

## Synthesis of Large Scorodite Particle Using Ultrasound Irradiation and Carbon Dioxide

超音波と二酸化炭素を用いた粗大なスコロダイト粒子の合成

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### 1. Introduction

Wastewater contaminated with arsenic, such as arsenious acid mine drainage, has been treated through the coprecipitation method using iron hydroxide generated by neutralization of the treatment solution including divalent iron ion (Fe(II)). However, iron hydroxide is not suitable for the storage of arsenic because it dissolves in acidic solutions and releases the adsorbed arsenic.<sup>1,2)</sup> Recently, scorodite has been studied as a promising storage material of arsenic.<sup>3,4)</sup> Scorodite releases little arsenic when the pH value of the solution is changed. Therefore, scorodite is an attractive material for storing arsenic. Scorodite is synthesized through a solution method using As(V)-Fe(II) containing acidic solution.<sup>5)</sup> Large scorodite particles (> 10  $\mu\text{m}$ ) are synthesized at high temperature (>90°C) solution in general. Particle size of scorodite can vary but larger ones are preferred because low surface-to-volume ratio makes it difficult to dissolve into the acidic solution. Previous study, it was obvious that ultrasound irradiation has effect to agglomerate precursors under oxygen gas bubbling into the solution. The purpose of our study is application of ultrasound irradiation to synthesize large scorodite particles (> 10  $\mu\text{m}$ ) by controlling the time, atmosphere, and timing of sonication.

### 2. Experimental

Arsenic acidic solution (As(V)) was prepared using  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$  and ion-exchange water. Then, Fe(II) solution was added to the As(V) solution. Finally Fe(II)-As(V) solution (50 ml) was adjusted to a Fe/As molar ratio of 1.5. As(V) concentration of the solution was 20 g/L. Sonication was performed with an ultrasonic generators (TA-4021; KAIJO) and submersible transducers (KAIJO). The Output and the frequency of the transducer were adjusted to 200 W and 200 kHz. A submersible transducer was placed at the bottom of a tank filled with water, and a flat-bottom flask containing the solution was placed directly

above the transducer. The temperature of the irradiated solution was controlled at 70°C using hot water circulation around the flat-bottom flask. Before the sonication of the solution, oxygen gas (100 ml/min) was flowed into the solution for 20 min to replace the air with oxygen gas in the flask. **Fig. 1** shows the experimental apparatus of ultrasound irradiation. Continuous sonication for 3 h generates both large (>10  $\mu\text{m}$ ) and small (<1  $\mu\text{m}$ ) scorodite particles. Small particles may come from the nucleation by cavitation during ultrasound irradiation. Therefore, to prevent the generation of small particles, ultrasound irradiation was used for only a short period (<30 min) immediately after beginning the synthesis to expect the agglomeration by ultrasound. So, this experimental procedure (partial ultrasound method) was as follows; 1) The precursor was generated at 70°C for 10 min using stirring (1000 rpm) with  $\text{O}_2$  bubbling. 2) Ultrasound was irradiated for 10 min into the suspension at 70°C with  $\text{O}_2$  or  $\text{CO}_2$  bubbling to enhance the agglomeration of the precursor. 3) Oxidation of the agglomeration was continued using stirring with  $\text{O}_2$  bubbling for 160 min without ultrasound irradiation (total 3 h). The precipitates from the above process were filtered using a 0.45  $\mu\text{m}$  pore diameter membrane filter. After drying, the precipitates were analyzed using X-ray diffraction (XRD) and scanning electron microscope (SEM).

