Arsenic(III) Oxidation by Birnessite and Precipitation of Manganese(II) Arsenate

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Solution chemical techniques were used to investigate the oxidation of As(III) to As(V) in 0.011 M arsenite suspension of well-crystallized hexagonal birnessite (H-birnessite, 2.7 g L−1) at pH 5. Products of the reaction were studied by scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), atomic force microscopy (AFM), and X-ray absorption near-edge structure spectroscopy (XANES). In the initial stage (first 74 h), chemical results have been interpreted quantitatively, and the reaction is shown to proceed in two steps as suggested by previous authors: 2 Mn n02 + H3AsO3 + H2O → 2 Mn n11-OOH + H2AsO4 + H+ and 2 Mn n11-OOH + H2AsO4 + 3H+ → 2 Mn n22 + H2AsO4− + 2H2O. The As(III) depletion rate was lower (0.02 h−1) than measured in previous studies because of the high crystallinity of the H-birnessite sample used in this study. The surface reaction sites are likely located on the edges of H-birnessite layers rather than on the basal planes. The ion activity product of Mn(II) and As(V) reached after 74 h reaction time was the solubility product of a protonated manganese arsenate, having a chemical composition close to that of krautite as identified by XANES and EDS. Krautite precipitation reaction can be written as follows: Mn n22 + H2AsO4− + H2O → Mn nHAsO4− H2O + H+ log Ks ≈ −0.2. Equilibrium was reached after 400 h. The manganese arsenate precipitate formed long fibers that aggregated at the surface of H-birnessite. The oxidation reaction transforms a toxic species, As(III), to a less toxic aqueous species, which further precipitates with Mn n22 as a mixed As−Mn solid characterized by a low solubility product.

Introduction

Manganese oxides play a distinctive role in superficial soil or near surface environments due to their narrow Eh−pH stability field. They are found in oxic soils, aquifers, and oceanic and aquatic systems (1, 2). They can be readily reductively dissolved by a variety of inorganic and organic compounds (3–5). Conversely, Mn n22+ should be oxidized in most oxic waters on the basis of thermodynamic considerations, but it is not oxidized by O2 within several years (6) unless mineral surfaces (7, 8) or microorganisms (9, 10) catalyze this slow redox reaction.

Morgan recognized such limitations in the chemical thermodynamics approach to dynamic natural systems (11). His broad contribution to aquatic chemistry includes kinetic studies of both the oxygenation of Mn2+ and the reductive dissolution of manganese oxides (e.g., refs 3 and 12–14). He further created the concept of oxidative capacity (OXC) of natural systems, which in the Eh−pH dimension is similar to that of buffer capacity in the pH dimension (15). These two achievements are of course linked together since manganese oxide is an important part of the OXC in natural waters.

One of the chemicals that can reductively dissolve manganese oxides is arsenious acid (H3AsO30), a toxic soluble As(III) species that plagues a variety of water-drinking bodies in the world (16). The oxidation of As(III) by manganese oxides has been shown to occur in surface water, after mixing of oxic and anoxic lake waters (17). The reaction could lead to some decontamination of surface and drinking water bodies since the acute toxicity of As(V) species is lower than that of As(III) species (18) and since As(V) can be easily removed from solution by precipitation and adsorption on a variety of minerals (7, 19). However, detailed kinetic and spectroscopic data are needed to optimize the application of MnO2/mineral mixtures as oxidants and sinks of arsenic in technical systems. Following the former investigation by Oscarson et al. (20), a number of studies have been devoted to the oxidation of As(III) by manganese oxides using either solution chemistry (21, 13) or spectroscopic tools (22), but none have combined the two types of technique.

In this study, the kinetics of arsenic transformation by hexagonal birnessite (H-birnessite) is examined. Solution chemistry, microscopic and spectroscopic tools were used, but microscopic and spectroscopic investigations imposed some constraints: high As concentration (~11 mM) and a great quantity of solid had to be used. This high As concentration is more representative of mine drainage water than of contaminated drinking water. In addition, the thorough chemical and morphological analysis of reaction products required the use of a well-crystallized birnessite whose chemical formula and structure are well-known. In contrast to hexagonal birnessite, natural phylomanganates are extremely fine-grained and are devoid of three-dimensional ordering. The structural formula of hexagonal birnessite is H0.33Mn3+0.11Mn5+0.18(Mn4+0.78Mn3+0.22O16)O22(H2O)10.5, where □ is a Mn vacancy in the octahedral layer (23). A polyhedral representation of its structure is presented in Figure 1, in which black dots stand for OH groups around octahedral cavities. These vacancies were shown to be the reactive sorption sites for Zn2+, Cr3+, and Co2+ (5, 24–26).

