Detoxification of wastewater containing As and Sb by hydrothermal mineralization

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Abstract: We demonstrate the detoxification of wastewater containing arsenic and antimony oxo-anions by hydrothermal mineralization treatment. The treatments at 150-200 °C with Ca(OH)₂ were carried out for the model wastewater containing 1-2000 mg/dm³ of arsenic and antimony species. These ions were removed as the precipitates of natural minerals of Ca₅(AsO₄)₂(OH) and Ca₅Sb₂O₇, respectively. In-situ solid/liquid separation under hydrothermal condition was also carried out in order to enhance the treatment efficiency. As a result, the removal rates and yields of respective ions increased drastically compared with those of the treatments by using an ordinary batch-type apparatus. The residual concentration of arsenic treated at 200 °C for 2 h was 0.02 mg/dm³ which was lower than the standard of discharged water in Japan and it was independent of the initial concentration of pollutants (1-2000 mg/dm³). Thus, the hydrothermal mineralization treatment is one of the effective treatment methods for detoxifying the polluted water containing As and Sb species.

Keywords: Hydrothermal Mineralization, Arsenic, Antimony, Wastewater

1. INTRODUCTION

Arsenic is one of the important raw materials for the production of advanced electronic materials. Chemical species containing arsenic are also discharged into wastewaters from petroleum refining plants and from thermal power plants¹-³. However, they have extremely high toxicity against human beings and the living things especially in case of the trivalent arsenite ion (As(III)O₃³⁻). On the other hand, antimony is also concerned with an adverse effect on human health due to its toxicity, although it is industrially used as fire retardants, ceramics and the other advanced materials⁴. Thus, the national effluent standard of Japan (NESJ) of arsenic species was set at 0.1 mg/dm³ and that of antimonic species was set at 0.02 mg/dm³ (reference value). An appropriate treatment is required frequently for industrial wastewaters to meet these standards. Furthermore, serious environmental problems by arsenic pollution of groundwater have emerged in Asian countries, such as Bangladesh, India and China⁵-⁷. On the contrary, there is no production of arsenic and antimonial ores in Japan, so that they are expected to be recycled. Therefore, the establishment of the removal and recycling system of arsenic from wastewaters is of global significance.

Several techniques to remove arsenic from aqueous media have been developed, for example, by adsorption, electro-coagulation, membrane permeation and biological methods⁸-¹⁰. Especially, the adsorption methods using iron hydroxide and zero-valent irons have been actively investigated¹¹-¹³. However, these have the following problems. (1) Removal yield is low, especially for arsenite ion (AsO₂³⁻). (2) The applicable concentration range is narrow. (3) Arsenic in aqueous media cannot be reused as resources. In addition, both the used adsorbent and collected residues must be properly treated again as hazardous wastes. The cause of these problems consists in the difficulty to form precipitate with low solubility in water because of high stability of arsenic oxoanins in aqueous media. Similarly, there is no effective technique to remove antimonic species from aqueous media, because it has similar property to arsenic. Thus, it is much expected to develop a new technique to recover arsenic and antimonic species as reusable solid precipitates from aqueous media regardless of its concentration, oxidation state and ionic species.

Compounds that contain high arsenic or antimony concentrations and are insoluble in water, are frequently found in natural minerals, for example, monimolite ((Pb,Ca)₅Sb₂O₇) haidingite (Ca₅AsO₄(OH)·(H₂O)) and Johnbaumite (Ca₅(AsO₄)₂(OH)). This fact suggests that nature has an ability to produce insoluble As(Sb)-bearing minerals. We reported in the previous studies that boron and fluorine can be removed from aqueous solutions containing borate, fluoride and fluoroborate ions by imitating natural mechanism to form insoluble minerals under hydrothermal conditions, using so-called “hydrothermal mineralization” technique¹⁴-¹⁶. In the present study, we investigated the recovery techniques of arsenic and antimony from model wastewater containing arsenite (As(III)O₃³⁻), arsenate (As(V)O₅³⁻) and antimonate (Sb(V)O₅³⁻) ions by using hydrothermal mineralization treatment.

