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Dissolution of nano-size Mg–Al–Cl hydrotalcite in aqueous media

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ABSTRACT

Aqueous dissolution of a synthetic chloride-containing Mg²⁺–Al³⁺ layered double hydroxide was studied at 298 K as a function of pH. Mild acidification (final pH 9–5) results in incongruent dissolution of Mg²⁺, exclusively. Formation of an amorphous Al(OH)₃ passive layer prevents further Mg²⁺ leaching, thus dissolved Mg²⁺ amounts for only 20% of the solid. At lower pH values, massive dissolution readily takes place in a congruent fashion. Congruent dissolution profiles are accounted for by a contracting volume kinetic law. The pH dependence of the observed rate constant shows that the kinetic order on proton concentration is 0.41, indicating that dissolution is surface controlled. The implications of these findings are discussed.

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1. Introduction

Among synthetic microporous solids, layered double hydroxides (LDHs), also known as anionic clays, are a focus of much attention in the field of materials science because of their multiple applications, such as, catalyst supports and catalyst precursors, anionic exchangers, sorption agents, intercalation and hybrid compounds, flame retardants, etc. (Rives, 2001). The general formula for these solids is typically expressed as [M(II)_{1-x}M(III)_x(OH)₂(A^{q-})_{x/a}·nH₂O], where the M(II) and M(III) are divalent and trivalent cations, ranging from Mg²⁺ and Al³⁺ to many transition metal cations (Bravo-Suarez et al., 2004). The main structure of the LDHs is composed of positively charged brucite-type sheets, where trivalent cations isomorphically replace a fraction *x* of the divalent cations in octahedral coordination. The interlamellar space is occupied by A^{q-} anions, which ensure the electroneutrality of the structure, and *n* water molecules (Evans and Slade, 2005). Since a purely electrostatic interaction holds the interlamellar anions, these solids easily undergo anion exchange reactions in aqueous media (Israeli et al., 2000; Jobbágy and Regazzoni, 2005; Miyata, 1983; Radha et al., 2007; Williams and O'Hare, 2005).

Undoubtedly, the most studied family of LDH compounds are synthetic forms derived from mineral hydrotalcites, Mg_{1-x}Al_x(OH)₂(CO₃)_{x/2}·nH₂O. Due to their inherent low toxicity and little cost, related chloride forms, Mg_{1-x}Al_x(OH)₂(Cl)_x·nH₂O, were tested as potential adsorbents for both medical (Ookubo et al., 1993) and environmental applications (Basciulla and Regazzoni, 2008; Goh et al., 2008; Prasanna and Kamath, 2008). Inspired on the rich intercalation

chemistry of LDHs (Ambroggi et al., 2003; Khan and O'Hare, 2002; Khan et al., 2001), recent studies view synthetic hydrotalcites as biocompatible-delivery matrixes for drug release (Choy et al., 2004; Costantino et al., 2008). In a different area of study, it has been recently shown that acid assisted decarbonation of highly crystalline hydrotalcites produces delaminated forms that exhibit outstanding properties as building blocks for self-assembled films or shells (Iyi et al., 2008; Li and Shi, 2008; Liu et al., 2006; Ma et al., 2006).

Despite of the variety of scopes and applications, all the aforementioned studies bear in common the exposure of hydrotalcite-like solids to aqueous solutions, in which dissolution can certainly take place. However, the subject has been unattended by the literature and the available evidence is scarce and qualitative (Kokot and Wojciechowska, 1993). The aim of the present study is to evaluate the chemical stability of synthetic chloride-containing hydrotalcite particles towards acid dissolution, and to assess the operating dissolution mechanisms.

2. Experimental

Mg_{0.73}Al_{0.27}(OH)₂Cl_{0.19}(CO₃)_{0.04}·H₂O, hereafter refers as HT(Cl), was synthesized by coprecipitation as described elsewhere (Jobbágy and Regazzoni, 2005); the so-prepared laminar crystalline powder (*a* = 0.305(1) nm and *c* = 2.358(6) nm) is composed of 100 ± 30 nm size hexagonal platelets (see Supplementary Information).

Dissolution experiments were performed by dispersing a weighted amount of HT(Cl) in a measured volume of an aqueous solution of a given HCl concentration, and letting the systems to evolve at 298.0 ± 0.1 K. Three sets of experiments were carried out. In the first set, the pH of the dispersions was allowed to drift freely for 72 h. Then, the solid was separated by filtration, and the supernatants stored for chemical analyses. The other sets of experiments were done at

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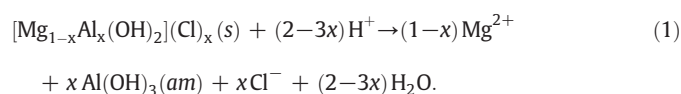
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constant pH, which was kept at a fixed value by addition of 2.5 M HCl from a 1 mL burette driven by a Titrimo unit (Metrohm) used in the pH-stat mode. In one of them, aliquots of the dispersions were withdrawn at different time intervals and filtered to quench the dissolution reaction; dissolved cations were then quantified. In the third set, the consumption of acid was recorded as a function of the reaction time.