FIGURE 1. X-ray powder diffraction pattern for the unreacted H-birnessite and structural model (23, 26). The structural formula is H0.33Mn3+0.11Mn5+0.18(Mn4+0.78Mn3+0.22O16)O22(H2O)10.5. Black dots represent OH groups around octahedral cavities.
As(III) aqueous species (As(OH)$_3^+$) may sorb either on these vacancies or on the edges of the octahedral Mn layers.

The objective of the present study is to elucidate the reaction mechanism occurring in the oxidative precipitation of arsenic in the presence of birnessite. The morphology and As/Mn stoichiometry of the precipitate were determined by field emission scanning electron microscopy (FE-SEM), and the dimensions of the precipitate particles were obtained by atomic force microscopy (AFM). X-ray absorption near-edge structure (XANES) spectroscopy was used to determine the oxidation state of manganese and arsenic in the solid phase.

**Materials and Methods**

**Standards and Reagents.** All solutions and suspensions were prepared with boiled MilliPore Milli-Q 18 MΩ water, which was cooled under a stream of argon. HNO$_3$ and HCl stock solutions were made from Titrisol solutions. Sodium arsenite salt and HNO$_3$ solution were used to prepare the pH 5 As(III) stock solution. ICP standards for As, Mn, and Na were prepared by dilution of 1000 ppm Alpha and Merck standards.

**Analytical Method.** Aqueous As(III) and As(V) species were separated by an anion-exchange resin (Dowex 1 × 8 anion-exchange resin 100–200 mesh) according to Ficklin (27). Total As (i.e., [As(III)] + [As(V)]) and As(III) concentrations were determined analytically, and the As(V) concentration was obtained by difference. Solid sample aliquots were dissolved in 10 mL of hot 4 M HCl solution before analysis. Arsenic, manganese, and sodium concentrations were measured on a Perkin-Elmer Optima 3300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES).

**Hexagonal Birnessite Preparation.** Sodium birnessite was prepared according to Giovanoli’s method (28), modified as follows. Initial solutions of MnCl$_2$ and NaOH were degassed with argon for 1 h. The final suspension obtained from the hydrolysis and oxidation of the Mn solution was stored 48 h at 110 °C to increase the crystallinity of birnessite. After the suspension was cooled, the solid was washed with deionized water and centrifuged 10 times to eliminate the excess in Na$^+$ and Cl$^-$. The Na-birnessite was subsequently transformed into H-birnessite at pH 5 according to Silvester et al.’s protocol (26). Equilibrium was reached after 20 days. The H-birnessite was then transferred into a 2.5-L glass reactor. The initial solid to liquid ratio, measured in triplicate, was equal to 2.73 ± 0.06 g L$^{-1}$. This birnessite content was chosen in order to collect enough material for XANES spectroscopy.

**Solid Characterization.** The unreacted H-birnessite was characterized with a Siemens D5000 X-ray powder diffractometer equipped with a KeVex Si(Li) solid-state detector and Cu Kα radiation. The diffraction pattern (Figure 1) was found to be in agreement with that reported by Lanson et al. for the H-birnessite standard (23). Mn K-edge XANES spectra were recorded at the LURE synchrotron radiation laboratory (Orsay, France) on the EXAFS 1 station, and As K-edge XANES spectra were recorded at the European Synchrotron Radiation Facility (ESRF, Grenoble France) on beamline BM32. The spectra were calibrated by taking the maximum of the derivative of the Mn metal foil at 6539 eV and that of erythrite [Co$_3$(AsO$_4$)$_2$·6H$_2$O] at 11867 eV. FE-SEM experiments were performed at the Institut für Nukleare Entsorgung (INE, Forschungszentrum Karlsruhe, Germany) using a CamScan CS44FE apparatus. AFM experiments were carried out at INE using a Topometrix Explorer apparatus operating in tapping mode.

