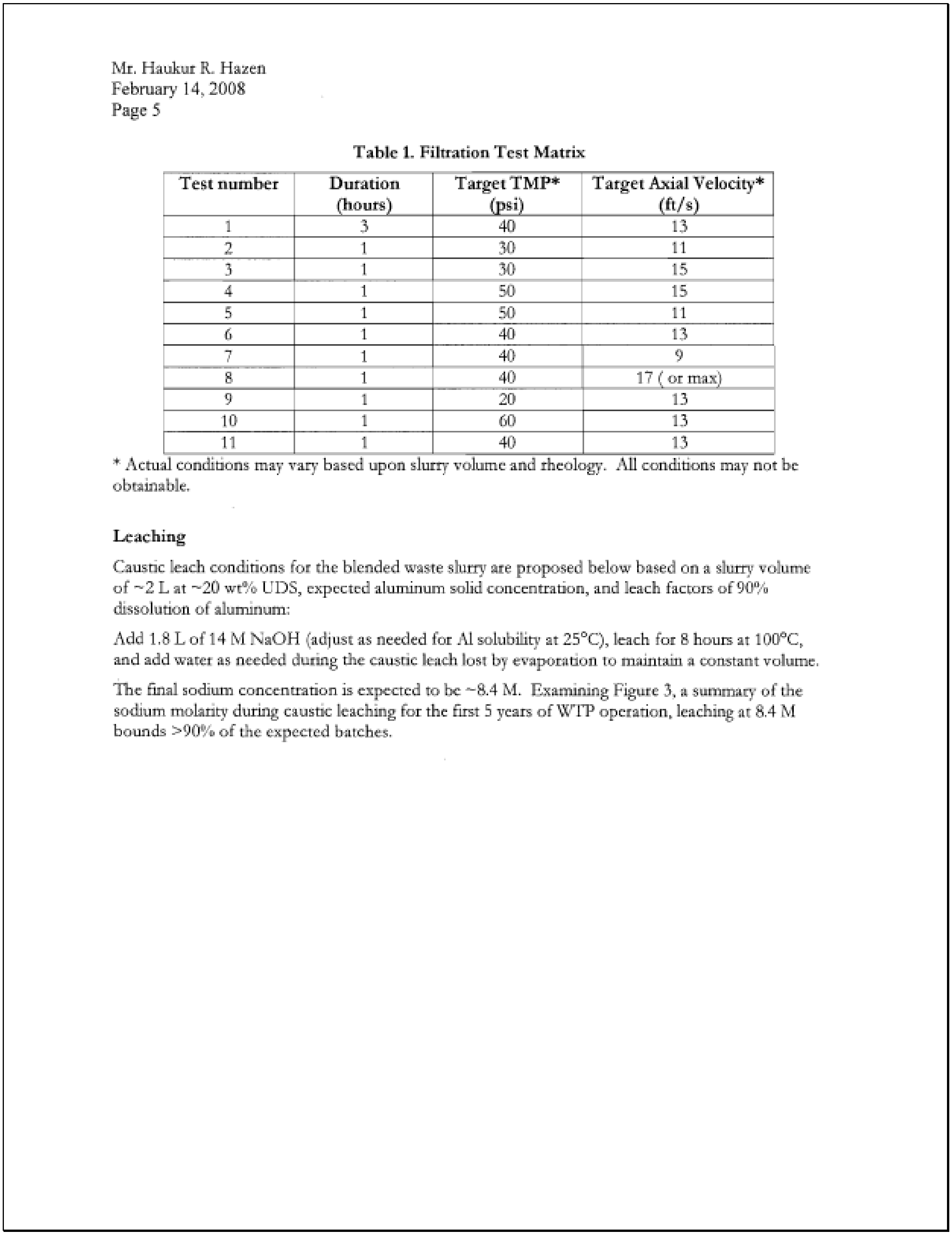


Table 1. Filtration Test Matrix

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 ~2 L at ~20 wt% UDS, expected aluminum solid concentration, and leach factors of 90% dissolution of aluminum:

Add 1.8 L of 14 M NaOH (adjust as needed for Al solubility at 25°C), leach for 8 hours at 100°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 ~8.4 M. Examining Figure 3, a summary of the sodium molarity during caustic leaching for the first 5 years of WTP operation, leaching at 8.4 M bounds >90% of the expected batches.

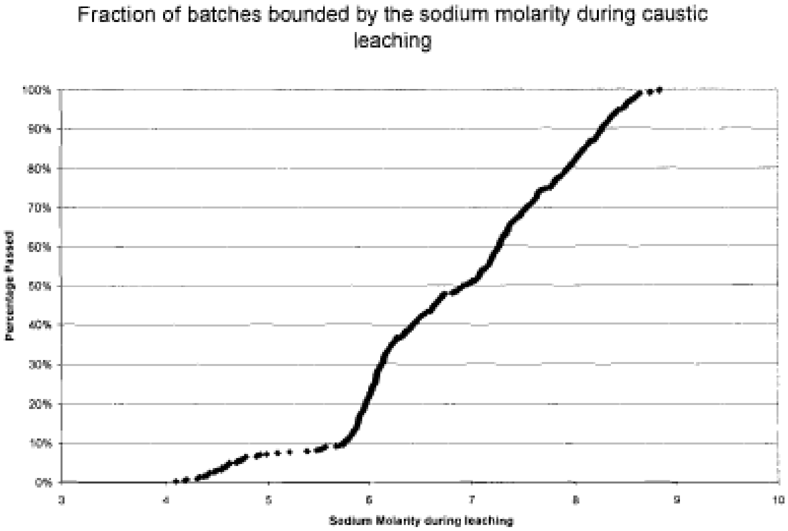


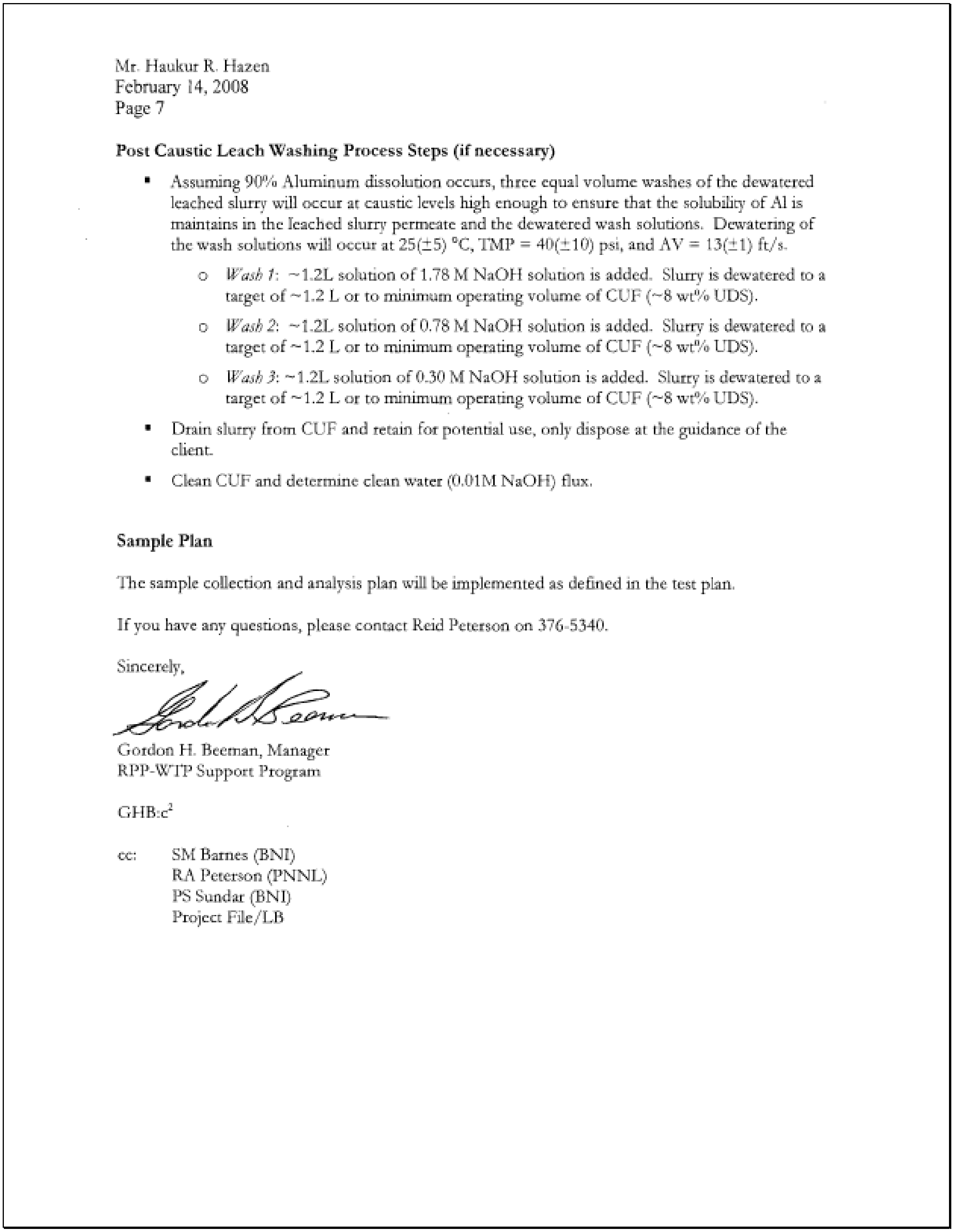
Figure 3. Projected WTP sodium molarity during caustic leaching.

Caustic Leaching Process Steps (more details provided in this section)

- Retrieve all solids from CUF and isolate in slurry feed reservoir for leaching.
- Assuming ~2 L of ~20 wt% UDS at 3 M sodium, add 1.8 L of 14 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.)
- Since no data is currently available on the gibbsite dissolution kinetics for these samples, the leach will be conducted at the WTP baseline process conditions:
    - Heat from 25°C to 100°C in 5.3 hours.
    - Leach for 8 hours at 100(+5/-10) °C.
    - Cool from 100°C to 25°C in 12 hours.

Post Caustic Leach Dewater Process Steps

- Dewater leached solids at 25(±5) °C, TMP = 40(±10) psi, and AV = 13(±1) ft/s. Dewater to a target of ~1.2 L or to minimum operating volume of CUF (~8 wt% UDS assuming aluminum is all gibbsite and 90% Al dissolution).
- Add back permeate to give a volume of ~2 L (~7 wt% UDS) and conduct a post leach filtration matrix as shown in Table 1.
- Dewater to a target of ~1.2 L or to minimum operating volume of CUF for washing.



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Post Caustic Leach Washing Process Steps (if necessary)

- Assuming 90% Aluminum dissolution occurs, three 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. Dewatering of the wash solutions will occur at 25(±5) °C, TMP = 40(±10) psi, and AV = 13(±1) ft/s.
    - *Wash 1*: ~1.2L solution of 1.78 M NaOH solution is added. Slurry is dewatered to a target of ~1.2 L or to minimum operating volume of CUF (~8 wt% UDS).
    - *Wash 2*: ~1.2L solution of 0.78 M NaOH solution is added. Slurry is dewatered to a target of ~1.2 L or to minimum operating volume of CUF (~8 wt% UDS).
    - *Wash 3*: ~1.2L solution of 0.30 M NaOH solution is added. Slurry is dewatered to a target of ~1.2 L or to minimum operating volume of CUF (~8 wt% UDS).
- 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.

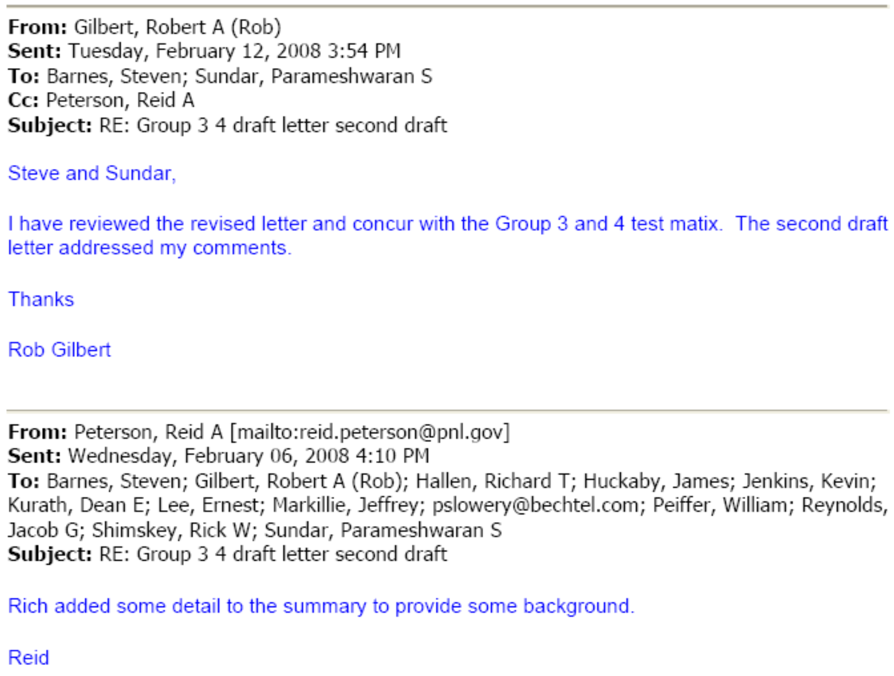
If you have any questions, please contact Reid Peterson on 376-5340.

Sincerely,

Gordon H. Beeman, Manager
RPP-WTP Support Program

GHB:c^2

cc: SM Barnes (BNI)
RA Peterson (PNNL)
PS Sundar (BNI)
Project File/LB



From: Gilbert, Robert A (Rob)
Sent: Tuesday, February 12, 2008 3:54 PM
To: Barnes, Steven; Sundar, Parameshwaran S
Cc: Peterson, Reid A
Subject: RE: Group 3 4 draft letter second draft

Steve and Sundar,

I have reviewed the revised letter and concur with the Group 3 and 4 test matix. The second draft letter addressed my comments.

Thanks

Rob Gilbert

From: Peterson, Reid A [mailto:reid.peterson@pnl.gov]
Sent: Wednesday, February 06, 2008 4:10 PM
To: Barnes, Steven; Gilbert, Robert A (Rob); Hallen, Richard T; Huckaby, James; Jenkins, Kevin; Kurath, Dean E; Lee, Ernest; Markillie, Jeffrey; pslowery@bechtel.com; Peiffer, William; Reynolds, Jacob G; Shimskey, Rick W; Sundar, Parameshwaran S
Subject: RE: Group 3 4 draft letter second draft

Rich added some detail to the summary to provide some background.

Reid

Appendix E

Group 3/4 CUF Particle Size Analysis (TDP-WTP-272)

Appendix E: Group 3/4 CUF Particle Size Analysis (TDP-WTP-272)

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TDP-WTP-272

Internal Distribution

Rick Shimskey

Amanda Casella

File/LB

Date	October 29, 2008
To	Rick Shimskey
From	Amanda Casella
Subject	<u>Particle Size Distribution for Group 3/4 [PUREX Cladding Waste Sludge and REDOX Cladding Waste Sludge Mixtures] CUF Samples</u>

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
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 3/4 wastes processed in the Cells Unit Filter (CUF) located at the RPL's Shielded Analytical Laboratory (SAL). Waste Group 3/4 corresponds to a mixture of PUREX Cladding Waste Sludge (Group 3) and REDOX Cladding Waste Sludge (Group 4).

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.

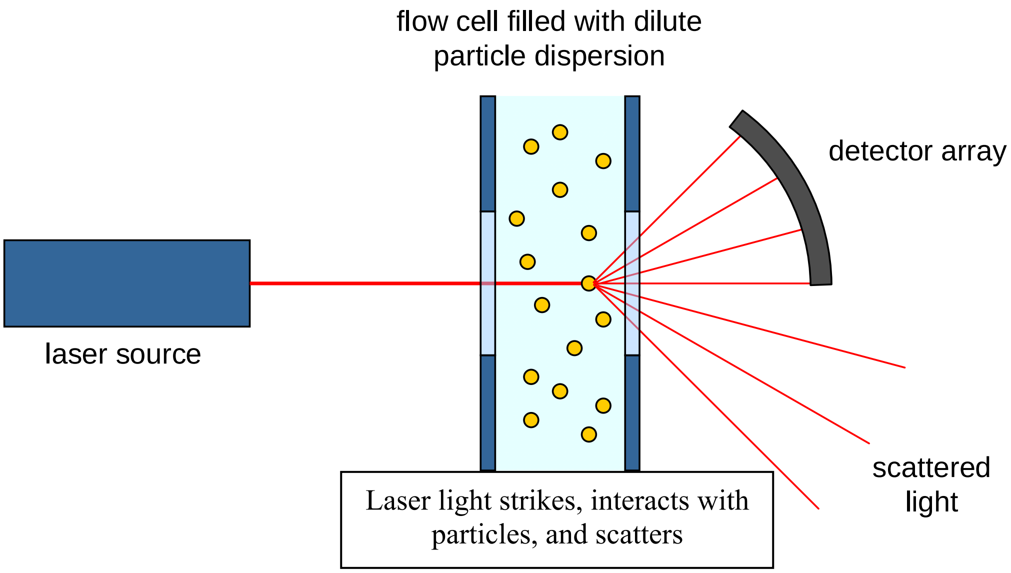


Figure 1. Schematic of a typical laser diffraction particle size analyzer.

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 3/4 CUF particle size measurement samples were derived as part of bench-scale crossflow ultrafiltration and leaching studies using actual tank waste. Source material for the studies included both Group 3 (PUREX Cladding Waste Sludge) and Group 4 (REDOX Cladding Waste Sludge) solids. Initially, Group 3 and Group 4 waste solids and supernate were combined in the CUF slurry reservoir to form a Group 3/4 tank waste slurry. The initial slurry mixture produced complications relating to the pump. Possibly fast-settling solids descended near the pump intake causing the pump to stall. After swapping the air pressure line from the compressor to the air motor to switch the motor direction, resulting in the pump working backwards, the solids plug was flushed from the inlet of the pump. After the motor direction was reconfigured in the forward direction improvement was observed in the velocity. Sample TI-601-G4-3-PSD was taken after the solids plug was flushed and the slurry began freely circulating. Various transmembrane pressures (TMP) and axial velocities (AV) were examined as the system velocity slowly improved over time. A second sample, TI-601-G4-3-Sheared-PSD was taken approximately 20 hours after continuous circulation to observe possible effects of particle alteration during this time. This slurry was then subjected to the following operations:

1. dewatering of the waste slurry to transform the low-concentration Group 3/4 slurry to a high-concentration Group 3/4 slurry
2. full-recycle ultrafiltration of the high-concentration waste slurry at various AV and TMP
3. caustic leaching of the waste slurry with 14M sodium hydroxide for 8 hours at 100°C (not including time for slurry heat-up, ~6 hrs, and cool-down, ~12 hrs)
4. dewatering of the caustically leached slurry
5. full-recycle ultrafiltration of the high-concentration caustically leached slurry at various AV and TMP
6. washing of the caustically leached slurry with relatively dilute sodium hydroxide solutions (includes three 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:

- loading the sample into the CUF and free circulation began,
- after 20 hours of circulation,
- dewatering the initial slurry (i.e. after step 1),
- after caustic leaching and dewatering (i.e., after step 4),
- 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. Table 1 provides a summary of the samples taken and their given sample identification number.

Table 1. Samples associated with Group 3/4 CUF particle size testing.

Sample Jar ID	Description
TI-601-G4-3-PSD	Slurry – Low-solids matrix Group 3/4 slurry before caustic leaching
TI-601-G4-3-Sheared-PSD	Slurry – Low-solids matrix Group 3/4-Sheared slurry before caustic leaching
TI-601-G4-6-PSD	Slurry – High-solids matrix Group 3/4 slurry before caustic leaching
TI-601-G4-9-PSD	Slurry – Dewatered Group 3/4 slurry after caustic leaching
TI-601-G4-12-PSD	Slurry – Washed Group 3/4 slurry after caustic leaching

4 Analysis

Particle size distributions for Group 3/4 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 3 and 4

Sample	Date
TI-601-G4-3-PSD	July 29, 2008
TI-601-G4-3-Sheared-PSD	July 31, 2008
TI-601-G4-6-PSD	July 31, 2008
TI-601-G4-9-PSD	August 1, 2008
TI-601-G4-12-PSD	August 1, 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.

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 checks employed NIST traceable polydisperse particle size standards purchased from Whitehouse Scientific (Waverton, Chester, CH3 7PB, UK). Table 4 provides a summary of the standard properties. Standards are traceable back to their 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 #	2101		
Weight:	0.10 g		
PSD Percentiles	List	Measured (µm)*	Absolute Error
d(10):	2.88 ± 0.24 µm	2.55	n/a
d(50):	4.18 ± 0.34 µm	4.22	0.98%**
d(90):	6.23 ± 0.56 µm	7.09	n/a

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

**Calculated before rounding of significant figures in List and Measured of d(50)

The instrument performance check covering size analysis of samples TI-601-G4-3-PSD, TI-601-G4-3-Sheared-PSD, TI-601-G4-6-PSD, TI-601-G4-9-PSD, and TI-601-G4-12-PSD was run on July 29, 2008. Performance check results for this period were recorded to the Malvern file "2008-07 July29-Group 4 PSD.mea".

Particle size standards are supplied as 0.10 g single shots of dry powder that must be dispersed in deionized water in order to achieve the appropriate distribution of particles. Dispersion was accomplished in the instrument flow cell, both through mechanical agitation of the flow cell pump and through sonication. A continuous pump speed of 3000 RPM was set to mix the flow cell contents. This pump speed was maintained through both powder dispersion and size measurement. As recommended by the manufacturer's instructions, the particle size standard dispersion was sonicated to eliminate particle agglomerates. Sonication was carried out at an instrument setting of 100%.

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 post-sonication measurements of the PSD indicated a d(50) of ~4.2 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 TI-601-G4-3-PSD, TI-601-G4-3-Sheared-PSD, TI-601-G4-6-PSD, TI-601-G4-9-PSD, and TI-601-G4-12-PSD.

8 Sample Handling

The Group 3/4 CUF testing 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 TI-601-G4-3-PSD, TI-601-G4-3-Sheared-PSD, TI-601-G4-6-PSD, TI-601-G4-9-PSD, and TI-601-G4-12-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).

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 in the initial characterization samples, so optical properties for boehmite [AlO(OH)] were employed in the measurement and analysis of Group 3/4 CUF 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.

Table 5. Material and suspending optical properties used for analysis of Group 3/4 CUF testing samples particle size distributions.

Sample Name	Material Selected for	Refractive	Absorption

	Optical Properties	Index (RI)	
TI-601-G4-3-PSD	Boehmite	1.655	1.0
TI-601-G4-3-Sheared-PSD	Boehmite	1.655	1.0
TI-601-G4-6-PSD	Boehmite	1.655	1.0
TI-601-G4-9-PSD	Boehmite	1.655	1.0
TI-601-G4-12-PSD	Boehmite	1.655	1.0
TI-601-G4-3-PSD	Boehmite	1.655	1.0
Suspending Phase	Water	1.33	n/a

Table 6. Particle size analysis test matrix used for samples TI-601-G4-3-PSD, TI-601-G4-3-Sheared-PSD, TI-601-G4-6-PSD, TI-601-G4-9-PSD, and TI-601-G4-12-PSD*.

Condition No.	Pump Speed (RPM)	Sonic Power	Comment
1	3000	0%	before sonication
2	4000	0%	before sonication
3	2000	0%	before sonication
4	3000	25%	during sonication
5	3000	50%	during sonication
6	3000	75%	during sonication
7	3000	0%	after sonication
8	4000	0%	after sonication
9	2000	0%	after sonication

*Sample TI-601-G4-12-PSD pump speeds before and after sonication were performed in a different order, resulting in the condition number order 1, 3, 2, 4, 5, 6, 7, 9, 8.

The size distribution of particles was measured under flow conditions before, during, and after 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 and/or sonic power for the next condition were set, the sample was given approximately 30 seconds to equilibrate, and the next set of measurements were taken. Measurements for TI-601-G4-3-PSD were logged to the Mastersizer 2000 file “2008-07

July29-Group 4 CUF PSD.mea". Measurements for TI-601-G4-3-Sheared-PSD and TI-601-G4-6-PSD were logged to the Mastersizer 2000 file "2008-07July30-Group 4 CUF PSD.mea". Measurements for TI-601-G4-9-PSD and TI-601-G4-12-PSD were logged to the Mastersizer 2000 file "2008-08Aug01-Group 4 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 except TI-601-G4-3-Sheared-PSD at conditions 1 and 2 in Table 6, and as such, no post-measurement alteration of these samples was required. Improper optical properties on TI-601-G4-3-Sheared-PSD at conditions 1 and 2 in Table 6 were changed from silica to boehmite after analysis.

The particle size results for Group 3/4 CUF testing samples appear large free of defects or data artifacts caused by air/bubble entrapment in the instrument except for three instances. In TI-601-G4-3-PSD, TI-601-G4-3-Sheared-PSD, and TI-601-G4-9-PSD at 4000 RPM after sonication a spurious peak is present around 1000 μm. This peak may be a result of bubbles in the sample or poor background. These peaks were not present in any of the adjacent measurements and were removed from the analysis.

10 Results and Discussion

Results from the initial characterization of Groups 3 [PUREX Cladding Waste Sludge] and 4 [REDOX Cladding Waste Sludge] and parametric testing of Group 4 are presented here for comparison to Group 3/4 CUF results. Complete descriptions of these tests including instrument performance check, experimental procedures, and post-measurement alterations are discussed in TDP-WTP-271.

10.1 Groups 3 and 4 Initial Characterization PSD Results

Results for TI550-G3-S-WL-PSD (Group 3 Initial Characterization)

Figures 2-4 and Tables 7 and 8 present the results of Group 3 initial characterization particle size analysis as a function of test condition. Figures 2-4 show the differential volume population distribution for the primary Group 3 initial characterization sample (see Appendix A for the duplicate sample results) and allow a qualitative examination of the PSD behavior with respect to pump speed and sonication. Table 7 is a summary of the measured oversize diameter percentiles (by volume/weight) for the primary sample, TI550-G3-S-WL-PSD-1. Table 8 presents the same results for the duplicate sample, TI550-G3-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 Appendix B 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 3 initial characterization sample as a function of pump speed before sonication. The distribution of particles ranges from 0.2 to 40 μm, with the exception of the 4000 RPM condition where the range extends to 200 μm. The peak maxima are between 11 and 15 μm, and all three conditions are continuous and uni-modal, although there is a weak shoulder near 2 μm. Distribution changes with respect to the flow rate are minor with the exception of the appearance of a larger shoulder population spanning 30-200 μm at 4000 RPM. This is expected as higher pump speeds are capable of suspending larger particles and particle agglomerates. Particle sizes appear to be stable with respect to flow, as they are not sheared apart at higher pump speeds.

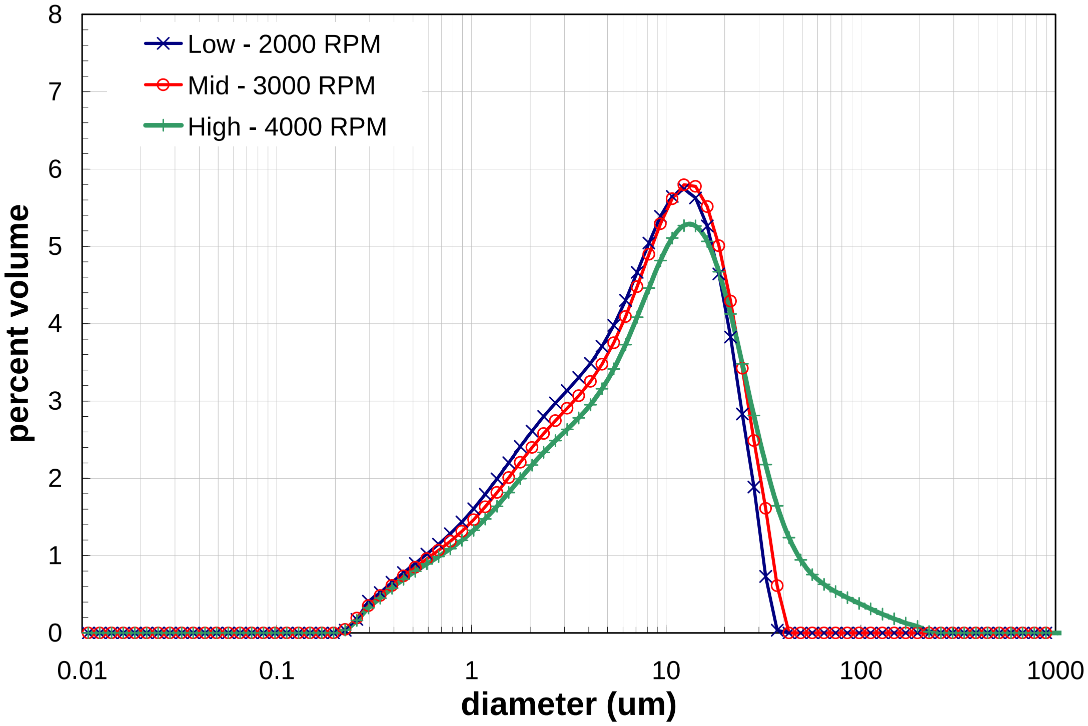


Figure 2. Pre-sonication volume distribution result for the primary Group 3 initial characterization sample as a function of pump speed.

Figure 3 shows the particle size distribution as a function of sonication. This figure indicates that sonication shifts the entire particle population to smaller diameters and increases the central (8-9 µm) population of particles, probably as a result of particle agglomerate disruption. Disruption is evidenced by a decreased fraction of 12-40 µm particles and an increased fraction of 0.2-12 µm particles. After sonication results show that although agglomerates larger than 14 µm do not reform within the time scale of the measurement, there may be some tendency of smaller particles to recombine, which results in an increase in the relative population of 5-10 µm particles.

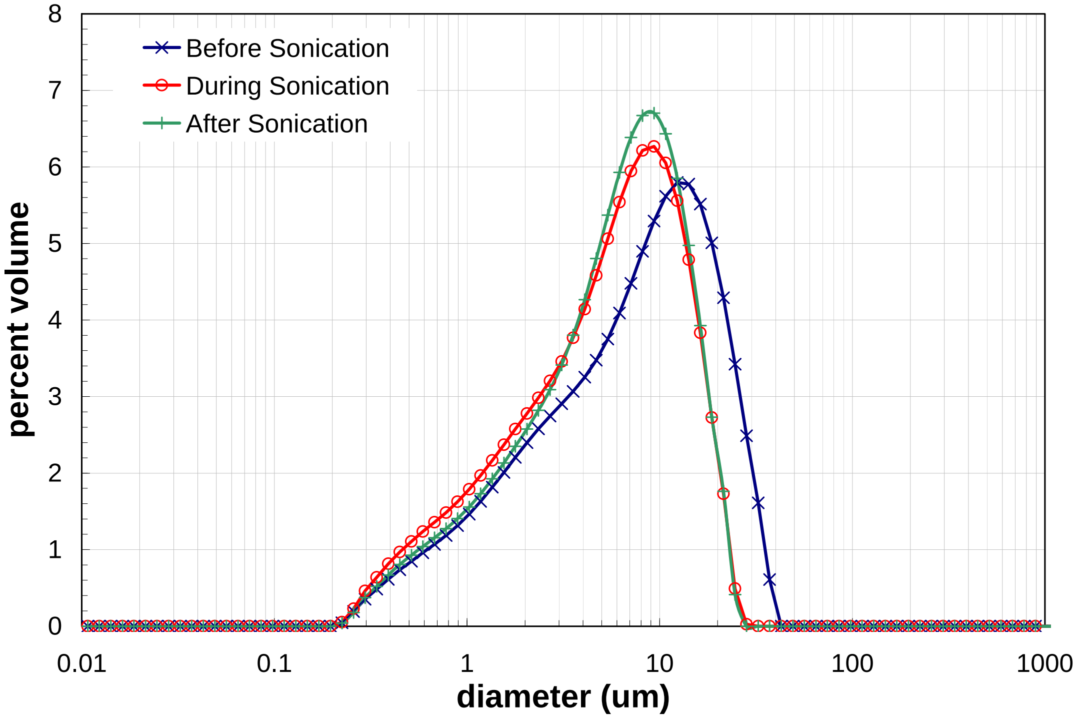


Figure 3. Volume distribution result for the primary Group 3 initial characterization sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

Figure 4 shows the primary Group 3 initial characterization PSD as a function of pump speed after the waste dispersion has been sonicated. Here, changes in pump speed do not appear to significantly change the distribution. Based on this observation, it can be concluded that the particles are still stable with respect to mechanical (shear-induced) break-up even after sonication. Changes as a result of sonication appear permanent as agglomerate recovery does not occur over the duration of the PSD measurement.

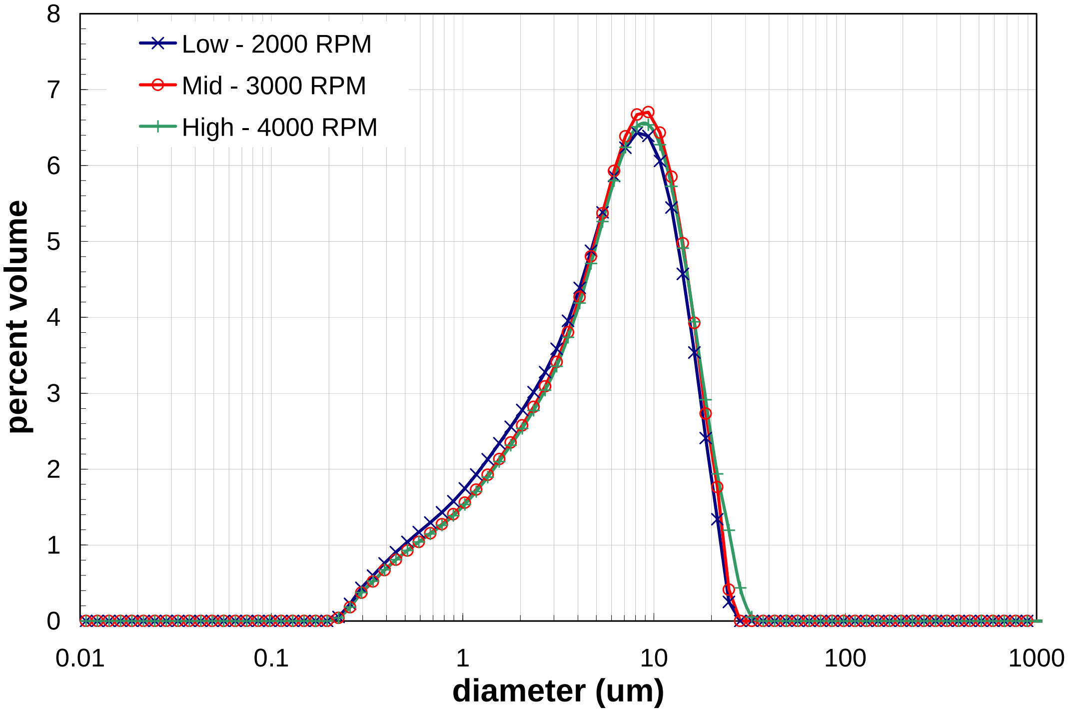


Figure 4. Post-sonication volume distribution result for the primary Group 3 initial characterization sample as a function of pump speed.

Tables 7 and 8 show select cumulative oversize percentiles for the primary and duplicate Group 3 particle dispersions. Using the primary results as a reference, the behavior of Group 3 initial characterization particle size as a function of pump speed and sonication can be quantitatively evaluated. Specifically, the following observations can be made:

- In general, the d(10) falls between 0.96 and 1.3 µm, the d(50) between 5.5 and 8.8 µm, and the d(90) between 14 and 30 µm
- The listed diameter percentiles appear to be slightly sensitive to changes in pump speed before sonication. Increases in flow appear to influence increases in the mean diameter [i.e., the d(50)]. For example, a decrease between 4000 and 2000 RPM before sonication decreases the particle diameter from 8.8 to 6.9 µm. This is a decrease of 22%, which is above the instrument limit of accuracy (10%) and therefore is significant and not merely random noise or measurement error.
- Sonication of the Group 3 solids dispersion decreases particle size. The PSD results at 3000 RPM indicate that sonication lowers the mean particle size from 7.7 to 6.0 µm. This represents a decrease of 22% in the mean particle size and is significant relative to the measurement accuracy (10%).
- After sonication the diameter percentiles appear to be less sensitive to changes in the pump speed. The mean diameter varies between 5.5 and 6.1 µm, which is a difference of 9.8% and is difficult to determine the significance.

Table 7. Particle size analysis percentile results from primary Group 3 initial characterization sample, TI550-G3-S-WL-PSD-1.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	1.2	7.7	22
2	4000	pre-sonic	1.3	8.8	30
3	2000	pre-sonic	1.1	6.9	20
4	3000	25%	0.97	6.3	18
5	3000	50%	0.97	6.0	16
6	3000	75%	0.96	5.6	15
7	3000	post-sonic	1.1	6.0	15
8	4000	post-sonic	1.1	6.1	15
9	2000	post-sonic	1.0	5.5	14

Table 8. Particle size analysis percentile results from duplicate Group 3 initial characterization sample, TI550-G3-S-WL-PSD-2.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	1.0	6.0	17
2	4000	pre-sonic	1.1	6.3	20
3	2000	pre-sonic	1.0	5.8	16
4	3000	25%	1.0	5.7	16
5	3000	50%	1.0	5.5	14
6	3000	75%	1.0	5.2	13
7	3000	post-sonic	1.0	5.1	13
8	4000	post-sonic	1.0	5.1	13
9	2000	post-sonic	1.0	5.1	13

Behavior of the duplicate sample PSD with respect to pump speed and sonication is similar to that of the primary sample. However, the PSD of the duplicate sample favors consistently smaller diameters 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 3 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 slight difference between samples.

Table 9. Absolute relative percent difference between primary and duplicate Group 3 initial characterization samples.

Measurement Condition	Pump Speed	Sonication	Absolute RPD		
			d(10)	d(50)	d(90)
1	3000	pre-sonic	11%	21%	20%
2	4000	pre-sonic	15%	28%	34%
3	2000	pre-sonic	5.8%	16%	16%
4	3000	25%	5.8%	8.8%	13%
5	3000	50%	5.5%	8.0%	12%
6	3000	75%	5.3%	6.9%	9.5%
7	3000	post-sonic	9.2%	15%	14%
8	4000	post-sonic	9.9%	17%	17%
9	2000	post-sonic	0.80%	9.0%	11%

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 3 initial characterization samples show RPDs that range from 0.80 to 34% 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. The largest RPDs are observed in the pre-sonication measurement conditions, indicating that sonication eliminates some size differences between the samples. Since, during sonication, the measurements lie close to or below 10% size differences between the primary and the duplicate sample may be largely influence by agglomeration.

Figures 5 and 6 show how the differences in the primary and duplicate PSDs described in the preceding paragraphs manifest in the differential volume distributions. Figure 5 compares the primary and duplicate PSDs at 3000 RPM before sonication. With respect to the pre-sonication comparison, both distributions show similar trends in population with peaks centered between 9-15 µm and spanning 0.2-40 µm. The main difference is that the primary sample has a significantly increased population of 10-40 µm. This causes the larger percentiles observed in Table 7 (relative to those in Table 8) and >10% RPDs in Table 9.

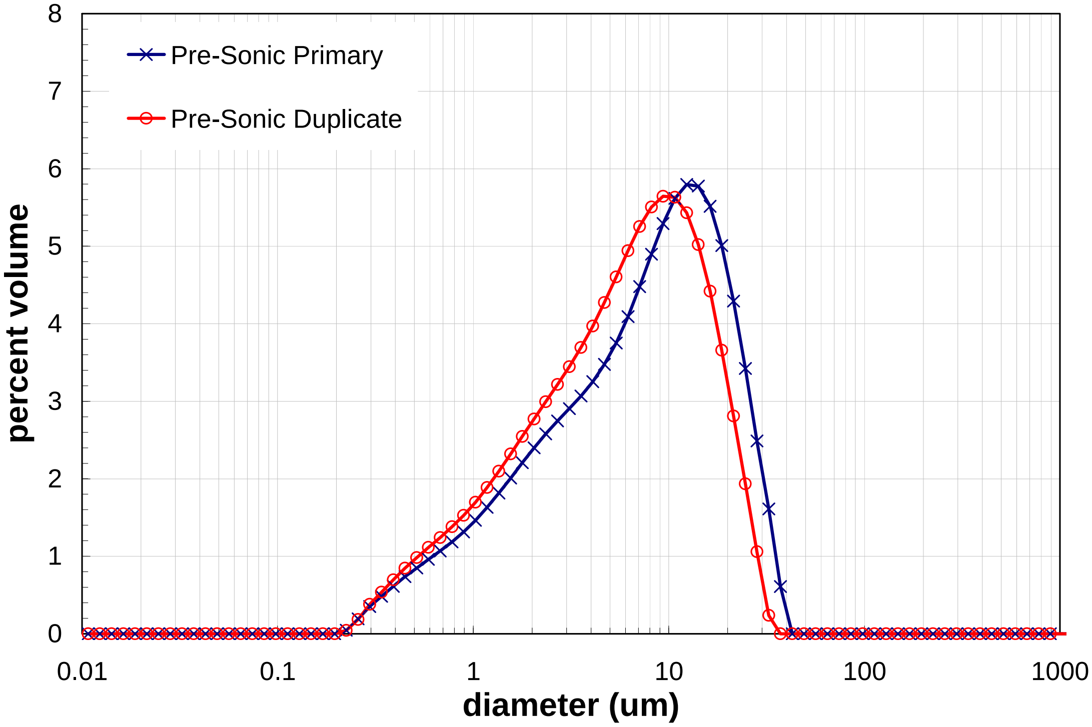


Figure 5. Comparison of primary and duplicate sample differential volume PSD of Group 3 initial characterization at 3000 RPM before sonication.

Figure 6 compares primary and duplicate distributions after sonication. Overall, the primary and duplicate distributions show a uni-modal particle size spanning 0.2-30 µm with the peak centered around 7-10 µm. After sonication results show that the increased particle size observed in the primary sample prior to sonication is maintained after sonication. The difference between the primary and duplicate distributions after sonication appears less than before sonication (an observation confirmed by the results in Table 9). This supports the earlier assertion that the difference between samples may be in their state of particle agglomeration.

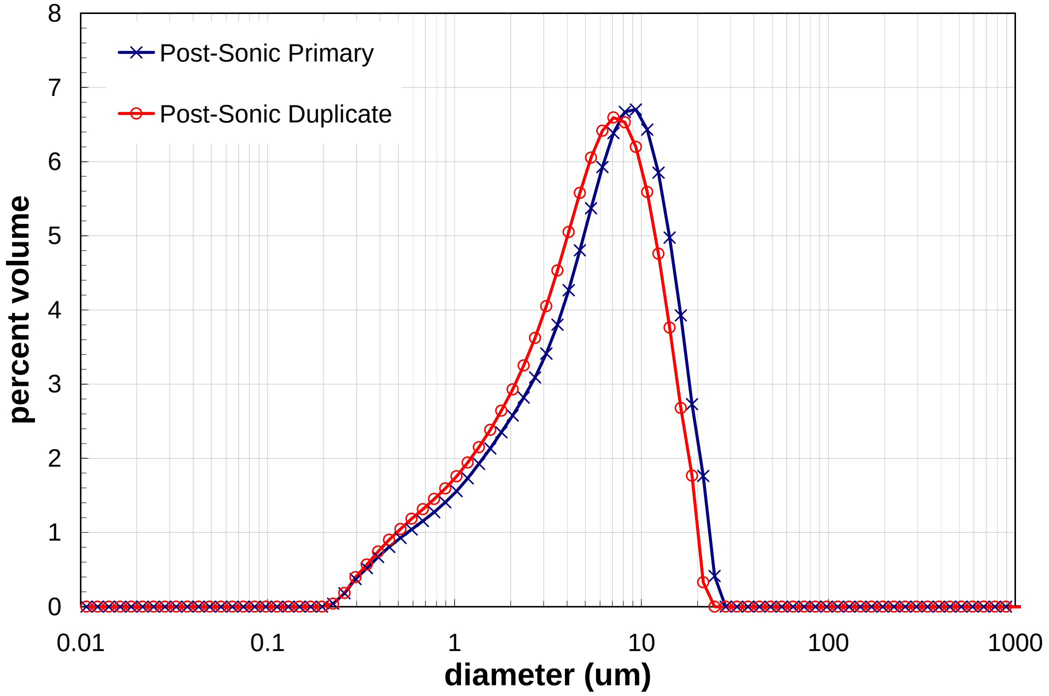


Figure 6. Comparison of primary and duplicate sample differential volume PSD of Group 3 initial characterization at 3000 RPM after sonication.

Particle size analysis of the initial characterization Group 3 (PUREX Cladding Waste Sludge) yielded a broad uni-modal particle size distribution with a peak centered between 11-15 µm and a range from 0.2-40 µm. The range extends to 200 µm at the high flow rate indicating the presence of some larger difficult to suspend particles or agglomerates. Sonication shifts the range to 0.2-20 µm suggesting that some of the larger particles may be agglomerates, which were disrupted during sonication. The agglomerate disruption due to sonication appeared stable during the time of the measurement.

Results for TI547-G4-S-WL-PSD (Group 4 Initial Characterization)

Figures 7-9 and Tables 10 and 11 present the results of Group 4 initial characterization particle size analysis as a function of test condition. Figures 7-9 show the differential volume population distribution for the primary Group 4 initial characterization sample (see Appendix A for the duplicate sample results) and allow a qualitative examination of the PSD behavior with respect to pump speed and sonication. Table 10 is a summary of the measured oversize diameter percentiles (by volume/weight) for the primary sample, TI547-G4-S-WL-PSD-1. Table 11 presents the same results for the duplicate sample, TI547-G4-S-WL-PSD -2. Both tables present cumulative oversize diameters corresponding to the d(10), d(50), and d(90). More extensive percentile results are provided in Appendix B of this interim report. These tables will be used to quantitatively examine reproducibility and changes in particle size.

Figure 7 shows the PSD for the primary Group 4 initial characterization sample as a function of pump speed before sonication. The distribution of particles ranges from 0.2-200 µm with varying peaks depending on the pump speed. At 2000 RPM the distribution is uni-modal with a maximum population between 12-14 µm and low shoulder populations on both ends of the range. As the pump speed increased the distribution became bi-modal with the primary peak between 55-65 µm and a secondary peak in the range of 12-14 µm. As in the 2000 RPM case there is a shoulder between 0.2-2 µm, although at 3000

RPM there is no shoulder at larger diameters after the peak. At 4000 RPM the major peak is between 50-60 µm and there are two shoulders, one between 0.2-2 µm and one between 12-14 µm. The distribution at 4000 RPM is dominated by the population of larger particles and the original 12-14 µm peak now exists as a shoulder distribution to the primary peak centered at 50-60 µm. These results indicate that the distribution was highly influenced by the flow rate and suggest the presence of large, difficult to suspend particles or particle agglomerates.

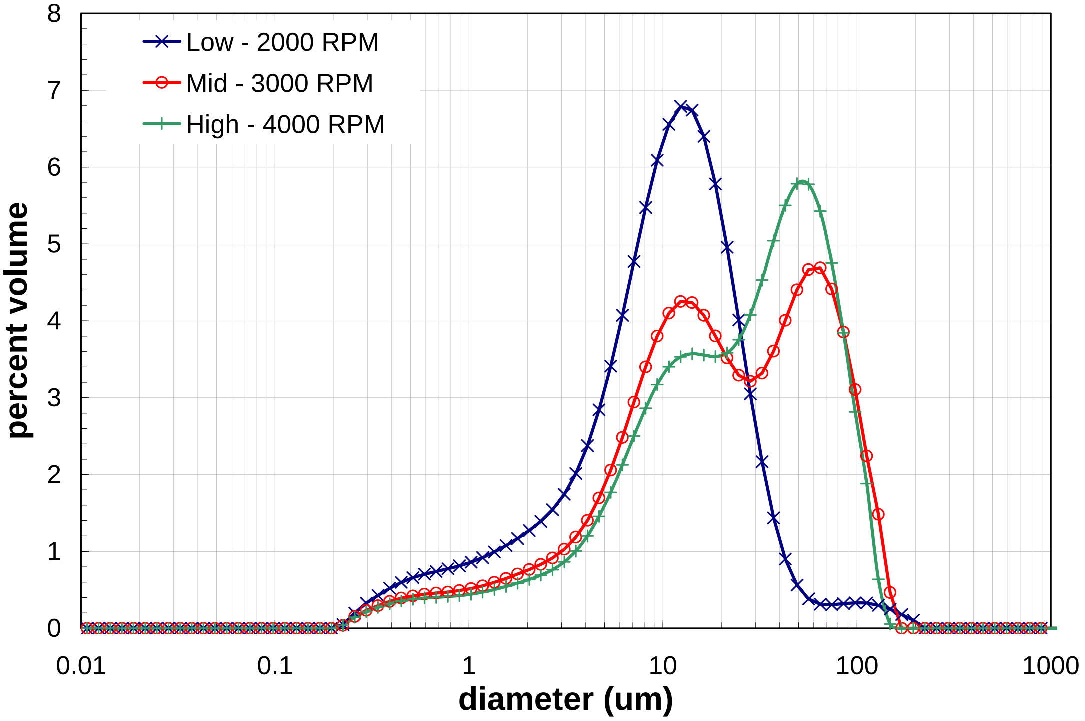


Figure 7. Pre-sonication volume distribution result for the primary Group 4 initial characterization sample as a function of pump speed.

Figure 8 shows the particle size distribution as a function of sonication. This figure indicates that sonication shifts the entire particle population to smaller diameters and substantially increases the central (9-11 µm) population of particles. This result suggests that the solid species making up the 20 to 200 µm population are particle agglomerates. During sonication the particle diameter range reduces from 0.2-200 µm to 0.2-35 µm. This reduction is likely a result of agglomerate disruption during sonication. After sonication agglomeration is again seen as the particle diameter range extends up to 0.2-150 µm. Therefore, although sonication may disrupt agglomerates, there is some recovery of these agglomerates.

