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Preparation and characterization of Zr-IV-containing Mg-Al-Cl layered double hydroxide

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Summary. In order to contribute to the long-term safety analysis of direct disposed research reactor fuel elements, the corrosion behavior of these fuel-types in final repository relevant salt brines was determined. Due to the corrosion processes, radionuclides were mobilized first, but then trapped by the formed secondary phases.

A Mg-Al layered double hydroxide (LDH) with chloride as interlayer anion was identified as one crystalline secondary phase component. The possibility to incorporate zirconium-IV into the lattice structure of the Mg-Al-Cl LDH was investigated by a co-precipitation process. The element zirconium was chosen because it has a low absorption cross section for neutrons, and is therefore used for nuclear energy applications, such as for cladding fuel elements. No zirconium release was detected, when the obtained LDH was treated with an ammonium carbonate solution. The molar stoichiometry with respect to Mg, Al and Zr remained stable and this is the first indication for the incorporation of zirconium.

For further examination, the material was analyzed by powder X-ray diffraction (XRD) combined with a Rietveld refinement. Due to a recursive calculation inside the Rietveld refinement, it was possible to derive structural parameters of the disordered LDH.

Further on, the Mg-Al-Zr-LDH was analyzed by EXAFS and the results did show that Zr is the central metal atom coordinated by 5 OH groups and by one chloride.

1. Introduction

In Germany, the direct disposal of spent fuel elements is under investigation. At the IEF-6 the work is focused on research reactor fuel element. Two different fuel-types are under investigation. The dispersed metallic UAl_x-type and the U_3Si_2-Al-type. At present three research reactors, the FRM-II-reactor (München), the FRG-I-reactor (Geesthacht) and the BER-II-reactor (Berlin) with a thermal output higher than 5 MW are in operation in Germany. In these reactors dispersed U_3Si_2-Al-fuel is used. In general, three possible back-end options for irradiated research reactor fuel elements exist in Germany [1]: first, irradiated research reactor fuel elements of USA origin can be sent back when these fuels were taken out of the reactor not later than May 2006. This affects basically the dispersed metallic UAl_x-Al-fuel, which was used in the FRJ-II-reactor (Jülich) till May 2006. Secondly, reprocessing in Great Britain or France is possible and it is performed with respect to economical reasons. Thirdly, dry interim storage and later on, direct disposal in deep geological formations has been taken into account too. A possible repository under consideration is a salt mine, and the accident scenario for long-term safety analysis is a water ingress. Different leaching experiments with the dispersed metallic UAl_x-Al-fuel (fuel used in the material test reactor FRJ-II)[1] in highly-concentrated salt brines at 90 °C showed that the radionuclides were rapidly mobilized, but then trapped by the corrosion products [2]. Investigations [3] of these secondary corrosion products as a near field barrier against radionuclide migration indicated that one component is a Mg-Al-Cl LDH, also referred as a hydrotalcite-like compound (HTlc).

LDHs may be described by the general formula: $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot m\,H_2O$, where M(II) and M(III) are di- and trivalent metals respectively, and A^{n-} is an anion. Their structure is based on brucite-like layers, in which a divalent cation is located in the center of oxygen octahedra and two-dimensional infinite layers are formed by edge-sharing of the octahedra. Partial isomorphous substitution of divalent cations for trivalent ones results in a positive charge on the layers. This charge is compensated by the presence of anions in the interlayer [4]. In the free space of this interlayer, water molecules are also present. The main features of LDH structures and of LDH properties are determined by the nature of the brucite-like sheet, by the type of stacking of the brucite-like sheets, by the amount of water and by the position and type of anions in the interlayer. It should be pointed out that a change in the brucite-like layer will result in differ-

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[1] The MTR-FE of the DIDO type contains 20 wt. % U-Al alloy with an initial enrichment of 80% in ^{235}U. The fuel alloy plates with a thickness of 0.6 mm (meat) are covered on both sides with aluminium claddings of 0.38 mm, the total thickness is then 1.36 mm. The spent fuel element will be disposed in a cast iron POLLUX container.

ent properties of the LDH. A change in the brucite-like sheet is possible by changing the stoichiometry of the metal ions present or by an exchange of the metal ions.

