# STUDYING Zn SORPTION ON CLAYS IN THE CONTEXT OF GEOLOGICAL DISPOSAL OF RADIOACTIVE WASTE

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## Introduction

Argillaceous rocks are studied intensively as suitable host formations for the deep geological disposal of radioactive waste, among others due to their strong radionuclide retention properties. As the retention of radiotoxic elements is strongly affected by mineral–water interface reactions, element specific solid/liquid distribution ratios ($K_d$ values) are one of the main parameters needed in safety assessment studies. Heavy metals are known to bind strongly, but their retention can be decreased in presence of complexing ligands in solution, like dissolved organic carbon.

In Belgium, Boom Clay is studied as a possible host rock. Since Boom Clay contains a considerable amount of organic matter (OM), it is expected that the dissolved fraction of the OM can play a significant role in the sorption and migration behaviour of the cationic radionuclides which tend to bind with OM too. Therefore we studied the sorption of Zn with the bottom-up approach: batch-type experiments in the absence and presence of OM were performed on illite, one of the main constitutive clay minerals present in the Boom Clay, and on the more complex system of Boom Clay itself (mix of illite, smectite and other minerals). Zinc is used as a reference for the divalent cations that sorb mainly via surface complexation. It is not a safety relevant radionuclide, but it has been chosen for practical aspects.

## Methods

The sorption isotherms with Boom Clay were performed in Real Boom Clay Water (RBCW - pore water extracted from the Boom Clay via piezometers, containing the natural present mobile OM ( ±160 mg C/L)) and Synthetic Boom Clay Water (SBCW – $NaHCO_3$ 0.015 M - similar chemical composition as RBCW but without OM). The sorption of Zn on purified Na-illite is studied in $NaClO_4$ 0.1 M buffered at pH 8.4 (pH Boom Clay) without and with humic acid (DOC 0, 15, 60 mg C $L^{-1}$) extracted from the RBCW. The total concentration of Zn varied between the detection limit and the solubility limit with each subsample containing an aliquot of $^{65}Zn$. The distribution coefficient $K_d$ was calculated in the usual manner: $K_d = \frac{A_{init}-A_{eq}}{A_{init}} \cdot \frac{V}{m}$ with $A_{init}$ and $A_{eq}$ the total initial activity and activity at equilibrium of the radionuclide in solution (Bq), V the volume of the liquid phase (L), and m the mass of the solid phase (kg). The solid – liquid ratio was 1 g/L for illite and 5 g/L for Boom Clay.

## Results

The sorption behaviour of Zn on illite at pH 8.4 at three different OM concentrations (0, 15 and 60 mg C/L) (Figure 1a) shows clearly an effect of the OM. In absence of OM, the sorption of Zn at trace concentrations on illite is very strong with log $K_d$ values ranging between 4 and 5. Adding OM (15 & 60 mg/C L) in the form of humic acids extracted from RBCW resulted in a significant decrease in sorption due to the formation of soluble complexes of Zn with OM. Sorption of Zn on Boom Clay showed a similar effect of OM (Figure 1b). When Boom Clay is equilibrated with SBCW, only the dissolved organic matter released from the clay is present in the experimental system (conc ±5 mg C/L). The log $K_d$ of Zn at trace concentrations is situated in between the log $K_d$ values obtained for Zn on illite with 0 and 15 mg C/L. The sorption increase above [Zn] $10^{-7}$ M can be attributed to the formation of insoluble complexes of Zn with the inorganic carbon of the SBCW. In equilibrium with RBCW (±160 mg C/L), Zn will sorb one order of magnitude less.

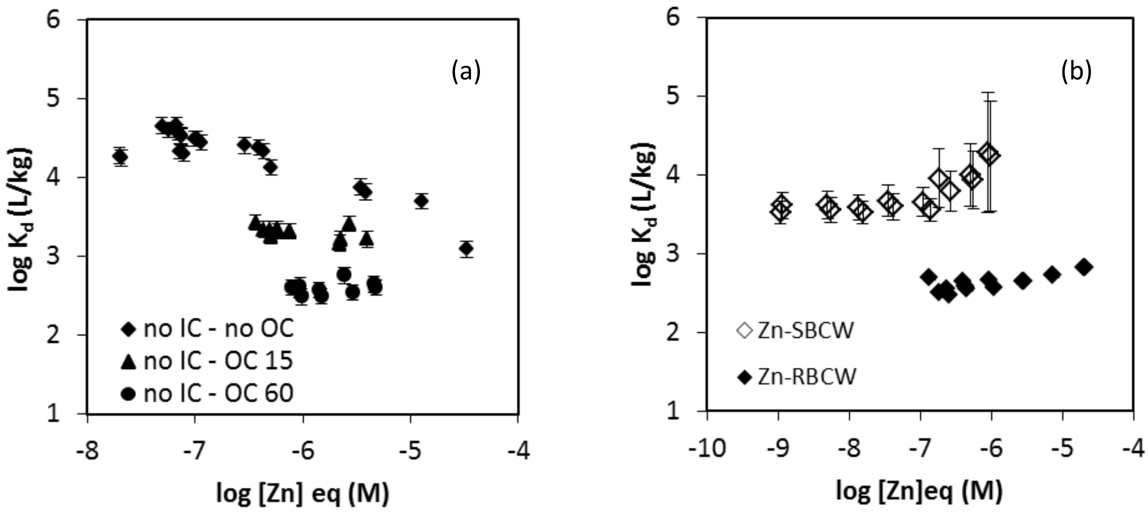


**Figure 1.** Sorption of Zn expressed as log $K_d$ in function of the Zn concentration in the solution. Graph (a) shows the sorption on illite in absence and presence of organic matter (0, 15 and 60 mg C/L), and graph (b) on Boom Clay in Real Boom Clay Water (160 mg C/L) and Synthetic Boom Clay Water (±5 mg C/L at equilibrium).

Experimental results will be compared with model calculations with the geochemical code PhreeqC using the 2SPNE-SC/CE model from Bradbury & Baeyens [1] to predict the sorption on illite. The complexation of Zn with OM will be implemented in PhreeqC by the Humic Ion-Binding Model VI [2].

## Conclusion

The sorption behaviour of Zn on the single clay mineral illite and on Boom Clay is clearly affected by the complexation of Zn with the dissolved organic matter, which makes Zn less available for sorption on the clay. This is an important issue towards safety assessment studies. In order to predict the sorption and migration of radionuclides in the clay precisely, it is important to implement the binding of the cations with organic matter in the predictive model in an accurate way.

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