2. EXPERIMENTAL DETAILS

Hydrothermal treatment

Model wastewaters with 1-2000 mg/dm³ of arsenite and arsenate ions were prepared by dissolving As₂O₃, As₂O₅ in 0.5 N NaOH solution, and neutralized by HCl in distilled and deionized water (Wako Pure Chemical Industries, Ltd.). Model wastewater containing 80 mg/dm³ of Sb₂O₃ was prepared by dissolving Sb₂O₃ into the same distilled and deionized water. These model wastewaters (30 mL) were sealed in a pressure vessel lined with fluorocarbon resin together with mineralizer.

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Ca(OH)$_2$, and moreover in some cases, with H$_2$O as oxidizer. Hydrothermal treatments were carried out by leaving the vessel in a dry oven for 2-96 h at a given temperature in the range of 100-230 °C. The pressure inside the vessel was not controlled intentionally, i.e., it depends on the saturation vapor pressure of water at each temperature. Thus, it was kept constant in the range from 0.5 MPa (150 °C) to 3.0 MPa (230 °C). After the hydrothermal treatment, the vessels were cooled down in atmospheric air for 1 h. Precipitates obtained by the hydrothermal treatment were filtered and collected.

Hydrothermal mineralization treatments by using the in situ sampling-type apparatus, which is shown in Figure 1, were carried out in order to enhance treatment efficiency, i.e., to prevent re-dissolution of the formed mineral precipitated under hydrothermal conditions. During the hydrothermal treatment, the reactive suspension is led into the sampling tube by its own vapor pressure, and the precipitates are separated from reaction suspension by 0.5 µm metal filter. After that, the samples were immediately cooled down at room temperature by using a cooling condenser. Collection of reaction solution during the hydrothermal treatment can be accomplished by the present in situ sampling-type apparatus.

Analysis

The precipitates were identified by X-ray diffraction (XRD: RIGAKU Rint-2500) using CuKα radiation. The microstructural observation and qualitative element analysis of the precipitates were performed by scanning electron microscopy (SEM: JEOL JSM-T20) equipped with energy dispersive X-ray spectrometry (EDS: JED-2140). Thermometric analyses of the precipitates were carried out by thermogravimetric and differential thermal analyzers (TG-DTA: RIGAKU Thermo plus, TG-8120). Quantitative analysis of the arsenate ion in the solvent was performed by inductively coupled plasma mass spectrometer (ICP-MS: Jobin-Yvon JY 24). A chemical formula of this unassignable compound was estimated as Ca(AsO$_3$)$_5$(OH)·4H$_2$O. According to the results of XPS, TG-DTA and SEM-EDS analyses, the chemical formula of this unassignable compound was estimated as Ca$_x$(AsO$_3$)$_y$(OH)$_z$·4H$_2$O. The formation of Ca$_x$(AsO$_3$)$_y$(OH)$_z$·4H$_2$O would be accomplished by the reaction Scheme 1(c). Solubility of this compound is relatively low, because the As concentration before the treatment (only by adding Ca(OH)$_2$) decreased from 2000 mg/dm$^3$ to 4 mg/dm$^3$. Figure 3 shows the XRD patterns of the precipitates before and after the treatment at 200 °C. Each precipitate in Fig. 4 were prepared under the following conditions. Figure 4-(a): the precipitate before the treatment. Figure 4-(b): Ca$_x$(AsO$_3$)$_y$(OH)

