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Applied Clay Science 13 (1998) 21–34

APPLIED  
CLAY  
SCIENCE

# Adsorption of Cr(VI) in layered double hydroxides

Rajib Lochan Goswamee<sup>a,\*</sup>, Pinaki Sengupta<sup>a</sup>,  
Krishna Gopal Bhattacharyya<sup>b</sup>, Dipak Kumar Dutta<sup>a</sup>

<sup>a</sup> *Material Science Division, Regional Research Laboratory (CSIR), Jorhat 785006, Assam, India*

<sup>b</sup> *Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India*

Received 18 February 1997; revised 19 January 1998; accepted 19 January 1998

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## Abstract

Adsorption of Cr(VI) by various uncalcined and calcined layered double hydroxides (LDH) of Mg–Al, Ni–Al and Zn–Cr types was investigated. Adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  through ion exchange in uncalcined LDH is slower in rate and smaller in amount than in calcined one where the adsorption occurs via rehydration. The nature and content of bi- and trivalent metal ions in LDH influence the adsorption. Calcined Mg–Al LDH with higher  $\text{Al}^{3+}$  content in the precursor structure shows higher adsorption capacity. Adsorption is higher in the Mg–Al LDH than in Ni–Al and Zn–Cr LDH. A two-step first-order rate kinetics was observed for the adsorption process which follows the Freundlich-type adsorption isotherm. The explanation of adsorption phenomenon has been supported by X-ray diffraction patterns. The pH of initial  $\text{Cr}_2\text{O}_7^{2-}$  solution has no effect on adsorption by calcined LDH. Release of  $\text{Cr}_2\text{O}_7^{2-}$  from the adsorbed product depends upon the type of anion in the aqueous phase and  $\text{CO}_3^{2-}$  being the most effective ion. Calcination of the  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed product up to 1250°C has not resulted in the formation of Cr-immobilized phases. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* layered double hydroxides; hydrotalcites; adsorption; memory effect

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## 1. Introduction

Layered double hydroxides (LDH) or mixed metal layered hydroxides (MMLH) have general formula  $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}\text{A}^{x-} \cdot n\text{H}_2\text{O}$  (von Allmann, 1970; Reichle, 1986), where M is metal cation and A is an exchangeable anion. These compounds possess a flat two-dimensional morphology composed of

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\* Corresponding author.

different elementary layers constituted by hydroxy framework of different metal ions like  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , etc. Isomorphous substitution of the bivalent metal ions in the brucite-like hydroxy framework by trivalent metal ions like  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , etc. gives rise to generation of additional charge over the layers which is counterbalanced by exchangeable anions like  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , etc. Calcination of these LDH produces intermediate non-stoichiometric oxides (Miyata, 1980) which undergo rehydration in aqueous medium and give back the hydroxide structure with different anions in the interlayers (memory effect).

This effect finds use in halide scavenging (Wang et al., 1985), adsorption of sulfuroxy anions (Sato et al., 1987), carboxylate anions (Yamagishi and Narita, 1990), metal complexes of ethylene-diaminetetraacetic acid (EDTA) (Narita et al., 1995), toxic oxometallate anions (Yamagishi et al., 1993), and  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$  (Chibwe and Jones, 1989) anions, etc.

Cr(VI) is present in the effluents of electroplating, tanning, mining and fertilizer industries. It causes problems of skin dermatitis, liver damage, carcinogenicity, etc. (Mudakavi et al., 1995). The United States Environment Protection Agency (USEPA) prescribes a maximum limit of  $50 \mu\text{g dm}^{-3}$  for total chromium in effluents. The magnitude of this problem of Cr ion in the environment is accentuated by the increase in discharge of chromium containing waste e.g., in Italy about 120 000 tonnes/year (Tiravanti et al., 1991), and in India about 150 000 tonnes/year (Knott, 1996) chromium containing sludges are released into the environment from the tanning industry effluents alone. Various methods like adsorption on activated carbon, etc. have been utilized for removing chromium from aqueous medium (Verma and Bhardwaj, 1994). Although adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  by calcined LDH is reported (Chibwe and Jones, 1989), detailed investigation on its removal from aqueous solution by various types of calcined LDH has not been carried out.

