New Treatment Method for Dilute Hydrochloric Acid Using Magnesium-Aluminum Oxide

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(Received July 13, 2001)

Magnesium-aluminum oxide (Mg-Al oxide) was shown to be superior to $CO_3{}^{2-}$ intercalated hydrotalcite (CO_3-HT) for removing dilute hydrochloric acid. Cl^- in a 0.5 M HCl solution could be quantitatively removed by adding 1.75-times the stoichiometric quantity of $Mg_{0.70}Al_{0.20}O$ at 60 °C for 1 h. The solution after the reaction was weakly alkaline. This reaction could be adequately described as being first order for the HCl concentration, and the apparent activation energy was 49.3 kJ mol^{-1}. The amount of Cl^- removal per 1 g of Mg-Al oxide in the first use was 3.08 meq at a Mg/Al molar ratio of 2.0 and 2.89 meq at a ratio of 3.5.

HT ($[Mg^{2+}{}_{1-x}Al^{3+}{}_x(OH)_2](A^{n-})_{x/n}\cdot mH_2O$: $0.20 \leqq x \leqq 0.33$) is a layered double hydroxide with anion-exchange properties.[1] CO_3-HT transforms into Mg-Al oxide when heated to 450–800 °C, as expressed by[2]

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \rightarrow (1 + x/2)Mg_{2(1-x)/(2+x)}Al_{2x/(2+x)}O + x/2CO_2 + H_2O. \quad (1)$$

The Mg-Al oxide can intercalate anions in solution, and then the original HT structure can be reconstructed, as expressed by[2–4]

$$(1 + x/2)Mg_{2(1-x)/(2+x)}Al_{2x/(2+x)}O + x/n\,A^{n-} + (1 + x/2)H_2O \rightarrow [Mg_{1-x}Al_x(OH)_2]A_{x/n} + xOH^-. \quad (2)$$

The feature of this reaction is the release of OH^- along with the intercalation of anions, and it is known that the selectivity of anion intercalation into the Mg-Al oxide increases with increasing charge density of the anion.[2] In the case of anions whose charge density is smaller than that of OH^-, $OH^- > F^- > Cl^- > Br^- > NO_3{}^- > I^-$, the Mg-Al oxide preferentially intercalates the released OH^- rather than those anions in a neutral solution. Therefore, the Mg-Al oxide can not be used as a remover of those anions in a neutral solution. In addition, because the solution after the reaction is strongly alkaline, it is difficult to apply Mg-Al oxide for treating a waste neutral saline solution. Accordingly, we propose that the Mg-Al oxide can be utilized for waste acid treatment as both a neutralizer and a fixative of anions.

There have been many studies on the reaction for such neutral saline solutions as NaCl, Na_2SO_4 and $NaNO_3$.[3–5] In contrast, no study had been made for an acidic solution below pH 2. We have thus reported briefly on this matter recently.[6] In this study, Mg-Al oxide was applied for treating dilute hydrochloric acid. The effects of the time, Mg-Al oxide quantity, HCl concentration, and temperature on Cl^- removal were revealed in detail. The difference on Cl^- removal between CO_3-HT and Mg-Al oxide was also examined.

Experimental

CO_3-HTs were prepared by a common precipitation method.[7] Mixed $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ solutions with Mg/Al molar ratios of 3.5 and 2.0 were added to 1.0 M Na_2CO_3 solutions. When the pH of the mixture was lower than 10, a solution of 2.0 M NaOH was added to maintain the pH at 10.0. The mixture was stirred and aged for a certain period of time, and the resulting product was washed, dried and calcined at 500 °C for 1 h. 0.01–0.5 M HCl solutions (10 mL) and $[Mg_{0.70}Al_{0.20}(OH)_{1.80}](CO_3)_{0.10}$, $Mg_{0.70}Al_{0.20}O$ or $Mg_{0.58}Al_{0.28}O$ of 0.5–2.0 times the stoichiometric quantity, according to Eqs. 3–5, were placed in a 50 ml screw tube and shaken at 25–80 °C for 0.2–3 h.

$$[Mg_{0.70}Al_{0.20}(OH)_{1.80}](CO_3)_{0.10} + 0.20HCl \rightarrow [Mg_{0.70}Al_{0.20}(OH)_{1.80}]Cl_{0.20} + 0.10CO_2 + 0.10H_2O \quad (3)$$

$$Mg_{0.70}Al_{0.20}O + 0.20HCl + 0.80H_2O \rightarrow [Mg_{0.70}Al_{0.20}(OH)_{1.80}]Cl_{0.20} \quad (4)$$

$$Mg_{0.58}Al_{0.28}O + 0.28HCl + 0.72H_2O \rightarrow [Mg_{0.58}Al_{0.28}(OH)_{1.72}]Cl_{0.28} \quad (5)$$

The pH of the solution was measured after the reaction, and the Cl^- concentration was determined by ion chromatography. The degrees of Mg^{2+} and Al^{3+} leaching were determined by ICP-AES. The precipitates were identified by X-ray diffraction (XRD).

