Sonochemical Synthesis of Large Scorodite Particles

for the Stable Storage of Arsenic

(超音波を用いた砒素の安定貯蔵を目的とする

粗大なスコロダイト粒子の合成に関する研究)

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Chapter 1

General introduction

Arsenic is used for a semiconductor compound of gallium arsenic (GaAs). GaAs is used in various applications [light emitting diode (LED), laser diode, high-frequencies switch for smart phones, and power amplifier] [1, 2]. However, arsenic is toxic for the human body and it is a causal substance of cancers (e.g., skin, lung, kidney, and liver); therefore, waste materials and factory effluents containing arsenic must be treated and stored using the appropriate methods [3, 4]. The values of environmental and effluent standard for arsenic are strictly established as below 0.01 ppm and 0.1 ppm, respectively in Japan [5, 6].

In the abandoned Matsuo mine (Iwate, Japan), divalent iron [Fe(II)] and arsenious acid [As(III)]-containing acid mine drainage has been discharged as wastewater. Arsenic concentration in the wastewater is several ppm. Arsenic removal has been performed by coprecipitation with iron hydroxide generated by neutralization with CaCO₃ after Fe(II) was oxidized to trivalent iron [Fe(III)] by iron-oxidizing bacteria [7, 8]. Subsequently, arsenic containing sludge is generated in the solution. The arsenic concentration of treated water is 0.01 ppm, and the value satisfies a criterion for the environmental standard. On the other hand, a smelting process in a smelter discharges highly-concentrated arsenic as by-products [9]. Arsenic is commonly found in the form of enargite (Cu₃AsS₄) and tennantite (Cu₁₀Fe₂AsS₁₃) sulfide minerals that are present in the copper ore deposits [3, 9–11]. The highly-concentrated arsenic is discharged as by-products such as anode slimes generated by electrolytic refining of copper and flue dust [12]. Arsenic in the flue dust

accrues in smelting furnace and converter, and it dominates approximately 80% in the total amount of arsenic accrued by copper smelting [13]. The flue dust often includes high-grade copper; therefore, they are repeatedly treated to recover as much copper as possible. Recently, copper grade in copper ore has been decreasing with the elapsed year of mining [14–17]. As a result, impurity (i.e., arsenic) concentration in copper ore has been increasing and it is concern of the stable smelting operation for copper. Currently, Japan has been imported copper concentrates of about 5 million per year and produced copper ingots of about 1.5 million per year [18, 19]. The amount of arsenic discharged in non-ferrous metals industry in Japan, based on PRTR (Pollutant Release and Transfer Register) law of Japan, is about 1,000 tons per year [20]. This value accounts for 99% of the total amount of arsenic discharged in Japan. Methods for arsenic removal from the highly-concentrated arsenic solutions and arsenic storage in the crystal structures such as iron arsenate (FeAsO4·2H₂O), calcium arsenate [Ca₃(AsO₄)₂], and arsenic sulfide (As₂S₃) have been recently reported [21–23]. However, arsenic sulfide is unstable at pH > 4 [21]. Calcium arsenate is unstable in the presence of atmospheric carbon dioxide or carbonate ions because they lead to the formation of calcium carbonate and the release of arsenate ions [21]. Thus, it is unsuitable for use as an arsenic storage material. On the other hand, scorodite (FeAsO₄·2H₂O) releases little arsenic when the pH of the solution is in the acidity and neutral regions [24, 25]. Fig. 1.1 shows a crystal structure of scorodite. Scorodite consists of FeO₆ octahedra and AsO₄ tetrahedra. The two water molecules surrounding Fe form hydrogen bonds with the O atoms in AsO₄ [26, 27]. Therefore, the strength of hydrogen bonds may affect the stability of the scorodite crystal structure.

Scorodite has been typically obtained by hydrothermal synthesis method in a solution containing trivalent iron [Fe(III)] and pentavalent arsenic [As(V)]. However, this method requires high temperature (>100 °C), high pressure, and expensive equipment [28]. To overcome these drawbacks, a new scorodite synthetic process using a stirrer with an O_2 gas flow for 7 h at <100 °C under atmospheric pressure was investigated in previous work [27, 29–34]. In this process, scorodite is synthesized in a sulfuric acidic solution containing divalent iron [Fe(II)] and pentavalent arsenic [As(V)]. The formula for the synthesis reaction of scorodite in Fe(II) and As(V) solution was given by Fujita et al. [29] as follows:

$$4H_3A_8(V)O_4 + 4Fe(II)SO_4 + O_2(g) + 6H_2O \rightarrow 4Fe(III)A_8O_4 \cdot 2H_2O + 4H_2SO_4. \quad (1.1)$$

The size of the synthesized scorodite particles plays an important role in arsenic storage. A larger particle size is preferred because a low surface-to-volume ratio makes it difficult to dissolve scorodite in an acidic solution as was demonstrated in the arsenic elution test based on the Japanese Ministry of the Environment Notification No. 13, where the large size of the scorodite particles (>10 μ m) prevents the elution of arsenic from scorodite to the solution (<0.02 mg/L) [29]. It is therefore important to synthesize scorodite with a large particle size in order to enable stable long-term arsenic storage. However, high energy consumption is a significant problem for scorodite synthesis. To reduce cost, primarily through a reduction of energy consumption, a process with a lower heating temperature and a shorter oxidation period is desirable. Fujita et al. reported the effect of reaction temperature on the scorodite synthesis using the above method [30]; although scorodite was synthesized at the lower temperature of 70 °C, the

resulting particles were small (3 μ m). Synthesis of scorodite using Fe(II) and As(V) is commonly synthesized by oxidation reaction of Fe(II) using O₂ gas. Oxidation-reduction potentials of Fe(II)/Fe(III) and O₂/H₂O are described as follows [35, 36]:

$$Fe^{2+} = Fe^{3+} + e^{-}$$
 $E^0 = +0.77 V \text{ vs. SHE}$ (1.2)

$$O_2 + 4H^+ + 4e^- = 2H_2O$$
 $E^0 = +1.23 \text{ V vs. SHE}$ (1.3)

The difference of oxidation-reduction potential between Fe(II)/Fe(III) and O₂/H₂O is 0.46 V. To enhance the oxidation of Fe(II) to Fe(III), the utilization of oxidants [e.g., OH radical (OH·), hydrogen peroxide (H₂O₂), and HO₂ radicals (HO₂·)] which have higher potential values than O₂ is necessary. Oxidation-reduction potentials of OH·/H₂O, H₂O₂/H₂O, and HO₂·/H₂O are described as follows [37]:

$$OH \cdot + H^+ + e^- = H_2O$$
 $E^0 = +2.38 V \text{ vs. SHE}$ (1.4)

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O$$
 $E^0 = +1.76 \text{ V vs. SHE}$ (1.5)

 $HO_2 + 3H^+ + 3e^- = 2H_2O$ $E^0 = +1.65 \text{ V vs. SHE}$ (1.6)

Oxidation-reduction potential of $OH \cdot /H_2O$ is the highest value above three oxidants. Therefore, $OH \cdot$ is attractive for the oxidant of Fe(II). Ultrasound has been used as one of the methods to generate $OH \cdot$. When ultrasound irradiation of high intensity forms a standing wave in the solution [38, 39] (Figs. 1.2 and 1.3), the acoustic pressure changes at the antinode with elapsed time and the dissolved gas generates fine bubbles (several µm) when the acoustic pressure is negative. The fine bubbles then first grow with time and then collapse when the acoustic pressure changes sign to positive (cavitation phenomena). The collapse of the bubbles forms local hotspots (5000 K, several thousand atm) and generates radicals (when the dissolved gas is O_2 gas) in and around babbles as follows [40]:

 $H_2O \rightarrow OH + H,$ (1.7)

$$OH \cdot + OH \cdot \rightarrow H_2O_2,$$
 (1.8)

$$H \cdot + H \cdot \rightarrow H_2(g),$$
 (1.9)

$$H \cdot + O_2 \rightarrow HO_2 \cdot .$$
 (1.10)

These products can act as oxidants (OH·, H₂O₂, and HO₂·) and reductant (H·) in solutions. These specific effects (high temperature and pressure field, oxidants, and reductants) of ultrasound irradiation have been applied to various fields [41–75]. For example, the feature of high temperature and pressure has been applied to the thermal decomposition of a hazardous organic compound [41]. Oxidant and reductant have been applied to the oxidation treatment of hazardous inorganic such as arsenite ion [48–54], the synthesis of metal nanoparticles (e.g., gold, palladium, and silver) [65–75], respectively.

Therefore, in this study, ultrasound was applied for oxidation of Fe(II) to Fe(III) during synthesis of scorodite with a large particle size (>10 μ m) at low reaction temperature and short reaction time. Furthermore, scorodite synthesis mechanism using ultrasound irradiation is clarified.



Orthorhombic structure
a = 8.937 Å, b = 10.278 Å, c = 9.996 Å
$\alpha = \beta = \gamma = 90.0^{\circ}$
Z = 8

Fig. 1.1 Crystal structure of scorodite.



Fig. 1.2 Schematic of a standing wave formed by ultrasound irradiation in a solution.



Fig. 1.3 Schematic of formation, growth, and collapse of cavitation bubbles under ultrasound irradiation.

In *Chapter 2*, the synthesis of large scorodite particles at low temperature, 70 °C, using ultrasound oxidation is investigated [76, 77]. The relationship between ultrasound intensity and the size of the generated scorodite particles is also investigated.

In *Chapter 3*, the effect of ultrasound agglomeration on the size of scorodite particles synthesized is investigated using various sonication frequencies (28 kHz, 200 kHz, and 1.7 MHz) [78].

In *Chapter 4*, the synthesis of large scorodite particles (>10 μ m) by adding CO₂ during the ultrasound agglomeration process is investigated [79]. Application of CO₂ gas during ultrasound irradiation would mitigate cavitation-related dispersion effect during the ultrasound agglomeration process of scorodite synthesis.

In *Chapter 5*, the effect of solution temperature on the size and morphology of scorodite synthesized using ultrasound irradiation is investigated. Solution temperature is conducted at 90, 70, 50, and 30 °C [80].

In *Chapter 6*, the effect of ultrasound irradiation on the size and morphology of scorodite particles synthesized under different acidic conditions is investigated. The pH of a solution is conducted at 2.0, 1.5, and 1.0.

In *Chapter 7*, scorodite is an arsenic storage material in the acidity and neutral regions. However, scorodite is unstable under an alkali solution. Therefore, the synthesis of Ca-Fe arsenates which are expected as arsenic storage materials under alkaline environment and the synthesis condition of these materials are investigated.

In Chapter 8, conclusions of this paper are described.

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Chapter 2

Synthesis of large scorodite particles using oxidation effect of ultrasound irradiation

2.1 Introduction

A larger particle size of scorodite is preferred because a low surface-to-volume ratio makes it difficult to dissolve scorodite in an acidic solution. It was reported that the large size of the scorodite particles (>10 µm) prevents the elution of arsenic from scorodite to the solution (<0.02 mg/L) which is evaluated by the arsenic elution test based on the Japanese Ministry of the Environment Notification No. 13 [29]. It is therefore important to synthesize scorodite with a large particle size in order to enable stable long-term arsenic storage [29]. Thus, understanding the generation process of scorodite particles is necessary. Shinoda et al. reported that a precursor is generated in the initial reaction stage prior to the formation of scorodite. Chemical state of iron in the precursor is ferrous ion [Fe(II)] with a small amount of ferric ion [Fe(III)] [27]. Faceted scorodite particles, crystalline scorodite particles, then grow from the precursor in solution at high temperature and under O₂ gas flow, however, the details of the crystal growth process are unclear. To synthesize faceted scorodite particles, the oxidation of the precursor containing Fe(II) is necessary. The oxidation of the precursor [Fe(II)-As(V)] by O₂ gas flow during ultrasound irradiation can be considered using the following formulas.

$$H_2O \rightarrow OH + H, \qquad (1.7)$$

$$OH \cdot + OH \cdot \rightarrow H_2O_2,$$
 (1.8)

$$H \cdot + O_2 \quad \rightarrow \quad HO_2 \cdot, \tag{1.10}$$

$$Fe(II)-As(V) + OH + H^{+} \rightarrow Fe(III)-As(V) + H_{2}O, \qquad (2.1)$$

$$Fe(II)-As(V) + H_2O_2 + H^+ \rightarrow Fe(III)-As(V) + OH + H_2O, \qquad (2.2)$$

$$3Fe(II)-As(V) + HO_2 + 3H^+ \rightarrow 3Fe(III)-As(V) + 2H_2O.$$
 (2.3)

In the proposed synthetic method, I expected the synthesis of large scorodite particles at low temperature by O_2 gas flow and sonochemical oxidation. In this study, ultrasound frequency of 200 kHz, which has a high oxidation effect, was chosen [81, 82]. Generation of oxidants (e.g., OH_{\cdot} , $HO_{2^{\cdot}}$) depends on the amount of fine bubbles generated during ultrasound irradiation. Generation amount of fine bubbles relates to the amplitude of a standing wave, which can be changed by ultrasound intensity [83].