In the present work, effect of various factors like (a) calcination of LDH, (b) trivalent metal ion content in precursor LDH, (c) variation of pH of starting  $\text{Cr}_2\text{O}_7^{2-}$  aqueous solution, (d) use of different bivalent and trivalent metal ion combinations viz., Mg–Al, Ni–Al and Zn–Cr, (e) calcination time in removing  $\text{Cr}_2\text{O}_7^{2-}$  ions from aqueous solution by adsorption in calcined LDH have been investigated. Further, the effect of calcination of  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed product and release of  $\text{Cr}_2\text{O}_7^{2-}$  from it by treatment with aqueous solution containing  $\text{CO}_3^{2-}$  and Cl<sup>-</sup> has also been investigated.

## 2. Experimental method

### 2.1. Synthesis of Mg–Al LDH

#### 2.1.1. Synthesis from aluminates (Mg–Al LDH1)

Mg–Al LDH1 was synthesised by following the reported method of Cox and Wise (1995). An amount of 1.88 g (0.07 M) of small pieces of aluminium metal

foil was dissolved in 100 cm<sup>3</sup> of 0.5 N NaOH solution. A 250 cm<sup>3</sup> of a solution containing 54.36 g (0.212 M) of Mg(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O was added in drops with constant stirring. The pH was maintained at 9.5–10.5 by adding drops of 1 N NaOH solution. The slurry was then rolled in a roller oven for 24 h at 65°C. The product was filtered, washed free of sodium ion and dried at 100 ± 5°C for 24 h in an air oven.

### 2.1.2. *Synthesis by coprecipitation (Mg–Al LDH2)*

The Mg–Al LDH2 was synthesised by following the method of Reichle (1985). A 188.32 g (0.502 M) of Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O and 230.79 g (0.9 M) of Mg(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O were dissolved in 700 cm<sup>3</sup> water. A mixture of 280 cm<sup>3</sup> of 12.5 M NaOH solution and 1000 cm<sup>3</sup> of 1 M Na<sub>2</sub>CO<sub>3</sub> solution was added in drops over a period of 4 h under stirring condition maintaining a pH of 9.5. The slurry was then rolled in a roller oven for 24 h at 65°C. The product was filtered, washed free of sodium ion and dried at 100 ± 5°C for 24 h in an air oven.

### 2.2. *Synthesis of Ni–Al LDH*

The Ni–Al LDH was synthesised by following the method of Vaccari et al. (1991). A 60.02 g (0.16 M) of Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O and 130.86 g (0.45 M) of Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O were dissolved in 320 cm<sup>3</sup> water. The solution was heated at 80°C. A 400 cm<sup>3</sup> of 1.8 M Na<sub>2</sub>CO<sub>3</sub> solution was added in drops under stirring condition maintaining the pH between 7 and 8. The process of addition was completed in 6 h. The slurry was set aside for 12 h. The pale green product was filtered, washed and dried in an air oven at 40°C for 48 h.

### 2.3. *Synthesis of Zn–Cr LDH*

The Zn–Cr LDH was synthesised by following the method of Boehm et al. (1977). To a suspension of 40 g (0.49 M) ZnO in 1000 cm<sup>3</sup> water, 200 cm<sup>3</sup> of 1 M aqueous solution of CrCl<sub>3</sub> · 6H<sub>2</sub>O was added in drops under stirring condition at 60°C. The slurry was stirred for 2 h. The decolorised supernatant liquid was decanted off and 200 cm<sup>3</sup> of fresh 1 M CrCl<sub>3</sub> · 6H<sub>2</sub>O solution was added in drops with stirring. The process was repeated once more. The pink coloured product was filtered, washed with water and dried in an air oven at 40°C for 48 h.

### 2.4. *Characterisation of the products*

Mg and Al content in the Mg–Al LDH was analysed by standard method for Magaldrate as proposed by US Pharmacopia (1990). Ni and Al content in Ni–Al LDH was determined by gravimetric method (Vogel, 1962). Zn and Cr content in Zn–Cr LDH was determined by atomic absorption spectroscopy (AAS). The

X-ray diffraction patterns of all the samples were recorded in a Jeol diffractometer (Cu-K  $\alpha$ ) with a step size of  $0.05^\circ/0.5$  s.

### 2.5. Calcination of LDH samples

Calcination of LDH was carried out in a muffle furnace at  $450^\circ\text{C}$  for different periods. The calcined products were stored in a desiccator over fused  $\text{CaCl}_2$ .

