SOLUBILITY AND STABILITY OF CALCIUM ARSENATES AT 25°C

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Abstract. The solubility and stability of calcium arsenates at 25°C was determined by both precipitation and dissolution experiments. Ca₃(AsO₄)₂·3H₂O(c), Ca₃(AsO₄)₂·21/4H₂O(c), Ca₅(AsO₄)₃(OH)(c) and Ca₄(OH)₂(AsO₄)₂·4H₂O(c) were identified in our experiment over a wide range of pH and for Ca/As molar ratios between 1.25 and 4.0. The solids precipitated at pH = 3 ~ 7 and Ca/As = 1.5 were phase-pure and well-crystallized Ca₃(AsO₄)₂·xH₂O(c) and had relatively larger grain size than those formed at pH > 7. Based on the analytical results and using the computer program PHREEQC, the solubility products for Ca₃(AsO₄)₂·3H₂O(c), Ca₃(AsO₄)₂·21/4H₂O(c), Ca₅(AsO₄)₃(OH)(c) and Ca₄(OH)₂(AsO₄)₂·4H₂O(c) were calculated as $K_{sp}$ of $10^{-21.14}$ ($10^{-20.01} \sim 10^{-22.02}$), $10^{-21.40}$ ($10^{-20.08} \sim 10^{-21.98}$), $10^{-40.12}$ ($10^{-37.33} \sim 10^{-42.72}$) and $10^{-27.49}$ ($10^{-26.10} \sim 10^{-28.91}$), respectively. Correspondingly, the free energies of forming ($\Delta G_f^\circ$) of these calcium arsenates were calculated to be $-3787.87$ kJ/mol, $-3611.50$ kJ/mol, $-5096.47$ kJ/mol and $-4928.86$ kJ/mol.

Keywords: calcium arsenates, free energies of forming, solubility products, stability

1. Introduction

Arsenic has been known from antiquity to be highly toxic for animals and the majority of plants (Fulladosa et al., 2004). The long-term intake of small doses of arsenic has a carcinogenic effect. Humans are exposed to arsenic in a variety of forms from sources such as food and water. Arsenic is released into the environment from natural processes such as weathering reactions, microbiological activity, and volcanic emissions (Smedley and Kinniburgh 2002), as well as through a range of anthropogenic activities, including: mining and smelting operations, refining operations, pharmaceutical and chemical manufacturing, burning of fossil fuels and wastes, wood preservatives, pulp and paper production, cement manufacturing, and former agricultural uses of arsenic (US EPA 1998; Bothe and Brown, 1999a; Karagas et al., 2001).

There have been a number of published investigations that have demonstrated that arsenic can be effectively removed from solution by lime precipitation. Lime additions to arsenic-containing wastes have been proven to be beneficial in reducing the mobility of dissolved arsenic, presumably through the formation of

low-solubility calcium arsenates (Bothe and Brown, 1999b). Lime softening has been also identified as an effective method of arsenic removal within the drinking water industry. As a whole, chemical precipitation such as lime softening is the most common of arsenic removal technologies and one of the most effective removal processes. Lime softening has been documented to achieve greater than a 95 percent removal of arsenate. The precipitation of metal arsenates as an arsenic removal mechanism is a preferred method to treat mine-processing effluents. Acid mine drainage and industrial waste waters are commonly treated with calcium oxide and calcium hydroxide to increase final pH and reduce the amount of dissolved matter discarded into aquatic systems (Robins, 1985; Magalhães, 2002). Metallic arsenates commonly crystallize during treatment of mine processing effluents or industrial wastes with a Ca(OH)₂ solution. Calcium arsenates were found in the oxidation zones in the As-containing ore districts and as oxidation products of As-bearing mineral wastes (Mihaljevic et al., 2003).

Precipitation of As with lime is still widely practiced, despite concerns about the long-term stability of the resulting precipitate (Valenzuela, 2000). There are a number of calcium arsenates that can be precipitated from arsenic(V) solutions, by lime addition to high pH (Nishimura et al., 1983; Nishimura and Tozawa, 1984; Nishimura and Robins, 1998). Bothe and Brown (1999a) identified several insoluble compounds, including Ca₄(OH)₂(AsO₄)₂·4H₂O, Ca₅(AsO₄)₃OH and Ca₃(AsO₄)₂·3²/₃H₂O. Nishimura and Tozawa (1985) used the formula Ca₃(AsO₄)₂·Ca(OH)₂ to represent the precipitates obtained from solutions containing As(V) ion. According to Swash and Monhemius (1995), the compounds most likely to precipitate at ambient temperature are CaHAsO₄·xH₂O, Ca₃H₂(AsO₄)₄ or Ca₃(AsO₄)₂-type compounds. The high Ca/As ratio during tailings neutralization would likely precipitate Ca₄(OH)₂(AsO₄)₂·4H₂O type Ca arsenate minerals (Donahue and Hendry, 2003). The presence of the rare calcium arsenate minerals weilite (CaHAsO₄), pharmacolite (CaHAsO₄·2H₂O), haidingerite (CaHAsO₄·3H₂O), and phaunouxite [Ca₃(AsO₄)₂·11H₂O] must indicate high concentrations of total dissolved arsenate, taking into account that calcium concentrations in the environment are usually controlled by equilibria with other less-soluble, calcium-containing solid phases (Magalhães, 2002).

