

Cation selectivity during re-crystallization of Layered Double Hydroxides from mixed (Mg, Al) oxides

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Abstract. The Layered Double Hydroxides (LDHs) with different cationic composition were obtained by regeneration process of mixed (Mg, Al) oxide (Mg:Al=2:1) with various regenerating solutions. Significant influence of pH on the cation composition of the LDH, obtained during regeneration process was found. The order of cation selectivity at pH 5-6 of regenerating solution is $\text{Zn} > \text{Fe}^{2+} > \text{Co} \geq \text{Ni} > \text{Cd} > \text{Mn} > \text{Mg} \gg \text{Ca}$, while at high pH values (> 10) Mg-Al LDH is preferably formed. The change of cationic ratio $\text{M}^{2+}:\text{Al}$ depends on the composition of regenerating solution. The regeneration of mixed (Mg, Al) oxide with solutions of M^{2+}Cl_2 or $\text{M}^{2+}(\text{NO}_3)_2$ causes an increase in $\text{M}^{2+}:\text{Al}$ ratio from 2:1 to 2.5:1. The use of regenerating solutions containing an excess of both OH groups and M^{2+} cations, such as $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3$, $\text{Mg}(\text{OH})_2$, $\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}_2$, etc., leads to formation of LDHs with $\text{M}^{2+}:\text{Al}$ ratio = 4.

The obtained influences and dependences of solution composition, pH and the order of selectivity on the LDH composition are very important and useful data in the case of removing of hazardous or useful cations from solutions through regeneration of mixed (Mg,Al) oxide.

Key words: Layered double hydroxide, mixed oxide, regeneration, cation selectivity, cation composition, environmental application

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Цвета Станимирова, Таня Стоилкова, Георги Киров. Катионна селективност при рекристализация на Слоисти Двойни Хидроксиди от смесени (Mg, Al) оксиди

Резюме. Чрез регенерация на смесен (Mg, Al) оксид (Mg:Al=2:1) с различни разтвори са получени различни по състав синтетични аналози на минерали Смесени Двойни Хидроксиди (СДХ). Установено е значително влияние на pH на регенериращия разтвор върху катионния състав на новополучените СДХ. Установява се, че при pH 5-6 на регенериращият разтвор редът на катионна селективност е $\text{Zn} > \text{Fe}^{2+} > \text{Co} \geq \text{Ni} > \text{Cd} > \text{Mn} > \text{Mg} \gg \text{Ca}$, докато при pH > 10 най-стабилен е Mg-Al-СДХ (минералите хидроталкит и майкснерит). Доказна е зависимост на катионното $\text{M}^{2+}:\text{Al}$ отношение от състава на регенериращия разтвор, като регенерацията на смесения оксид с M^{2+}Cl_2 или $\text{M}^{2+}(\text{NO}_3)_2$ води до повишаване на отношението от 2:1 до 2.5:1, а при присъствие и на допълнителен източник на OH групи в регенериращия разтвор (напр. от $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3$, $\text{Mg}(\text{OH})_2$, $\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}_2$), отношението нараства до 4:1.

Установените ред на селективност на M^{2+} катиони, влияние и взимоотношения на различните фактори на регенерационния процес са важни и полезни данни при прилагане на регенерацията на смесен (Mg, Al) оксид за извличане на полезни или вредни катиони от разтвори.

Introduction

The Layered Double Hydroxides (LDHs) with a formula $M^{2+}_{1-x}M^{3+}_x(OH)_2A_{x/m}^{m-}(1-3x/2)H_2O$ gain increasing interest in recent years, because of their wide scope of various applications, easy synthesis and possibilities for post-synthetic modification (Cavani et al., 1991; Newman, Jones, 1998; Vaccari, 1999; Rives, Ulibarri, 1999; Williams, O'Hare, 2006; Duan, Evans, 2006).

An important method for preparation of the LDHs with various inorganic, organic anions and pillared structures is a regeneration in water solution of a mixed Mg, Al oxide (MO) which is a product of thermal decomposition of Mg-Al- CO_3 LDH at 400-800°C (Reichle et al., 1985; Chibwe, Jones, 1989; Newman, Jones, 1998; Rives, Ulibarri, 1999; Rocha et al., 1999). This reaction was also successfully used for extraction of anions from solutions (Kovanda et al., 1999; You et al., 2001a, b; Diaz-Nava et al., 2003; Dusova et al., 2003; Kameda et al., 2003a; Lazaridis, Asouidou, 2003; Cardoso et al., 2003).

