

Behavior of Sulfate Ion During Formation of Bioscorodite for Arsenite Immobilization

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Abstract

Removal of arsenic as scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) from As(III)-bearing metal refinery wastewaters has been studied using chemical or biological techniques. Biological scorodite formation can be effectively applied for dilute As(III) solutions, and we have previously demonstrated one-step As(III) immobilization using the Fe(II)- and As(III)-oxidizing archaeon *Acidianus brierleyi* at pH 1.5, 70°C. Prior to crystallization of pale-green scorodite, yellowish amorphous ferric-arsenate precursors are typically formed. To clarify the process of bioscorodite crystallization through the transformation of the precursors into crystalline scorodite, this study investigated uptake of sulfate ions (SO_4^{2-}) in the crystal structure.

1. Introduction

Scorodite is considered as one of the ideal As disposal forms due to high thermodynamic stability, high density and low Fe demand.^[1] The past studies started with hydrothermal methods and developed to atmospheric and more recently to biological methods. Compared to other chemical methodologies, biological approach can become more important for dilute As solutions, since chemical methods display difficulties in treating such low As concentrations. For bioscorodite formation, our research group has been utilizing the thermo-acidophilic Fe-oxidizing archaeon, *Acidianus brierleyi*. We have found that *Ac. brierleyi* has not only Fe(II)- but also As(III)-oxidizing ability to enable one-step crystalline bioscorodite formation.^[2] Prior to crystallization of pale-green bioscorodite, yellowish amorphous ferric arsenate precursors are typically formed. To clarify the process of bioscorodite crystallization, this study investigated the factors possibly affecting the formation of precursors and their transformation into crystalline scorodite. The effects of SO_4^{2-} ions were previously reported in chemical scorodite studies.^{[3][4]} Also, the fact that copper refinery wastewaters often contain high concentrations of SO_4^{2-} motivated us to investigate behavior of SO_4^{2-} during

bioscorodite formation by liquid and solid characterization analyses.

2. Materials and Methods

Pregrown *Ac. brierleyi* cells were inoculated (1.0×10^7 cells/ml) in 500 ml Erlenmeyer flasks containing 200 ml of heterotrophic basal salts medium (pH 1.5 with H_2SO_4) with 18 mM Fe(II) (as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 13 mM As(III) (as NaAsO_2) and 0.02% (w/v) yeast extract. Flasks were incubated at 70°C, shaken at 150 rpm. Precipitates were regularly taken and washed once by pure water. After freeze-drying, samples were digested in 35% HCl to determine the chemical composition. Liquid samples were regularly taken to monitor pH, Eh vs SHE, cell density, and the concentrations of total Fe/As/S by ICP-OES, As(III) by stripping voltammetric method, and Fe(II) by o-phenanthroline method. Precipitates were freeze-dried overnight for XRD, SEM, FT-IR (KBr pellet method), and TG-DTA (heated from room temperature to 1200°C at 10°C/min with N_2 gas 100 ml/min).

3. Results and Discussion

3.1. Precursor Formation and Transformation into Scorodite

Fe(II) and As(III) were completely oxidized within 4 days by *Ac. brierleyi*.

Consequently, yellowish amorphous ferric arsenate was precipitated as precursors (1st stage As precipitation at day 4–10). The color then turned pale-green (typical color of bioscorodite) overnight to form crystalline scorodite (2nd stage As precipitation at day 10~). To observe the behavior of Fe^{3+} , AsO_4^{3-} and SO_4^{2-} ions in solid, amorphous precipitates were digested in 35% HCl. The results showed that SO_4^{2-} ion was one of the constituents of precursors. The measured $[\text{AsO}_4]_{\text{im}}/[\text{Fe}]_{\text{im}}$ molar ratio at day 5 was smaller (0.78) than the theoretical value of scorodite (1.0), while $[\text{AsO}_4+\text{SO}_4]_{\text{im}}/[\text{Fe}]_{\text{im}}$ was 0.94. At the end of reaction, $[\text{SO}_4]_{\text{im}}/[\text{Fe}]_{\text{im}}$ decreased from 0.16 to 0.08 as $[\text{AsO}_4]_{\text{im}}/[\text{Fe}]_{\text{im}}$ increased to 0.94. This indicates that excess Fe was precipitated due to incorporation of SO_4^{2-} ions instead of AsO_4^{3-} ions. In order to confirm the uptake of SO_4^{2-} ions, chemical scorodite synthesis was attempted with or without use of H_2SO_4 . When other acids such as HCl and HNO_3 were used instead of H_2SO_4 , no precipitates were obtained in 1 week. In contrast, yellowish precipitates readily formed within 1 hour when H_2SO_4 was used, and were transformed into scorodite at day 7. Although inhibitory effects of SO_4^{2-} ions on chemical scorodite synthesis have been reported^[3], uptake of SO_4^{2-} ion was shown to be the key for precursor formation for dilute As(III) solutions.

3.2. Behavior of SO_4^{2-} Ions During Transformation of Precursors into Bioscorodite

From changes in FT-IR spectra of precipitates, distinct SO_4^{2-} peaks (1062 cm^{-1}) originally present in precursors disappeared after day 9, corresponding to the clear color change to pale-green. This was accompanied by the emergence of OH peaks deriving from water molecules (3523 cm^{-1}), which indicates occurrence of H-bond cleavage. SO_4^{2-} ions were once incorporated in the precursor structure by weak H-bonding, and then released to form final scorodite products. In order to elucidate precise chemical formula of the precipitates, TG-DTA measurement was

conducted. Based on the TG curve previously reported in the hydrothermal study^[4], the precursors formed in this study can be considered basic ferric arsenate sulfate $(\text{Fe}(\text{AsO}_4)_{1-x}(\text{SO}_4)_x(\text{OH})_x \cdot w\text{H}_2\text{O})$. Consequently, the chemical formula of precursors was determined as $\text{Fe}(\text{AsO}_4)_{0.8}(\text{SO}_4)_{0.2}(\text{OH})_{0.3} \cdot 2.4\text{H}_2\text{O}$. In contrast, the typical scorodite TG curve was obtained with the final bioscorodite product at day 14. Its chemical formula was calculated as $\text{Fe}(\text{AsO}_4)_{0.9}(\text{SO}_4)_{0.1} \cdot 1.9\text{H}_2\text{O}$. One fifth of the AsO_4^{3-} locus was occupied by SO_4^{2-} ions, which were then released from precursors to form final product with a chemical formula close to theoretical scorodite.

4. Conclusions

Uptake of SO_4^{2-} ions in scorodite precursors was shown one of the key factors for effective bioscorodite crystallization from dilute As(III) solutions (~13 mM). Amorphous precursors were determined as basic ferric arsenate sulfate. Transformation of amorphous precursors into crystalline bioscorodite proceeded via release of SO_4^{2-} ions.

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