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Formation of Mg–Al layered double hydroxides intercalated with nitrilotriacetate anions

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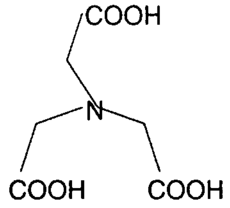
The formation, by coprecipitation, of a Mg–Al layered double hydroxide (LDH) intercalate containing nitrilotriacetate (NTA) anions has been observed. The intercalated LDH has a basal spacing close to 12 Å (gallery height 7.2 Å). The rehydration of a Mg-Al mixed oxide (formed by calcination at 500 °C of a Mg–Al carbonate-containing LDH) in the presence of NTA also results in the formation of a NTA intercalated LDH, indicating the ability of the mixed oxide for adsorptive removal of NTA. It was further shown that nitrate-containing LDHs may be ion-exchanged by NTA, whereas for carbonate-containing materials exchange is difficult. In some cases the formation of the intercalate is accompanied by considerable sequestration of the magnesium and aluminium cations. It is proposed that NTA may exist in the interlayer of the LDH as a trivalent or a divalent anion or under certain circumstances as a $[Mg–NTA]^-$ complex.

Introduction

Layered double hydroxides (LDHs) are host–guest materials that are of interest because of their potential application as catalysts, sorbents, hosts for nanoscale reactions as well as in medicine as antacids.[1–3] In general, LDHs may be represented by the general formula $[M^{2+}{}_{1-x}\ M^{3+}{}_x(OH)_2][x/n\ A^{n-}]\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, x is equal to the ratio $M^{3+}/(M^{2+} + M^{3+})$ and A^{n-} is an exchangeable anion of charge n. Possible M^{2+} and M^{3+} species include Mg^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} or Zn^{2+} and Al^{3+}, Cr^{3+}, Ga^{3+} or Fe^{3+}, respectively. The combination of Mg^{2+} and Al^{3+} is one of the most frequent studied and with carbonate as the balancing anion is found in nature as the mineral hydrotalcite.[4–7]

A particular class of intercalate formed with LDHs is one in which the interlayer anion is organic. The properties, characterisation and application of such organo-LDHs have recently been reviewed.[3] Three main methods for preparing organo-LDHs have been reported. The first is by conventional anion exchange.[8,9] The second is based on the fact that M^{2+}–M^{3+} mixed oxides, obtained by calcination of a LDH in the range of temperatures 450–800 °C, adsorb anions from water during reconstruction of the LDH structure (the so-called memory effect).[10–12] Thirdly, organic anions may be incorporated directly by coprecipitation.[1,9] In the context of organo-LDHs the presence of organic contaminants in natural waters is of current concern and in this respect the adsorptive removal of organic anions by LDHs or their calcined products has been studied for phenols,[14,15] aromatic sulfonates[16] and carboxylates.[17]

Nitrilotriacetic acid (NTA) **1** is widely used industrially and as a result becomes released into the environment. Although it has been regarded as a detergent builder, its possible link to birth defects has resulted in its use being banned in the USA.[18] It is also known to be a carcinogen.[19] In addition, when NTA is released into the environment (*e.g.* water streams) it is able to chelate heavy metals rendering them mobile.[20] Previously, the adsorptive removal of NTA has been studied using either gibbsite[21] or titanium oxide[22] as the sorbent. For these materials adsorption of NTA occurs essentially on the surface of particles. LDH sorbents, however, have the potential to adsorb anions into the bulk of the solid *via* intercalation or anion exchange.



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The aim of the present paper is to study the formation of NTA intercalated Mg–Al LDHs. A comparison is made between coprecipitation, exchange and reconstruction as methods of synthesis and the effect of the strong chelating ability of NTA is discussed. The possible usefulness of LDHs and their calcined products for removal of NTA from water is considered.

Experimental

Starting materials

The trisodium salt of nitrilotriacetic acid (Na_3NTA) was purchased (Aldrich) and used without purification. The free acid form of NTA (H_3NTA) was obtained as a precipitate by the addition of nitric acid to a solution of Na_3NTA.

Carbonate- and nitrate-containing LDHs with Mg and Al as the octahedral cations (designated Mg–Al–CO_3 and Mg-Al-NO_3, respectively) with Mg : Al ratios close to 2 and 4 : 1 were prepared using established methods.[23] 240 ml of a mixed metal nitrate solution, containing 0.12 mol of total metal and with Mg : Al ratio of 2 or 4 : 1, was added dropwise to 340 ml of aqueous solution containing $NaNO_3$ or Na_2CO_3. Four equivalents of anion for each Al^{3+} were used. The initial pH of the solutions was adjusted to 10 by the addition of HNO_3 or NaOH solution as appropriate and maintained at 10 by the simultaneous addition of 1 M NaOH(aq). The reaction mixtures were aged at 65 °C for 18 h.

For the rehydration studies, a Mg–Al mixed oxide was prepared by calcination of the ratio 2 and 4 : 1 Mg-Al-CO_3 LDH at 500 °C in air for 4 h.