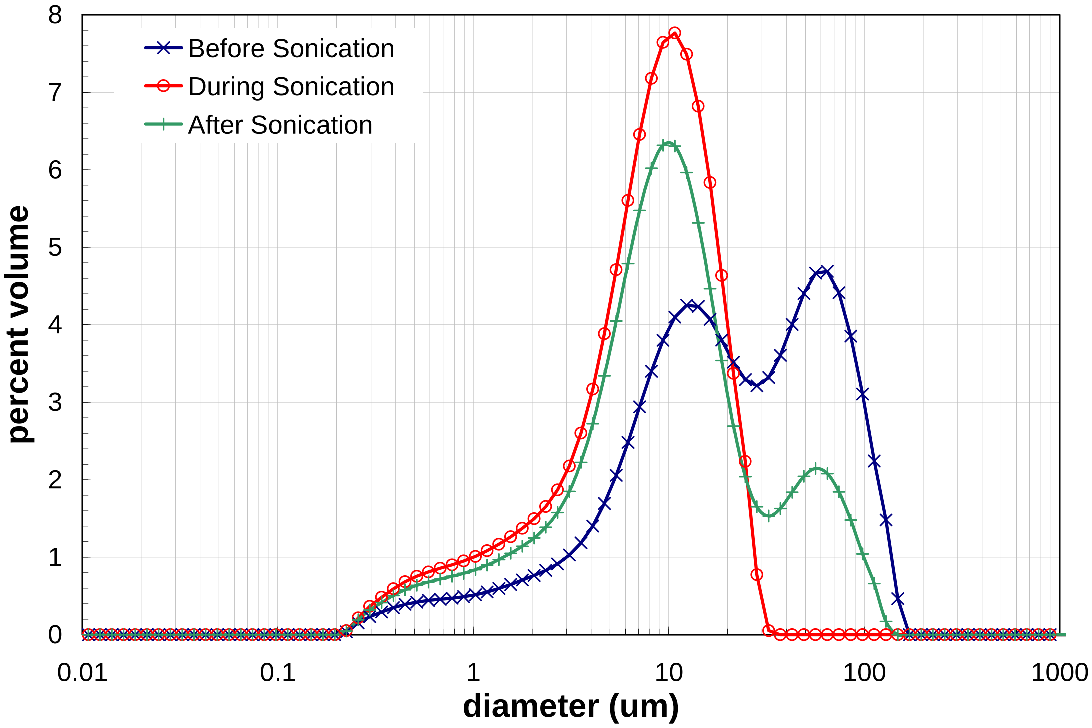


Figure 8. Volume distribution result for the primary Group 4 initial characterization sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

Figure 9 shows the primary Group 4 initial characterization PSD as a function of pump speed after the sample has been sonicated. Here again, changes in pump speed show a large discrepancy in particle diameter distribution. At 2000 RPM the particle diameter ranges from 0.2-40 µm with a peak around 9-11 µm. As the pump speed increases to 3000 RPM, larger particle diameters are seen as evident by the broader range of 0.2-150 µm. At both 3000 and 4000 RPM there is a secondary peak between 45-65 µm. The percent volume of particles and/or agglomerates within this range increases significantly at 4000 RPM, indicating that higher pump speeds are able to keep more larger diameter particles and/or agglomerates in suspension, while at 2000 RPM these may quickly settle out.

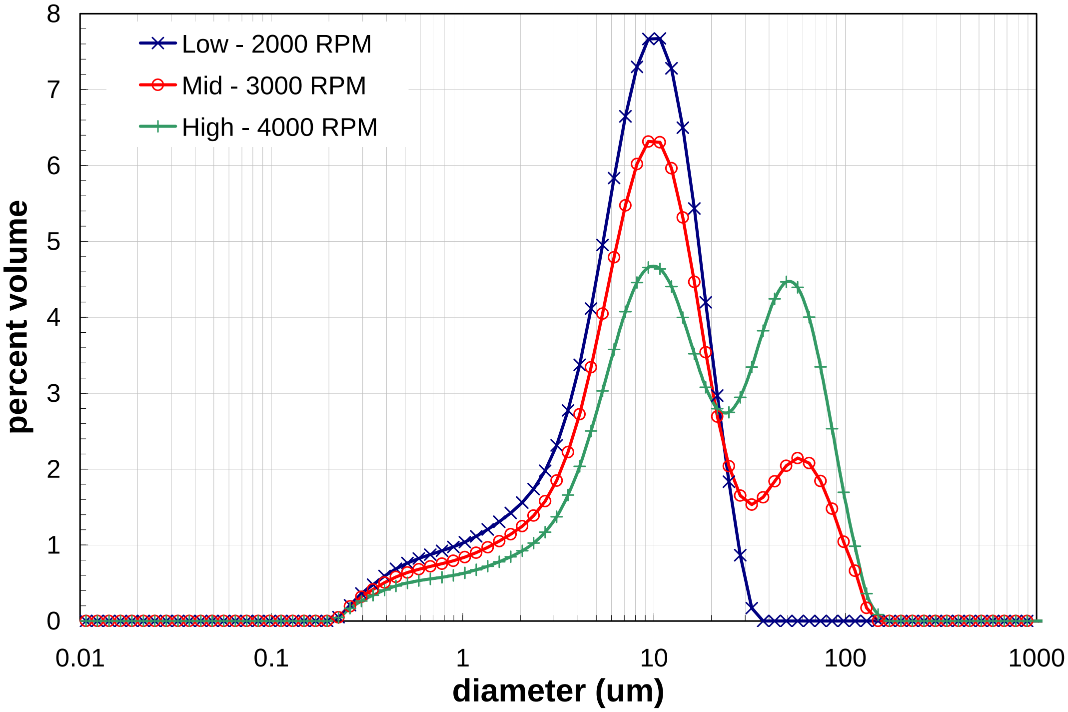


Figure 9. Post-sonication volume distribution result for the primary Group 4 initial characterization sample as a function of pump speed.

Tables 10 and 11 show select cumulative oversize percentiles for the primary and duplicate Group 4 particle dispersions. Using the primary results as a reference, the behavior of Group 4 initial characterization particle size as a function of pump speed and sonication can be quantitatively evaluated. Specifically, the following observations can be made:

- In general, the d(10) falls between 1.4 and 3.9 µm, the d(50) between 7.9 and 26 µm, and the d(90) between 17 and 83 µm
- The listed diameter percentiles appear to be sensitive to changes in pump speed, both before and after sonication. Increases in flow rate appear to influence increases in the mean diameter [i.e., the d(50)]. For example, a decrease from 4000 RPM to 2000 RPM reduces the mean diameter from 26 to 10 µm which is a difference of ~62%. This effect is reduced after sonication although it is still prevalent as a difference of the same reading is ~44%.
- Sonication of the Group 4 solids dispersion decreases particle size. The PSD results at 3000 RPM indicate that sonication lowers the mean particle diameter from 20 to 9.7 µm. This represents a decrease of ~52% and is significant relative to the measurement accuracy (10%).

Table 10. Particle size analysis percentile results from primary Group 4 initial characterization sample, TI547-G4-S-WL-PSD-1.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	3.2	20	83

2	4000	pre-sonic	3.9	26	78
3	2000	pre-sonic	1.7	10	27
4	3000	25%	1.6	10	23
5	3000	50%	1.5	9.1	21
6	3000	75%	1.5	8.2	18
7	3000	post-sonic	1.8	9.7	51
8	4000	post-sonic	2.5	14	67
9	2000	post-sonic	1.4	7.9	17

Table 11. Particle size analysis percentile results from duplicate Group 4 initial characterization sample, TI547-G4-S-WL-PSD-2.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	2.1	12	34
2	4000	pre-sonic	2.5	15	48
3	2000	pre-sonic	1.8	11	27
4	3000	25%	1.8	11	25
5	3000	50%	1.7	9.3	21
6	3000	75%	1.5	8.0	17
7	3000	post-sonic	1.6	8.0	19
8	4000	post-sonic	1.8	9.2	36
9	2000	post-sonic	1.5	7.7	17

Behavior of the duplicate sample PSD with respect to pump speed and sonication is similar to that of the primary sample. However, the PSD of the duplicate sample favors consistently smaller diameters than that of the primary at equivalent measurement conditions. Table 12 shows the absolute relative percent difference, calculated according to Eq. 1, between the d(10), d(50), and d(90) values determined for the primary and duplicate Group 4 initial characterization samples. The listed RPDs indicate that there is a difference between samples.

Table 12. Absolute relative percent difference between primary and duplicate Group 4 initial characterization samples.

Measurement Condition	Pump Speed	Sonication	Absolute RPD		
			d(10)	d(50)	d(90)
1	3000	pre-sonic	34%	39%	59%
2	4000	pre-sonic	34%	43%	38%
3	2000	pre-sonic	5.9%	4.9%	2.4%
4	3000	25%	11%	7.7%	9.9%
5	3000	50%	8.7%	2.8%	1.7%
6	3000	75%	4.8%	1.9%	2.7%
7	3000	post-sonic	13%	17%	63%
8	4000	post-sonic	28%	35%	46%
9	2000	post-sonic	4.4%	2.3%	3.6%

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 4 initial characterization samples show RPDs that range from 1.7 to 63% depending on the measurement condition and percentile examined. As the pre-sonic and post-sonic measurements display a large number of RPDs greater than 10% in Table 12, and during sonication, the measurements lie close to or below 10% size differences between the primary and the duplicate sample may be largely influence by agglomeration.

Figures 10 and 11 show how the differences in the primary and duplicate PSDs described in the preceding paragraphs manifest in the differential volume distributions. Figure 10 compares the primary and duplicate PSDs at 3000 RPM before sonication. There are two major discrepancies, in the pre-sonic measurements, between the particle size distribution of the primary and the duplicate. The duplicate sample demonstrates a uni-modal peak which ranges from 0.2-100 µm, while the primary sample exhibits a bi-modal peak with a range from 0.2-170 µm.

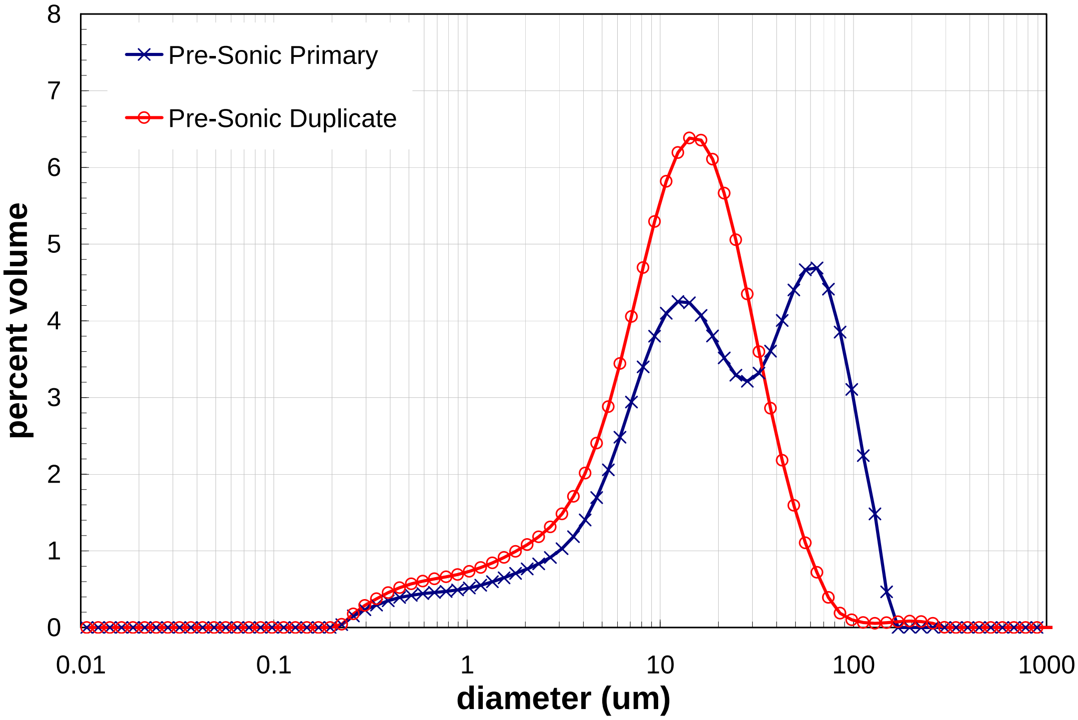


Figure 10. Comparison of primary and duplicate sample differential volume PSD of Group 4 initial characterization at 3000 RPM before sonication.

The after sonic distribution, shown in Figure 11, exhibits more similar trends than were observed before sonication. Both the primary and duplicate ranged from approximately 0.2-130 µm although the primary extended slightly to 150 µm. In both instances a major peak was observed around 9-11 µm, and a minor peak was observed around 50-75 µm. The primary had a larger secondary peak, which, in accordance with the before sonication comparison, would indicate that the primary sample had higher affinity for agglomeration as this secondary peak did not exist during sonication. Therefore, the primary sample may have resulted in a higher fraction of larger particles and/or agglomerates than the secondary.

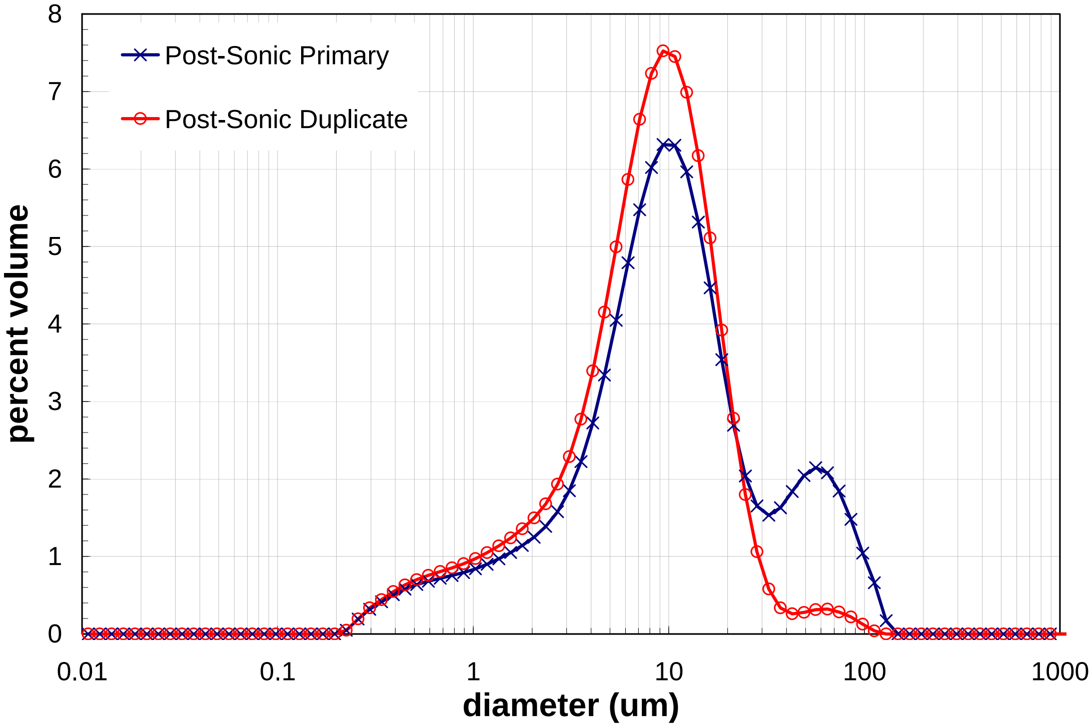


Figure 11. Comparison of primary and duplicate sample differential volume PSD of Group 4 initial characterization at 3000 RPM after sonication.

The results of the initial characterization of Group 4 (REDOX Cladding Waste Sludge solids) samples indicate a broad distribution ranging from 0.2-200 µm. The particle size distribution was heavily influenced by the pump speed, with a rise in population of > 30 µm particles as the flow rate was increased. The larger solids appear to be agglomerates as they are easily disrupted by sonication. Recovery of these agglomerates occurs after sonication although it was not complete during the time of the measurement.

10.2 Group 3/4 CUF Testing PSD Results

The following sub-sections discuss the PSD results for Group 3/4 CUF testing samples. A brief outline of how select cumulative oversize diameter percentiles behave as a function of test condition is given, and graphs of particle size distributions are given 1) as a function of flow rate before and after sonication and 2) at 3000 RPM before, during and after 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 PSD to one another to highlight effects of CUF processing shall be examined in Section 10.3.

Results for TI-601-G4-3-PSD (Low-Solids Matrix)

Sample TI-601-G4-3-PSD is representative of the low-solids matrix (dilute) slurry that was initially run in the CUF system. The source slurry is a chemically unmodified mixture of homogenized wastes from Group 3 and 4. Table 13 shows select cumulative undersize percentiles for sample TI-601-G4-3-PSD, more extensive percentile results are shown in Appendix B. Here the d(10) ranges between 0.98 and 1.1 µm, the d(50) between 5.4 and 6.4 µm, and the d(90) between 15 and 27 µm. With regards to pump speed effects, the d(50) and d(90) percentiles before sonication show a significant increase in size at 4000 RPM, indicating the presence of large, difficult-to-suspend particles. Sonication appears to have minimal effects on the percentiles except at 4000 RPM where the d(90) is reduced from 27 to 18 µm, signifying that larger difficult-to-suspend particles may be results of agglomeration.

Table 13. Particle size analysis percentile results the Group 3/4 low-solids matrix sample (TI-601-G4-3-PSD).

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	0.97	5.5	17
2	4000	pre-sonic	1.1	6.4	27
3	2000	pre-sonic	0.99	5.4	16
4	3000	25%	0.98	5.4	16
5	3000	50%	0.98	5.6	16
6	3000	75%	0.98	5.7	15
7	3000	post-sonic	1.0	5.8	16
8	4000	post-sonic	1.1	6.2	18
9	2000	post-sonic	1.0	5.6	15

Figure 12 shows the PSD for Group 3/4 low-solids matrix (TI-601-G4-3-PSD) sample as a function of pump speed before sonication. The distribution of particles ranges from 0.2 to 40 µm, with the range extending to 200 µm at 4000 RPM. The peak maxima are around 9 µm and all three conditions are continuous and uni-modal, although there is a small shoulder near 0.4 µm and at 4000 RPM there is also a shoulder around 70 µm. Changes with respect to the flow rate are minor with the exception of some suspension of larger particle diameters at 4000 RPM. This is expected as higher pump speeds are capable of suspending larger particles and particle agglomerates.

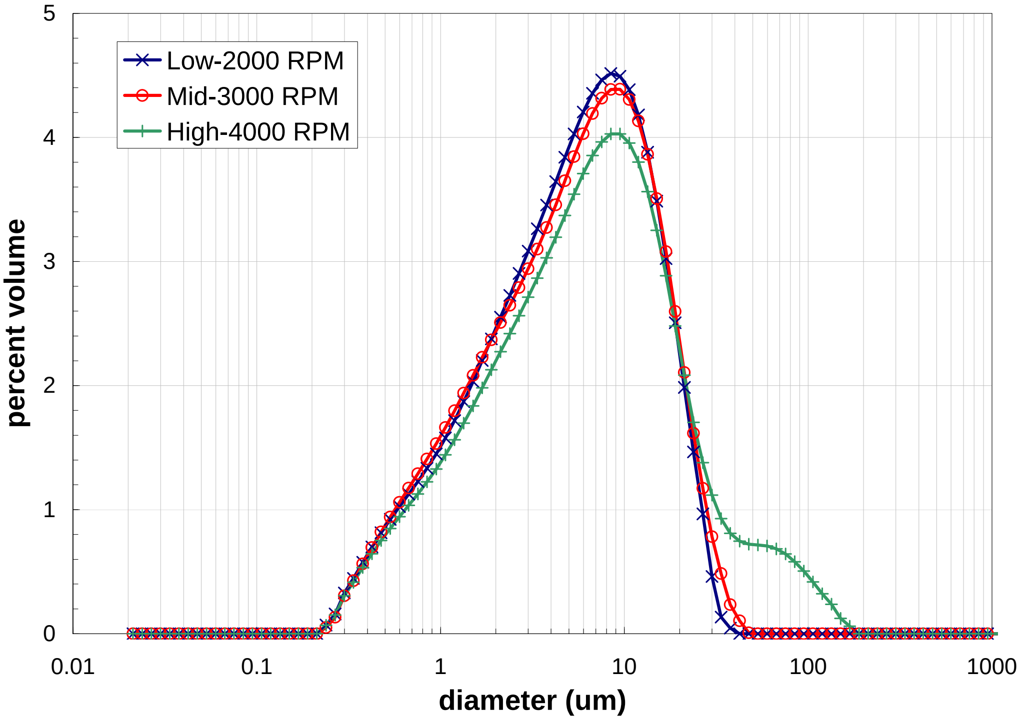


Figure 12. Pre-sonication volume distribution result for the Group 3/4 low-solids matrix (TI-601-G4-3-PSD) sample as a function of pump speed.

Figure 13 shows the particle size distribution as a function of sonication. This figure indicates that the effects of sonication are minimal on the Group 3/4 low-solids matrix sample. During sonication the distribution remains uni-modal and continuous with a peak maximum around 9 µm. After sonication a small increase is seen in particles of approximately 50 µm, which may be a result of agglomerate formation or more likely is noise or a spurious flocculate.

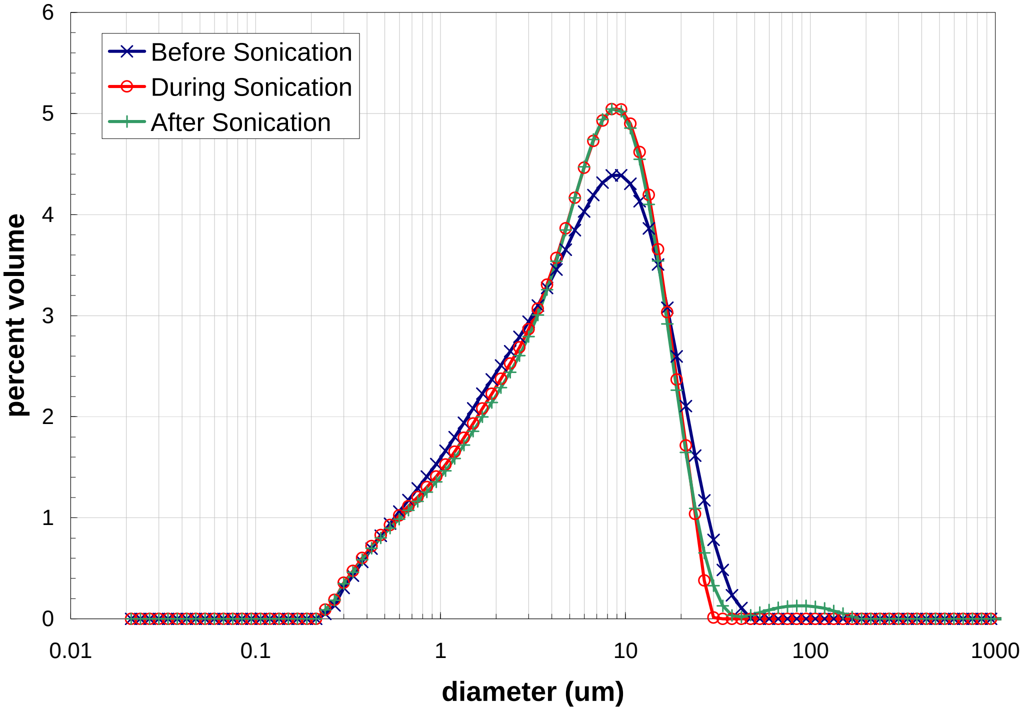


Figure 13. Volume distribution result for the Group 3/4 low-solids matrix (TI-601-G4-3-PSD) sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

Figure 14 shows the Group 3/4 low-solids matrix (TI-601-G4-3-PSD) PSD as a function of pump speed after the waste dispersion has been sonicated. Here, changes in pump speed do not appear to significantly change the distribution, with the exception of a small increase in the quantity of larger particles 3000 and 4000 RPM. This fraction of larger particles appears less than in pre-sonication measurements shown in Figure 12. Based on this observation, sonication can disrupt agglomerates, although there is some recovery afterwards.

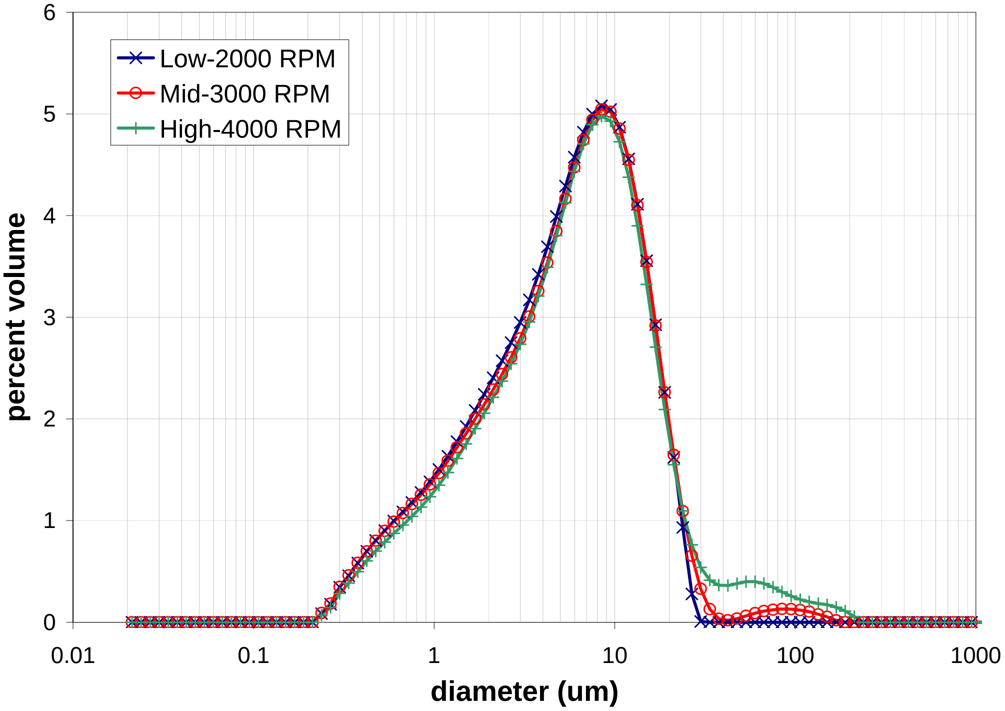


Figure 14. Post-sonication volume distribution result for the Group 3/4 low-solids matrix (TI-601-G4-3-PSD) sample as a function of pump speed.

Particle size analysis of the Group 3/4 low-solids matrix (TI-601-G4-3-PSD) yielded a broad particle size distribution with a peak centered around 9 µm and a range from 0.2-40 µm. The range extends to 200 µm as the flow rate increases, indicating the presence of some larger difficult to suspend particles or agglomerates. Sonication increases the relative peak population and decreases the fraction of > 11 µm particles suggesting that some of the larger particles may be agglomerates, which were disrupted during sonication. After sonication, some larger particles and/or agglomerates were again present at 4000 RPM, although this fraction was reduced relative to the pre-sonication measurements. Therefore, particles in this size range are most likely agglomerates which can be disrupted by sonication.

Results for TI-601-G4-3-Sheared-PSD (Low-solids matrix-Sheared)

Sample TI-601-G4-3-Sheared-PSD is again representative of the low-solids matrix (dilute) slurry that was initially run in the CUF system. This sample was taken approximately 20 hours after TI-601-G4-3-PSD, where the slurry had been continuously circulated through the CUF possibly resulting in the shearing of particles or particle agglomerates. Table 14 shows select cumulative undersize percentiles for sample TI-601-G4-3-Sheared-PSD, more extensive percentile results are shown in Appendix B. Here the d(10) ranges between 0.94 and 1.0 µm, the d(50) between 4.6 and 6.4 µm, and the d(90) between 14 and 37 µm. With regards to pump speed effects, the d(50) and d(90) percentiles before sonication show a significant increase in size at 4000 RPM, indicating the presence of large, difficult-to-suspend particles. Sonication appears to have minimal effects on the percentiles except at 4000 RPM where the d(90) is reduced from 37 to 18 µm, signifying that larger difficult-to-suspend particles may be results of agglomeration.

Table 14. Particle size analysis percentile results the Group 3/4-Sheared low-solids matrix (TI-601-G4-3-Sheared-PSD) sample.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	0.94	5.2	19
2	4000	pre-sonic	1.0	6.4	37
3	2000	pre-sonic	0.97	4.6	14
4	3000	25%	0.97	4.6	14
5	3000	50%	0.99	5.0	15
6	3000	75%	0.99	5.1	14
7	3000	post-sonic	1.0	5.2	15
8	4000	post-sonic	1.0	5.6	18
9	2000	post-sonic	1.0	5.2	15

Figure 15 shows the PSD for the Group 3/4 sheared low-solids matrix (TI-601-G4-3-Sheared-PSD) sample as a function of pump speed before sonication. At 2000 RPM the PSD is uni-modal with the peak around 5 µm. Particle sizes range from 0.2-30 µm, and a weak shoulder is present around 0.4 µm. At higher pump speeds the range increases up to 200 µm and the peak maximum shifts to around 8 µm. This is expected as higher pump speeds are capable of suspending larger particles and particle agglomerates that may settle out at lower pump speeds.

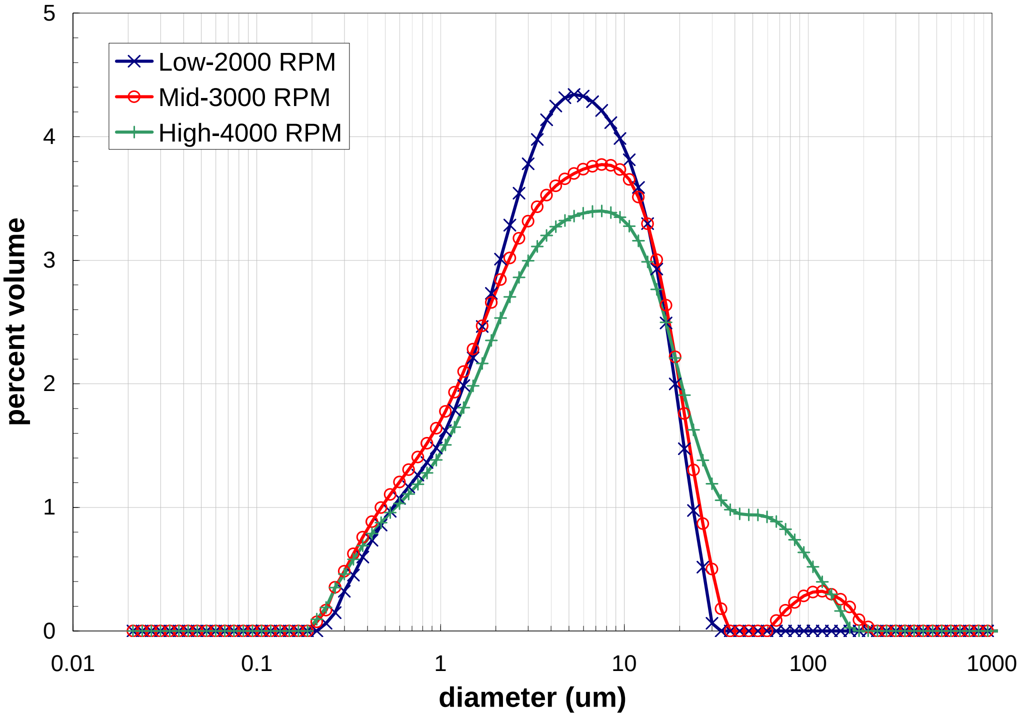


Figure 15. Pre-sonication volume distribution result for the Group 3/4-Sheared low-solids matrix (TI-601-G4-3-Sheared-PSD) sample as a function of pump speed.

Figure 16 shows the particle size distribution as a result of applied sonication. This figure indicates particles > 30 µm may be mostly agglomerates that are disrupted during sonication. The 100 µm peak present before sonication does not exist during or after sonication. The relative peak maxima are shifted to larger volumes as a result of the agglomerate disruption. Similarities between the during- and after- sonication distribution suggest that the changes which occur during sonication are irreversible over the time frame of the post-sonication particle size analyses.

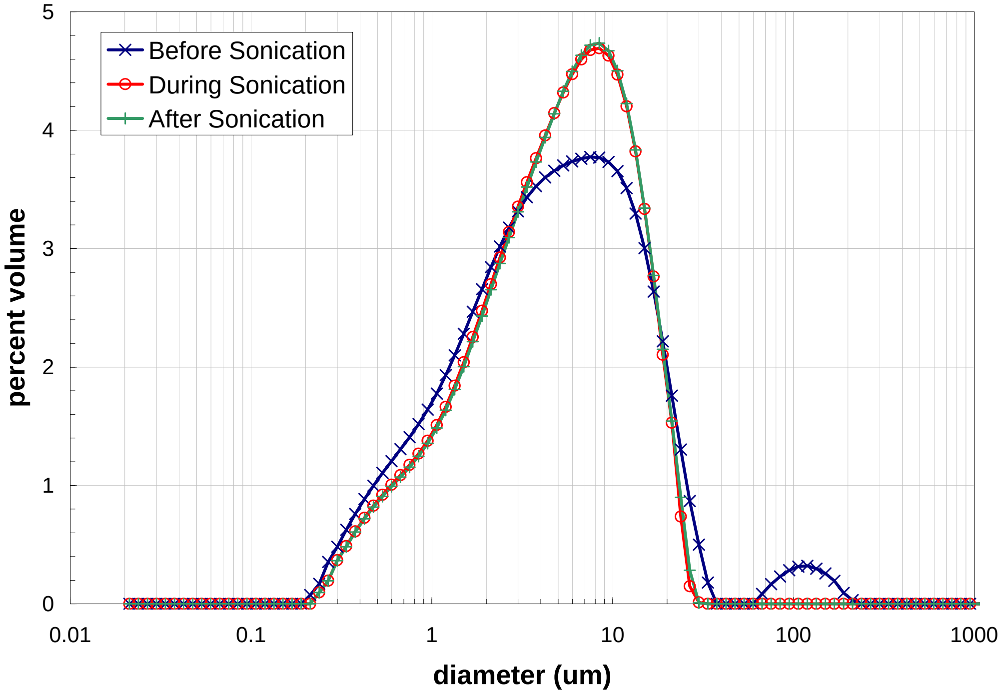


Figure 16. Volume distribution result for the Group 3/4-Sheared low-solids matrix (TI-601-G4-3-Sheared-PSD) sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

Figure 17 shows TI-601-G4-3-Sheared-PSD as a function of pump speed after the sample has been sonicated. Changes in pump speed show little discrepancy in particle size distribution at smaller particle sizes. As in the pre-sonication measurements, at 4000 RPM a large particle peak is present around 100 µm, and is most likely a result of increased suspension of heavier particles and/or agglomerates due to increased flow rate. This fraction of larger particles appears less than in pre-sonication measurements shown in Figure 15. Therefore, particles in this range are most likely a result of agglomerate formation.

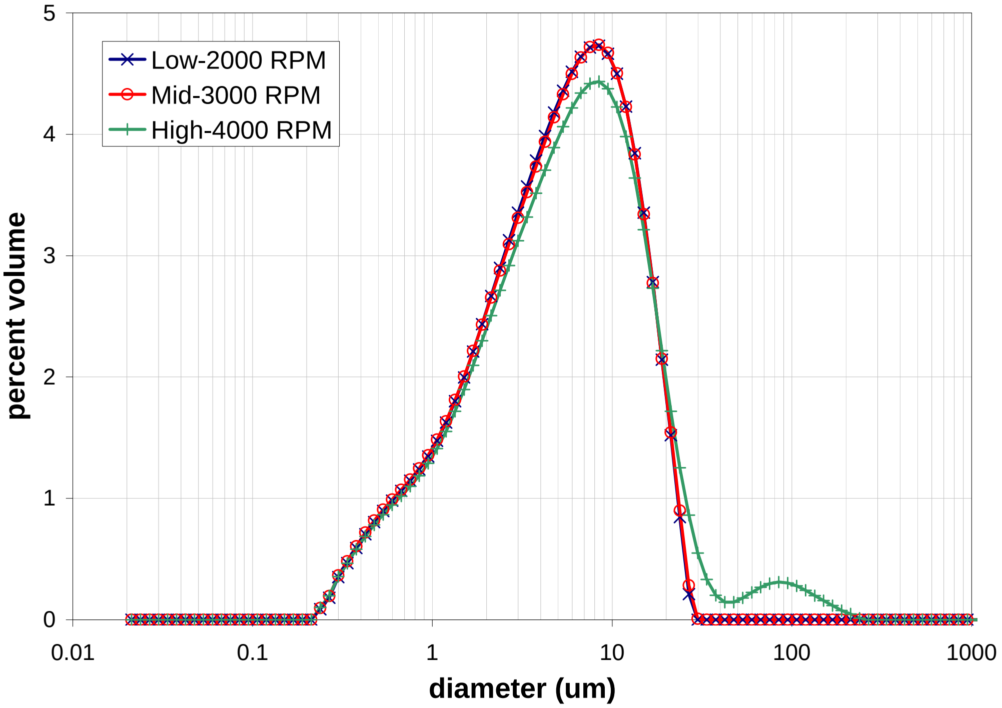


Figure 17. Post-sonication volume distribution result for the Group 3/4-Sheared low-solids matrix (TI-601-G4-3-Sheared-PSD) sample as a function of pump speed.

Particle size analysis of the Group 3/4 sheared low-solids matrix (TI-601-G4-3-Sheared-PSD) yielded a broad particle size distribution with a peak between 5-9 µm and a range from 0.2-40 µm. The range extends to 200 µm as the flow rate increases, indicating the presence of some larger difficult to suspend particles or agglomerates. Sonication increases the relative peak population and decreases the fraction of > 11 µm particles suggesting that some of the larger particles may be agglomerates, which were disrupted during sonication. After sonication, some larger particles and/or agglomerates were again present at 4000 RPM, although this fraction was reduced relative to the pre-sonication measurements. Therefore, particles in this size range are most likely agglomerates which can be disrupted by sonication.

Results for TI-601-G4-6-PSD (High-solids matrix Group 3/4 before caustic leach)

Sample TI-601-G4-6-PSD is representative of the high-solids matrix slurry that results from dewatering the initial 3/4 CUF slurry. Table 15 shows select cumulative undersize percentiles for sample TI-601-G4-6-PSD, more extensive percentile results are shown in Appendix B. Here the d(10) ranges between 0.91 and 1.1 µm, the d(50) between 4.6 and 5.7 µm, and the d(90) between 14 and 36 µm. With regards to pump speed effects, the d(50) and d(90) percentiles before sonication show a significant increase in size at 4000 RPM, indicating the presence of large, difficult-to-suspend particles and/or agglomerates. Sonication appears to have minimal effects on the percentiles except at 4000 RPM where the d(90) is reduced from 36 to 21 µm, signifying that larger difficult-to-suspend particles may be results of agglomeration.

Table 15. Particle size analysis percentile results the Group 3/4 high-solids matrix (TI-601-G4-6-PSD) sample.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	0.91	4.8	19
2	4000	pre-sonic	1.0	5.7	36
3	2000	pre-sonic	0.93	4.6	17
4	3000	25%	0.99	4.6	15
5	3000	50%	0.99	4.8	15
6	3000	75%	1.0	4.9	15
7	3000	post-sonic	1.1	5.2	17
8	4000	post-sonic	1.1	5.5	21
9	2000	post-sonic	1.0	4.9	14

Figure 18 shows the PSD for the Group 3/4 high-solids matrix (TI-601-G4-6-PSD) sample as a function of pump speed before sonication. The particle size distribution ranges from 0.2-200 µm with a peak centered around 5 µm and a weak shoulder around 0.5 µm. There is also a shoulder or separate peak at diameters > 40 µm. These particles have an increasing population as the pump speed increases. This is expected as higher pump speeds are capable of suspending larger particles and particle agglomerates that may settle out at lower pump speeds.

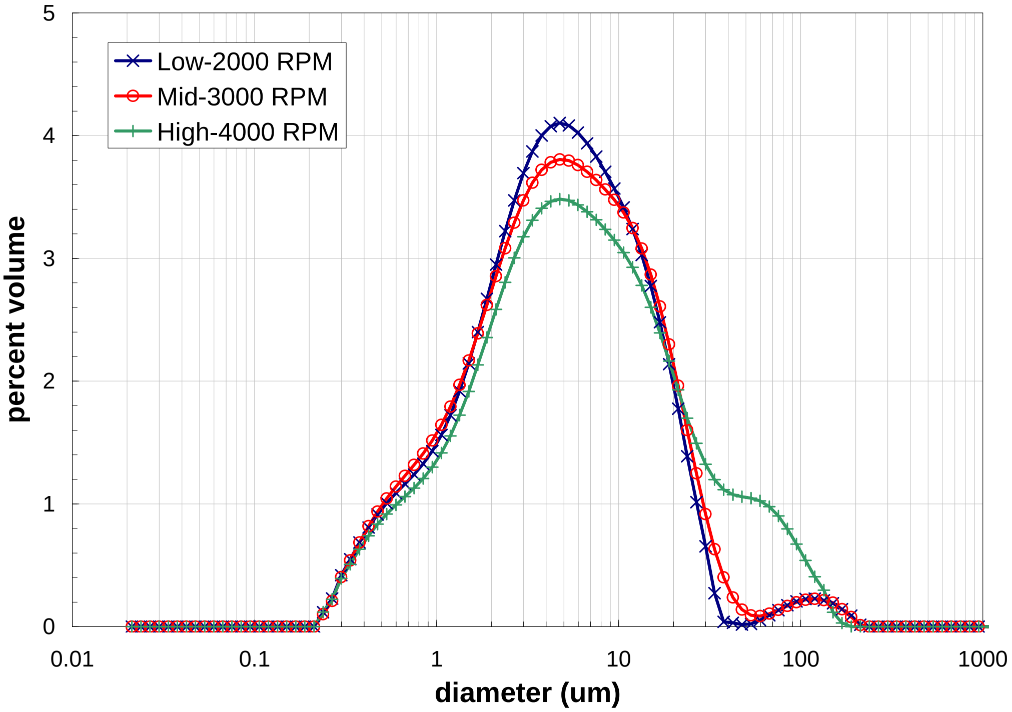


Figure 18. Pre-sonication volume distribution result for the Group 3/4 high-solids matrix (TI-601-G4-6-PSD) sample as a function of pump speed.

Figure 19 shows the particle size distribution as a result of applied sonication. Sonication shifts the range from 0.2-200 µm to 0.2-30 µm, eliminating the secondary peak centered around 120 µm. The primary peak is shifted from 5 to 7 µm, which is likely a result of the disruption of >30 µm agglomerates. Agglomerate recovery is observed after sonication, as the range extends to 200 µm, although the peak population remains centered around 7 µm.

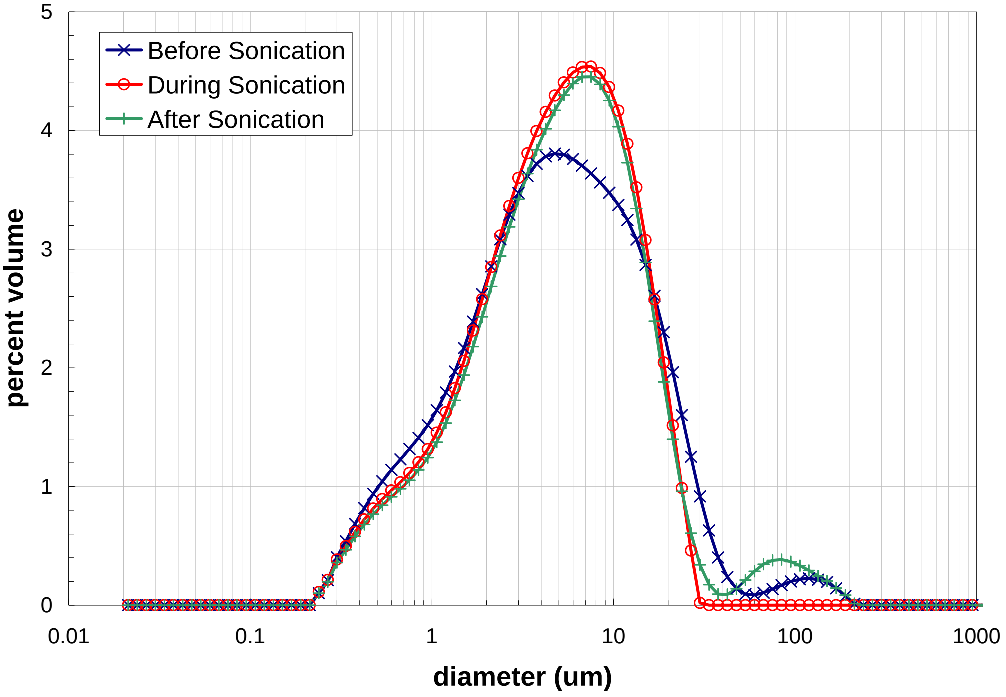


Figure 19. Volume distribution result for the Group 3/4 high-solids matrix (TI-601-G4-6-PSD) sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

Figure 20 shows TI-601-G4-6-PSD as a function of pump speed after the sample has been sonicated. Changes in pump speed show little discrepancy in particle size distribution at smaller particle sizes. At faster pump speeds a large particle peak is present between 30-200 µm, and is most likely a result of increased suspension of heavier particles and/or agglomerates due to increased flow rate. This fraction of larger particles appears less than in pre-sonication measurements shown in Figure 18. Therefore, particles in this range are most likely a result of agglomerate formation.

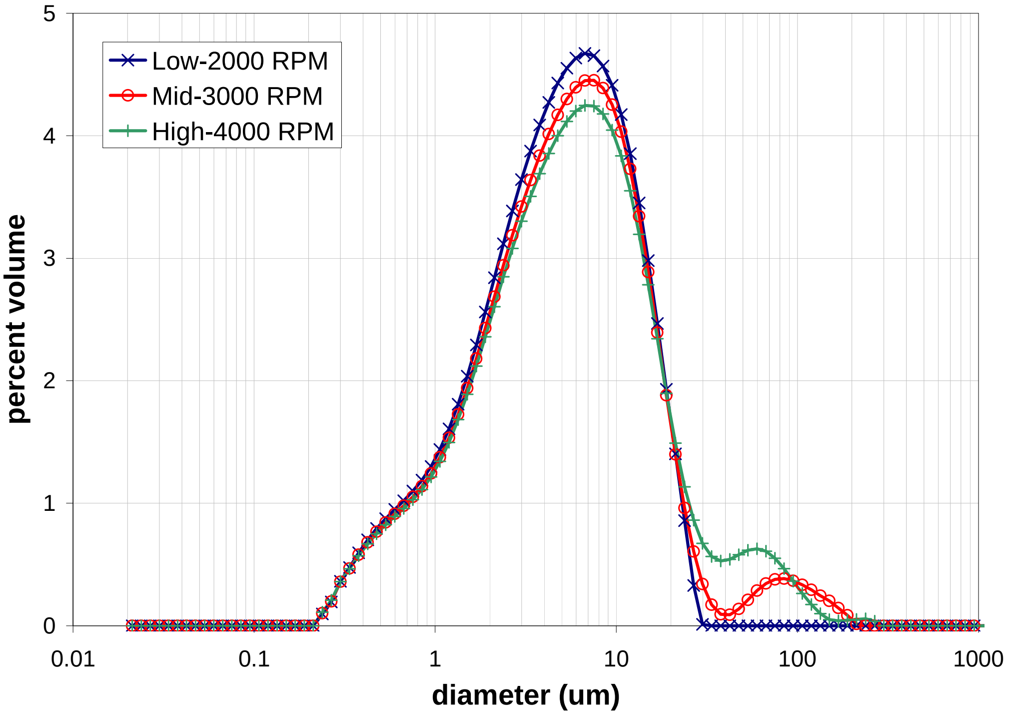


Figure 20. Post-sonication volume distribution result for the Group 3/4 high-solids matrix (TI-601-G4-6-PSD) sample as a function of pump speed.

Particle size analysis of the Group 3/4 high-solids matrix (TI-601-G4-6-PSD) yielded a broad particle size distribution with a range from 0.2-200 µm. The relative population of particles > 30µm increases as the flow rate increases, indicating the presence of some larger difficult to suspend particles or agglomerates. Sonication increases the relative peak population suggesting that some of the larger particles may be agglomerates, which are disrupted during sonication. After sonication, recovery of particle agglomerates was again present at 3000 and 4000 RPM, although the fraction at 4000 RPM was reduced relative to the pre-sonication measurements. Therefore, particles in this size range are most likely agglomerates which are difficult-to-suspend and may be poorly sampled.

Results for TI-601-G4-9-PSD (Dewatered Group 3/4 after caustic leach)

Sample TI-601-G4-9-PSD is representative of waste solids that result from caustic-leaching and subsequent dewatering of the initial 3/4 CUF slurry. Table 16 shows select cumulative undersize percentiles for sample TI-601-G4-9-PSD, more extensive percentile results are shown in Appendix B. Here the d(10) ranges between 0.61 and 1.0 µm, the d(50) between 2.6 and 8.8 µm, and the d(90) between 14 and 82 µm. With regards to pump speed effects, the d(50) and d(90) percentiles before sonication show a large increase in size at 4000 RPM, indicating the presence of large, difficult-to-suspend particles and/or agglomerates. Sonication appears to enlarge the percentiles except at 2000 and 4000 RPM where the d(90) is reduced.

Table 16. Particle size analysis percentile results the dewatered Group 3/4 after caustic leach (TI-601-G4-9-PSD) sample.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	0.61	2.6	14
2	4000	pre-sonic	0.78	8.4	82
3	2000	pre-sonic	0.70	4.4	23
4	3000	25%	0.66	4.6	17
5	3000	50%	0.69	5.8	17
6	3000	75%	0.77	6.3	18
7	3000	post-sonic	0.82	6.5	18
8	4000	post-sonic	1.0	8.8	65
9	2000	post-sonic	0.83	6.1	17

Figure 21 shows the PSD for the dewatered Group 3/4 after caustic leach (TI-601-G4-9-PSD) sample as a function of pump speed before sonication. At 2000 RPM the distribution ranges from 0.2-200 µm and is non-continuous and tri-modal. Three peaks are present with the primary peak centered around 10 µm, the secondary peak centered around 1.5 µm, and a third peak centered around 100 µm. At 3000 RPM, the distribution ranges from 0.2-30 µm and is continuous and bi-modal with the primary peak centered around 1.5 µm and the secondary peak centered around 10 µm. At 4000 RPM, the distribution ranges from 0.2-200 µm and is continuous and tri-modal with the primary peak centered around 70 µm, the secondary peak centered around 1.5 µm, and the third peak centered around 10 µm. The fraction of > 20 µm at 4000 RPM most likely indicates a significant quantity of large difficult-to-suspend particles or agglomerates. As the conditions ran 3000, 4000, 2000 RPM the 100 µm peak at 2000 RPM is likely carry over of slowly settling particles or agglomerates suspended at 4000 RPM.