**Experimental Conditions.** The experiment was carried out at 25.0 ± 0.5 °C under controlled argon atmosphere. The H-birnessite suspension was allowed to equilibrate at pH 5.0 ± 0.1 in a 0.03 M NaN$O_3$ background ionic medium for 1 week before the introduction of As(III). The suspension pH was monitored with a pH-stat apparatus (Impulsomat (Metrohm 614) and Dosimat (Metrohm 665)). Proton addition (HNO$_3$ 0.1 M) was controlled by a computer (Figure 2). At t = 0, 0.1 mol m$^{-3}$ of As(III) was added to the suspension, corresponding to an As/Mn molar ratio of 0.44 and to a 0.011 M arsenite concentration in water. Samples were collected with a plastic syringe and filtered through a 0.1-μm filter membrane (Durapore 0.1 μm VVLP). The first milliliter of the filtered supernatant was discarded to limit losses due to sorption on the filter membrane. This filtration step lasted less than 1 min. The filtered solution was then diluted prior to analysis. The solid collected on the filter was either dissolved for chemical analysis or lyophilized for spectroscopic analysis.

**Results and Discussion**

**Concentration of Dissolved Species versus Time.** Figure 3 reports the changes in moles of aqueous As(III), As(V), and Mn(II) in the reactor and moles of added protons with time, consecutively to the addition of As(III) to the H-birnessite suspension. The depletion of As(III) from solution was quite...
the Scott thesis (29).

From 74 to 400 h, As(III)(aq) depletion was slower, of As(III)(aq), which paralleled the increase in moles of As-
occurred in three distinct steps, which are discussed below. slow, and As(III) was not completely oxidized even after 600 h of reaction time. The decrease in As(III)(aq) content occurred in three distinct steps, which are discussed below. The first 74 h were characterized by a rapid decrease in moles of As(III)(aq), which paralleled the increase in moles of As-
(V)(aq). From 74 to 400 h, As(III)(aq) depletion was slower, and arsenic started to be incorporated in the solid phase. Beyond 400 h, As(V)(aq) concentration remained approximately constant, while As(III)(aq) concentration progressively approached zero.

**Initial Reaction Step (0–74 h) and Particle Size Effect.**
In the first 74 h of reaction time, aqueous As(III) species were transformed to aqueous As(V) species. Since the only oxidant present in solution was H-birnessite and since at any time a very little amount of As was present in the solid phase, As(III) must have been oxidized by H-birnessite in a multistep oxidation reaction in which the release of As(V) in solution was faster than both the As(III) sorption and the electron-transfer reaction step at the H-birnessite surface. One mole of Mn$^{2+}$ and 1 mol of H$_2$AsO$_4^-$ (the predominant As(V) species at pH 5, according to the Minteq database) were produced for every consumed mole of H$_3$AsO$_3^0$ (the predominant As(III) species at pH 5) and for nearly every mole of proton removed from solution. Therefore, the chemical reaction can be written as follows:

\[ >\text{Mn}^{IV}O_2 + H_2\text{AsO}_4^- + H^+ \rightarrow \text{Mn}^{2+} + H_2\text{AsO}_4^- + H_2O \]

where $>\text{MnO}_2$ is a Mn$^{IV}$ reactive H-birnessite surface functional group.

The apparent first-order rate equation for the depletion of As(III) can be written as

\[ \frac{d[\text{As(III)}]}{dt} = k_{obs}[\text{As(III)}] \]

or after integration:

\[ \ln\left(\frac{[\text{As(III)}]}{[\text{As(III)}]_0}\right) = -kt \]

where $[\text{As(III)}]_0$ is the concentration of As(III) remaining in solution at time $t$, and $k_{obs}$ is the apparent first-order rate constant. The measured $k_{obs}$ value, 0.02 h$^{-1}$, is 30–200 times lower than those reported previously in the literature (Table 1). This difference could arise from a difference in pH and As to Mn ratio. The influence of these parameters was studied by Oscarson et al. (20), Moore et al. (21), Scott (29), and Scott and Morgan (13). An increase in pH led to a decrease in As(III) depletion rate: $k_{obs}$ was found to decrease from 4.2 to 1.96 h$^{-1}$ as pH was increased from 4.0 to 6.8 (29) (Table 1, experiments MnAs1 and MnAs10, respectively). Moore et al.’s (21) experiment was conducted at the same As to Mn ratio and temperature as in the present study, but their $k_{obs}$ value was much larger (0.57 h$^{-1}$) than ours, although they worked at pH 7.5. Therefore, differences in experimental conditions cannot account for our low $k_{obs}$ value, and it will be argued below that this difference is due to the higher crystallinity of our birnessite sample.

**Initial Step (0–74 h) and Oxidation Mechanism.** To quantify the transfer between species (Sp) in solution (Sp =
Mn$^{2+}$, As(III), or As(V), in the solid (Sp = Mn(II), Mn(III), Mn(IV) or As), together with the amount of added H$^+$, these species are expressed in moles rather than in concentration.