Synthesis of NTA-containing LDHs

Coprecipitation. The constant pH method was used (at pH 7 or 10), with a procedure similar to that previously reported.[13] 120 ml of a mixed Mg–Al nitrate solution containing 0.06 mol of total metal and with a Mg : Al ratio of 2 or 4 : 1 was added dropwise to 340 ml of the NTA solution containing sufficient NTA to provide upon mixing a NTA : Al molar ratio of 3.33 : 1. The NTA solution was prepared by dissolving a mixture of Na_3NTA and H_3NTA, the relative amounts of each being varied in order to adjust the pH of the solution to 7 or 10. The pH was then maintained during the reaction at either 7 or 10 by the addition of 1 M NaOH(aq). The reaction mixture was aged at 65 °C for 18 h. Coprecipitation was carried out under a nitrogen atmosphere. The resulting slurry was filtered, washed with deionised water, and dried in air at room temperature. A comparative coprecipitation of a terephthalate-containing Mg–Al LDH was also performed at pH 10 and Mg : Al = 2 : 1 in order to investigate how the yield of LDH varied with the identity of the anion.[13]

Rehydration. A starting NTA solution was prepared from H_3NTA and Na_3NTA with a pH value of 6.1. Sufficient mixed oxide (prepared by calcination at 500 °C for 4 h of the carbonate LDHs described above) to provide 2 mmol Al was added to a 100 ml aqueous solution containing either 6.67 or 1 mmol of NTA (giving a NTA : Al molar ratio of 3.3 or 0.5 : 1 respectively). The resulting slurry was placed in a tightly capped flask (in air) and shaken at room temperature for 4 h. The slurry was then filtered and washed with deionised water and air-dried. Samples are designated as 2RH06L, 2RH06H, 4RH06L and 4RH06H: the first figure indicates the Mg : Al ratio of the mixed oxide and the letter L or H the ratio of NTA : Al in the mixture, *i.e.* L for 0.5 and H for 3.3 : 1. The value 06 approximates to the pH of the starting solution.

Rehydration was also performed with a solution containing only H_3NTA. To 100 ml water, 5 or 2.5 mmol of H_3NTA were added. Only partial dissolution occurred. To this slurry was then added sufficient of the mixed oxide to provide approximately 20 mmol Mg (and an NTA : Al ratio of 0.5 : 1). The mixture was stirred and reaction carried out in tightly sealed flasks under nitrogen. Stirring was continued for 6 h at 65 °C. The slurry was then quickly filtered and dried under vacuum for 16 h at room temperature (to give 2RHX or 4RHX for Mg/Al = 2 and 4 : 1, respectively). Portions of these suspensions were also hydrothermally treated at *ca.* 200 °C and 1.5 MPa for 2 h using a pressure-controlled microwave oven (2RHXM and 4RHXM). The products were filtered off and dried under vacuum at room temperature for 16 h.

Anion exchange. The possible exchange of nitrate and carbonate by NTA was studied using the LDH–CO_3 and LDH-NO_3 samples (Mg : Al approximately 2 and 4 : 1). Sufficient LDH to provide approximately 2 mmol of Al was added to a 100 ml aqueous solution containing 6.67 or 1 mmol of NTA [molar ratio NTA : Al of 3.3 (H) or 0.5 : 1 (L), respectively]. The pH of the solutions was adjusted to 6.1 or 11.4 in a way similar to that described for coprecipitation. Other procedures were the same as for the rehydration experiments. EN and EC indicate exchange of nitrate and carbonate LDHs respectively.

Reverse anion exchange. Selected samples of NTA–LDH containing about 0.5 mmol Al were individually dispersed in a solution containing 0.5 mmol Na_2CO_3 or 2.5 mmol $NaNO_3$. The solutions were placed in a tightly capped flask, shaken at room temperature for 4 h and then filtered.

Sample characterisation

Chemical analysis of C, H and N was carried out using an Exeter Analytical CE-400 Elemental Analyser. Al and Mg were analysed by atomic absorption spectrometry using a Varian Spectra AA-40 spectrophotometer. Weight loss on ignition at 1000 °C was also used to provide information concerning chemical composition. Powder X-ray diffraction (PXRD) data were obtained using a Phillips PW1710 diffractometer with Cu-Kα radiation with a nickel filter for Kβ attenuation. A step scan of 0.04° 2θ at a rate of 0.04° s^{-1} was used. Fourier transform infrared (FTIR) spectra were recorded with a Perkin-Elmer Paragon 1000 spectrometer using the KBr pellet technique. Thermogravimetric analysis (TGA) was carried out using a Polymer Laboratories TGA 1500 instrument. Data were recorded from room temperature to 1000 °C in air with a temperature ramp rate of 20 °C min^{-1}.

