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Laboratory Tests on Post-Filtration Precipitation in the WTP Pretreatment Process

RL Russell
RA Peterson
DE Rinehart
JV Crum

November 2009

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Test Specification: 24590-PTF-TSP-RT-07-001, Rev 2
Test Plan: TP-WTP-PEP-044, Rev 0.2
Test Exceptions: 24590-WTP-TEF-RT-09-0001, Rev 1
24590-WTP-TEF-RT-09-0002, Rev 0
R&T focus area: Pretreatment
Test Scoping Statement: 24590-WTP-PL-RT-07-0002 Rev 0. SS: M6-3

Pacific Northwest National Laboratory
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by Test Exceptions 24590-WTP-TEF-RT-09-0001 Rev 1 and 24590-WTP-TEF-RT-09-0002 Rev 0 under Test Specification, 24590-PTF-TSP-RT-07-001, Rev 2 and Test Plan TP-WTP-PEP-044, Rev 0.2. The work followed the quality assurance requirements outlined in the Test Specification and Test Plan. The descriptions provided in this 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:

11/20/09

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

Date

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Abbreviations and Acronyms

AFA	anti-foam agent
APEL	Applied Process Engineering Laboratory
ASME	American Society of Mechanical Engineers
BNI	Bechtel National Incorporated
BS	blank spike
CFR	Code of Federal Regulations
DIW	deionized water
DOE	U.S. Department of Energy
EFRT	External Flowsheet Review Team
HDI	How Do I….?
IC	ion chromatography
ICP	inductively coupled plasma
IW	inhibited water
LCS	laboratory control sample
OM	optical microscopy
PDLW	Process Development Laboratory West
PEP	Pretreatment Engineering Platform
PLM	polarized light microscopy
PNNL	Pacific Northwest National Laboratory
PSD	particle-size distribution
PTF	Pretreatment Facility
QAM	Quality Assurance Manual
QAP	quality assurance program
QARD	Quality Assurance Requirements and Descriptions (document)
QC	quality control
RPP	River Protection Project
R&T	research and technology
SEM	scanning electron microscopy
UDS	undissolved solids
UFP	ultrafiltration process
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-ray diffraction

Testing Summary

This report includes the results of the precipitation study testing performed in accordance with Test Exception 24590-WTP-TEF-RT-09-0001, Rev 1, for Test Plan TP-WTP-PEP-044, Rev 0.2,[a] which was prepared and approved in response to Test Specification 24590-WTP-TSP-RT-07-001, Rev 2 (Huckaby 2008).

Significant post-filtration precipitation was observed in the post-caustic leachate and wash solutions while the leaching and ultrafiltration processes were demonstrated in the Pretreatment Engineering Platform (PEP). Precipitation in these streams could lead to precipitates accumulating in filtrate receipt vessels and in the feed to ion exchange columns. Post-filtration precipitation in the feed to the ion-exchange column, if it occurs, will severely impact the operability of the unit and the pretreatment process. Therefore, a laboratory study was carried out to develop an understanding of the phenomenon of post-filtration precipitation and the help in identifying the pathways to mitigate it. This report summarizes the results from the laboratory studies to support this objective. The salient findings from the study are as follows:

- The polarized light microscopy (PLM) mineralogical characterizations and the chemical compositions found the precipitates observed in the PEP to be predominantly sodium phosphate and sodium oxalate.
- The presence of phosphate, sulfate, and fluoride anions do not appear to have an effect on this final equilibrium composition of oxalate, but do appear to slow down the rate of precipitation of oxalate.
- Phosphate precipitates rapidly with the solution reaching close to equilibrium in about 12 hours in the absence of fluoride. However, the presence of fluoride anions appears to slow down the approach of phosphate to equilibrium and has a strong effect on the final equilibrium phosphate concentration. There appears to be no significant effects on the rate of phosphate precipitation from the presence of oxalate, sulfate, and silicate anions in solution.
- The precipitation of sulfate appears to be affected very significantly by the presence of fluoride anions. However, the presence of fluoride appeared to have no effect on the rate of approach of sulfate to its apparent equilibrium concentration.
- The fluoride appears to reach equilibrium composition very rapidly within 12 hours. The presence of both phosphate and oxalate anions appears to suppress the equilibrium concentration of fluoride very significantly at 25°C, while sulfate may not have an effect. The presence of other anions does not appear to affect the rate of approach of fluoride to equilibrium concentration.
- In all cases, precipitates when observed settled very rapidly in less than 1 hour.
- In the presence of fluoride and phosphate anions, the precipitate observed was $Na_7F(PO_4)_2 \cdot 19H_20$. In the absence of fluorides, the phosphate anion appeared to form $Na_3(PO_4) \cdot 12H_2O$.
- The particle-size analysis performed using the I-mage software on the polarized light micrographs indicates that the $Na_7F(PO_4)_2 \cdot 19H_2O$ particles ranged from a minimum of 20 μm × 20 μm (length × width) to a maximum of 2600 μm × 1400 μm with the mean size in the range of 225 μm to 715 μm in length and 30 μm to 175 μm in width. Primary crystals of $Na_7F(PO_4)_2 \cdot 19H_2O$ appeared to be hexahedrons in shape.

(a) RL Russell. 2008. "Test Plan for the PEP Parallel Laboratory Testing." TP-WTP-PEP-044, Rev 0.2. Pacific Northwest National Laboratory, Richland, Washington.

- The $Na_3(PO_4).12H_2O$ particles were significantly smaller in size, ranging from a minimum of 108 µm × 16 µm to a maximum of 2500 µm × 76 µm, with a mean of 610 µm × 35 µm. The primary crystals of $Na_3(PO_4).12H_2O$ were needle like in shape.
- The precipitates redissolve upon dilution with water. The degree of dilution varied, but in general complete dissolution of the precipitates could be achieved through dilution.
- The phosphate precipitates could be redissolved at temperatures ≤35°C, when heated.
- Precipitates of oxalate could form when leachate and wash solutions are blended together because of a common ion effect from the increased sodium ion concentration in the blend relative to the wash solutions.

Objective

The test objectives for the work addressed in TP-WTP-PEP-044, Rev 0.2[(a)] are summarized in Table S.1 along with a discussion of how the objectives were met. Only the fifth test objective is addressed in this report as the others were all addressed in previous reports.

Table S.1. Test Objectives from TP-WTP-PEP-044, Rev 0.2

Test Objective	Objective Met? (Y/N)	Discussion
1) Establish scale factors between laboratory process measurements (e.g., leach factors, filter fluxes) and those of the Pretreatment Engineering Platform (PEP).	NA	This objective was addressed in reports WTP-RPT-186, Rev 0, WTP-RPT-188, Rev 0, and WTP-RPT-197, Rev 0.
2) Maximize the comparability of the laboratory and PEP process measurements and simplify the development of the scaling relationships. Slurry samples will be collected from the PEP at appropriate points during the testing, transported to a laboratory, and subjected to analogous laboratory testing. Filter flux measurements for slurries with low and high solids concentrations, caustic leaching, and oxidative leaching will each be examined in this fashion.	NA	This objective was addressed in reports WTP-RPT-186, Rev 0, WTP-RPT-188, Rev 0, and WTP-RPT-197, Rev 0.
3) Permeate precipitation testing will be performed to evaluate the propensity of the Phase I simulant permeates to precipitate solids.	NA	This objective was addressed in report WTP-RPT-200, Rev 0.

Table S.1. Test Objectives from TP-WTP-PEP-044, Rev 0.2

Test Objective	Objective Met? (Y/N)	Discussion
4) Develop an understanding of the post-precipitation phenomenon.	NA	This objective was addressed in report WTP-RPT-200, Rev 0.
5) Develop empirical information needed to 1) understand the operating bounds in concentration and temperature to avoid post-filtration precipitation in the caustic leach process solutions, and 2) identify and assess a need for a change to the flowsheet, if required, to improve process operability.	Y	Empirical data were developed to identify the extent of supersaturation that was achieved during recent PEP tests. In addition, empirical data were obtained to assess the extent of supersaturation using a typical process cooling curve. This information provides understanding about the temperature or dilution required to avoid post-filtration precipitation. This empirical information will also provide the necessary information for WTP to assess the need for a change to the flowsheet. It was determined that the majority of the precipitates in these PEP washes were primarily sodium phosphates and sodium oxalates. The phosphates are sensitive to temperature in precipitating whereas the oxalates are not. It was also determined from the PEP washes that phosphates precipitated in the more concentrated washes (the earlier ones) whereas oxalates precipitated in the more dilute washes (the later ones). Most of the precipitates from the PEP washes can be dissolved by dilution with deionized water (DIW). When different combinations of leachate, permeate, and wash from the PEP are blended together, they form precipitates almost immediately. Therefore, to avoid precipitation in the wash solutions, a change to the flowsheet needs to be considered.

Test Exceptions

There were two Test Exceptions issued for Test Plan TP-WTP-PEP-044, Rev 0.2. These test exceptions are summarized in Table S.2 along with a brief description of how each test exception impacted existing objectives and the test plan scope.

Table S.2. Test Exceptions for Test Plan TP-WTP-PEP-044, Rev 0.2

List Test Exceptions	Describe Test Exceptions
24590-WTP-TEF-RT-09-0001, Rev 1	This Test Exception did not affect any existing test plan objectives. It added test objectives concerned with 1) understanding the operating bounds in concentration and temperature to avoid post-filtration precipitation in the caustic leach process solutions, and 2) identifying and assessing a need for a change to the flowsheet, if required, to improve process operability. This is objective 5 in Table S.1.
24590-WTP-TEF-RT-09-0002, Rev 0	This Test Exception did not affect any existing test plan objectives. It added test objectives concerned with developing an understanding of the post-filtration precipitation process. This is objective 4 in Table S.1.

Results and Performance Against Success Criteria

The success criterion described in TP-WTP-PEP-044, Rev 0.2 that this testing met is presented in Table S.3.

Table S.3. Results and Performance Against Success Criteria of TP-WTP-PEP-044, Rev 0.2

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
1. Generate testing results that allow a scale-up factor from the laboratory testing to the PEP testing to be generated.	1. This criterion is not addressed in this report. This was addressed in reports WTP-RPT-186, Rev 0, WTP-RPT-188, Rev 0, and WTP-RPT-197, Rev 0.
2. Determine the mineralogy of the precipitate phase, precipitate composition, and the solution phase saturation composition for the composite samples from demonstration Test A.	2. This criterion was met by performing chemical analysis using inductively coupled plasma (ICP) spectroscopy and ion chromatography (IC) on the solution and on the dissolved solids. The solids were also analyzed by polarized light microscopy (PLM) and X-ray diffraction (XRD), and three of them were found to be sodium phosphate, and one of them was found to be sodium oxalate with all analytical methods being in agreement. These results are discussed further in Section 3.0.
3. Determine the rate at which the anions-phosphate, oxalate, sulfate, silicate, and fluoride-approach equilibrium solution composition (saturation concentration) in post-caustic-leach slurry at 25°C before filtration.	3. The criterion was met by preparing 11 different synthetic caustic leachate blends of the target anions from UFP-2 that were prepared by spiking different anions to a higher concentration before beginning the test. These were then heated to 85°C, held at 85°C for 24 hours, cooled to 25°C, and then held for

Table S.3. Results and Performance Against Success Criteria of TP-WTP-PEP-044, Rev 0.2

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
	24 hours. The samples were then cooled to 16°C, held for 24 hours, heated back to 25°C, and then held 96 hours. The solutions were sampled periodically throughout the test and analyzed for the presence of these anions. These results showed that oxalate appears to be fairly slow to precipitate, taking nearly 24 hours before reaching equilibrium. The presence of phosphate, sulfate, or fluoride did not significantly change the equilibrium concentration of oxalate, but the kinetics appears to be faster in the presence of the other anions. In the absence of fluoride, phosphate appears to equilibrate very quickly. However, in the presence of fluoride, phosphate equilibrates much slower and to a significantly lower solubility limit. Phosphate solubility appears to be a strong function of fluoride. The presence of fluoride does appear to impact the sulfate solubility. Interestingly, fluoride appears to equilibrate fairly quickly. The presence of oxalate appears to impact the fluoride solubility, but fluoride did not impact the oxalate solubility. These results are discussed further in Section 4.0.
4. Identify precipitates formed at ambient temperature in the presence of phosphate, oxalate, sulfate, silicate, and fluoride anions in the post-caustic leachate solution. Also, determine particle-size distribution (PSD), crystal shape and habit (morphology), quantity, and the settling rate of precipitates formed.	4. This criterion was met by preparing 11 different blends (which corresponded to the supernate concentration of those in Success Criterion 3) of the target anions that were prepared and held at 35°C for 24 hours and filtered. Then the supernate was cooled to 20°C and held for 96 hours. The objective of this task was to collect precipitate samples for physical and chemical characterization. Five of the 11 tests produced precipitate, which was then analyzed to determine PSD crystal shape and habit (morphology), quantity, and the settling rate of precipitates formed. These results showed that four of the precipitates were sodium fluoride phosphates, and one precipitate was sodium phosphate. No oxalate, sulfate, or silicate solids were observed. The solids settled fairly quickly. These results are discussed further in Section 5.0.
5. Determine the dilution required to redissolve the post-filtration precipitate through incremental dilution of the slurry with water at 25°C.	5. This criterion was met by testing seven samples from the PEP Integrated Tests (A, B, and D). A total of 100-mL of solution with precipitate in it was placed in a centrifuge tube and diluted with 5-mL DIW each

Table S.3. Results and Performance Against Success Criteria of TP-WTP-PEP-044, Rev 0.2

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
	day until the precipitate completely dissolved. The amount of solids remaining was measured each day by centrifuging at 1000G for 15 minutes and recording the volume of solids present. More DIW was added, and the solids were resuspended. These results showed that the solids are essentially soluble if enough DIW is added. These results are discussed further in Section 6.0.
6. Determine solution supersaturation in the post-caustic-leach filtrate during the dewatering period, based on the samples collected at discrete times during Integrated Test B in the PEP. The supersaturation shall be expressed as both the centrifuged volume fraction and as weight fraction of the slurry sample. Also, determine the temperature at which the precipitate goes into total solution.	6. This criterion was met by placing 10 post-caustic-leach filtrate and wash solutions from the PEP Integrated Test B in an incubator at 20°C for 96 hours. The temperature of the incubator was raised 1°C each day up to 35°C. Samples were taken at 20°C, 25°C, and 35°C. Some of the precipitate did not dissolve even at 35°C. These results showed that in the more concentrated solutions, it was phosphate dissolving, and in the more dilute solutions, it was oxalate dissolving. The solids remaining were determined to be sodium oxalate in all but one sample, which was sodium phosphate. These results are discussed further in Section 7.0.
7. Determine the effects of blending on precipitation during the post-caustic-leach dewatering and wash periods in Integrated Test B in the PEP.	7. This criterion was met by preparing five different blends from the PEP Integrated Test B post-caustic-leach dewatering and wash solutions to determine if precipitate formed after 48 hours at 25°C. It was found that the blends containing leachate and permeate all formed precipitate almost immediately whereas the blends containing just wash solutions did not precipitate during this time period at this temperature. These results are discussed further in Section 8.0.

Quality Requirements

The Pacific Northwest National Laboratory (PNNL) Quality Assurance Program is based upon the requirements as 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* (a.k.a.

the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, *Requirements for Quality Assurance Programs for Nuclear Facilities*.
- ASME NQA-1-2000, Part II, Subpart 2.7, *Quality Assurance Requirements for Computer Software for Nuclear Facility Applications.*
- ASME NQA-1-2000, Part IV, Subpart 4.2, *Graded Approach Application of Quality Assurance Requirements for Research and Development.*

The procedures necessary to implement the requirements are documented through PNNL's "How Do I…?" (HDI).(a)

PNNL implements 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),* as applicable. 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). The requirements of DOE/RW-0333P Rev 13, *Quality Assurance Requirements and Descriptions (QARD),* and 10 CFR 830, Subpart A, were not required for this work.

RPP-WTP addresses 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 procedure is part of PNNL's *RPP-WTP Quality Assurance Manual* (RPP-WTP-QA-003). Following this procedure, a technical review would verify that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the objectives.

R&T Test Conditions

The research and technology (R&T) test conditions, as defined in the Test Specifications 24590-PTF-TSP-RT-07-001, Rev 2 (Huckaby 2008) associated with Test Plan TP-WTP-PEP-044, Rev 0.2 are summarized in Table S.4.

(a) PNNL's system for managing the delivery of laboratory-level policies, requirements, and procedures.

Table S.4. R&T Test Conditions from TP-WTP-PEP-044, Rev 0.2

List R&T Test Conditions	Were Test Conditions Followed?
1) Filter flux measurements will be conducted on two low-solids concentration simulants and on two high-solids concentration simulants to demonstrate the scale-up of crossflow filtration.	Not applicable to this report. It is addressed in report RPT-WTP-203, Rev 0.
2) Caustic-leaching tests will be performed with slurry samples collected from the PEP leaching vessels just before steam heating is initiated in the PEP to obtain laboratory caustic-leaching data that can be used as a baseline to evaluate caustic-leaching performance in the PEP.	Not applicable to this report. It is addressed in report RPT-WTP-200, Rev 0.
3) Oxidative leaching tests will be performed with slurry samples collected from the PEP leaching vessels just before the permanganate is added in the PEP to obtain laboratory oxidative leaching data that can be used as a baseline to evaluate oxidative leaching performance in the PEP.	Not applicable to this report. It is addressed in report RPT-WTP-200, Rev 0.
4) Permeate precipitation testing will be conducted using the post-caustic wash solutions, the permeate near the end of the initial solids concentration process, and the permeate near the end of the post-caustic-leach solids concentration process to evaluate the propensity of the simulant permeates to precipitate solids.	Not applicable to this report. It is addressed in report RPT-WTP-200, Rev 0.
5) Permeate precipitation tests will be performed to determine the operating bounds in concentration and temperature to avoid post-filtration precipitation in the caustic-leach process and to assess a need for a change to the flowsheet to improve process operability using caustic leach and wash solutions collected during PEP Integrated Tests A, B, and D.	The test conditions were followed by characterizing the washes and precipitates, diluting the wash solutions with 5 vol% DIW every 24 hours, raising the temperatures by 1°C per 24 hours from 20°C to 35°C, and blending different solutions as discussed in Sections 3, 6, 7, and 8, respectively. A simplified simulant spiked with the anions of interest was also used and heated to 85°C for 24 hours, cooled to 25°C for 24 hours, cooled to 16°C for 24 hours, and then heated to 25°C again for 96 hours as discussed in Section 4. Another test was performed with the same spiked simulant by heating to 35°C for 46 hours and then filtering and cooling to 20°C for 96 hours as discussed in Section 5.

Simulant Use

Testing for Tasks 2 and 3 of the Test Exception 24590-WTP-TEF-RT-09-0001, Rev 1 used a base simplified simulant (derived from PEP Integrated Test A) that contained simulant solids made up of the filtration sludge and a supernate containing sufficient aluminate to represent dissolved gibbsite/boehmite, nitrate, nitrite, carbonate, and hydroxide only. The composition of the base simulant was based on UFP-1 leaching conditions.

Testing for Tasks 1, 4, 5, and 6 used caustic leach and wash solution samples provided by WTP from the PEP Integrated Tests A, B, and D. Integrated Test A corresponded to caustic leaching in the UFP-1 vessel, and Integrated Tests B and D corresponded to caustic leaching in the UFP-2 vessel.

The simulant used for the PEP tests does not represent any particular Hanford tank waste type or a blend of Hanford tank wastes. The simulant used for the PEP testing was blended from components listed below (Barnes and Voke 2006). The simulant recipe for Phase I PEP testing did not include phosphate simulant. The basis for selecting the individual components and the comparison to actual waste behavior is provided where applicable in the indicated references.

- Boehmite component (for Al) (Russell et al. 2009a)
- Gibbsite component (for Al) (Russell et al. 2009b)
- Oxalate component (Barnes and Voke 2006)
- Filtration Inerts component (Russell et al. 2009c)
- Supernatant component (Barnes and Voke 2006)
- Chromium component (Rapko et al. 2007).

Discrepancies and Follow-on Tests

None.

1.0 Background

Pacific Northwest National Laboratory (PNNL) has been tasked by Bechtel National Inc. (BNI) on the River Protection Project-Hanford Tank Waste Treatment and Immobilization Plant (RPP-WTP) project to perform research and development activities to resolve technical issues identified for the Pretreatment Facility (PTF). The Pretreatment Engineering Platform (PEP) was designed, constructed, and operated as part of a plan to respond to issue M12, "Undemonstrated Leaching Processes," of the External Flowsheet Review Team (EFRT) issue response plan (Barnes et al. 2006). The PEP is a $^1/_{4.5}$-scale test platform designed to simulate the WTP pretreatment caustic leaching, oxidative leaching, ultrafiltration solids concentration, and slurry washing processes. The PEP replicates the WTP leaching processes using prototypic equipment and control strategies. A simplified flow diagram of the PEP system is shown in Figure 1.1.

Two operating scenarios are being evaluated for the ultrafiltration process (UFP) and leaching operations. The first scenario has caustic leaching performed in the UFP-2 ultrafiltration feed vessels (i.e., vessel UFP-VSL-T02A in the PEP; and vessels UFP-VSL-00002A and B in the WTP PTF). The second scenario has caustic leaching conducted in the UFP-1 ultrafiltration feed preparation vessels (i.e., vessels UFP-VSL-T01A and B in the PEP; vessels UFP-VSL-00001A and B in the WTP PTF).

In both scenarios, 19-M sodium hydroxide solution (NaOH, caustic) is added to the waste slurry in the vessels to leach solid aluminum compounds (e.g., gibbsite, boehmite). Caustic addition is followed by a heating step that uses direct injection of steam to accelerate the leach process. Following the caustic leach, the vessel contents are cooled using vessel cooling jackets and/or external heat exchangers. The main difference between the two scenarios is that for leaching in UFP-VSL-T01A and B, the 19-M NaOH is added to feed waste slurry (3 to 8-wt% solids), while for leaching in UFP-VSL-T02A, the slurry is concentrated to nominally 20-wt% solids using crossflow ultrafiltration before adding the caustic.

The PEP testing program was conducted under Test Plan TP-RPP-WTP-506(a) using a waste simulant that was developed in response to Task 5 from the M-12 EFRT issue response plan(b). The testing included the following tests with the PEP simulant:

- Shakedown/Functional Testing: Tested process operations (e.g., slurry transfers, steam heating of the vessels and the accumulation of condensate, filter backpulsing, and flushing), process controls (e.g., transmembrane pressure and axial flow velocity in the filter loop), certain test functions (e.g., in-line slurry sampling accuracy and precision).
- Integrated Test A: Demonstrated integrated processing when caustic leaching (98°C) is performed in UFP-VSL-00001A/B with the Cr simulant component added after the post-caustic-leach washing step.
- Integrated Test B: Demonstrated integrated processing when the caustic leaching (98°C) is performed in UFP-VSL-00002A with the Cr simulant component added after the post-caustic-leach washing step.

(a) GB Josephson, OP Bredt, JK Young, and DE Kurath. 2008. *Pretreatment Engineering Platform (PEP) Testing(Phase I).* TP-RPP-WTP-506, Rev 0.4, Pacific Northwest National Laboratory, Richland, Washington.

(b) RD Scheele, GN Brown, and DE Kurath. 2009. *Scale-Up, Production, and Procurement of PEP Simulants.* WTP-RPT-204, Rev 0, Pacific Northwest National Laboratory, Richland Washington.

- Integrated Test D: Demonstrated integrated processing when the caustic leaching is performed at a lower temperature (85°C) in UFP-VSL-00002A and with the Cr simulant component added to the initial batch of simulant.

Integrated Test C was deleted from the scope of the testing (ICN-TP-RPP-WTP-506_R0.2).

Whether caustic leaching was carried out in UFP-VSL-T01A/B or UFP-VSL-T02A, the leached solids wash steps occurred in vessel UFP-VSL-T02A and used the same procedure. Periodically, measured volumes of inhibited water (IW) (0.01 M NaOH) were added incrementally upstream of the first recirculation pump and mixed inline. At the same time, permeate was removed from the ultrafilters in the loop and collected in UFP-VSL-T62A and/or UFP-VSL-T62B. The wash liquid addition line flowmeter was used to monitor and control the wash volume.

Significant post-filtration precipitation was observed in the post-caustic leachate and wash solutions while the leaching and ultrafiltration processes were demonstrated in the PEP. Precipitation in these streams could lead to precipitates accumulating in filtrate receipt vessels and in the feed to ion exchange columns. Post-filtration precipitation in the feed to the ion-exchange column will have a very significant effect on the operability of the unit and the pretreatment process. Therefore, it is essential to develop an understanding of the post-filtration-precipitation phenomenon.

The test objective was divided into several tasks to develop an understanding of the post-filtration-precipitation phenomenon. The post-filtration precipitate mineralogy, precipitate phase compositions, and solution saturation compositions in the post-caustic leachate and wash solution samples from Integrated Test A are described in Section 3. The rate at which the anions approach equilibrium solution composition upon cooling in the post-caustic-leach slurry is discussed in Section 4 of this report. Section 5 identifies and characterizes the precipitates formed in the post-caustic leachate solution through controlled laboratory experiments. Section 6 describes the potential to redissolve the post-filtration precipitate in Integrated Tests A, B, and D in the PEP through dilution with water. Determination of solution supersaturation in the post-caustic-leach filtrate during the dewatering and washing period based on the samples collected during Integrated Test B in the PEP is described in Section 7. The effects of blending during the post-caustic-leach dewatering and wash periods in Integrated Test B in the PEP are discussed in Section 8.

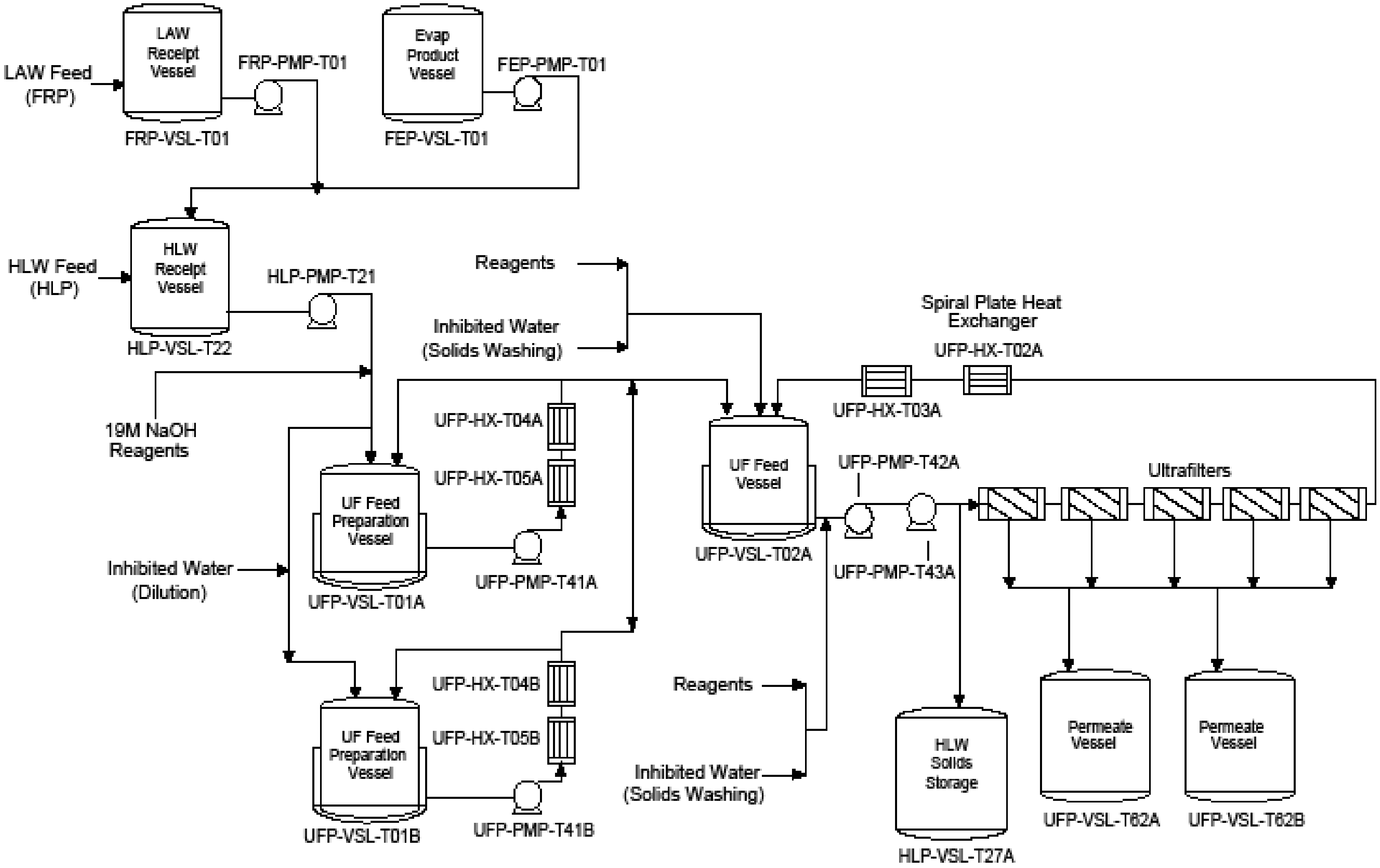

Figure 1.1. PEP Simplified Flow Diagram

2.0 Quality Assurance

The PNNL Quality Assurance Program is based upon the requirements as 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* (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, *Requirements for Quality Assurance Programs for Nuclear Facilities*.
- ASME NQA-1-2000, Part II, Subpart 2.7, *Quality Assurance Requirements for Computer Software for Nuclear Facility Applications.*
- ASME NQA-1-2000, Part IV, Subpart 4.2, *Graded Approach Application of Quality Assurance Requirements for Research and Development.*

The procedures necessary to implement the requirements are documented through PNNL's "How Do I…?" (HDI).[a]

PNNL implements 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)* as applicable. 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). The requirements of DOE/RW-0333P Rev 13, *Quality Assurance Requirements and Descriptions (QARD),* and 10 CFR 830, Subpart A, were not required for this work.

The applicable quality control (QC) parameters for chemical analysis and the acceptance criteria are delineated in Table 2.1. Blank spike and/or laboratory control sample QC failures will result in reanalyzing the sample for the particular analyte for which the spike failed. Matrix spike and/or duplicate analysis QC failures will not result in reanalyzing the sample, but probable reasons for the failure will be discussed in the analytical report to be stored in the project files.

RPP-WTP addresses 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 procedure is part of PNNL's *RPP-WTP Quality Assurance Manual* (RPP-WTP-QA-003). Following this procedure, a technical review would verify that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the objectives.

(a) PNNL's system for managing the delivery of laboratory-level policies, requirements, and procedures.

Table 2.1. QC Acceptance Criteria

QC Sample	QC Acceptance Criteria
Processing Blanks	<EQL (estimated quantitation limit)
Duplicate (Precision)	≤20%
Laboratory Control Sample (LCS) /Blank Spike (BS)	80% to 120%
Matrix Spike (Accuracy)	None prepared
Post Spike (Accuracy)	75% to 125%
Serial Dilution	≤10%
System QC Samples	90% to 110%

3.0 Post-Filtration Precipitate and Solution Characterizations

The objective of these tests was to determine the post-filtration precipitate mineralogy, precipitate phase compositions, and the solution saturation compositions in the post-caustic leachate and wash solution samples from the PEP Integrated Test A at ambient temperature. These tests were specified in Test Exception WTP-TEF-RT-09-0001, Rev 1, Task 1, associated with Test Plan TP-WTP-PEP-044, Rev 0.2.