The reverse reactions Mg-Al LDH $\rightarrow$ MO $\rightarrow$ Mg-Al LDH were described in literature as "memory effect" with topotactical character of the regeneration reaction (Sato et al., 1988; Marchi, Apestenguia, 1998). On the basis of estimated reaction kinetic, (Millange et al., 2000) and of the results of detailed SEM and XRD investigations (Stanimirova et al., 2001), it was proved that the regeneration is a processes of dissolution of MO and subsequent crystallization of LDH. The dissolution-crystallization mechanism of MO regeneration explains well the formation of LDH with new anions and implies a possibility of changing of cation composition of LDH during regeneration process. Using this phenomenon, we succeeded to change the cationic $Mg^{2+}:Al^{3+}$ ratio by addition of Mg^{2+} or Al^{3+} cations from soluble and low-soluble compounds

(Stanimirova, Kirov, 2003). A zonal catalyst with Ni rich surface was prepared by Takehira et al. (2004) through substitution of Mg^{2+} with Ni^{2+} during regeneration of (Mg, Al) oxide. More recent papers describing simultaneous extraction of cations and anions from water solutions through (Mg, Al) oxide have been also published (Kameda et al., 2003b; Lazaridis, 2003). Therefore, in the present paper it was of interest to determine the exact conditions of extraction of particular divalent cation from solution. We investigated the products and conditions of interaction between MO and aqua solutions with various cation and anion compositions. Both the order of cation selectivity during regeneration and the influence of some factors (pH, solution composition) on the cation substitution and selectivity were studied.

Experimental

The mixed Mg,Al oxide (MO) was obtained by heating of the synthetic Mg-Al- CO_3 LDH (Mg:Al=2:1) at 500°C for 2 hours. The regeneration of MO was carried out at room temperature for 24 h with periodical stirring. Two sets of experiments were performed:

1. Regeneration with solutions containing one type of M^{2+} cations: The 0.25 g MO was added to 40 mL solutions of each $M^{2+}Cl_2$ ($M^{2+} = Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+}$), $CdSO_4$, $Cd(NO_3)_2$, $Ca(OH)_2$, $Na_2Zn(OH)_4$, $Ni(NH_3)_4(H_2O)_2Cl_2$ and $Ni(NH_3)Cl_2$. During the experiments with Ni-ammonia complexes, pH of the solution was maintained constant - 8.6 or 13 by addition of NH_4OH . The content of each mentioned above M^{2+} cation was calculated to be 2-fold excess in regenerating solution.
2. Regeneration with mixed solutions of $Mg^{2+} + M^{2+}$ cations in ratio $M^{2+}/(M^{2+}+Mg^{2+}) = 0.2$,

0.4, 0.6, 0.8 and 1.0, where M^{2+} was Ni^{2+} or Zn^{2+} . The 0.25 g MO was added to 30 mL of solutions which provides 2-fold excess of M^{2+} into solutions.

3. Regeneration with mixed solutions of Mg^{2+} + Ni^{2+} + Zn^{2+} cations in ratio 1:1:1. The 0.25 g MO was added to 30 mL of solutions which provides 2-fold excess of M^{2+} into solutions. The compositions and concentrations of the solutions are shown in Table 1.

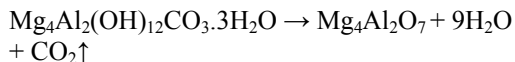
After regenerating process, the samples were washed with distilled water and air dried. For the experiments, chemicals with purity for analysis were used.

The initial sample and final products were characterized by X-ray powder diffraction (XRD) and SEM. The powder XRD patterns were recorded on a TUR M62 diffractometer using Co $K\alpha$ radiation in the 2θ range $4-80^\circ$, continuous scan at 2° min^{-1} . SEM observations were done on microscope JEOL 5510.

The content of Mg, Ni, Zn, Co, Mn, Cd, and Ca were determined by atomic absorption spectroscopy (AAS) - Perkin Elmer 3030 and the Al content was determined by complexometry, as well.

