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Effect of DTPA on europium sorption onto quartz – batch sorption experiments and surface complexation modeling

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Abstract

Sorption of radionuclides on mineral surfaces retards their migration in the environment of a repository. Presence of organic ligands, however, affects sorption and consequently influences their transport behavior. In this study, we quantify the sorption of Eu(III) onto quartz surfaces as a function of pH in the absence and presence of diethylenetriaminepentaacetic acid (DTPA). Batch sorption experiments show a pH-dependent sorption of Eu(III) on quartz. The presence of DTPA results in slightly higher sorption of Eu(III) at neutral to slightly acidic pH and considerably lower sorption at alkaline conditions. Sorption experiments were simulated using the Diffuse Double Layer Model (DDLDM) with single sorption sites ($\equiv\text{QOH}$) and monodentate surface complexation. The reactions were established based on the aqueous speciation calculation under the experimental conditions, and the thermodynamic constants of surface reactions were obtained and refined by numerical optimization. Results of surface complexation modeling show the formation of a surface species $\equiv\text{QOHEuDTPA}^{2-}$, explaining the elevated sorption of Eu(III) at neutral to slightly acidic pH. In contrast, dissolved EuDTPA^{2-} complex species are present at alkaline pH, resulting in an enhanced mobility of Eu(III).

Keywords:

Sorption, Europium, Radionuclides, Diethylenetriaminepentaacetic acid, Surface complexation modeling

1 Introduction

Radionuclide migration in natural aqueous systems is a critical process in the long-term safety assessment of nuclear waste repositories. Sorption and desorption on mineral surfaces and complexation with organic ligands are major processes controlling the mobility of actinides and lanthanides in the subsurface. Therefore, quantitative experimental data on effects of organic complexing ligands are required for a fundamental and mechanistic understanding of migration. This is a prerequisite for both the prediction of radionuclide transport and the successful remediation of a contaminated environment.

In this context, several studies were conducted to investigate effects of organic complexing ligands on sorption of lanthanides and actinides on mineral surfaces (Fairhurst et al., 1995; Takahashi et al., 1998; Alliot et al., 2005; Lippold et al., 2005; Pathak and Choppin, 2007; Schott et al., 2012; Ye et al., 2014). Specifically, it was found that organic ligands are able to elevate as well as to suppress the sorption of radionuclides in dependence on pH and ionic strength. The two major groups of organic complexing ligands to be considered are: (a) polycarboxylic acids including citric acid and oxalic acid and (b) aminopolycarboxylic acids such as EDTA, NTA and DTPA (Choppin, 1995). Alliot et al. (2005) studied the effects of small organic ligands such as oxalate, acetate and carbonic acid on sorption of Am(III) onto α -alumina and found that these complexing ligands are able to prevent sorption. In another study, Pathak and Choppin (2007) showed that oxalate enhanced sorption of Eu(III) on silica due to the formation of ternary surface complexes, whereas acetate, citrate and EDTA reduced sorption of Eu(III) due to the formation of a binary complex ligand/Eu(III) in solution. Only few studies were performed to investigate the influence of aminopolycarboxylic acids on sorption of radionuclides onto minerals. Most of them are focused on EDTA (Sylwester, 2001) and NTA (Reinoso-Maset et al., 2012).

Surface complexation models (SCMs) can describe sorption of radionuclides onto mineral surfaces under variable geochemical conditions. They include surface properties such as the format of electrical interfacial layers and define surface/dissolved complexes based on theoretical calculations and/or spectroscopic studies. A couple of studies have quantified and modeled the sorption of Eu(III) and trivalent actinides on quartz and silica in the absence of organic ligands (Wang et al., 2001; Kuta et al.,

2011; Britz, 2018). Wang et al. (2001) published an SCM for sorption of Am(III) on amorphous silica. They used a Diffuse Double Layer Model (DDLm) in which the effect of changing aqueous speciation on the formation of surface complexes was taken into account. By means of laser-induced fluorescence spectroscopy, Kuta et al. (2011) performed a molecular dynamics simulation to predict sorption of Eu(III) onto α -quartz and showed that both inner- and outer-sphere complexes of lanthanide ions formed on surface edge sites of quartz. Britz (2018) compared a DDLm, a Basic Stern Model (BSM), and a Non-Electrostatic Double Layer Model (noEDLM) to explain sorption of Eu(III) onto quartz and suggested a monodentate, bidentate, and a combination of mono- and bidentate binding on the surface edge sites. However, few works aimed to model and predict sorption of lanthanides on mineral surfaces in ternary systems with complexing organic ligands.