In order to achieve to the safety of long-term disposed fuel elements in an underground disposal site, the migration of radiotoxic elements through the geosphere must be evaluated. The existing multibarrier-system should prevent that, due to corrosion processes of the fuel containment and of the fuel itself, the mobilized radionuclides will be released to the biosphere. The corrosion products (secondary phases) formed can be regarded as first barrier with respect to radionuclide mobilization. As controlling retardation processes the surface complexation, the ion exchange and the co precipitation can be mentioned. Ionic exchange or surface complexation reactions are reversible processes. On the contrary the co precipitation process leads to an incorporation of the element in the lattice structure and is an irreversible process. A remobilization of the element is only possible when a change in the chemical condition is that significant that the host component itself will dissolve.

We already demonstrated that an isomorphous substitution of the trivalent aluminum, present in the Mg-Al-Cl LDH, by the trivalent europium [5], and by the trivalent samarium [6], is possible. Within this substitution the net positive charge in the brucite layer remains constant, hence the value of the AEC (anion exchange capacity) remains constant too. An increase of the AEC value can be achieved by increasing the number of trivalent ions in the layer within permissible limits. Alternatively, partial substitution of the Mg-II or Al-III ion by a tetravalent metal ion, may increase the net positive charge in the brucite layer and hence the AEC value, too. An increase in the AEC value is desirable because then the LDH can remove higher amounts of anionic radionuclide species. In future work the retention of repository-relevant radionuclide anionic species like selenite, iodine and pertechnetate in repository-relevant aquatic phases is aspired. The influence of the increased AEC-value in view of the retardation of anionic species was already studied by Das *et al.* [7]. They investigated the adsorption of hexavalent chromium and selenite on uncalcinated and calcinated Mg-Al-LDHs containing zirconium-IV in the main layer. The first synthesis of a Mg-Al-LDH containing Zr in the brucite layer but with carbonate as interlayer anion was reported by Velu *et al.* [8]. Nevertheless, these results were discussed by Intissar *et al.* [9] in detail. By use of X-ray absorption and Mössbauer spectroscopy they showed, that the tetravalent cation is segregated from the LDH structure and forms amorphous M-IV oxide-like particles.

In the present paper we report the preparation and detailed characterization of a layered material possessing the hydrotalcite-like structure containing magnesium, aluminum and the tetravalent element zirconium in the hydroxide layer with chloride as interlayer anion. From XRD and EXAFS measurements the presence of Zr IV oxide particles can be ruled out.

2. Experimental

Deionised water was boiled and stored under an argon atmosphere before use. The chemicals were of analytical grade and used without further treatment. All experiments were performed under an argon atmosphere.

2.1 Synthesis of the Mg-Al-Zr-Cl LDH

The Mg-Al-Zr-Cl LDH was obtained according to the following co precipitation process: 250 mL of water were placed in a three-necked glass flask and a pH of 10 was adjusted using 2 M NaOH. A mixed aqueous solution of $MgCl_2 \cdot 6H_2O$ (0.3 M) and $AlCl_3 \cdot 6H_2O$ (0.09 M) and $ZrOCl_2 \cdot 8H_2O$ (0.01 M) in 250 mL water was added over a period of 5 h while the pH was maintained at 10 by addition of 2 M NaOH. The temperature was maintained at 70 °C. After the addition was complete, the temperature was raised to 90 °C and stirring was continued for 24 h. After cooling to room temperature, the formed precipitate was filtered and then dialyzed at 60 °C. For that purpose a dialysis hose was filled with the substance and placed in 2 L vessel containing deionised water. The water was changed until it was chloride-free (chloride measurements were performed with the cuvette test LCK 311, DR. LANGE). The precipitate was filtered and dried in a desiccator.

2.2 Chemical analysis

The obtained substance was characterized by photometry, DTA-TGA, FTIR, ICP-OES, SEM-EDX, EXAFS and XRD. For DTA-TGA, SEM-EDX, XRD, EXAFS and FTIR measurements, dry samples were milled to powder. For photometric and ICP-OES measurements the solid samples were dissolved in 2 M HNO_3. Furthermore 1 g of the synthesized Mg-Al-Zr-Cl LDH was treated with 50 mL of an ammonium carbonate solution (1 mol/L) at room temperature for 24 h. This procedure was performed to distinguish between sorbed and incorporated Zr species. A change in the metal ion stochiometry is expected, when Zr is only sorbed and not incorporated. Then the solid was separated by filtration, washed with 10 mL water and dried at 70 °C.

