Compositional and Structural Control on Anion Sorption Capability of Layered Double Hydroxides (LDHs)

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ABSTRACT

Layered double hydroxides (LDHs) have shown great promise as anion getters. In this paper, we demonstrate that the sorption capability of a LDH for a specific oxyanion can be greatly increased by appropriately manipulating material composition and structure. A large set of LDH materials have been synthesized with various combinations of metal cations, interlayer anions, and the molar ratios of divalent cation M(II) to trivalent cation M(III). The synthesized materials have then been tested systematically for their sorption capabilities for pertechnetate (TcO_4^-). It is discovered that for a given interlayer anion (either CO_3^{2-} or NO_3^-) the Ni-Al LDH with a Ni/Al ratio of 3:1 exhibits the highest sorption capability among all the materials tested. The distribution coefficient (K_d) is determined to be as high as 307 mL/g for $Ni_6Al_2(OH)_{16}CO_3 \cdot nH_2O$ and 1390 mL/g for $Ni_6Al_2(OH)_{16}NO_3 \cdot nH_2O$ at a pH of 8. The sorption of TcO_4^- on M(II)-M(III)-CO_3 LDHs is dominated by the edge sites of LDH layers and strongly correlated with the basal spacing d_{003} of the materials, which increases with the decreasing radii of both divalent and trivalent cations. The sorption reaches its maximum when the layer spacing is just large enough for a pertechnetate anion to fit into a cage space between two neighboring octahedra of metal hydroxides at the edge. Furthermore, the sorption is found to increase with the crystallinity of the materials. For a given combination of metal cations and an interlayer anion, a best crystalline LDH material is obtained generally with a M(II)/M(III) ratio of 3:1. Replacement of interlayer carbonate with readily exchangeable nitrate greatly increases the sorption capability of a LDH material for

pertechnetate, due to the enhanced adsorption on edge sites and the possible contribution from interlayer anion exchanges. The work reported here will help to establish a general structure-property relationship for the related layered materials.

INTRODUCTION

Layered double hydroxides (LDHs) are a group of anionic clays that have positively charged layers of metal hydroxides, between which are located anions and, in general, some water molecules [1]. The metal hydroxide layers have structures similar to brucite $Mg(OH)_2$ in which divalent cations are octahedrally surrounded by hydroxyl groups with the resulting octahedra sharing edges to form infinite sheets. A certain amount of these divalent cations are isomorphously replaced by trivalent cation, giving rise to positively charged metal hydroxide layeres; and the excessive charges are then balanced by interlayer anions. The general formula of LDHs are represented by $M(II)_{1-x}(M(III)_x(OH)_2Y_{x/n}$, where $M(II)$ and $M(III)$ represent the divalent and trivalent cation respectively; Y is the interlayer anion; and n is the charge of the interlayer anion. Most common LDHs are based on double hydroxides of main group metals such as Mg, Ca and Al and transition metals such as Ni, Co, Cr, Zn, Fe, etc. Among the interlayer anions known to incorporate into LDHs are a variety of negatively charged species including CO_3^{2-}, SO_4^{2-}, NO_3^-, and even complexes of metals [2].

LDH materials are known to have high anion sorption capacities[1], with a typical ion exchange capacity of ~ 3.5 meq/g [3]. Both interlayer exchange and surface adsorption probably contribute to the measured sorption capacity of a LDH material, since the point of zero charge (PZC), for example, for Mg-Al-CO_3 LDH can be as high as 12-12.5 [4]. LDH materials have been suggested for removal of chromate, phosphate, chloride ion, anionic surfactants, ionic dyes, and humic substances from water [5-14]. Calcination of LDHs generally increases the sorption capability of the materials [15-17].

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[1] Hereafter term "sorption" is referred to a general sense of ion uptake that could include both surface adsorption and interlayer ion exchange.

The enhanced reactivity is probably due to the removal of strongly bound carbonate ions from the interlayer during heating and the subsequent replacement by readily-exchangeable hydroxyl groups during rehydration [15].

The primary objective of the work reported here is to develop a getter material for large-scale removal or immobilization of anionic radionuclides such as ^{99}Tc, ^{79}Se, and ^{129}I in radioactive waste treatment and disposal. These long-lived radionuclides are highly soluble and poorly retarded by geologic materials under oxidizing conditions, thus posing a serious environmental concern [17]. Among the candidate getter materials identified so far, LDHs have shown the most promise [18-20]. In this paper, we demonstrate that the sorption capability of a LDH for pertechnetate (TcO$_4^-$) can be greatly enhanced by appropriately manipulating material composition and structure in their synthesis. The results reported here will help to establish a general structure-property relationship for LDH materials that will guide us to engineer these materials for optimal removal of a specific oxyanion.

EXPERIMENTAL SECTION

Synthesis of LDH Materials

The LDH materials used in this study were prepared by co-precipitation. A divalent metal M(II) salt solution was mixed with a trivalent metal M(III) salt solution at a desired M(II)/M(III) molar ratio. The mixture was then titrated with a basic solution, either a Na$_2$CO$_3$ (15%) or a 4 M NaOH solution, in the presence of a chosen interlayer anion - either carbonate, sulfate or nitrate - with vigorous stirring at a room temperature. The pH of the solution was monitored, and the titration was concluded when the pH reached above the logarithmic values of the hydrolysis constants of the corresponding metal cations. The resulting suspension was subsequently aged for several hours at 60 °C in an isothermal oven. The suspension was then cooled to a room temperature, filtered with 0.2 μm membranes, and rinsed with deionized water thoroughly to remove any

excess salt. The resulting solid was vacuum-dried at 40 °C, and a LDH material was finally obtained.