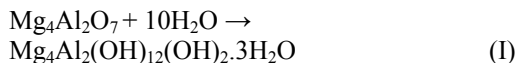
Results and Discussion

The thermal decomposition of Mg-Al- CO_3 LDH ($400-800^\circ\text{C}$) leads to the formation of mixed (Mg,Al)O solid solution (MO) with a periclase-like cubic structure:



The hydration of MO in water solution can be explained as a reaction of hydrolysis, likely to the simple oxides with periclase-like structure. A number of reactions can be observed:

1. Regeneration with pure water:



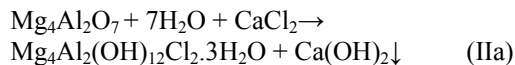
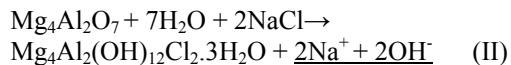
During reaction (I), beside the OH groups formatting LDH hydroxide layers, an extra OH group per each Al atom can be added to the LDH structure as an interlayer anion. Our results supported the proceeding of the

reaction. The obtained product after the regeneration of MO in distilled water (Table 1 - exp. 1) was a Mg-Al LDH with $\text{Mg}^{2+}:\text{Al}^{3+}$ ratio = 2:1 and lattice parameters similar to these published for Mg-Al-OH LDH (Miyata, 1983; Cavani et al., 1991).

On the SEM micrograph, the obtained Mg-Al-OH LDH is built of complex spheroidal aggregates unlike the aggregates of single, platy, hexagonally shaped crystallites of the initial Mg-Al- CO_3 LDH and those of the MO (Fig. 1a, b).

2. Regeneration with solutions containing cations, which are not able to occupy octahedral sites in the brucite-like hydroxide layers of LDH structure:

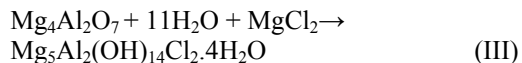
In this case, LDH and soluble or insoluble hydroxides are formed. For example:



The reaction (II) has been described by Sato et al. (1993) as “caustification” of Na_2CO_3 during regeneration of MO, as well as by Kameda et al. (2003a, b) for interpretation of regenerating process of MO with solution of NaCl and acids.

Our experiment of regeneration of MO with CaCl_2 solution (Table 1, exp. 2) confirmed the proceeding of the reaction (IIa). Due to the washing of the products to $\text{pH}=8$, the XRD data showed the presence of CaCO_3 , which had been formed by reaction of unwashed $\text{Ca}(\text{OH})_2$ in the solution with the atmospheric CO_2 .

3. Regeneration with solutions containing cations, which are able to occupy the octahedral sites of hydroxide layers:



According to the reaction (III), only one additional Mg^{2+} cation per formula unit can join to the LDH structure causing an increase in the $\text{Mg}^{2+}:\text{Al}^{3+}$ ratio to 2.5:1. The results of our experiment support such type of regeneration reactions. The regeneration of MO

Table 1. Conditions of regeneration reactions, XRD and chemical results of the products obtained after regeneration of MO

Experiment No	Regenerating solution			pH after reaction MO + solution	X-ray data of reaction products					Chemical analysis of LDH obtained after regeneration M ²⁺ : Mg: Al
					phases	LDH with interlayer anion:				
	Cl ⁻									
	a, nm	c, nm	c, nm			M ²⁺ :Al				
	composition	M	pH		Initial LDH	0.3044	2.280	~ 2:1	0.00: 1.97: 1.00	
1	distilled H ₂ O	-			LDH	0.3046	2.286	2.280 ~ 2:1	0.00: 2.02: 1.00	
2	CaCl ₂	0.5	10.03	11.38	LDH CaCO ₃ >1%	0.3046	2.283	2.283 ~ 2:1	0.00: 2.03: 1.00	
3	MgCl ₂	0.5	8.23	8.34	LDH	0.3056	2.394	2.304 ~ 2.5:1	0.00: 2.51: 1.00	
4	NiCl ₂	0.5	5.90	6.40	LDH	0.3036	2.397	2.307 ~ 2.5:1	2.41: 0.13: 1.00	
5	CoCl ₂	0.5	5.67	6.38	LDH	0.3060	2.396	2.301 ~ 2.5:1	2.32: 0.14: 1.00	
6	ZnCl ₂	0.5	6.02	6.98	LDH	0.3088	2.395	2.304 ~ 2.5:1	2.49: 0.02: 1.00	
7	MnCl ₂	0.5	5.14	6.47	LDH	n.d.	2.397	2.299 ~ 2.5:1	2.24: 0.20: 1.00	
8	Cd(NO ₃) ₂	0.5	5.58	6.77	LDH	0.3264	2.562	LDH <5% CdCO ₃ > 95%	2.35: 0.14: 1.00	
9	Ni(NH ₃) ₄ (H ₂ O) ₂ Cl ₂	0.75	8.60	8.60	LDH	0.3062	2.469	2.393 ~ 4:1	2.51: 1.54: 1.00	
10	Ca(OH) ₂	0.2	13.00	12.80	LDH CaCO ₃ ~13%	0.3044	2.281	2.281 ~ 2:1	0.00: 1.97: 1.00	
11	Ni(NH ₃) ₆ Cl ₂	0.5	13.20	13.15	LDH	0.3040	2.319	2.280 ~ 2:1	0.17: 1.90: 1.00	
12	Na ₂ Zn(OH) ₄	0.15	12.20	12.32	LDH	0.3052	2.285	2.283 ~ 2:1	0.26: 1.84: 1.00	