500 µL of the filtrate was added to 49.5 mL of a 0.1 M nitric acid solution and this solution was analyzed by ICP-OES in order to determine the amounts of Mg, Al and Zr. To determine the Mg, Al and Zr molar ratios of the solid, an ICP-OES analysis was performed as follows:

100 mg of the solid was dissolved in 10 mL 2 M nitric acid. This solution was diluted (1 : 1000) with a 0.1 M nitric acid solution and the measurement was performed.

To obtain detailed information about the incorporation of Zr, investigations with XRD and EXAFS were performed.

2.3 X-ray diffraction (XRD)

Prior to the X-ray diffraction measurements, an internal standard (10.0 wt.-% zincite) was added and the sample was hand-ground in an agate mortar. For the specimen preparation the top loading technique was used. The sample was measured on a 3003TT (General Electric) diffractometer (Bragg–Brentano geometry, Cu K_α radiation generated at 40 kV and 40 mA) equipped with an automatic divergence slit irradiating 10 mm sample length, a 0.5 mm detector slit, a secondary beam graphite monochromator, a point detector and a sample spinner. The sample was measured from 5° to

85° 2Θ with a step size of 0.03° 2Θ and a measuring time of 20 s per step.

2.4 Rietveld refinement

The principle of the Rietveld method [10] consists of the computation of synthetic diffraction patterns from a given structural model. This data will be fitted to experimental data by a non-linear least squares minimization. The quality of the refinement can be judged by the agreement index R_{wp}, which contains the differences of measured and observed data and its comparison to R_{exp}, the theoretical minimum value for R_{wp} [11].

The Rietveld analysis allows an insight in structural details of crystalline materials and therefore it is suitable for the characterization of the LDH.

For the refinement, the program BGMN was used [12]. BGMN contains a structure description language and offers the possibility of a complex manipulation of the structure factors and a solver for linear equation systems. Therefore a recursive treatment of diffraction effects from faulted layer stackings, similar to DIFFaX simulations [13] can be performed within a Rietveld refinement [6].

From previous investigations [5] it is known that LDHs develop a disordered stacking of the two polytypes $2H_1$ and $3R_1$. Both polytypes form trigonal prismatic interlayer polyhedra. In the $3R_1$ structure adjacent layers are translated by a stacking vector (2/3, 1/3, 1/3) relative to each other. The $2H_1$ polytype is formed by an alternate stacking of layers which are rotated around 180° parallel to the adjacent layers. In this work the probability of these two stackings could be refined. The layer structure is derived from a description of a Cl-LDH ($3R_1$) by Ennadi *et al.* [14] Due to the disordered stacking, the symmetry is reduced from the original point group R-$32/m$ (3 layers per unit cell) to $P3m1$ (one layer per unit cell). In addition to the atomic positions of the interlayer atoms (Cl and oxygen to represent water) as proposed by Ennadi *et al.* [14], several further positions were tested. The initial occupancies of atomic positions are derived from chemical analysis. The occupancies of the cations were not refined. For ZnO only lattice parameters, peak broadening parameters and a scaling factor was refined. As non-structural parameters, the zero point, the sample displacement error and a Lagrange polynomial of 5th degree for background modeling were refined. BGMN includes a fundamental parameter approach to model the peak profiles [15]. The instrument-dependent part of the diffraction profile is predetermined by a ray tracing procedure.

2.5 Extended X-ray absorption fine structure (EXAFS)

Zr K X-ray absorption fine structure (XAFS) spectra are recorded at the INE-beamline (ANKA, Karlsruhe, Germany). Spectra are energy calibrated to the first inflection point in the XANES of a Zr foil (17.998 keV) measured simultaneously. The Zr-doped LDH XAFS is recorded at room temperature in transmission-mode using Ar-filled ionization chambers at ambient pressure. Ge⟨422⟩ crystals are used in the monochromator, operating in fixed-exit mode. The incident intensity is held constant by means of a piezo-driven feedback system. The parallel alignment of the crystal faces is detuned to ∼ 70% of the maximum beam intensity. The XAFS sample is pressed in dried form into a polyethylene pellet of 13 mm diameter.

Table 1. Metric parameters of the LDH with Mg/Al as center (R = distance between the central atom chosen, here Mg/Al (both share the same crystallolgraphic site) and the backscattering atom, N = coordination numbers) [18].