In this work, we investigated the influence of diethylenetriaminepentaacetic acid (DTPA), which is used as a decontamination agent during operation of a final repository (Sharma et al., 2010; Randall et al., 2011), on the sorption of Eu(III) to quartz sand to derive implications for the mobility of radionuclides in case of release together with organic complexants. Quartz is a widespread mineral with a relatively simple structure. It is the predominant constituent of many soils and rocks which are involved in many physical, chemical and biological processes in subsurface environments. For this reason, quartz was chosen as a representative sorbent in this study. Because of their similar chemical behavior, it is widely accepted that trivalent lanthanides are, to some extent, suitable as analogues of trivalent actinides such as Am(III), Cm(III) or Pu(III) (Choppin, 1995). We quantified and predicted the effects of pH and ligand concentration on Eu(III) sorption by conducting a series of batch sorption experiments in the pH range between 3 and 9. Speciation calculations were conducted to determine the Eu(III) and Eu(III)-DTPA species present in solution under the experimental conditions. A DDLm was applied to explain sorption of Eu(III) and the influence of DTPA on Eu(III) sorption on quartz surfaces. Surface complexation reactions were established based on the speciation calculation, and surface complexation parameters were estimated and optimized from data fitting.

2 Materials and methods

2.1 Materials

Quartz sand with a grain size of 0.2 - 0.8 mm was obtained from Merck KGaA, Germany. It was washed three times with 0.01 M NaClO₄ (Merck, Germany) and three times with deionized water to remove impurities. A 10 mL stock solution of 2×10^{-4} mol/L Eu(NO₃)₃ (Merck, Germany) in ultrapure water (≥ 18 M Ω /cm) was spiked with ¹⁵²Eu as a radiotracer (POLATOM, Poland) at an activity of 0.3 MBq. The solution was adjusted to pH 3 to avoid formation of colloids, precipitation, and sorption on walls. DTPA (acid form) was provided by Sigma Aldrich, Germany. The pH of the stock solution (10^{-2} mol/L DTPA) was adjusted to 6.5. NaClO₄ was used as a background electrolyte at a concentration of 0.01 M.

2.2 Experimental

Batch sorption experiments were performed in 50 mL polypropylene plastic tubes containing 0.2 g quartz sand and 20 mL 10^{-6} M [¹⁵²Eu]Eu(III) in 0.01 M NaClO₄ with an activity concentration of 0.03 kBq/L. The pH of the suspensions was varied between 3.5 and 9 using HClO₄ and NaOH for adjusting. Experiments were done in the absence and in the presence of DTPA ([DTPA]/[Eu] = 0.5, 1, 2, 10, and 30). Additional experiments at pH 6.5 and 8.5 and [DTPA]/[Eu] = 0.2, 0.7, and 6 were done to study sorption of Eu(III) as a function of DTPA concentration. For the experiments done in the presence of organic ligand, the DTPA stock solution was added to the suspension lastly. After rotating the suspensions for about 40 h with an end-over-end shaker (ROTATHERM), the pH of the solutions were measured again, and the samples were centrifuged at 5000 rpm for 10 min to separate quartz from supernatant. The equilibration time was verified to be sufficient for surface complexation reactions in kinetic sorption experiments with Eu(III) and Eu(III)/DTPA mixtures at pH 6 over a period of 100 h.

The amount of Eu(III) sorption on quartz was determined by counting the decays of ¹⁵²Eu in 8 mL samples of the respective initial solutions and of the supernatant solutions after sorption. Count rates were measured for 5 minutes with a gamma counter 1480 Wallac Wizard 3" (Perkin Elmer, USA), set at the full energy range of 0 - 2 MeV as Eu was the only radionuclide in the sample. The percentage of Eu(III) sorption was determined as:

$$\% \text{ sorbed} = \left[\frac{A_i - A_f}{A_i} \right] \times 100$$

where A_i and A_f are the initial and final count rates in the aliquots (before and after sorption, respectively).

