4.2.2 Influence of carbonate and gluconate on the Eu(III) and Cm(III) sorption onto clay minerals

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Introduction

Trivalent actinides generally show a strong interaction with clay mineral surfaces in terms of sorption reactions [1]. This strong retention was demonstrated recently also for highly saline conditions [2]. A significant decline in sorption is, however, to be expected in presence of organic complexing ligands, either naturally occurring like e.g. humic acids [3] or originating from the waste form or the concrete used as construction material. Among other relevant complexing ligands, gluconate as a representative of α–hydroxo carboxylic acids and an analogue to isosaccharinic acid (main product of cellulose degradation) and an important cement additive, might significantly decrease the sorption of trivalent actinides. In a recent study related to the impact of gluconate on the sorption of ^{63}Ni onto TiO_2, a decrease in sorption was observed at pH > 8, which was significantly enhanced in $CaCl_2$ containing aqueous solutions [4]. Such insufficiently understood findings prompted us to address this topic in more detail.

Sorption of europium in presence of carbonate or gluconate onto clay minerals

Only a few detailed studies are available in the literature dealing with the influence of carbonate as an omnipresent and strongly complexing groundwater ligand on actinide sorption onto clay minerals [4] and virtually no published data are available for higher ionic strength conditions, which is relevant for some nuclear waste disposal safety case studies. In order to assess the strong radionuclide retention capacity of clay minerals either in bentonite barriers or claystone host rocks of nuclear waste repositories, the potential impact of strong complexing anionic ligands on sorption must be quantified. For a sound mechanistic understanding and a reliable prediction of the metal ion sorption under relevant conditions a sufficient number of experimental data under variation of sensitive parameters (e.g. pH, ligand concentration, variation of background electrolyte concentration and composition etc.) is essential. Spectroscopic techniques such as the time resolved laser fluorescence spectroscopy (TRLFS) by using Cm provide a powerful tool to get direct information on the complexation in solution and on the mineral surface complexation by identifying different species. By combining all available information reliable thermodynamic models can be derived or validated.

In the present work batch sorption experiments in presence of carbonate or gluconate were performed with Illite du Puy (Na-IdP-2), montmorillonite (Na-SWy-2) and a synthetic iron free montmorillonite (IFM) [5], using a solid to liquid ratio of 1 g/L and

different NaCl background electrolytes concentrations (0.1, 1, 3 M). For the gluconate system experiments were done additionally also in $CaCl_2$ background electrolyte solutions (0.06, 0.6, 2 M). The radionuclide concentration was limited to $2\cdot10^{-8}$ M ^{152}Eu (carrier free) for batch experiments and $1\cdot10^{-7}$ M ^{248}Cm for TRLFS. In case of the gluconate studies all experiments were performed under argon atmosphere with $1\cdot10^{-2}$ M sodium or calcium gluconate, depending on the background electrolyte. Experiments with carbonate were performed in equilibria with different CO_2 containing atmospheres by selecting $p_{CO2}=10^{-3.3}$ (atmospheric conditions; partial pressure slightly higher compared to the obsolete standard value of $p_{CO2}=10^{-3.5}$, in consideration of the increasing global CO_2 content of the atmosphere) and 10^{-2} bar (1% CO_2 in a glove box; higher carbonate contents are expected for deep repository conditions). To guarantee equilibrium conditions with the gas phase, calculated (using the geochemical code PHREEQC and the databases THEREDA or the PSI/Nagra Chemical Thermodynamic Database) amounts of bicarbonate, carbonate and hydroxide ions were added to the solutions to achieve fixed pH values under equilibrium conditions. For TRLFS measurements with Cm in carbonate containing systems a reduced solid to liquid ratio of 0.25 g/L for measurements in suspension and 1 g/L for measurements of wet pastes were selected. Besides TRLFS spectra also fluorescence lifetime measurements have been performed.