In the PEP Integrated Test A, the concentrated caustic-leached solids in UFP-VSL-T02A were washed incrementally with 0.01 M NaOH. The wash solution was added in 100 incremental steps. Each step had a target volume of 11 gallons. A 1-L sample was taken from the line carrying the permeate stream from the first ultrafilter to the pulse-pot, which represented each wash step for a total of 100 samples. The wash steps occurred in tank UFP-VSL-T02A, which contained the leached and concentrated slurry, by periodically adding a small volume of inhibited water (IW, 0.01 M NaOH) upstream of the first recirculation pump and mixing inline. At the same time, permeate was removed from the ultrafilters in the loop and collected in UFP-VSL-T62A and/or UFP-VSL-T62B. The flowmeter for the line where wash liquid is added was used to monitor and control the wash volume.

During every third wash step, an anti-foam agent (AFA) was added to maintain a target concentration of 350 ppm. Wash liquid additions were initiated when the level in vessel UFP-VSL-T02A dropped below a set value occurring approximately every 4 minutes, except between batches 7 and 8. Between batches 7 and 8, there was a 14-hr hold time to address recirculation pump problems. Following each addition, the slurry and wash liquid were recirculated and therefore mixed continuously while permeate was continuously removed at a rate between 4-kg/min and 17-kg/min by ultrafiltration through all five filter bundles.

The caustic-leach wash samples were collected from February 14, 2009, 1:13 until February 15, 2009 22:50. All 100 samples were stored at ambient temperature of the Process Development Laboratory-West (PDL-W) facility and were then transferred to the Applied Process Engineering Laboratory (APEL) on February 17, 2009. These samples were stored at room temperature of the APEL (~18-22°C) for 13 to 14 days. Samples 2341 (wash 3), 2349 (wash 11), 2363 (wash 25), and 2369 (wash 31) were chosen for further characterization and all contained precipitates that were then separated from the supernate by vacuum filtration using a 0.45-µm filter on March 2-3, 2009, in the APEL.

Even after filtering, the samples continued to form precipitate over time. Therefore, these four samples (2341, 2349, 2363, and 2369) were placed in an oven at 38.4°C on June 8, 2009, 17:30 until June 11, 2009, 9:30 to allow the precipitate to redissolve. After the precipitate had redissolved, supernate samples were taken at approximately 38°C for chemical analysis and density measurement after filtering.

Samples 2341 (wash 3), 2349 (wash 11), 2363 (wash 25), and 2369 (wash 31) were analyzed by inductively coupled plasma (ICP) spectroscopy for Al, Na, P, and S (shown in Table 3.1) and ion chromatography (IC) for oxalate, phosphate, sulfate, nitrate, and nitrite (shown in Table 3.2) to determine the solution saturation compositions as well as supernate density and hydroxide concentration (shown in Table 3.3). The chemical analysis and density measurements were performed at room temperature. The chemical analysis involved dissolving any precipitates that may have formed, and the density measurements ignored any precipitates that may have formed.

Table 3.1. ICP Results for Integrated Test A Post-Caustic Wash Solutions Composition

Sample ID	Wash #	Al (µg/g)	Na (µg/g)	P (µg/g)	S (µg/g)
2341	3	7,710	117,000	586	2,700
2349	11	5,840	91,800	744	2,060
2363	25	4,060	63,900	1,500	1,370
2369	31	3,200	54,000	1,950	1,140

Table 3.2. IC Results for Integrated Test A Post-Caustic Wash Solutions Composition

Sample ID	Wash #	C_2O_4 (µg/g)	PO_4 (µg/g)	SO_4 (µg/g)	NO_3 (µg/g)	NO_2 (µg/g)
2341	3	242	1,530	7,810	47,100	10,900
2349	11	622	2,250	6,020	36,100	8,280
2363	25	1,750	4,990	4,140	24,700	5,670
2369	31	2,500	6,370	3,360	20,000	4,620

Table 3.3. Density Results for Integrated Test A Post-Caustic Wash Solutions Composition

Sample ID	Wash #	Density (g/mL)	OH (µg/mL)
2341	3	1.28	7.08E+04
2349	11	1.22	5.05E+04
2363	25	1.15	3.25E+04
2369	31	1.13	2.66E+04

The analytical results of the solution phase in Table 3.2 indicate that the sodium oxalate and sodium phosphate dissolved and increased in concentration throughout the washes whereas the other analytes decreased in concentration progressively during the post-caustic-leach wash. The progressive increase in the oxalate and phosphate concentrations during the wash period is attributed to redissolution of the precipitated oxalate and phosphate during the caustic-leach operation. The redissolution of precipitated oxalate was initially suppressed because of common ion effect from the higher concentration of sodium ions in solution. The phosphate dissolved and appeared earlier than the oxalate during the wash operation, until it was fully dissolved (after approximately 24 washes). The phosphate concentration in the wash solutions began to decrease subsequently as it was gradually diluted with each incremental wash. This is shown in Figure 3.1.

Table 3.4 shows the amount of solids present along with the wt% undissolved solids (UDS). Figure 3.2 shows the solids after they were air-dried. No solids are visible for sample 2369 since so few were present that they were all on the filter paper. Even after filtering, crystals continued to form in the supernate over the next couple of months as the samples sat at room temperature of the APEL (~18-22°C). It should also be noted that phosphate is significantly more temperature sensitive as shown in Figure 5.6. Results shown in Section 5 indicate that a 5°C drop in temperature will result in the precipitation of only about 5% of the soluble oxalate. However, the same 5°C drop will result in the precipitation of about 40% of the soluble sodium phosphate.

A material balance based on the data presented in Table 3.7 (to be discussed later) is consistent with six waters of hydration for the solids measured in. Using this estimate of the waters of hydration, the solids found in samples 2341 (wash 3), 2349 (wash 11), and 2363 (wash 25) are all consistent with the precipitation of approximately 25% of the soluble phosphate. This quantity of precipitation would be consistent with the approximately 3°C temperature drop observed (from 25°C to 22°C upon storage in APEL). However, the quantity of solids formed in sample 2369 (wash 31) represents roughly 10% of the soluble oxalate. This is much greater than the expected 2% to 6% solids based on the observed temperature drop. The results suggest that the oxalate samples may have achieved more supersaturation than simply that due to temperature effects. This could possibly have been from the common ion effect of blending the streams in the shell side of the filter bundle.

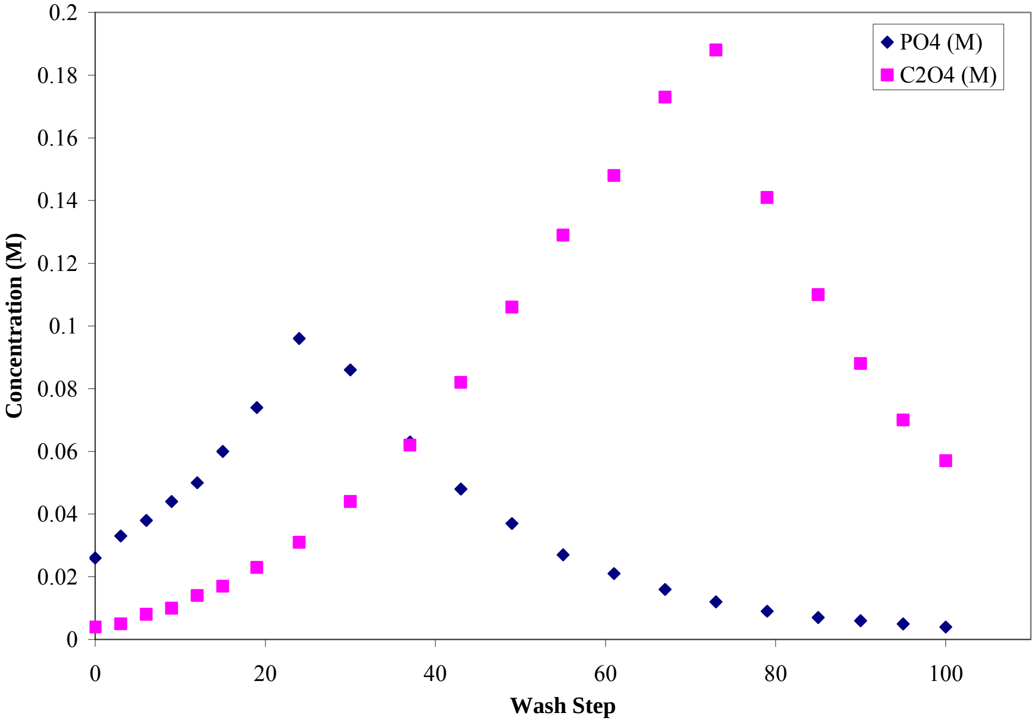

Figure 3.1. Phosphate and Oxalate Concentration Plot with PEP Integrated Test A Wash Step

Table 3.4. Weights of Filtered Solids in Integrated Test A Samples

Sample ID	Wash #	Weight of Solids (g)	Wt% UDS
2341	3	1.99	0.17
2349	11	2.61	0.24
2363	25	4.69	0.44
2369	31	0.388	0.038

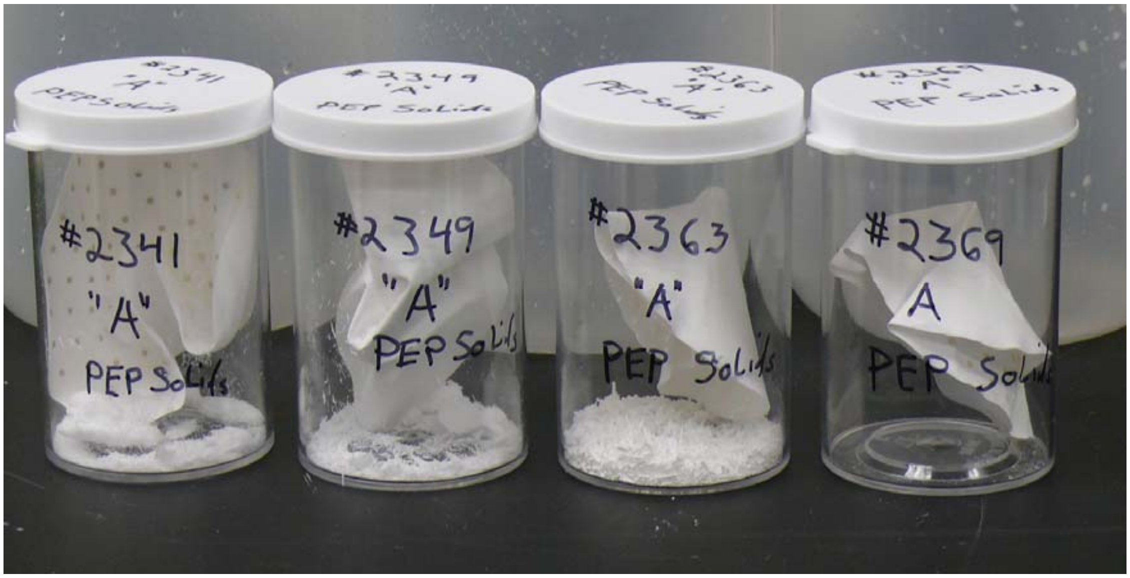

Figure 3.2. Filtered Solids and Filter Paper from the PEP Integrated Test A Samples Analyzed

The solids from this set of samples (2341, 2349, 2363, and 2369) were filtered and air dried, and the mineral form and approximate mean particle size of the solids were determined using polarized light microscopy (PLM). The mineral form was then confirmed using x-ray diffraction (XRD).

Pictures were taken of the samples in polarized light, cross-polarized light, and cross-polarized light with a full wave plate (which introduces a vivid red interference color to the image). Interference patterns were only obtained for samples 2341 (wash 3), 2349 (wash 11), and 2363 (wash 25), which were all determined to be sodium phosphate based on the crystal shape and color refraction. Sample 2369 (wash 31) indicated sodium oxalate based on the crystal shape. The microscope light source was unfiltered. These pictures are shown in Figure 3.3 through Figure 3.12.

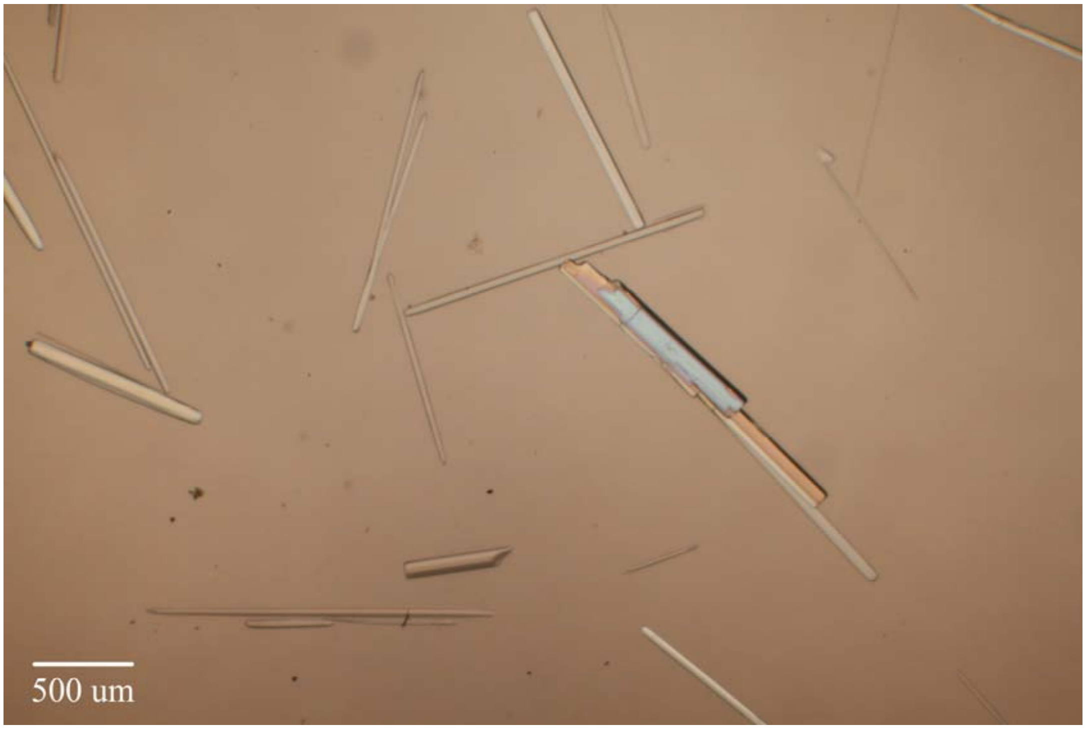

Figure 3.3. Polarized Light Optical Microscopy (OM) of Sodium Phosphate in Sample 2341 (Wash 3)

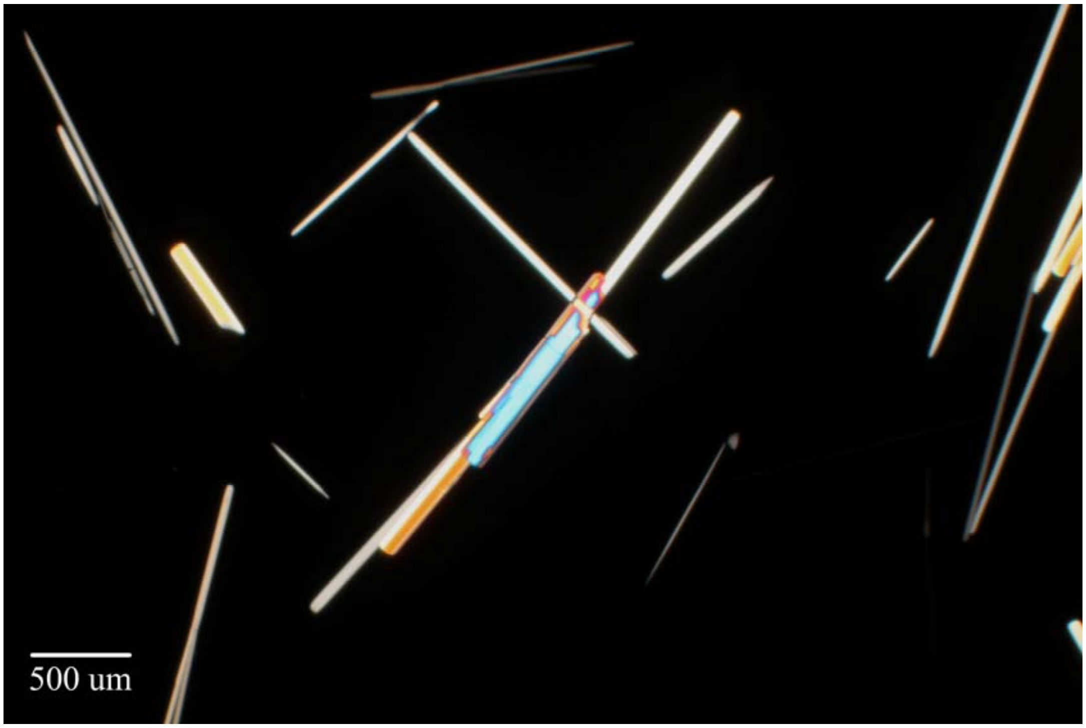

Figure 3.4. Cross-Polarized Light OM of Sodium Phosphate in Sample 2341 (Wash 3)

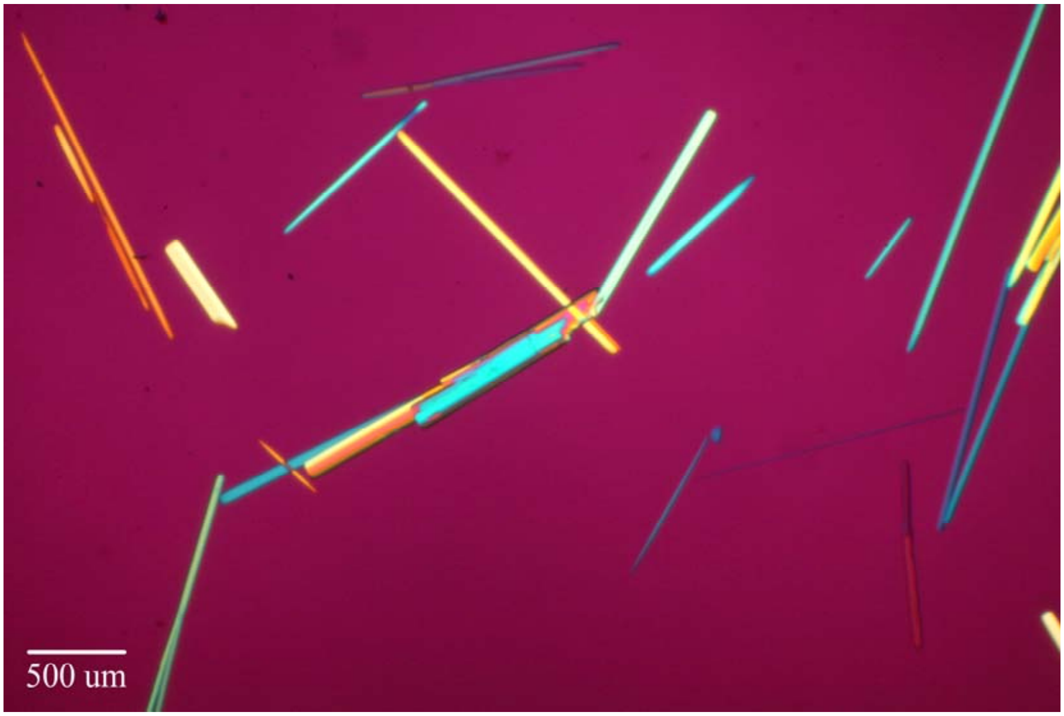

Figure 3.5. Cross-Polarized Light OM of Sodium Phosphate in Sample 2341 (Wash 3) with Full Wave Plate

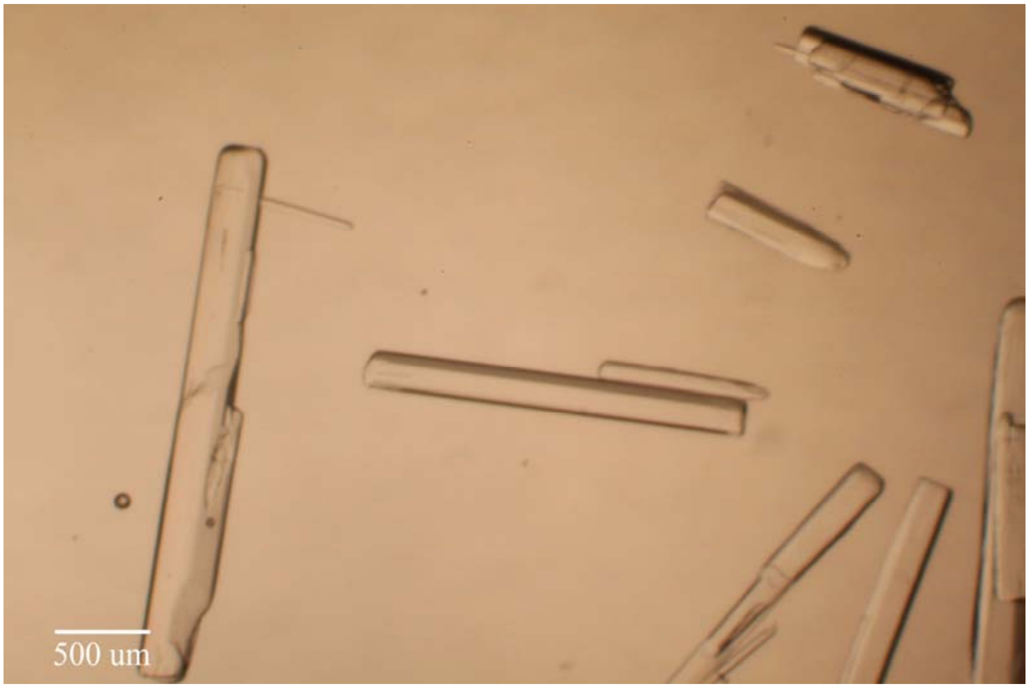

Figure 3.6. Polarized Light OM of Sodium Phosphate in Sample 2349 (Wash 11)

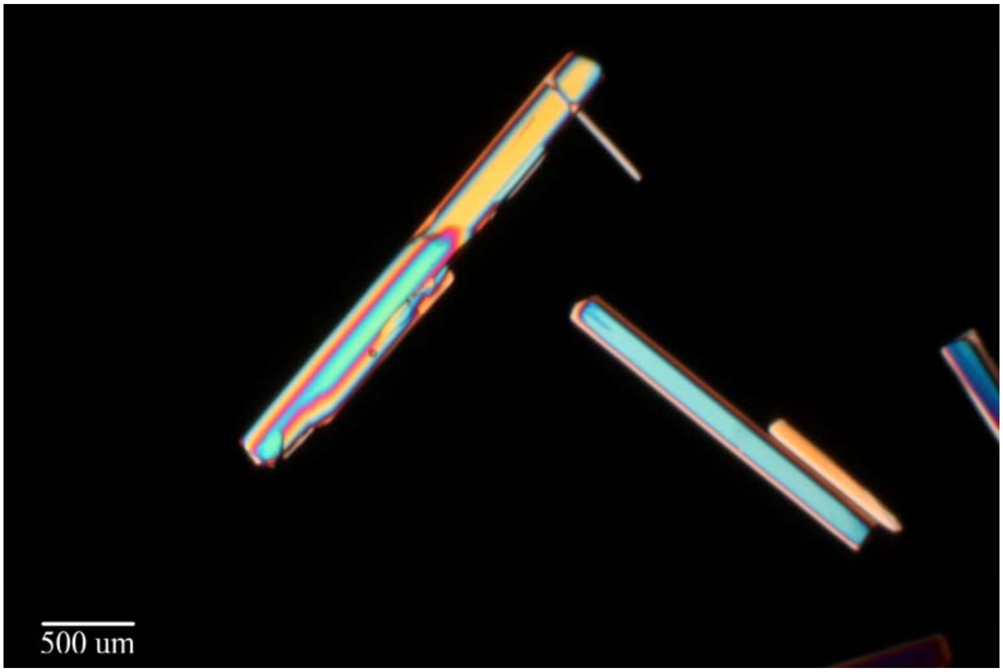

Figure 3.7. Cross-Polarized Light OM of Sodium Phosphate in Sample 2349 (Wash 11)

Figure 3.8. Cross-Polarized Light OM of Sodium Phosphate in Sample 2349 (Wash 11) with Full Wave Plate

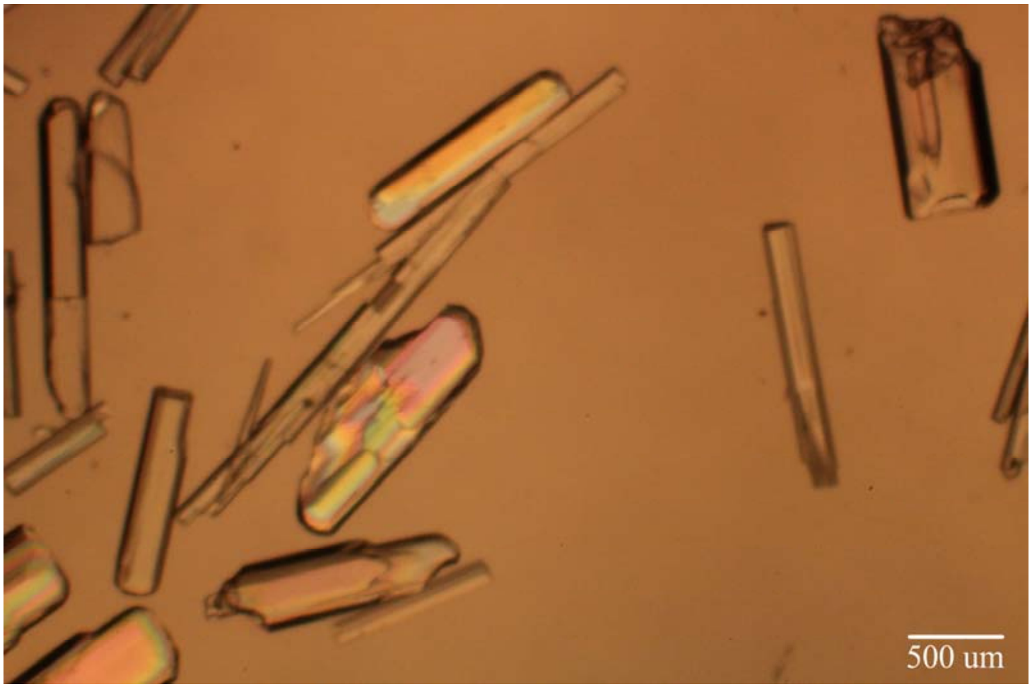

Figure 3.9. Polarized Light OM of Sodium Phosphate in Sample 2363 (Wash 25)

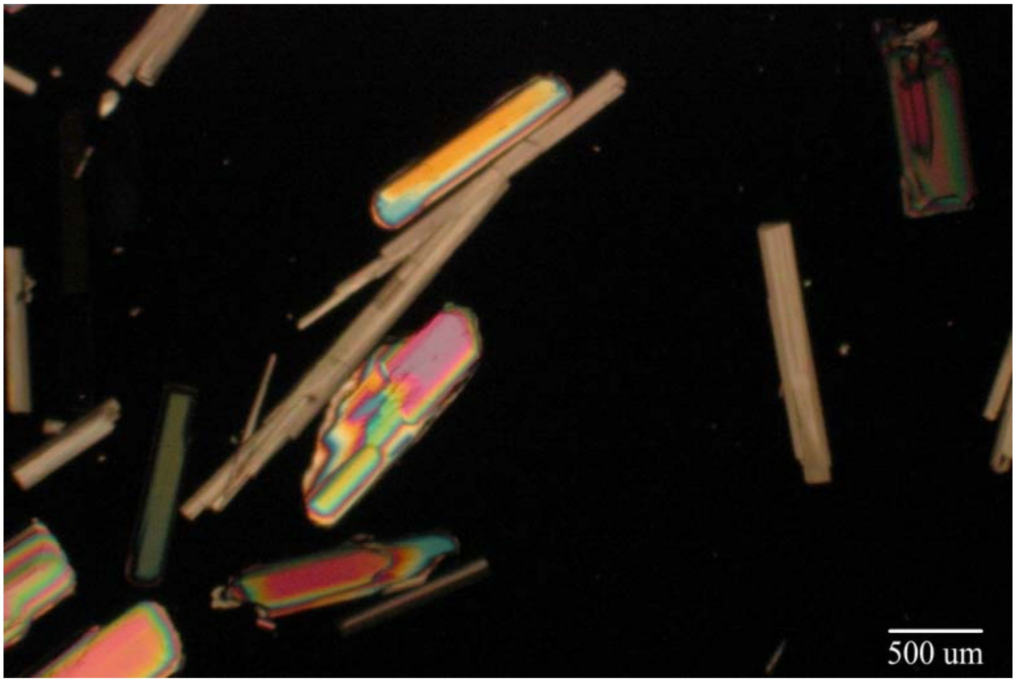

Figure 3.10. Cross-Polarized Light OM of Sodium Phosphate in Sample 2363 (Wash 25)

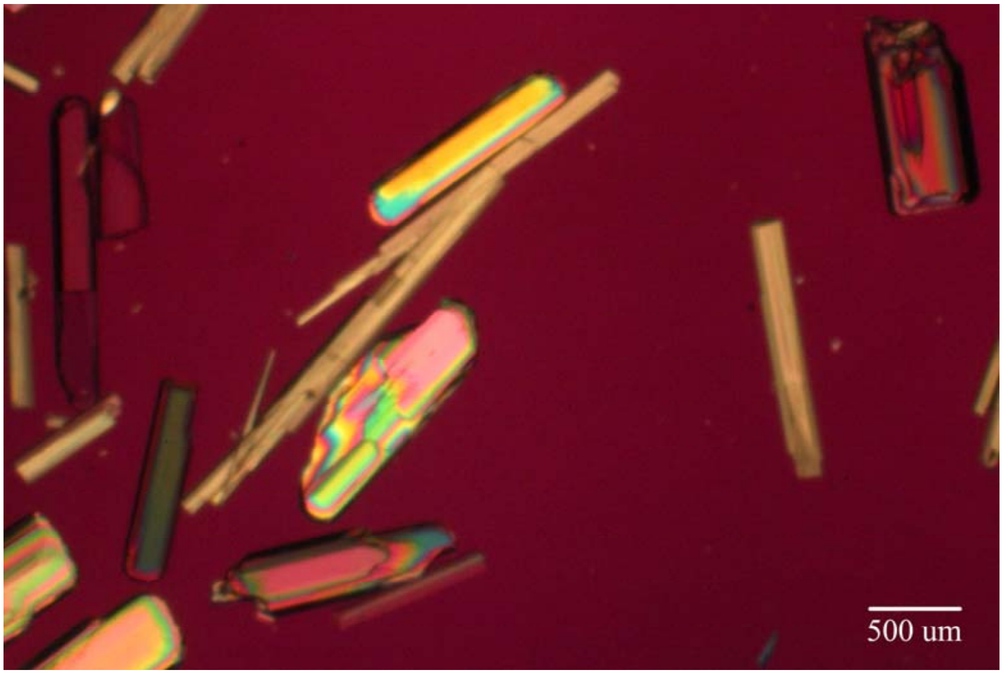

Figure 3.11. Cross-Polarized Light OM of Sodium Phosphate in Sample 2363 (Wash 25) with Full Wave Plate

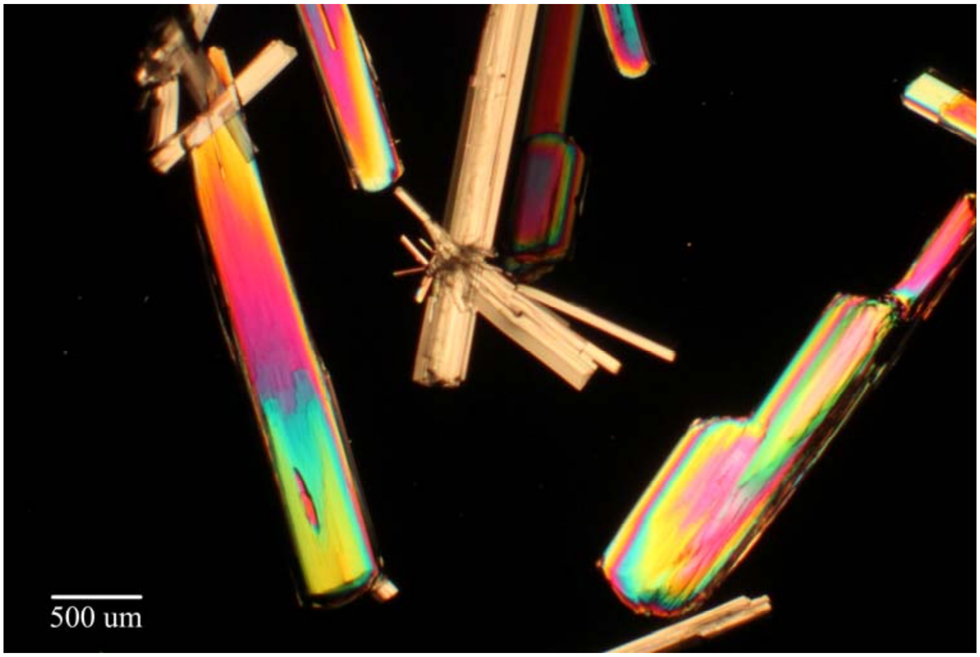

Figure 3.12. Cross-Polarized Light OM of Sodium Oxalate in Sample 2369 (Wash 31)

Particle size analysis was performed using I-mage software on polarized light micrographs. The crystals were manually fit using the multiline function to define the crystal perimeter. The software then calculated the crystal area, maximum length, and maximum width. The summary of results is shown in Table 3.5 with the complete results shown in Appendix A, Table A.10 through Table A.13.

