Stabilization of arsenic by precipitation of large crystalline scorodite (FeAsO$_4$·2H$_2$O) particles is considered to be a promising option for treating As(V) contained in industrial by-products. In this study, scorodite synthesis by direct addition of hematite particles as a Fe(III) source to Fe(II) solution containing As(V) was investigated with different initial Fe(II) concentrations. During scorodite formation, the Fe(II) concentration and pH of the reaction solution are almost constant, and the residual arsenic concentration in the solution is low. The initial Fe(II) concentration strongly affects scorodite formation, and larger faceted crystalline scorodite particles are obtained with higher initial Fe(II) concentration. The observed scorodite particle size is larger than that formed by the conventional DMSP method. Coarse faceted scorodite can also be obtained by direct addition of hematite powder to FeSO$_4$ solution with As(V). From the results of environmental leaching tests, O$_2$ gas blowing for a short time to convert the remaining unstable gel-like precursor to crystalline scorodite is very effective to prevent arsenic leaching. Furthermore, for the gel-like precursor formed in the initial stage of the scorodite synthesis process, chemical state analysis by X-ray absorption spectroscopy in the range of the X-ray absorption near-edge structure at the Fe K absorption edge for iron reveals that the precursor contains Fe(II) as well as Fe(III). This indicates that scorodite does not directly form from Fe(II) ions from hematite and arsenate ions from solution, but a gel-like precursor initially forms from Fe(II) ions in solution and is then converted to crystalline scorodite.

Keywords: scorodite, arsenic, hematite, gel-like precursor

1. Introduction

Pentavalent arsenic (As(V)) removal and stabilization by formation of crystalline scorodite (FeAsO$_4$·2H$_2$O) is considered to be promising for treating As(V) contained in industrial by-products, such as fly ash from non-ferrous smelters. The degree of As dissolution from large crystalline scorodite particles is small,\textsuperscript{1,11} which can minimize the environmental impact of As. Conversion of arsenic to scorodite requires an autoclave reactor that can be operated under pressurized oxidation conditions and temperatures above 100°C.\textsuperscript{2,3,10}

To avoid the use of an expensive autoclave reaction system, Dowa Metals and Mining Co., Ltd. developed a new method for producing large crystalline scorodite particles with improved filtration and washability properties under normal atmospheric pressure and at temperatures below 100°C.\textsuperscript{4-10} This process was trademarked as the Dowa Mining Scorodite Process (DMSP). In this method, oxygen gas (O$_2$) is blown into a solution containing a high concentration of As(V) and ferrous (Fe(II)) ions at 95°C. The Fe(II) ions are oxidized to ferric ions (Fe(III)), resulting in formation of large scorodite particles (median diameter of 20.7 µm).\textsuperscript{9} The reactions in the process can be expressed as follows:

\[
\text{Oxidation of } \text{Fe}^{2+} \text{ by } O_2 \text{ blowing:} \\
\text{Fe}^{2+} + H^+ + \frac{1}{4} O_2(g) \rightarrow \text{Fe}^{3+} + \frac{1}{2} H_2O(l) \quad (1)
\]

Subsequent scorodite precipitation:

\[
\text{Subsequent scorodite precipitation:} \\
\text{Fe}^{3+} + H_2\text{AsO}_4^- + 2H_2O(l) \rightarrow \text{FeAsO}_4\cdot2H_2O(s) + 3H^+ \quad (2)
\]

Thus, the overall reaction formula is

\[
\text{Fe}^{2+} + H_2\text{AsO}_4^- + \frac{1}{4} O_2(g) + \frac{3}{2} H_2O(l) \rightarrow \text{FeAsO}_4\cdot2H_2O(s) + 2H^+ \quad (3)
\]