Our study requires synthesis of a large set of LDH materials that encompass sufficient compositional variability. More than 40 LDH materials were synthesized with various combinations of divalent and trivalent metal cations: M(II) - Mg, Zn, Co, Ni, Cu, Fe, Cd, Pd, and Mn; and M(III) - Al, Fe, Cr, V, Y, Yb, La, Ga, and Bi. Interlayer anions of interest include carbonate, nitrate, and sulfate. The ratio of M(II)/M(III) in the synthesized materials spanned from 1 to 10. A single phase of LDH was relatively easily obtained with a M(II)/M(III) ratio between 2 and 5 for most metal cations. However, not all metal combinations had led to the formation of a pure LDH phase at desired M(II)/M(III) ratios, and the data presented below are only for those that have been confirmed by powder X-ray diffraction (XRD).

The XRD analysis was carried out using a Bruker analytical X-ray diffractometer with a Cu-K□ anode target ($\lambda = 0.154$ nm) and operating at 40kV and 40 mA. The XRD analysis was used to check whether the material obtained from each synthesis consisted of a pure LDH phase. The ratio of M(II)/M(III) was determined by the total amounts of divalent and trivalent salts added during the synthesis. At the end of each synthesis, the aqueous solution was analyzed for the amounts of metals remaining in the solution. The analysis was performed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The amounts of metals remaining in the solution were found to be negligible.

Sorption Experiments

All the synthesized LDH materials were tested for their adsorption capabilities for pertechnetate (TcO_4^-). In each test, 0.1 g of a dry LDH material was weighed into a 40-mL centrifuge tube and equilibrated with 20 mL de-ionized water overnight. The pH of the solution was adjusted to approximately neutral (7.25 ± 0.25). 0.1 mL of TcO_4^- (10^{-4} M) was then spiked into each centrifuge tube. The tubes were shaken for 24 hours. The samples were then centrifuged at 3500 rpm for 5 min. 1 mL of the supernatant of each

sample was placed into a vial containing 15 mL cocktail solution. The solution was well mixed and subjected to a liquid scintillation count. The equilibrium pH for sorption was measured at the end of each experiment.

Liquid scintillation counts were performed on Tri-CARB Liquid Scintillation Analyzer (Model Standard 2700TR) equipped with the patented Time-Resolved Liquid Scintillation Counting technique and able to perform a three-dimensional analysis (counts/channel, pulse height in keV, and time) during collecting counts from a sample. Each analysis was performed at a count time of 10 minutes per sample on a channel-by-channel basis. The □-activity was recorded and then converted to a mass concentration. A distribution coefficient (K_d) of Tc between the solid and the liquid was calculated from two replicates of measurements at an initial Tc concentration of 1.24×10^{-6} M.

RESULTS AND DISCUSSION

Compositional control on crystal structures

For a given interlayer anion, the basal spacing d_{003} (i.e., the thickness of a brucite layer plus the interlayer spacing) of a LDH material strongly depends on the choice of both divalent and trivalent cations (Figure 1). The basal spacing d_{003} is found to linearly decrease with the radii of both divalent and trivalent cations. The actual mechanism for this is still unknown. In general, an oxygen atom in a M-O(H) structure is bound preferentially to a metal cation with a small radius, making the hydrogen ion more easily dissociated from the oxygen atom [21]. In a LDH, the same polarizing effect may weaken the bonding between the brucite layer and the interlayer anions, thus causing the expansion of interlayer spacing for small metal cations. Figure 1 also shows that divalent cations apparently have a much larger impact on the basal spacing d_{003} than trivalent cations, probably because the former account for a major fraction of total metal cations in the materials.

Furthermore, for chosen metal cations and an interlayer anion, the crystallinity of LDH materials depends on the ratio of M(II)/M(III) (Figure 2). The best crystalline phase of Ni-Al-CO$_3$ LDH is obtained with a Ni/Al ratio of 3:1, corresponding to the Mg/Al ratio in the naturally occurring LDH – hydrotalcite [22]. It is thus postulated that this specific ratio gives rise to a LDH phase that may be energetically more stable than those with other M(II)/M(III) ratios. Two competing factors may affect the stability of a LDH phase: The more M(II) cations are substituted by M(III), the more positive charges would result on brucite layers, thus leading to the stronger bonding between the brucite layers and the interlayer anions and therefore a more stable LDH phase; on the other hand, upon a cation substitution, additional energy would be introduced due to the lattice distortion created by the size difference between the two cations. Therefore, the most stable LDH phase is expected to be the one with a M(II)/M(III) ratio that best compromises the two competing factors.

Finally, as shown in Figure 2, the interlayer spacing of the synthesized materials remain practically unchanged as the M(II)/M(III) ratio varies, which is consistent with the observation that the d-spacing of pyroaurites - a Mg-Fe(III)-CO$_3$ LDH - only slightly increases as the Mg/Fe(III) ratio changes from 2 to 4 [23]. A similar observation was reported for Mg-Al-CO$_3$ and Ni-Al-CO$_3$ LDHs [24].

Effect of pH and ionic strength

TcO$_4^-$ sorption on Ni-Al-CO$_3$ LDHs is sensitive to both the pH and the ionic strength changes in the solution (Figure 3), thus strongly suggesting that the sorption take place mostly on the external surface sites of the materials. Since divalent anions are known to have higher affinities for the interlayer sites than monovalent anions [25-26], it is reasonable to expect that a significant interlayer ion exchange of TcO$_4^-$ for interlayer CO$_3^{2-}$ is unlikely. A linear extrapolation of log K$_d$ data to high pH values in Figure 3 leads the sorption lines for three different ionic strengths to crossover at a pH of 10.7, which falls in the estimated range of the point of zero charge (PZC) of Ni-Al-CO$_3$ LDH. This range is estimated from Ni hydroxide, based on the consideration that hydrotalcite –

Mg-Al-CO$_3$ LDH – has a PZC similar to Mg hydroxide [4, 27]. Ni hydroxide has been reported to have PZC values ranging from 10.3 to 11.2 [28-29].