All experiments were carried out under a N₂ blanket in a 250 mL reactor fitted with jacket through which water from a thermostat was circulated. Dispersions were filtered through 0.05 μm pore-size membranes. Dissolved Al³⁺ and Mg²⁺ were determined by atomic absorption spectroscopy; the detection limits were 0.5 and 0.003 ppm, respectively. pH values were measured using a combined glass electrode calibrated against NIST buffers.

3. Results and discussion

It is well-known that the natural pH of Mg²⁺–Al³⁺ LDHs dispersed in pure water lies around 9.3 ± 0.1 (Jobbágy and Regazzoni, 2005). This rise in pH reveals proton consumption by either H⁺ adsorption or partial dissolution of the layered solid, or both. The concentrations of Al³⁺ and Mg²⁺ in the supernatant of an equilibrated 1 g L⁻¹ HT(Cl) dispersion were, however, below detection. Acidification, nonetheless, triggered measurable dissolution. Fig. 1 shows the fraction of Mg²⁺ and Al³⁺ dissolved 72 h after the addition of HCl to the dispersion; for clarity, the data are presented as a function of the attained pH. Depending on the attained pH value, i.e., on the amount of added HCl, two very different dissolution behaviors can be inferred. In the range 5.0 ≤ pH < 9.0, dissolution of Al³⁺ was null, and only leaching of Mg²⁺ was observed. The fraction of leached Mg²⁺ increased rapidly with decreasing pH, but soon it leveled off, despite the solution was undersaturated with respect to Mg(OH)₂. Thermodynamically, within this pH range, the aqueous phase is supersaturated with respect to amorphous Al(OH)₃, thus dissolution of hydrotalcite is incongruent, and should be accounted for by



Amorphous Al(OH)₃, therefore, formed a passive layer that hindered further Mg²⁺ leaching. Whether this layer formed by reprecipitation or by condensation of the Al(OH)₆ octahedra left behind in the Mg²⁺-depleted brucite sheets, is an open question.

When the amount of added HCl was large enough to achieve pH values lower than, say, 4.7, the passive shell became thermodynamically unstable, and massive dissolution ensued; below pH 4.0, total

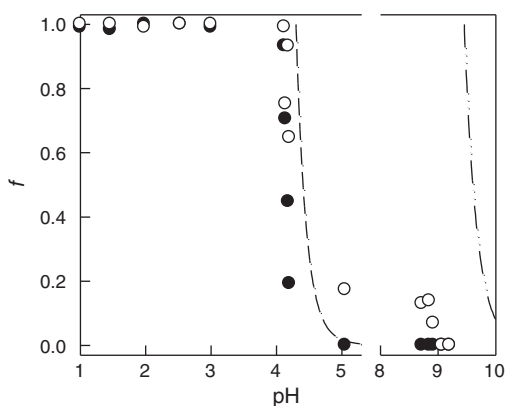
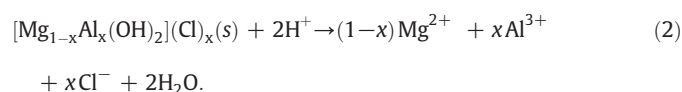


Fig. 1. Fraction of Al³⁺ (●) and Mg²⁺ (○) dissolved from HT(Cl) after 72 h at 298 K as a function of the attained pH. The dashed and dashed-dotted lines depict the solubility limit of amorphous Al(OH)₃ and Mg(OH)₂, respectively.

dissolution of hydrotalcite took place in less than 72 h (Fig. 1). The measured $f_{\text{Al}^{3+}}/f_{\text{Mg}^{2+}}$ ratios (where f stands for the dissolved fraction) suggest that dissolution is congruent (Eq. (2)) only at pH ≤ 4.0. They further suggest that the change in the dissolution behavior takes place in a rather narrow pH interval.



Strictly, congruent dissolution implies that the rate of leaching of the constituent cations must be equal at any reaction time, viz. the concentration ratio of dissolved Al³⁺ and Mg²⁺ must match that of the solid phase during the entire dissolution process; that is, $f_{\text{Al}^{3+}}/f_{\text{Mg}^{2+}} = 1$, and independent of time. The data in Fig. 2 demonstrate that dissolution of hydrotalcite at pH 4.0 is in fact congruent, at least within the experimental uncertainty.