Results and Discussion

1. Difference between CO_3-HT and Mg-Al Oxide.

Figure 1 shows the effect of time on Cl^- removal using $Mg_{0.70}Al_{0.20}O$ or $[Mg_{0.70}Al_{0.20}(OH)_{1.80}](CO_3)_{0.10}$ of 1.75-times

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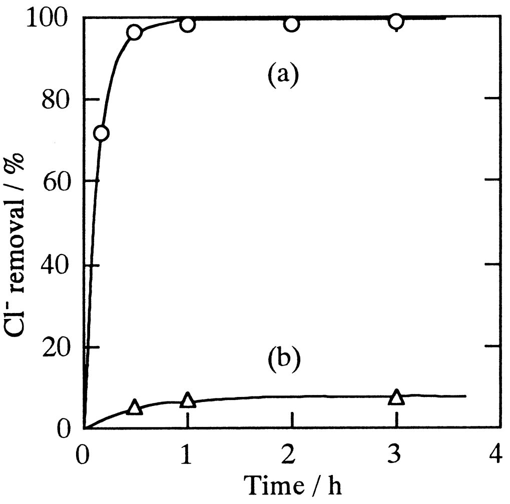

Fig. 1. Effect of time on Cl^- removal using (a) $Mg_{0.70}Al_{0.20}O$ or (b) $[Mg_{0.70}Al_{0.20}(OH)_{1.80}](CO_3)_{0.10}$ of 1.75-times the stoichiometric quantity. HCl concd: 0.5 M, Temp.: 60 °C.

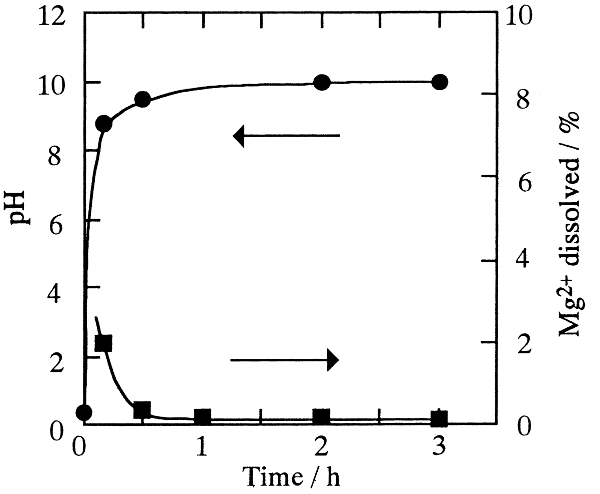

Fig. 2. Effect of time on the pH or Mg^{2+} dissolved using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. HCl concd: 0.5 M, Temp: 60 °C.

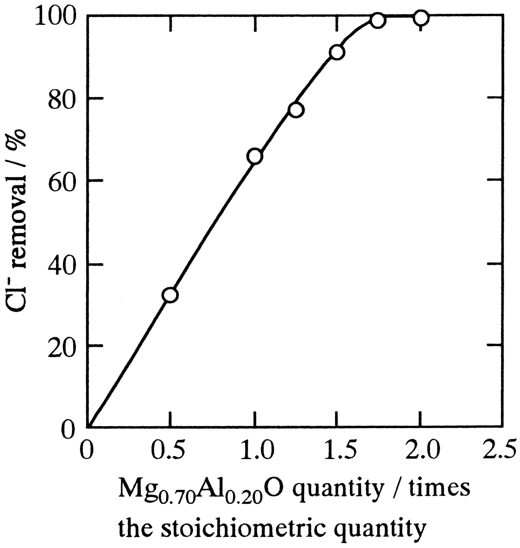

Fig. 3. Effect of the $Mg_{0.70}Al_{0.20}O$ quantity on Cl^- removal. HCl concd: 0.5 M, Temp: 60 °C, Time: 3 h.

the stoichiometric quantity. The CO_3-HT removed hydrochloric acid slightly. When a 0.1 M HCl solution (20 mL) and CO_3-HT of the stoichiometric quantity were shaken at 37 °C, Cl^- was removed 55% by an exchange reaction of HCl and CO_3^{2-}, as shown in Eq. 3.[8] Because the HCl concentration was high in this study, it is conjectured that the CO_3-HT was mainly dissolved in addition to the slight exchange reaction. From the fact that the solution after the reaction was neutral, it may be deduced that Cl^- could hardly exchange with the CO_3^{2-}.

