

Background

In Belgium the Boom Clay is considered as a reference formation for methodological studies for deep geological disposal of high level radioactive waste and spent fuel. The Boom Clay has many favourable physical and geochemical characteristics, like diffusion-dominated transport (very low permeability), and pronounced capability for an efficient retardation (by sorption processes) of mobile radionuclides (slightly alkaline pH and reducing conditions). A focussed research programme was started on radionuclide sorption on Boom Clay with a two-fold goal: 1) to acquire and select sorption parameters that serve as an input for safety assessment calculations 2) to scientifically underpin the selected data by demonstrating a comprehensive understanding of the radionuclide uptake processes in the host formation. This latter goal necessitates the ability to sufficiently describe the most relevant radionuclide uptake processes by means of quasi-mechanistic chemical formulations.

In Boom Clay pore water, the most important reactions for lanthanide and actinide ions influencing their speciation and mobility, are hydrolysis and complexation with naturally occurring ligands such as inorganic carbonate and dissolved organic matter (OM ~ 100 ppm C). Interaction with dissolved OM generally leads to a decreased sorption to the mineral surface, thus increasing the mobility of the radionuclide. A good description of these interactions is therefore needed for making trustworthy predictions.

Objectives

- To obtain high quality sorption datasets for representative trivalent (Eu) and tetravalent (Th) RN (radionuclides) on Boom Clay while scoping the influence of organic matter on the sorption behaviour.
- To describe RN uptake on Boom Clay in presence of OM by a (quasi)-mechanistic model which enables predictions to be made.

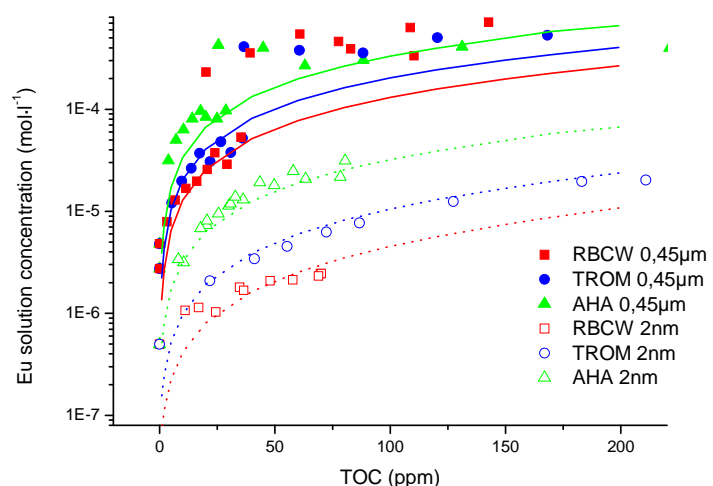
Principal results

The methodology followed is a bottom-up approach: from separate well-defined systems to more complex mixtures. First we investigate the interaction of the RN with OM in the aqueous phase (mostly by means of solubility-type experiments) and try to describe the observed behaviour by means of interaction constants. Secondly we investigate the interaction of the RN with a major component of the Boom Clay, e.g. illite and describe this in terms of (quasi-mechanistic) surface complexation constants.

Thirdly, we investigate the interaction of RN with the selected major Boom Clay component in presence of OM and check if this can be described by combining the obtained interaction parameters of the subsystems into one consistent model.

Finally, we check if RN sorption onto the complex Boom Clay matrix, consisting of more than 10 different components, can be described based on the model derived for the simplified systems. Currently this study is finalised for the system Eu-OM-illite.