Depending on their constituents, different LDH materials can have quite different stability ranges in pH, and it is thus difficult to measure the distribution coefficients of all the synthesized LDH materials under similar pH conditions. Therefore, in order to compare the sorption capabilities of these materials, the measured K_d values must be corrected for the pH effect. As shown in Figure 3, the log K_d for TcO_4^- sorption on Ni-Al-CO$_3$ LDH in de-ionized water is roughly proportional to 1/3 pH. A similar relationship is also found for Ni-Al-NO$_3$ LDH. As a first order approximation, this functionally linear relationship is used to correct all K_d values obtained from our sorption experiments, and the corrected K_d values are tabulated in Tables 1 through 3.

TcO_4^- sorption to edge sites: A cage effect

For a given interlayer anion, the sorption capability of a LDH material strongly depends on the choice of both divalent and trivalent cations (Figures 4 and 5). Among all the combinations of metal cations tested, Ni-Al-LDH exhibits the highest sorption capability for TcO_4^-, with a K_d value of 307 mL/g for Ni-Al-CO$_3$ LDH at a pH of 8. The sorption capabilities of LDH materials follow the order of Al > Cr > Ga > Bi for trivalent cations and Ni > Co > Mg > Zn > Fe > Cu □Cd for divalent cations.

A strong correlation has been found between the measured K_d values and the basal spacing d_{003} of LDH materials (Figure 6). With a small increase (~ 0.5 Å) in the basal spacing, the distribution coefficient K_d increases by more than two orders of magnitude. This suggests that TcO_4^- sorption onto the external surface of a carbonate LDH may actually take place at the edge sites of LDH layers since the chemical environment of these sites are expected to be very sensitive to layer-spacing changes. As demonstrated in Figure 1, the layer spacing of LDH materials increases with the decreasing radii of both divalent and trivalent cations. The combination of Ni and Al gives rise to the largest basal spacing and therefore the highest K_d among all the metal combinations we have tested.

One would then expect that the sorption of TcO_4^- could be enhanced by further increasing the basal spacing d_{003}. To test the idea, we replace interlayer CO_3^{2-} anions with large SO_4^{2-} anions. The resulting LDHs have much larger layer spacing than the original carbonate LDHs. For instance, the basal spacing d_{003} of Ni-Al-SO$_4$ LDH is determined to be 8.5 Å as compared to 7.7 Å of Ni-Al-CO$_3$ LDH. Also note that the layer spacing of sulfate LDHs can be further expanded by hydration after the materials are exposed to water [30]. Then, according to Figure 6, sulfate LDHs should have higher K_d values than their carbonate counterparts for TcO_4^- sorption. However, to our surprise, the sorption of TcO_4^- on sulfate LDHs is found to be very poor (i.e., no sorption was detected for all sulfate LDHs synthesized in our experiments), even though SO_4^{2-} is more readily exchangeable than CO_3^{2-} [25] and both SO_4^{2-} and TcO_4^- share a similar molecular configuration (i.e., both S and Tc are tetrahedrally coordinated by oxygen atoms). One plausible explanation for this is that the maximum sorption of TcO_4^- onto LDH edge sites occurs when the basal spacing is just large enough for a pertechnetate anion to fit into a cage space at the edge of LDH layers.

As illustrated in Figure 7, a cage space for TcO_4^- sorption does exist between two neighboring octahedra of metal hydroxides at the edge of LDH layers. Tc is tetrahedrally coordinated in TcO_4^-. A TcO_4^- anion is adsorbed into a cage space by attaching its top vertex to an OH$^-$ site and its base vertices to an interlayer anion position at the edge. The size of the cage along the c-axis direction is the brucite-layer thickness plus half the interlayer spacing. The thickness of a brucite layer in LDHs is about 2 Å [22, 31]. Given the basal spacing d_{003} of 7.7 Å for Ni-Al-CO$_3$ LDH (Figure 1), the interlayer spacing for this material is estimated to be ~ 5.7 Å and thus the cage size to be ~ 4.85 Å, which can perfectly accommodate a pertechnetate anion of a size of ~ 4.54 Å (estimated from ReO$_4^-$ [32]). Either a too large or a too small cage size would tend to destabilize the adsorbed pertechnetate anion. In addition to the cage size, the sorption of TcO_4^- is also expected to depend on how easily the OH$^-$ group and the interlayer anion at the edge can be displaced by the target anion as it fits into the cage. Apparently, this displacement is affected by the chemistry of the contacted solution, for example, the pH as shown in Figure 3.

Effect of crystallinity

For a given choice of metal cations, the sorption capability of a LDH material is also controlled by the M(II)/M(III) ratio of the material (Figure 8). For example, the maximum sorption of pertechnetate by Ni-Al-CO$_3$ LDH is attained at the Ni/Al ratio of 3:1 (Figure 7). Interestingly, this optimal ratio corresponds to the LDH phase with the best crystallinity (Figure 2), thus suggesting that the sorption of TcO$_4^-$ is closely related to the ordering degree of layer structures. This result is consistent with the observation of ReO$_4^-$ sorption onto a calcined Mg-Al-CO$_3$ LDH [33]. ReO$_4^-$ is generally used as a chemical analog to TcO$_4^-$ since both anions exhibit a similar sorption behavior [19]. LDH calcined at less than 300°C rapidly rehydrates and structurally reconstitutes when exposed to water or even to humid air [34]. It has been found that, different from other anions (such as SeO$_4^{2-}$ and AsO$_4^{3-}$), ReO$_4^-$ sorption on a calcined LDH material is to a large extent controlled by the degree of layer structure reconstruction after the material is immersed in water [33]. It is also reported that the better the crystallinity the higher the I$^-$ sorption is on Mg-Al-NO$_3$ LDHs with the same Mg/Al ratio [35].

