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Anion substitution of nitrate-saturated layered double hydroxide of Mg and Al

G.P. Gillman [a,*], M.A. Noble [a], M.D. Raven [b]

[a] *CSIRO Land and Water, PMB Aitkenvale, Qld. 4814, Australia*
[b] *CSIRO Land and Water, Private Bag 2, Glen Osmond, SA 5064, Australia*

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Abstract

In the context of producing industrial-grade hydrotalcite-like (HT) materials containing phosphate and sulfate for use as slow-release fertilizers, the ease with which nitrate-HT can be converted to phosphate-HT and sulfate-HT has been examined. Graded amounts of di-ammonium hydrogen phosphate and ammonium sulfate were added to nitrate-HT, while maintaining pH at 9.5, to produce substitutions ranging from approximately 50% to 100%. Chemical and X-ray diffraction analysis of the products confirmed that the substitution could be easily effected by simple topotactic exchange.
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1. Introduction

The unique properties of a range of inorganic clay-like materials generally known as Layered Double Hydroxides (LDH) make them candidates for a number of industrial applications. Cavani et al. (1991) comprehensively reviewed the properties and application of LDH compounds referred to as Hydrotalcite-Type Anionic Clays based on the structure of Hydrotalcite, an hydroxycarbonate of Mg and Al that occurs naturally in specimen quantities in some areas and is represented by the formula:

$$[\mathrm{Mg}_{1-x}\mathrm{Al}_x(\mathrm{OH})_2]^{x+}\ \cdot(\mathrm{CO}_3)_{0.5x}.y\mathrm{H}_2\mathrm{O}.$$

Occupying the interlayer spacings between positively charged sheets of Mg/Al hydroxide, a great range of inorganic and organic anions can theoretically be introduced into this structure by simple anion exchange reactions, though it is recognized that chemical and physical properties result in an order of adsorption specificity such as CO_3, $PO_4 > NO_3$, Cl.

It is generally assumed that the above-mentioned anion exchange reaction proceeds topotactically, i.e. with the stacked sheet structure of the hydrotalcite-like clay (HT) remaining intact, as is the case when cations are exchanged on negatively charged smectitic clays, but Radha et al. (2005) have questioned this assumption. The latter authors propose that replacement of one anion for another involves the dissolution of the original HT and its subsequent re-precipitation containing the new anion, providing that the latter is present in solution in sufficiently high concentration, and that solution composition is not conducive to the formation of low-solubility salts of the new anion and Mg and/or Al. These authors conceded, however, that topotactic exchange can

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[*] Corresponding author.
E-mail address: Gavin.Gillman@csiro.au (G.P. Gillman).

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occur if the pH of the exchange reaction is higher than the pH of HT formation.

It has recently been proposed (Gillman and Noble, 2005) that technical grade HT can be used as slow-release fertilizer, thereby avoiding the financial and environmental consequences of applying soluble compounds to freely drained soils. The production of nitrate-saturated HT (NO_3-HT) could be integrated into ammonium nitrate manufacture, as shown schematically in Fig. 1a. It is further proposed (Fig. 1b) that HPO_4-HT and SO_4-HT would also be manufactured on site using simple anion exchange reactions. For the entire range of HT products, the only by-product is ammonium nitrate, the relevant chemical reactions being:

$$2Mg(NO_3)_2 + Al(NO_3)_3 + 6NH_4OH \rightarrow Mg_2Al(OH)_6.NO_3 + 6NH_4NO_3 \qquad \text{Eqtn.1}$$

$$Mg_2Al(OH)_6.NO_3 + 0.5(NH_4)_2HPO_4 \rightarrow Mg_2Al(OH)_6.0.5HPO_4 + NH_4NO_3 \qquad \text{Eqtn.2}$$

$$Mg_2Al(OH)_6.NO_3 + 0.5(NH_4)_2SO_4 \rightarrow Mg_2Al(OH)_6.0.5SO_4 + NH_4NO_3 \qquad \text{Eqtn.3}$$

To assess the feasibility of the NO_3-HT substitution reactions, especially under bulk production conditions, a number of laboratory studies have been conducted to ensure that NO_3-HT can be stoichiometrically converted to HPO_4-HT and SO_4-HT while keeping the HT structure intact. There was no attempt to exclude atmospheric CO_2 during the anion substitution experiments described below, to allow better simulation of large-scale manufacturing conditions.