The classic work on arsenate solubility that is often referred to in the literature is the work of Chukhlantsev (Chukhlantsev, 1956). He gave a value of $1.5 \times 10^{-3} - 3.5 \times 10^{-3}$ mol/l for the solubility of Ca₃(AsO₄)₂. Plots of his data as log solubility versus pH have been extrapolated to predict extremely low solubilities for individual metal arsenates. These extrapolations have been shown to be greatly in error (Nishimura, et al., 1978; Robins, 1981). Mahapatra et al. (1986) reported a value of $9 \times 10^{-3}$ mol/l for the solubility of weilite in a $10^{-3}$ mol/l NaNO₃ solution at pH 5. Other arsenates, for example 3:2 Ca arsenate, also have high solubilities, $9.1 \times 10^{-5}$ mol/l for Ca₃(AsO₄)₂ (Stephanakis and Kontopoulos, 1988). The solubility of 1:1 Ca arsenate was studied by Swasch and Monhemius (1995) who used the US EPA TCLP test on synthetic compounds. The arsenic solution concentrations
for the calcium arsenate compounds were in the range 900-4,400 mg/L As. They reported high solubilities for weilite (CaHAsO₄), ranging from 2.9 to 4.8 × 10⁻² mol/l, and for haidingerite (CaHAsO₄·H₂O) and pharmacolite (CaHAsO₄·2H₂O), ranging from 4.1 to 5.8 × 10⁻² mol/l. Geochemical modeling suggested that if the pore fluids were brought to equilibrium with Ca₄(OH)₂(AsO₄)₂·4H₂O type Ca arsenate minerals, the long-term dissolved As concentrations would range between 13 and 126 mg/l (Donahue and Hendry, 2003). The lowest value for arsenic concentration in equilibrium with solid calcium arsenates, 0.01 mg/L arsenic, was found at pH 12.6 in closed systems (Bothe and Brown, 1999b).

There exists a series of calcium arsenates that can form from aqueous solutions. However, the role of calcium arsenate formation in reducing the concentrations of dissolved arsenic has not been well established. Neutralization of an As(V) solution with lime leads to the formation of a series of calcium arsenate compounds, whose compositions have not been completely established. Nishimura and Robins (1998) recently reevaluated the solubility and stability regions of various calcium arsenate hydrates but were not able to synthesize the arsenate apatite Ca₅(PO₄)₃OH (johnbaumite), for which little information exists in the literature. Bothe and Brown (1999b) determined the solubility product constants and free energies of formation of a variety of calcium arsenates, but only by analysis of slurries and suspensions made with varying molar Ca/As ratios. Therefore, a study was undertaken to determine the solubility and stability of calcium arsenates by both precipitation and dissolution.

2. Experimental methods

2.1. Mixing and precipitation experiments

These experiments were made in HDPE bottles by mixing CO₂-free 2.0 M Ca(OH)₂ slurry with 2.0 M H₃AsO₄ solution or by 1.0 M Ca(OH)₂ slurry with 1.0 M H₃AsO₄ solution in different Ca/As molar ratios (1.0, 1.25, 1.5, 1.67, 2.0 and 4.0), which were adjusted to a certain initial pH with KOH or HNO₃ solutions before mixing. The bottles were then sealed with capsules to minimize intrusion of atmospheric CO₂, stored at 25°C and periodically agitated. After reaction for more than 90 days, the pH values of the mixing solutions in the bottles were measured. Simultaneously, 10 ml samples were extracted from each bottle and centrifuged. The liquid fraction was filtered through a 0.20 μm filter into a vial, and then diluted and stabilized with 0.2% HNO₃ in 100-ml volumetric flasks. The concentrations of calcium and arsenic were analyzed by Atomic Absorption Spectrometer (Perkin-Elmer AAnalyst 700). The solid fractions were extracted via filtration, air-dried, and then characterized using an automated Brucker D8Advance X-ray diffractometer with CuKα X-ray radiation. The morphology was analyzed by scanning electron microscopy (SEM, Joel JSM-5610LV).
2.2. DISSOLUTION EXPERIMENTS

2.2.1. Solid preparation and characterization
Calcium arsenate solids were precipitated by mixing a CO₂-free 0.5 M Ca(OH)₂ slurry and a 0.5 M H₃AsO₄ solution in 1.25:1 or 1.5:1 Ca/As molar ratio proportions under pH = 5 or pH = 7 condition and in 1.67:1 or 2.0:1 Ca/As molar ratio proportions under pH = 12 ∼ 13 condition. The mixture was reacted at 50°C for a 24-h period. The white precipitates were separated by filtration, washed with absolute ethanol, oven-dried at 50°C for 24 h. Some samples were characterized using TGA (TA Instruments model 2050). The heating rate used during TGA analysis was 10°C/min in air. The four precipitates were characterized by XRD, SEM and TG analysis and identified as Ca₃(AsO₄)₂·3H₂O(c), Ca₃(AsO₄)₂·21/4H₂O(c), Ca₅(AsO₄)₃(OH)(c) and Ca₄(OH)₂(AsO₄)₂·4H₂O(c).

