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# Scorodite Crystal Formation on Hematite (Fe<sub>2</sub>O<sub>3</sub>) Surface in Fe(II) Solution Containing As(V)

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Scorodite crystal formation on a hematite (Fe<sub>2</sub>O<sub>3</sub>) surface in excess Fe(II) solution containing As(V) was observed under various conditions using the direct hematite addition method. Gel-like precursors initially formed and covered the entire hematite surface. Scorodite crystal nuclei then appeared preferentially on the grain boundaries of each hematite crystal, rather than on the flat hematite crystal surface. These grew into faceted crystalline scorodite particles through stepwise structure formation. The effects of solution temperature (50, 70, and 95°C), initial solution pH (0.6, 0.9, and 1.6), initial Fe(II) concentration (0, 25, and 55.9 g/L), and initial As concentration (25 and 50 g/L) on gel-like precursor and scorodite crystal formation were comprehensively investigated. The reaction temperature only affected the scorodite crystal formation rate and not the crystal shape in the studied range of 50–95°C. Octahedral faceted scorodite was obtained at all temperatures studied. The solution pH strongly affected scorodite crystal formation, with a higher pH favoring scorodite formation in the studied range of pH 0.6–1.6. Scorodite crystals were not obtained at pH 0.6 because of the lower AsO<sub>4</sub><sup>3-</sup> concentration in solution. Octahedral faceted scorodite crystals were also obtained at a lower Fe(II) concentration (25 g/L), but the gel-like precursor and scorodite crystals were not obtained in the absence of Fe(II). The As(V) concentration in solution affected the overall scorodite formation rate. Imperfect octahedral-shaped scorodite crystals with larger diameters were observed at lower As(V) concentration (25 g/L), which was attributed to the lower AsO<sub>4</sub><sup>3-</sup> concentration. This study provides important information for As treatment through scorodite crystal formation using the hematite addition method.

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**Keywords:** scorodite, arsenic, hematite, gel-like precursor, tablet surface

## 1. Introduction

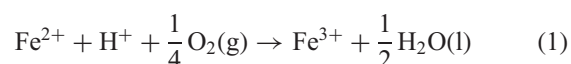
Arsenic is highly toxic to most plants and animals, with long-term exposure to As having various adverse health effects, including skin cancer.<sup>1)</sup> Preventing As distribution into the environment is important, necessitating the development of effective methods for As removal and stabilization. Pentavalent As removal and its stabilization as crystalline scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O) is a promising method for treating As in industrial byproducts, such as flue gas dust from nonferrous smelters. Large highly crystalline scorodite particles can achieve suppressed As dissolution,<sup>2)</sup> which reduces its environmental impact.

Conventionally, the conversion of As into scorodite is performed in an autoclave reactor operated under pressurized oxidation conditions at temperatures above 100°C.<sup>3,4)</sup> To avoid using expensive autoclave reactors, Demopoulos and coworkers reported scorodite synthesis below 100°C by adding scorodite seed;<sup>5–11)</sup> however, this method requires strict control of the ferric arsenate solution pH by adding magnesium or calcium hydroxides. The biological scorodite crystallization method, which utilizes bacterial oxidation of Fe(II) and As(III) in a solution with lower arsenic concentration at a lower temperature, has also been investigated.<sup>12–15)</sup>

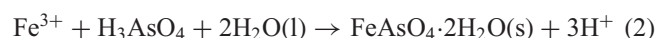
DOWA Metals & Mining Co., Ltd. developed the DMSP (DOWA Metals & Mining Scorodite Process) method to produce large crystalline scorodite particles at normal atmospheric pressure and temperatures below 100°C.<sup>16–22)</sup> In this method, large scorodite particles (median diameter

(D<sub>50</sub>), 20.7 μm) are obtained by blowing O<sub>2</sub> gas into a reaction solution containing As(V) and Fe(II) ions at high concentration.<sup>21)</sup> The Fe(III) ions needed for scorodite synthesis are supplied by converting Fe(II) into Fe(III) using blown O<sub>2</sub>. A membrane-type (gel-like) substance containing iron arsenate is formed as the precursor of faceted crystalline scorodite particles. These particles grow through conversion of the gel-like precursor. The reactions in this process are expressed by eqs. (1)–(3).

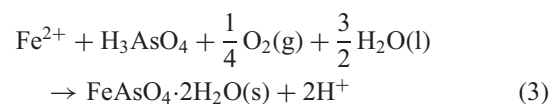
Oxidation of Fe<sup>2+</sup> by blown O<sub>2</sub>:



Subsequent scorodite precipitation:



Overall reaction:



Shinoda *et al.*<sup>23)</sup> used X-ray absorption near-edge structure spectroscopy to investigate the chemical state of Fe in the gel-like precursor. Their results showed that the precursor mainly consists of Fe(II) with a small amount of Fe(III). This indicated that scorodite particles formed from the gel-like precursor containing Fe(II). The conversion of Fe(II) into Fe(III) by blowing with O<sub>2</sub> gas was therefore not an essential step, because direct addition of Fe(III) into an As(V)-containing FeSO<sub>4</sub> solution also resulted in the formation of faceted crystalline scorodite particles.

Scorodite formation through the direct addition of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, as an Fe(III) source, to an FeSO<sub>4</sub> solution containing As(V), without oxidation by O<sub>2</sub> gas, has been

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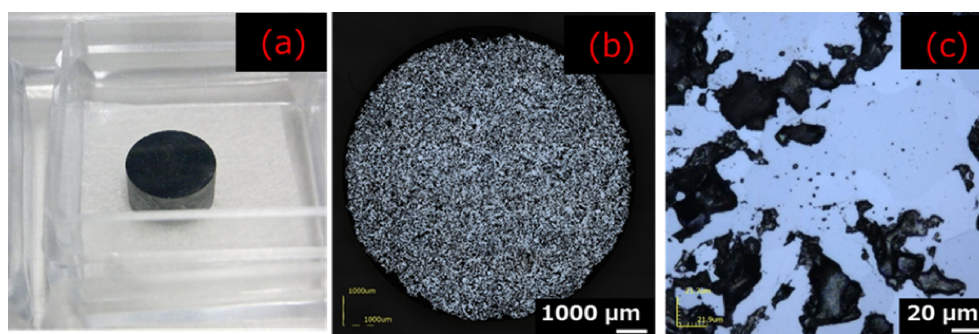
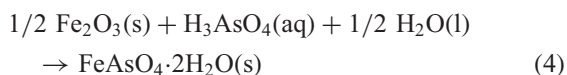


Fig. 1 Sintered and polished hematite tablet (porosity before sintering, 15%): (a) photograph of tablet, (b) image of polished surface, and (c) enlarged image of polished surface.

investigated.<sup>24–26</sup>) The results indicated that the size of the formed scorodite particles increased with increasing initial Fe(II) concentration, through formation of a gel-like precursor. Large faceted scorodite particles also formed in solution with an initial Fe(II) concentration of 75 g/L (initial As(V), 70 g/L; pH 1.43; temperature, 95°C; Fe(III) solution continuously added to the reaction solution). This showed that a high initial Fe(II) concentration was necessary to produce faceted scorodite crystalline particles through conversion of the gel-like precursor when using the method of direct addition of Fe(III) to the solution.

