Research paper

Competition between chloride and sulphate during the reformation of calcined hydrotalcite

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ABSTRACT

The layered double hydroxides (LDH) have been widely investigated for their use as sorbents, exchangers and delivery shuttles for anionic compounds in aqueous environments. We synthesized hydrotalcite (HT), calcined it to increase its sorption capacity and quantified the affinities of chloride and sulphate for intercalation, in mixed anion solutions. To better simulate natural systems, no particular measures were taken to exclude air, with its inherent CO_2. Thus, a small amount of dissolved carbonate (<1 mM) was present under all tested conditions. The results show that: i) LDH, that has reformed in the presence of minor amounts of CO_2, always contains some interlayer carbonate; ii) chloride competes with carbonate for intercalation sites, whereas sulphate does not; iii) when chloride and sulphate are present in equal concentrations, the affinity of sulphate is higher than chloride for intercalation, regardless of the total anion concentration; iv) at anion concentrations <100 mM, sulphate outcompetes chloride, even when chloride is in 3 times molar excess; and v) at anion concentrations ≥ 100 mM, the most abundant anion (3–5 times in molar excess) has the highest affinity. The results bring us closer to a clear description of the structure, composition and behavior of Mg^{2+}, Al^{3+} LDH that forms in multi ion solutions. This can be used to predict geochemical behavior in natural systems such as determining saturation states of minerals and to optimize wastewater treatment and remediation of contaminated soil and groundwater.

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1. Introduction

Layered double hydroxides (LDH), also known as anionic clays or hydrotalcite like compounds, have received attention over the past decades because of their unique structural properties and simple, low cost synthesis (Reichle, 1986; Cavani et al., 1991; Roy et al., 2001). These compounds are highly tunable, multifunctional and generally non-toxic (Evans and Duan, 2006), which makes them effective as sorbents, exchangers, stabilizing agents and delivery shuttles (Khan et al., 2001; Evans and Duan, 2006; Choy et al., 2007) in fields such as agriculture, medicine and catalysis (Giannelis et al., 1987; Meyn et al., 1990; Basile and Vaccari, 2001; Costantino and Nocchetti, 2001; Monzón et al., 2001; Sels et al., 2001; Khan et al., 2009), as well as for remediation of groundwater and soil, for immobilization of arsenate, chromate and phosphate (Ulibarri and Hermosin, 2001; Skovbjerg et al., 2006; Goh et al., 2008; Xu et al., 2010).

LDH consists of positively charged layers with brucite structure ($M(OH)_2$) that sandwich interlayers composed of water and anions (A^{m-}) for charge compensation. M in the formula typically represents divalent cations, M(II), which are partially substituted by trivalent cations, M(III). The metals in the main layers are octahedrally coordinated to hydroxide but the type and distribution of the cations can vary. Possible divalent cations include Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+} and Zn^{2+}, and trivalent cations are Al^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Cr^{3+} and Ga^{3+} (Drits and Bookin, 2001; Roy et al., 2001; Mills et al., 2012). Some LDH contain cations in the interlayer along with anions (Drits and Bookin, 2001), e.g. the mixed valent Fe(II)/Fe(III) LDH, green rust (Christiansen et al., 2009; Christiansen et al., 2014). The general chemical formula for LDH is:

$$\left[M(II)_{1-x} M(III)_x (OH)_2 \right]^{x+} \left[A^{m-}_{x/m} \cdot nH_2O \right]^{x-},$$
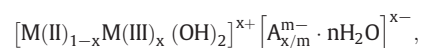
where m represents the charge of the interlayer anion and x, the molar fraction of the trivalent cation within the hydroxide layer:

