Note

THERMAL STABILITY OF Mg,Al DOUBLE HYDROXIDES MODIFIED BY ANIONIC EXCHANGE *

O. MARINO and G. MASCOLO

Istituto di Chimica Applicata, Facoltà di Ingegneria, Università di Napoli, 80125 Napoli (Italy)

(Received 11 December 1981)

A recent synthesis [1] has given Mg, Al hydroxides which are relatively low in carbon dioxide. These compounds have compositions of type $[Mg_{1-x}Al_x(OH)_2][OH_x \cdot H_2O_{0.81-x}]$. The structure consists of brucite-like layers with a net positive charge x because of substitution of Al^{3+} for Mg^{2+}. The hydroxyl groups and water molecules form interlayers interleaved between the basic layers which are stacked with rhombohedral symmetry and three layers per unit cell [2]. The layer spacing $c' = c/3$ of these hydroxides diminishes with increase in Al^{3+} ions due to increase in electrostatic attraction between positive layers and negative interlayers [1,3]. The parameter a also decreases with increase of Al^{3+} ions because of their smaller size. The composition limits of these phases [4] indicate that the maximum substitution is $x = 0.33$, which corresponds to the composition Mg_2Al, while the lower limit of $x = 0.25$, corresponding to the ratio Mg_3Al, is commonly found in mineral hydrotalcite.

Meixnerite [5], a rare mineral with a hydroxide interlayer and synthetic Mg,Al hydroxides, has a strong capability for trapping CO_2 giving hydrotalcite-like phases [6]. On the other hand, the ability of hydrotalcite to exchange different anions has been demonstrated [7].

The aim of the present work has therefore been to study the anion exchange of the synthetic Mg,Al hydroxides and the thermal stability of the more extensively exchanged forms.

EXPERIMENTAL

Synthetic Mg,Al hydroxides were prepared according to a previous paper [1]. The exchange runs were carried out at 25°C by placing samples of 1–4 g in 1 l of 0.02 N $CoCl_2$, $CaCl_2$, KCl or NaCl solution. The time allowed for exchange was 24 h. Exchanges were also performed at 25 and 80°C employ-

ing $4N$ $MgCl_2$. $MgSO_4$ or $Mg(NO_3)_2$ solution. It must be noted that it was practically impossible to avoid the carbonation of the samples during the ion exchange. Atomic absorption spectroscopy (Perkin-Elmer 300s apparatus) was employed for analyzing Ca. K. Co and Na. The amount of Cl^- was determined by the Mohr method. The weight loss was determined by TG using 100 mg samples at a heating rate of $6°C$ min^{-1} using a Stanton Mass flow balance. A DuPont 900 thermal analyzer was used for the DTA under the following conditions: heating rate $10°C$ min^{-1}. sample weight 20 mg, reference sample powdered Al_2O_3. T and ΔT sensitivity 0.4 and 0.008 mV in. $^{-1}$. respectively. X-Ray powder patterns were obtained using a Guinier de Wolff Camera with CuK_α radiation. $Pb(NO_3)_2$ was used as a reference material and the films were measured using a Kipp and Zonen micro-densitometer.

RESULTS AND DISCUSSION

Preliminary ionic exchange runs were performed using Mg,Al hydroxide with $x = 0.30$ and diluted chloride-containing solutions of different cations. The data in Fig. 1 show that the OH^- groups can be exchanged with Cl^- anions.

An unexpected cation exchange has also been observed, especially for Co^{2+}. This suggests that Co^{2+} can replace Mg^{2+} in the hydroxide layer structure as their size and charge are very similar. On the other hand, Co^{2+} ions are unlikely to occur between the layers because of the overall positive
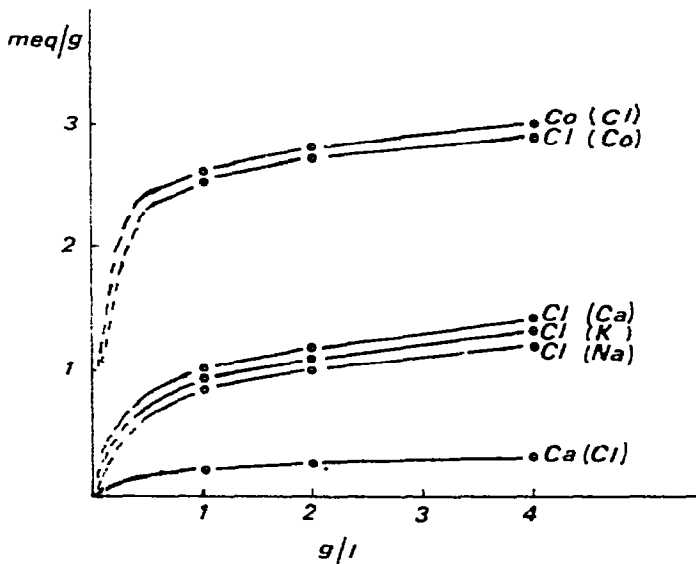