2.2.2. Dissolution and equilibration
The solubility experiments were conducted in much the same manner as those used for determining the solubility of magnesite [MgCO₃] by Kittrick and Peryea (1986) and for determining the solubility of barium arsenate by Essington (1988). The equilibrium solubility experiments were conducted under different ionic strength conditions. All equilibrium solubility systems were replicated fivefold.

One or three gram solid samples of calcium arsenates were placed in 50-ml polypropylene bottles. 50 ml of either pure water or 0.1 M KOH solution was added to each bottle. The bottles were capped and placed in a temperature-controlled water bath (25°C). The samples were equilibrated, with periodic shaking, for time periods varying from 90 to 100 d. After equilibration, the aqueous phase pH was determined and 10-ml samples were extracted from each bottle, centrifuged and filtered. The liquid fractions and the solid fractions were analyzed and characterized using AAS, XRD and SEM in the same manner as described in the previous mixing and precipitation experiments.

2.3. SIMULATION AND CALCULATION OF EXPERIMENTAL DATA USING PHREEQC

Associated with each mixing and each dissolution is an assemblage of solid phases, a solution phase containing dissolved calcium and arsenic (sometimes also containing K⁺ and NO₃⁻), and a pH value. Assuming equilibrium has been reached, the values of these parameters can be calculated using established theoretical principles (Bothe and Brown, 1999b). In this study, the simulations were performed using PHREEQC, a program based on the ion-association aqueous model. The input is free-format and uses order-independent keyword data blocks that facilitate the building of models that can simulate a wide variety of aqueous-based scenarios (Parkhurst and Appelo, 1999). The aqueous species considered for total calcium in the calculations were Ca²⁺, CaOH⁺, Ca₃AsO₄⁻, CaHAsO₄ and CaH₂AsO₄⁺. For total arsenate, the species
considered were H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻, AsO₄³⁻, CaAsO₄⁻, CaHAsO₄ and CaH₂AsO₄⁺.

3. Results

3.1. XRD and SEM analyses

3.1.1. Precipitation experiments

The structure of the calcium arsenate compounds, which precipitated from the mixing of As solution with Ca(OH)₂ slurry, depended on the pH and the Ca/As molar ratio. Three types of calcium arsenates, i.e., Ca₃(AsO₄)₂·xH₂O(c), Ca₅(AsO₄)₃(OH)(c) and Ca₄(OH)₂(AsO₄)₂·4H₂O(c), were identified in our experiment over a wide range of pH and for Ca/As molar ratios between 1.25 and 4.0.

The mixture of Ca₃(AsO₄)₂·xH₂O(c) and Ca₄(OH)₂(AsO₄)₂·4H₂O(c) was observed to form at pH 3.0 ~ 7 and at Ca/As ratios of 1.0 and 1.25.

The XRD and SEM analysis of eleven separate precipitation experiments of this work for the Ca/As = 1.5 suggested that four solid samples precipitated at low initial pH (3.06, 4.06, 4.75, 5.45) and low final pH (3.70, 4.13, 5.94, 5.54) were identified as pure Ca₃(AsO₄)₂·xH₂O(c) (Figures 1 and 2), seven solids precipitated at initial pH 6.84 ~ 12.94 and final pH 7.14 ~ 7.50 were mainly Ca₃(AsO₄)₂·xH₂O with somewhat Ca₅(AsO₄)₃(OH)(c) as the solutions were in the process of precipitating the solids. However, at equilibrium the Ca₃(AsO₄)₂·xH₂O solid appeared to be the most dominant at the final pH 7.14 ~ 7.50.

At the Ca/As ratios of 1.67 and 4.0, the precipitated solids comprised mainly Ca₅(AsO₄)₃(OH)(c) and partially Ca₃(AsO₄)₂·xH₂O(c). The predominant compound formed at Ca/As = 2.0 was Ca₄(OH)₂(AsO₄)₂·4H₂O(c), appeared in conjunction with Ca₅(AsO₄)₃(OH)(c) and Ca₃(AsO₄)₂·xH₂O(c), but in minor amount.