$$x = \frac{M(III)}{M(II) + M(III)}.$$

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The molar fraction of trivalent ions, x, commonly ranges between 0.20 and 0.33. When x is large, charge density in the hydroxide layers is high so electrostatic interaction with the interlayer anions is stronger, leading to tighter packing (Brindley and Kikkawa, 1979). Each LDH type is characterized by a specific basal plane spacing (*d*-spacing) and this is determined by the nature of the cations (i.e., the charge density), the interlayer anions and their structural arrangement, the degree of hydration and the stacking sequence of the hydroxide layers (Cavani et al., 1991). Most LDH crystallize in either the double layer hexagonal stacking sequence (2H) or the triple layer rhombohedral stacking sequence (3R) (Bookin and Drits, 1993; Drits and Bookin, 2001). Hydrotalcite (HT), $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, which is a naturally occurring LDH of polytype 3R with interlayer carbonate and a 3:1 Mg^{2+}/Al^{3+} ratio (x = 0.25), has a *d*-spacing of 7.69 Å (Miyata, 1980). In contrast, quintinite ($Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$), also with interlayer carbonate but 2:1 Mg^{2+}/Al^{3+} ratio (x = 0.33), has a *d*-spacing of 7.57 Å for the 3R polytype (Jambor et al., 1998).

The interlayer anions are bound by electrostatic interactions and hydrogen bonding, which gives LDH compounds the ability to exchange anions with the surrounding environment, especially in their hydrated state (Miyata, 1983). LDH can intercalate various anions, including halides, oxo-anions, oxo- and polyoxo-metallates and organic anions (Cavani et al., 1991; Roy et al., 2001; Xu et al., 2010; Theiss et al., 2014). However, their affinity for intercalation differs and is controlled by the charge density of the anions. For example, for a Mg^{2+}/Al^{3+} LDH (x = 0.29) with interlayer CO_3^{2-} and NO_3^- in a 2:1 ratio, Miyata (1983) observed an exchange selectivity for monovalent anions in the sequence: $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ and for divalent anions: $CO_3^{2-} > SO_4^{2-}$. The carbonate ion has the strongest affinity for LDH and once it is intercalated, it resists exchange with other anions (Miyata, 1983; Parker et al., 1995).

A unique property of LDH is its "memory effect". Calcination of LDH at temperatures from 400 to 800 °C produces a mixed oxide $(M(II)_{1-x}M(III)_xO_{1+x/2})$ (Miyata, 1980; Sato et al., 1986), which when exposed to air or water, rehydrates and reforms with the same structure as the original LDH, incorporating the anions that are available in its surroundings. Thus, interlayer anions can easily be exchanged and a variety of LDH types, with a range of properties can be created. For example, for calcined HT (cHT, $Mg_{0.75}Al_{0.25}O_{1.125}$), the anion selectivity during reformation follows the sequence: $CO_3^{2-} > SO_4^{2-} > F^- > HPO_4^{2-} > Cl^- > B(OH)_4^- > NO_3^-$ (Parker et al., 1995), which agrees with the anion exchange affinities reported by Miyata (1983). Sato et al. (1986) found that sorption extent and rates for calcined LDH ($Mg_{0.7}Al_{0.3}O_{1.15}$) are much higher for divalent than for monovalent anions. The reformation process is known to begin immediately after the compound is exposed to solution and to be complete within a day (Sato et al., 1986; Millange et al., 2000). However in air, where water comes from humidity and the anion from hydrated CO_2, reformation takes several days (Parker et al., 1995).

Natural waters contain a variety of dissolved salts at various concentrations. Each anion has its own impact on reformation and exchange capacity. Natural LDH compounds have been observed to contain multiple interlayer anions and these have also been synthesized in experiments (Drits et al., 1987). However, little is known about the parameters that control LDH structure and composition in complex solutions. This knowledge is particularly important for tuning LDH properties, to optimize them for specific applications. So far, most studies have focused on maximizing the exchange and sorption capacities of the various LDH types for individual anions (Parker et al., 1995; Lv et al., 2006; Goh et al., 2008; Hamidi and Kazemi, 2015; Wan et al., 2015). These studies have demonstrated that sorption capacity is determined by the amount of LDH, i.e. solid to liquid ratio, temperature, reaction time and whether the LDH was thermally activated or not (i.e. calcined). In comparison, experimental studies on LDH formation and reformation in mixed anion solutions are scarce. Chatelet et al. (1996) showed that the sorption of divalent anions such as CrO_4^{2-} and SO_4^{2-} by calcined