Scorodite synthesis by direct addition of solid Fe(III) compounds, namely hematite (Fe<sub>2</sub>O<sub>3</sub>)<sup>24,26,27</sup> and magnetite (Fe<sub>3</sub>O<sub>4</sub>),<sup>28,29</sup> to an FeSO<sub>4</sub> solution containing As(V) has also been reported. For hematite addition, the overall scorodite formation reaction can be expressed as shown in eq. (4):



Hematite powder is a cheaper source of Fe(III) than Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution. Furthermore, H<sup>+</sup> is not generated during the reaction, so only a small change in solution pH occurs during scorodite formation. The DMSP method, which uses blowing O<sub>2</sub> gas, generates H<sup>+</sup>, which leads to a decrease in pH that suppresses both scorodite formation and As removal from the solution. In methods involving the direct addition of Fe(III) ions, the Fe(II) concentration is maintained because Fe(II) ions are not consumed. This is of industrial importance because the FeSO<sub>4</sub> solution can be recycled without wastewater treatment for further scorodite formation through repeated addition of hematite and the As source. Notwithstanding, details of the mechanism of scorodite crystal formation in the hematite powder addition method remain unknown. This mechanism must be complex because different reaction steps involve various solids, including hematite, the gel-like precursor, and scorodite.

In this study, scorodite crystal formation on a hematite (Fe<sub>2</sub>O<sub>3</sub>) surface, as a solid Fe(III) source, in excess Fe(II) solution containing As(V) was observed under various conditions. Preliminary results for scorodite formation on a hematite surface were previously reported.<sup>30–33</sup>) The effects of solution temperature (50, 70, and 95°C), initial solution pH (0.6, 0.9, and 1.6), initial Fe(II) concentration (0, 25, and 55.9 g/L), and initial As concentration (25 and 50 g/L) on the gel-like precursor and scorodite crystal formation were thoroughly investigated.

## 2. Experimental

### 2.1 Materials

An FeSO<sub>4</sub> solution containing As(V) was prepared from FeSO<sub>4</sub>·7H<sub>2</sub>O, arsenic(V) acid (60 mass% H<sub>3</sub>AsO<sub>4</sub>), and ion-exchanged water, and used as the original experimental solution. These chemicals were of reagent grade and obtained from Wako Pure Chemical Industries, Ltd. (Japan). Cylindrical hematite (Fe<sub>2</sub>O<sub>3</sub>) tablets (φ, 10 mm; thickness, 5 mm) were purchased from Kojundo Chemical Laboratory Co., Ltd. (Japan). The hematite tablets were sintered at 1300°C in a box furnace (Koyo Thermo Systems Co., Ltd., Japan) and then allowed to cool in the furnace. Sintering was conducted to reduce the gaps between the hematite crystals and obtain sufficient flat area for observation by increasing the size of the primary hematite crystals. Dense hematite tablets of 5% porosity were first sintered for 48 h, and then used for detailed observation of generation of the gel-like precursor and its conversion to scorodite crystals. Hematite tablets of 15% porosity were first sintered for 120 h and then used to investigate the effects of solution conditions on scorodite crystal formation. One of the circular surfaces on the sintered tablet was mechanically polished for observation of scorodite formation on the hematite surface. Images of the sintered and polished tablets are shown in Fig. 1. Black regions observed on the polished surface in Figs. 1(b) and 1(c) are recessed areas derived from gaps between the hematite crystals comprising the tablet.

### 2.2 Methods

Figure 2 shows the experimental apparatus used for scorodite synthesis. The apparatus consisted of a 500-mL Pyrex flask equipped with a condenser, a glass tube as a gas inlet, and a pH/oxidation–reduction potential electrode. The reaction solution volume was 400 mL and scorodite formation was performed without stirring the solution. The reaction solution in the flask was heated with a mantle heater and the temperature measured using a K-type thermocouple. Experiments were conducted under Ar at a flow rate of 400 mL/min to prevent oxidation of Fe(II) ions during heating. The amount of As(V) in solution was set at 25 or 50 g/L (corresponding to 0.33 or 0.67 mol/L of As, respectively) and the Fe(II) content was set at 0, 25, or 55.9 g/L (corresponding to 0, 0.448, and 1.00 mol/L of Fe, respectively). A small amount of Sb impurity was present in the arsenic(V) acid used to prepare the reaction solution,

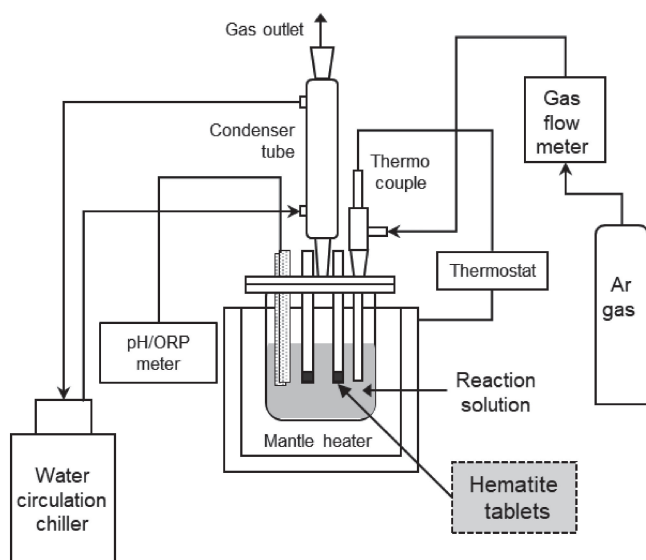


Fig. 2 Experimental apparatus for scorodite crystal formation on polished hematite surface.

which might affect scorodite synthesis. The initial Sb concentration in the solution was about 50 mg/L for all conditions studied. The solution temperature was set at 50, 70, or 95°C. The solution pH was adjusted to 0.6, 0.9, or 1.6 by adding H<sub>2</sub>SO<sub>4</sub>. The change in solution composition during the scorodite formation experiments was considered negligible because the amount of scorodite generated was very small when considering the excess of Fe(II) solution containing As(V). Hematite consumption by scorodite generation was also small, so the overall shape of the hematite tablet was maintained throughout the experiments.

