

Oxidative leaching of chromium from layered double hydroxides: Mechanistic studies

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Abstract. The layered double hydroxide (LDH) of Zn with Cr on treatment with a hypochlorite solution releases chromate ions as a result of oxidative leaching by a dissolution–reprecipitation mechanism. The residue is found to be ϵ -Zn(OH)₂. The LDH of Mg with Cr on the other hand is resistant to oxidative leaching. In contrast, a X-ray amorphous gel of the coprecipitated hydroxides of Mg and Cr yields chromate ions. These results suggest that the oxidation potential of Cr(III) in LDHs is determined by the nature of the divalent ion and the crystallinity of the phase while being unaffected by the nature of the intercalated anions.

Keywords. Layered double hydroxide; stichtite; oxidative leaching; dissolution–reprecipitation.

1. Introduction

Anionic clays based on mineral stichtite, Mg₆Cr₂(OH)₁₆(CO₃)₄·4H₂O, comprise positively charged layers having the composition [M(II)_{1-x}Cr_x(OH)₂]^{x+} (Taylor 1973). Anions such as CO₃²⁻ are intercalated between the layers for the restoration of charge neutrality. A host of divalent ions such as Mg, Ni (Kooli *et al* 1995), Co (del Arco *et al* 1996), Cu (Grosso *et al* 1992) and Zn (Boehm *et al* 1977) can take the place of M(II) to yield a large number of compounds, which are more generally referred to as ‘layered double hydroxides’, (LDHs) (Cavani *et al* 1991). While other LDHs exhibit considerable compositional flexibility (0.2 ≤ x ≤ 0.33) (Miyata 1980), the LDH of Zn with Cr³⁺ has a unique composition corresponding to x = 0.33 (Bocclair and Braterman 1998). This leads to the formula, Zn₂Cr(OH)₆(CO₃)_{1/2}·yH₂O (y = 2.0). We abbreviate the formula of these LDHs as M–Cr–A (M = Mg, Zn; A = NO₃⁻, CO₃²⁻, Cl⁻).

We have for some time been working on the use of Ni-based LDHs as candidate electrode materials for alkaline secondary batteries (Kamath *et al* 1994). The LDH of Ni²⁺ with Cr³⁺ was shown to deliver a higher discharge capacity as compared to nickel hydroxide (Jayashree and Kamath 2002), but capacity fading was observed on cycling due to the oxidative leaching of Cr³⁺ in the form of the soluble CrO₄²⁻ ion. This observation got us interested in the mechanism of Cr³⁺ oxidation in LDHs. To examine this we employed the LDHs of Cr³⁺ with divalent ions such as Mg and Zn, which, in contrast with Ni, do not have any redox chemistry of their own.

The motivation for the present investigation was (i) to determine the mechanism of oxidative leaching of Cr from the LDH lattice and (ii) to characterize the residue obtained at the end of the reaction.

2. Experimental

2.1 Preparation of LDHs

The Zn–Cr–A (A=NO₃⁻, Cl⁻) LDH was prepared by the method of Boehm *et al* (1977). 2.5 g of ZnO was first suspended in 10 ml of water. To this suspension, 10 ml of 1 M CrA₃ solution was added drop wise and stirred for a day. The Cr salt solution was fully decolourized and was replaced with a fresh aliquot. The suspension was then stirred for 6 days, after which the LDH was filtered, washed with copious quantities of water and dried at 65°C. The Zn–Cr–CO₃²⁻ LDH was prepared by ion exchange, by suspending a pre-weighed batch of the Zn–Cr–NO₃⁻ LDH in 100 ml of an aqueous Na₂CO₃ solution containing three times the stoichiometric requirement of CO₃²⁻ ions for 24 h. The suspension was then filtered, washed with water and dried at 65°C.