Fig. 2 also denotes the presence of highly reactive surface sites, accounting for the nearly 6% dissolution observed during the first minute of the reaction. In addition, Fig. 2 shows that complete dissolution of HT(Cl) took place in about 3 h at pH 4.0. The apparent discrepancy with the data in Fig. 1 is a consequence of the different experimental designs. In this latter case, the driving force for dissolution was let to drift freely during the dissolution process, whereas in the former, it was kept constant (by fixing pH), large and negative. Dissolution rates depend on the actual driving force (Blesa et al., 1983), i.e.,

$$\partial C/\partial t = C_\infty(\partial f/\partial t) = R_0 A(t) \left[1 - \exp\left(\frac{\Delta G(t)}{RT}\right) \right] \quad (3)$$

where C_∞ is the total concentration, R_0 is the specific dissolution rate, $A(t)$ is the instantaneous surface area, and $\Delta G(t)$ is the driving force.

According to Eq. (2) (note that due to the composition of the studied solid, 2.08 proton are consumed per mole of dissolved hydrotalcite), the rate of congruent dissolution of HT(Cl) can be followed by recording the volume of acid (V) added to the reacting system to keep pH constant; in this case, $f = V/V_\infty$. The evolution of f at pH 3.5 is shown in Fig. 3. Kinetic runs at other pH values depicted similar deceleratory profiles. The shape of these profiles is the result of the decreasing interfacial area, and can be accounted for by an isotropic contracting volume rate law (Eq. (4)) as it can be seen in the inset of Fig. 3.

$$(1-f)^{1/3} = 1 - k_{\text{obs}} t \quad (4)$$

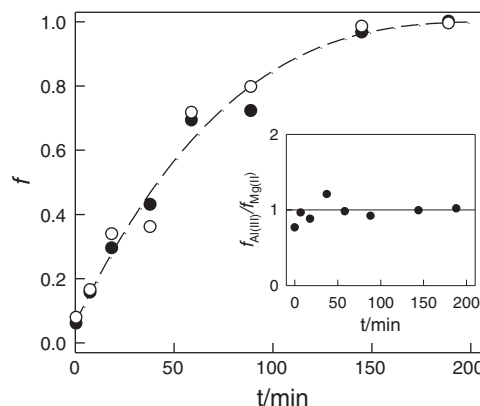


Fig. 2. Time evolution of $f_{\text{Al}^{3+}}$ (●) and $f_{\text{Mg}^{2+}}$ (○) at pH 4.00; $T = 298$ K. The dashed line shows the best fit according to Eq. (4); the non-zero ordinate discounts the contribution of highly reactive sites. Inset: evolution of the $f_{\text{Al}^{3+}}/f_{\text{Mg}^{2+}}$ ratio.

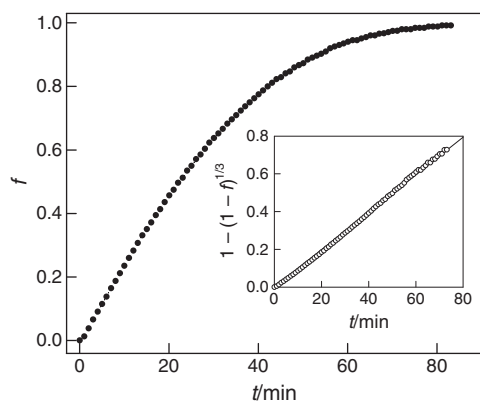


Fig. 3. Dissolved fraction of HT(Cl) as a function of reaction time; pH = 3.5; $T = 298$ K. Inset: linearized dissolution profile according to Eq. (4).

where k_{obs} is the observed rate constant, which is related to R_0 , the initial particle dimensions, and the molar volume of the solid (\bar{V}); for spherical particles of radius r_0 ,

$$k_{\text{obs}} = R_0 \bar{V} / r_0. \quad (5)$$

Eq. (4) is indeed a good descriptor of the congruent dissolution of HT(Cl). Nonetheless, no especial significance must be credited to the noted agreement (Fig. 3 inset). Due to the unlike coordination environments of the basal and the 100 (and analogous) surfaces of the hexagonal hydroxalite crystals, the latter are expected to be much more prone to proton attack, thus dissolving hydroxalite particles should match the symmetry of a contracting cylinder (Eq. (6)). The use of this rate equation resulted, however, in much poorer fittings, a fact that must be attributed to polydispersity, which usually blurs the assessment of the reaction front geometry and leads to unexpected exponents (Taplin, 1974; Urrutia and Blesa, 1988). In what follows, we shall use Eq. (4) to derive k_{obs} values.