Table 3.5. Summary Table of Measured Crystal Dimensions for Each Sample

Sample #	# of particles	Statistical Measure	Area, μm^2	Max Length, µm	Max Width, µm
2341	18	Mean	47,440	994	53.6
		Min	2,288	102	20.6
		Max	194,030	1,750	148
2349	20	Mean	536,183	2,040	301
		Min	80,973	673	71
		Max	2,206,430	4,200	656
2363	12	Mean	297,616	1,350	272
		Min	93,673	668	143
		Max	543,611	2,470	537
2369	21	Mean	126,568	951	144
		Min	1,157	83	30
		Max	425,482	2,030	426

The solids in sample 2341 (wash 3) were identified as primarily sodium hydrogen phosphate when analyzed by XRD as shown in Figure 3.13. Samples 2349 (wash 11) in Figure 3.14 and 2363 (wash 25) in Figure 3.15 were also identified as sodium hydrogen phosphate dihydrate by XRD. These results are all in agreement with the chemical analysis and PLM for these samples indicating that the precipitates are phosphates, but they disagree on the form of phosphate. It appears that the sodium phosphate may have disproportionated to sodium hydrogen phosphate and sodium hydroxide upon drying. However, this was not confirmed. The XRD identified sample 2369 (wash 31) to be sodium oxalate, as seen in Figure 3.16. This result is in agreement with the chemical analysis and PLM for this sample.

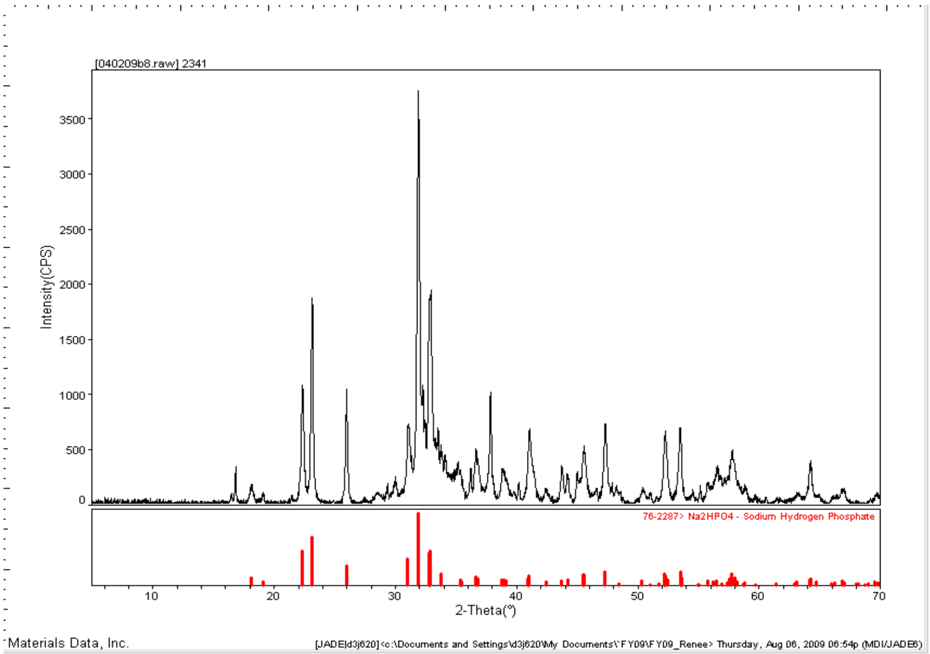

Figure 3.13. XRD Pattern of Crystals from Integrated Test A Wash 3 (Sample Bottle 2341) Identified to be Sodium Hydrogen Phosphate (Na_2HPO_4)

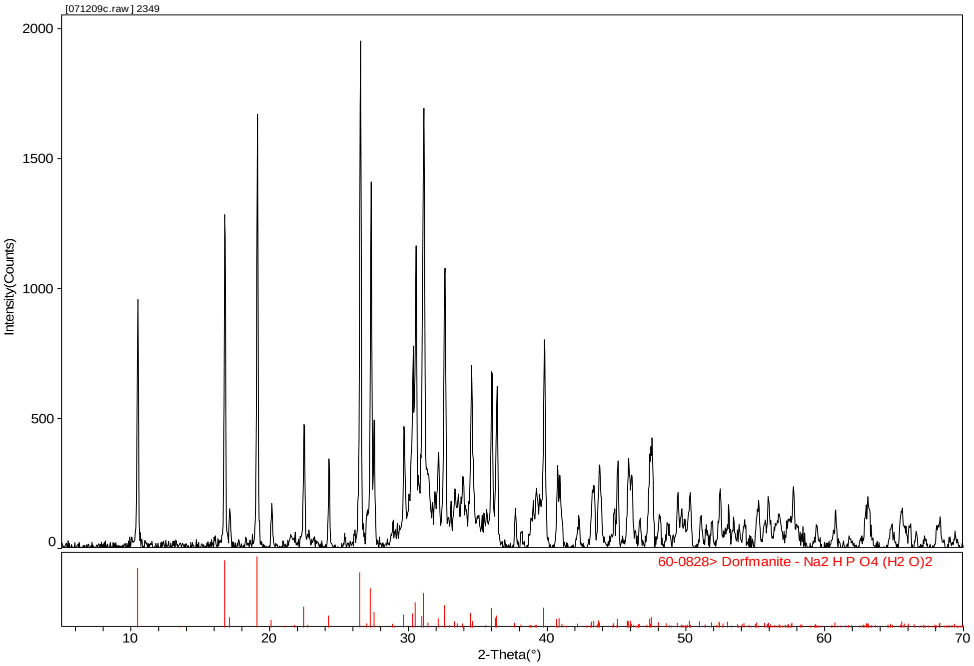

Figure 3.14. XRD Pattern of Crystals from Integrated Test A Wash 11 (Sample Bottle 2349) Identified to be Sodium Hydrogen Phosphate (Na_2HPO_4-$2H_2O$)

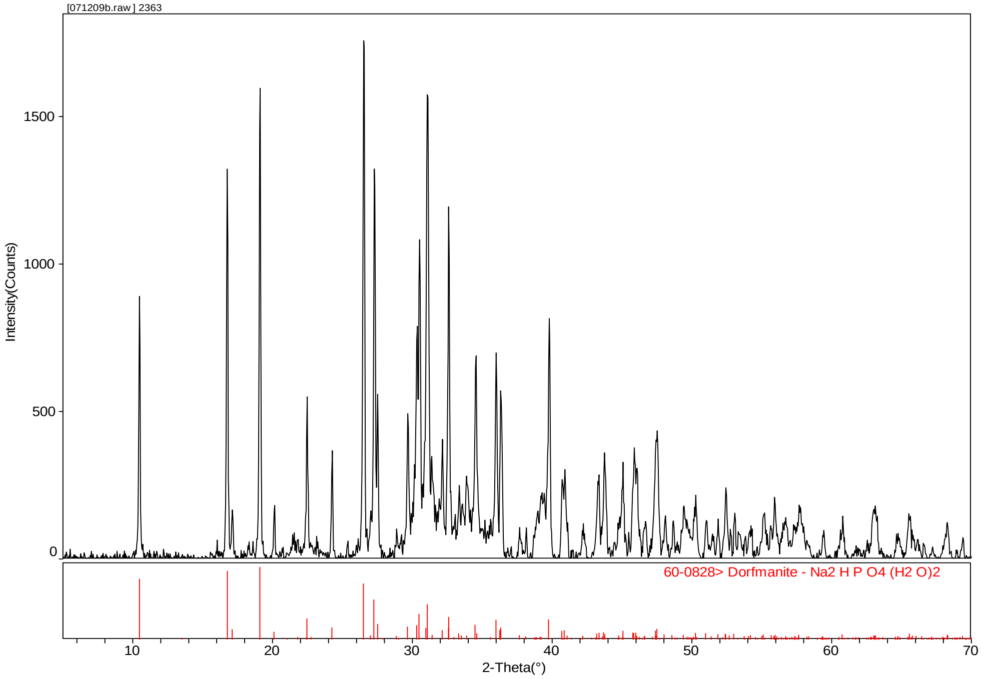

Figure 3.15. XRD Pattern of Crystals from Integrated Test A Wash 25 (Sample Bottle 2363) Identified to be Sodium Hydrogen Phosphate (Na_2HPO_4-$2H_2O$)

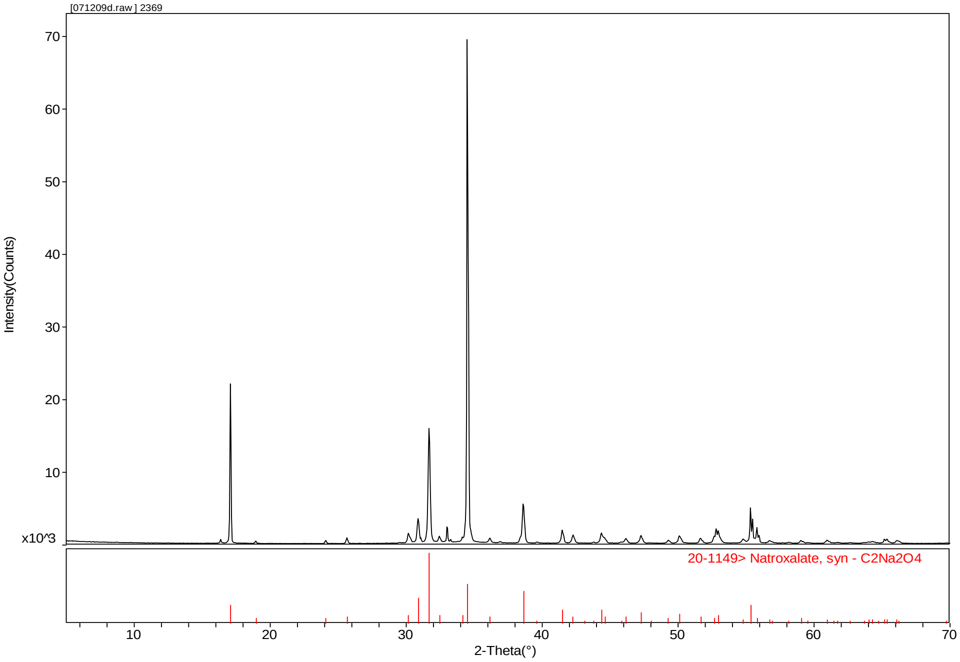

Figure 3.16. XRD Pattern of Crystals from Integrated Test A Wash 31 (Sample Bottle 2369) Identified to be Sodium Oxalate ($Na_2C_2O_4$)

For samples 2341 (wash 3), 2349 (wash 11), 2363 (wash 25), and 2369 (wash 31), a portion of the filtered and air-dried solids were dissolved in deionized water (DIW) in a ratio of approximately 40:1 and analyzed by ICP (Table 3.6) and IC (Table 3.7). These results confirmed what the PLM and XRD showed, namely that samples 2341, 2349, and 2363 were sodium phosphate whereas sample 2369 was sodium oxalate. This can be explained by 1) differences in the solubilities of sodium phosphate and sodium oxalate as a function of sodium ion concentrations in solution, and 2) the quantities of precipitated phosphates and oxalates at the end of the caustic leaching operation. Aluminum compounds were not observed to precipitate in these washes.

Analysis of the data presented in Table 3.7 indicates that the phosphate contains approximately six waters of hydration, while the oxalate contains no apparent waters of hydration. Also note that these samples contained very little soluble salts after drying. The ratio of Na to P of 3.5:1 suggests that only about 14% (0.5 of 3.5) of the salt present in the solids after drying is from soluble salts (or bound sodium hydroxide).

Table 3.6. ICP Results for Integrated Test A Post-Caustic-Precipitate Composition Dissolved in DIW

Sample ID	Wash #	Solids Wt (g)	DIW Wt (g)	Al (µg/mL)	Na (µg/mL)	P (µg/mL)	S (µg/mL)
2341	3	0.5147	20.3946	39.1	7,240	2,590	77
2349	11	0.5037	20.4030	23.0	6,990	2,600	34
2363	25	0.4975	20.2410	9.54	6,980	2,700	<2.45
2369	31	0.1725	8.4439	11.2	7,030	<1.75	<2.45

Table 3.7. IC Results for Integrated Test A Post-Caustic-Precipitate Composition Dissolved in DIW

Sample ID	Wash #	Solids Wt (g)	DIW Wt (g)	C_2O_4 (µg/mL)	PO_4 (µg/mL)	SO_4 (µg/mL)	NO_3 (µg/mL)	NO_2 (µg/mL)
2341	3	0.5147	20.3946	<23	8,250	63	260	32
2349	11	0.5037	20.4030	<23	8,350	36	170	23
2363	25	0.4975	20.2410	26	8,700	<34	82	<23
2369	31	0.1725	8.4439	13,400	45	<34	58	<23

4.0 Determination of Rate of Approach to Equilibrium Concentrations

The objective of these tests was to determine the rate at which the anions of interest (phosphate, oxalate, sulfate, silicate, and fluoride) approach equilibrium solution composition in post-caustic-leach slurry at 25°C before filtration using controlled laboratory experiments. These tests were specified in Test Exception WTP-TEF-RT-09-0001, Rev 1, Task 2 associated with Test Plan TP-WTP-PEP-044, Rev 0.2.

These tests were performed using simplified post-caustic-leach slurry simulant (derived from the PEP Integrated Test A) with the composition shown in Table 4.1. This simulant contained filtration sludge and a supernate containing sufficient aluminate to represent dissolved gibbsite/boehmite, nitrate, nitrite, carbonate, and hydroxide only. The other anions were deleted from the simulant composition so that they could be spiked and the concentration controlled. The post-caustic-leach slurry simulant was spiked with each anion of interest (phosphate, oxalate, sulfate, silicate, and fluoride) in the form of a sodium salt as shown in Table 4.2.

Table 4.1. Simplified Post-Caustic-Leach Slurry Simulant Composition

Chemical	Amount (g/kg)
Fe-rich slurry	40.0
$NaNO_3$	75.3
$NaNO_2$	18.5
NaOH	149.6
$NaAl(OH)_4$	36.9
Na_2CO_3	7.42
DIW	677.2

Table 4.2. Test Matrix Identification for Task 2

Test ID	Post-Caustic-Leach Slurry (g)	$Na_2C_2O_4$-$2H_2O$ (g)	Na_3PO_4-$12H_2O$ (g)	Na_2SO_4 (g)	NaF (g)	Na_2SiO_3-$9H_2O$ (g)
T2-1a	1000.06	80.88	52.63	14.75	13.59	14.33
T2-1b	1000.03	80.88	52.63	14.75	13.59	14.33
T2-1c	1000.06	80.88	52.63	14.75	13.59	14.33
T2-2	1000.07	80.88	52.63	14.75	0.00	0.00
T2-3	1000.03	0.00	52.63	0.00	13.59	14.33
T2-4	1000.05	0.00	52.63	0.00	0.00	0.00
T2-5	1000.08	0.00	52.63	14.75	13.59	14.33
T2-6	1000.01	0.00	0.00	14.75	0.00	0.00
T2-7	1000.07	80.88	0.00	0.00	13.59	14.33
T2-8	1000.03	80.88	0.00	0.00	0.00	0.00
T2-9	1000.05	0.00	0.00	0.00	0.00	0.00

The slurries in the test matrix above were processed as follows:

- Heated to 85°C for 25.5 hours, shaken once an hour for the first 12 hours, and allowed to sit for the remaining 13.5 hours.
- Sampled for IC and ICP (T2-1a-85°C to T2-9 -85°C). See Appendix A for data summary.
- Cooled with shaking to 25±1°C over 5.5 hours. This cooling period corresponds to the estimated cooling time in Integrated Test A.
- Held at 25±1°C with shaking for 24 hours and sampled at 0, 1, 2, 4, 8, 12, and 24 hours for IC and ICP (T2-1a-25°C-0 to T2-9 -25°C-24).
- Cooled with shaking to 16±1°C over 4.3 hours and held at 16±1°C for 20 hours.
- Sampled for IC and ICP after the 20 hours (T2-1a-15°C to T2-9 -15°C).
- Heated with shaking to 25°C over 3.5 hours.
- Held at 25±1°C with shaking for 96 hours and sampled at 24 and 96 hours for IC and ICP (T2-1a-25°C-b-24 to T2-9 -25°C-b-96).

The 11 test bottles were placed in an oven at 85°C for 25.5 hours, shaken manually once an hour for the first 12 hours to mix them well, and then allowed to sit for the remaining 13.5 hours. After 25.5 hours at 85°C, the test bottles were removed from the oven and sampled by placing approximately 1.5-mL of supernate (filtered through a 0.45-µm filter immediately) into a sample bottle containing approximately 15-mL of DIW to dilute it approximately 10 times. Then the slurry test bottles were placed into an incubator at a temperature of 71.1°C and cooled to 25±1°C over 5.5 hours as shown in Figure 4.1 while shaking at 150 rpm. Note that the liquid blank was at 71.1°C—but the actual test bottles were at 85°C at the beginning—so the liquid blank temperature was slightly low for the first few readings while the test solutions were losing heat, and therefore the curve is flat at the beginning. The liquid blank was used for tracking temperature and was surrounded by the test bottles.

These test bottles were then held at 25±1°C for 24 hours in the incubator while shaking at 150 rpm. They were each sampled at 0, 1, 2, 4, 8, 12, and 24 hours. After holding for 24 hours at 25±1°C, the temperature of the incubator was lowered to 16±1°C over 4.3 hours as shown in Figure 4.2 while continuing to shake at 150 rpm. Another sample was taken from each of the test bottles after they had been held at 16±1°C for 20 hours. The temperature of the incubator was then increased to 25±1°C over 3.5 hours and held at temperature for 92.75 hours with samples taken from each of the test bottles at 24 and 96 hours after the temperature had been raised with the shaker remaining at 150 rpm. In all cases, samples for analysis were prepared by placing approximately 1.5-mL of supernate (immediately filtered through a 0.45-µm filter) into a labeled sample bottle containing approximately 15-mL of DIW to dilute it approximately 10 times.

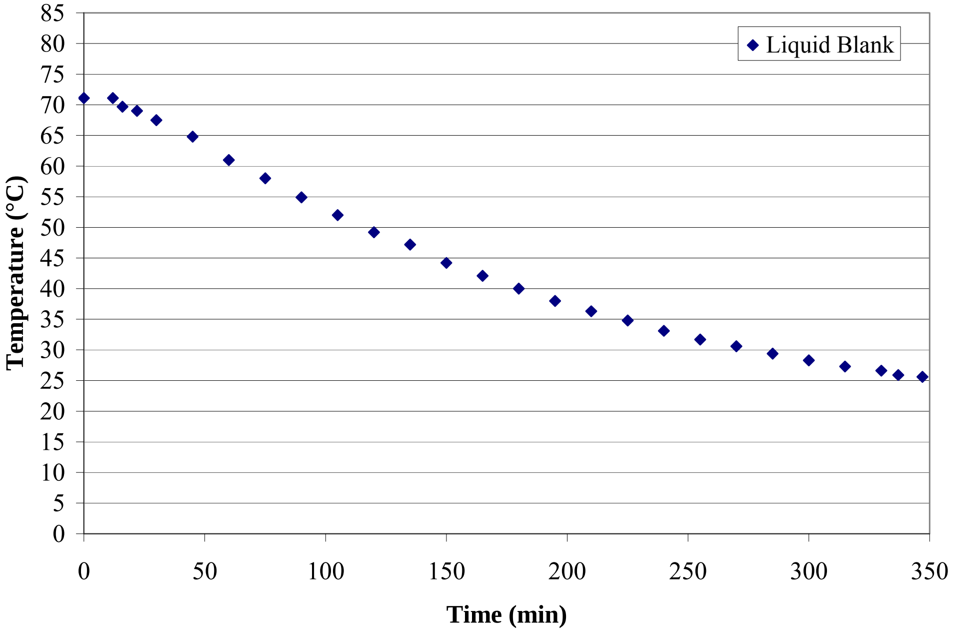

Figure 4.1. Cooling Curve of Test Solutions from 85°C to 25°C

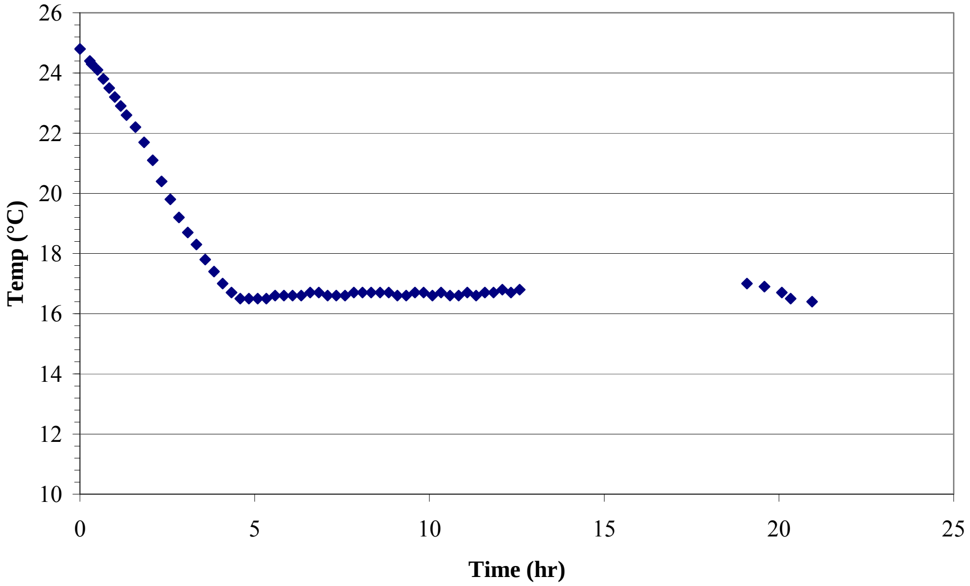

Figure 4.2. Task 2 Cooling Curve from 25°C to 16°C

All of the supernate samples taken while the slurry temperature was at 85°C for 24 hours developed an orange-brown precipitate after being diluted with DIW and allowed to sit at ambient temperature (~18 to 22°C) for 26 hours. Figure 4.3 shows three of the samples. The Fe-rich slurry from Table 4.1 is believed to be the source of the brown precipitate since sample T2-9 (without any anion spikes and shown on the far left in Figure 4.3) had just as much precipitate as the other samples. Chemical analysis confirmed that it was an iron compound. Iron was present in the post-caustic-leach slurry component.

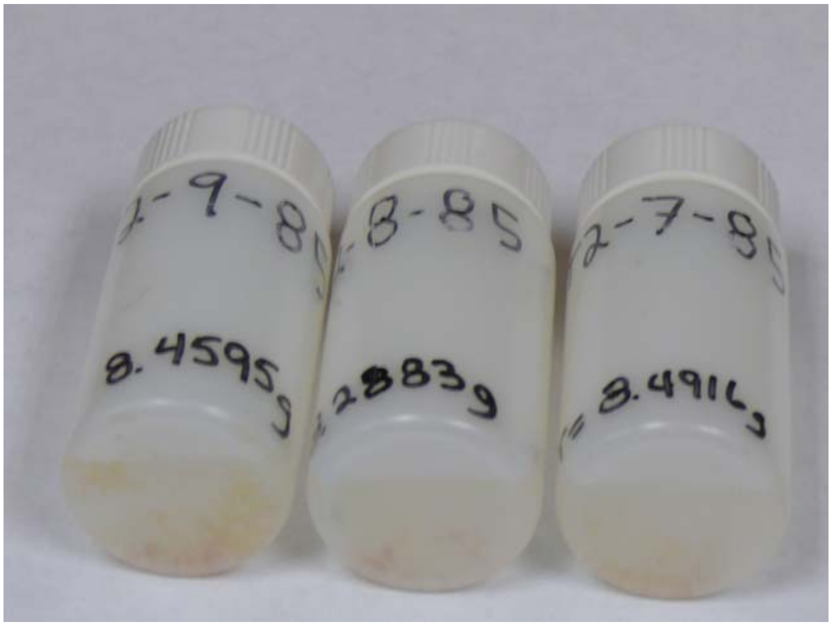

Figure 4.3. Precipitate in 85°C Samples from Tests T2-7, T2-8, and T2-9 (from right to left) after 24 Hours at Ambient Temperature (~18 to 22°C)

Each sample was analyzed by ICP for Al, Na, K, P, S, Si, and Fe and by IC for oxalate, phosphate, sulfate, fluoride, nitrate, and nitrite as shown in Tables A.1 and A.2, respectively. The ICP results showed very low levels of silicon present and no evidence of alumino-silicate precipitation.

Figure 4.4 shows the precipitation of oxalate in the samples by the decrease in oxalate concentration. Oxalate appears to be fairly slow to precipitate, taking nearly 24 hours before reaching equilibrium. The presence of phosphate, sulfate, or fluoride did not significantly change the equilibrium concentration of oxalate, but the kinetics appeared to be slower in the presence of the other anions. The average oxalate concentration is 137-mg/kg after approximately 48 hours. Note that the initial concentration in the full matrix at 25°C is significantly higher, up to 200-mg/kg. The concentration of oxalate at 85°C was approximately 450-mg/kg. Results discussed in Section 5 show that oxalate solubility is relatively insensitive to temperature. The solubility at 35ºC in this matrix is approximately 160-mg/kg (see Section 5). Thus, this initial supersaturation is significantly in excess of 10ºC.

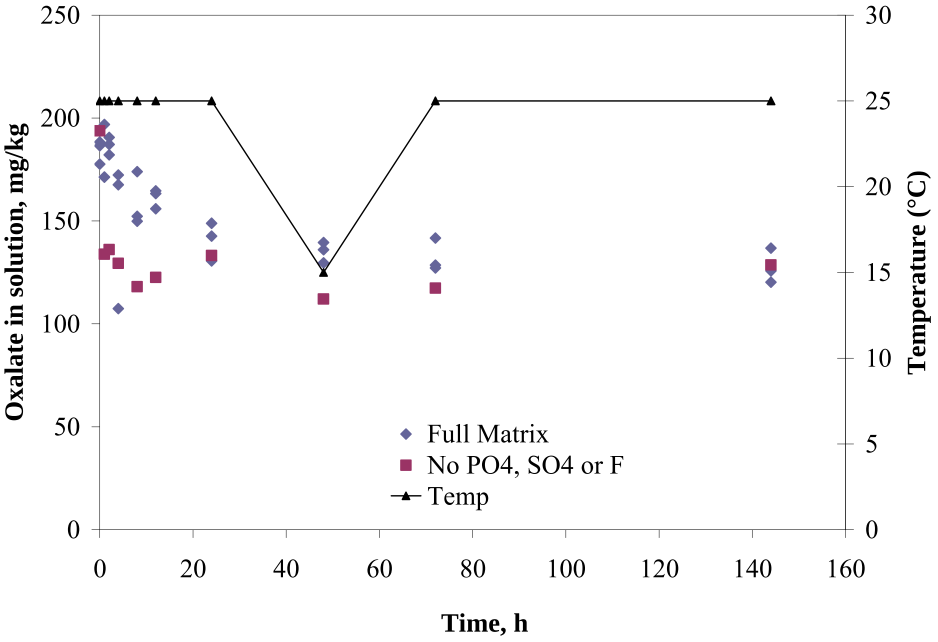

Figure 4.4. Oxalate Precipitation in the Task 2 Tests

Figure 4.5 shows the precipitation of phosphate in the samples. In the absence of fluoride, phosphate appears to equilibrate very quickly. However, in the presence of fluoride, phosphate equilibrates much slower and to a significantly lower solubility. Phosphate solubility appears to be a strong function of fluoride. Figure 4.6 shows the average of the last two phosphate and fluoride measurements from each of these tests that contained both phosphate and fluoride. The solubility of phosphate supersaturation seen for sodium fluoride phosphate is approximately 600-mg/kg. This extent of supersaturation is again significantly more than 10°C of supersaturation. The observed saturation at 35°C (see Section 5) is approximately 1000-mg/kg, while the initial concentration at 25°C was over 1600-mg/kg in these tests. At 85°C, the phosphate concentration was approximately 12,000-mg/kg. The initial samples at 25°C were very high—greater than 10,000-mg/kg. Then the subsequent samples rapidly reached a steady state value. However, in the absence of fluoride for Tests 2 and 4, there appeared to be some delay in the crystallization.