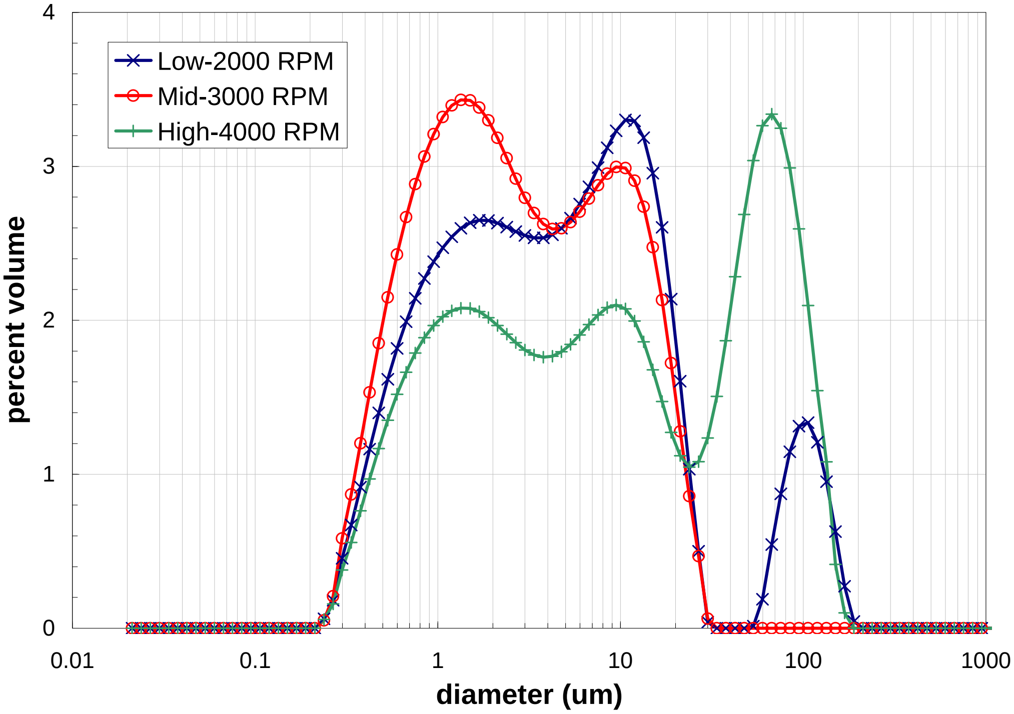


Figure 21. Pre-sonication volume distribution result for the dewatered Group 3/4 after caustic leach (TI-601-G4-9-PSD) sample as a function of pump speed.

Figure 22 shows the particle size distribution as a result of applied sonication. The range of the particles appears to remain unaffected as a result of sonication. There is a significant peak shift where the majority of the particle population moves from 1.5 µm to 12 µm. This effect may be a result of increased suspension of particles as a result of input of sonic energy, or more likely may be a result of increased disruption of larger settled particles as indicated below.

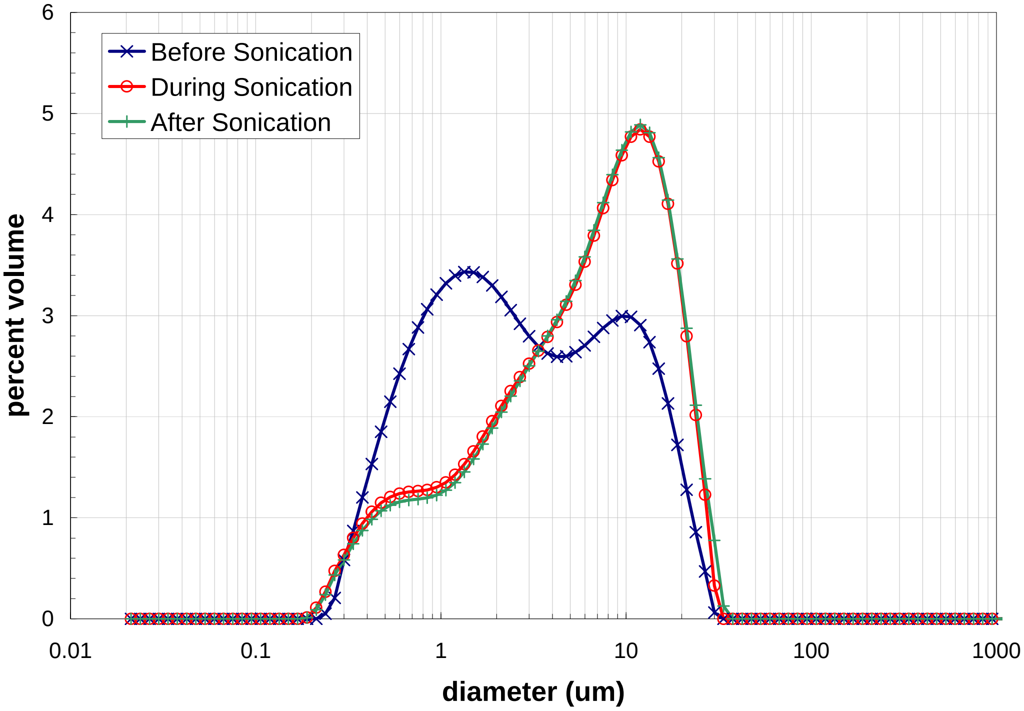


Figure 22. Volume distribution result for the dewatered Group 3/4 after caustic leach (TI-601-G4-9-PSD) sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

Figure 23 shows the PSD as a function of pump speed after the sample has been sonicated. At 2000 and 3000 RPM the distribution is continuous and uni-modal ranging between 0.2-30 µm with a peak at 12 µm and a shoulder at 0.5 µm. At 4000 RPM the distribution is continuous and bi-modal with the same primary peak and shoulder diameters as at the lower speeds only an additional peak is present around 80 µm which extends the range to 200 µm. The fraction of >20 µm particles at 4000 RPM relative to pre-sonic conditions is greatly reduced and no peak is observed at 2000 RPM in this range. This may indicate that there was sonic disruption of particles not previously suspended at 3000 RPM.

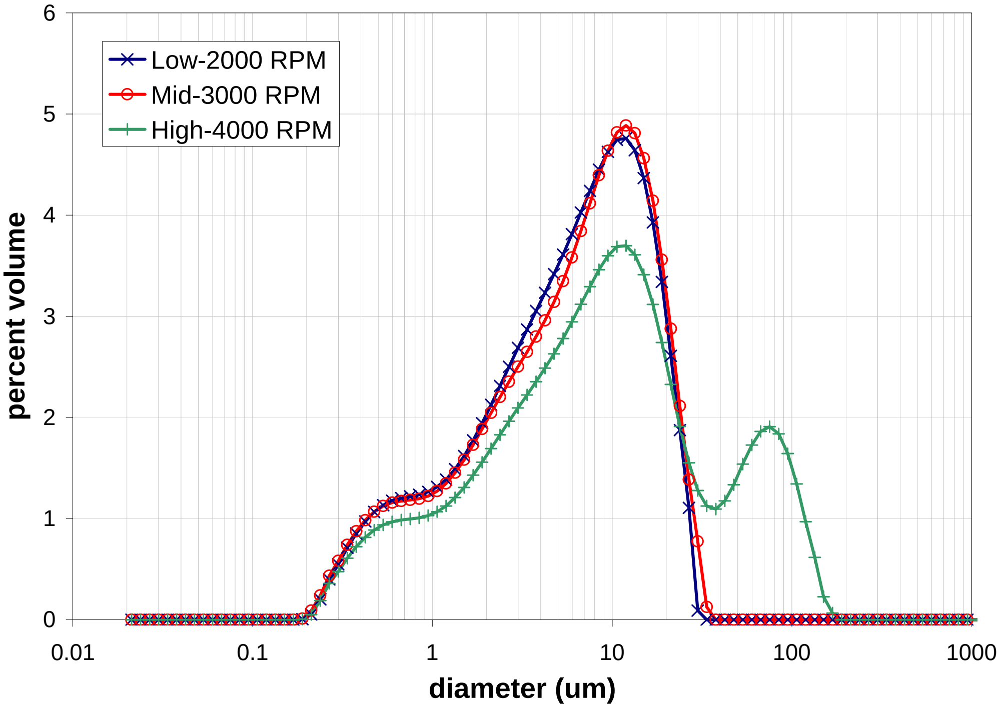


Figure 23. Post-sonication volume distribution result for the dewatered Group 3/4 after caustic leach (TI-601-G4-9-PSD) sample as a function of pump speed.

Particle size analysis of the dewatered Group 3/4 after caustic leach (TI-601-G4-9-PSD) sample yielded a broad particle size distribution with a range from 0.2-200 µm. Pre-sonic distribution displayed a significant fraction of large difficult-to-suspend particles and/or agglomerates at 4000 RPM, which may be slow settling relative to the measurement as a portion of these were also seen at 2000 RPM. Sonication shifted the peak population to larger diameters, which was most likely a result of sonic induced break-up of larger agglomerates not suspended until after disruption. After sonication larger particles and/or agglomerates are still observed at 4000 RPM, although the fraction is significantly less than before sonication. This also supports the conclusion that sonication of settled particles may have led to the increase in peak particle diameter.

Results for TI-601-G4-12-PSD (Washed Group 3/4 after caustic leach)

Sample TI-601-G4-12-PSD is representative of waste solids that result from washing of the caustic-leached and dewatered 3/4 CUF slurry with increasingly dilute NaOH solutions. Table 17 shows select cumulative undersize percentiles for sample TI-601-G4-12-PSD, more extensive percentile results are shown in Appendix B. Here the d(10) ranges between 0.42 and 0.82 µm, the d(50) between 1.7 and 31 µm, and the d(90) between 13 and 94 µm. With regards to pump speed effects, the d(50) and d(90) percentiles before sonication show a large increase in size at 4000 RPM, indicating the presence of large, difficult-to-suspend particles and/or agglomerates. Sonication appears to increase the d(50) and d(90) at lower pump speeds and decrease them at 4000 RPM.

Table 17. Particle size analysis percentile results for the washed Group 3/4 after caustic leach (TI-601-G4-12-PSD) sample.

Measurement Condition	Pump Speed	Sonication	d(10) [µm]	d(50) [µm]	d(90) [µm]
1	3000	pre-sonic	0.58	1.8	21
3	4000	pre-sonic	0.75	31	94
2	2000	pre-sonic	0.55	1.7	15
4	3000	25%	0.47	2.1	13
5	3000	50%	0.43	2.5	13
6	3000	75%	0.42	2.6	13
7	3000	post-sonic	0.60	7.7	87
9	4000	post-sonic	0.82	23	83
8	2000	post-sonic	0.48	3.1	14

Figure 24 shows the PSD for the washed Group 3/4 after caustic leach (TI-601-G4-12-PSD) sample as a function of pump speed before sonication. At 2000 RPM the distribution is tri-modal and non-continuous with a primary peak at 1 µm, a secondary peak at 10µm and a third peak at 120 µm. At 3000 RPM the distribution is similar to 2000 RPM although the distribution is continuous and the 11-100 µm relative contribution is larger. At 4000 RPM the distribution remains tri-modal and continuous, although the primary peak is at 60 µm, the secondary peak is at 1 µm, and a weak peak exists at 8 µm. The strong primary peak at 4000 RPM suggests that there are numerous large difficult-to-suspend particles and/or agglomerates in the sample.

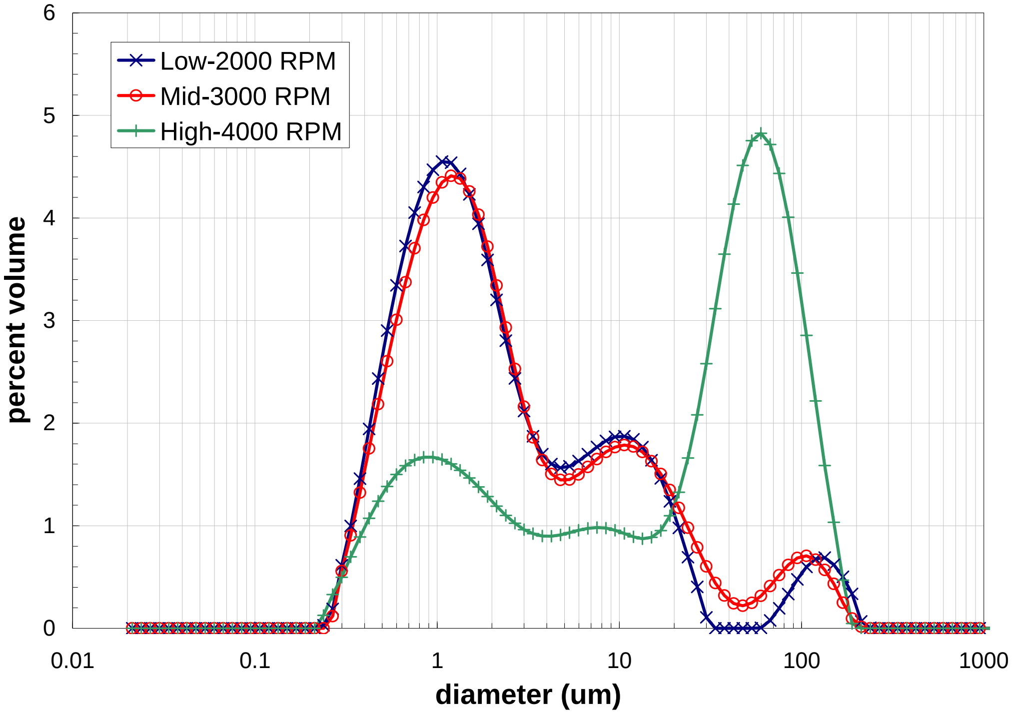


Figure 24. Pre-sonication volume distribution result for the washed Group 3/4 after caustic leach (TI-601-G4-12-PSD) sample as a function of pump speed.

Figure 25 shows the particle size distribution as a result of applied sonication. During sonication the particle size range is shifted from 0.23-200 µm to 0.2-30 µm, resulting in a tri-modal continuous distribution with peak maxima around 0.5, 2.4, and 10 µm. Sonication appears to disrupt particles around 1.2 µm, as indicated by the reduced relative fraction of particles in this size range. This peak population may be been comprised of agglomerates or may have been more susceptible to sonic induced shearing. This 1.2 µm peak reduction during sonication may also be a result of > 30 µm agglomerates preferentially reducing to particles around 0.5 and 2.4 µm increasing their relative population. After sonication a significant increase occurs for > 30 µm particles, indicating rapid agglomerate recovery. As the distribution for 0-30 µm particles displays similar qualities during and after sonication the effects on the primary pre-sonication 1.2 µm peak appear to remain stable throughout the duration of the experiment.

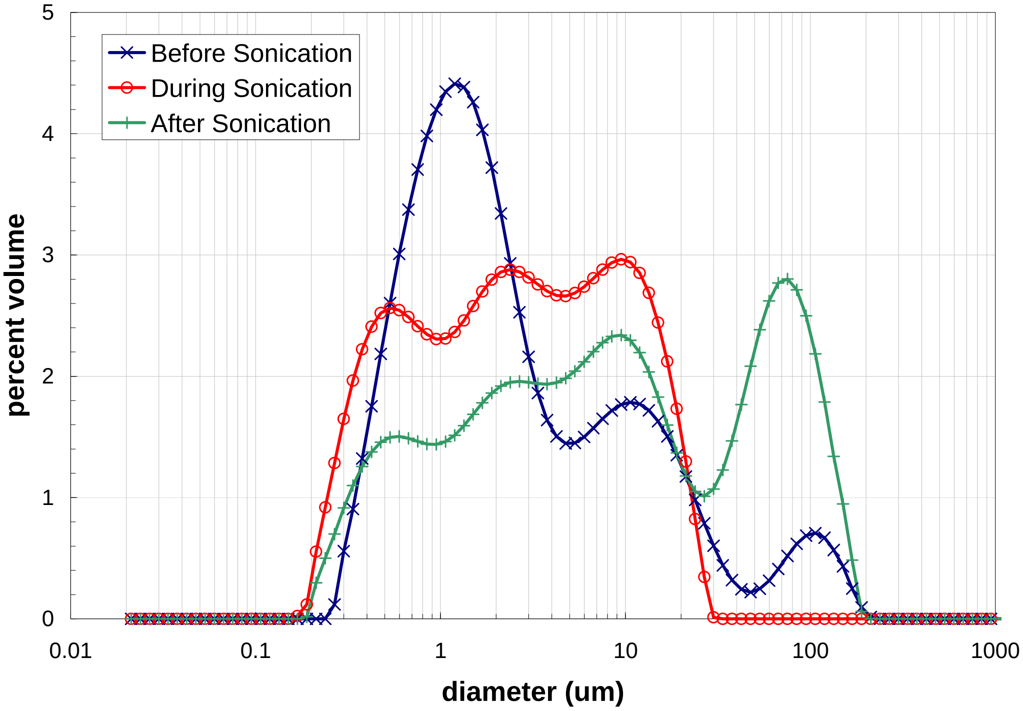


Figure 25. Volume distribution result for the washed Group 3/4 after caustic leach (TI-601-G4-12-PSD) sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

Figure 26 shows the PSD as a function of pump speed after the sample has been sonicated. The distribution remains multi-modal and ranges from 0.2-30 µm at 2000 RPM with the range extending to 200 µm at higher pump speeds. Increasing relative populations of > 20 µm particles and/or agglomerates are suspended at faster pump speeds, indicating that there is a significant fraction of large difficult-to-suspend particles and/or agglomerates.

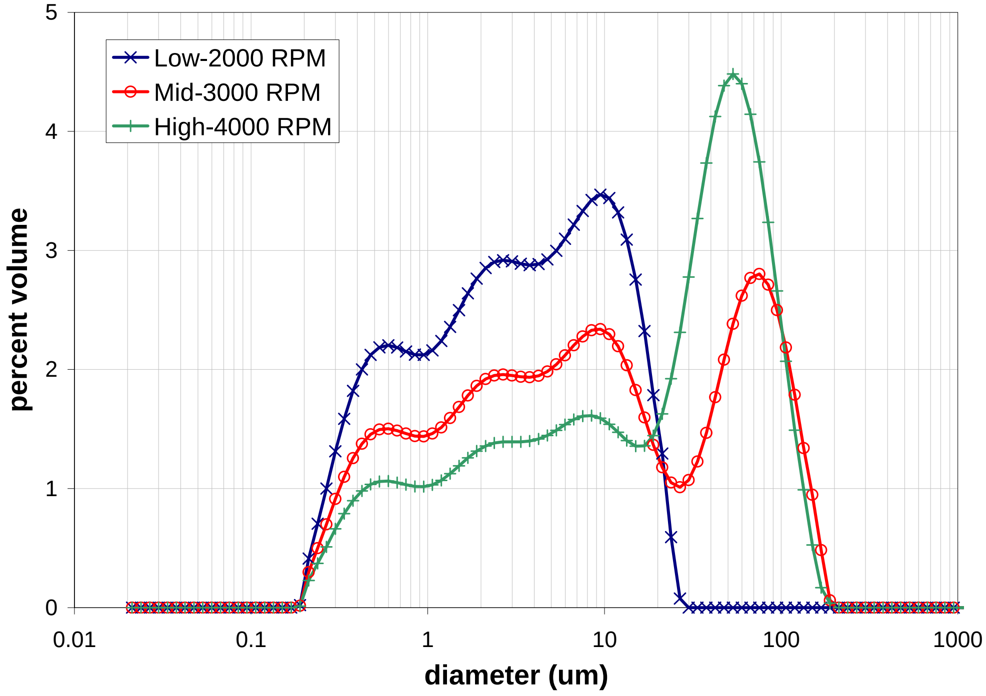


Figure 26. Post-sonication volume distribution result for the washed Group 3/4 after caustic leach (TI-601-G4-12-PSD) sample as a function of pump speed.

Particle size analysis of the washed Group 3/4 after caustic leach (TI-601-G4-12-PSD) sample yielded a broad particle size distribution with a range from 0.2-200 µm. Before and after sonication results displayed a significant fraction of large difficult-to-suspend particles and/or agglomerates at higher pump speeds. Sonication showed disruption of particles and/or agglomerates around 1.2 µm and > 30 µm. After sonication, rapid agglomerate recombination occurs increasing the relative fraction of > 30 µm particles compared to pre-sonic measurements.

10.3 CUF Processing Effects on Group 3/4 Solids

Mixing of Group 3 and Group 4 Waste Solids

The influence of mixing Group 3 and Group 4 waste solids can be evaluated by comparing PSD for the source materials (i.e., those for the initial characterization samples TI550-G3-S-WL-PSD-1 and TI547-G4-S-WL-PSD-1) to the initial low-solids matrix slurry PSD (sample TI-601-G4-3-PSD). The PSD measurement for the primary initial characterization samples is used for this comparison. Some caution must be used when interpreting these results, as the initial characterization samples have not been subjected to the same level of shear that the CUF testing sample undergoes during circulation through the filtration loop.

Table 18 and Figure 27 show the influence of mixing Groups 3 and 4 solids in the CUF on the waste sample PSD. In overall behavior, the mixed waste PSD most resembles the Group 3 initial characterization sample PSD in that almost the entirety of the sample is < 30 µm. Similar to Group 4 the mixed waste does have a small fraction of 30-150 µm particles. Although, the relative population in this region to the primary peak is much lower than in the Group 4 PSD. This fraction in the 30-150 µm range also account for the lower primary peak in comparison with the Group 3 PSD. It is possible that circulation of the Group 3/4 waste mixture in the CUF has sheared a majority of the 30-150 µm particles characteristic of Group 4 waste solids. Overall, the range of sizes observed in the Group 3/4 CUF testing sample is reasonable relative to the source materials. However, the mixed Group 3/4 waste solids PSD indicates shear breakage of particles as a result of circulation of the CUF slurry at low solids concentration.

Table 18. Cumulative undersize percentiles showing the influence of mixing on the PSD of Group 3 and 4 solids at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Sample	**d(10) [µm]**	**d(50) [µm]**	**d(90) [µm]**
Group 3 Initial Characterization (TI550-G3-S-WL-PSD-1)	1.1	6.0	15
Group 4 Initial Characterization (TI547-G4-S-WL-PSD-1)	1.8	9.7	51
Group 3/4 Low Solids Matrix Slurry (TI-601-G4-3-PSD)	1.0	5.8	16

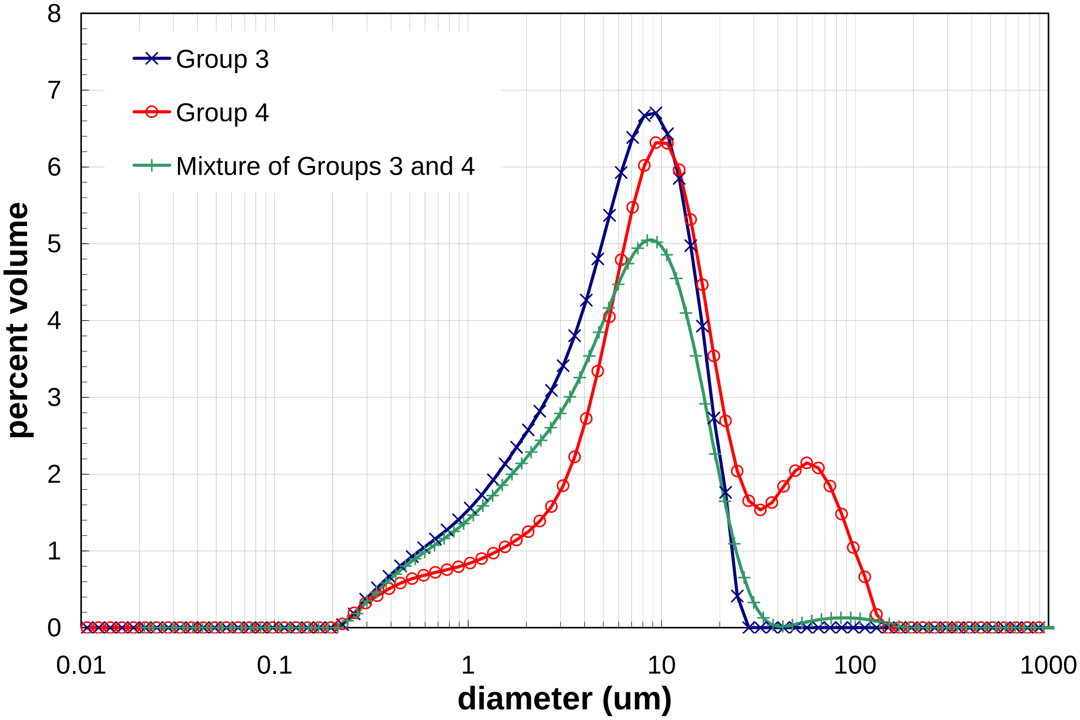


Figure 27. Influence of mixing Group 3 and Group 4 waste solids on PSD. All PSDs taken at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Shearing Effect on Group 3/4 (Low-solids matrix-Sheared)

Table 19 and Figure 28 show the influence of shearing on the PSD of Group 3/4 mixed waste solids. Here, select cumulative undersize percentiles and PSD for the low-solids matrix slurry (TI-601-G4-3-PSD) are compared to that of the sheared low-solids matrix slurry (TI-601-G4-3-Sheared-PSD), which had been further circulated through the CUF for an additional ~20 hours. Differences between the samples are minimal. The unsheared sample exhibits a small peak in the 30-120 µm range, although this is most likely a spurious flocculate or a measurement artifact such as noise. Overall, it appears the additional ~20 hour circulation does not highly influence particle size distribution.

Table 19. Cumulative undersize percentiles showing the influence of ~20 hours circulation on low-solids Group 3/4 PSD at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Sample	**d(10) [µm]**	**d(50) [µm]**	**d(90) [µm]**
Group 3/4 Low Solids Matrix Slurry (TI-601-G4-3-PSD)	1.0	5.8	16
Sheared Group 3/4 Low Solids Matrix Slurry (TI-601-G4-3-Sheared-PSD)	1.0	5.2	15

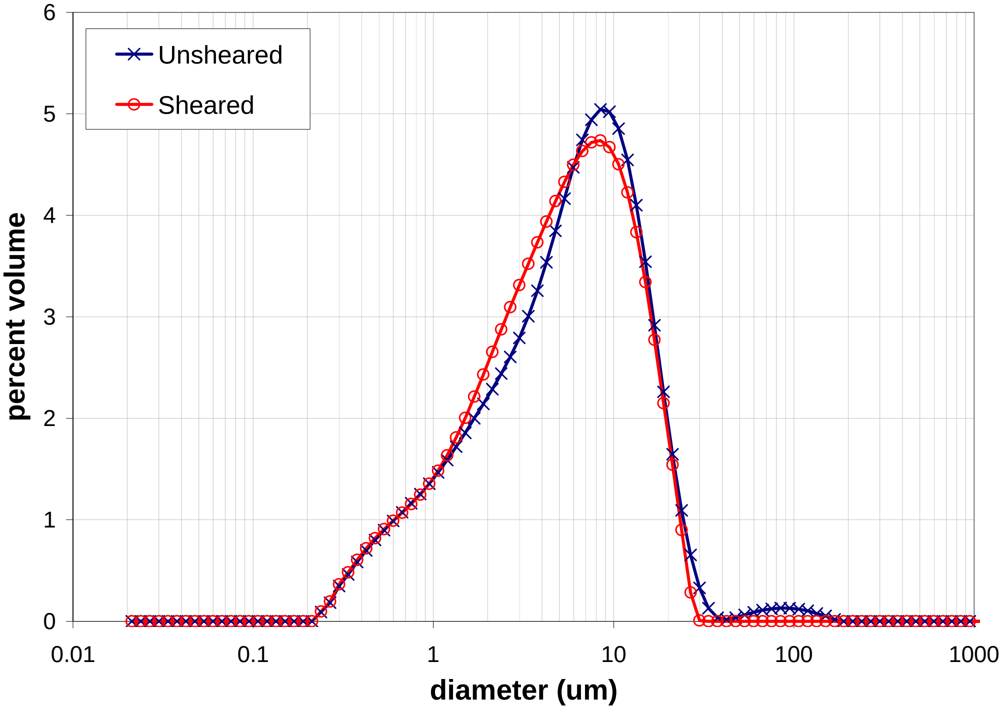


Figure 28. Influence of ~20 hours circulation on low-solids Group 3/4 PSD. All PSDs taken at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Filtration and Shear of Group 3/4 Mixed Solids

Table 20 and Figure 29 show the influence of filtration and shearing on the PSD of Group 3/4 mixed waste solids. Here, select cumulative undersize percentiles and PSD for the low solids matrix slurry (TI-601-G4-3-Sheared-PSD) are compared to that of the high solids matrix slurry (TI-601-G4-6-PSD). Overall both PSDs are similar indicating that prolonged CUF circulation and dewatering did not impact the range of sizes in the waste solids greatly, with the exception of the presence of a small fraction of larger particles in the high-solids matrix. The high-solids matrix PSD indicates the formation of 30-200 µm agglomerates, which are also shown in the slight increase in d(90) in Table 20 It is possible that the dewatering operation (and increase slurry concentration) facilitates increased particle contact and, in turn, agglomeration.

Table 20. Cumulative undersize percentiles showing the influence of filtration and shear on the PSD of Group 3/4 mixed solids at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Sample	**d(10) [µm]**	**d(50) [µm]**	**d(90) [µm]**
Low Solids Matrix Slurry (TI-601-G4-3-Sheared-PSD)	1.0	5.2	15
High Solids Matrix Slurry (TI-601-G4-6-PSD)	1.1	5.2	17

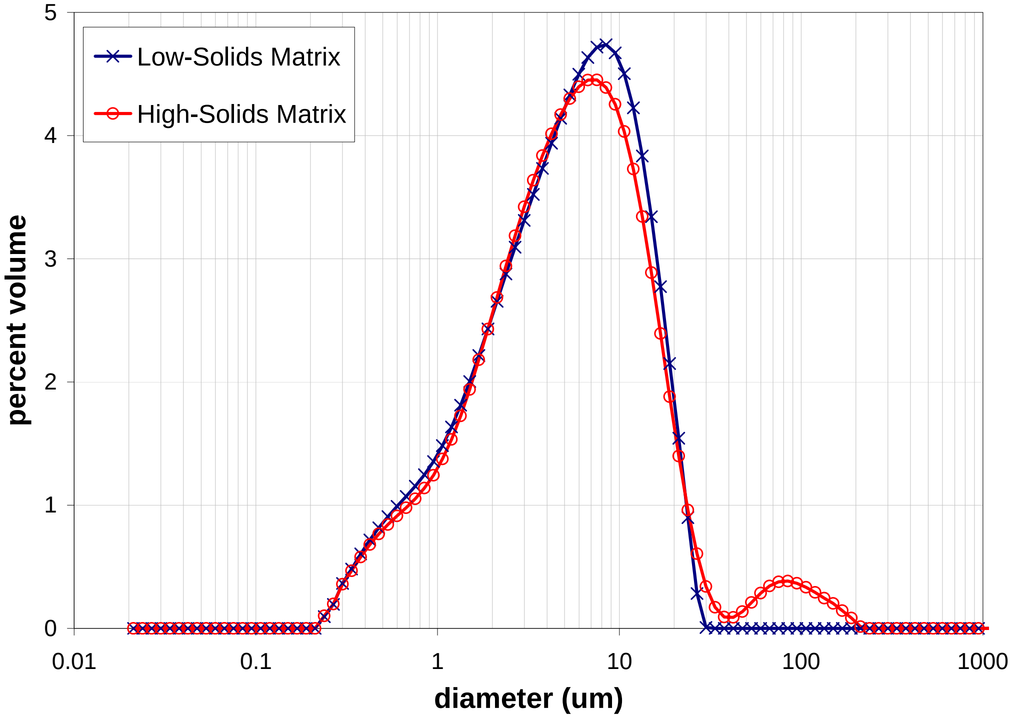


Figure 29. Influence of filtration and shearing on the PSD of Group 3/4 waste solids on PSD. All PSDs taken at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Caustic-Leaching and Dewatering of Group 3/4 Mixed Solids

Table 21 and Figure 30 show the influence of caustic-leaching and dewatering on the PSD of Group 3/4 mixed waste solids. Here, select cumulative undersize percentiles and PSD for the caustic-leached and dewatered slurry (TI-601-G4-9-PSD) are compared to that of the high solids matrix slurry (TI-601-G4-6-PSD). Caustic leaching shows shifting in relative size distributions. The differences observed after leaching are 1) a disruption of the 40-200 µm particles, 2) an increase in the relative contribution of 0.2-1 µm particles, 3) a decrease in the relative contribution of 1-7 µm particles, and 4) a shift in the peak population from 7 to 12 µm. The decrease in 1-7 µm and > 40 µm particles may be a result of complete particle dissolution, dissolution of material holding agglomerates together, and/or dissolution of material off the surface of agglomerates. The increase in 0.2-1 µm particles may represent particles that have reduced in size as a result of dissolution, particle/agglomerate fragments resulting that have detached from parent particles during dissolution, and/or material previously masked by leached material.

Table 21. Cumulative undersize percentiles showing the influence of caustic-leaching and dewatering on the PSD of Group 3/4 mixed solids at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Sample	**d(10) [µm]**	**d(50) [µm]**	**d(90) [µm]**
High Solids Matrix Slurry (TI-601-G4-6-PSD)	1.1	5.2	17
Caustic-Leached and Dewatered Slurry (TI-601-G4-9-PSD)	0.82	6.5	18

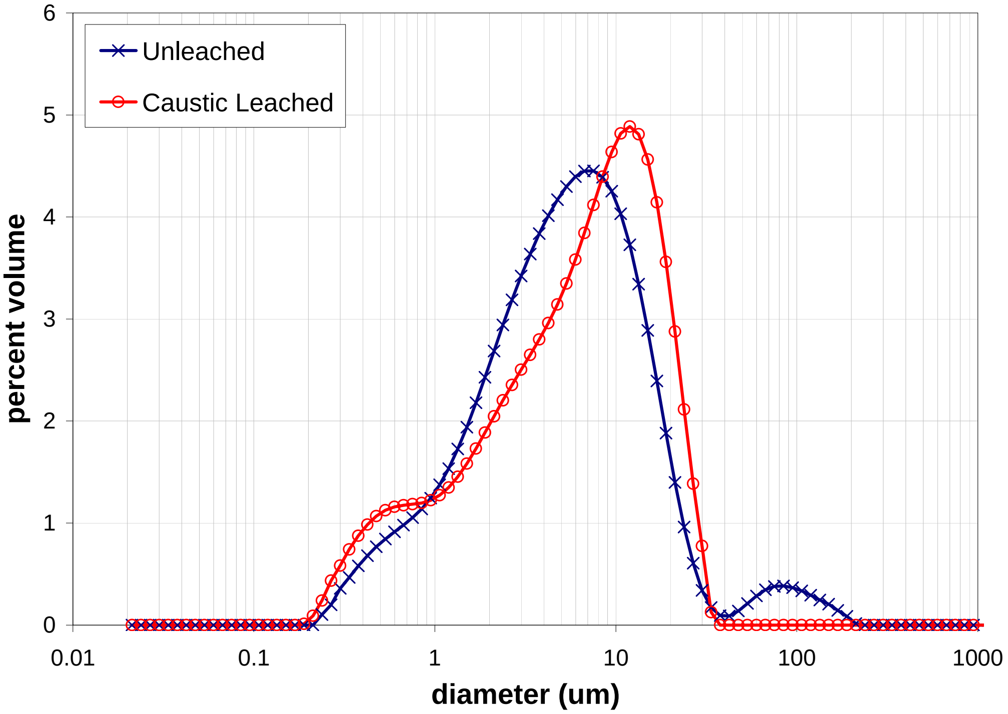


Figure 30. Influence of caustic-leaching and dewatering on the PSD of Group 3/4 waste solids on PSD. All PSDs taken at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Post Caustic-Leach Washing of Group 3/4 Mixed Solids

Table 22 and Figure 31 show the influence of post caustic-leach washing on the PSD of Group 3/4 mixed waste solids. Here select cumulative undersize percentiles and PSD for the caustic-leached dewatered, and washed slurry (TI-601-G4-12-PSD) are compared to that of the caustic-leached and dewatered slurry (TI-601-G4-9-PSD). Washing the caustic leached sample changes the PSD from a bi-modal to a multi-modal distribution. The three peaks in the washed PSD that are < 20 µm roughly line up with the two peaks and the weak shoulder seen before washing. The main difference observed after washing is the presence of a large 75 µm peak, which extends the range from 0.2-40 µm to 0.2-200 µm. This effect is also observed in the decrease of the d(10) and the increase in the d(50) and d(90) in Table 24. Therefore washing may induce agglomeration resulting in larger diameters, possibly as a result of the change in ionic strength of the solution or the increased particle to particle interaction.

Table 22. Cumulative undersize percentiles showing the influence of post caustic-leach washing on the PSD of Group 3/4 mixed solids at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

Sample	d(10) [µm]	d(50) [µm]	d(90) [µm]
Caustic-Leached Only (TI-601-G4-9-PSD)	0.82	6.5	18
Caustic-Leached and Washed (TI-601-G4-12-PSD)	0.60	7.7	87

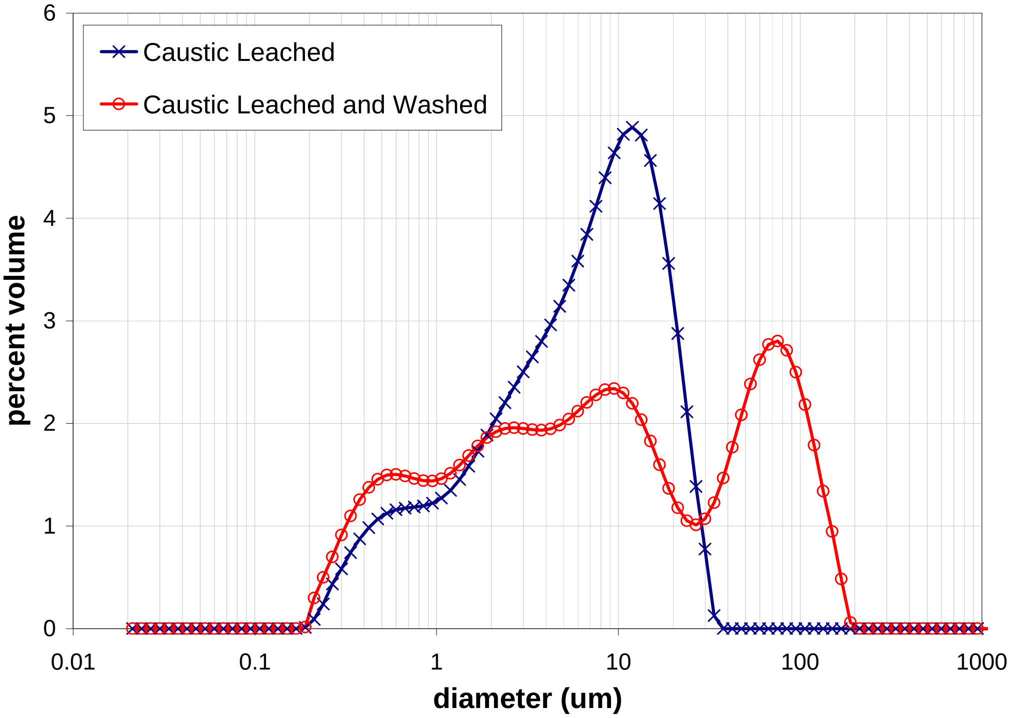


Figure 31. Influence of post caustic-leach washing on the PSD of Group 3/4 waste solids on PSD. All PSDs taken at measurement condition 7 – 3000 RPM, post-sonication (see Table 6).

11 Records

Data records relating to Group 3/4 CUF particle size distribution measurements and post-measurement analysis exist in original Malvern Mastersizer 2000 data files and Laboratory Record Books (LRBs):

- Malvern Mastersizer Files: "2008-07July29-Group 4 CUF PSD.mea", "2008-07July30-Group 4 CUF PSD.mea", "2008-08Aug01-Group 4 CUF PSD.mea"
- LRB BNW 56933: Pages 115-117
- Test Data Package: TDP-WTP-272, TDP-WTP-271, CCP-WTPSP-548, and CCP-WTPSP-613

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.

Appendix A – Duplicate Sample Differential Particle Size Plots

Figures A-1, A-2, and A-3 show the differential volume distribution as a function of particle diameter for the duplicate Group 3 initial characterization sample, TI550-G3-S-WL-PSD-2. Specifically, A-1 shows the pre-sonication PSDs as a function of pump speed, A-2 shows the PSDs as a function of sonication, and A-3 shows the post-sonication PSDs as a function of pump speed. These results are not discussed either here or in the main body of this interim report.

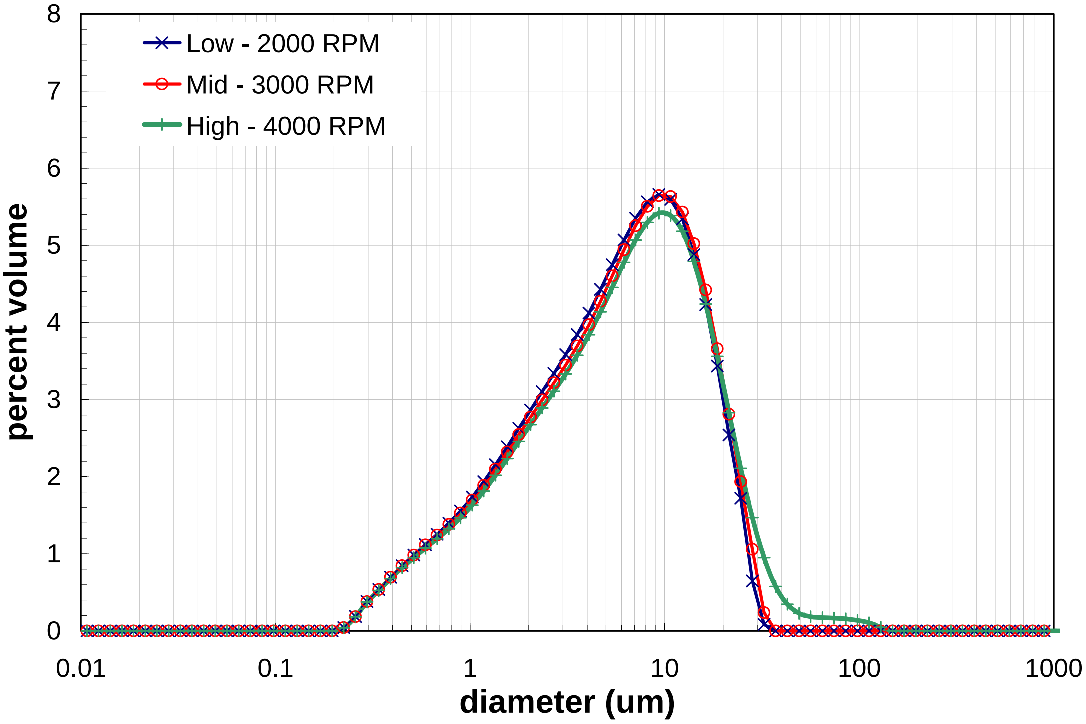


Figure A-1. Pre-sonication volume distribution result for the duplicate Group 3 initial characterization sample as a function of pump speed.

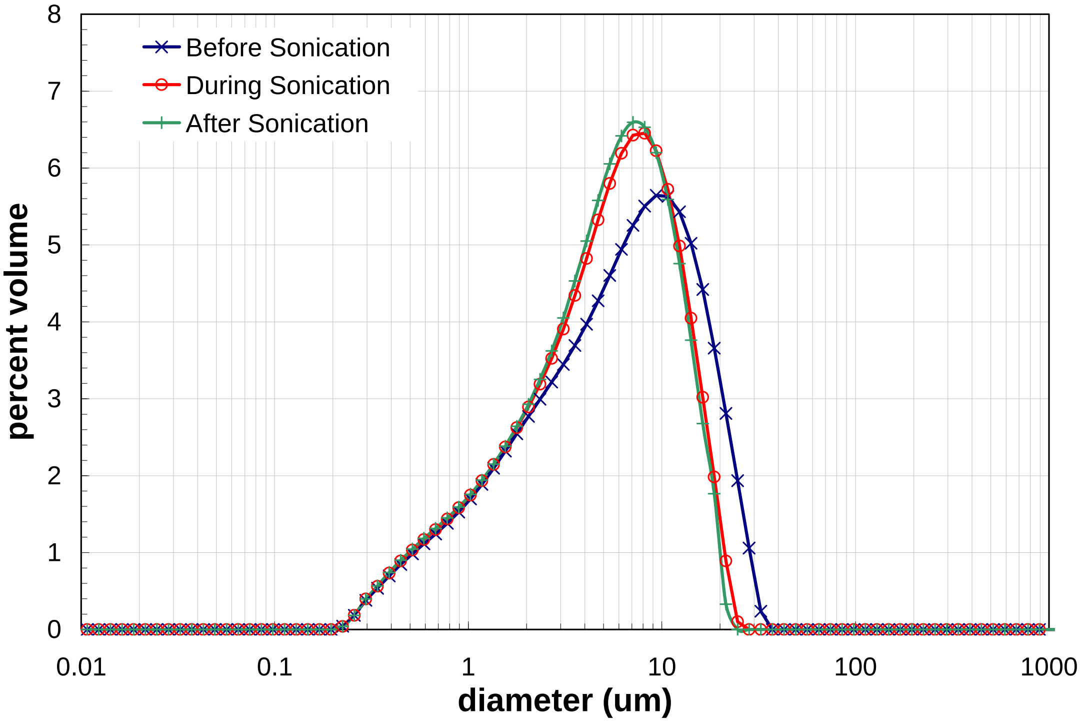


Figure A-2. Volume distribution result for the duplicate Group 3 initial characterization sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

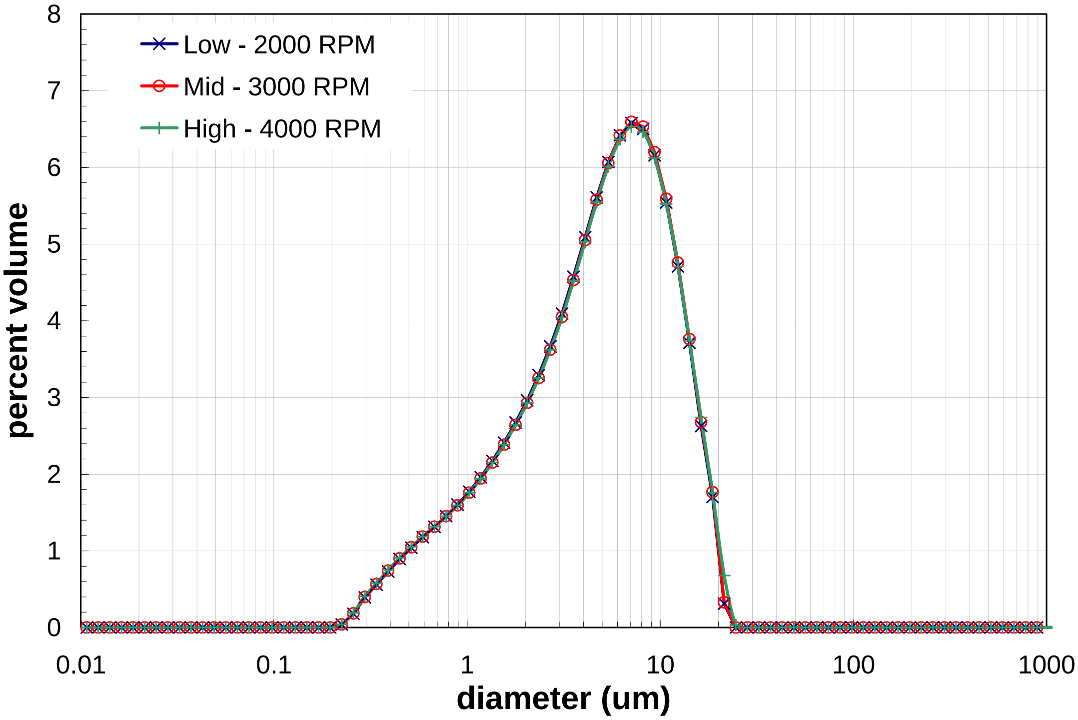


Figure A-3. Post-sonication volume distribution result for the duplicate Group 3 initial characterization sample as a function of pump speed.

Figures A-4, A-5, and A-6 show the differential volume distribution as a function of particle diameter for the duplicate Group 4 initial characterization sample, TI547-G4-S-WL-PSD-2. Specifically, A-4 shows the pre-sonication PSDs as a function of pump speed, A-5 shows the PSDs as a function of sonication, and A-6 shows the post-sonication PSDs as a function of pump speed. These results are not discussed either here or in the main body of this interim report.

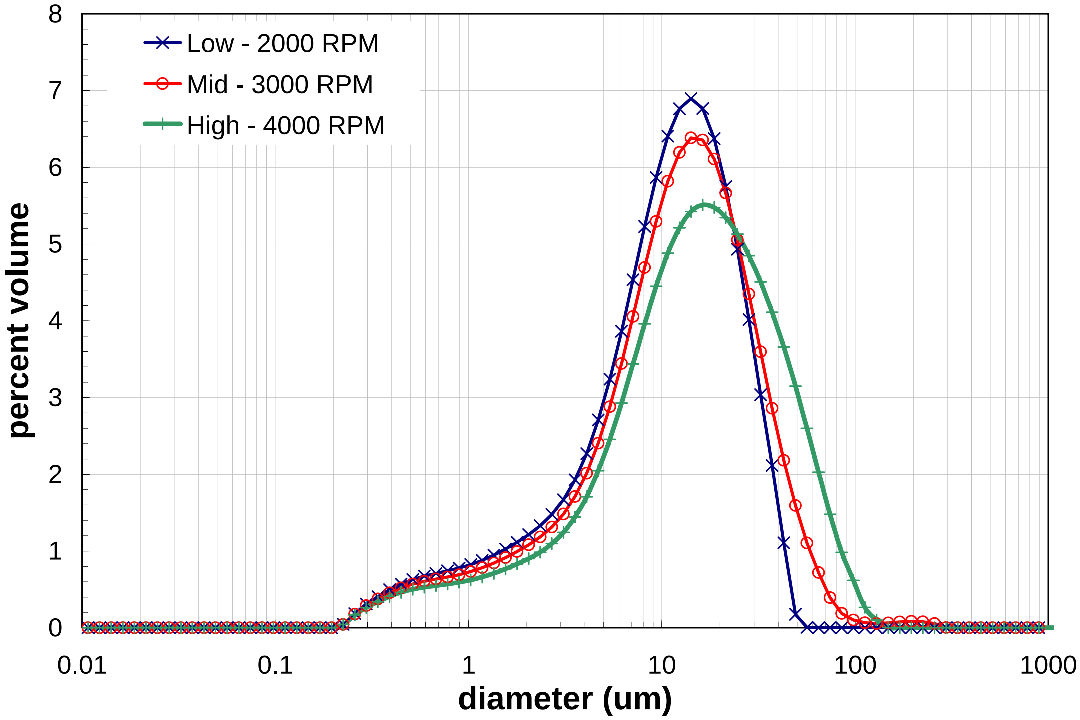


Figure A-4. Pre-sonication volume distribution result for the duplicate Group 4 initial characterization sample as a function of pump speed.

