Coprecipitation of Large Scorodite Particles from Aqueous Fe(II) and As(V) Solution by Oxygen Injection

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A novel method for synthesizing large scorodite (FeAsO₄·2H₂O) particles was recently developed for the fixation of arsenic. This method involves the coprecipitation of scorodite particles from an Fe(II) and As(V) aqueous solution at approximately 95 °C by oxygen injection. In order to understand the process of coprecipitation of scorodite particles by this method, X-ray diffractometry (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were used for characterizing reaction products extracted from the suspension during the reaction. The SEM observation showed that the formation of large scorodite particles was almost completed after a reaction time of 3 h, and then, fine particles precipitated on the large particles by further reactions. The XRD results indicated that scorodite particles with specific lattice parameters were formed in the reaction. The XPS results indicated that the arsenic composition on the surface of the scorodite particles decreased until 3 h from the start of precipitation reaction and increased thereafter. These results correspond to the results on the morphology of the scorodite particles obtained by SEM. Furthermore, X-ray absorption spectra (XAS) in the range of X-ray absorption near edge structure (XANES) were measured for gel-like reaction products formed in the initial stages of the reaction. The spectra revealed that the gel-like reaction products were composed of Fe(II) and Fe(III). The coprecipitation of scorodite particles synthesized by the novel method is discussed on the basis of these results together with previous results on the analyses of iron and arsenic concentrations in solution.


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1. Introduction

Elements such as arsenic (As), antimony (Sb), bismuth (Bi), tellurium (Te), and selenium (Se) are major impurity elements in nonferrous metal ores. Although these elements are produced as byproducts in nonferrous metal processes, typically copper smelting, As is particularly required to be immobilized as a stable compound. This is because As is toxic to animals and plants. Among a large number of As compounds, ferric sulfate compounds containing arsenate, such as jarosite (MFe₃(SO₄)₂(OH)₆, M = H₃O⁺, Na⁺, K⁺, Ag⁺, NH₄⁺, etc.), and ferric arsenate compounds such as scorodite (FeAsO₄·2H₂O) appear to be the most effective compounds for the immobilization or disposal of As. Thus far, several studies have been conducted on the solubility and stability of ferric arsenate compounds in water¹⁻⁵ and on the dissolution of As from ferric arsenate compounds.⁶⁻⁷ Fundamental studies on E-pH diagrams of arsenic relevant systems⁸ and experimental studies on adsorption characteristics of arsenate on ferric compounds⁹⁻¹⁵ have also been conducted. These studies show that the chemical and physical properties of As, such as solubility and adsorption, strongly depend on the structure and morphology of ferric arsenate compounds, which may be controlled by their synthesis routes. For instance, it has been reported that different solubilities of As were obtained for different scorodite particles.¹,⁴

In order to synthesize stable ferric arsenate compounds, precipitation processes of scorodite in water have been investigated by examining the precipitates and analyzing the solution.¹⁶⁻¹⁹ In these studies, scorodite particles were precipitated by reacting Fe(III) with As(V) in water; it should be noted that the solution conditions in these studies were different in each study. In the coprecipitation of scorodite, the following reaction is considered to occur:

$$\text{Fe(III)} + \text{H}_3\text{AsO}_4 + \text{2H}_2\text{O} \rightarrow \text{Fe(III)AsO}_4\cdot\text{2H}_2\text{O(s)} + 3\text{H}^+$$  (1)

The size of scorodite particles formed by this reaction is typically in the range of sub-micrometers due to the very high precipitation reaction rate. Therefore, the dissolution level of As in water appears to be relatively high. Furthermore, the fine particles form aggregates with low dewaterability.