In the scorodite formation experiments, certain amounts of ion-exchanged water and FeSO<sub>4</sub>·7H<sub>2</sub>O were fed into a separable flask and the mixture was stirred using an impeller at 200 rpm under Ar gas flow. The solution was heated and arsenic(V) acid solution was added when the temperature reached 40°C. Precipitation was observed at around 70–75°C. The solution was then filtered; the filtrate was fed into a new separable flask and used for further experiments. When the temperature reached 95°C, polished hematite tablets attached to glass rods or rubber plugs were inserted and immersed in the reaction solution to initiate scorodite formation (reaction time, 0 min). Excess Fe(II) and As, with respect to the amount of scorodite formed, were present in solution during scorodite crystal formation and their concentrations remained constant even after a long reaction period. After a predetermined reaction time, the hematite tablets were removed from the solution and cleaned by immersion in ion-exchanged water (approximately 50 mL) in a 50-mL beaker for 30 s. The tablets were then placed in weighing bottles, frozen using liquid nitrogen, and freeze-dried overnight in a freeze dryer.

The gel-like precursors formed on the hematite tablet surface were observed by scanning electron microscopy (SEM; SU8000, Hitachi High-Technologies Corp., Japan) and analyzed by energy-dispersive X-ray spectroscopy (EDX; X-Max, Oxford Instruments, UK). The generated scorodite crystal shapes were examined by SEM (SU6600,

Hitachi High-Technologies Corp., Japan). The interface between the hematite crystal boundary and the generated scorodite crystal was treated with a focused ion beam (FIB; Helios NanoLab 600i, Thermo Fisher Scientific, USA) and then examined by SEM–EDX (SEM: standard-loading SEM with Helios NanoLab 600i; EDX: EDAX Octane Super, Ametek, Inc., USA). The hematite tablet surface was examined by X-ray diffraction (XRD; D2PHASER, Bruker Corp., USA; radiation source: Cu K $\alpha$ ).

### 3. Results and Discussion

#### 3.1 Investigation of gel-like precursor generation and conversion into scorodite crystals

Generation of the gel-like precursor and its conversion into scorodite crystals were investigated under standard scorodite synthesis conditions (95°C; pH 1.6; As(V) concentration, 50 g/L; Fe(II) concentration, 55.9 g/L).

Figure 3 shows images of the gel-like precursor generated on the hematite tablet surface in the initial reaction stage (10 min). Blue and brown areas and some crystals were observed in the laser microscopy photograph of the hematite tablet surface (Fig. 3(a)). SEM–EDX images (Figs. 3(b) and 3(c)) showed that the colored areas contained As. The enlarged SEM image (Fig. 3(d)) showed fibrous gel-like precursor generation. These results confirmed that a fibrous gel-like precursor covered the hematite tablet surface in the initial reaction stage. The blue and brown areas observed in the laser microscopy photograph were both considered to be gel-like precursors layers, with the difference in color derived from the layer thickness. These results suggested that scorodite crystals with diameters of several microns were generated from within accumulated gel-like precursors.

Figure 4 shows laser microscopy images of the hematite tablet surface before and after reacting for 60 min. Single crystals of hematite, tens of microns in diameter, and crystal boundaries can be observed in Fig. 4(a). After scorodite synthesis for 60 min, the hematite tablet surface was totally covered by the gel-like precursor (blue- and brown-colored areas) and the surface color had changed, as shown in Fig. 4(b). Compared with the hematite tablet surface before the reaction, the hematite crystal boundaries were clearer and scorodite crystals (black-colored particles) were generated around the hematite crystal boundaries. This indicated that the gel-like precursor formed first and covered the entire hematite surface, with consumption of hematite as the Fe(III) source. Scorodite crystal nuclei then appeared preferentially on the grain boundaries of each hematite crystal rather than on the flat surface of the hematite crystals.

Figure 5 shows SEM images of the hematite tablet surface after scorodite synthesis for 180 min. The nuclei grew to give faceted crystalline scorodite particles through stepwise structure formation. Figure 6 shows SEM images of the hematite tablet surface at different reaction times (60–300 min). Flat scorodite crystals that formed after 60 min grew into faceted crystalline scorodite particles with diameters of up to 30  $\mu$ m, which then aggregated.

Figure 7 shows SEM–EDX images of the interface between the hematite crystal boundary and scorodite crystal generated on the boundary. This interface was flat. At this



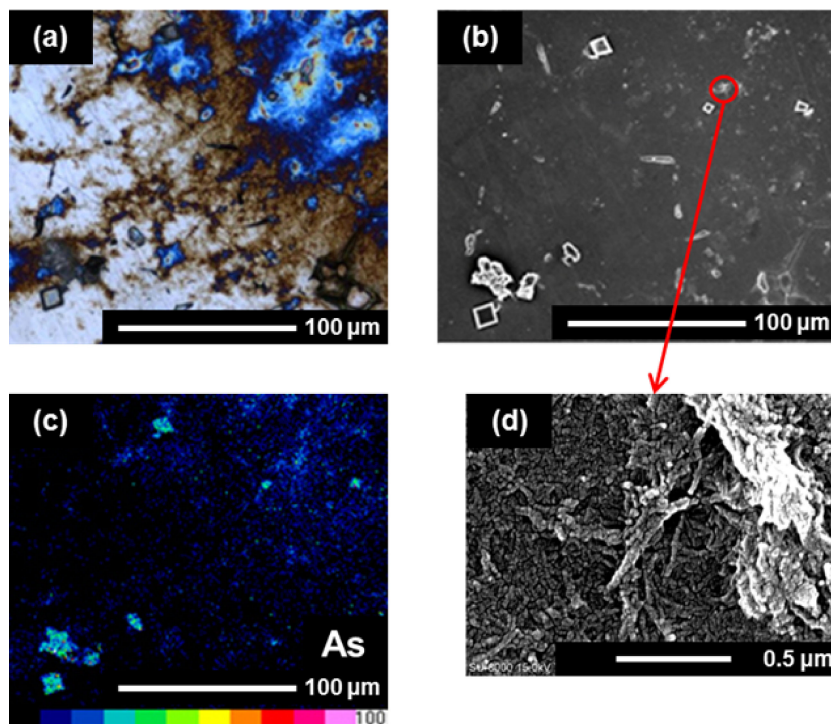


Fig. 3 Gel-like precursors on hematite tablet surface in the initial reaction stage (10 min): (a) Laser microscopy photograph, (b) SEM image, (c) As elemental mapping, and (d) enlarged SEM image of gel-like precursor (taken from Ref. 21), with revisions).