Effect of interlayer anion

As discussed above, the adsorption of TcO$_4^-$ into a cage space of a LDH depends on how easily the interlayer anion at the edge can be displaced by the target anion as it fits into the cage. It is expected that replacement of the interlayer anion CO$_3^{2-}$ with a readily exchangeable anion such as NO$_3^-$ could further enhance the sorption capability of a LDH for TcO$_4^-$, if the resulting cage size remains more or less the same. A XRD analysis has confirmed that nitrate LDHs we synthesized with a M(II)/M(III) ratio of 3:1 have the basal spacing d_{003} either similar to or slightly larger than their carbonate counterparts[2]; for instance, the basal spacing of Mg-Al-NO$_3$ LDH is determined to be 7.86 Å as compared to 7.64 Å for Mg-Al-CO$_3$ LDH. As shown in Figures 4 and 5, nitrate LDH

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[2] We notice that a relatively large variation in the basal spacing has been reported for nitrate LDHs. For example, the reported basal spacing for Mg-Al-NO$_3$ LDHs ranges from 7.92 to 8.79 Å [25, 30, 36]. The large layer spacing seems to appear in the materials with low M(II)/M(III) ratios (~ 2:1) and has been attributed to the steric repulsion between the interlayer anions the causes nitrate anions to tilt away from the *a-b* plan [36].

materials indeed have systematically higher sorption capabilities for TcO_4^- than their carbonate counterparts. The K_d value for $Ni_6Al_2(OH)_{16}NO_3 \cdot nH_2O$ has been found to be as high as 1390 mL/g at pH 8. It is also interesting to note that the effect of metal cations on pertechnetate sorption onto nitrate LDHs seems to follow the same pattern as the carbonate LDHs, with the Ni-Al phases having the highest K_d values among all the metal combinations (Figures 4 and 5). All these observations seem to support the concept of TcO_4^- adsorption into a cage space at the edge of LDH layers as postulated above. Finally, the enhanced sorption capabilities of nitrate LDHs may also be partly due to the contribution from actual interlayer anion exchanges, given that NO_3^- is highly exchangeable as an interlayer anion [25].

Toward a general functional relationship for material manipulations

The results presented here will help to establish a general structure-property relationship for LDH materials that will allow us to purposefully manipulate these materials for optimal sorption of a specific oxyanion. The cage effect on edge site sorption proposed above is of particular interest. For instance, to develop a TcO_4^- getter material for radioactive waste disposal, we must be able to demonstrate the long-term stability of the material. For this purpose, the replacement of interlayer anion CO_3^{2-} with a more readily exchangeable anion such as NO_3^- may not be a viable approach, because carbonate ions are ubiquitously present in natural systems and can easily exchange with interlayer NO_3^-, thus quickly rendering the material ineffective. An alternative approach would be to enhance the sorption capabilities of carbonate LDHs - the phases thermodynamically stable in the nature - by engineering the adsorption cages at the edge of LDH layers through the choices of an appropriate combination of metal cations and the ratio of M(II)/(M(III). As demonstrated in this paper, $Ni-Al-CO_3$ LDH with the Ni/Al ratio of 3:1 may be a good candidate for this specific application.

CONCLUSION

A series of LDH materials have been synthesized with various combinations of metal cations, interlayer anions, and the molar ratios of divalent cation to trivalent cation. The synthesized materials have been systematically tested for their sorption capabilities for pertechnetate (TcO_4^-). It is discovered that for a given interlayer anion the Ni-Al LDH with a Ni/Al ratio of 3:1 exhibits the highest sorption capability among all the materials tested. The distribution coefficient (K_d) is determined to be as high as 307 mL/g for $Ni_6Al_2(OH)_{16}CO_3 \cdot nH_2O$ and 1390 mL/g for $Ni_6Al_2(OH)_{16}NO_3 \cdot nH_2O$ at a pH of 8. The sorption of TcO_4^- on M(II)-M(III)-CO_3 LDHs is strongly correlated with the basal spacing d_{003} of the materials, which systematically decreases with the radii of both divalent and trivalent cations. The sorption seems to take place at edge sites of LDH layers, and it reaches the maximum when the layer spacing is just large enough for a pertechnetate anion to fit into a cage space between two neighboring octahedra of metal hydroxides at the edge. Furthermore, the sorption also increases with the crystallinity of the materials. For a given choice of metal cations and interlayer anion, the best crystalline LDH phase is generally obtained with a M(II)/M(III) ratio of 3:1. Replacement of interlayer carbonate with nitrate significantly increases the sorption capabilities of LDH materials for pertechnetate, due to the enhanced adsorption on the edge sites and the possible contribution from interlayer anion exchanges. The results reported here will help establish a general structure-property relationship that will guide to engineer LDH materials for removal of a specific oxyanion.

ACKNOWLEDGMENTS

providing Ni-Al-NO$_3$ LDH material.

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FIGURE CAPTIONS

Figure 1. Correlation of the basal spacing d_{003} of M(II)-M(III)-CO$_3$ LDHs with the radii of cations. Radii of cations are from references [37 - 38].

Figure 2. X-ray diffraction patterns of Ni-Al-CO$_3$ LDHs with various Ni/Al ratios. Note that the material with a Ni/Al ratio of 3:1 has the best crystallinity.

Figure 3. Effects of pH and ionic strength on pertechnetate sorption on Ni-Al-CO$_3$ LDH. Linear extrapolations of the data lead the sorption lines for three ionic strengths to crossover at a pH of 10.7, within the range of the point of zero charge (PZC) of Ni-Al-CO$_3$ LDH estimated from Ni(OH)$_2$. The PZC range is represented by the horizontal bar.

Figure 4. Distribution coefficients (K$_d$) of pertechnetate sorption on carbonate LDHs as a function of trivalent cations. No data is available for Ni-Ga-CO$_3$ LDH.

Figure 5. Distribution coefficients (K$_d$) of pertechnetate sorption on carbonate LDHs as a function of divalent cations.