On the other hand, it has been recently found that large scorodite particles coprecipitate through the oxidation of aqueous Fe(II) and As(V) solution.¹⁻²² The coprecipitation occurs when an oxidizing gas such as oxygen and air is injected into the aqueous solution by the novel method. The diameter of scorodite particles synthesized under these conditions is over 10 μm, which is much larger than the size of scorodite particles obtained from Fe(III) and As(V) solution. Because the surface of scorodite particles appears to be flat, the concentration of As dissolved from these particles in aqueous solution is relatively less than that dissolved from particles obtained from the Fe(III) and As(V) solution. These characteristics of scorodite particles synthesized by the novel method are advantageous to the disposal and storage of As. In this process, coprecipitation of scorodite particles occurs at approximately 95 °C as follows:

$$4\text{H}_3\text{AsO}_4 + 4\text{Fe(II)SO}_4 + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe(III)AsO}_4\cdot\text{2H}_2\text{O(s)} + 4\text{H}_2\text{SO}_4$$  (2)

The advantages of this reaction are that it does not require hydrothermal processes, and it can be carried out under atmospheric conditions.

Therefore, the novel scorodite synthesis process in which the coprecipitation rate is controlled by regulating the rate of oxidation of Fe(II) to Fe(III) is promising for the primary
fixation of As in the solution, since scorodite particles synthesized by this method appear to be well crystallized and stable. In order to carry out this process, it is important to understand the coprecipitation of scorodite particles using the crystal structure and surface composition analyses. In this study, scanning electron microscopy (SEM), X-ray diffractometry (XRD), and X-ray photoelectron spectroscopy (XPS) were used for characterizing products extracted from the suspension during the reaction. X-ray absorption spectroscopy (XAS) in the range of X-ray absorption near edge structure (XANES) spectra of the products during the reaction was also used for analyzing the chemical state of iron in the products. In this paper, the coprecipitation of scorodite particles is discussed on the basis of these results and those obtained by analyses of iron and As in the aqueous solution obtained from the previous studies.

2. Experimental

2.1 Sample preparation

Solid particles, which are later identified as scorodite particles, were synthesized by injecting oxygen into an aqueous solution containing As(V) and Fe(II) ions at approximately 95°C following the previous method.21) Aqueous As(V) solution derived from the purification and concentration of waste containing arsenic compounds from refinery was used for the synthesis of scorodite particles. The procedure is briefly described as follows. First, a 0.7 L of reaction solution, in which concentration of As(V) was 50 g/L and Fe/As molar ratio was 1.5, was prepared in a beaker by adding Fe(II) sulfate hexahydrate to the As(V) solution. The solution was heated and stirred at 200 rpm till it attained the reaction temperature. Next, O2 gas was injected into the solution, which was stirred by a propeller at 1000 rpm. This process produced a suspension containing solid particles coprecipitated in the solution. A part of the suspension was sampled from the beaker after a given reaction time, and the suspension was filtered through a membrane at 0.4 MPa to separate the solid particles. Finally, the solid particles were rinsed with distilled water, pressure filtered, and dried. The pH value of the reaction solution was varied from 1.02 at before O2 gas injection to 0 after 1 h of reaction time, and no significant change of pH was observed thereafter.

In order to compare the structure of solid particles synthesized by the above method with that of solid particles synthesized using As(V) and Fe(III) solution, a conventional method was used for preparing the solid particles from aqueous solution containing As(V) and Fe(III) in an autoclave as reactor.19)

2.2 Measurements

The crystalline components of the solid particles prepared by the above method were identified by the powder XRD. The apparatus used in this study was Rigaku RINT2000, in which Cu Kα radiation was used. The lattice parameters of the samples were estimated from the positions of peaks in the diffraction patterns by using the algorithm developed by Pawley.23) SEM observation was also performed by using a Hitachi S-4100L electron microscope in order to characterize the morphology of the solid particles.

In order to determine the molar ratio of As to Fe on the surface of the solid particles, Fe 2p and As 3d XPS spectra were measured using an XPS apparatus PHI 5600. The Mg Kα radiation served as the incident X-ray, and the take-off angle of emitted photoelectron was 45°. The molar ratio of As to Fe was estimated from their spectral intensities coupled with their sensitivity factors.

