



Removal of antimonate ions and simultaneous formation of a brandholzite-like compound from magnesium–aluminum oxide

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ABSTRACT

Magnesium–aluminum oxide (Mg–Al oxide), obtained by thermal decomposition of a Mg–Al layered double hydroxide (Mg–Al LDH), was found to remove $\text{Sb}(\text{OH})_6^-$ (Sb(V)) in solution because of rehydration, and to combine with Sb(V) to form a brandholzite-like structure. Although the Sb concentration decreased with increasing amounts of Mg–Al oxide, differences in the Mg/Al molar ratio had little effect on this relationship. The removal of Sb(V) in solution by Mg–Al oxide was partially prevented by coexistent anions with high charge densities (SO_4^{2-} and CO_3^{2-}). In this case, Mg–Al oxide likely rehydrates and competitively combines with Sb(V) in solution to construct a brandholzite-like structure or with anions to reconstruct the LDH structure. However, in the case of coexistent anions with low charge densities (Cl^- and OH^-), Mg–Al oxide likely rehydrates and preferentially combines with Sb(V) in solution to construct the brandholzite-like structure. A high concentration of Cl^- and SO_4^{2-} had little effect on the decrease in Sb concentration, whereas a high concentration of CO_3^{2-} had a large effect.

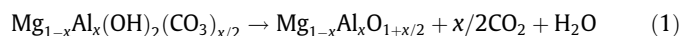
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1. Introduction

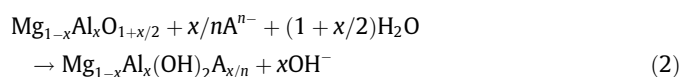
Antimony (Sb), in addition to selenium (Se) and arsenic (As), is a typical unwanted constituent of most ores and concentrates which are processed in the nonferrous metallurgical industry. Various types of Sb-bearing intermediate products and process wastes must be treated in an environmentally acceptable manner. Coprecipitation techniques with Fe(III) species have been studied to eliminate Sb from process liquors and effluents [1,2]. Although Fe(III) species effectively reduce the concentration of residual Sb in solution, their reaction with $\text{Sb}(\text{OH})_6^-$ (Sb(V)), is found to be much slower than their reaction with $\text{Sb}(\text{OH})_4^-$ (Sb(III)), particularly in a pH range advantageous for Sb elimination [2]. Furthermore, these techniques have the potential to generate large amounts of sludge, which is contaminated with small amounts of Sb if the appropriate reaction conditions are not set [3]. Thus, the development of a new treatment method for Sb(V) in an aqueous solution is desired.

Magnesium–aluminum layered double hydroxide (Mg–Al LDH), which has anion-exchange capability [4], is represented by the formula $[\text{Mg}_{1-x}\text{Al}_x^{3+}(\text{OH})_2](\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where x denotes the Al/(Mg + Al) molar ratio ($0.20 \leq x \leq 0.33$) and A^{n-} is CO_3^{2-} , Cl^- , etc. [5,6]. Mg–Al LDH consists of a stack of Al^{3+} -bearing brucite-like octahedral layers in which the positive layer charge due to the

replacement of some Mg^{2+} ions with Al^{3+} is electrically neutralized by the interlayer anions. The interlayer space is occupied by water molecules in the hydration shell of the intercalated anions. Mg–Al LDH intercalated with CO_3^{2-} (CO_3 -Mg–Al LDH) can be transformed into Mg–Al oxide by calcination at 450–800 °C, as expressed by Eq. (1):



The Mg–Al oxide can rehydrate and combine with anions to reconstruct the LDH structure:



Recently, high expectations have been placed on Mg–Al LDH and Mg–Al oxide to be applied to water preservation and purification. For example, these materials are able to take up oxometalates such as arsenite, arsenate, chromate, phosphate, selenite, and selenate from aqueous solutions [7–12]. We have previously reported treatments of hydrochloric acid, fluoride, borate, and tetrafluoroborate ions in aqueous solutions using Mg–Al oxide [13–18].

