**Pacific Northwest
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Mechanism of Phosphorus Removal from Hanford Tank Sludge by Caustic Leaching

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Test specification: 24590-PTF-TSP-RT-06-003, Rev. 1

Test Plan: TP-RPP-WTP-467, Rev. 1

Test exceptions: None

R&T focus area: Pretreatment

Test scoping statement(s): None

Completeness of Testing

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

Approved:

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Gordon H. Beeman, Manager
RPP-WTP Support Program

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Date

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Acronyms

ASO	Analytical Service Operations
DOE	U.S. Department of Energy
FTIR	Fourier Transform Infrared
HLW	high-level waste
IC	ion chromatrography
ICDD	International Centre for Diffraction Data
ICP	inductively coupled plasma
LAW	low-activity waste
M&TE	measuring and test equipment
NQA	Nuclear Quality Assurance
OES	optical emission spectroscopy
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
QAM	Quality Assurance Manual
QAP	Quality Assurance Plan
QARD	Quality Assurance Requirements and Descriptions
QC	quality control
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project
TP	test plan
WTP	Waste Treatment and Immobilization Plant
WTPSP	Waste Treatment Plant Support Program
XRD	X-ray diffraction

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Testing Summary

Two experiments were conducted to explore the mechanism by which phosphorus is removed from Hanford tank sludge by caustic leaching. In the first experiment, a series of phosphate salts were treated with 3 M NaOH under conditions prototypic of the actual leaching process to be performed in the Waste Treatment and Immobilization Plant (WTP). The phosphates used were aluminum phosphate, bismuth phosphate, chromium(III) phosphate, and β-tri-calcium phosphate; all of these phases have previously been determined to exist in Hanford tank sludge. The leachate solution was sampled at selected time intervals and analyzed for the specific metal ion involved (Al, Bi, Ca, or Cr) and for P (total and as phosphate). The solids remaining after completion of the caustic leaching step were analyzed to determine the reaction product. In the second experiment, the dependence of P removal from bismuth phosphate was examined as a function of the hydroxide ion concentration. It was anticipated that a plot of log[phosphate] versus log[hydroxide] would provide insight into the phosphorus-removal mechanism.

This report describes the test activities outlined in Section 6.3.2.1, Preliminary Investigation of Phosphate Dissolution, in Test Plan TP-RPP-WTP-467, Rev.1. The objectives, success criteria, and test conditions of Section 6.3.2.1 are summarized here.

Objectives

Table S.1 describes the test objectives and whether the objectives were met.

Table S.1. Description of Test Objectives

Test Objective	Objective Met (Y/N)	Discussion
Determine the mechanism(s) involved in removing phosphorus from phosphate phases prototypic of those in Hanford tank sludges by caustic leaching.	Y	The key features of the reactions between aluminum phosphate, bismuth phosphate, chromium(III) phosphate, and β-tri-calcium phosphate with aqueous sodium hydroxide were elucidated. Whereas solublization of P from $AlPO_4$ and $CrPO_4 \cdot 4H_2O$ can be explained in terms of simple metathesis reactions, the behavior of $BiPO_4$ is more complex, with the formation of a bismuth oxide/phosphate phase. The ability to leach phosphorus from $Ca_3(PO_4)_2$ is limited because of the formation of hydroxyapatite.

Test Exceptions

None.

Results and Performance Against Success Criteria

Table S.2 describes the success criterion and explains how the criterion was met or not.

Table S.2. Success Criterion

Success Criterion	Explain How the Tests Did or Did Not Meet the Success Criterion
Determine reaction products from caustic leaching of aluminum phosphate, bismuth phosphate, chromium(III) phosphate, and β-tri-calcium phosphate	The product from the reaction of $BiPO_4$ with NaOH was identified to be a sillenite phase of the type $Bi_{12}P_1O_{20}$ (the best match to the X-ray diffraction (XRD) pattern was to the phase $Bi_{9.872}Bi_{1.223}P_{0.853}O_{20}$). The product from the reaction of $CrPO_4 \cdot 4H_2O$ with NaOH was hydrous chromium hydroxide. The product from the reaction of $Ca_3(PO_4)_2$ with NaOH was hydroxyapatite. In the case of $AlPO_4$, very little residual solid was present after reaction with NaOH, and this residue was most probably due to an impurity in the starting $AlPO_4$. Essentially all of the Al and P dissolved into the NaOH solution.
Determine the influence of hydroxide concentration in the removal of P from $BiPO_4$ to determine if the P removal mechanism was a simple metathesis reaction.	The plot of log[P] versus log[OH] for reaction of $BiPO_4$ did not display a slope of 3, indicating that the mechanism for P removal from $BiPO_4$ is not a simple metathesis reaction. This is consistent with the reaction product being identified to be a sillenite phase rather than bismuth hydroxide.

Quality Requirements

Pacific Northwest National Laboratory (PNNL) implemented the River Protection Project (RPP)-WTP quality requirements by performing work in accordance with the RPP-WTP Support Program Quality Assurance Plan (RPP-WTP-QA-001, QAP). Work was performed to the quality requirements of NQA-1-1989 Part I, *Basic and Supplementary Requirements*, NQA-2a-1990, Part 2.7, and DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions (QARD)*. These quality requirements were implemented through the RPP-WTP Support Program Quality Assurance Manual (RPP-WTP-QA-003, QAM). The requirements of DOE/RW-0333P, Rev 13, QARD were not required for this work.

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

R&T Test Conditions

Table S.3 lists the research and technology test conditions and whether they were followed.

Table S.3. List of R&T Test Conditions and Whether they Were Followed

List R&T Test Conditions	Were Test Conditions Followed?
As described in Section 6.3.2.1 of Test Plan TP-RPP-WTP-467, Rev.1: *Experiment 1:* Leaching of $AlPO_4$, $BiPO_4$, $Ca_3(PO_4)_2$, and $CrPO_4$ in 3 M NaOH at 90°C for up to 48 h.[a] *Experiment 2:* Leaching of $BiPO_4$ with a sub-stoichiometric (four or five different molar ratios of OH^- to Bi will be tested) amount of NaOH at 60°C. Leaching will be allowed to progress to equilibrium as determined by Raman spectroscopy.	Yes. *Experiment 1:* Samples of $AlPO_4$, $BiPO_4$, $Ca_3(PO_4)_2$, and $CrPO_4$ were leached with 3 M NaOH at 90°C. The leaching experiments for $AlPO_4$, $BiPO_4$, and $CrPO_4 \cdot 4H_2O$ were continued to 24 h, but at some point between 8 and 24 hours, the temperature-control apparatus failed; therefore, the total length of heating could not be precisely determined. However, the ICP-OES data indicated that the reactions for $AlPO_4$ and $BiPO_4$ were complete well within the 8-h heating period and that the reaction for $CrPO_4 \cdot 4H_2O$ was 96% complete after 8 h (with no additional changes between the 8-h and 24-h samples). The leaching duration was 48 h for the $Ca_3(PO_4)_2$ experiment. *Experiment 2:* $BiPO_4$ was leached in NaOH at 60°C with OH^-/Bi ratios of 0.5, 1.0, 1.5, 2.0, and 2.5. Equilibrium was verified at 93 h of leaching using Raman spectroscopy.

(a) Previous caustic leaching tests performed with actual Hanford tank sludges suggested phosphate removal to be fairly rapid at 100°C. A slightly lower temperature (90°C) was chosen for these experiments to slow down the reactions so that at least a qualitative assessment of the reaction kinetics could be performed (although the focus of this work was on determining the final reaction products, rather than on assessing the kinetics). Similarly for Experiment 2, 60°C was used so as to maintain a distribution between product species and reactants at equilibrium (i.e., to avoid complete consumption of the reactants).