$$(1-f)^{1/2} = 1 - k_{\text{obs}} t = 1 - (R_0 \bar{V} / a_0 \cos 30^\circ) t \quad (6)$$

where a_0 is the initial edge length of the hexagonal particles. Comparison of the profiles shown in Figs. 2 and 3 indicates that the rate of congruent dissolution of hydroxalite is strongly pH dependent. For large and negative ΔG values, the influence of all chemical variables is lumped in R_0 (Eq. (3)), which is embodied within k_{obs} (Eq. (5)). Fig. 4, which illustrates the pH dependence of k_{obs} , shows that the kinetic order on proton concentration is 0.41, viz.

$$k_{\text{obs}} = k_0 [\text{H}^+]^n = 0.23 [\text{H}^+]^{0.41} / \text{min}^{-1} \quad (7)$$

where k_0 is the specific rate constant. Fractional kinetic orders on proton concentration are common for metal (hydr)oxide dissolution reactions (Blesa et al., 1983); typically, they lie around 0.5. They are characteristic of surface controlled dissolution processes, and reflect the necessity of forming an ensemble of i adjacent protonated surface OH groups, prior to electrophilic attack on M–OH–M bonds; note that Eq. (7) resembles a Freundlich adsorption isotherm, which, for most oxides, is a good descriptor of surface protonation away from the point of zero charge (Wieland et al., 1988).

The above description also applies to early stages of the dissolution of hydroxalite in near-neutral solutions. In such a case, however, formation of amorphous $\text{Al}(\text{OH})_3$ blocks the dissolution reaction, thus Eq. (4) soon breaks down.

Most synthetic LDHs are composed of metal ions that form individual hydroxides with very different solubilities, thus their overall dissolution behavior must be similar to that illustrated in the

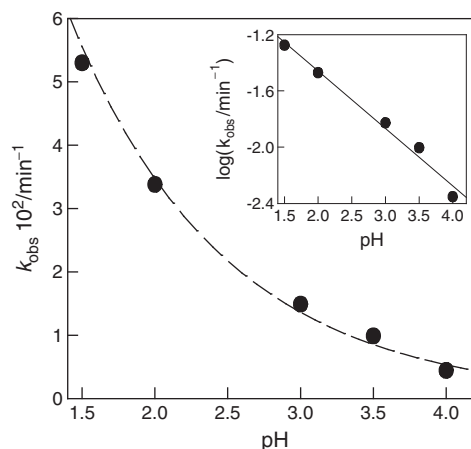


Fig. 4. Dependence of k_{obs} with pH. The inset shows the same data set presented as a log–log plot.

present work. Nonetheless, due account of the unlike labilities of the metal ions, especially of the more soluble divalent ones, ought to be made, because they must determine the kinetic stability of the LDH. Let us for instance reason the cases of Zn^{2+} – Al^{3+} and Ni^{2+} – Al^{3+} LDHs. $\text{Zn}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ bare roughly the same solubility (Baes and Mesmer, 1976), but Zn^{2+} aqueous ions exchange water molecules at a significantly higher rate than Ni^{2+} ions do (Margerum et al., 1978), hence Ni^{2+} – Al^{3+} LDHs should be kinetically more stable than Zn^{2+} – Al^{3+} LDHs, under both congruent and incongruent dissolution conditions. Obviously, the dissolution driving force is dictated by thermodynamics, and the unlike solubilities of the LDHs, which are determined by the nature of the constituent metal ions, as well as by the nature of the intercalated anions (Allada et al., 2002; Bravo-Suarez et al., 2004), ought not to be left aside from consideration.

In summary, this work demonstrates indisputably that hydroxalite is rather unstable in aqueous solutions, even in slightly alkaline media. This fact, somehow disregarded in the literature, poses a warning on common practices involving hydroxalite and other LDHs. For example, acid assisted decarbonation processes (Iyi et al., 2004) will produce a significant loss of material, and alter the stoichiometry of the brucite-like sheets, even if the acid treatment is performed at a moderately acidic pH (Iyi and Sasaki, 2008). Furthermore, if complexing anions are being intercalated, they will attack the $\text{Al}(\text{OH})_3$ passive layer, enhancing dissolution (Blesa et al., 2000). Likewise, water treatment or remediation processes performed outside the stability pH range of hydroxalite would deteriorate its capacity to be regenerated, once it becomes saturated with anionic contaminants (Kuzawa et al., 2006). Massive dissolution at extreme pH values, however, may not prevent the scavenging of anions, such as, chromate and phosphate (Terry, 2004), but removal should be attributed to the precipitation of solid phases rather than to adsorption or anion exchange. Despite dissolution of hydroxalite, either congruent or incongruent, may result detrimental for environmental applications, the instability of hydroxalite in acid media may be instrumental to drug delivery. In fact, in most scenarios it is conceivable that the pace of drug release would be determined by the rate of dissolution of the brucite-like slabs. Extrapolation of the present results to such a situation, however, is not warranted, for the amphiphilic nature of most of the intercalated drugs should arrest dissolution.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.clay.2010.11.027.

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