In contrast, $Mg_{0.70}Al_{0.20}O$ exhibited a much higher degree of Cl^- removal, and Cl^- was quantitatively removed above 1 h. Figure 2 shows the effect of time on the pH or Mg^{2+} dissolved using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. The pH was rapidly increased and kept constant at about 10. Although Mg from $Mg_{0.70}Al_{0.20}O$ was dissolved at first, the dissolution was not recognized after 1 h. The precipitate after 1 h was a mixture of HT and a slight amount of $Mg(OH)_2$. The reaction until about 0.2 h was interpreted by both the intercalation of Cl^- and the dissolution of $Mg_{0.70}Al_{0.20}O$, as expressed in Eq. 4 and

$$Mg_{0.70}Al_{0.20}O + H_2O \rightarrow 0.70Mg^{2+} + 0.20Al^{3+} + 2OH^-. \quad (6)$$

It is conjectured that Cl^- was removed as follows at 0.2–1 h:

$$Mg_{0.70}Al_{0.20}O + 0.10Mg^{2+} + 0.20Cl^- + H_2O \rightarrow [Mg_{0.70}Al_{0.20}(OH)_{1.80}]Cl_{0.20} + 0.10Mg(OH)_2. \quad (7)$$

Since the dissolution of Al was not recognized at 0.2 h, it is supposed that Al was promptly hydrolyzed.

In sum, because an increase in the OH^- concentration was prevented by the precipitation of $Mg(OH)_2$, as expressed in Eq. 7, it may be concluded that Cl^- was easily intercalated into $Mg_{0.70}Al_{0.20}O$ for a small amount of OH^-.

2. Dilute Hydrochloric Acid Removal Using Mg-Al Oxide. Figure 3 shows the effect of the $Mg_{0.70}Al_{0.20}O$ quantity on Cl^- removal. Cl^- removal increased with increasing $Mg_{0.70}Al_{0.20}O$ quantity, and Cl^- was removed above 99% adding $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. However, Cl^- was not quantitatively removed at the stoichiometric quantity. This was due to the formation of OH-HT, as expressed by

$$Mg_{0.70}Al_{0.20}O + H_2O \rightarrow [Mg_{0.70}Al_{0.20}(OH)_{1.80}](OH)_{0.20} \quad (8)$$

after the release of OH^-, as expressed by

$$Mg_{0.70}Al_{0.20}O + 0.20Cl^- + H_2O \rightarrow [Mg_{0.70}Al_{0.20}(OH)_{1.80}]Cl_{0.20} + 0.20OH^-. \quad (9)$$

Additionally, this is also attributable to the dissolution of

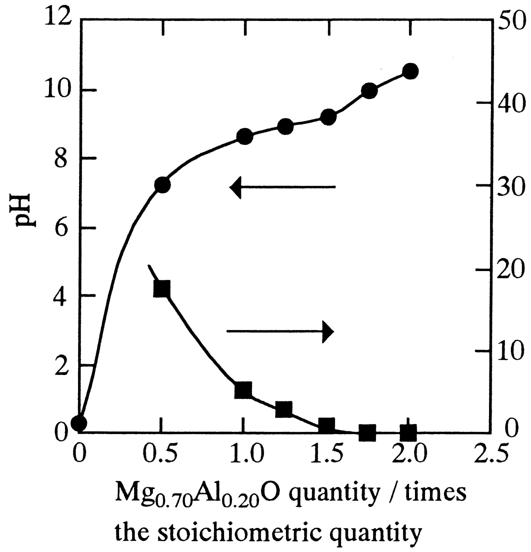

Fig. 4. Effect of the $Mg_{0.70}Al_{0.20}O$ quantity on the pH or Mg^{2+} dissolved. HCl concd: 0.5 M, Temp: 60 °C, Time: 3 h.

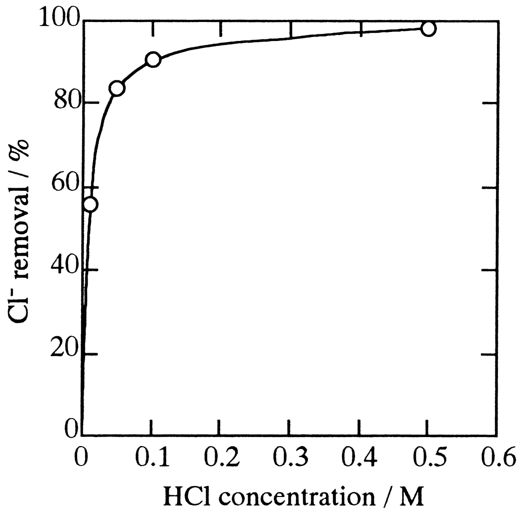

Fig. 5. Effect of the HCl concentration on Cl^- removal using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. Temp: 60 °C, Time: 1 h.