Simulant Use

This work was conducted using pure phosphate compounds that were previously identified to be present in Hanford tank sludges. Using the pure phases allowed the reaction products to be clearly identified, which cannot easily be done with actual waste samples. Qualitative comparisons to results obtained in upcoming experiments with actual tank-waste samples will be made, as appropriate, in the reports for the actual waste testing.

Discrepancies and Follow-on Tests

It was originally planned to run the 3 M NaOH/90°C leaching experiments with aluminum phosphate, bismuth phosphate, chromium(III) phosphate, and β-tri-calcium phosphate for 48 h. However, during leaching of $AlPO_4$, $BiPO_4$, and $CrPO_4 \cdot 4H_2O$, the temperature controller failed sometime between 8 and 24 h; therefore, the total length of heating could not be precisely determined. This was deemed to have no impact on the results because the ICP-OES and ion chromatography (IC) data indicated that the reactions for $AlPO_4$ and $BiPO_4$ were complete well within the 8-h heating period and that the reaction for $CrPO_4 \cdot 4H_2O$ was 96% complete after 8 h (with no additional changes between the 8-h and 24-h samples).

Follow-on testing should be considered if analysis of the actual waste samples reveals significant amounts of phosphorus-containing phases that were not considered in this work.

Acknowledgements

1.0   Introduction

The Hanford Waste Treatment and Immobilization Plant (WTP) is being designed and constructed to immobilize the large volumes of radioactive wastes that are stored in underground tanks at the Hanford Site in southeastern Washington state. These wastes were generated during past plutonium production and other operations. In the WTP, the wastes will be partitioned into low-activity and high-level fractions. Both fractions will be immobilized in borosilicate glass waste forms suitable for final disposition. The low-activity waste (LAW) fraction will be disposed of by shallow burial onsite, while the high-level waste (HLW) will be disposed of in a geologic repository (Stewart et al. 1998).

Caustic leaching is the baseline method for pretreating the water-insoluble fraction of the waste (generally referred to as the *sludge*). Caustic leaching is primarily designed to remove a large fraction of the aluminum, based on the amphoteric nature of this element (Lumetta et al. 1998). If aluminum is not removed, the minimum amount of HLW glass produced in immobilizing this fraction of the waste will be defined by this element. Caustic leaching has also been shown to remove some Cr—another problematic waste component for producing the HLW glass form—from the HLW solids, but this process is relatively slow. In some cases, an oxidative leaching method will be used to separate Cr from the HLW solids by converting it to the soluble CrO_4^{2-} form (Lumetta and Rapko 1999). Phosphorus is another component that is removed from the HLW solids by caustic leaching. Like Cr, there is relatively low tolerance for P in the HLW melter feed, so its removal is important with respect to reducing the HLW volume. Previous experiments conducted with actual tank-waste samples have indicated that caustic leaching is generally effective at removing P from the HLW solids (Lumetta et al. 1998 and 2003). However, little effort has been directed at understanding the mechanism of P removal by caustic leaching.

This report presents the results of experiments conducted to examine the P-removal mechanism using pure phosphate phases that correspond to phases identified by microscopic examination of actual tank samples (Lumetta et al. 2003). The compounds examined were aluminum phosphate, bismuth phosphate, chromium(III) phosphate, and β-tri-calcium phosphate. Two experiments were performed. First, the phosphate salts were treated with 3 M NaOH under conditions prototypic of the actual leaching process to be performed. The leachate solution was sampled at selected time intervals and analyzed for the specific metal ion involved (Al, Bi, Ca, or Cr) and for P (total and as phosphate). The solids remaining after completion of the caustic leaching step were analyzed to determine the reaction product.

In the second experiment, the dependence of P removal from bismuth phosphate was examined as a function of the hydroxide ion concentration. This was done to probe the hypothesis that the P-removal mechanism is one of metathesis as described by the equation:

$$BiPO_4(s) + 3NaOH(aq) \rightarrow Bi(OH)_3(s) + Na_3PO_4(aq) \tag{1.1}$$
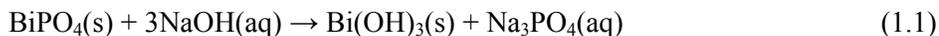
Were this reaction responsible for P removal from the $BiPO_4$ phase, a plot of log[phosphate] versus log[hydroxide] would be linear with a slope of 3. This turned out not to be the case, as will be discussed in Section 3.

2.0   Experimental Section

This section provides the experimental details for the work described in this report. Included are descriptions of the general materials and methods used and specifics of the experiments performed.

2.1 General Materials and Methods

Aluminum phosphate, bismuth phosphate, bismuth oxide, and chromium(III) phosphate tetrahydrate were obtained from Alfa Aesar (Ward Hill, Massachusetts). β-tri-calcium phosphate was procured from Fluka Chemika (Steinheim, Switzerland) and hydroxyapatite from Calbiochem (La Jolla, California). All of these phosphate salts were used as-received. The NaOH solution used (3.11 M) was standardized by titration with HCl before use. Fourier-transform infrared (FTIR) spectra were recorded as KBr pellets on a Nicolet 750 FTIR spectrometer. Raman spectra were recorded using an InPhotonics Model RS2000-3b-670 Raman spectrometer (Norwood, Massachusetts) equipped with a fiber-optic probe with a 670-nm excitation laser. To measure the Raman spectra, the probe was placed in an inverted vertical position, and an 8-mL glass vial containing the sample was placed directly on top of the probe. The contribution from the glass vial was subtracted from the spectra using GRAMS/AI (v. 7.02) software (Thermo Galactic, Salem, NH).

Samples for powder X-ray diffraction (XRD) measurements were prepared by slurrying the sample with an amyl acetate-based, low X-ray background, glue, placing the slurry on a glass slide and drying the prepared sample before analysis. The XRD measurement was performed on a Sintag PAD V X-ray Powder diffractometer using a Cu-Kα radiation and a solid-state detector. Measurement parameters include operation at 2-KW power, 0.02 degrees/step, and a 20 sec/step over a 2θ range of 5 to 65 degrees. The diffraction patterns were compared with known 2-theta/intensity data from the International Centre for Diffraction Data (ICDD) database 49 (through 1999) to identify crystalline phases. This measurement was performed according to the technical procedure PNL-ALO-268, Solids Analysis, X-ray Diffraction.

The free hydroxide concentrations were determined by titration with standard HCl using a Brinkman 636 auto-titrator. Inductively coupled plasma optical emission spectroscopy (ICP-OES) and ion chromatography analyses were performed by Southwest Research Institute (San Antonio, Texas).

2.2 Leaching with 3 M NaOH

The four phosphate salts were placed in separate 60-mL polypropylene bottles. The quantities used were 0.637 g $AlPO_4$ (5.22 mmole), 1.577 g $BiPO_4$ (5.19 mmole), 1.138 g $CrPO_4 \cdot 4H_2O$ (5.20 mmole), and 0.810 g $Ca_3(PO_4)_2$ (2.61 mmole; 5.22 mmole PO_4^{2-}). The NaOH solution (50 mL of 3.11 M) was added to each bottle, giving an OH^-/PO_4^{3-} molar ratio of 30. The bottles were placed in an aluminum heating block set at 90°C and were shaken using an orbital shaker. Samples were withdrawn for analysis at 1, 2, 4, and 8 h. In the case of $Ca_3(PO_4)_2$, the experiment was extended to 48 h with additional samples being taken at 25.5 h and 48 h. The leaching experiments for $AlPO_4$, $BiPO_4$, and $CrPO_4 \cdot 4H_2O$ were continued to 24 h, but at some point between 8 and 24 hours, the temperature-control apparatus failed; therefore, the total length of heating could not be precisely determined. However, the ICP-OES data indicated that the reactions for $AlPO_4$ and $BiPO_4$ were complete well within the 8-h heating period and that the reaction for $CrPO_4 \cdot 4H_2O$ was 96% complete after 8 h (with no additional changes between the 8-h and 24-h samples). Each sampling event involved withdrawing 0.7 mL of the slurry and filtering the sample through a 0.45-μm nylon syringe filter that had been pre-heated at ~100°C. Aliquots of the filtered solution were taken for ICP-OES, IC, and free hydroxide analysis.