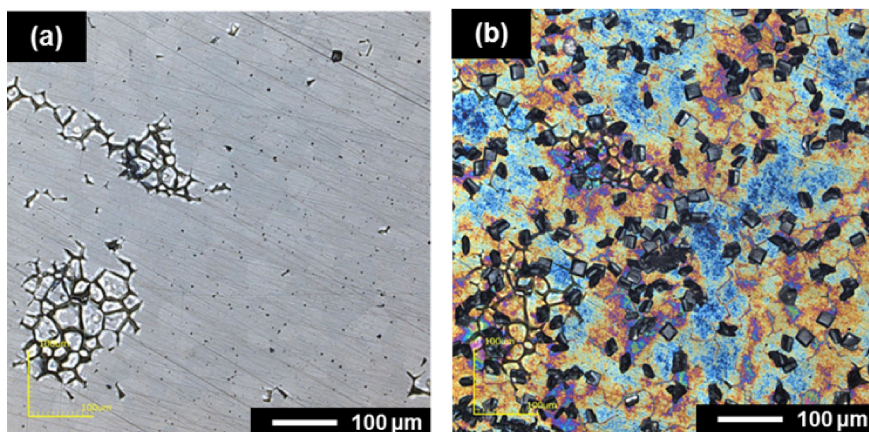


Fig. 4 Laser microscopy images of hematite tablet surface (a) before and (b) after reacting for 60 min (taken from Ref. 19), with revisions).

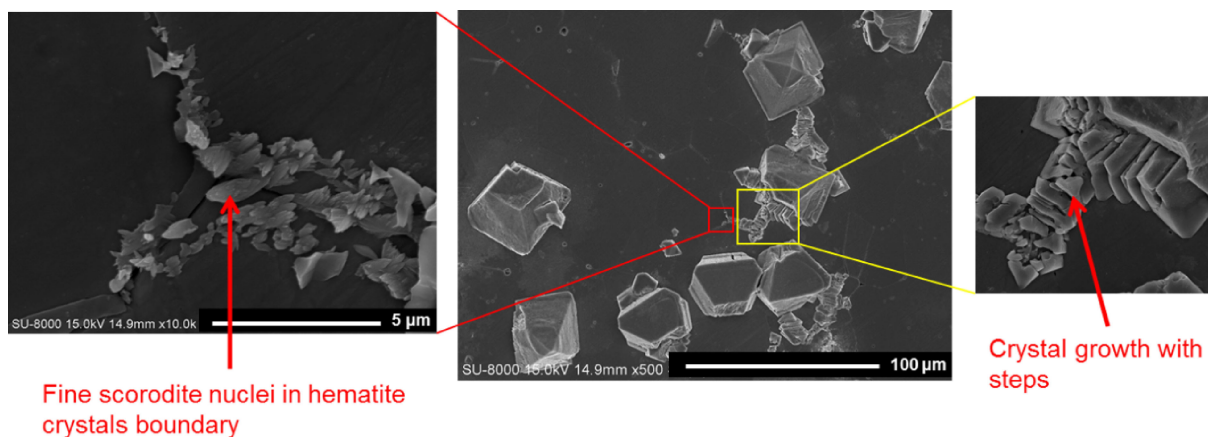


Fig. 5 SEM images of hematite tablet surface after scorodite synthesis for 180 min (taken from Refs. 19) and 20), with revisions).

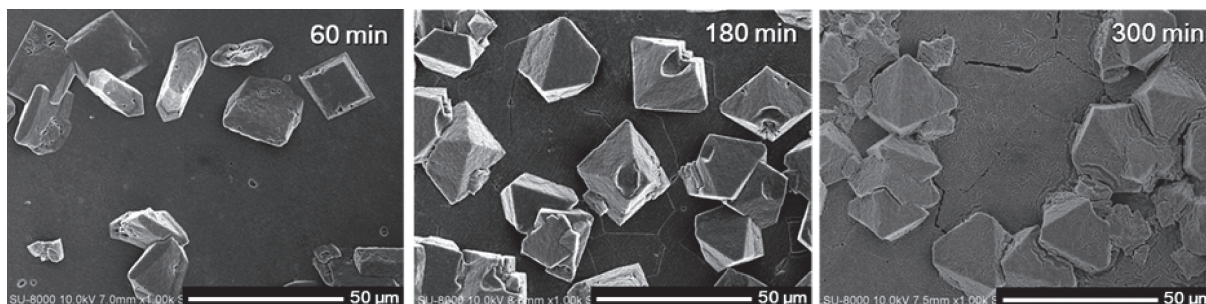


Fig. 6 SEM images of hematite tablet surface at different reaction times (60–300 min) (taken from Ref. 21), with revisions).