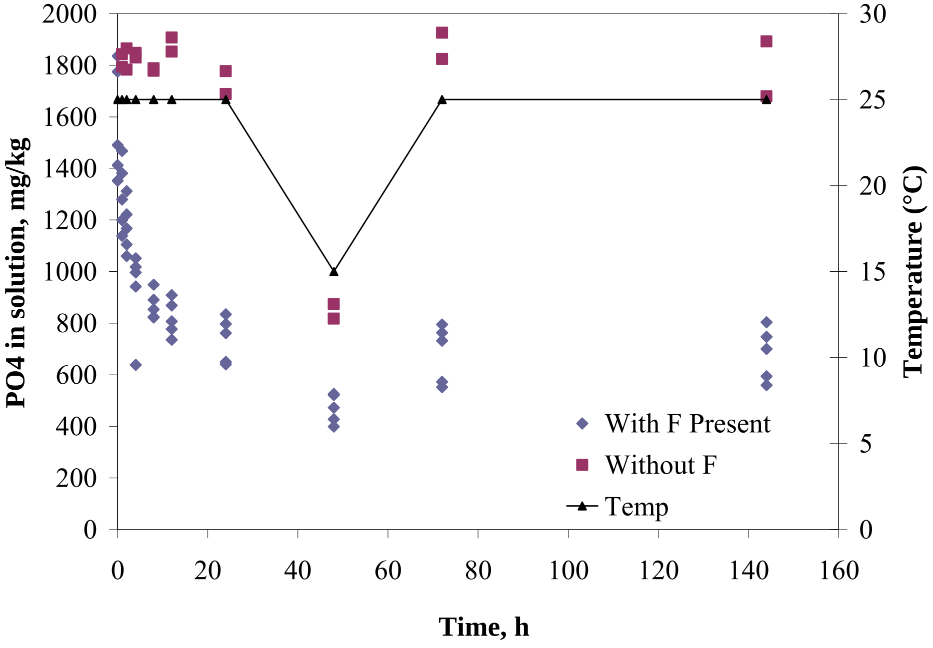

Figure 4.5. Phosphate Precipitation in the Task 2 Tests

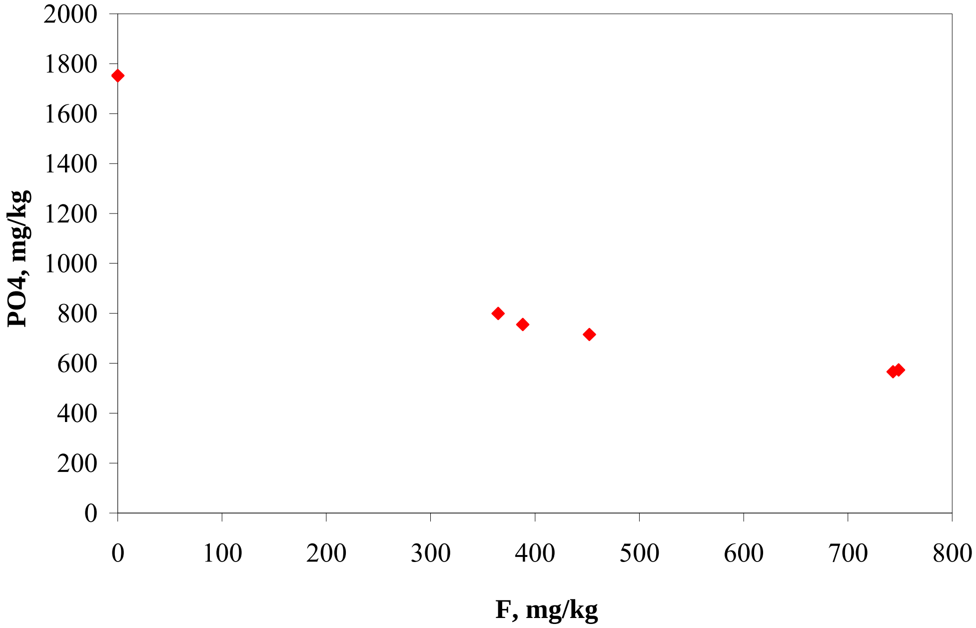

Figure 4.6. Effect of Fluoride Concentration on the Phosphate Concentration 144 Hours After Cooling from 85°C to 25°C

Figure 4.7 shows that the presence of fluoride does appear to impact the sulfate solubility by significantly decreasing it. It should be noted that for the tests without fluoride, the quantity of sulfate was likely all of the sulfate in the simulant. As such, this test is not a good measure of sulfate kinetics or solubility, but does indicate that sulfate is very soluble in this matrix.

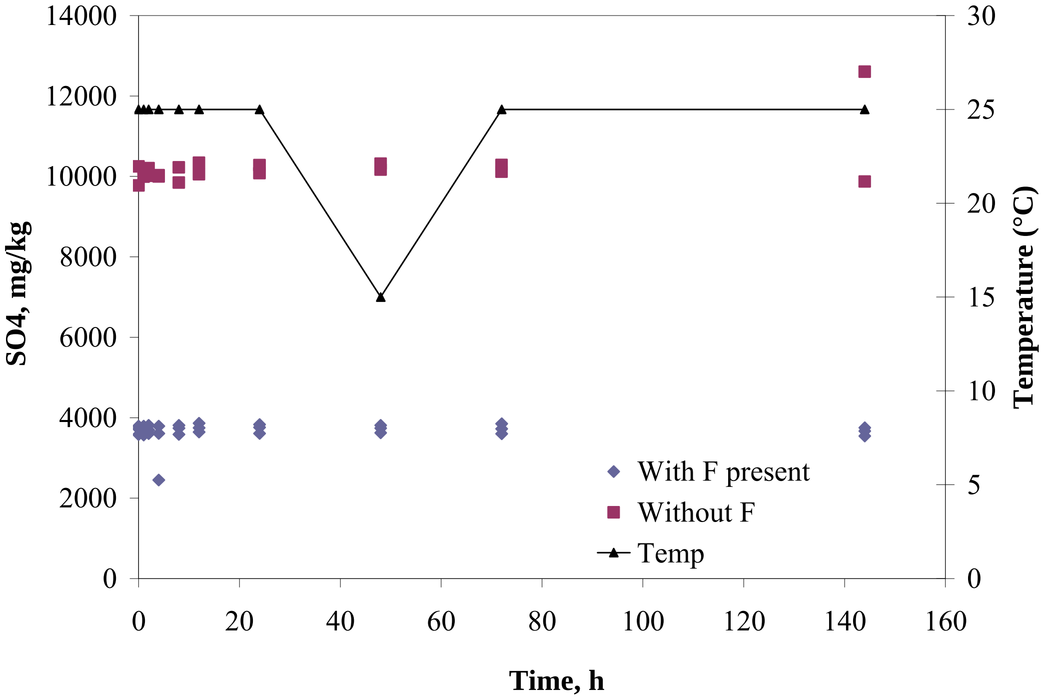

Figure 4.7. Sulfate Precipitation in the Task 2 Tests

Interestingly, fluoride appears to equilibrate within a few hours for all the samples as shown in Figure 4.8. However, the presence of oxalate appears to impact the fluoride solubility, but fluoride did not impact the oxalate solubility.

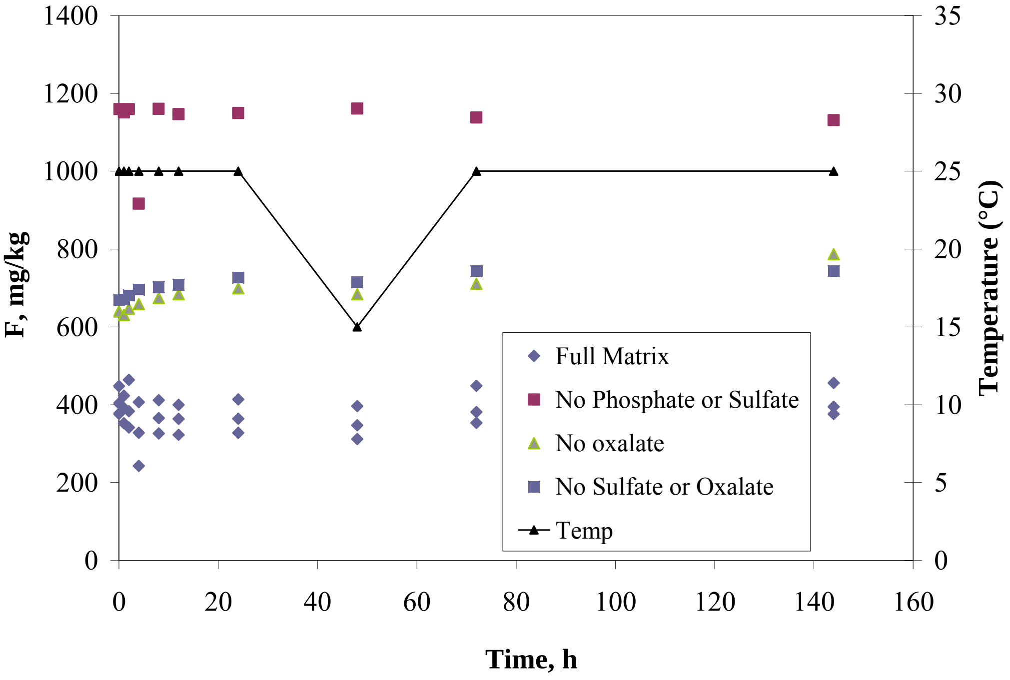

Figure 4.8. Fluoride Precipitation in the Task 2 Tests

5.0 Identification and Characterization of Precipitates

The objective of these tests was to identify precipitates formed at ambient temperature (20°C) in the presence of phosphate, oxalate, sulfate, silicate, and fluoride anions in the post-caustic leachate solution. These precipitates were also characterized for particle-size distribution (PSD), crystal shape and habit, quantity of precipitate formed, and settling rate. These tests were specified in Test Exception WTP-TEF-RT-09-0001, Rev 1, Task 3 associated with Test Plan TP-WTP-PEP-044, Rev 0.2.

These tests were performed using simulated post-caustic-leach slurry (derived from the PEP Integrated Test A) with the composition shown in Table 4.1. The simulated post-caustic-leach slurry was spiked with each anion of interest (phosphate, oxalate, sulfate, silicate, and fluoride) in the form of a sodium salt as shown in Table 5.1.

Table 5.1. Test Matrix Identification

Test ID	Post-Caustic-Leach Slurry (g)	$Na_2C_2O_4$-$2H_2O$ (g)	Na_3PO_4-$12H_2O$ (g)	Na_2SO_4 (g)	NaF (g)	Na_2SiO_3-$9H_2O$ (g)
T3-1a	1000.03	80.88	52.63	14.75	13.59	14.33
T3-1b	1000.04	80.88	52.63	14.75	13.59	14.33
T3-1c	1000.02	80.88	52.63	14.75	13.59	14.33
T3-2	1000.02	80.88	52.63	14.75	0.00	0.00
T3-3	1000.05	0.00	52.63	0.00	13.59	14.33
T3-4	1000.03	0.00	52.63	0.00	0.00	0.00
T3-5	1000.01	0.00	52.63	14.75	13.59	14.33
T3-6	1000.03	0.00	0.00	14.75	0.00	0.00
T3-7	1000.00	80.88	0.00	0.00	13.59	14.33
T3-8	1000.01	80.88	0.00	0.00	0.00	0.00
T3-9	1000.04	0.00	0.00	0.00	0.00	0.00

These slurries were processed as follows:

- All slurries were heated to 35±1°C for 46 hours with shaking.
- All slurries were centrifuged, then filtered through a 0.45-µm filter at 35°C, producing a supernate, which was sampled for IC and ICP (T3-1a-35°C to T3-9-35°C).
- All slurries were filtered and sampled over a period of 22 hours because of difficulty in filtering iron-containing slurries. Each slurry was filtered over a period of 1 to 2 hours at 35±5°C.
- All supernates were split into two samples, the smaller for settling tests and the larger for all other testing.
- All supernates were cooled to 20°C with shaking and held there for 92 to 96 hours and then sampled for IC and ICP (T3-1a-20°C to T3-9-20°C).

- Supernates that did not produce crystals during the first hold (T3-2, T3-6, T3-7, T3-8, and T3-9) were seeded from T3-4 and T3-1a and held at 20°C for another 96 hours.
- Settling tests were performed per discussion below.

These test samples were placed in the incubator at 35±1°C and held there for at least 46 hours while shaking at 150 rpm. After 46 hours, the test samples were first centrifuged and then filtered through a 0.45-μm filter at 35°C, and an aliquot was taken for analysis by placing approximately 1.5-mL of supernate (filtered through a 0.45-μm filter) into a sample bottle containing approximately 15-mL of DIW to dilute it approximately 10 times. This filtering was very difficult because of filter clogging from the iron oxyhydroxide present in the slurry. Multiple filters were used during the filtering of each test sample, which required more time per analytical sample (~1 to 2 hours), increasing the test sample time at 35±1°C. This analytical sample collecting was continued over 22 hours before all of the test samples were filtered. Immediately after filtering, the test samples were split by pouring the supernate into two bottles—one 250-mL bottle and one 1-L bottle. The smaller bottle was used for the settling test and the crystal size testing. The larger bottle was used for all of the other analyses. The filtered test samples were cooled to 20°C in the incubator over 5 hours while shaking at 165 rpm. After being held at 20°C for 92 to 96 hours, another sample was taken by placing approximately 1.5-mL of supernate (filtered through a 0.45-μm filter) into a sample bottle containing approximately 15-mL of DIW to dilute it approximately 10 times. These samples were submitted for ICP analysis of Al, Na, S, Si, Fe, K, and P and for IC analysis of oxalate, phosphate, sulfate, nitrate, nitrite, and fluoride. These results are shown in Appendix A, Table A.3, and Table A.4, respectively.

The test precipitate results are shown in Table 5.2. Tests T3-2, T3-6, T3-7, T3-8, and T3-9 did not produce solids. Test T3-4 with only phosphate added produced the most solids (see Figure 5.1). Tests T3-1a, T3-1b, T3-1c, T3-3, and T3-5 only produced approximately 1-mL or less of solids. Tests T3-2, T3-6, T3-7, T3-8, and T3-9 were seeded with a drop of supernate containing crystals from each of Test T3-4 and T3-1a and allowed to mix over the weekend. However, they still did not produce any crystals after 96 hours at 20°C.

Table 5.2. Test Precipitate Results

Test ID	Precipitate Formed?	Amount of Precipitate (g)	Type of Precipitate
T3-1a	Yes	1.61	$Na_7F(PO_4)_2 \cdot 19H_2O$
T3-1b	Yes	1.15	$Na_7F(PO_4)_2 \cdot 19H_2O$
T3-1c	Yes	1.24	$Na_7F(PO_4)_2 \cdot 19H_2O$
T3-2	No	0.112	NA
T3-3	Yes	2.33	$Na_7F(PO_4)_2 \cdot 19H_2O$
T3-4	Yes	14.9	$Na_3PO_4 \cdot 12H_2O$
T3-5	Yes	0.176	$Na_7F(PO_4)_2 \cdot 19H_2O$
T3-6	No	0.112	NA
T3-7	No	0.104	NA
T3-8	No	0.100	NA
T3-9	No	0.110	NA

In the settling test, the samples with just the small amount of solids settled in 2 to 3 minutes. These tests settled so fast and with such little solids that it was not possible to obtain a settling curve. Test T3-4 settled with an interface where the majority of the solids settled, but the supernate above them remained cloudy longer as shown in Figure 5.2. The settling curves for Test T3-4 are shown in Figure 5.3 and Figure 5.4.

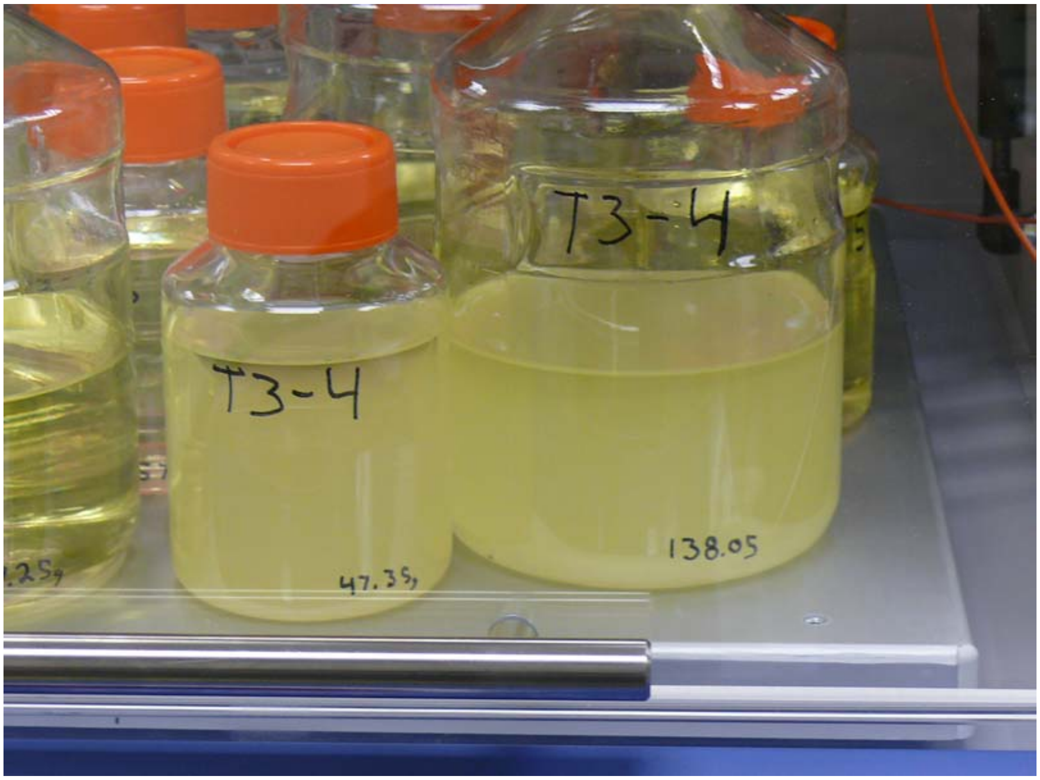

Figure 5.1. Solids Produced in Test T3-4 (Spiked with Sodium Phosphate)

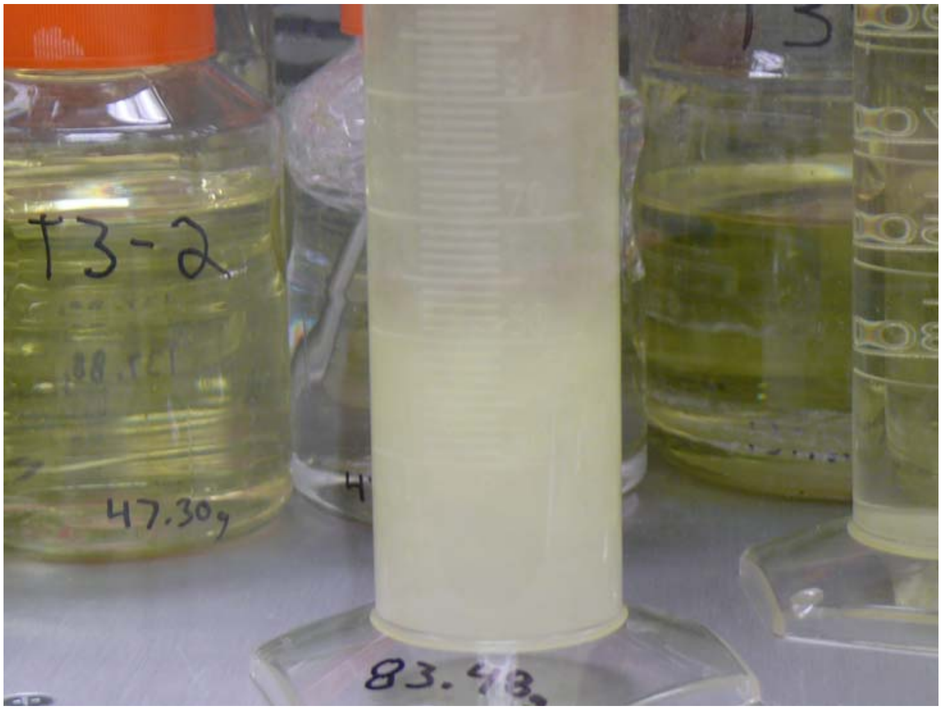

Figure 5.2. Test T3-4 (Spiked with Sodium Phosphate) Solids Settling

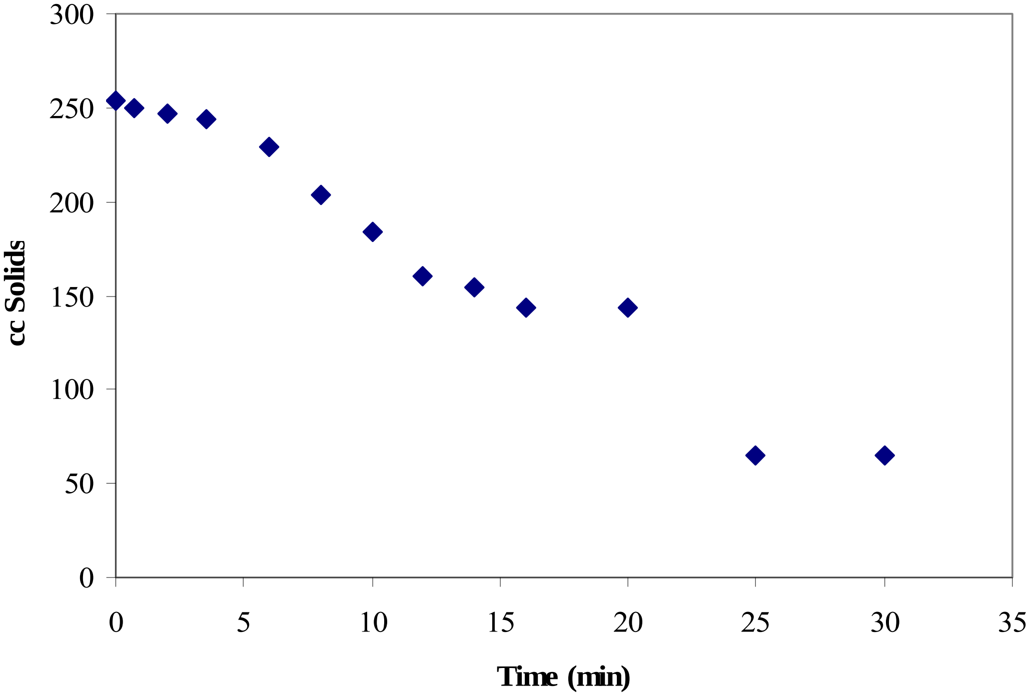

Figure 5.3. Initial Settling Rate of Test T3-4 (Spiked with Sodium Phosphate)

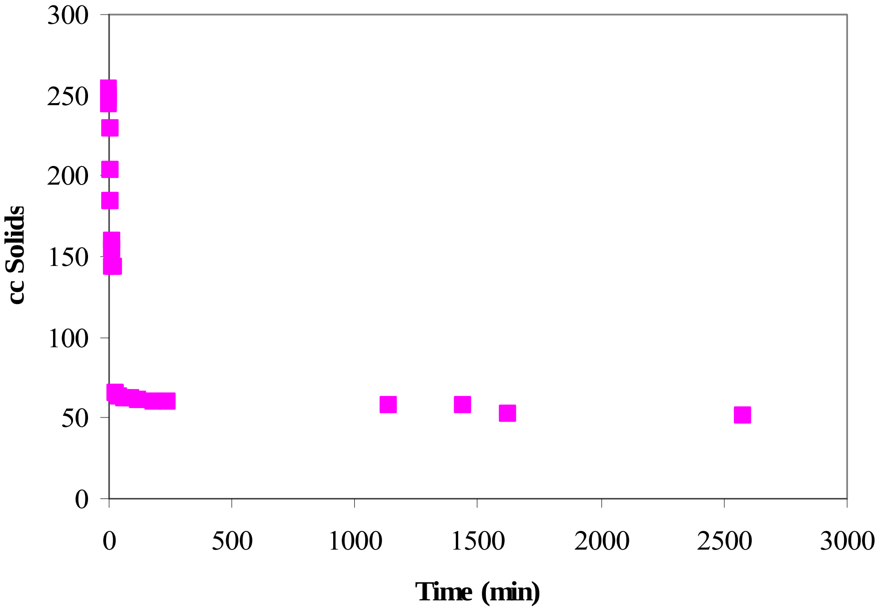

Figure 5.4. Overall Settling Rate of Test T3-4 (Spiked with Sodium Phosphate)

Table 5.3 provides the measured difference in ion concentrations between the 35°C and 20°C samples where a greater amount of precipitation was expected with a higher concentration difference. The blank entries represent tests where the species of interest was omitted from the slurry matrix. This table indicates that Tests T3-1a, T3-1b, T3-1c, T3-3, T3-4, and T3-5 should have a significant amount of precipitation. Tests T3-2, T3-7, and T3-8 should have a small amount of precipitation with Test T3-6 and Test T3-9 having no precipitation. These results indicate that very low quantities of oxalate and sulfate will precipitate upon cooling. The results indicate that larger quantities of sodium fluoride phosphate will precipitate upon cooling.

Table 5.3. Measured Difference in Ion Concentration between 35°C and 20°C

Test ID	F (µg/g)	C_2O_4 (µg/g)	PO_4 (µg/g)	SO_4 (µg/g)	Amt of Precip. (g)
T3-1a	62	25	590	-20	1.61
T3-1b	24	7	315	-16	1.15
T3-1c	21	-5	265	-43	1.24
T3-2	—	9	19	4	0.112
T3-3	84	—	876	—	2.33
T3-4	—	—	2906	—	14.9
T3-5	79	—	817	13	0.176
T3-6	—	—	—	-94	0.112
T3-7	-6	14	—	—	0.104
T3-8	—	15	—	—	0.100
T3-9	—	—	—	—	0.110

Sodium phosphate solubility from the results of Tasks 2 and 3 tests is shown in Figure 5.5. The amount of phosphate in solution at 35°C in Test T3-2 appears to be anomalously low. At this point, there is not a good reason why this value was low, but the sample did not appear to be at equilibrium at 35°C. This may be due to either the sample re-equilibrating quickly upon cooling during the separation process or the sample not yet reaching equilibrium during storage at temperature. The amount of phosphate in solution is about ¼ of the expected amount based on Test T3-4 (phosphate only test).

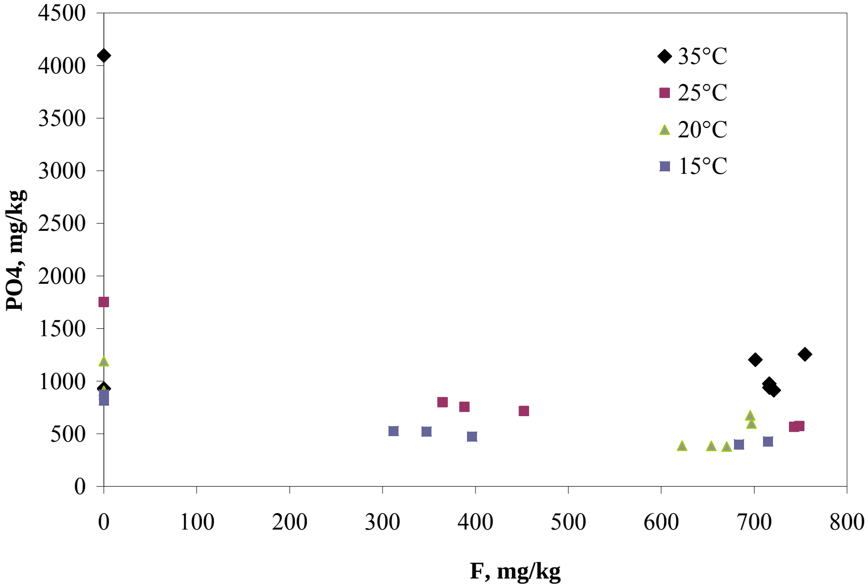

Figure 5.5. Phosphate Solubility

Figure 5.6 shows the impact of temperature on solubility of the different anions measured at 24 hours from Task 2 for 15°C and 25°C (see Section 4) and Task 3 for 20°C and 35°C. This shows that only sodium phosphate and sodium fluoride phosphate exhibit any significant change in solubility with temperature. The other main components appear to be relatively insensitive to temperature.

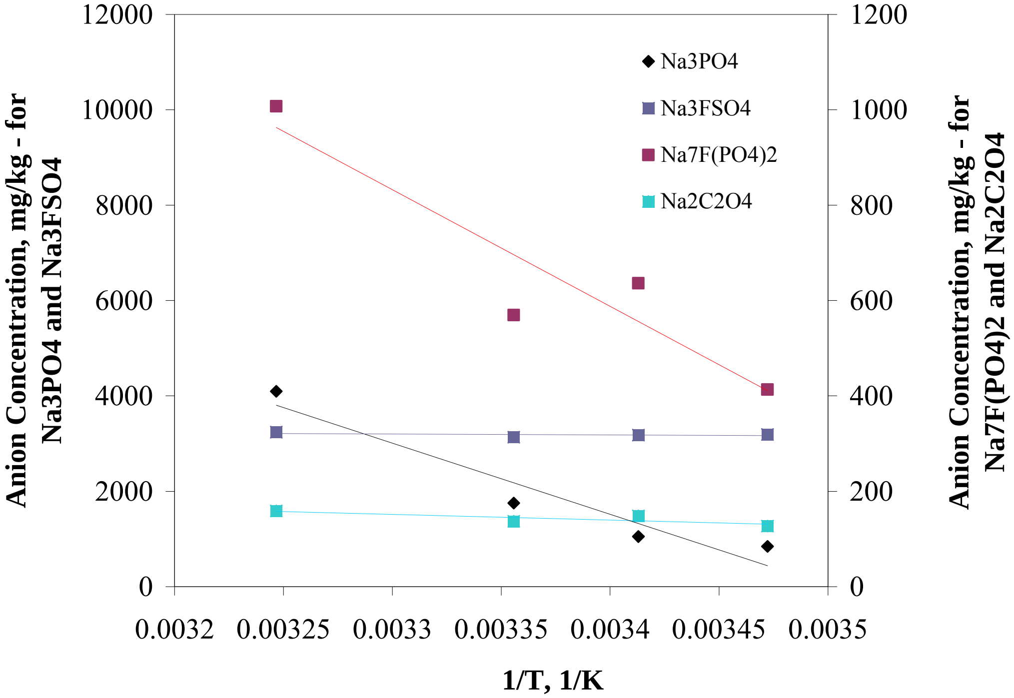

Figure 5.6. Impact of Temperature on Solubility Measured at 24 Hours

Task 3 sample solutions containing precipitated crystals were analyzed by OM to gather optical properties of the crystals as well as particle size. All of the Task 3 samples, with the exception of T3-4, contained the same cubic crystal type as shown in Figure 5.7 through Figure 5.11. The crystals were determined to be cubic because of the observed morphology when under cross-polarized light is extinct at all angles. These crystals are likely $Na_7F(PO_4)_2{\cdot}19H_2O$ based on the high refractive index of the crystals.