At the conclusion of the 3 M NaOH leaching experiment, the residual solids were washed with three successive 5-mL portions of 0.01 M NaOH. After mixing with the 0.01 M NaOH solution, the mixtures

were centrifuged and the liquid decanted. The washed solids were transferred into 8-mL glass vials using several small portions of deionized water. The solids were centrifuged, and the water was removed. The solids were then dried in a vacuum oven at ~50°C over Drierite. The residual solids were characterized by FTIR, Raman, and XRD.

2.3 Leaching of Bismuth Phosphate with Variable NaOH

Bismuth phosphate and NaOH were mixed together in 60-mL polypropylene bottles in the amounts indicated in Table 2.1, and the mixtures were diluted to 30 mL with deionized water. The bottles were placed in an aluminum heating block set at 60°C and were shaken using an orbital shaker. At selected time intervals (3, 20, 44, 71, and 93 h), mixing was stopped, and the solids were allowed to settle. A 2-mL portion of the liquid phase was placed in an 8-mL glass vial, and the Raman spectrum was recorded through the bottom of the glass vial. Immediately after taking the Raman measurement, the solution was returned to the reaction bottle, and shaking was resumed. After 93 h of mixing, the reaction bottles were allowed to cool to ambient temperature. Approximately 15 mL of solution from each bottle was filtered through a 0.45-µm nylon syringe filter. Aliquots of the clarified liquids were taken for ICP-OES, IC, and free hydroxide analysis.

Table 2.1. Amounts of Bismuth Phosphate and Sodium Hydroxide Used

Target OH⁻/Bi Ratio (mol/mol)	Mass $BiPO_4$, g	Vol. 3.11 M NaOH, mL
0.5	0.500	0.26
1.0	0.504	0.53
1.5	0.506	0.79
2.0	0.506	1.00
2.5	0.502	1.32

2.4 Quality Assurance

2.4.1 Quality Assurance and Quality Control

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

2.4.2 Application of RPP-WTP Quality Assurance Requirements

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

PNNL implemented the RPP-WTP quality requirements by performing work in accordance with the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Plan* (RPP-WTP-QA-001, QAP). Work was performed to the quality requirements of NQA-1-1989 Part I,

Basic and Supplementary Requirements, NQA-2a-1990, Part 2.7, and DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions (QARD)*. These quality requirements are implemented through the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Manual* (RPP-WTP-QA-003, QAM).

2.4.3 Conduct of Experimental and Analytical Work

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

Reported hydroxide analyses were performed by RPL-ASO according to procedure RPG-CMC-228, Rev 1. No QC issues were associated with these data.

Solution metals concentrations were determined by ICP-OES at Southwest Research institute according to procedure TAP01-0406-130, Rev 5. No QC issues were associated with these data.

Solution anion analyses were determined by ion chromatography (IC) at Southwest Research institute according to procedure TAP01-0406-042, Rev 4. No QC issues were associated with these data.

Additional M&TE that were used included balances, thermocouples, and a temperature controller. The thermocouples and temperature controller were calibrated by the PNNL Instrument Calibration Facility. Balances are calibrated annually by a certified contractor, QC Services, Portland, Oregon. A balance performance check was conducted each day the balance was used.

2.4.4 Internal Data Verification and Validation

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

3.0   Results and Discussion

This section details the results of the phosphorus-removal experiments. The two experiments conducted are discussed separately, starting with the leaching of the individual phosphate phases in 3 M NaOH and then a discussion of the reaction of bismuth phosphate at different NaOH concentrations.

3.1 Leaching with 3 M NaOH

3.1.1   Aluminum Phosphate

After leaching with 3.11 M NaOH at 90°C for 1 h, visual inspection indicated that most of the $AlPO_4$ had dissolved. Analysis of the leachate for Al and P by ICP-OES confirmed this to be true. If all of the $AlPO_4$ dissolved, the concentrations of Al and P in the leachate solution would have been 0.104 M. After leaching for 1 h, the Al and P concentrations were 0.0919 and 0.103 M, respectively. Thus, at this point in the experiment, essentially all of the P and 88% of the Al were in solution. The complete transfer of P into solution within the first hour of leaching was confirmed by the IC analysis, which indicated the P concentration (as PO_4^{3-}) to be 0.106 M. The incomplete Al dissolution after 1 h is perhaps due to an initial conversion of the Al to solid gibbsite, which then subsequently dissolves in the NaOH solution. After 2 h of leaching, the Al concentration was 0.103 M, suggesting essentially complete dissolution.

Only a very small amount (0.003 g) of residual solids remained after the leaching of $AlPO_4$. Both the FTIR and Raman spectra indicated that the residual solids were significantly different from the starting $AlPO_4$. The FTIR spectrum of $AlPO_4$ displayed a very strong v_3 stretching band for PO_4^{3-} at 1128 cm^{-1}, although this band was clearly split into multiple bands. In contrast, the FTIR spectrum of the residual Al solids was essentially featureless in this area of the spectrum. The Raman spectrum of $AlPO_4$ was largely featureless in the range 400 to 1500 cm^{-1}, whereas the residual Al solids displayed two sharp bands at 482 and 512 cm^{-1} in the Raman spectrum. Because of the limited amount of material available, the XRD analysis of the residual Al solids was inconclusive. The XRD pattern suggested the presence of $LiAlSi_2O_6$ and $AlPO_4$ (Berlinite), although the pattern is very weak. Therefore, the exact identity of the residual Al solids is not known, but it is most likely attributable to an impurity in the $AlPO_4$ starting material and, perhaps, a small amount of un-reacted $AlPO_4$.

3.1.2   Bismuth Phosphate

The appearance of the solids changed rapidly during the leaching of $BiPO_4$ with 3.11 M NaOH at 90°C. Within 10 min, the color of the solids changed from white to yellow, and they remained yellow throughout the course of the experiment. The ICP-OES and IC analyses indicated rapid removal of P from $BiPO_4$ under the leaching conditions investigated. After 1 h of leaching, the total P concentration (by ICP-OES) was 0.098 M, and the PO_4^{2-} concentration (by IC) was 0.114 M, giving a mean value of 0.106 mol P/L. Since the expected P concentration upon completely removing the P from the starting $BiPO_4$ was 0.104 M, it can be concluded that complete removal of P from $BiPO_4$ occurred within 1 h of leaching with 3.11 M NaOH at 90°C.

XRD analysis of the starting material verified it to be crystalline $BiPO_4$. The yellow product from the reaction with NaOH was also highly crystalline, and the XRD analysis indicated it to be one of the compounds in the family of sillenite phases that have the general formula $Bi_{24}M_2O_{40}$. In this case, the best fit to the XRD data was for the sillenite with the empirical formula $Bi^{3+}_{9.872}Bi^{5+}_{1.223}P_{0.853}O_{20}$ (Wignacourt et al. 1991); however, other sillenite formulations also reasonably fit the XRD data, including $Bi_{24}P_{1.86}O_{40}$. Although sillenite phases are generally produced in high-temperature solid-state syntheses, the latter phase has been reported to form from alkaline aqueous solutions under conditions not unlike those used here (Horowitz et al. 1989). The P non-stoichiometry in the phase $Bi_{24}P_{1.86}O_{40}$ could be

explained in terms of either 20% vacancies on the P sites in the sillenite structure or by 25% incorporation of Na^+ ions into the structure.