Fig. 1. Ionic exchange of a Mg,Al hydroxide with chloride-containing solutions of different cations.

charge on the layers [8]. The higher value of exchanged chloride from Co-containing solution may be explained by the formation of compounds of the type $MgOHCl$ and $Mg_2(OH)_3Cl$. In fact, the Mg^{2+} ions, deriving from the exchange with Co^{2+}, react both with the exchanged OH^- and with the Cl^- of the contact solution. A small amount of Ca was exchanged, while no exchanged Na or K was observed owing to the different size and charge, respectively. The Co-exchanged form was green in colour. It must be pointed out that on treating the white carbonate form with Co-containing solution no colour change was observed, indicating no cation exchange in this case. Such a behaviour might be explained considering that cation exchange takes place simultaneously with the anion exchange. Because the carbonate form is more stable than the chloride [7], no significant anion exchange was recorded and consequently no cation exchange was observed. Further evidence of the foreign cations in the basic layers of Mg,Al hydroxides appears in Fig. 2 where the a and c' parameters of pure Mg,Al hydroxide (lines a) and those of the same samples obtained in the presence of $Ca(OH)_2$-saturated solution (lines b) are reported. Over all the range of compositions, the Ca-doped samples showed higher values of both the a and c' parameters than the undoped Mg,Al hydroxides [9]. This may be explained with the larger size of the Ca^{2+} compared with that of the Mg^{2+} ion.

The research has been continued by keeping constant the composition of the basic layer. To this end, further exchange runs were performed with homocationic solutions containing Mg^{2+}. To speed and extend the anion exchange, a concentrated solution at 80°C was used.

The X-ray powder diffraction of treated samples confirms that the OH^- groups of the Mg,Al hydroxides with $x = 0.30$ can be easily exchanged with Cl^-, NO_3^- and SO_4^{2-} anions both at room temperature and 80°C. Some $Mg(OH)_2$ or $MgOHCl$ (in the case of treatment with solutions of $MgCl_2$) was found to be present because of the reaction of Mg^{2+} contained in the solutions with the OH^- ions deriving from the exchange.