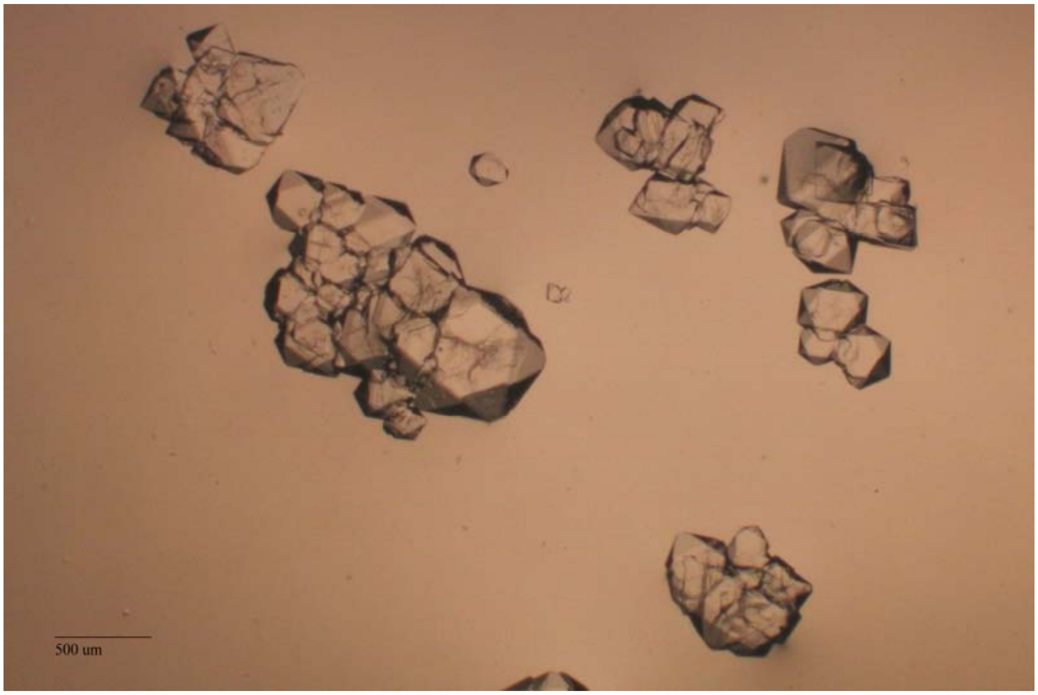

Figure 5.7. Sample T3-1a ($Na_7F(PO_4)_2{\cdot}19H_2O$) OM in Polarized Light

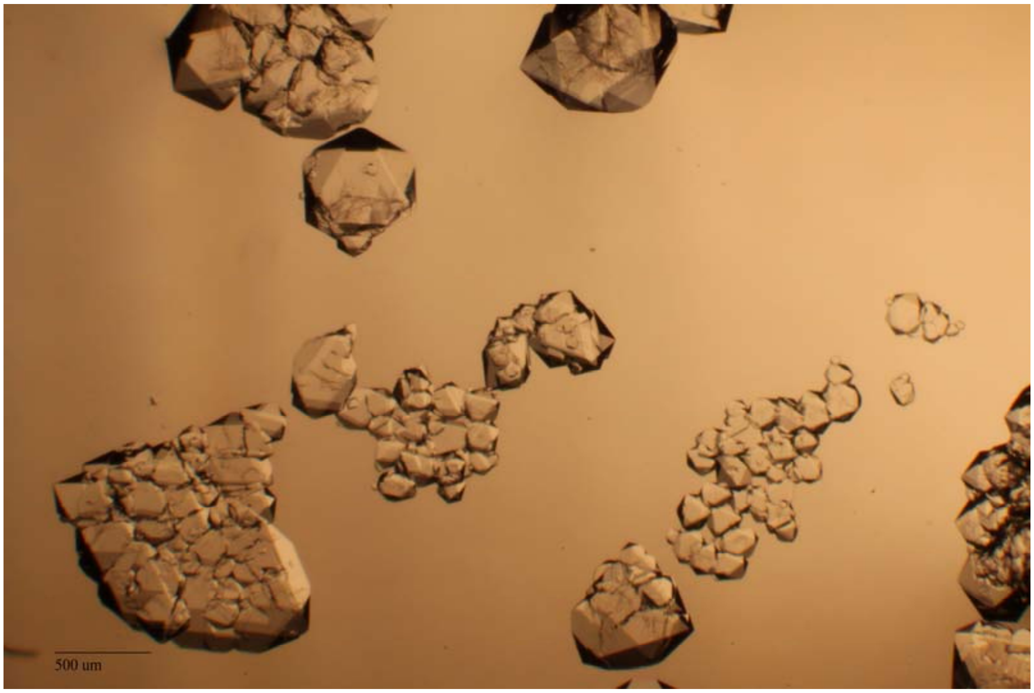

Figure 5.8. Sample T3-1b ($Na_7F(PO_4)_2{\cdot}19H_2O$) OM in Polarized Light

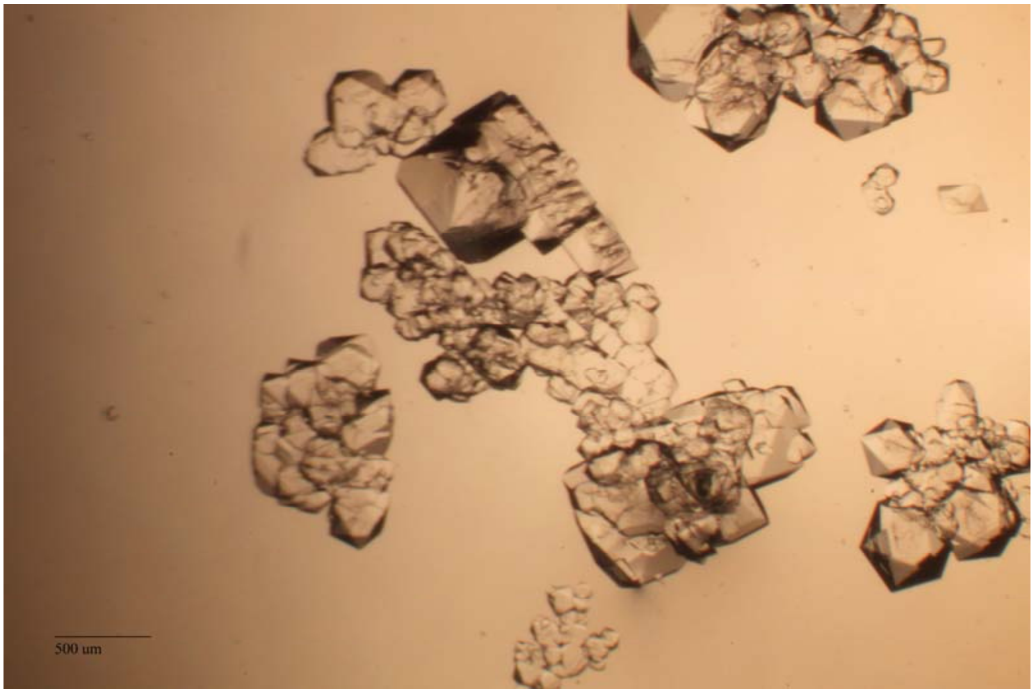

Figure 5.9. Sample T3-1c ($Na_7F(PO_4)_2 \cdot 19H_2O$) OM in Polarized Light

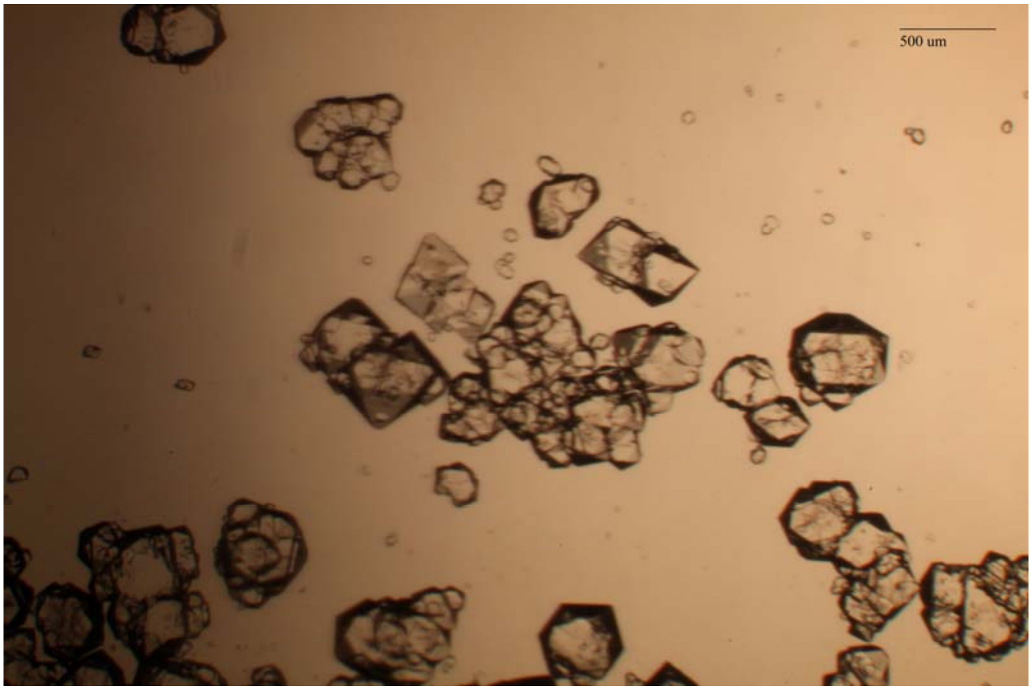

Figure 5.10. Sample T3-3 ($Na_7F(PO_4)_2 \cdot 19H_2O$) OM in Polarized Light

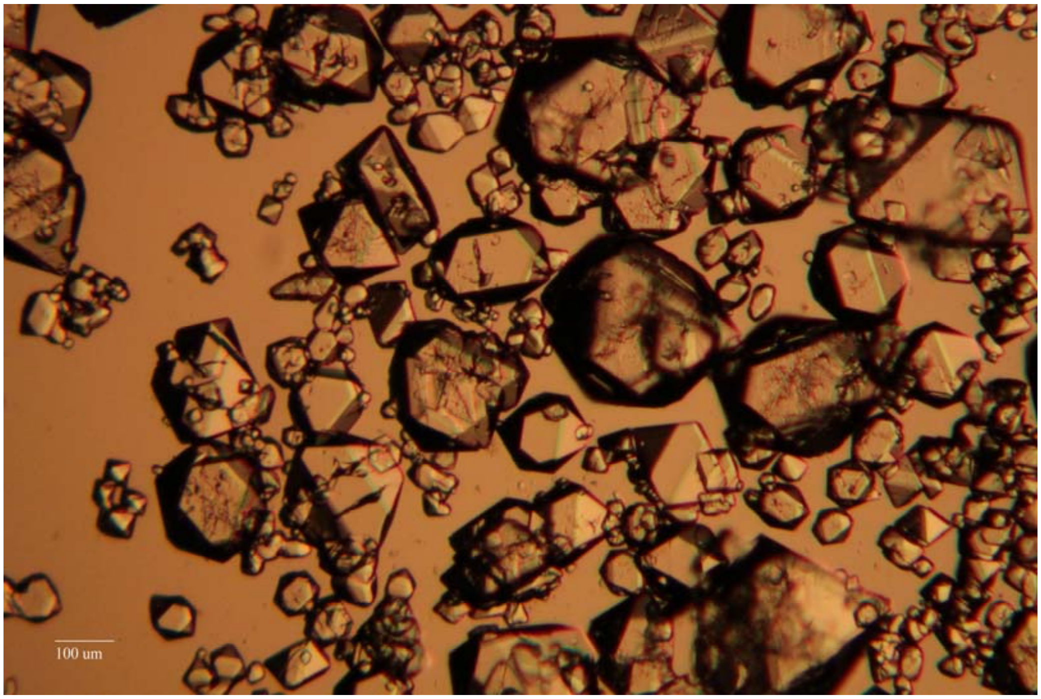

Figure 5.11. Sample T3-5 ($Na_7F(PO_4)_2{\cdot}19H_2O$) OM in Polarized Light

Sample T3-4 contains long, thin, needle-shaped crystals that appear white under cross-polarized light as shown in Figure 5.12. When a full wave plate is inserted into the cross-polarized light, the crystals appear blue when the long axis of the crystal and the wave plate are parallel, and yellowish-orange when perpendicular, as shown in Figure 5.13. Therefore, these crystals are most likely $Na_3PO_4{\cdot}12H_2O$.

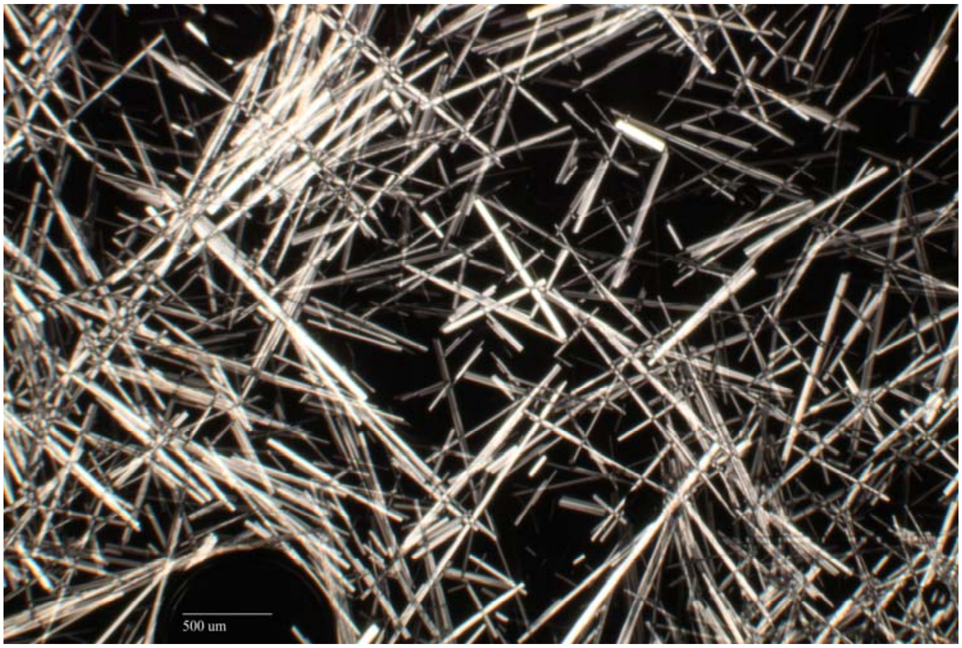

Figure 5.12. Sample T3-4 in ($Na_3PO_4{\cdot}12H_2O$) OM Cross-Polarized Light

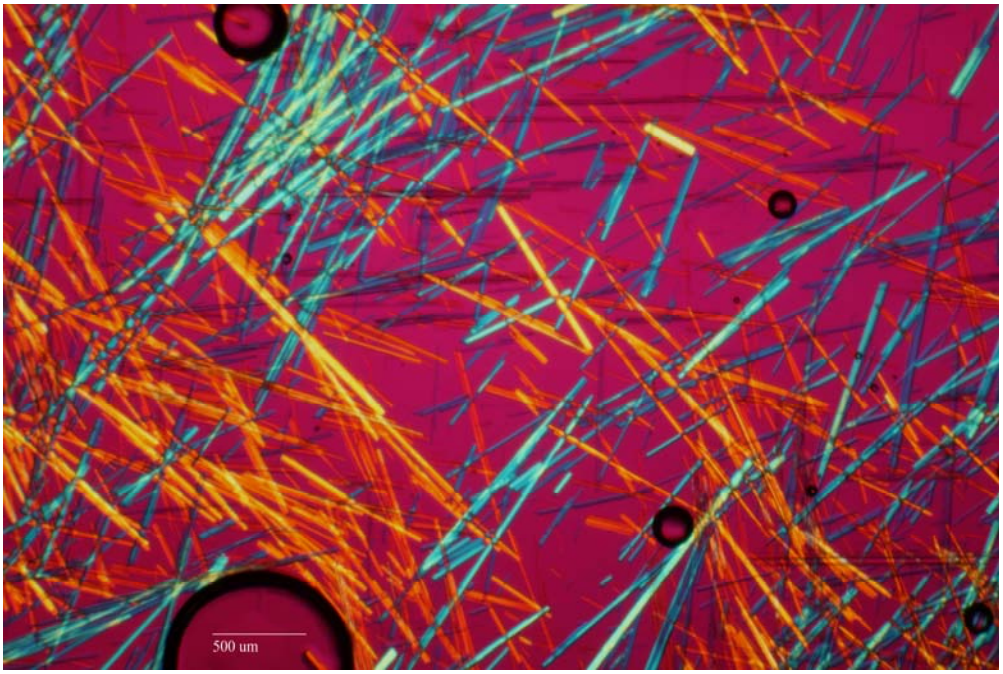

Figure 5.13. Sample T3-4 $Na_3PO_4 \cdot 12H_2O$ Crystals in OM Cross-Polarized Light with Full Wave Plate

Particle size analysis was performed using I-mage software on polarized light micrographs. Particles were fit manually with the polygon, circle, or ellipse functions. The cubic crystals appear to nucleate and grow from existing crystals and as a result significantly interfere with the size measurements of the individual crystals. Often the size of the combined group of crystals was all that could be accurately measured for the cubic crystals. In the case of T3-4, the crystals were individually fit as it is much easier to distinguish individual crystals when overlap occurs. The software then calculated the crystal area, maximum length, and maximum width with a summary of these results shown in Table 5.4. The complete results are shown in Appendix A, Table A14 through Table A.19.

Table 5.4. Summary Table of Measured Crystal Dimensions for Each Sample

Sample #	Particle Mineralogy	# of Particles	Statistical Measure	Area, μm^2	Max Length, μm	Max Width, μm
T3-1a	$Na_7F(PO_4)_2{\cdot}19H_2O$	28	Mean	201,352	556	410
			Min	8,776	126	95
			Max	1,240,400	1,700	1,055
T3-1b	$Na_7F(PO_4)_2{\cdot}19H_2O$	3	Mean	293,314	652	457
			Min	4,134	98	60
			Max	618,588	984	818
T3-1c	$Na_7F(PO_4)_2{\cdot}19H_2O$	14	Mean	546,288	1,052	712
			Min	32,220	279	174
			Max	1,876,168	2,610	1,385
T3-3	$Na_7F(PO_4)_2{\cdot}19H_2O$	38	Mean	96,352	301	227
			Min	315	19	19
			Max	830,846	1,429	1,038
T3-4	$Na_3PO_4{\cdot}12H_2O$	75	Mean	18,410	606	35
			Min	2,175	108	16
			Max	69,947	2,486	76
T3-5	$Na_7F(PO_4)_2{\cdot}19H_2O$	42	Mean	87,513	279	211
			Min	654	29	29
			Max	819,871	1,421	1,044

6.0 Dilution Required to Redissolve the Precipitate

The objective of these tests was to determine the potential to redissolve the post-filtration precipitate observed in PEP Integrated Tests A, B, and D through dilution with DIW at 25±1°C. These tests were specified in Test Exception WTP-TEF-RT-09-0001, Rev 1, Task 4 associated with Test Plan TP-WTP-PEP-044, Rev 0.2.

Two samples from the PEP Integrated Test A (2367—wash 30 and 2587—wash 70), two samples from the PEP Integrated Test B (4232—wash 10 and 4267—wash 45), and three samples from the PEP Integrated Test D (5652--post-caustic-leach, 5457—wash 21, and 5478—wash 42) were used for this task. These tests were performed in duplicate by placing 100-mL of these test samples into 200-mL centrifuge tubes and holding them at 25°C for 48 hours while shaking at 150 rpm. After 48 hours, they were centrifuged, the volume of solids was measured, and then 5-mL of DIW was added to them. They were well mixed by shaking to resuspend the solids and then held at 25°C for 24 hours while shaking at 150 rpm with the process repeated until the solids completely dissolved or the centrifuge tubes became full.

Table 6.1 shows the amount of dilution required for each test to achieve complete solids dissolution or when the centrifuge tube became full. Figure 6.1 shows how the solids decreased with the dilution for each test with 10% error bars included. After a certain point in several of the samples, the solids dissolved an unobservable amount so that it appeared they were not dissolving. The dilution was stopped after 85-mL of DIW was added because the centrifuge tube was full. However, these results show that the solids are essentially soluble if enough DIW is added. The dried remaining solids weighed 50-mg for Integrated Test D 5652 (post-caustic-leach) and 5-mg for Integrated Test B 4267 (wash 45).

Table 6.1. Amount DIW Required to Achieve Complete Dissolution of Solids

Test ID	Sample ID	Wash #	Sample Amt (mL)	DIW Added (mL)	Comments
T4-A-2367a	Test A 2367	30	105	30	No solids at this point
T4-A-2367b	Test A 2367	30	110	30	No solids at this point
T4-A-2587a	Test A 2587	70	105	30	No solids at this point
T4-A-2587b	Test A 2587	70	105	30	No solids at this point
T4-B-4232a	Test B 4232	10	100	30	No solids at this point
T4-B-4232b	Test B 4232	10	105	30	No solids at this point
T4-B-4267a	Test B 4267	45	110	85	Stopped with skiff of solids left
T4-B-4267b	Test B 4267	45	113	85	Stopped with skiff of solids left
T4-D-5652a	Test D 5652	Post-caustic-leach	98	85	Stopped with skiff of solids left
T4-D-5652b	Test D 5652	Post-caustic-leach	99	85	Stopped with skiff of solids left
T4-D-5457a	Test D 5457	21	101	50	No solids at this point
T4-D-5457b	Test D 5457	21	103	50	No solids at this point
T4-D-5478a	Test D 5478	42	105	55	No solids at this point
T4-D-5478b	Test D 5478	42	104	50	No solids at this point

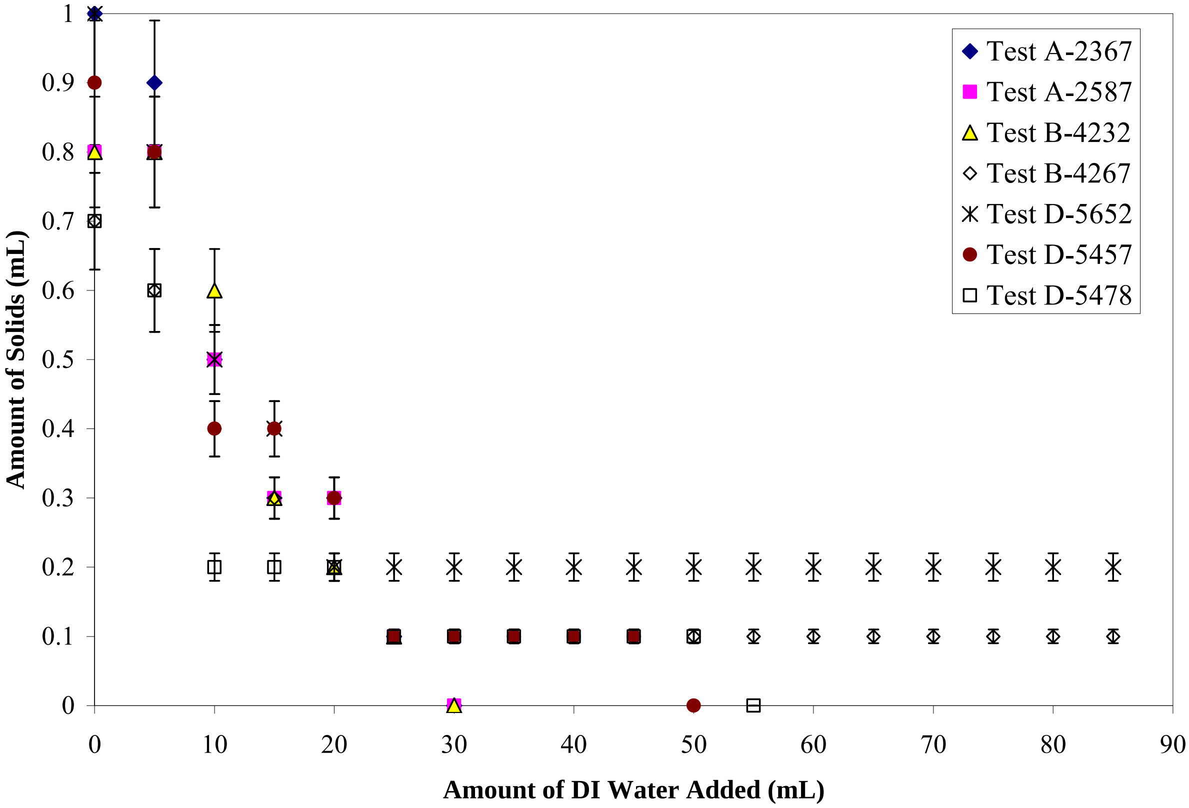

Figure 6.1. Solids Dissolution with DIW Addition

7.0 Supersaturation in Post-Caustic-Leach Filtrates from PEP Integrated Test B

The objective of these tests was to determine the solution supersaturation in the post-caustic-leach filtrate during the dewatering and washing period based on the samples collected during PEP Integrated Test B. These tests were specified in Test Exception WTP-TEF-RT-09-0001, Rev 1, Task 5 associated with Test Plan TP-WTP-PEP-044, Rev 0.2.

The concentrated caustic-leached solids in UFP-VSL-T02A were washed incrementally with 0.01 M NaOH in the PEP Integrated Test B. The wash liquid was added in steps with 11 gallon target volume for each step and 52 steps total. Samples were taken in 1-L sample bottles. Each 1-L sample number represented a wash step with a total of 52 samples taken. During every third or fourth wash step, AFA was added to maintain a target concentration of 350 ppm. Wash liquid additions were initiated when the level in the vessel UFP-VSL-T02A dropped below a set value, occurring approximately every 4 minutes. Permeate was continuously removed at a rate between 1-kg/min and 8-kg/min by ultrafiltration through all five filter bundles.

The caustic-leach wash samples were collected from March 19, 2009, 16:27 until March 20, 2009, 1:03. All 52 samples were stored at ambient temperature of the PDL-W facility and were then transferred to the APEL laboratory on March 20, 2009.

These supernate and wash samples from the post-caustic-leach slurry concentration period were processed as follows:

- All 52 samples were stored at room temperature (~18 to 22°C) in the APEL laboratory for 94 days.
- A subset of samples (4153, 4154, 4223, 4225, 4227, 4229, 4231, 4234, 4237, and 4240) was held at 20°C for 72 hours and then sampled for characterization of the solution phase by ICP and IC analysis.
- The temperature of this subset of samples was raised incrementally by 1°C and held there for 24 hours until 30°C was reached. The solution phase of the subset was sampled after 24 hours at 25°C for chemical characterization by ICP and IC analyses.
- The temperature was then raised from 30°C to 35°C in a single increment and the samples held at 35°C. Again, the solution phase of the subset was sampled for chemical characterization after 24 hours at 35°C by ICP and IC analyses.

Samples 4153 (caustic leachate), 4154 (caustic leachate), 4223 (wash 1), 4225 (wash 3), 4227 (wash 5), 4229 (wash 7), 4231 (wash 9), 4234 (wash 12), 4237 (wash 15), and 4240 (wash 18) were tested by placing them in an incubator at 20°C for 72 hours while shaking at 150 rpm. After 72 hours at 20°C, supernate samples were taken by placing approximately 1.5-mL of supernate (filtered through a 0.45-μm filter immediately) into a sample bottle containing approximately 15-mL of DIW to dilute it approximately 10 times.

The temperature was then increased 1°C every 24 hours and the samples allowed to equilibrate for 24 hours. After each 24-hour period, the samples were inspected for remaining solids. This continued until the temperature reached 30°C. After the samples reached 30°C, solids still remained in the majority of the samples. Therefore, the temperature was increased to 35°C, and the samples were allowed to equilibrate for 24 hours at 35°C. Supernate samples were taken at 25°C and at 35°C by placing approximately 1.5-mL of supernate (filtered through a 0.45-µm filter immediately) into a sample bottle containing approximately 15-mL of DIW to dilute it approximately 10 times.

The supernate samples were analyzed by ICP for Al, Na, P, and S (shown in Appendix A Table A.5), IC for oxalate, phosphate, sulfate, nitrate, and nitrite (shown in Appendix A Table A.6) to determine the solution saturation compositions and solution density (shown in Appendix A Table A.7).

The results of the oxalate dissolution for these samples are shown in Figure 7.1 with wash numbers increasing from right to left in the figure. Figure 7.1 shows that there was little to no dissolution of oxalate after heating the solutions from 20°C to 35°C except for washes 15 (sample 4237) and 18 (sample 4240) (the two on the far left of the figure) where an increase occurs from 25°C to 35°C. This is because of the lower solubility of oxalate at high sodium ion concentrations in the earlier wash solutions. The tests show a low sensitivity of sodium oxalate solubility to temperature at high sodium concentrations in solution. However, in washes 15 and 18, the concentration of sodium ion was low enough for oxalate to dissolve. Therefore, when the temperature was increased, the amount of oxalate in the supernate increased in these samples.

The results of the phosphorus (phosphate) dissolution for these samples are shown in Figure 7.2 with wash numbers increasing from right to left in the figure. It can be seen in Figure 7.2 that the phosphorus (phosphate) concentration in solution increased significantly upon heating to 35°C for most of the samples with the exception of washes 12 (sample 4234), 15 (sample 4237), and 18 (sample 4240) (the three on the far left of the figure). This can be explained by the fact that by this point, all of the phosphorus (phosphate) had been dissolved and washed out, and therefore, there was no more to dissolve when the temperature was increased in these tests.

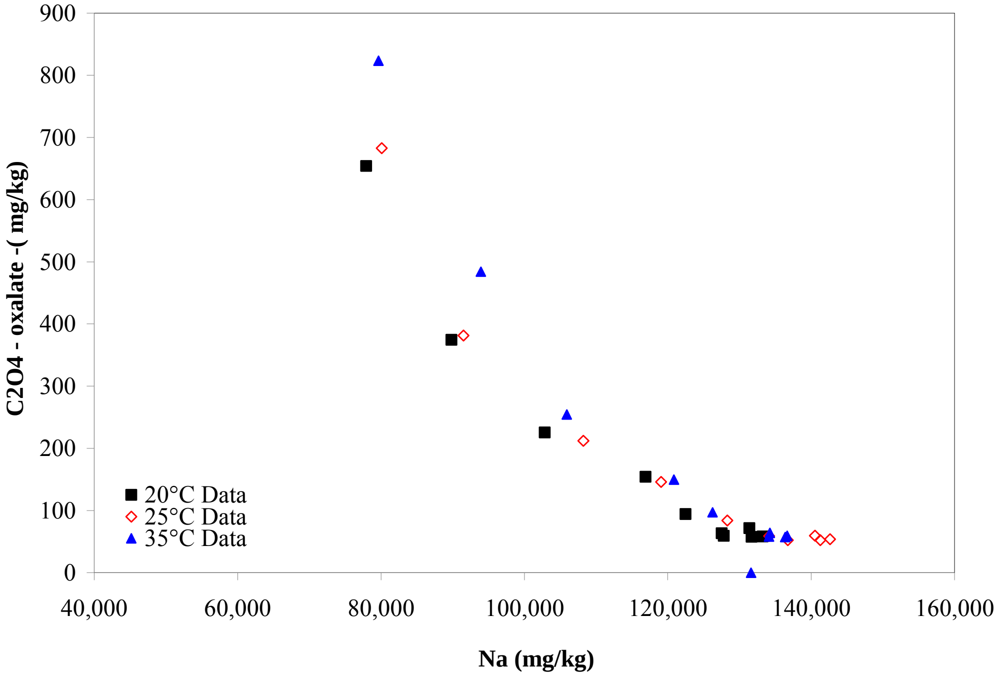

Figure 7.1. Oxalate Concentration Relative to Na During PEP Integrated Test B Washes

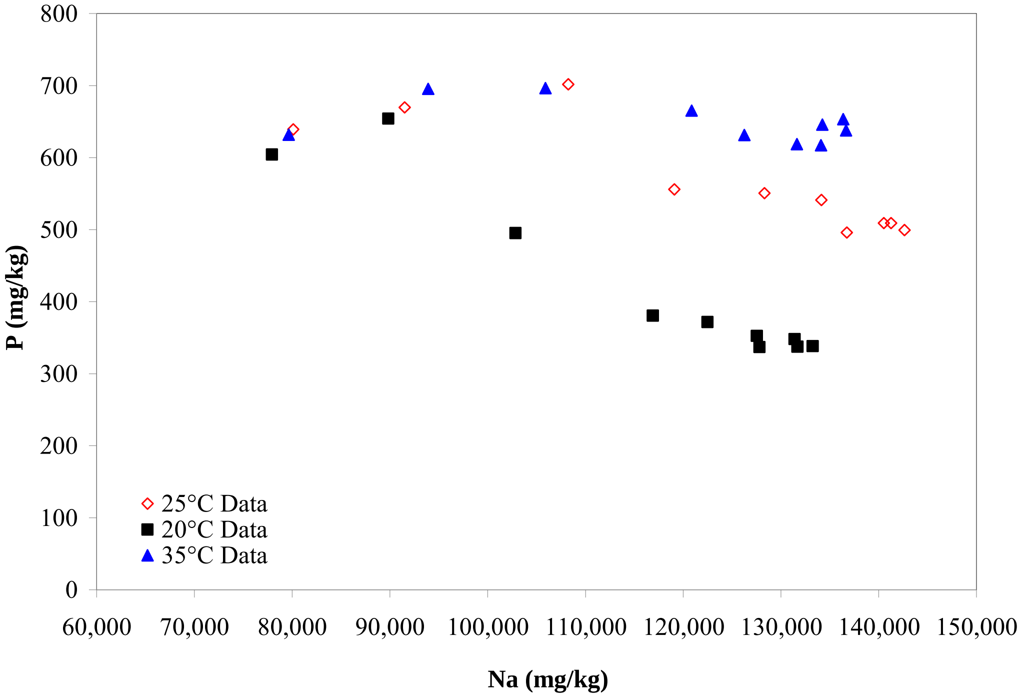

Figure 7.2. Phosphorus Concentration Relative to Na During PEP Integrated Test B Washes

At the end of the test, the supernate was filtered rapidly at 35°C using 0.45-µm filters to determine how many solids were left in each test bottle. These solids were air-dried and then weighed, and the results are shown in Table 7.1. Figure 7.3 shows the photos of the filtered solids. Each sample contained brownish solids on the filter, and some of them had crystals also.