* c parameter of LDH obtained after exchange of Cl⁻ anions with CO₃²⁻ anions in solution of 0.5 M Na₂CO₃

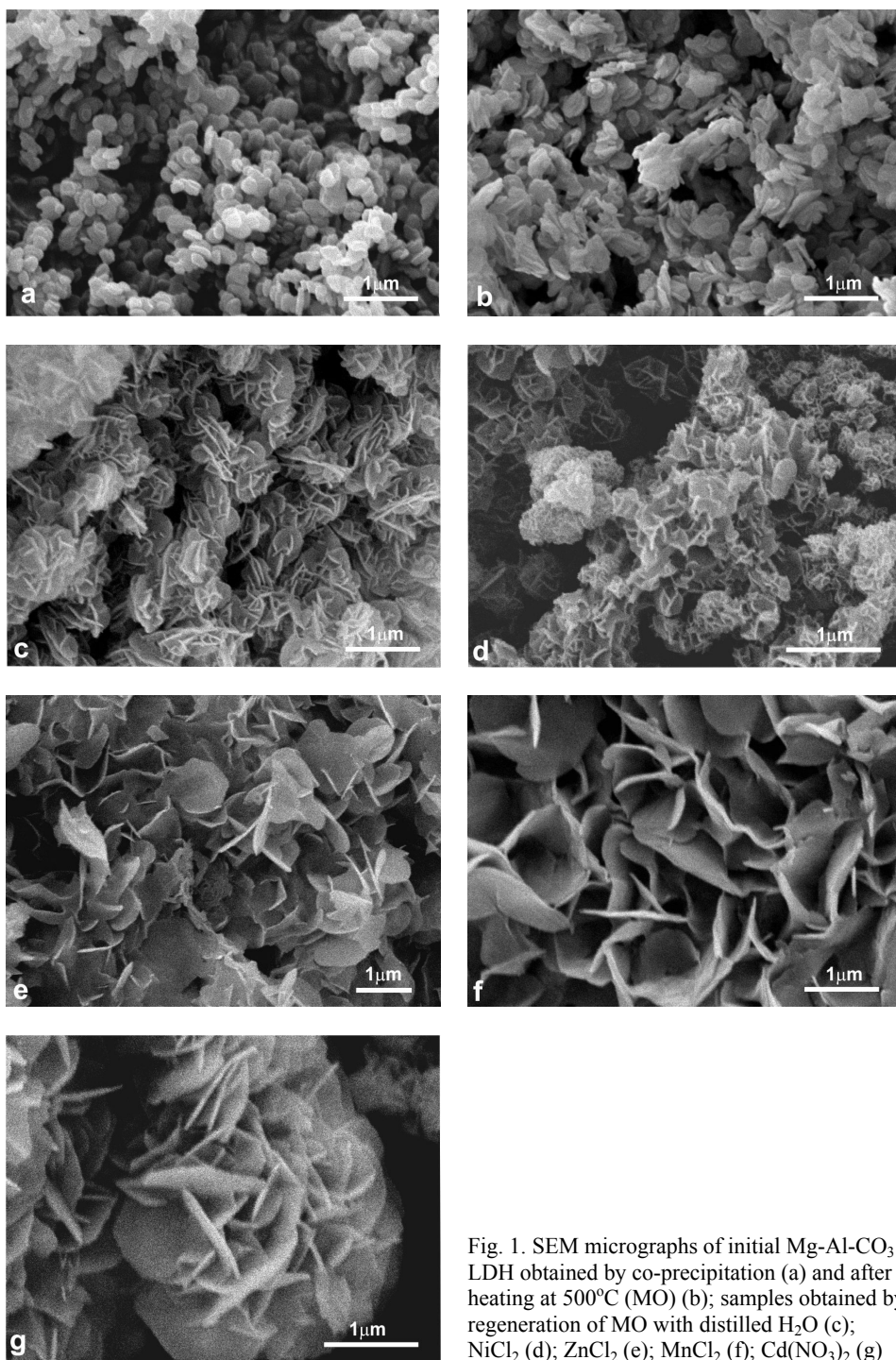
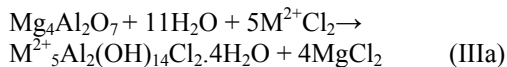