2.3 Modeling

The aqueous chemical speciation of Eu(III), DTPA, and 1:1 Eu(III)-DTPA were calculated by means of the geochemical speciation code PHREEQC (Version 3.4 (Parkhurst, 2013)). The Nagra/PSI Chemical Thermodynamic Database (Thoenen et al., 2014), which contains thermodynamic data for a range of lanthanides and actinides, was used to calculate the Eu(III) speciation. Additional equilibrium constants for DTPA acidity and Eu(III)-DTPA complexation (Grimes and Nash 2014), which are not contained in the database, were used in the model. Surface complexation reactions were described on the basis of the Diffuse Double Layer Model (DDLm) of Dzombak and Morel (1990). We assumed monodentate surface complexation of the metal on a single edge site of quartz sand ($\equiv\text{QOH}$). Surface reactions were defined based on the aqueous species, and the equilibrium constants ($\log k$) of surface complexation reactions were optimized from fitting the simulated sorption curves to the experimental data using the parameter estimation code PEST (Doherty, 2018) coupled with PHREEQC. The optimization of $\log k$ values for the surface complexation reactions was done for the binary sorption system (no DTPA) and the ternary system at $[\text{DTPA}]/[\text{Eu}] = 1$. A weighted residuals model was used to find the best fit. The defined thermodynamic constants were then used to calculate sorption of Eu on quartz in the ternary sorption system at $[\text{DTPA}]/[\text{Eu}] = 0.5, 2, \text{ and } 10$. Both surface complexation modeling as well as speciation modeling were performed for equilibrium conditions, and no kinetic processes were considered.

3 Results and discussion

We quantified sorption of Eu(III) onto quartz sand in dependence on pH and DTPA concentration by conducting a series of batch sorption experiments and surface complexation modeling.

3.1 Aqueous speciation

In the absence of DTPA, the ionic form of europium (Eu^{3+}) as well as the europium hydroxyl complexes EuOH^{2+} , $\text{Eu}(\text{OH})_2^+$, and $\text{Eu}(\text{OH})_3$ are the dominant Eu(III) species in the studied pH range (Fig. 1a). Figure 1b depicts the species distribution of DTPA. The change in Eu speciation in the presence of DTPA at equal concentration is shown in Fig. 1c. It is evident that at $3.5 < \text{pH} < 9$ in the presence of organic ligand the total amount of Eu is present in complexed form with DTPA (EuDTPA^{2-} is the only Eu aqueous species formed). The acidity constants for DTPA as well as the stability constants for Eu-DTPA complexation used in the speciation modeling were determined by potentiometric titration by Grimes and Nash (2014), listed in Table 1.

3.2 Sorption kinetics

Kinetic experiments have been performed in order to determine the time needed to reach equilibrium for both binary and ternary ($[\text{Eu}]/[\text{DTPA}] = 1$) sorption systems at pH 6. The percentages of Eu(III) sorption on quartz versus time are plotted in Fig. 2 for systems with and without organic ligand. Initially, equilibration proceeds fast and then continues slowly till equilibrium is reached. Presence of DTPA affects the rate of europium sorption. In general, the initial rapid sorption occurred within the first 2 h, and equilibrium sorption was reached after 20 h and 36 h for Eu(III) and Eu-DTPA sorption systems, respectively. A similar rate trend was reported by Pathak and Choppin (2007) for adsorption of Eu (10^{-5} M) on silica at pH 6 in 0.2 M NaClO_4 (included in Fig. 2).

3.3 Batch sorption experiments

3.3.1 Sorption of Eu(III)

In Fig. 3a, sorption of Eu(III) onto quartz in the absence of DTPA is shown as a function of pH. The results show a continuous increase in the percentage of Eu sorption with pH from 5 to 6.5. Above pH 6.5, the total amount of Eu(III) is adsorbed. This behavior can be related to increasing ionization of surface

hydroxyl groups ($\equiv QO^-$) with increasing solution pH. In general, sorption of Eu(III) on oxides increases with pH due to deprotonation of sorption sites (Wang et al., 2011; Qiu et al., 2018). Eu(III) bonding with mineral surface hydroxyl groups reduces the negative charges of the ionized hydroxyl groups. By means of time-resolved laser fluorescence spectroscopy (TRLFS), Stumpf et al. (2008) observed the formation of inner-sphere complexes of Am(III) on deprotonated surface sites of quartz (QO^-) and found a similar pH-dependent sorption behavior.