Table 7.1. Solids Left in Samples after Test Completed

Sample ID	Description	Solids Left (g)	Sample ID	Description	Solids Left (g)
4153	leachate	0.1591	4229	Wash 7	0.1608
4154	leachate	0.1350	4231	Wash 9	0.1532
4223	Wash 1	0.2116	4234	Wash 12	0.2535
4225	Wash 3	0.1094	4237	Wash 15	0.3445
4227	Wash 5	0.1098	4240	Wash 18	0.5374

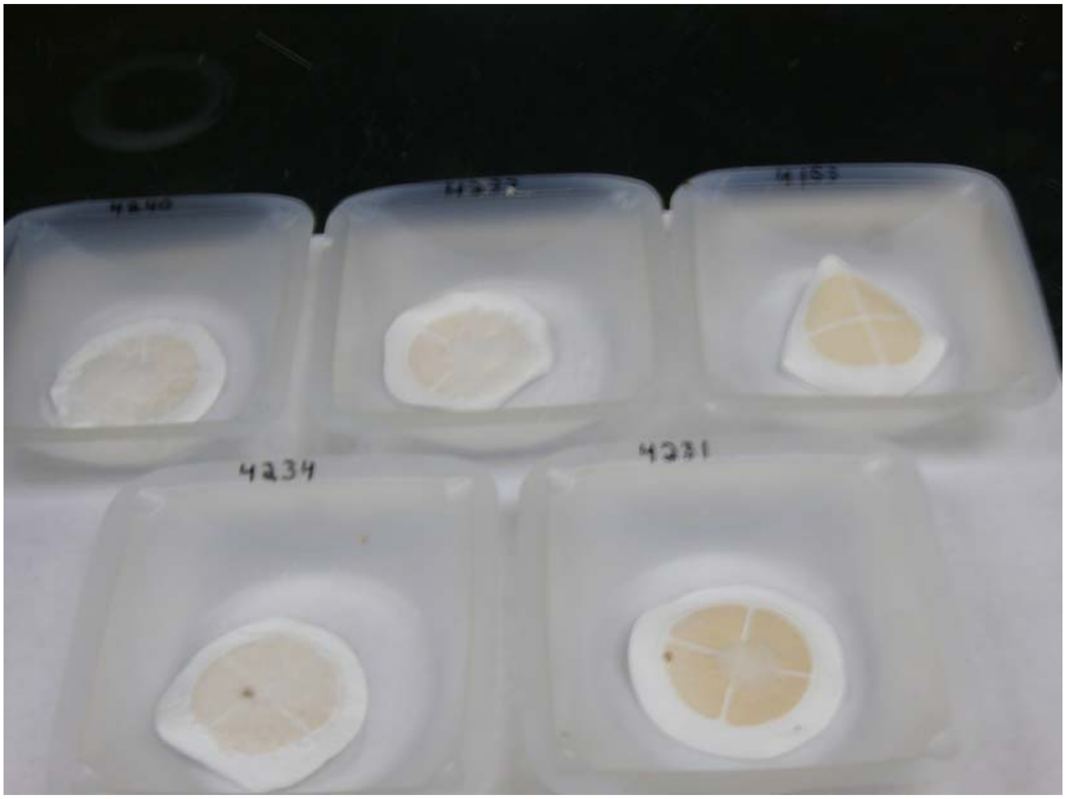

Figure 7.3. Solid Crystals Remaining After Temperature Increased to 35°C

These crystals were then analyzed by a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) by fixing the crystals onto carbon sticky tape and coating the crystals with a conductive coating of Pd using a sputter coater to determine their composition. Note that EDS-measured compositions are limited to elements with a mass equal to or greater than carbon.

The morphology of sample 4231 is fibrous and fans out at the tips of the crystals, as shown in Figure 7.4 and Figure 7.5. The crystals also tend to form another crystal 90° from the long axis. EDS analysis of the crystals reveals a chemistry of mainly Na, O, and C, with minor amounts of Al, S, and Cu, as given in Table 7.2. Samples 4234, 4237, and 4240 were all similar in chemical composition to sample #4231. The micrographs of samples 4234, 4237, and 4240, shown in Figure 7.6 through Figure 7.10, are similar to one another, but the tips of the crystals did not fan out as distinctly as those observed in sample 4231. Samples 4231 through 4240 all appear to be $Na_2C_2O_4$, based on the thin needle crystals and measured chemistry.

Sample 4153 is quite different from the other samples in terms of morphology and chemistry. The morphology of the crystals is wide large crystals that appear to have cracked significantly, presumably upon drying, as shown in Figure 7.11. The measured chemistry of sample 4153 is mainly Na, P, and O, with minor amounts of Al, C, Cu, and S, as given in Table 7.2. Sample 4153 appears to be $Na_3PO_4{\cdot}12H_2O$, based on the measured chemistry and the large needle-shaped crystals.

Table 7.2. Measured Compositions of Task 5 Dried Crystals

Weight % by Element										
Sample #	Filename	C	O	Na	Al	Sr	P	S	Cu	Total
4231	Area 1.spc	13.68	34.06	47.17	2.06	0.00	0.00	1.19	1.84	100.00
4234	Area 2.spc	14.76	34.82	48.98	0.77	0.00	0.00	0.19	0.48	100.00
4237	Area 3.spc	5.79	34.72	58.43	0.48	0.00	0.00	0.08	0.5	100.00
4237	Area 4.spc	15.6	33	47.45	2.37	0.00	0.00	0.41	1.17	100.00
4240	Area 5.spc	6.19	30.33	61.01	0.93	0.00	0.00	0.23	1.31	100.00
4153	Area 6.spc	2.4	23.46	30.1	7.28	2.91	31.7	0.8	1.36	100.01
Atomic % by Element										
Sample #	Filename	C	O	Na	Al	Sr	P	S	Cu	Total
4231	Area 1.spc	20.85	38.98	37.56	1.40	0.00	0.00	0.68	0.53	100.00
4234	Area 2.spc	22.03	39.03	38.19	0.51	0.00	0.00	0.10	0.14	100.00
4237	Area 3.spc	9.24	41.56	48.66	0.34	0.00	0.00	0.05	0.15	100.00
4237	Area 4.spc	23.43	37.21	37.21	1.59	0.00	0.00	0.23	0.33	100.00
4240	Area 5.spc	10.05	36.98	51.76	0.67	0.00	0.00	0.14	0.4	100.00
4153	Area 6.spc	4.6	33.72	30.11	6.21	0.76	23.54	0.57	0.49	100.00

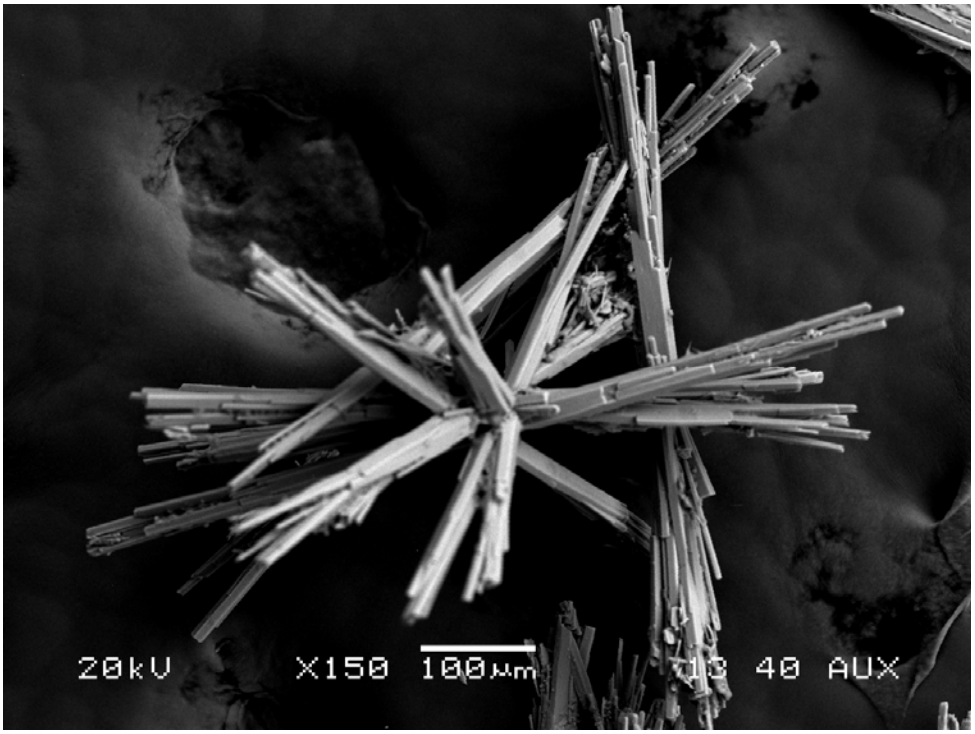

Figure 7.4. SEM Micrograph of Sample 4231 Wash 9 ($Na_2C_2O_4$)

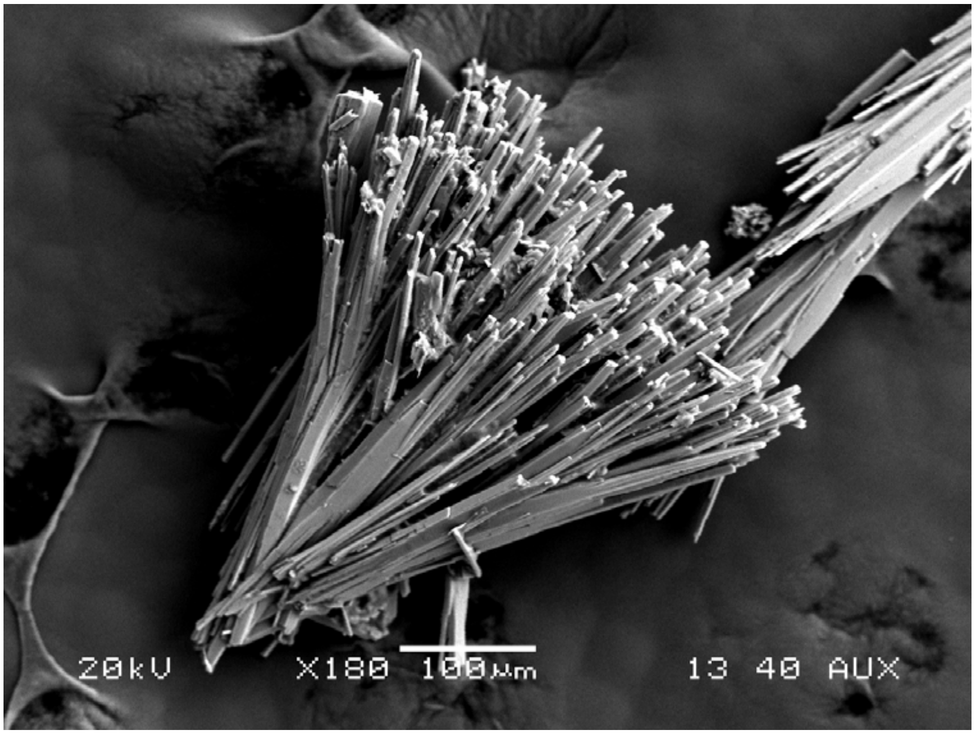

Figure 7.5. SEM Micrograph of Sample 4231 Wash 9 ($Na_2C_2O_4$)

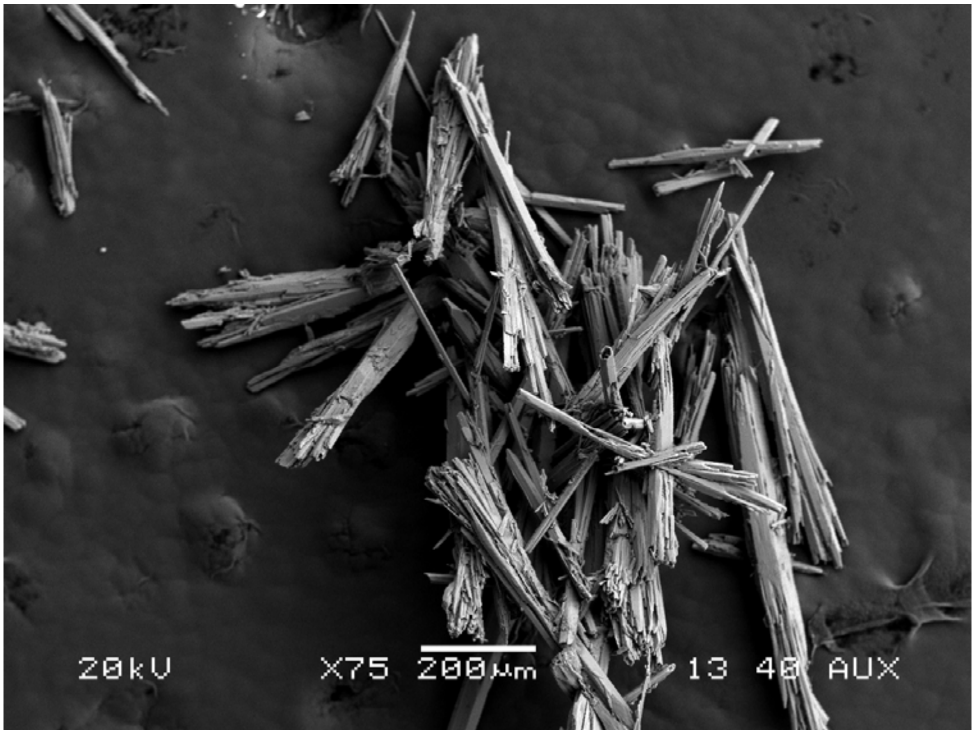

Figure 7.6. SEM Micrograph of Sample 4234 Wash 12 ($Na_2C_2O_4$)

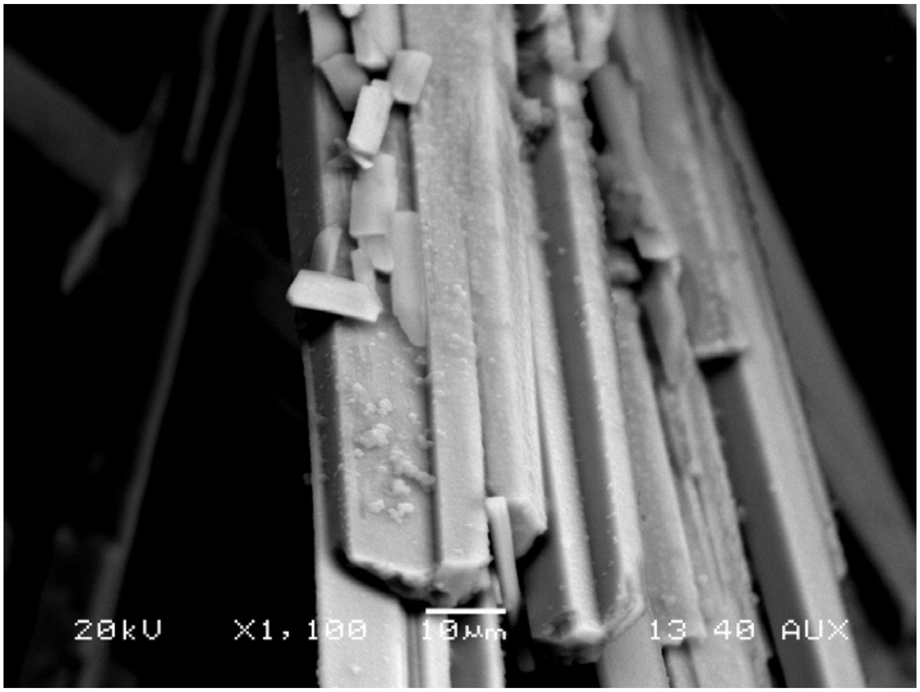

Figure 7.7. SEM Micrograph of Sample 4234 Wash 12 ($Na_2C_2O_4$)

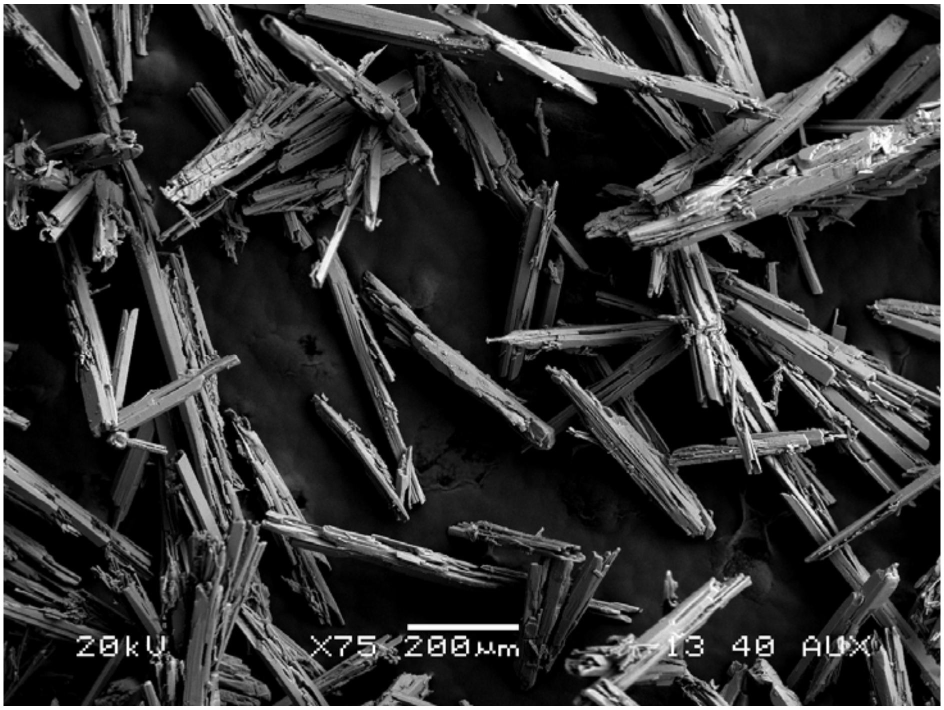

Figure 7.8. SEM Micrograph of Sample 4237 Wash 15 ($Na_2C_2O_4$)

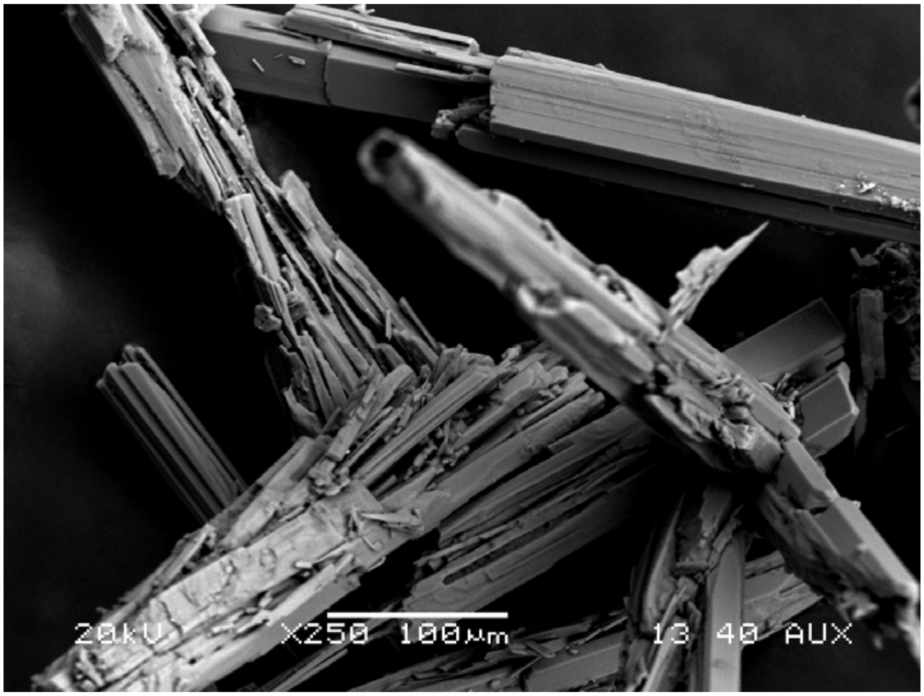

Figure 7.9. SEM Micrograph of Sample 4237 Wash 15 ($Na_2C_2O_4$)

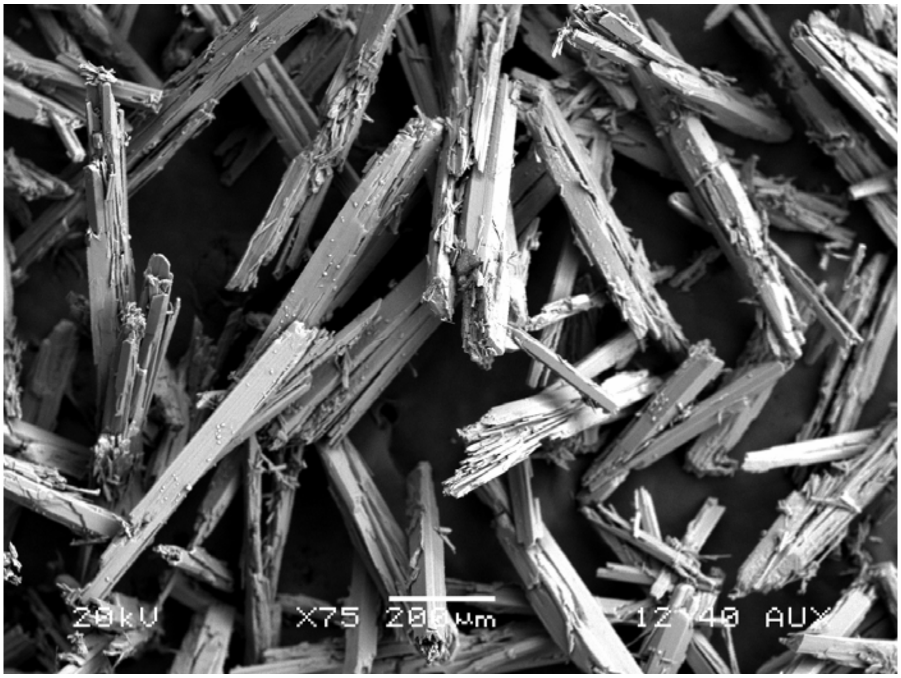

Figure 7.10. SEM Micrograph of Sample 4240 Wash 18 ($Na_2C_2O_4$)

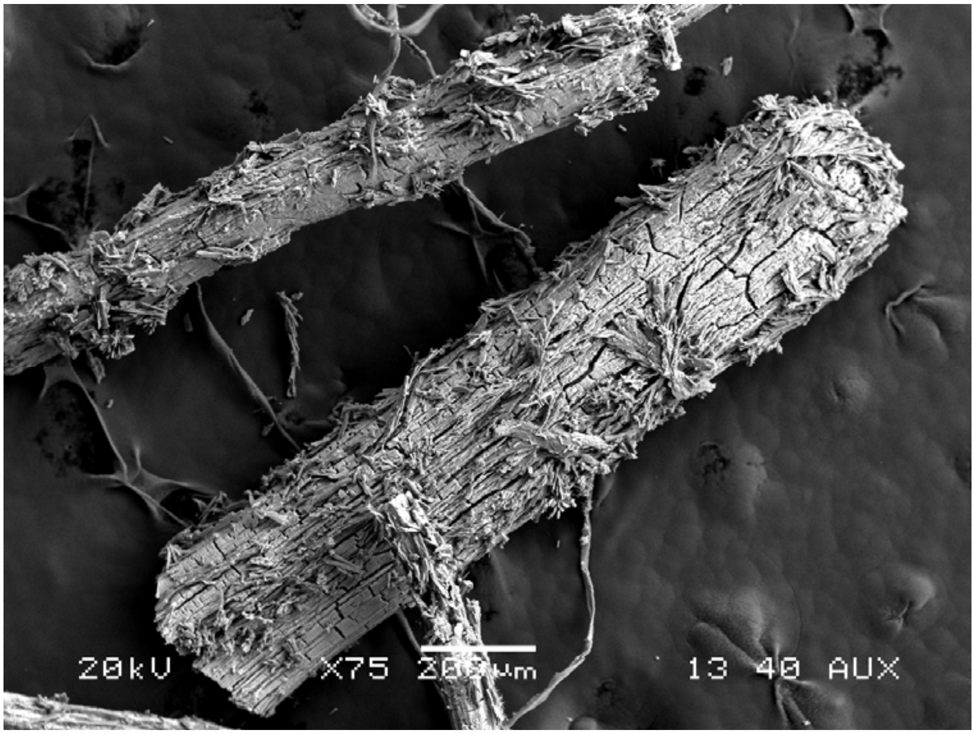

Figure 7.11. SEM Micrograph of Sample 4153 Leachate ($Na_3PO_4 \cdot 12H_2O$**)**

8.0 Effects of Blending During the Post-Caustic-Leach Dewatering and Wash Cycle

The objective of these tests was to determine the effects of blending permeate, leachate, and wash solution during the post-caustic-leach dewatering and wash periods in the PEP Integrated Test B. These tests were specified in Test Exception WTP-TEF-RT-09-0001, Rev 1, Task 6 associated with Test Plan TP-WTP-PEP-044, Rev 0.2.

Several of the PEP Integrated Test B permeate, leachate, and wash solution samples were blended together in different combinations to determine the effect of these blends on precipitation. Five blends were prepared for this testing as shown in Table 8.1. Blend 1 represented mixing the filtrates from Integrated Test B, Blend 2 represented mixing the leachate and concentrated wash (wash liquids down to 2.6 M Na), Blend 3 represented mixing the leachate, concentrated wash (wash liquids down to 2.6 M Na), and dilute wash (wash liquids from 2.6 to 0.3 M Na), Blend 4 represented mixing the concentrated (wash liquids down to 2.6 M Na) and dilute washes (wash liquids from 2.6 to 0.3 M Na), and Blend 5 represented mixing concentrated washes (wash liquids down to 2.6 M Na) only.

Table 8.1. PEP Integrated Test B Blend Compositions

PEP ID	Description	Blend 1 (mL)	Blend 2 (mL)	Blend 3 (mL)	Blend 4 (mL)	Blend 5 (mL)
4037	permeate	115	—	—	—	—
4153	leachate	30	125	62.5	—	—
4224	Wash 2	—	25	12.5	15	50
4225	Wash 3	7.5	—	—	—	—
4226	Wash 4	—	25	12.5	15	50
4228	Wash 6	7.5	—	—	—	—
4229	Wash 7	—	25	12.5	15	50
4231	Wash 9	7.5	25	12.5	15	50
4234	Wash 12	7.5	25	12.5	15	50
4237	Wash 15	15	—	25	35	—
4243	Wash 21	15	—	25	35	—
4250	Wash 28	15	—	25	35	—
4256	Wash 34	15	—	25	35	—
4261	Wash 39	15	—	25	35	—

The solutions were mixed together in a 500-mL bottle and then placed in an incubator for 48 hours at 25±1°C shaking at 150 rpm. Blends 1, 3, and 4 became cloudy when the solutions were added, indicating precipitate forming at time zero. Blends 2 and 5 remained clear throughout the addition of solutions. After 9 days, Blend 2 also contained slight visible precipitate. These blends were then filtered at the end of the test using 0.45-µm filters to determine how many solids were formed in each blend. These solids were air-dried and then weighed, and the results are shown in Table 8.2. The final composition of the blend supernates was also analyzed by ICP and IC and is shown in Appendix A, Table A.8 and Table A.9, respectively. Note that Blends 1, 3, and 4 all contained a mix of leachate and later washes. These later washes would have contained high concentrations of oxalate. Thus, it is likely that the cause of the immediate precipitate in Blends 1, 3 and 4 was sodium oxalate. Blends 2 and 5 did not contain those later washes and as such, did not achieve as great a degree of supersaturation.

Table 8.2. Solids Formed in Blends after Test Completed

Sample ID	Total Slurry Wt (g)	Solids Left (g)	Wt% Solids
Blend 1	292.54	0.5301	0.18
Blend 2	307.85	0.1525	0.05
Blend 3	282.33	0.8973	0.32
Blend 4	273.78	0.7834	0.29
Blend 5	304.73	0.0937	0.03

After sitting at ambient temperature (~18 to 22°C) for a couple of weeks, Blend 2 and Blend 5 formed precipitate on the bottom of the bottle as shown in Figure 8.1 and Figure 8.2. This may have been due to the slight drop in temperature, which caused the phosphate to precipitate.

Figure 8.1. Blend 2 Solids Formed after Sitting at Ambient Laboratory Temperature

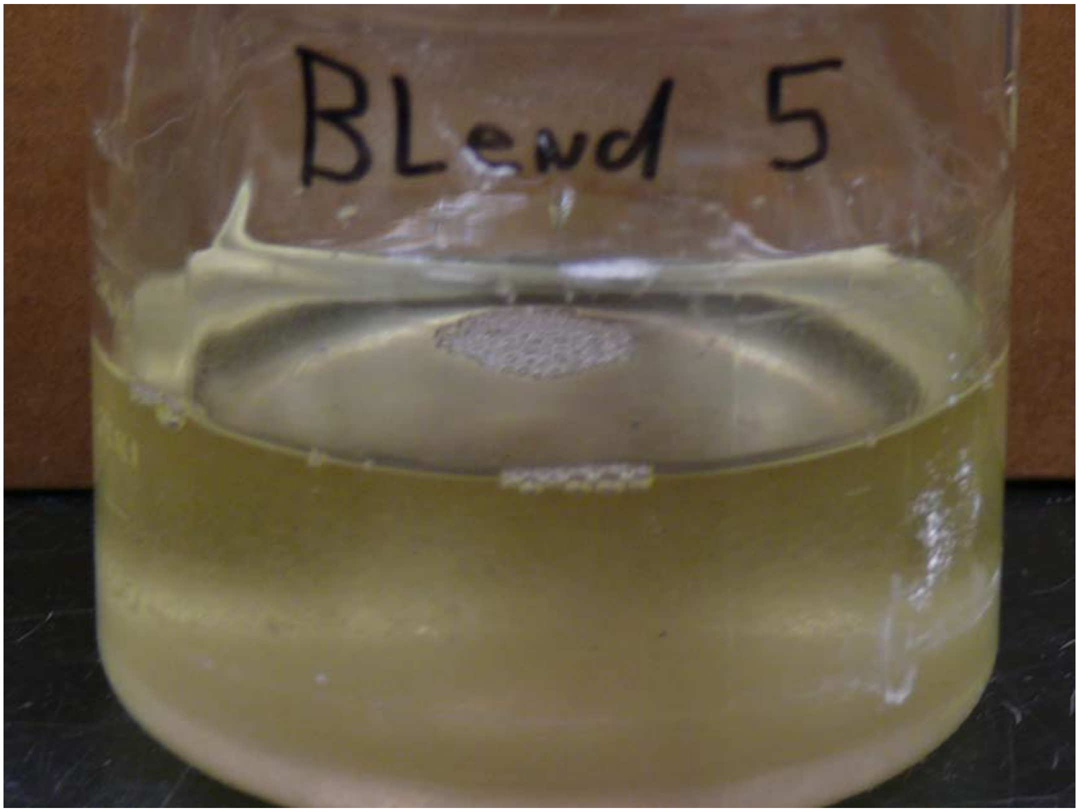

Figure 8.2. Blend 5 Solids Formed after Sitting at Ambient Laboratory Temperature

9.0 Summary

During demonstration of the leaching and ultrafiltration processes in the PEP, significant post-filtration precipitation was observed in the post-caustic leachate and wash solutions. Precipitation in this stream could lead to accumulation of precipitates in filtrate receipt vessels and in the feed to ion exchange columns. Post-filtration precipitation in the feed to the ion-exchange column will have a very significant effect on the operability of the unit and the pretreatment process. This work scope was completed to develop an understanding of the phenomenon of precipitation after filtration. The results of the test objective are documented according to tasks in Sections 3.0 through 8.0. The following is a summary of the preceding sections.