In the DMSP method, during scorodite formation, a membrane-type (gel-like) substance containing iron arsenate forms as a precursor of faceted crystalline scorodite particles. The faceted crystalline scorodite particles grow by conversion of the gel-like precursor. The gel-like precursor is consumed and is not observed in latter stage of scorodite formation. Shinoda et al.\textsuperscript{11} analyzed the chemical state of iron in the gel-like precursor by X-ray absorption near-edge structure (XANES) spectroscopy at the Fe K absorption edge. According to their results, the gel-like precursor mainly consists of Fe(II) with a small amount of Fe(III). This indicates that the scorodite particles form from the gel-like precursor containing Fe(II), although the detailed mechanism of conversion of the gel-like precursor to scorodite particles is still unclear. Thus, it is considered that conversion of Fe(II) to Fe(III) is not essential, and direct addition of Fe(III) to As(V)-containing FeSO$_4$ solution will also result in formation of faceted crystalline scorodite particles.

The scorodite formation process by direct addition of Fe$_2$(SO$_4$)$_3$ solution as a Fe(III) source to As(V)-containing FeSO$_4$ solution has been investigated.\textsuperscript{12-14} The influence of the initial Fe(II) ion concentration on scorodite formation was also investigated in these studies. The overall scorodite formation reaction in the process can be expressed as follows:

\[
\text{Subsequent scorodite precipitation:} \\
\text{Fe}^{3+} + H_2\text{AsO}_4^- + 2H_2O(l) \rightarrow \text{FeAsO}_4\cdot2H_2O(s) + 3H^+ \quad (4)
\]

The results indicated that formation of scorodite particles is rather slow for a solution without Fe(II) ions, and resulted in formation of cauliflower-shaped aggregates of small scorodite particles. In addition, the gel-like precursor was not observed for a solution without Fe(II) ions. The size of the scorodite

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particles increased with increasing initial Fe(II) concentration, together with formation of a gel-like precursor. The initial Fe(II) concentration of 75 g/L favored formation of large well-faceted scorodite particles. Thus, a high initial Fe(II) concentration is necessary to produce a gel-like precursor and direct addition of Fe(III) also results in conversion of the precursor to faceted scorodite crystalline particles.

2.1 Materials

Laboratory Co. Ltd. (Sakado, Saitama, Japan) were used. The chemical reagents were purchased from Kojundo Chemical Industries, Ltd. (Osaka, Japan). For the standard materials for the XAS measurements, scorodite synthesized by the DMSP method and hematite obtained from Kojundo Chemical Laboratory Co. Ltd. (Sakado, Saitama, Japan) were used.

2.2 Methods

The apparatus for scorodite synthesis consisted of a Pyrex flask with capacity 1 L equipped with a condenser, a glass tube for the gas inlet, and a pH/oxidation–reduction potential (ORP) electrode. In a typical experiment, 720 mL of the reaction solution was agitated by polytetrafluoroethylene turbine blades driven by a stirring motor. During the process, the reaction solution in the flask was heated by a mantle heater. The temperature was controlled at 95°C, as measured by a K-type thermocouple. The experiments were performed under an Ar atmosphere to prevent oxidation of Fe(II) ions during the heating process. The initial concentration of As(V) in the solution was set to 50 g/L (0.67 mol/L), while the initial content of Fe(II) in the solution was varied from 0 to 55 g/L (0 to 0.98 mol/L). There was a small amount of antimony (Sb) in the arsenic(V) acid used for preparation of the reaction solution as an impurity, which may affect synthesis of scorodite. The initial Sb concentration in the solution ranged from 84.3 to 164.2 mg/L. The determined amount of hematite powder (40.03 g) was added to 720 mL of the solution (0.69 mol/L. Fe(III)) at 95°C under Ar blowing at 700 mL/min with constant stirring at 1000 rpm by a Teflon propeller (reaction time = 60 min). Thus, the molar ratio of Fe(III) to As in the reaction system is 1.04 (0.69/0.67) for all of conditions studied, which it is more than the stoichiometric amount of Fe(III) needed for scorodite (FeAsO4·2H2O) synthesis. The pH and ORP of the solution were continuously measured during the reaction by the pH/ORP electrode. The total reaction time was set to 420 min, and sampling of the formed slurry was performed at 10 and 60 min.