### 2.6. Adsorption studies

Adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  was carried out by rehydrating calcined LDH in aqueous solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  in a roller oven with a rolling rate of 21 rpm at room temperature for 10 h. The effect of pH on the adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  was investigated by using aqueous solutions prepared by dissolving  $\text{Cr(VI)O}_3$  and adjusting the pH with NaOH solution.  $\text{Cr}_2\text{O}_7^{2-}$  concentration in solutions before and after adsorption were estimated by standard titrimetric and spectrophotometric methods (Vogel, 1962). In case of solutions of  $\text{Cr}_2\text{O}_7^{2-}$  with concentration less than  $7.75 \text{ meq dm}^{-3}$ , spectrophotometric method was used.

### 2.7. Release study

Release of  $\text{Cr}_2\text{O}_7^{2-}$  from the  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed Mg–Al LDH2 by treatment with water and aqueous solutions of  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$  was investigated for different periods of contact time. The  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed Mg–Al LDH2 for this purpose, was prepared by rolling  $20 \text{ cm}^3$  of  $0.028 \text{ N K}_2\text{Cr}_2\text{O}_7$  solution with  $200 \text{ mg}$  of precalcined Mg–Al LDH2 for 48 h. The calcination was done at  $450^\circ\text{C}$  for 10 h. The yellow adsorbed product was filtered, washed and dried in air oven at  $110^\circ\text{C}$  for 1 h. A  $150 \text{ mg}$  of the dried solid was then treated with  $15 \text{ cm}^3$  of (a) water (b)  $0.028 \text{ N}$  aqueous  $\text{CO}_3^{2-}$  solution ( $\text{Na}_2\text{CO}_3$ ) and (c)  $0.028 \text{ N}$  aqueous  $\text{Cl}^-$  solution (KCl). The suspensions were then rolled at room temperature for 30 min, 6 h and 48 h, respectively. The supernatants were estimated for  $\text{Cr}_2\text{O}_7^{2-}$ . To investigate the effect of calcination on  $\text{Cr}_2\text{O}_7^{2-}$  release from the  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed Mg–Al LDH2, the latter was calcined up to  $1250^\circ\text{C}$  for 30 min. Release behaviour of these products was studied by rolling in water for 48 h.

## 3. Results and discussion

The Mg:Al mole ratio in Mg–Al LDH1 and Mg–Al LDH2 was found to be 5.0:1 and 2.2:1, respectively. The Ni:Al mole ratio in Ni–Al LDH and Zn:Cr mole ratio in Zn–Cr LDH were 1.77:1 and 2:1, respectively.

All the synthesised LDH were found to give XRD patterns typical of layered structures with high intensity (00 $l$ ) peaks at regular interval of  $d$ -spacings along

Table 1

Effect of bi-/trivalent metal ion ratio on  $\text{Cr}_2\text{O}_7^{2-}$  adsorption in calcined Mg–Al LDH

Mg/Al <sup>a</sup> (mole ratio)	Calcination time (h)	Concentration <sup>b</sup> of $\text{Cr}_2\text{O}_7^{2-}$ in solution ( $\text{meq dm}^{-3}$ )	Amount adsorbed ( $\text{meq g}^{-1}$ )
LDH1 (5.0:1)	10	30.19	1.944
LDH2 (2.2:1)	10	30.19	2.264

<sup>a</sup>0.2 g; <sup>b</sup>25 cm<sup>3</sup> of sample; contact time 600 min.

with specific positions for other (*hkl*) reflections, e.g., Mg–Al LDH2 gave XRD pattern with (003), (006), (009) and (110) reflections at 7.63, 3.80, 2.58 and 1.52 Å, respectively (Mortland et al., 1967; Miyata, 1975; Vaccari et al., 1991).

The empirical formulae of Mg–Al LDH1 and Mg–Al LDH2 (calculated from the Mg and Al content and considering the  $\text{CO}_3^{2-}$  as the interlayer anion) are  $[\text{Mg}_5\text{Al}(\text{OH})_{12}](\text{CO}_3)_{0.5} \cdot x\text{H}_2\text{O}$  and  $[\text{Mg}_{2.2}\text{Al}(\text{OH})_{6.4}](\text{CO}_3)_{0.5} \cdot x\text{H}_2\text{O}$ , respectively. Mg–Al LDH2, containing higher amount of  $\text{Al}^{3+}$  should have higher amount of positive charge in the layer and higher adsorption capacity. Table 1 shows that Mg–Al LDH2 adsorbs higher amount of  $\text{Cr}_2\text{O}_7^{2-}$  than the Mg–Al LDH1. The Mg–Al LDH2 was, therefore, utilized for studying various aspects of  $\text{Cr}_2\text{O}_7^{2-}$  adsorption.

