

A new synthesis and characterization of magnesium–aluminium hydroxides¹

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SUMMARY. A new synthesis of Mg–Al double hydroxides is described, that gives products relatively low (0.8–1.0%) in CO₂. The general formula [Mg_{1-x}Al_x(OH)₂][(OH)_x(H₂O)_{0.81-x}] with 0.23 ≤ x ≤ 0.33 is proposed. Cell parameters and thermal data are given. The *c*-axial length decreases with Al-content; this is attributed to increased electrostatic attraction between layers.

NUMEROUS studies of synthetic phases similar to natural hydrotalcite or manasseite have been reported; these compounds are composed of positively charged brucite-like layers of formula [Mg_{1-x}Al_x(OH)₂] and interlayers consisting of anions and water molecules; according to Allmann (1971), 0.20 ≤ x ≤ 0.33. All previous experiments show the difficulty of synthesizing a pure mixed hydroxide with no additional anions.

Feitknecht and Gerber (1942) were the first to prepare Mg–Al double hydroxide by titrating a solution containing MgCl₂ and AlCl₃ with NaOH, but the Cl content of the sample so prepared was considerable. The mixed Mg–Al hydroxide has been indexed on the basis of a rhombohedral lattice having *a* = 3.10 and *c* = 23.8 Å. Roy *et al.* (1953), on investigating the phase equilibria of the system MgO–Al₂O₃–H₂O, found no mixed hydroxide. Only after adding CO₂ or N₂O₅ were hydrotalcite-like phases obtained. Mortland and Gastuche (1962), using the Feitknecht method, prepared Mg–Al double hydroxides of variable composition with a molar ratio 0.7 < Mg/(Mg + Al) < 0.8. To remove the absorbed ions the suspensions containing the precipitates were dialysed for 30 days at 60 °C against distilled water. During the dialysis the samples were transformed to Mg–Al carbonate hydroxides, as showed by Ross and Kodama (1967). In further investigations Gastuche *et al.* (1967) prepared carbonate-hydroxides with Mg/Al ratios 2:1 and 5:1. The lattice constants are = 3.048 and *c*' = 7.60–7.90 Å. Meixnerite, a natural Mg₆Al₂(OH)₁₈·4H₂O, is a nearly CO₂-free

mineral (<2%) that avidly takes up CO₂ during grinding, Koritnig and Susse (1975). This paper proposes a new synthesis of nearly CO₂-free Mg–Al double hydroxides together with their characterization.

Experimental. Alumina gel of Merck and MgO from decomposition at 650 °C for 6 hours of magnesium basic carbonate of C. Erba, both R.C. grade, were employed. Ranging the Mg/(Mg + Al) molar ratio, marked X_{Mg}, from 0 to 1, different suspensions were prepared by utilizing distilled and boiled water. The suspensions were kept in sealed teflon containers and rotated for a week at 80 ± 1 °C in air thermostated oven. After filtration under CO₂-free conditions the products were dried over silica-gel. A part of the samples was chemically analysed: MgO and Al₂O₃ were determined by atomic absorption methods (Perkin-Elmer 300 s apparatus) by dissolving the solid in dilute nitric acid; the H₂O content was determined by thermogravimetric analysis (TG) on 50 mg sample at a heating rate of 6 °C/min, using a Stanton Massflow apparatus; a calimeter was used for the CO₂ determination. A Du Pont thermal analyser was used for differential thermal analysis (DTA) with the following conditions: Pt/Rh thermocouples, heating rate 10 °C/min, samples of 20 mg in Pt crucibles, reference sample Al₂O₃ and sensitivity of 0.02 mV/in.

X-ray powder patterns were obtained using a Guinier de Wolff camera with Cu radiation. Pb(NO₃)₂ was used as a reference material and the films were measured using a Kipp and Zonen microdensitometer. Accurate *d*-spacings of selected reflections from specimens were measured by scanning 1/8° (2θ) per minute with a Philips diffractometer using Pb(NO₃)₂ as a spacing standard.

