SYNTHESIS OF A Mg-Cd-Al LAYERED DOUBLE HYDROXIDE AND SORPTION OF SELENIUM

Birte Hansen*, Hilde Curtius, and Reinhard Odoj

Institute for Energy Research − Safety Research and Reactor Technology (IEF-6), Research Centre Jülich GmbH, D-52428 Jülich, Germany

Abstract—Leaching experiments with metallic uranium-aluminum research-reactor fuel elements in repository-relevant MgCl$_2$-rich salt brine (brine 2) were performed. A Mg-Al layered double hydroxide (LDH) with chloride as the interlayer anion was identified as a crystalline secondary-phase component. In the present study, the incorporation of Cd into the structure of the Mg-Al-Cl LDH was investigated. Synthesis by a coprecipitation method was performed and the Mg-Cd-Al-Cl LDH obtained was characterized. The sorption behavior of selenium on the LDH was investigated in water, clay pore-water (Mont-Terri-type), and brine 2. Using a LDH concentration of 10 g/L, the sorption kinetics were rapid and equilibrium was reached within 12 h. The sorption of selenium decreased with increasing amount of chloride anions in the solutions. The chloride anions acted as competing anions for the sorption of selenium. The effect of pH on selenium sorption was investigated and a large buffer capacity of the LDH was observed. For the range of selenium concentration used, linear sorption isotherms were obtained which obeyed the Freundlich and Dubinin-Radushkevich models. From these, the energies of selenium sorption were calculated to be in the range of ion-exchange processes.

Key Words—Clay Pore-water, Layered Double Hydroxides, MgCl$_2$-rich Salt Brine, Sorption.

INTRODUCTION

On the basis of the political decision that there should be no reprocessing of spent research-reactor fuel elements in Germany, direct disposal is explored. The disposal repository may be in a salt mine. A possible accident scenario for long-term safety analysis in a salt repository is a hypothetical water ingress, whereby highly concentrated salt brines will arise. Leaching experiments with metallic uranium-aluminum research-reactor fuel elements in repository-relevant MgCl$_2$-rich salt brine (brine 2) were therefore undertaken (Curtius *et al.*, 2006). The fuel elements corroded completely within 1 y. The radionuclides were mobilized rapidly, but most were immobilized again by the secondary corrosion products showing that these secondary phases act as a near-field barrier against radionuclide migration. A Mg-Al-Cl LDH was identified as a crystalline component of these secondary phases.

Structurally, the LDHs comprise brucite-like layers, in which some of the divalent cations are replaced isomorphously by trivalent cations (Reichle, 1986). The resultant positive charge excess is compensated by anions in the interlayer. Water is also present in the interlayer. Layered double hydroxides have attracted attention recently because of their structures and their large anion exchange capacities − they are amongst the

few inorganic anion exchangers with capacities of up to ~3 meq/g (Miyata, 1983). Layed double hydroxides can be synthesized readily by coprecipitation methods (Miyata, 1975; Cavani *et al.*, 1991).

Preparation of a LDH with Cd instead of Mg and CO$_3^{2-}$ as the counter ion was first reported by Miyata and Kumura (1973), but the product obtained by those authors included small amounts of CdCO$_3$. Vichi and Alves (1997) successfully synthesized pure Cd/Al LDHs with NO$_3^-$ and CO$_3^{2-}$ in the interlayer. Cadmium is important because of its toxicity. In nuclear power plants and other facilities in the nuclear fuel cycle, Cd is used as a neutron poison because of its large neutron-absorption capacity. Therefore, Cd is often found in nuclear waste streams. Furthermore, it is of interest to know whether a cation with such a large ionic radius, in comparison to that of Mg (Mg^{2+}: 72 pm, Cd^{2+}: 95 pm, coordination number 6, Riedel, 1990), can be embedded in the lattice structure of a Mg-Al LDH. Cadmium is seen as an analog for radionuclides with similar ionic radii.

[79]Se accrues as a fission product in irradiated research-reactor fuel elements. Due to its half-life of 6.5×10^4 y, it is considered to be a long-term, safety-relevant radionuclide for repositories. In this work, experiments were performed with selenite, because this is the most likely Se compound to arise under the expected reductive, final-disposal conditions.

A great deal of literature on the sorption of Se on LDHs is available. Most of it describes the sorption of Se on Mg-Al LDHs from pure water (Das *et al.*, 2002, 2004). Studies of the sorption of Se on a Mg-Al LDH by You *et al.* (2001) and Yang *et al.* (2005) were performed

* E-mail address of corresponding author:
b.hansen@fz-juelich.de

in pure water or in aqueous solutions containing competing anions in concentrations of up to only 0.025 mol/L and 0.02 mol/L, respectively. The sorption of selenite in brine 2, a repository-relevant salt solution, on a Mg-Al LDH and on a Mg-Al-Eu LDH was carried out by Curtius *et al.* (2008).