Fig. 1 shows that adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  through rehydration of calcined LDH is considerably higher than the adsorption through anion exchange of uncalcined LDH. The former reaches a plateau at a  $\text{Cr}_2\text{O}_7^{2-}$  concentration of 30.19  $\text{meq dm}^{-3}$  while the latter shows a slowly increasing adsorption with increase in concentration of  $\text{Cr}_2\text{O}_7^{2-}$ . The latter result is due to the slow anion exchange ability of the uncalcined LDH caused by tightly held layers with  $\text{CO}_3^{2-}$  in the interlayer positions (Miyata, 1980; Wang et al., 1985).

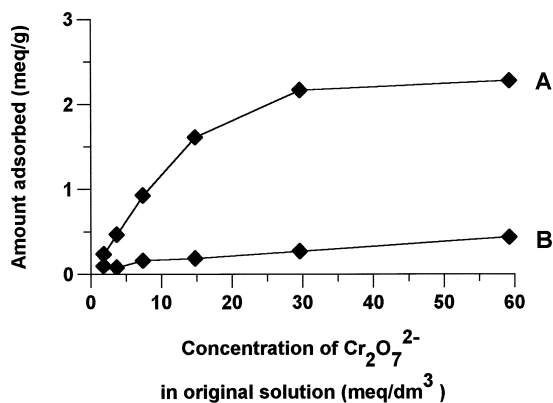


Fig. 1. Adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  in (A) calcined (B) uncalcined Mg–Al LDH2 (amount of solid adsorbent taken 200 mg).

Table 2

Effect of pH of solution on adsorption  $\text{Cr}_2\text{O}_7^{2-}$  by calcined Mg–Al LDH2

pH of solution		Amount adsorbed (meq g <sup>-1</sup> )
Before adsorption	After adsorption	
5.45	11.5	0.96
6.84	11.5	0.99
10.8	11.5	0.99

$\text{Cr}_2\text{O}_7^{2-}$  concentration 10.08 meq dm<sup>-3</sup>; volume 20 cm<sup>3</sup>; adsorbent 0.2 g; contact time 10 h.

In case of calcined Mg–Al LDH2, the plateau may be attributed to saturation of adsorption by the reconstituted metal hydroxide layers. The anion exchange capacity (AEC) of calcined Mg–Al LDH2 calculated from the empirical formula is 6.2 meq g<sup>-1</sup>. The amount of  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed by the calcined LDH at saturation (Fig. 1) is 2.3 meq g<sup>-1</sup>. The difference between two values might be due to the competitive adsorption of  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  from the solution (Ulibarri et al., 1995). The  $\text{CO}_3^{2-}$  must have resulted from  $\text{CO}_2$  absorption from air. Infrared spectra of the product obtained from the rehydration of the calcined LDH even in high  $\text{Cr}_2\text{O}_7^{2-}$  concentration ( $\approx 118$  meq dm<sup>-3</sup>) shows a strong band at 1390 cm<sup>-1</sup> ( $\nu\text{CO}_3$ ) indicating the presence of  $\text{CO}_3^{2-}$  (Nakamoto, 1978). Table 2 shows that the calcined oxide materials being highly basic, the solution after rehydration becomes alkaline (pH 11.5) resulting in adsorption of  $\text{OH}^-$  in the interlayer positions even when starting solution was acidic (pH 5.5). Consequently the amount of  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed remains constant irrespective of the starting  $\text{Cr}_2\text{O}_7^{2-}$  solution pH.

It appears from Fig. 2 that the amount of adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  from 20 cm<sup>3</sup> (10.18 meq dm<sup>-3</sup>) solution, rises with an increase in the amount of adsorbent. However the amount of adsorption reaches a near constant value when the adsorbent amount is 200 mg or more. The plateau therefore corresponds to the

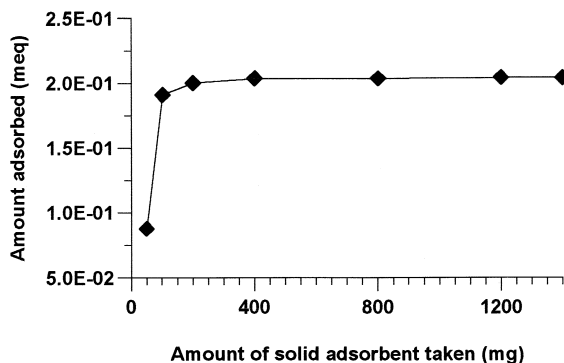


Fig. 2. Adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  by calcined Mg–Al LDH2 at fixed concentration of  $\text{Cr}_2\text{O}_7^{2-}$  (10.18 meq dm<sup>-3</sup>).

adsorption of all the available  $\text{Cr}_2\text{O}_7^{2-}$  from the given solution and is well below the AEC.