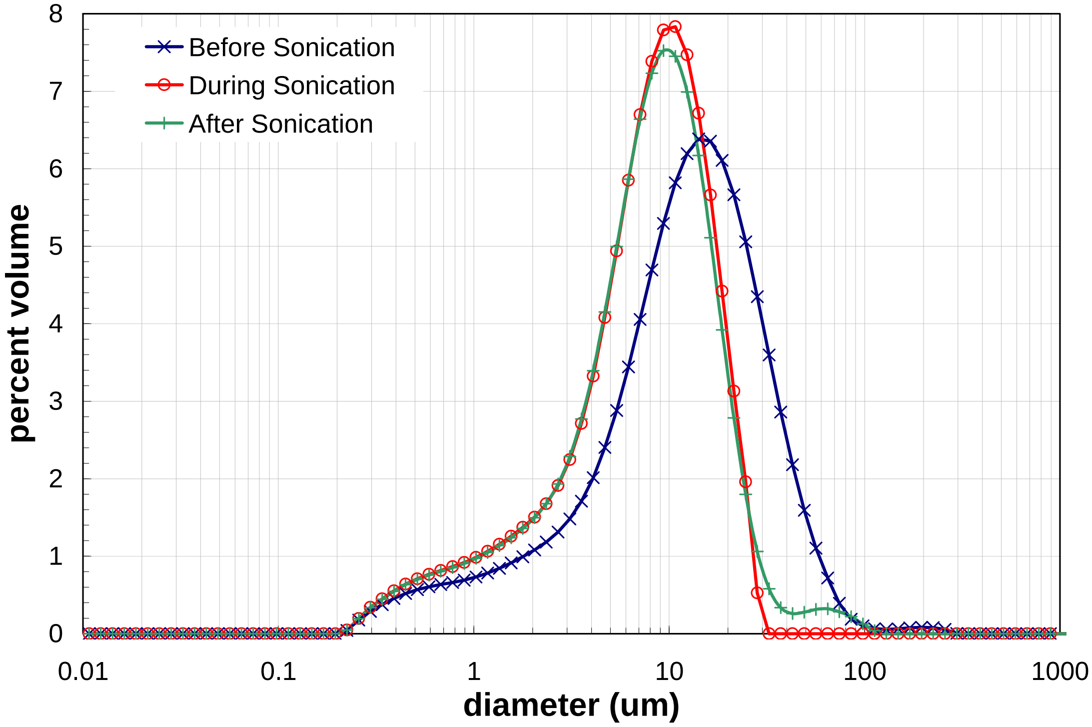


Figure A-5. Volume distribution result for the duplicate Group 4 initial characterization sample as a function of sonication. Note: the during-sonication condition corresponds to measurement condition 6 (see Table 6).

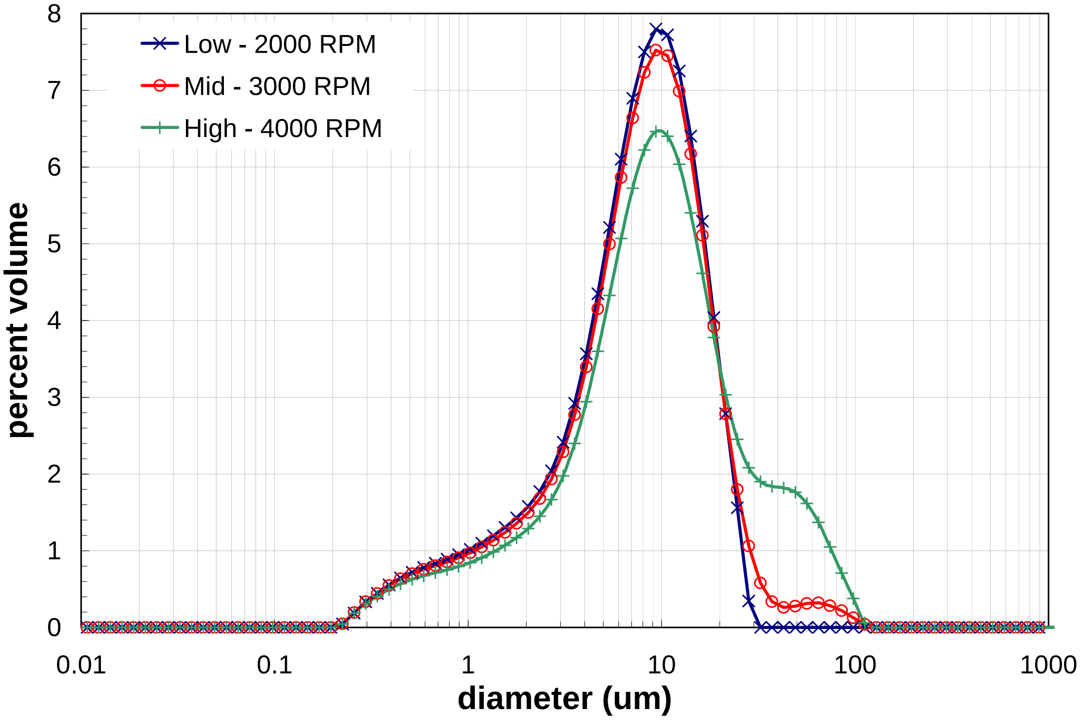


Figure A-6. Post-sonication volume distribution result for the duplicate Group 4 initial characterization sample as a function of pump speed.

Appendix B – Detailed Cumulative PSD

Results: TI550-G3-S-WL-PSD (Group 3 Initial Characterization)

Table B-1 and B-2 present detailed cumulative oversize distributions (by volume/weight) for Group 3 initial characterization samples TI550-G3-S-WL-PSD-1 and -2, respectively. Results are reported as a function of test condition (see Table 6). This appendix 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 the main body of this interim report.

Table B-1. Cumulative oversize diameter distributions for the primary Group 3 initial characterization sample, TI550-G3-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 / pre-sonic	0.36	0.70	1.2	2.3	2.9	3.7	5.5	7.7	10	13	14	16	22	26	33
2 - 4000 / pre-sonic	0.37	0.73	1.3	2.5	3.3	4.2	6.3	8.8	12	15	17	20	30	44	100
3 - 2000 / pre-sonic	0.35	0.67	1.1	2.1	2.7	3.3	4.9	6.9	9.1	12	13	15	20	23	30
4 - 3000 / 25%	0.34	0.61	0.97	1.9	2.4	3.0	4.4	6.3	8.4	11	12	14	18	22	27
5 - 3000 / 50%	0.34	0.60	0.97	1.8	2.4	3.0	4.4	6.0	7.8	10	11	13	16	20	25
6 - 3000 / 75%	0.34	0.60	0.96	1.8	2.3	2.9	4.2	5.6	7.2	9.0	10	11	15	17	22
7 - 3000 / post-sonic	0.35	0.67	1.1	2.1	2.7	3.3	4.6	6.0	7.5	9.2	10	11	15	17	22
8 - 4000 / post-sonic	0.35	0.67	1.1	2.1	2.7	3.4	4.7	6.1	7.7	9.5	11	12	15	19	25
9 - 2000 / post-sonic	0.34	0.62	1.0	1.9	2.4	3.0	4.2	5.5	7.0	8.7	9.7	11	14	17	21

Table B-2. Cumulative oversize diameter distributions for the duplicate Group 3 initial characterization sample, TI550-G3-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 / pre-sonic	0.35	0.65	1.0	2.0	2.5	3.1	4.4	6.0	7.9	10	11	13	17	21	27
2 - 4000 / pre-sonic	0.35	0.66	1.1	2.0	2.6	3.2	4.6	6.3	8.3	11	12	14	20	25	51

3 - 2000 / pre-sonic	0.35	0.65	1.0	1.9	2.4	3.0	4.3	5.8	7.5	9.6	11	12	16	20	26
4 - 3000 / 25%	0.35	0.64	1.0	1.9	2.4	3.0	4.3	5.7	7.4	9.4	11	12	16	19	25
5 - 3000 / 50%	0.35	0.64	1.0	1.9	2.4	3.0	4.2	5.5	7.0	8.8	9.9	11	14	17	22
6 - 3000 / 75%	0.35	0.63	1.0	1.9	2.4	2.9	4.0	5.2	6.6	8.2	9.1	10	13	16	20
7 - 3000 / post-sonic	0.35	0.63	1.0	1.9	2.4	2.9	4.0	5.1	6.4	7.9	8.7	9.8	13	15	19
8 - 4000 / post-sonic	0.35	0.62	1.0	1.9	2.4	2.9	3.9	5.1	6.4	7.9	8.8	9.8	13	15	19
9 - 2000 / post-sonic	0.35	0.63	1.0	1.9	2.4	2.9	3.9	5.1	6.3	7.8	8.7	9.7	13	15	19

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

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

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 appendix does not provide discussion of the RPD results; however, the RPD for the 10th, 50th, and 90th diameter percentiles are presented and discussed in the main body of this interim report.

Table B-3. Relative percent difference between primary and duplicate Group 3 initial characterization samples (TI550-G3-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 / pre-sonic	1.4	7.3	11	14	15	17	20	22	22	21	21	21	20	20	19
2 - 4000 / pre-sonic	3.6	10	15	19	22	24	27	28	29	29	30	30	34	42	50
3 - 2000 / pre-sonic	0.00	3.7	5.8	7.6	8.8	10	14	16	17	17	17	17	16	15	13
4 - 3000 / 25%	3.9	5.9	5.7	3.4	2.1	0.40	4.3	8.8	12	13	13	13	13	12	11
5 - 3000 / 50%	3.9	5.6	5.5	3.8	2.5	0.58	4.1	8.0	10	12	12	12	12	12	12
6 - 3000 / 75%	3.6	5.5	5.3	3.7	2.1	0.14	4.0	6.9	8.5	9.3	9.5	9.6	9.5	9.2	8.8
7 - 3000 / post-	1.4	6.0	9.2	11	12	13	15	15	15	15	15	15	14	13	14

sonic															
8 - 4000 / post-sonic	2.0	6.3	9.9	12	14	15	16	17	17	17	17	17	17	18	21
9 - 2000 / post-sonic	3.2	2.1	0.80	0.80	2.2	3.9	7.0	9.0	10	11	11	11	11	10	11

Results: TI547-G4-S-WL-PSD (Group 4 Initial Characterization)

Table B-4 and B-5 present detailed cumulative oversize distributions (by volume/weight) for Group 4 initial characterization samples TI547-G4-S-WL-PSD-1 and -2, respectively. Results are reported as a function of test condition (see Table 6). This appendix 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 the main body of this interim report. Table A-6 shows the absolute relative percent difference (RPD) between primary and duplicate results as calculated in Eq. B-1.

Table B-4. Cumulative oversize diameter distributions for the primary Group 4 initial characterization sample, TI547-G4-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 / pre-sonic	0.41	1.3	3.2	6.9	8.6	10	14	20	31	45	52	61	83	100	130
2 - 4000 / pre-sonic	0.42	1.5	3.9	8.0	10	12	18	26	36	47	53	59	78	93	120
3 - 2000 / pre-sonic	0.36	0.83	1.7	4.1	5.2	6.3	8.4	10	13	16	18	20	27	37	110
4 - 3000 / 25%	0.36	0.79	1.6	3.9	4.9	6.0	7.9	9.9	12	15	16	18	23	27	34
5 - 3000 / 50%	0.35	0.77	1.5	3.6	4.6	5.6	7.3	9.1	11	13	15	16	21	24	30
6 - 3000 / 75%	0.35	0.75	1.5	3.4	4.3	5.1	6.6	8.2	9.8	12	13	14	18	21	26
7 - 3000 / post-sonic	0.37	0.85	1.8	4.0	5.0	5.9	7.7	9.7	12	16	18	23	51	70	100
8 - 4000 / post-sonic	0.39	1.1	2.5	5.3	6.5	7.7	10	14	22	35	41	48	67	82	110
9 - 2000 / post-sonic	0.35	0.74	1.4	3.2	4.1	4.9	6.4	7.9	9.5	11	12	14	17	21	26

Table B-5. Cumulative oversize diameter distributions for the duplicate Group 4 initial characterization sample, TI547-G4-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 / pre-sonic	0.38	0.95	2.1	4.9	6.2	7.4	9.8	12	15	19	22	25	34	44	72
2 - 4000 / pre-sonic	0.39	1.1	2.5	5.8	7.2	8.6	12	15	19	25	29	34	48	62	91
3 - 2000 / pre-sonic	0.37	0.87	1.8	4.3	5.5	6.6	8.8	11	13	17	18	20	27	32	41
4 - 3000 / 25%	0.37	0.86	1.8	4.2	5.4	6.5	8.5	11	13	16	17	19	25	30	38
5 - 3000 / 50%	0.36	0.82	1.7	3.9	4.9	5.8	7.6	9.3	11	13	15	16	21	25	31
6 - 3000 / 75%	0.36	0.78	1.5	3.4	4.3	5.1	6.5	8.0	9.6	11	13	14	17	20	25
7 - 3000 / post-sonic	0.36	0.79	1.6	3.4	4.3	5.1	6.5	8.0	9.6	12	13	14	19	24	60
8 - 4000 / post-sonic	0.37	0.86	1.8	3.9	4.9	5.7	7.4	9.2	11	15	17	20	36	53	81
9 - 2000 / post-sonic	0.36	0.78	1.5	3.3	4.1	4.9	6.3	7.7	9.2	11	12	13	17	20	24

Table B-6. Relative percent difference between primary and duplicate Group 4 initial characterization samples (TI547-G4-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 / pre-sonic	7.4	28	34	29	28	28	31	39	50	57	59	60	59	56	44
2 - 4000 / pre-sonic	7.4	29	34	28	28	29	36	43	47	46	45	43	38	33	22
3 - 2000 / pre-sonic	1.7	4.3	5.9	5.4	5.0	4.8	4.8	4.9	4.8	4.4	3.8	2.9	2.4	13	64
4 - 3000 / 25%	2.5	8.3	11	10	9.1	8.4	7.8	7.7	7.9	8.3	8.6	8.9	9.9	11	12
5 - 3000 / 50%	2.3	7.2	8.7	7.1	5.7	4.8	3.6	2.8	2.4	2.1	1.9	1.8	1.7	1.7	1.9
6 - 3000 / 75%	2.0	4.8	4.8	1.5	0.14	0.65	1.5	1.9	2.2	2.4	2.4	2.5	2.7	2.9	2.7
7 - 3000 / post-sonic	1.4	7.3	13	15	15	15	16	17	20	25	30	38	63	66	41
8 - 4000 / post-sonic	5.2	20	28	26	25	26	29	35	47	58	59	59	46	35	26

9 - 2000 / post-sonic	2.3	4.7	4.4	1.0	0.29	1.1	1.9	2.3	2.6	2.8	2.9	3.1	3.6	4.5	7.2

Results: TI-601-G4-3-PSD (Low-solids matrix Group 3/4)

Table B-7 present detailed cumulative oversize distributions (by volume/weight) for Group 3/4 CUF testing sample TI-601-G4-3-PSD. Results are reported as a function of test condition (see Table 6). This appendix 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 the main body of this interim report.

Table B-7. Cumulative oversize diameter distributions for the Group 3/4 CUF testing sample, TI-601-G4-3-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 / pre-sonic	0.36	0.63	0.97	1.8	2.2	2.8	4.0	5.5	7.3	9.5	11	12	17	22	31
2 - 4000 / pre-sonic	0.36	0.66	1.1	2.0	2.6	3.2	4.6	6.4	8.5	11	13	16	27	50	100
3 - 2000 / pre-sonic	0.36	0.63	0.99	1.8	2.3	2.8	4.0	5.4	7.1	9.2	10	12	16	20	27
4 - 3000 / 25%	0.35	0.62	0.98	1.8	2.3	2.8	4.0	5.4	7.1	9.2	10	12	16	20	26
5 - 3000 / 50%	0.35	0.62	0.98	1.8	2.3	2.9	4.1	5.6	7.3	9.3	11	12	16	19	25
6 - 3000 / 75%	0.35	0.62	0.98	1.9	2.4	2.9	4.2	5.7	7.3	9.1	10	12	15	18	23
7 - 3000 / post-sonic	0.35	0.63	1.0	1.9	2.5	3.1	4.4	5.8	7.5	9.4	11	12	16	20	52
8 - 4000 / post-sonic	0.37	0.69	1.1	2.1	2.7	3.3	4.7	6.2	7.9	10	11	13	18	30	100
9 - 2000 / post-sonic	0.35	0.63	1.0	1.9	2.4	3.0	4.2	5.6	7.1	9.0	10	11	15	18	23

Results: TI-601-G4-3-Sheared-PSD (Sheared Low-solids matrix Group 3/4)

Table B-8 present detailed cumulative oversize distributions (by volume/weight) for Group 3/4 CUF testing sample TI-601-G4-3-Sheared-PSD. Results are reported as a function of test condition (see Table 6). This appendix 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 the main body of this interim report.

Table B-8. Cumulative oversize diameter distributions for the Group 3/4 CUF testing sample, TI-601-G4-3-Sheared-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 / pre-sonic	0.35	0.60	0.94	1.7	2.2	2.7	3.8	5.2	7.1	9.7	11	13	19	25	140
2 - 4000 / pre-sonic	0.35	0.63	1.0	2.0	2.5	3.1	4.5	6.4	8.9	13	15	19	37	67	120
3 - 2000 / pre-sonic	0.36	0.62	0.97	1.7	2.1	2.6	3.5	4.6	6.0	7.8	9.0	10	14	18	24
4 - 3000 / 25%	0.35	0.62	0.97	1.7	2.1	2.5	3.5	4.6	6.0	7.9	9.0	10	14	18	24
5 - 3000 / 50%	0.35	0.62	0.99	1.8	2.2	2.7	3.7	5.0	6.6	8.5	9.6	11	15	18	23
6 - 3000 / 75%	0.34	0.62	0.99	1.8	2.3	2.8	3.8	5.1	6.6	8.5	9.6	11	14	17	22
7 - 3000 / post-sonic	0.35	0.62	1.0	1.9	2.3	2.8	3.9	5.2	6.7	8.6	9.7	11	15	18	23
8 - 4000 / post-sonic	0.35	0.63	1.0	1.9	2.4	3.0	4.2	5.6	7.3	9.5	11	13	18	25	110
9 - 2000 / post-sonic	0.35	0.63	1.0	1.9	2.3	2.8	3.9	5.2	6.7	8.5	9.6	11	15	18	23

<u>Results: TI-601-G4-6-PSD (High-solids matrix Group 3/4)</u>

Table B-9 present detailed cumulative oversize distributions (by volume/weight) for Group 3/4 parametric testing sample TI-601-G4-6-PSD. Results are reported as a function of test condition (see Table 6). This appendix 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 the main body of this interim report.

Table B-9. Cumulative oversize diameter distributions for the Group 3/4 CUF testing sample, TI-601-G4-6-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 / pre-sonic	0.34	0.58	0.91	1.7	2.1	2.5	3.5	4.8	6.5	8.9	11	13	19	26	110
2 - 4000 / pre-sonic	0.34	0.61	1.0	1.9	2.4	2.9	4.1	5.7	8.0	11	14	18	36	61	110
3 - 2000 / pre-sonic	0.33	0.58	0.93	1.7	2.1	2.6	3.5	4.6	6.2	8.3	9.7	12	17	23	110
4 - 3000 / 25%	0.34	0.61	0.99	1.8	2.2	2.6	3.5	4.6	6.0	8.0	9.2	11	15	19	26

5 - 3000 / 50%	0.34	0.60	0.99	1.8	2.2	2.7	3.6	4.8	6.4	8.3	9.6	11	15	19	25
6 - 3000 / 75%	0.34	0.62	1.0	1.9	2.3	2.7	3.7	4.9	6.4	8.2	9.3	11	15	18	24
7 - 3000 / post-sonic	0.35	0.64	1.1	2.0	2.4	2.9	4.0	5.2	6.8	8.8	10	12	17	24	110
8 - 4000 / post-sonic	0.34	0.64	1.1	2.0	2.5	3.0	4.1	5.5	7.2	9.5	11	13	21	41	94
9 - 2000 / post-sonic	0.35	0.63	1.0	1.9	2.3	2.8	3.7	4.9	6.3	8.1	9.1	10	14	17	23

Results: TI-601-G4-9-PSD (Dewatered Group 3/4 after caustic leach)

Table B-10 present detailed cumulative oversize distributions (by volume/weight) for Group 3/4 CUF testing sample TI-601-G4-9-PSD. Results are reported as a function of test condition (see Table 6). This appendix 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 the main body of this interim report.

Table B-10. Cumulative oversize diameter distributions for the Group 3/4 CUF testing sample, TI-601-G4-9-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 / pre-sonic	0.33	0.46	0.61	0.91	1.1	1.3	1.8	2.6	4.0	6.1	7.5	9.2	14	17	24
2 - 4000 / pre-sonic	0.35	0.55	0.78	1.4	1.8	2.5	4.7	8.4	15	37	48	58	82	100	130
3 - 2000 / pre-sonic	0.34	0.51	0.70	1.1	1.4	1.8	2.8	4.4	6.7	9.7	12	14	23	96	140
4 - 3000 / 25%	0.30	0.47	0.66	1.2	1.5	1.9	3.1	4.6	6.7	9.2	11	12	17	20	25
5 - 3000 / 50%	0.29	0.45	0.69	1.5	2.0	2.5	4.0	5.8	7.9	10	12	13	17	21	26
6 - 3000 / 75%	0.29	0.48	0.77	1.7	2.3	2.9	4.4	6.3	8.4	11	12	14	18	21	26
7 - 3000 / post-sonic	0.30	0.50	0.82	1.8	2.4	3.1	4.7	6.5	8.6	11	12	14	18	22	28
8 - 4000 / post-sonic	0.31	0.56	1.0	2.3	3.1	4.0	6.2	8.8	12	17	21	28	65	89	120
9 - 2000 / post-sonic	0.31	0.51	0.83	1.8	2.4	3.0	4.4	6.1	8.1	10	12	13	17	21	26

Results: TI-601-G4-12-PSD (Washed Group 3/4 after leaching)

Table B-11 present detailed cumulative oversize distributions (by volume/weight) for Group 3/4 CUF testing sample TI-601-G4-12-PSD. Results are reported as a function of test condition (see Table 6). This appendix 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 the main body of this interim report.

Table B-11. Cumulative oversize diameter distributions for the Group 3/4 CUF testing sample, TI-601-G4-12-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 / pre-sonic	0.33	0.46	0.58	0.81	0.93	1.1	1.4	1.8	2.6	4.9	7.2	10	21	63	140
2 - 4000 / pre-sonic	0.32	0.44	0.55	0.76	0.87	0.99	1.3	1.7	2.3	4.0	5.8	8.1	15	26	160
3 - 2000 / pre-sonic	0.32	0.51	0.75	1.5	2.4	4.4	15	31	44	56	63	71	94	110	150
4 - 3000 / 25%	0.28	0.38	0.47	0.66	0.77	0.93	1.4	2.1	3.2	5.1	6.5	8.2	13	16	23
5 - 3000 / 50%	0.25	0.34	0.43	0.65	0.80	1.0	1.7	2.5	3.7	5.8	7.3	9.0	13	17	23
6 - 3000 / 75%	0.23	0.33	0.42	0.67	0.85	1.1	1.7	2.6	3.9	6.0	7.4	9.0	13	17	23
7 - 3000 / post-sonic	0.26	0.41	0.60	1.3	1.8	2.5	4.5	7.7	13	29	44	57	87	110	150
8 - 4000 / post-sonic	0.25	0.36	0.48	0.81	1.1	1.4	2.1	3.1	4.7	6.8	8.1	9.6	14	17	22
9 - 2000 / post-sonic	0.28	0.48	0.82	2.2	3.4	5.1	11	23	36	48	54	62	83	100	140

Appendix F

Group 3/4 Rheology Analysis (TDP-WTP-302)

Appendix F: Group 3/4 Rheology Analysis (TDP-WTP-302)

MEMORANDUM

Pacific Northwest
NATIONAL LABORATORY

Date:	**October 31, 2008**	Project No.:	**53019**
To:	**Rick Shimskey**	Internal Distribution:	**Rick Shimskey** **Richard Daniel** **File/LB**
From:	**Richard Daniel**		
Subject:	**Rheology of PUREX Cladding Waste Sludge (Group 3) and REDOX Cladding Waste Sludge (Group 4) Mixtures**		

Acronyms and Abbreviations

Acronym	Definition
AV	Axial Velocity
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
TMP	Transmembrane Pressure
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 mixture of PUREX Cladding Waste Sludge (Group 3) and REDOX Cladding Waste Sludge (Group 4) derived from Cells Unit Filter (CUF) testing efforts. This mixture is hereafter referred to as the Group 3/4 waste mixture or the cladding waste mixture. Although the studies described herein are limited to flow-curve testing of waste materials, discussion of shear strength measurements for Group 3 and 4 initial characterization (i.e., as-homogenized) samples is included for reference.

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 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.

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.

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.

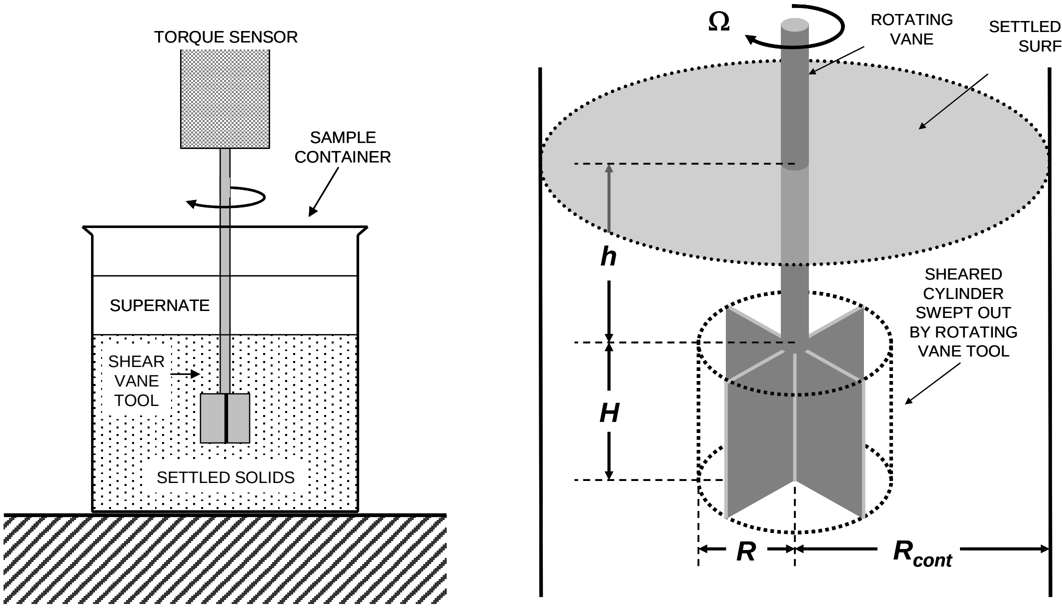


Figure 1. Typical shear strength experimental setup. A sludge / slurry sample in a container of radius R_{cont} is allowed to settle over a given period of time. A vane tool attached to a viscometer (i.e., a torque sensor) is immersed into the settled solids portion of a sludge or slurry to a depth h (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.

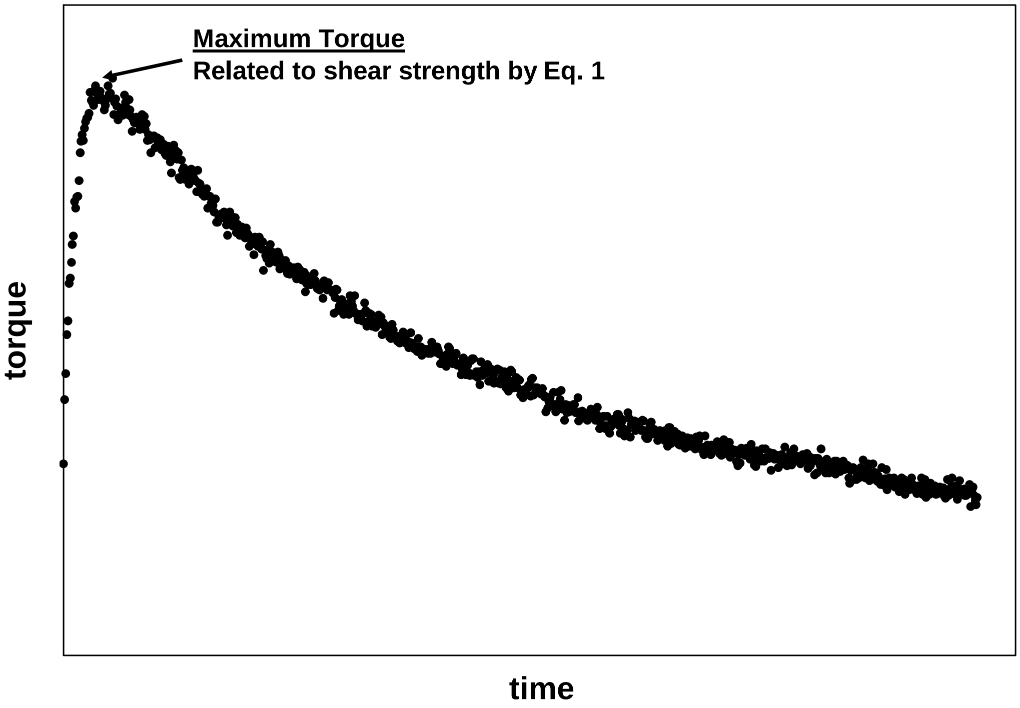


Figure 2. Example shear strength torque versus time curve. The maximum torque corresponds to the onset of motion. Here, the stress applied by vane rotation is finally sufficient to overcome frictional, cohesive, and other structural forces stabilizing the settled solids.

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 [1/s]. 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.

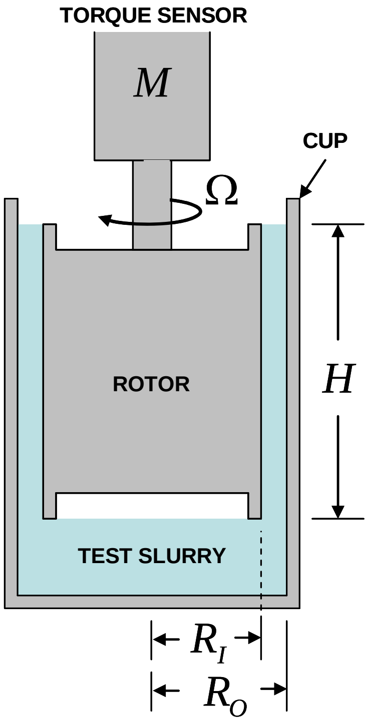


Figure 3. Rotor and cup geometry used in rotational viscometry testing.

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 typically 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-Bulkely 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 Samples

Group 3/4 CUF rheology samples were derived as part of bench-scale cross-flow filtration and leaching studies using actual tank waste. Source material for the studies included both Group 3 [PUREX Cladding Waste Sludge] and Group 4 [REDOX Cladding Waste Sludge] solids. Initially, Group 3 and Group 4 waste solids and supernate were combined in the CUF slurry reservoir to form a low-solids concentration Group 3/4 tank waste slurry. This initial slurry stalled the pump during the initial attempt to circulate it through the cross-flow filtration loop. The suspected cause of the failure was the formation of an immobile plug of material at the pump inlet. This plug likely formed during initial mixing of the fast-settling Group 3 and Group 4 waste solids.

Attempts to "power-through" the plug by running the pump in the forward direction failed. The plug was eventually disrupted by running the air motor in reverse. After recovery, pump performance was erratic and suggestive of transient system blockage. Prolonged circulation of the low-solids concentration Group 3/4 mixed slurry observed a noticeable improvement in pump performance: at the end of 20 hours of continuous operation, pump flow rates had stabilized and were free of transient spikes. After stabilization, this initial low-solids concentration slurry was subjected to the following operations:

1. dewatering of the waste slurry to transform the low-concentration Group 3/4 slurry to a high-concentration Group 3/4 slurry
2. full-recycle ultrafiltration of the high-concentration waste slurry at various AV and TMP
3. caustic leaching of the waste slurry with 14M sodium hydroxide for 8 hours at 100°C (not including time for slurry heat-up, ~6 hrs, and cool-down, ~12 hrs)
4. dewatering of the caustically leached slurry
5. full-recycle ultrafiltration of the high-concentration caustically leached slurry at various AV and TMP
6. washing of the caustically leached slurry with relatively dilute sodium hydroxide solutions (includes three successive washes with increasingly dilute NaOH solutions)

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

- before 20 hours of circulation at the low-solids concentration,
- dewatering the initial slurry to the high-solids concentration (i.e. after step 1),
- after caustic leaching and dewatering of the slurry (i.e., after step 4),
- after washing the caustic-leached slurry (i.e., after step 6),

Permeate samples were collected during dewatering of the initial and caustic leached slurry.

For sampling, approximately 60-100 mL of sample was placed into a pre-labeled 120 mL Qorpak jar. Slurry samples were taken at valve V5, which is located near the slurry pump outlet. Valve V5 was selected for slurry sampling because it resides in the filtration loop and likely provides a representative sample of the slurry in-contact with the filter element. Permeate samples were taken from the dewater collection bottles. Table 2 provides a summary of the samples taken and their given sample identification number.

Table 2. Samples associated with Group 3/4 CUF rheology testing.

Sample Jar ID	Description
TI601-G4-R1	Slurry – Low-solids Group 3/4 slurry before caustic leaching (unsheared)
TI601-G4-R2	Slurry – High-solids Group 3/4 slurry before caustic leaching (highly sheared)
TI601-G4-R2S	Permeate – Group 3/4 permeate collected during dewater to high-solids slurry
TI601-G4-R3	Slurry – Dewatered Group 3/4 slurry after caustic leaching
TI601-G4-R3S	Permeate – Group 3/4 permeate collected during post-leach dewater operation
TI601-G4-R4	Slurry – Washed Group 3/4 slurry after caustic leaching

4 Analysis

Flow curve testing of Group 3/4 waste mixtures was initially planned to be run in parallel with the filtration testing, which began on February 17th and finished on February 23rd, 2008. Samples TI601-G4-R1, TI601-G4-R2, and TI601-G4-R3 were run during CUF testing; however, rheology tests on subsequent samples could not be run because of extensive issues with rotor centering and binding between the water jacket and measuring cup. All slurry sample TI601-G4-R4 and both permeate samples were saved for later tested. Table 3 provides a list of sample test dates for Group 3/4 CUF rheology.

Table 3. Sample testing dates for Groups 3/4 CUF rheology.

Sample Jar ID	Date Tested
TI601-G4-R1	February 19, 2008
TI601-G4-R2	February 20, 2008
TI601-G4-R2S	June 20, 2008
TI601-G4-R3	February 22, 2008
TI601-G4-R3S	July 17, 2008
TI601-G4-R4	July 23, 2008

Flow curve testing produced the following reportable data for the Group 3/4 CUF samples:

- flow curve data for Group 3/4 slurries at 25°C, 40°C, and 60°C at various points in the filtration and leaching process
- flow curve data for Group 3/4 permeates at 25°C, 40°C, and 60°C before and after caustic leaching
- best-fit Newtonian, Bingham Plastic, and Casson (as applicable) parameters for Group 3/4 waste slurries at 25°C, 40°C, and 60°C
- Newtonian viscosities for Group 3/4 permeates at 25°C, 40 C, and 60°C

5 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 4 summarizes the M5 measuring system information.

Table 4. 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 5.

Table 5. 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 6. 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 before May of 2008 employed thermocouple 22888 and display 22889, whereas control and measurement during and after May of 2008 employed thermocouple 22887 and display 22890. For shear strength measurement of Group 3 settled solids, the ambient in-cell temperature recorded during testing was based on the thermocouple attached to the Cells Unit Filter (CUF) slurry reservoir installed in SAL Cell 5 (Calibration Barcode 24072).

Table 6. Calibration information for temperature measurement and display systems.

System	Serial #	Calibration Barcode	Range Calibrated	Date Calibrated	Date Due
Type-K Thermocouple	n/a	22888	0° to 100° C (±2° C)	5/4/2007	5/4/2008
Temperature Display	6070759	22889	0° to 100° C (±2° C)	5/7/2007	5/7/2008
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

Waste slurries were tested "as-is". No sample treatment was performed during the interval between sample extraction from the CUF and rheology testing, with exception of the mechanical agitation required to disperse any settled waste solids in the test sample jar.

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 7 to 10 provide a summary of each viscosity standard's properties. Rheology tests performed before March 2008 used Silicone Oil

Batch 1, whereas tests performed after April 2008 used Silicone Oil Batch 2. Standards are traceable back to their certificate of analysis through a unique lot number.

Table 7. Properties of Brookfield Fluid 10.

(Batch 1)

Fluid	10
Viscosity	9.6 cP
Temperature	25
Lot Number	121306
Expires	March 2008

Table 8. Properties of Brookfield Fluid 100 (Batch 1).

Fluid	100
Viscosity	96.0 cP
Temperature	25
Lot Number	021507
Expires	May 2008

Table 9. Properties of Brookfield Fluid 10.

(Batch 2)

Fluid	10
Viscosity	9.1 cP
Temperature	25
Lot Number	021308
Expires	April 2009

Table 10. Properties of Brookfield Fluid 100 (Batch 2).

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 measurements reported herein were covered by three separate performance checks covering the months of February, June, and July. Table 11 provides a summary of which performance checks cover the period of performance for measurement of the test samples listed in Table 2

Table 11. Periods of performance for Group 3/4 CUF rheology.

Period of Performance	Performance Check Date	Silicone Oils Used	Applicable Sample Analyses
February 2008	February 11, 2008	Fluids 10 and 100 (Batch 1)	TI601-G4-R1 TI601-G4-R2 TI601-G4-R3
June 2008	June 12, 2008	Fluids 10 and 100	TI601-G4-R2S

		(Batch 2)	
July 2008	July 16, 2008	Fluids 10 and 100 (Batch 2)	TI601-G4-R3S TI601-G4-R4

In all cases, execution of performance verification 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 relative percent difference, *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 3/4 CUF rheology, the RV20-M5 was verified to be in acceptable performance. Table 12 lists the results of each performance verification/check carried out in association with Group 3/4 CUF characterization efforts. As indicated in the table, the RV20-M5 measuring system showed acceptable performance for both test fluids.

Table 12. Results of rheometer performance checks.

Fluid	Period of Performance	List Viscosity (cP)	Measured Viscosity (cP)	*E*	Acceptable
Brookfield Fluid 10 (Batch 1)	February '08	9.6	9.5	1.2%	Yes
Brookfield Fluid 100 (Batch 1)	February '08	96.0	95.4	0.6%	Yes
Brookfield Fluid 10 (Batch 2)	June '08	9.1	8.5	6.7%	Yes
Brookfield Fluid 100 (Batch 2)	June '08	98.2	102	4.1%	Yes
Brookfield Fluid 10 (Batch 2)	July '08	9.1	9.9	2.7%	Yes
Brookfield Fluid 100 (Batch 2)	July '08	98.2	101	8.7%	Yes

Shear Strength Testing

No shear strength testing was performed in association with Group 3/4 CUF rheology testing. As such, the experimental test procedure for shear strength is not presented in detail herein. Shear strength results for Group 3 and 4 initial characterization samples are provided for reference only. Additional details regarding how Group 3 and 4 initial characterization shear strength measurements were performed are given in TDP-WTP-285 [5] and TDP-WTP-286 [6], respectively. It should be noted that because the volume of settled solids in both Group 3 and Group 4 test samples, it was not possible to satisfy the geometric constraints outlined for vane immersion in Table 1 nor was it possible to fully immerse the vane tool without contacting the bottom of the sample jar. As such, the shear strength result reported herein is not independent of container geometry and is likely a factor of two lower than would be observed for a fully immersed vane.

Flow Curve Testing

Flow curve testing for Group 3/4 CUF testing samples 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. This shear step used a constant rotational speed of 200 RPM (470 s^{-1}). During this shear step, the rotor torque was recorded as a function of time to record any shear-induced changes in the stress-response of the sample and (in cases of certain Newtonian slurries) provide a secondary measurement of viscosity.
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. In certain measurements, a lower maximum shear rate than 1000 s^{-1} was selected to avoid regions of unstable flow.
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.

In most cases, visual inspection of the cup contents after testing was complete found a significant layer (1-2 mm thick) of settled solids. It is likely that solids settling influenced rheology measurements. The consequence of solids settling would be lowered solids concentration in the suspending phase (especially of large aggregates), which would yield a weaker fluid rheology (i.e., lowered yield stress and consistency).

At the end of each flow curve 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, and Herschel-Bulkley flow models). This analysis utilized the least-squares data regression routine native to the RheoWin 2.96 software. Regressions typically included both up-ramp, constant rotation, and down-ramp portions of the flow curve, resulting in an "average" set of model parameters for the total flow curve. In a number of cases, only limit portions of the flow curve data (e.g., up-ramp only) were fit. For example, model fits were often limited to specific shear rate ranges to avoid flow curve anomalies such as Taylor Vortices (at high shear rates).

8 Results and Discussion

The following sections discuss the results of flow curve testing for Group 3/4 CUF samples. Before discussing these results, flow curve and shear strength measurements for the Group 3 and Group 4 source materials, namely those derived from homogenization efforts, will be introduced and reviewed as a point-of-reference for discussion of the CUF flow curves. Following that discussion, the slurry flow curves for each sample will be introduced and discussed one-by-one, with an emphasis on the temperature effects and flow curve behavior of each particular sample. After all flow curve measurement data has been presented, the results will be compared to one another to elucidate the effect of CUF processing on relative sample rheology. Next, a discussion of permeate rheology will be given. Finally, the results of flow curve testing will be summarized.

8.1 Source Input Materials

Before discussing the rheology results for Group 3/4 CUF testing, the rheology of both Group 3 and Group 4 reference materials shall be introduced in detail. The source material presented for these groups correspond to those measured for the initial characterization samples derived from waste homogenization.

Samples TI513-G3-AR-RH1 and TI513-G3-AR-J1: Source Group 3 Material

Samples TI513-G3-AR-RH1 and TI513-G3-AR-J1 were derived from homogenization efforts and are representative of the source Group 3 material used for CUF testing. Both waste slurries correspond to the Group 3 initial characterization sludge samples and have an undissolved solids concentration of ~29-wt%.

Sample TI513-G3-AR-J1 was employed for measurement of Group 3 settled solids shear strength. The result is shown in Table 13 and indicates a settled solids shear strength of ~700 Pa after 72 hours of settling. This result likely underestimates the actual shear strength of Group 3 settled solids because only half vane immersion could be achieved as a result of limited settled solids. It is likely that the actually shear strength for this sample is on the order of 1500 Pa.

Table 13. Shear strength of Group 3 Initial Characterization settled solids at ambient hot-cell temperature (26.4° C)

Test Sample	Settling Time	Shear Strength [Pa]
TI513-G3-AR-RH1	72 hours	700 Pa*

* Value corresponds to test where only half vane immersion is

achieved. Actually shear strength is likely on the order of 1500 Pa.

Sample TI513-G3-AR-RH1 was employed for flow curve testing. Figure 4 shows the results of the measurement and indicates that flow behavior is Newtonian with a zero yield stress. Although some of the curves show a finite offset of ~0.2 Pa, this falls below the instruments yield sensitivity of 0.5 Pa and, as such, is not significantly different than zero. 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 400 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 effected data unusable.

Rotational viscometry operates under the assumption of laminar flow. Because most rotational viscometers employ small gap sizes (~1 mm) and because most tests fluids are non-Newtonian or are Newtonian with high viscosity (i.e., greater than 10 cP), flow conditions within the gap are typically laminar. However, turbulent flow conditions will be realized during flow curve measurement for low viscosity fluids. For example, flow curve measurements of water (which has a viscosity of 1 cP) in the MV1 measurement cup system show a transition from laminar to turbulent flow around 200 s^{-1}. This transition point scales approximately with viscosity, such that prediction of transition points for higher viscosity fluids can be made simply by multiplying 200 s^{-1} by the ratio of the current viscosity to that of water. Thus, 5 cP fluids should have a transition point around 1000 s^{-1}, which is the measurement limit for the flow curves discussed herein. As such, laminar-to-turbulent flow transitions should not be observed for fluids with viscosities greater than 5 cP.

Turbulent flow dissipates more energy than laminar flow. As a result, more force is required to maintain constant rotation of the measurement systems in turbulent flow. This is observed in flow curve measurements as an increase in the slope of the shear stress versus shear rate curve (like observed in Figure 4). This increase is not predictable and cannot be analyzed to extract the actual viscosity of the test fluid. Thus, any flow curve data beyond the transition point is usually discarded.

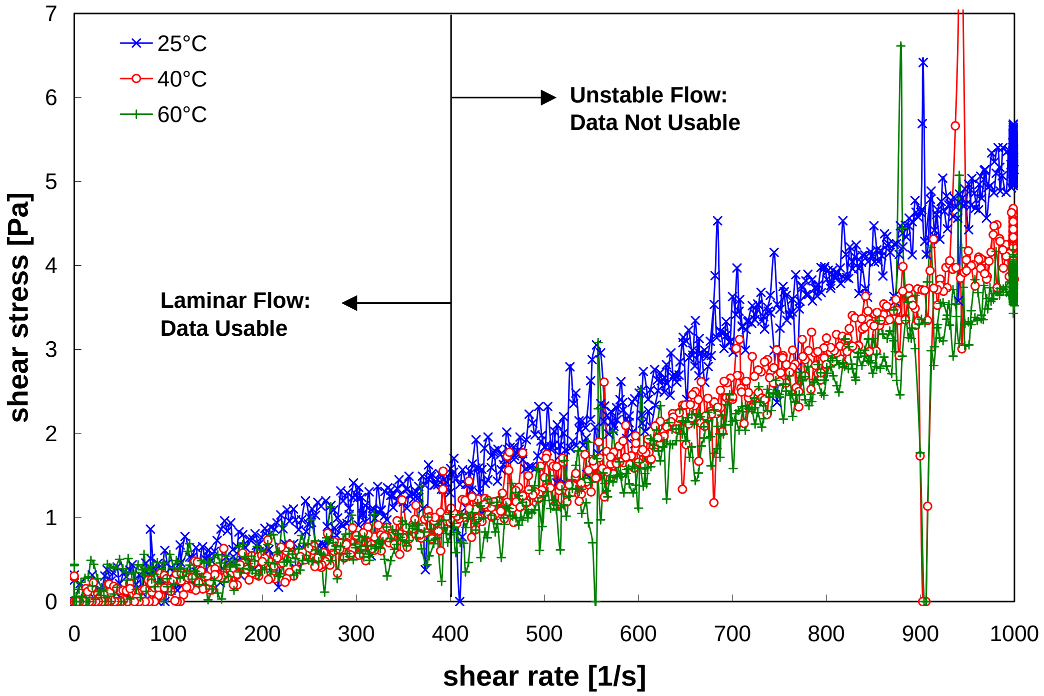


Figure 4. Flow curve (shear stress versus shear rate) for the Group 3 initial characterization slurry sample TI513-G3-AR-RH1 at 25° C, 40° C, and 60° C. Note: the second repeat measurement for 25° C is shown here, as it is the closest to the 40° and 60° C measurements in time.

The flow curves shown in Figure 4 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 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 affects are absent, as any changes could have taken place during the shearing step or before analysis took place. As stated before, significant settled solids were observed on the bottom of the measuring after completion of the measurement. It is likely that these solids settled out before the measurement took place. The effect of settling on the measurement results reported herein is that viscosities regressed from the flow curve may be lower than for the fully dispersed slurry. Unfortunately, without additional information on how slurry rheology acts as a function of solids concentration, it is difficult to evaluate how large a decrease in slurry viscosity occurs as a result of settling.

Analysis of the flow curve data is affected by the small (but statistically insignificant) stress offset and the formation of Taylor vortices. Given the ±0.2 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. However, the analysis employed a Bingham-Plastic fitting model to account for the small but finite stress offset. Here, Newtonian viscosity is equated with the Bingham consistency index (i.e., Bingham-Plastic slope). Next, data believed to be influenced by Taylor vortex formation are excluded from the fits. The shear rate range for all fits is limited to between 0 and 400 s^{-1}. Finally, rotor inertial effects and measurement noise sometimes caused down-ramp stress data to fall below zero. Less than zero stress measurements are reported as zero by the RheoWin software, which can result in fit bias. Both the replicate 25°C and 40°C down-ramp flow curve measurements were impacted significantly by less than zero stress correction by the RheoWin software. To correct for this, the fitting analysis for the replicate 25°C and 40°C measurements was limited to the up-ramp data.

In addition to determination of Newtonian viscosity from the flow curve, secondary viscosities are derived from the constant rotation (shearing) step performed before each measurement. Here, the apparent viscosity is averaged over the period of constant rotation at 470 s^{-1}. It should be noted that the rate of rotation during these measurements fell in the range where Taylor vortex formation was observed. As such, viscosity determinations from constant rotation should be approached with caution, as they may be biased to higher values as a result of flow turbulence.

Table 14 summarizes the best-fit Newtonian viscosity for flow curve data for sample TI513-G3-AR-RH1. The results indicate a Newtonian viscosity that generally falls between 1.7 and 3.6 cP depending on temperatures. Increased temperature yields a decrease in the slurry viscosity, likely as a result of suspending phase viscosity decrease. The viscosities determined by flow curve fitting analysis and by constant rotation analysis typically agree within the standard deviation of the measurements (i.e., the error associated with each constant rotation measurement). The exception to this is the measurement at 60°C. Here, the constant rotation viscosity is significantly higher than that determined from the flow curve. It should be noted that since the 60°C measurement corresponds to the lowest viscosity, the transition point from laminar to turbulent flow will also occur at the lowest shear rate for this temperature. As such, the deviation between constant rotation and flow curve fit viscosities at this temperature is likely a result of turbulent flow biasing the constant rotation measurement to higher viscosity.