Figure 6. Correlation of the distribution coefficients of pertechnetate sorption on M(II)-M(III)-CO$_3$ LDHs with the basal spacing d_{003} of the materials

Figure 7. Schematic representation of pertechetate sorption on M(II)-M(III)-CO$_3$ LDHs. Pertechnetate anions tend to fit into the cage spaces between the two octahedra of metal hydroxides. The size of the cage spaces depends on the layer spacing.

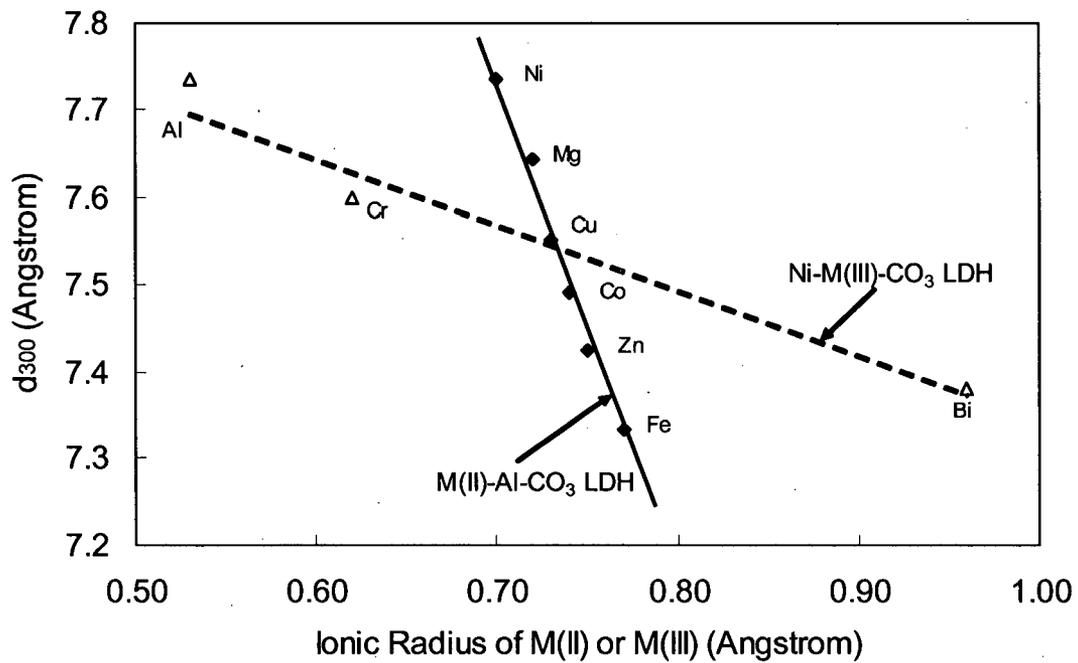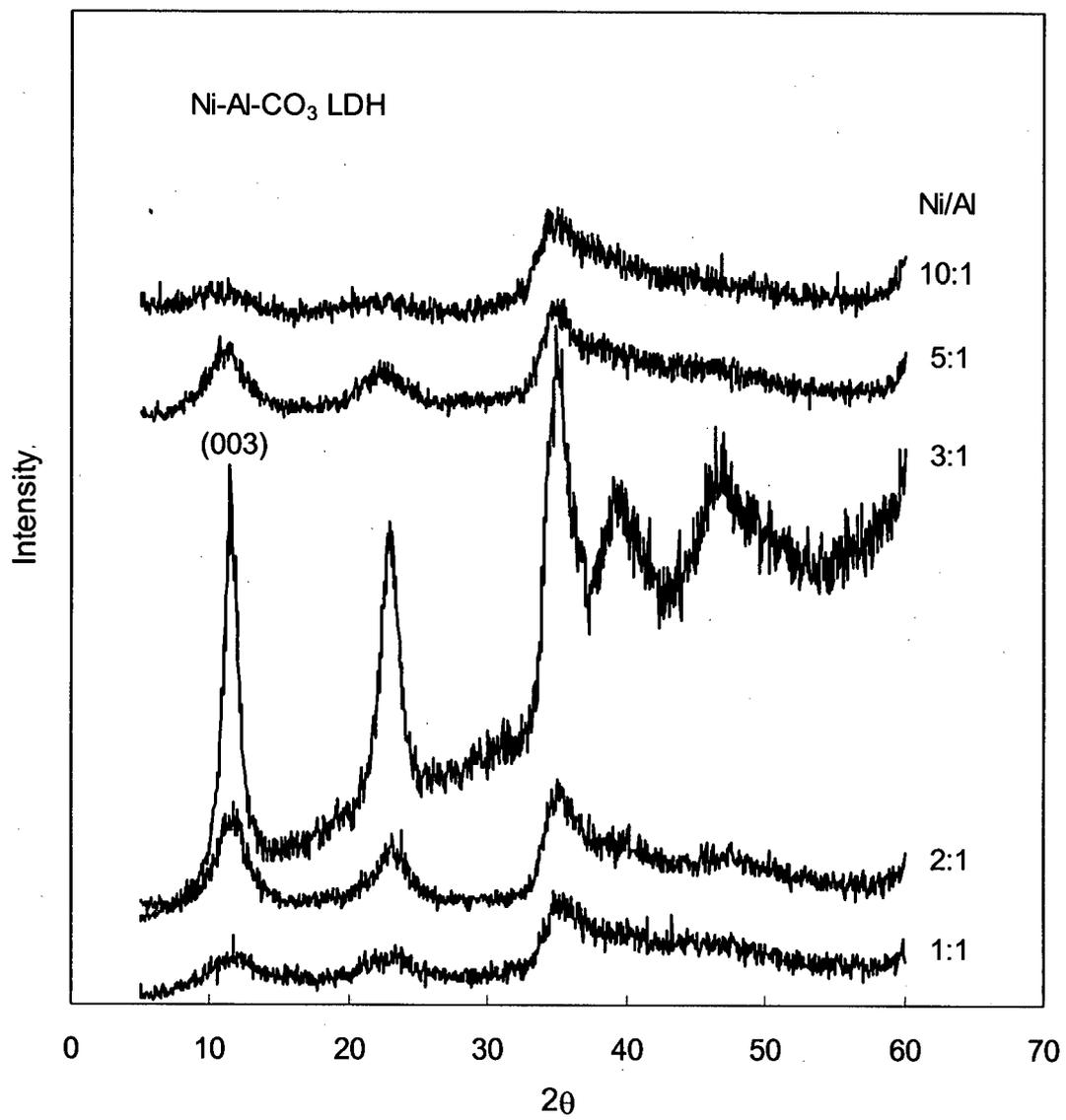**Figure 8.