The rate of depletion of  $\text{Cr}_2\text{O}_7^{2-}$  concentration (Fig. 3) shows that the reaction proceeds in two stages, each with first order rate kinetics, satisfying an equation of the type:

$$\ln[\text{Cr}_2\text{O}_7^{2-}] = -k_n t + C \quad (1)$$

where  $k_n$  is the rate constant and  $t$  is time in min. The data were fitted by least square technique and standard deviation was found out to be 0.24 for the first stage. The slope or rate constant for the first stage,  $k_1$  is  $0.0419 \text{ min}^{-1}$ . The rate constant for comparatively slower second stage is  $k_2 = 0.0020 \text{ min}^{-1}$ , and the standard deviation for the same is 0.07. The first stage is faster than the second stage by a factor of approximately 20 ( $\approx k_1/k_2$ ). Such a multiple reaction rate results from the heterogeneous systems involved in the adsorption reaction (Oscarson et al., 1983). It is evident from Fig. 3 that the adsorption equilibrium is reached at 600 min of contact time.

Fig. 4 shows that the adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  by the calcined Mg–Al LDH2 (contact time 600 min) follows the Freundlich adsorption isotherm (Narita et al., 1995) which satisfies an equation of the type:

$$\log(X/M) = 1/n(\log C_e) + \log K \quad (2)$$

where  $K$  and  $1/n$  are constants, and are considered to be relative indicators of adsorption capacity and adsorption intensity, respectively ( $1/n$  is usually  $< 1.0$  for favourable adsorption),  $C_e$  is the equilibrium  $\text{Cr}_2\text{O}_7^{2-}$  concentration ( $\text{meq dm}^{-3}$ ) and  $X$  is the amount of  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed ( $\text{meq dm}^{-3}$ ) and  $M$  is the

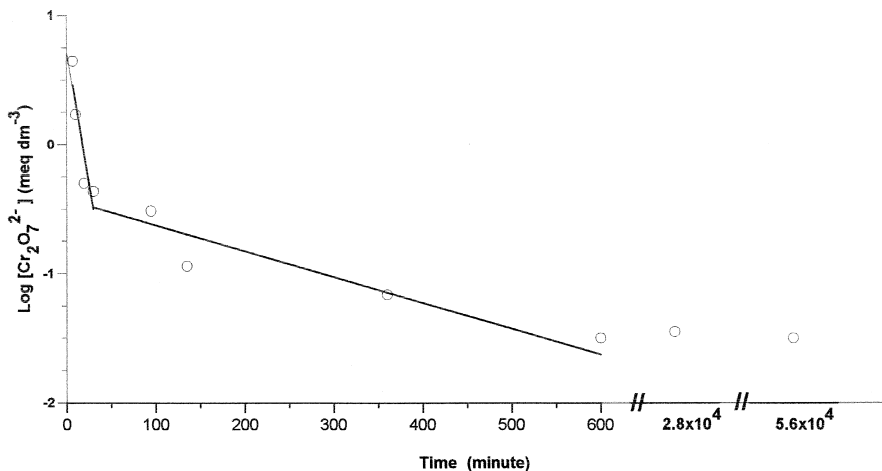


Fig. 3. Rate of depletion of  $\text{Cr}_2\text{O}_7^{2-}$  concentration due to adsorption on Mg–Al LDH2 at  $30^\circ\text{C}$  (initial concentration  $9.4 \text{ meq dm}^{-3}$ , amount of adsorbent 200 mg).