3. RESULTS AND DISCUSSION

3.1. Hydrothermal mineralization treatment for As containing wastewater with Ca(OH)$_2$ mineralizer

Treatment time dependence of the As concentration in the model wastewater (As: 2000 mg/dm$^3$) treated at 100 °C with Ca(OH)$_2$ is shown in Fig. 1. The arsenic content decreased only by adding Ca(OH)$_2$ mineralizer to the model wastewater, and it was decreased down to 4 mg/dm$^3$ (even before the hydrothermal mineralization treatment). This decrease in As concentration is due to the formation of arsenic calcium compound as described later. However, this concentration does not meet NESJ (0.1 mg/dm$^3$). By performing the hydrothermal mineralization in the model wastewater added with Ca(OH)$_2$, As concentration draws concave curves against treatment time, i.e., a proper treatment time exists for decreasing As concentration. The increase of As concentration at longer treatment-time might be caused by the nature of As compound formed during the treatment. At the optimal treatment condition, the As concentration reduced down to ca. 0.4 mg/dm$^3$, which is one tenth of As concentration before the hydrothermal treatment, but is still higher than the NESJ.
prepared by heat treatment of the precipitate before the treatment at 200 °C for 4 h in order to eliminate crystal water. Figure 4-(c): Arsenate apatite (Ca$_5$AsO$_4$$_3$) formed by hydrothermal mineralization treatment of arsinite ion (AsV$^{3+}$) with Ca(OH)$_2$ minerizer at 200 °C for 24 h. Figure 4-(d): Precipitate after the hydrothermal treatment for the model wastewater containing arsinite ion (As$_3$O$_4$$_3$) at 200 °C for 8 h. These results indicate that the precipitate after the treatment is a mixture of Ca$_3$(As$_3$O$_4$$_3$)$_3$(OH) and Ca$_5$(As$_3$O$_4$$_3$)(OH). Thus, crystal water of Ca$_3$(As$_3$O$_4$$_3$)$_3$(OH)-4H$_2$O would be removed during the hydrothermal mineralization treatment according to Scheme 1-(f). After that, As in the precipitate were oxidized and formed Ca$_5$(As$_3$O$_4$$_3$)(OH). XPS spectra of the precipitates obtained at the treatment temperature of 200 °C showed the same oxidation number of arsenic. Gas analysis by GC-TCD suggested that the oxidizer was H$_2$O$_2$, because generation of hydrogen was confirmed. Thus, the oxidation of As was accomplished by the reaction between AsO$_3$$_3$ and H$_2$O shown in Scheme 1-(j). After that, the formation of Ca$_5$(As$_3$O$_4$$_3$)(OH) would occur by the reaction between AsO$_3$$_3$ and precipitate of Ca(OH)$_2$ (Scheme 1-(k)). Additionally, the solubility of Ca$_5$(As$_3$O$_4$$_3$)(OH)-4H$_2$O and Ca$_5$(As$_3$O$_4$$_3$)(OH) in water, which was measured by a simple solubility test, was 13.79 mg As/100 dm$^3$ H$_2$O and 29.10 mg As/100 dm$^3$ H$_2$O, respectively. Therefore, the concave tendency in Fig. 1 would be caused by the removal of crystal water from Ca$_5$(As$_3$O$_4$$_3$)(OH)-4H$_2$O and the formation of Ca$_5$(As$_3$O$_4$$_3$)(OH), which has higher solubility in water with an increase of treatment time. These results also indicate that the solubility of the formed precipitates such as Ca$_5$(As$_3$O$_4$$_3$)(OH)-4H$_2$O have negative solubility curve against the increase in temperature. In contrast, the solubility of Ca$_5$(As$_3$O$_4$$_3$)(OH) was less than 0.2 mg As/100 dm$^3$ that was very low compared with the above trivalent arsenic compounds. It is expected, therefore, that intentional oxidation of arsenite ion to form Ca$_5$(As$_3$O$_4$$_3$)(OH) would be effective for precipitation of arsenic species.

\[ \text{(a) Ca(OH)$_2$ + H}_2\text{O$_2$} \rightarrow \text{CaO$_2$ + 2H}_2\text{O} \]
\[ \text{(b) 2CaO$_2$ + 2H}_2\text{O} \rightarrow 2\text{Ca(OH)$_2$ + O}_2} \]
\[ \text{(c) 2 H}_2\text{O$_2$} \rightarrow 2 \text{H}_2\text{O + O}_2} \]
\[ \text{(d) CaO + H}_2\text{O$_2$} \rightarrow \text{Ca(OH)$_2$} \]
\[ \text{(e) 3AsO$_3$$_3$ + 5 Ca(OH)$_2$ + 4 H}_2\text{O} \rightarrow \text{Ca$_5$(As$_3$O$_4$$_3$)(OH)-4 H}_2\text{O + 9OH} \]
\[ \text{(f) Ca$_5$(As$_3$O$_4$$_3$)(OH)-4 H}_2\text{O} \rightarrow \text{Ca$_5$(As$_3$O$_4$$_3$)(OH) + 4 H}_2\text{O} \]
\[ \text{(h) AsO$_3$$_3$ + CaO$_2$ \rightarrow AsO$_4$$_3$ + CaO} \]
\[ \text{(i) AsO$_3$$_3$ + H}_2\text{O$_2$} \rightarrow \text{AsO$_4$$_3$ + H}_2\text{O} \]
\[ \text{(j) AsO$_3$$_3$ + H}_2\text{O} \rightarrow \text{AsO$_4$$_3$ + H}_2} \]
\[ \text{(k) 3 AsO$_4$$_3$ + 5Ca(OH)$_2$ \rightarrow \text{Ca$_5$(As$_3$O$_4$$_3$)(OH) + 9OH}} \]