In this chapter, I aim to investigate the relationship between ultrasound intensity and the size of the generated scorodite particles. I also investigate the synthesis of large scorodite particles using the oxidation effect of ultrasound irradiation.

2.2 Experimental procedure

A solution containing divalent iron and arsenic acid [Fe(II)-As(V)] was prepared using Na₂HAsO₄·7H₂O (Wako, >99%), FeSO₄·7H₂O (Kanto Chemical, >99%), and ion exchange water. The Fe(II)-As(V) solution (50 mL) was adjusted to an Fe/As molar ratio of 1.5. The As(V) concentration was 20 g/L and the solution pH was adjusted to 2.0 using H_2SO_4 (Wako, >97%). A schematic illustration of the experimental apparatus is shown in Fig. 2.1. Ultrasound irradiation was performed using an ultrasonic generator (Kaijo TA-4021) and a submersible transducer at a frequency of 200 kHz (Kaijo). The ultrasound power applied to the solution in the flask was 11.6, 8.4, 5.3, and 2.1 W, as calculated calorimetrically [84]. The condition without ultrasound irradiation is referred to as 0 W. A submersible transducer was placed on the bottom of a tank filled with water, and a flat-bottom flask containing the sample solution was placed directly above the transducer. The temperature of the irradiated solution was maintained at 70 °C using hot water circulation around the flat-bottom flask. The solution temperature was raised gradually over 20 min until the required temperature (70 °C) was reached. Prior to the ultrasound irradiation of the solution, oxygen (100 mL/min) was flowed into the solution through the inlet port (inner diameter: 4 mm) without filter to generate fine bubbles for 20 min in order to replace the air in the flask. Ultrasound irradiation was conducted at 70 °C for 3 h under oxygen gas flow. Upon completion of the reaction, the precipitates were filtered through a membrane filter with a 0.45 µm pore diameter (Advantec) and collected. The precipitates were then dried and analyzed by X-ray diffraction (XRD; Rigaku, RINT2000, Cu Ka), scanning electron microscopy (SEM; Hitachi, TM-1000), a particle size analyzer (Nikkiso, Microtrac MT3300EXII), and using specific surface area measurement (MicrotracBEL, Belsorp-miniII). The amount

of collapsed bubbles are related to the amount of generated radicals during irradiation at 200 kHz. Since the generated oxidizing radicals such as OH radicals function as oxidants, I evaluated the amount of the generated fine bubbles by ultrasound irradiation using the potassium iodide (KI) method [81, 82, 85, 86]. A 0.1 M KI solution (50 mL) was prepared using KI for oxidant analysis (Wako, >99.5%) and ion exchange water. The solution was irradiated for 30 min at various ultrasound powers after oxygen (100 mL/min) was flowed into the solution for 30 min in order to replace the air in the flask. The temperature of the irradiated solution was maintained at 70 °C using hot water circulation around the flat-bottom flask. After the solution was irradiated, I measured its absorbance of it at 355 nm (absorption wavelength of triiodide ions) to evaluate the amount of triiodide ions (molar absorptivity $\epsilon = 26,303 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) using ultraviolet-visible spectrophotometry (JASCO, V-630iRM). The synthesized scorodite was then evaluated using the arsenic dissolution test based on the procedure specified by the Japanese environmental ministry [87]. Here, 2 g of the sample and 20 g of ion-exchanged water adjusted to pH 5.1 using HCl (weight ratio of the sample and the solvent was 1:10) were mixed. The mixture was placed in a polyethylene container and horizontally shaken for 6 h. After the test, the amount of eluted arsenic was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Seiko Instruments, SPS5510).



Fig. 2.1 Schematic of the experimental apparatus [79].

2.3 Results and discussion

Fig. 2.2 shows the XRD patterns of the precipitated particles synthesized at 70 °C for 3 h using various ultrasound intensities. Examination of the peaks shows that the samples were scorodite for all experimental conditions, according to the powder diffraction file (PDF) No. 00-037-0468 for all experimental conditions; no impurity peaks were present. The XRD peak of 0 W showed the lowest intensity and the intensities of the peaks for 2.1–11.6 W irradiation were approximately same.

Examination of oxidation-reduction potential (ORP) values and yields for scorodite under different irradiation conditions shown in Fig. 2.3 indicates that ORP clearly shows the oxidation from Fe(II) to Fe(III) to be favored by a higher irradiation intensity. Here, I followed the approach of Fujita who used the ORP values measured before and after reaction to confirm the oxidation of Fe(II) in the solution [29]. The ΔORP values were 137 (11.6 W), 117 (8.4 W), 117 (5.3 W), 115 (2.1 W), and 86 (0 W) mV. The highest $\triangle ORP$ value and yield were observed for 11.6 W irradiation, implying that 11.6 W irradiation leads to the fastest Fe(II) oxidation among the examined conditions. I also confirmed that $\triangle ORP$ value and yield were lower at lower ultrasound intensity. The particles synthesized by low intensity ultrasound may include precursor (non-crystalline) and low-crystallinity particles. Previous work has shown that irradiation of the solution with high intensity ultrasound leads to miniaturization of the bubbles and an increase in the amount of generated bubbles [88–91]. This increases the area of the interface between the liquid phase and the gas phase (oxygen gas), promoting oxidation. Oxidation is also promoted by the formation of radical species (OH, HO_2) generated by the collapse of the bubbles during ultrasound irradiation [40,

92]. Therefore, high ultrasound intensity promoted oxidation from Fe(II) to Fe(III), as observed in my experiments.



Fig. 2.2 XRD patterns of precipitated particles synthesized at 70 °C for 3 h using various ultrasound intensities [76].



Fig. 2.3 ORP values and yields of scorodite synthesized at various ultrasound intensities [76].

I then examined the dependence of size of the synthesized particles on irradiation intensity. Fig. 2.4 shows the SEM images of the scorodite particles synthesized at 70 °C for 3 h at different ultrasound intensities. For high intensity irradiation (11.6 W), I confirmed that a mixture of large (>10 µm) and small (<1 µm) particles was obtained. On the other hand, generation of small ($<1 \mu m$) particles was prevented at low intensity of irradiation (2.1 W), possibly because the low intensity results in only a low amount of fine bubbles. Fine bubbles generated by ultrasound irradiation promote the formation of nuclei [93, 94] and the jet flow and the shock wave generated by the collapse of the fine bubbles during ultrasound irradiation can disperse the particles [95]. A low intensity of ultrasound irradiation may lead to agglomeration of fine particles by the ultrasound vibration due to the low formation amount of nuclei and the low dispersion effect. For irradiation with 2.1–11.6 W, I observed large scorodite particles (>10 µm) with faceted surfaces. However, at 0 W (without ultrasound irradiation), a high number of fine particles and secondary particles arising from agglomeration of fine particles were observed. Such a nonmonotonic dependence of particle size on irradiation intensity can be explained as follows. At 0 W (without ultrasound), many fine particle are present because particle agglomeration is not promoted by the ultrasound vibration. In contrast, large scorodite particles are obtained because of the increased amount of supplied oxygen and solute [Fe(III), As(V)] to the nuclei during particle growth under low intensity ultrasound irradiation. Further increase in ultrasound intensity leads to the formation of the bubbles as described above, generating many nuclei and giving rise to a large number of fine particles.



Fig. 2.4 SEM images of scorodite particles synthesized at 70 °C for 3 h by each ultrasound intensity [76].

To elucidate the effect of ultrasound intensity on the morphology of the synthesized particles, I observed the particle surfaces. The surfaces of the particles synthesized at high irradiation intensity of 11.6 W were faceted, whereas rough surfaces were observed for particles synthesized under irradiation intensity of 2.1 W. The difference in the surface morphology may arise from the difference in the reaction rates (oxidation, solute supply, dissolution, and deposition). The reaction at low intensity is s lower than that at high intensity. The distribution curves, which are plotted on the volume standard, for the size of scorodite particle synthesized at different irradiation intensities were measured using a particle size analyzer (Fig. 2.5) and were used to calculate the average particle size. The obtained average particle sizes and the specific surface areas measured by BET method are shown in Fig. 2.6. The obtained average particle size values were 8.27 (0 W), 12.57 (2.1 W), 8.94 (5.3 W), 8.20 (8.4 W), and 11.49 (11.6 W) µm and the specific surface area values were 11.76 (0 W), 5.52 (2.1 W), 2.25 (5.3 W), 1.77 (8.4 W), and 1.27 (11.6 W) m²/g. Thus, the specific surface area increases with lower ultrasound intensity, verifying that the surfaces of particles synthesized at low intensity are rougher than those of particles synthesized under high irradiation intensity. The highest average particle size was obtained for irradiation intensity of 2.1 W. This is due to a combination of the weakening of the stirring effects, the jet flow generated by the collapse of the bubbles, and the physical stirring by the ultrasound and the agglomeration effect by the ultrasound vibration. However, at low irradiation intensity, the number of dissolved fine particles in solution and the amount of supplied solute to the nuclei decreased by reduction of the jet flow and physical stirring. This leads to an insufficiently high reaction rate and gives rise to the rough surfaces of the particles synthesized at low ultrasound intensity.

Examination of the particle distribution curves shows that approximately the same amount of fine particles is generated at 2.1 W and 11.6 W. At first glance, the amount of the generated fine particles (<1 μ m) should be higher with the increased amount of fine bubbles associated with ultrasound irradiation. However, in addition to leading to the generation of fine particles, high intensity ultrasound also gives rise to their dissolution. Therefore, high intensity ultrasound promotes Ostwald ripening, resulting in a lower amount of fine particles [96]. On the other hand, low ultrasound intensity prevents the generation of fine bubbles that form particle nuclei, but does not promote Ostwald ripening. Hence, many particles were agglomerated (secondary particles) and rough surfaces were displayed for the reaction time of 3 h.

To examine the particle growth at different ultrasound intensities, I observed particle growth at ultrasound intensities of 11.6 W and 2.1 W using SEM (Fig. 2.7). After 20 min irradiation, many particles agglomerated with fine particles were observed for both intensities. After irradiation for 120 min with 11.6 W, agglomerated particles transform into a single particle with faceted surface. For high ultrasound intensity, the oxidation reaction and solute supply quantity promote the growth during the elapsed time. Therefore, particles with faceted surfaces were obtained at the early stage of crystal growth for high ultrasound intensity.



Fig. 2.5 Particle size distribution of scorodite synthesized at various ultrasound intensities [76].



Fig. 2.6 Relationships of average particle size and specific surface area at various ultrasound intensities [76].



Fig. 2.7 Particle growth with elapsed time using ultrasound intensity of (a) 11.6 W and (b) 2.1 W [76].

I then compared the amount of the oxidizing radicals generated by ultrasound at each intensity to further elucidate the influence of ultrasound intensity on particle growth. For a given frequency, fine bubble generation depends on the irradiation intensity [88–90] and the generation amount of radicals is related to the amount of collapsed bubbles during irradiation at 200 kHz. Therefore, I evaluated the generation amount of oxidizing radicals, OH radicals, using potassium iodide (KI) method [81, 82]. The chemical reactions of KI method are given by

$$H_2 O \to O H^{\cdot} + H^{\cdot}, \qquad (1.7)$$

$$2OH \cdot + 2I^{-} \rightarrow I_{2} + 2OH^{-}, \qquad (2.4)$$

$$I_2 + I^- \to I_3^-. \tag{2.5}$$

The KI method evaluation was performed using 0.1 M iodine solution under oxygen atmosphere by measuring the amount of triiodide ions. Iodine ions were oxidized by OH radicals to iodine [Eq. (2.4)], and then iodine was changed to the stable triiodide ions [Eq. (2.5)]. Therefore, I can compare the amount of oxidizing radicals at different ultrasound conditions by comparing the amount of triiodide ions generated at each condition. Fig. 2.8 shows the results obtained by the KI method for the amount of triiodide ions generated for each ultrasound intensity. I found that the amount of generated triiodide ions increases with higher ultrasound intensity. Thus, higher ultrasound intensity generates larger amount of fine bubbles, which then collapse, leading to the formation of radicals. Therefore, high ultrasound intensity promotes oxidation of Fe(II) by increasing the surface contact area of oxygen bubbles (gas phase) and Fe(II) (liquid phase) and also by promoting nuclei formation associated with generation of fine bubbles. However, only a low amount of fine particles (<1 μ m) was generated (Fig. 2.5). This is due to the enhanced dissolution of fine particles and the enhancement of particle growth by provision of the solute to the particles caused by the application of high ultrasound power.