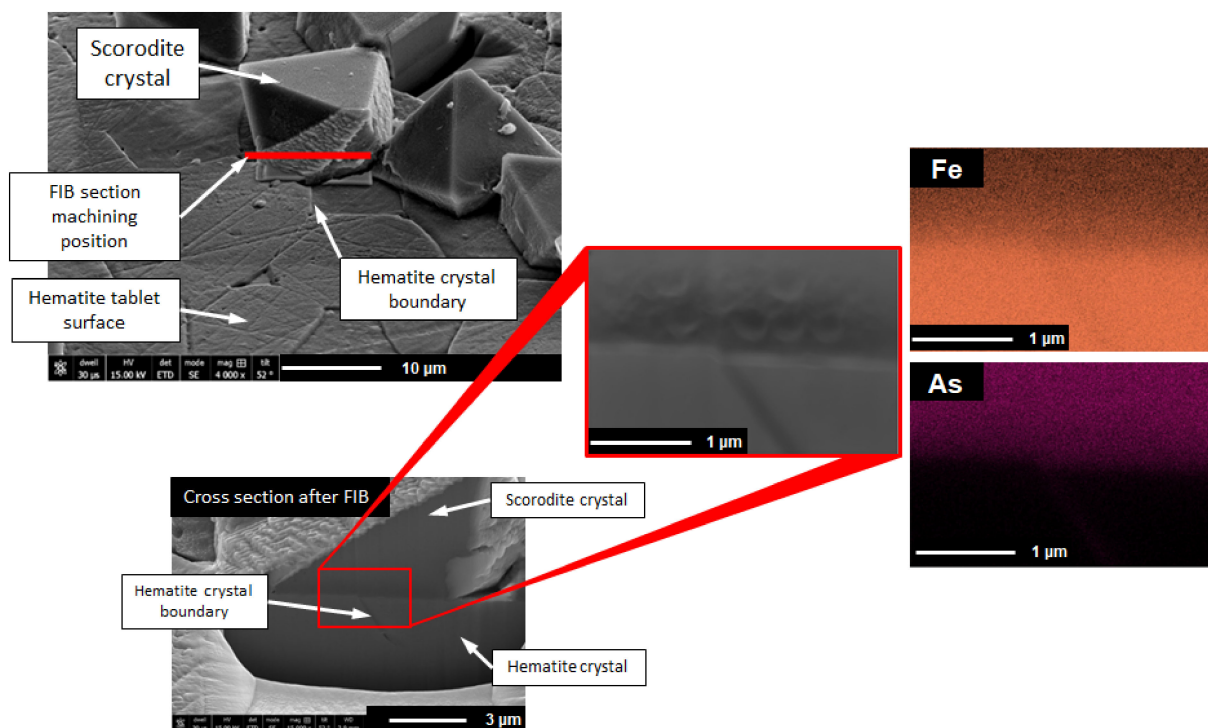


Fig. 7 SEM-EDX images of interface between hematite crystal boundary and generated scorodite crystal after reaction for 180 min (taken from Ref. 21), with revisions).

resolution, no intermediate layer was observed at the interface and having Fe or As concentrations that differed from those of the scorodite and hematite layers.

### 3.2 Effect of solution temperature on scorodite crystal formation

Scorodite synthesis experiments were performed at 50, 70, and 95°C to investigate the effects of solution temperature on scorodite crystal formation. The other experimental conditions were as follows: As concentration, 50 g/L; Fe concentration, 55.9 g/L; and pH 1.6. The initial oxidation–reduction potential (ORP) values at 50, 70, and 95°C were 135, 98.8, and 72.3 mV (vs. Ag/AgCl electrode), respectively. Figure 8 shows SEM images of scorodite crystals synthesized by reacting at each temperature for 420 min. The scorodite crystals synthesized at 95°C were octahedral faceted crystals with diameters of <math><20\ \mu\text{m}</math>. The gel-like precursor was still observed after 420 min. The change in solution composition during the scorodite formation experiments was considered negligible because the amount of

scorodite generated was very small when considering the excess of Fe(II) solution containing As(V), resulting in continuous formation of the gel-like precursor. The rate of scorodite crystal formation decreased with decreasing temperature. At 70°C, octahedral faceted scorodite crystals were also obtained after 420 min. The amount of gel-like precursor observed at this temperature was smaller than that observed at 95°C throughout the reaction period, while gel-like precursors were rarely observed at 420 min (observed only at the edge of scorodite crystals connecting the hematite surface). However, at 50°C, scorodite crystal growth was low after 420 min and XRD peaks assigned to scorodite were weak, as shown in Fig. 9. No gel-like precursor was observed throughout the reaction period at 50°C. The formation of octahedral faceted scorodite crystals was confirmed at 50°C when the reaction was continued for up to 98 h (data not shown).

These results showed that reaction temperature affected the scorodite crystal formation rate, but not the crystal shape, in the studied range of 50–95°C.



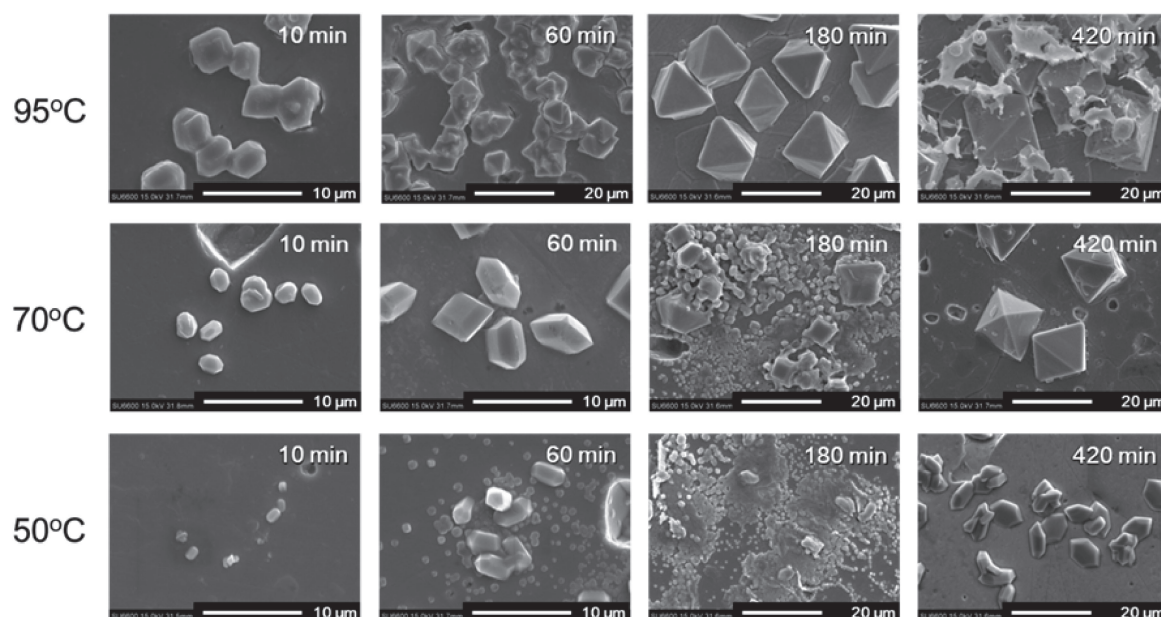


Fig. 8 SEM images of scorodite crystals synthesized at different reaction temperatures (taken from Ref. 22), with revisions).