Scheme 1. Possible reactions in the hydrothermal mineralization treatment.

- Gas analysis by GC-TCD suggested that the oxidizer was H$_2$O$_2$. 
- Ca$_5$(As$_3$O$_4$$_3$)(OH) had lower solubility than Ca$_5$(As$_3$O$_4$$_3$)(OH)-4H$_2$O.
- Prolonged treatment at 200 °C resulted in the formation of Ca$_5$(As$_3$O$_4$$_3$)(OH).

![Figure 5](image-url) Dependence of As concentration on treatment time with 0.18 g of Ca(OH)$_2$ and 3% H$_2$O$_2$. As(III): 2000 mg/dm$^3$. ○: 100 °C, □: 150 °C

Effect of H$_2$O$_2$ addition
The effects of H$_2$O$_2$ addition on oxidation of arsenite ions and precipitation of Ca$_5$(AsO$_3$)$_3$(OH) were examined. Figure 5 shows the dependence of concentration of As on treatment time under the hydrothermal conditions for 0-16 h at 100 or 150 °C with the addition of 0.18 g Ca(OH)$_2$ and 3% H$_2$O$_2$. As concentration before the treatment (only by adding Ca(OH)$_2$ and H$_2$O$_2$) was approximately 150 mg/dm$^3$ which was higher than that of the treatment with Ca(OH)$_2$ only. Decrease of As concentration before the treatment shown in Fig. 1 was derived from the formation of Ca$_5$(AsO$_3$)$_3$(OH)$·4$H$_2$O. The addition of H$_2$O$_2$ inhibits the formation of Ca$_5$(AsO$_3$)$_3$(OH)$·4$H$_2$O and forms CaO$_2$. On the other hand, residual concentration of As is 0.15 mg/dm$^3$ at the optimum treatment time of 12 h. Figure 6 shows the XRD patterns of the precipitates formed under the above hydrothermal conditions. Diffraction peaks of CaO$_2$ are observed at short treatment times (0 h to 8 h) and then the diffraction peaks of Ca(OH)$_2$ appear with decreasing the intensities of CaO$_2$ peaks. This result shows that the oxidation of Ca(OH)$_2$ occurred at the beginning of treatment (Scheme 1-(a)), after which it gradually reacts with H$_2$O to form Ca(OH)$_2$ (Scheme 1-(b)). High values of As concentrations before the treatment (compared with the case of no H$_2$O$_2$ addition in Fig. 1) would be caused by decomposition of Ca$_5$(AsO$_3$)$_3$(OH)$·4$H$_2$O (Scheme 1-(g)) and CaO$_2$. On the other hand, only the diffraction peaks of Ca$_5$(AsO$_3$)$_3$(OH) was observed after the hydrothermal treatment. Therefore, the minimum value of As concentration at the optimum treatment time is attributed to the result of oxidation of arsenite to arsenate (As(V)) by H$_2$O$_2$ or CaO$_2$, and formation of Ca$_5$(AsO$_3$)$_3$(OH) (Scheme 1-(h), (i), (j), (k)). However, a concave curve tendency is still observed in Fig. 5 against the treatment time and the NESJ could not be overcome. Oxidation of arsenite ion would be insufficient, because arsenite ion still existed mainly in the treated-water by detailed analysis (though figure not shown here).