Fig. 2.8 Generation amount of triiodide ions in each ultrasound intensity using the KI method [76].

Finally, arsenic elution was examined for the scorodite synthesized at different ultrasound intensities. I also measured the specific surface area of the samples that has an effect on the elution tests (Fig. 2.9). The amount of arsenic eluted from the synthesized scorodite was 320.41 (0 W), 144.09 (2.1 W), 42.98 (5.3 W), 17.36 (8.4 W), and 15.40 (11.6 W) mg/L. The arsenic elution rate was calculated from the amount of the arsenic eluted in the solution, and was 0.987 (0 W), 0.444 (2.1 W), 0.132 (5.3 W), 0.053 (8.4 W), and 0.047 (11.6 W) %. Thus, the scorodite synthesized under highest irradiation intensity of 11.6 W showed the smallest arsenic elution rate. The amount of eluted arsenic increased with lower ultrasound intensity. Although large scorodite particles were obtained for low ultrasound intensity of 2.1 W, this condition also showed a high amount of eluted arsenic. This may be due to the presence of fine particles including precursor (non-crystalline) and large particles with rough surface (low-crystalline). It is supported by the results of a specific surface area of the samples, the sample synthesized at an intensity of 2.1 W and showed high specific surface area. Previous studies reported that the amount of eluted arsenic was low for the highly crystalline faceted scorodite [29, 30]. Therefore, it is advantageous to synthesize faceted particles, even if the particle size is small. Crystallization at the early stage is favored oxidation promotion and dissolution enhancement due to high intensity ultrasound, which also enables the synthesis of large faceted scorodite particles. Since it is possible to obtain faceted scorodite particles at the early stage of the reaction by using high intensity irradiation, scorodite synthesis under high ultrasound intensity is desirable.



Fig. 2.9 Relationships of specific surface area and arsenic elution amount of scorodite samples synthesized at various ultrasound intensities [76].

2.4 Conclusions

In this chapter, the relationship between ultrasound intensity and the size and morphology of the generated scorodite particles was investigated. I also synthesized the large scorodite particles (>10 μ m) using the oxidation effect of ultrasound irradiation at low temperature (70 °C) for short reaction time (3 h). $\triangle ORP$ value and yield were higher for high intensity irradiation, implying that oxidation of Fe(II) was promoted in the reaction solution. When ultrasound irradiates with high intensity into the solution, the area of the interface between the liquid phase and the gas phase (oxygen gas) becomes high due to the miniaturization of the oxygen gas bubbles and an increase in the amount of bubbles. Thus, high ultrasound intensity promotes oxidation reaction from Fe(II) to Fe(III). Oxidation is also promoted by radicals generated by the collapse of the bubbles under ultrasound irradiation. Large scorodite particles (>10 µm) with faceted surface were observed in SEM images of the samples synthesized with 2.1-11.6 W irradiation. However, it was found that particles synthesized with low intensity irradiation have rough surfaces, possibly due to the slower reaction at the lower irradiation intensity. Many fine particles and secondary particles, (agglomerates consisting of fine particles) were observed after the synthesis at 0 W (without ultrasound irradiation). I concluded that low intensity of ultrasound leads to the synthesis large particles with rough surfaces as well as fine particles including precursor (non-crystalline) and low crystalline particles due to the low oxidation. Therefore, while low intensity is effective for prevention of the generation of fine bubbles that favor formation of the nuclei, it also leads to low dissolution of fine particles. An additional contribution to Fe(II) oxidation and crystal growth is made by the radicals synthesized by ultrasound irradiation in solutions. Dissolution tests showed that the smallest amount

of eluted arsenic was obtained for the scorodite synthesized at the high intensity condition of 11.6 W. Under high ultrasound intensity irradiation, faceted scorodite particles can be synthesized as oxidation is promoted by the increase area of the interface between Fe(II) (liquid phase), the oxygen bubbles (gas phase) and the oxidation radicals generated by the ultrasound irradiation. To synthesize the large scorodite particles with facet, it was necessary to increase the supply quantity of solute [Fe(III), As(V)] from the solution to the nuclei during synthesis process. Therefore, higher intensity of ultrasound is suitable for the synthesis of large faceted scorodite particles at low temperature (70 °C) in a short reaction time (3 h).

Chapter 3

Effect of ultrasound agglomeration on size of scorodite particles synthesized using stirring

3.1 Introduction

In chapter 2, large scorodite particles (>10 µm) were synthesized at low temperature (70 °C) and for a short reaction time (3 h) using 200 kHz ultrasound irradiation with load power of ≤ 200 W. Although the low intensity ultrasound makes low oxidation effect of ultrasound irradiation, the large scorodite particles (>10 µm) were synthesized at various intensities, 11.6, 8.4, 5.3, and 2.1 W, which are calculated by calorimetrically [76]. Thus, I consider that the agglomeration effect of the ultrasound irradiation contributed synthesis of large scorodite particles (>10 µm). High intensity ultrasound (11.6 W) generates not only large particles but also small scorodite particles. Small particles may be because of the nucleus formation by the collapse of the bubbles (cavitation phenomena) during ultrasound irradiation [93, 94]. The timing difference of particles generation during the synthesis process will relate to size difference of synthesized particles. Therefore, it is necessary to adjust the timing of the particles generation. To synthesize the large particles without including the fine particles, I applied ultrasound irradiation for only a short time period (10 min) immediately after the beginning the synthesis. The purpose of this chapter is to clarify the effect of the agglomeration effect of ultrasound irradiation on the size and morphology of scorodite particles and to apply short time sonication for the synthesis of large scorodite particles without small particles. I also investigate the effects of the changes in ultrasound frequency on the size of the generated scorodite particles.

3.2 Experimental procedure

A solution containing divalent iron and arsenic acid [Fe(II)-As(V)] was prepared using Na₂HAsO₄·7H₂O (Wako, >99%), FeSO₄·7H₂O (Kanto Chemical, >99%), and ion exchange water. The Fe(II)-As(V) solution (50 mL) was adjusted to an Fe/As molar ratio of 1.5. The As(V) concentration was 20 g/L. The pH of the solution was adjusted to 2.0 using H_2SO_4 (Wako, >97%). A schematic of the experimental apparatus is shown in Fig. 2.1. Ultrasound irradiation was performed using an ultrasonic generator (Kaijo TA-4021), 200 and 28 kHz submersible transducers (Kaijo), and a 1.7 MHz submersible transducer (Seiko giken). The ultrasound power applied to the solution was 11.4 W (200 kHz), 13.4 W (28 kHz), and 5.3 W (1.7 MHz) as calculated calorimetrically [84]. A submersible transducer was placed at the bottom of a tank filled with water, and a flat-bottom flask containing the sample solution was placed directly above the transducer. The temperature of the irradiated solution was set at 70 °C using hot water circulation around the flat-bottom flask. The solution temperature was raised gradually over 20 min until the required temperature (70 °C) was reached. Before the ultrasound irradiation of the solution, oxygen gas (100 mL/min) was flowed into the solution for 20 min to replace the air in the flask with the oxygen gas. Ultrasound irradiation or stirring (1,000 rpm) was then conducted at 70 °C for 3 h under oxygen gas atmosphere. When the reaction was completed, the precipitates were filtered through a membrane filter with a 0.45 µm pore diameter (Advantec) and collected. After drying, the precipitates were analyzed by X-ray diffraction (XRD; Rigaku RINT2000, Cu Ka) and scanning electron microscopy (SEM; Hitachi TM-1000), and with a particle size analyzer (Nikkiso Microtrac MT3300EXII).

3.3 Results and discussion

I first investigated the effect of variation in the ultrasound irradiation frequency on the size and the morphology of the scorodite particles. Fig. 3.1 shows the XRD patterns obtained from the precipitated particles indicating that scorodite was successfully synthesized for each frequency. The intensities of the XRD peaks were approximately same for all the samples, indicating that the particles synthesized using stirring and ultrasound irradiation of various frequencies exhibited similar levels of crystallinity. As shown in the SEM images of the precipitated samples (Fig. 3.2), the scorodite particles are polyhedron for all synthesis conditions. Fig. 3.3 shows the particle size distribution of the precipitated samples obtained using a particle size analyzer. The average size of the particles synthesized by stirring and ultrasound irradiation at 200 kHz, 28 kHz, and 1.7 MHz were 7.3, 15.5, 7.0, and 16.9 µm, respectively. While the particle sizes of the scorodite synthesized using 28 kHz ultrasound or stirring were similar, ultrasound irradiations at 200 kHz and 1.7 MHz leads to a significant increase in the particle size. I attribute the smaller size of the particles synthesized by 28 kHz ultrasound to the promotion of the nucleation and dispersion by the low-frequency physical motion as crystal nucleation may have been caused by the cavitation during the ultrasound irradiation [97, 98]. For 200 kHz ultrasound irradiation, while most of the particles were large (>10 μ m), small (<1 μ m) particles were obtained as well. Synthesis using 1.7 MHz ultrasound resulted in large scorodite particles (>10 µm) and a low amount of the fine particles because of the decreased cavitation effect by high frequency ultrasound. Therefore, 200 kHz or 1.7 MHz high frequency ultrasound irradiation is more favorable for the synthesis of large scorodite particles (>10 µm) than the 28 kHz low frequency irradiation. Next, I
investigated the synthesis conditions that would prevent the formation of fine particles. Although I could be synthesized large scorodite particles (>10 μ m) by continuous irradiation for 3 h using 200 kHz or 1.7 MHz ultrasound, 200 kHz ultrasound irradiation synthesis generated both large and small scorodite particles.



Fig. 3.1 XRD patterns of the samples synthesized using stirring or ultrasound irradiation (200 kHz, 28 kHz, and 1.7 MHz) for 180 min [78].



Fig. 3.2 SEM images of the precipitated samples obtained using stirring or ultrasound irradiation (200 kHz, 28 kHz, and 1.7 MHz) for 180 min [78].



Fig. 3.3 Particle size distributions of the precipitated samples obtained using stirring or ultrasound irradiation (200 kHz, 28 kHz, and 1.7 MHz) for 180 min [78].