** Dependence of distribution coefficient of pertechnetate sorption on the ratio of M(II)/M(III) in LDHs.
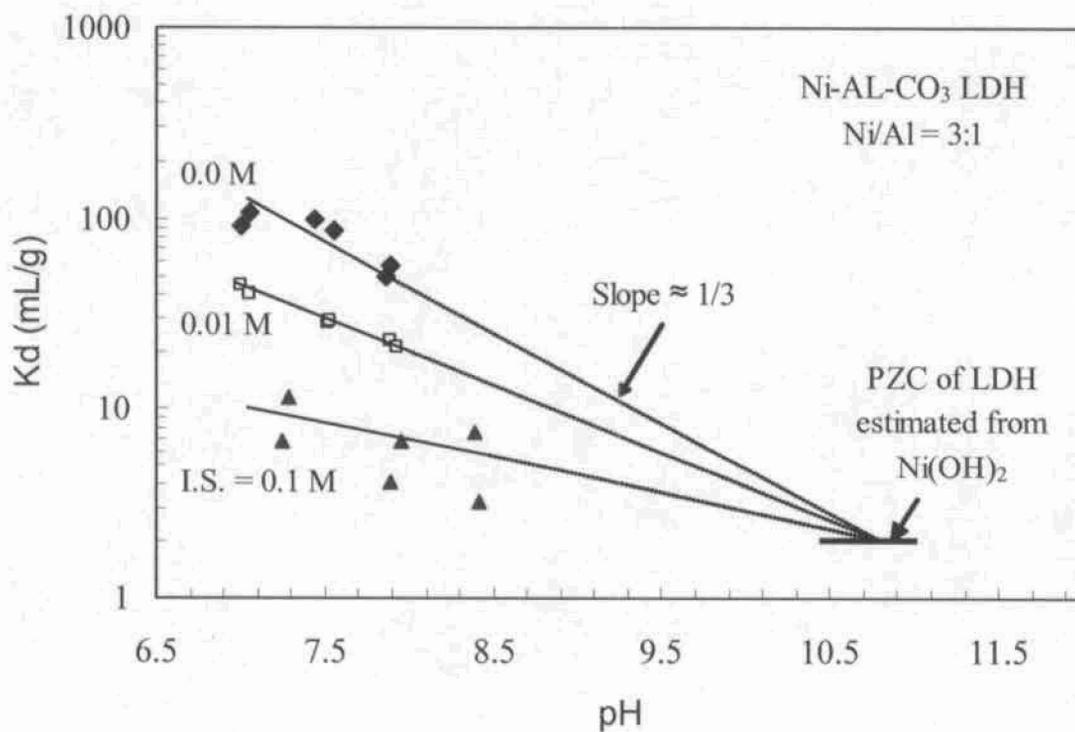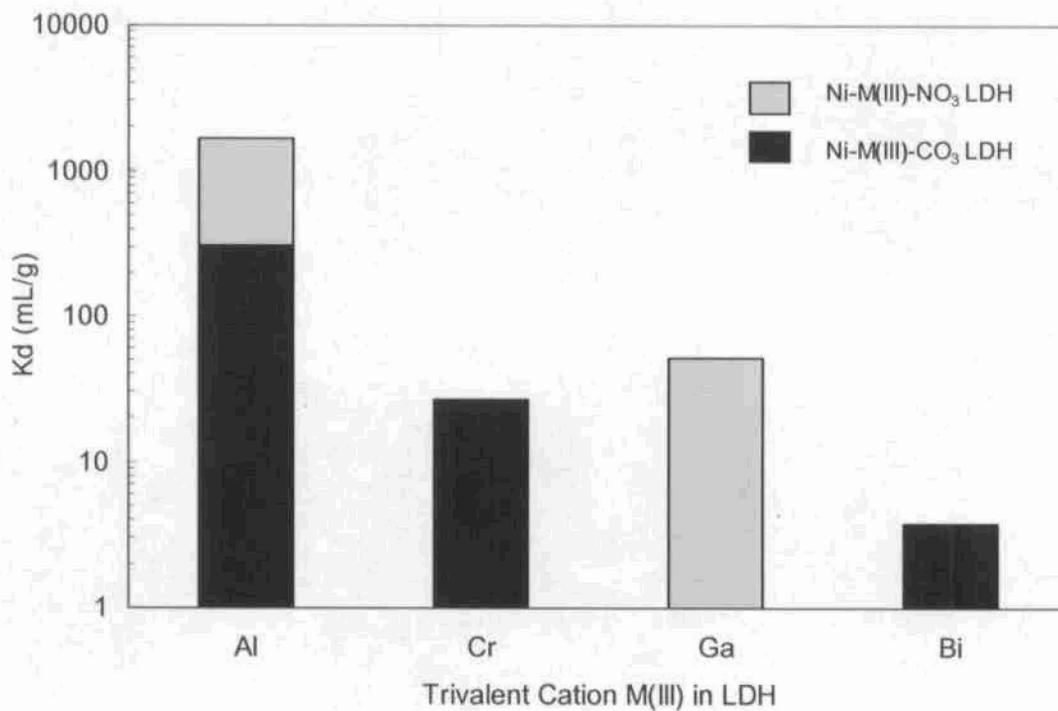
Figure 1
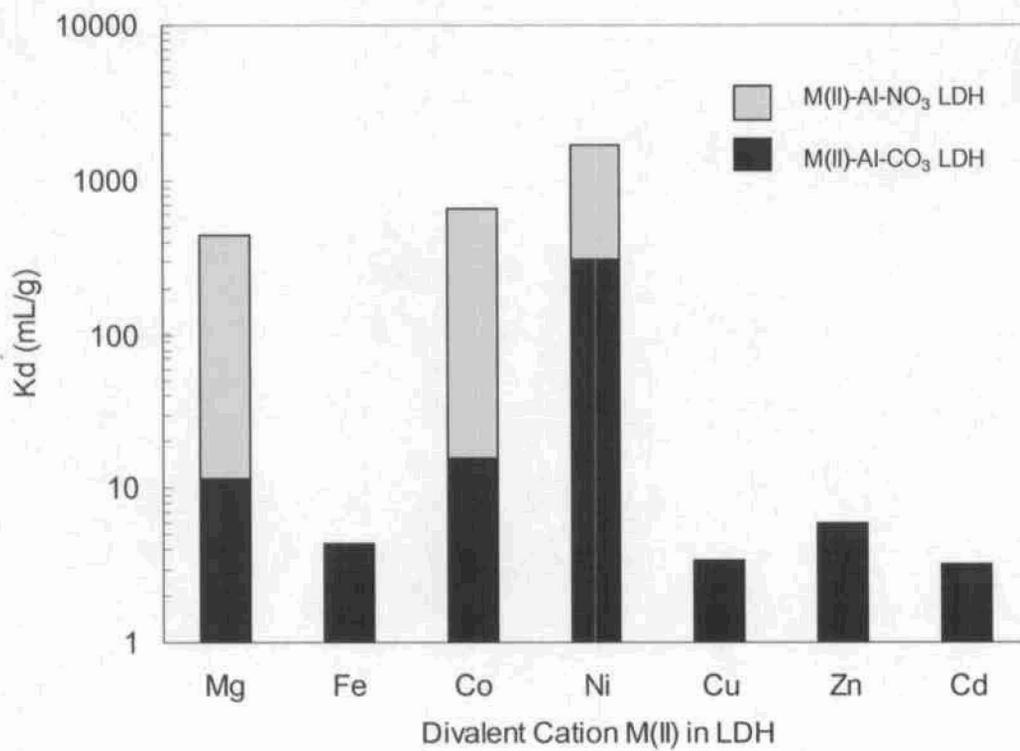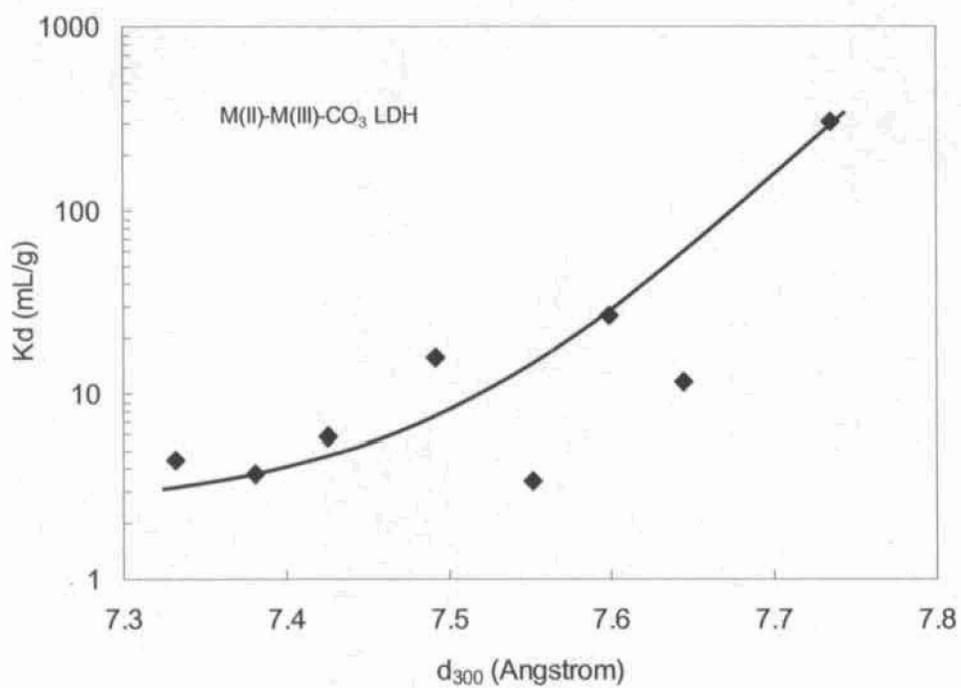
Figure 2