Results and discussion. The chemical analyses of the contact liquid phases of the reaction products, obtained after filtration, showed a negligible magnesium and aluminium content, therefore the Mg:Al ratios of the products equal those of the starting materials. Fig. 1 summarizes the crystalline phases formed from the range of initial compositions. Slow diffractometric scanning showed that no asymmetry of *d* spacings was observed for the double hydroxide (*D.H.*), hence no mixtures of *D.H.* with different composition were formed. The

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TABLE I. X-ray powder data for synthetic Mg-Al double hydroxides spacing in Å

$X_{Mg} = 0.09$	$X_{Mg} = 0.69$	$X_{Mg} = 0.71$	$X_{Mg} = 0.73$	$X_{Mg} = 0.95$	<i>hkil</i>	<i>I/I₀</i>
7.55	7.60	7.64	7.70	7.80	0003	100
3.77	3.80	3.82	3.85	3.89	0006	40
2.608	2.612	2.614	2.617	—	10 $\bar{1}$ 1	5
2.562	2.568	2.572	2.573	2.580	01 $\bar{1}$ 2	.20
2.516	2.533	2.547	—	—	0009	6
2.274	2.281	2.288	2.293 (b)	2.302 (b)	01 $\bar{1}$ 5	20
1.928	1.936	1.941	1.947 (b)	1.957 (b)	01 $\bar{1}$ 8	25
1.701 (b)	1.723 (b)	1.731 (b)	1.738 (vb)	1.750 (vb)	1, 0, $\bar{1}$, 10	8
1.6219 (b)	1.6380 (b)	1.6345 (vb)	1.6400 (vb)	1.6530 (vb)	0, 1, $\bar{1}$, 11	9
1.5188	1.5215	1.5228	1.5240	1.5268	11 $\bar{2}$ 0	14
1.4885	1.4916	1.4932	1.4955	1.4980	11 $\bar{2}$ 3	13
1.4528	1.4590 (b)	1.4650 (vb)	1.4735 (vb)	1.4850 (vb)	1, 0, $\bar{1}$, 13	7
1.4092	1.4120	1.4142	1.4166	1.4204	11 $\bar{2}$ 6	8

The *d* spacing were measured on samples dried on silica-gel.
(b) = broad; (vb) = very broad.

observed reflections and related indexing of powder patterns of pure *D.H.* and their end members are reported in Table I. The data in fig. 1 show that *c* varies linearly with X_{Mg} and that the composition range of the *D.H.* is given by $0.67 \leq X_{Mg} \leq 0.77$. The cell parameters were found to be a 3.038, c 22.6 Å for the Al-rich, and a 3.054, c 23.4 Å for the Mg-rich end-member; these values were determined using samples with $X_{Mg} = 0.09$ and 0.95 respectively.

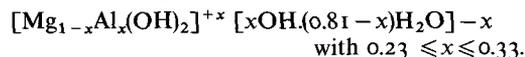
Allmann (pers. comm.) suggests that $X_{Mg} = 0.67$ is only possible if Mg and Al are ordered and that the disordered pure phases have somewhat less Al. This theorem is supported by the present results; X_{Mg} does not fall below 0.67, and at higher values of X_{Mg} the X-ray reflections are broadened (Table I). Allmann (1968, 1970) found similar results

for most of the natural minerals. The chemical analyses of pure *D.H.* phases are reported in Table II. The low amounts of CO₂ shows the existence of nearly CO₂-free *D.H.* phases having mainly OH anions in the interlayer sheet.