Results and discussion

(a) Coprecipitation (CP)

Mixing of the solutions at pH 7 did not result in any precipitation. The absence of a precipitate is unusual given that, even though this pH might not be appropriate for the formation of a pure LDH, other aluminium (oxy)hydroxide phases might be expected to precipitate.[24] We also note that it has been reported that a Mg–Al LDH containing terephthalate anion has been obtained by coprecipitation at pH 6.5.[25] The absence of a precipitate in this instance, however, appears a characteristic of NTA in that it has the capacity strongly to chelate Mg and Al. Precipitation did occur, however, at pH 10. The resulting samples are designated 2CP10 and 4CP10, with 2 and 4 referring to the Mg : Al ratio in the starting solution.

PXRD. The PXRD patterns observed for 2CP10 and 4CP10 (Fig. 1) indicate that NTA-intercalated LDHs, with a basal spacing of approximately 12 Å, are present in both products. The patterns reveal, however, that in the case of 2CP10 some AlOOH (boehmite)[26] is also present. For 4CP10 a reflection at 8.2 Å is also observed. This may be assigned to the presence of an LDH phase with nitrate and/or carbonate as the charge-balancing anion.

Chemical composition. For both precipitates (Table 1) the Mg : Al ratio appears to be lower than within the starting solution. Carbon and nitrogen microanalysis suggests that NTA is present in the product. The presence of impurity carbonate (broad band close to 1360 cm^{-1}) in both samples

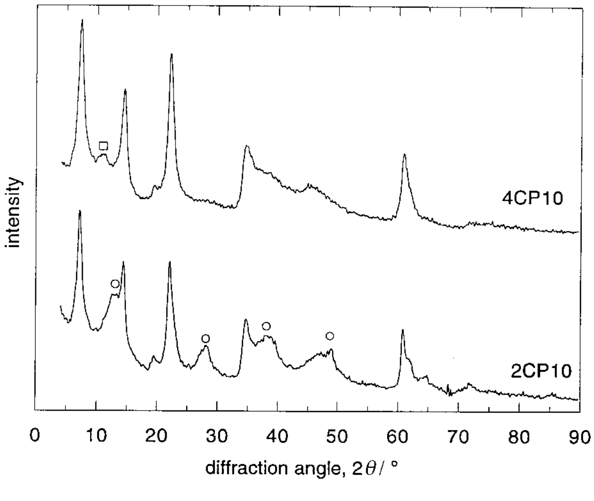

Fig. 1 Powder XRD patterns for the coprecipitation products resulting from precipitation at pH 10 for Mg : Al = 2 and 4 : 1 (2CP10 and 4CP10). NTA-intercalated LDHs with basal spacing ≈12 Å were formed. ○ indicates the peaks due to AlOOH, boehmite, and □ indicates those for that of LDH–NO_3/CO_3.

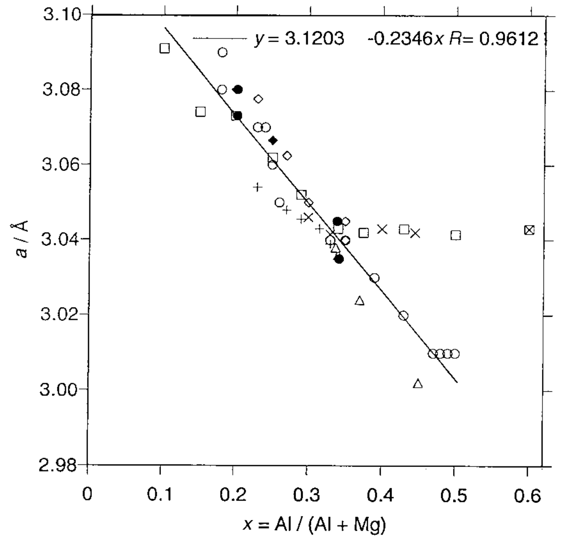

Fig. 2 The relationship between lattice parameter *a* and composition of the Mg, Al hydroxide layer: (□) from ref. 27, (◇) from ref. 28, (+) from ref. 29, (×) synthesized, (◆) natural hydrotalcite from Snarum, Norway in ref. 30; these are also reviewed in ref. 2; (○) from ref. 13, (△) from ref. 25 and (●) are the starting materials (NO_3 and CO_3) of the present work.

and nitrate (sharp absorption at 1380 cm^{-1}) in 4CP10 was also indicated by FTIR (data not shown).

PXRD patterns for LDHs are usually indexed on the basis of a hexagonal unit cell. It is, furthermore, well known that there is strong correlation between the *a* parameter of the unit cell (as measured from the position of the 110 reflection and the relation $a = 2d_{110}$, where d_{110} is the *d* spacing of the 110 reflection) and the Mg : Al ratio within the LDH sheets, with the *a* parameter increasing with increasing Mg : Al ratio.[2,13,27–30] Fig. 2 indicates the relationship between the *a* parameter and the Mg : Al ratio. As shown in Table 1, for 2CP10 the difference in Mg : Al between the total precipitated product and the LDH component within the precipitate is large (2.1 : 1 within LDH compared with 0.93 : 1 within the precipitate). This difference arises as a result of the presence of the boehmite phase. For 4CP10 the difference is smaller (2.26 : 1 within the precipitate and 2.0 : 1 in the LDH, in agreement with the PXRD pattern for 4CP10 which shows little evidence for separate Mg or Al (oxy)hydroxide phases.