LDH ($Mg_{0.67}Al_{0.33}O_{1.16}$) is slightly decreased in the presence of Cl^-, whereas the sorption of Cl^- is strongly decreased in the presence of SO_4^{2-}. Similarly, Wan et al. (2015) showed that fluoride sorption by cHT decreased when other anions were added along with fluoride and the added anions decreased fluoride sorption in the order: $PO_4^{3-} > SO_4^{2-} > Cl^-$. However, it is still unknown how anion affinity for the LDH interlayer is affected by changes in anion concentration and anion ratio and although several studies have analyzed changes in solution composition, little is known about how and to what extent such changes affect the intrinsic LDH structure. This information is essential for a full understanding of LDH behavior and key to predicting and tuning its properties.

In this study, we have investigated the reformation of calcined hydrotalcite in mixed Cl^- and SO_4^{2-} solutions, as a function of total anion concentration, $[Cl^-]/[SO_4^{2-}]$ ratio and temperature (ambient conditions and 150 °C). To simulate natural conditions, the initial reformation solutions were not excluded from air with its inherent CO_2. Thus, a small amount of carbonate was present from the beginning in all experiments conducted here. The reformed crystalline solids were investigated by X-ray diffraction (XRD) and infrared spectroscopy (IR) to establish anion affinity as a function of concentration and molar ratio. Establishing anion affinities provides information for determining the design rules for LDH (re-)formation in mixed ion solutions, which is needed for determining the in situ chemical composition of natural waters and improving techniques for producing compounds for specific purposes. To the best of our knowledge, no previous studies have analyzed the reformed LDH structures to quantify the anion affinities during reformation of cHT in mixed anion solutions.

2. Experimental details

2.1. Hydrotalcite (HT) synthesis and calcination

HT was synthesized using the coprecipitation method, by increasing pH, as described by Seron and Delorme (2008). A base stock solution (0.78 M Na_2CO_3 and 0.77 M NaOH) and cation stock solution (1.5 M $Mg(NO_3)_2 \cdot 6H_2O$ and 0.50 M $Al(NO_3)_3 \cdot 9H_2O$) were prepared by dissolving reagent grade chemicals (Sigma-Aldrich) in ultrapure deionized water (MilliQ, resistivity >18 M$\Omega \cdot$cm). Solutions were stored in plastic bottles to avoid silica contamination, which has been shown to affect LDH formation and transformation (Kwon et al., 2007).

For HT synthesis, the cation stock solution was diluted 3 times with ultrapure water and placed in a perfluoroalkoxy alkane (PFA) beaker. The base solution was then added at a rate of 1.6 ± 0.1 ml/min using a peristaltic pump, while the solution was continuously stirred and pH monitored. Titration stopped once pH leveled off at 12.8 ± 0.1. The product was aged at 64 ± 2 °C for 20 h and then centrifuged for 3 min at 4322 *g*. The supernatant was removed and the remaining wet paste was washed with ultrapure water 5 to 7 times until the supernatant pH was constant. The paste was dried in the fume hood and then ground to a fine powder. The synthesized HT was calcined at 550 °C for 2 h and stored in a PFA beaker under nitrogen atmosphere to minimize exposure to CO_2 and H_2O, i.e., to avoid premature LDH reformation.

2.2. Reformation experiments

A series of solutions with varying Cl^- and SO_4^{2-} concentrations was prepared (Table 1). Reagent grade Na_2SO_4 and NaCl (Sigma-Aldrich) were dissolved in ultrapure water, then freshly calcined HT, i.e. cHT, was added to give a solid/liquid ratio of 20 mg/ml. All reformation experiments were performed at two sets of P and T conditions, i.e., at 25 °C, 1 bar, called the room temperature bench (RTB) experiments and at 150 °C, 3–5 bar, called the high temperature vessel (HTV) experiments. For HTV experiments, reactions were set up in Teflon tubes, sealed with Teflon tape and performed inside a high temperature vessel, filled with ultrapure water. For RTB experiments, polypropylene tubes