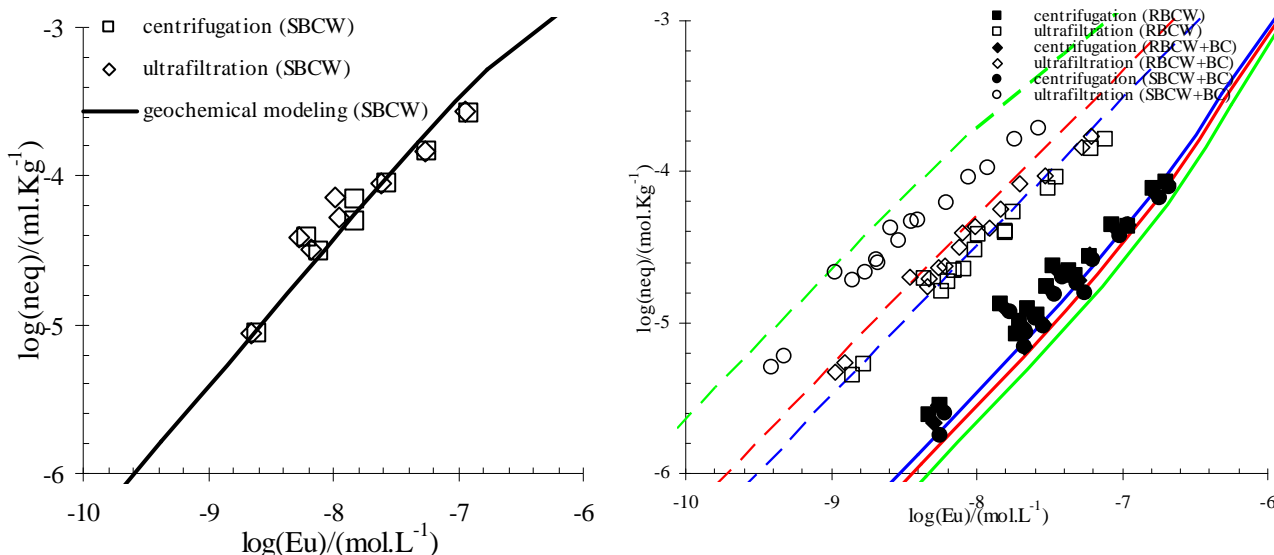
The interaction of Eu with OM was investigated by looking at the influence of dissolved organic matter on the solubility of Eu in Synthetic Boom Clay Water electrolyte (SBCW). Crystalline $\text{Eu}(\text{OH})_3$ was mixed with SBCW containing different concentrations of OM. With increasing OM, the Eu concentration increased which indicated a complexation-like interaction mechanism between inorganic Eu species and dissolved OM colloids. All of the data sets could be modelled (using PHREEQC geochemical modelling code) using a combination of solubility calculations (using the Nagra/PSI thermodynamic database) and complexation reactions between Eu^{3+} and OM functional groups. For the description of the interaction of Eu and NOM, a simple free ligand approach and a more sophisticated



Effect of increasing OM concentrations on the Eu solubility in synthetic Boom Clay water and simulations based on Tipping's humic ion binding model VI

Tipping humic ion-binding model VI were successfully introduced into the PHREEQC geochemical code and tested. Both models provided good fits to the data, but the parameters obtained from the first model are only valid for similar geochemical conditions ("conditional" complexation constants) while the latter model provides "intrinsic" binding constants between Eu^{3+} and NOM independent of the geochemical conditions.

The sorption behaviour of Eu on purified illite in SBCW electrolyte (binary sorption system) was successfully modelled by the 2SPNE SC/CE model (2 site protolysis non-electrostatic surface complexation/cation exchange model, developed by Bradbury and Baeyens, 1997, 2005).



Eu sorption isotherms on illite in absence (left) and presence (right) of organic matter. The lines denote simulated sorption isotherms based on the 2SPNE SC/CE sorption model in combination with Tipping's Humic ion binding model VI

With some reasonable modification to the Eu-OM interaction parameters obtained from the Eu solubility experiments, the influence of organic matter on the Eu sorption on illite (ternary sorption system) could be well described using the 2SPNE SC/CE model combined with the Tipping humic ion-binding model VI (using PHREEQC geochemical code).

We are now able to describe in a (quasi)-mechanistic way the interaction of trivalent Eu onto illite clay in presence of complexing organic matter. This will help us to interpret and simulate the sorption behaviour of trivalent RN onto Boom Clay and it will enable us to make more trustworthy predictions.

Future developments

- Simulation of Am sorption onto BC in representative BC water based on the Eu-NOM-illite system.
- Finalisation of a similar study for Th as a representative for tetravalent RN.

Main contact person

Christophe Bruggeman, christophe.bruggeman@sckcen.be

Sonia Salah, sonja.salah@sckcen.be

Norbert Maes, norbert.maes@sckcen.be

Main reference

D.J. Liu, C. Bruggeman, N. Maes, "Influence of Natural Organic Matter on the Solubility of Eu in Boom Clay pore water", submitted for publication in Radiochimica Acta (2007)

D.J. Liu, C. Bruggeman, N. Maes, "Influence of Boom Clay Organic Matter on the adsorption of Eu^{3+} by illite", paper in preparation (2007)

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