On the assumption that all the NTA exists within the LDH (there being no PXRD evidence for other phases which might contain NTA) the ratio of NTA : Al in the LDH phase may be calculated from the chemical analysis data. For both samples the ratio is close to 0.3 : 1, suggesting that NTA is present as the trivalent anion within the interlayer. Proposed chemical formulae, based on the chemical analysis data, FTIR and PXRD, for 2CP10 and 4CP10 are shown in Table 1.

Material balances. Material balances for 2CP10 and 4CP10 are shown in Table 1. At pH 7 all the magnesium and aluminium cations remain in solution and a precipitate is not formed. Even at pH 10 a large proportion of the Mg and Al cations (and approximately twice as much Mg than Al) remains in solution and is not precipitated. A comparative preparation of a terephthalate LDH at pH 10 resulted in product with greater than 90% yield based on Mg and Al. In the preparation of carbonate and nitrate containing LDHs, the yield based on available Mg and Al cations within the solution also exceeded 90%. Thus the significant loss of cations in terms of precipitate yield appears to be a characteristic of the NTA system.

Kukkadapu *et al.*[25] have reported the formation of bayerite as a second phase in the coprecipitation of a MgAl–terephthalate LDH. The precipitation was performed from a solution with a Mg : Al ratio of 2 : 1 at pH 6.5. The Mg : Al ratio in the total precipitation product was equal to 1.1 : 1, with the precipitate consisting of a mixture of an LDH along with an excess of aluminium in the form of bayerite. Traversa *et al.*[31] have reported coprecipitation of an oxalate LDH at pH ≈9.5 from a solution with Mg : Al ratio <1 : 1, which resulted in the formation of a mixture of an LDH and gibbsite. We suggest that in the case of NTA the cause for the 2CP10 precipitate being Al-rich is the chelating capacity of NTA, which while interfering with the precipitation of both metals interferes more with Mg than Al. In the case of Kukkadapu *et al.* the formation of a separate aluminium phase appears to be the result of differences in the solubility of the Mg and Al cations at pH 6.5. It is known, however, that NTA will chelate Al stronger than Mg (log *K* for Mg–NTA = 5.5 and for Al-NTA = 11.4, *K* [M–NTA]/[M][NTA]).[32] Thus the effect which we observe in our case reflects the fact that the solubility will be determined jointly by the pH and the amount of NTA present in the solution.

The chemical analysis data presented in Table 1 also suggest

Table 1 Chemical analysis for total precipitate along with data from PXRD for the LDH phase. Also shown are proposed formulae of the precipitates and the reaction yields

	2CP10		4CP10	
Chemical analysis	Analysed (wt%)	Calculated (wt%)[a]	Analysed (wt%)	Calculated (wt%)
Mg	13.92	13.85	18.41	18.29
Al	16.70	16.76	9.04	9.13
C	6.00	6.11	7.08	7.17
N	1.12	1.16	1.56	1.59
weight loss at 1000 °C	45.36	45.36	52.41	52.42
LDH phase a^b/Å		3.044		3.038
Mg : Al estimated		2.1		2.0
Basal spacing[c]/Å		12.3		12.0
Proposed chemical formula of product[d]	$[Mg_{0.67}Al_{0.33}(OH)_2](NTA^{3-})_{0.097}(CO_3{}^{2-})_{0.016}\cdot 0.84H_2O + 0.40AlOOH$		$[Mg_{0.69}Al_{0.31}(OH)_2](NTA^{3-})_{0.09}(CO_3{}^{2-})_{0.007}(NO_3{}^{-})_{0.015}\cdot 0.79H_2O$	
% Metal in precipitate				
Mg		36		44
Al		77		77
% NTA uptake in LDH		3.2		7.3

[a] Based on proposed chemical formulae of product. [b] Assuming hexagonal unit cells. [c] d_{001} value of assumed hexagonal unit cells. [d] The figures in front of the chemical formula of additional phases show the relative molar amount of the phase (LDH phase = 1).

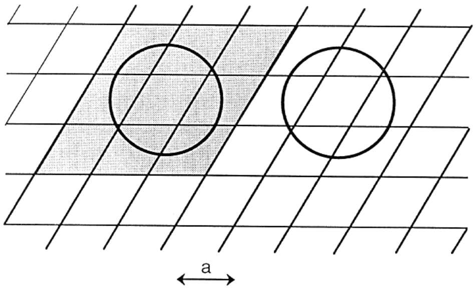

Fig. 3 Schematic of brucite-like layer and corresponding size of the NTA anion.

that only a small fraction of the actual NTA available in the solution is precipitated (3 and 7%). This is to be expected since there is a large excess of NTA over Al^{3+} present in the solution (only 0.33 mol of NTA^{3-} is required for each Al^{3+} in the layer compared with the 3.33 mol available in the solution). Such an excess of anion is frequently used to avoid competitive uptake of nitrate and/or carbonate anions. Narita *et al.*[17], however, have reported the removal of aliphatic and aromatic carboxylate anions through coprecipitation of an LDH. They reported that when Al^{3+} is present in fourfold excess the precipitation process can be made nearly 100% efficient for the removal of the organic anion.

