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The Interaction of ^{152}Eu and ^{228}Th with Calcite Under Alkaline Conditions

Jan Tits (jan.tits@psi.ch), **Erich Wieland** (erich.wieland@psi.ch),
Michael H. Bradbury (michael.bradbury@psi.ch) & **Jean-Pierre Dobler**

Paul Scherrer Institute, Laboratory for Waste Management, Villigen PSI, CH5232, Switzerland

The work described in this paper was carried out to elucidate the processes controlling the sorption of radionuclides in the alkaline disturbed zone around a nuclear waste repository. In Switzerland, it is proposed to dispose of low and short-lived intermediate level radioactive waste in a cement based repository situated in a Palfris Marl formation (NAGRA 1992). After closure, a hyperalkaline plume of cement pore water could migrate from the near-field into the marl, thus generating an alkaline disturbed zone in the host rock around the repository. Calcite makes up between 40 wt% and 70 wt% of the primary minerals in Palfris marl and will remain largely unaffected by the hyperalkaline plume. Due to its stability, calcite could play an important role in the retention of radionuclides under hyperalkaline conditions. The present study describes the adsorption of ^{152}Eu as an analogue for the trivalent actinides and ^{228}Th, a member of the tetravalent actinides respectively, on calcite, as well as the effect of gluconic acid (GLU), a frequently used cement additive, on the uptake process. The experiments were conducted in an artificial cement pore water (ACW) to simulate high pH conditions. The solution contained 0.18 M KOH, 0.114 M NaOH, 1.7 mM $Ca(OH)_2$, and had a pH of 13.3. Sorption values for ^{152}Eu and ^{228}Th were determined using the batch technique. The data are presented in terms of a distribution ratio, R_d (L kg^{-1}), which relates the quantity of radionuclide sorbed (mol kg^{-1}) to the equilibrium radionuclide concentration in the aqueous solution (M).

Prior to the sorption studies the stability of ^{152}Eu and ^{228}Th solutions in ACW was tested. The solutions were stable up to total concentrations of approximately 10^{-9} M.

Kinetic tests reveal that the adsorption of ^{152}Eu and ^{228}Th by calcite in ACW is fast reaching equilibrium within less than 2 days. Both radionuclides exhibit a very high affinity for calcite with constant R_d values of (6±4) 10^4 L kg^{-1} (^{152}Eu) and (3±2) x 10^4 L kg^{-1} (^{228}Th) over the range of concentrations investigated. The linear sorption isotherms and the fast kinetics suggest that the dominant process governing the uptake of both radionuclides is due to an adsorption process.

Increasing GLU concentrations progressively decrease the sorption values of both radionuclides due to the formation of aqueous GLU complexes. This is illustrated for ^{152}Eu in Figure 1. Note that ^{228}Th exhibits a similar behaviour. The data show that ^{152}Eu (and ^{228}Th) sorption decrease with increasing GLU concentration at levels >10^{-7} M.

VERCAMMEN (2000) has demonstrated that isosaccharinic acid (ISA), which has a similar structure to GLU, forms stable complexes with Eu(III) and Th(IV) in an ACW solution. Eu(III) co-ordinates with one ISA ligand to form a 1:1 complex, whereas Th(IV) co-ordinates with two ISA ligands and two Ca ions to form a 1:2:2 complex. With the following it is assumed that both ligands form complexes with the same stoichiometry with trivalent and tetravalent cations. The solid line in Figure 1 represents a fit of the data assuming a 1:1 Eu:GLU complex. Such a fit allows the determination of the conditional complexation constant for I=0.3: log $\beta^{0.3}$(EuGLU) = -28.1±0.2. Extrapolation to zero ionic strength using the Davies equation gives: log β^0(EuGLU) = -27.8±0.2. In a similar way data for ^{228}Th sorption in the presence of increasing GLU concentrations can be fitted assuming the formation of a 1:2:2 Th:GLU:Ca complex. The conditional complexation constant for I=0.3 is determined to be: log $\beta^{0.3}$(ThGLU) = -1.1±0.1 and extrapolation to I=0 gives: log β^0(ThGLU) = -2.4±0.

The GLU concentration in the pore water of a cementitious repository was estimated to be <10^{-7} M. Assuming that this cement pore water leaves the repository unchanged and controls the GLU concentration in the alkaline disturbed zone, the effect on the retention of ^{152}Eu and ^{228}Th will not be significant.

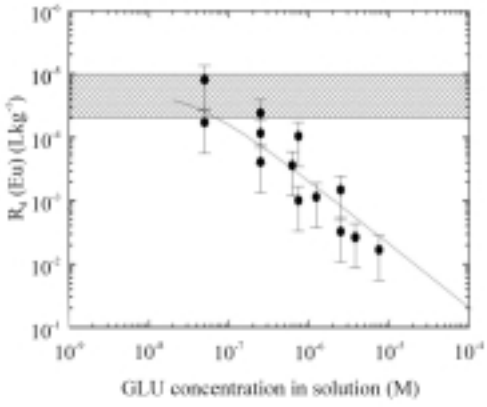

Figure 1: Influence of equilibrium GLU concentration on the uptake of ^{152}Eu by calcite in ACW at pH 13.3. The total Eu concentration was 10^{-9} M. The cross-hatched area indicates the 95% confidence interval for the R_d value in the absence of GLU. The solid line represents the best fit to the experimental data with the Eu and Th complexation constants given in the text.

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