The XRD and SEM analysis indicated that the Ca₃(AsO₄)₂·xH₂O compound presented in all precipitates independent on the Ca/As ratio and the pH of the mixing solution. These compounds were crystalline and had the distinct XRD pattern of Ca₃(AsO₄)₂·xH₂O(c). However, the structure and the grain size were related to the forming pH. For example, at the Ca/As = 1.25 and the initial pH = 4.09, and at the Ca/As = 1.5 and the initial pH = 3.04 and 4.06, the precipitated Ca₃(AsO₄)₂·xH₂O(c) was granular or platy (Figure 2: Ca-As-1.5-4). At the Ca/As = 1.5 and the initial pH = 4.75, the precipitated compound was equigranular and had a grain size of 5 ~ 40 μm (Figure 2: Ca-As-1.5-5). At the Ca/As = 1.5 and the initial pH = 5.45, the small platy or leafy Ca₃(AsO₄)₂·xH₂O(c) with a grain size of 2 ~ 10 μm formed (Figure 2: Ca-As-1.5-6). In a word, the Ca₃(AsO₄)₂·xH₂O solids precipitated at lower pH were more crystalline and had relatively larger grain size than those formed at higher pH.
Figure 1. The X-ray diffraction analysis of the reaction products precipitated from mixing 2.0 M Ca(OH)$_2$ slurry with 2.0 M H$_3$AsO$_4$ solution in Ca/As molar ratio = 1.5 at pH = 3 ~ 7. The solids precipitated under lower pH conditions were phase-pure Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c).

On the basis of TGA, the hydrate formed at low pH was determined to have the composition Ca$_3$(AsO$_4$)$_2$·3H$_2$O, whereas the hydrate formed at the higher pH contained less waters of crystallization having the composition Ca$_3$(AsO$_4$)$_2$·21/4H$_2$O. TGA also showed that the detailed structure of their weight loss profiles differed as well.

3.1.2. Dissolution experiments

X-ray diffraction and SEM analysis of Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) was performed on the solids before and after the equilibration experiments (Figure 3 ~ Figure 6). As illustrated in Figures 3 and 5, the results of the analyses on materials before equilibrium reaction were indistinguishable from the following equilibrium reaction. Morphological analysis of the Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) precipitate was also performed by scanning electron microscopy (SEM) before and after the equilibration experiments (Figures 4 and 6). The examination of the X-ray data indicated differences among the weaker diffraction peaks depending on the forming pH value and the Ca/As ratio, which means a structural dependence on the pH and the Ca/As ratio of the solution from which the hydrate precipitates. TGA indicated that the
detailed structure of their weight loss profiles differed. The TGA results showed that the form of the $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c)$ crystal was related to their precipitation pH and the Ca/As ratios. The $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c)$ precipitate acquired at pH = 4.08 and the Ca/As ratio = 1.25 was the larger leafy crystal (10- to 20-μm diam.) and was determined to have the composition $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}(c)$. Whereas, the $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c)$ solid precipitated at pH = 7.22 and the Ca/As ratio = 1.5 existed mainly as the smaller leafy crystal (1- to 5-μm diam.) and contained less waters of crystallization having the composition $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\frac{1}{4}\text{H}_2\text{O}(c)$. After the dissolution equilibration experiments at 25 °C, the crystal shape did not change for the leafy $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\frac{1}{4}\text{H}_2\text{O}(c)$ solid (Figure 6), but the $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}(c)$ solid became well-crystallized (Figure 4).

XRD and SEM analyses were also performed on the $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c)$ and $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}(c)$ solids before and after the equilibration experiments. As illustrated in Figure 7 ~ Figure 10, the results of the XRD analyses on materials before equilibrium reaction were indistinguishable from the following equilibrium reaction. The phase-pure $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c)$ was observed by SEM to have a
Figure 3. The X-ray diffraction analysis of Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) where (A) shows the solid prior to the solubility experiments and (B) shows the solid after the 100-d equilibrium. The Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) solid used in the dissolution experiments was obtained at pH = 5 and Ca/As = 1.25.

Figure 4. The SEM analysis of Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) where (A) shows the solid prior to the solubility experiments and (B) shows the solid after the 100-d equilibrium. The Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) solid used in the dissolution experiments was obtained at pH = 5 and Ca/As = 1.25.

very fine granular morphology (<1 µm diam.) (Figure 8). The Ca$_5$(AsO$_4$)$_3$(OH)(c) solid had no levels of constitutional water on the basis of the TGA analysis. The Ca$_4$(OH)$_2$(AsO$_4$)$_2$·4H$_2$O(c) solid existed as the fine needle-like crystal (Figure 10).

3.2. SOLUBILITY OF CALCIUM ARSENATE [Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c)]

The dissolution of Ca$_3$(AsO$_4$)$_2$·xH$_2$O can be described by the following reaction:

$$\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O} = 3\text{Ca}^{2+}(\text{aq}) + 2\text{AsO}_4^{3-}(\text{aq}) + x\text{H}_2\text{O}$$  (1)
SOLUBILITY AND STABILITY OF CALCIUM ARSENATES

Figure 5. The X-ray diffraction analysis of Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) where (A) shows the solid prior to the solubility experiments and (B) shows the solid after the 100-d equilibrium. The Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) solid used in the dissolution experiments was obtained at pH = 7 and Ca/As = 1.5.

