Detoxification of Antimonic Contaminated Water and Precipitation Recovery of Antimony by Mineralization under Hydrothermal Condition

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The detoxification of water contaminated by antimony and its resource recovery are achieved by hydrothermal mineralization treatment. The treatment is based on the precipitation method of a mineral from aqueous media by imitating natural mineralization mechanism derived from activity of magma. The treatment could reduce Sb concentration in aqueous media, when the formed mineral was $Ca_2(Sb_2O_7)$, which resembled natural mineral of Monimolite ($(Pb,Ca)_2Sb_2O_7$). The antimony concentration in water after the hydrothermal mineralization under optimal conditions was 0.06 mg/dm^3. Additionally, the rapid cooling of the treated water made much progress in the treatment efficiency to disturb the re-dissolution of the formed mineral. Therefore, this treatment is effective for detoxification of water polluted by antimonic species and its resource recovery.

There has been a growing concern over the adverse effect of antimony on human health due to its toxicity and increase in industrial use.[1] Antimony has been used in large quantities for fire retardants, ceramics, and the other advanced materials manufacturing. The World Health Organization (WHO) allows 50 μg/dm^3 for antimony by the guideline.[2] National drinking water contaminant standard of the United States is set at 60 μg/dm^3. Similarly, reference value of drinking water contamination of antimony is set at 20 μg/dm^3 for Sb in Japan.[3] Generally, the standard for effluent is set at ten times higher than that of drinking water e.g., 200 μg/dm^{-3} in Japan. This value is five times lower than that of standard of arsenic, and it indicates the high toxicity of antimony. Thus, it is apparent that the standard of antimony concentration in the wastewater and drinking water would be regulated by Water Pollution Control Law in future. However, there are no techniques to remove antimony contained in aqeous media. Therefore, establishment of the detoxification treatment for wastewater containing Sb is strongly desired.

It is well known that the dominant oxidation state of antimony in most oxygenated environmental water is Sb^V from the examination to determine the type of antimony for estimation of health risk.[4] Various removal treatments for Sb from polluted water were investigated e.g., by adsorption,[5–10] electro-coagulation,[11] solvent extraction,[12] and membrane methods.[4,13] However, these methods have less removal ability, especially for treating a heavily contaminated water. Additionally, chemical species collected by these methods cannot be reused as resources for production. In our previous study, we investigated the recovery of As from $As^VO_4{}^{3-}/As^{III}O_3{}^{3-}$, or B from $B(OH)_4{}^-/BF_4{}^-$ contained in aqueous media as natural mineral by hydrothermal mineralization.[14–16] Properties of Sb^V resemble the same group elements in the periodic table, such as phosphoric acid ($P^VO_4{}^{3-}$) and arsenate ($As^VO_4{}^{3-}$) acid. Thus, we expected to apply the hydrothermal mineralization treatment to the wastewater contaminated by Sb^VO_3 for recovering Sb as precipitate and detoxifying the polluted water.

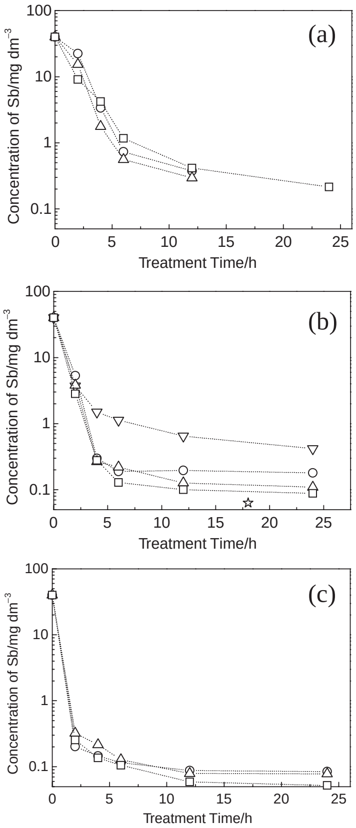

Figure 1. Dependence of the Sb concentration on the treatment time with ▽; 0.05 g, ○; 0.1 g, △; 0.2 g, □ and ☆; 0.3 g $Ca(OH)_2$ mineralizer. (a); 150 °C, (b); 200 °C, (c); 230 °C. ☆; rapidly cooled down by ice water for 5 min.