Backscatterer	N	R (Å) LDH
O (from OH)	6	2.03
Al/Mg	6	3.06
O (from OH)	6	3.67
C	2	4.00
O	6	4.19

EXAFS fits are performed with Artemis [16] part of the Ifeffit package [17], using phase and amplitude data calculated for a 9 atom cluster derived from the undoped LDH structure [18] (Table 1). The cell parameters are increased to account for the larger size of the Zr cation. Single path scattering files for phase and amplitude are used for the second coordination sphere. The k-range used for the fit is (2.33–13.93 Å^{-1}) and fits are performed in the R-space on the k^2-weighted data.

3. Results and discussions

3.1 Characteristics of LDHs

The Mg-Al-Zr-Cl LDH was prepared according to a described co-precipitation method [19]. Little modifications were performed with regard to the purification and drying steps. For the synthesized double layered hydroxide a Mg/Al/Zr mole ratio of 3 : 0.93 : 0.099 was determined by ICP-OES. Chloride was determined photometrically using a cuvette test LCK 311 (DR. LANGE). Due to the molar stoichiometry of the metal ions present in the main layer, the number of hydroxylgroups in the main layer must be eight

In the DTA-TGA thermogram the first endothermic peak occurs between room temperature and 275 °C, with its maximum at 142.5 °C, corresponding to a weight loss of 14.7%, and is due to desorption of the interlayer water. The second endothermic peak between 275 °C and 600 °C indicates partial dehydroxylation in the main layer and elimination of chloride in the interlayer. This assumption was drawn due to the results from Roelofs *et al.* [20], who investigated the thermal decomposition of Mg-Al-LDHs in detail. They showed that the dehydroxylation in the main layer depend on the basic properties of the interlayer anion.

The IR-spectra show strong hydroxyl and water stretching and bending bands at 3482 and 1636 cm^{-1}. Metal–O-vibration bands appear in the region 1000 to 550 cm^{-1}. A very weak adsorption band due to adsorbed CO_3^{2-} was present at 1376 cm^{-1}. The presence of the divalent carbonate ion can be explained by the preparation of the KBr phase, which was not performed under an inert gas atmosphere, and by the high affinity of this ion towards LDHs.

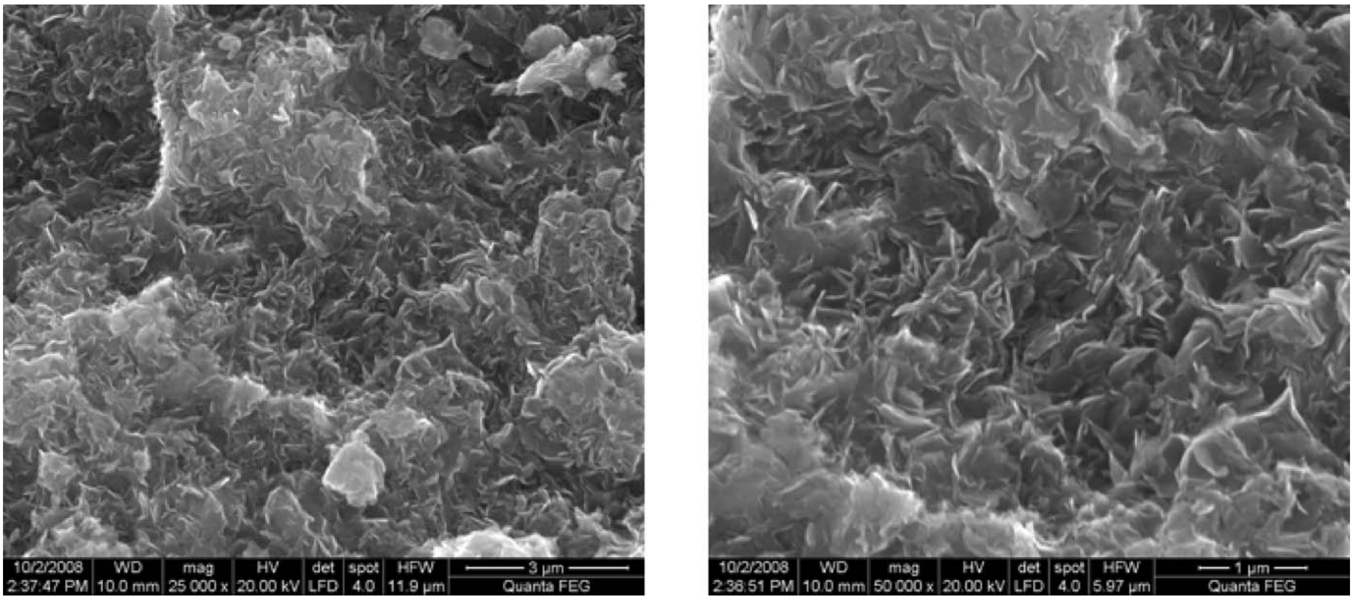

Fig. 1. Morphology of the Mg-Al-Zr-LDH, investigated by SEM.