The Mg–Cr–CO₃²⁻ LDH was prepared by the method of coprecipitation (Kooli *et al* 1995). A mixed metal (Mg²⁺ + Cr³⁺) nitrate solution containing the required quantity of the metals in 3 : 1 ratio (total strength, 0.6 M) was added drop wise to a solution of NaOH + Na₂CO₃ containing the stoichiometric requirement of OH⁻ ions and a three-fold excess of CO₃²⁻ ions using a Metrohm Model 718 STAT titrino operated in the DOS mode at the rate of 3 ml min⁻¹. The resulting slurry was filtered, washed free of excess alkali and carbonate ions and dried at 65°C. This as-prepared material was found to be X-ray amor-

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phous. To obtain a well crystallized LDH, the slurry obtained in a separate experiment was hydrothermally treated in a teflon lined autoclave (75% filling, 180°C, 72 h) under autogenous pressure. The solid was then filtered, washed and dried to constant weight at 65°C.

2.2 Cr leaching experiments

Oxidative leaching of Cr was carried out by suspending a pre-weighed (500 mg) amount of the LDH in 50 ml of 5% sodium hypochlorite (Nice Reagents, India) solution (pH > 12) for 26 h under constant stirring. The residue was then filtered through a previously weighed sintered glass crucible, washed and dried at room temperature over P₂O₅. The percentage weight loss could thus be determined. The filtrate had the yellow colour of dissolved CrO₄²⁻ ions. The amount of CrO₄²⁻ in the leachate was determined gravimetrically as BaCrO₄ using the standard procedure (Vogel 1978).

2.3 Wet chemical analysis

The residues obtained from the leaching experiments were subjected to chemical analysis. A preweighed amount of the residue was dissolved in a known amount of excess dilute HCl. The hydroxyl content was estimated by back titrating the excess acid against standard NaOH pH metrically. The metal content was estimated by EDTA titrations. The unaccounted weight was attributed to water to arrive at an approximate formula, which was then found to be consistent with results of thermal analysis.

2.4 Characterization

All the samples were characterized by PXRD (Jeol Model JDX8P powder X-ray diffractometer, Co K α source, $l =$

1.79 Å or Siemens D5005 diffractometer, Cu K α source, $l = 1.541$ Å), infrared spectroscopy (Nicolet Model Impact 400D FTIR spectrometer, 4000–400 cm⁻¹, KBr pellets, resolution, 4 cm⁻¹) and thermogravimetry (lab. built system, heating rate, 5°C min⁻¹).

3. Results and discussion

Mg(OH)₂ crystallizes in a layered structure (space group *P*-3 m 1; $a = 3.148$ Å and $c = 4.772$ Å) comprising a hexagonal close packing of hydroxyl ions, with Mg²⁺ occupying alternate layers of octahedral sites (Oswald and Asper 1977). When a fraction, x , of the Mg²⁺ ions are substituted by Cr³⁺, the layers acquire a composition, [Mg_{1-x}Cr_x(OH)₂]^{x+} with a positive charge, to neutralize which, carbonates/nitrates are intercalated in the interlayer region. This causes an increase in the interlayer spacing from 4.77 Å seen in Mg(OH)₂ (bivalent hydroxides) to a higher value, 7.6 Å, seen in the LDHs. In figures 1a and 2a are shown the PXRD patterns of the LDHs of Cr³⁺ with Zn and Mg, respectively. Both the LDHs exhibit a low angle ($2\theta = 10$ –14°) reflection corresponding to their enlarged basal spacing. This is 8.86 Å in the case of the Zn–Cr–NO₃ LDH characteristic of the intercalated nitrate and is 7.73 Å in the case of the Mg–Cr–CO₃²⁻ LDH characteristic of the intercalated CO₃²⁻ ion (Miyata 1983). In figure 3a is given an illustrative IR spectrum of the Zn–Cr–NO₃ LDH. Strong vibrations due to the intercalated NO₃⁻ ion can be seen at 1350–1380 cm⁻¹ (n_3).

The oxidative leaching of Cr from the LDHs can take place by two possible mechanisms:

(I) The oxidation of Cr³⁺ to Cr(VI) followed by the topo-tactic removal of Cr(VI) from the lattice. Cr(VI) has a very small ionic radius (0.26 Å in 4-coordination and 0.44 Å in 6-coordination) (Shannon 1976) and can in principle