A Mg-Cd-Al LDH with chloride in the interlayer was prepared in the present work. In this LDH, 3.3% of the molar amount of Mg was replaced successfully by Cd. A characterization of this Mg-Cd-Al LDH was performed and the sorption behavior of SeO_3^{2-} in water, clay pore-water (Mont-Terri-type), and brine 2 was investigated. The investigations were time-dependent analyses and sorption isotherm studies taking into consideration the influence of pH and LDH concentration.

EXPERIMENTAL

Materials and equipment

Deionized water was boiled and stored under an argon atmosphere before use. Chemicals of analytical grade (obtained from Merck, Germany) were used without further treatment. All experiments were performed under an argon atmosphere.

For 1 L of the clay pore-water (Mont-Terri-type), the following amounts of salts were dissolved: 12.38 g of NaCl, 0.12 g of KCl, 3.457 g of $MgCl_2 \cdot 6H_2O$, 3.793 g of $CaCl_2 \cdot 2H_2O$, 0.136 g of $SrCl_2 \cdot 6H_2O$, 2.00 g of Na_2SO_4, and 0.04 g of $NaHCO_3$. Finally, the pH was adjusted to 7.6.

For 1 L of brine 2, the following amounts of salts were dissolved: 937.08 g of $MgCl_2 \cdot 6H_2O$, 0.126 g of $MgSO_4 \cdot 7 H_2O$, 1.42 g of KCl, 39.68 g of $CaCl_2 \cdot 2H_2O$, and 4.13 g of NaCl. The salt solutions were stored under an argon atmosphere.

For the selenium experiments, the ^{75}Se isotope was used. Radioactive ^{75}Se solutions were prepared from a standardized stock solution (mass of solution: 4.9893±0.0002 g in a 5 mL V-vial; chemical form of [75]Se: H_2SeO_3 in 0.1 M HCl; contained activity: 4.12±0.12 MBq).

Synthesis of the Mg-Cd-Al-Cl LDH

The Mg-Cd-Al-Cl LDH was prepared from the chloride salts according to the coprecipitation method of Weiss and Toth (1996). Minor modifications were made to the purification and drying steps. Firstly, 250 mL of water was placed in a round flask. A mixed aqueous solution of $MgCl_2 \cdot 6H_2O$ (0.29 mol), $CdCl_2 \cdot H_2O$ (0.01 mol), and $AlCl_3 \cdot 6H_2O$ (0.1 mol) in 250 mL of water was added over a period of 3 h. The pH was maintained at 10 by adding 2 M NaOH, dropwise, at a temperature of 70ºC. After the addition of the chloride salt solution, the temperature was increased to 90ºC and stirring was continued for 24 h. The precipitate formed was filtered, and then dialyzed at 60ºC using dialysis tubing. During the dialysis, the water was changed occasionally, until free of chloride (cuvette test LCK

311, Lange). The solid was filtered and dried in a desiccator under an argon atmosphere.

Chemical analysis

For X-ray diffraction (XRD) and differential thermal analysis-thermogravimetric analysis (DTA-TGA) the dry Mg-Cd-Al LDH was milled to powder. Prior to XRD measurement, some of the sample was mixed with an internal standard (10.0 wt.% zincite). The measurement was performed with and without zincite in Bragg-Brentano geometry. For specimen preparation, the top-loading technique in round sample holders (diameter 27 mm) was used. A Panalytical X'Pert Pro θ-θ diffractometer (CuKα radiation generated at 40 kV and 30 mA, Ni filtered) with a 240 mm goniometer radius, equipped with a 0.04 rad primary Søller slit, an automatic divergence slit irradiating a 20 mm sample length, an automatic anti-scattering slit, a 0.04 rad secondary Søller slit, and a X'Celerator Scientific PSD detector (0.518º active length) was used. The sample was measured from 2 to 90º2θ with a step size of 0.0167º2θ and a total measuring time of 57 min, using a sample spinner. Fourier transform infrared spectroscopy (FTIR) was performed using the KBr pellet technique. The amount of Mg, Cd, and Al was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Examination of the amount of chloride was accomplished by photometry. For the ICP-OES measurements and the chloride-content determination, 200 mg of the sample was dissolved in 20 mL of a 2 M nitric acid. For ICP-OES, this solution was diluted (1 to 1000) with 0.1 M nitric acid. The specific surface area was determined by BET after sieving the milled solid to a particle size of <0.050 mm. In addition, 1 g of the sample was treated with 30 mL of a 1 M ammonium carbonate solution at room temperature for 24 h. Then the solid was filtered, washed with water, and dried at 80ºC. An ICP-OES measurement was performed as above.