From these results the formula of the Mg-Al-Zr-Cl LDH can be derived as $[Mg_3Al_{0.93}Zr_{0.099}(OH)_8]Cl_{0.94}(CO_3{}^{2-})_{0.03}\cdot 2.71H_2O$.

Eight hydroxyl-groups must be present in the main layer because the LDH structure is based on brucite-like layers, in which the divalent cation is located in the center of oxygen octahedra and two-dimensional infinite layers are formed by edge-sharing of the octahedral.

The morphology of the Mg-Al-Zr LDH obtained was investigated by SEM. The sand rose crystal structure (Fig. 1), typical for LDHs [21], can be clearly seen.

Then the element distribution was determined by EDX and theses results did show a homogeneous distribution and no other phase was observed.

For the solid a specific surface area of 48 m^2/g was determined by BET and a cationic exchange capacity of 66 mmol/100 g was obtained by a complexation reaction with Cu-II-triethylentetraamin.

Furthermore, the treatment of the Mg-Al-Zr-Cl LDH with an ammoniumcarbonate solution [22] did not result in any change of the Mg-Al-Zr molar ratios, indicating that the Zr is incorporated. For Zr species, which are sorbed at the LDH surface, we expect an interaction with the strong complexation agent, leading to the formation of carbonate complexes. These components were neither detected in solution nor in the solid.

3.2 XRD measurements

Table 2 shows the structural results of the Rietveld refinement of the Mg-Al-Zr-Cl LDH. It was found that the original position for the interlayer chloride, as proposed by Ennadi *et al.* [14] did not lead to a satisfying result. Attempts to refine the position in the *a*1-*a*2 plane showed that the chloride has a tendency to move on a position perpendicular to the hydrogen, which corresponds to the Wyckoff position *b* (space group *P*3*m*1). In the final refinement only the interlayer water was positioned on the site proposed by Ennadi *et al.* [14] and chloride was fixed on Wyckoff position *b*. However, the occupancy of the chloride strongly decreased. This indicates that this position is also not suitable for a satisfying description of the atomic arrangement. This is illustrated in the strong misfit of the intensity of the 110 reflection (angular position at 60.06) (Fig. 2).

Table 2. Refinement results of Mg-Al-Zr-Cl LDH (R_{wp} and R_{exp} = agreement indices, *a* and *c* = lattice constants, $p(3R1)$ = probability for $3R1$ stacking, $p(Cl)$ and $p(H_2O)$ = occupancy of Cl resp. H_2O, ESD = estimated standard deviation).

	Start parameters	Refinement	ESD
R_{wp} (%)		9.14	
R_{exp} (%)		3.38	
a (Å)	3.06	3.0718	0.0011
c (Å)	8.00	8.0002	0.0045
$p(3R1)$	0.5	0.5129	0.0044
$p(Cl)$	0.235	0.0264	0.0051
$p(H_2O)$	0.25	0.0777	0.0012
LDH (wt. %)		89.04	0.14
ZnO (wt. %)		10.96	0.14

Unfortunately, so far there exists no suitable model in literature to describe the position of the chloride. Apart from this drawback, the refinement produced some significant structural parameters. The probability for the $3R_1$ stacking is close to 0.5, this shows that this LDH is highly disordered. The *a* and *c* lattice constant show typical values for a Cl LDH. Both values, the stacking probability and the lattice constants, have no influence on the intensity of the 110 reflection [5].

The initial content of the ZnO admixture was refined as 10.96 wt. %. This overestimation could be explained by an additional amorphous component (9.7 wt. %, ESD = 1.3 wt. %). However, the uncertainties in the determination of the amorphous content are relatively high and, consequently, a quantification of a small amount with large error seems to be critical.

Table 3. Metric parameters (R = distances, N = coordination numbers, σ^2 = EXAFS Debye–Waller factors, ΔE_0 = relative energy shifts) from least squares analysis of FT data. S_0^2 is held constant at 1.0.