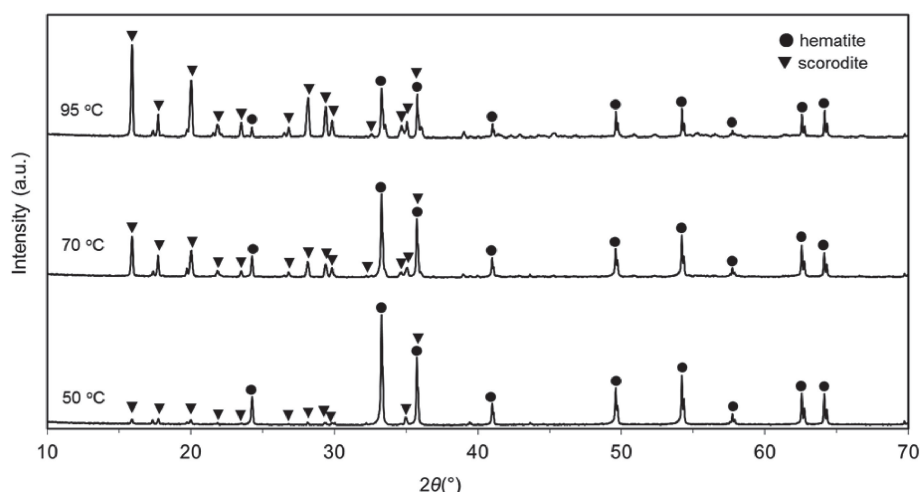


Fig. 9 XRD patterns of hematite tablet surfaces reacted at different temperatures for 420 min.

### 3.3 Effect of initial solution pH

Scorodite synthesis experiments were performed at solution pH values of 0.6, 0.9, and 1.6 to investigate the effect of pH on scorodite crystal formation. The other experimental conditions were as follows: As concentration, 50 g/L; Fe concentration, 55.9 g/L; and 95°C. The initial ORP values at solution pH values of 0.6, 0.9, and 1.6 were 249, 203, and 72.3 mV (vs. Ag/AgCl electrode), respectively.

Figure 10 shows SEM images of scorodite crystals synthesized in solutions with different pH values. As mentioned in Section 3.2, the scorodite synthesized at pH 1.6 for 420 min formed octahedral faceted crystals with diameters of <math><20\ \mu\text{m}</math>. When the solution pH was 0.9, faceted scorodite crystals were also obtained, but the crystal formation rate was low. At pH 0.6, no obvious faceted scorodite crystals were obtained, even after 420 min and no XRD peaks were assigned to scorodite (Fig. 11). This was confirmed by SEM–EDX. Several hollow particles (diameters of around 2  $\mu\text{m}$ ) were observed in the SEM image after

reaction at pH 0.6 for 180 min, which were attributed to carbonaceous impurities originally present in the hematite tablet.

These results confirmed that solution pH strongly affected scorodite crystal formation. A higher pH was preferable for scorodite formation in the studied range of pH 0.6–1.6. This was attributed to changes in the concentrations of ionic species from  $\text{H}_3\text{AsO}_4$  in the reaction solution and the  $\text{AsO}_4^{3-}$  content decreasing with decreasing pH.  $\text{AsO}_4^{3-}$  in solution is considered to initially be taken up to form the gel-like precursor and then converted into crystalline scorodite, so pH affects the formation of the gel-like precursor. A more detailed investigation is needed to clarify the mechanism of the effect of solution pH on the complex scorodite crystal formation process.

### 3.4 Effect of initial Fe(II) concentration

Scorodite synthesis experiments were performed at Fe(II) concentrations of 0, 25, and 55.9 g/L (corresponding to

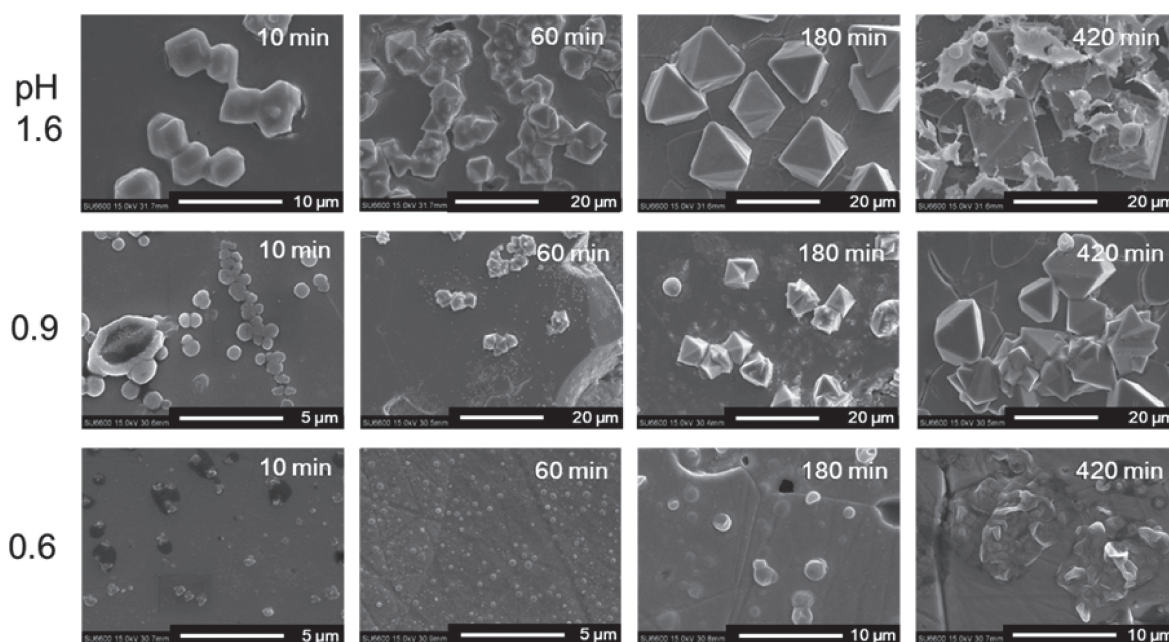


Fig. 10 SEM images of scorodite crystals synthesized at different solution pH values.

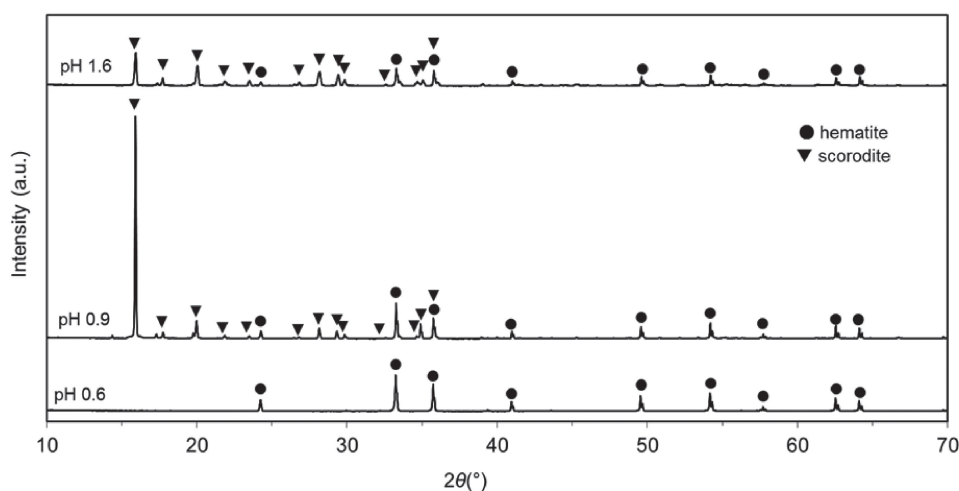


Fig. 11 XRD patterns of hematite tablet surfaces reacted at different solution pH values for 420 min.