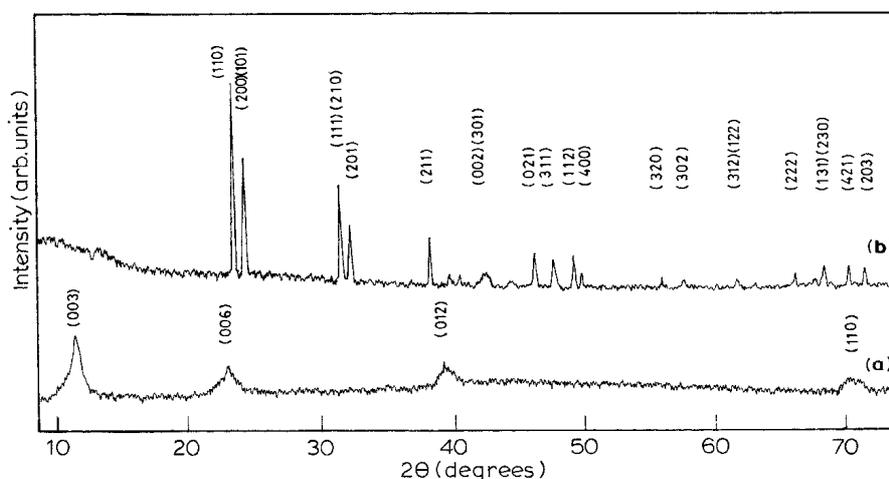


Figure 1. Powder X-ray diffraction patterns of Zn–Cr–NO₃ LDH (a) before and (b) after Cr leaching.

diffuse through the triangular face of the $[M(OH)_6]$ octahedron of the LDH layer, by a process known as diadachy. The Cr(VI) can then be hydrolyzed to the CrO_4^{2-} ion in the solution outside the LDH lattice. Cation exchange of divalent ions in LDHs has been shown to occur by this mechanism despite their much larger size (Komarneni *et al* 1998).

(II) The direct removal of Cr^{3+} as the CrO_4^{2-} ion by the disruption of the hydroxide layer, with Cr(VI) drawing away the oxygen of the lattice. The LDH would effectively dissolve and the bivalent hydroxide would then re-

precipitate as an unary hydroxide. We refer to this as the dissolution-reprecipitation (D-R) mechanism.

If the former mechanism were to prevail, the end product of the reaction would also be a layered phase with a structure related to the original LDH. The loss of Cr^{3+} would result in the elimination of the positive charge on the layer. Consequently there should be an equivalent reduction in the negative charge. Release of the intercalated carbonate/nitrate ions would yield a hydrated unary hydroxide of the formula, $M(OH)_2 \cdot yH_2O$ ($y = 0.66-1.0$).

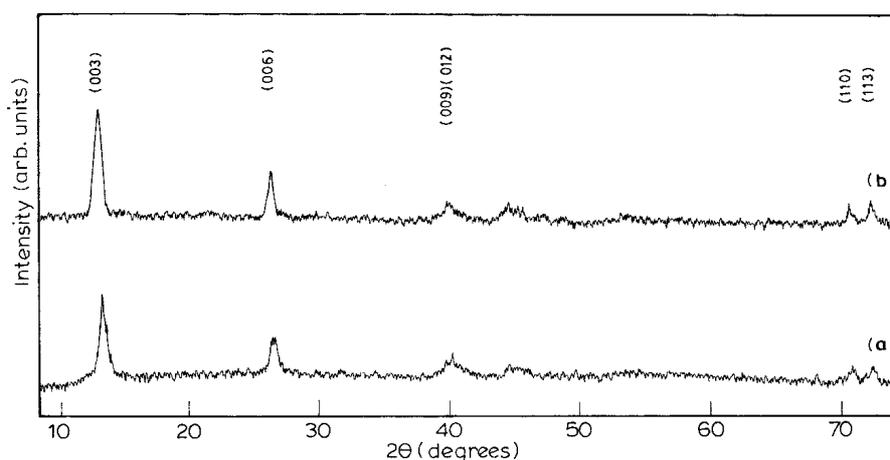


Figure 2. Powder X-ray diffraction patterns of Mg-Cr-CO₃ LDH (a) before and (b) after Cr leaching.