$\Delta$Sp is the difference between the moles of Sp in the reactor at t and at $t = 0$. A detailed examination of Figure 3B shows a discrepancy between experimental and predicted $\Delta$H$^+$ and

FIGURE 4. SEM images of the As(III)-reacted H-birnessite particles. (A) 1–2 $\mu$m H-birnessite particles just after adding As(III) in suspension. (B) Particles after 6 h of reaction. Particles are smaller and edges are smoother than initially. (C) Particles after 162 h of reaction with krautite-like fibers. H-birnessite particles and krautite-like fibers are aggregated. (D) Isolated fiber on the edge of an aggregate. (E) Krautite-like fibers at the end of the experiment. (F) AFM image of fibers. (G) Topographic transect from the previous image. Width and height values are in agreement with SEM scale.
\[ \Delta \text{As(V)} \] calculated according to reaction 1, specifically in the very beginning of the reaction. Indeed, whereas \( \Delta \text{Mn}^{2+}/\Delta t \) and \( \Delta \text{As(V)}/\Delta t \) are equal within experimental error, \( \Delta H^{+}/\Delta t \) and \( \Delta \text{Mn}^{2+}/\Delta t \) are not (Figure 38). Scott and Morgan (13) found also that Mn\(^{2+}\) was released in solution with some delay relative to As(V). A preliminary interpretation of this phenomenon was warranted by Nesbitt et al. (22) using X-ray photoelectron spectroscopy (XPS). They suggested a two-step reaction mechanism:

\[
2\rightarrow \text{Mn}^{IV}_2 + H_2\text{AsO}_3 + H_2O \rightarrow \\
2\rightarrow \text{Mn}^{III}_2\text{OH} + H_2\text{AsO}_4^- + H^+ \tag{2}
\]

\[
2\rightarrow \text{Mn}^{III}_2\text{OOH} + H_2\text{AsO}_3 + 3H^+ \rightarrow \\
2\text{Mn}^{2+} + H_2\text{AsO}_4^- + 2H_2O \tag{3}
\]

where \( >\text{Mn}^{III}_2\text{OH} \) is a Mn(III) H-birnessite reactive site. On the basis of our results, this reaction scheme can be quantitatively evaluated in the following way. The net release and consumption of Mn\(^{2+}\) and H\(^+\) will be assumed to be only due to reactions 2 and 3. Arsenic present in the solid phase will be neglected during the first 74 h as it has been shown to account for less than 1% of the total arsenic mass balance. Net changes in aqueous moles of As(III) and As(V), denoted as \( \Delta \text{As(III)} \) and \( \Delta \text{As(V)} \), can then be calculated according to

\[
\Delta \text{Mn}^{2+} = 2\Delta \text{As(V)} = - \frac{2}{3} \Delta H^{+} = -2\Delta \text{As(III)} = -\Delta >\text{Mn}^{III}_2\text{OOH} \tag{A}
\]

\[
\Delta H^+ = \Delta H^+_2 + \Delta H^+_3 \tag{C}
\]

\[
\Delta \text{As(III)} = \Delta \text{As(III)}_2 + \Delta \text{As(III)}_3 \tag{D}
\]

and

\[
\Delta \text{As(V)} = \Delta \text{As(V)}_2 + \Delta \text{As(V)}_3 \tag{E}
\]

where the (2) and (3) subscripts refer to concentration changes due to the advancement of reactions 2 and 3, respectively. Combining eqs A–C, one obtains

\[
\Delta \text{As(V)} = 2\Delta \text{Mn}^{2+} + \Delta H^+ \tag{F}
\]

\[
\Delta \text{As(III)} = -2\Delta \text{Mn}^{2+} - \Delta H^+ \tag{G}
\]

Concentrations of As(III) and As(V) were computed according to eqs F and G on the basis of \( \Delta H^+ \) and \( \Delta \text{Mn}^{2+} \). The computed and experimental \( \Delta \text{As(III)} \) and \( \Delta \text{As(V)} \) values now agree within experimental errors (Figure 5A).