Table 14. Results of fitting analysis for rheology sample TI513-G3-AR-RH1. Unless specified otherwise, flow curve viscosities are determined by fitting both up- and down-ramp data. The error listed for the constant rotation fits corresponds to the standard deviation associated with each measurement.

MODEL	TEMPERATURE [°C]	RANGE	VISCOSITY [MPA·S]	ERROR	R
Newtonian	25 (1 of 2)	0-400 s^{-1}	3.2	n/a	0.92
(Flow Curve)	25 (2 of 2)	0-400 s^{-1} (a)	3.4	n/a	0.95
	40	0-400 s^{-1} (a)	2.3	n/a	0.92
	60	0-400 s^{-1}	1.7	n/a	0.76
Constant Rotation	25 (1 of 2)	n/a	3.2	0.2	n/a
(At 470 s^{-1})	25 (2 of 2)	n/a	3.6	0.3	n/a
	40	n/a	2.2	0.7	n/a
	60	n/a	2.2 (b)	0.2	n/a

(a) Based on fit of up-ramp data only.

(b) Value likely affected by flow turbulence. For Information Only.

Test Plan TP-RPP-WTP-467 requests determination of apparent viscosity at 33 s-1. For the current measurement, measurement noise and the low slurry viscosity (< 5 cP) makes determination of apparent viscosity at this shear rate difficult and subject to significant error. In terms of calculated apparent viscosities, the Newtonian results reported in Table 14 represent the apparent viscosity over the entire range of shear and should provide a reasonable estimation of the apparent viscosity at 33 s^{-1}. Thus, determination apparent viscosity from measurement data is forgone in favor for the results in Table 14.

In summary, flow curve analysis for Group 3 Initial Characterization slurry sample, TI513-G3-AR-RH1, suggests Newtonian rheology. Regression analysis of the flow curve data finds a slurry viscosity ranging from 3.4-3.6 cP at 25°C and ~1.7 cP at 60°C. As indicated by the results, increased slurry temperature yields lower slurry viscosity, likely as a result of lowering of the suspending phase viscosity. The flow curve data are relatively free of hysteresis, which suggests that settling and/or shearing affects are minimal or occur before flow curve measurement

Sample TI514-G4-AR-RH1: Source Group 4 Material

Sample TI514-G4-AR-RH1 is derived from Group 4 waste homogenization and is representative of the source Group 4 material used for CUF testing. This waste slurry corresponds to the initial characterization REDOX cladding waste sludge sample and has an undissolved solids concentration of ~30-wt%.

The results of Group 4 initial characterization shear strength testing are shown in Table 15. Three separate observations after 72 hours of settling time indicate a shear strength ranging from 100 to 340 Pa. The single measurement at the central location suggests a shear strength of approximately 100 Pa. Significantly higher shear strengths were encountered during measurements made near the container walls. The two radial measurements indicate shear strengths of 340 and 290 Pa, and are likely influenced by vane-wall interactions.

These results should be approached with caution. The geometric constraints required for shear strength testing could not be met because of limited settled solids volume. As a result, all reported values are likely influenced by container geometry. In addition, because only half vane immersion could be achieved in these tests, the shear strength values listed in Table 15 likely underestimate shear strength. It is expected that full vane immersion would yield a factor of 2 increase in the reported values. Based on this, it is speculated that the actual shear strength for Group 4 settled solids ranges from 200 to 700 Pa.

Table 15. Shear strength of Group 4 Initial Characterization settled solids at ambient hot-cell temperature (sample TI514-G4-AR-RH1)

Test Number	**Location**	**Temperature [°C]**	**Settling Time**	**Shear Strength [Pa]**
1	Center	27.7	72 hours	100 Pa
2	Radial (Near Wall)	27.8	72 hours	340 Pa
3	Radial (Near Wall)	27.9	72 hours	290 Pa

Figure 5 shows the initial flow curve measured for the Group 4 initial characterization slurry sample, TI514-G4-AR-RH1, at 25°C. This measurement indicates Newtonian flow behavior. Although the curves shows a finite offset of ~0.1 Pa, this falls below the instruments yield sensitivity limit of 0.5 Pa. Flow curve data show a linear stress response over shear rates from zero up to ~500 s^{-1}. At higher shear rates, 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 effected data unusable. The flow curves at 40°C and 60°C show similar stress response (see Reference 6 for full results), and suggest Newtonian slurry behavior of the entire range of temperatures tested (25°C to 60°C). At higher temperature, the slope of the linear portion of the flow curve is reduced, indicating a decrease in slurry viscosity at increased slurry temperature (cf. Table 16). This viscosity-temperature trend is likely a result of lowered of the suspending phase viscosity at increased temperature.

The flow curve shown in Figure 5 is 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 affects are absent, as any changes could have taken place during the shearing step or before analysis took place. As stated before, significant settled solids were observed on the bottom of the measuring after completion of the measurement. It is likely that these solids settled out before the measurement took place. The effect of settling on the measurement results reported herein is that viscosities regressed from the flow curve may be lower than for the fully dispersed slurry. Unfortunately, without additional information on how slurry rheology acts as a function of solids concentration, it is difficult to evaluate how large a decrease in slurry viscosity occurs as a result of settling.

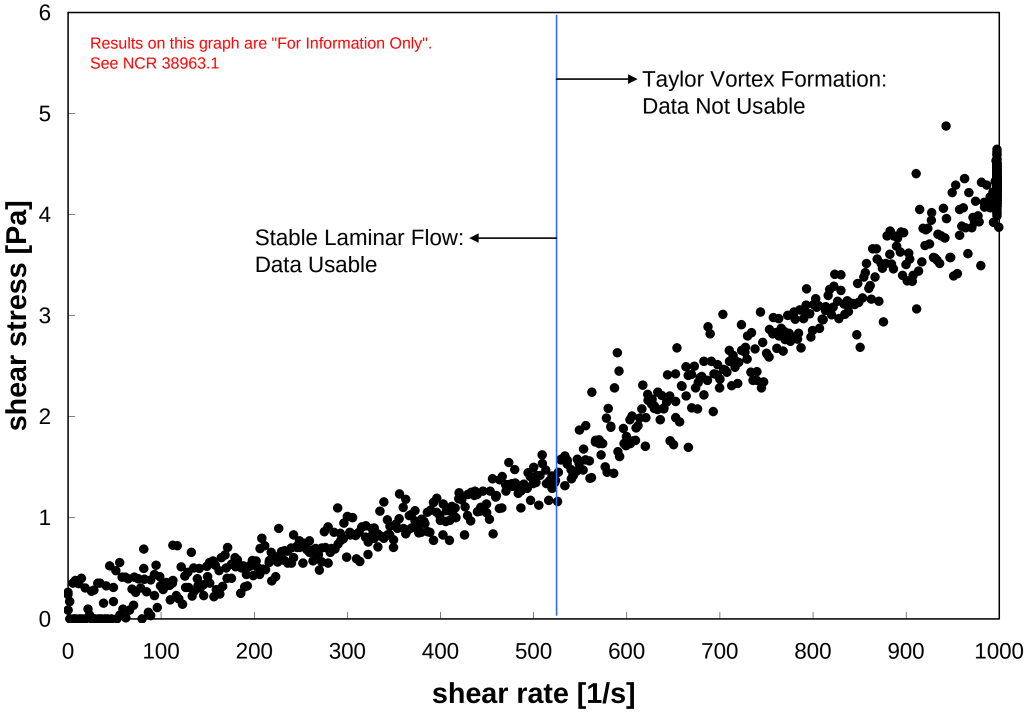


Figure 5. Flow curve (shear stress versus shear rate) for the Group 4 initial characterization slurry sample TI514-G4-AR-RH1 at 25° C (initial measurement). Measurements at other temperature set points produced similar results. Temperature corresponding to this measurement could not be verified. Result is “For Information Only”; see NCR 38963.1 for details.

Analysis of the flow curve data is affected by the small (but statistically insignificant) stress offset and the formation of Taylor vortices. Given the ±0.1 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. However, the analysis employed a Bingham-Plastic fitting model to account for the small but finite stress offset. Here, Newtonian viscosity is equated with the Bingham consistency index (i.e., Bingham-Plastic slope). Next, data believed to be influenced by Taylor vortex formation are excluded from the fits. The shear rate range for all fits is limited to data below 450 s^{-1}, 270 s^{-1}, and 240 s^{-1} at 25°C, 40°C, and 60°C, respectively. Finally, rotor inertial effects and measurement noise sometimes caused down-ramp stress data to fall below zero. Less than zero stress measurements are reported as zero by the RheoWin software, which can result in fit bias. The replicate 25°C down-ramp flow curve measurement was impacted significantly by less than zero stress correction by the RheoWin software. To correct for this, the fitting analysis for the replicate 25°C measurement was limited to the up-ramp data.

Table 16 summarizes the Newtonian viscosity results derived from flow curve data for sample TI514-G4-AR-RH1. It should be stressed that these results are "For Information Only" – NCR 38963.1 provides additional details regarding the quality status for this data. Table 16 indicates a Group 4 slurry viscosity that generally falls between 1.1 and 2.4 cP 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 measurement at 25°C compare well with each other and are within the accepted limit of variation (15%).

Table 16. Results of fitting analysis for Group 4 Initial Characterization Sample TI514-G4-AR-RH1. Unless specified otherwise, flow curve viscosities are determined by fitting both up- and down-ramp data.

MODEL	TEMPERATURE [°C]	RANGE	VISCOSITY [MPA·S]	R
Newtonian	25 (1 of 2)	0-450 s^{-1}	2.3	0.91
(Flow Curve)	25 (2 of 2)	0-450 s^{-1} (a)	2.4	0.91
	40	0-270 s^{-1}	1.4	0.76
	60	0-240 s^{-1}	1.1	0.41

(a) Based on fit of up-ramp data only.

Results are "For Information Only". See NCR 38963.1

Test Plan TP-RPP-WTP-467 requests determination of apparent viscosity at 33 s^{-1}. For the current measurement, measurement noise and the low slurry viscosity (< 5 cP) makes determination of apparent viscosity at this shear rate difficult and subject to significant error. In terms of calculated apparent viscosities, the Newtonian results reported in Table 16 represent the apparent viscosity over the entire range of shear and should provide a reasonable estimation of the apparent viscosity at 33 s^{-1}. Thus, determination apparent viscosity from measurement data is forgone in favor for the results in Table 16.

In summary, flow curve analysis for Group 4 Initial Characterization slurry sample, TI514-G4-AR-RH1, suggests Newtonian rheology. Regression analysis of the flow curve data finds a slurry viscosity ranging from 2.3-2.4 cP at 25°C and 1.1 cP at 60°C. As indicated by the results, increased slurry temperature yields lower slurry viscosity, likely as a result of lowering of the suspending phase viscosity. The flow curve data are relatively free of hysteresis, which suggests that settling and/or shearing affects are minimal or occur before flow curve measurement.

8.2 Rheology of Group 3/4 CUF Slurry Samples

The following sub-sections discuss the rheology results for Group 3/4 CUF slurry test samples. A short discussion on how the measured flow curve data behave as a function of temperature is given. Next, measurement anomalies, such as Taylor vortices, slip, and rotor inertia, are identified and quantified. Finally, application of flow curve models to the data is discussed and best-fit flow curve parameters reported. In this regard, both Bingham-Plastic and Casson constitutive equation analyses are applied. The current section focuses on flow curve data behave as a function of temperature. Section 9.3 will examine how the different sample flow curves compare to one another in an effort to highlight the effects of CUF processing on Group 3/4 waste mixture rheology.

Sample TI601-G4-R1: Low Solids Concentration Group 3/4 Slurry

Sample TI601-G4-R1 corresponds to the low-solids concentration (dilute) Group 3/4 mixed slurry initially run in the CUF system. It represents a chemically unmodified mixture of homogenized wastes from Group 3 and 4 and has an undissolved solids concentration of ~6-wt%. This slurry sample was aliquoted before extensive CUF processing (i.e., shearing) of the Group 3/4 slurry, and as such, is considered an “unsheared” sample.

Figure 6 shows the results of flow curve testing for sample TI601-G4-R1. The flow curves indicate that the slurries are Newtonian, having a linear slope up to ~450 to 550 s^{-1}. At shear rates higher than 550 s^{-1}, an increase in the flow curve slopes is observed and suggests the formation of Taylor vortices. As such, flow curve data beyond 450 s^{-1} are likely influenced by flow instabilities and, as such, are not useable for determination of slurry viscosity. With respect to other data anomalies, the flow curve data are generally free of hysteresis (with exception of rotor inertial effects) but are subject to a significant noise-to-signal ratio. Given that the total range of shear stress over shear rates between 0 to 450 s^{-1} is only 1.0 to 1.5 Pa, it is likely that the noise is substantial for the current measurements because the viscosity of the test slurry is approaching the M5 measuring system’s limit of accuracy of ±0.5 cP.

Temperature effects appear to fall within the measurement noise. There is significant overlap of flow curve data at all but the highest shear rates studied. Based on the overall variation of the data in Figure 6, it appears that the slope of the flow curve data (i.e., the slurry viscosity) appears to decrease with increasing temperature. However, because of significant overlap of data between 0 and 450 s^{-1}, any decrease in slurry viscosity with increased temperature is likely insignificant relative to the experimental error.

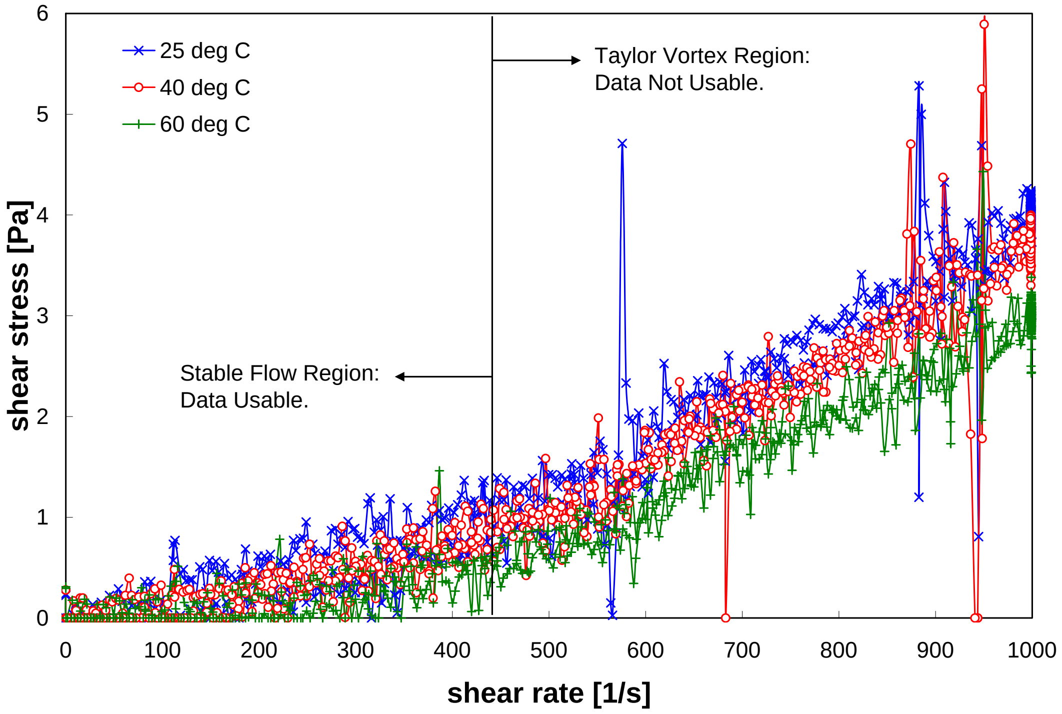


Figure 6. Flow curve for the Group 3/4 CUF testing slurry sample TI601-G4-R1 at 25° C, 40° C, and 60° C. Only the replicate flow curve measurement at 25° C is shown.

The flow curve data in Figure 6 were analyzed to derive Newtonian viscosity as a function of temperature. Least squares analysis of this employed a Bingham-Plastic model to account for any finite stress offset in the M5 measuring system. The slurry viscosity is associated with the Bingham-Plastic consistency index. Bingham fits confirmed Newtonian behavior, as all regressed Bingham-Plastic yield indices were above the limit of stress sensitivity for the MV1 cup and rotor (0.5 Pa). To avoid the inclusion of data affected by Taylor vortex formation, the range of flow curve data fit is limited to 0 to 400 s^{-1}.

Table 17 summarizes the best-fit Newtonian viscosities for sample TI601-G4-R1. Results confirm that viscosity shows a decrease with increasing temperature. At 25°C, both initial and replicate flow curves yield a viscosity of 2.0 cP. Viscosity decreases to 1.6 cP and 0.9 cP at 40°C and 60°C, respectively. Measurement noise affects the quality of the fit, as indicated by the low R values of 0.57 to 0.85. Finally, the change in viscosity with increasing temperature is near the limit of measurement accuracy (±0.5cP). From 25°C to 40°C, shows an insignificant 0.4 cP decrease. The change in viscosity from 40°C and 60°C of 0.7 cP is near the limit of significance.

Table 17. Results of fitting analysis for rheology sample TI601-G4-R1. Viscosities were determined by fitting both up- and down-ramp data.

MODEL	TEMPERATURE [°C]	RANGE	VISCOSITY [MPA·S]	R
Newtonian	25 (1 of 2)	0-400 s^{-1}	2.0	0.75
	25 (2 of 2)	0-400 s^{-1}	2.0	0.85
	40	0-400 s^{-1}	1.6	0.79
	60	0-400 s^{-1}	0.9	0.57

R is the correlation coefficient.

In summary, the initial low-solids concentration Group 3/4 slurry sample TI601-G4-R1 shows Newtonian rheology. Viscosity ranges from 2.0 cP at 25°C down to 0.9 cP at 60°C. The measurements are affected by significant noise, but this is expected for slurries with viscosities near the lower measuring limit for the instrument (~0.5 cP).

Sample TI601-G4-R2: High Solids Concentration Group 3/4 Slurry

Sample TI601-G4-R2 corresponds to the high-solids concentration Group 3/4 mixed slurry that results from dewatering of the initial low-solids concentration slurry. Like the previous sample, it represents a chemically unmodified mixture of homogenized wastes from Group 3 and 4. It has an undissolved solids concentration of ~13-wt%. This slurry sample was aliquoted after prolonged circulation of the Group 3/4 CUF slurry, and as such, is considered a highly “sheared” but chemically unmodified Group 3/4 slurry.

Figure 7 shows the results of flow curve testing for sample TI601-G4-R2. The flow behavior is non-Newtonian. Flow curve data indicate that the dewatered slurry has a finite yield stress of approximately 2 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. The 40°C measurement data is subject to noise between shear rates of 150 to 250 s^{-1} and shear rates above 850 s^{-1}. This noise is likely associated with a slight rotor misalignment during measurement as a result of in-cell disturbance (such as cell floor vibration) during measurement.

Flow curve data indicate that slurry rheology tends to become weaker at higher temperatures. Although changes in the slurry yield stress are small and difficult to determine given the ±0.5 Pa limit of instrument accuracy, the slope of the flow curve data does appears to decrease with increasing temperature (indicating a lower slurry consistency at high temperature). The stress response of the slurry at 25°C and 40°C is similar such that there is some overlap between the two data sets as a result of measurement noise. Overall, the majority of 40°C flow curve data fall below those at 25°C. Flow curve data at 60°C show a significantly reduced stress response relative to the lower test temperatures. The decrease in slope and reduced stress response are consistent with a reduction in rheology at higher temperatures.

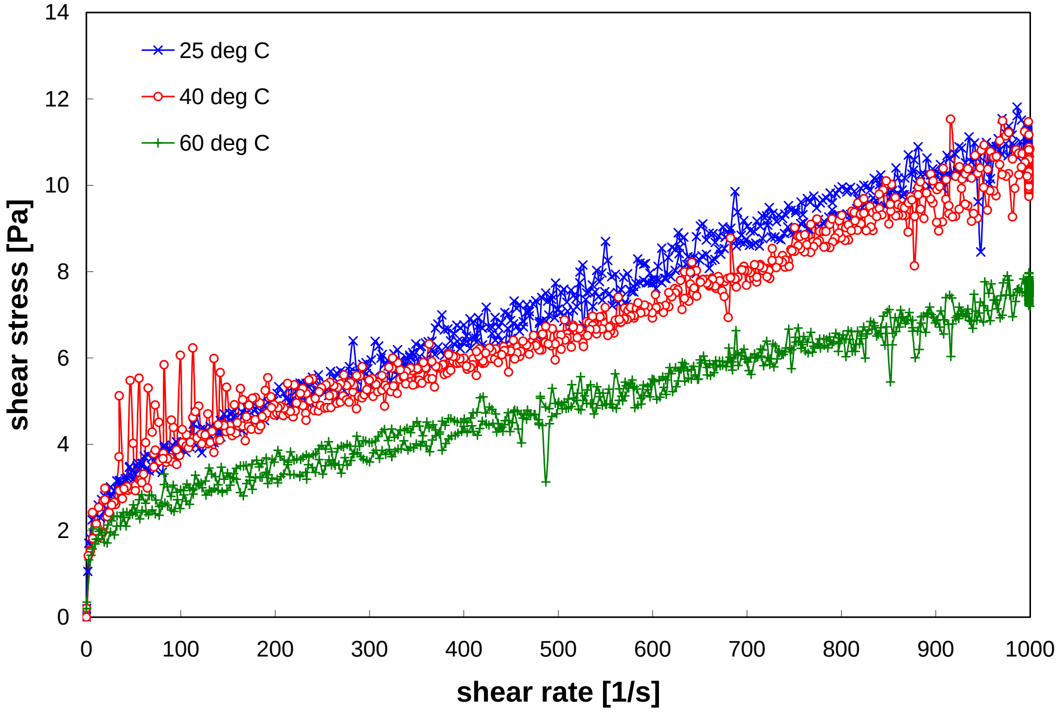


Figure 7. Flow curve for the Group 3/4 CUF testing slurry sample TI601-G4-R2 at 25° C, 40° C, and 60° C. Only the replicate flow curve measurement at 25° C is shown.

To obtain a quantitative description from the flow behavior illustrated in Figure 7, the flow curve data are fit to both Bingham-Plastic and Casson models. Since the data were not influenced by Taylor vortex formation, the full range of shear rates (0-1000 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 100-1000 s^{-1} to avoid bias introduced by slurry shear thinning at low shear rates.

Table 18 summarizes the best-fit Bingham-Plastic and Casson parameters for sample TI601-G4-R2. An example of "how-well" the Bingham-Plastic and Casson models fit data is provided in Figure 8. Both models provide reasonable fits of the data. While the Casson model provides a better description of the flow curve (especially over 0-100 s^{-1}), it tends to overstate shear thinning at shear rates beyond 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.

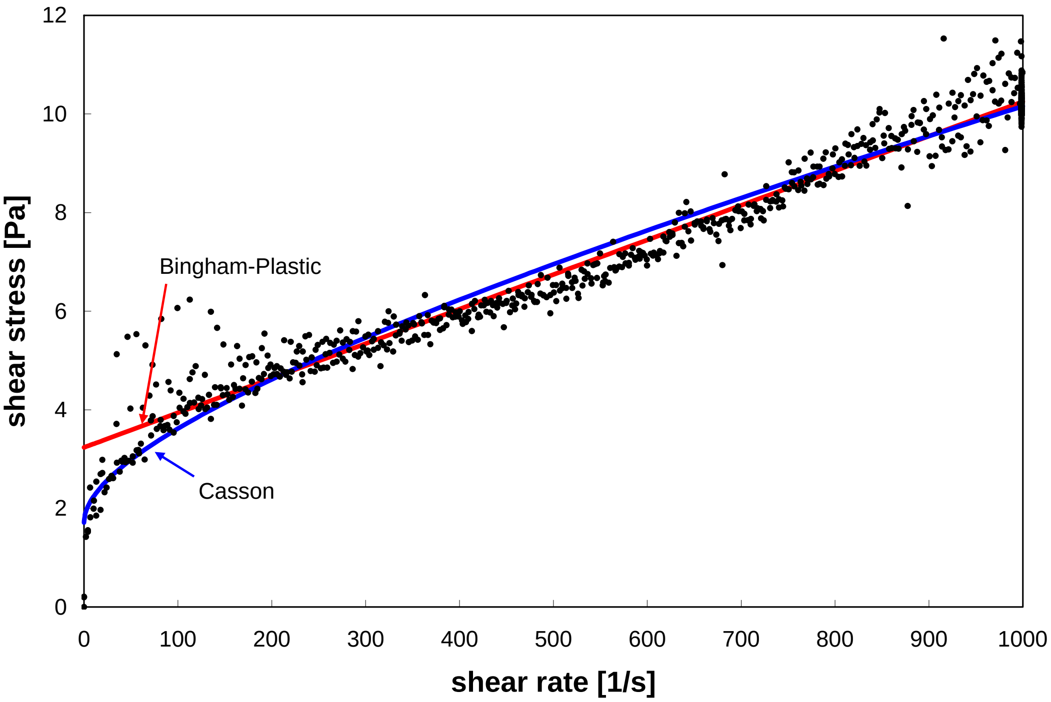


Figure 8. Example result for the fitting analysis of Group 3/4 CUF slurry test sample TI601-G4-R2. Data points (solid circles) correspond to the measurement at 40°C. The solid lines correspond to the best-fit Bingham-Plastic and Casson model calculations.

Based on the Bingham-Plastic results, the slurry can be characterized as a having a yield stress and consistency of 2.3-3.4 Pa and 5.2-7.6 cP, respectively. Casson model results are lower, suggesting a yield and consistency of 1.2 to 1.7 Pa and 2.7 to 4.0 cP, respectively. For both model fits, initial and replicate results agree to within the expected limits of instrument accuracy (0.5 Pa for stress, 0.5 cP for consistency). Likewise, the fitting results obtained for 25°C and 40°C flow curve data are also similar. Finally, a significant decrease is observed in the fitting parameters at 60°C and is consistent with the observed decrease in the 60°C flow curve in Figure 7.

Table 18. Results of fitting analysis for rheology sample TI601-G4-R2. Viscosities were determined by fitting both up- and down-ramp data.

MODEL	TEMPERATURE [°C]	RANGE	YIELD STRESS [PA]	CONSISTENCY [MPA·S]	R
Bingham-Plastic	25 (1 of 2)	100-1000 s^{-1}	3.1	7.1	1.00
	25 (2 of 2)	100-1000 s^{-1}	3.4	7.6	0.99
	40	100-1000 s^{-1}	3.2	7.0	0.99
	60	100-1000 s^{-1}	2.3	5.2	0.99

Casson	25 (1 of 2)	0-1000 s^{-1}	1.5	3.8	1.00
	25 (2 of 2)	0-1000 s^{-1}	1.7	4.0	0.99
	40	0-1000 s^{-1}	1.7	3.5	0.98
	60	0-1000 s^{-1}	1.2	2.7	0.99

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 18. The results of these analyses are provided in Table 19.

Table 19. Select apparent viscosities for sample TI601-G4-R2.

Source	Temperature [°C]	Apparent Viscosity [cP]			
		@ 33 s^{-1}	@ 100 s^{-1}	@ 500 s^{-1}	@ 1000 s^{-1}
Measured	25 (1 of 2)	86	37	13	10
	25 (2 of 2)	94	39	14	11
	40	93	48	13	10
	60	68	28	9.9	7.6
Bingham-Plastic	25 (1 of 2)	100	38	13	10
	25 (2 of 2)	110	42	14	11
	40	110	39	13	10
	60	75	28	9.9	7.5
Casson	25 (1 of 2)	76	34	14	10
	25 (2 of 2)	84	38	15	11
	40	82	36	14	10
	60	58	26	10	7.5

In summary, the initial high-solids concentration Group 3/4 slurry sample TI601-G4-R2 shows non-Newtonian rheology. Analysis of flow curve data against the Bingham-Plastic flow curve model suggests a yield stress ranging from 2.3 to 3.4 Pa and a consistency ranging from 5.2 to 7.6 cP. Similar analysis with the Casson model finds a yield and consistency that range from 1.2 to 1.7 Pa and 2.7 to 4.0

cP, respectively. With regards to temperature effects, the flow curves at 25°C and 40°C are statistically similar, whereas the flow curve at 60°C shows a significant reduction in stress response relative to lower temperatures.

Sample TI601-G4-R3: Caustic-Leached and Dewatered Group 3/4 Slurry

Sample TI601-G4-R3 corresponds to the caustic-leached and dewatered Group 3/4 mixed slurry. This slurry has an undissolved solids concentration of ~3-wt%. Figure 9 shows the results of flow curve testing for sample TI601-G4-R3. Below 500 s^{-1}, the flow curve stress data exhibit a linear response with shear rate. The low shear rate data are free of hysteresis, with exception of the 25°C flow curve, which exhibits a lower stress response during the down-ramp portion of the measurement. This hysteresis is either a result of shear disruption of internal sample structure or could indicate settling of the solids material. The latter is supported by observation of a 1-2 mm layer of settled solids on the bottom of the test cup after testing.

Up-ramp measurement data for the 25°C and 40°C above 500 s^{-1} are not linear and show an anomalous increase between 600 and 700 s^{-1}. This increase persists into the constant rotation step but is absent on the down ramp. Such behavior is characteristic of rotor misalignment. It is speculated that in-cell vibration or vibration of the instrument as it reached 700 s^{-1} yielded the misalignment and that constant rotation at 1000 s^{-1} re-seated the rotor properly for the down-ramp portion. With regard to its effect on the overall data, this anomaly only appears to affect up-ramp data at shear rates above 600 s^{-1}.

In general, the flow curve data indicate that the slurry is Newtonian. The slurry exhibits a decreased stress response with increasing temperature which is consistent with reduced slurry viscosity at higher temperatures. Although the TI601-G4-R3 slurry is Newtonian, it shows a significant stress response at all temperatures tested. For example, the TI601-G4-R3 slurry exhibits an approximately 7 Pa shear stress at a shear rate of 500 s^{-1} at 25°C. In comparison, the stress response of the TI601-G4-R1 slurry at 500 s-1 and 25°C is only ~1 Pa. As a result of the significant stress response, the flow curve data for TI601-G4-R3 have a much higher signal-to-noise ratio relative to the TI601-G4-R1 slurry flow curve data.

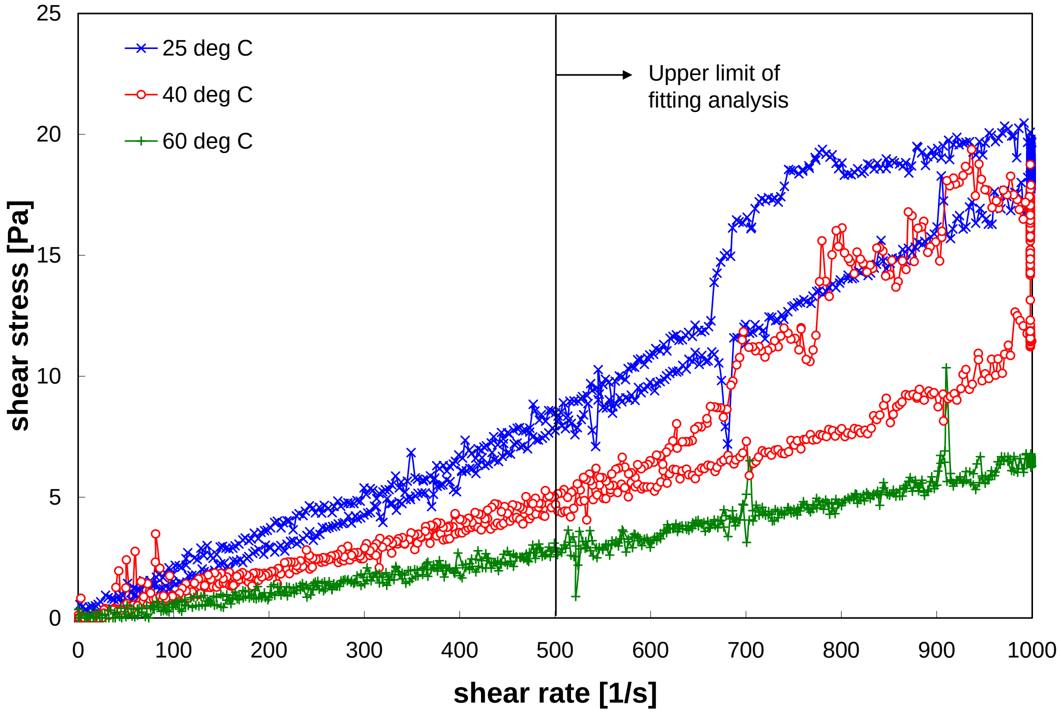


Figure 9. Flow curve for the Group 3/4 CUF testing slurry sample TI601-G4-R3 at 25° C, 40° C, and 60° C. Only the replicate flow curve measurement at 25° C is shown.

Flow curve data for sample TI601-G4-R3 were fit to a Newtonian flow model. Because of the higher signal-to-noise ratio for this sample, there was less need to account for finite stress offset using the Bingham-Plastic model (as was done for the TI601-G4-R1 fitting analysis). Both up- and down-ramp data were included in the fitting analysis. However, the range of shear rates fit was limited to 0 to 500 s^{-1} to prevent inclusion of data affected by the apparent rotor misalignment anomaly over 700 to 1000 s^{-1}.

Table 20 summarizes the best-fit Newtonian viscosities for sample TI601-G4-R3. These results indicate a viscosity of 15-16 cP at 25°C which decreases to 9.5 and 5.4 cP at 40 and 60°C. The initial and replicate flow curve measurements agree within the 10% accepted limit of instrument accuracy. In addition, the correlation coefficient of the fit (R) is high (0.97-0.99) suggesting good correlation between the data and model.

Table 20. Results of fitting analysis for rheology sample TI601-G4-R3. Viscosities were determined by fitting both up- and down-ramp data.

MODEL	TEMPERATURE [°C]	RANGE	VISCOSITY [MPA·S]	R
Newtonian	25 (1 of 2)	0-500 s^{-1}	15	0.99
	25 (2 of 2)	0-500 s^{-1}	16	0.99
	40	0-500 s^{-1}	9.5	0.97
	60	0-500 s^{-1}	5.4	0.99

In summary, the caustic-leached and dewatered Group 3/4 slurry (sample TI601-G4-R3) shows Newtonian rheology. The slurry viscosity is 15-16 cP at 25°C, 9.5 cP at 40°C, and 5.4 cP at 60°C. The measurements show a high signal-to-noise ratio relative to previous Newtonian Group 3, Group 4, and Group 3/4 samples which is likely in part to high viscosity of the TI601-G4-R3 slurry.

Sample TI601-G4-R4: Caustic-Leached, Dewatered, and Washed Group 3/4 Slurry

Sample TI601-G4-R4 corresponds to the caustic-leached, dewatered, and washed Group 3/4 mixed slurry. This slurry has an undissolved solids concentration of ~2-wt%. Flow curve testing indicated that the slurry was Newtonian behavior and exhibited a weak stress response (i.e., a shear stress of ~1 Pa at 500 s^{-1} and 25°C). As shown in Figure 10, measurements made with the appropriate zero torque offset were affected by significant negative torque correction. To account for this, an artificial positive torque offset was introduced on sample measurements used for data analysis. Figure 11 shows a typical flow curve measurement where the artificial offset (~0.5 Pa) was included. The data corresponds to the initial flow curve measurement at 25°C. Because of the low stress response of the material, the signal-to-noise ratio is low relative to the previous sample (TI601-G4-R3). The data appear relatively free of flow curve hysteresis although such effects may be lost in the measurement noise. Measurements at 40°C and 60°C show similar behavior, but with a decreased stress response over the range of shear rates tested.

For the current measurements, the shear rate range tested was limited to 0 to 500 s^{-1} at 25°C and 40°C to avoid the formation of Taylor vortices. Flow curve data at 40°C suggest vortex formation starting around 300 s^{-1}. As a result, the flow curve measurement at 60°C was limited to a range of 0 to 300 s^{-1}.

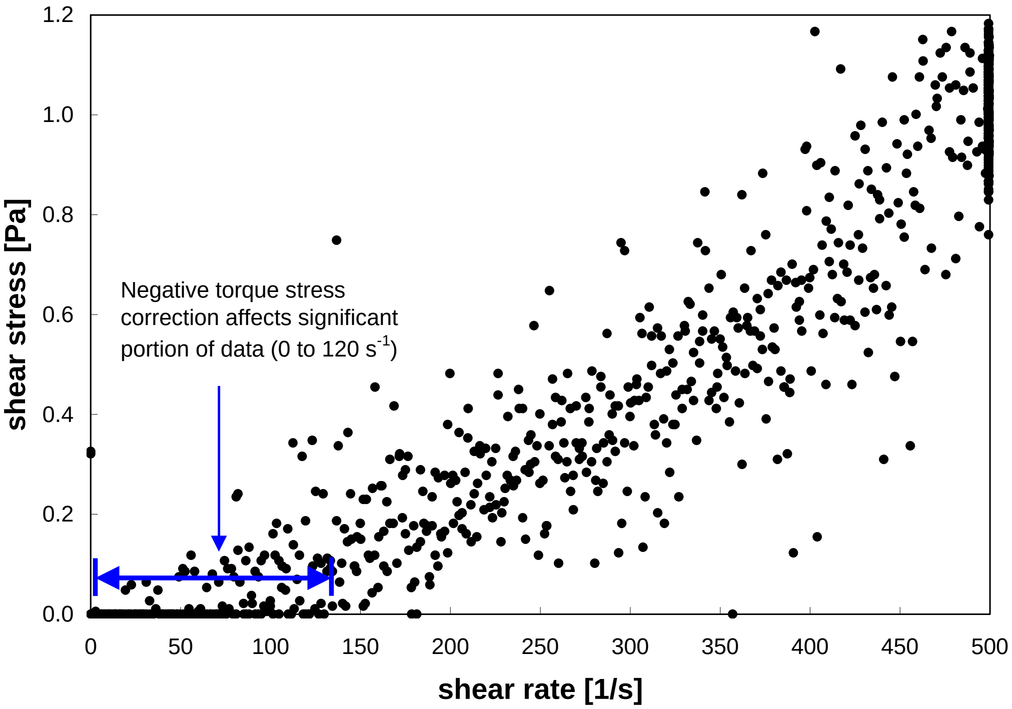


Figure 10. Example flow curve for the Group 3/4 CUF testing slurry sample TI601-G4-R4 showing significant negative torque correction over 0 to 120 s^{-1}. Data are provided “For Information Only”.

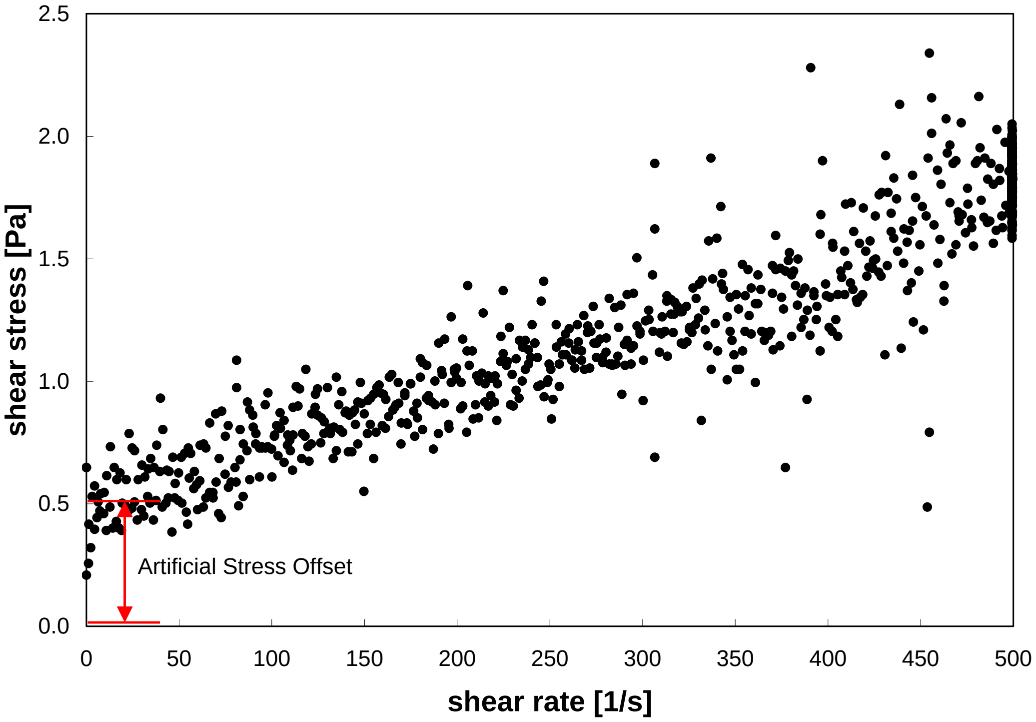


Figure 11. Sample flow curve for the Group 3/4 CUF testing slurry sample TI601-G4-R4 the initial flow curve measurement at 25°C is shown. An artificial stress offset was introduced to the

measurement to avoid negative stress readings resulting from noise and rotor inertia. Negative stress readings are recorded as zero by the RheoWin software and can bias viscosity estimates.

Based on the measurements above, the flow behavior of sample TI601-G4-R4 is assumed Newtonian. To account for the inclusion of the finite torque offset, the data are analyzed using a Bingham plastic model. For all cases, both up- and down-ramp data are included in the analysis. Fits of measurement data at 25°C use a shear rate range of 0-500 s^{-1}. Fits at higher temperatures (25°C and 40°C) use a reduced shear rate range of 0 to 300 s^{-1} to avoid inclusion of data influenced by Taylor vortex formation. The Newtonian viscosity for each set of flow curve data is associated with the regressed value of Bingham-Plastic consistency index.

Table 21 summarizes the regressed Newtonian viscosities for TI601-G4-R4. The results indicate a Newtonian viscosity of 2.3-2.7 cP at 25°C, 1.4 cP at 40°C, and 0.7 cP at 60°C. The decrease in viscosity with increasing temperature is consistent with previous Group 3/4 CUF testing samples. The quality of the fit, as given by the correlation coefficient (R), decreases at higher temperatures and is indicative of the reduced stress response at higher temperature (which yield a lower signal-to-noise ratio). With regards to measurement reproducibility, the initial and replicate measurements at 25°C agree within the expected limit of instrument accuracy (±0.5 cP for fluids with a viscosity lower than 5 cP).

Table 21. Results of fitting analysis for rheology sample TI601-G4-R4. Viscosities were determined by fitting both up- and down-ramp data.

MODEL	TEMPERATURE [°C]	RANGE	VISCOSITY [MPA·S]	R
Newtonian	25 (1 of 2)	0-500 s^{-1}	2.7	0.95
	25 (2 of 2)	0-500 s^{-1}	2.3	0.89
	40	0-300 s^{-1}	1.4	0.89
	60	0-300 s^{-1}	0.7	0.52

In summary, the caustic-leached, dewatered, and washed Group 3/4 slurry (sample TI601-G4-R4) shows weak Newtonian rheology. Slurry viscosity is 2.3-2.7 cP at 25°C, 1.4 cP at 40°C, and 0.7 cP at 60°C.

8.3 Effects of CUF Processing on Group 3/4 Rheology

This section examines the effect waste mixing and CUF processing has on Group 3/4 waste mixture rheology. Because Group 3/4 samples are mixtures of two separate waste streams, it is not possible to examine or infer the effect of CUF processing on the rheology of the separate waste groups. Instead, comparisons will primarily focus on the changes that occur in sample rheology between processing steps. The data analysis and discussion presented in this section details impacts to the waste slurry rheology during the following four processes:

1. mixing of the Group 3 and Group 4 waste solids
2. shear and dewatering of the Group 3/4 waste mixture
3. caustic-leaching of the initial Group 3/4 mixture
4. washing of the caustic-leached Group 3/4 mixture

To discuss the influence of each of these processes on the CUF slurry rheology, flow curve data along with best-fit Newtonian viscosity and Bingham-Plastic parameters shall be employed. Comparisons shall be made using best-fit parameters based on 25°C replicate measurement flow curve data. In addition to the processes outlined above, a general discussion of the effect of temperature for Group 3/4 CUF samples is given at the end of this section.

Mixing of Group 3 and Group 4 Waste Solids

Table 22 compares the rheology of the source Group 3 and Group 4 slurries to the low-solids matrix (dilute) Group 3/4 CUF slurry. Both source materials have a relatively high undissolved solids concentration (~30-wt%) and are Newtonian. The viscosities of the Group 3 and 4 source materials are 3.4 and 2.4 cP, respectively, at 25°C. In comparison, the dilute Group 3/4 slurry mixture is Newtonian with a viscosity of 2.0 cP at 25°C. The lower mixture viscosity relative to the source materials is expected, as the dilute CUF slurry only has an undissolved solids concentration of ~6-wt%. However, given the significant difference in undissolved solids concentrations, the mixed slurry viscosity is remarkably similar to that of the source materials. Indeed, the difference between the Group 4 source material and dilute CUF mixture viscosities falls within the limit of instrument accuracy (±0.5 cP). As such, solids concentration affects appear weak. It is speculated that the viscosity of these samples is governed primarily by that of the suspending phase. On the other hand, the similarity in viscosity between samples of disparate solids concentrations could also be a consequence of significant solids settling before and during flow curve analysis. This latter assertion is supported by the observation of significant settled solids at the end of all Group 3/4 CUF rheology tests.

Table 22. Effect of waste stream mixing on Group 3/4 CUF rheology (at 25°C). Note: Group 4 source material (TI514-G4-AR-RH1) rheology result is "For Information Only". See NCR 38963.1 for details.

DESCRIPTION	UNDISSOLVED SOLIDS CONCENTRATION	RHEOLOGY	YIELD STRESS [PA]	CONSISTENCY [CP]
Group 3 Source (TI513-G3-AR-RH1)	~29-wt%	Newtonian	n/a	3.4
Group 4 Source (TI514-G4-AR-RH1)	~30-wt%	Newtonian	n/a	2.4
Dilute Group 3/4 Mixture (TI601-G4-R1)	~6-wt%	Newtonian	n/a	2.0

* Non-Newtonian properties reported are Bingham-Plastic model parameters.

Shear and Dewatering of Group 3/4 Waste Mixture

Table 23 shows the effect that dewatering has on the pre-caustic-leach rheology of the Group 3/4 CUF slurry. The initial dilute slurry shows Newtonian behavior with a low viscosity of 2.0 cP at 25°C. After dewatering, the slurry is non-Newtonian with a finite yield and a higher consistency index. Based on the Bingham-Plastic parameters, the yield and consistency of the dewatered slurry are 3.4 Pa and 7.6

cP, respectively, at 25°C. Based on these results, it can be concluded that prolonged shear and subsequent dewatering effect a significant increase in overall Group 3/4 slurry rheology.

With respect to undissolved solids, dewatering only changes the slurry concentration from ~6-wt% to ~13-wt%. The significant change in rheology associated with this relatively minor change in solids concentration (compared to the source material dilution) indicates a strong solids concentration dependence for rheology that contrasts starkly with the results in Table 22, which suggest a weak dependence of Group 3/4 slurry rheology on solids concentration. The difference in rheology-solids concentration dependencies observed during mixing and dewatering operations suggests that prolonged solids shearing as a result of CUF processing has changed how the bulk sample rheology depends on solids concentrations.

Table 23. Effect of pre-caustic-leach dewatering on Group 3/4 CUF rheology (at 25°C)

DESCRIPTION	UNDISSOLVED SOLIDS CONCENTRATIO N	RHEOLOGY	YIELD STRESS [PA]	CONSISTE NCY [CP]
Dilute Group 3/4 Mixture (TI572-G2-R1)	~6-wt%	Newtonian	n/a	2.0
Concentrated Group 3/4 Mixture (TI601-G4-R2)	~13-wt%	Non-Newtonian*	3.4	7.6

* Non-Newtonian properties reported are Bingham-Plastic model parameters.

Caustic-Leaching of Group 3/4 Waste Mixture

Table 24 shows the effect of caustic-leaching and dewatering on the rheology of the Group 3/4 CUF slurry. Before leaching, the slurry shows Newtonian behavior at low solids concentrations and non-Newtonian behavior at high solids concentration. After leaching, the slurry is Newtonian but exhibits a significant viscosity (or consistency) relative to the pre-leach slurries. At 25°C, leached slurry viscosity is ~16 cP. In comparison, the pre-leach dilute slurry was only 2.0 cP at 25°C, and the pre-leach concentrated slurry indicates an infinite shear viscosity of 7.6 cP at 25°C. The high viscosity of the post-leach slurry can be attributed to increased suspending phase viscosity resulting from significant dissolved solids. This conclusion is supported by comparison of pre- and post-leached dissolved solids concentrations, ~20-wt% and ~35-wt%, respectively. The origin of the high dissolved solids content in the post-leach sample includes both addition of concentrated caustic for caustic-leaching and dissolution of aluminum species during caustic-leaching.

Table 24. Effect of caustic-leaching and dewatering on Group 3/4 CUF rheology (at 25°C)

DESCRIPTION	UNDISSOLVED SOLIDS CONCENTRATIO N	RHEOLOGY	YIELD STRESS [PA]	CONSISTE NCY [CP]
Dilute Group 3/4 Mixture (TI572-G2-R1)	~6-wt%	Newtonian	n/a	2.0

Concentrated (TI601-G4-R2)	~13-wt%	Non-Newtonian*	3.4	7.6
Caustic-Leached / Dewatered (TI601-G4-R3)	~3-wt%	Newtonian	n/a	16

* Non-Newtonian properties reported are Bingham-Plastic model parameters.

Washing of Caustic-Leached Group 3/4 Waste Mixture

Table 25 shows the effect of post-caustic-leach washing on the rheology of the Group 3/4 CUF slurry. The results indicate that washing effects a significant reduction in viscosity. Before washing, the slurry is Newtonian and exhibits a significant viscosity of 16 cP at 25°C. After washing, the slurry is Newtonian with a weak viscosity of 2.3 cP at 25°C. Because the pre- and post-wash undissolved solids concentrations are similar, the reduction in post-wash slurry viscosity can be attributed to the lowered suspending phase dissolved solids concentration. Washing of the Group 3/4 slurry, while employs dilute caustic with a final wash caustic concentration of ~0.01M NaOH, reduces dissolved solids from ~35-wt% to ~12-wt%. This reduction in dissolved solids content yields a corresponding reduction in viscosity.