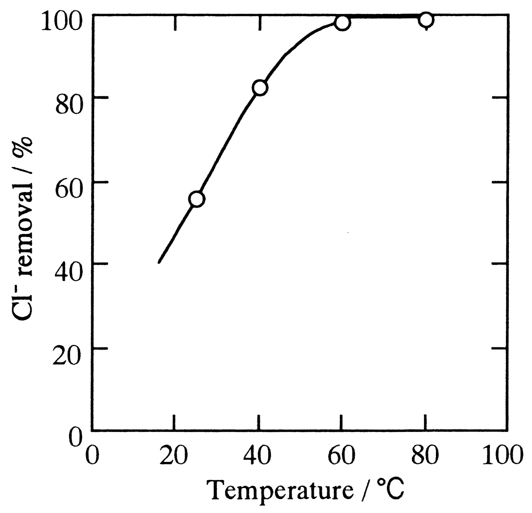

Fig. 6. Effect of the temperature on Cl^- removal using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. HCl concnd: 0.5 M, Time: 1 h.

$Mg_{0.70}Al_{0.20}O$. About 5% of Mg was dissolved at the stoichiometric quantity, as shown in Fig. 4. Considering the formation of OH-HT and the dissolution of Mg, Mg-Al oxide is required above the stoichiometric quantity for a quantitative removal of Cl^-.

Figure 5 shows the effect of the HCl concentration on Cl^- removal using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. Cl^- removal increased with increasing HCl concentration. With increasing HCl concentration, the concentration of Cl^- should be higher than that of OH^- at the pH at which the once dissolved Mg^{2+} catch the released OH^- to precipitate as $Mg(OH)_2$. Consequently, it can be stated that Cl^- was easily intercalated into $Mg_{0.70}Al_{0.20}O$. The intercalation capacity of Mg-Al oxide for Cl^- has been investigated in a NaCl solution,[3,5] and it is known that Cl^- removal is low, since OH^- is mainly intercalated due to an increase in the OH^- concentration due to the formation of NaOH, as expressed by

$$\begin{aligned}&Mg_{0.70}Al_{0.20}O + 0.20NaCl + H_2O \rightarrow \\ &[Mg_{0.70}Al_{0.20}(OH)_{1.80}]Cl_{0.20} + 0.20NaOH. \qquad (10)\end{aligned}$$

It must be emphasized that the capacity of Mg-Al oxide for Cl^- removal could be attained maximally in a strong hydrochloric acid below 0.1 M.

Figure 6 shows the effect of the temperature on Cl^- removal using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. Cl^- removal increased with increasing temperature, and Cl^- was quantitatively removed above 60 °C. The thermostable temperature of the anion-exchange resin is below 60 °C. It should be noted that a hydrochloric acid treatment at over 60 °C is possible using Mg-Al oxide instead of the resin.

From the fact that the removal rate of Cl^- was fast with increasing temperature, it is implied that this reaction proceeded under chemical reaction control. The Cl^- removal rate at 25–60 °C was arranged according to the following equation using the results shown in Fig. 1 and 6:

$$-\ln(1-x) = kt, \qquad (11)$$

where x is the degree of Cl^- removal, and k (min^{-1}) is the apparent rate constant. Figure 7 shows a first-order plot of Cl^- removal using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. This reaction is described as being first order for the HCl concentration because of the good linearity at each temperature. An Arrhenius plot of k, determined from the slope of the straight lines in Fig. 7, is shown in Fig. 8. The apparent activation energy was 49.3 kJ mol^{-1}. This value confirms that Cl^- removal by Mg-Al oxide proceeded under chemical reaction control.