The formed scorodite precipitate was separated by vacuum filtration of the sampled slurry using a membrane filter (cellulose acetate type, pore size 0.45 µm, q = 47 mm). The scorodite precipitate was washed several times with distilled water and then freeze-dried. The total Fe and As contents in the solution were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES, Spectro Arcos, Ametek Co. Ltd., Tokyo, Japan). The Fe(II) content in the solution was determined by redox titration using 0.02 M KMnO4 solution. The Fe(III) content in the solution was determined from the difference of total Fe concentration and the Fe(II) content. The crystallinity and structure of the as-formed scorodite samples were analyzed by X-ray diffraction (XRD, RINT2000, RIGAKU Corp., Akishima, Tokyo, Japan). In addition, the morphology of the particles was observed by scanning electron microscopy (SEM, S-U6600, Hitachi High-Technologies Corp., Tokyo, Japan)–energy-dispersive X-ray spectroscopy (EDX, X-act, Oxford Instruments Plc., Oxford, UK). The scorodite particle size was determined by a laser diffraction particle size analyzer (MT3000I, MicrotracBEL Corp.). The environmental testing latches of the generated scorodite particles were performed according to the procedure specified by the Japanese Environmental Ministry (1973).17

XAS at the Fe K absorption edge of the gel-like precursor formed in the early stage and scorodite crystals of the final product was performed to analyze the chemical state of iron. For the measurements, we used a solid powder sample obtained after the initial reaction stage (30 min) containing a
lot of gel-like precursor and a sample after the final reaction stage (420 min) containing crystalline scorodite (with a small amount of adhered gel-like precursor on the crystal surfaces) obtained with the initial concentrations of Fe(II) and As(V) in the solution of 55 and 50 g/L, respectively. The XAS experiments using synchrotron radiation were performed in transmission and conversion electron yield mode using a Si(111) double-crystal monochromator at beamline BL11 of the SAGA Light Source (Tosu, Japan). The sample powders for the XAS measurements in transmission mode were diluted with powdered boron nitrate and compressed to form a disk with a diameter of 10 mm. For the XAS measurements in conversion electron yield (CEY) mode, the sample powders were well crushed and homogeneously dispersed on a conductive layer. The XAS measurement in CEY mode is a more surface sensitive method, so it was expected that the difference between the surface and bulk compositions of the samples can be obtained from the results obtained in these two modes. The backgrounds of the measured spectra were subtracted and the spectra were then normalized using the absorbance calculated under the assumption that the Fe atoms are isolated. The presence of Fe(II) ions in the samples was determined from the energy position of the Fe K absorption edge in the XANES spectra.

3. Results and Discussion

3.1 Scorodite formation with different initial Fe(II) concentrations

Figure 1 shows the changes in the solution pH, ORP, and total arsenic, Fe(II), and Fe(III) concentrations with time after addition of hematite powder. Figure 2 shows SEM images of the scorodite particles generated with the different initial Fe(II) concentrations after 10, 60, and 420 min. Without Fe(II) in the reaction solution (initial Fe(II) concentration = 0 g/L), the scorodite formation rate is very slow and the final arsenic concentration is high. In the SEM images, hematite particles are observed even after 420 min and some small flakey scorodite crystals with sizes of about 1 µm are observed. This tendency is consistent with the Fe(III) solution addition method. With Fe(II) in the reaction solution (initial Fe(II) concentration = 5, 17, 34, and 55 g/L), a gel-like precursor with unreacted hematite is observed in the initial stage of the reaction, similar to the DMSP method. The final arsenic concentrations are lower than those for the DMSP method, which is because of the stable pH in the hematite addition method. The solution pH slightly increases in the late reaction stage because of removal of arsenic acid from the solution system owing to scorodite formation (eq. (5)). From the overall scorodite formation reaction (eq. (5)), the Fe(II) concentration in the reaction solution is almost constant. Larger particles of faceted scorodite are observed for higher initial Fe(II) concentration. This confirms that coarse faceted scorodite forms with hematite powder addition to the As(V)-containing FeSO₄ solution. However, a membrane-type (gel-like) precursor and residual hematite are observed on the surface of the formed faceted scorodite crystals even after 420 min, as shown in the Fig. 3. The presence of the precursor will be caused by the stable Fe(II) concentration and pH in the final stage of the reaction.