Vibrational spectroscopy was also consistent with the formation of a sillenite phase during leaching of $BiPO_4$ with 3.11 M NaOH at 90°C. Examination of the residual Bi solids by vibrational spectroscopy indicated significant differences from the starting $BiPO_4$. The FTIR spectrum (Figure 3.1a) of $BiPO_4$ displayed a series of four well-resolved ν_3 stretching frequencies for PO_4^{3-} at 924, 955, 1002, and 1075 cm^{-1}, consistent with the spectrum reported in the literature for $BiPO_4$ with the monazite-type structure (Romero et al. 1994). On the other hand, the FTIR spectrum of the residual Bi solids (Figure 3.1b) displayed a band at 942 cm^{-1} that can be attributed to $\nu_3(PO_4^{3-})$ of the sillenite phase. The FTIR spectral pattern observed is very similar to that reported for $Bi_{12}Fe_{0.5}P_{0.5}O_{20}$ (Devalette et al. 1982), except that the $\nu_3(PO_4^{3-})$ band is shifted to lower energy (it is at 965 cm^{-1} for the Fe-substituted sillenite). The differences between $BiPO_4$ and the residual Bi solids were also quite pronounced in the Raman spectra (Figure 3.2). The $\nu_1(PO_4^{3-})$ bands at 967 and 1038 cm^{-1} in the Raman spectrum of $BiPO_4$ were completely absent in the spectrum of the Bi residual, and these were replaced by a very weak band at 901 cm^{-1}. Figure 3.2 also compares the Raman spectrum of the residual Bi solids with that of $Bi(OH)_3$, which was prepared by adding a solution of $Bi(NO_3)_3$ in 1 M HNO_3 to an excess of concentrated aqueous ammonium hydroxide. It is clear from comparing Figure 3.2b and Figure 3.2c that the product of the leaching experiment was not the hydroxide; this conclusion is also supported by the fact that the residual Bi solids were yellow compared to the white color of bismuth hydroxide. Because of the yellow coloration of the Bi residual solids, it was hypothesized that the product is Bi_2O_3, which is also yellow. However, this hypothesis was not supported by comparing the Raman spectrum of the residual solid to Bi_2O_3 (obtained from Alfa Aesar; Figure 3.3d). The Raman spectral pattern is also very similar to that reported for $Bi_{12}Fe_{0.5}P_{0.5}O_{20}$ (Devalette et al. 1982), which displayed a weak $\nu_1(PO_4^{3-})$ at 905 cm^{-1}.

It can be concluded that the mechanism of phosphate removal from $BiPO_4$ by caustic leaching is more complex than the simple metathesis reaction (Equation 1.1) originally hypothesized. The reaction is best described as:

$$12BiPO_4(s) + 33NaOH(aq) + 0.25O_2 \rightarrow Bi^{3+}_{11}Bi^{+5}PO_{20}(s) + 11Na_3PO_4(aq) + 16.5H_2O \qquad (3.1)$$

Note that this mechanism implies that 100% removal of the P from the $BiPO_4$ phase should not occur, with roughly 8% remaining in the sillenite phase. This small difference between the expected phosphorus concentration in solution and the values measured by ICP-OES and IC could not be discerned within the experimental uncertainty of the measurements.

3.1.3   Calcium Phosphate

The leaching of $Ca_3(PO_4)_2$ with 3.11 M NaOH at 90°C showed several interesting features. The ICP-OES analysis of the leachate solution indicated relatively little transfer of P into the solution phase, but there was clearly some transfer of P into solution, and this increased with increasing leaching time (Figure 3.3). Interestingly, there were significant differences between the total P concentrations determined by ICP-OES and the P concentrations determined as PO_4^{3-} ion by IC analysis (Table 3.1). During the first 8 h of leaching, only ~50% of the P was present in solution as the PO_4^{3-} ion; however, after 48 h of leaching, the total P concentration was essentially the same as the PO_4^{3-} concentration. Thus, it appears that initially a significant fraction of the P is leached from $Ca_3(PO_4)_2$ in some form other than PO_4^{3-}, but eventually, the P in solution is converted to PO_4^{3-}. Throughout the course of the experiment, Ca was found to be below the ICP-OES detection limit ($< 6.1 \times 10^{-4}$ M).
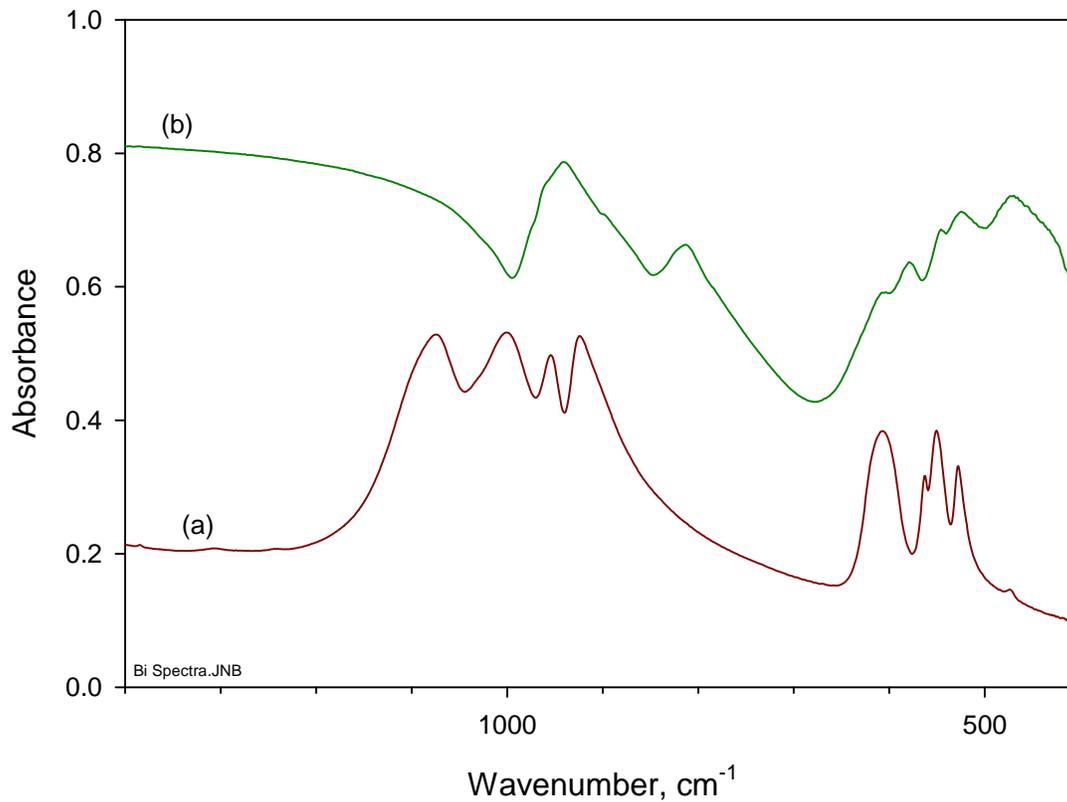
Figure 3.1. FTIR Spectra of a) BiPO$_4$ and b) the Residual Solids Remaining After Leaching BiPO$_4$ in 3.11 M NaOH at 90°C

Table 3.1. Comparison of Phosphorus Concentrations Determined by ICP-OES and by IC During Leaching of Ca$_3$(PO$_4$)$_2$ with 3.11 M NaOH at 90 °C