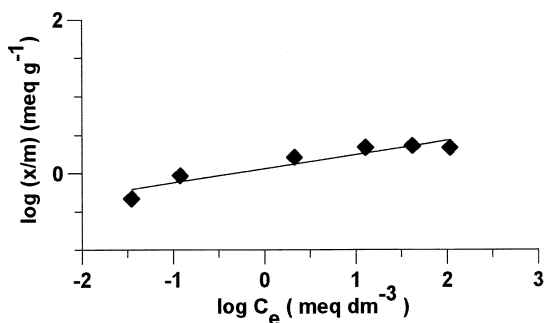


Fig. 4. Freundlich isotherm for adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  on calcined Mg–Al LDH2 at 30°C.

amount of adsorbate ( $\text{g dm}^{-3}$ ) added. The values of  $K$  and  $1/n$  are found to be 1.15 and 0.1845, respectively, indicating a considerable amount of favourable adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  on calcined Mg–Al LDH2.

Fig. 5 shows X-ray diffraction patterns of Mg–Al LDH2 and LDH reconstructed from rehydration of calcined Mg–Al LDH2 in water as well as in  $117.92 \text{ meq dm}^{-3}$   $\text{Cr}_2\text{O}_7^{2-}$  solution.  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed calcined Mg–Al LDH2 shows the existence of a broad peak around  $10 \text{ \AA}$  which can be ascribed due to turbostratic distortion (Brindley and Brown, 1984; Lal and Howe, 1981) and mixed layer formation (Carroll, 1970). Apart from intercalation of  $\text{CrO}_4^{2-}$  derived from depolymerisation of  $\text{Cr}_2\text{O}_7^{2-}$  in basic interlayer positions, the experimental conditions also permit formation of layers with  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  in the interlayers. The stereochemical factors do not permit that all these anions are present in the same interlayer space forming a hetero anionic composition therein (Drits et al., 1993; Schoellhorn and Otto, 1986). Therefore, these ions would form different elementary layers which will together stack up in the form of mixed layers as shown by broad peak. However, Misra and Perrotta (1992) when conducting the experiments in carbonate free medium, obtained a relatively sharp peak at  $8.4 \text{ \AA}$  due to  $\text{CrO}_4^{2-}$  in the interlayer. Depege et al. (1994) reported values of  $8.35 \text{ \AA}$  and  $8.08 \text{ \AA}$  for  $[\text{Cu-Cr-Cr}_2\text{O}_7]$  and  $[\text{Cu-Cr-CrO}_4]$ , respectively. Chibwe and Jones (1989) however, obtained a peak at  $10 \text{ \AA}$  due to  $\text{Cr}_2\text{O}_7^{2-}$  intercalated in hydrotalcite.

Fig. 6 shows the comparative ability of the calcined LDH for adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  from its aqueous solution having concentration  $1.89 \text{ meq dm}^{-3}$ ,  $7.75 \text{ meq dm}^{-3}$ ,  $30.19 \text{ meq dm}^{-3}$ . In case of Mg–Al hydrotalcite, the amount of adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  increases with increase in calcination time and this is attributed to an increase in amount of the calcined product having higher adsorption capacity. Fig. 6 shows that Mg–Al LDH1 and Mg–Al LDH2 calcined at  $450^\circ\text{C}$  for 10 h adsorbs (from a solution of strength  $30.19 \text{ meq dm}^{-3}$ )  $19.44 \text{ meq g}^{-1}$  and  $22.64 \text{ meq g}^{-1}$ , respectively. This clearly indicates that higher adsorption ability of Mg–Al LDH2 is due to higher  $\text{Al}^{3+}$  content



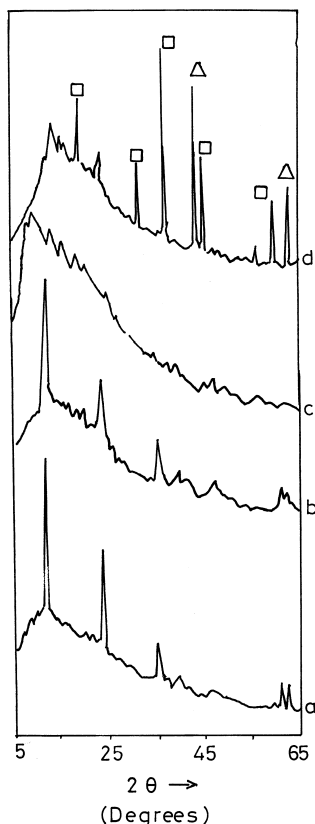


Fig. 5. XRD patterns of (a) Mg–Al LDH2 (b) Mg–Al LDH2 after calcination and rehydration in distilled water (c) Mg–Al LDH2 after calcination and rehydration in  $117.92 \text{ meq dm}^{-3}$  aqueous solution of  $\text{Cr}_2\text{O}_7^{2-}$  ion (d) after calcination of adsorbed species (in Mg–Al LDH2) at  $1250^\circ\text{C}$  ( $\Delta$ , MgO;  $\square$ ,  $\text{MgAl}_2\text{O}_4$ ).

than in Mg–Al LDH1. In case of Zn–Cr LDH and Ni–Al LDH, there is a gradual decrease in adsorption capacity with increase in calcination time.