The reason for the remaining hematite is excess hematite addition (molar Fe(III)/As(V) ratio = 1.04) than the stoichiometric ratio of 1.0 for scorodite. Thus, hematite addition should be optimized to minimize the remaining hematite content.
Figure 4 shows the XRD pattern of the scorodite particles formed after 420 min with an initial Fe(II) concentration of 55 g/L. The result confirms formation of crystalline scorodite and residual hematite.

Table 1 summarizes the median particle diameters and specific surface areas of the particles after 420 min scorodite synthesis for different initial Fe(II) concentrations. Larger scorodite particles form for higher initial Fe(II) concentration,
concentrations in the leachate are 14.0 and 1.4 mg/L, respectively. The pH of the leachate is 3.7. This higher initial As concentration of 50 g/L and the pH is 3.1. The iron concentration in the leachate are 14.0 and 1.4 mg/L, respectively. The pH of the leachate is 3.7. This higher initial Fe(II) concentration of 34 and 55 g/L are 46 and 34 µm, respectively, which are larger than the median diameter for the DMSP method (20.7 µm).9)

Table 1 Median particle diameters and specific surface areas of the scorodite particles after 420 min scorodite synthesis with different initial Fe(II) concentrations.

<table>
<thead>
<tr>
<th>Initial solution</th>
<th>Median particle diameter after 420 min (µm)</th>
<th>Brunauer-Emmett-Teller specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V) concentration (g/L)</td>
<td>Fe(II) concentration (g/L)</td>
<td>pH (c)</td>
</tr>
<tr>
<td>50 g/L</td>
<td>4.53</td>
<td>12.3</td>
</tr>
<tr>
<td>17</td>
<td>1.61</td>
<td>21.6</td>
</tr>
<tr>
<td>34</td>
<td>1.74</td>
<td>24.6</td>
</tr>
<tr>
<td>55</td>
<td>1.79</td>
<td>24.0</td>
</tr>
</tbody>
</table>

which is consistent with the SEM results (Fig. 2). The median diameters of the scorodite particles for initial Fe(II) concentrations of 34 and 55 g/L are 46 and 34 µm, respectively, which are larger than the median diameter for the DMSP method (20.7 µm).9)

3.2 Leaching tests of the scorodite particles

For an initial Fe(II) concentration of 55 g/L and an initial As concentration of 50 g/L, the arsenic and iron concentrations in the leachate are 14.0 and 1.4 mg/L, respectively. The pH of the leachate is 3.7. This higher arsenic concentration in the leachate is because of arsenic leaching from the membrane-type (gel-like) precursor adhered to the scorodite crystal surfaces, as shown in Fig. 3. Final gas oxidation treatment to convert the precursor to crystalline scorodite is effective for preventing arsenic leaching from the remaining precursor. O₂ gas blowing into the reaction solution was performed for 1 h after 420 min reaction time with Ar blowing. The arsenic concentration in the leachate dramatically decreases to 0.21 mg/L. The iron concentration in the leachate is 34 mg/L and the pH is 3.1. From these results, O₂ gas blowing for a short period of time to convert the remaining unstable precursor to crystalline scorodite is very effective for preventing arsenic leaching from the remaining precursor.