Orientation of NTA in the interlayer. The molecular size of NTA is estimated to be approximately 6 Å diameter and 4 Å thickness.[33] Fig. 3 illustrates schematically, within the basal plane, the size of the LDH unit cell. The intersections correspond to the positions of the metal ions. In a LDH with Mg : Al ratio of 2 : 1, the shaded area corresponds to a positive charge of three electron units, *i.e.* one NTA^{3-}. Represented within the figure as circles and to scale are NTA anions in a hypothetical 'flat' orientation, *i.e.* when all three carboxylic groups of the anion are fixed to the same hydroxide layer. At ratio 2 : 1, therefore, there is clearly sufficient space for the anions to adopt a 'flat' orientation. The observed basal spacing for the intercalate is approximately 12 Å and since the thickness of the brucite-like layer is 4.8 Å[4,5] we propose an orientation as in Fig. 4(a), *i.e.* a bilayer of planar NTA anions oriented parallel to the sheets. The possibility also exists of a 'bridging' orientation with one fixed to one layer and the other two carboxylic groups to the other, as shown in Fig. 4(b). At this moment we are not able to distinguish between these possibilities.

(b) Rehydration (RH)

Chemical analysis data for the products obtained by rehydration of the mixed oxide are shown in Table 2. Also given are theoretical values based on proposed compositions from analytical data along with information from PXRD, FTIR and thermal analysis. PXRD patterns (Fig. 5) indicate in general the formation of a phase with a similar basal spacing to that observed for the coprecipitation products, confirming the formation of a NTA-intercalated LDH. The pattern of 2RHXM in addition suggests the possible formation of boehmite (compare with 2CP10). Boehmite may also be present to a smaller extent in 2RHX although in this case it is less clear since the pattern is quite broad. For 2RH06L, 4RH06L, 4RHX and 4RHXM we do not find evidence for a separate Mg or Al (oxy)hydroxide phase and may regard these products as being composed of LDH phases.

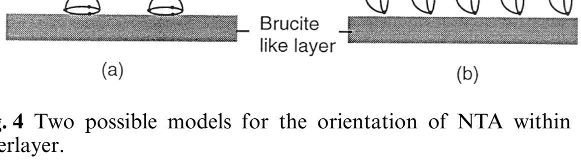

Fig. 4 Two possible models for the orientation of NTA within the interlayer.

For 2RH06H the PXRD pattern is similar to that of the starting Mg–Al mixed oxide phase and an LDH phase does not appear to have formed. This is consistent with the chemical analysis data which indicate a large loss of metal and little uptake of NTA. Among the rehydration experiments 2RH06H was the only case where the starting NTA : Al ratio employed was 3.3 : 1 (*i.e.* NTA was in excess). We conclude, therefore, that the presence of an excess of NTA results in dissolution of Mg and Al rather than formation of LDH. In the case of 4RH06L the resulting PXRD pattern is very similar to that of a carbonate LDH. This observation is consistent with the relatively small amount of NTA found in this sample.

For 2RHX, 2RHXM and 4RHXM the ratio of NTA : Al within the LDH exceeds 0.33 : 1, suggesting that NTA is intercalated either partially or entirely as the divalent anion. This is a reasonable conclusion at the final pH of approximately 8.5 conditions when the ease of the three steps of ionisation of NTA is considered (pK_{a1}, pK_{a2}, $pK_{a3} = 1.89$, 2.49, 9.37).[32] In addition, for 2RHX and 2RHXM the basal spacing of the NTA-intercalated phase is slightly larger (*ca.* 1 Å) than that obtained by coprecipitation. This is consistent with there being more anion within the gallery as a result of the decrease in anion charge from 3 to 2.

In the powder XRD pattern of 4RHX, though the reflections are broad, a phase of basal spacing ≈8.6 Å is observed in addition to the LDH-NTA phase at 11.8 Å. The 8.6 Å phase appears to be also formed in 4RHXM as suggested by a shoulder in the diffraction pattern. One possible explanation for this spacing is the formation of a monolayer of planar anions oriented parallel to the hydroxide sheets (Fig. 4); such an arrangement would give rise to a basal spacing of approximately 8.7 Å. Chemical analysis does not suggest that carbonate is present in these samples.

For 4RHX and 4RH06L we further note that the Mg : Al ratio within the LDH sheets is estimated to be lower than the ratio within the precipitate overall, although no additional Mg-containing phases are observed by PXRD. In the case of 4RH06L, the total charge carried by the interlayer anion, if present as trivalent anion, also exceeds the apparent charge on the LDH sheet (a trivalent anion is the most likely given the final pH of the reaction mixture) or even if completely divalent. One possibility is that NTA is intercalated as a $[Mg–NTA]^{-}$ chelate complex in both 4RHX and 4RH06L, and to a lesser extent in 4RHXM. The reason why $[Mg–NTA]^{-}$ would prefer to adopt a monolayer arrangement as opposed to a bilayer one is still not clear, although it is possible that the presence of the central metal changes some property and behaviour in a LDH interlayer.