Fig. 1. SEM micrographs of initial Mg-Al-CO₃ LDH obtained by co-precipitation (a) and after heating at 500°C (MO) (b); samples obtained by regeneration of MO with distilled H₂O (c); NiCl₂ (d); ZnCl₂ (e); MnCl₂ (f); Cd(NO₃)₂ (g)

with solution of MgCl_2 caused a formation of LDH with lattice parameters and chemical composition corresponding to LDH with 2.5:1 $\text{Mg}^{2+}:\text{Al}^{3+}$ ratio (Table 1, exp. 3).

The regenerating reactions of MO with solution containing M^{2+} cations different from Mg^{2+} , for example Zn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Mn^{2+} , Fe^{2+} etc., can be summarized as follows:



The results of chemical analysis of LDHs obtained after regeneration of MO with solutions containing Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} and Cd^{2+} cations (Table 1, exp. 4, 5, 6, 7, 8), showed that cationic $\text{M}^{2+}:\text{Al}^{3+}$ ratios of all new crystallized LDHs were 2.5:1 (Table 1). On the other hand, the chemical analyses pointed out that the cation compositions of the LDHs were changed, too. The Mg^{2+} cations of the initial MO were almost entirely substituted by other divalent cations. The values of the lattice parameters estimated from XRD patterns of these LDHs corresponded to the chemical analysis. The parameter a of LDHs obtained after regeneration is changed as the values are in correlation with the corresponding ionic radius of the incorporated M^{2+} cations (Table 1).

The values of the parameter c corresponded to the size of the interlayer anions. The calculated parameter c of LDHs obtained after regeneration, showed that products are either chloride Mg-, Ni-, Co-, Zn-, or Mn-Al LDHs and nitrate Cd-Al LDH. In the case of treatment of MO with solution of different Cd-salts, only regeneration with $\text{Cd}(\text{NO}_3)_2$ was successful and led to formation of Cd-Al LDH, while treatment of MO with CdCl_2 or CdSO_4 , caused destruction of MO and crystallization of $\text{Cd}(\text{OH})\text{Cl}$ or $\text{Cd}_2\text{SO}_4(\text{OH})_2$, respectively.

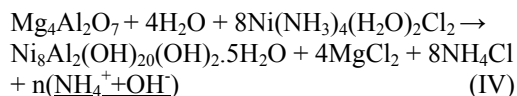
All obtained LDH were exchanged with Na_2CO_3 , in order to use the values of d_{003} ($=c/3$) for comparison of the various LDHs and for determination of the $\text{M}^{2+}:\text{Al}^{3+}$ ratio. The results showed that the interlayer anions of all LDHs were completely exchanged, except Cd-Al LDH which was converted to CdCO_3 . The $\text{M}^{2+}:\text{Al}^{3+}$ ratios estimated from d_{003} values of

CO_3 LDHs were in excellent correlation with those obtained by chemical analysis (Table 1).

The SEM investigation shows that all regenerated samples are represented by typical for LDHs, obtained by regeneration process rose-like aggregates, and the newly formed hexagonal plates have different sizes, depending on the incorporated M^{2+} cation only (Fig. 1 c-g).