The presence of the small particles may be because of the nucleus formation by cavitation during the ultrasound irradiation. Therefore, I considered several modifications to the synthesis procedures to prevent the generation of fine particles. I first investigated the effect of the differences in the stirring time. Fig. 3.4 shows the SEM images of the scorodite particles after different elapsed times of stirring at 70 °C. In the initial reaction stage, a gel-like reaction product appeared in the solution. This product was not a crystalline structure, which was confirmed by XRD measurement. Furthermore, Shinoda et al. reported that this product is mainly composed of Fe(II) with a small amount of Fe(III) [27]. Thus, the gel-like reaction product differs from scorodite and becomes scorodite by oxidation in Fe(II) and As(V) aqueous solution at 70 °C. Here, I defined the gel-like product as the precursor of scorodite. The generation and growth of the precursor with longer stirring time is clearly observed, with the precursor size of $<1 \mu m$ at 0 min, approximately 1 μm at 10 min and $>3 \mu m$ at 20 min, respectively. Then, I investigated the effect of the short time ultrasound irradiation on the precursors. The scorodite synthesis was performed following three different procedures such that the precursors of different size described above were irradiated by each ultrasound frequency for 10 min during the 180 min oxidation process with stirring. Fig. 3.5 shows the flowchart of this experiment. Procedure (1) was as follows: 1) Ultrasound was irradiated without stirring for 10 min into the suspension at 70 °C to enhance the agglomeration of the precursor. 2) The oxidation of the agglomerated precursor was continued using stirring with oxygen flow for 170 min without ultrasound irradiation (total 3 h). Procedure (2) was as follows: 1) To increase the precursor size, stirring was conducted at 70 °C for 10 min with oxygen flow. 2) Ultrasound was irradiated for 10 min at 70 °C. 3) Oxidation of the agglomerated precursor was continued using stirring

with oxygen flow for 160 min without ultrasound irradiation (total 3 h). Procedure (3) was as follows; 1) To increase the precursor size, stirring was conducted at 70 °C for 20 min with oxygen flow. 2) Ultrasound was irradiated for 10 min at 70 °C. 3) Oxidation of the agglomerated precursor was continued using stirring with oxygen flow for 150 min without ultrasound irradiation (total 3 h). Fig. 3.6 shows the SEM images of the precipitated samples synthesized using procedures (1)-(3) and using 200 kHz ultrasound irradiation. Majority of the particle size of scorodite obtained by procedures (1)–(3) were 3–8 µm. However, procedure (1) contained a considerable amount of fine particles (approximately 1 μ m). The primary particle size obtained by procedure (2) was larger than that obtained by procedures (1) and (3). Fig. 3.7 shows the particle size distribution of the precipitated samples measured by the particle size analyzer. The average sizes of the particles synthesized by procedures (1)-(3) were 10.9, 12.5, and 10.9 µm, respectively. The average size of synthesized particles including not only primary particle but also secondary particle was over 10 µm from the laser diffraction particle size analysis. The large part of primary particle size was less than 10 µm which was confirmed by SEM observation. The precipitated sample yields were 81, 78, and 79% for procedures (1)-(3), respectively. The yield for procedure (1) was slightly higher than for procedures (2) and (3). Thus, the largest average particle size was obtained by procedure (2). Fig. 3.8 shows the SEM images of the precipitated samples synthesized using procedures (1)–(3) and using 28 kHz ultrasound irradiation. The sizes of the scorodite particles obtained by procedures (1)–(3) were 1, 3–5, and 3–5 μ m, respectively. Fig. 3.9 shows the particle size distributions for the precipitated samples measured by the particle size analyzer. The average size of the particles synthesized by procedures (1)-(3) were 5.0, 7.0, and 8.7 µm, respectively. The precipitated sample

yields were 82, 81, and 80% for procedures (1)-(3), respectively. Thus, the size of the particles synthesized by procedure (3) was larger than that synthesized by procedure (1) or (2). Fig. 3.10 shows the SEM images of the precipitated samples synthesized using procedures (1)-(3) and using 1.7 MHz ultrasound irradiation. The size of scorodite particles obtained by the procedures (1)–(3) were 5–8, 3, and 3 µm, respectively. Fig. 3.11 shows the particle size distributions for the precipitated samples measured by the particle size analyzer. The average size of the particles synthesized by procedures (1)-(3) were 13.9, 7.6, and 8.0 µm, respectively. The precipitated particle yields were 80, 80, and 77% for the conditions (1)-(3), respectively. The precipitated yield for procedure (3) was slightly lower than for procedure (1) or (2). In this case, procedure (1) obtained scorodite particles with the largest average size. These results show that the most favorable procedure for the generation of large scorodite particles varies depending on the ultrasound frequency used during the synthesis. I attribute the differences in the optimal procedure at different ultrasound frequencies to the effect of particle agglomeration that is controlled by both the precursor size and the ultrasound frequency. To confirm the importance of particle agglomeration, I used the dynamic agglomeration formula. Dynamic agglomeration by ultrasound irradiation has been reported by Brandt [99] as follows:

$$\frac{X_p}{X_l} = \frac{1}{\sqrt{1 + \left(\frac{\pi\rho_p f d_p^2}{9\mu}\right)^2}},$$
(3.1)

where X_p is the particle amplitude, X_l is the amplitude of the liquid, ρ_p is particle density, *f* is ultrasound frequency, d_p is particle diameter, and μ is the viscosity of the liquid. According to Brandt, particles can aggregate when the X_p/X_l ratio is 0.2–0.8. Using Eq. (3.1) and the X_p/X_l ratio values varying from 0.2 to 0.8 for the 200 kHz, 28 kHz, and 1.7 MHz ultrasound frequencies, the particle size that would lead to agglomeration was calculated as 1.1–2.9 µm (200 kHz), 3.0–8.0 µm (28 kHz), and 0.4–1.0 µm (1.7 MHz). For 200 kHz, 28 kHz, and 1.7 MHz ultrasound irradiation, the largest particles were obtained for precursor size of >1 µm, >3 µm, and <1 µm, respectively. These sizes are in the range of the sizes that enable agglomeration as calculated from Eq. (3.1).



Fig. 3.4 SEM images of the precipitated samples obtained using stirring after elapsed time [78].



Fig. 3.5 Experimental procedures (1)–(3) [78].



Fig. 3.6 SEM images of the precipitated samples obtained using 200 kHz ultrasound irradiation and procedures (1)–(3) [78].



Fig. 3.7 Particle size distributions of the precipitated samples obtained using 200 kHz ultrasound irradiation and procedures (1)–(3) [78].



Fig. 3.8 SEM images of the precipitated samples obtained using 28 kHz ultrasound irradiation and procedures (1)–(3) [78].



Fig. 3.9 Particle size distribution of the precipitated samples obtained using 28 kHz ultrasound irradiation and procedures (1)–(3) [78].



Fig. 3.10 SEM images of the precipitated samples obtained using 1.7 MHz ultrasound irradiation and procedures (1)–(3) [78].



Fig. 3.11 Particle size distributions of the precipitated samples obtained using 1.7 MHz ultrasound irradiation and procedures (1)–(3) [78].

I now compare the particle size obtained by the optimal procedure at each ultrasound frequency. Fig. 3.12 shows the particle size distribution of the precipitated samples obtained using the particle size analyzer. The average size of the particles synthesized using procedure (3) and 28 kHz ultrasound irradiation is larger than that obtained by stirring. However, the average size of the particles synthesized using 28 kHz ultrasound irradiation and procedure (3) is smaller than those obtained using high-frequency 200 kHz or 1.7 MHz ultrasound irradiation. I attribute this to the nucleation by cavitation during the ultrasound irradiation and to the inhibition of particle growth and the generation of fine particles by the physical action of low frequency irradiation. The scorodite particles synthesized using high ultrasound frequencies of 200 kHz and 1.7 MHz were larger than those obtained by stirring only; using high-frequency ultrasound irradiation, I could also be prevented the generation of fine particles (<1 µm). Therefore, two conditions were necessary to obtain large particles and eliminate fine particles. First, the cavitation was successfully prevented by the short period of the ultrasound irradiation. Second, the agglomeration of the precursor during the particle growth process reduced the number of nuclei for crystal growth and enhanced the supply of solute [Fe(III), As(V)] from the solution to the precursor (Fig. 3.13). Thus, the agglomeration of the precursor was assisted by the dynamic agglomeration effect of ultrasound irradiation and the resulting preference for the precursor particles. This enabled the synthesis of large scorodite particles at a low temperature (70 °C) by irradiation for only 10 min during the total reaction time of 180 min. Further studies will explore the optimization of the ultrasound irradiation conditions such as the ultrasound power and irradiation time for the agglomeration of scorodite precursors.



Fig. 3.12 Particle size distributions of the samples synthesized by the optimal procedures for stirring only and using 200 kHz, 28 kHz, and 1.7 MHz ultrasound irradiation frequencies [78].



Synthesis process using ultrasound irradiation followed by stirring

Fig. 3.13 Image of the crystal growth of scorodite with and without ultrasound irradiation for a short period during the oxidation process [78].

3.4 Conclusions

In this chapter, I investigated the effect of the ultrasound agglomeration on the size and morphology of scorodite particles. The particle growth of the precursor during the oxidation using a stirrer was confirmed by the SEM observation. The precursor size was changed by the elapsed time and was $<1 \mu m$ at 0 min, approximately 1 μm at 10 min, and >3 µm at 20 min, respectively. Then, I synthesized the scorodite particles using three different procedures where a different size of the precursor was irradiated for 10 min during the oxidation process of 3 h of total reaction time. Even at the same frequency of ultrasound irradiation, the obtained scorodite particles size was different for the different irradiated precursor size. The largest average particle size was obtained for the 200 kHz irradiation using the >1 μ m precursor [procedure (2)], for the 28 kHz irradiation using the >3 μ m precursor [procedure (3)], and for the 1.7 MHz irradiation using $<1 \mu m$ precursor [procedure (1)]. The average particle size obtained using the above procedures were 12.5, 8.7, and 13.9 µm for the 200 kHz, 28 kHz, and 1.7 MHz ultrasound irradiation frequencies, respectively. The relationship between the optimal frequencies and precursors sizes can be explained by the dynamic action agglomeration formula. Using the 200 kHz, 28 kHz, and 1.7 MHz frequency values, the obtained ranges of the agglomeration size were 1.1–2.9 µm (200 kHz), 3.0–8.0 µm (28 kHz), and 0.4–1.0 µm (1.7 MHz). The agglomeration of precursor reduces the number of nuclei and enhances amount of solute supplied to the nuclei during the crystal growth process, leading to a larger particle size. Although the sizes of the particles synthesized using 10 minutes irradiation of 200 kHz [procedure (2)] and 1.7 MHz [procedure (1)] were smaller than that for the particles synthesized using continuous irradiation for 3 h, the scorodite particles synthesized using 10 min irradiation with high frequencies of 200

kHz or 1.7 MHz were larger than those synthesize with stirring only (7.3 μ m). The use of high frequency ultrasound irradiation also prevented the generation of fine particles (<1 μ m) due to the effectiveness of the short period ultrasound irradiation for the prevention of cavitation that is related to the generation of crystal nuclei. Thus, I found that it is possible to synthesize large scorodite particles (average particle size 10 μ m) at low temperature (70 °C) using high-frequency ultrasound irradiation for only 10 min on precursors of a suitable size during the total reaction time of 180 min.

Chapter 4

Utilization of carbon dioxide to synthesize large scorodite particles under ultrasound irradiation

4.1 Introduction

In chapter 3, the growth process was monitored using scanning electron microscopy (SEM) and revealed that the precursors make agglomerations during the early stage of scorodite synthesis (Fig. 3.4). As reaction time increased, the agglomerates were transformed to scorodite by the crystal growth during further oxidation. The effect of ultrasound irradiation on particle agglomeration is well known [99–103]. Brandt proposed the following equation to describe ultrasound-induced dynamic agglomeration [99]:

$$\frac{X_p}{X_l} = \frac{1}{\sqrt{1 + \left(\frac{\pi\rho_p f d_p^2}{9\mu}\right)^2}},$$
(3.1)

where X_p is the particle amplitude, X_l is the smplitude of the liquid, ρ_p is the particle density, *f* is the ultrasound frequency, d_p is the particle diameter, and μ is the viscosity of the liquid. According to Brandet, particles aggregate when $X_p / X_l = 0.2$ –0.8, For an ultrasound frequency of 200 kHz and X_p / X_l range of 0.2–0.8, the particle size of the scorodite precursor calculated using Eq. (3.1) is 1.1–2.9 µm. The particle size of the scorodite precursor varies for different ultrasound frequencies (e.g., 1.7 MHz: 0.4–1.0 µm; 28 kHz: 3.0–8.0 µm). In chapter 3, ultrasound was irradiated to each precursor of the particle size which can be aggregated with each frequency [Fig. 4.1 (b), (c), and (d)] [78]. I successfully synthesized larger scorodite particles using ultrasound than those obtained under only stirring because of the agglomeration of the precursor during the early stage of scorodite synthesis [Fig. 4.1 (a)]. The average size of synthesized particles including not only primary particle but also secondary particle was over 10 µm from a laser diffraction particle size analyzer. The large part of primary particle size was less than 10 µm which was confirmed by SEM observation. In addition, size of synthesized particles was different with ultrasound frequency, and high ultrasound frequencies (1.7 MHz and 200 kHz) were desirable to synthesize large size scorodite particles. The size of the synthesized scorodite particles was minimized at the low ultrasound frequency (28 kHz). It is a well-known fact that the lower ultrasound frequency has a stronger physical effect [97, 104-107]. I consider that these findings were attributed to dispersion resulting from cavitation. Cavitation generates by ultrasound not only the oxidants (e.g., OH·, H₂O₂) [40, 108] but also the physical action (jet flow, shock wave) [109–111]. The oxidants promoted the oxidation of scorodite precursor in chapter 2 [76]. However, I consider that the dispersion effect (jet flow, shock wave) resulting from cavitation during ultrasound irradiation led to the potential for the inhibition of the precursor agglomeration by ultrasound vibration.

