



## Treatment of hydrochloric acid using Mg–Al layered double hydroxide intercalated with carbonate



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### ABSTRACT

Mg–Al layered double hydroxide intercalated with  $\text{CO}_3^{2-}$  ( $\text{CO}_3\text{-Mg-Al LDH}$ ) was found to take up only low amounts of  $\text{Cl}^-$  during the treatment of hydrochloric acid. Low pH promotes the removal of  $\text{Cl}^-$ . HCl is considered to react with  $\text{CO}_3^{2-}$  in the interlayers of Mg–Al LDH as a result of which  $\text{Cl}^-$  is probably intercalated in the interlayers. High pH of the Mg–Al LDH suspension leads to a lower extent of reaction between HCl and Mg–Al LDH, owing to the neutralization of the acid. We can state that the adsorption of  $\text{Cl}^-$  on Mg–Al LDH is best described by the Dubinin–Radushkevich adsorption isotherm. The maximum adsorption amounts were calculated to be 1.4 and 0.6 mmol/g for  $\text{CO}_3\text{-Mg-Al LDH}$  with Mg/Al molar ratios of 2 and 4, respectively, whereas the adsorption energies were calculated to be 82 and 124 kJ/mol, respectively. In summary, the removal of  $\text{Cl}^-$  is caused by both the reaction between hydrochloric acid and  $\text{CO}_3^{2-}$  in the interlayers of Mg–Al LDH as well as anion exchange between the  $\text{HCO}_3^-$  produced and a different  $\text{Cl}^-$  ion in hydrochloric acid. This explains why the adsorption is best expressed by the D–R adsorption isotherm, which assumes a heterogeneous surface and non-constant adsorption potential. © 2016 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

### Introduction

Mg–Al layered double hydroxides (Mg–Al LDHs) exhibit anion exchange properties and are typically represented by the formula  $[\text{Mg}^{2+}_{1-x}\text{Al}^{3+}_x(\text{OH})_2](\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ , where  $x$  is the  $\text{Al}^{3+}/(\text{Mg}^{2+} + \text{Al}^{3+})$  molar ratio ( $0.20 \leq x \leq 0.33$ ) and  $\text{A}^{n-}$  is an anion such as  $\text{CO}_3^{2-}$  or  $\text{Cl}^-$  [1–3]. Mg–Al LDHs consist of a stack of brucite-like octahedral layers in which some of the  $\text{Mg}^{2+}$  is replaced with  $\text{Al}^{3+}$ . The positive charge in the layer arising from this substitution is neutralized by the interlayer anions [4] and the interlayer space is occupied by water molecules in the hydration shell of these anions. Recently, LDHs have been examined for solid-state photoluminescence, magnetic properties, and UV-blocking materials [5–9]. Mg–Al LDHs and their calcined derivatives (i.e., Mg–Al oxides) are known to adsorb anions and have been applied to wastewater treatment [10,11]. Although there are various types of LDHs, such as Zn–Al LDH, Ni–Al LDH, and Cu–Al LDH, Mg–Al LDH is a basic hydroxide material in the LDH family. Unlike other LDHs, Mg–Al LDH is not harmful to humans, even when dissolved in wastewater during treatment (i.e., the dissolved  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  are not harmful).

The treatment of hydrochloric acid is very important in the chemical industry because waste hydrochloric acid corrodes concrete and drainpipes if it is discharged in drains. Usually, the waste hydrochloric acid is neutralized by  $\text{Ca}(\text{OH})_2$  and NaOH. However,  $\text{CaCl}_2$  and NaCl produced in wastewater must be further treated to prevent severe salt damage to the surrounding water environment. Therefore, a new treatment method for waste hydrochloric acid is desired.

We previously clarified that Mg–Al oxide is effective for the treatment of hydrochloric acid, where Mg–Al oxide works as a neutralizing reagent for the acid as well as a scavenger for  $\text{Cl}^-$  [12–15]. Mg–Al oxide was also found to remove  $\text{Cl}^-$  during the treatment of gaseous HCl [16–18]. Similarly, Mg–Al LDH intercalated with  $\text{CO}_3^{2-}$  ( $\text{CO}_3\text{-Mg-Al LDH}$ ) was able to remove  $\text{Cl}^-$  during the treatment of gaseous HCl [19], suggesting that  $\text{CO}_3\text{-Mg-Al LDH}$  could potentially also remove  $\text{Cl}^-$  during the treatment of hydrochloric acid. Generally,  $\text{CO}_3\text{-Mg-Al LDH}$  is used as an acid-reducing agent [1]. In the 1970s, the antacid efficacy of  $\text{CO}_3\text{-Mg-Al LDH}$  was examined [20–23]. Furthermore, deintercalation of  $\text{CO}_3^{2-}$  from  $\text{CO}_3\text{-Mg-Al LDH}$  using a mixed acid-salt solution was examined [24]. However, the removal of  $\text{Cl}^-$  from hydrochloric acid was not investigated.