The a and c' parameters (Å), for variously anion-exchanged forms of Mg,Al hydroxides with $x = 0.30$ appear in Table 1. The a parameter, depending mainly on the composition of the hydroxide layer, is not affected by the different anionic treatment except in the case of the chloride form, probably due also to the replacement of OH^- by Cl^- in the basic layer. The layer spacing, c', is slightly larger for carbonate and chloride indicating that the interlayer arrangement in these exchanged samples is similar to that of the hydroxide sample. The expanded basal spacing for nitrate and sulphate forms suggests a different interlayer arrangement. Intermediate values of the basal spacing, depending on moisture [6], were also observed for these exchanged forms. That involves a different amount of anion exchange as all the samples were dried on silica gel. On the other hand, the X-ray powder diffraction revealed that the entity of the anionic exchange depends on the treatment temperature and on the composition of the Mg,Al hydroxide.
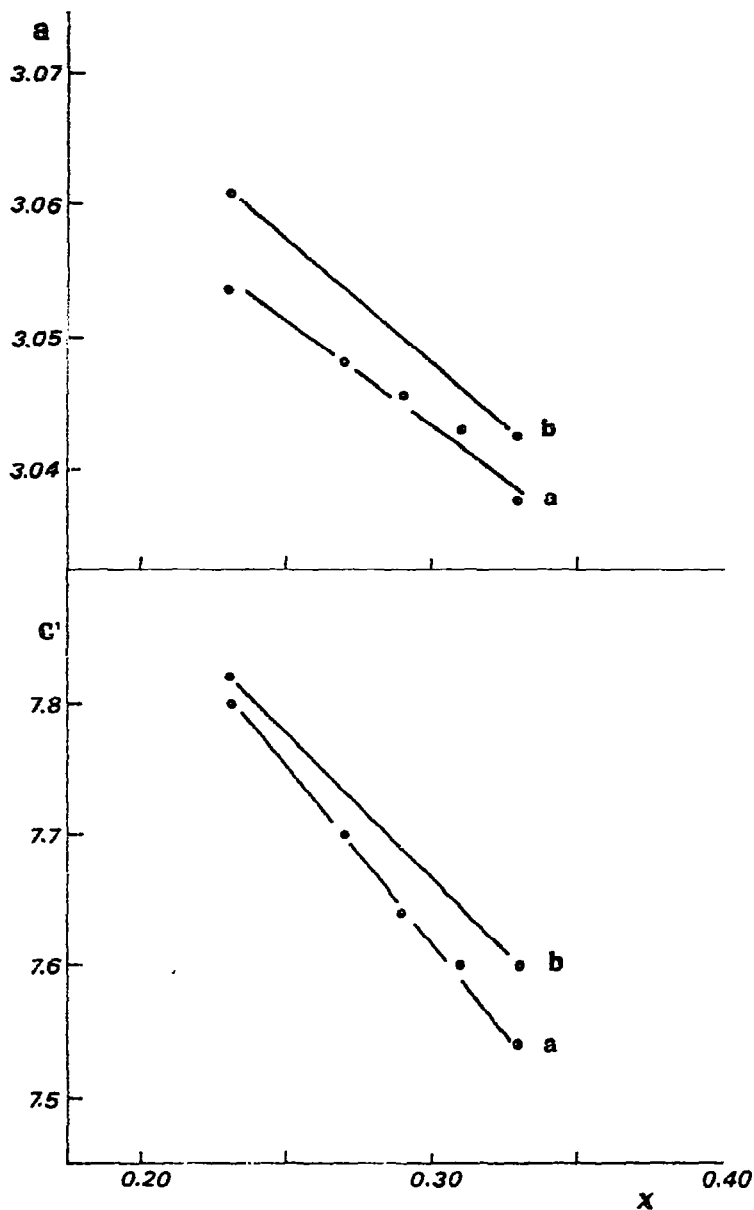
Fig. 2. c' and a parameters (Å) of (a) undoped and (b) Ca-doped Mg.Al hydroxides as a function of x.

Splitting and broadening of X-ray powder diffraction lines, especially for nitrate and sulphate forms, were also observed. The different anion forms were easily re-exchanged to that of the carbonate form by bubbling CO_2 gas through the suspensions containing the different anion forms.

The DTA curves of samples listed in Table 1 are reported in Fig. 3. The lower temperature endothermic peak for hydroxy hydrotalcite (this name is rightly suggested by Bish [7]) due to the loss of water molecules from the interlayer [6] is shifted to higher temperature for CO_3^{2-}, SO_4^{2-} and Cl^-

TABLE 1

The a and c' parameters for variously anion-exchanged forms of Mg,Al hydroxides with $x=0.30$

	Anion				
	OH^-	CO_3^{2-} *	NO_3^-	Cl^-	SO_4^{2-}
a	3.046	3.046	3.047	3.052	3.046
c'	7.62	7.67	8.36	7.79	8.05

* Ref. 6.