Material balance. Using the rehydration method the loss of metals increases with decreasing pH or increasing NTA : Al ratio. The dissolution of metal in solution during rehydration is not likely to be unique to NTA, though it may be enhanced in this case because of the strong chelating capacity of NTA. Hermosín *et al.*[15] reported that 10% of metal was dissolved during the removal of trinitrophenol during reconstruction of a Mg–Al oxide derived from an LDH. In terms of the precipitated fraction of NTA which we observe, Sato and Okuwaki[11] reported that during rehydration benzenepolycarboxylate anions were adsorbed to nearly the full anion exchange capacity. Our results are comparable.

Use of a calcined LDH as a sorbent for NTA. The efficiency of adsorptive removal is higher at low pH values. It is not appropriate to compare the efficiency (in terms of removed NTA) reported here with values reported for other sorbents.

Table 2 Analytical data for rehydration products

	2RH06L		2RH06H		2RHX		2RHXM		4RH06L		4RHX		4RHXM	
Chemical analysis (wt%)	anal.	calc.	anal.[d]	calc.	anal.	calc.	anal.	calc.	anal.	calc.	anal.	calc.	anal.	calc.
Mg	17.86	17.94	16.32		13.75	13.72	15.78	15.79	23.28	23.20	23.16	23.01	23.19	23.02
Al	9.90	9.81	17.09		12.94	12.98	13.02	13.01	6.35	6.45	6.32	6.49	6.22	6.39
C	6.59	6.63	3.90		10.08	10.13	10.35	10.57	5.11	5.09	7.31	7.59	7.46	7.51
N	1.15	1.16	0.48		2.01	1.97	2.03	2.05	0.77	0.77	1.48	1.48	1.50	1.46
Weight loss at 1000 °C	51.68	51.71	40.65		52.73	52.72	49.23	49.23	49.40	49.34	49.66	49.58	49.79	49.75
LDH phase														
a^{a}/Å	3.044		LDH		(3.026)[e]		3.040		3.065		3.067		3.038	
Mg : Al estimated	1.9		not formed		(1.5)[e]		1.9		3.2		3.4		4.2	
Basal spacing[b]/Å	12.3				(12.7)[e]		13.3		8.02		(11.8, 8.6)[e]		11.8	
% Metal in precipitate														
Mg	86		15		66		67		77		96		98	
Al	93		28		100		100		76		71		71	
% NTA uptake in LDH	36		0.43		60		59		38		69		72	
Final pH	12.3		10.6		8.5		8.3		12.6		9.8		9.4	
Proposed chemical formulae[c]														
2RH06L	$[\mathrm{Mg_{0.67}Al_{0.33}(OH)_2}](\mathrm{NTA^{3-}})_{0.075}(\mathrm{CO_3^{2-}})_{0.051}\cdot 0.80\mathrm{H_2O}$													
2RHX	$[\mathrm{Mg_{0.61}Al_{0.39}(OH)_2}](\mathrm{NTA^{3-}})_{0.088}(\mathrm{HNTA^{2-}})_{0.064}\cdot 0.68\mathrm{H_2O}+0.13\mathrm{AlOOH}$													
2RHXM	$[\mathrm{Mg_{0.66}Al_{0.34}(OH)_2}](\mathrm{NTA^{3-}})_{0.041}(\mathrm{HNTA^{2-}})_{0.108}\cdot 0.29\mathrm{H_2O}+0.15\mathrm{AlOOH}$													
4RH06L	$[\mathrm{Mg_{0.79}Al_{0.21}(OH)_2}](\mathrm{Mg{-}NTA^{-}})_{0.048}(\mathrm{CO_3^{2-}})_{0.084}\cdot 0.76\mathrm{H_2O}$													
4RHX	$[\mathrm{Mg_{0.79}Al_{0.21}(OH)_2}](\mathrm{NTA^{3-}})_{0.055}(\mathrm{Mg{-}NTA^{-}})_{0.037}\cdot 0.57\mathrm{H_2O}$													
4RHXM	$[\mathrm{Mg_{0.80}Al_{0.20}(OH)_2}](\mathrm{NTA^{3-}})_{0.025}(\mathrm{HNTA^{2-}})_{0.063}\cdot 0.50\mathrm{H_2O}$													

[a–c]See Table 1. [d]NTA content of 2RH06H is 6.45 wt%. [e]Diffraction peaks were quite broad.