If  $\text{CO}_3\text{-Mg-Al LDH}$  can effectively remove  $\text{Cl}^-$  during the treatment of hydrochloric acid, then  $\text{CO}_3\text{-Mg-Al LDH}$  is expected to act as a neutralizing reagent for the acid and a scavenger for

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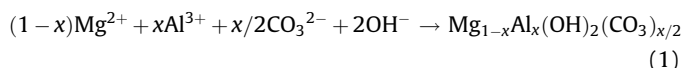
$\text{Cl}^-$ . We can develop new treatment methods for waste hydrochloric acid to solve the above problem, i.e., the use of Mg–Al oxide and  $\text{CO}_3\cdot\text{Mg}$ –Al LDH can be combined. Therefore, in the present study, the removal of  $\text{Cl}^-$  by  $\text{CO}_3\cdot\text{Mg}$ –Al LDH during the treatment of hydrochloric acid was examined. Adsorption isotherms were measured and a reaction mechanism is proposed.

## Experimental

All the reagents were of chemical reagent grade and were used without further purification.

### Preparation of $\text{CO}_3\cdot\text{Mg}$ –Al LDH

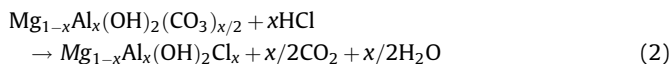
The co-precipitation reactions that occur during the synthesis of  $\text{CO}_3\cdot\text{Mg}$ –Al LDH are shown in Eq. (1). In the present study, stoichiometric coefficient ( $x$ ) values of 0.33 or 0.20 were used for  $\text{CO}_3^{2-}$ , which were calculated based on the neutralization of the positive charge of the Al-bearing, brucite-like octahedral layers, assuming that Mg was replaced with Al at a Mg/Al molar ratio of 2 or 4.



$\text{CO}_3\cdot\text{Mg}$ –Al LDH was prepared by the dropwise addition of an Mg–Al nitrate solution into a  $\text{Na}_2\text{CO}_3$  solution maintained at pH 10.5. The Mg–Al nitrate aqueous solutions with initial Mg/Al molar ratios of 2 or 4 were composed of 0.33 M  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  and 0.17 M  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ , or 0.40 M  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  and 0.10 M  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ , respectively. To prepare  $\text{CO}_3\cdot\text{Mg}$ –Al LDH, 500 mL of the Mg–Al nitrate solution was added dropwise to 500 mL of 0.1 M  $\text{Na}_2\text{CO}_3$  solution at a rate of  $10 \text{ mL min}^{-1}$ . This solution was maintained at  $30^\circ\text{C}$  and gently agitated. The pH was maintained at a value of 0.5 by adding appropriate amounts of 1.25 M NaOH and the resulting suspension was allowed to settle at  $30^\circ\text{C}$  for 1 h. The particles were then recovered by filtration, repeatedly washed with deionized water, and then dried under reduced pressure (133 Pa) at  $40^\circ\text{C}$  for 40 h. The  $\text{CO}_3\cdot\text{Mg}$ –Al LDHs prepared using initial Mg/Al molar ratios of 2 or 4 are referred to as LDH 4Mg2Al- $\text{CO}_3$  and LDH 8Mg2Al- $\text{CO}_3$ , respectively, hereafter [4].

### Treatment of hydrochloric acid

The  $\text{CO}_3\cdot\text{Mg}$ –Al LDHs were added to 0.1 M hydrochloric acid (20 mL) and the resultant suspensions were shaken at  $10$ – $60^\circ\text{C}$  for 10–360 min. Samples of the suspension were filtered through a  $0.45 \mu\text{m}$  membrane filter after measuring the pH. The filtrates were analyzed for residual  $\text{Cl}^-$  as well as dissolved  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ . Stoichiometric amount of LDH (as indicated in Eq. (2)) was used for the treatment of hydrochloric acid, and is indicated using the notation eq1.



To measure the adsorption isotherms for  $\text{Cl}^-$  adsorbed on to the LDHs, 20 mL of hydrochloric acid (0.001–0.1 M) and 0.2 g of the LDHs were placed in 50 mL screw-top tubes and shaken at  $30^\circ\text{C}$  for 24 h.