forms, while a broad peak appears at 156°C for the nitrate form. The splitting for the hydroxy form might be due to the mentioned partial carbonation of this sample, while the one for the nitrate form probably indicates a different arrangement of water molecules in this sample. On the other hand, the peak shifted at higher temperature for bivalent anion-treated samples indicates a higher thermal stability due to a higher electrostatic attraction between basic layer and interlayer. The evolution of H_2O from structural hydroxyl groups occurs at higher temperatures with one peak for hydroxide and sulphate forms; in fact, for the sulphate form, SO_3 evolves at
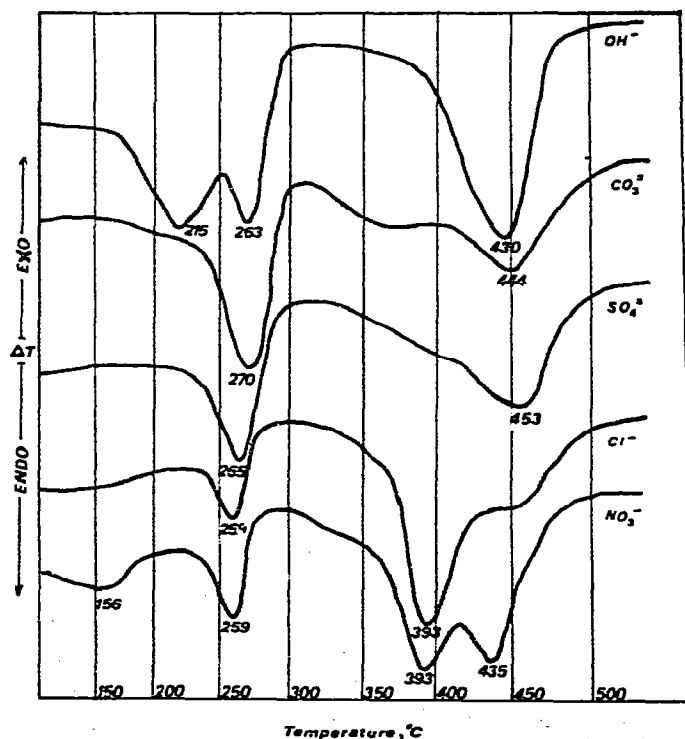

Fig. 3. DTA curves of the samples listed in Table 1.

temperatures higher than 950°C, as determined by TG. In the case of the carbonate form, the decarbonation and dehydroxylation occur in the order between 300 and 500°C.

The evolution of chloride as HCl or as Cl_2 from the chloride form seems to coincide with that of N_2O_5 from the nitrate at 390°C before the dehydroxylation.

The weight loss associated with the interlayer water molecules for various anion forms decrease according to the order $OH^- > SO_4^{2-} \simeq CO_3^{2-} > Cl^- \simeq NO_3^-$. Quantitative data for anion exchange and for GEA are not available because of the presence of free $Mg(OH)_2$ in all the samples and their partial carbonation. It may be hypothesized, from the above sequence, that the anion exchange with the interlayer content takes place according to the following substitutions: $2OH^- + H_2O$ for CO_3^{2-}, recently verified [6], $OH^- + 2H_2O$ for NO_3^- and $OH^- + nH_2O$ for Cl^-, that involves even anions having planar structures geometrically similar (e.g. nitrate and carbonate), if exchanged in different amounts, may substantially affect the interlayer arrangement. To this end, it is interesting to point out the change of basal spacing for the nitrate forms having different amounts of nitrate. The low form with low nitrate amounts shows no significant change of basal spacing with respect to untreated Mg,Al hydroxides, while the full nitrate-exchanged form, obtained by keeping the hydroxy form in saturated concentrated HNO_3 solution, showed a basal spacing of 8.60 Å. This involves an additional sheet of oxygen atoms for the interlayer composition.

CONCLUSIONS

The interlayer OH^- ions of Mg,Al hydroxides can be easily exchanged with different anions: cation exchange in the basic layer is also sometimes observed when ingoing and outgoing cations have similar size and equal charge.

The interlayer arrangement of the Mg,Al hydroxides variously anion exchanged depends not only on the size and geometry but also on the amount and the charge of the exchangeable anion.

The thermal stability of the variously anion-exchanged forms increases by increasing the charge of the anion.

REFERENCES

1 G. Mascolo and O. Marino, Mineral. Mag., 43 (1980) 619.
2 R. Allmann, Chimia, 24 (1970) 99.
3 G.W. Brindley and S. Kikkawa, Am. Mineral., 64 (1979) 836.
4 G.W. Brindley, Mineral. Mag., 43 (1980) 1047.

5 S. Koritnig and P. Süsse, Tschermaks Mineral. Petrogr. Mitt., 22 (1975) 79.
6 G. Mascolo and O. Marino, Thermochim. Acta, 35 (1980) 93.
7 D.L. Bish, Bull. Mineral., 103 (1980) 170.
8 G.W. Brindley, personal communication, 1980.
9 G. Mascolo and O. Marino. 7th Int. Cong. Chem. Cement. Paris, Vol. 2, 1980, Theme III, p. 58.