Sample	Backscatterer	R (Å) (±0.01)	N (±20%)	σ^2 (Å^2) × 10^{-3}	ΔE_0 (eV)	goodness of fit (%)
Zr-doped LDH	O	2.13	5.0	7.0	−9.7	1.0
Zr-doped LDH	Cl	2.45	0.9	9.8	−5.6	1.0
Zr-doped LDH	Al/Mg	3.51	2.3	6.3	−0.9	1.0

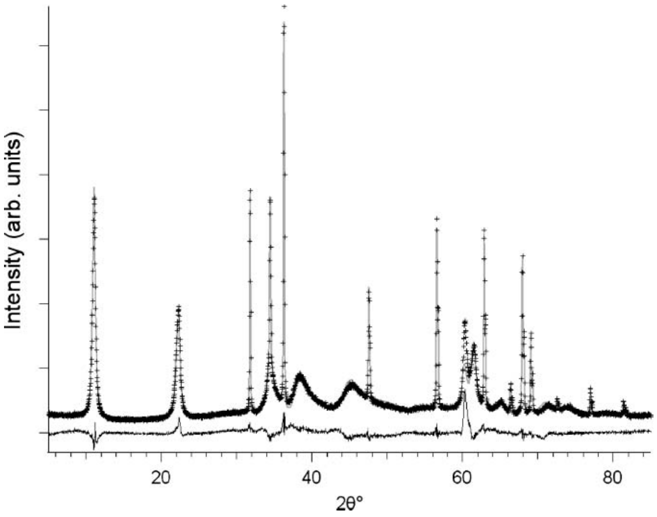

Fig. 2. Rietveld refinement of the Mg-Al-Zr-Cl LDH. Gray line: calculated intensity; +: observed intensity, black line: difference curve.

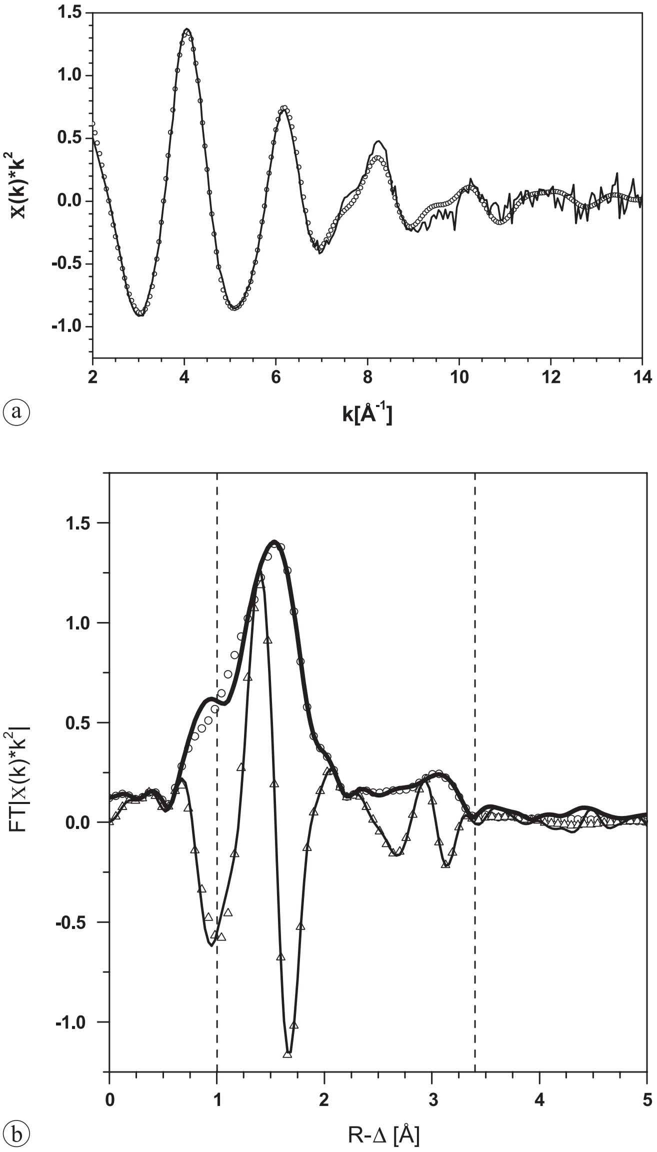

Fig. 3. (**a**) k^2-weighted Zr L_3 EXAFS of the sample (solid line) and fit result (open circles); (**b**) FT magnitude (thick solid line), imaginary part (thin solid line), and fit result (open triangles and circles). FT is performed in the range 2.3–13.9 Å^{-1}. FT fit range borders are indicated with dashed lines.