3.3.2 Effect of DTPA on Eu(III) sorption

In Fig. 3a, sorption of Eu(III) in the presence of DTPA onto quartz at ligand/metal ratios of 0.5, 1, 2, 10, and 30 is shown as a function of pH. In general, presence of DTPA affects the shape of the sorption curve. Results show that under slightly acidic conditions (pH 4-5), presence of DTPA slightly enhances Eu(III) uptake (by ~ 5 -10%). This was observed at [DTPA]/[Eu] ratios of 0.5 to 30 with similar effects. It can be interpreted as sorption of Eu-DTPA complexes on the surface sites of quartz. Increase of metal sorption in the presence of organic ligands at neutral to slightly acidic conditions was also found in a previous study (Karimzadeh et al., 2017). By using TRLFS, Pathak and Choppin (2007) identified Eu-oxalate surface species on silica at neutral pH. In addition, Ye et al. (2014) found that in the presence of fulvic acid and at acidic to neutral pH, sorption of Eu(III) was enhanced due to the formation of a Eu-FA surface complex on the surface edge sites of quartz. They found that fulvic acid forms a bridge between Eu ions and quartz, thereby increasing metal uptake. However, our results show that in the presence of DTPA and above pH 5, Eu(III) uptake is inhibited (Fig 3a). Compared to the binary sorption system, at [DTPA]/[Eu] = 0.5 and pH > 6 the adsorbed amount of Eu is reduced by $\sim 20\%$. By increasing the ligand/metal ratio from 0.5 to 30, the percentage of adsorbed Eu decreases in dependence on the solution pH. At [DTPA]/[Eu] = 30 and pH 9, only 22% of Eu is adsorbed. Speciation modeling (Fig. 1) shows that at pH > 5 , the total amount of aqueous europium is present in complexed form with DTPA ($EuDTPA^{2-}$). Sorption of DTPA on quartz at alkaline conditions does not take place due to its negative charge. Thus, the major influence of DTPA on Eu sorption results from the formation of Eu-ligand complexes in solution. Under alkaline conditions, the

Eu(III) surface complex is weaker than the complex with DTPA in solution. Therefore, DTPA is able to mobilize Eu and to reduce its sorption at high pH.

Figure 3b shows the effect of DTPA concentration in mol/L on the amount of Eu(III) adsorbed per mass of adsorbent (mol/g) at pH 6.5 and 8.5. Both curves exhibit two regions with different slopes. This figure shows that with increasing DTPA concentration, the mobilizing effect of DTPA (the ability of DTPA to keep Eu in the solution phase) sharply declines at equimolar ligand/metal ratio ($[DTPA] = [Eu] = 10^{-6} \text{ M}$), which confirms the 1:1 stoichiometry as it is shown in the aqueous speciation in Fig. 1c, too.

3.4 Surface complexation modeling

A surface complexation model was developed to explain Eu sorption in the absence of DTPA as well as the effect of DTPA on Eu sorption onto quartz sand. A preliminary assessment of the possible mode of Eu(III) complexation on quartz sorption sites suggested Eu binding in a monodentate and/or bidentate manner (Stumpf et al., 2008; Kumar et al., 2012; Britz, 2018). Kumar et al. (2012) showed by TRLFS that a monodentate surface complex of Eu is formed on silica surfaces. Monodentate binding of Eu on surface sites of quartz was also proposed in the published surface complexation models (Ye et al., 2014; Britz, 2018). In our model, we assumed monodentate surface complexation of Eu on single edge sites of quartz ($\equiv QOH^0$ and $\equiv QO^-$). It has been described in the literature that metal sorption onto crystalline quartz is dominated by the edge sites (Britz (2018)). Based on the previous work (Stumpf et al. (2008)), the number of sites at the quartz surface was set to 3.6 nm^{-2} and the specific surface area measured $0.165 \text{ m}^2/\text{g}$. The surface parameters and the surface complexation reactions for the considered binary and ternary surface complexes together with the estimated $\log k$ values are given in Table 2. In Fig. 4, the overall model fit and the distribution of surface species for binary and ternary sorption systems are presented. The thermodynamic constants for reactions 3, 4, 5, and 6 in Table 2 are optimized from the Eu sorption experiments in the absence of DTPA. The modeling results presented in Fig. 4a show that in the absence of organic ligand, surface reactions 4 and 5 reproduce the sorption edge of europium, and the contributions of surface species $\equiv QOEu^{2+}$ and $\equiv QOHEu(OH)_3$ described by equations 3 and 5 are