Table 25. Effect of post-caustic-leach washing on Group 3/4 CUF rheology (at 25°C)

DESCRIPTION	UNDISSOLVED SOLIDS CONCENTRATION	RHEOLOGY	YIELD STRESS [PA]	CONSISTENCY [CP]
Caustic-Leached / Dewatered (TI601-G4-R3)	~3-wt%	Newtonian	n/a	16
Caustic-Leached / Dewatered / Washed (TI601-G4-R4)	~2-wt%	Newtonian	n/a	2.3

Temperature Trends

Table 26 shows the effect of post-caustic-leach washing on the rheology of the Group 3/4 CUF slurry. In all cases, increased slurry temperature effects a decrease in slurry viscosity. The high solids slurry (TI601-G4-R2) is non-Newtonian and shows a decreasing yield stress with increased temperature. Specifically, the Bingham-Plastic yield for this slurry decreases from 3.4 Pa at 25°C to 2.3 Pa at 60°C. Overall, the simplest explanation for this decrease in slurry rheology with increased temperature is a lowered suspending phase viscosity at higher temperatures. However, other mechanisms such as solids structuring can also yield similar behaviors.

Table 26. Effect of temperature on slurry consistency/viscosity for the Group 3 source material (G3), Group 4 source material (G4), low-solids (LS), high-solids (HS), caustic-leached and dewatered (CLD), and caustic-leached dewatered and washed (CLDW) slurries.

Temperature	Slurry Consistency / Viscosity [cP]

[°C]	**G3**	**G4***	**LS**	**HS****	**CLD**	**CLDW**
25 (replicate)	3.4	2.4	2.0	7.6	16	2.3
40	2.3	1.4	1.6	7.0	9.5	1.4
60	1.7	1.1	0.9	5.2	5.4	0.7

* Result for Group 4 are "For Information Only". See NCR 38963.1 for details.

** Non-Newtonian slurry. Bingham-Plastic consistency index reported.

8.4 Rheology of Group 3/4 CUF Permeate Samples

The following sub-sections discuss the rheology results for Group 3/4 CUF permeate test samples TI601-G4-R2S and TI601-G4-R3S. A short discussion on how the measured flow curve data behave as a function of temperature is given. Next, measurement anomalies, such as Taylor vortices, slip, and rotor inertia, are identified and quantified. Finally, application of flow curve models to the data is discussed and best-fit flow curve parameters reported.

Sample TI601-G4-R2S: Initial (Pre-Leach) Permeate

Sample TI601-G4-R2S corresponds to permeate collected during dewatering of the initial (i.e., pre-caustic-leach) slurry. Figure 12 shows an example results of flow curve testing for this sample and corresponds to the replicate flow curve measurement at 25°C. The flow behavior is Newtonian with a weak stress response (~0.5 Pa at 250 s^{-1}) indicative of a solution with near water viscosity. The weak stress response of the sample results in two difficulties with the flow curve data: 1) a finite stress offset and 2) a low signal-to-noise ratio. The finite offset is an artifact of the instrument zero and is noticeable because of the low stress response of the sample. For samples with low viscosity, it is advantageous to introduce positive artificial offsets using the instrument zero to avoid negative torque readings, which are set to zero by the RheoWin software and, as a result, can bias viscosity analysis.

The initial measurement at 25°C employed the full shear rate range of 0 to 1000 s^{-1}. Taylor vortex formation was observed near ~300 s^{-1}. Initial measurement flow curve data below 300 s^{-1} were affected by significant negative torque correction. To correct for this, subsequent flow curve measurement for sample TI601-G4-R2S employed a reduced stress range of 0 to 250 s^{-1} to avoid formation of Taylor vortices and provide better data resolution over the linear range. As shown in Figure 12, measurements also included the finite stress offset to avoid negative torque correction.

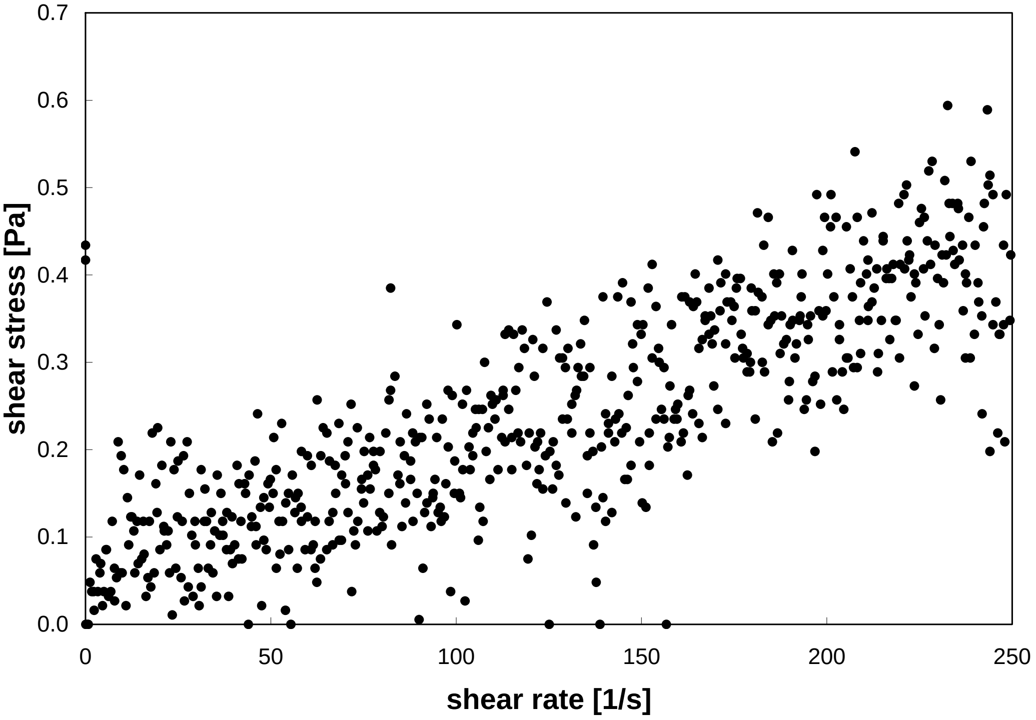


Figure 12. Sample flow curve for the Group 3/4 CUF testing permeate sample TI601-G4-R2S. The replicate flow curve measurement at 25°C is shown. Here, the maximum shear rate was limited to 250 s^{-1} to avoid the formation of Taylor vortices.

Based on flow curve measurements, permeate sample TI601-G4-R2S was assumed Newtonian. To account for both the low stress response of the sample and finite torque offset, flow curve data were fit to a Bingham-Plastic model. The Newtonian viscosity of the permeate was then associated with the Bingham-Plastic consistency index. The initial measurement data at 25°C were fit over a shear rate range of 50 to 250 s^{-1}. The lower bound of 50 s^{-1} limits inclusion of negative torque measurements set to zero by the RheoWin software. The upper bound of 250 s^{-1} prevents inclusion of stress influenced by Taylor vortex formation. The replicate 25°C measurement and higher temperature measurement fits for sample TI601-G4-R2S employed a shear rate range of 0 to 250 s^{-1} with the upper limit in place to again prevent inclusion of data affected by Taylor vortices. All fits use included both up- and down-ramp data.

Table 27 summarizes the best-fit Newtonian viscosities for sample TI601-G4-R2S. Viscosity ranges from 1.0 to 1.6 cP and appears to decrease with increasing temperature. The significance of the decrease is difficult to ascertain, as the total range of viscosity change of 0.6 cP falls near the accepted limit of instrument accuracy (0.5 cP).

Table 27. Results of fitting analysis for rheology sample TI601-G4-R2S. Viscosities were determined by fitting both up- and down-ramp data.

MODEL	TEMPERATURE [°C]	RANGE	VISCOSITY [MPA·S]	R
Newtonian	25 (1 of 2)	50-250 s^{-1}	1.4	0.73
	25 (2 of 2)	0-250 s^{-1}	1.6	0.88
	40	0-250 s^{-1}	1.3	0.79
	60	0-250 s^{-1}	1.0	0.70

In short, the initial (pre-leach) Group 3/4 permeate sample (TI601-G4-R2S) shows weak Newtonian rheology. The permeate viscosity is 1.4-1.6 cP at 25°C, 1.3 cP at 40°C, and 1.0 cP at 60°C. Although the flow curve fitting results indicate a decrease in permeate viscosity with increasing temperature, the total change in viscosity over the temperature range tested is only 0.6 cP and falls near the limit of instrument accuracy (0.5). As such, it is difficult to ascertain if this change is significant.

Sample TI601-G4-R3S: Final (Post-Leach) Permeate

Sample TI601-G4-R3S corresponds to permeate collected during dewatering of the caustic-leached slurry. Dewatering takes place before washing of the slurry, and the permeate collected is rich in ionic species. Figure 13 shows the flow curve measurement result for the initial measurement of TI601-G4-R3S at 25°C. In keeping with the test method developed for the pre-leach permeate sample (TI601-G4-R2S), flow curve measurements were limited to a lower shear rate range of 0 to 400 s^{-1} than typically employed (i.e., 0 to 1000 s^{-1}). A small positive artificial stress offset was introduced using the instrument zero to prevent negative stress correction by the RheoWin software. Measurement data, such as those shown in Figure 13, indicate Newtonian flow behavior with a significant stress response. For the example shown in Figure 13, a shear stress of ~3.5 Pa is measured at 400 s^{-1}. The data are relatively free of anomalies such as flow curve hysteresis and Taylor vortex formation. Flow curve measurements also exhibit a strong signal to noise ratio.

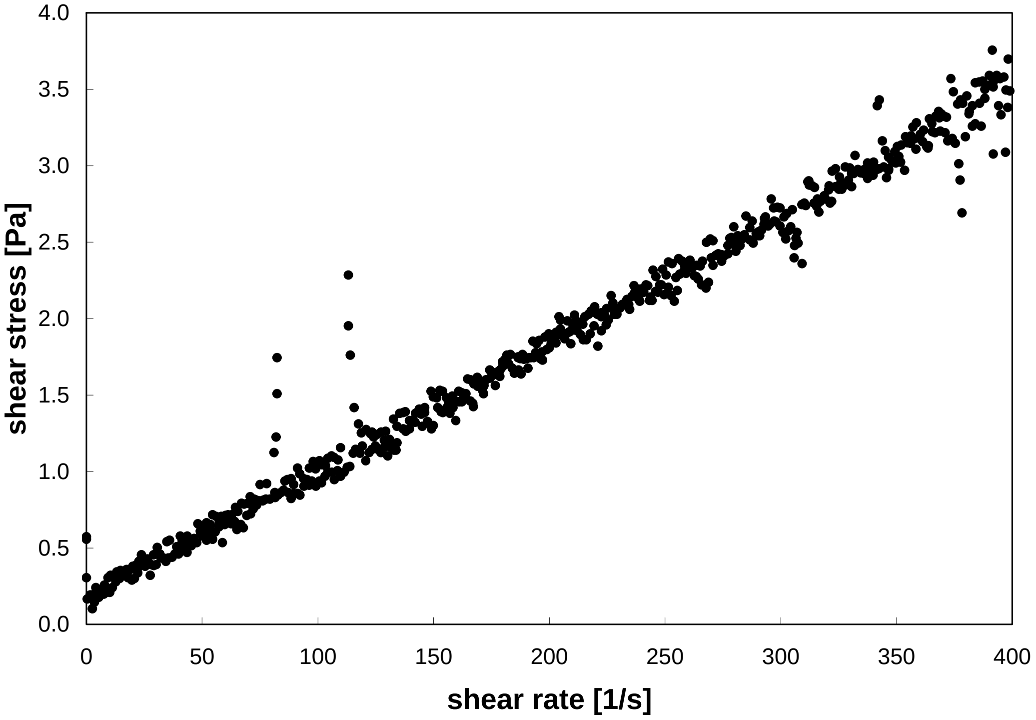


Figure 13. Sample flow curve for the Group 3/4 CUF testing permeate sample TI601-G4-R3S. The initial flow curve measurement at 25°C is shown. Here, the maximum shear rate was limited to 400 s^{-1}.

Based on the flow curve measurements, permeate sample TI601-G4-R3S was assumed Newtonian. To account for the inclusion of artificial stress offset, flow curve data for this sample were analyzed with a Bingham-Plastic model. The Newtonian viscosity of the sample is associated with the regressed Bingham-Plastic consistency index. Least-squares analysis employs both up- and down-ramp data over the full range of shear rates (i.e., 0 to 400 s^{-1}).

Table 28 summarizes the best-fit Newtonian viscosities for sample TI601-G4-R3S. The results indicate that the permeate viscosity decreases with temperature. The viscosity is 8.2 cP, 4.9 cP, and 2.9 cP, at 25°C, 40°C, and 60°C, respectively. Changes in permeate viscosity with temperature exceed the expected limits of accuracy of ±10% for these measurements, suggesting that the change is significant. Overall, the quality of the fits appears to be reasonable. Good correlation between the Bingham model and the data is confirmed by fit correlation coefficients (R values) that are close to unity. In addition, initial and replicate measurements compare well with each other.

Table 28. Results of fitting analysis for rheology sample TI601-G4-R3S. Viscosities were determined by fitting both up- and down-ramp data.

MODEL	TEMPERATURE [°C]	RANGE	VISCOSITY [MPA·S]	R
Newtonian	25 (1 of 2)	0-400 s^{-1}	8.2	0.99
	25 (2 of 2)	0-400 s^{-1}	8.2	0.99
	40	0-400 s^{-1}	4.9	0.99
	60	0-400 s^{-1}	2.9	0.97

In short, the final (post-leach) Group 3/4 permeate sample (TI601-G4-R3S) shows significant Newtonian rheology. The permeate viscosity is 8.2 cP at 25°C, 4.9 cP at 40°C, and 2.9 cP at 60°C. The flow curve fitting results indicate a decrease in permeate viscosity with increasing temperature. Given that the variation in viscosity between temperature set points exceeds 10%, it is likely that the temperature correlation observed for this sample is significant.

9 Conclusions

The preceding sections detail the rheology of Group 3/4 tank waste slurries and permeates as a function of CUF processing and sample temperature. Newtonian behavior was observed for all waste slurries with exception of the initial high solids Group 3/4 waste mixture. For the latter case, the waste was non-Newtonian and exhibited a significant yield stress and was slightly shear-thinning. Using the best-fit Newtonian viscosity and Bingham-Plastic parameters as a guide, the slurry rheology as a function of waste processing in the CUF may be described as follows:

1. *Group 3 Source Material (TI513-G3-AR-RH1)* – the source material for Group 3 is Newtonian with a viscosity of 3.2-3.4 cP at 25°C, 2.3 cP at 40°C, and 1.7 cP at 60°C.

2. *Group 4 Source Material (TI514-G4-AR-RH1)* – the source material for Group 4 is Newtonian with a viscosity of 2.3-2.4 cP at 25°C, 1.4 cP at 40°C, and 1.1 cP at 60°C.

3. *Group 3/4 Initial Dilute Slurry (TI601-G4-R1)* – this is a dilute initial Group 3/4 slurry (~6-wt%) created by mixing source material from Group 3 and Group 4 wastes. It is Newtonian with a viscosity of 2.0 cP at 25°C, 1.6 cP at 40°C, and 0.9 cP at 60°C.

4. *Group 3/4 Initial Concentrated Slurry (TI601-G4-R2)* – this is a concentrated Group 3/4 slurry (~13-wt%) that results from prolonged shearing and subsequent dewatering of the initial dilute slurry. It shows non-Newtonian rheology with a Bingham-Plastic yield stress of 3.1-3.4 Pa at 25°C, 3.2 Pa at 40°C, and 2.3 Pa at 60°C and a Bingham-Plastic consistency index of 7.1-7.6 cP at 25°C, 7.0 cP at 40°C, and 5.2 cP at 60°C.

5. *Group 3/4 Caustic-Leached and Dewatered Slurry (TI601-G4-R3)* – this is a concentrated Group 3/4 slurry (~3-wt%) that results from caustic-leaching and dewatering of the initial slurry concentrate. It is Newtonian with a viscosity of 15-16 cP at 25°C, 9.5 cP at 40°C, and 5.4 cP at 60°C.

6. *Group 3/4 Caustic-Leached, Dewatered, and Washed Slurry (TI601-G4-R4)* – this is a concentrated Group 3/4 slurry (~2-wt%) that results from washing of the caustic-leached and dewatered slurry. It is Newtonian with a viscosity of 2.3-2.7 cP at 25°C, 1.4 cP at 40°C, and 0.7 cP at 60°C.

7. *Group 3/4 Initial (Pre-Leach) Permeate (TI601-G4-R2S)* – this is Group 3/4 permeate collected during dewatering of the initial slurry. It is Newtonian with a viscosity of 1.4-1.6 cP at 25°C, 1.3 cP at 40°C, and 1.0 cP at 60°C.

8. *Group 3/4 Final (Post-Leach) Permeate (TI601-G4-R3S)* – this is Group 3/4 permeate collected during dewatering of the caustic-leached slurry. It is Newtonian with a viscosity of 8.2 cP at 25°C, 4.9 cP at 40°C, and 2.9 cP at 60°C.

10 Records

Data records relating to rheological characterization of Group 3 and 4 Initial Characterization samples and of Group 3/4 CUF Testing samples include Test Data Packages (TDPs), Computational Computer Programs (CCPs), and LRBs:

- **LRB BNW 59633** – Pages 80-83, 118-125, 140-141, and 147-148
- **TDP-WTP-285** – flow curve and shear strength measurement data, results, and graphs for sample TI513-G3-AR-RH1 / TI513-G3-AR-J1
- **TDP-WTP-286** – flow curve and shear strength measurement data, results, and graphs for sample TI514-G4-AR-RH1
- **CCP-WTPSP-553** – flow curve measurement data, results, and graphs for sample TI601-G4-R1
- **CCP-WTPSP-554** – flow curve measurement data, results, and graphs for sample TI601-G4-R2
- **CCP-WTPSP-556** – flow curve measurement data, results, and graphs for sample TI601-G4-R3
- **CCP-WTPSP-558** – flow curve measurement data, results, and graphs for sample TI601-G4-R4
- **CCP-WTPSP-555** – flow curve measurement data, results, and graphs for sample TI601-G4-R2S
- **CCP-WTPSP-557** – flow curve measurement data, results, and graphs for sample TI601-G4-R3S

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-285, Revision 0, "Rheology of Waste Processing Group 3 (PUREX Cladding Waste Sludge): Initial Characterization," RC Daniel, Pacific Northwest National Laboratory, October 2008.

6. 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.

Rheograms

This appendix contains detailed rheograms (shear stress and apparent viscosity as a function of shear rate) for 3/4 CUF testing samples. No discussion of these results is provided.

<u>Sample TI601-G4-R1: Initial Dilute Group 3/4 CUF Slurry</u>

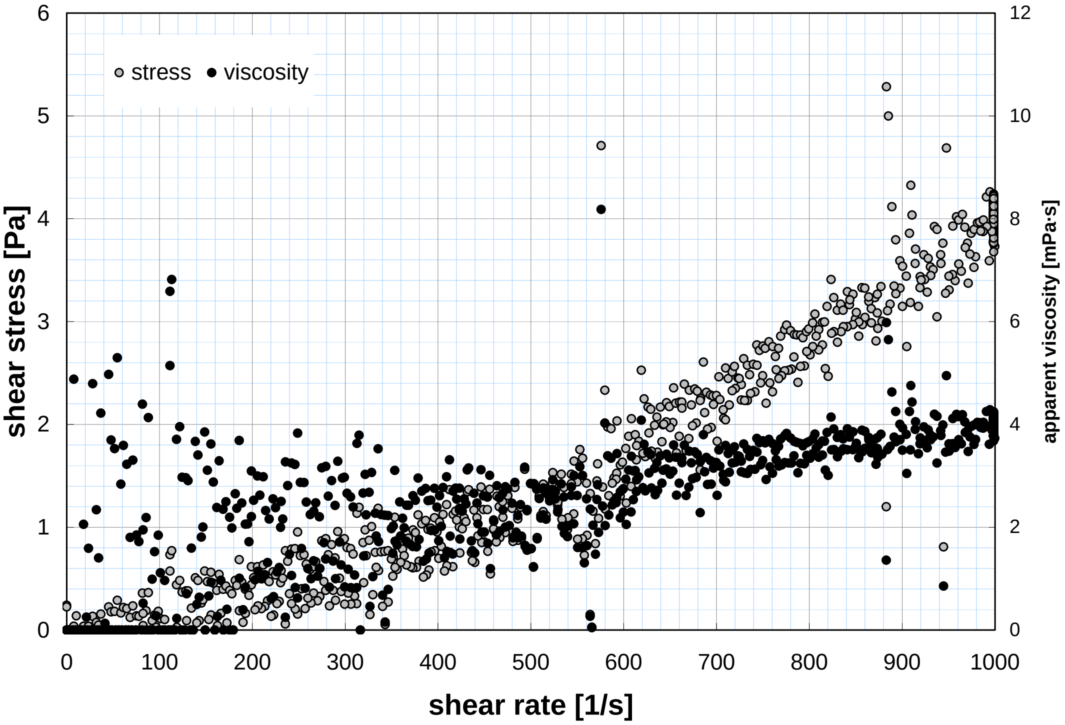


Figure R-1. Rheogram for TI601-G4-R1 at 25°C (measurement 1 of 2).

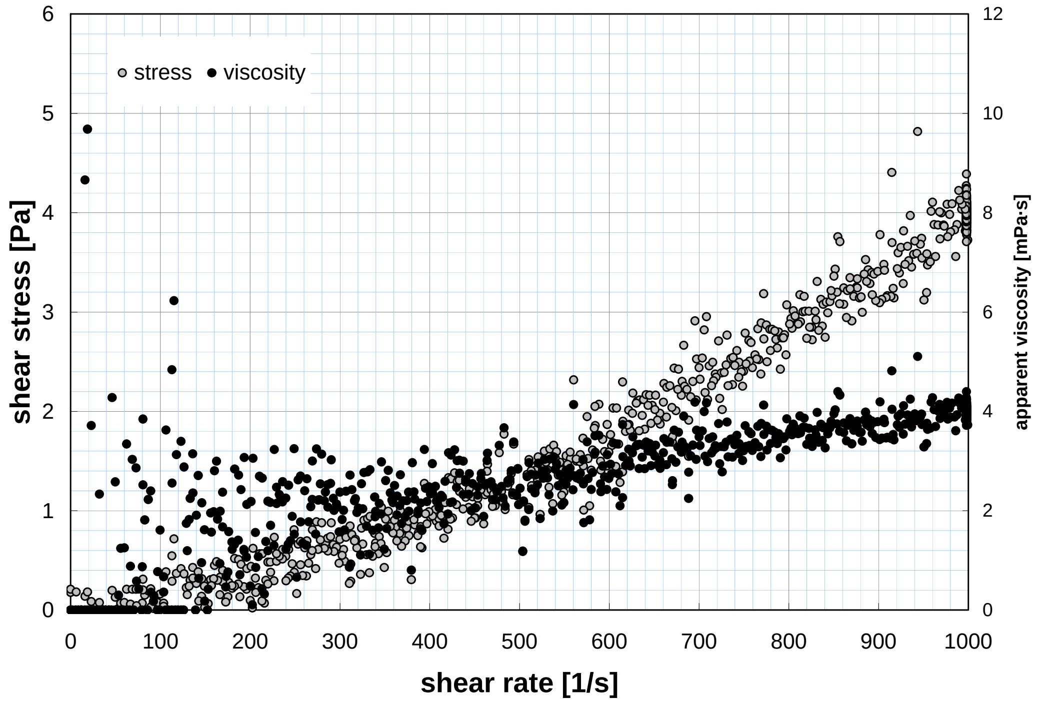


Figure R-2. Rheogram for TI601-G4-R1 at 25°C (measurement 2 of 2).

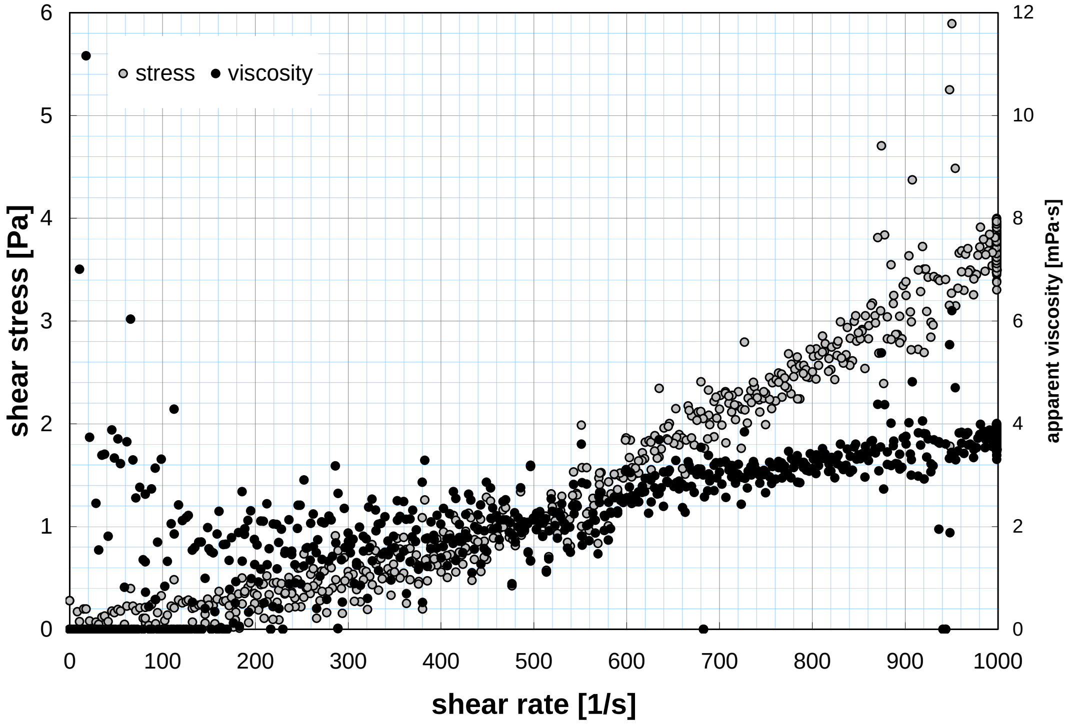


Figure R-3. Rheogram for TI601-G4-R1 at 40°C.

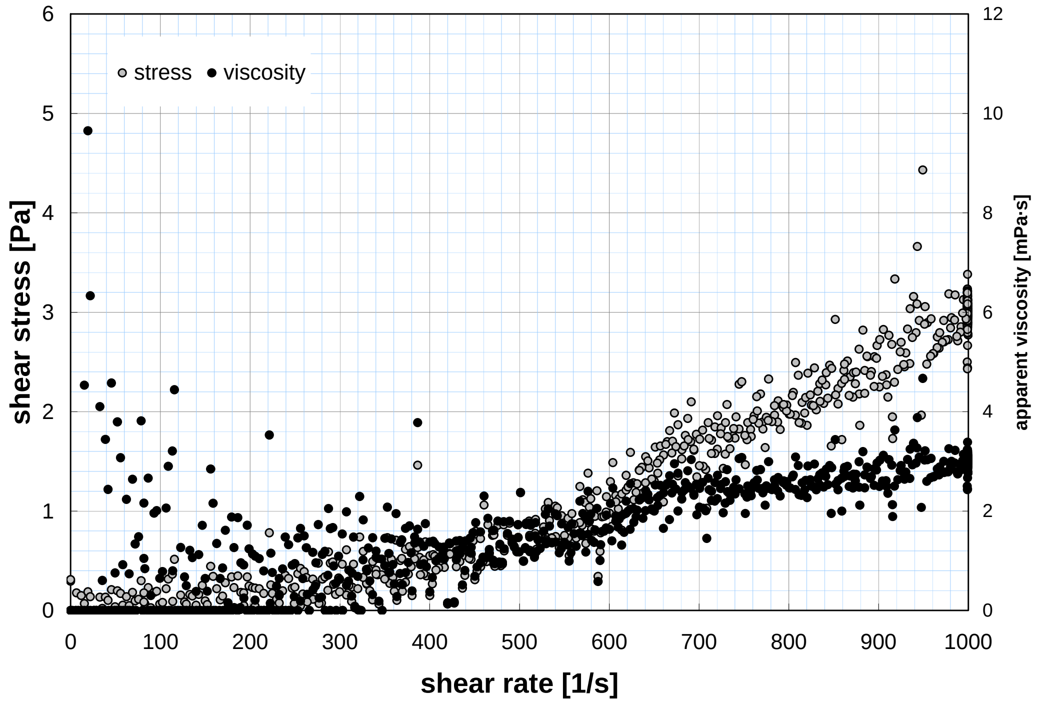


Figure R-4. Rheogram for TI601-G4-R1 at 60°C.

Sample TI601-G4-R2: Initial Concentrated Group 3/4 CUF Slurry

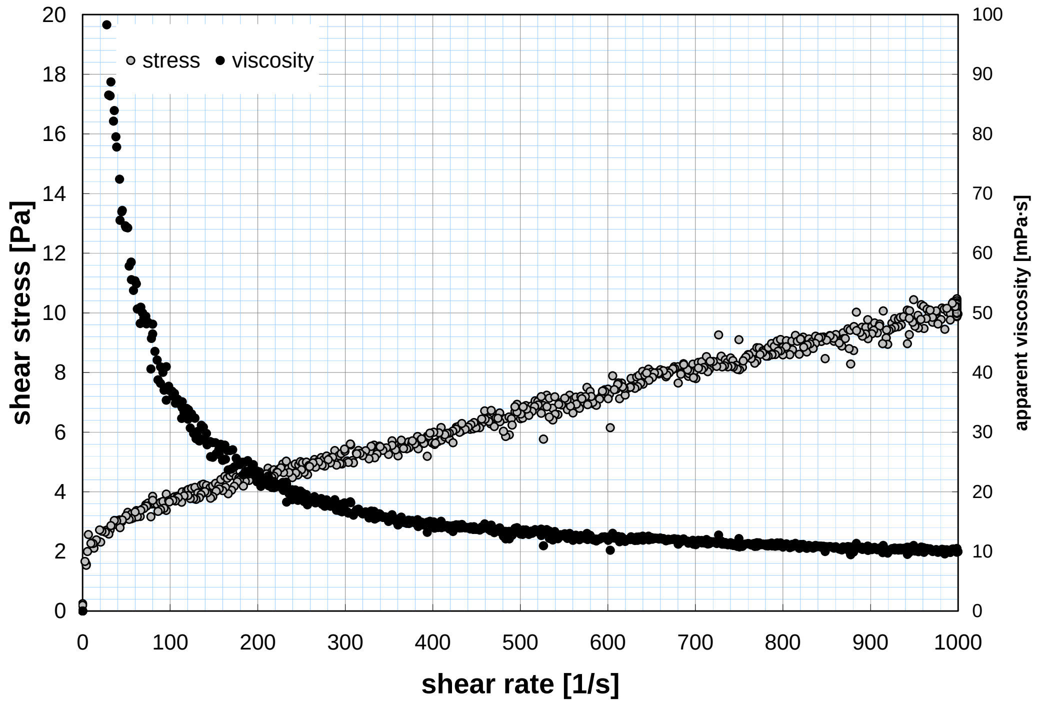


Figure R-5. Rheogram for TI601-G4-R2 at 25°C (measurement 1 of 2).

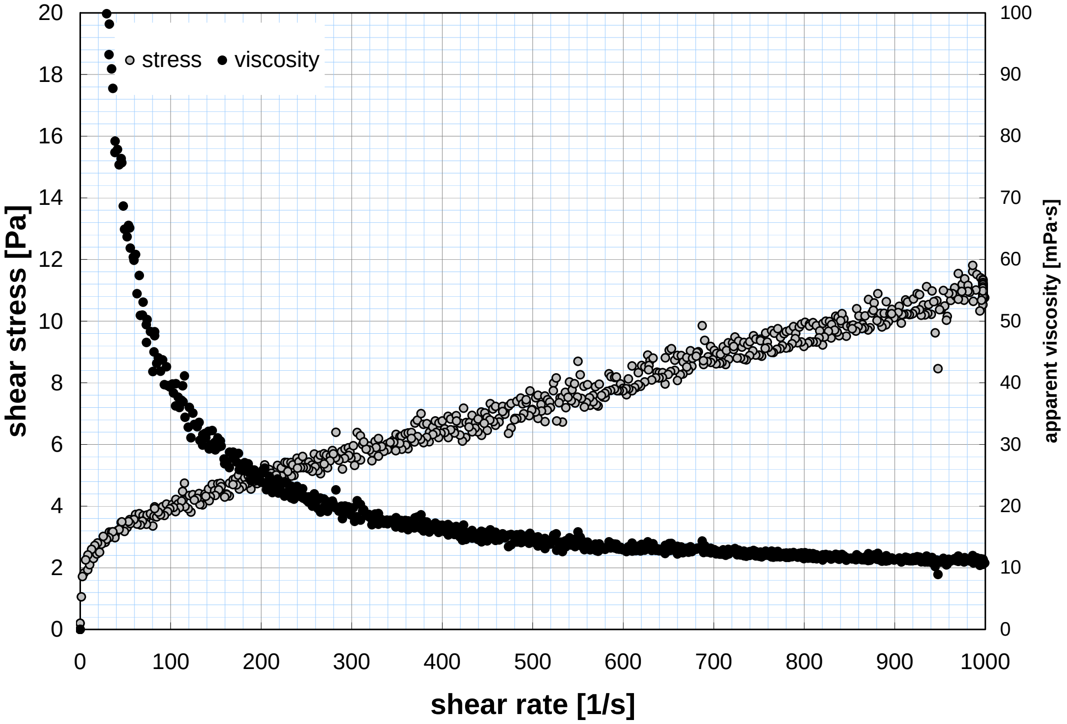


Figure R-6. Rheogram for TI601-G4-R2 at 25°C (measurement 2 of 2).

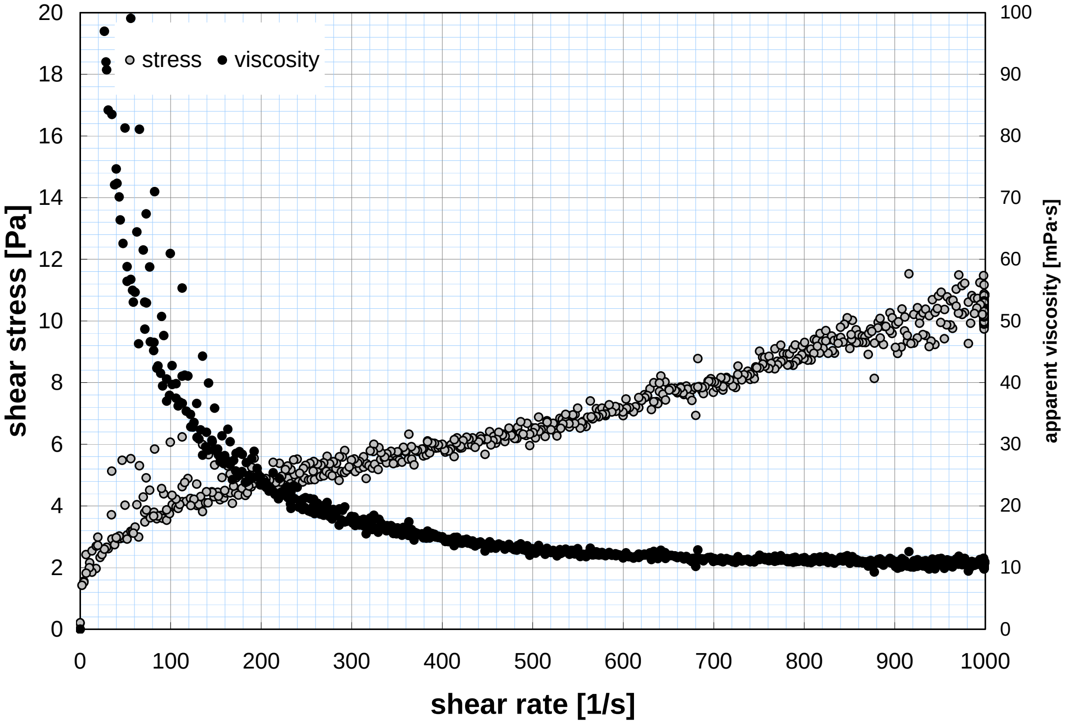


Figure R-7. Rheogram for TI601-G4-R2 at 40°C.

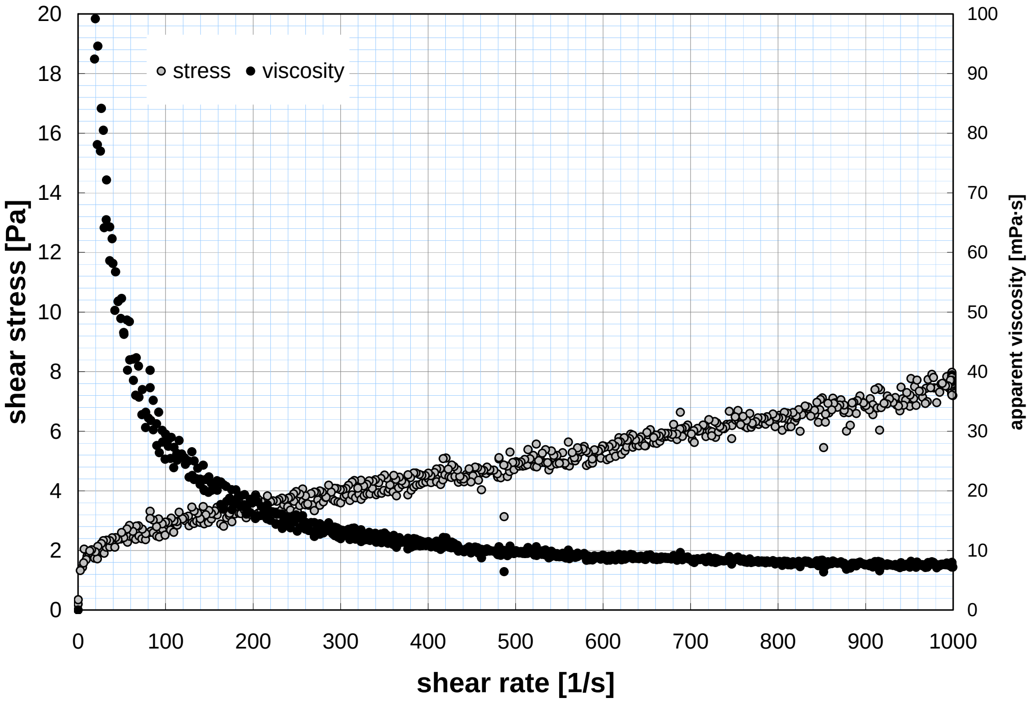


Figure R-8. Rheogram for TI601-G4-R2 at 60°C.

<u>Sample TI601-G4-R3: Caustic-Leached and Dewatered Group 3/4 CUF Slurry</u>

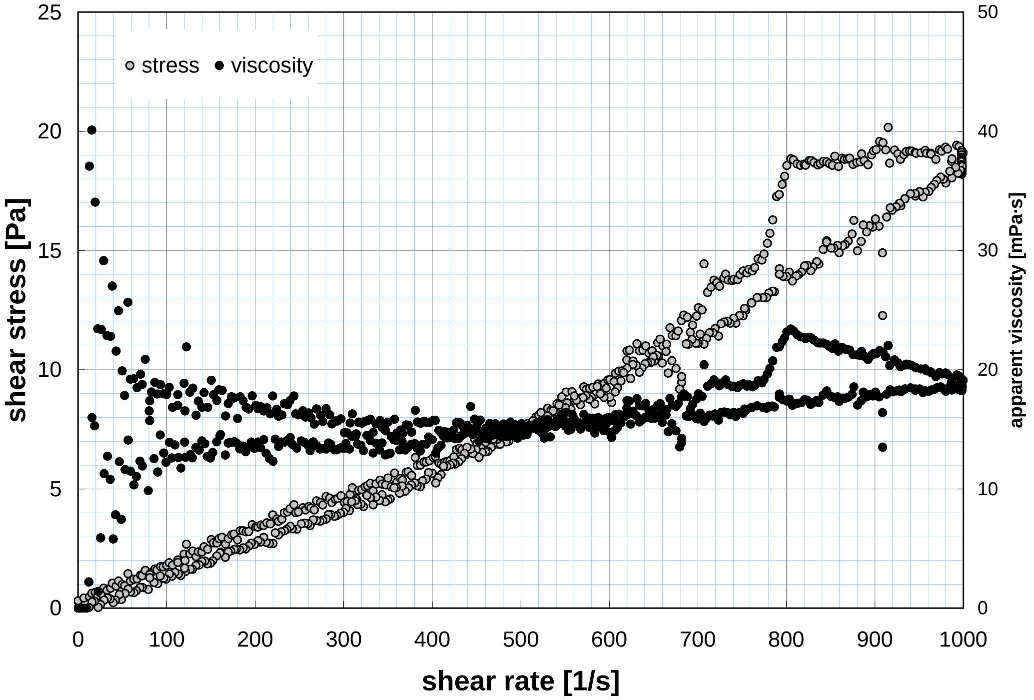


Figure R-9. Rheogram for TI601-G4-R3 at 25°C (measurement 1 of 2).

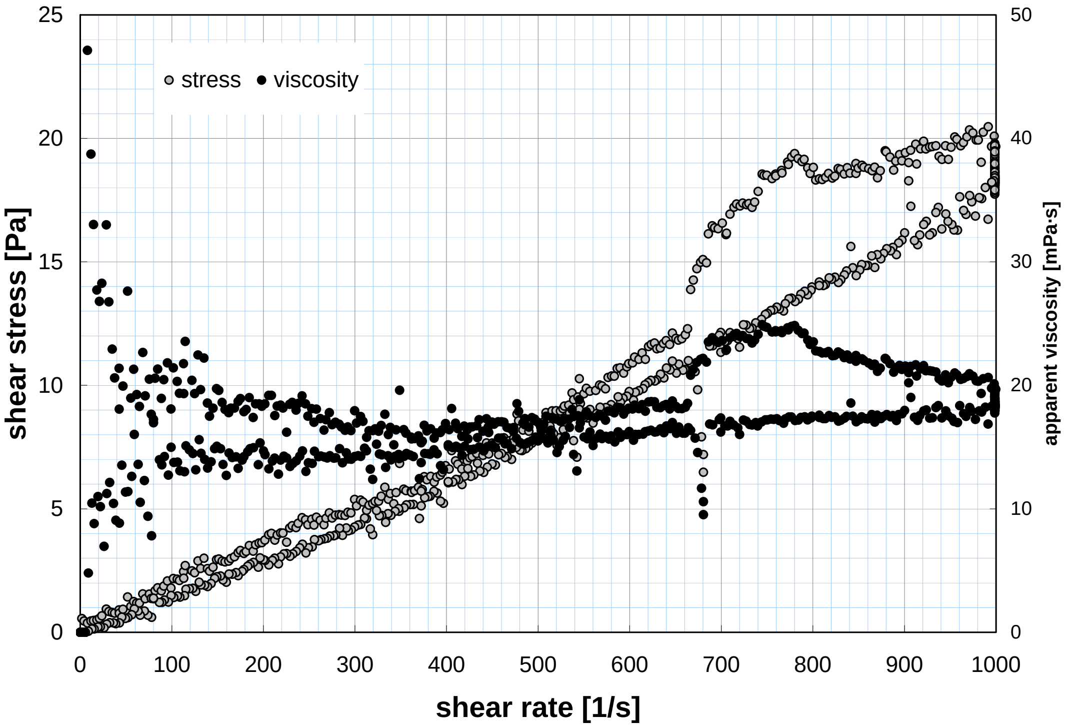


Figure R-10. Rheogram for TI601-G4-R3 at 25°C (measurement 2 of 2).

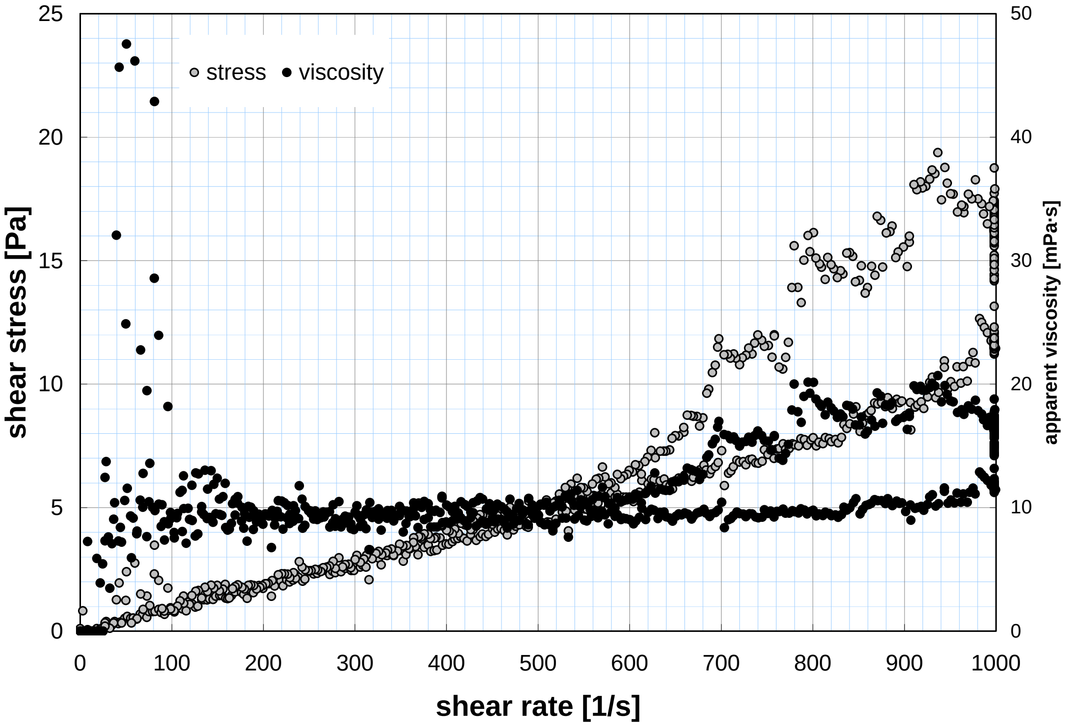


Figure R-11. Rheogram for TI601-G4-R3 at 40°C.

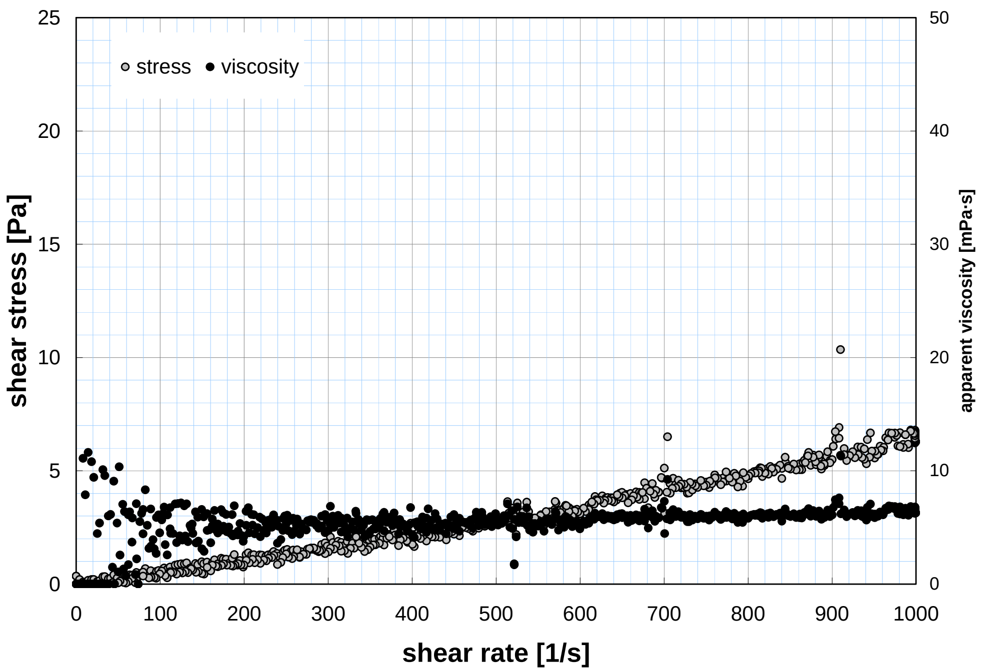


Figure R-12. Rheogram for TI601-G4-R3 at 60°C.

<u>Sample TI601-G4-R4: Caustic-Leached, Dewatered, and Washed Group 3/4 CUF Slurry</u>

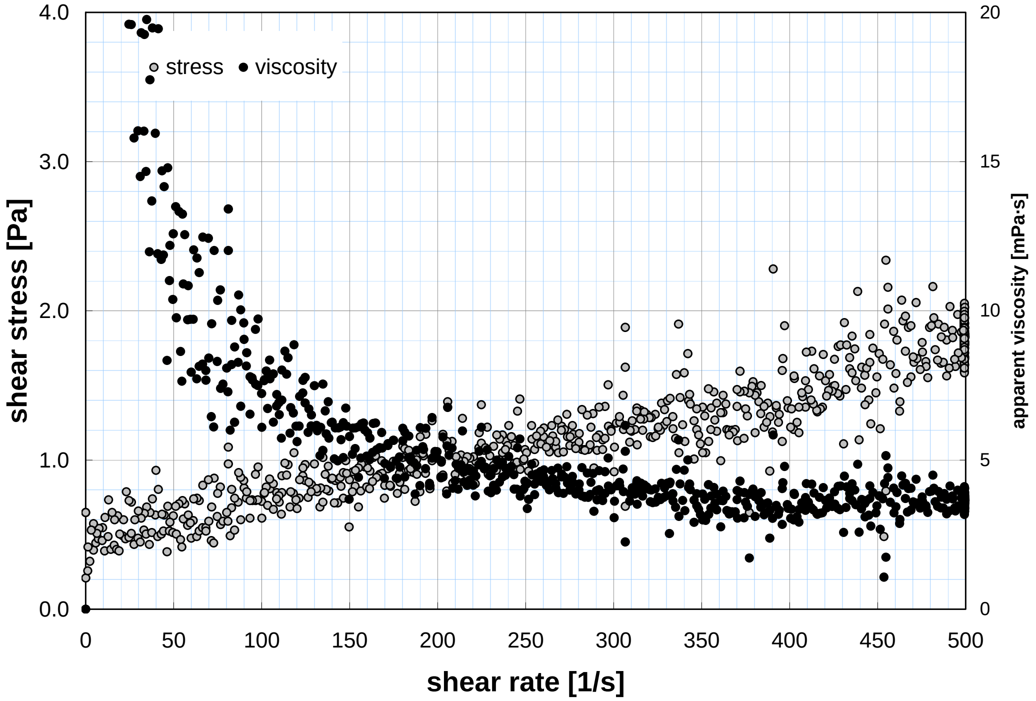


Figure R-13. Rheogram for TI601-G4-R4 at 25°C (measurement 1 of 2). For the measurement, an artificial stress offset of 0.5 Pa was included to prevent negative torque correction.