3. An Application of Mg-Al Oxide to Dilute Waste Hydrochloric Acid Treatment. Table 1 gives the amounts of Cl^- removed per 1 g of Mg-Al oxide in the first use. The Mg-Al oxide has a large capacity for removing Cl^- relatively, be-

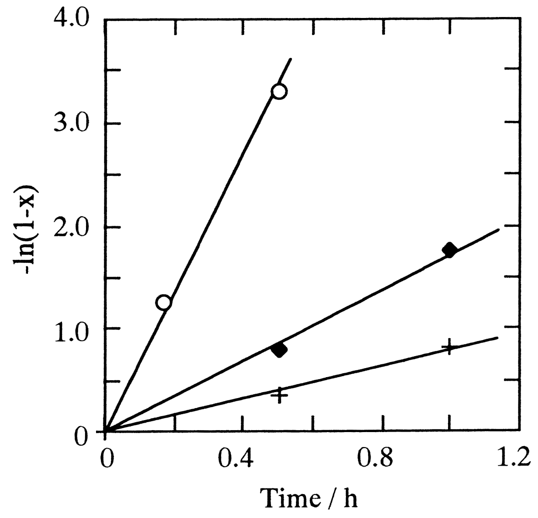

Fig. 7. First-order plot of Cl$^-$ removal using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. HCl concd: 0.5 M.

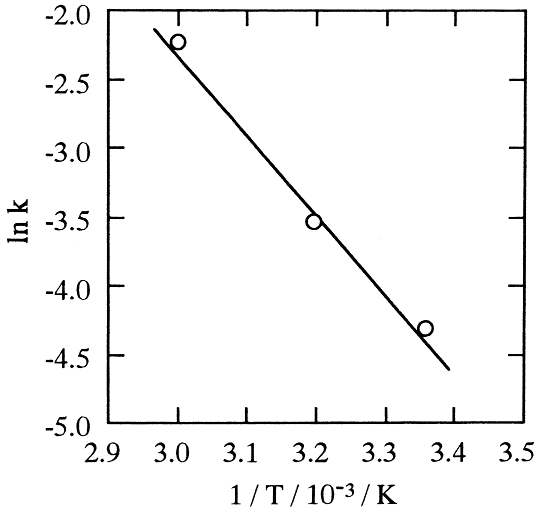

Fig. 8. Arrhenius plot of the apparent rate constant of Cl$^-$ removal using $Mg_{0.70}Al_{0.20}O$ of 1.75-times the stoichiometric quantity. HCl concd: 0.5 M.

Table 1. Amounts of Cl$^-$ Removed per 1 g of Mg-Al Oxide in the First Use

Mg/Al molar ratio in Mg-Al oxide	mg/g	meq/g
2.0	109	3.08
3.5	103	2.89

HCl concd: 0.5 M, Temp: 60 °C, Time: 1 h,
Mg-Al oxide: 1.75-times the stoichiometric quantity.

cause the ion-exchange capacity of the anion-exchange resin is 3.5 (meq/g). A Mg-Al oxide at Mg/Al molar ratio of 2.0 has a larger capacity for removing Cl$^-$ than that at 3.5. However, it is advisable utilizing Mg-Al oxide with a large Mg/Al molar ratio for practical use, since the price of Al is higher than that of Mg.

An exaust gas containing hydrogen chloride from garbage incinerators is generally treated by blowing slaked lime powder, and the produced calcium chloride etc. are discharged into landfill.[9] However, the calcium chloride generates highly concentrated saline leachate, and the leachate becomes a cause of damage from salt to the surrounding water environment.[10,11] We thus propose that Mg-Al oxide can be applied for treating hydrochloric acid produced by washing waste hydrogen chloride with venturis scrubbers. After this treatment and a filtration process, the produced Cl-HT can be used as an ion exchanger for removing phosphorus to prevent eutrophication of surface water by an algae bloom.[12,13] It is known that the use of Cl-HT in various anion intercalated HTs is suitable for treating phosphate ion.[12] In the case of calcining Cl-HT at 450–800 °C, Mg-Al oxide can be reproduced with hydrochloric acid.[14,15] This reproduction method doesn't produce any new drainage, contrary to the reproduction of an ion-exchange resin. The reproduced Mg-Al oxide can be used for another treatment.

Conclusion

From the present results concerning the removal of dilute hydrochloric acid using Mg-Al oxide, the following conclusions may be drawn:

1. Mg-Al oxide was superior to CO_3-HT as a remover of dilute hydrochloric acid.
2. 0.5 M hydrochloric acid could be quantitatively removed by adding 1.75-2 times the stoichiometric quantity of $Mg_{0.70}Al_{0.20}O$ at 60–80 °C over a period of 1 h.
3. The reaction of Cl$^-$ removal by Mg-Al oxide could be adequately described by first order for the HCl concentration. The apparent activation energy was 49.3 kJ mol^{-1}.
4. The amount of Cl$^-$ removal per 1 g of Mg-Al oxide in the first use was 3.08 meq at a Mg/Al molar ratio of 2.0, and 2.89 meq at a ratio of 3.5.

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