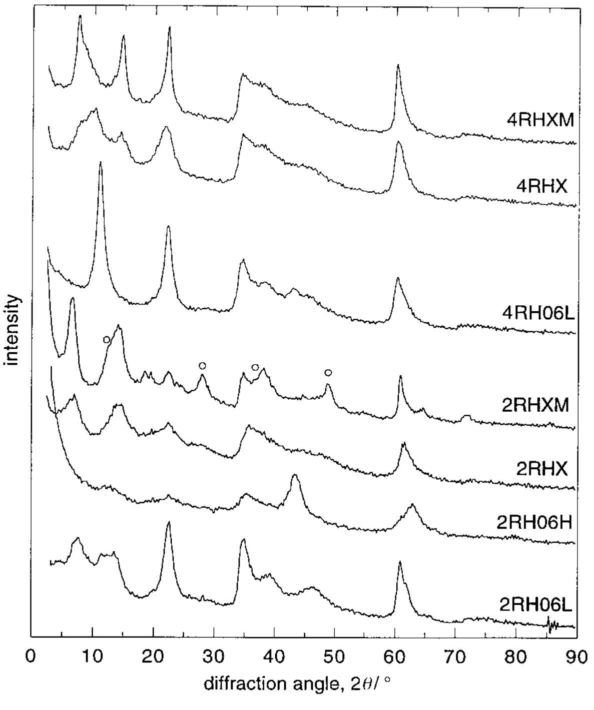

Fig. 5 Powder XRD patterns of the rehydration products obtained from ratio 2 and 4: samples. H and L refer to NTA/Al ratios of 3.33 and 0.5 : 1, respectively. X is for acidic solution with NTA/Al = 0.5 : 1 and M refers to hydrothermal treatment. NTA-intercalated LDHs are formed, except for 2RH06H and 4RH06L (see text). ○ indicates the peaks due to AlOOH, boehmite.

In the literature, for example, removal values greater than 90% have been reported from significantly more dilute ($<10^{-4}$ M) solutions with similar amounts of absorbent to those used here.[21,22] We may claim, however, that the saturated adsorption limit of this work, ≈2 mmol (g absorbent)$^{-1}$, is larger than the value of 85 μmol g^{-1} reported by Vohra and Davis[22] for TiO_2 from 10^{-3} M solutions of NTA.

(c) Anion exchange

Analytical data for the samples prepared by anion exchange are shown in Table 3 along with proposed chemical formulae. Powder XRD patterns of the products are shown in Fig. 6; those of 2EN06H and 2EC06H are omitted, with that for 2EN06H being similar to that for 2EN06L and 2EC06H similar to 2EC06L. Except for 4EN06L, the Mg : Al ratios for the total products were not very different to those for the starting materials. We conclude, therefore, during anion exchange, the Mg : Al ratio in the LDH sheets is preserved.

The anion exchange of 2EN06L and 2EN11L results in the formation of NTA-intercalated phases. 2EC06L and 4EN06L, however, were not significantly ion-exchanged by NTA, the patterns being similar to those of the original carbonate and nitrate phases. (The uptake of NTA in these cases was small.) We conclude that CO_3^{2-} is strongly fixed in the interlayer region. The preparation of alkyl sulfonate[8] and alkyl sulfate[9] intercalated LDH through anion exchange starting from NO_3[8] or Cl[9] LDHs has been previously reported and our results are consistent with these. The difficulty of anion exchange of LDH–CO_3 has been reported by several workers.[1,2,6,7] Ulibarri, Hermosín and co-workers[14,15] reported that a carbonate-containing LDH worked for the removal of trinitro- or trichloro-phenol only at low initial pH (<2).

The case of 4EN06L is more complicated. We suggest, however, that it is difficult to expand the interlayer region of 4EN by comparison with 2EN because the relatively smaller charge of the layers weakens the repulsion between them.

For the adsorptive removal of NTA, therefore, we conclude that among the samples examined only LDH–NO_3 with a comparatively low Mg : Al ratio, was satisfactory. An important feature of this method is that the adsorption of NTA can be achieved even when starting from high pH solutions, which is in contrast to the rehydration method.

(d) Reverse anion exchange

Powder XRD patterns for NTA intercalated LDHs treated with solutions containing either nitrate or carbonate anions are shown in Fig. 7. The patterns clearly demonstrate that the

Table 3 Analytical data for anion-exchange samples

	2EN06L		2EN06H	2EN11L		2EC06L	2EC06H	4EN06L
Chemical analysis (wt%)	anal.	calc.	analysed	anal.	calc.	analysed	analysed	analysed
Mg	16.64	16.61	n.m.[f]	18.15	18.30	n.m.[f]	n.m.[f]	n.m.[f]
Al	10.81	10.82	n.m.[f]	10.15	10.01	n.m.[f]	n.m.[f]	n.m.[f]
C	8.49	8.48	8.47	7.33	7.55	2.89	3.10	1.97
N	1.52	1.52	1.40	1.36	1.40	0.24	0.24	2.02
Weight loss at 1000 °C	51.97	52.01	52.86	50.72	50.74	44.45	45.52	46.27
NTA content (wt%)		20.4	18.8		18.3	3.22	3.22	4.12
LDH phase								
a^a/Å	3.038		3.040	3.040		3.047	3.044	3.082
Mg:Al estimated	1.9		1.9	1.9		2.2	2.1	5.1
Basal spacing[b]/Å	11.8		11.8	12.0		7.64	7.56	8.02
Precipitated Mg	84		56[e]	93		83[e]	68[e]	81[e]
fraction (%)[c] Al	94			90				
NTA	53		4.7	48		6.7	0.83	14
Final pH	9.0		9.1	11.5		9.8	8.8	10.8
Proposed chemical formula[d]								
2EN06L	$[Mg_{0.63}Al_{0.37}(OH)_2](NTA^{3-})_{0.068}(HNTA^{2-})_{0.032}(CO_3^{2-})_{0.051}\cdot 0.61H_2O$							
2EN11L	$[Mg_{0.67}Al_{0.33}(OH)_2](NTA^{3-})_{0.089}(CO_3^{2-})_{0.025}\cdot 0.64H_2O$							