Ultrasound cavitation is influenced by ultrasound power and the dissolved gas species present [76, 83, 112–116]. The cavitation effect decreases with decreasing ultrasound power [76] because as power decreases, the amplitude of the resulting standing wave also decreases. And it is reducing the likelihood that the standing wave will exceed the cavitation threshold, which is the required energy to generate fine bubbles at each frequency of ultrasound, necessary to generate bubbles. A lower ultrasound power also results in a smaller agglomeration effect because the frequency of particle collision decreases with decreasing power. Using the solution with CO₂ gas has been shown to prevent the physical action (jet flow, shock wave) by cavitation [114–116] because of the high solubility of CO₂ in water (mole fraction of gas in water; CO₂ 3.81×10^{-4} , O₂ 1.50×10^{-5}) [117]. Gases with high solubility are easily dissolved into the solution, thereby inhibiting the contraction of bubbles during ultrasound irradiation [112]. Thus, I hypothesized that the addition of CO₂ gas during ultrasound irradiation might prevent cavitation-related dispersion during the ultrasound agglomeration process of scorodite synthesis. This would lead to the enhancement of precursor agglomeration.

In this chapter, I attempted to synthesize large (>10 μ m) scorodite particles by adding CO₂ during the ultrasound agglomeration process. In conventional methods, the synthesis of scorodite, which is synthesized by oxidizing a precursor containing Fe(II), requires O₂ gas. Thus, I used a mixed (O₂ + CO₂) gas during ultrasound irradiation and investigated the effect of CO₂ on the oxidation reaction to synthesize scorodite. This chapter is the development study of chapter 3. Therefore, I used 200 kHz ultrasound that mainly has been used in chapter 2 and 3.

4.2 Experimental procedure

A solution containing divalent iron and arsenic acid [Fe(II)-As(V)] was prepared using Na₂HAsO₄·7H₂O (Wako, >99%), FeSO₄·7H₂O (Kanto Chemical, >99%), and ion-exchange water. The Fe/As molar ratio of the Fe(II)-As(V) solution (50 mL) was adjusted to 1.5. The As(V) concentration was 20 g/L, and the solution pH was adjusted to 2.0 using H_2SO_4 (Wako, >97%). The experimental apparatus is schematically illustrated in Fig. 2.1. Ultrasound irradiation was performed using an ultrasonic generator (Kaijo TA-4021) and a submersible transducer at a frequency of 200 kHz (Kaijo). The ultrasound power applied to the solution in the flask was 12.1 W, as calorimetrically calculated [84]. A submersible transducer was placed on the bottom of a water-filled tank, and the flat-bottom flask containing the sample solution was placed directly above the transducer. By circulating hot water around the flat-bottom flask, the solution temperature was gradually raised to 70 °C over a period of 20 min and then maintained at this temperature during irradiation. Prior to ultrasound irradiation, O2 gas (100 mL/min) was flowed into the solution for 20 min to replace the air in the flask and the air dissolved in the solution. The condition of ultrasound irradiation in this chapter is same with that in chapter 3, Fig. 4.1 (c) except for type of gas. First, to increase the precursor size, the solution was stirred at 1,000 rpm and 70 °C for 10 min under O₂ gas flow (100 mL/min). Subsequently, 200 kHz ultrasound was irradiated to the precursor of the size $(1.1-2.9 \,\mu\text{m})$ which can be aggregated with 200 kHz frequency for 10 min at 70 °C. During irradiation, different mixed gases (100 vol% O₂; 80 vol% O₂ + 20 vol% CO₂; 50 vol% O₂ + 50 vol% CO₂; and 100 vol% CO₂) were injected into the solution. Finally, the oxidation reaction continued with stirring under O₂ gas flow for 160 min without ultrasound irradiation (total reaction time = 3 h). Upon reaction completion, the

precipitates were filtered through a membrane filter with a 0.45 µm pore diameter (Advantec) and collected. The precipitates were then dried at 55 °C under vacuum and analyzed by X-ray diffraction (XRD; Rigaku RINT2000, Cu K α), SEM (Hitachi TM-1000), and particle size analysis (Nikkiso Microtrac MT3300EXII). Since oxidizing radicals (e.g., OH-) generated during the reaction function as oxidants, I evaluated the amount of triiodide ions oxidized by radicals produced during ultrasound irradiation using the potassium iodide (KI) method [81, 82, 85, 86]. A KI solution (0.1 M, 50 mL) was prepared using KI for oxidant analysis (Wako, >99.5%) and ion-exchange water. After different mixed gases were flowed into the solution (100 mL/min) for 30 min to replace the air in the flask and in the solution, the solution was irradiated for 30 min using 200 kHz ultrasound. The temperature of the irradiated solution was maintained at 70 °C by circulating hot water around the flat-bottom flask. After irradiation, solution absorbance was measured at 355 nm (the absorption wavelength of triiodide ions) using ultraviolet–visible spectrophotometry (JASCO V-630iRM) to evaluate the amount of triiodide ions (molar absorptivity $\epsilon = 26,303 \, \text{dm}^3 \, \text{mol}^{-1} \, \text{cm}^{-1}$).



Fig. 4.1 Images of scorodite crystals grown with and without ultrasound irradiation during the oxidation process: (a) stirrer, (b) 28 kHz ultrasound, (c) 200 kHz ultrasound, and (d) 1.7 MHz ultrasound [79].

4.3 Results and discussion

Fig. 4.2 shows the XRD patterns of the particles synthesized at 70 °C for 3 h using various mixed gases under the proposed sonication condition using 200 kHz frequency. To identify those synthesized samples, powder diffraction file (PDF) of No. 00-034-0468 was also drawn in Fig. 4.2. The patterns indicate that all synthesized samples were scorodite, and no impurity peaks were observed. The crystallinities of the scorodite particles synthesized using the different mixed gases were >90%, and the scorodite yields were approximately 78% for all experimental conditions. Thus, the injection of mixed gases for 10 min during ultrasound irradiation did not affect the crystallinity or yield of the synthesized scorodite particles.

SEM images and particle size distribution of the scorodite particles synthesized using different mixed gases under the proposed sonication condition are shown in Figs. 4.3 and 4.4. Particle size analysis indicated that the scorodite particles formed using CO₂ gas were larger in value than those synthesized using only O₂ gas; the average particle sizes of the scorodite particles measured using the particle size analyzer were 12.1 μ m (100 vol% O₂), 13.8 μ m (80 vol% O₂ + 20 vol% CO₂), 12.6 μ m (50 vol% O₂ + 50 vol% CO₂), and 12.6 μ m (100 vol% CO₂). To compare the primary particle size, I observed these particle using SEM. From these photos, it is obvious that the condition of CO₂ gas of 100 vol%. To investigate the effect of ultrasound irradiation, I synthesized scorodite particles without ultrasound (Fig. 4.5) and compared the samples with those generated using ultrasound (Fig. 4.3). Without ultrasound irradiation, inhomogeneous particles with sizes of approximately 5 μ m were obtained under all gas conditions, and the use of CO₂ gas for 10 min did not affect the particle size from SEM

observation (Fig. 4.5). The effect of a dissolved gas on the strength of physical action (jet flow, shock wave) is related to the type of dissolved gas [114–116]. Argon gas, which has low solubility in water (mole fraction of Ar gas in water = 1.51×10^{-5}) as same as O₂ gas [117], results in strong physical action related to cavitation. However, mixing Ar with CO₂ (80 vol% Ar + 20 vol% CO₂) drastically reduces the physical action caused by cavitation [116]. Therefore, CO₂ gas mitigated the dispersion attributed to cavitation, thereby enhancing precursor agglomeration. As the result, the number of nuclei decreased, and the amount of solute [Fe(III), As(V)] supplied per a nuclei increased, resulting in the formation of large (>10 µm) scorodite particles when CO₂ gas was added during ultrasound agglomeration for 10 min.

As indicated above, the scorodite particles synthesized using various mixed gases were analyzed by SEM and particle size analysis. Large (>10 μ m) scorodite particles were generated when the CO₂ content was 50 vol% or greater; otherwise, small (\leq 3 μ m) particles were obtained (Fig. 4.3). The particle size distribution also indicated the generation of smaller particles in the presence of \geq 50 vol% CO₂ compared with the utilization of mixed gas containing 20 vol% CO₂ (Fig. 4.4). Small particles are unfavorable for arsenic storage because they increase the rate of arsenic leaching from scorodite. I consider that these results come from the decrease of the O₂ gas content in flowing mixed gas during the ultrasound agglomeration process on scorodite synthesis.



Fig. 4.2 XRD patterns of particles synthesized at 70 °C for 3 h with the agglomeration process using ultrasound irradiation with mixed gases of various O₂/CO₂ percentages for 10 min [79].



Fig. 4.3 SEM images of scorodite particles synthesized at 70 °C for 3 h with the agglomeration process using ultrasound irradiation with mixed gases of various O₂/CO₂ percentages for 10 min. O₂/CO₂ percentages are (a) 100 vol% O₂, (b) 80 vol% O₂ + 20 vol% CO₂, (c) 50 vol% O₂ + 50 vol% CO₂, and (d) 100 vol% CO₂ [79].



Fig. 4.4 Particle size distributions of samples synthesized at 70 °C for 3 h with the agglomeration process using ultrasound irradiation with mixed gases of various O₂/CO₂ percentages for 10 min [79].



Fig. 4.5. SEM images of scorodite particles synthesized at 70 °C for 3 h using combination of stirring with O₂ gas for 170 min and standing with mixed gases of various O₂/CO₂ percentages for 10 min. O₂/CO₂ percentages are (a) 100 vol% O₂, (b) 80 vol% O₂ + 20 vol% CO₂, and (c) 100 vol% CO₂ [79]. To confirm the effect of ultrasound irradiation on oxidation, I evaluated the amount of triiodide ions oxidized by oxidant radicals (e.g., $OH \cdot$) generated by cavitation during ultrasound irradiation using the KI method [81, 82], which involves the following chemical reactions:

$$H_2 O \to O H^{\cdot} + H^{\cdot}, \tag{1.7}$$

$$2OH \cdot + 2I^- \rightarrow I_2 + 2OH^-, \tag{2.4}$$

$$\mathbf{I}_2 + \mathbf{I}^- \to \mathbf{I}_3^-. \tag{2.5}$$

The generation of oxidant radicals is due to the thermal decomposition of the water by the high temperature reached of bubbles during collapse. I consider that CO₂ gas could not reach the high pressure of temperature of bubbles during collapse because of its high solubility in the reaction solution [112, 113]. After replacing the air present in the flask and solution using each gas (100 mL/min), the prepared KI solution (pH 6.0) was continuously irradiated using a 200 kHz transducer at 70 °C for 30 min. The amounts of triiodide ions generated by ultrasound irradiation under different gas mixtures were 3.77×10^{-5} mol/L (100 vol% O₂), 2.64×10^{-5} mol/L (80 vol% O₂ + 20 vol% CO₂), 0.54×10^{-5} mol/L (50 vol% O₂ + 50 vol% CO₂), 0.30×10^{-5} mol/L (20 vol% O₂ + 80 vol% CO₂), and 0.25×10^{-5} mol/L (100 vol% CO₂) (Fig. 4.6). The amount of generated triiodide ions was highest for pure O₂ gas (100 vol%) and decreased with increasing CO₂ content. I consider that the gas mixture containing 20 vol% CO₂ mitigated the physical action while retaining the oxidation effect. In contrast, the mixture with \geq 50 vol% CO₂ prevented physical action along with oxidation resulting from bubble collapse. In chapter 2, oxidant radicals generated under 200 kHz

ultrasound irradiation and O₂ gas flow contribute to the oxidation reaction to synthesize scorodite [76]. Thus, when the gas mixture contains more than 50 vol% of CO₂, the oxidation reaction during the ultrasound agglomeration process is inhibited because of the reduction in O₂ gas and oxidant radicals, which are responsible for oxidation. Therefore, a large proportion of CO_2 gas (≥ 50 vol%) prevented nuclei formation by oxidation of radicals and O₂ gas during ultrasound irradiation (10 min) at the early reaction stage. Subsequently, during the stirring process (160 min), nuclei also began to form along with the growth of agglomerated particles. Hence, a mixture of large (>10 μ m) and small ($\leq 3 \mu$ m) particles was obtained. The small particles ($\leq 3 \mu$ m) in the generated ones at \geq 50 vol% of CO₂ indicated similar in size to the scorodite particles produced under O₂ gas flow and stirring at 70 °C for 3 h [78]. However, the scorodite yield was the same (78%) under all experimental conditions, and the average particle size was larger when CO_2 gas was used compared to when only O_2 gas (100 vol%) was employed (Fig. 4.4). These results indicate that the prevention of the dispersion effect by cavitation is more important than the decrease of the oxidation effect in the ultrasound agglomeration process (10 min).