Sorption experiments

Sorption experiments were performed using the batch technique. All samples were stored under an argon atmosphere in glass tubes with occasional shaking. For the sampling procedure the samples were filtered using a 450 nm filter and the pH was measured. The concentration of ^{75}Se in solution was determined by liquid scintillation counting (LSC). The mol amount of ^{75}Se in the selenite solution was calculated from the formula:

$$n = A/(\lambda \; N_A) \tag{1}$$

in which n is the mol amount of ^{75}Se, A is the activity of [75]Se (s^{-1}), λ is the decay constant of [75]Se ($6.69 \times 10^{-8} s^{-1}$), and N_A is Avogadro's number (mol^{-1}). The molar concentration, C, of ^{75}Se in the mixture was obtained from:

$$C = n/V \tag{2}$$

where V is the volume of the mixture (0.0101 L).

For time-dependent sorption studies, 100 µL of selenite solution (containing 5.61×10^{-15} mol of Se) and 100 mg of Mg-Cd-Al LDH was added to 10 mL of solution (water, clay pore-water, or brine 2). The selenite concentration in this mixture was 5.55×10^{-13} mol/L. Samples were taken at different time intervals. Blank experiments which were carried out in an analogous manner indicated that sorption of Se on the glass walls was insignificant. The time-dependent sorptions were also investigated with a LDH concentration of 0.1 g/L. The suspension was prepared by adding 50 mg of the milled LDH to 500 mL of solution (water, clay pore-water, or brine 2) and dispersing ultrasonically for 15 min. Then, 100 µL of selenite solution (containing 4.30×10^{-15} mol of Se) was added to 10 mL of the suspension.

Desorption investigations were performed using the dilution method. First, 10 mL of solution (water, clay pore-water, or brine 2) with 100 µL of selenite solution and 100 mg of LDH was equilibrated. Then 5 mL of the equilibrated solution was removed and 5 mL of new solution (water, clay pore-water, or brine 2) was added in each case. The solution removed was analyzed as described above. The desorption procedure was repeated five times for each sample. For the suspension (0.1 g LDH/L), the desorption investigations were only performed in water.

To evaluate the adsorption isotherms for 10 mL of solution (water, clay pore-water, or brine 2), different quantities of the selenite solution and 100 mg of Mg-Cd-Al LDH were added. The selenite concentration in the mixtures ranged from 5.33×10^{-14} mol/L to 2.67×10^{-12} mol/L. The samples were stored for 2 days before sampling.

The effect of pH on the sorption of selenite was investigated as follows. After 10 mL of the solution (water, clay pore-water, or brine 2) and 100 µL of selenite solution (containing 5.16×10^{-15} mol of Se) had

been placed in the glass tubes, the pH was adjusted and 100 mg of LDH added. The samples were stored for 2 days before sampling (as described above).

RESULTS AND DISCUSSION

Chemical analysis

For the Mg-Cd-Al LDH, a Mg/Cd/Al mole ratio of 2.91:0.09:1 was determined by ICP-OES, indicating that a 3:1 LDH-type in respect of the ratio of divalent and trivalent cations was synthesized. The amount of interlayer water was obtained from the DTA-TGA analysis. From these results and from the photometric chloride determination, the empirical formula of the Mg-Cd-Al LDH was derived as: $[Mg_{2.91}Cd_{0.09}Al(OH)_8]Cl_{0.98}(CO_3)_{0.01} \cdot 1.91H_2O$.

Based on the empirical formula, the theoretical anion exchange capacity (TAEC) was calculated, ignoring the presence of carbonate in the interlayer. For monovalent anions it is 3.12×10^{-3} mol/g. This means that, at most, 3.12×10^{-3} mol/g of chloride can be exchanged by other monovalent anions. For divalent anions the TAEC is reduced to 1.56×10^{-3} mol/g.