The XAS spectra of the solid particles at the Fe K absorption edge were measured using a Rigaku R-XAS Looper24) in order to analyze the chemical state of iron. In these measurements, white X-ray radiation from a Mo anode, generated by applying a tube voltage and current of 14 kV and 100 mA (1.4 kW), respectively, was monochromized by using a Si(400) Johansson-type bent single crystal and irradiated on to the sample. Sample powders for XAS measurement were diluted with powdered boron nitrate and compressed to form a disk 20 mm in diameter. In the case of measurements of a gel-like sample extracted from the reaction suspension at an early stage of the precipitation process, the undried gel-like sample was filled in a punched hole of 20 mm in diameter in a sample holder comprising an acrylic plate, and covered by a kapton film serving as an X-ray path window. Backgrounds of the measured spectra were subtracted, and then, the spectra were normalized using absorbance calculated under the assumption that the Fe atoms were isolated. The presence of Fe(II) ions in the samples was examined from the energy position of the Fe K absorption edge in the XANES spectra.

3. Results and Discussion

3.1 Morphology of solid particles

Figure 1 shows SEM images of solid particles extracted from the suspension oxidized for 1, 3, 5, and 9 h at different magnifications. The shape of the solid particles coprecipitated from the suspension oxidized for 1 h was polyhedral, and their diameter was approximately 10 μm, as shown in Figs. 1(a) and 1(b). Although the surface of the particles was almost flat, secondary micrometer-sized particles were formed on the surfaces of the primary solid particles. In the case of solid particles obtained from the suspension oxidized for 3 h, as shown in Figs. 1(c) and 1(d), the fundamental shapes of the primary and secondary particles were also polyhedral; however, submicron-sized particles precipitated on their surfaces.

Fine particles less than 100 nm in diameter coprecipitated on the primary 10-μm, secondary micron-sized, and submicron-sized particles’ surfaces when the reaction occurred for 5 h, as shown in Figs. 1(e) and 1(f). Finally, the surfaces of relatively large particles were almost completely covered with such fine particles when the reaction occurred for 9 h, as shown in Figs. 1(g) and 1(h). Thus, the SEM results revealed that the hierarchical formation of the primary 10-μm and secondary micron-sized solid particles is likely to occur during the reaction for 3 h, and submicron-sized or much finer particles are subsequently formed on the surface of the primary particles. However, the major solid particles coprecipitated in the aqueous solution are regarded as primary solid particles because the volume fraction of small and fine precipitates is relatively small.
3.2 Structure of solid particles

The X-ray powder diffraction method was used for identifying the crystalline phase and analyzing the lattice parameters of the solid particles synthesized by the above-mentioned method. Figures 2(a) and 2(b) show the XRD patterns of the solid particles formed by reaction for 1 and 9 h, respectively. For comparison, the XRD pattern of solid particles synthesized from aqueous As(V) and Fe(III) solution at 175°C using an autoclave is shown in Fig. 2(c). The solid particles were identified as scorodite particles since all the diffraction peaks correspond to those of scorodite. However, small differences in these diffraction patterns were found between scorodite particles coprecipitated by the conventional process and those coprecipitated by the novel reaction process. The crystal structure of scorodite is orthorhombic, Pcab. Figure 3 shows the XRD patterns in the range of scattering angle, 2θ, including 200, 020, and 002 diffraction peaks, whose positions are directly related to the lattice constants a, b, and c. The differences in the peak positions indicate that the lattice constants of these scorodite...
particles changed depending on the reaction conditions, although the fundamental structure of these scorodite particles was orthorhombic. The lattice constants $a$, $b$, and $c$ of scorodite synthesized by the novel method from the As(V) and Fe(II) solution under ambient atmospheric conditions are listed in Table 1, along with the lattice constants obtained from the diffraction data of scorodite particles synthesized from the As(V) and Fe(III) solution by the conventional method using the autoclave. The lattice constants of the powdered scorodite samples synthesized by the novel method are almost independent of the reaction time. They are clearly different from those of the scorodite particles synthesized from the As(V) and Fe(III) solution by the conventional method. The lattice constants $a$ and $b$ are larger, and $c$ is smaller than those of the scorodite synthesized by the conventional method.