TABLE II. Chemical analyses of Mg-Al double hydroxides dried on silica-gel (% by weight)

X_{Mg}	MgO	Al ₂ O ₃	H ₂ O	CO ₂
0.69	37.53	21.12	39.71	1.0
0.71	39.00	19.79	40.03	0.9
0.73	40.03	18.49	40.32	0.8

Considering the small amount of CO₂ as equivalent to 2H₂O, from data in Table II, the oxygen contents of the interlayer sheet have been calculated for three samples. The values were identical at 0.81 per metal cation, and the following general formula is proposed:



This constancy in the oxygen content of the interlayer sheet can be reconciled with the variation in layer thickness if, following Brown and Gastuche (1967), it is assumed that the electrostatic attraction between the brucite-like layers and the interlayers increases with Al-content. Allmann (1971) found that on increase of *x* from 0.20 to 0.33 the O-H . . . O distances decreased from 2.9 to 2.8 Å in many double-layer minerals if triply charged ions are introduced into brucite-like layers. The OH⁻

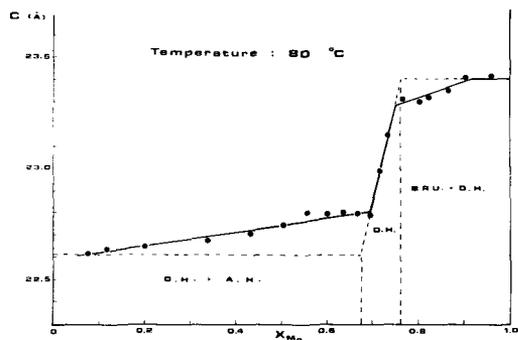
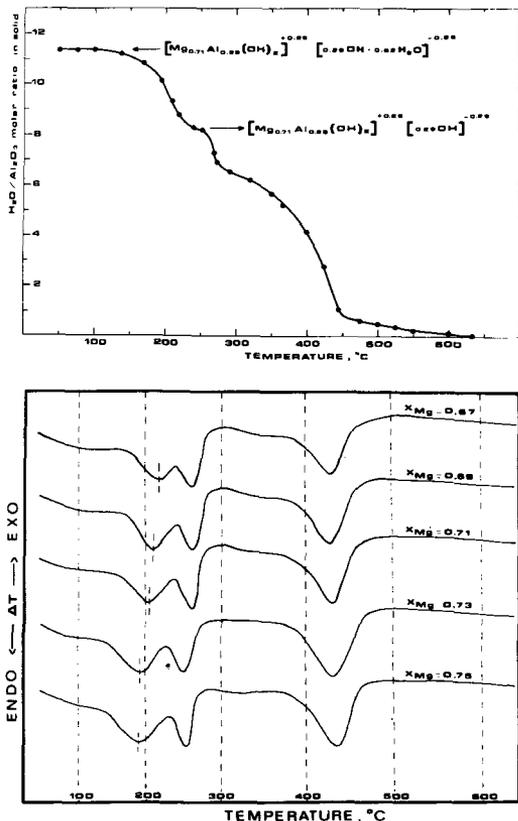


FIG. 1. *c* parameter of unit cell for Mg-Al double hydroxides and crystalline phases formed as a function of the initial composition X_{Mg} ; ($X_{Mg} = Mg/(Mg + Al)$). *D.H.* = double hydroxide, *A.H.* = aluminium hydroxide, *BRU* = brucite.



FIGS. 2 and 3. FIG. 2 (above). TG curve of a sample with $X_{Mg} = 0.71$. FIG. 3 (below). DTA curves.

groups on average have to compensate a charge of $(1+x/2)$, which is made possible by decreasing the OH bond strength to $(1-x/2)$ as a result of hydrogen bonding. The percentage decrease in the above O-H . . . O distances is 3.4%; this value agrees perfectly with the percentage variation in the

c value of the unit cell for the corresponding values of x found in the present work. On the other hand the small differences in the a -axial lengths for the end-member ($a = 3.038$ to 3.054 Å) make it impossible to accommodate different numbers of oxygen atoms in the interlayer sheet.

The TG curve of a sample with $X_{Mg} = 0.71$ (fig. 2) shows a step at about 250 °C; the weight loss below this temperature corresponds to the content of molecular water. In the DTA curves (fig. 3), the peaks below 300 °C move to lower temperatures as X_{Mg} increases. This is attributed to progressively weaker bonding of the water molecules as the Al-content is reduced.

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