Model wastewaters containing 40 mg/dm^3 of pentavalent antimony (dissolved as $Sb^VO_3{}^-$) were prepared by dissolving Sb_2O_5 in distilled and deionized water. Then, 30 dm^3 of the model wastewater was sealed in a pressure vessel lined with fluorocarbon resin together with mineralizer $Ca(OH)_2$. Hydrothermal mineralization treatments were carried out by leaving the vessel in a dry oven for 2–12 h at 150, 200, and 230 °C. The pressure inside the vessel was not controlled intentionally, i.e., it depends on the pressure of 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 treatment, the vessel was cooled down in room temperature for 1 h or in ice water for 10 min. Determination of Sb concentration and the analysis of the precipitates before and after the treatment were

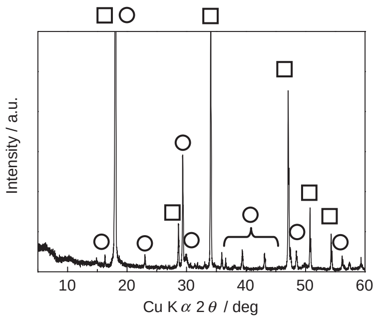

Figure 2. XRD pattern of the precipitate obtained by hydrothermal treatment at 200 °C for 24 h with 0.05 g of $Ca(OH)_2$. ○: $Ca_2Sb_2O_7$, □: $Ca(OH)_2$.

carried out by inductively coupled plasma mass spectrometry and X-ray diffraction, respectively.

Figure 1 shows the treatment time dependence of the Sb concentration in the water treated at 150–230 °C with 0.05–0.3 g of $Ca(OH)_2$ mineralizer. Sb concentration only by addition of $Ca(OH)_2$ (i.e., before the hydrothermal treatment) did not reduce. However, it decreased drastically by applying the hydrothermal mineralization treatment. Residual Sb concentrations were decreased with an increase of treatment temperature and it was 0.06 mg/dm^3 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 2 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 $Ca_2Sb_2O_7$, which has the structure similar to Monimolite ($(Pb,Ca)_2Sb_2O_7$). The recovered $Ca_2Sb_2O_7$ 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^{2+} concentration in solution is provided by only 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 1b). It is expected that the cause of this low recovery rate is shortage of the precipitate of $Ca(OH)_2$. Figure 3 shows the SEM photograph of the precipitate obtained by the treatment at 200 °C for 24 h. Result of EDS analysis showed that the $Ca_2Sb_2O_7$ was formed as fine crystals on the surface of hexagonal $Ca(OH)_2$. Thus, it is expected that $Ca_2Sb_2O_7$ would be formed by the reaction of SbO_3^- with hydroxy 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.[16]

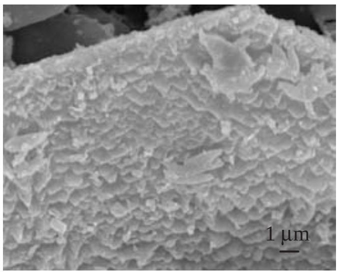

Figure 3. SEM photograph of the precipitate obtained by the hydrothermal mineralization treatment at 200 °C for 24 h.

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 $Ca_2Sb_2O_7$. Furthermore, residual Sb concentration decreased to 0.05 mg/dm^3 treated at 200 °C with rapid cooling in ice water (see the value at ☆ in Figure 1b) 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 $Ca_2Sb_2O_7$ 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 $Ca_2Sb_2O_7$ would occur and Sb concentration increase. On the other hand, a rapid cooling of the vessel prevented the re-dissolution of $Ca_2Sb_2O_7$ in shorter cooling process (typically for 10 min). Decrease of Sb concentration was achieved through the separation of the solvent from precipitate before re-dissolving a large amount of $Ca_2Sb_2O_7$ into treated water. This result suggests that every Sb concentration after the treatment in this study would be higher than that in situ under hydrothermal condition. Therefore, the system construction to separate reaction solution from precipitate in situ under hydrothermal condition would improve the efficiency to remove and recover Sb by hydrothermal mineralization.

We conclude that hydrothermal mineralization treatment is effective for recovering Sb^V from aqueous media. The recovered mineral was $Ca_2Sb_2O_7$, 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 $Ca_2Sb_2O_7$ under hydrothermal condition was lower than that under room temperature and pressure. Therefore, it is expected that the separation of reaction solution and precipitate in situ under hydrothermal condition bring about the improvement of higher yield recovery of Sb.

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