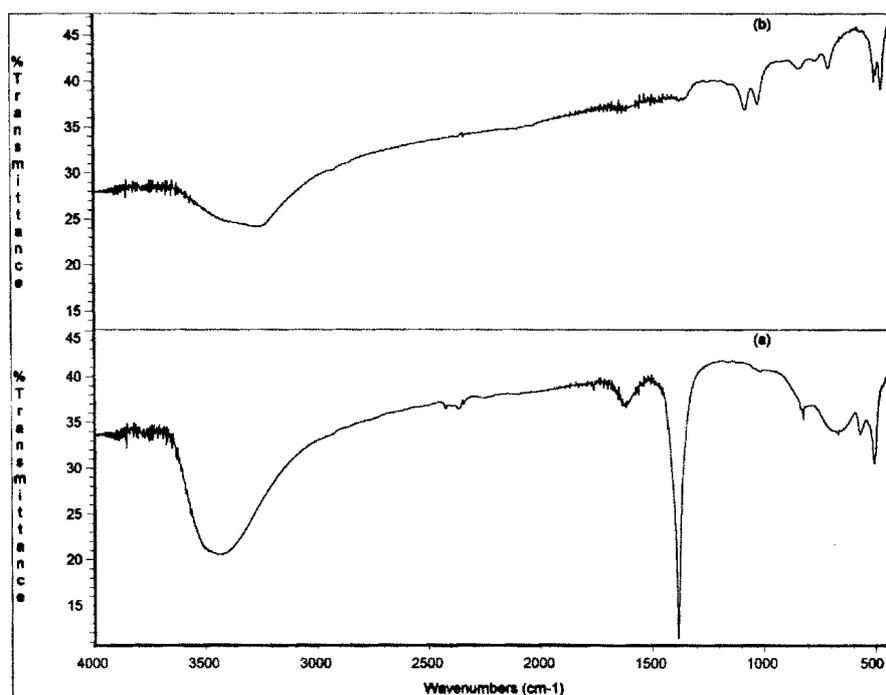


Figure 3. IR spectra of the Zn-Cr-NO₃ LDH (a) before and (b) after Cr leaching.

Table 1. Results of the oxidative leaching of Cr in different LDH systems.

LDH system	Weight loss after Cr leaching (wt.%)	Amount of Cr leached out (wt.%)	
		Observed	Expected*
Zn–Cr–NO ₃	48.11	14.53	13.6
Zn–Cr–CO ₃	43.56	15.02	(13.4)
Zn–Cr–Cl	44.0	15.24	14.6
Mg–Cr–CO ₃	11.04	< 1	15.9**
Mg–Cr–CO ₃ slurry	35.63	8.71	—***

*Calculated for the formula, $Zn_2Cr(OH)_6(A^{n-})_{x/n} \cdot 2H_2O$ (value in parentheses calculated for four molecules of water); **calculated for the formula, $Mg_6Cr_2(OH)_{16}(CO_3) \cdot 4H_2O$; ***composition unknown.

Such hydroxides are known as α -hydroxides (Oliva *et al* 1982). Release of hydroxyl ions on the other hand would yield phases of the composition, $M(OH)_{2-x}(A^{n-})_{x/n}$ (Gallezot and Prettre 1969). These are better known as hydroxysalts or basic salts. While both these types of phases have been shown to have a topotactic relationship with the LDHs (Kamath *et al* 1997; Rajamathi *et al* 2001), α -hydroxides of Mg and Zn have not been stabilized and characterized with certainty.

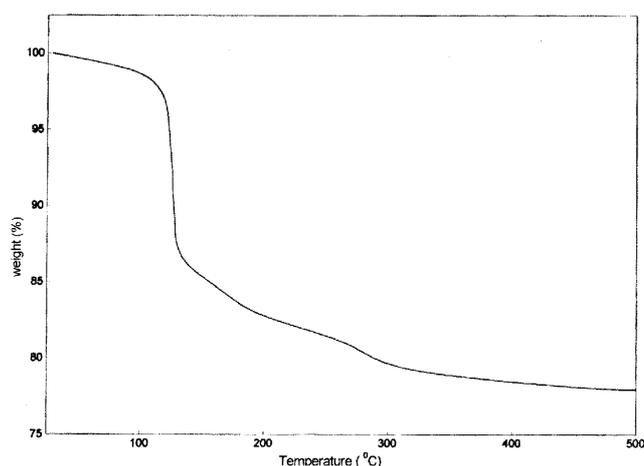
If the D–R mechanism is valid, the product is expected to be the thermodynamically most stable modification. In the case of the Mg–Cr LDH, the D–R mechanism is expected to yield brucite-like $Mg(OH)_2$ as the latter is not known to exhibit any polymorphism or interlayer chemistry. Among the various polymorphic modifications of $Zn(OH)_2$, the stable form is *e*- $Zn(OH)_2$, which resembles the 3-dimensional structure of cristobalite with Zn^{2+} in tetrahedral coordination (Oswald and Asper 1977).