Figure 6. The SEM analysis of Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) where (A) shows the solid prior to the solubility experiments and (B) shows the solid after the 100-d equilibrium. The Ca$_3$(AsO$_4$)$_2$·xH$_2$O(c) solid used in the dissolution experiments was obtained at pH = 7 and Ca/As = 1.5.

Assuming unit activity of the solid phase

$$K_{sp} = \text{(Ca}^{2+}\text{)}^3\text{(AsO}_4^{3-}\text{)}^2$$

where ( ) denotes thermodynamic activity of the species enclosed and $K_{sp}$ is the equilibrium constant of dissolution for Eq. (1).
Figure 7. The X-ray diffraction analysis of the phase-pure Ca₅(AsO₄)₃(OH)(c). (A) solid analysis before solubility experiments; (B) solid analysis after solubility experiments. The Ca₅(AsO₄)₃(OH)(c) solid used in the dissolution experiments was obtained at pH > 12 and Ca/As = 1.67.

Figure 8. The SEM analysis of Ca₅(AsO₄)₃(OH)(c) where (A) shows the solid prior to the solubility experiments and (B) shows the solid after the 100-d equilibrium. The Ca₅(AsO₄)₃(OH)(c) solid used in the dissolution experiments was obtained at pH > 12 and Ca/As = 1.67.

The standard free energy of reaction ($\Delta G_r^\circ$), in kJ/mol, is related to $K_{sp}$ at standard temperature (298.15 K) and pressure (0.101 MPa) by

$$\Delta G_r^\circ = -5.708 \log K_{sp}$$

(3)

For Eq. (1),

$$\Delta G_r^\circ = 3 \Delta G_f^\circ [\text{Ca}^{2+}] + 2 \Delta G_f^\circ [\text{AsO}_4^{3-}] + x \Delta G_f^\circ [\text{H}_2\text{O}]$$

$$- \Delta G_f^\circ [\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}]$$

(4)
Rearranging,

$$\Delta G_f^0[Ca_3(AsO_4)_2 \cdot xH_2O] = 3\Delta G_f^0[Ca^{2+}] + 2\Delta G_f^0[AsO_4^{3-}]$$

$$+ x\Delta G_f^0[H_2O] - \Delta G_r^0$$  \hspace{1cm} (5)

The chemical characteristics of equilibrium solutions in contact with $Ca_3(AsO_4)_2 \cdot xH_2O$ and the calculated log $K_{sp}$ using PHREEQC are shown in Table I. The log $K_{sp}$ of $-21.14$ (−20.31 $\sim$ −22.02) for $Ca_3(AsO_4)_2 \cdot 3H_2O(c)$ and the log $K_{sp}$ of $-21.40$ (−20.08 $\sim$ −21.98) for $Ca_3(AsO_4)_2 \cdot 2^{1/4}H_2O(c)$ were obtained by averaging over all precipitation and dissolution experiments at different pH values between 5.54 $\sim$ 6.68 with reaction times of 90 or 100 days. As the data illustrate, there was a high degree of correspondence in the calculated log $K_{sp}$ values under the experimental conditions of precipitation and dissolution. The As solubility of the precipitation experiments was same as that of the dissolution experiments.

The calculated log $K_{sp}$ values for $Ca_3(AsO_4)_2 \cdot 3H_2O(c)$ and $Ca_3(AsO_4)_2 \cdot 2^{1/4}H_2O(c)$ were in good agreement with those for the $Ca_3(AsO_4)_2 \cdot 3^{2/3}H_2O$ precipitate and the $Ca_3(AsO_4)_2 \cdot 4^{1/4}H_2O$ precipitate, which were determined only through precipitation experiments by Bothe and Brown (1999b) to be $-21.02$ and $-21.12$, respectively.
The experimentally observed mean $K_{sp}$ values ($10^{-21.14}$ and $10^{-21.40}$) were used to calculate the free energy of formation of Ca$_3$(AsO$_4$)$_2$·3H$_2$O(c) and Ca$_3$(AsO$_4$)$_2$·21/4H$_2$O(c). The $\Delta G_f^\circ$ values for Ca$_3$(AsO$_4$)$_2$·3H$_2$O(c) and Ca$_3$(AsO$_4$)$_2$·21/4H$_2$O(c) were computed as $-3787.87$ kJ/mol and $-3611.50$ kJ/mol, respectively, by using Eqs. (6)–(8) and by assuming $\Delta G_f^\circ$ for Ca$^{2+}$ = $-553.00$ kJ/mol, $\Delta G_f^\circ$ for AsO$_3^{3-}$ = $-648.39$ kJ/mol and $\Delta G_f^\circ$ for H$_2$O = $-237.141$ kJ/mol.