X-ray diffraction patterns given in Fig. 7 show that Mg–Al LDH2 and Ni–Al LDH on calcination at  $450^\circ\text{C}$  give MgO and NiO, respectively. In case of Mg–Al LDH2, the calcined product gives back the layered hydroxide on rehydration (Fig. 5b). Miyata (1980) has reported that on calcination of Mg–Al LDH below  $800^\circ\text{C}$ ,  $\text{Al}^{3+}$  in the structure remains inside the MgO formed, giving Mg–Al oxide solid solution which is capable of forming back LDH on rehydration. Segregation of this solid solution to MgO and  $\text{MgAl}_2\text{O}_4$  takes place only above  $800^\circ\text{C}$  beyond which it is incapable of reconstruction of layered hydroxide. Although the same is true for Ni–Al LDH, the  $450^\circ\text{C}$  calcined product shows much lower adsorption ability (Fig. 6). This may be attributed to the requirement of hydrothermal treatment for rehydration of the calcined Ni–Al LDH (Kooli et al., 1995). Zn–Cr LDH, on the other hand, on calcination at

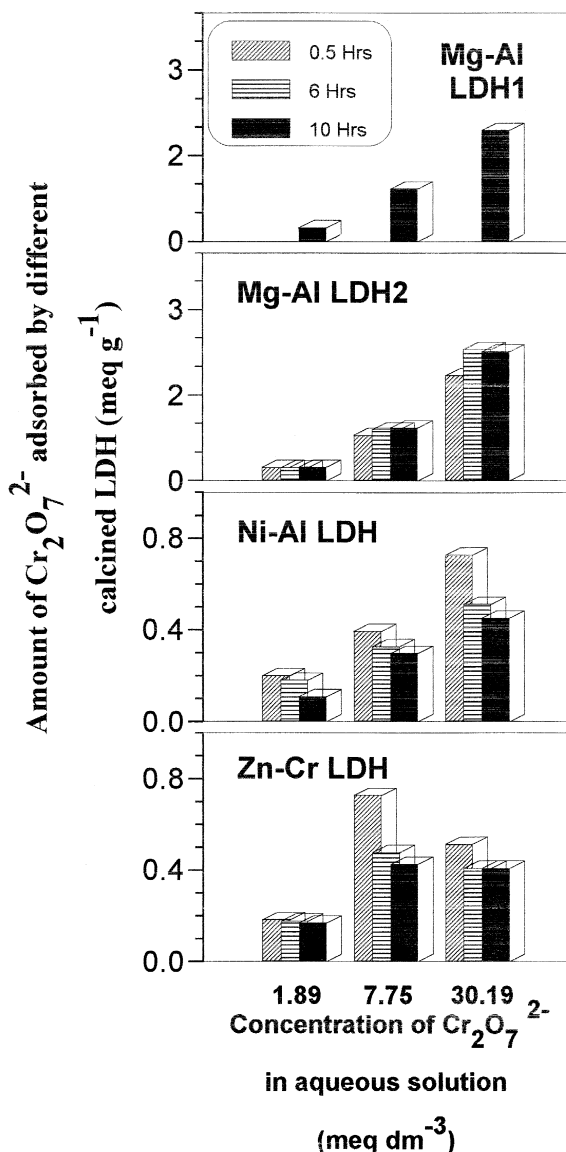


Fig. 6. Adsorption abilities of different calcined LDH.

450°C decomposes by complete segregation to  $\text{ZnO}$  and  $\text{ZnCr}_2\text{O}_4$  (Fig. 7) which are incapable of rehydration and reconstruction.

