

# Synthesis and sulfate ion-exchange properties of a hydrotalcite-like compound intercalated by chloride ions

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## Abstract

To reduce the generation of hydrogen sulfide gas from sulfate ions, we synthesized a layered double hydroxide hydrotalcite-like compound intercalated with chloride ions in the interlayer (HT-Cl) using a coprecipitation reaction. The resultant HT-Cl material had a Mg/Al molar ratio of approximately 2, and the molar fraction of the chloride ions on the intercalated anion layer of the HT was 0.90. A higher molar fraction of chloride ions can be inserted into the interlayers of the HT by increasing the initial concentration ratio of chloride ions to aluminum ions  $[Cl^-]_0/[Al^{3+}]_0$  in the solution. Approximately 98% of the sulfate ions in the solution were removed within 10 min after adding 1.12 times the stoichiometric quantity of synthesized HT-Cl, which contained a Mg/Al molar ratio of 2 equal to a solution containing a 12 mM calcium sulfate solution. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Hydrotalcite-like compound; Anion exchange; Sulfate ion; Chloride ion

## 1. Introduction

A serious environmental issue has been raised by the detection of high concentrations of harmful hydrogen sulfide gas in many anaerobic subsurface environments, such as landfill sites. Current measures, such as capture-fixed methods or diffusion, are being applied to the emission of hydrogen sulfide gas, which is principally due to the reduction of sulfates by sulfate-reducing bacteria, linked to the degradation of naturally occurring and contaminant forms of organic matter under anaerobic conditions [1–3]. In these cases, one of the methods for controlling the emission of H<sub>2</sub>S gas is to remove the sulfate ions (SO<sub>4</sub><sup>2-</sup>), *i.e.*, the source of the sulfur, thereby moderating the activity of sulfate-reducing bacteria.

Traditionally, the use of clay material as an anion exchanger is a method used for removing SO<sub>4</sub><sup>2-</sup> to lower the emission of harmful gases into the environment. Hydrotalcite-like compounds (HTs) are layered double hydroxides with anion-exchange properties [4,5]. The chemical composition of a

HT is Mg<sub>1-x</sub><sup>2+</sup>Al<sub>x</sub><sup>3+</sup>(OH)<sub>2</sub>(A<sup>n-</sup>)<sub>x/n</sub>·mH<sub>2</sub>O, where A<sup>n-</sup> is an *n* valent anion, such as CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, or Cl<sup>-</sup>, and 0.20 ≤ *x* ≤ 0.33. The crystal structure consists of positively charged brucite-like octahedral hydroxide layers, which are charge neutralized by the interlayer anion. Water molecules occupy the remaining interlayer space inside the crystal lattice. Since CO<sub>3</sub><sup>2-</sup> has an exceptionally high affinity for HTs, CO<sub>3</sub><sup>2-</sup> intercalated in the interlayer (HT-CO<sub>3</sub>) is a preferred solution, which can be synthesized using a coprecipitation method. An aqueous solution containing Mg<sup>2+</sup> and Al<sup>3+</sup> ions is continuously added to the appropriate aqueous solution of anions at a slow flow rate maintaining at pH from 8 to 10 by the drop-wise addition of a base such as NaOH and/or Na<sub>2</sub>CO<sub>3</sub>. This method can yield HTs intercalated with anions such as CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, and Cl<sup>-</sup> in interlayers [6–9]. It has been reported that Cl<sup>-</sup>-intercalated hydrotalcite (HT-Cl) [10,11] is an excellent phosphate ion exchanger [12–14].

The selectivity for the HT increases with the increasing electric charge of the anion and decreasing anion size, for example, CO<sub>3</sub><sup>2-</sup> > SO<sub>4</sub><sup>2-</sup> > OH<sup>-</sup> > F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > I<sup>-</sup> [7,15]. The anion, which has the highest electric density, exhibits the highest electrostatic force toward the host layer. When a higher amount of Cl<sup>-</sup> is intercalated inside the HT layer, a smaller concentration of CO<sub>3</sub><sup>2-</sup> and/or OH<sup>-</sup> is present in the intercalated layer; therefore, the SO<sub>4</sub><sup>2-</sup> in the solution can be removed more

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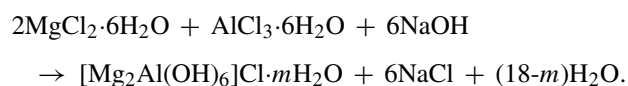
effectively. The charge density in the interlayer is proportional to the number of  $\text{Al}^{3+}$  ions, and the number of intercalated anions is determined by the charge density. The selectivity for the HT increases with anions containing a higher electric field density due to a higher electrostatic field interaction between the HT and the anion.  $\text{SO}_4^{2-}$  can be intercalated in the HT more rapidly than other anions, decreasing the Mg/Al molar ratio in the host layer. Consequently, HT-Cl, in which the Mg/Al molar ratio is 2, is highly suitable for removing the  $\text{SO}_4^{2-}$  in the solution.

In this study, we prepared a HT-Cl material containing a Mg/Al molar ratio of 2, and conducted experiments examining the possible variables to reduce  $\text{SO}_4^{2-}$  by varying the concentrations of  $\text{MgCl}_2$  and  $\text{AlCl}_3$  in the solution, the aging time, and the dripping method for the solution. We report the conditions for synthesizing the optimal ratio of  $\text{Cl}^-$  intercalated within the HT, and describe the  $\text{SO}_4^{2-}$  exchange for the synthesized HT-Cl material.