The mentioned limitation of increasing of the $\text{M}^{2+}:\text{Al}^{3+}$ ratio to 2.5:1 during regeneration of the MO losses validity when the regenerating solution comprises additional sources of OH groups.

The highest cationic ratio $\text{M}^{2+}:\text{Al}^{3+}$ of 4:1 was achieved by regeneration of MO with Ni-ammonia-chloride complex ($\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}_2$) at $\text{pH}=8.6$ (Table 1 - exp. 9). According to ammonia chemistry, the NH_3 and water molecules in solutions are in equilibrium with NH_4^+ and OH^- ($\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$). The same OH^- groups make an increase in the $\text{M}^{2+}:\text{Al}^{3+}$ ratio possible:

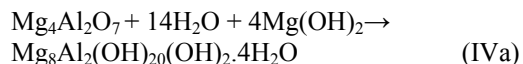


The observed 4:1 $\text{M}^{2+}:\text{Al}^{3+}$ ratio was confirmed by chemical analysis and by the calculated lattice parameters from the XRD pattern of LDH after CO_3 exchange. The chemical analysis of this LDH showed that there is no complete substitution of Mg^{2+} cations with Ni^{2+} ones. The divalent cation composition of the final product is mixed (Mg-Ni)-Al LDH with ratio $\text{Mg}^{2+}:\text{Ni}^{2+}=1:1.6$.

On the other hand, the pH of the regenerating solution influences the substitution of Mg^{2+} cations with various divalent cations and increases the $\text{M}^{2+}:\text{Al}^{3+}$ ratio. A significant substitution took place at pH 6.5-8.0 (Table 1, exp. 3-9), but a very low rate of substitution of Mg^{2+} was observed during regeneration in solutions with high $\text{pH}=12-13$.

As known, Ca-Al LDH is crystallized by co-precipitation at $\text{pH} > 11$. Therefore, it could be expected that during regeneration of MO with $\text{Ca}(\text{OH})_2$ at high pH (Table 1, exp. 10),

Ca-Al LDH would be formed. However, we found that at high pH no substitution of Mg^{2+} from MO took place, which led to crystallization of Mg-Al LDH. The latter suggested that at $\text{pH} > 10$ the Mg-Al LDH is the most stable phase. Similar results were obtained for the regeneration of MO at high pH with solutions containing other M^{2+} cations. The amount of incorporated Ni^{2+} or Zn^{2+} cations into the new formed LDH is less than 10% (Table 1 - exp. 11 and 12). The $\text{M}^{2+}:\text{Al}^{3+}$ ratio of the LDHs obtained during these experiments remained 2:1, because the Mg^{2+} cations in the solution originated from the dissolution of the MO with initial 2:1 ratio. If an excess of Mg^{2+} cations is provided in the regenerating solution, than LDH with maximum $\text{Mg}^{2+}:\text{Al}^{3+}$ ratio of 4:1 would be crystallized. As previously described (Stanimirova, Kirov, 2003), regeneration of MO ($\text{Mg}^{2+}:\text{Al}^{3+}=2:1$) with Mg-rich solutions of $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3$ (hydromagnesite) or $\text{Mg}(\text{OH})_2$ (brucite) result in the formation of LDHs with $\text{Mg}^{2+}:\text{Al}^{3+}=4:1$.



4. Regeneration with mixed M^{2+} -Mg chloride solutions:

Tichit et al. (2001) suggested that the order of cation selectivity during preparation of LDH by direct co-precipitation from multi-component solutions depends on the pH values of precipitation of $\text{M}^{2+}(\text{OH})_2$ as follows: $\text{Ca}(\text{OH})_2$ ($\text{pH}=12.4$), $\text{Mg}(\text{OH})_2$ (9.4), $\text{Mn}(\text{OH})_2$ (7.8), $\text{Cd}(\text{OH})_2$ (7.2), $\text{Ni}(\text{OH})_2$ (6.7), $\text{Co}(\text{OH})_2$ (6.6), $\text{Fe}(\text{OH})_2$ (6.5), $\text{Zn}(\text{OH})_2$ (5.4)

The results obtained from regeneration of MO with Mg-Ni, Mg-Zn and Mg-Ca chloride solutions and regeneration in Mg-Ni-Zn chloride solution, are presented on Figs. 2 and 3, respectively.