0, 0.448, and 1.00 mol/L of Fe, respectively) to investigate the effects of Fe(II) concentration on scorodite crystal formation. The other experimental conditions were as follows: As concentration, 50 g/L; pH 1.6; and 95°C. The initial ORP values at Fe(II) concentrations of 0, 25, and 55.9 g/L were 513, 96.5, and 72.3 mV (vs. Ag/AgCl electrode), respectively.

Figure 12 shows SEM images of scorodite crystals synthesized at different Fe(II) concentrations. Under the standard conditions at an Fe(II) concentration of 55.9 g/L, the synthesized scorodite obtained after reacting for 420 min consisted of octahedral faceted crystals with diameters of <math><20\ \mu\text{m}</math>. In this case, membrane-shaped gel-like precursors were observed on the scorodite crystals, even after 420 min. When the Fe(II) concentration was 25 g/L, faceted scorodite crystals were also obtained. Gel-like precursor covering the scorodite crystal surface was also observed after 420 min. At an Fe(II) concentration of 0 g/L, amorphous iron arsenate particles were observed after 180 min and small leaf-shaped

crystals containing arsenic were observed after 420 min. The chemical form of the generated crystals could not be determined from the XRD pattern, as shown in Fig. 13. SEM-EDX analysis confirmed that the hollow particles (diameters of around 2  $\mu\text{m}$ ) observed in the SEM image from an Fe(II) concentration of 0 g/L after 60 min were carbonaceous impurities.

These results confirmed that the Fe(II) concentration in the reaction solution affected the gel-like precursor generation rate and octahedral faceted scorodite crystals were obtained at a low Fe(II) concentration (25 g/L). No gel-like precursor or scorodite crystals were obtained without Fe(II) in the reaction solution.

### 3.5 Effect of initial As concentration

Scorodite synthesis experiments were performed with As(V) concentrations of 25 and 50 g/L (corresponding to 0.33 and 0.67 mol/L of As, respectively) to investigate the effects of As(V) concentration on scorodite crystal formation.



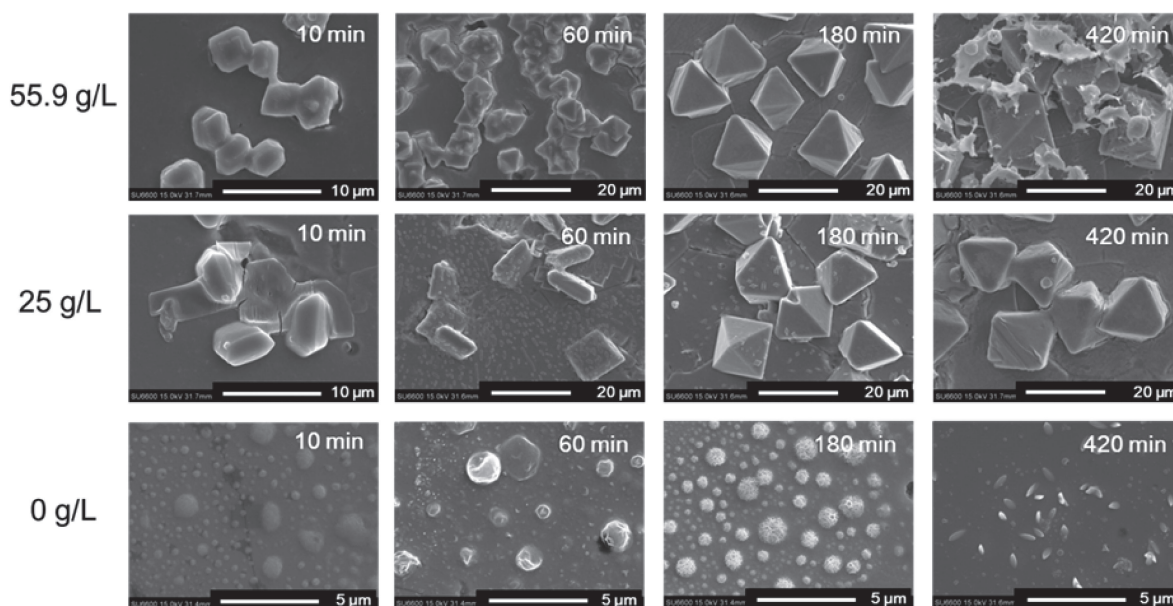


Fig. 12 SEM images of scorodite crystals synthesized at different Fe(II) concentrations.

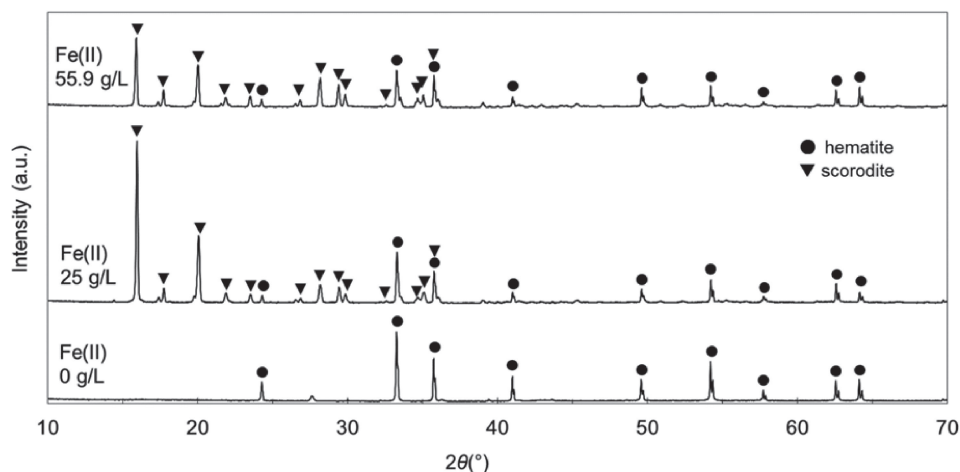


Fig. 13 XRD patterns of hematite tablet surfaces reacted at different Fe(II) concentrations for 420 min.