The use of a mixed gas containing 80 vol% O_2 and 20 vol% CO_2 mitigated the physical action while retaining the oxidation effect attributed to O_2 gas and oxidant radicals. Large scorodite particles (>10 µm) were successfully synthesized by adding CO_2 gas during a short period (10 min) of sonication in the overall 3 h reaction process at 70 °C. Further studies will explore the effects of CO_2 gas during ultrasound agglomeration using low-frequency ultrasound, which has the higher dispersion effect of cavitation than 200 kHz ultrasound experimented in this study.



Fig. 4.6 Amount of triiodide ions generated by ultrasound irradiation using mixed gases with various content ratio of CO₂ [79].

4.4 Conclusions

In this chapter, I used CO₂ and ultrasound irradiation to synthesize large scorodite particles from a precursor containing Fe(II) via oxidation under O₂ gas flow. Mixed gases containing O₂ and CO₂ were applied during the ultrasound agglomeration process for a short time period (10 min). At first, precursor size was increased under stirring and flowing O₂ gas at 70 °C for 10 min (until the precursor size was large enough for the precursor to be aggregated by 200 kHz ultrasound). Next, the reaction solution was ultrasonically irradiated for 10 min at 70 °C under the flow of different mixed gases (O2 + CO₂). Finally, the agglomerated precursor was oxidized under flowing O₂ gas with stirring for 160 min without ultrasound irradiation (total reaction time = 3 h). The scorodite particles synthesized using only O₂ gas (100 vol%) were approximately 5-6 μm in size by SEM observation. In contrast, large scorodite particles (>10 μm) were synthesized when mixed gases containing CO2 were used. Thus, CO2 gas mitigated dispersion caused by cavitation, which decreased the number of crystal nuclei and increased the amount of solute [Fe(III), As(V)] supplied per crystal nuclei. However, when the CO₂ content of the mixed gas exceeded 50 vol%, a mixture of large (>10 μ m) and small ($\leq 3 \mu m$) particles was obtained. In this case, scorodite nuclei formed along with the growth of agglomerated particles during the stirring process (160 min) after ultrasound agglomeration (10 min). In contrast, the mixed gas containing 20 vol% CO₂ gas prevented cavitation-related dispersion while preserving oxidation by O₂ and oxidant radicals, thereby resulting in the formation of large scorodite particles (>10 μm).

Chapter 5

Effect of reaction temperature on the size and morphology of scorodite synthesized using ultrasound irradiation

5.1 Introduction

In chapter 2, a mixture of fine (<1 μ m) and large scorodite particles (>10 μ m) with faceted surfaces is synthesized at low temperature (70 °C) and a short reaction time (3 h) using 200 kHz ultrasound irradiation [76]. I consider that fine particles (<1 μ m) are generated because of the nuclei formation caused by fine bubbles, which are the order of several micrometers, generated by ultrasound. In chapter 3, I applied the dynamic agglomeration formula (Eq. 3.1) to synthesize large scorodite particles without the fine particles. However, the effect of fine bubbles, such as a dispersion effect for particles in the solution, is not considered in the dynamic agglomeration formula (Eq. 3.1). Generation amount of fine bubbles depend on the solution temperature [112, 118]. Investigation of the effect of reaction temperature on the size and morphology of scorodite synthesized using ultrasound irradiation is necessary. At reaction temperatures higher than 70 °C, I hypothesize that large scorodite particles (>10 µm) without fine particles (<1 µm) can be synthesized by decreasing the amount of fine bubbles and promoting the agglomeration effect with ultrasound irradiation. In this chapter, I focused on dynamic agglomeration of ultrasound and applied it to the current synthesis method [29] of scorodite particles at 90 °C to prevent the generation of fine bubbles and to utilize the agglomeration effect of ultrasound selectively. At reaction temperatures lower than 70 °C, synthesis of scorodite at low temperatures using ultrasound irradiation is expected to promote agglomeration and dissolution and deposition, as well as the
oxidation of the Fe(II)-containing precursor. To the best my knowledge, there are no reports of scorodite synthesis at 30 °C; thus, in this chapter, I aim to investigate the relationship between ultrasound irradiation and reaction temperature on scorodite synthesis.

5.2 Experimental procedure

A solution containing divalent iron and arsenic acid [Fe(II)-As(V)] was prepared using Na₂HAsO₄·7H₂O (Wako, >99%), FeSO₄·7H₂O (Kanto Chemical, >99%), and ion-exchange water. The Fe(II)-As(V) solution (50 mL) was adjusted to an Fe/As molar ratio of 1.5. The As(V) concentration was 20 g/L, and the solution pH was adjusted to 2.0 using H_2SO_4 (Wako, >97%). A schematic illustration of the experimental apparatus is shown in Fig. 2.1. Ultrasound irradiation was performed using an ultrasonic generator (Kaijo TA-4021) and a submersible transducer at a frequency of 200 kHz (Kaijo). The ultrasound power applied to the solution in the flask was 12.6 W, as calculated calorimetrically [84]. A submersible transducer was placed on the bottom of a tank filled with water, and a flat-bottom flask containing the sample solution was placed directly above the transducer. The temperature of the irradiated solution was set to 90, 70, 50, and 30 °C using hot water circulation around the flat-bottom flask. The solution temperature was raised gradually over 20 min until the desired temperature was reached. Prior to ultrasound irradiation of the solution, O₂ gas (100 mL/min) was flowed into the solution for 20 min to replace the air in the flask. Ultrasound irradiation was conducted at 90, 70, 50, and 30 °C, each, for 3 h under O₂ gas flow. Upon completion of the reaction, the precipitates were filtered through a membrane filter with a 0.45 µm pore diameter (Advantec) and collected. The precipitates were then dried at 55 °C with vacuum and analyzed by X-ray diffraction (XRD; Rigaku RINT2000, Cu Ka), and scanning electron microscopy (SEM; Hitachi TM-1000).

5.3 Results and discussion

The synthesis of scorodite using ultrasound irradiation or stirring at various temperatures was conducted. The oxidation-reduction potential (ORP) of the reacted solution and the yield of scorodite and the precursor are shown in Fig. 5.1 (a and b). Here, I follow the approach of Fujita, who used the ORP values measured before and after the reaction to confirm the oxidation of Fe(II) in the solution [29]. For stirring, the differences in the ORP values ($\triangle ORP$) before and after the reaction were 225 (90 °C), 170 (70 °C), 153 (50 °C), and 77 (30 °C) mV and the yields were 2.89 (90 °C), 2.42 (70 °C), 1.42 (50 °C), and 0.52 (30 °C) g. As illustrated in Fig. 5.1 (a), the yield and $\triangle ORP$ increase with the reaction temperature. Therefore, a higher reaction temperature leads to faster oxidation of Fe(II). On the other hand, when ultrasound irradiation was used, the $\triangle ORPs$ were 71 (90 °C), 144 (70 °C), 59 (50 °C), and 53 (30 °C) mV and the yields were 1.51 (90 °C), 1.79 (70 °C), 1.19 (50 °C), and 0.74 (30 °C) g. Results obtained using ultrasound irradiation were similar to those obtained using stirring. Ultrasound irradiation of the solution at high reaction temperature resulted in an increase in the yield and $\triangle ORP$. However, as shown in Fig. 5.1 (b), the order of ORP values at 70 and 90 °C with ultrasound irradiation was reversed from that when stirring was used (i.e., the ORP and yield decreased with an increase in temperature from 70 to 90 °C). Additionally, I compared these results to those obtained from the synthesis using only O₂ flow at 100 mL/min at temperatures of 70 and 90 °C [without ultrasound irradiation and stirring, Fig. 5.1 (b)]. Oxygen gas generates the precursor (amorphous) containing Fe(II), Fe(III), and As(V) at each temperature through Fe(II) oxidation in the solution. The only difference observed without ultrasound irradiation and stirring was a decrease in the yield at 70 °C. These results may be because of a decrease in the number

of bubbles during ultrasound irradiation at 90 °C; therefore, jet flow becomes weak and the amount of radicals generated by the collapse of the bubbles is reduced. As a result, oxidation by ultrasound irradiation promotes the synthesis of scorodite at 70 °C.

The XRD patterns of the particles synthesized using ultrasound irradiation or stirring for 3 h at each reaction temperature with an O₂ flow are shown in Fig. 5.2 (a and b). When using stirring at temperatures above 70 °C, the synthesized material was identified as scorodite from the powder diffraction file (PDF) No. 00-037-0468. Crystallinity values of scorodite synthesized at different temperatures (30 °C, 50 °C, and >70 °C) were 1, 7, and >90%, respectively. Thus, a reaction temperature of >70 °C is necessary to synthesize scorodite. When using ultrasound irradiation, XRD peaks from scorodite were observed at temperatures >30 °C. Sharp peaks of scorodite are observed above 50 °C. Crystallinity values of scorodite synthesized at different temperatures were 46% (30 °C) and >90% (>50 °C). This is attributed to the promotion of Fe (II) oxidation in the precursor by ultrasound irradiation and O₂ gas. Thus, even at 50 °C, ultrasound irradiation. To the best of my knowledge, crystalline scorodite has never been synthesized at temperatures as low as 30 °C for 3 h.



Fig. 5.1 ORP values and yields of scorodite synthesized at different reaction temperatures using (a) stirring and (b) ultrasound irradiation [80].



Fig. 5.2 XRD patterns of precipitated particles synthesized at different reaction temperatures using (a) stirring and (b) ultrasound irradiation [80].

SEM images of the products synthesized by ultrasound irradiation or stirring for 3 h at each reaction temperature are shown in Fig. 5.3. Under stirring conditions at 30 and 50 °C, fine particles (<1 µm), which are amorphous, agglutinated and formed secondary particles. Particles of polyhedral scorodite (5-6 µm) were synthesized at temperatures >70 °C and were agglutinated. Under ultrasound irradiation, polyhedral scorodite particles (3 µm) were formed at 50 °C. Furthermore, the appearance of scorodite particles with faceted crystals starts to be observed at this temperature. This may result from oxidation assisted by radicals generated from the collapse of bubbles and the enhancement of the solubility of the precursor by jet flow to promote the crystalline growth of scorodite. Large numbers of scorodite particles (>10 µm) with faceted crystals were found at 70 °C, although fine particles (<1 µm) were also observed. At 90 °C, the size of scorodite particles was broad and inhomogeneous, from fine particles (<1 μ m) to large particles (>10 μ m). These results are very similar to those of scorodite particles (Fig. 5.4) synthesized using only O₂ flow without ultrasound irradiation and stirring at 90 °C, although large particles (>10 µm) were not observed. I believe that the formation of large particles (>10 μ m) with ultrasound irradiation comes from the acceleration of agglomeration of the precursor by dynamic agglomeration.

The degree to which particles dynamically agglomerated by ultrasound irradiation is regulated by the frequency of the ultrasound; a particular frequency can agglomerate a particular size particle. As the reaction temperature increases, the crystal growth rate of the precursor increases. Therefore, shorter aggregation period of a precursor leads to a lower agglomeration-promoting effect of ultrasound. The value of Δ ORP and the yield at 90 °C were lower than that observed at 70 °C when ultrasound irradiation was used. This is likely caused by the reduction in the number of cavitation

bubbles generated by ultrasound irradiation at 90 °C compared to 70 °C. Therefore, under high-temperature conditions, cavitation bubbles formed by ultrasound irradiation for nucleation of the precursor are difficult to generate. This reduces the cavitation effects, resulting in inhomogeneous particle size and low yield, cause by a decrease in the oxidation of Fe(II) to Fe(III) by radicals, and less promotion of dissolution by jet flow generated by the collapse of bubbles. At 90 °C of solution temperature, I hypothesized that large scorodite particles (>10 μ m) without fine particles (<1 μ m) can be synthesized by decreasing the amount of fine bubbles and promoting the agglomeration effect with ultrasound irradiation. This reduction of the cavitation effect was as expected from my hypothesis. However, the results, inhomogeneous particle size and low yield of scorodite, were different. These results indicate that the agglomeration effect of the ultrasound are necessary to synthesize scorodite as homogeneous and large particles even though including some fine particles.