The XRD pattern obtained for the Mg-Cd-Al LDH showed symmetric 00*l* basal reflections (Figure 1). In the range $32-55°2\theta$, very broad and asymmetric reflections were observed indicating a highly disordered structure. Curtius and Ufer (2007) described this structure as a mixture of the trigonal $3R_1$ polytype and rhombohedral symmetry and the hexagonal $2H_1$ polytype; these polytypes have different *c* spacings. At $17.7°2\theta$ and $30.2°2\theta$, two additional peaks were present which were assigned to $Cd(OH)_2$. Quantification of the amount of this impurity by an internal standard, as described by Curtius and Ufer (2007), showed that the Mg-Cd-Al LDH contained $0.3-0.4$ wt.% of $Cd(OH)_2$; therefore, nearly all of the cadmium could be incorporated because no other by-products were observed. From
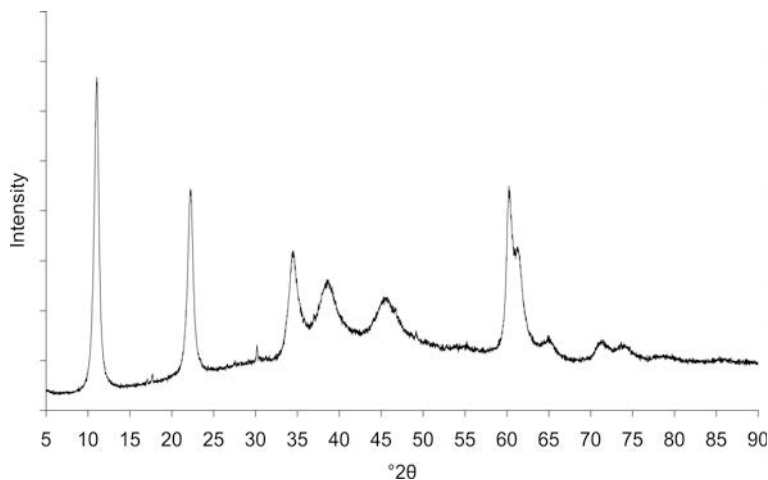

Figure 1. XRD pattern of the Mg-Cd-Al LDH. CuKα radiation.

the basal reflection at 11.1º2θ, the spacing was calculated to be 7.998 Å and from the *hk*0 reflection (110) at 60.3º2θ the *a* lattice parameter was calculated to be 3.067 Å, in agreement with the values of Miyata (1975). The aforementioned Mg-Al LDHs contain chloride as the interlayer anion. When the interlayer anion is a carbonate, the value for the layer spacings will decrease to 7.67 Å (Miyata, 1975).

In the infrared (IR) spectrum, strong hydroxyl and water stretching and bending bands at 3484 cm^{-1} and 1630 cm^{-1} are clearly seen. Al-O and Mg-O vibration bands as well as Al-O bending bands appeared in the region 1100 to 500 cm^{-1}. At 1371 cm^{-1}, a weak stretching band due to adsorbed CO_3^{2-} was present, an artefact of KBr-pellet preparation and not caused by the synthesis (evidence for this comes from IR measurements taken directly after synthesis and dialysis of the Mg-Cd-Al LDH by single-reflection diamond attenuated total reflection − ATR − no carbonate was observed).

A specific surface area of 46 m^2/g was established by the BET (Brunauer, Emmet, Teller) method. After treatment of the solid with the ammonium carbonate solution, only traces of Cd were released. The molar stoichiometry of the Mg-Cd-Al LDH did not change in relation to Mg, Cd, and Al, taking into account the error range of element analysis by ICP-OES. Leaching with ammonium carbonate solution did not remove coprecipitated elements (Duff *et al.*, 2002). Therefore, it can be assumed that nearly all of the Cd was incorporated. The traces of Cd released after treatment with ammonium carbonate solution agreed with the impurity observed by XRD measurement.

Sorption experiments

For the time-dependent sorption investigations of selenite on the Mg-Cd-Al LDH in water (10 g/L), equilibrium was reached in <1 h (Figure 2). Selenite adsorbed quantitatively, according to an anion exchange capacity of 1.12×10^{-14} mol/g. The equilibrium pH was 6.78 (±0.16). In clay pore-water, selenite sorbed up to 62% at an equilibrium pH of 6.52 (±0.25). This corresponds to an anion exchange capacity of 6.94×10^{-15} mol/g. The selenite sorption in brine 2 reached 23% corresponding to an anion exchange capacity of 2.58×10^{-15} mol/g. In brine 2 the equilibrium pH was 6.26 (±0.02). During the sorption process, no release of Cd^{2+} was observed because the cadmium was incorporated into the lattice structure of the Mg-Cd-Al LDH. Only the interlayer chloride anions were exchanged by selenium, which was present as selenite.

The decrease in selenite sorption in the sequence water, clay pore-water, and brine 2 may be explained by the increasing amount of chloride as a competing anion in the solutions, as observed by Curtius *et al.* (2008), who investigated the sorption of selenite on a Mg-Al LDH and on a Mg-Al-Eu LDH in water, a 0.1 M $MgCl_2$ solution and brine 2. The competing anions caused by the high chloride concentration reduced the ion-exchange capacities of the LDHs. Compared to the selenite concentration used, the chloride anions represented a molar excess of ~5.4×10^{11} in clay pore-water and ~1.8×10^{13} in brine 2. Hence the sorption in water was better than the sorption in clay pore-water or in brine 2. Miyata (1983) discovered that the selectivity in the exchange reaction increased with increasing anion-charge density. This allowed the sorption of selenite in spite of the large chloride concentrations.