Scorodite contains a ferric cation, an arsenate anion, and the water of crystallization. The orthorhombic structure of an ideal scorodite particle is described using FeO$_6$ octahedral and AsO$_4$ tetrahedral units, as shown in Fig. 4. In the FeO$_6$ unit, Fe is coordinated by four O atoms shared by four AsO$_4$ tetrahedra and two water molecules. All the O atoms coordinating Fe form the bridge between Fe and As and produce four Fe-O-As linkages. On the other hand, the two water molecules surrounding Fe form hydrogen bonds with the O atoms in AsO$_4$. Because the strength of hydrogen bonds may affect the stability of the scorodite crystal structure, differences in hydrogen bond lengths and crystalline imperfections may lead to differences between the lattice constants of the scorodite particles synthesized by the different reaction processes, as listed in Table 1. It should be noted that there are several stable crystallographic planes in the structure. The facets of the primary scorodite particles, as shown in Fig. 1, are considered stable planes, indicating that the primary scorodite particles consist of several grains since the number of facets is not very large.

### 3.3 Surface composition of scorodite particles

In order to understand the coprecipitation of scorodite particles, the composition of Fe and As in the surface layer of particles extracted from the suspension oxidized for different reaction times was analyzed by XPS. The compositions of Fe and As and the atomic As/Fe ratio on the surface of the scorodite particles were plotted as a function of the reaction time, as shown in Figs. 5(a) and 5(b), respectively. The concentrations of Fe and As in the reaction solution decreased with the reaction time, and after 3 h, the rate of decrease became quite small, which implies that the coprecipitation of the scorodite particles was almost completed when the reaction time was around 3 h. The average bulk atomic composition of As in the scorodite particles analyzed by ICP-AES decreased monotonically with the reaction time. The

<table>
<thead>
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<th>Sample</th>
<th>$a$(nm)</th>
<th>$b$(nm)</th>
<th>$c$(nm)</th>
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<tr>
<td>Novel process</td>
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<tr>
<td>(As(V), Fe(II))</td>
<td>0.89543 (1)</td>
<td>1.03253 (1)</td>
<td>1.00479 (2)</td>
</tr>
<tr>
<td>reaction time, $t$/h</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.89544 (1)</td>
<td>1.03256 (1)</td>
<td>1.00479 (1)</td>
</tr>
<tr>
<td>3</td>
<td>0.89548 (1)</td>
<td>1.03254 (1)</td>
<td>1.00473 (1)</td>
</tr>
<tr>
<td>5</td>
<td>0.89542 (1)</td>
<td>1.03252 (1)</td>
<td>1.00487 (1)</td>
</tr>
<tr>
<td>7</td>
<td>0.89545 (1)</td>
<td>1.03253 (1)</td>
<td>1.00487 (1)</td>
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<tr>
<td>Conventional process</td>
<td>0.89421 (1)</td>
<td>1.02755 (2)</td>
<td>1.00606 (2)</td>
</tr>
<tr>
<td>(As(V), Fe(III))</td>
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Fig. 2 XRD patterns of solid particles coprecipitated by injecting oxygen for 1 h (a) and 9 h (b) and scorodite particles synthesized by coprecipitation from the solution containing As(V) and Fe(III) (c) for reference.

Fig. 3 Expanded XRD patterns of those shown in Fig. 2 in the range of the diffraction angle including 020, 002, and 200 diffraction peaks.

Fig. 4 Packing of FeO$_6$ octahedra and AsO$_4$ tetrahedra in the unit cell of scorodite.
surface composition of As analyzed by XPS, as shown in Fig. 5(b), also decreased until when the reaction time was 5 h, which corresponds to the bulk composition of the particles. However, the surface composition of As increased when the reaction time exceeded 5 h, while the bulk composition of As decreased. This may be due to morphological changes occurring in the scorodite particles over time, as shown in Fig. 1. In the initial stage of the precipitation process until the reaction time was 1 h, scorodite particles precipitated subsequent to oxidation of Fe(II) to Fe(III). However, when the reaction time was 5 h or later, the precipitates on the surface of scorodite particles were formed directly by coprecipitation of Fe(III) and As(V) ions. According to this fact, As ions present in the surface area of the particles would be located in the lattice of scorodite with different crystallinity though the resultant value of As composition on the surface was similar at the reaction time of 1 and 7 h. On the other hand, it is known that arsenate ions can be adsorbed on fine ferric oxides,9–15) hence, the fine particles formed on the scorodite particles’ surfaces were partially such ferric oxides and may act as adsorption sites for the arsenate ions. The formation of ferric oxides implies that the concentration of Fe(III) in the solution is higher than that of As(V), although the ferric oxides are not identified by the XRD measurements. It is then considered that the surface composition of As apparently increased when the reaction time exceeded 5 h: thus, large heterogeneous scorodite particles are formed when the reaction time is long.