Time, h	*Total P by ICP-OES, M*	*P as PO$_4^{3-}$ by IC, M*	*PO$_4^{3-}$/Total P, mol/mol*
1	1.96×10^{-3}	9.28×10^{-4}	0.47
2	2.30×10^{-3}	1.18×10^{-3}	0.51
4	3.19×10^{-3}	1.26×10^{-3}	0.39
8	3.95×10^{-3}	2.14×10^{-3}	0.54
24	1.04×10^{-2}	8.69×10^{-3}	0.84
48	1.66×10^{-2}	1.79×10^{-3}	1.08

Bi Spectra.JNB

(d)

(c)

(b)

(a)

Wavenumber, cm^{-1}

1000

500
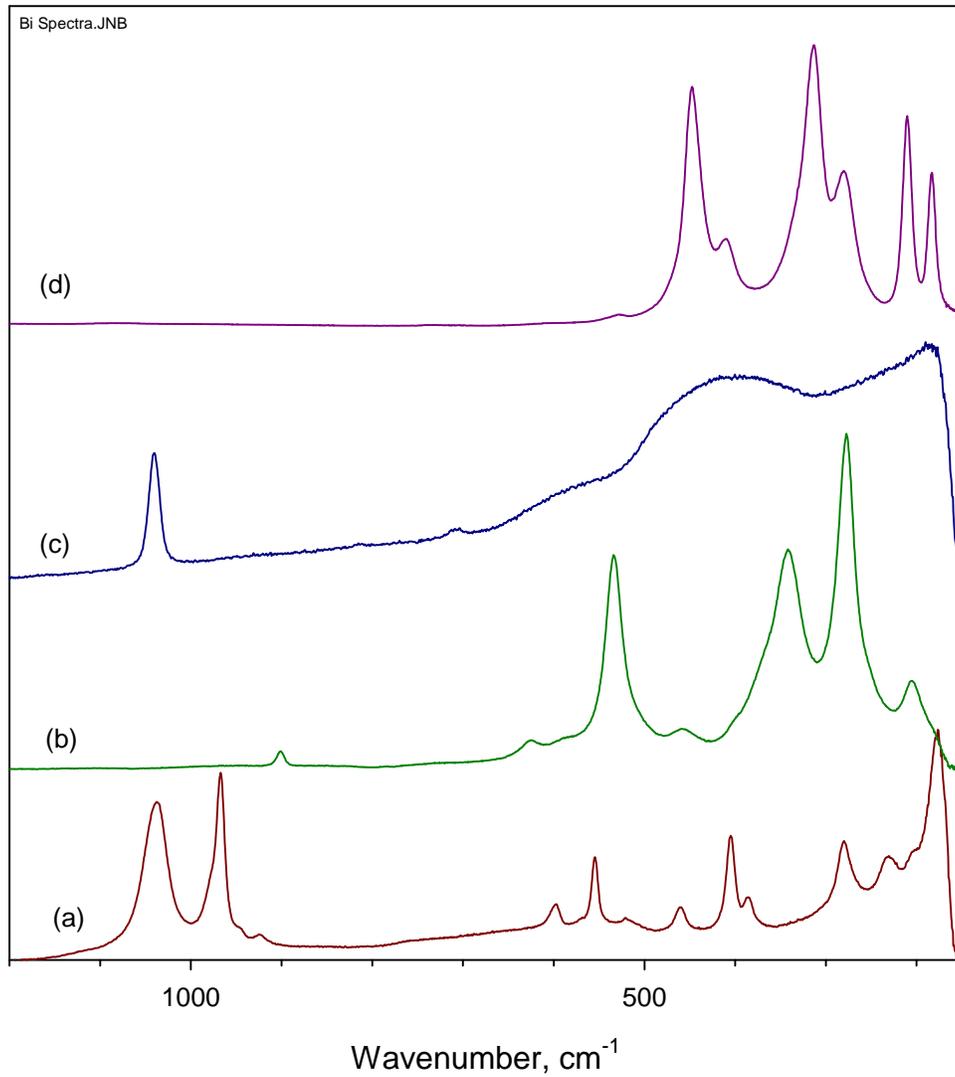
Figure 3.2. Raman Spectra of a) BiPO$_4$, b) the Residual Solids Remaining After Leaching BiPO$_4$ in 3.11 M NaOH at 90 °C, c) Bismuth Hydroxide, and d) Bi$_2$O$_3$

3.4
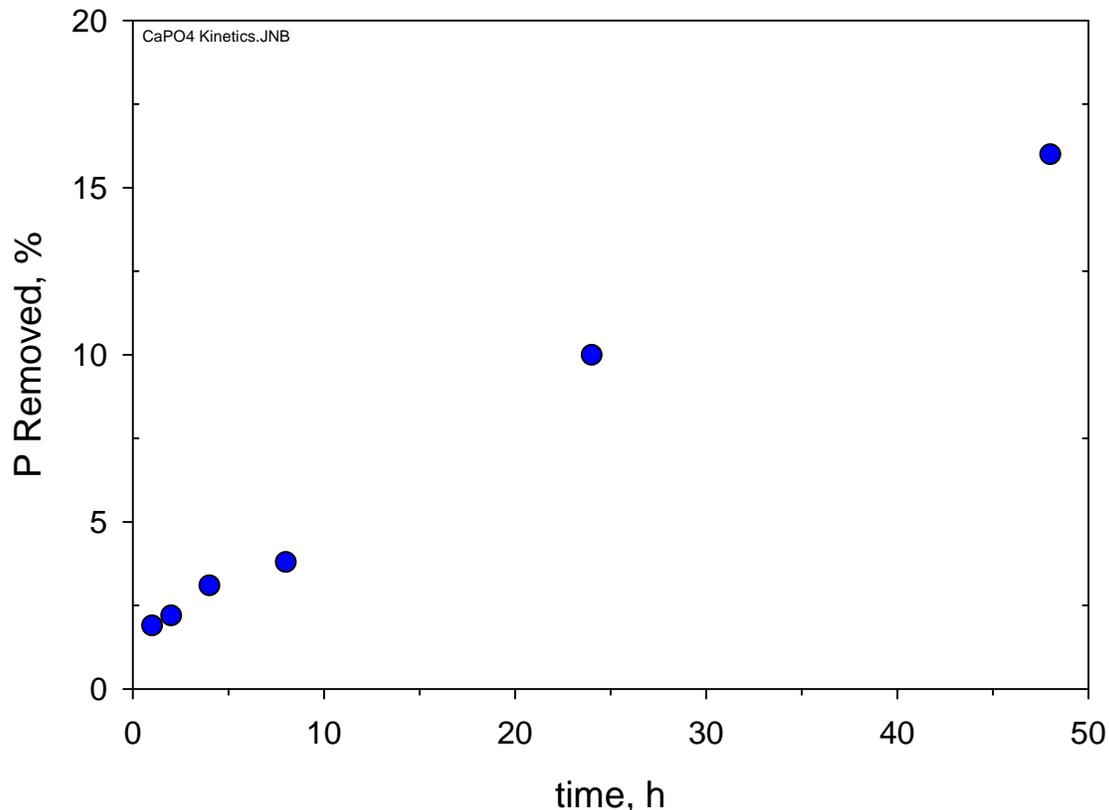
Figure 3.3.   Phosphorus Removal (as % removed) as a Function of Time During Leaching of Ca$_3$(PO$_4$)$_2$ in 3.11 M NaOH at 90 °C