During the sorption investigations of selenite as a function of pH, the adjusted initial pH ranged from 3.5 to 8 for water and clay pore-water, and from 3.5 to 6 for brine 2 (Figure 3). The equilibrium pH in water obtained was 6.61 (±0.46), in clay pore-water, 5.81 (±0.12), and in brine 2, 6.23 (±0.03). From comparison of these initial and equilibrium pH values, the assumption could be drawn that the Mg-Cd-Al LDH must have a high pH-buffering capacity and the sorption of selenite does not depend on pH in the investigated initial pH ranges.
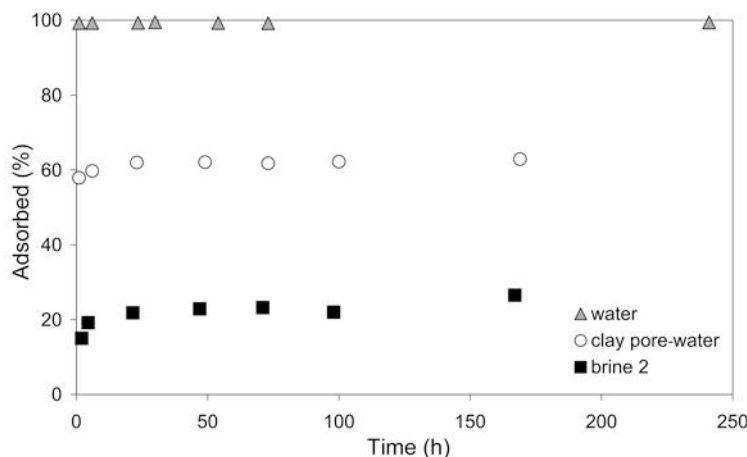

Figure 2. Sorption kinetics of selenite on the Mg-Cd-Al LDH in water, clay pore-water, and brine 2.
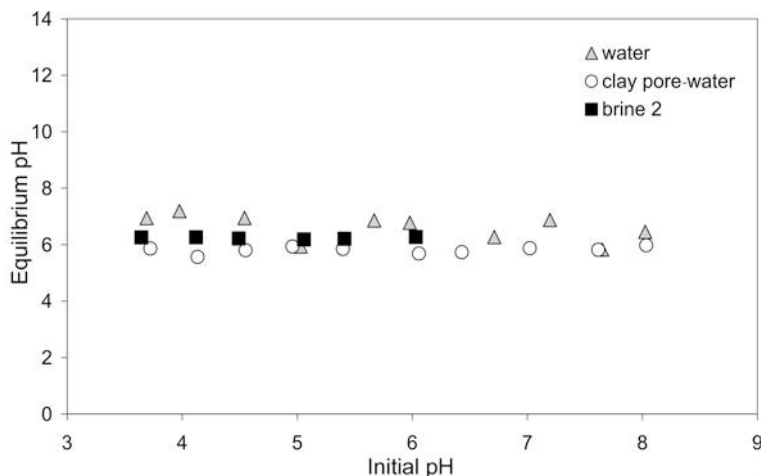
Figure 3. pH dependency of the sorption of selenite on the Mg-Cd-Al LDH in water, clay pore-water, and the brine 2.

Lv *et al.* (2007) investigated the sorption of fluoride on Mg-Al-CO$_3$ LDHs from water with high fluoride concentrations and observed that the metal cations in the LDHs began to dissolve when the pH was reduced to 5.0. During the sorption investigations of selenium on the Mg-Cd-Al LDH, no dissolution of the LDH was observed in the pH ranges used, perhaps because the equilibrium was reached very quickly and the equilibrium pH values ranged from 5.81 to 6.61 because of the high buffering capacity of the LDH.

In general, the results from the desorption studies showed that no selenite desorbed in water (Figure 4). In clay pore-water and in brine 2, selenite desorbed continuously over the course of time. The desorption rate in clay pore-water represented ~2% in each case, in brine 2 it averaged ~10%. In the time period investigated no equilibrium was reached and no statement could be made whether the selenium will be desorbed completely over the years.

For the adsorption isotherms, the amount of selenite sorbed on the Mg-Cd-Al LDH, C_{ads}, was plotted *vs.* the equilibrium selenite concentration, C_e, in clay pore-water, and in brine 2 (Figure 5). The pH averaged 5.99 (±0.24) in clay pore-water and 6.28 (±0.05) in brine 2. The linearity shows that no saturation was reached in the concentration range used. Châtelet *et al.* (1996) suggested that the linearity in the range before saturation indicates an exchange mechanism in which the possible adsorption sites in LDHs are located within the interlayer.