The model also allows obtaining the \( >\text{Mn}^{IV}_2\text{O}_2 \) and \( >\text{Mn}^{III}_2\text{OOH} \) proportions in the solid phase:

\[
>\text{Mn}^{III}_2\text{OOH} = 2\Delta \text{Mn}^{2+} + 2\Delta H^+ \tag{H}
\]

\[
>\text{Mn}^{IV}_2\text{O}_2 = -3\Delta \text{Mn}^{2+} - 2\Delta H^+ \tag{I}
\]

According to eqs H and I, the Mn(III)/Mn(IV) ratio in the solid phase increases rapidly in the first 2 h of the reaction (from 31% to 37%) and is then stable. Besides, the Mn(III)/Mn(IV) slope parallels the As(V) slope (Figure 5A). This suggests that reaction 3, i.e., the oxidation of As(III) by Mn(III), is the rate-limiting step of reaction 1. This finding agrees with XPS results by Nesbitt et al. (22), who showed (reaction 2) the appearance of intermediate Mn(III) and hydroxyl groups.

**Intermediate Nucleation Step (74–162 h).** After 100 h of reaction time, no more protons had to be added to maintain the pH constant. Mn\(^{2+}\) and As(V) concentrations reached their maximum at 162 h and then decreased gradually later on. In light of the data obtained during the 162–583-h period, the 74–162-h interval corresponds to the nucleation of a new solid.

**Manganese Arsenate Precipitation (162–583 h).** From 162 to 583 h, the As(III) content in solution decreased with no net production of aqueous As(V) and Mn(II). Instead, As(V) and Mn(II) contents decreased at the same rate. These ions either coprecipitated or were uptaken by birnessite. The position in energy of XANES spectra and the shape of the edge maximum indicated that As was predominantly pentavalent in the solid phase (Figure 6). The As average oxidation state in the solid could not be determined accurately because of the lack of reference products with intermediate As oxidation states. Semiquantitative estimate indicated that the As(V) to total As ratio was greater than 90%. This value was confirmed by EXAFS spectroscopy (Tournassat et al., manuscript in preparation). Therefore, the precipitated solid was a manganese arsenate, and the As(III) removal from solution resulted from an oxidative precipitation reaction.

Numerous manganese arsenate compounds have been reported in the literature with different As:Mn molar ratio, but Mn\(_5\text{As}_4\text{O}_{16}\cdot 8\text{H}_2\text{O(s)}\) is the only manganese arsenate compound for which a thermodynamic solubility product is available. It will be shown below that the precipitation of this manganese(II) arsenate was plausible on the basis of solubility thermodynamic considerations but did not fit the stoichiometry of the produced species.
A large range of solubility products have been reported for the manganese(II) arsenate solid. For the dissociation reaction

\[ \text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O} + 6\text{H}^+ = 3\text{Mn}^{2+} + 2\text{H}_2\text{AsO}_4^0 + 8\text{H}_2\text{O} \] (5)

Sadiq (19) reported an equilibrium constant of \( K_{\text{sadiq}} = 10^{9.5} \), whereas the Minteq and Wateqf4 thermodynamic databases yielded \( K_{\text{database}} = 10^{12.5} \). The possible precipitation of \( \text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O} \) during our experiment was assessed by computing with phreeqc2 the ion activity product \( \text{IAP} = (\text{Mn}^{2+})^3(\text{H}_2\text{AsO}_4^0)^2(\text{H}^+)^6 \) at each sampling time (Table 2). Log IAP increased from 0 to 12.1 between 0 and 162 h and then leveled off to 11.4 at 583 h. The concentration of solution species was thermodynamically consistent with the precipitation of \( \text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O} \) according to Sadiq (19) as log IAP became greater than log(\( K_{\text{sadiq}} \)) at t = 25 h. The final log IAP value (at 583 h) was reached only at t = 74 h, meaning that the beginning of the precipitation may have occurred actually from 74 h and not from 25 h. In this case, \( \text{Mn}^{2+} \) concentration in the solid phase is expected to have increased after the 74th hour. This assumption was confirmed by XANES spectroscopy. Figure 7 shows \( \text{Mn K-edge} \) spectra as function of reaction time together with the position of the edge maximum for \( \text{Mn}^{4+} (6553 \text{ eV}), \text{Mn}^{3+} (\sim 6558 \text{ eV}), \) and \( \text{Mn}^{2+} (6562 \text{ eV}) \) reported in the literature (10). A shift of the edge position toward lower energy and a concomitant apparition of a shoulder at 6562 eV were observed after 74 h, attesting for the apparition of \( \text{Mn}^{3+} \). The divalent manganese present in the solid phase necessarily originated from the solution as the solid phase was devoid of \( \text{Mn}^{2+} \) before 74 h.