3.3. SOLUBILITY OF CALCIUM ARSENATE [Ca$_5$(AsO$_4$)$_3$(OH)(c)]

The dissolution of Ca$_5$(AsO$_4$)$_3$(OH)(c) can be described by the following reaction:

$$\text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c) = 5\text{Ca}^{2+}(aq) + 3\text{AsO}_3^{3-}(aq) + \text{OH}^- \quad (6)$$

Assuming unit activity of the solid phase

$$K_{sp} = (\text{Ca}^{2+})^5(\text{AsO}_3^{3-})^3(\text{OH}^-) \quad (7)$$

where ( ) denotes thermodynamic activity of the species enclosed and $K_{sp}$ is the equilibrium constant of dissolution for Eq. (6).

The standard free energy of reaction ($\Delta G_r^\circ$), in kJ/mol, is related to $K_{sp}$ at standard temperature (298.15 K) and pressure (0.101 MPa) by Eq. (3).

For Eq. (6),

$$\Delta G_r^\circ = 5\Delta G_f^\circ[\text{Ca}^{2+}] + 3\Delta G_f^\circ[\text{AsO}_3^{3-}] + \Delta G_f^\circ[\text{OH}^-]$$

$$-\Delta G_f^\circ[\text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c)] \quad (8)$$
Rearranging,

\[
\Delta G_f^o [\text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c)] = 5\Delta G_f^o [\text{Ca}^{2+}] + 3\Delta G_f^o [\text{AsO}_4^{3-}] \\
+ \Delta G_f^o [\text{OH}^-] - \Delta G_f^o 
\]

Table II gives the observed Ca and As analyses as a function of the pH, together with estimated \(K^+\) and \(\text{NO}_3^-\) concentrations. The \(\log K_w\) were calculated by using PHREEQC as described previously. The results of the precipitation experiments are in accordance with those of the dissolution experiments. This indicates solution equilibrium with respect to \(\text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c)\) and lends support to the significance of the calculated \(K_w\) value.

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### TABLE I

Analytical data and solubility determination of \(\text{Ca}_5(\text{AsO}_4)_3\cdot x\text{H}_2\text{O}(c)\) at 25 °C

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Reacted time (days)</th>
<th>Final pH</th>
<th>(K^{++})</th>
<th>(\text{NO}_3^-)</th>
<th>Ca</th>
<th>As</th>
<th>(\log K_w)</th>
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<td>(\text{Ca}_3(\text{AsO}_4)_2\cdot 3\text{H}_2\text{O})</td>
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<td>Ca-As-1.0-5</td>
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<td>Ca-As-1.25-7</td>
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<td>Ca-As-1.5-5</td>
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<td>Ca-As-1.5-6</td>
<td>5.54 0.2323</td>
<td>0.2324966</td>
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<td>Ca-As-1.25-4-2</td>
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<td>Ca-As-1.25-4-3</td>
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<td>(\text{Ca}_3(\text{AsO}_4)_2\cdot 2\frac{1}{4}\text{H}_2\text{O})</td>
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<tr>
<td>Ca-As-1.5-7</td>
<td>90 precipitation</td>
<td>7.14</td>
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<td>0.0317007</td>
<td>0.0265611</td>
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<td>Ca-As-1.5-8</td>
<td>7.19 0.0160</td>
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<td>0.0293373</td>
<td>−20.42</td>
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<td>Ca-As-1.5-9</td>
<td>7.38 0.0032</td>
<td>0.0051899</td>
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<td>Ca-As-1.5-11</td>
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<td>0.0385470</td>
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<td>Ca-As-1.5-8-1</td>
<td>100 dissolution</td>
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<td>0.0065819</td>
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<td>Ca-As-1.5-8-3</td>
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<tr>
<td>Ca-As-1.5-8-4</td>
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<td>0.0065717</td>
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<td>−21.42</td>
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<td>Ca-As-1.5-8-5</td>
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<td>0.0287100</td>
<td>−21.41</td>
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</tbody>
</table>

*Calculated from original concentration.
TABLE II
Analytical data and solubility determination of Ca\(_5\)(AsO\(_4\)\(_3\))(OH)(c) at 25 °C