negligible (less than 0.1% at their peak). This shows that the europium hydroxide species $\text{Eu}(\text{OH})^{2+}$ and $\text{Eu}(\text{OH})_2^+$ are bound to deprotonated surface edge sites of quartz ($\equiv\text{QO}^-$, Fig. 1a). As shown in Fig. 4a, the model predicts a small fraction of Eu hydroxide $\text{Eu}(\text{OH})^{2+}$ to be sorbed in form of $\equiv\text{QOEuOH}^+$ (9% at peak at pH 6) and the major part of Eu to be sorbed as neutral surface species to form $\equiv\text{QOEu}(\text{OH})_2$.

The thermodynamic constant for surface reaction 7 was estimated from fitting the modeling results to the experimental data presented in Fig. 4c ($[\text{Eu}]/[\text{DTPA}] = 1$) and was then used together with the log k values obtained for the binary sorption system to simulate sorption of Eu in the presence of organic ligand at $[\text{DTPA}]/[\text{Eu}] = 0.5, 2, \text{ and } 10$ (Figs. 4b, 4d, and 4e). The DDLM provides a close fit to the experimental data. Our model results show that in the presence of DTPA and at a ligand-to-metal ratio of 0.5 (Fig. 4b), the surface species $\equiv\text{QOEuOH}^+$, $\equiv\text{QOEu}(\text{OH})_2$, and $\equiv\text{QOHEuDTPA}^{2-}$ are formed on the quartz surface (surface reactions 4, 5, and 7, Table 2). However, at $[\text{DTPA}]/[\text{Eu}] \geq 1$, surface reactions 5 and 7 dominate the Eu(III) sorption profile (Figs. 4c, 4d, and 4e), i.e., mainly the surface species $\equiv\text{QOEu}(\text{OH})_2$ and $\equiv\text{QOHEuDTPA}^{2-}$ are formed if DTPA is present in excess. Figures 4b - 4e show that with increasing $[\text{DTPA}]/[\text{Eu}]$ ratio in ternary sorption systems, the contribution of $\equiv\text{QOHEuDTPA}^{2-}$ in the sorption edge is elevated and at $[\text{DTPA}]/[\text{Eu}] = 10$ the sorption curve of this surface species extends over the whole studied pH range. At neutral to slightly acidic pH, DTPA can form a bridge between quartz surface and Eu(III) and thus enhances Eu(III) sorption. This is well displayed in the modeling results. Figures 4b - 4e show that the surface species $\equiv\text{QOHEuDTPA}^{2-}$ is formed mostly at $\text{pH} < 8$, where neutral surface hydroxyl groups ($\equiv\text{QOH}^0$) are available. As mentioned before, due to the ionization of surface hydroxyl groups at alkaline conditions, the quartz surface mostly consists of $\equiv\text{QO}^-$. At $\text{pH} > 7.5$, the surface species $\equiv\text{QOEu}(\text{OH})_2$ dominates total Eu(III) sorption on deprotonated quartz surface edge sites ($\equiv\text{QO}^-$), i.e., surface reaction 5 constitutes the major part of Eu sorption.