Fig. 5.3 SEM images of scorodite particles synthesized at different reaction temperatures using (a) stirring and (b) ultrasound irradiation [80].



Fig. 5.4 SEM image of scorodite particles synthesized at 90 °C using O₂ gas flow without stirring and ultrasound irradiation [80].

In chapter 2, I successfully synthesized large particles (>10 μ m) at 70 °C for 3 h [76, 77]. However, fine particles (<1 μ m) were also formed, resulting from Fig. 2.4. The jet flow generated by the collapse of the bubbles promotes dissolution and deposition to grow scorodite faceted crystals. Therefore, oxidation of Fe(II) in the precursor, for reaction temperatures below 70 °C, is promoted by both O₂ gas and the OH radical, and hydrogen peroxide generated by ultrasound irradiation under an O₂ atmosphere [40].

Low-temperature and short-time synthesis of highly crystalline scorodite at 30 °C for 3 h has not been reported. Using ultrasound irradiation, XRD peaks of scorodite synthesized over 30 °C were observed [Fig. 5.2 (b)]. XRD patterns of the products synthesized at 30 °C under ultrasound irradiation or stirring are shown in Fig. 5.5. Accelerated oxidation of precursors containing Fe(II) by ultrasound irradiation leads to the observation of scorodite. Thus, it is possible to synthesize highly crystalline scorodite by the promotion of oxidation using ultrasound irradiation in shorter times than stirring. Accordingly, I attempted low-temperature synthesis of highly crystalline scorodite with longer reaction times (7 h). Low-temperature synthesis of scorodite by hydrogen peroxide (H₂O₂) addition was also attempted. Hydrogen peroxide (0.013 mol of H₂O₂ resulting in a H₂O₂/Fe(II) molar ratio of 2/3) was added slowly, with a drop rate of about 0.17 mL/min, to the prepared Fe(II) solution. XRD patterns of the precipitate synthesized at 30 °C for 7 h with ultrasound irradiation, stirring, or the addition of hydrogen peroxide (with stirring or ultrasound) are shown in Figs. 5.6 and 5.7. Under stirring, crystal peaks of scorodite were not observed because the oxidation of the precursors containing Fe(II) was too slow. After ultrasound irradiation for 7 h at 30 °C, XRD peaks indicated the presence of scorodite, with an intensity stronger than that observed after 3 h. The addition of hydrogen peroxide under all conditions provided

amorphous products. Shinoda et al. reported that highly crystalline scorodite is synthesized by the oxidation of Fe(II)-Fe(III)-As(V) precursor in a solution containing a high concentration of Fe(II) [27]. Synthesis of scorodite from Fe(III) solution requires long reaction times when Fe(II) is not present in the solution "E. Shibata, unpublished results". Therefore, the addition of hydrogen peroxide to the Fe(II) solution leads to the oxidation of Fe(II) to Fe(III) in the bulk solution, rather than the oxidation of precursors, and crystalline scorodite is not formed.



Fig. 5.5 XRD patterns of the precipitated particles synthesized at 30 °C using ultrasound irradiation or stirring [80].



Fig. 5.6 XRD patterns of the precipitated particles synthesized at 30 °C for 7 h using stirring with and without the addition of hydrogen peroxide [80].



Fig. 5.7 XRD patterns of the precipitated particles synthesized at 30 °C for 7 h using ultrasound irradiation with and without the addition of hydrogen peroxide [80].

The amount of oxidant generated by ultrasound irradiation at 200 kHz was estimated by utilizing the KI method [Eq. (1.7), (2.4), and (2.5)] [81, 82]. The prepared KI solution (pH 6.0) was irradiated using a 200 kHz transducer at 30 °C for 15 min after replacement of air in the solution using each gas (100 mL/min). The amount of triiodide ions generated by ultrasound irradiation or stirring under different atmospheric conditions (O₂, air, Ar) is shown in Fig. 5.8. When stirring was used, no triiodide ion was generated under any condition. However, when using ultrasound irradiation, the O₂ atmosphere showed the largest amount of triiodide ions, with the second highest yield under air, followed by argon. Specific heat ratios of 1.396 (O₂), 1.402 (air), and 1.670 (Ar) [119] at a temperature of 27 °C and a pressure of 1.0 atm did not match the order of the amount of generated triiodide ions. It is reported that the amount of OH radicals generated by 200 kHz irradiation under O₂ atmosphere is larger than that under Ar atmosphere [120].

I also considered the relationship between the amount of oxygen in the atmosphere to that of generated triiodide ions. O_2 gas captures H radical under O_2 atmosphere [Eq. (1.10)] and prevents the recombination of OH radical and H radical [121].

$$H \cdot + O_2 \rightarrow HO_2 \cdot .$$
 (1.10)

Thus, the amount of triiodide ions increases because of the formation of OH radical, hydrogen peroxide, and HO₂ radical. At low temperatures, oxidizing Fe(II) to Fe(III) by O_2 gas is difficult; therefore, the synthesis of scorodite was promoted by oxidation from radicals generated by ultrasound irradiation under an O_2 atmosphere.



Fig. 5.8 The amount of triiodide ion generated, using KI method, under different atmospheres [80].

Finally, to confirm the promotion of the precursor [including Fe (II)] oxidation, scorodite synthesis was conducted at 30 °C for 7 h under different atmospheres (O2, air, Ar). Fig. 5.9 shows the values of ORP values and yields of scorodite synthesized using ultrasound irradiation. Under an O_2 atmosphere, the highest value of $\triangle ORP$ and the yield was observed. When the amount of oxygen is lower (air), the value of $\triangle ORP$ and the yield decreases. Fig. 5.10 shows the XRD patterns of the samples precipitated under different atmospheres at 30 °C. Scorodite peaks in the XRD patterns are observed in the precipitates under every atmospheric condition. The Ar atmosphere showed the highest intensity peaks attributed to crystalline scorodite. The precipitate from the O₂ atmosphere showed the lowest intensity peaks from scorodite. The precursor [Fe(II)-F e(III)-As(V)] was generated easily by oxidation of Fe(II) in the solution from O₂ gas; however, because the crystal growth of scorodite is slow, oxidation of the precursor at low temperatures is slow. Conversely, under an Ar atmosphere, the precursor was not generated because Fe(II) solution cannot be oxidized by Ar gas. Hence, the amount of generated precursor was lower than that observed from the reactions carried out under an O_2 or air atmosphere (Fig. 5.9). The amount of precursor that forms is low under an Ar atmosphere, and is related to the amount of oxidation of the precursor by radicals generated from ultrasound irradiation. Thus, I demonstrated that highly crystalline scorodite can be obtained under an Ar atmosphere. In conventional methods, the synthesis of scorodite requires O₂ gas. However, I confirmed that radicals generated by ultrasound irradiation contribute to the synthesis of scorodite because it can be synthesized under an Ar gas flow (without O2 gas). Although, up to 70 °C, fine scorodite particles (<1 µm) are easily generated by the nucleation effect of fine bubbles during ultrasound irradiation, generation and collapse of cavitation bubbles contribute

significantly to enable not only the synthesis of scorodite at temperatures as low as 30 °C but also the crystal growth of particles (>10 μ m) at 70 °C by oxidation from radicals and dissolution–deposition by jet flow.

In this chapter, I synthesized scorodite particles using ultrasound irradiation at four temperatures (90, 70, 50, and 30 °C). Under the ultrasound irradiation condition, the size of the particles decreased when the temperature increased from 70 to 90 °C. I concluded that 70 °C is a suitable temperature in this experimental condition to synthesize large scorodite particles. However, it is unclear whether 70 °C is the best temperature, because detailed temperature data, such as those for 85, 80, 75, and 65 °C, have not yet been investigated.



Fig. 5.9 ORP value and yield of scorodite synthesized at 30 °C for 7 h using ultrasound irradiation [80].



Fig. 5.10 XRD patterns of the precipitated particles synthesized at 30 °C using ultrasound irradiation under different atmospheres [80].

5.4 Conclusions

I have investigated the synthesis of large scorodite particles (>10 µm) from fine sized precursor using dynamic agglomeration by ultrasound irradiation (70 °C, 3 h). Generation of fine bubbles depends on the solution temperature, but the relationship between ultrasound irradiation and reaction temperature on scorodite synthesis has not yet been investigated. The effect of different reaction temperatures (90, 70, 50, and 30 °C) on the formation, size, and morphology of scorodite particles was investigated under an O_2 gas flow with ultrasound irradiation. I expected to synthesize large scorodite particles without fine particles using the agglomeration effect of ultrasound irradiation at 90 °C. However, the size of the particles was inhomogeneous from fine (<1 µm) to large (>10 µm). Ultrasound irradiation contributed to the generation of large particles through assisting the agglomeration effect. The value of Δ ORP and yield decreased when the temperature increased from 70 to 90 °C. In that case, the oxidation and dissolution and deposition effect were lower because of a decrease in the number of bubbles, which reduces the amount of radicals and jet flow generated by ultrasound, leading to inhomogeneous formation of particles.

Chapter 6

Effect of ultrasound irradiation on size and morphology of scorodite particles synthesized under different acidic conditions

6.1 Introduction

It is reported that large scorodite particles (>10 μ m) with polyhedron shape is synthesized using a stirrer under O₂ gas flow at 95 °C after 7 h in a sulfuric acidic solution at pH 1.0 [29]. The size and morphology of scorodite particles are also influenced by the pH of the reaction solution [34]. However, effect of different acidic concentrations, which means different pH values, for reaction solution of scorodite on property of synthesized scorodite particles has not yet been investigated. In this chapter, I synthesized scorodite particles using ultrasound irradiation in acidic solutions of different pH and investigated the effect of ultrasound irradiation on the size and morphology of scorodite particles.

6.2 Experimental procedure

A solution containing divalent iron and arsenic acid [Fe(II)-As(V)] was prepared using Na₂HAsO₄·7H₂O (Wako, >99%), FeSO₄·7H₂O (Kanto Chemical, >99%), and ion exchange water. The Fe(II)-As(V) solution (50 mL) was adjusted to an Fe/As molar ratio of 1.5. The As(V) concentration was 20 g/L, and The solution pH was adjusted to 2.0, 1.5, and 1.0, respectively using H_2SO_4 (Wako, >97%). A schematic illustration of the experimental apparatus is shown in Fig. 2.1. Ultrasound irradiation was performed using an ultrasonic generator (Kaijo TA-4021) and a submersible transducer at a frequency of 200 kHz (Kaijo). The ultrasound power applied to the solution in the flask was 11.6 W (200 kHz) as calculated calorimetrically [84]. A submersible transducer was placed on the bottom of a tank filled with water, and a flat-bottom flask containing the sample solution was placed directly above the transducer. The temperature of the irradiated solution was set to 70 °C using hot water circulation around the flat-bottom flask. The solution temperature was raised gradually over 20 min until the desired temperature was reached. Prior to ultrasound irradiation of the solution, O₂ gas (100 mL/min) was flowed into the solution for 20 min to replace the air in the flask. Ultrasound irradiation was conducted at 70 °C for 3 h under O₂ gas flow in different acidic solutions (pH 2.0, 1.5, and 1.0). Upon completion of the reaction, the precipitates were filtered through a membrane filter with a 0.45 µm pore diameter (Advantec) and collected. The precipitates were then dried at 55 °C with vacuum and analyzed by X-ray diffraction (XRD; Rigaku RINT2000, Cu Ka), and scanning electron microscopy (SEM; Hitachi TM-1000).

6.3 Results and discussion

XRD patterns of the precipitate synthesized using with and without 200 kHz ultrasound irradiation under different pH conditions are shown in Figs. 6.1 and 6.2, respectively. The patterns indicate that all synthesized samples were scorodite. However, the intensity of XRD peaks of scorodite synthesized at pH 1.0 differs between two conditions (with or without ultrasound irradiation). In the case of without ultrasound, oxidation of the precursor (crystallization) is difficult because the precursor is easily dissolute into the strong acidic solution (pH 1.0). Therefore, I consider that 200 kHz ultrasound effectively oxidized Fe(II) to Fe(III) and the oxidation rate by ultrasound may be higher than dissolution rate of precursor with or without ultrasound in the strong acidic solution.