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Reacted time (days)</th>
<th>Final pH</th>
<th>K(^{++})</th>
<th>NO(_3^-)</th>
<th>Ca</th>
<th>As</th>
<th>(\log K_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-As-1.67-6</td>
<td>90 precipitation</td>
<td>5.61</td>
<td>0.3731</td>
<td>0.5022</td>
<td>0.2503867</td>
<td>0.0723690</td>
<td>-41.45</td>
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<tr>
<td>Ca-As-1.67-7</td>
<td>6.98</td>
<td>0.0800</td>
<td>0.1440</td>
<td>0.0721593</td>
<td>0.0125972</td>
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<tr>
<td>Ca-As-1.67-8</td>
<td>7.21</td>
<td>0.1921</td>
<td>0.0858701</td>
<td>0.0016270</td>
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<tr>
<td>Ca-As-1.67-9</td>
<td>6.98</td>
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<td>0.0503119</td>
<td>0.0047223</td>
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<td>0.0287240</td>
<td>0.0016457</td>
<td>-38.15</td>
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<td>Ca-As-1.67-11</td>
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<td>0.0170</td>
<td>0.0005555</td>
<td>0.0022247</td>
<td>-37.53</td>
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<td>Ca-As-1.67-12</td>
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<td>0.0058434</td>
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<tr>
<td>Ca-As-1.67-13</td>
<td>13.03</td>
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<td>0.0000455</td>
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<tr>
<td>Ca-As-1.67-12-1</td>
<td>100 dissolution</td>
<td>13.38</td>
<td>0.1000</td>
<td>0.0004736</td>
<td>0.0000119</td>
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<tr>
<td>Ca-As-1.67-12-2</td>
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<td>0.1000</td>
<td>0.0001692</td>
<td>0.0000418</td>
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<tr>
<td>Ca-As-1.67-12-3</td>
<td>13.39</td>
<td>0.1000</td>
<td>0.0002954</td>
<td>0.0000151</td>
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<tr>
<td>Ca-As-1.67-12-4</td>
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<td>0.0001377</td>
<td>0.0000326</td>
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<tr>
<td>Ca-As-1.67-12-5</td>
<td>13.40</td>
<td>0.1000</td>
<td>0.0000973</td>
<td>0.0000343</td>
<td>-42.72</td>
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<td></td>
</tr>
</tbody>
</table>

*Calculated from original concentration.

A mean \(K_{sp}\) value was calculated for Ca\(_5\)(AsO\(_4\)\(_3\))(OH)(c) solid of \(10^{-38.04}\) (\(10^{-37.53} \sim 10^{-42.72}\)). This value is approximately 2.08 log units lower than \(10^{-38.04}\) reported by Bothe and Brown (1999b). On the basis of the obtained \(\log K_{sp}\) values, the \(\Delta G^\circ\|_{\text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c)}\) of \(-5096.47\) kJ/mol was calculated using Eqs. (3), (8), and (9), which is only 9.47 lower than \(-5087\) kJ/mol determined by Bothe and Brown (1999b).

3.4. SOLUBILITY OF CALCIUM ARSENATE \([\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2\cdot4\text{H}_2\text{O}(c)]\)

The dissolution of Ca\(_4\)(OH)\(_2\)(AsO\(_4\)\(_2\))\(_2\cdot4\text{H}_2\text{O}(c)\) can be described by the following reaction:

\[
\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}(c) = 4\text{Ca}^{2+}(\text{aq}) + 2\text{AsO}_4^{3-}(\text{aq}) + 2\text{OH}^- + 4\text{H}_2\text{O}
\] (10)

Assuming unit activity of the solid phase

\[
K_{sp} = (\text{Ca}^{2+})^4(\text{AsO}_4^{3-})^2(\text{OH}^-)^2
\] (11)

where ( ) denotes thermodynamic activity of the species enclosed and \(K_{sp}\) is the equilibrium constant of dissolution for Eq. (10).
TABLE III
Analytical data and solubility determination of Ca₄(OH)₂(AsO₄)₂·₄H₂O(c) at 25°C

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Process</th>
<th>Reacted time (days)</th>
<th>pH</th>
<th>K⁺⁺</th>
<th>NO₃⁻</th>
<th>Ca</th>
<th>As</th>
<th>log Kₛₚ</th>
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<tbody>
<tr>
<td>Ca-As-2.0-10</td>
<td>Precipitation</td>
<td>90</td>
<td>11.07</td>
<td>0.0947</td>
<td>0.0536853</td>
<td>0.0000187</td>
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<td>12.26</td>
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<td>Ca-As-2.0-12</td>
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<td>Ca-As-2.0-13</td>
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<td>13.38</td>
<td>0.0870</td>
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<td>0.6400</td>
<td>0.3969759</td>
<td>0.0000509</td>
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<td>12.69</td>
<td>0.0987</td>
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<td>Dissolution</td>
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<td>0.0057335</td>
<td>0.0000056</td>
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<td>0.0000060</td>
<td>-27.87</td>
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</tbody>
</table>

*Calculated from original concentration.

The standard free energy of reaction \( \Delta G_r \), in kJ/mol, is related to \( K_{sp} \) at standard temperature (298.15 K) and pressure (0.101 MPa) by Eq. (3).

