Complexation and Adsorption of $^{152}\text{Eu}$ to Superplasticizers and Bentonite at Variable Salt Concentrations

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Abstract

The preferred method for the storage of spent nuclear fuel (HLW) is the disposal in deep geological formations. The repository will consist not only of the geological barrier but also of an engineered barrier and has to isolate the waste for at least $10^6$ years from the biosphere [1]. In this barrier, several materials like concrete or bentonite are effective in retention of radionuclides. In modern concrete, several additives are used to improve the properties of the cement paste. Superplasticizers of the polycarboxylateether (PCE)-family are widely used for this purpose [2]. These organic materials might have an influence on the mobility of radionuclides. Hence, it is necessary to study their complexation and adsorption behaviour with radionuclides, cement-phases like C-S-H and buffer materials like bentonite considering a possible leaching of PCE from cement in consequence of water influx. In this study, the complexation and adsorption behaviour of the superplasticizer MasterGlenium® 51 was investigated by means of the radionuclide $^{152}\text{Eu}$, which is an analogue for trivalent actinides such as Cm(III) or Am(III), at a fixed pH and variable salt concentrations (NaCl, CaCl$_2$). Complexation constant and loading capacity for the PCE with $^{152}\text{Eu}$ were determined on the basis of the Langmuir isotherm equation as well as of the charge neutralisation model [3]. Furthermore the adsorption behaviour of $^{152}\text{Eu}$ to bentonite with and without MasterGlenium51® in the presence of different background electrolytes was studied.

Introduction

Considering the situation of a deep geological repository for spent nuclear fuel, possible water intrusion and therefore the corrosion of the engineered barriers like the waste bearing canisters may take place in a few hundreds of years after inclosure of the waste. As a consequence, radionuclides may be released into the nearfield of the repository. The mobility of the radionuclides in presence of superplasticizers under alkaline conditions and high salinity up to 4 mol/L has to be investigated to evaluate the performance of the engineered barrier consisting of cement-phases like C-S-H and buffer materials such as bentonite. Complexation and adsorption of $^{152}\text{Eu}$ with MasterGlenium® 51 and bentonite were studied in batch experiments.

Methods

A stock solution of $^{152}\text{Eu(NO}_3)_3$ was prepared with a concentration of $2 \cdot 10^{-4}$ mol/L and an activity of 0.3 MBq. The solution was adjusted to pH 3 to avoid formation of colloids and wall adsorption. For recording an isotherm of binding of Eu to the superplasticizer, solutions with different concentrations of Eu(NO$_3)_3$ were prepared ranging from $10^{-7}$ mol/L down to $10^{-2}$ mol/L spiked with $^{152}\text{Eu}$ at an activity of 0.6 kBq. Experiments on the effect of electrolytes (NaCl and CaCl$_2$ up to 4 M) on complexation were carried out at a fixed $^{152}\text{Eu}$ concentration of $10^{-6}$ M. The superplasticizer was added as last component, resulting in a concentration of 100 mg/L. Separation of bound and non-bound Eu was carried out after 24 hours of contact time by ultrafiltration with polyethersulfon-membrane centrifuge filters (Vivaspin, Sartorius) with an MWCO of 3kDa. Concentrations of Eu in the filtrate were determined relative to reference samples with a Perkin Elmer Wizard 1470 automatic γ-counter in an energy window of 0 - 2 keV. Wall adsorption during equilibration in 4 mL PP tubes was found to be negligible. The amount of $^{152}\text{Eu}$ complexed to the superplasticizer was calculated from the difference in the count rates between reference and filtrates. To determine the carboxyl-content of the superplasticizer a direct titration with 0.1 M NaOH was carried out in 0.1 M NaClO$_4$ under a N$_2$ atmosphere using a WTW inoLab 720 pH meter [4]. For batch adsorption experiments, two stock suspensions of 5.05 g/L bentonite without and with NaCl or CaCl$_2$ (4.5 mol/L) were mixed at variable ratios.
before adding $^{152}$Eu and MasterGlenium® 51 at concentrations of $10^{-6}$ M and 100 mg/L, respectively. After 24 hours of end-over-end rotation at 20 rpm, the samples were centrifuged at 7000 rpm for 60 min. 3 mL of the supernatant solution was taken for analysis by γ-counting relative to reference solutions.

**Results/Discussion**

Titration of the superplasticizer MasterGlenium® 51 resulted in a carboxyl-group-content of $(1.17 \pm 0.01)$ meq/g, taken from an equivalence-point at pH 9.3. The isotherm of binding of $^{152}$Eu to the organic material exhibits a linear range from $10^{-7}$ mol/L up to $10^{-4}$ mol/L with the Langmuir parameters $\Gamma_{\text{max}} = (0.32 \pm 0.01)$ mmol/g Eu and $K_L = (15.59 \pm 0.01)$ L/mmol at pH 5.8. According to the charge neutralization model, the maximum loading $\Gamma_{\text{max}}$ is expressed as a loading capacity (LC), which is normalized to the measured content of carboxyl groups. It represents the molar fraction of the maximum available complexing sites under the given setup of experimental conditions. The Langmuir constant $K_L$ is normalized to the charge of the cation giving a stability constant $\beta$. A good agreement was obtained for the constants derived from the Langmuir isotherm equation and from charge neutralization model with $LC = 0.827 \pm 0.003$ and $\beta = (12.86 \pm 0.01)$ L/mmol. Batch sorption experiments with bentonite, MasterGlenium® 51 and $^{152}$Eu show a quantitative adsorption of Eu for all concentrations of NaCl, whereas for the CaCl$_2$ system, a pronounced decrease in adsorption was found for higher salt concentrations (down to 20 % of total Eu). The effect of the superplasticizer is relatively small in both cases, resulting in an increase in Eu adsorption approximately 5 %.

**Conclusion**

For the first time, metal complexation with a polycarboxylateether (superplasticizer) was quantitatively investigated for the example of the system Eu / MasterGlenium® 51. Interaction parameters based on the Langmuir isotherm equation and the charge neutralisation model were shown to be analogous. Competition effects of NaCl and CaCl$_2$ with respect to complexation and adsorption turned out to be very different. At the chosen pH of 5.8, the influence of the superplasticizer on adsorption of Eu onto bentonite is rather small, in spite of significant complexation. Further experiments are planned at alkaline conditions (pH 9 – 13), including the adsorption behaviour of the organic component, which will allow an elucidation of its effect on Eu adsorption.

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**References and citations**