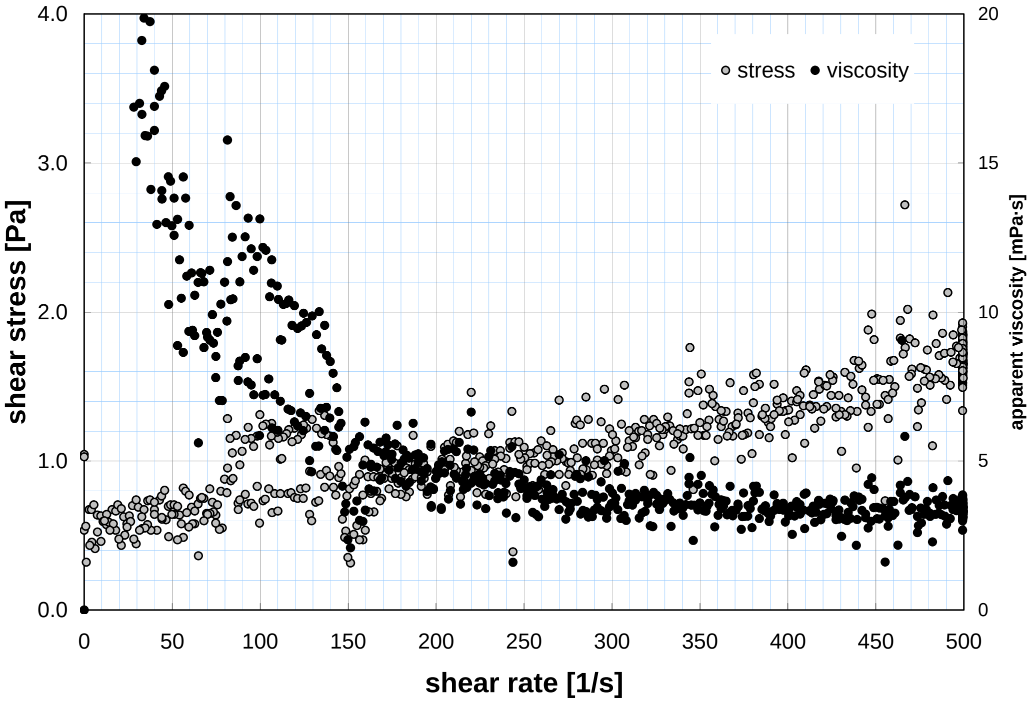


Figure R-14. Rheogram for TI601-G4-R4 at 25°C (measurement 2 of 2). For the measurement, an artificial stress offset of 0.5 Pa was included to prevent negative torque correction.

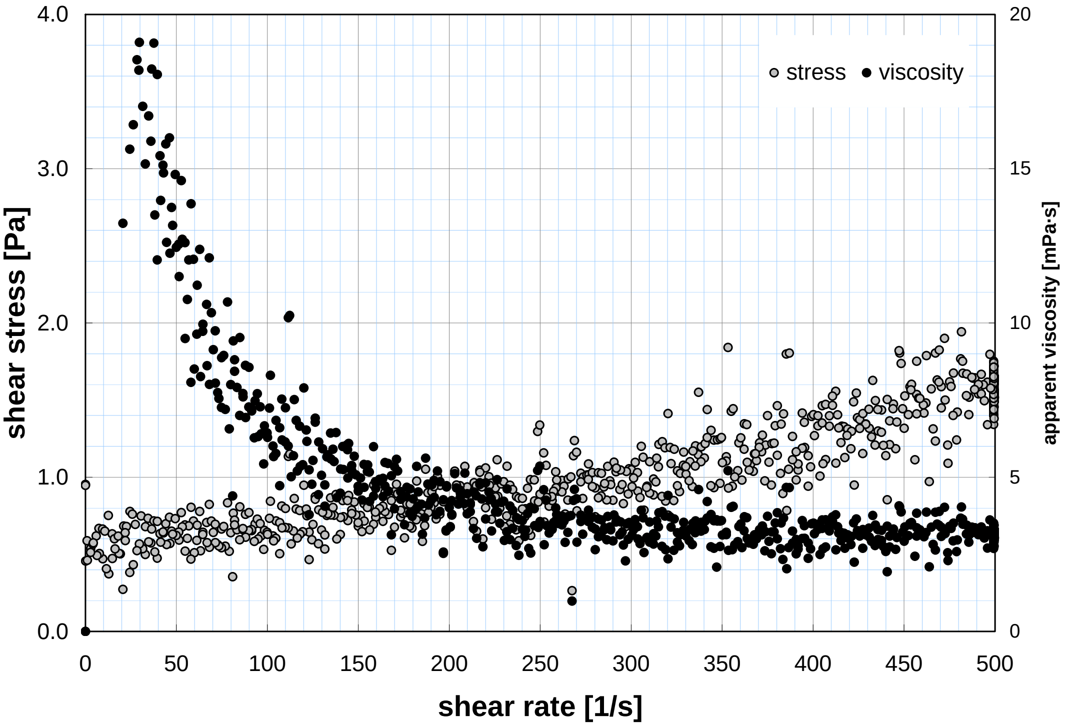


Figure R-15. Rheogram for TI601-G4-R4 at 40°C. For the measurement, an artificial stress offset of 0.5 Pa was included to prevent negative torque correction.

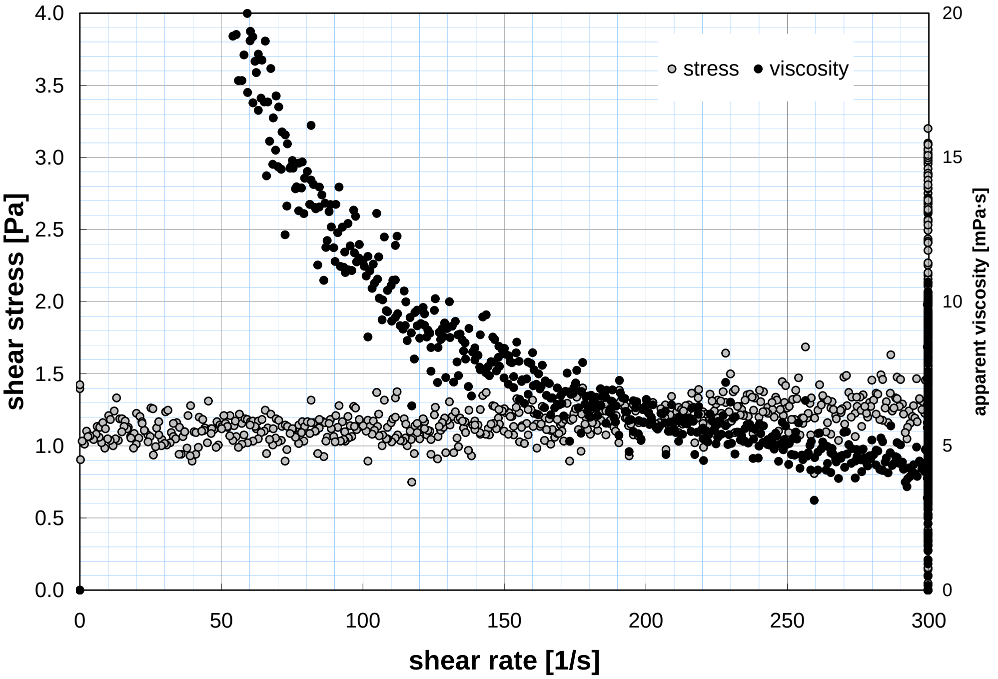


Figure R-16. Rheogram for TI601-G4-R4 at 60°C. For the measurement, an artificial stress offset of ~1 Pa was included to prevent negative torque correction.

Sample TI601-G4-R2S: Initial (Pre-Leach) Group 3/4 CUF Permeate

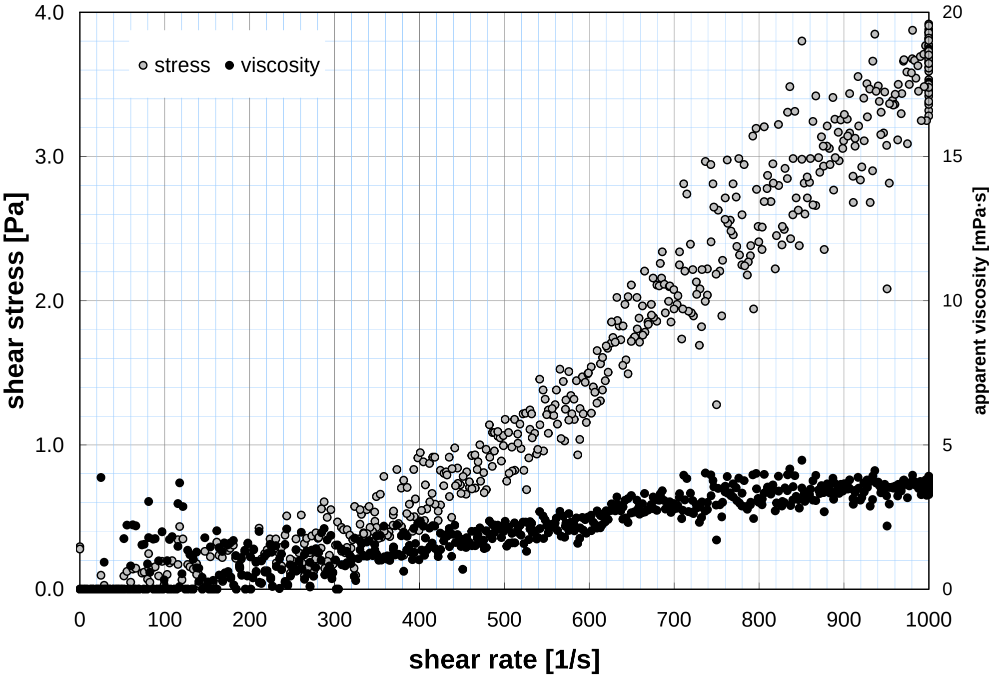


Figure R-17. Rheogram for TI601-G4-R2S at 25°C (measurement 1 of 2).

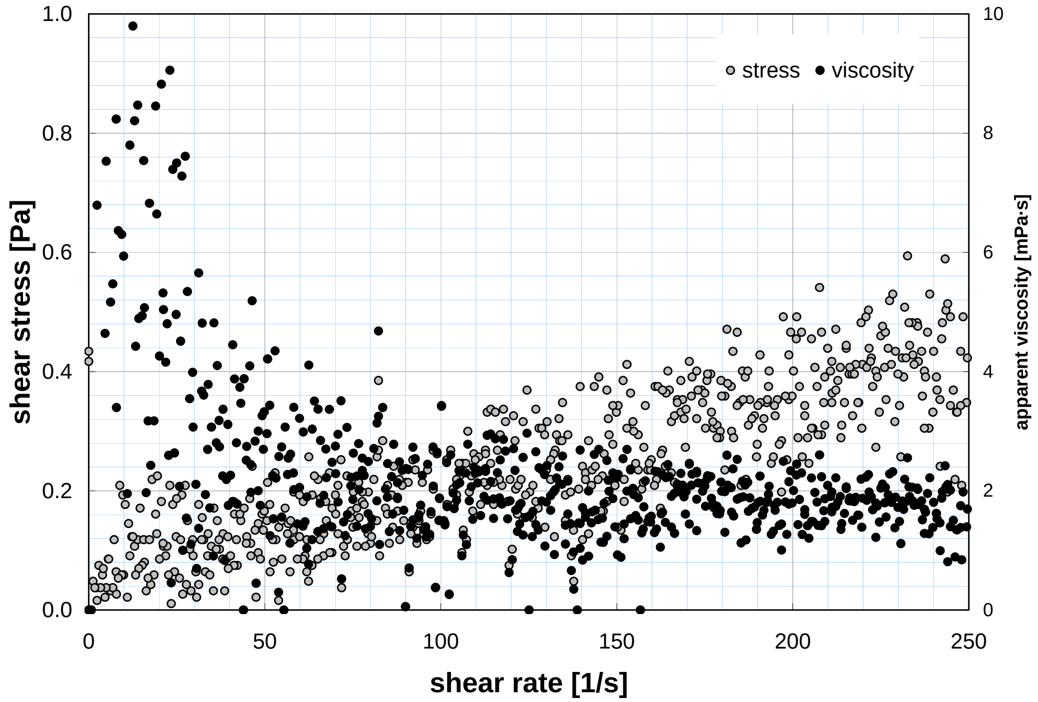


Figure R-18. Rheogram for TI601-G4-R2S at 25°C (measurement 2 of 2). For the measurement, an artificial stress offset of ~0.1 Pa was included to prevent negative torque correction.

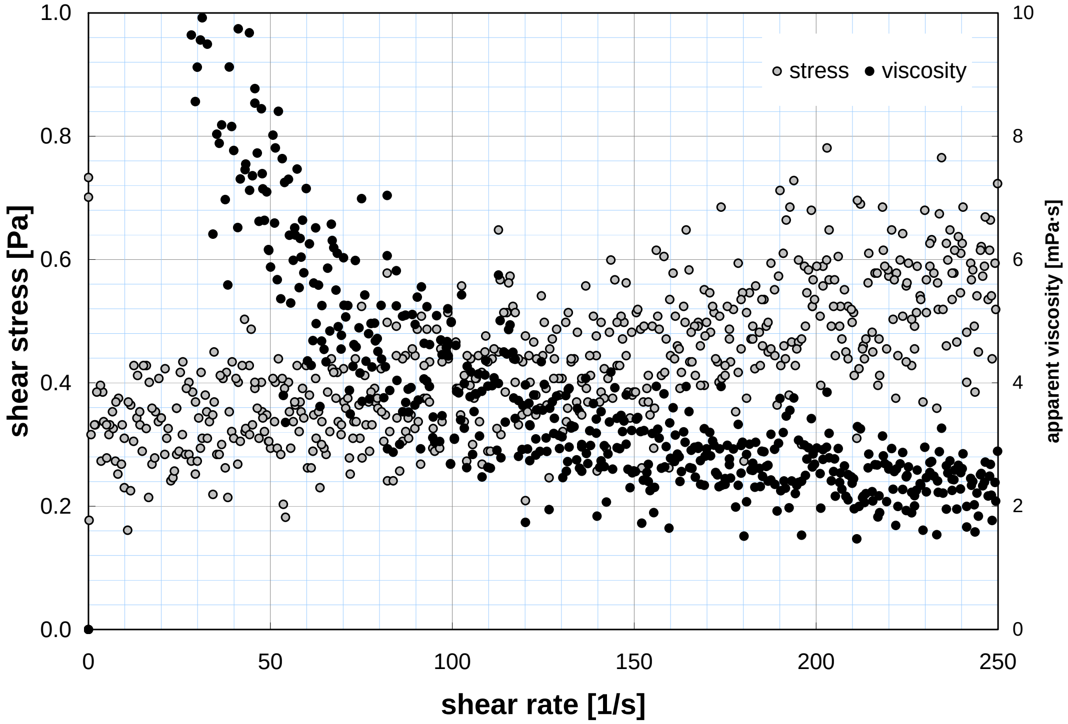


Figure R-19. Rheogram for TI601-G4-R2S at 40°C. For the measurement, an artificial stress offset of ~0.3 Pa was included to prevent negative torque correction.

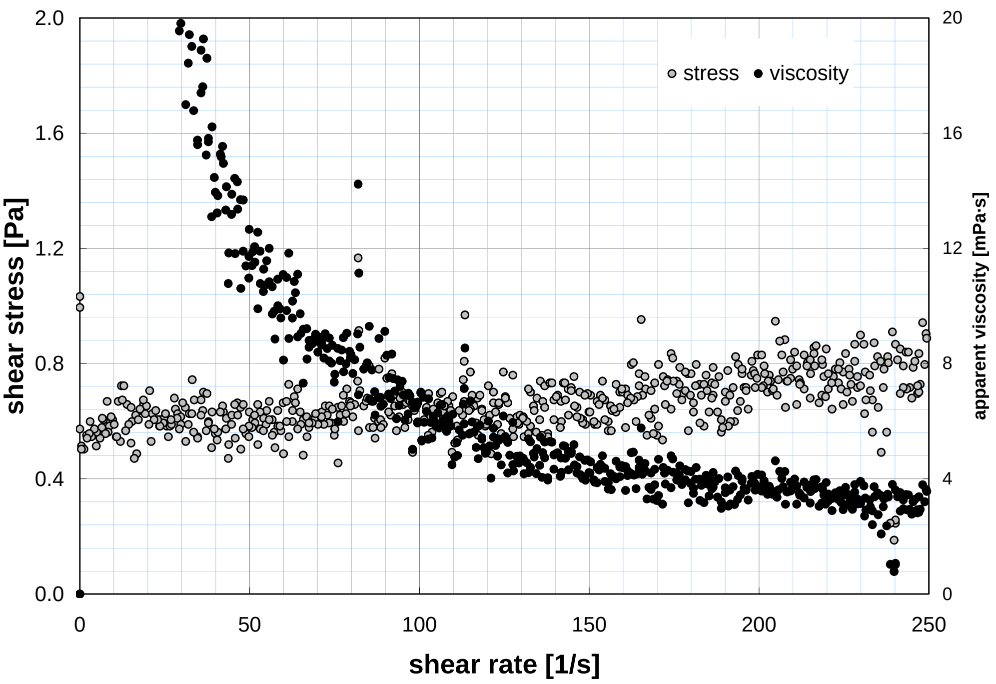


Figure R-20. Rheogram for TI601-G4-R2S at 60°C. For the measurement, an artificial stress offset of ~0.6 Pa was included to prevent negative torque correction.

Sample TI601-G4-R3S: Final (Post-Leach) Group 3/4 CUF Permeate

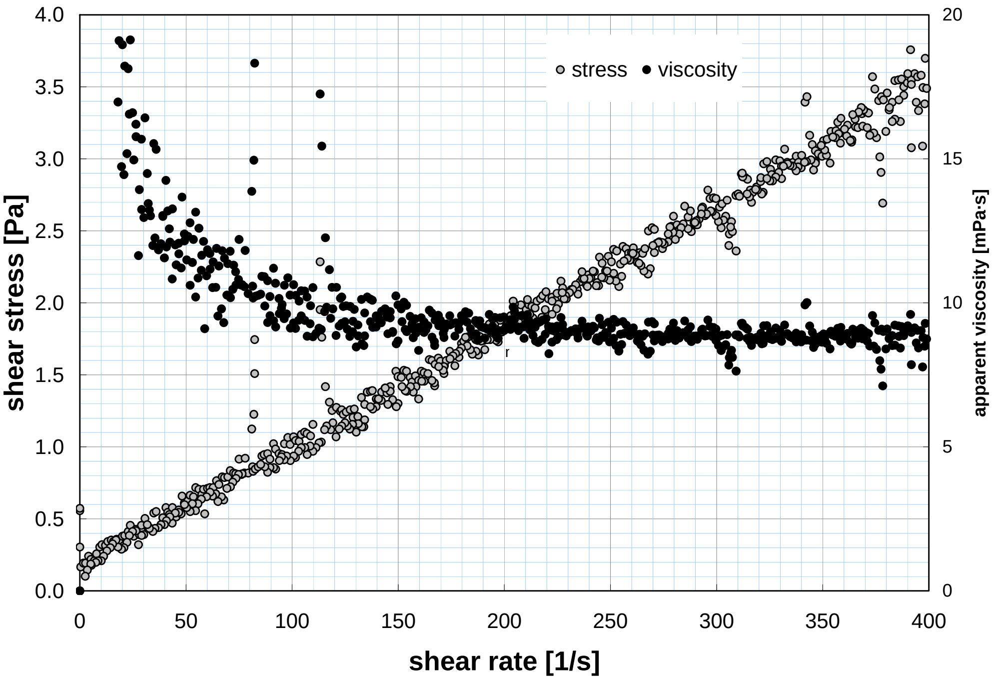


Figure R-21. Rheogram for TI601-G4-R3S at 25°C (measurement 1 of 2). For the measurement, an artificial stress offset of ~0.2 Pa was included to prevent negative torque correction.

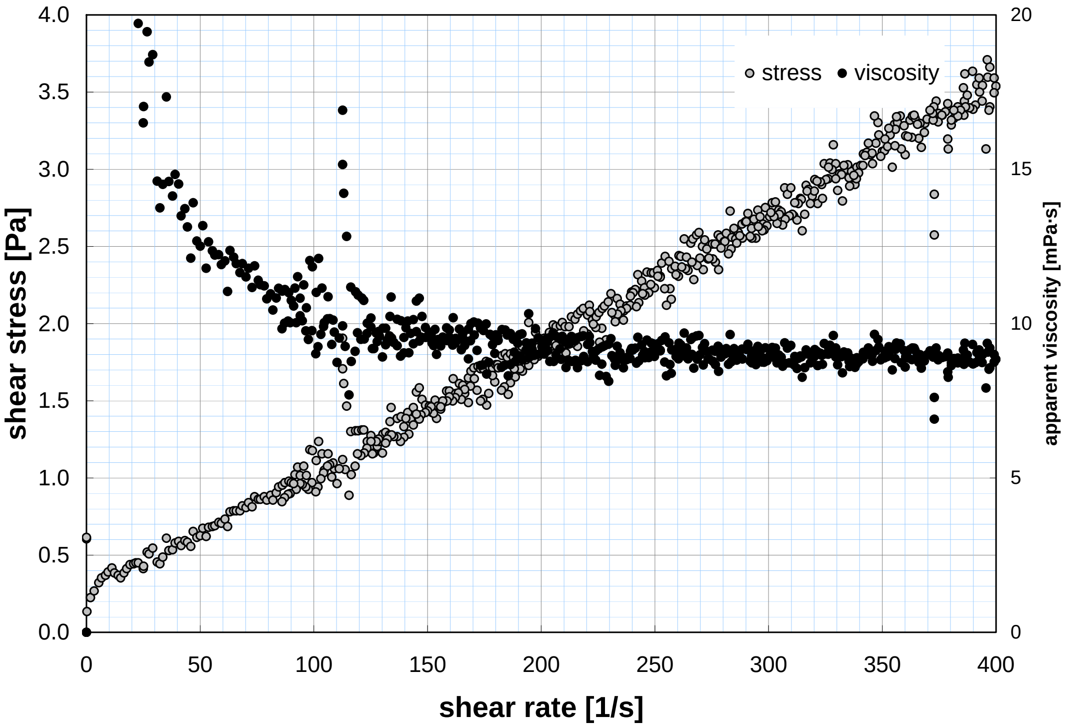


Figure R-22. Rheogram for TI601-G4-R3S at 25°C (measurement 2 of 2). For the measurement, an artificial stress offset of ~0.3 Pa was included to prevent negative torque correction.

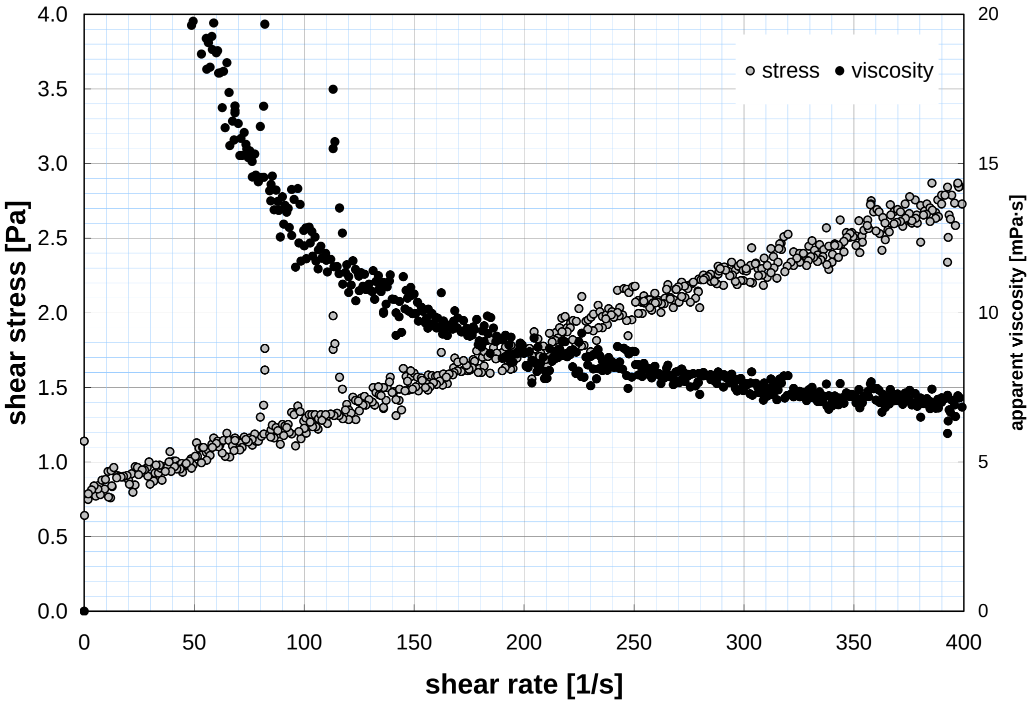


Figure R-23. Rheogram for TI601-G4-R3S at 40°C. For the measurement, an artificial stress offset of ~0.8 Pa was included to prevent negative torque correction.

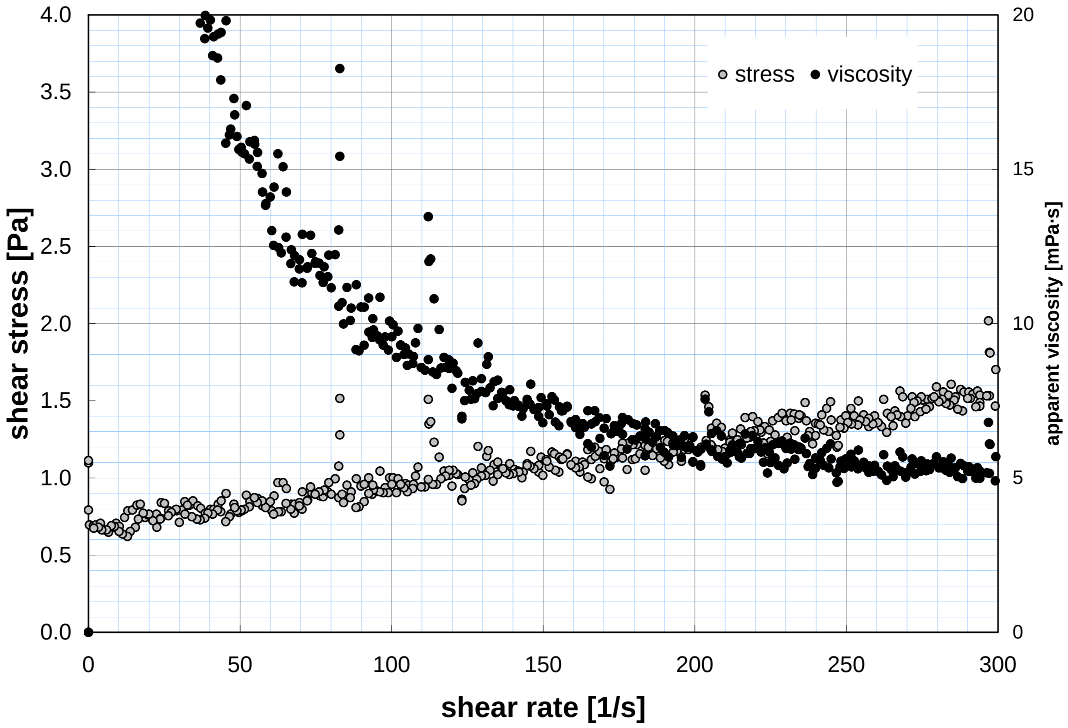


Figure R-24. Rheogram for TI601-G4-R3S at 60°C. For the measurement, an artificial stress offset of ~0.7 Pa was included to prevent negative torque correction.

Appendix G

Group 3/4 CUF Analytical Results

Appendix G: Group 3/4 CUF Analytical Results

Special Instructions for the
CUF Group 3/4 PUREX/REDOX Cladding Waste Treatability Study
Analysis Requirements

A blend of two composite materials containing liquid and sludge from Hanford waste tanks was subjected to CUF process as per TI-RPP-WTP-601. The first composite blend was from tanks B-108, B-109, BY-109, C-103, C-104, and C-105, representing waste described as PUREX Cladding Waste Sludge (Group 3). The second composite blend was comprised of material from tanks 241-U-105, 241-U-204, 241-U-201, 241-U-202, and 241-U-203, representing tank waste described as REDOX Cladding Waste Sludge (Group 4). The start date for this treatability study is February 17th, 2008. Color code: `Fluorescent Orange`.

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.

SAL Preparation/Analysis

Please record observations associated with the dissolution preparations. 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) will be provided. For radiochemistry, the reference date shall be February 17, 2008 for samples from TI-RPP-WTP-601.

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.**

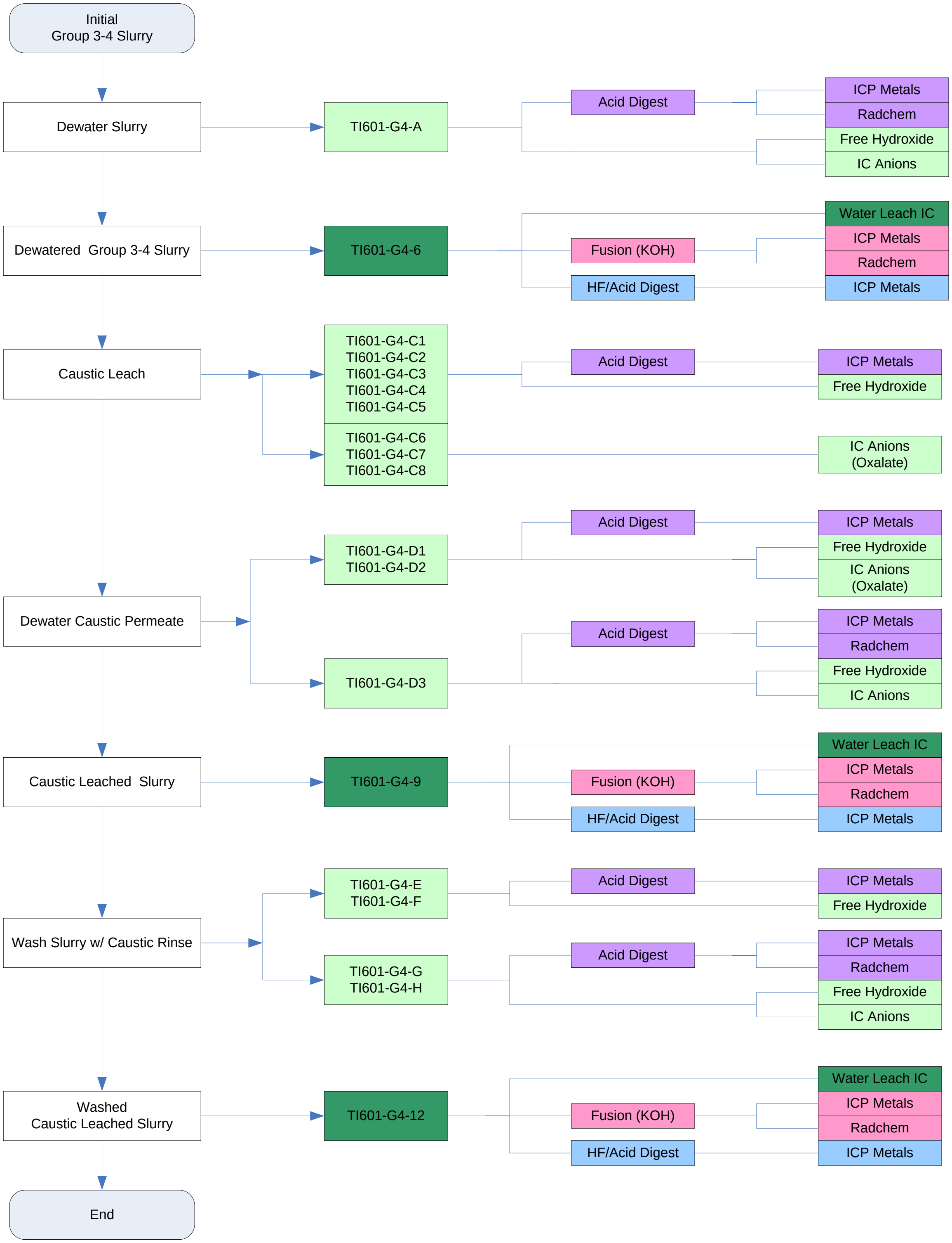


Figure 1: TI-RPP-WTP-601 Process Sampling Plan

Table 1. Cross-Reference of Process component, Sample ID, and RPL ID

Component	Sample ID	ASO ID
Dewater filtrate	TI601-G4-A	08-01365
Dewatered Caustic leach, End of Matrix	TI601-G4-D3	08-01366
wash 3 permeate	TI601-G4-G	08-01367
Wash 4 permeate	TI601-G4-H	08-01368
Caustic leach filtrate, 1 hour heat up	TI601-G4-C1	08-01369
Caustic leach filtrate, 3 hour heat up	TI601-G4-C2	08-01370
Caustic leach filtrate, 0 hour leach	TI601-G4-C3	08-01371
Caustic leach filtrate, 4 hour leach	TI601-G4-C4	08-01372
Caustic leach filtrate, 8 hour leach	TI601-G4-C5	08-01373
wash 1 permeate	TI601-G4-E	08-01374
wash 2 permeate	TI601-G4-F	08-01375
Dewatered Caustic leach, Initial	TI601-G4-D1	08-01376
Dewatered Caustic leach, Final	TI601-G4-D2	08-01377
Caustic leach filtrate, 0 hour cool-down	TI601-G4-C6	08-01378
Caustic leach filtrate, 6 hour cool-down	TI601-G4-C7	08-01379
Caustic leach filtrate, 12 hour cool-down	TI601-G4-C8	08-01380
Dewatered Slurry	TI601-G4-6	08-01381
Caustic Leached Slurry	TI601-G4-9	08-01382
Washed Caustic Leached Slurry	TI601-G4-12	08-01383

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-601			
Dewatered slurry **(TI601-G4-6)**		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 **(TI601-G4-A)**		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 **(TI601-G4-C1, TI601-G4-C2, TI601-G4-C3, TI601-G4-C4, TI601-G4-C5)**		Direct distribution • Free hydroxide	
		Acid digestion • ICP metals (Table 3)	
Time interval Caustic Leach filtrates - Oxalate **(TI601-G4-C6, TI601-G4-C7, TI601-G4-C8)**		Direct distribution • Anions / Oxalate Only	
Caustic-leached permeate **(TI601-G4-D1, TI601-G4-D2)**		Acid digestion • ICP metals (Table 3)	
		Direct distribution • Free hydroxide • Anions / Oxalate Only	
Caustic-leached permeate **(TI601-G4-D3)**		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 (TI601-G4-9)		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 (TI601-G4-E, TI601-G4-F)		Direct distribution • Free hydroxide	
		Acid digestion • ICP metals (Table 3)	
Third wash and combined wash composite following caustic leach (TI601-G4-G, TI601-G4-H)		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 (TI572-G2-12)		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)	

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

Analyte	Analytical Technique	Liquids			Solids		
		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)

APR 15 TTC

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)

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*

If *Yes*, Contact ASO Lead before submitting Samples
☐ 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

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

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:**
  5/26/08
  (*To be completed by ASO Lead*)

KNP, LRG, LPD, CZS, KJC, KKT, MJS, RGS, BMO, IEB

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: 4/29/08
Delivered By (optional) ____________________
Time Delivered (optional) ____________________
Group ID (optional) _RPP-WTP/Task No: [ ]
CMC Waste Sample? X No ☐ Yes

Received By: T Teang-Le
ASR Number: ____**8125**________ Rev.: ___**00**______
RPL Numbers: _____**08-01365 to 08-01383**______
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** Karl N. Pool 4/15/08

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 RPL Number	Client Sample ID	Sample Description (& Matrix, If Varies)	Analysis Requested	ASO Staff Use Only Test	ASO Staff Use Only Library
08-01365	TI601-G4-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 Analys "
08-01366	TI601-G4-D3	Dewater Caustic Leach – End of Run		Prep-128 ICP GEA	Lab Analys Radchem
08-01367	TI601-G4-G	Wash 3 Permeate		Alpha Beta Pu-AEA SR-90	↓
08-01368	TI601-G4-H	Wash 4 Permeate		U-KPA	
08-01369	TI601-G4-C1	Caustic Leach Filtrate – 1 hour heat	Direct Analyses 1) OH 2) IC (08- 01376 and 08- 01377 only – Oxalate only) Acid Digest – 128 (Prep Lab) 1) ICP/OES	OH	Lab Analyses
08-01370	TI601-G4-C2	Caustic Leach Filtrate – 3 hour heat		IC	Lab Analyse
08-01371	TI601-G4-C3	Caustic Leach Filtrate – 0 hour heat			
08-01372	TI601-G4-C4	Caustic Leach Filtrate – 4 hour heat			
08-01373	TI601-G4-C5	Caustic Leach Filtrate – 8 hour heat		Prep-128	
08-01374	TI601-G4-E	Wash 1 permeate		ICP	Lab Analyses
08-01375	TI601-G4-F	Wash 2 permeate			
08-01376	TI601-G4-D1	Dewatered Caustic Leach, Initial			
08-01377	TI601-G4-D2	Dewatered Caustic Leach, Final			
08-01378	TI601-G4-C6	Oxidative Wash 1 Permeate	Direct Analyses 1) IC – Oxalate Only	IC	Lab Analyse
08-01379	TI601-G4-C7	Oxidative Wash 2 Permeate			
08-01380	TI601-G4-C8	Group 5/6 Slurry Permeate			

ASR # 8125 Rev.: 00

Page 1 of 2

ASR 8125 - Group 3-4 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
08-01381	TI601-G4-6	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	Lab Analy Radchem
08-01382	TI601-G4-9	Caustic Leach Slurry		Alpha Beta Pu-AEA Sr-90 U-KPA	↓
08-01383	TI601-G4-12	Washed Caustic Leached Slurry		Prep-138 ICP Prep-103 IC	Lab Analy Lab Analy

ASR # 8125 Rev.: 00

Page 2 of 2

Battelle PNNL/RS&E/Inorganic Analysis ... ICPOES Analysis Report

PO Box 999, Richland, Washington 99352

Project / WP#: 52964 / F99189
ASR#: 8125
Client: R. Shimskey
Total Samples: 3 (solid)

	First	Last
RPL#:	08-01381	08-01383
Client ID:	TI6-1-G4-6	TI6-1-G4-12
Sample Preparation: PNL-ALO-115, "Solubilization of Metals from Solids using a KOH-KNO_3 Fusion", 4/23/08 (SAL/dk).		

Procedure: RPG-CMC-211, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICPOES)", Rev 2.

Analyst: P. Berry

Analysis Date (File): 04-28-2008 (C0127)

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE Number: N827583 (ICPOES instrument)
M19445 (Mettler AT400 Balance)

B.M. Oliver 4/30/08
Preparer

C. G. Ylampe 5/2/08
Review and Concur

Battelle PNNL/RS&E/Inorganic Analysis ... ICPOES Analysis Report

Three samples submitted under Analytical Service Request (ASR) 8125 were analyzed by ICPOES. 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 ICPOES 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 ICPOES 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 8125 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).

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the fusion process. Except for manganese, 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. The manganese was measured at a level of about 50 µg/g, which exceeded the 5% requirement for Samples 08-01381 (and duplicate) and 08-01382. The source of the magnesium is not known but is believed to be from contamination originating in the SAL.

Blank Spike (BS)/Laboratory Control Sample (LCS):

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. Except for silicon (49%), the recovery values were within the acceptance criterion of 80% to 120% for all AOIs meeting the above requirement. The reason for the silicon under-recovery is not understood, but is believed to be an issue with the preparation process in the SAL. All other QC for silicon was within appropriate acceptance requirements. Because of the under-recovery, the reported values for silicon in the samples should be considered as being potentially biased low.

Matrix-Spiked Sample:

No matrix spike sample was provided for analysis.

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 (~40%), 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 sample heterogeneity as all other analytes were well within the acceptance criterion.

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, S, 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, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	4/28/2008	4/28/2008	4/28/2008	4/28/2008	4/28/2008
		Multiplier >	3420.6	3465.0	3429.4	3061.8	3808.1
		RPL/LAB >	08-01381-115-B @5	08-01381-115-S @5 rr	08-01381-115-D @5	08-01382-115-S @5	08-01383-115-S @5
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Prep Blank	TI6-1-G4-6		TI6-1-G4-9	TI6-1-G4-12
(µg/mL)	(µg/mL)	(Analyte)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
0.2900	2.900	Al	--	127,000	129,000	54,700	56,300
0.0077	0.077	B	[80]	[210]	[230]	[130]	[190]
0.0240	0.240	Bi	--	[730]	[710]	[630]	3,090
0.0029	0.029	Cd	--	--	--	--	[16]
0.0024	0.024	Cr	[59]	690	655	552	2,200
0.1800	1.800	Fe	--	[5,700]	[5,500]	5,750	28,300
4.0000	40.000	K	na	na	na	na	na
0.0011	0.011	Mn	49.7	546	526	539	2,300
1.9000	19.000	Na	--	180,000	175,000	386,000	343,000
0.0400	0.400	Ni	na	na	na	na	na
0.0540	0.540	P	--	12,400	11,500	7,890	6,140
0.1600	1.600	S	--	[2,000]	[2,100]	--	[730]
0.2300	2.300	Si	--	[5,600]	[5,400]	[5,400]	22,900
0.0003	0.005	Sr	[0.97]	25.5	25.8	35.8	155
0.0410	0.820	U	--	3,710	3,620	3,640	15,700
0.0032	0.064	Zn	[93]	262	287	[140]	[220]
0.0035	0.035	Zr	--	1,310	870	593	825
Other Analytes							
0.0015	0.015	Ag	--	--	--	--	[20]
0.0390	0.390	As	[350]	[230]	[170]	[420]	[320]
0.0005	0.010	Ba	[5.3]	[30]	[32]	[31]	118
0.0000	0.000	Be	--	[1.1]	[1.1]	[0.42]	[0.72]
1.1000	11.000	Ca	--	--	--	--	--
0.0083	0.083	Ce	--	--	--	--	[81]
0.0027	0.027	Co	--	--	--	--	[40]
0.0020	0.020	Cu	[28]	[60]	[61]	[41]	102
0.0029	0.029	Dy	--	--	--	--	--
0.0004	0.004	Eu	--	--	--	--	--
0.0027	0.027	La	--	[11]	--	--	[65]
0.0019	0.019	Li	[11]	[16]	[16]	[15]	[29]
0.0052	0.052	Mg	--	[160]	[150]	[130]	646
0.0072	0.072	Mo	--	--	--	[26]	--
0.0062	0.062	Nd	--	[34]	[35]	[25]	[110]
0.0320	0.320	Pb	--	1,130	[1,000]	[610]	1,640
0.0064	0.064	Pd	--	--	--	--	--
0.0130	0.130	Rh	[50]	--	[60]	--	--
0.0067	0.067	Ru	--	--	--	[33]	[53]
0.0310	0.310	Sb	--	--	--	--	--
0.1100	1.100	Se	--	--	--	--	--
0.0250	0.250	Sn	--	--	--	--	--
0.0200	0.200	Ta	--	--	--	[70]	[100]
0.0260	0.260	Te	--	--	--	--	--
0.0084	0.084	Th	--	[62]	[54]	[54]	[240]
0.0005	0.005	Ti	[3.1]	33.5	31.8	32.9	137
0.0300	0.300	Tl	--	--	[140]	--	--
0.0032	0.032	V	--	[14]	--	[13]	[26]
0.0210	0.210	W	--	--	--	--	--
0.0003	0.003	Y	[2.1]	[4.7]	[4.4]	[5.3]	16.1

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 4/28/08

Criteria >	≤ 25%	80%-120%	70%-130%	70%-130%	70%-130%	≤ 10%
QC ID >	08-01381 Dup	LCS/BS (01381)	MS (none)	08-01381 + AS-A	08-01381 + AS-B	08-01381 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	1.1	97		111		7.0
B				100		
Bi				92		
Cd				92		
Cr	5.2			99		9.5
Fe		95		104		
K	na	na	na	na	na	na
Mn	3.8	97		96		6.1
Na	3.0			101		
Ni	na	na	na	na	na	na
P	7.6			97		4.3
S					94	
Si		49		103		
Sr	1.2			102		
U	2.4				97	
Zn	9.2	94		100		
Zr	40.3			100		5.9
Other Analytes						
Ag				92		
As				93		
Ba		95		98		
Be				99		
Ca				99		
Ce					95	
Co				96		
Cu		97		100		
Dy					97	
Eu					95	
La					93	
Li				101		
Mg		95		97		
Mo				97		
Nd					92	
Pb		92		95		
Pd					93	
Rh					98	
Ru					92	
Sb				95		
Se				93		
Sn				92		
Ta				98		
Te					95	
Th					93	
Ti	5.3	88		95		
Tl				89		
V				93		
W				92		
Y				95		

Shaded results are outside the acceptance criteria.

nr = not recovered; spike concentration less than 25% of sample concentration.

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/RS&E/Inorganic Analysis ... ICPOES Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#: 52964 / F99189
ASR#: 8125
Client: R. Shimskey
Total Samples: 13 (liquid)

	First	Last
RPL#:	08-01365	08-01377
Client ID:	TI601-G4-A	TI601-G4-D2
Sample Preparation: RPG-CMC-128, "HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater", 6/2/08 (SRPL/ld).		

Procedure: RPG-CMC-211, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICPOES)", Rev 2.

Analyst: J. Deschane

Analysis Date (File): 06-04-2008 (C0138)

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE Number: N827583 (ICPOES instrument)
M19445 (Mettler AT400 Balance)

B.M. Olsen 6/12/08
Preparer

6/16/08
Review and Concur

Battelle PNNL/RS&E/Inorganic Analysis ... ICPOES Analysis Report

Thirteen samples submitted under Analytical Service Request (ASR) 8125 were analyzed by ICPOES. 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 ICPOES 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 ICPOES 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 8125 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, -2B, and -3 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

Page 1 of 3

		Run Date >	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008
		Multiplier >	24.4	121.9	122.3	611.5	123.7	123.4	123.8
		RPL/LAB >	BLK-01365	08-01365 @5	08-01366 @5	08-01366 @25	08-01367 @5	DUP-01367 @5	08-01368 @5
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Prep blank	TI601-G4-A	TI601-G4-D3		TI601-G4-G		TI601-G4-H
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0060	0.060	Al	--	1,440	24,000		3,580	3,590	8,620
0.0048	0.096	B	[0.16]	16.5	38.8		[5.0]	[3.9]	[11]
0.0300	0.300	Bi	[7.2]	--	[29]		[5.3]	--	[8.2]
0.0034	0.034	Cd	[0.32]	[2.2]	[1.7]		[1.4]	[1.1]	[1.3]
0.0017	0.017	Cr	--	58.1	73.8		11.8	12.2	28.2
0.0024	0.048	Fe	[0.10]	[1.7]	23.3		[2.2]	[2.1]	[5.5]
0.0720	0.720	K	[6.5]	436	595		96.7	102	202
0.0002	0.005	Mn	--	[0.078]	[0.20]		[0.040]	[0.053]	[0.085]
0.0160	0.320	Na	--	68,100	over-range	180,000	41,900	42,100	80,800
0.0024	0.024	Ni	--	8.32	[2.1]		--	[0.41]	[0.71]
0.0500	0.500	P	--	3,550	542		1,650	1,630	1,390
0.1600	1.600	S	[4.5]	728	370		[54]	[56]	[140]
0.0056	0.056	Si	--	19.2	101		12.8	12.8	27.6
0.0001	0.002	Sr	[0.0021]	[0.068]	[0.020]		--	--	--
0.0320	0.320	U	--	[31]	--		[4.3]	--	--
0.0028	0.056	Zn	[1.2]	[1.3]	42.0		8.24	[6.8]	15.7
0.0011	0.011	Zr	--	--	3.32		[1.3]	[1.3]	4.22
Other Analytes									
0.0021	0.021	Ag	--	--	--		--	--	--
0.0430	0.430	As	--	--	--		--	--	--
0.0003	0.005	Ba	[0.10]	[0.25]	[0.32]		[0.11]	[0.14]	[0.17]
0.0001	0.001	Be	--	--	0.176		[0.023]	[0.031]	0.0651
0.0061	0.061	Ca	[0.84]	[7.4]	--		--	--	--
0.0100	0.100	Ce	--	--	--		--	--	--
0.0024	0.024	Co	[0.070]	[0.35]	[0.43]		--	--	--
0.0014	0.014	Cu	--	[0.27]	4.70		[0.43]	[0.18]	[1.3]
0.0029	0.029	Dy	--	--	--		--	--	--
0.0011	0.011	Eu	--	--	--		--	--	--
0.0028	0.028	La	--	--	--		--	--	--
0.0006	0.012	Li	[0.043]	[0.46]	[1.4]		[0.66]	[0.75]	[0.90]
0.0023	0.023	Mg	--	--	--		--	--	--
0.0052	0.052	Mo	--	[2.5]	[3.0]		--	[0.67]	[1.2]
0.0054	0.054	Nd	--	--	--		--	--	--
0.0320	0.320	Pb	[1.7]	[38]	177		[14]	[14]	53.9
0.0063	0.063	Pd	--	--	--		--	--	--
0.0120	0.120	Rh	--	--	--		--	--	--
0.0085	0.085	Ru	--	[1.2]	--		--	--	--
0.0200	0.200	Sb	[0.89]	--	--		--	--	--
0.0700	0.700	Se	--	--	--		--	--	--
0.0270	0.270	Sn	[0.85]	--	--		[4.3]	--	[3.4]
0.0170	0.170	Ta	--	--	--		--	--	--
0.0260	0.260	Te	--	--	--		--	--	--
0.0098	0.098	Th	--	--	[1.4]		--	--	--
0.0004	0.004	Ti	--	--	--		--	[0.057]	--
0.0380	0.380	Tl	--	--	--		--	--	--
0.0007	0.007	V	[0.025]	1.46	[0.23]		1.33	1.31	0.998
0.0190	0.190	W	--	[5.5]	[6.3]		--	--	[2.8]
0.0004	0.004	Y	--	--	--		--	--	--

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%.