In Fig. 5, experimental and modeling results of Eu sorption on quartz in the absence of organic ligand are compared with the results provided by Pathak and Choppin (2007), Stumpf et al. (2008) and Ye et al. (2014). All sorption curves show the same trend, and the shapes are comparable. Nevertheless, they display slight differences in curvature and starting point, which is mostly due to differences in the

experimental conditions (initial metal concentration, background electrolyte concentration and solid/liquid ratios). Furthermore, the lines are based on different modeling approaches. In contrast to our DDLM, Stumpf et al. (2008) used the Basic Stern Model in combination with the charge distribution concept and assumed bidentate surface complexation of Am(III) on single sites of quartz. However, the Eu sorption profile obtained with our model is close to the sorption profile simulated by Stumpf et al. (2008). The experimental results of Eu sorption onto silica provided by Ye et al. (2014) are more heterogeneous compared to the results provided by Stumpf et al. (2008) and Pathak and Choppin (2007) and show a noticeable Eu sorption at acidic conditions ($\text{pH} < 5$), which can be caused by minor surface impurities as it is addressed by Britz (2018) and Lützenkirchen (1996). On the other hand, the model results provided by Ye et al. (2014) show no Eu sorption under acidic conditions. A comparison of the surface complexation parameters used in our model in binary and ternary sorption systems with those used in the selected models explained above is provided in Table S1 (supporting data). Note that there are differences in the modeling approaches, surface complexation reactions and surface parameters (e.g., surface area and site density), which is reflected in the thermodynamic constants.

4 Summary and conclusions

We described the sorption behavior of Eu(III) on quartz, in the presence and absence of DTPA, by a combination of experimental data and surface complexation modeling. DTPA reduces sorption of Eu(III) at alkaline pH and therewith enhances its mobility due to the formation of Eu(III)-ligand complexes in solution. At $[\text{Eu}]/[\text{ligand}]$ ratios > 1 , the mobilization effect of DTPA is higher than at $[\text{Eu}]/[\text{ligand}]$ ratios < 1 , confirming the 1:1 stoichiometry. Under acidic conditions, DTPA slightly decreases the mobility of Eu(III), indicating the formation of ternary surface complexes (Eu/ligand/quartz). The applied DDLM successfully described the experimental data. These results show that mobility of trivalent lanthanides and most likely actinides can be changed in the presence of aminopolycarboxylic acids. Their usage as a decontamination agent in the operation phase of a nuclear waste repository should thus be avoided. The

obtained thermodynamic data are substantial for reactive transport models simulating long-term radionuclide migration in the far-field of a repository.

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References

- Alliot, C., Bion, L., Mercier, F., Vitorge, P., Toulhoat, P., 2005. Effect of aqueous acetic, oxalic and carbonic acids on the adsorption of americium onto α -alumina. *Radiochim. Acta* 93(8), 435-442.
- Britz, S.M., 2018. Europium sorption experiments with muscovite, orthoclase, and quartz: Modeling of surface complexation and reactive transport (Doctoral dissertation). Technical University of Braunschweig, Braunschweig.
- Choppin, G.R., 1995. Comparative solution chemistry of the 4f and 5f elements. *Journal of Alloys and Compounds* 223, 174-179.
- Doherty, J., 2018. PEST, Model-independent parameter estimation—user manual. 7th edition, watermark numerical computing. Brisbane, Australia.
- Dzombak, D.A., Morel, F., 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley & Sons, New York.
- Fairhurst, A.J., Warwick, P., Richardson, S., 1995. The Effect of pH on Europium-Mineral Interactions in the Presence of Humic Acid. *Radiochimica Acta* 69, 103-111.
- Grimes, T.S., Nash, K.L., 2014. Acid Dissociation Constants and Rare Earth Stability Constants for DTPA. *Journal of Solution Chemistry* 43, 298-313.
- Karimzadeh, L., Barthen, R., Stockmann, M., Gruendig, M., Franke, K., Lippmann-Pipke, J., 2017. Effect of glutamic acid on copper sorption onto kaolinite - Batch experiments and surface complexation modeling. *Chemosphere* 178, 277-281.
- Kumar, S., Kar, A.S., Tomar, B.S., Bhattacharyya, D., 2012. X-ray absorption fine structure spectroscopy study of Eu(III) sorption products onto amorphous silica and γ -alumina: Effect of pH and substrate. *Polyhedron* 33, 33-40.
- Kuta, J., Wander, M.C.F., Wang, Z., Jiang, S., Wall, N.A., Clark, A.E., 2011. Trends in Ln(III) Sorption to Quartz Assessed by Molecular Dynamics Simulations and Laser-Induced Fluorescence Studies. *The Journal of Physical Chemistry C* 115, 21120-21127.
- Lippold, H., Müller, N., Kupsch, H., 2005. Effect of humic acid on the pH-dependent adsorption of terbium (III) onto geological materials. *Applied Geochemistry* 20, 1209-1217.
- Lützenkirchen, J., 1996. Description des interactions aux interfaces liquide - solide à l'aide des modèles de complexation et de précipitation de surface (Doctoral dissertation). Université Louis Pasteur, Strasbourg.
- Parkhurst, D.L., 2013. Description of input and examples for PHREEQC version 3--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Reston, Virginia : U.S. Department of the Interior, U.S. Geological Survey.
- Pathak, P.N., Choppin, G.R., 2007. Effect of complexing anions on europium sorption on suspended silica: a TRLFS study for ternary complex formation. *Radiochimica Acta* 95, 267-272.