[a,b,d]See Table 1. [c]Precipitated amount/content in total reaction mixture. [e]Precipitated fraction of the total metal. [f]Not measured.

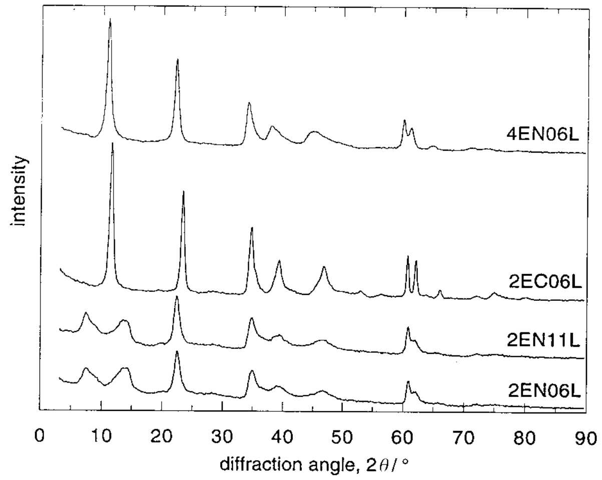

Fig. 6 Powder XRD patterns of some products of anion exchange. EN and EC are for exchange of nitrate and carbonate LDHs, respectively, at pH 6 or 11. L indicates a NTA:Al ratio 0.5:1. A NTA-intercalated phase was obtained only from LDH–NO_3 with Mg:Al ≈2:1.

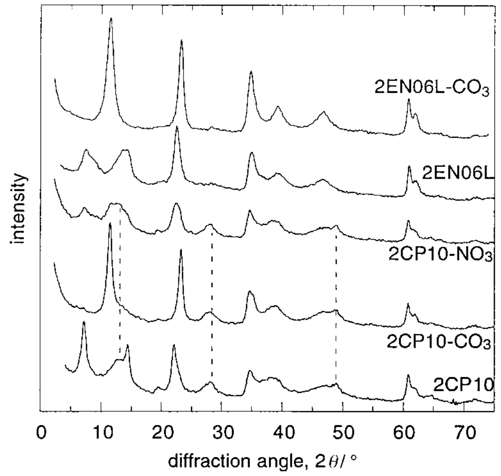

Fig. 7 Powder XRD patterns of two examples of NTA intercalated LDHs and their reverse anion-exchange products. See Fig. 1 and 6; CO_3 and NO_3 indicate the identity of the inorganic anion in the exchange solution. The dashed lines show peaks due to AlOOH, boehmite.

NTA anions are readily and completely exchanged by CO_3^{2-} (2CP10-CO_3, 2EN06L-CO_3) but not by NO_3^- (2CP10-NO_3).Certain reflections in the case of 2CP10 which remain after exchange by CO_3^{2-} are associated with boehmite. The results suggest that the removal of NTA will be difficult in the presence of carbonate anions.

Conclusion

NTA is intercalated into Mg–Al LDHs as either the trivalent or divalent anion and also possibly as [Mg–NTA]$^-$. NTA-intercalated LDHs may be prepared by direct coprecipitation when the pH of the solution is held at 10. Coprecipitation is, however, accompanied by considerable loss of metals, with more Mg than Al being retained in solution. Thus the Mg:Al ratio in the total product becomes lower than in the starting mixture and may result in the formation of boehmite as an additional phase. At pH 7 coprecipitation does not occur. The results reflect the chelating capacity of NTA. Rehydration of a Mg-Al mixed oxide (derived from a carbonate-containing LDH) in the presence of NTA also results in the formation of an NTA-intercalated phase. The mixed oxide may therefore be used as an absorbent for NTA. A LDH–NO_3 with Mg:Al ≈2:1 may be ion-exchanged by NTA and is suitable for the removal of NTA from aqueous solutions. For LDH–CO_3 and LDH–NO_3 with Mg:Al ≈4:1, however, ion exchange remains a difficult and more restrictive method for NTA removal. The results of reverse anion exchange (*i.e.* de-intercalation of NTA) confirm that the affinity of NTA anions to the LDH is stronger than of NO_3 but weaker than of CO_3.

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