The results of the oxidative leaching of Cr are summarized in table 1. It is seen that in the case of the Zn–Cr LDHs, Cr leaching is quantitative, whereas, Mg–Cr LDH does not yield any Cr. In figure 3b is shown the infrared spectrum of the residue obtained from the Zn–Cr system. The strong absorptions due to the intercalated nitrates are absent, indicating that the intercalated nitrate ions have been eliminated from the lattice together with the removal of Cr. In the Mg–Cr system however, the anion related vibrations are retained (data not shown).

The question now arises as to the nature of residues. In the case of the Mg–Cr LDH, the residue retains the LDH structure as is to be expected (see figure 2b) from the results of the Cr leaching experiments. In the case of the Zn–Cr LDH, the residue exhibits a PXRD pattern (see figure 1b) that can be assigned to *e*- $Zn(OH)_2$ (PDF: 38-0385). The *e*- $Zn(OH)_2$ has been further characterized by wet chemical analysis (table 2) and TG studies (figure 4). Wet chemical analysis shows a ratio of $Zn/OH = 0.5$ and an approximate formula, $Zn(OH)_2 \cdot 0.22H_2O$ and thermogravimetry exhibits a total weight loss of 22.0% (expected 21.3%) corresponding to the decomposition

**Table 2.** Results of wet chemical analysis of *e*- $Zn(OH)_2$ sample.

Zn ²⁺ (wt.%)	OH ⁻ (wt.%)	H ₂ O (wt.%)	Approximate formula
62.89	32.78	4.59	$Zn(OH)_2 \cdot 0.22 H_2O$

**Figure 4.** Thermogravimetric data of the residue obtained after Cr leaching from Zn–Cr–NO₃.

In figure 5 we compare the structure of the Zn–Cr LDH with that of *e*- $Zn(OH)_2$. While Zn occupies octahedral sites in the former, the latter contains Zn in the tetrahedral sites. Clearly the transformation involving as it does a change in the coordination number of Zn proceeds via the D–R mechanism.

To see if the difference in reactivity between the two LDHs is merely due to the greater bulk solubility of the Zn–Cr LDH compared to the Mg–Cr LDH, they were suspended in a NaOH solution (pH > 12) having the same pH as that of the oxidant. The Zn–Cr–NO₃ LDH exhibited a final weight loss of 8.2%. The following observations were made: (i) there was no trace of dissolved Zn^{2+} or Cr^{3+} in the liquid phase, even after 26 h of soaking; (ii) the residue obtained after 26 h of soaking retained the LDH structure (see figure 6) with an interlayer spacing of

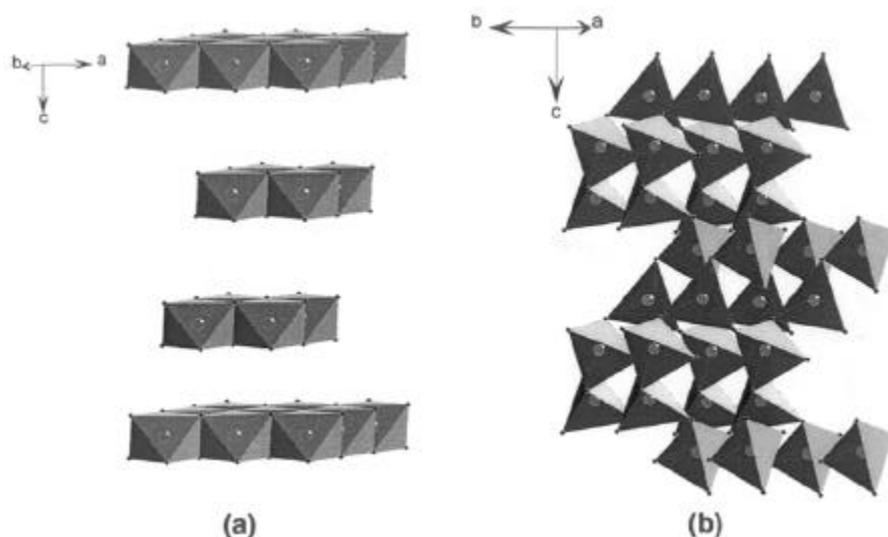
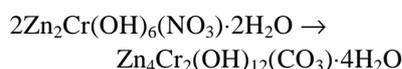