The objective of the Task 1 tests was to determine the post-filtration precipitate mineralogy, precipitate phase compositions, and solution saturation compositions in the post-caustic leachate and wash-solution samples from the PEP Integrated Test A at ambient temperature. These washes all formed precipitate and then were filtered using a 0.45-μm filter after 16 days at an ambient temperature of 18 to 22°C. After drying, the wt% undissolved solids ranged from 0.038-wt% to 0.44-wt%. However, even after filtering, crystals continued to form at ambient temperature (~18 to 22°C) in the supernate over the next couple of months.

The analytical results of the solution phase indicate that the sodium oxalate and sodium phosphate dissolved and increased in concentration throughout the washes whereas the other analytes decreased in concentration progressively during the post-caustic-leach wash. This allowed sodium phosphate and sodium oxalate to become supersaturated and precipitate as the temperature dropped over time to form precipitated solids. The oxalates appeared to dissolve in more dilute solution because of the reduced common ion effect of sodium. The phosphate dissolved and appeared earlier as the caustic leached slurry was washed until it was all dissolved.

Pictures were taken of the dried solids from the samples in polarized light, cross-polarized light, and cross-polarized light with a full wave plate. Interference patterns were only obtained for samples 2341 (wash 3), 2349 (wash 11), and 2363 (wash 25) and indicated sodium phosphate based on the crystal shape and color refraction. Sample 2369 (wash 31) indicated sodium oxalate based on the crystal shape. These results are all in agreement with the chemical analysis and XRD. This can be explained by 1) differences in the solubilities of sodium phosphate and sodium oxalate as a function of sodium ion concentrations in solution, and 2) the quantities of precipitated phosphates and oxalates at the end of the caustic leaching operation. Aluminum compounds were not observed to precipitate in these washes.

The objective of the Task 2 tests was to determine the rate at which the anions of interest (phosphate, oxalate, sulfate, silicate, and fluoride) approach equilibrium solution composition in post-caustic-leach slurry at 25°C before filtration using controlled laboratory experiments. These tests were performed using simplified simulated post-caustic-leach slurry (derived from the PEP Integrated Test A). The simulated post-caustic-leach slurry was spiked with each target anion (phosphate, oxalate, sulfate, silicate, and fluoride) in the form of a sodium salt.

Eleven different blends of the target anions were prepared and held at 85°C for 24 hours and then cooled to 25°C and held for 24 hours. The samples were then cooled to 16°C and held for 24 hours and heated back to 25°C and held 96 hours. The solutions were sampled periodically throughout the test and analyzed for the presence of these anions.

All of the samples taken while the supernate temperature was at 85°C for 24 hours developed an orange-brown precipitate after being diluted with DIW and sitting at ambient temperature (~18 to 22°C) for 26 hours. The Fe-rich slurry is believed to be the source of the brown precipitate since sample T2-9 (null test without any anion spikes) had just as much precipitate as the other samples. Chemical analysis confirmed that it was an iron compound. Iron was present in the post-caustic-leach slurry component.

From these tests, oxalate appears to be fairly slow to precipitate, taking nearly 24 hours before reaching equilibrium. However, the presence of phosphate, sulfate, or fluoride did not significantly change the equilibrium concentration of oxalate, but the kinetics appeared to be faster in the presence of the other anions. In the absence of fluoride, phosphate appears to equilibrate very quickly. However, in the presence of fluoride, phosphate equilibrates much slower and to a significantly lower solubility. Phosphate solubility appears to be a strong function of fluoride. The presence of fluoride does appear to suppress the sulfate solubility. Interestingly, fluoride appears to equilibrate within a few hours. However, the presence of oxalate appears to suppress the fluoride solubility, but fluoride had no effect on the oxalate solubility.

The objective of the Task 3 tests was to identify precipitates formed at ambient temperature in the presence of phosphate, oxalate, sulfate, silicate, and fluoride anions in the post-caustic leachate solution. Eleven different blends of the target anions were prepared and held at 35°C for 24 hours and filtered, and then the supernate was cooled to 20°C and held for 96 hours. Five of the 11 tests produced precipitate, which was then analyzed to determine PSD crystal shape and habit (morphology), quantity, and the settling rate of precipitates formed.

The amount of phosphate in solution at 35°C appears to be anomalously low. At this point, there is not a good reason why this value was low, but that the sample may not have reached equilibrium at 35°C. This may be due to either the sample re-equilibrating quickly upon cooling during the separation process or the sample not yet reaching equilibrium during storage at temperature. The amount of phosphate in solution is about ¼ of the expected amount based on the amount in the test with phosphate only.

Only sodium phosphate and sodium fluoride phosphate exhibit any significant change in solubility with temperature. The other main components appear to be relatively insensitive to temperature.

Task 3 sample solutions containing precipitated crystals were analyzed by OM to gather optical properties of the crystals as well as particle size. All of the Task 3 samples, with the exception of the phosphate only test, contained the same cubic crystal type. These samples were determined to be cubic because of the observed morphology, which is extinct at all angles when under cross-polarized light. These crystals are likely $Na_7F(PO_4)_2 \cdot 19H_2O$ based on the high refractive index of the crystals. The phosphate only test sample contains long, thin, needle-shaped crystals that appear white under cross-polarized light. When a full wave plate is inserted into the cross-polarized light, the crystals appear blue when the long axis of the crystal and the wave plate are parallel and yellowish-orange when perpendicular. Therefore, these crystals are most likely $Na_3PO_4 \cdot 12H_2O$.

The objective of the Task 4 tests was to determine the potential to redissolve the post-filtration precipitate in Integrated Tests A, B, and D in the PEP through dilution with DIW at 25±1°C. DIW was added in 5-mL increments every 24 hours until the solids were completely dissolved. These results showed that the solids are essentially soluble if enough DIW is added.

The objective of the Task 5 tests was to determine the solution supersaturation in the post-caustic-leach filtrate during the dewatering and washing period based on the samples collected during the PEP Integrated Test B. Ten post-caustic-leach filtrate and wash solutions from the PEP Integrated Test B were placed in an incubator at 20°C for 96 hours. The temperature of the incubator was raised 1°C every 24 hours until 30°C was reached. The temperature was then raised from 30°C to 35°C for 24 hours while shaking at 150 rpm. Samples were taken at 20°C, 25°C, and 35°C.

There was little to no dissolution of oxalate after heating the solutions from 20°C to 35°C, except for wash 15 (sample 4237) and wash 18 (sample 4240) where an increase occurred from 25°C to 35°C. This is because of the lower solubility of oxalate at high sodium ion concentrations in the earlier wash solutions. The tests show a low-sensitivity sodium oxalate solubility to temperature at high sodium concentrations in solution. However, in washes 15 and 18, the concentration of sodium ions was low enough for the precipitated oxalate to dissolve. Therefore, when the temperature was increased, the amount of oxalate in the supernate increased in these samples as the precipitated oxalate dissolved.

The results of the phosphate (phosphorus) dissolution for these samples show that the phosphate (phosphorus) concentration in solution increased significantly upon heating to 35°C for most of the samples with the exception of washes 12 (sample 4234), 15 (sample 4237), and 18 (sample 4240). This can be explained by the fact that by this point, all of the phosphorus (phosphate) had dissolved and washed out when the temperature was increased in these tests.

The crystals that did not dissolve were analyzed by SEM equipped with an EDS. Samples 4231 (wash 9) through 4240 (wash 18) all appear to be $Na_2C_2O_4$, based on the thin needle crystals and measured chemistry. Sample 4153(leachate) appears to be $Na_3PO_4 \cdot 12H_2O$, based on the measured chemistry and the large needle-shaped crystals.

The objective of the Task 6 tests was to determine the effects of blending during the post-caustic-leach dewatering and wash periods in the PEP Integrated Test B. Several of the PEP Integrated Test B permeate, leachate, and wash solution samples were blended together in different combinations to determine the effect of these blends on precipitation. Blend 1 represented mixing the filtrates from Integrated Test B, Blend 2 represented mixing the leachate and concentrated wash (wash liquids down to 2.6 M Na), Blend 3 represented mixing the leachate, concentrated wash (wash liquids down to 2.6 M Na), and dilute wash (wash liquids from 2.6 to 0.3 M Na), Blend 4 represented mixing the concentrated (wash liquids down to 2.6 M Na) and dilute washes (wash liquids from 2.6 to 0.3 M Na), and Blend 5 represented mixing concentrated washes (wash liquids down to 2.6 M Na) only.

The solutions were mixed together in a 500-mL bottle and then placed in an incubator for 48 hours at 25±1°C while shaking at 150 rpm. Blends 1, 3, and 4 became cloudy when the solutions were added, indicating precipitate forming at time zero. Blends 2 and 5 remained clear throughout the addition of solutions. After 9 days, Blend 2 also contained slight visible precipitate. These blends were then filtered at the end of the test using 0.45-µm filters to determine how many solids were formed in each blend. The wt% UDS ranged from 0.03-wt% in Blend 5 to 0.32-wt% in Blend 3. Note that Blends 1, 3, and 4 all contained a mix of leachate and later washes. These later washes would have contained high concentrations of oxalate. Thus, it is likely that the cause of the immediate precipitate in Blends 1, 3, and

4 was sodium oxalate. Blends 2 and 5 did not contain those later washes and as such, did not achieve as great a degree of supersaturation.

10.0 Conclusions

The following conclusions were drawn from this work:

- The analytical results of the PEP Integrated Test A washes from the solution phase indicate that the sodium oxalate and sodium phosphate dissolved and increased in concentration throughout the washes whereas the other analytes decreased in concentration progressively during the post-caustic-leach wash.
- The oxalates appeared to dissolve in more dilute solution because of the reduced common ion effect of sodium. The phosphate dissolved and appeared earlier as the caustic leached slurry was washed until it was all dissolved.
- Aluminum compounds were not observed to precipitate in these washes.
- Oxalate appears to be fairly slow to precipitate, taking nearly 24 hours before reaching equilibrium. However, the presence of phosphate, sulfate, or fluoride did not significantly change the equilibrium concentration of oxalate, but the kinetics appeared to be faster in the presence of the other anions.
- In the absence of fluoride, phosphate appears to equilibrate very quickly. However, in the presence of fluoride, phosphate equilibrates much slower and to a significantly lower solubility. Phosphate solubility appears to be a strong function of fluoride.
- The presence of fluoride does appear to suppress the sulfate solubility.
- Fluoride appears to equilibrate within a few hours. However, the presence of oxalate appears to suppress the fluoride solubility, but fluoride had no effect on the oxalate solubility.
- Only sodium phosphate and sodium fluoride phosphate exhibit any significant change in solubility with temperature. The other main components appear to be relatively insensitive to temperature.
- All of the Task 3 samples, with the exception of the phosphate-only test, contained the same cubic crystal type, which is most likely $Na_7F(PO_4)_2 \cdot 19H_2O$.
- The precipitated solids are essentially soluble if enough DIW is added.
- Blends containing a mix of leachate and later washes (containing high concentrations of oxalate) precipitated immediately. This is likely due to the high concentration of sodium oxalate present. Blends 2 and 5 did not contain those later washes and as such, did not achieve as great a degree of supersaturation with oxalate.

11.0 References

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Appendix A

Chemical Analysis Results

Appendix A: Chemical Analysis Results

Dilution factors were calculated by adding the sample weight and the DIW weight and dividing the sum by the sample weight for all sample results reported from these analytical results.

Table A.1. ICP Results for Task 2 Supernate

Test ID	Sample ID	Sample Wt (g)	DIW (g)	Al (mg/L)	Na (mg/L)	P (mg/L)	S (mg/L)	Si (mg/L)	Fe (mg/L)	K (mg/L)
T2-1a	85°C	1.9347	14.5796	1,140	14,400	456	133	1.93	2.31	86.0
	25°C-0 hr	2.0784	14.7004	1,260	15,000	52.1	135	1.60	1.66	97.4
	25°C-1 hr	2.0404	14.6059	1,240	15,200	45.2	147	1.55	0.968	95.6
	25°C-2 hr	1.8480	14.6221	1,130	13,600	36.9	134	1.47	0.845	88.0
	25°C-4 hr	2.9329	13.6433	1,140	14,200	32.8	139	1.49	0.900	89.8
	25°C-8 hr	2.1474	14.2005	1,360	15,700	36.9	156	1.69	0.918	106
	25°C-12 hr	2.2690	14.5718	1,400	15,700	36.7	169	1.78	1.14	108
	25°C-24 hr	2.4826	14.5781	1,610	18,600	36.8	202	2.0	1.44	117
	15°C	2.2433	14.7031	1,410	16,900	27	178	2.0	1.09	103
	25°C-b 24 hr	2.1247	14.7548	1,330	16,100	33	162	1.5	0.56	98.5
	25°C-b 96 hr	1.9635	14.9026	1,220	14,600	32	145	1.6	0.62	90.5
T2-1b	85°C	1.9840	14.6905	1,020	14,700	466	139	4.43	3.23	89.1
	25°C-0 hr	2.0413	14.6731	1,060	14,900	54.1	142	3.39	1.10	92.7
	25°C-1 hr	2.0380	14.6793	1,070	14,900	47.8	149	3.40	1.09	94.9
	25°C-2 hr	2.1003	14.5745	1,090	15,300	44.4	152	3.52	1.11	98.5
	25°C-4 hr	2.0558	14.8148	1,040	14,700	36.5	149	3.23	1.00	92.9
	25°C-8 hr	2.2809	14.2522	1,310	17,700	40.7	174	3.9	2.93	109
	25°C-12 hr	2.6159	14.6052	1,450	19,300	39.0	200	4.4	1.84	124
	25°C-24 hr	2.4337	14.9196	1,310	17,600	37.2	189	3.9	1.51	111
	15°C	2.0434	14.7266	1,120	15,700	26	169	3.2	1.16	96.2
	25°C-b 24 hr	2.0906	14.7012	1,130	15,800	36.7	168	3.2	0.73	97.6
	25°C-b 96 hr	1.9644	14.8275	1,070	14,800	35.1	142	2.8	0.945	91.2
T2-1c	85°C	1.8050	14.5581	937	13,600	426	124	5.42	4.19	81.7
	25°C-0 hr	1.7735	14.7670	924	12,700	43.9	120	3.17	0.932	81.1
	25°C-1 hr	1.6038	14.5611	850	12,000	34.8	114	2.94	0.946	75.3
	25°C-2 hr	2.0213	14.7139	1,050	14,800	38.0	142	3.48	1.47	94.6
	25°C-4 hr	2.1133	14.7556	1,070	15,100	33.2	148	3.50	1.18	96.4
	25°C-8 hr	1.7146	14.3404	963	12,800	27.5	123	3.16	1.19	85.2
	25°C-12 hr	2.5116	14.5171	1,400	18,600	35.3	180	4.7	1.61	120
	25°C-24 hr	2.0306	14.7696	1,130	15,400	32	169	3.6	1.43	94.2
	15°C	2.1823	14.4569	1,230	16,800	26	167	3.7	1.22	102
	25°C-b 24 hr	2.1155	14.5348	1,150	16,200	32	151	3.5	0.868	98.1
	25°C-b 96 hr	2.1425	14.6962	1,150	15,900	31	145	3.3	1.08	99.2
T2-2	85°C	1.8534	14.6473	1,110	14,000	442	339	1.88	2.78	83.4
	25°C-0 hr	2.0774	14.7051	1,180	15,400	456	379	1.57	1.01	89.8
	25°C-1 hr	1.8355	14.5439	1,120	13,800	61.4	364	1.36	0.549	86.9
	25°C-2 hr	2.0746	14.6716	1,230	15,200	68.9	407	1.48	0.784	96.4
	25°C-4 hr	1.8476	14.6463	1,100	13,800	58.8	363	1.31	0.715	86.3
	25°C-8 hr	2.1863	14.5029	1,360	16,100	72.5	428	1.57	0.806	106
	25°C-12 hr	2.2154	14.2873	1,390	16,100	79.6	448	1.70	0.716	107
	25°C-24 hr	1.7871	14.5852	1,190	14,000	63.3	394	1.7	1.68	86.2
	15°C	2.1842	14.2713	1,430	17,300	38.2	470	1.7	0.866	106
	25°C-b 24 hr	1.9851	14.4748	1,230	15,500	67.3	403	1.4	0.40	93.5

Table A.1. ICP Results for Task 2 Supernate

Test ID	Sample ID	Sample Wt (g)	DIW (g)	Al (mg/L)	Na (mg/L)	P (mg/L)	S (mg/L)	Si (mg/L)	Fe (mg/L)	K (mg/L)
	25°C-b 96 hr	1.9673	14.6357	1,230	15,100	74.8	393	1.5	0.57	91.0
T2-3	85°C	2.0784	14.5842	1,090	15,200	470	4.5	5.63	3.37	95.4
	25°C-0 hr	1.9028	14.6491	982	13,600	61.0	3.5	3.62	1.74	85.9
	25°C-1 hr	1.8022	14.5220	953	13,200	49.2	4.0	3.43	1.44	83.9
	25°C-2 hr	1.9830	14.6939	1,040	14,300	46.9	3.6	3.60	0.895	92.7
	25°C-4 hr	2.1745	14.6349	1,100	15,400	38.4	4.8	3.75	0.917	99.0
	25°C-8 hr	2.4737	14.5557	1,400	18,500	41.0	---	4.8	1.24	117
	25°C-12 hr	2.6938	14.1919	1,550	20,200	40.4	13	5.4	1.42	129
	25°C-24 hr	2.2044	14.6542	1,230	16,700	32	6.3	4.2	1.39	104
	15°C	2.1798	14.7643	1,190	16,300	24	12	4.2	1.53	101
	25°C-b 24 hr	1.8987	14.3184	1,070	14,800	22	12	3.5	0.72	90.6
	25°C-b 96 hr	2.1041	14.7122	1,150	15,500	25	6.1	3.5	0.82	96.3
T2-4	85°C	1.9295	14.6504	1,160	14,100	460	3.0	1.56	2.31	88.0
	25°C-0 hr	1.8547	14.6407	1,080	13,900	435	3.3	1.36	1.00	81.6
	25°C-1 hr	1.7289	14.5278	1,070	12,800	59.3	3.9	1.67	1.07	82.5
	25°C-2 hr	1.6947	14.8147	1,030	12,300	55.5	4.1	1.2	0.842	79.8
	25°C-4 hr	1.7707	14.5044	1,130	13,000	60.6	2.2	1.28	0.783	85.8
	25°C-8 hr	2.2147	14.5003	1,410	15,600	74.0	4.6	1.69	0.826	108
	25°C-12 hr	2.3471	14.5062	1,560	17,600	85.7	5.9	2.1	1.65	118
	25°C-24 hr	1.4177	14.8626	933	10,900	53.6	---	1.4	1.01	67.7
	15°C	2.1631	14.5262	1,410	16,300	40.7	6.3	1.9	0.62	104
	25°C-b 24 hr	2.2338	14.1825	1,450	17,200	82.0	---	1.7	0.73	106
	25°C-b 96 hr	1.8569	14.9544	1,170	13,400	69.9	---	1.3	0.47	85.9
T2-5	85°C	1.7839	14.5761	939	13,600	422	115	4.10	2.11	81.5
	25°C-0 hr	1.9830	14.7133	1,030	14,500	64.8	117	3.22	0.897	90.2
	25°C-1 hr	1.9396	14.5921	1,020	14,200	48.6	121	3.08	0.852	89.8
	25°C-2 hr	2.0978	14.6534	1,090	15,200	45.2	131	3.24	0.907	96.7
	25°C-4 hr	1.9987	14.4554	1,180	13,400	65.4	---	1.3	0.84	87.9
	25°C-8 hr	2.6800	14.5296	1,450	19,600	40.9	162	4.5	1.19	120
	25°C-12 hr	2.2884	14.5495	1,220	16,200	30.9	141	3.63	1.13	106
	25°C-24 hr	2.2854	14.3548	1,260	17,500	34	147	3.8	1.26	105
	15°C	2.0191	14.4203	1,150	15,700	21	136	3.2	0.85	95.0
	25°C-b 24 hr	1.9792	14.5692	1,090	15,100	24	118	3.0	0.70	91.2
	25°C-b 96 hr	1.8897	14.6265	1,160	15,800	19	123	3.3	0.83	96.1
T2-6	85°C	1.7960	14.7075	1,110	13,400	2.9	339	1.36	2.02	84.1
	25°C-0 hr	1.9644	14.6695	1,170	14,400	3.1	388	1.37	1.22	89.0
	25°C-1 hr	1.9153	14.4953	1,180	14,400	2.7	389	1.25	1.20	91.0
	25°C-2 hr	2.0430	14.9063	1,200	14,700	2.3	391	1.35	1.24	92.7
	25°C-4 hr	2.0169	14.4284	1,270	15,000	2.1	396	1.40	1.26	97.8
	25°C-8 hr	2.2635	14.6261	1,460	17,100	----	451	2.4	1.48	108
	25°C-12 hr	2.6059	14.5537	1,680	20,000	4.6	551	1.8	1.71	124
	25°C-24 hr	2.0623	14.7645	1,300	15,600	8.4	430	1.8	1.21	95.5
	15°C	2.0792	14.6726	1,340	16,000	11	438	1.4	1.00	96.9
	25°C-b 24 hr	1.7681	14.4679	1,130	14,000	11	360	1.6	0.996	84.1
	25°C-b 96 hr	1.7895	14.6742	1,140	13,700	---	354	1.3	0.83	82.8
T2-7	85°C	1.8875	14.6665	1,010	13,700	3.2	3.7	4.09	2.93	89.2
	25°C-0 hr	2.1034	14.6025	1,090	15,200	3.1	4.5	3.87	1.28	96.3
	25°C-1 hr	2.0705	14.3632	1,110	15,300	3.5	4.5	3.84	1.51	99.2
	25°C-2 hr	1.8141	14.7511	948	13,200	1.9	4.9	3.46	1.27	85.0
	25°C-4 hr	2.4228	14.7919	994	13,400	2.6	4.5	3.42	1.20	88.2

Table A.1. ICP Results for Task 2 Supernate

Test ID	Sample ID	Sample Wt (g)	DIW (g)	Al (mg/L)	Na (mg/L)	P (mg/L)	S (mg/L)	Si (mg/L)	Fe (mg/L)	K (mg/L)
	25°C-8 hr	1.9031	14.4453	1,050	13,700	2.8	4.7	3.62	1.29	92.0
	25°C-12 hr	2.6049	14.5551	1,480	20,000	4.4	7.2	4.9	1.90	126
	25°C-24 hr	2.1033	14.3416	1,190	16,200	9.4	14	4.2	1.71	101
	15°C	2.1423	14.7736	1,190	16,200	8.9	----	4.4	1.20	103
	25°C-b 24 hr	1.8924	14.6728	1,040	14,500	14	---	3.2	0.83	89.0
	25°C-b 96 hr	1.7792	14.5848	985	13,500	---	---	3.4	1.07	82.6
T2-8	85°C	2.2064	14.4293	1,250	14,400	3.6	3.8	1.44	2.73	97.2
	25°C-0 hr	2.2816	14.7210	1,380	16,200	2.7	5.0	1.66	1.59	108
	25°C-1 hr	2.1011	14.4441	1,310	15,300	2.2	4.2	1.63	1.50	101
	25°C-2 hr	2.2037	14.4611	1,340	15,600	3.4	5.1	1.45	1.30	106
	25°C-4 hr	2.3403	14.4867	1,550	17,600	4.3	---	1.8	1.90	114
	25°C-8 hr	2.4455	14.5387	1,610	17,800	---	----	2.1	1.90	119
	25°C-12 hr	2.6974	14.7022	1,740	19,900	----	16	1.9	1.89	128
	25°C-24 hr	1.9945	14.6163	1,320	15,500	9.8	9.3	1.7	1.48	95.0
	15°C	2.2289	14.4289	1,450	16,700	---	7.4	1.6	0.80	108
	25°C-b 24 hr	2.2675	14.3639	1,460	17,000	8.0	11	1.7	0.982	109
	25°C-b 96 hr	2.2303	14.6369	1,370	15,800	---	---	1.8	1.29	101
T2-9	85°C	1.9753	14.7040	1,230	14,000	3.5	3.0	1.43	2.79	94.3
	25°C-0 hr	2.4214	14.4338	1,560	18,200	---	8.3	1.5	1.60	114
	25°C-1 hr	2.0979	14.7994	1,280	14,900	2.9	4.3	1.51	1.32	98.4
	25°C-2 hr	1.6679	14.4493	1,040	12,500	2.3	3.0	1.1	1.01	81.3
	25°C-4 hr	1.9033	14.5538	1,200	13,800	2.4	3.6	1.37	1.23	92.1
	25°C-8 hr	2.1504	14.1977	1,370	15,200	3.6	5.6	1.56	1.29	105
	25°C-12 hr	2.6758	14.3778	1,760	20,000	---	----	2.2	1.71	128
	25°C-24 hr	1.8892	14.2807	1,270	15,100	10	13	1.5	1.21	94.8
	15°C	2.2648	14.5778	1,450	16,700	7.0	---	1.3	1.02	106
	25°C-b 24 hr	2.0236	14.4929	1,330	15,400	8.3	14	1.8	1.06	97.3
	25°C-b 96 hr	2.2298	14.5495	1,400	16,100	---	---	1.7	1.36	102

Table A.2. IC Results for Task 2 Supernate

Test ID	Sample ID	Sample Wt (g)	DIW (g)	C_2O_4 (mg/L)	PO_4 (mg/L)	SO_4 (mg/L)	F (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)
T2-1a	85°C	1.9347	14.5796	55	1,480	433	136	6,430	1,440
	25°C-0 hr	2.0784	14.7004	22	175	461	50	7,130	1,600
	25°C-1 hr	2.0404	14.6059	21	147	454	48	7,060	1,580
	25°C-2 hr	1.8480	14.6221	21	124	414	43	6,470	1,420
	25°C-4 hr	2.9329	13.6433	19	113	433	43	6,590	1,460
	25°C-8 hr	2.1474	14.2005	20	117	491	48	7,490	1,650
	25°C-12 hr	2.2690	14.5718	22	117	505	49	7,770	1,720
	25°C-24 hr	2.4826	14.5781	19	116	547	53	8,430	1,870
	15°C	2.2433	14.7031	18	69	495	46	7,690	1,710
	25°C-24 hr	2.1247	14.7548	16	96	469	48	7,280	1,610
	25°C-96 hr	1.9635	14.9026	14	87	427	46	6,650	1,470
T2-1b	85°C	1.9840	14.6905	57	1,480	449	140	6,380	1,450
	25°C-0 hr	2.0413	14.6731	23	182	463	46	6,840	1,550
	25°C-1 hr	2.0380	14.6793	24	156	462	43	6,860	1,550
	25°C-2 hr	2.1003	14.5745	24	147	480	43	7,160	1,600
	25°C-4 hr	2.0558	14.8148	21	124	462	40	6,740	1,510
	25°C-8 hr	2.2809	14.2522	24	131	526	45	7,700	1,720
	25°C-12 hr	2.6159	14.6052	25	138	587	49	8,520	1,860
	25°C-24 hr	2.4337	14.9196	20	117	537	46	7,940	1,780
	15°C	2.0434	14.7266	17	64	464	38	6,890	1,550
	25°C-24 hr	2.0906	14.7012	16	99	479	44	7,100	1,590
	25°C-96 hr	1.9644	14.8275	16	94	439	44	6,560	1,460
T2-1c	85°C	1.8050	14.5581	52	1,350	399	134	5,890	1,330
	25°C-0 hr	1.7735	14.7670	20	145	384	48	6,100	1,380
	25°C-1 hr	1.6038	14.5611	17	113	354	42	5,540	1,250
	25°C-2 hr	2.0213	14.7139	22	128	435	56	6,820	1,520
	25°C-4 hr	2.1133	14.7556	21	118	452	51	6,970	1,560
	25°C-8 hr	1.7146	14.3404	16	88	383	44	5,930	1,320
	25°C-12 hr	2.5116	14.5171	23	119	537	59	8,320	1,880
	25°C-24 hr	2.0306	14.7696	18	92	436	50	6,780	1,520
	15°C	2.1823	14.4569	17	62	475	52	7,470	1,680
	25°C-24 hr	2.1155	14.5348	18	93	457	57	7,190	1,610
	25°C-96 hr	2.1425	14.6962	16	89	451	58	7,160	1,590
T2-2	85°C	1.8534	14.6473	52	1,400	1,090	<3	6,120	1,370
	25°C-0 hr	2.0774	14.7051	20	1,510	1,210	<3	6,780	1,520
	25°C-1 hr	1.8355	14.5439	17	201	1,120	<3	6,420	1,430
	25°C-2 hr	2.0746	14.6716	19	231	1,240	<3	7,110	1,560
	25°C-4 hr	1.8476	14.6463	15	205	1,120	<3	6,310	1,390
	25°C-8 hr	2.1863	14.5029	17	233	1,290	<3	7,440	1,640
	25°C-12 hr	2.2154	14.2873	19	256	1,350	<3	7,690	1,710
	25°C-24 hr	1.7871	14.5852	14	194	1,100	<3	6,240	1,380
	15°C	2.1842	14.2713	17	116	1,350	<3	7,680	1,710
	25°C-24 hr	1.9851	14.4748	15	220	1,220	<3	6,960	1,530
	25°C-96 hr	1.9673	14.6357	18	199	1,170	<3	6,770	1,490
T2-3	85°C	2.0784	14.5842	<4	1,460	11	196	6,780	1,540
	25°C-0 hr	1.9028	14.6491	<4	204	10	77	6,450	1,460
	25°C-1 hr	1.8022	14.5220	<4	162	10	74	6,220	1,410
	25°C-2 hr	1.9830	14.6939	<4	156	10	81	6,730	1,500