The Raman spectrum of the Ca solids remaining after leaching with 3.11 M NaOH for 48 h clearly indicated that the β-tri-calcium phosphate was converted to hydroxyapatite during the leaching process. Figure 3.4 compares the Raman spectra of Ca$_3$(PO$_4$)$_2$, the residual Ca solids, and commercially procured Ca$_5$(PO$_4$)$_3$(OH). The Raman spectrum of the Ca$_3$(PO$_4$)$_2$ used in this work agreed very well with that reported in the literature, with the ν$_1$ phosphate stretch split into two bands at 948 and 971 cm^{-1}, compared to the literature values of 949 and 970 cm^{-1} (de Aza et al. 1997a). The Raman spectrum of the Ca residual was nearly identical to that of hydroxyapatite, although there was a minor difference in the band positions measured—a single ν$_1$ phosphate band was observed at 963 cm^{-1} for the residual Ca solids compared to 960 cm^{-1} for hydroxyapatite. These results also agree with the literature data for polycrystalline hydroxyapatite (ν$_1$ at 962 cm^{-1}) (de Aza et al. 1997b). The FTIR spectra (Figure 3.5) also indicated the product of the reaction to be primarily hydroxyapatite. The FTIR spectrum of Ca$_3$(PO$_4$)$_2$ displayed a complex series of phosphate bands in the region 925 to 1230 cm^{-1}, consistent with spectra reported in the literature (Kutty 1970). In contrast, the residual Ca solids displayed a very strong band at 1036 cm^{-1}, with surrounding weaker bands at 962 and 1093 cm^{-1}. The FTIR spectral pattern for the Ca residual was similar to that for hydroxyapatite itself and agrees with literature reports (Zhang et al. 2005). The appearance of bands at 1417 and 1457 cm^{-1} in the FTIR spectrum of the Ca residual suggests that there might be some other, as yet identified, product present (these bands were not evident in the hydroxyapatite spectrum). XRD examination of the residual Ca solid also indicated the reaction product to be hydroxyapatite.

Ca Spectra.JNB

(c)

(b)

(a)

1000   500

Wavenumber, cm^{-1}
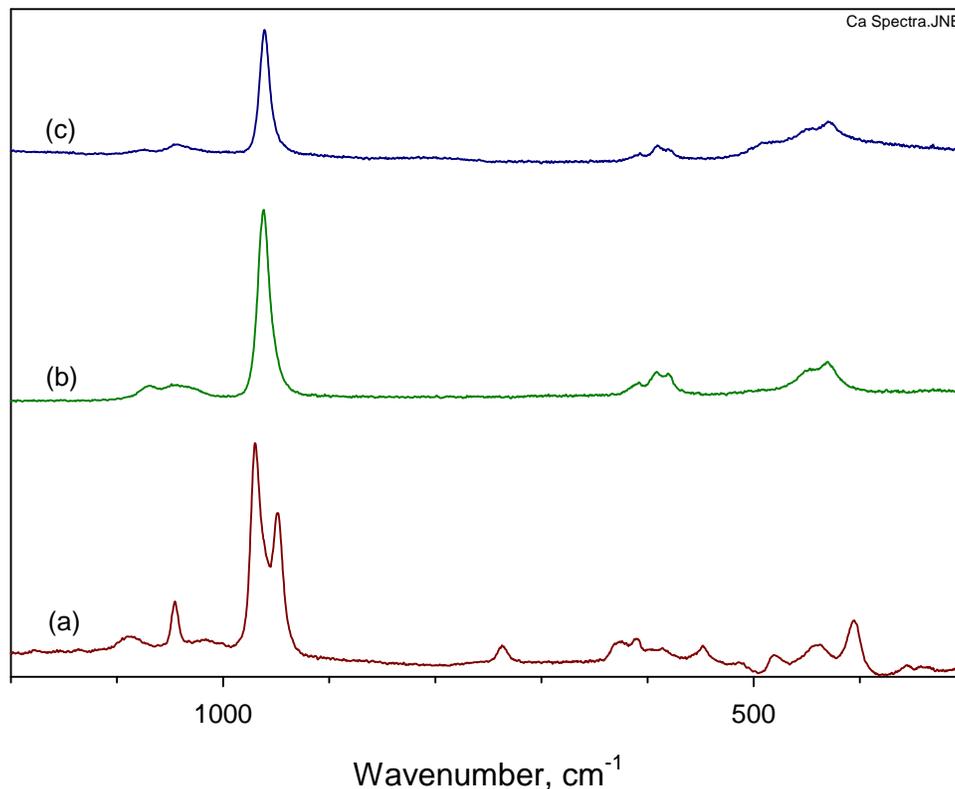
Figure 3.4. Raman Spectra of a) Ca$_3$(PO$_4$)$_2$, b) the Residual Solids Remaining After Leaching Ca$_3$(PO$_4$)$_2$ in 3.11 M NaOH for 48 h at 90 °C, and c) Hydroxyapatite

Based on these observations, the behavior of Ca$_3$(PO$_4$)$_2$ during caustic leaching can be described by the following equation:

$$5Ca_3(PO_4)_2 + 3NaOH \rightarrow 3Ca_5(PO_4)_3(OH) + Na_3PO_4 \qquad (3.2)$$

It should be noted that, although some phosphorus can be removed the β-tri-calcium phosphate phase by caustic leaching, at best, only 10% of the phosphorus can be removed from this phase by implementing the caustic-leaching process. However, the data in Figure 3.4 indicate that slightly more P is transferred into solution than would be expected from Equation 3.2 after 48 h of leaching. Thus, it appears that further slow leaching of P from hydroxyapatite is possible. This is further supported by the unidentified bands in the FTIR spectrum of the residual Ca solids (Figure 3.4).
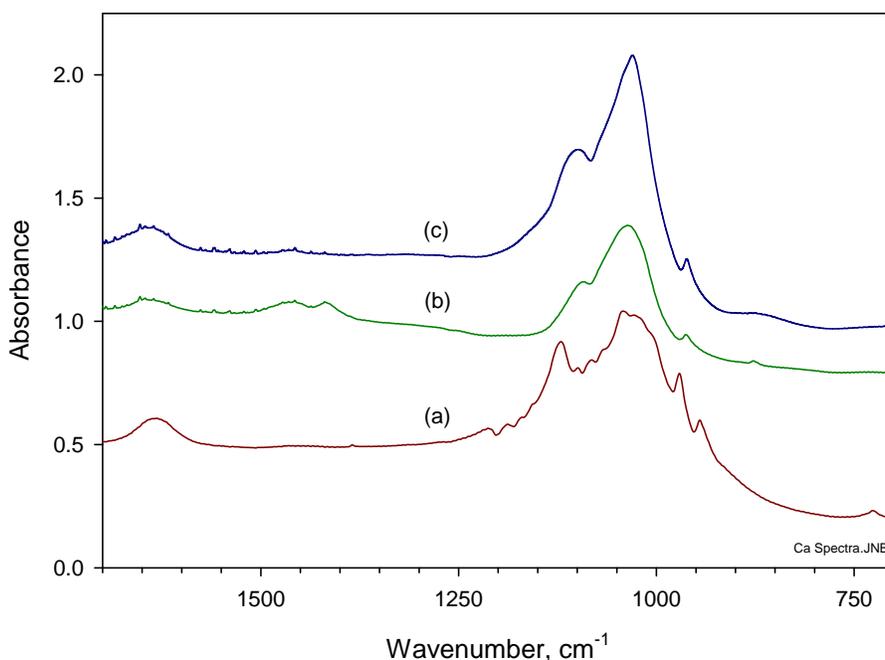
Figure 3.5. FTIR Spectra of a) Ca$_3$(PO$_4$)$_2$, b) the Residual Solids Remaining After Leaching Ca$_3$(PO$_4$)$_2$ in 3.11 M NaOH for 48 h at 90 °C, and c) Hydroxyapatite

3.1.4   Chromium Phosphate

The removal of P from CrPO$_4$·4H$_2$O was considerably slower than that observed for AlPO$_4$ and BiPO$_4$. However, nearly quantitative removal of the P was achieved after 8 h (Figure 3.6). The ICP-OES results also indicate some dissolution of Cr (13% after 8 h; Figure 3.6). Based on the yellow coloration of the leachate and previous observations during leaching of actual tank waste, the Cr in solution is most probably present as CrO$_4^{2-}$, resulting from Cr(III) oxidation by adventitious oxygen.