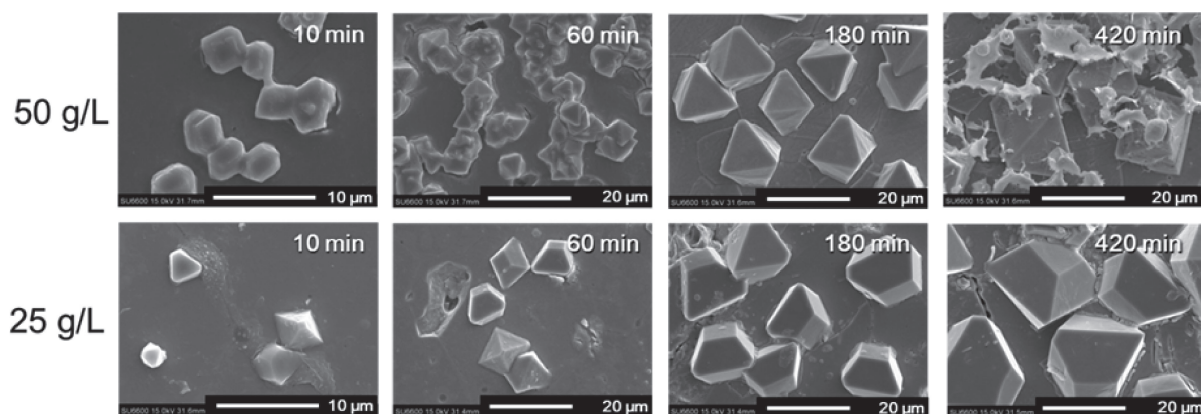


Fig. 14 SEM images of scorodite crystals synthesized at different As(V) concentrations.

The other experimental conditions were as follows: Fe concentration, 55.9 g/L; pH 1.6; and 95°C. The initial ORP values at As(V) concentrations of 25 and 50 g/L were 94.1 and 72.3 mV (vs. Ag/AgCl electrode), respectively.

Figure 14 shows SEM images of scorodite crystals synthesized at different As(V) concentrations. The scorodite obtained under the standard conditions at an As(V) concentration of 50 g/L after reacting for 420 min formed

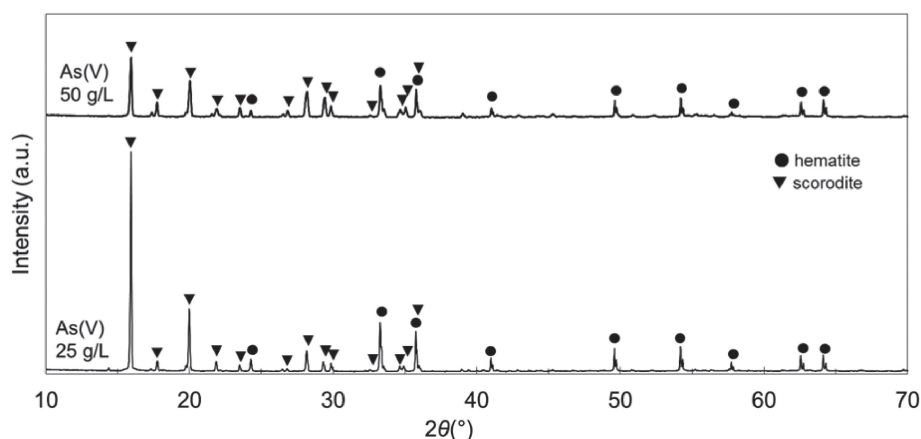


Fig. 15 XRD patterns of hematite tablet surfaces reacted at different As(V) concentrations for 420 min.

octahedral faceted crystals with diameters of  $<20\ \mu\text{m}$ . Even when the As(V) concentration was 25 g/L, faceted scorodite crystal growth was observed; however, even after 420 min, a perfect octahedral shape was not achieved. Furthermore, the diameter of the obtained crystals was greater than  $20\ \mu\text{m}$ . The XRD patterns in Fig. 15 indicate that the crystallinity of the scorodite crystals formed at an As(V) concentration of 25 g/L was higher than that of crystals formed at 50 g/L.

These results showed that the As(V) concentration in the reaction solution affected the overall scorodite formation rate. Imperfect octahedral-shaped scorodite crystals with a larger diameter were obtained at a lower As(V) concentration in solution (25 g/L). As discussed in Section 3.3, the solution As(V) concentration could affect gel-like precursor formation. A more detailed investigation is needed to clarify the effect of solution As(V) concentration on the complex scorodite crystal formation process.

#### 4. Conclusions

In this study, scorodite crystal formation on a hematite ( $\text{Fe}_2\text{O}_3$ ) surface, as a solid Fe(III) source, in excess Fe(II) solution containing As(V) was observed under various conditions.

The results confirmed that a gel-like precursor initially formed and covered the entire hematite surface. Nuclei of scorodite crystals then appeared on the grain boundaries of each hematite crystal preferentially over the flat surface of hematite crystals. The nuclei grew to give faceted crystalline scorodite particles through stepwise structure formation.

The effects of solution temperature (50, 70, and  $95^\circ\text{C}$ ), initial solution pH (0.6, 0.9, and 1.6), initial Fe(II) concentration (0, 25, and 55.9 g/L), and initial As concentration (25 and 50 g/L) on gel-like precursor and scorodite crystal formation were comprehensively investigated.

The reaction temperature only affected the scorodite crystal formation rate and not the crystal shape in the studied range of  $50\text{--}95^\circ\text{C}$ . Octahedral faceted scorodite was obtained at all temperatures studied. Solution pH strongly affected scorodite crystal formation, with a higher pH preferable for scorodite formation in the studied range of pH 0.6 to 1.6. No obvious faceted scorodite crystals were obtained at a solution pH of 0.6. Octahedral faceted scorodite crystals were obtained even

at a lower Fe(II) concentration (25 g/L). Only amorphous iron arsenate particles and small leaf-shaped crystals containing arsenic were observed when Fe(II) was not present in the reaction solution.

The As(V) concentration in the reaction solution affected the overall scorodite formation rate. Imperfect octahedral-shaped scorodite crystals with a larger diameter were obtained at a lower As(V) concentration in solution (25 g/L). Further investigations are needed to clarify the complex formation mechanisms of the gel-like precursor and scorodite crystal in the direct hematite addition method. This study provides important information for using this method to form crystalline scorodite through As treatment.

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