2. Experimental

2.1. Preparation of NO_3-HT slurry for substitution experiments

For each of the substitution experiments described in Sections 2.2 to 2.5 below, a bulk NO_3-HT slurry was prepared by pumping 500 ml of a mixed nitrate solution (1.0 M in Mg, 0.5 M in Al) into 250 ml of vigorously stirred 70% ammonia solution over 3–4 min. The final pH of the resultant NO_3-HT slurry was about 9.5. The slurry was heated to 80 °C and kept at this temperature with moderate stirring for 8 h. The nitrate content, in other words the anion exchange capacity (AEC), of washed and dried NO_3-HT previously produced in this laboratory ranged from 335 to 355 cmol/kg.

2.2. Conversion of NO_3-HT to Cl-HT

The 750 ml of NO_3-HT slurry described in Section 2.1 was divided into 5 × 150 ml portions. By-product ammonium nitrate concentration of the slurry was reduced by centrifuging the suspensions, discarding the supernatant solution, re-suspending the ‘cake’ in 50 ml of water, centrifuging, discarding the supernatant solution, and finally re-suspending the cake in a further 50 ml of distilled water. With vigorous stirring, 15, 20, 25, 30, and 35 ml of 2 M ammonium chloride solution was added to the respective suspensions that were then allowed to stand for 3 days to allow a reasonable period for anion exchange. The slurries were centrifuged, the supernatant solution retained for chloride analysis, and the HT ‘cake’ subjected to ‘centrifuge washing’ whereby distilled water addition and centrifugation were repeated until a ‘point of dispersion’ was reached (clear supernatant solution could not be obtained). The cake was then dried at 80 °C and samples digested in A.R. nitric and hydrochloric acids for analysis of chloride and nitrate respectively.

2.3. Conversion of NO_3-HT to HPO_4-HT

Another 750 ml of NO_3-HT slurry produced as in Section 2.1 was divided into 5 × 150 ml portions to which were added with vigorous stirring 15, 20, 25, 30, and 35 ml of 1 M di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) solution respectively. Following overnight standing, the slurries were centrifuged, and the supernatant solutions were retained for phosphate analysis. The HT cake was then subjected to ‘centrifuge washing’ as described in Section 2.2, and after drying at 80 °C, a sample was digested in hydrochloric acid for nitrate and phosphate determination. Powdered samples of the final products were also subjected to X-ray diffraction (XRD) analysis.

2.4. Conversion of NO_3-HT to SO_4-HT

The same procedure was used as in Section 2.3, but using 1 M ammonium sulfate instead of 1 M di-ammonium hydrogen phosphate. The solution from the first centrifugation was analysed for sulfate, and the final washed and dried products were digested in hydrochloric acid for sulfate and nitrate determination as well as XRD analysis.

2.5. XRD analysis

The samples were ground in an agate mortar and pestle before being pressed into aluminium sample holders for X-ray diffraction analysis. XRD patterns were recorded with a Philips PW1800 microprocessor-controlled diffractometer using Co Kα radiation, variable divergence slit, and graphite monochromator. The diffraction patterns were recorded in steps of 0.05° 2-theta with a 2.0 s counting time per step, and logged to data files on an IBM-compatible PC for analysis.

3. Results and discussion

3.1. Chloride substitution of NO_3-HT

In view of previously encountered difficulty in being able to completely exchange nitrate with chloride, the

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