Fig. 6.3 shows the SEM images of the scorodite particles synthesized at 70 °C for 3 h in a solution at pH 1.0. When without using ultrasound, size of scorodite particles was inhomogeneous from fine particles (<1 μ m) to large particles (>10 μ m). Size and morphology of scorodite particles synthesized using ultrasound irradiation were 1–6 μ m and rod-like particles with faceted crystals. The difference of the size and morphology of scorodite synthesized using with or without 200 kHz ultrasound should come from the oxidation effect by oxidants (i.e., OH· and HO₂·) generated by ultrasound irradiation [40].



Fig. 6.1 XRD patterns of precipitated samples synthesized in different pH solutions using 200 kHz ultrasound irradiation under O₂ gas flow.



Fig. 6.2 XRD patterns of precipitated samples synthesized in different pH solutions under O_2 gas flow without ultrasound irradiation.



Fig. 6.3 SEM images of scorodite particles synthesized using O_2 gas with or without 200 kHz ultrasound irradiation in the solution at pH 1.0.

6.4 Conclusions

To investigate the effect of ultrasound irradiation on the size and morphology of scorodite synthesized at different pH conditions, scorodite particles were synthesized in different pH solutions (pH 2.0, 1.5, and 1.0) for 3 h under O_2 gas flow. The intensity of XRD peaks of scorodite synthesized at pH 1.0 without ultrasound was lower than that of scorodite synthesized using ultrasound irradiation. In addition, the size of scorodite particles was inhomogeneous from fine particles (<1 μ m) to large particles (>10 μ m) at without ultrasound irradiation condition. On the other hand, high crystalline scorodite particles with rod-like was synthesized at ultrasound irradiation condition. Oxidation of the precursor (crystallization) in the strong acidic solution of pH 1.0 is difficult because the precursor is easily dissolved. The different results at pH 1.0 should come from the difference of oxidation amount by radicals generated by 200 kHz ultrasound irradiation.

Chapter 7

Synthesis of calcium iron arsenate for stable storage of arsenic under alkali condition

7.1 Introduction

Scorodite can store arsenic stability for acidic to neutral solutions [24, 25]. However, scorodite is unstable for an alkali solution. Thus, study of arsenic storage material under an alkali solution is needed. In mining and metallurgical smelter, Ca-Fe arsenates [e.g., yukonite (Ca₂Fe₃(AsO₄)₄(OH)·12H₂O), arseniosiderite (Ca₃Fe₄(AsO₄)₄(OH)₆·3H₂O)] are generally generated as secondary products of iron arsenates at tailing containing calcium at neutral-alkali environment [122–129]. However, formation conditions of yukonite and arseniosiderite are not yet fully clarified. Therefore, I investigated the synthesis conditions of these materials, yukonite and arseniosiderite, by varying the solution pH from 6 to 11.

7.2 Experimental procedure

А solution containing calcium, trivalent iron. arsenic acid and [Ca(II)-Fe(III)-As(V)] was prepared using $Ca(NO_3)_2 \cdot 4H_2O$ (Wako, >99%), Fe(NO₃)₃·9H₂O (Wako, >99%), Na₂HAsO₄·7H₂O (Wako, >99%), and ion exchange water. The Ca(II)-Fe(III)-As(V) solution (50 mL) was adjusted to an Ca/Fe/As molar ratio = 1.0/1.5/1.5. The As(V) concentration was 11 g/L (0.15 M), and pH values of solutions were adjusted to 6.0, 7.0, 7.5, 8.0, 9.0, 10.0, and 11.0 respectively using 5 M NaOH (Wako, >97%). The reaction solutions were stirred at 85 °C for 36 h using hotplate stirrer (200 rpm). After completion of the reaction, the precipitates were filtered through a membrane filter with a 0.45 µm pore diameter (Advantec) and collected. The precipitates were then dried at 55 °C with vacuum and identified by X-ray diffraction (XRD; Rigaku RINT2000, Cu Kα).

7.3 Results and discussion

In this experimental condition, precipitates, i.e. iron hydroxide, are generated immediately before the start of the reaction. Fig. 7.1 shows the XRD patterns of precipitated samples synthesized for 36 h in various acidic solutions. Arseniosiderite peaks (PDF No. 00-026-1002) and yukonite peaks (PDF No. 00-045-1358) were shown at pH 7-9 and pH 10, respectively. The samples obtained at pH 6 and 11 were amorphous. It is reported that arseniosiderite forms in the weakly acidic to neutral solutions and yukonite forms in the neutral to weakly alkaline solutions at high concentration (3 M As, Ca/Fe/As=1.0/1.5/1.5). In this experiment, Ca-Fe-arsenates were obtained in the alkaline solution (pH \geq 7) at the condition of low concentration (0.15 M As, Ca/Fe/As=1.0/1.5/1.5). Yukonite transforms to arseniosiderite due to the supply of solute (ferric ion and calcium ion) with an elapsed time [129]. Considering from above sentences, yukonite has a tendency to transform to arseniosiderite by the supply of ferric ion, but yukonite did not change to arseniosiderite in this experiment. The reason may come from the supply speed of ferric ion from the solution to yukonite. In this experimental condition, the concentration of raw materials is low. Additionally, the high pH makes iron hydroxide which consumes ferric ion in the solution. Therefore, the supply speed of ferric ion from the solution to yukonite became low and it relates to the stabilization of yukonite in strong base solution of pH 10.



Fig. 7.1 XRD patterns of precipitated samples synthesized at 85 °C for 36 h using stirring (200 rpm) in various acidic solutions.

7.4 Conclusions

Synthesis of yukonite and arseniosiderite was conducted at various pH values of 6–11, and synthesis conditions of these materials were investigated. Ca-Fe-arsenates were synthesized at 85 °C for 36 h using stirring (200 rpm) under different pH conditions (pH 6.0, 7.0, 7.5, 8.0, 9.0, 10.0, and 11.0). Arseniosiderite peaks and yukonite peaks were appeared at pH 7–9 and pH 10, respectively. In general, yukonite transforms to arseniosiderite by the supply of solute (ferric ion and calcium ion) with an elapsed time. Therefore, I consider that yukonite was generated at high pH condition (pH 10) because supply speed of ferric ion from the solution to yukonite becomes low by the generation of iron hydroxide.

Chapter 8

Conclusions

In this paper, the sonochemical synthesis of large scorodite particles for the stable storage of arsenic was investigated.

In *chapter* 2, the synthesis of large scorodite particles (>10 μ m) at a low temperature using oxidation effect of ultrasound irradiation was investigated. Large scorodite particles (>10 μ m) with faceted surface were observed in SEM images of the samples synthesized with 2.1–11.6 W irradiation. Many fine particles and secondary particles, (agglomerates consisting of fine particles) were observed after the synthesis at 0 W (without ultrasound irradiation). Dissolution tests showed that the smallest amount of dissolved arsenic was obtained for the scorodite synthesized at the high intensity condition of 11.6 W. Under high ultrasound intensity irradiation, faceted scorodite particles can be synthesized as oxidation is promoted by the increase area of the interface between Fe(II) (liquid phase), the oxygen bubbles (gas phase) and the oxidation radicals generated by the ultrasound irradiation. To synthesize the large scorodite particles with facet, it was necessary to increase the supply quantity of solute [Fe(III), As(V)] from the solution to the nuclei during synthesis process. Therefore, higher intensity of ultrasound is suitable for the synthesis of large faceted scorodite particles at low temperature in a short reaction time.

In *chapter 3*, the effect of the ultrasound irradiation frequency on the generation of scorodite particles was investigated. Even at the same frequency of ultrasound

irradiation, the obtained scorodite particles size was different for the different irradiated precursor size. The average particle sizes obtained were 12.5, 8.7, and 13.9 μ m for the 200 kHz, 28 kHz, and 1.7 MHz ultrasound irradiation frequencies, respectively. The relationship between the optimal frequencies and precursors sizes was explained by the dynamic action agglomeration formula. The agglomeration of precursor reduces the number of nuclei and enhances amount of solute supplied to the nuclei during the crystal growth process, leading to a larger particle size. The use of high frequency ultrasound irradiation for the prevention of cavitation that is related to the generation of crystal nuclei. Thus, I found that it is possible to synthesize large scorodite particles (average particle size 10 μ m) at low temperature (70 °C) using high-frequency ultrasound irradiation for only 10 min on precursors of a suitable size during the total reaction time of 180 min.

In *chapter 4*, the synthesis of large (>10 μ m) scorodite particles by adding CO₂ during the ultrasonic agglomeration process was investigated. Mixed gases containing O₂ and CO₂ were applied during the ultrasonic agglomeration process for a short time period (10 min). The scorodite particles synthesized using only O₂ gas (100 vol%) were approximately 5–6 μ m in size by SEM observation. In contrast, large scorodite particles (>10 μ m) were synthesized when mixed gases containing CO₂ were used. Thus, CO₂ gas mitigated dispersion caused by cavitation, which decreased the number of crystal nuclei and increased the amount of solute [Fe(III), As(V)] supplied per crystal nuclei. However, when the CO₂ content of the mixed gas exceeded 50 vol%, a mixture of large (>10 μ m) and small (≤3 μ m) particles was obtained. In this case, scorodite nuclei formed along with the growth of agglomerated particles during the stirring process (160 min) after ultrasonic agglomeration (10 min). In contrast, the mixed gas containing 20 vol% CO₂ gas prevented cavitation-related dispersion while preserving oxidation by O₂ and oxidant radicals, thereby resulting in the formation of large scorodite particles (>10 μ m).

In chapter 5, the relationship between ultrasound irradiation and reaction temperature on scorodite synthesis was investigated. The effect of different reaction temperatures (90, 70, 50, and 30 °C) on the formation, size, and morphology of scorodite particles was investigated under an O₂ gas flow with ultrasound irradiation. I expected to synthesize large scorodite particles without fine particles using the agglomeration effect of ultrasound irradiation at 90 °C. However, the size of the particles was inhomogeneous from fine (<1 µm) to large (>10 µm). Ultrasound irradiation contributed to the generation of large particles through assisting the agglomeration effect. The value of $\triangle ORP$ and yield decreased when the temperature increased from 70 to 90 °C. In that case, the oxidation and dissolution and deposition effect were lower because of a decrease in the number of bubbles, which reduces the amount of radicals and jet flow generated by ultrasound, leading to inhomogeneous formation of particles. On the other hand, XRD peaks from scorodite were observed at temperatures >30 °C when using ultrasound irradiation. To the best of my knowledge, crystalline scorodite has never been synthesized at temperatures as low as 30 °C for 3 h. Thus, it is possible to synthesize highly crystalline scorodite by the promotion of oxidation using ultrasound irradiation in shorter times than stirring.

In *chapter 6*, the effect of ultrasound irradiation (200 kHz) on the size and morphology of scorodite particles synthesized under different acidic conditions (pH 2.0, 1.5, and 1.0) was investigated under O_2 gas flow for 3 h at 70 °C. In the case of without ultrasound, the intensity of XRD peaks of scorodite synthesized at pH 1.0 was lower than that of scorodite synthesized using ultrasound irradiation. Oxidation of the precursor (crystallization) is difficult without using ultrasound because the precursor is easily dissolute into the strong acidic solution (pH 1.0). Oxidation effect of ultrasound irradiation on scorodite synthesize at pH 1.0 contributed fast crystallization of scorodite.

In *chapter* 7, scorodite can store arsenic stably in acidic and neutral solutions. However, scorodite is unstable under an alkali solution. In mining and metallurgical smelter, Ca-Fe arsenates [e.g., yukonite (Ca₂Fe₃(AsO₄)₄(OH)·12H₂O), arseniosiderite (Ca₃Fe₄(AsO₄)₄(OH)₆·3H₂O)] are generally generated as secondary products of iron arsenates at tailing containing calcium under neutral-alkali environment. Therefore, syntheses of yukonite and arseniosiderite were conducted at various solutions of pH (6– 11), and the synthesis conditions of these materials were investigated. Arseniosiderite peaks and yukonite peaks were appeared at pH 7–9 and pH 10, respectively. Yukonite transforms to arseniosiderite by the supply of solute (ferric ion and calcium ion) with an elapsed time. Therefore, I consider that yukonite was able to be stayed at high pH condition (pH 10) because of the low supply speed of ferric ion from the solution to arseniosiderite by generation of iron hydroxide which consumes ferric ion and reduces ferric ion concentration of the solution.
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