### Characterization methods

The LDHs were analyzed before and after the treatment of HCl using X-ray diffraction (RINT-2200VHF XRD, RIGAKU Co.) measurements with Cu  $K\alpha$  radiation. The LDHs were dissolved in 1 M

$\text{HNO}_3$ , and the Mg and Al contents were analyzed using inductively coupled plasma-atomic emission spectrometry (iCAP 6500 Duo ICP-AES, Thermo Fisher Scientific Co.). For the adsorption experiments, the residual concentration of  $\text{Cl}^-$  in the filtrates was determined using a Dionex DX-120 ion chromatograph and Dionex model AS-12A column (eluent: 2.7 mM  $\text{Na}_2\text{CO}_3$  and 0.3 mM  $\text{NaHCO}_3$ ; flow rate:  $1.3 \text{ mL min}^{-1}$ ). The amounts of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  dissolved from the LDHs were determined using ICP-AES.

## Results and discussion

### Preparation of $\text{CO}_3\cdot\text{Mg}$ –Al LDH

Fig. 1(a) and (b) shows the XRD patterns for LDH 4Mg2Al- $\text{CO}_3$  and LDH 8Mg2Al- $\text{CO}_3$ , respectively. The XRD peaks of both products may be attributed to hydroxycarbonate (JCPDS card 22-700), a naturally occurring hydroxycarbonate of magnesium and aluminum with the formula  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$  and having an LDH structure. This suggests that all the products had the basic LDH structure. Table 1 presents the elemental compositions of  $\text{CO}_3\cdot\text{Mg}$ –Al LDHs. The LDHs were shown to contain both  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ , and the Mg/Al molar ratios for LDH 4Mg2Al- $\text{CO}_3$  and LDH 8Mg2Al- $\text{CO}_3$  were 2.1 and 3.9, respectively. These values are close to the Mg/Al molar ratios of 2 and 4, respectively, in the initial Mg–Al solution, and suggest that most of the  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  in the solution precipitated as the LDH. These results also indicate the formation of  $\text{CO}_3\cdot\text{Mg}$ –Al LDHs and are consistent with the reactions shown in Eq. (1).

### Treatment of hydrochloric acid

Fig. 2(a) and (b) shows the effect of temperature on the removal of  $\text{Cl}^-$  over time in LDH 4Mg2Al- $\text{CO}_3$  and LDH 8Mg2Al- $\text{CO}_3$  suspensions in 0.1 M hydrochloric acid at eq1, respectively. In both the cases, less than 40% of  $\text{Cl}^-$  was removed at all time durations. This low degree of removal is attributed to the difficulty in anion exchange between the  $\text{CO}_3^{2-}$  in  $\text{CO}_3\cdot\text{Mg}$ –Al LDH and  $\text{Cl}^-$  in hydrochloric acid, owing to the larger charge density of  $\text{CO}_3^{2-}$  compared to that of  $\text{Cl}^-$ . Fig. 3(a) and (b) shows the effect of temperature on the amount of  $\text{Mg}^{2+}$  dissolved over time in the LDH 4Mg2Al- $\text{CO}_3$  and LDH 8Mg2Al- $\text{CO}_3$  suspensions in 0.1 M hydrochloric acid at eq1, respectively. In both the cases,  $\text{Mg}^{2+}$  was found to dissolve from the LDHs, whereas no  $\text{Al}^{3+}$  dissolution was observed. The amount of  $\text{Mg}^{2+}$  dissolved increased rapidly over time until it reached a plateau.

Fig. 4(a) and (b) shows the effect of temperature on pH over time in the LDH 4Mg2Al- $\text{CO}_3$  and LDH 8Mg2Al- $\text{CO}_3$  suspensions in 0.1 M hydrochloric acid at eq1, respectively. In both the cases, the

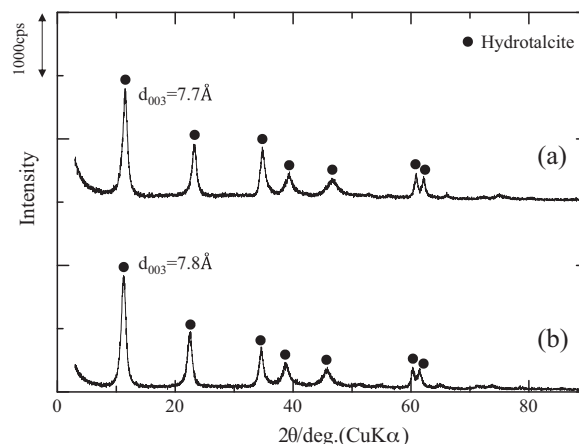


Fig. 1. XRD patterns of (a) LDH 4Mg2Al- $\text{CO}_3$  and (b) LDH 8Mg2Al- $\text{CO}_3$ .

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