## 2. Materials and methods

### 2.1. Synthesis of $\text{Cl}^-$ -intercalated hydrotalcite

The HT-Cl was prepared using a standard coprecipitation method (*i.e.*, mixing  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  solutions, which had a  $[\text{Mg}^{2+}]_0/[\text{Al}^{3+}]_0$  molar ratio of 2 and total  $[\text{Mg}^{2+}]_0$  and  $[\text{Al}^{3+}]_0$  concentrations of 1 M) in water or NaCl solution in a five-necked, round-bottomed flask using a peristaltic pump at a rate of 5 ml/min. The resulting solution was kept at pH 10 by adding 2 M sodium hydroxide solution using a peristaltic pump through another port in the flask. Two glass bars were placed between the injection ports for the added solutions and bulk solution in order to add solutions that were moving along the glass bars to the bulk solution continuously. The solution was stirred at 600 rpm and 25 °C, continuously venting the nitrogen gas in order to prevent carbon dioxide gas from being dissolved. A pH of 10 was kept constant to maintain the following stoichiometric equation:

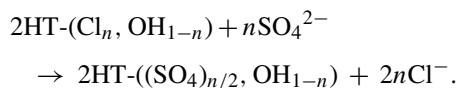


The formed precipitate was stirred between 1 and 24 h at 300 rpm and 70 °C, and then cooled at ambient temperature for 2 h. The HT-Cl material was isolated by centrifuging the resulting suspension, washing it four times with deionized water, and drying it at 105 °C for 24 h. The precipitates were analyzed by X-ray diffraction (XRD) using a Rigaku Denki RINT-2200VHF. The precipitates were dissolved with nitric acid and the chloride concentration was determined by ion chromatography using Dionex QIC and a Dionex model AS4A column (eluent: 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate, flow rate: 1.5 ml/min, detection limit: 0.06 mg/l). The Mg and Al concentrations were quantified by ICP-AES using a Seiko Instruments SPS7800. The hydroxide concentration in the HT-Cl material was estimated from a charge balance assuming that the excess charge with the  $\text{Al}^{3+}$  ion in the host layer was compensated by the  $\text{Cl}^-$  and  $\text{OH}^-$ .

### 2.2. $\text{SO}_4^{2-}$ removal by HT-Cl

A solution containing 1.2–12 mM  $\text{CaSO}_4$  with a volume of 30 ml and a prescribed amount of HT-Cl (chemical composition:  $[\text{Mg}_{1.98}\text{Al}(\text{OH})_{5.95}]\text{Cl}_{0.71}(\text{OH})_{0.29} \cdot 1.48\text{H}_2\text{O}$ ) were placed in a 50-ml screw-tube and shaken at 10–60 °C for up to 60 min at 150 strokes per minute.

Assuming that only the  $\text{Cl}^-$  is exchanged for  $\text{SO}_4^{2-}$  in the interlayer of the HT, a stoichiometric quantity of HT-Cl should be regarded according to the following theoretical ion-exchange equation, replacing  $\text{Cl}^-$  for the  $\text{SO}_4^{2-}$ :



The pH of the suspended solution was measured after shaking, and the solids were filtered and washed with deionized water. The  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations were determined by ion chromatography as described in Section 2.1.

## 3. Results and discussion

### 3.1. Synthesis of HT-Cl

Fig. 1 shows the XRD patterns of HT-Cl, which has a chemical composition of  $[\text{Mg}_{1.98}\text{Al}(\text{OH})_{5.95}]\text{Cl}_{0.71}(\text{OH})_{0.29} \cdot 1.48\text{H}_2\text{O}$ . Since all of the XRD peaks of HT-Cl corresponded to those of hydrotalcite, the prepared HT-Cl was confirmed to have the structure of HT. The interlayer thickness of 2.95 Å was estimated by subtracting the brucite layer thickness 4.77 Å from the basal spacing ( $d_{006}$ ) 7.72 Å. The value of the basal spacing was slightly smaller than that of HT- $\text{CO}_3$  (7.84 Å) shown in JCPDS card 22-700. These calculated values were in good agreement with the reported interlayer spacing values of synthesized HT-Cl materials [7,9,16]. This suggests that the  $\text{Cl}^-$  is not only absorbed on the surface of the HT but also intercalated in the interlayer of the HT material.

Inside the structure of hydrotalcite-like compounds, the excess charge of the host layer is caused by  $\text{Al}^{3+}$  ions. To maintain a charge balance, the amount of  $\text{Al}^{3+}$  in the host layer must

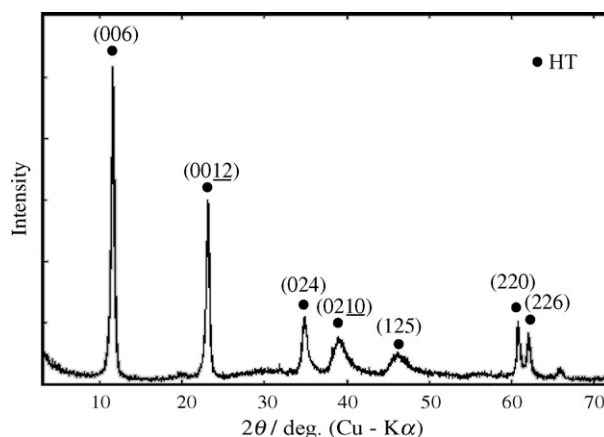


Fig. 1. X-ray powder diffraction pattern of the synthesized HT-Cl.

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