The sorption data obtained were fitted to a Freundlich equation and gave linear isotherms with slopes of ~1 indicating that a concentration-independent adsorption of selenite in clay pore-water and brine 2 exists in the concentration range used (Curtius *et al.*, 2008). As an alternative to the Freundlich isotherm, the data were fitted to the Dubinin-Radushkevich (D-R) equation (Atun *et al.*, 1996):
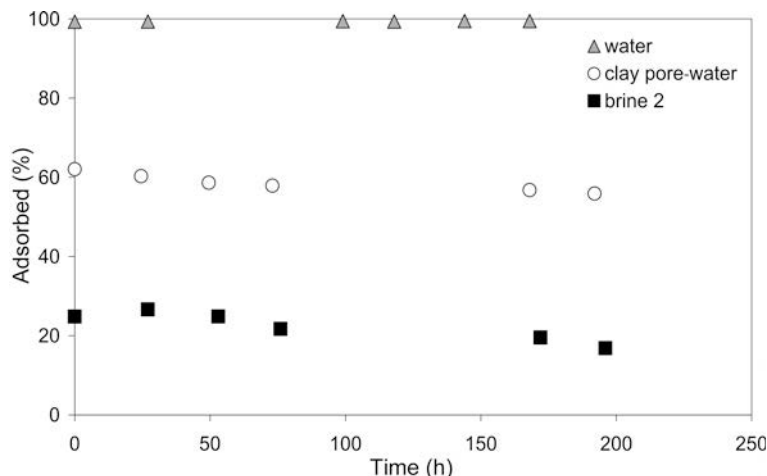

Figure 4. Desorption kinetics of selenite on the Mg-Cd-Al LDH in water, clay pore-water and brine 2.
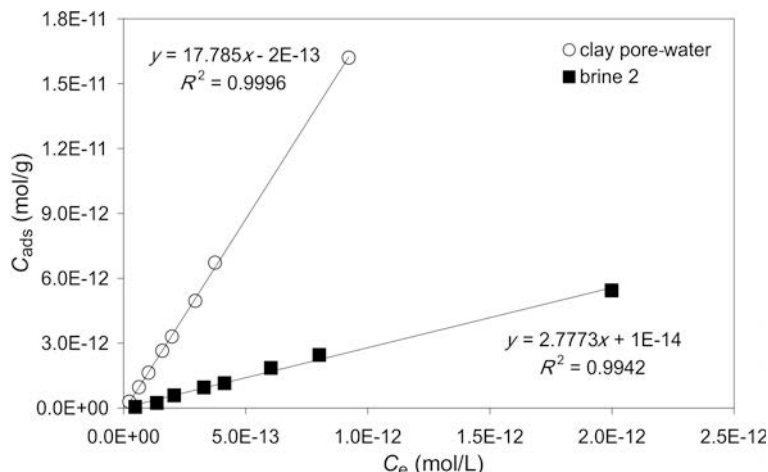
Figure 5. Isotherms of selenite sorption on the Mg-Cd-Al LDH in clay pore-water and brine 2.

$$X = X_m \exp(-K\varepsilon^2) \qquad (3)$$

in which X is the amount of solute adsorbed per unit weight of solid (mol/g), X_m the maximum sorption capacity of adsorbent per unit weight (mol/g), ε the Polanyi potential $= RT \ln(1+1/C_e)$, R the gas constant (kJ/K mol), C_e the equilibrium concentration of solute in solution (mol/L), T the temperature (K), and K the constant related to the sorption energy (mol²/kJ²).

The mean energy of sorption, E, is the free energy change when one mol of ion is transferred to the surface of the solid from infinity in the solution, and it is calculated from:

$$E = (-2K)^{-1/2} \qquad (4)$$

The D-R equations gave satisfactory fits to the results obtained ($R^2 = 0.9997$ for clay pore-water and $R^2 = 0.9819$ for brine 2, Figure 6). The mean energy of sorption in clay pore-water was calculated to be 12.9 kJ/

mol and in brine 2, 11.8 kJ/mol, both values being in the range of ion-exchange processes (Khan *et al.*, 1995). The maximum sorption capacities (X_m) were obtained from the intercept points of the functions with the ordinate. In clay pore-water, X_m was found to be 2.37×10^{-5} mol/g and in brine 2 it was 6.27×10^{-5} mol/g. Compared to the TAEC for divalent anions (1.56×10^{-3} mol/g), these values were significantly smaller. One reason could be the large amount of chloride in the solutions meaning that ion exchange could only take place at the edges of the interlayer of the Mg-Cd-Al LDH.