In this study, we examined the removal of Sb(V) in an aqueous solution by Mg–Al oxide as a new treatment method. We investigated the effects of Mg–Al oxide quantity, Mg/Al molar ratio, and coexistent anions on Sb(V) removal. In addition, we compared the effects of Mg–Al oxide in removing Sb(V) in an aqueous solution to those of MgO and Al_2O_3 , which were used as reference materials.

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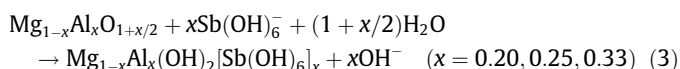
2. Experimental

2.1. Reagent preparation

Firstly, CO₃-Mg-Al LDHs were prepared by co-precipitation according the following method. Two hundred milliliter of mixed 0.5 mol/L solutions composed of Mg(NO₃)₂ and Al(NO₃)₃ with Mg/Al molar ratios of 2, 3, and 4 were added to 200 mL of Na₂CO₃ solution while stirring at 30 °C. A 0.5 mol/L NaOH solution was added to maintain the pH of the reaction mixture at 10.5, and the mixture was stirred continuously at 30 °C for 1 h. The CO₃-Mg-Al LDHs that formed were isolated by filtering the resulting suspensions, washing them thoroughly with deionized water, and drying them under reduced pressure (133 Pa) for 40 h. Mg-Al oxides were prepared by calcining the CO₃-Mg-Al LDHs at 500 °C for 2 h to yield compounds with Mg/Al molar ratios of 2, 3, and 4.

2.2. Removal of Sb(V) in an aqueous solution

The Sb(V) solution, which contained Sb(OH)₆⁻ (Sb(V)) in an aqueous solution, was prepared by shaking Sb₂O₅ (Sb(V)) in deionized water at 50 °C for 72 h. The Mg-Al oxides were added to 200 mL of a 40 mg/L Sb(V) solution, and the resultant suspension was kept standing at 30 °C for 120 min while stirring. N₂ was bubbled into the solution throughout the operation. The Mg-Al oxide quantity was 1–10 times the stoichiometric amount indicated by Eq. (3):



The stoichiometric amount can be expressed by the molar ratio of Al in the Mg-Al oxide to Sb in the Sb(V) solution, i.e., the Al/Sb molar ratio. In other words, the Mg-Al oxide quantity was prepared at Al/Sb molar ratios of 1–10. Samples of the suspension were withdrawn at different time intervals and immediately filtered through a 0.45-μm membrane filter after measuring the pH. The filtrates were analyzed for their residual Sb and dissolved Mg. MgO and Al₂O₃ were also used as reference materials to investigate their capacities for adsorbing Sb(V). Furthermore, NaCl, Na₂SO₄, and Na₂CO₃ were added to the Sb(V) solution at molar ratios (Cl⁻/Sb, SO₄²⁻/Sb, and CO₃²⁻/Sb) of 1 or 100 each, to investigate the effect of the coexistent anions on the removal of Sb(V).

2.3. Characterization methods

The concentrations of Sb and Mg in the filtrates were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The Mg-Al oxide and products obtained from the suspensions in Sb(V) solution were analyzed by X-ray diffraction (XRD) using Cu Kα radiation.

3. Results and discussion

3.1. Formation of the brandholzite-like compound

Fig. 1 shows the effects of Mg-Al oxide (Mg/Al molar ratio of 4), MgO, and Al₂O₃ on the residual Sb concentrations during suspension in Sb(V) solution. At all Al/Sb molar ratios, Mg-Al oxide reduced Sb concentrations with time. The Sb concentration decreased with increasing Al/Sb molar ratio, and was less than 1 mg/L at Al/Sb molar ratios of 5 and 10 within 60 min. In contrast, neither MgO nor Al₂O₃ reduced the Sb concentration over time. Fig. 2 shows the XRD patterns for (a) Mg-Al oxide (Mg/Al molar ratio of 4) and for the products obtained from the suspensions in