3.2. Hydrothermal mineralization treatment for As containing wastewater by in situ sampling-type treatment apparatus

Figure 7 shows similar concave curves against treatment time in case of 5% H$_2$O$_2$ addition at 100 °C and 150 °C, which means that arsenite ion also exists in the water. However, the As concentration was less than the value of NESJ, 0.1 mg/dm$^3$ at the optimum treatment conditions attained at 5% H$_2$O$_2$ addition at 150 °C for 4-12 h. This result shows that the oxidation of 2000 mg/dm$^3$ of arsenite ion and the formation of Ca$_5$(AsO$_3$)$_3$(OH) were nearly complete by the hydrothermal treatment with H$_2$O$_2$ addition. Obviously, the optimum amount of H$_2$O$_2$ addition depends on the initial concentration of arsenite ion, which needs at least 5% H$_2$O$_2$ in this case to oxidize 2000 mg/dm$^3$ of arsenite ion to arsenate. These results indicate that the hydrothermal mineralization treatment is effective for removing and recovering five valence arsenic species such as arsenate ion. Therefore, it is concluded that the hydrothermal mineralization treatment is an effective technique for the recovery of arsenic from arsenic-bearing wastewaters.
Hydrothermal mineralization treatment by using the in situ sampling-type treatment apparatus (see Fig. 1) was carried out for the model wastewater containing 2000 mg/dm³ of arsenate ion (As\(^{5+}\)O\(_4\)\(^{-3}\)) in order to prevent re-dissolution of the formed mineral during cooling process for 1 h. Figure 8 shows the result of hydrothermal mineralization treatment by using ordinary batch type and in situ sampling-type treatment apparatuses. As concentration after the treatment in using the latter apparatus for 3 h was ca. 0.016 mg/dm³. This result shows that the separation of reaction solution from the precipitate under hydrothermal condition enables not only an improved yield recovery, but also a shortened optimal treatment time. Shortening of the optimal treatment time is caused by crystal and/or grain growth of mineral. The re-dissolution rate of the formed mineral would be affected by crystallinity and crystal radius. The decrease in As concentration at longer treatment time is expected in using ordinary batch type hydrothermal apparatus (e.g. Figure 1), which is actually accomplished by crystal growth of Ca\(_2\)(AsO\(_4\))\(_3\)(OH). Larger crystal or grain size causes its slow re-dissolution of Ca\(_2\)(AsO\(_4\))\(_3\)(OH) precipitate during the cooling process. However, when the solution is separated from precipitate under hydrothermal condition, crystal growth has no effect on decreasing As concentration in treated-water, because this treatment can completely prevent re-dissolution of the formed minerals regardless of crystal growth. Therefore, the optimal treatment time to reduce As concentration was shortened by using the in situ sampling-type hydrothermal treatment apparatus.

### 3.3. Hydrothermal mineralization treatment for Sb containing wastewater

Figure 9 shows the treatment time dependence of Sb concentration in the water treated at 150-230 °C with 0.05 - 0.3 g of Ca(OH)\(_2\) mineralizer. Sb concentration did not decrease only by addition of Ca(OH)\(_2\) (i.e., before the hydrothermal treatment). However, it decreased drastically by applying the hydrothermal mineralization treatment. Residual Sb concentration was found to decrease with an increase of treatment temperature, and it was 0.06 mg/dm³ at 230 °C for 12 h with 0.3 g of Ca(OH)\(_2\). Therefore, the hydrothermal mineralization treatment is definitely effective for reducing Sb in aqueous media. Figure 10 shows the XRD pattern of the precipitate obtained by the treatment with 0.05 g Ca(OH)\(_2\) at 200 °C for 12 h. The precipitate formed by the treatment was Ca\(_3\)Sb\(_2\)O\(_6\); which had the crystal structure similar to Monimolite [(Pb,Ca)\(_2\)Sb\(_2\)O\(_6\)]. The recovered Ca\(_3\)Sb\(_2\)O\(_6\) would be easily reused by the conventional resource manufacturing process. Although residual Sb concentration did not vary drastically by changing the added Ca(OH)\(_2\) amount in the range of 0.1-0.3 g, it was gradually decreased. Ca\(_3\)Sb\(_2\)O\(_6\) in solution is dependent only on the solubility of Ca(OH)\(_2\) into water at a given hydrothermal condition, even when enough amount of Ca(OH)\(_2\) is added. However, the treatment with 0.05 g of Ca(OH)\(_2\) showed low recovery rate of Sb (Figure 9b). This low recovery rate is responsible for the shortage of Ca(OH)\(_2\) precipitate.