The Raman spectra of CrPO$_4$ and the residual Cr solids were uninformative because they were mostly featureless in the phosphate region. On the other hand, the FTIR spectra (Figure 3.7) indicated conversion to Cr(OH)$_3$·xH$_2$O. The FTIR spectrum (Figure 3.7a) of CrPO$_4$·4H$_2$O displayed a broad ν_3 band centered at 1077 cm^{-1} with a shoulder at 902 cm^{-1}, consistent with the spectrum reported in the literature (Petit et al. 1995). This band was absent (or at least greatly diminished) in the FTIR spectrum of the residual Cr solids (Figure 3.7b). The FTIR spectral pattern for the residual Cr solids resembled that for Cr(OH)$_3$·xH$_2$O (Figure 3.7c), which was separately prepared by adding a solution of CrCl$_3$ to excess aqueous NaOH. Both the Cr(OH)$_3$·xH$_2$O and the Cr residual displayed a pattern of three bands between 1300 and 1800 cm^{-1}, which are likely attributable to hydroxyl bending modes. However, there are some slight differences in the band positions for these materials—1362, 1488, and 1632 cm^{-1} for the Cr residual and 1388, 1480, and 1629 cm^{-1} for Cr(OH)$_3$·xH$_2$O—suggesting some subtle differences in the structures of the Cr residual and the separately prepared hydroxide. XRD analysis of the residual Cr solids indicated the material to be amorphous.

Based on these observations, it can be concluded that the removal of P from chromium(III) phosphate by caustic leaching is due to the simple metathesis reaction:

$$CrPO_4(s) + 3NaOH(aq) \rightarrow Cr(OH)_3(s) + Na_3PO_4(s) \qquad (3.3)$$

3.7
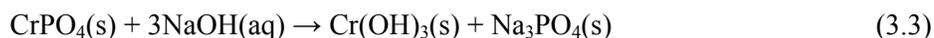
This reaction, although slower than that observed for AlPO$_4$ and BiPO$_4$, is rapid enough that nearly all P contained in the chromium(III) phosphate in the tank sludge can be removed by leaching with 3 M NaOH at 90°C for 8 h.
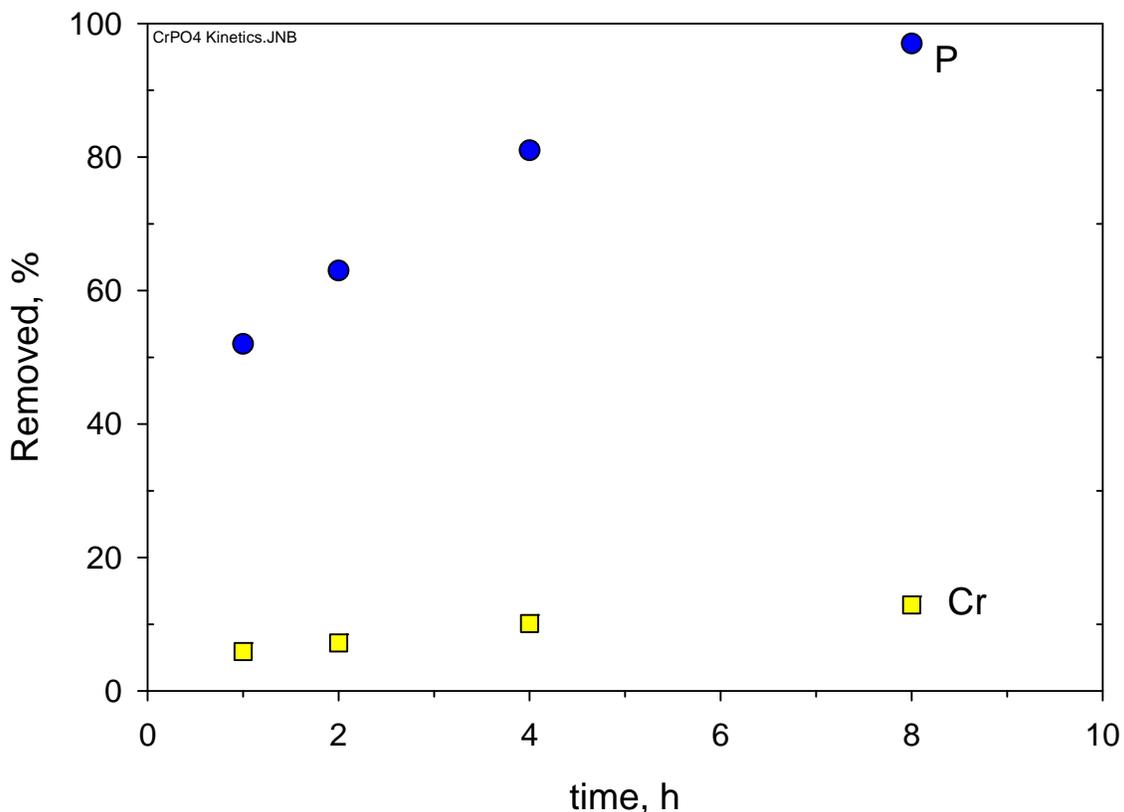

Figure 3.6. Phosphorus and Chromium Removal (as % removed) as a Function of Time During Leaching of CrPO$_4$·4H$_2$O in 3.11 M NaOH at 90 °C

3.2 Leaching of Bismuth Phosphate with Variable NaOH

The progress of the reaction of BiPO$_4$ with variable ratios of NaOH was monitored by Raman spectroscopy, tracking the intensity of the ν_1 phosphate band at 935 cm^{-1}. The intensity of this band was low at the concentrations of phosphate used in the experiment. Nevertheless, in most cases (the phosphate in solution during the OH$^-$/Bi = 0.5 reaction was below the Raman detection limit), the Raman technique was useful in determining that the equilibrium had been reached after reacting for 93 h. This was evidenced by no change in the intensity of the ν_1 band between the spectra recorded at 71 h and that at 93 h.
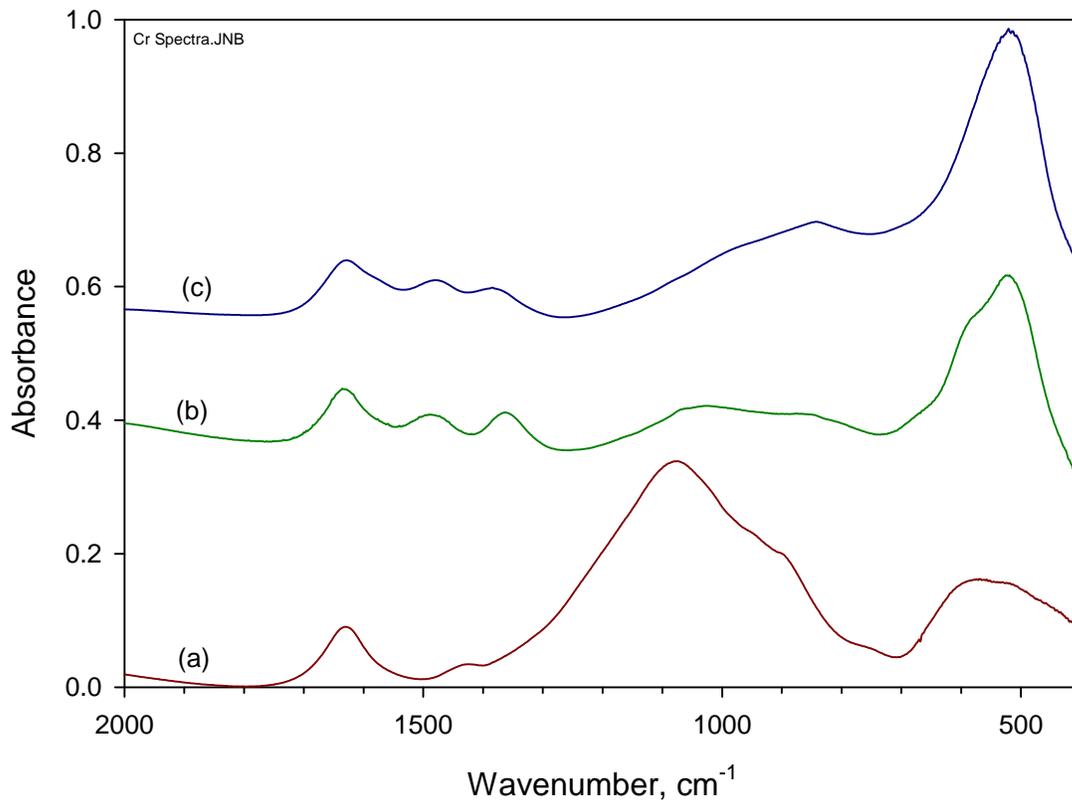
Figure 3.7. FTIR Spectra of a) CrPO$_4$·H$_2$O, b) the Residual Solids Remaining After Leaching CrPO$_4$·H$_2$O in 3.11 M NaOH at 90 °C, and c) Cr(OH)$_3$·xH$_2$O