The sorption of selenite was also investigated under different LDH concentrations, from 10 g/L to 0.1 g/L. In water, the sorption equilibrium was reached within 2 h and selenite adsorbed quantitatively. The equilibrium pH was 7.71 (± 0.22). In clay pore-water, up to 20% adsorption was observed, but due to the large degree of fluctuation in the adsorption values obtained, the results were not interpreted. In brine 2, the sorption of
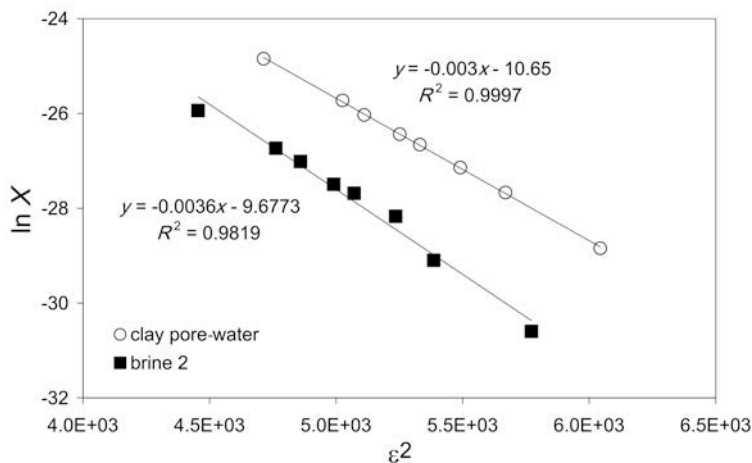

Figure 6. D-R plots of selenite sorption on the Mg-Cd-Al LDH in clay pore-water and brine 2.

selenite was negligible. The pH values are similar to those from the time-dependent sorption investigations with a LDH concentration of 10 g/L, so the lesser degree of sorption could not be explained by the pH values. It is assumed that the LDH concentration of 0.1 g/L is insufficient. The desorption investigations were performed in water only. No desorption of selenite was detected.

CONCLUSIONS

Incorporation of cadmium into the lattice structure of a Mg-Al LDH with chloride in the interlayer was investigated. A Mg-Cd-Al LDH in which 3.3% of the molar amount of Mg was exchanged by Cd was synthesized *via* coprecipitation. The formula of the Mg-Cd-Al LDH was derived (from chemical analysis) as $[Mg_{2.91}Cd_{0.09}Al(OH)_8]Cl_{0.98}(CO_3)_{0.01} \cdot 1.91H_2O$.

The purity of the Mg-Cd-Al LDH was investigated by XRD. Only minor amounts of $Cd(OH)_2$ were measured. Thus, nearly all of the cadmium must have been incorporated by the LDH because no other by-products were observed. The calculated layer-spacing values and the *a* lattice parameter agreed with those of other Mg-Al LDHs which had chloride as the interlayer anion. Another indication of the incorporation of Cd was obtained after treatment of the solid with an ammonium carbonate solution. The molar ratio did not change, within error. Successful preparation of the Mg-Cd-Al LDH shows that even Cd, with its larger ionic radius compared to that of Mg, can be incorporated into the lattice structure of a Mg-Al LDH.

The sorption behavior of selenite on the Mg-Cd-Al LDH was investigated in water, clay pore-water, and brine 2. Mainly time-dependent and isotherm studies were performed. The influence of pH, competing anions, and LDH concentration was furthermore investigated. The sorption of selenite in water, clay pore-water, and brine 2 was very fast and the equilibrium in water was reached in <1 h. In clay pore-water and brine 2 the equilibrium was reached within 12 h. During the desorption investigations with water, no release of selenite was observed. In clay pore-water and in brine 2, selenite desorbed continuously over the course of time. The adsorption isotherms obtained were all linear. The sorption energies determined were in the range of ion-exchange processes. For pH-dependent studies, the equilibrium pH in water was established as 6.61 (±0.46), and in clay pore-water, 5.81 (±0.12). In brine 2 the equilibrium pH was 6.23 (±0.03). These results demonstrate the buffering capacity of the Mg-Cd-Al LDH. Decreasing the LDH concentration from 10 g/L to 0.1 g/L, meant that only in water was a satisfactory level of sorption of selenite observed.

The competing chloride anions decreased the degree of sorption of selenite. Considering final disposal in clay or salt, the Mg-Cd-Al LDH will retard the formation of selenite, though the molar chloride excess is as large as that in the solutions used.