Result of SEM-EDS analysis showed that the Ca\(_3\)Sb\(_2\)O\(_6\) was formed as fine crystals on the surface of hexagonal Ca(OH)\(_2\). Thus, it is expected that Ca\(_3\)Sb\(_2\)O\(_6\) would be formed by the reaction of SbO\(^{3-}\) with hydroxyl group on the surface of Ca(OH)\(_2\) precipitate. This mechanism is similar to the case of hydrothermal mineralization treatment of aqueous media containing boric acid. Improvement of yield recovery of Sb would be attained by increasing the surface area of Ca(OH)\(_2\) precipitate used for the formation reaction of Ca\(_3\)Sb\(_2\)O\(_6\). Furthermore, residual Sb concentration decreased to 0.05 mg/dm³ treated at 200 °C with rapid cooling in ice water (see the value at ☆ in Figure 9b) which is lower than the Sb concentration treated with 0.3 g of Ca(OH)\(_2\) at 230 °C. This result indicates that the solubility of Ca\(_3\)Sb\(_2\)O\(_6\) under hydrothermal condition is lower than that under ordinary temperature and pressure. In this study, a batch type of pressure vessel was cooled down to room temperature for 1 h after the treatment. During this process, re-dissolution of Ca\(_3\)Sb\(_2\)O\(_6\) would occur and Sb concentration increase. On the other hand, a rapid
cooling of the vessel prevented the re-dissolution of Ca\textsubscript{2}Sb\textsubscript{2}O\textsubscript{7} in shorter cooling process (typically for 10 min). Decrease of Sb concentration was achieved through the separation of solvent from the precipitate before re-dissolving a large amount of Ca\textsubscript{2}Sb\textsubscript{2}O\textsubscript{7} into treated-water. This result suggests that Sb concentration after the treatment in this study (by an ordinary batch-type) would be higher than that by the in-situ sampling-type under hydrothermal condition. Therefore, the system construction for in-situ separation of reaction solution from the precipitate under hydrothermal condition would improve the efficiency to remove and recover Sb by hydrothermal mineralization.

4. CONCLUSIONS

We have demonstrated the precipitation and recovery system of arsenite, arsenate and antimonate ions by hydrothermal mineralization technique, which imitates the natural mechanism to form insoluble minerals in the Earth’s crust. Simultaneous oxidation and mineralization of arsenite by using Ca(OH)\textsubscript{2} mineralizer and H\textsubscript{2}O\textsubscript{2} oxidizer were effective enough to precipitate arsenic as johnbaumite with high yield. The hydrothermal mineralization treatment for the model wastewater, which containing 2000 mg/dm\textsuperscript{3} of arsenite ion, at optimum treatment condition could reduce arsenic concentration lower than that of NESJ, 0.1 mg/dm\textsuperscript{3}. The separation of aqueous solution from precipitate under hydrothermal condition could completely prevent re-dissolution of the formed mineral and it enables detoxification of wastewater and resource recovery with high-efficiency. On the other hand, the hydrothermal mineralization treatment with Ca(OH)\textsubscript{2} could form precipitates from aqueous media containing antimonite ions. The recovered mineral was Ca\textsubscript{2}Sb\textsubscript{2}O\textsubscript{7}, which had a structure similar to Monimolite. Thus, reuse of the formed precipitate would become possible by incorporating this process into the traditional resource manufacturing process. Rapid cooling test showed that the solubility of Ca\textsubscript{2}Sb\textsubscript{2}O\textsubscript{7} under hydrothermal condition was lower than that under room temperature and pressure. It is expected that the separation of reaction solution and precipitate in-situ under hydrothermal condition enables the improvement of yield recovery of Sb. Therefore, we conclude that the hydrothermal mineralization treatment is effective technique to precipitate and recover arsenite, arsenate and antimonate ions from wastewater and even from ground water.

REFERENCES