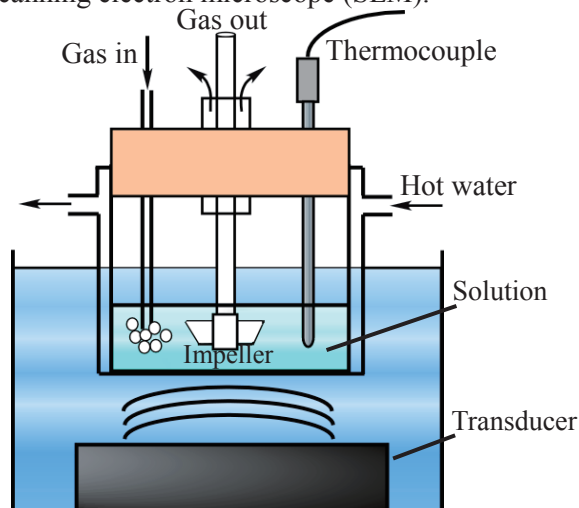


Fig. 1 Experimental apparatus

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### 3. Results

At first, we performed scorodite synthesis by partial ultrasound irradiation or continuous stirring under O<sub>2</sub> bubbling (without using CO<sub>2</sub>). **Fig. 2** shows the XRD patterns of the precipitated samples synthesized by this process or stirring without using ultrasound. Scorodite was successfully synthesized at 70°C by this partial sonication. **Fig. 3** shows the SEM images of precipitated samples by partial ultrasound irradiation. The shape of particles was polyhedron. In addition, partial ultrasound irradiation prevented the generation of fine particles. The average size of the particles synthesized by stirring was 11.3 μm, and that of the particles synthesized by partial ultrasound irradiation was 13.3 μm. Fujita et al. reported that the size of the scorodite particles was approximately 10 μm through the oxidation using stirrer under high temperature (95°C) and long reaction time (7 h).<sup>3)</sup> The specific surface area of scorodite particles synthesized by partial ultrasound irradiation was 0.41 m<sup>2</sup>/g, which is smaller than that in a previous report (0.5 m<sup>2</sup>/g).<sup>3)</sup> Thus, it is obvious that the scorodite particles obtained by ultrasound irradiation were the primary particles rather than the agglomerates.

Secondly, we performed scorodite synthesis using CO<sub>2</sub>. To confirm the effect of CO<sub>2</sub>, the solution was stirred at 70°C for 10 min with O<sub>2</sub> bubbling to generate precursors, followed by stirring with CO<sub>2</sub> bubbling for 10 min. After that, oxidation of the agglomeration was continued using stirring with O<sub>2</sub> bubbling (without CO<sub>2</sub> bubbling) at 100 mL/min for 160 min (total 3 h). **Fig. 4** shows the SEM images of precipitated samples using stirrer with and without CO<sub>2</sub> bubbling for 10 min in 3 h reaction time. The figure of particles was polyhedron. However, the size of particles synthesized using 10 min CO<sub>2</sub> bubbling was finer than that using O<sub>2</sub> bubbling only. This reason comes from the lack of enough oxidation for precursor due to CO<sub>2</sub> introduction. Therefore, both of agglomeration and oxidation is necessary to synthesize scorodite as large particles.

### 4. Conclusion

Partial ultrasound irradiation was successfully synthesized large size of scorodite. Not only the oxidation but also agglomeration of precursors was necessary to gain the large size of scorodite. We also performed scorodite synthesis using short time CO<sub>2</sub> bubbling to confirm the effect of CO<sub>2</sub> bubbling during agglomeration process of precursors. However, the particles size became fine.

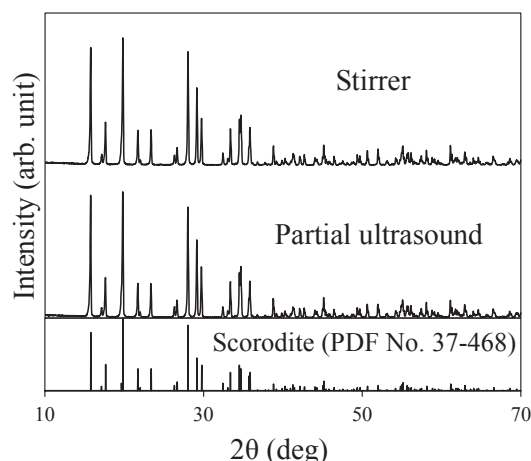


Fig. 2 XRD patterns of precipitated samples synthesized at 70°C

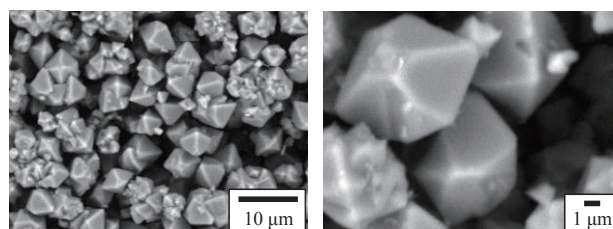


Fig. 3 SEM images of precipitated samples at 70°C using partial ultrasound irradiation.

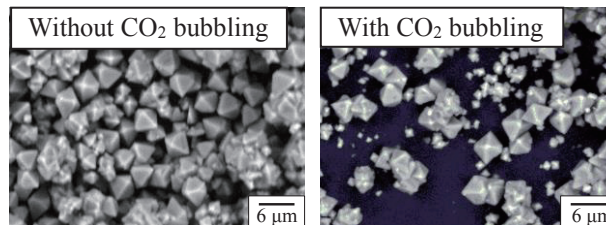


Fig. 4 SEM images of precipitated samples at 70°C using stirrer with and without CO<sub>2</sub> bubbling for 10 min in 3 h of total reaction time.

### Acknowledgment

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