3.4 Chemical state of iron in initial reaction products

Besides the coprecipitation process of the scorodite particles from the iron and arsenic aqueous solution, the nucleation process of scorodite particles was also studied using XANES measurements. A suspension with high viscosity was formed in early stage of coprecipitation when the initial condition of pH value was approximately above 2. The gel-like sample was extracted from the suspension reacted for approximately 15 min. XRD measurements using Mo Kα radiation confirmed that no crystalline phase was present in the gel-like sample. XANES spectra at the Fe K absorption edge for an as-prepared sample and a sample kept under ambient atmospheric conditions for approximately 100 h are shown in Fig. 6, along with data on dried powdered samples synthesized from the As(V) and Fe(III) solution by the conventional method for reference. The spectra reveal that the scorodite particles used as reference consisted of Fe(III), and the gel-like sample consisted of Fe(II) with a small amount of Fe(III). Moreover, Fe(II) in the gel-like sample kept under ambient atmospheric conditions was partially oxidized. The gel-like sample was only filtered and not dried. Therefore, Fe(II) detected in the XANES spectra can be obtained from the remaining solution. However, it can be considered that the concentration of Fe(II) in the remaining solution was very small. This implies that the scorodite particles were formed from the gel-like intermediate products containing Fe(II), although the transformation processes of the gel-like intermediates into scorodite particles should be further elucidated.

In order to understand the coprecipitation process of scorodite particles, the Fe and As compositions in the precipitated scorodite particles during the reaction were considered for comparing their average composition ratio with that on the surface of the particles. The total concentration of Fe and As in the reaction solution decreased with the reaction time,21) which corresponds to the coprecipitation of large scorodite particles. However, Fe(II) ions in the solution are one of the most important parameters of the reaction. The chemical and electrochemical characteristics of Fe(II) are considerably different from those of Fe(III). In fact, Fe(II) ions are known to play a crucial role in the formation of different ferric oxyhydroxides, for example, corrosion products of iron, since Fe(II) is reactive to oxygen.26–28) The
reactivity of Fe(II) appears to induce the formation of large scorodite particles. It should be noted that scorodite particles are relatively larger than colloidal particles of iron oxides formed in an aqueous solution. This may be attributed to the nearly optimum reaction conditions such as the dissolved amounts of iron, arsenic, and oxygen, pH and oxidation-reduction potential of water, and the reaction temperature which are conducive to the formation of large scorodite particles. Further optimization of the process conditions will help in developing a continuous process for synthesizing large scorodite particles.

4. Concluding Remarks

Analytical methods such as XRD, SEM, XPS, and XAS were used for characterizing scorodite particles that were coprecipitated from Fe(II) and As(V) aqueous solution at approximately 95°C by injecting oxygen. The main results obtained in this study are as follows:

(1) SEM observations revealed that the formation of the morphology of large scorodite particles was almost completed when the reaction time was 5 h. Then, fine particles precipitated on the large particles by further reactions. XRD results showed that scorodite particles with specific lattice parameters coprecipitated when the reaction time was 1 h.

(2) XPS results indicated that the surface composition of As decreased for a reaction time of 5 h and increased thereafter. These results are in agreement with the results obtained by morphological observation of the scorodite particles using SEM and the results of the analyses of As and Fe in the reaction solution.

(3) XANES spectra indicated that gel-like reaction products formed in the initial reaction stage were composed of Fe(II) and Fe(III), and they were oxidized to an Fe(III) arsenate compound. These gel-like reaction products appear to be a precursor of scorodite particles, although elemental processes should be further studied.

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REFERENCES