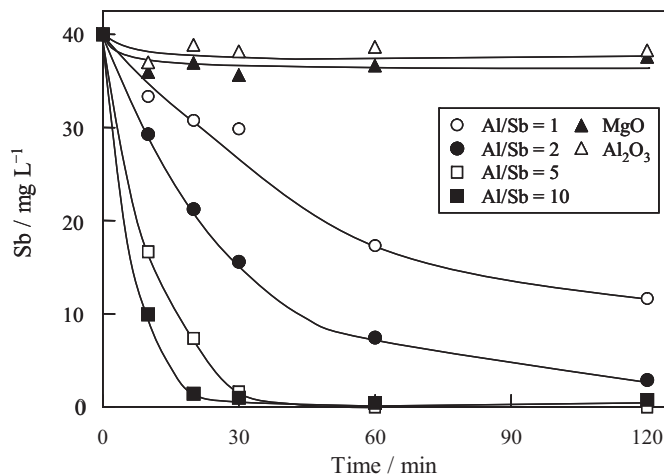


Fig. 1. Effects of Mg-Al oxide (Mg/Al molar ratio of 4), MgO, and Al₂O₃ on the residual Sb concentrations during suspension in an Sb(V) solution. *Al/Sb is the molar ratio of Al in Mg-Al oxide to Sb in solution. **The amounts of MgO and Al₂O₃ were equal to that of Mg-Al oxide at Al/Sb = 2.

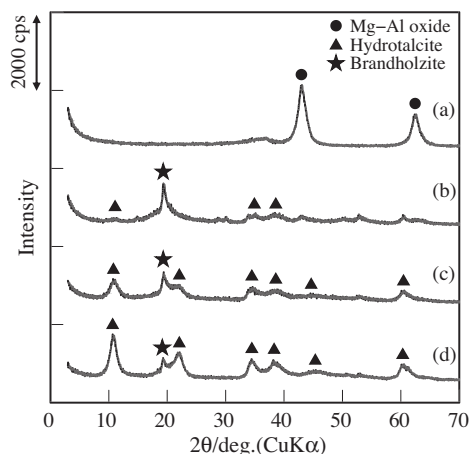


Fig. 2. XRD patterns for (a) Mg-Al oxide (Mg/Al molar ratio of 4) and products obtained from suspension in an Sb(V) solution at Al/Sb molar ratios of (b) 2, (c) 5, and (d) 10 after 120 min.

Sb(V) solution at Al/Sb molar ratios of (b) 2, (c) 5, and (d) 10 after 120 min. For all products, some peaks of the XRD patterns were ascribed to hydroxalcite (JCPDS card 22-700), a hydroxycarbonate of magnesium and aluminum (Mg₆Al₂(OH)₁₆CO₃·4H₂O), which occurs naturally and has the structure of a layered double hydroxide. This suggests that Mg-Al oxide was changed to Mg-Al LDH as a result of the reconstruction reaction. In addition, other peaks in the XRD patterns were ascribed to brandholzite (JCPDS card 40-335), a magnesium antimony hydrate hydroxide (MgSb₂(OH)₁₂·6H₂O). Friedrich et al. [19] have described brandholzite as follows. The crystal structure of brandholzite, Mg(H₂O)₆[Sb(OH)₆]₂, is built up of nearly regular-shaped, isolated Mg(H₂O)₆ and Sb(OH)₆ octahedra interconnected solely by hydrogen bonds. These octahedra are arranged in two types of layers stacked along the *c* axis. One layer consists of Sb(OH)₆ octahedra only, while the other consists of Mg(H₂O)₆ and Sb(OH)₆ octahedra with a Mg/Sb ratio of 2:1. The resulting compositions of these layers are {[Sb(OH)₆]₆}⁹⁻ and {[Sb(OH)₆]₃[Mg(H₂O)₆]₆}⁹⁺, respectively. For Fig. 2(b) in particular, the peak intensity of brandholzite was much larger than that of hydroxalcite. Thus, the product at an Al/Sb molar ratio of 2 was thought to be mainly composed of brandholzite, suggesting that

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