In this experiment, it was assumed that the product of the reaction was the same as that when BiPO$_4$ was leached with 3 M NaOH at 90°C; that is, the sillenite phase Bi$^{3+}_{11}$Bi^{+5}PO$_{20}$. Base on the yellow coloration of the solids formed in this experiment with variable Bi/OH ratios, this seems a reasonable assumption. Based on reaction 3.1, a plot of log[P] versus log[OH] should yield a straight line with a slope of 3. However, this proved not to be the case (Figure 3.8). The plot is not very linear, and the regression line has a slope somewhat less than 1. The reason for this behavior is not clear at present. The equilibrium constant for reaction 3.1 includes terms that were not controlled during this experiment, such as the oxygen activity and the water activity, which might have affected the experimental outcome. Therefore, no definitive conclusions should be drawn from this particular experiment.
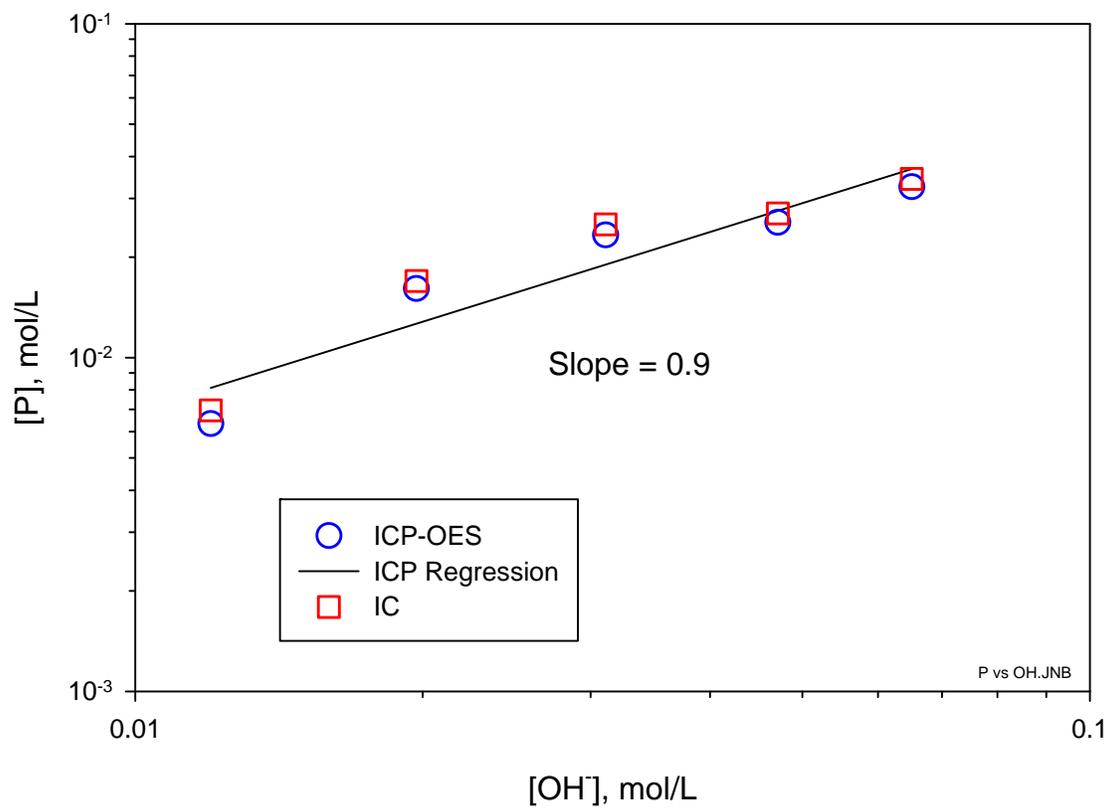
Figure 3.8. Log-Log Plot of the Phosphorus Concentration Versus the Hydroxide Concentration in the Reaction of BiPO₄ with NaOH

4.0   Summary and Conclusions

The results of this study indicate that the behavior of phosphorus during caustic leaching is somewhat more complex than originally hypothesized. Aluminum phosphate and chromium phosphate behave as expected. Phosphorus removal from these phases can be explained in terms of metathesis reactions of the type (M = Al or Cr):

$$MPO_4(s) + 3NaOH(aq) \rightarrow M(OH)_3(s) + Na_3PO_4(aq) \tag{4.1}$$
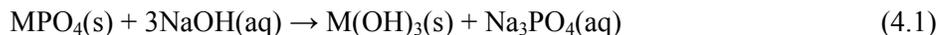
In the case of Al, the resulting hydroxide dissolves in the NaOH solution so that complete dissolution of the $AlPO_4$ phase occurs. The hydrous chromium hydroxide formed at the elevated leaching temperature is insoluble, but some Cr reports to the leachate due to oxidation of Cr(III) to Cr(VI) from adventitious oxygen.

Efficient removal of phosphorus from $Ca_3(PO_4)_2$ by caustic leaching was not expected due to its insolubility in aqueous media. However, it was shown that some phosphorus can be removed because of the conversion of $Ca_3(PO_4)_2$ to $Ca_5(PO_4)_3(OH)$. Complete conversion to hydroxyapatite would result in removal of 10% of the P from $Ca_3(PO_4)_2$. On the other hand, this conversion is slow. Only ~4% of the P was removed from $Ca_3(PO_4)_2$ after leaching in 3 M NaOH at 90°C for 8 h. So for tanks containing both Ca and P, it should probably be assumed that all the Ca is present as $Ca_3(PO_4)_2$ and that the phosphorus from this phase will not be removed during the caustic-leaching process. An interesting feature of the $Ca_3(PO_4)_2$/NaOH reaction is that a significant fraction of the P is leached from $Ca_3(PO_4)_2$ in some form other than PO_4^{3-}, but eventually, the P in solution is converted to PO_4^{3-}.

The release of phosphorus from $BiPO_4$ by leaching with 3 M NaOH at 90°C is rapid, but this does not proceed via a simple metathesis reaction. Rather, conversion to a sillenite phase (e.g., $Bi_{12}PO_{20}$) occurs. This will result in some of the P (~8%) remaining in the solid phase. On the other hand, the high stability of sillenite phases and the generality of their formation offer the intriguing possibility of substitution of Tc for P in the crystal lattice. Were this to occur, it would provide a means for sequestering Tc into the HLW solids, routing the Tc away from the LAW fraction.

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