Table A.2. IC Results for Task 2 Supernate

Test ID	Sample ID	Sample Wt (g)	DIW (g)	C_2O_4 (mg/L)	PO_4 (mg/L)	SO_4 (mg/L)	F (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)
	25°C-4 hr	2.1745	14.6349	<4	136	11	90	7,240	1,620
	25°C-8 hr	2.4737	14.5557	<4	124	13	102	8,100	1,780
	25°C-12 hr	2.6938	14.1919	<4	124	14	113	9,070	2,040
	25°C-24 hr	2.2044	14.6542	<4	85	11	95	7,450	1,670
	15°C	2.1798	14.7643	<4	55	11	92	7,330	1,640
	25°C-24 hr	1.8987	14.3184	<4	67	10	87	6,650	1,480
	25°C-96 hr	2.1041	14.7122	<4	70	11	93	7,050	1,570
T2-4	85°C	1.9295	14.6504	<4	1,460	10	<3	6,430	1,440
	25°C-0 hr	1.8547	14.6407	<4	1,420	10	<3	6,200	1,390
	25°C-1 hr	1.7289	14.5278	<4	196	9	<3	6,160	1,470
	25°C-2 hr	1.6947	14.8147	<4	183	9	<3	5,960	1,310
	25°C-4 hr	1.7707	14.5044	<4	201	9	<3	6,200	1,370
	25°C-8 hr	2.2147	14.5003	<4	237	14	<3	7,640	1,690
	25°C-12 hr	2.3471	14.5062	<4	258	12	<3	8,080	1,800
	25°C-24 hr	1.4177	14.8626	<4	147	8	<3	5,020	1,110
	15°C	2.1631	14.5262	<4	106	12	<3	7,610	1,680
	25°C-24 hr	2.2338	14.1825	<4	262	12	<3	7,980	1,760
	25°C-96 hr	1.8569	14.9544	<4	209	10	<3	6,370	1,400
T2-5	85°C	1.7839	14.5761	<4	1,370	361	148	5,850	1,320
	25°C-0 hr	1.9830	14.7133	<4	218	380	76	6,640	1,500
	25°C-1 hr	1.9396	14.5921	<4	162	371	74	6,580	1,490
	25°C-2 hr	2.0978	14.6534	<4	153	402	81	7,080	1,580
	25°C-4 hr	1.9987	14.4554	<4	121	387	80	6,790	1,510
	25°C-8 hr	2.6800	14.5296	<4	128	499	105	8,810	1,980
	25°C-12 hr	2.2884	14.5495	<4	100	437	93	7,710	1,730
	25°C-24 hr	2.2854	14.3548	<4	88	438	96	7,780	1,740
	15°C	2.0191	14.4203	<4	49	390	84	6,940	1,560
	25°C-24 hr	1.9792	14.5692	<4	66	375	85	6,790	1,520
	25°C-96 hr	1.8897	14.6265	<4	68	383	90	7,140	1,590
T2-6	85°C	1.7960	14.7075	<4	10	1,110	<3	6,230	1,390
	25°C-0 hr	1.9644	14.6695	<4	10	1,210	<3	6,780	1,520
	25°C-1 hr	1.9153	14.4953	<4	10	1,190	<3	6,710	1,500
	25°C-2 hr	2.0430	14.9063	<4	10	1,230	<3	6,950	1,530
	25°C-4 hr	2.0169	14.4284	<4	10	1,230	<3	6,970	1,540
	25°C-8 hr	2.2635	14.6261	<4	11	1,370	<3	7,730	1,710
	25°C-12 hr	2.6059	14.5537	<4	13	1,570	<3	8,810	1,950
	25°C-24 hr	2.0623	14.7645	<4	10	1,260	<3	7,120	1,580
	15°C	2.0792	14.6726	<4	11	1,280	<3	7,200	1,590
	25°C-24 hr	1.7681	14.4679	<4	9	1,120	<3	6,260	1,380
	25°C-96 hr	1.7895	14.6742	<4	9	1,110	<3	6,210	1,370
T2-7	85°C	1.8875	14.6665	50	10	12	133	6,480	1,470
	25°C-0 hr	2.1034	14.6025	21	11	13	146	7,160	1,620
	25°C-1 hr	2.0705	14.3632	19	11	13	145	7,190	1,630
	25°C-2 hr	1.8141	14.7511	17	9	11	127	6,190	1,380
	25°C-4 hr	2.4228	14.7919	16	9	11	129	6,230	1,390
	25°C-8 hr	1.9031	14.4453	16	10	12	135	6,630	1,490
	25°C-12 hr	2.6049	14.5551	21	13	16	174	8,710	1,960

Table A.2. IC Results for Task 2 Supernate

Test ID	Sample ID	Sample Wt (g)	DIW (g)	C_2O_4 (mg/L)	PO_4 (mg/L)	SO_4 (mg/L)	F (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)
	25°C-24 hr	2.1033	14.3416	18	11	13	147	7,340	1,650
	15°C	2.1423	14.7736	15	11	13	147	7,290	1,630
	25°C-24 hr	1.8924	14.6728	14	10	12	130	6,520	1,450
	25°C-96 hr	1.7792	14.5848	14	9	11	123	6,180	1,380
T2-8	85°C	2.2064	14.4293	55	10	13	<3	7,030	1,570
	25°C-0 hr	2.2816	14.7210	26	11	14	<3	7,820	1,750
	25°C-1 hr	2.1011	14.4441	17	11	14	<3	7,450	1,660
	25°C-2 hr	2.2037	14.4611	18	11	14	<3	7,730	1,720
	25°C-4 hr	2.3403	14.4867	18	12	15	<3	8,080	1,780
	25°C-8 hr	2.4455	14.5387	17	12	15	<3	8,420	1,870
	25°C-12 hr	2.6974	14.7022	19	13	17	<3	9,110	2,020
	25°C-24 hr	1.9945	14.6163	16	10	13	<3	7,080	1,560
	15°C	2.2289	14.4289	15	11	14	<3	7,880	1,740
	25°C-24 hr	2.2675	14.3639	16	12	15	<3	8,000	1,770
	25°C-96 hr	2.2303	14.6369	17	11	14	<3	7,740	1,710
T2-9	85°C	1.9753	14.7040	<4	10	11	<3	6,910	1,550
	25°C-0 hr	2.4214	14.4338	<4	12	13	<3	8,460	1,890
	25°C-1 hr	2.0979	14.7994	<4	10	11	<3	7,260	1,620
	25°C-2 hr	1.6679	14.4493	<4	9	9	<3	5,810	1,270
	25°C-4 hr	1.9033	14.5538	<4	10	10	<3	6,660	1,470
	25°C-8 hr	2.1504	14.1977	<4	11	12	<3	7,600	1,690
	25°C-12 hr	2.6758	14.3778	<4	13	14	<3	9,260	2,050
	25°C-24 hr	1.8892	14.2807	<4	9	10	<3	6,880	1,520
	15°C	2.2648	14.5778	<4	12	12	<3	7,920	1,750
	25°C-24 hr	2.0236	14.4929	<4	10	11	<3	7,160	1,580
	25°C-96 hr	2.2298	14.5495	<4	12	12	<3	7,770	1,710

Table A.3. ICP Results for Task 3 Supernate

Sample ID	Sample Wt (g)	DIW Wt (g)	Al (mg/L)	Fe (mg/L)	Na (mg/L)	P (mg/L)	S (mg/L)	Si (mg/L)	K (mg/L)
T3-1a-35	1.9441	14.8330	1,180	1.78	15,000	35	111	45.9	89.2
T3-1a-20	2.1873	14.6421	1,240	1.28	15,900	15.5	116	48.1	103
T3-1b-35	1.9116	14.6978	1,080	1.53	13,900	32.4	113	38.2	87.7
T3-1b-20	2.0293	14.8129	1,150	1.29	14,800	22.6	118	39.7	93.9
T3-1c-35	2.0960	14.5894	1,200	1.61	15,000	35.5	114	37.9	98.1
T3-1c-20	2.4174	14.7447	1,440	1.63	18,400	29	137	46.0	114
T3-2-35	1.8990	14.7282	1,150	1.41	13,900	31.4	206	1.32	89.8
T3-2-20	2.1255	14.5286	1,260	0.878	15,600	35.1	233	1.40	100
T3-3-35	1.9538	14.6158	1,050	1.48	14,100	45.0	3.7	35.7	89.6
T3-3-20	2.3100	14.5261	1,300	1.70	17,600	17	8.3	41.0	105
T3-4-35	1.4855	14.6971	894	0.960	10,900	113	3.0	0.97	69.2
T3-4-20	2.1851	14.6996	1,290	1.20	15,400	47.0	3.9	1.32	102
T3-5-35	2.0900	14.5645	1,140	1.62	15,100	46.7	154	49.2	96.5
T3-5-20	2.1006	14.4504	1,160	1.36	15,500	15.5	157	47.6	97.5
T3-6-35	1.8776	14.7100	1,110	1.15	13,700	2.6	353	1.2	86.4
T3-6-20	2.2394	14.5784	1,390	0.989	17,500	---	440	1.9	104
T3-7-35	1.5991	14.5299	940	1.32	11,900	2.2	3.4	33.4	77.1
T3-7-20	2.1413	14.5140	1,200	1.39	15,400	2.9	5.4	42.1	101
T3-8-35	1.9431	14.8338	1,150	1.24	13,800	2.5	4.3	1.23	90.9
T3-8-20	2.1305	14.6274	1,270	0.894	15,400	2.9	3.7	1.32	101
T3-9-35	1.8035	14.6740	1,100	1.35	13,000	2.4	3.5	1.1	86.4
T3-9-20	2.1095	14.3832	1,280	0.861	15,500	3.2	4.2	1.34	102

Table A.4. IC Results for Task 3 Supernate

Sample ID	Sample Wt (g)	DIW Wt (g)	F (mg/L)	C_2O_4 (mg/L)	PO_4 (mg/L)	SO_4 (mg/L)	NO_3 (mg/\L)	NO_2 (mg/L)
T3-1a-35	1.9441	14.8330	83	19	113	332	6,450	1,420
T3-1a-20	2.1873	14.6421	85	18	50	375	7,380	1,620
T3-1b-35	1.9116	14.6978	83	18	105	364	6,440	1,420
T3-1b-20	2.0293	14.8129	84	18	72	383	6,810	1,490
T3-1c-35	2.0960	14.5894	90	19	118	370	6,980	1,540
T3-1c-20	2.4174	14.7447	98	22	95	421	8,030	1,760
T3-2-35	1.8990	14.7282	<3	18	106	668	6,400	1,410
T3-2-20	2.1255	14.5286	<3	19	116	746	7,260	1,590
T3-3-35	1.9538	14.6158	89	<4	148	10	6,520	1,440
T3-3-20	2.3100	14.5261	92	<4	52	13	7,760	1,710
T3-4-35	1.4855	14.6971	<3	<4	376	8	5,080	1,110
T3-4-20	2.1851	14.6996	<3	<4	154	11	7,410	1,620
T3-5-35	2.0900	14.5645	88	<4	151	499	6,980	1,540
T3-5-20	2.1006	14.4504	79	<4	49	503	7,140	1,560
T3-6-35	1.8776	14.7100	<3	<4	10	1,120	6,340	1,390
T3-6-20	2.2394	14.5784	<3	<4	10	1,330	7,560	1,650
T3-7-35	1.5991	14.5299	75	16	8	10	5,550	1,220
T3-7-20	2.1413	14.5140	98	19	10	14	7,330	1,600
T3-8-35	1.9431	14.8338	<3	19	9	11	6,580	1,440
T3-8-20	2.1305	14.6274	<3	19	10	13	7,320	1,590
T3-9-35	1.8035	14.6740	<3	<4	8	10	6,190	1,360
T3-9-20	2.1095	14.3832	<3	<4	10	11	7,370	1,600

Table A.5. ICP Results for Task 5 Test B Post-Caustic Wash Solutions Composition

Sample ID	Wash #	Sample Wt (g)	DIW Wt (g)	Al (mg/L)	Na (mg/L)	P (mg/L)	S (mg/L)
B-4153-20°C	supernate	1.3946	10.0360	2,070	16,400	42.5	258
B-4153-25°C	supernate	2.2456	15.0487	2,220	18,800	68.1	265
B-4153-35°C	supernate	1.4634	14.3978	1,490	12,600	60.6	185
B-4154-20°C	supernate	1.3441	10.0310	2,030	16,000	41.0	255
B-4154-25°C	supernate	2.2520	15.0916	2,250	18,900	68.1	266
B-4154-35°C	supernate	1.6064	14.6050	1,630	13,800	64.4	208
B-4223-20°C	1	1.3278	10.0397	2,020	16,000	40.6	252
B-4223-25°C	1	2.1873	15.0821	2,220	18,600	65.1	266
B-4223-35°C	1	1.6984	14.8256	1,680	14,300	68.5	217
B-4225-20°C	3	1.3149	10.1141	1,920	15,100	39.8	240
B-4225-25°C	3	2.6304	15.1703	2,490	20,900	75.8	295
B-4225-35°C	3	1.6611	14.7887	1,630	13,800	63.5	207
B-4227-20°C	5	1.4020	10.0191	2,020	16,100	44.5	252
B-4227-25°C	5	2.3055	15.1890	2,180	18,200	73.4	261
B-4227-35°C	5	1.6452	14.9335	1,600	13,300	62.5	202
B-4229-20°C	7	1.2877	10.0189	1,800	14,300	43.4	224
B-4229-25°C	7	2.2096	15.1316	2,000	16,800	72.1	240
B-4229-35°C	7	1.6685	14.8253	1,550	13,000	65.0	200
B-4231-20°C	9	1.2212	10.0932	1,610	12,900	42.0	198
B-4231-25°C	9	2.0699	15.1061	1,760	14,700	68.6	209
B-4231-35°C	9	1.6151	14.7775	1,430	12,100	66.6	182
B-4234-20°C	12	1.2234	10.0356	1,430	11,400	54.9	177
B-4234-25°C	12	2.2353	15.0780	1,710	14,300	92.7	202
B-4234-35°C	12	1.4997	14.6018	1,180	9,990	65.7	151
B-4237-20°C	15	1.1844	10.0864	1,200	9,600	69.9	146
B-4237-25°C	15	1.7792	15.0304	1,180	9,840	72.0	140
B-4237-35°C	15	1.6064	14.4460	1,120	9,510	70.4	140
B-4240-20°C	18	0.9912	10.1280	873	7,030	54.5	104
B-4240-25°C	18	1.8278	15.0411	1,040	8,800	70.2	124
B-4240-35°C	18	1.4759	14.6444	863	7,350	58.3	106

Table A.6. IC Results for Task 5 Test B Post-Caustic Wash Solutions Composition

Sample ID	Wash #	Sample Wt (g)	DIW Wt (g)	C_2O_4 (mg/L)	PO_4 (mg/L)	SO_4 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)
B-4153-20°C	supernate	1.3946	10.0360	9	142	788	4,570	1,100
B-4153-25°C	supernate	2.2456	15.0487	8	217	832	4,850	1,160
B-4153-35°C	supernate	1.4634	14.3978	6	202	588	3,430	812
B-4154-20°C	supernate	1.3441	10.0310	7	134	750	4,380	1,050
B-4154-25°C	supernate	2.2520	15.0916	7	211	832	4,840	1,160
B-4154-35°C	supernate	1.6064	14.6050	6	206	632	3,700	875
B-4223-20°C	1	1.3278	10.0397	7	133	768	4,470	1,070
B-4223-25°C	1	2.1873	15.0821	7	202	814	4,740	1,140
B-4223-35°C	1	1.6984	14.8256	6	223	659	3,860	912
B-4225-20°C	3	1.3149	10.1141	7	128	714	4,160	999
B-4225-25°C	3	2.6304	15.1703	8	236	937	5,420	1,300
B-4225-35°C	3	1.6611	14.7887	6	203	630	3,690	872
B-4227-20°C	5	1.4020	10.0191	8	141	752	4,380	1,050
B-4227-25°C	5	2.3055	15.1890	8	228	813	4,740	1,140
B-4227-35°C	5	1.6452	14.9335	7	200	609	3580	847
B-4229-20°C	7	1.2877	10.0189	11	137	662	3,860	930
B-4229-25°C	7	2.2096	15.1316	11	225	747	4,370	1,050
B-4229-35°C	7	1.6685	14.8253	10	208	595	3,480	822
B-4231-20°C	9	1.2212	10.0932	17	140	586	3,410	818
B-4231-25°C	9	2.0699	15.1061	18	221	660	3,860	929
B-4231-35°C	9	1.6151	14.7775	15	214	542	3,160	747
B-4234-20°C	12	1.2234	10.0356	25	178	522	3,040	729
B-4234-25°C	12	2.2353	15.0780	28	292	622	3,650	874
B-4234-35°C	12	1.4997	14.6018	24	210	446	2,590	612
B-4237-20°C	15	1.1844	10.0864	40	231	433	2,520	604
B-4237-25°C	15	1.7792	15.0304	41	232	438	2,550	610
B-4237-35°C	15	1.6064	14.4460	49	221	417	2,420	569
B-4240-20°C	18	0.9912	10.1280	59	178	309	1,770	423
B-4240-25°C	18	1.8278	15.0411	75	222	384	2,220	530
B-4240-35°C	18	1.4759	14.6444	76	187	324	1,870	438

Table A.7. Density Results for Task 5 Test B Post-Caustic Wash Solutions Composition

Sample ID	Wash #	Density (g/mL)	Sample ID	Wash #	Density (g/mL)
4153-20°C	supernate	1.329	4229-20°C	7	1.300
4153-25°C	supernate	1.327	4229-25°C	7	1.300
4153-35°C	supernate	1.323	4229-35°C	7	1.294
4154-20°C	supernate	1.329	4231-20°C	9	1.281
4154-25°C	supernate	1.328	4231-25°C	9	1.280
4154-35°C	supernate	1.323	4231-35°C	9	1.277
4223-20°C	1	1.330	4234-20°C	12	1.248
4223-25°C	1	1.328	4234-25°C	12	1.244
4223-35°C	1	1.324	4234-35°C	12	1.240
4225-20°C	3	1.320	4237-20°C	15	1.212
4225-25°C	3	1.319	4237-25°C	15	1.209
4225-35°C	3	1.314	4237-35°C	15	1.206
4227-20°C	5	1.315	4240-20°C	18	1.178
4227-25°C	5	1.311	4240-25°C	18	1.177
4227-35°C	5	1.307	4240-35°C	18	1.172

Table A.8. ICP Results for Task 6 Supernate

Sample ID	Sample Wt (g)	DIW Wt (g)	Al (mg/L)	Na (mg/L)	P (mg/L)	S (mg/L)
Blend 1	1.8414	14.9795	839	10,200	112	306
Blend 2	2.1074	14.9407	1,920	15,900	64.5	237
Blend 3	1.9291	14.7809	1,340	11,200	56.9	162
Blend 4	1.7653	14.9762	972	8,160	49.9	117
Blend 5	2.0636	15.1189	1,880	15,600	67.5	226

Table A.9. IC Results for Task 6 Supernate

Sample ID	Sample Wt (g)	DIW Wt (g)	C_2O_4 (mg/L)	PO_4 (mg/L)	SO_4 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)
Blend 1	1.8414	14.9795	75	336	903	5,260	1,270
Blend 2	2.1074	14.9407	15	210	736	4,220	1,020
Blend 3	1.9291	14.7809	48	172	487	2,750	653
Blend 4	1.7653	14.9762	90	149	347	1,940	465
Blend 5	2.0636	15.1189	19	208	676	3,880	931

Table A.10. Particle Size Analysis Statistics for Sample # 2341

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	39,709	1,326	30.9
2	26,843	1,275	30.7
3	64,265	924.3	71.5
4	29,013	996.4	33.1
5	30,413	1,141	27.3
6	43,489	1,344	35.9
7	61,072	1,213	52.0
8	30,857	738.0	51.3
9	58,964	1,570	39.3
10	121,290	905.0	148
11	194,030	1,747	143
12	15,177	832.6	20.6
13	2,287.8	101.6	45.5
14	9,646.9	393.4	31.4
15	44,843	549.0	95.2
16	51,087	1,738	35.0
17	14,633	431.3	42.0
18	16,300	669.0	32.0
Mean	47,440	994.1	53.6
Min	2,288	101.6	20.6
Max	194,030	1,747	148
Sum	853,920	17,893	965
Std. Dev.	45,712	467.4	37.8
Variance	2,089,577,158	218,491	1430
Skew	2.281	-0.069	1.860
Excess	6.015	-0.639	2.574
Var. Coeff.	96	47	71
Obj. Count	18	—	—
Img. Area	19,091,308	—	—
Total Obj. Count	20	—	—
Total Img. Area	38,182,615	—	—

Table A.11. Particle Size Analysis Statistics for Sample # 2349

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	1,036,690	4,044	314
2	118,719	1,424	90
3	133,681	673	275
4	188,341	715	480
5	688,911	2,595	273
6	484,776	3,138	256
7	329,057	1,300	314
8	2,206,430	4,204	656
9	805,433	2,827	344
10	395,698	2,018	203
11	80,973	901	104
12	154,128	804	220
13	235,374	1,024	302
14	638,549	1,949	417
15	107,937	1,288	99
16	173,975	2,663	71
17	1,091,160	2,088	575
18	893,284	2,332	496
19	512,003	3,448	166
20	448,552	1,431	356
Mean	536,183	2,043	301
Min	80,973	673	71
Max	2,206,430	4,204	656
Sum	10,723,664	40,869	6,011
Std. Dev.	506,335	1,092	163
Variance	256,374,682,000	1191920	26,559
Skew	2	1	1
Excess	5	-1	0
Var. Coeff.	94	53	54
Obj. Count	8	—	—
Img. Area	19,091,308	—	—
Total Obj. Count	20	—	—
Total Img. Area	76,365,230	—	—

Table A.12. Particle Size Analysis Statistics for Sample # 2363

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	498,504	1,065	537
2	242,586	1,439	183
3	276,394	1,242	243
4	236,186	2,183	143
5	429,159	2,469	215
6	543,611	1,420	502
7	110,800	877	146
8	359,130	1,261	373
9	239,529	1,095	241
10	184,379	801	281
11	357,441	1,687	233
12	93,673	668	170
Mean	297,616	1,351	272
Min	93,673	668	143
Max	543,611	2,469	537
Sum	3,571,392	16,207	3,266
Std. Dev.	143,171	542	132
Variance	20,497,989,504	293,402	17,346
Skew	0	1	1
Excess	-1	0	0
Var. Coeff.	48	40	48
Obj. Count	12	—	—
Img. Area	19,091,308	—	—
Total Obj. Count	33	—	—
Total Img. Area	38,182,615	—	—

Table A.13. Particle Size Analysis Statistics for Sample # 2369

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	10,788	389	30
2	205,169	1,162	252
3	101,625	1,410	81
4	93,851	880	124
5	339,532	2,027	176
6	425,482	1,982	268
7	1,157	83	45
8	11,795	347	44
9	144,725	994	182
10	235,350	1,833	152
11	25,156	359	75
12	88,001	941	108
13	43,204	551	97
14	120,611	1,165	110
15	35,127	261	136
16	118,232	1,329	135
17	86,454	735	172
18	143,424	1,276	121
19	20,013	250	95
20	250,255	1,471	187
21	157,966	530	426
Mean	126,568	951	144
Min	1,157	83	30
Max	425,482	2,027	426
Sum	2,657,918	19,975	3,016
Std. Dev.	112,641	590	90
Variance	12,688,102,534	348,099	8,062
Skew	1	0	2
Excess	1	-1	4
Var. Coeff.	89	62	63
Obj. Count	21	—	—
Img. Area	19,091,308	—	—
Total Obj. Count	33	—	—
Total Img. Area	38,182,615	—	—

Table A.14. Particle Size Analysis Statistics for Sample # T3-1a

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	142,427	523	364
2	46,147	340	243
3	258, 589	708	505
4	203,049	672	427
5	379,026	986	530
6	275,267	716	593
7	270,194	783	497
8	253,255	689	509
9	95,054	402	335
10	154,059	561	418
11	27,421	207	180
12	17,593	209	195
13	86,955	386	298
14	96,563	423	283
15	201,314	625	441
16	42,315	310	202
17	10,101	148	95
18	11,213	137	112
19	65,894	320	269
20	94,311	398	346
21	369,832	851	785
22	26,030	210	174
23	8,776	126	97
24	1,240,400	1,700	1,055
25	335,305	838	687
26	383,128	883	698
27	187,736	627	466
28	355,909	786	678
Mean	201,352	556	410
Min	8,776	126	95
Max	1,240,400	1,700	1,055
Sum	5,637,863	15,565	11,482
Std. Dev.	240,034	339	231
Variance	57,616,500,370	115,173	53,302
Skew	3	1	1
Excess	13	3	1
Var. Coeff.	119	61	56
Obj. Count	28	—	—
Img. Area	19,091,307.52	—	—
Total Obj. Count	28	—	—
Total Img. Area	57,273,922.57	—	—

Table A.15. Particle Size Analysis Statistics for Sample # T3-1b

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	618,588	984	818
2	4,134	98	60
3	257,220	873	493
Mean	293,314	652	457
Min	4,134	98	60
Max	618,588	984	818
Sum	879,942	1,955	1,371
Std. Dev.	308,813	483	380
Variance	95,365,214,697	233,182	144,691
Skew	1	-2	0
Var. Coeff.	32,512,997	35,789	31,668
Obj. Count	3	—	—

Table A.16. Particle Size Analysis Statistics for Sample # T3-1c

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	571,708	954	867
2	755,779	1,416	1,023
3	608,736	1,119	771
4	284,476	834	558
5	664,337	1,372	900
6	165,977	629	479
7	1,876,168	2,610	1,385
8	636,772	1,160	963
9	32,220	280	174
10	35,091	279	201
11	1,137,143	1,455	1,092
12	538,023	1,161	729
13	145,457	656	397
14	196,143	807	436
Mean	546,288	1,052	712
Min	32,220	279	174
Max	1,876,168	2,610	1,385
Sum	7,648,030	14,731	9,975
Std. Dev.	496,941	588	354
Variance	246,950,088,862	346,313	125,029
Skew	2	1	0
Excess	3	3	-1
Var. Coeff.	91	56	50
Obj. Count	14	—	—
Img. Area	2,065,067	—	—

Table A.17. Particle Size Analysis Statistics for Sample # T3-3

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	215,732	583	523
2	15,238	170	141
3	90,927	439	298
4	8,636	138	78
5	4,340	89	63
6	2,351	64	53
7	4,006	86	69
8	3,401	76	67
9	6,501	106	89
10	168,024	627	375
11	2,416	64	55
12	4,243	110	56
13	3,460	94	59
14	296,814	760	538
15	168,648	601	417
16	206,653	588	504
17	39,255	267	212
18	830,846	1,429	1,038
19	140,541	552	344
20	5,705	95	98
21	209,325	561	524
22	334,094	875	533
23	142,545	491	419
24	356,291	815	621
25	123,341	431	399
26	257,780	755	520
27	4,723	90	74
28	2,503	70	47
29	2,460	63	62
30	1,400	41	41
31	1,699	46	46
32	751	30	30
33	870	33	33
34	1,400	41	41
35	2,445	56	56
36	1,243	40	40
37	472	24	24
38	315	19	19
Mean	96,352	301	227
Min	315	19	19
Max	830,846	1,429	1,038
Sum	3,661,394	11,422	8,607
Std. Dev.	163,243	332	241
Variance	26,648,164,956	110,420	58,276
Skew	3	1	1
Excess	10	2	2

Table A.17. Particle Size Analysis Statistics for Sample # T3-3

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
Var. Coeff.	169	111	107
Obj. Count	38	—	—
Img. Area	2,065,067	—	—
Total Obj. Count	2,394	—	—
Total Img. Area	27,380,421	—	—

Table A.18. Particle Size Analysis Statistics for Sample # T3-4

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	10,212	630	17
2	7,488	333	27
3	18,494	503	47
4	37,108	895	42
5	16,430	651	29
6	28,884	840	48
7	13,430	486	29
8	20,914	667	37
9	28,289	976	33
10	10,680	490	26
11	7,544	325	31
12	21,606	806	40
13	8,503	393	24
14	6,839	247	29
15	16,178	584	42
16	7,185	336	27
17	36,720	1,153	54
18	49,274	1,393	41
19	2,300	118	25
20	28,847	1,025	33
21	21,238	510	51
22	49,881	1,285	52
23	4,941	288	22
24	9,780	540	22
25	20,687	775	39
26	11,063	345	53
27	11,048	454	28
28	5,905	312	20
29	27,472	986	36
30	3,404	178	20
31	7,715	272	30
32	4,598	213	27
33	8,077	300	29
34	5,385	271	20
35	22,605	612	48
36	8,426	219	43
37	5,126	234	26

Table A.18. Particle Size Analysis Statistics for Sample # T3-4

Crystal No.	Area, μm^2	Max Length, μm	Max Width, μm
38	5,981	280	23
39	39,101	1,009	56
40	18,161	561	40
41	3,612	156	24
42	16,470	622	39
43	2,954	210	16
44	2,175	108	24
45	69,947	1,240	76
46	5,120	211	31
47	10,356	676	18
48	14,546	690	25
49	40,166	1,011	55
50	11,748	413	31
51	8,715	300	37
52	7,709	380	22
53	17,839	487	39
54	15,568	695	24
55	12,295	576	23
56	11,245	345	38
57	4,506	186	28
58	7,273	295	26
59	35,916	845	47
60	6,726	184	40
61	17,001	647	27
62	26,482	703	47
63	50,799	1,239	58
64	21,121	672	47
65	6,441	238	38
66	2,792	206	16
67	6,022	272	39
68	23,072	1,272	28
69	15,243	448	50
70	13,413	351	43
71	21,379	969	27
72	68,440	2,486	31
73	53,959	2,025	37
74	36,668	824	62
75	45,500	954	51
Mean	18,410	606	35
Min	2,175	108	16
Max	69,947	2,486	76
Sum	1,380,736	45,432	2,632
Std. Dev.	15,622	428	12
Variance	244,054,513	183,254	154
Skew	1	2	1
Excess	2	5	0
Var. Coeff.	85	71	35
Obj. Count	75	—	—

Table A.18. Particle Size Analysis Statistics for Sample # T3-4

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
Img. Area	19,091,308	—	—
Total Obj. Count	75	—	—
Total Img. Area	19,091,308	—	—

Table A.19. Particle Size Analysis Statistics for Sample # T3-5

Crystal No.	Area, µm^2	Max Length, µm	Max Width, µm
1	210,189	599	518
2	93,997	439	298
3	6,794	125	77
4	14,733	149	149
5	8,256	141	83
6	169,265	624	370
7	144,364	577	348
8	201,878	563	504
9	174,709	627	425
10	310,782	774	553
11	43,544	296	224
12	819,871	1,421	1,044
13	202,143	589	494
14	335,397	899	523
15	140,226	441	452
16	352,606	821	606
17	258,058	749	525
18	5,156	98	67
19	4,440	123	44
20	1,677	48	44
21	1,628	48	43
22	2,805	78	46
23	4,570	75	75
24	4,043	72	72
25	2,445	56	56
26	2,658	57	57
27	1,243	40	40
28	4,297	73	73
29	3,287	64	64
30	3,556	67	67
31	654	29	29
32	1,116	37	37
33	751	30	30

Table A.19. Particle Size Analysis Statistics for Sample # T3-5

Crystal No.	Area, μm^2	Max Length, μm	Max Width, μm
34	751	30	30
35	870	33	33
36	654	29	29
37	6,975	93	93
38	6,775	113	86
39	119,515	420	372
40	2,658	57	57
41	2,658	57	57
42	3,556	67	67
Mean	87,513	279	211
Min	654	29	29
Max	819,871	1,421	1,044
Sum	3,675,548	11,728	8,862
Std. Dev.	156,301	325	234
Variance	24,429,993,253	105,867	54,708
Skew	3	2	2
Excess	11	2	2
Var. Coeff.	179	117	111
Obj. Count	42	—	—
Img. Area	19,091,308	—	—
Total Obj. Count	2,394	—	—
Total Img. Area	27,380,421	—	—

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