For Eq. (10),

\[
\Delta G_r = 4\Delta G_f[Ca^{2+}] + 2\Delta G_f[AsO_4^{3-}] + 2\Delta G_f[OH^-] + 4\Delta G_f[H_2O] - \Delta G_f[Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O(c)] 
\]

Rearranging,

\[
\Delta G_f[Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O(c)] = 4\Delta G_f[Ca^{2+}] + 2\Delta G_f[AsO_4^{1-}] + 2\Delta G_f[OH^-] + 4\Delta G_f[H_2O] - \Delta G_f 
\]

The mean \( \log K_{sp} \) value of \(-27.49 \) (-26.10 to -28.91) for \( Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O(c) \) was obtained by averaging over all precipitation and dissolution experiments at different pH values between 9.63 to 13.40 with reaction times of 90 or 100 days (Table III). This value is approximately 1.71 log units higher than that (\( 10^{-29.20} \) at \( 23^\circ \)C) reported by Bothe and Brown (1999b). Based on our experimental result, the values of \( \Delta G_f \) for \( Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O(c) \) was calculated to be \(-4928.86\) kJ/mol, which is \( 12.14 \) higher than \(-4941\) kJ/mol given by Bothe and Brown (1999b) and \( 8.86 \) lower than \(-4920\) kJ/mol by Nishimura and Robins (1998).

4. Conclusions

The structure of the calcium arsenate precipitates obtained from the mixing of As solution with \( Ca(OH)_2 \) slurry depended on the pH and the Ca/As
ratio. \( \text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c) \), \( \text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c) \) and \( \text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}(c) \) were identified in our experiment over a wide range of pH and for Ca/As molar ratios between 1.25 and 4.0. The solid samples precipitated at low pH (3 \( \sim \) 7) and Ca/As = 1.5 were phase-pure \( \text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c) \) and well-crystallized, the solids precipitated at pH > 7 and Ca/As = 1.5 were mainly \( \text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c) \) with somewhat \( \text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c) \). The mixture of \( \text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c) \) and \( \text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}(c) \) was observed to form at pH = 3 \( \sim \) 7 and at Ca/As = 1.0 and 1.25. At the Ca/As ratio of 1.67, the precipitated solids comprised \( \text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c) \). The predominant compound formed at the Ca/As ratio 2.0 was \( \text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}(c) \), however, in some suspensions this hydrate precipitated in conjunction with minor amount of \( \text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c) \) and \( \text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c) \).

The \( \text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}(c) \) solids precipitated at lower pH were more crystalline and had much larger grain size than those formed at higher pH. Studies modeling the solubility behavior of arsenates using thermodynamic data have used \( \text{Ca}_3(\text{AsO}_4)_2 \) as the prototype mineral responsible for arsenic uptake in the presence of calcium (Bothe and Brown, 1999b), but anhydrous \( \text{Ca}_3(\text{AsO}_4)_2 \) was not identified during precipitation from an aqueous solution over a wide range of pH and Ca/As ratios. The hydrated forms are thermodynamically stable in aqueous solutions. Different from the results of Bothe and Brown (1999a), the \( \text{Ca}_3(\text{AsO}_4)_2 \cdot (\frac{3}{4})\text{H}_2\text{O}(c) \) precipitate consisting of large platy crystals with dimensions on the order of 10 \( \sim \) 30 \( \mu \text{m} \) across was not observed, rather the large granular \( \text{Ca}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}(c) \) (5 \( \sim \) 40 \( \mu \text{m} \) diam.) and the small leafy \( \text{Ca}_3(\text{AsO}_4)_2 \cdot (\frac{3}{4})\text{H}_2\text{O}(c) \) (1 \( \sim \) 5 \( \mu \text{m} \) diam.) had formed.

The analytical concentrations of calcium and arsenic and pH were used to estimate solubility of calcium arsenates. The solubility products for \( \text{Ca}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}(c) \), \( \text{Ca}_3(\text{AsO}_4)_2 \cdot (\frac{3}{4})\text{H}_2\text{O}(c) \), \( \text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c) \) and \( \text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}(c) \) were verified by both precipitation and dissolution experiments as \( K_{sp} \) values of \( 10^{-21.14}(10^{-20.01} \sim 10^{-22.02}) \), \( 10^{-21.40}(10^{-20.08} \sim 10^{-21.99}) \), \( 10^{-40.12}(10^{-37.53} \sim 10^{-42.72}) \) and \( 10^{-27.49}(10^{-26.10} \sim 10^{-28.91}) \), respectively. Based on the \( K_{sp} \) values determined, \( \Delta G_f^0 \) values for \( \text{Ca}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}(c) \), \( \text{Ca}_3(\text{AsO}_4)_2 \cdot (\frac{3}{4})\text{H}_2\text{O}(c) \), \( \text{Ca}_5(\text{AsO}_4)_3(\text{OH})(c) \) and \( \text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}(c) \) were calculated to be \(-3787.87 \text{ kJ/mol} \), \(-3611.50 \text{ kJ/mol} \), \(-5096.47 \text{ kJ/mol} \) and \(-4928.86 \text{ kJ/mol} \), respectively. There was no difference between the solubility products of \( \text{Ca}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}(c) \) and \( \text{Ca}_3(\text{AsO}_4)_2 \cdot (\frac{3}{4})\text{H}_2\text{O}(c) \) in the dissolution experiments.

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