Release of  $\text{Cr}_2\text{O}_7^{2-}$  from adsorbed solid is dependent upon the nature of anion present in the aqueous phase. When the anion present is stereochemically suitable for inclusion into interlayers of LDH, release of  $\text{Cr}_2\text{O}_7^{2-}$  becomes higher. Fig. 8 shows that the amount and rate of release  $\text{Cr}_2\text{O}_7^{2-}$  by  $\text{CO}_3^{2-}$  solution is much higher than that of  $\text{Cl}^-$  solution. It is because  $\text{CO}_3^{2-}$  is highly

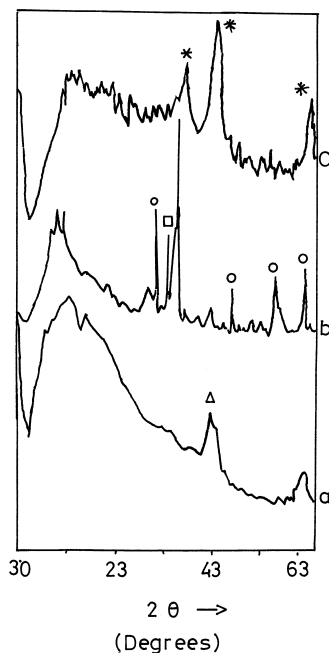


Fig. 7. XRD patterns of LDH calcined at 450°C for 10 h (a) Mg–Al LDH2 ( $\Delta$  MgO), (b) Zn–Cr LDH ( $\circ$  ZnO,  $\square$   $\text{ZnCr}_2\text{O}_4$ ), (c) Ni–Al LDH ( $*$  NiO).

stabilised in the interlayers of LDH (von Allmann, 1970). In comparison to aqueous solutions containing  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$  ion, release with distilled water was found to be very small.

The  $\text{Cr}_2\text{O}_7^{2-}$  adsorbed Mg–Al LDH2 calcined up to 1250°C resulted in the formation of discrete MgO and  $\text{MgAl}_2\text{O}_4$  as the predominant phases along with

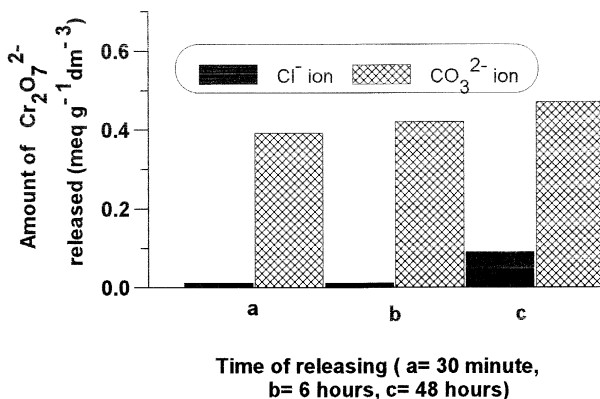


Fig. 8. Release of adsorbed  $\text{Cr}_2\text{O}_7^{2-}$  by  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  ion.

some other minor phases (Fig. 5). These minor phases could not be matched completely with the database of the International Center for Diffraction Data (1996) for different possible combination of elements in the system. Release of  $\text{Cr}_2\text{O}_7^{2-}$  from the calcined product in water for 48 h was found to be higher than in uncalcined product. This higher  $\text{Cr}_2\text{O}_7^{2-}$  release may be due to complete structural breakdown on calcination. However, immobilization of Cr in silicate framework of common building bricks after calcination with tannery sludge has been reported (Knott, 1996).

#### 4. Conclusions

Adsorption capacity of Mg–Al LDH with higher  $\text{Al}^{3+}$  content in the structure is higher than the product with lower  $\text{Al}^{3+}$  content. Adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  in Mg–Al LDH calcined at  $450^\circ\text{C}$  is higher and faster than in uncalcined Mg–Al LDH and calcined ( $450^\circ\text{C}$ ) Ni–Al and Zn–Cr LDH. The  $\text{Cr}_2\text{O}_7^{2-}$  adsorption in calcined Mg–Al LDH follows a two-stage first-order rate kinetics with an approximately 20 times faster reaction rate for the first stage. The adsorption behaviour follows a Freundlich type adsorption isotherm. pH of the initial solutions has no influence on adsorption by calcined Mg–Al LDH. The amount of release of  $\text{Cr}_2\text{O}_7^{2-}$  from the adsorbed products by different agents follows the order  $\text{CO}_3^{2-} > \text{Cl}^- > \text{water}$ . Calcination of adsorbed Mg–Al LDH at  $1250^\circ\text{C}$  does not immobilize the Cr in solid state structure.

#### Acknowledgements

The authors thank Dr. R.K. Baruah, Dr. P.C. Borthakur and Director R.R.L. Jorhat for helping us greatly at different stages of this work.

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