ASR 8125 128 Final from C0138 R. Shimskey (ASR-8125 128's).XLS

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

Run Date >	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008	6/4/2008
Multiplier >	122.4	612.2	620.2	616.0	622.2	614.0	609.5	611.2	617.2	616.0
RPL/LAB >	08-01369 @5	08-01369 @25	08-01370 @25	08-01371 @25	08-01372 @25	08-01373 @25	08-01374 @25	08-01375 @25	08-01376 @25	08-01377 @25
Client ID >	TI601-G4-C1		TI601-G4-C2	TI601-G4-C3	TI601-G4-C4	TI601-G4-C5	TI601-G4-E	TI601-G4-F	TI601-G4-D1	TI601-G4-D2
(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
Al	7,960		26,800	26,600	29,100	26,500	13,400	6,960	18,100	25,000
B	12.4		--	[9.3]	[21]	[19]	--	--	[12]	[17]
Bi	[26]		[40]	[66]	[60]	[70]	--	--	[22]	[28]
Cd	[1.6]		--	--	--	[2.4]	--	--	--	--
Cr	43.2		53.5	58.8	69.5	68.0	43.7	22.8	67.7	67.3
Fe	37.4		53.4	60.9	55.1	70.8	[9.6]	[3.9]	[18]	[25]
K	578		505	537	550	512	[340]	[250]	481	508
Mn	5.62		14.1	18.7	12.8	20.5	--	--	[1.1]	--
Na	over-range	183,000	198,000	191,000	209,000	192,000	115,000	71,500	153,000	176,000
Ni	5.36		[5.3]	[4.4]	--	[2.5]	[1.8]	--	[3.6]	--
P	523		2,010	581	1,490	2,180	800	1,800	2,270	534
S	383		[440]	[380]	[460]	[430]	[200]	[120]	[560]	[370]
Si	66.3		103	130	108	90.7	39.7	[21]	55.2	56.4
Sr	[0.096]		[0.11]	[0.062]	--	[0.12]	--	--	[0.072]	--
U	[17]		--	[23]	--	[22]	--	--	--	--
Zn	15.7		43.8	44.5	51.0	47.2	[24]	[13]	[33]	43.8
Zr	4.30		12.0	8.86	12.8	11.9	[3.8]	[4.6]	10.6	[3.8]

Ag	--		--	--	--	[1.3]	--	--	--	--
As	--		--	--	--	--	--	--	--	--
Ba	[0.61]		[0.56]	[0.49]	[0.62]	[0.68]	[0.54]	[0.38]	[0.58]	[0.55]
Be	0.143		[0.20]	[0.23]	[0.25]	[0.23]	[0.15]	[0.085]	[0.15]	[0.21]
Ca	[1.9]		--	[4.2]	[18]	[4.9]	--	--	[14]	[12]
Ce	--		--	--	--	--	--	--	--	--
Co	--		--	--	[1.5]	--	--	--	--	--
Cu	2.35		[4.1]	[3.8]	[5.2]	[4.1]	[1.3]	--	[2.7]	[4.9]
Dy	--		--	--	--	--	--	--	--	--
Eu	--		--	--	--	--	--	--	--	--
La	--		--	--	--	--	--	--	--	--
Li	[1.5]		[3.4]	[4.2]	[3.9]	[3.4]	[0.61]	[0.63]	[2.7]	[3.7]
Mg	--		--	--	--	--	--	--	--	--
Mo	[1.5]		[3.3]	--	[4.9]	[4.0]	[3.3]	--	[4.4]	[3.4]
Nd	--		[3.5]	--	--	--	--	[4.4]	--	--
Pb	117		211	202	221	209	[85]	[31]	[150]	[170]
Pd	--		--	--	--	--	--	--	--	--
Rh	--		--	--	--	--	--	--	--	--
Ru	--		--	--	--	--	--	--	--	--
Sb	--		--	--	--	[14]	--	[14]	--	--
Se	--		--	--	--	--	--	--	--	--
Sn	--		--	--	--	--	--	--	--	--
Ta	--		--	--	--	--	--	--	--	--
Te	--		--	--	--	--	--	--	--	--
Th	--		--	--	--	--	--	--	--	--
Ti	--		--	--	--	--	--	[0.27]	--	--
Tl	--		--	--	--	--	--	--	--	--
V	[0.49]		[1.7]	[1.4]	[1.5]	[2.3]	[1.4]	[2.1]	[1.9]	[1.4]
W	[4.6]		[12]	[15]	[18]	[13]	[12]	[17]	[16]	[16]
Y	--		--	--	--	--	--	--	--	--

QC Performance 6/4/2008

Criteria >	≤ 20%	80%-120%	75%-125%	75%-125%	75%-125%	≤ 10%
QC ID >	08-01367 Dup	LCS/BS	08-01367 MS	08-01365 + PS-A	08-01365 + PS-B	08-01365 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	0.3	100	100	102		3.7
B		104	100	103		
Bi		89	94	93		
Cd		96	96	93		
Cr	3.6	101	102	101		1.3
Fe		97	99	98		
K	5.2	102	100	98		
Mn		99	99	99		
Na	0.4	97	nr	nr		2.3
Ni		99	100	102		
P	1.2	98	94	101		0.1
S		99	99		101	
Si	0.3	95	104	105		
Sr		104	103	102		
U		100	99		100	
Zn		95	98	102		
Zr		93	91	100		
Other Analytes						
Ag		107	106	91		
As				103		
Ba		98	98	99		
Be		99	100	100		
Ca		102	102	100		
Ce		95	94		96	
Co				99		
Cu		100	101	105		
Dy					99	
Eu					98	
La		97	96		97	
Li		103	99	99		
Mg		100	100	100		
Mo		100	99	101		
Nd		97	95		94	
Pb		98	99	98		
Pd					95	
Rh					100	
Ru					93	
Sb				98		
Se				100		
Sn				102		
Ta				99		
Te					98	
Th		96	95		96	
Ti		102	101	99		
Tl				97		
V	1.6	94	92	95		
W		98	102	100		
Y				97		

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 ... ICPOES Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#: 52964 / F99189
ASR#: 8125
Client: R. Shimskey
Total Samples: 3 (solid)

	First	Last
RPL#:	08-01381	08-01383
Client ID:	TI601-G4-6	TI601-G4-12
Sample Preparation: RPG-CMC-138, "HNO_3-HF-HCl Acid Digestion of Solids for Metals Analysis Using a Dry-Block Heater", 4/22/08 (SAL/dk).		

Procedure: RPG-CMC-211, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICPOES)", Rev 2.

Analyst: P. Berry

Analysis Date (File): 5-15-2008 (C0133)

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE Number: N827583 (ICPOES instrument)
M19445 (Mettler AT400 Balance)

5/20/08
Preparer

5/23/08
Review and Concur

Battelle PNNL/RS&E/Inorganic Analysis ... ICPOES Analysis Report

Three samples submitted under Analytical Service Request (ASR) 8125 were analyzed by ICPOES. The samples were prepared following RPL procedure RPG-CMC-138 using a nominal 0.1 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 ICPOES 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 ICPOES 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-8125 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).

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.

Battelle PNNL/RS&E/Inorganic Analysis ... ICPOES Analysis Report

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, S, 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, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

Page 1 of 2

		Run Date >	5/15/2008	5/15/2008	5/15/2008	5/15/2008	5/15/2008
		Multiplier >	967.6	967.1	968.1	856.9	1283.7
		RPL/LAB >	08-01381-138-B	08-01381-138-S	08-01381-138-D	08-01382-138-S	08-01383-138-S
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Prep Blank	TI601-G4-6		TI601-G4-9	TI601-G4-12
(µg/mL)	(µg/mL)	(Analyte)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
0.0060	0.060	Al	[7.1]	139,000	140,000	50,700	58,800
0.0048	0.096	B	[27]	158	153	101	179
0.0300	0.300	Bi	--	869	865	673	3,260
0.0034	0.034	Cd	--	[8.1]	[10]	[6.3]	[38]
0.0017	0.017	Cr	--	720	720	501	2,130
0.0024	0.048	Fe	[21]	6,040	6,150	5,350	28,400
0.0720	0.720	K	--	697	756	[490]	[360]
0.0002	0.005	Mn	--	597	604	507	2,470
0.0160	0.320	Na	--	186,000	187,000	350,000	354,000
0.0024	0.024	Ni	[5.4]	372	371	352	1,860
0.0500	0.500	P	--	14,300	14,200	8,190	13,500
0.1600	1.600	S	--	1,990	2,050	[1,000]	[840]
0.0056	0.056	Si	na	na	na	na	na
0.0001	0.002	Sr	--	28.2	28.5	32.7	162
0.0320	0.320	U	--	3,890	3,970	3,370	16,000
0.0028	0.056	Zn	[33]	284	292	128	164
0.0011	0.011	Zr	--	2,930	2,960	2,480	11,700
Other Analytes							
0.0021	0.021	Ag	--	[4.2]	[3.9]	[3.4]	[21]
0.0430	0.430	As	--	--	--	--	--
0.0003	0.005	Ba	--	30.3	31.3	27.1	115
0.0001	0.001	Be	--	0.971	1.00	[0.37]	[0.66]
0.0061	0.061	Ca	[10]	541	557	482	2,320
0.0100	0.100	Ce	--	[29]	[20]	[19]	[110]
0.0024	0.024	Co	--	[6.0]	[5.0]	[2.4]	[28]
0.0014	0.014	Cu	--	36.1	36.2	19.3	71.6
0.0029	0.029	Dy	--	--	--	--	--
0.0011	0.011	Eu	--	--	--	--	--
0.0028	0.028	La	--	[21]	[20]	[19]	82.8
0.0006	0.012	Li	--	[11]	[11]	[8.6]	21.9
0.0023	0.023	Mg	--	194	200	170	825
0.0052	0.052	Mo	--	[19]	[21]	[14]	[65]
0.0054	0.054	Nd	--	[34]	[32]	[30]	129
0.0320	0.320	Pb	--	1,330	1,330	772	1,770
0.0063	0.063	Pd	[12]	--	--	--	[13]
0.0120	0.120	Rh	--	--	--	--	--
0.0085	0.085	Ru	--	[11]	--	--	[37]
0.0200	0.200	Sb	--	--	--	--	--
0.0700	0.700	Se	--	--	--	--	[100]
0.0270	0.270	Sn	--	--	--	--	[48]
0.0170	0.170	Ta	--	--	--	--	--
0.0260	0.260	Te	--	--	--	--	--
0.0098	0.098	Th	--	[87]	[91]	[75]	369
0.0004	0.004	Ti	[0.62]	32.6	32.4	27.9	138
0.0380	0.380	Tl	[65]	--	--	--	[68]
0.0007	0.007	V	[1.4]	11.5	12.1	7.88	20.4
0.0190	0.190	W	--	[23]	[32]	[24]	[37]
0.0004	0.004	Y	--	[4.1]	[4.0]	[3.6]	17.3

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 5/15/2008

Criteria >	≤ 20%	80%-120%	75%-125%	75%-125%	75%-125%	≤ 10%
QC ID >	08-01381 Dup	1381 LCS	MS (none)	08-01381 + AS-A	08-01381 + AS-B	08-01381 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	0.8	99		nr		2.3
B	2.8			102		
Bi	0.5			93		
Cd		84		98		
Cr	0.0			100		0.8
Fe	1.9	98		98		4.1
K	8.0			98		
Mn	1.2	101		98		3.7
Na	0.1	96		98		2.0
Ni	0.4	109		99		4.1
P	0.6	88		94		0.5
S	2.9	105			98	
Si	na	na	na	na	na	na
Sr	0.9			102		3.0
U	1.9				94	1.1
Zn	2.8	99		101		1.7
Zr	1.2			97		2.4
Other Analytes						
Ag		96		93		
As		89		97		
Ba	3.2	97		98		
Be	3.1			96		
Ca	2.9	98		99		19.6
Ce					94	
Co				100		
Cu	0.3	96		98		
Dy					94	
Eu					93	
La					94	
Li				100		
Mg	3.1	98		99		1.5
Mo				99		
Nd					93	
Pb	0.1	101		100		
Pd					88	
Rh					95	
Ru					94	
Sb				98		
Se				95		
Sn				94		
Ta				101		
Te					94	
Th					93	
Ti	0.6	94		96		5.1
Tl		nr		93		
V	5.0	93		93		
W				94		
Y				95		

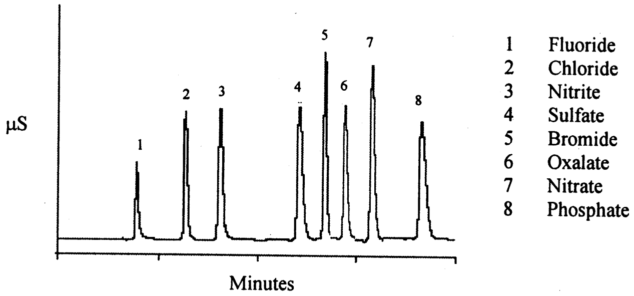
Shaded results are outside the acceptance criteria.

nr = not recovered; spike concentration less than 25% of sample concentration.

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 - 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 #:***	8125
Project #:	52964	***# Samples:***	9 liquids
Charge Code:	F99189		

***** RPL Numbers: 08-01365 through 08-01368, 08-1376 through 08-01380*****

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 5/20 and 21/08)
Analyst	MJ Steele
Analysis Dates	05/20 through 22/08
Calibration Date	5/08/08
Cal/Ver Stds Prep Date	Cal 05/08/08; Ver 05/20/08
Excel Data File	Results ASR 8125 Shimsky.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-0162)

Prepared By 5-23-08
Date

Reviewed By 5/29/08
Date

IC Report

Sample Results

See Attachment: Direct Liquid Sample Results ASR 8125

Sample Analysis/Results Discussion

Nine liquid samples were submitted to the ASO for analysis under ASR 8125. The specified analytes of are fluoride, nitrite, nitrate, sulfate, oxalate and phosphate. The sample was 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.

After screening the sample, the final analysis was performed using additional dilution factors ranging from ~105 to 5250. All results have been adjusted for all analytical dilutions. The prep dilution blank (water used to dilute samples at the IC workstation) is reported as analyzed, no dilution factors were applied to this sample. 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).

For sample numbers 08-01376 thru 08-01380, oxalate only was requested. The data summary table includes the requested oxalate results along with opportunistic results for F, NO_2, NO_3, SO_4 and PO_4.

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). The processing blank met the QA Plan acceptance criteria for all analytes of interest.

Duplicate (Precision): One sample was analyzed in duplicate (08-01368). The relative percent difference is reported for all analytes of interest which were measured at or above the EQL. The reported RPDs ranged from less than 1 to 1%, which meets the Project acceptance criteria (Table 4 of ASR) of <20%.

Laboratory Control Sample/Blank Spike (LCS/BS): The routine instrument LCS/blank spike was analyzed with the data set and had recoveries ranging from 98% to 105% for the analytes of interest. These recoveries meet the Project acceptance criteria (Table 4 of ASR) of 80% to 120% recovery.

IC Report

Matrix Spike: (Accuracy) None prepared. Sample did not undergo sample preparation; therefore, an analytical post spike was prepared and analyzed.

Post Spike: (Accuracy) Multiple analytical spikes (i.e., standard added during dilution) were prepared for sample 08-01365 and analyzed. Sample 08-01365 was diluted by 105, 525, 2625, and 5250 in order to obtain spikes concentrations at least 20% greater than measured sample concentration. The recovery range was from 99% to 111% for all analytes of interest, which meets the QA Plan post spike recovery acceptance criteria of 75% to 125%. The reported post spike value for nitrate was slightly higher than the highest calibration standard, but this did not significantly impact the spike value.

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

The reported post spike value for nitrate was slightly higher than the highest calibration standard, but this did not significantly impact the spike value.

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 8125

RPL Number	Client Sample ID	F MDL µg/mL	F 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
08-01365	TI601-G4-A	3.3	472		130	11,800		7.9	7.9	U
08-01366	TI601-G4-D3	3.3	15.0	J	26	5,670		7.9	1,040	
08-01367	TI601-G4-G	3.3	425		5.3	857		7.9	163	
08-01368	TI601-G4-H	3.3	289		26	1,970		7.9	371	
08-01376	TI601-G4-D1	3.3	6.7	J	130	OvrRng		7.9	1,450	
08-01377	TI601-G4-D2	3.3	12.0	J	26	5,480		7.9	996	
08-01378	TI601-G4-C6	3.3	159		26	2,470		7.9	457	
08-01379	TI601-G4-C7	3.3	126		26	2,770		7.9	515	
08-01380	TI601-G4-C8	3.3	5.0	J	26	2,090		7.9	392	
Dilution Blank 1	DB 5-20-08	0.031	0.031	U	0.050	0.050	U	0.076	0.076	U
Dilution Blank 2	DB 5-21-08	0.031	0.031	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
08-01365	TI601-G4-A	26	3,370		530	104,000		160	11,300	
08-01366	TI601-G4-D3	5.2	30.0	J	260	50,200		31	2,290	
08-01367	TI601-G4-G	5.2	964		53	7,550		31	5,530	
08-01368	TI601-G4-H	5.2	960		260	17,200		31	5,060	
08-01376	TI601-G4-D1	5.2	185		260	OvrRng		31	2,390	
08-01377	TI601-G4-D2	5.2	34.0	J	260	OvrRng		31	1,630	
08-01378	TI601-G4-C6	5.2	200		260	OvrRng		31	3,860	
08-01379	TI601-G4-C7	5.2	94.8		260	OvrRng		31	3,790	
08-01380	TI601-G4-C8	5.2	49.0	J	260	OvrRng		6.3	1,340	
Dilution Blank 1	DB 5-20-08	0.050	0.050	U	0.10	0.10	U	0.060	0.060	U
Dilution Blank 2	DB 5-21-08	0.050	0.050	U	0.10	0.10	U	0.060	0.060	U

Direct Liquid Sample QC Results ASR 8125

Sample/Replicate Precision Results [(a)]

		F		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	Sample ID	µg/mL	%RSD	µg/mL	%RSD	µg/mL	%RSD	µg/mL	%RSD	µg/mL	%RSD	µg/mL	%RSD
08-01368	Sample	289	--	1970	--	371	--	960	--	17200	--	5060	--
	Duplicate | RPD	292	1	1980	1	374	1	963	0	17100	1	5080	0

Sample Spike Results - At IC Workstation

RPL Number	Sample ID	F		NO_2		SO_4		C_2O_4		NO_3		PO_4	
		µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec
08-01365	Sample	472	--	11800	--	U	--	3370	--	104000	--	11300	--
	AS Sample	3.29	104	4.76	101	4.17	111	5.88	107	24.5	107	5.23	99

▨ Nitrate spike sample results were slightly above the highest calibration standandard

LCS Results - IC System

RPL Number	Run ID	F %Rec	NO_2 %Rec	SO_4 %Rec	C_2O_4 %Rec	NO_3 %Rec	PO_4 %Rec
LCS	5/21/2008 12:45	101	101	101	105	104	98

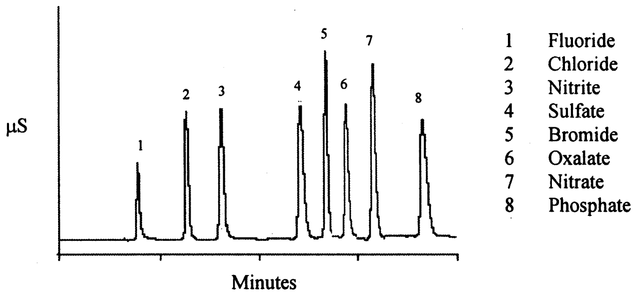
AS = Analytical Spike: Spike performed at IC Workstation on liquid Sample.
LCS = Laboratory Control Sample (Standard analyzed at IC Workstation)
RPD = Relative Percent Difference
%Rec = Percent Recovery
U = Not Detected Above Method Detection Limit
J = Detected, Result are Qualitative: Result >MDL but <EQL (estimated quantitation limit)
-- = Value Not Calculated, place holder for blank cell
a = %RPD is not calculated for results which are below the EQL

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 #:***	8125
Project #:	52964	***# Samples:***	3 Solids
Charge Code:	F99189		

*** RPL Numbers: 08-01381 through 08-01383***

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 5/20 and 21/08) Water leach in SAL – RPG-CMC-103 (05/21/08)
Analyst	MJ Steele
Analysis Dates	05/20 through 22/08
Calibration Date	05/08/08
Cal/Ver Stds Prep Date	Cal 05/08/07; Ver 05/20/08
Excel Data File	Results ASR 8125 Shimsky.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-0162)

Prepared By 5-23-08
Date

Reviewed By 5/29/08
Date

IC Report

Sample Results

See Attachment: Leached Dry Solids Sample Results ASR 8125

Sample Analysis/Results Discussion

Three solid/slurry samples were submitted to the ASO for analysis under ASR 8125. The specified analytes of are fluoride, nitrite, nitrate, sulfate, oxalate and phosphate. The samples were prepared for IC analysis by drying the solids/slurry and then leaching the dry solids (~1g sample/slurry to 10 mL of deionized water), which included the preparation of matix spikes and sample replicates. 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 make further dilutions were analyzed as the process sample. All sample results are reported as µg/g; the leach deionized water samples have been normalized to the average solid/slurry processing factor of 9.48.

After screening the samples, the final analysis was performed using additional dilution factors ranging from ~50 to 1500. All results have been adjusted for all leaching and analytical dilution factors. 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

The Laboratory Control Sample (Blank Spike) processed through the leaching process failed for oxalate (only 70% of the oxalate was recovered). This is not uncommon for leaches performed in the hot cell; however, the loss mechanism is unknown. Based on the leached LCS recovery, oxalate results for all samples have been manually J-flagged (indicating that the oxalate results are qualitative estimates only).

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. None of the analytes of interest were detected in the process leach blank.

Duplicate (Precision): Sample 08-01381 was analyzed in duplicate. The relative percent difference is reported for all analytes which were measured at or above the EQL. The reported

IC Report

RPDs ranged from 1 to 2% for all analytes of interest, which meets the Project acceptance criteria (Table 4 of ASR) of <25%.

Processing Laboratory Control/Blank Spike (LCS/BS): The leaching process LCS/blank spike was analyzed with the data set and, except for oxalate (See Data Limitations), had a recoveries ranging from 94% to 101% for the analytes of interest. These recoveries meet the Project acceptance criteria (Table 4 of ASR) of 80% to 120% recovery. Since oxalate only recovered at 70%, all oxalate results have been J-flagged.

Matrix Spike: (Accuracy) A matrix spike was prepared for Sample 08-01383. 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 08-01383 and analyzed. Sample 08-01383 was diluted by 50, 250 and 750 in order to obtain spikes concentrations at least 20% greater than measured sample concentration. The recovery range was from 99% to 114% for all analytes of interest (including oxalate), 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.

Leached Dry Solids Sample Results ASR 8125

RPL Number	Client Sample ID	F MDL µg/g	F Result µg/g	DF	NO_2 MDL µg/g	NO_2 Result µg/g	DF	SO_4 MDL µg/g	SO_4 Result µg/g	DF
08-01381-103-PB	Process Blank	0.294	0.294	U	0.474	0.474	U	0.720	0.720	U
08-01381-103-S	TI601-G4-6	15	2,830		120	25,500		35	4,740	
08-01382-103-S	TI601-G4-9	59	1,950		98	10,300		143	1,910	
08-01383-103-S	TI601-G4-12	17	2,630		26	5,570		40	1,130	
Dilution Blank 1	DB 5-20-08	0.031	0.031	U	0.050	0.050	U	0.076	0.076	U
Dilution Blank 2	DB 5-21-08	0.031	0.031	U	0.050	0.050	U	0.076	0.076	U

RPL Number	Client Sample ID	C_2O_4 MDL µg/g	C_2O_4 Result µg/g	DF	NO_3 MDL µg/g	NO_3 Result µg/g	DF	PO_4 MDL µg/g	PO_4 Result µg/g	DF
08-01381-103-PB	Process Blank	0.474	0.474	U	0.95	0.95	U	0.569	0.569	U
08-01381-103-S	TI601-G4-6	111	8,790	J	1,380	230,000		415	41,600	
08-01382-103-S	TI601-G4-9	90	6,880	J	565	94,100		339	28,200	
08-01383-103-S	TI601-G4-12	126	8,600	J	263	61,000		473	40,900	
Dilution Blank 1	DB 5-20-08	0.050	0.050	U	0.10	0.10	U	0.060	0.060	U
Dilution Blank 2	DB 5-21-08	0.050	0.050	U	0.10	0.10	U	0.060	0.060	U

Leached Dry Solids Sample Results ASR 8125

Sample/Replicate Precision Results [a]

		F		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	Sample ID	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD	µg/g	%RSD
08-01381-103-S	Sample	2,830	--	25,500	--	4,740	--	8,790	--	230,000	--	41,600	--
	Dup (RPD)	2,900	2	26,000	2	4,840	2	8,920	2	235,000	2	42,100	1

Sample Spike Results - At IC Workstation

		F		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	Sample ID	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec
08-01381-103-BS	Proc Blk	U	--	U	--	U	--	U	--	U	--	U	--
	LCS Sample	5.2	100	9.76	94	15.7	100	7.27	70	18.5	101	12.8	99
08-01383	Sample	255	--	586	--	122	--	821	--	5810	--	3940	--
	PS Sample	1.64	113	3.7	101	4.92	99	4.48	114	16.3	107	11	100

LCS Results - IC System

RPL Number	Run ID	F %Rec	NO_2 %Rec	SO_4 %Rec	C_2O_4 %Rec	NO_3 %Rec	PO_4 %Rec
LCS	5/21/2008 12:45	101	101	101	105	104	98

AS = Analytical Spike: Spike performed at IC Workstation on liquid Sample.
LCS = Laboratory Control Sample (Standard analyzed at IC Workstation)
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
▨ QC recovery did not meet QA Plan or client specifications
a = %RPD is not calculated for results which are below the EQL

Battelle

. . . Putting Technology To Work

Client: Rick Shimskey

Report Date: 5/7/2008
Analysis Date: 5/5/2008

Subject: Hydroxide Analyses for: **Group 3/4 PUREX/REDOX Cladding Waste Waste Treatability Study**

ASR: **8125** Rev-0
Sample ID. 08-01365 thru 08-01377

Procedure: RPG-CMC-228-Rev 1

Direct sample aliquots of Group 3/4 PUREX/REDOX Cladding 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 99%, well within the allowed ± 20% recovery range. Although not required in this ASR, a matrix spike was analyzed and the recovery was 97%. No hydroxide was detected in the reagent blank.

The initial pH is reported on attached Report Summary along with the free hydroxide molarities (generally the 1st inflection point whenever the initial pH is 12 or more). In such cases, generally the 2nd inflection point around pH 7-8, indicates the total hydroxide molarity. Generally, the analysis used very small volumes (0.05ml) due to high caustic, yet surprisingly these results showed excellent Relative Percent Deviation (RPD) for the first inflection point, well within ± 20% allowed range. Many of the samples also indicated a third inflection point around pH 4-5, and most RPD's for 2nd and third points were within ± 20% allowed range even though this is not a requirement. Again this data is very acceptable considering the small sample size, undissolved species in some samples, and the fact that other base constituent molarities were very miminal compared to the hydroxide.

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: 5/7/08

Reviewed by: ________________ Date: 5/7/08

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

ASR # 8125

WP# F99189

Hydroxide and Alkalinity Determination
Procedure: RPG-CMC-228-Rev 1

Equip # WB76843

Report Summary for ASR # -- 8125
Revision # **Rev-0**

Report Date: 5/6/2008
Analysis Date: 5/5/2008

				Concentration, moles / Liter					
				First Point		**Second Point**		**Third Point**	
RPG #	**Client ID**	**Initial pH**	**OH conc ug/mL**	**Molarity**	**RPD**	**Molarity**	**RPD**	**Molarity**	**RPD**
08-01365	**TI-601-G4-A**	**11.71**	4.66E+03	**0.27**		**0.45**		**0.45**	
08-01365-Dup	**TI-601-G4-A**	**11.90**	5.16E+03	**0.30**	10.2%	**0.40**	12.1%	**0.44**	2.4%
08-01366	**TI-601-G4-D3**	**12.53**	9.37E+04	**5.51**		**1.33**		**0.21**	
08-01366-Dup	**TI-601-G4-D3**	**12.59**	9.51E+04	**5.60**	1.5%	**1.36**	2.0%	**0.21**	1.2%
08-01367	**TI-601-G4-G**	**12.48**	2.23E+04	**1.31**		**0.31**		**0.15**	
08-01367-Dup	**TI-601-G4-G**	**12.25**	2.21E+04	**1.30**	0.7%	**0.33**	4.1%	**0.14**	3.5%
08-01368	**TI-601-G4-H**	**12.30**	4.74E+04	**2.79**		**0.56**		**0.12**	
08-01368-Dup	**TI-601-G4-H**	**12.26**	4.77E+04	**2.80**	0.6%	**0.64**	12.0%	**0.10**	20.6%
08-01369	**TI-601-G4-C1**	**12.47**	1.16E+05	**6.84**		**0.63**		**0.30**	
08-01369-Dup	**TI-601-G4-C1**	**12.50**	1.13E+05	**6.66**	2.6%	**0.67**	7.5%	**0.41**	29.5%
08-01370	**TI-601-G4-C2**	**12.44**	1.00E+05	**5.91**		**1.32**		**0.14**	
08-01370-Dup	**TI-601-G4-C2**	**12.45**	9.83E+04	**5.78**	2.2%	**1.39**	5.3%	**0.22**	43.2%
08-01371	**TI-601-G4-C3**	**11.72**	1.03E+05	**6.05**		**1.50**		**0.31**	
08-01371-Dup	**TI-601-G4-C3**	**12.77**	9.82E+04	**5.77**	4.6%	**1.51**	0.7%	**0.31**	0.7%

OH conc (mg/L) = M (g/L) * 17,000
free OH as specified in ASR

µg/ml or mg/L MDL	Molarity MDL	Required RPD
1.70E+03	**0.100**	+/- 20%

	Initial pH	Molarity	Allowed Recovery Range
Reag. Blk.1		**0**	
Standard 1	**11.82**	**99.4%**	+/- 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: 5/7/08

Reviewer: 5/7/08

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

ASR # 8125

WP# F99189

Hydroxide and Alkalinity Determination
Procedure: RPG-CMC-228-Rev 1

Equip # WB76843

Report Summary for ASR # -- 8125
Revision # **Rev-0**

Report Date: 5/6/2008
Analysis Date: 5/5/2008

				Concentration, moles / Liter					
				First Point		Second Point		Third Point	
RPG #	**Client ID**	**Initial pH**	**OH conc ug/mL**	**Molarity**	**RPD**	**Molarity**	**RPD**	**Molarity**	**RPD**
08-01372	**TI-601-G4-C4**	**12.41**	1.11E+05	**6.55**		**1.45**		**0.23**	
08-01372-Dup	**TI-601-G4-C4**	**12.44**	1.14E+05	**6.70**	2.2%	**1.52**	5.1%	**0.23**	0.0%
08-01373	**TI-601-G4-C5**	**12.72**	1.10E+05	**6.45**		**2.10**		**0.78**	
08-01373-Dup	**TI-601-G4-C5**	**12.53**	1.07E+05	**6.32**	2.0%	**1.40**	39.8%	**0.25**	103.2%
08-01374	**TI-601-G4-E**	**12.42**	6.66E+04	**3.92**		**0.80**		**0.25**	
08-01374-Dup	**TI-601-G4-E**	**12.47**	6.91E+04	**4.06**	3.7%	**0.79**	0.3%	**0.38**	41.0%
08-01375	**TI-601-G4-F**	**12.36**	4.08E+04	**2.40**		**0.56**		**0.10**	
08-01375-Dup	**TI-601-G4-F**	**12.25**	3.98E+04	**2.34**	2.4%	**0.56**	0.7%	**0.14**	40.7%
08-01376	**TI-601-G4-D1**	**12.36**	6.36E+04	**3.74**		**0.95**		**0.46**	
08-01376-Dup	**TI-601-G4-D1**	**12.41**	6.40E+04	**3.76**	0.5%	**1.03**	8.0%	**0.56**	18.7%
08-01377	**TI-601-G4-D2**	**12.52**	9.10E+04	**5.35**		**1.30**		**0.21**	
08-01377-Dup	**TI-601-G4-D2**	**12.50**	9.47E+04	**5.57**	4.1%	**1.37**	5.0%	**0.26**	21.6%

	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%

				Allowed Recovery Range
Reag. Blk.1			**0**	
Standard 1		**11.82**	**99.4%**	+/- 20%
08-01375MS	**Matrix spike**	**12.59**	**96.9%**	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: 5/7/08

Reviewer: 5/7/08

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

ASR # and Rev # 8125 Rev-0
Client: Rick Shimskey
WP# F99189

File: R:\radchem\hydroxide\asr **8125**
Report Date: **5/6/2008**
Analysis Date: **5/5/2008**

Procedure: **RPG-CMC-228-Rev 1** Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates

Spreadsheet: OH-TemplateLocked07.xls 4/1/2007

using a Brinkman 636 Auto Titrator Equip # WB76843 Lab Loc. 525

Analyst: 5/7/08

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
08-01365	TI-601-G4-A		na	0.100	na		3	11.710	0.270	10.805	0.027	0.274	
08-01365-Dup	TI-601-G4-A	Replicate	na	0.200	na		5	11.895	0.598	10.696	0.061	0.304	10.2%
08-01366	TI-601-G4-D3		na	0.200	na		6,7,8	12.531	10.851	10.399	1.102	5.512	
08-01366-Dup	TI-601-G4-D3	Replicate	na	0.050	na		9	12.588	2.754	10.367	0.280	5.596	1.5%
08-01367	TI-601-G4-G		na	0.200	na		10	12.482	2.582	10.344	0.262	1.312	
08-01367-Dup	TI-601-G4-G	Replicate	na	0.200	na		11	12.252	2.563	10.407	0.260	1.302	0.7%
08-01368	TI-601-G4-H		na	0.200	na		12,13	12.295	5.489	10.286	0.558	2.788	
08-01368-Dup	TI-601-G4-H	Replicate	na	0.050	na		14	12.263	1.380	10.196	0.140	2.804	0.6%
08-01369	TI-601-G4-C1		na	0.050	na		15	12.469	3.366	9.992	0.342	6.840	
08-01369-Dup	TI-601-G4-C1	Replicate	na	0.050	na		16	12.498	3.278	10.107	0.333	6.661	2.6%
08-01370	TI-601-G4-C2		na	0.050	na		17	12.441	2.907	10.347	0.295	5.907	
08-01370-Dup	TI-601-G4-C2	Replicate	na	0.050	na		18	12.448	2.845	10.462	0.289	5.781	2.2%
08-01371	TI-601-G4-C3		na	0.050	na		19	11.720	2.975	10.450	0.302	6.045	
08-01371-Dup	TI-601-G4-C3	Replicate	na	0.050	na		20	12.766	2.842	10.393	0.289	5.775	4.6%
Reag. Blk.1		OH vol	OH Wt.		na		1	4.692	na		**OH % Recovery**		
Standard 1	0.1118 M NaOH	2.0	2.0190	2.000	na		2	11.816	2.109	8.179	0.2143	**95.8%**	
		OH vol	OH Wt.										
08-01368MS	+ 2mL 0.1118 M NaOH	2.0			na						0.0000	0.0%	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: 95.8%
init.pH 7 check: 7.002

verif. pH reading
start 6.998
end 7.013

Performance checks using Balance # 360--01-06-037

Pipet #	Vol.	Wt.	Pipet #	Vol.	Wt.	
92501	0.100	0.0995	00545	0.0500	0.0499	
		0.1001			0.0502	
		0.1004			0.0499	
		0.1001			0.0502	
		0.1003			0.05	
	Ave	0.1000	% eror	Ave	0.0500	% eror
	Std. Dev.	0.0005	0.46%	Std. Dev.	0.0002	0.30%

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

ASR # and 8125

WP# F99189

File: R:\radchem\hydroxide\asr

0

Procedure:
Alkalinity of Aqueous Solutions, Leachates and Supernates

using a Brinkman 636 Auto Titrator Equip # WB76843

5/7/08

Titrant	Molarity
HCl	0.1016

0

RPG #		Sample Vol. (mL	2nd Equivalence Point Titrant ol. (mL)	pH	Found millimoles base	Molarity base	nillimole RPD	3rd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
08-01365	0	0.100	0.709	7.425	0.045	0.446		1.152	4.176	0.045	0.450	
08-01365-Dup	Replicat	0.200	1.376	7.706	0.079	0.395	12%	2.241	4.478	0.088	0.439	2%
08-01366	0	0.200	13.470	7.802	0.266	1.330		13.891	5.426	0.043	0.214	
08-01366-Dup	Replicat	0.050	3.422	7.758	0.068	1.357	2%	3.526	5.459	0.011	0.211	1%
08-01367	0	0.200	3.198	7.322	0.063	0.313		3.486	3.991	0.029	0.146	
08-01367-Dup	Replicat	0.200	3.205	7.394	0.065	0.326	4%	3.483	4.354	0.028	0.141	4%
08-01368	0	0.200	6.599	7.456	0.113	0.564		6.835	4.721	0.024	0.120	
08-01368-Dup	Replicat	0.050	1.693	6.413	0.032	0.636	12%	1.741	4.503	0.005	0.098	21%
08-01369	0	0.050	3.674	6.976	0.031	0.626		3.824	3.522	0.015	0.305	
08-01369-Dup	Replicat	0.050	3.610	7.266	0.034	0.675	7%	3.812	3.398	0.021	0.410	30%
08-01370	0	0.050	3.555	7.604	0.066	1.317		3.624	5.641	0.007	0.140	
08-01370-Dup	Replicat	0.050	3.528	8.028	0.069	1.388	5%	3.635	5.768	0.011	0.217	43%
08-01371	0	0.050	3.715	7.973	0.075	1.504		3.869	5.134	0.016	0.313	
08-01371-Dup	Replicat	0.050	3.587	7.924	0.076	1.514	1%	3.740	5.319	0.016	0.311	1%
						2-nd Recovered						
Standard 1		2.000	2.188	4.058	0.2223	99.4%						
						Total OH recovery						
08-01368MS		0.000			0.0000	0.0%	MS					

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 #	8125 Rev-0	File: R:\radchem\hydroxide\asr 8125	
Client:	Rick Shimskey	Report Date:	5/5/2008
WP#	F99189	Analysis Date:	5/2/2008

Procedure: **RPG-CMC-228-Rev 1** Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates

Spreadsheet: OH-TemplateLocked07.xls 4/1/2007

using a Brinkman 636 Auto Titrator Equip # WB76843 Lab Loc. 525

Analyst: 5/7/08

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
08-01372	TI-601-G4-C4		na	0.050	na		21	12.409	3.225	10.343	0.328	6.553	
08-01372-Dup	TI-601-G4-C4	Replicate	na	0.050	na		22	12.442	3.296	10.190	0.335	6.697	2.2%
08-01373	TI-601-G4-C5		na	0.050	na		23	12.723	3.172	10.432	0.322	6.446	
08-01373-Dup	TI-601-G4-C5	Replicate	na	0.050	na		24	12.530	3.108	10.395	0.316	6.315	2.0%
08-01374	TI-601-G4-E		na	0.050	na		25	12.421	1.927	10.243	0.196	3.916	
08-01374-Dup	TI-601-G4-E	Replicate	na	0.050	na		26	12.467	2.000	10.218	0.203	4.064	3.7%
08-01375	TI-601-G4-F		na	0.050	na		27	12.357	1.180	10.250	0.120	2.398	
08-01375-Dup	TI-601-G4-F	Replicate	na	0.050	na		28	12.250	1.152	10.304	0.117	2.341	2.4%
08-01376	TI-601-G4-D1		na	0.050	na		30	12.355	1.842	10.220	0.187	3.743	
08-01376-Dup	TI-601-G4-D1	Replicate	na	0.050	na		31	12.405	1.852	10.402	0.188	3.763	0.5%
08-01377	TI-601-G4-D2		na	0.050	na		32	12.524	2.633	10.468	0.268	5.350	
08-01377-Dup	TI-601-G4-D2	Replicate	na	0.050	na		33	12.498	2.742	10.364	0.279	5.572	4.1%
			na		na								
		Replicate	na		na								
Reag. Blk.1		OH vol	OH Wt.		na		1	4.692	na		**OH % Recovery**		
Standard 1	0.1118 M NaOH	2.0	2.0154	2.000	na		2	11.816	2.109	8.179	0.2143	**95.8%**	
		OH vol	OH Wt.										
08-01375MS	+ 2mL 0.1118 M NaOH	2.0		0.050	na		29	12.586	3.247	10.239	0.3299	94.6%	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
95.8%

init.pH 7 check
7.002

verif. pH reading
start
end 7.002

Performance checks using Balance # 360--01-06-037

Pipet #	Vol.	Wt.	Pipet #	Vol.	Wt.	
92501	0.100	0.0995	00545	0.0500	0.0499	
		0.1001			0.0502	
		0.1004			0.0499	
		0.1001			0.0502	
		0.1003			0.05	
	Ave	0.1000	% eror	Ave	0.0500	% eror
	Std. Dev.	0.0005	0.46%	Std. Dev.	0.0002	0.30%

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building

ASR # and 8125

WP# F99189

File: R:\radchem\hydroxide\asr

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Procedure:
Alkalinity of Aqueous Solutions, Leachates and Supernates
using a Brinkman 636 Auto Titrator Equip # WB76843

5/7/08.

Titrant	Molarity
HCl	0.1016
	0

			2nd Equivalence Point					3rd Equivalence Point				
RPG #		Sample Vol. (mL	Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	nillimole RPD	Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
08-01372	0	0.050	3.938	7.995	0.072	1.449		4.053	5.556	0.012	0.234	
08-01372-Dup	Replicat	0.050	4.046	7.793	0.076	1.524	5%	4.161	5.583	0.012	0.234	0%
08-01373	0	0.050	4.205	6.288	0.105	2.099		4.587	3.839	0.039	0.776	
08-01373-Dup	Replicat	0.050	3.798	7.939	0.070	1.402	40%	3.920	5.024	0.012	0.248	103%
08-01374	0	0.050	2.319	7.115	0.040	0.797		2.441	3.855	0.012	0.248	
08-01374-Dup	Replicat	0.050	2.391	7.579	0.040	0.795	0%	2.576	3.521	0.019	0.376	41%
08-01375	0	0.050	1.455	6.615	0.028	0.559		1.502	4.324	0.005	0.096	
08-01375-Dup	Replicat	0.050	1.429	7.061	0.028	0.563	1%	1.500	4.283	0.007	0.144	41%
08-01376	0	0.050	2.308	7.567	0.047	0.947		2.536	3.642	0.023	0.463	
08-01376-Dup	Replicat	0.050	2.357	7.868	0.051	1.026	8%	2.632	3.787	0.028	0.559	19%
08-01377	0	0.050	3.272	7.696	0.065	1.298		3.375	5.039	0.010	0.209	
08-01377-Dup	Replicat	0.050	3.414	7.966	0.068	1.366	5%	3.542	5.319	0.013	0.260	22%
						2-nd Recovered						
Standard 1		2.000	2.188	4.058	0.2223	**99.4%**						
						Total OH recovery						
08-01375MS		0.050	3.575	6.927	0.3632	**96.9%**	MS					

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: 08-1365_Shimskey
Rev 0
Report date: 6/20/2008

Client: R. Shimskey
Project 52964, charge code F99189
ASR 8125, 7 Samples

Prepared by: C. Soderquist 6-20-08
Concur: T Trang-Le 6/20/08

Samples processed between May and June 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
TI601-G4-A	08-1365
TI601-G4-D3	08-1366
TI601-G4-G	08-1367
TI601-G4-H	08-1368
TI601-G4-6	08-1381
TI601-G4-9	08-1382
TI601-G4-12	08-1383

Battelle, Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename 08-1365_Shimskey
6/20/2008

Client: R. Shimskey
ASR 8125

The Samples

These samples originated in the hot cells and arrived in the analytical lab in late April 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 in two samples, where the Compton background from high Cs-137 activity raised the detection limit for Eu-155. The hot cell blanks are small compared to the accompanying samples. All pairs of duplicates agree closely, within two standard deviations in every case. 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. 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.

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filename 08-1365_Shimskey
6/20/2008

Client: R. Shimskey
ASR 8125

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 08-1365_Shimskey
6/20/2008

Client: R. Shimskey
ASR 8125

Procedures: RPG-CMC-128, Sample digestion in dilute nitric acid (liquid samples only)
PNL-ALO-115, Potassium hydroxide fusion sample preparation (solid samples only)
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-154**	**Eu-155**	**Am-241**
TI601-G4-A	08-1365	**5.54E-4 ± 7%**	**5.99E+0 ± 6%**	< 3.E-4	< 2.E-3	< 9.E-4
TI601-G4-D3	08-1366	< 1.E-4	**3.20E+0 ± 3%**	< 3.E-4	< 2.E-3	< 2.E-3
TI601-G4-G	08-1367	< 7.E-5	**4.60E-1 ± 4%**	< 2.E-4	< 7.E-4	< 1.E-3
	08-1367 Dup	< 7.E-5	**4.58E-1 ± 4%**	< 2.E-4	< 7.E-4	< 1.E-3
	RPD	--	0.4%	--	--	--
TI601-G4-H	08-1368	< 7.E-5	**1.12E+0 ± 3%**	< 2.E-4	< 1.E-3	< 2.E-3
Acid digestion blank		< 8.E-5	< 8.E-5	< 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 08-1365_Shimskey
6/20/2008

		Measured Activity, **µci per g** ± 1s counting error				
Sample	Lab ID	**Co-60**	**Cs-137**	**Eu-154**	**Eu-155**	**Am-241**
TI601-G4-6	08-1381	**1.29E-2 ± 7%**	**2.58E+1 ± 4%**	**1.07E-1 ± 3%**	**4.69E-2 ± 15%**	**3.70E-1 ± 11%**
	08-1381 Dup	**1.23E-2 ± 7%**	**2.57E+1 ± 4%**	**1.07E-1 ± 2%**	**4.02E-2 ± 17%**	**4.03E-1 ± 11%**
	RPD	5%	0.4%	0%	15%	8%
TI601-G4-9	08-1382	**9.95E-3 ± 7%**	**1.64E+1 ± 4%**	**9.55E-2 ± 3%**	**3.32E-2 ± 16%**	**3.63E-1 ± 7%**
TI601-G4-12	08-1383	**5.03E-2 ± 4%**	**4.73E+1 ± 3%**	**4.51E-1 ± 2%**	**1.66E-1 ± 8%**	**1.42E+0 ± 5%**
Hot Cell KOH fusion blank		3.99E-3 ± 18%	1.15E+0 ± 3%	< 5.E-3	< 8.E-3	< 2.E-2
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 08-1365_Shimskey
6/20/2008

Client: R. Shimskey
ASR 8125
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**
TI601-G4-A	08-1365	**1.15E-3 ± 16%**	**6.05E+0 ± 4%**	**1.43E-1 ± 2%**	**5.97E-4 ± 2%**	**5.91E-5 ± 4%**	**8.63E+2 ± 4%**
TI601-G4-D3	08-1366	< 4.E-4	**2.94E+0 ± 4%**	**2.90E-2 ± 2%**	**2.90E-4 ± 2%**	**2.99E-5 ± 5%**	**3.16E+2 ± 4%**
TI601-G4-G	08-1367	< 4.E-4	**3.69E-1 ± 4%**	**5.52E-3 ± 2%**	**2.58E-5 ± 5%**	**2.63E-6 ± 16%**	**1.03E+2 ± 4%**
	08-1367 Dup	< 4.E-4	**3.95E-1 ± 4%**	**5.42E-3 ± 2%**	**2.63E-5 ± 7%**	**2.55E-6 ± 26%**	**1.01E+2 ± 4%**
	RPD	--	7%	2%	2%	3%	2%
TI601-G4-H	08-1368	< 4.E-4	**9.63E-1 ± 4%**	**1.18E-2 ± 2%**	**9.21E-5 ± 3%**	**9.27E-6 ± 9%**	**1.89E+2 ± 4%**
	Acid digestion blank	< 5.E-5	< 1.E-5	< 8.E-5	< 6.E-7	< 6.E-7	--
	Requested detection limit	4.0E-3	1.0E-3	1.0E-3	1.0E-4	1.0E-4	6.0E+1

		Measured Activity, µCi per g ± 1s total uncertainty					
Sample	Lab ID	**Gross Alpha**	**Gross Beta**	**Sr-90**	**Pu-239+240**	**Pu-238**	**Total Uranium, µg/g**
TI601-G4-6	08-1381	**6.16E-1 ± 11%**	**1.33E+2 ± 4%**	**6.05E+1 ± 2%**	**2.16E-1 ± 4%**	**2.56E-2 ± 11%**	**3.87E+3 ± 4%**
	08-1381 Dup	**5.32E-1 ± 12%**	**1.29E+2 ± 4%**	**6.23E+1 ± 2%**	**2.24E-1 ± 3%**	**3.01E-2 ± 8%**	**3.93E+3 ± 4%**
	RPD	15%	2%	3%	4%	16%	2%
TI601-G4-9	08-1382	**6.08E-1 ± 10%**	**1.19E+2 ± 4%**	**5.96E+1 ± 2%**	**2.41E-1 ± 4%**	**2.02E-2 ± 12%**	**3.73E+3 ± 4%**
TI601-G4-12	08-1383	**2.43E+0 ± 6%**	**5.43E+2 ± 4%**	**2.53E+2 ± 2%**	**8.77E-1 ± 2%**	**9.89E-2 ± 5%**	**1.57E+4 ± 4%**
	Hot cell KOH fusion blank	< 1.E-2	1.59E+0 ± 4%	3.04E-1 ± 2%	2.03E-3 ± 4%	5.38E-3 ± 3%	1.34E+1 ± 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-7	<3.E-6	<4.E-8	<5.E-8	3.48E-3 ± 3%
	Reagent spike	91%	81%	97%	95%	--	102%
	Matrix spike	83%	83%	94%	95%	--	99%, 97%
		--	--	--	--	--	

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	

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