The possible \( \text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O} \) formation was further checked by mass balance computations according to

\[ \Delta \text{As}(\text{III}) + \frac{2}{3} \Delta \text{Mn}(\text{II}) + \frac{2}{3} \Delta \text{H}^+ = \Delta \text{As}(\text{V}) - \frac{1}{3} \Delta \text{Mn}^{2+} \] (6)

The inferred \( \text{Mn}/\text{As} \) stoichiometry is unrealistic because of the following:

(i) The calculated amount of \( \text{Mn}(\text{II}) \) consumed exceeded largely the quantity of \( \text{Mn}(\text{III}) \) available in the solid (i.e., the sum of initial structural \( \text{Mn}(\text{III}) \) and \( \text{Mn}(\text{III}) \) produced by reaction 2).

(ii) The calculated amount of \( \text{Mn}(\text{IV}) \) in the solid would be expected to increase with reaction time, whereas XANES spectroscopy showed a decrease in average Mn oxidation state.

Other manganese(II) arsenate compounds with \( \text{Mn}/\text{As} \) ratio comprised between 1 (krautite; 32) and 3.5 (allacite; 33) may have precipitated. No solubility product is available for any of these compounds (K. Nordstrom, personal communication). The possible precipitation of one of these compounds was tested only on the basis of stoichiometry considerations using eqs A–J because it could not be tested on the basis of solubility considerations. The best fit to our experimental data was obtained assuming the formation of krautite (Mn\text{HAsO}_4\cdot\text{H}_2\text{O}) (Figure 5b). However, 0.2H\text{+} per As had to be added to the solid to obtain a good fit to experimental data. For this Mn\text{As} stoichiometry, the Mn\text{IV} content in the solid should decrease and the Mn(III) content should remain constant in agreement with XPS (22). Further support for the precipitation of a krautite-like solid was obtained by SEM-EDS and AFM (Figure 4). Large 0.05–
characterized by a fast As(III) depletion, lasted less than 1 h. Therefore, one can reasonably reject the hypothesis that these fibers are the result of the dissolution of birmesite platelets. In addition, the EDS analysis (Figure 8) of one isolated fiber shown in Figure 4d indicated that the precipitate had a Mn to As ratio close to 1, in agreement with krautite chemical composition.

The krautite precipitation/dissolution reaction can be written as

\[
\text{MnHAsO}_4 \cdot \text{H}_2\text{O} + \text{H}^+ = \text{Mn}^{2+} + \text{H}_2\text{AsO}_4^- + \text{H}_2\text{O}
\]

The ion activity product for this reaction (IAP_{krautite}) has been calculated with phreeqc2 at each step in our experiment, as well as in Moore et al.'s (21) and Scott’s (29) experiments (Table 2). For our experiment, log IAP_{krautite} reached a maximum (0.07) at 162 h and then leveled off to –0.21 at the end of the experiment. Therefore, one can consider this value to be the solubility product of krautite (K_{krautite}^s). Earlier, i.e., after 74 h, log IAP_{krautite} was greater than –0.21, and krautite nucleation may have occurred. In the experiment of Moore et al. (21), log IAP_{krautite} became larger than –0.21 after only 2 h because of a faster kinetics and a higher pH. In this case, precipitation may have occurred already after 1 h. After 4 h, they observed the formation of a gel having a Mn/As molar ratio of 1.05 ± 0.05, in agreement with the present study. Although Oscarson et al. (20) did not measure [Mn(III)]_aq, they probably precipitated a krautite-like solid because their initial As(III) concentration and pH value were similar to those of Moore et al. (21). In contrast, Scott (29) did not observe any precipitate as expected from the low log IAP_{krautite} values reported in Table 2. They used a lower pH value in their MnAs1 experiment and a lower As concentration and solid to solution ratio in their MnAs10 experiment.

The precipitation or not of a Mn(II)–As(V) solid phase provides a clue to the discrepancies in As(III) oxidation rates reported in the literature. Moore et al. (21) and Oscarson et al. (20) observed a two-step reaction kinetics. The first step, characterized by a fast As(III) depletion, lasted less than 1 h (i.e., up to the point where IAP reached the K_{krautite}^s value). In the second step, the As(III) depletion was limited and lasted up to the disappearance of As(III) from solution. In contrast, no low As(III) depletion was observed by Scott and Morgan (13). Therefore, the existence of a slow As(III) depletion step can be correlated to the onset of a manganese(II) arsenate precipitation. If precipitation occurred on the edge of the birmesite platelets, it would obstruct the reactive surface functional groups, further decreasing the As(III) depletion rate.

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