The data of regeneration of MO with mixed Mg-Ca chloride solutions suggested that

the Ca^{2+} cations were not incorporated in LDH. Therefore the obtained LDH is composed of Mg-Al-Cl LDH (Fig. 2). The composition of products obtained after regeneration of MO with Mg-Ni and Mg-Zn chloride solutions showed distinctive selectivity of the LDH to incorporated Ni^{2+} and Zn^{2+} cations in comparison with Mg^{2+} . The Zn^{2+} cations were preferably included into LDH in comparison with Ni^{2+} ones (Fig. 2). The same tendency is seen on the diagram of chemical composition of LDH obtained by regeneration of MO with mixed Mg-Ni-Zn chloride solution (Fig. 3). The Zn^{2+} content is ~62 mol %, which is approximately twice more than Ni^{2+} cations (36 mol %), while the Mg-content is insignificant (~2.5 mol %). The lattice parameter a of the obtained Mg-Ni-Zn-Al LDH was 0.3076 nm, very close to the estimated average weighted value (0.3068 nm) of the parameters a of Zn-Al LDH (0.3088 nm), Ni-Al LDH (0.3036 nm) and Mg-Al LDH (0.3044 nm). This result is in agreement to Vegard's rule of isomorphic substitution of ions in structures, which confirmed that the obtained Mg-Ni-Zn-Al LDH is a homogenous solid solution.

Conclusions

The results show that during regeneration of MO at high pH values (>10) the most stable phase is the Mg-Al LDH. At low pH (5.5-8.0) the Mg^{2+} cations were substituted by all of each used cations (Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , Cd^{2+}) except Ca^{2+} ones. At $\text{pH} = 5-6$ during regeneration of MO with chloride or nitrate solutions the order of selectivity of M^{2+} is $\text{Mg}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+}$. This order exactly corresponds to the order of precipitation of simple $\text{M}^{2+}(\text{OH})_2$. Therefore the following order of M^{2+} selectivity during regeneration of MO could be proposed:

$\text{Ca}^{2+} \ll \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Cd}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Zn}^{2+}$. The obtained order is important in the case of removing of hazardous or useful cations from solutions through regeneration of MO.

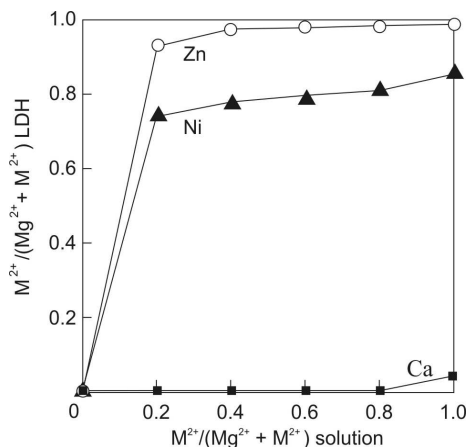


Fig. 2. Composition diagram of the products obtained after regeneration of MO with mixed Mg^{2+} - M^{2+} chloride solutions

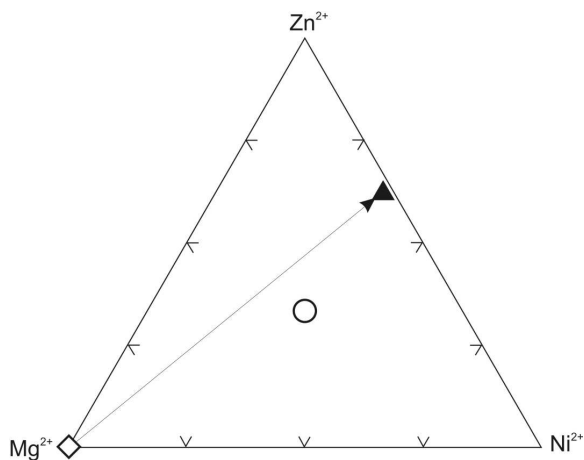


Fig. 3. Ternary diagram of the cation composition of starting MO (◇), regenerating solution (○) and resulting LDH (▲)

The cationic ratio $M^{2+}:Al^{3+}$ during regeneration of MO with chloride or nitrate solutions is changed from 2:1 to 2.5:1. The higher values of cationic ratio (up to 4:1) are reached by providing an excess of both OH groups and M^{2+} cations. This result is useful for determination of quantities of removed cations from solutions.

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