- Qiu, L., Scott, K., Rousseau, S., 2018. Kinetic and equilibrium studies of Cs(I), Sr(II) and Eu(III) adsorption on a natural sandy soil. *Radiochimica Acta* 107, 55-66.
- Randall, M., Lennon, C., Rigby, B., 2011. Biogeochemical Aspects of the Waste Acceptance Criteria at LLWR. NNL Report (10) 11348 Issue 3.
- Reinoso-Maset, E., Worsfold, P.J., Keith-Roach, M.J., 2012. The effect of EDTA, NTA and picolinic acid on Th(IV) mobility in a ternary system with natural sand. *Environmental Pollution* 162, 399-405.
- Schott, J., Acker, M., Barkleit, A., Brendler, V., Taut, S., Bernhard, G., 2012. The influence of temperature and small organic ligands on the sorption of Eu(III) on Opalinus Clay. *Radiochimica Acta* 100, 315-324.
- Sharma, D., Kamboj, S., Kamboj, S., Nair, A., Ali, J., 2010. Nuclear and radiological agents: Contamination and decontamination of human beings. *International Journal of Pharmaceutical Sciences Review and Research* 5, 95-101.
- Stumpf, S., Stumpf, T., Lützenkirchen, J., Walther, C., Fanghänel, T., 2008. Immobilization of trivalent actinides by sorption onto quartz and incorporation into siliceous bulk: Investigations by TRLFS. *Journal of Colloid and Interface Science* 318, 5-14.
- Sverjensky, D.A., Sahai, N., 1996. Theoretical prediction of single-site surface-protonation equilibrium constants for oxides and silicates in water. *Geochimica et Cosmochimica Acta* 60, 3773-3797.
- Sylwester, E.R., 2001. Effect of EDTA on plutonium migration. *Journal of Radioanalytical and Nuclear Chemistry* 250, 47-53.
- Takahashi, Y., Minai, Y., Kimura, T., Tominaga, T., 1998. Adsorption of europium(III) and americium(III) on kaolinite and montmorillonite in the presence of humic acid. *Journal of Radioanalytical and Nuclear Chemistry* 234, 277-282.
- Thoenen, T., Hummel, W., Berner, U., Curti, E., 2014. The PSI/Nagra Chemical Thermodynamic. Database 12/07, Paul Scherrer Institut, Villigen PSI, Switzerland.
- Wang, P., Anderko, A., Turner, D.R., 2001. Thermodynamic modeling of the adsorption of radionuclides on selected minerals. I: cations. *Industrial & Engineering Chemistry Research* 40, 4428-4443.
- Wang, Y.Q., Fan, Q.H., Li, P., Zheng, X.B., Xu, J.Z., Jin, Y.R., Wu, W.S., 2011. The sorption of Eu(III) on calcareous soil: effects of pH, ionic strength, temperature, foreign ions and humic acid. *Journal of Radioanalytical and Nuclear Chemistry* 287, 231-237.
- Ye, Y., Chen, Z., Montavon, G., Jin, Q., Guo, Z., Wu, W., 2014. Surface complexation modeling of Eu(III) adsorption on silica in the presence of fulvic acid. *Science China Chemistry* 57, 1276-1282.