Figure 3

Figure 4

Figure 5
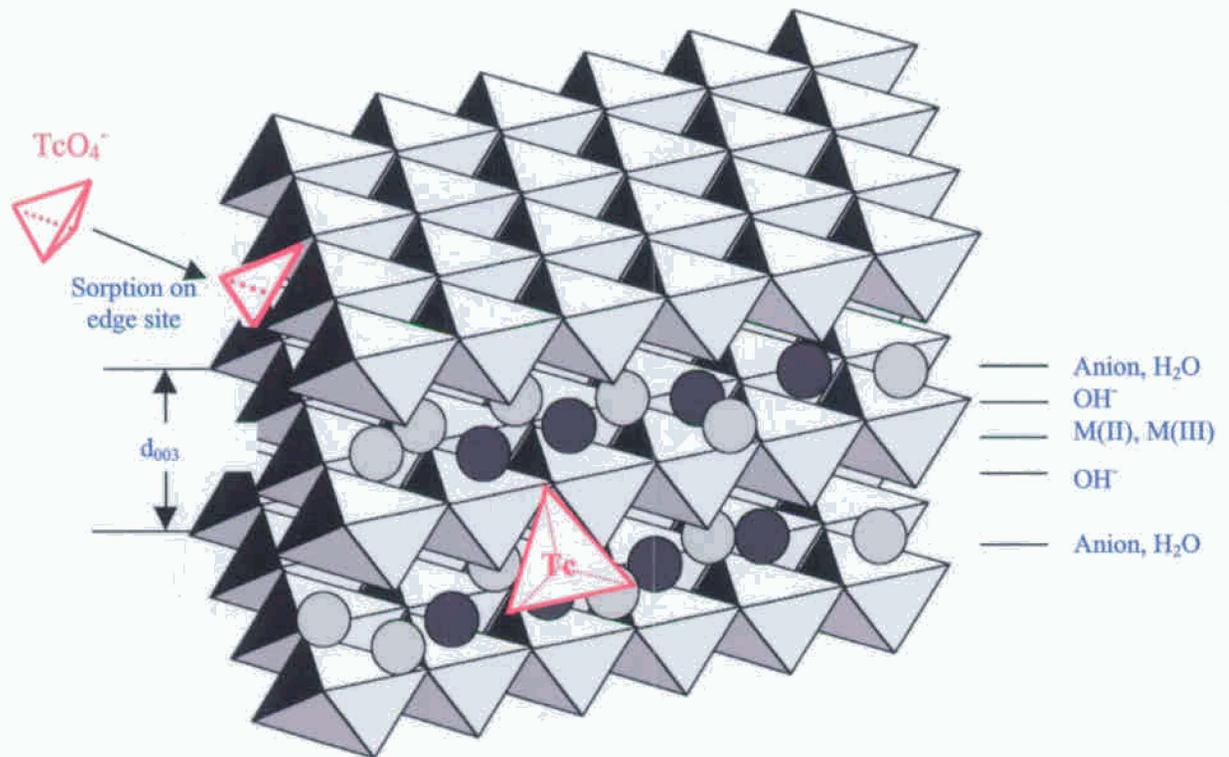
Figure 6

Figure 7

20

Figure 8

Table 1. Sorption capabilities of Ni-M(III) LDH materials for pertechnetate (TcO_4^-)

M(III)	pH	K_d (mL/g)	K_d (mL/g) corrected to pH of 8.0
		Ni-M(III)-CO$_3$ LDH[*]	Ni-M(III)-CO$_3$ LDH[*]
Al	8.5	209	307
Cr	7.8	31	27
Bi	7.9	4	4
		Ni-M(III)-NO$_3$ LDH[*]	Ni-M(III)-NO$_3$ LDH[*]
Al	7.9	1501	1390
Ga	7.5	74	50

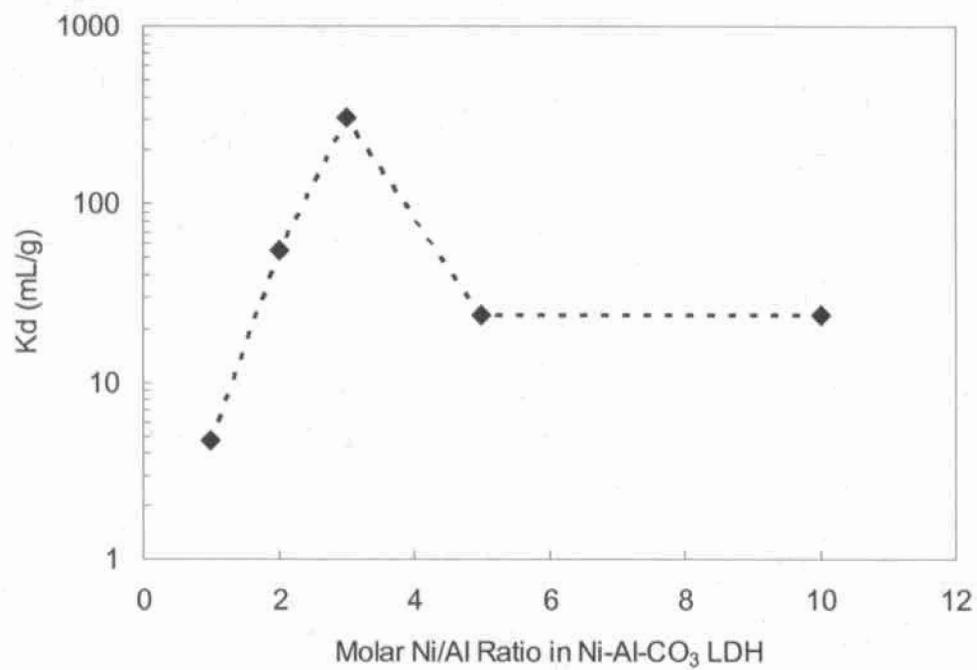[*] Ni/M(III) = 3:1 for all materials.

Table 2. Sorption capabilities of M(II)-Al LDH materials for pertechnetate (TcO_4^-)

M(II)	pH	K_d (mL/g)	K_d (mL/g) corrected to pH of 8.0
		M(II)-Al-CO$_3$ LDH	M(II)-Al-CO$_3$ LDH
Mg	9.4	4	12
Fe	8.5	3	4
Co	7.7	20	16
Ni	8.5	209	307
Cu	7.8	4	3
Zn	8.5	4	6
Cd	8.1	3	3
		M(II)-Al-NO$_3$ LDH	M(II)-Al-NO$_3$ LDH
Mg	9.1	187	435
Co	8.0	631	631
Ni	7.9	1501	1390

* M(II)/Al = 3:1 for all materials.

Table 3. Sorption capabilities of Ni-Al-CO$_3$ LDHs with various Ni/Al ratios for TcO$_4^-$

Ni:Al molar ratio	pH	K$_d$ (mL/g)	K$_d$ (mL/g) corrected to pH of 8.0
10	7.8	28	24
5	7.8	28	24
3	8.5	209	307
2	7.4	87	55
1	7.3	8	5