3.3 EXAFS measurements

The data are well reproduced using 3 shells within the FT range (1.1–3.4 Å) as shown Fig. 3. The fit results are given in Table 3. The first coordination sphere contains 5 O atoms at 2.13 Å with a Debye–Waller factor (σ^2) of 7.0×10^{-3} Å^2 and 1 Cl atom at 2.45 Å with a σ^2 of 9.8×10^{-3} Å^2. The Debye–Waller factor is a parameter accounting for the molecular structural and thermal disorder of a sample, static and thermal disorder from the point of view of the absorber atom (here Zr). It traduces the distance distribution of the coordination shell considered.

The presence of a Cl atom was not expected in the first coordination shell but no satisfactory fit can be achieved without adding the chlorine atom.

The structural incorporation of the Zr dopant is comparable to Eu in LDH [5]. The Zr is six-fold coordinated but a chlorine atom has replaced an oxygen atom in the first coordination shell.

As for Eu-doped LDHs, the Al shell is more distant as expected for isotropic extension of the unit cell. Circa 2 Al atoms are found at 3.51 Å (1.7 Al at 3.45 Å for Eu). The reduced Al coordination number compared to the expected value of 6 (see Table 1) as well as the missing associated O shell (from OH), indicates either disorder in the Zr near neighbour structure, with larger radius, or that Zr does not replace Al/Mg exactly at their lattice position. No Zr−Zr interaction can be evidenced, excluding the formation of cluster or polynuclear species such in Zr oxide or hydroxide within the EXAFS detection limit. It is likely that the Zr is located out of the Al/Mg layer, bonding then with two Al/Mg. The Cl atom will then come in the vicinity of Zr and could explain that one Cl integrates the first coordination shell. These results are also compatible with a bidentate sorption species but this possibility of a sorption species is ruled out by the results of the treatment of the Mg-Al-Zr-Cl LDH with an ammonium carbonate solution as reported in this paper. Therefore, we argue as for the Eu case that the Zr atom is likely incorporated into the LDH structure but as a defect.

4. Conclusions

Within a couple of months a non-irradiated metallic UAl_x-Al fuel element sample corroded completely in the presence of Fe-II ions in a final repository salt brine solution at 90 °C. In the corrosion products a crystalline phase component was identified as Mg-Al-Cl LDH. The ability of this component to retard radionuclide species by incorporation was investigated. As element species the tetravalent zirconium was chosen.

A synthesis of a Mg-Al-Zr LDH with chloride as interlayer anion was performed. From the analytical data the formula of the Mg-Al-Zr-Cl LDH can be derived as $[Mg_3Al_{0.93}Zr_{0.099}(OH)_8]Cl_{0.94}(CO_3{}^{2-})_{0.03} \cdot 2.71H_2O$. Proofs for the successful incorporation of the tetravalent Zr can be given as follow:

- The molar ratio of Mg-Al-Zr did not change, when this LDH was treated with an ammonium carbonate solution. No Zr was detected in solution and the remaining solid, analyzed by XRD, showed only the typical LDH reflexes.
- SEM-EDX investigations clearly showed the typical sand rose structure and a homogeneous element distribution. No by products were detected.
- The Rietveld refinement of the XRD measurement showed that the synthesized material consists of a LDH with a high degree of stacking disordering. No additional phases could be detected directly.
- Investigations performed by EXAFS spectrometry did show clearly, that in the first coordination shell of the Zr atom 5 OH groups and one chloride atom is present, hence Zr possess an octahedral No Zr−Zr interaction can be evidenced, excluding the formation of cluster or polynuclear species such in Zr oxide or hydroxide within the EXAFS detection limit.

Nevertheless, the exact position of the Zr in the crystal lattice structure of the LDH is not clear yet. Because of the high degree of stacking disordering of the LDH, especially improvements of the structural models are necessary. This work is in progress.