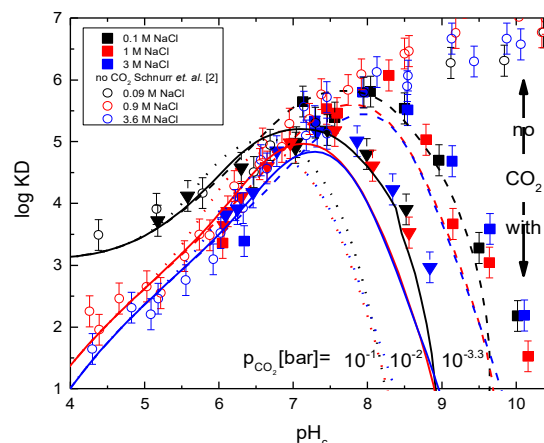A strong reduction of Eu (III) / Cm(III) retention

Fig. 1: *Sorption of Eu(III) onto Illite, from low to high salinity in absence (open symbols [2]) and presence of carbonate (closed symbols, this work) at different p_{CO2} values. Drawn, dashed and dotted lines represent calculated sorption data acc. to the 2 SPNE/CE model combined with the Pitzer approach for elevated ionic strength conditions.*
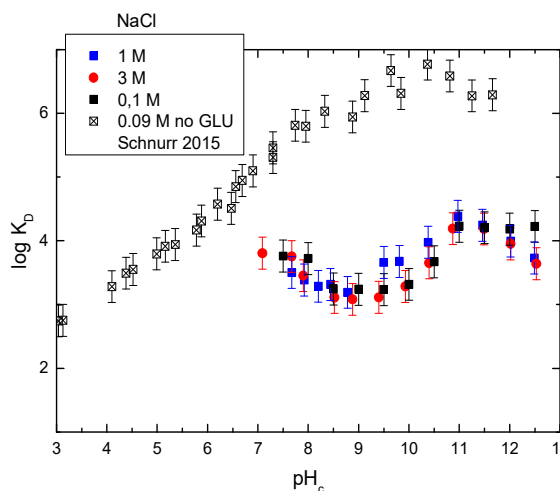
Fig. 2: *Sorption of Eu(III) onto Illite, from low to high salinity in absence (open symbols [2]) and presence of 0.01 M gluconate (closed symbols, this work) at different p_{CO2} value.*

with increasing p_{CO2} for pH > 7.5 is obvious in agreement with previous studies (Figure 1). Compared to carbonate free conditions K_D values were up to 3 orders of magnitude lower at pH ~ 9.5. No significant effect of increasing the NaCl background electrolyte concentration could be detected. The modelling of experimental data using the 2 SPNE/CE model [1] combined with the Pitzer approach to take ion-ion interactions in solution into account is in good agreement with the experimental findings. TRLFS spectra and lifetime measurements clearly point to the presence of different carbonate containing surface sorbed Cm(III) species. According to previous studies model calculations were performed using two ternary carbonate-Eu/Cm(III)-surface species (in agreement with TRLFS observations) with a slight increase of respective log K values (e.g. Illite: $\equiv$SOEuCO$_3$ with log K = 10.4, and $\equiv$SOEu(OH)CO$_3^-$ with log K = 1.8). Virtually no ionic strength effect is visible for experimental data in the pH range > 8, where carbonate influences sorption. Model calculations, however, predict a slightly decreasing sorption at increasing ionic

strength. Yet, the agreement of model calculations and experiment is still good.

First experimental results for studies with gluconate indicate a significant reduced Eu(III) sorption in the alkaline pH range consistent with previous findings obtained for ^{63}Ni and rutile. However, experiments are still ongoing and yet incomplete. Additional studies will be performed and finally complemented with establishing a geochemical sorption model to describe experimental findings.

Conclusions

The presence of competing ligands like carbonate or gluconate shows a major effect on the sorption behavior of trivalent lanthanides and actinides. First Eu(III) sorption experiments in presence of a relatively high gluconate concentration show a significantly reduced retention over the whole pH-range covered in this study. Sorption experiments in presence of carbonate were performed in equilibrium with different CO_2 containing atmospheres. This generates a pH dependent increase of carbonate concentrations, which results in strongly decreasing K_D-values with increasing pH.

References

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