Figure 5. Structures of (a) Zn–Cr LDH (interlayer anions are not shown for clarity) and (b) *e*-Zn(OH)₂ viewed along the *b*-direction.

7.73 Å characteristic of the intercalated carbonate ions and (iii) the IR spectrum of the residue (data not shown) indicated the absence of NO₃⁻ ions and the incorporation of CO₃²⁻ ions (1367 cm⁻¹ and 1393 cm⁻¹).

On the basis of these observations, we conclude that the observed weight loss is not due to the bulk dissolution of the LDH, but due to the exchange of intercalated nitrates for carbonates present in the alkaline liquid phase according to the equation



(Calculated mass change: 8.36%; observed: 8.2%).

The Mg–Cr–CO₃²⁻ LDH exhibits a weight loss of < 1%. As this LDH already contains carbonate ions, there is no avenue for further anion exchange. Unfortunately solubility products of Cr based LDHs have not been reported to date. The Mg–Cr slurry exhibits a weight loss of 3.81% for unspecified reasons.

These results indicate that both LDHs have no significant bulk solubility. Cr leaching from Zn–Cr LDH is therefore not a trivial case of bulk dissolution of LDH followed by the oxidation of the free Cr³⁺ species to CrO₄²⁻. On the other hand this is genuine solid–solid transformation, dissolution–reprecipitation being a microscopic phenomenon that occurs only at the solid–liquid interface. Indeed our results indicate that the dissolution of the Zn–Cr LDH at the microscopic level is driven by the Cr³⁺ oxidation reaction and not *vice-versa*.

The Cr³⁺ oxidation potential therefore appears to be different in the two LDHs. Several factors can in principle affect the oxidation potential of Cr. Besides the nature of the divalent ion, other factors to be considered are (i)

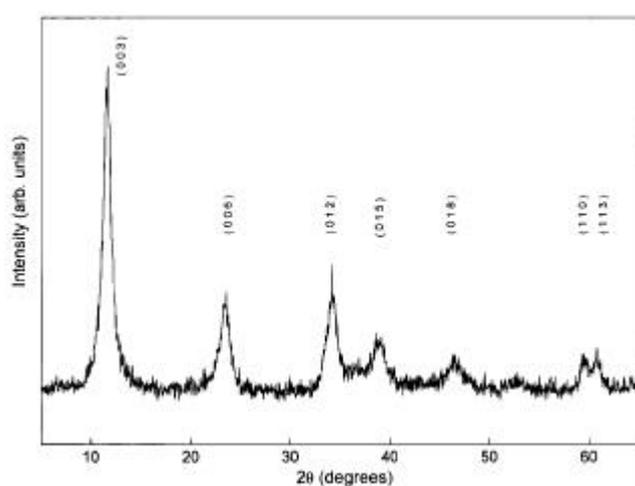


Figure 6. Powder X-ray diffraction patterns of Zn–Cr–NO₃ LDH aged in NaOH at pH 12 (Source, Cu K α radiation).

nature of the intercalated anion and (ii) the crystallinity of the solid.

To examine these factors, Cr leaching was carried out from the Zn–Cr–A (A = CO₃²⁻, Cl⁻) LDHs as well. The fact that the Zn–Cr LDH yields Cr for all the three anions studied (table 1) suggests that the effect of the anion is not significant. To investigate the effect of crystallinity, Cr leaching experiments were carried out on the as precipitated X-ray amorphous gel of the Mg–Cr LDH as a control experiment to the well crystallized hydrothermally treated Mg–Cr LDH. In contrast to that of the well crystallized LDH, the gel yielded Cr, showing that a long range ordering of the LDH lattice critically determines the reactivity of the solid.

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