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References

1. Thamm, G.: Disposal of irradiated fuel elements from German research reactors – Status and Outlook, Trans. Int. Conf. Research Reactor Fuel Management (RRFM 1999), Bruges, Belgium (1999), p. 159.
2. Brücher, H., Curtius, H., Fachinger, J., Kaiser, G., Mazeina, L., Nau, K.: Untersuchungen zur Radionuklidfreisetzung und zum Korrosionsverhalten von bestrahltem Kernbrennstoff aus Forschungsreaktoren unter Endlagerbedingungen. Report Forschungszentrum Jülich, Jül-4104, ISSN 0944-2952 (2002).
3. Mazeina, L., Curtius, H., Fachinger, J., Odoj, R.: Characterisation of secondary products of uranium-aluminium material test reactor fuel element corrosion in repository-relevant brine. J. Nucl. Mater. **323**, 1 (2003).
4. Miyata, S.: The synthesis of hydrotalcite-like compounds and their structures and physico-chemical properties. Clays Clay Miner. **31**, 369 (1975).
5. (a) Stumpf, T., Curtius, H., Walther, C., Dardenne, K., Ufer, K., Fanghänel, T.: Incorporation of Eu(III) into hydrotalcite: a TRLFS and EXAFS study. Environ. Sci. Technol. **41**(9), 3186 (2007); (b) Curtius, H., Ufer, K.: Eu incorporation behaviour of a Mg-Al-Cl layered double hydroxide. Clays Clay Miner. **55**(4), 354 (2007).
6. Ufer, K., Kleeberg, R., Bergmann, J., Curtius, H., Dohrmann, R.: Refining realstructure parameters of disordered layer structures within the Rietveld method. Z. Kristallogr. Suppl. **27**, 151 (2008).
7. Das, N. N., Konar, J., Mohanta, M. K., Srivastava, S. C.: 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. J. Colloid Interface Sci. **270**, 1 (2004).
8. Velu, S., Ramaswamy, V., Ramani, A., Handa, B. M., Sivasanker, S.: New hydrotalcite-like anionic clays containing Zr^{4+} in the layers. Chem. Commun. 2107 (1997).
9. Intissar, M., Jumas, J.-C., Besse, J.-P., Leroux, F.: Reinvestigation of the layered double hydroxide containing tetravalent cations: Unambiguous response provided by XAS and Mössbauer spectroscopy. Chem. Mater. **15**, 4625 (2003).
10. Rietfeld, H. M.: Line profiles of neutron-powder-diffraction peaks for structure refinement. Acta Cryst. **22**, 151 (1967).
11. Hill, R. J., Fischer, R. X.: Profile agreement indices in Rietfeld and pattern-fitting analysis. J. Appl. Cryst. **23**, 462 (1990).
12. Bergmann, J., Friedel, P., Kleeberg, R.: BGMN – a new fundamental parameter based Rietveld program for laboratory X-ray sources, it's use in quantitative analysis and structure investigations. Commission of Powder Diffraction, International Union of Crystallography, CPD Newsletter Vol. 20, p. 5 (1998).
13. Treacy, M. M. J., Newsam, J. M., Deem, M. W.: A general recursion method for calculating diffracted intensities from crystals containing planar faults. Proc. R. Soc. Lond. Ser. A **433**, 499 (1991).
14. Ennadi, A., Legrouri, A., De Roy, A., Besse, J. P.: X-ray diffraction pattern simulation for thermally treated [Zn-Al-Cl] layered double hydroxide. J. Solid State Chem. **152**, 568 (2000).
15. Cheary, R. W., Coelho, A. A.: A fundamental parameters approach to X-ray line-profile fitting. J. Appl. Cryst. **25**, 109 (1992).
16. Newville, M.: IFEFFIT interactive XAFS analysis and FEFF fitting. J. Synchrotron Radiat. **8**, 322 (2001).
17. Ravel, B., Newville, M.: ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. **12**, 537 (2005).
18. Bellotto, M., Rebours, B., Clause, O., Lynch, J., Bazin, D., Elkaim, E.: A reexamination of hydrotalcite crystal chemistry. J. Phys. Chem. **100**, 8527 (1996).
19. Weiss, A., Toth, E.: Untersuchungen zur Synthese, Quellungseigenschaften und Anionenaustausch von kristallchemisch modifizierten Doppelhydroxiden vom Hydrotalkit-Typ. Jahrestagung der DTTG, Freiberg (1996), p. 267.
20. Roelofs, J. C. A. A., van Bokhoven, J. A., Van Dillen, A. J., Geus, J. W., de Jong, K. P.: The thermal decomposition of Mg-Al Hydrotalcites: Effects of interlayer anions and characteristics of the final structure. Chem. Eur. J. **8**, 5571 (2002).
21. Mistra, C., Perrota, J.: Composition and properties of synthetic hydrotalcites. Clays Clay Miner. **40**, 145 (1992).
22. Duff, C. M., Coughlin, J. U., Hunter, D. G.: Uranium co-precipitation with iron oxide minerals. Geochim. Cosmochim. Acta **66**, 3533 (2002).