REFERENCES

Atun, G., Bilgin, B., and Mardinli, A. (1996) Sorption of cesium on montmorillonite and effects of salt concentration. *Journal of Radioanalytical and Nuclear Chemistry, Articles*, **211**, 435−442.
Cavani, F., Trifirò, F., and Vaccari, A. (1991) Hydrotalcite-type anionic clays: preparation, properties and applications. *Catalysis Today*, **11**, 173−301.
Châtelet, L., Bottero, J.Y., Yvon, J., and Bouchelaghem, A. (1996) Competition between monovalent and divalent anions for calcined and uncalcined hydrotalcite: anion exchange and adsorption sites. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*, **111**, 167−175.
Curtius, H. and Ufer, K. (2007) Eu incorporation behavior of a Mg-Al-Cl layered double hydroxide. *Clays and Clay Minerals*, **55**, 354−360.
Curtius, H., Kaiser, G., Paparigas, Z., Ufer, K., Müller, E., Enge, R., and Brücher, H. (2006) Untersuchungen zum Verhalten von Forschungsreaktor-Brennelementen (FR-BE) in den Wirtsgesteinsformationswässern möglicher Endläger (Investigations of the behavior of research reactor fuel elements in host rock waters of possible repositories). *Berichte des Forschungszentrums Jülich*, 4237, ISSN 0944-2952.
Curtius, H., Paparigas, Z., and Kaiser, G. (2008) Sorption of selenium on Mg-Al and Mg-Al-Eu layered double hydroxides. *Radiochimica Acta*, **96**, 651−655.
Das, J., Das, D., Dash, G.P., and Parida, K.M. (2002) Studies on Mg/Fe hydrotalcite-like-compound (HTlc) − I. Removal of inorganic selenite (SeO_3^{2-}) from aqueous medium. *Journal of Colloid and Interface Science*, **251**, 26−32.
Das, N.N., Konar, J., Mohanta, M.K., and Srivastava, S.C. (2004) Adsorption of Cr(VI) and Se(IV) from their aqueous solutions onto Zr^{4+}-substituted ZnAl/MgAl-layered double hydroxides: effect of Zr^{4+} substitution in the layer. *Journal of Colloid and Interface Science*, **270**, 1−8.
Duff, M.C., Coughlin, J.U., and Hunter, D.B. (2002) Uranium co-precipitation with iron oxide minerals. *Geochimica et Cosmochimica Acta*, **66**, 3533−3547.
Khan, S.A., Reman, R.-U., and Khan, M.A. (1995) Adsorption of Cs(I), Sr(II) and Co(II) on Al_2O_3. *Journal of Radioanalytical and Nuclear Chemistry, Articles*, **190**, 81−96.
Lv, L., He, J., Wei, M., Evans, and D.G., Zhou, Z. (2007) Treatment of high fluoride concentration water by MgAl-CO_3 layered double hydroxides: Kinetic and equilibrium studies. *Water Research*, **41**, 1534−1542.
Miyata, S. (1975) The synthesis of hydrotalcite-like compounds and their structures and physico-chemical properties − I: The systems Mg^{2+}-Al^{3+}-NO_3^-, Mg^{2+}-Al^{3+}-Cl^-, Mg^{2+}-Al^{3+}-ClO_4^-, Ni^{2+}-Al^{3+}-Cl^- and Zn^{2+}-Al^{3+}-Cl^-. *Clays and Clay Minerals*, **23**, 369−375.
Miyata, S. (1983) Anion-exchange properties of hydrotalcite-like compounds. *Clays and Clay Minerals*, **31**, 305−311.
Miyata, S. and Kumura, T. (1973) Synthesis of new hydrotalcite-like compounds and their physico-chemical properties. *Chemistry Letters*, 843−848.
Reichle, W.T. (1986) Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). *Solid State Ionics*, **22**, 135−141.

Riedel, E. (1990) *Anorganische Chemie (Inorganic Chemistry)*. Walter de Gruyter, Berlin, New York.

Vichi, F.M. and Alves, O.L. (1997) Preparation of Cd/Al layered double hydroxides and their intercalation reactions with phosphonic acids. *Journal of Materials Chemistry*, **7**, 1631−1634.

Weiss, A. and Toth, E. (1996) Untersuchungen zur Synthese, Quellungseigenschaften und Anionenaustausch von kristallchemisch modifizierten Doppelhydroxiden vom Hydrotalkit-Typ (Investigations of synthesis, swelling properties and anion exchange of crystallochemical modified double hydroxides of the hydrotalcite type). Pp. 267−276 in: *Contributions to the annual DTTG meeting Freiberg, Germany* (D. Wolf, R. Starke, and R. Kleeberg, editors).

Available at: http://www.dttg.ethz.ch/band4_en.html. ISSN 1432-7007.

Yang, L., Shahrivari, Z., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T. (2005) Removal of trace levels of arsenic and selenium from aqueous solutions by calcined and uncalcined layered double hydroxides (LDH). *Industrial & Engineering Chemistry Research*, **44**, 6804−6815.

You, Y., Vance, G.F., and Zhao, H. (2001) Selenium adsorption on Mg-Al and Zn-Al layered double hydroxides. *Applied Clay Science*, **20**, 13−25.