3.3 XAS measurements

Figure 5 shows the normalized XANES spectra at the Fe K absorption edge obtained in transmission and CEY mode. From the results obtained in transmission mode (Fig. 5(a)), the position of the Fe K absorption edge for the solid sample obtained after the initial reaction stage (30 min) containing a lot of gel-like precursor is located in a lower energy region than the positions for hematite and scorodite (both contain Fe(III)). This shows that Fe(II) is contained in the gel-like precursor. The Fe K absorption edge position for the sample obtained after the final reaction stage (420 min) containing crystalline scorodite is located in the higher energy region and close to the position for scorodite. This indicates that the relative Fe(III) content increases. Fitting the measured Fe K XANES spectrum under the assumption that the final product consists of only the precursor and crystalline scorodite gives the best agreement in terms of the ratio of precursor to crystalline scorodite of 43:57. Although the presence and amount of unreacted hematite in the initial product sample (gel-like precursor) and final product (scorodite) should be taken into account for more accurate analysis, this confirms that gel-like precursor is contained in the final scorodite sample. In the surface-sensitive CEY mode (Fig. 5(b)), the Fe K XANES spectra for the initial (gel-like precursor) and final (scorodite) product samples are almost the same.

Figure 6 shows the radial structure functions (RSFs) calculated by Fourier transformation of the X-ray absorption fine-structure spectra at the Fe K absorption edge. The RSFs obtained from the transmission mode measurements indicate that the local structure near the Fe atom for the initial product sample (gel-like precursor) is close to amorphous with a small amount of unreacted residual hematite, and that for the final product sample (scorodite) is close to the scorodite structure (Fig. 6(a)). The RSFs obtained from the X-ray absorption fine-structure spectra in CEY mode are slightly different from those in transmission mode in the second nearest neighbor region (Fig. 6(b)). The RSF profiles for the initial and final samples can be explained by the samples being a mixture of Fe(II)-containing amorphous solid (gel-like precursor) and Fe(III) crystalline compounds, which are hematite and scorodite, respectively. From the absorption edge position, the ratios of Fe(II) to Fe(III) are similar. However, more detailed investigation with different reaction products is needed.

From the results, the gel-like precursor includes Fe(II) and the chemical state of Fe is different on the surface and inside the product. This indicates that a gel-like precursor first forms from Fe(II) ions in solution and is then converted to crystalline scorodite rather than scorodite directly forming from Fe(III) ions from hematite and arsenate ions from solution. Considering the fact that the Fe(II) concentration in the reaction solution is constant during scorodite formation, the same amount of Fe(II) consumed by gel-like precursor formation must be compensated for by Fe(II) release from the gel-like precursor accompanied by conversion to scorodite crystals or Fe(II) release from unreacted hematite with iron reduction (Fe(III) to Fe(II)). However, further investigation of the behaviour of the Fe(II) and Fe(III) ions during scorodite crystal formation is required. This information about the chemical state and local structure is important to understand the reaction mechanisms of arsenic stabilization and arsenic separation from water.

4. Conclusions

We have investigated crystalline scorodite synthesis by direct addition of hematite particles as a Fe(III) source to As(V)-containing FeSO₄ solutions with different initial
Fe(II) concentrations. During scorodite formation, the Fe(II) concentration and solution pH are almost constant, and the residual arsenic concentration in the solution is low. The initial Fe(II) concentration strongly affects scorodite synthesis, and larger faceted scorodite particles form with higher initial Fe(II) concentration. The observed scorodite particle size is larger than that obtained by the conventional DMSP method. Coarse faceted scorodite can also be formed by hematite powder addition to As(V)-containing FeSO$_4$ solution. From the results of leaching tests, O$_2$ gas blowing for a short period of time to convert the remaining unstable gel-like precursor to crystalline scorodite is very effective to prevent arsenic leaching. XAS in the range of the XANES was performed for the gel-like precursor formed in the initial stage of the reaction. The results reveal that the gel-like precursor is composed of Fe(II) and Fe(III). This indicates that scorodite does not directly form from Fe(III) ions from hematite and arsenate ions from solution, but a gel-like precursor initially forms from Fe(II) ions in solution and is then converted to scorodite crystals. This information about the chemical state and local structure is very important to understand the reaction mechanisms of arsenic stabilization and arsenic separation from water.

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