

A CONSISTENT PHENOMENOLOGICAL MODEL FOR NATURAL ORGANIC MATTER LINKED MIGRATION OF Cm(III), Pu(III/IV), Np(IV), Tc(IV) AND Pa(V) IN THE BOOM CLAY

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As Natural Organic Matter (NOM) may modify/enhance the mobility of radionuclides (RNs) through complexation or colloidal interactions, it is essential to evaluate the impact of these processes before performing safety assessments aiming at demonstrating the suitability of deep-seated clayey formations for geological disposal of radioactive waste.

Column migration experiments (Figure 1) with Cm, Pu, Np, Tc and Pa in Boom Clay, initiated about 10 years ago, showed strikingly similar features despite their different chemical speciation. On a relative short time, these RNs began percolating through the clay core until a constant concentration at the outlet side was reached (Figure 1). As most of the aqueous forms of these RNs are supposed to sorb strongly onto the Boom Clay solid phase, it was assumed that their relative fast transport was due to colloids (either intrinsic colloids or NOM-colloids). The constant concentration percolating from the core was thought to result from a solubility limiting phase precipitated at the source position. However, the concentrations in the percolate were systematically lower than the thermodynamic calculated solubilities, and all the more, complexation to NOM would likely result in an increased RN concentration. Although these curves could be modelled by a simple diffusion-advection relationship with linear sorption, they could not be backed up by a mechanistic understanding (Wang *et al.*, 2001).

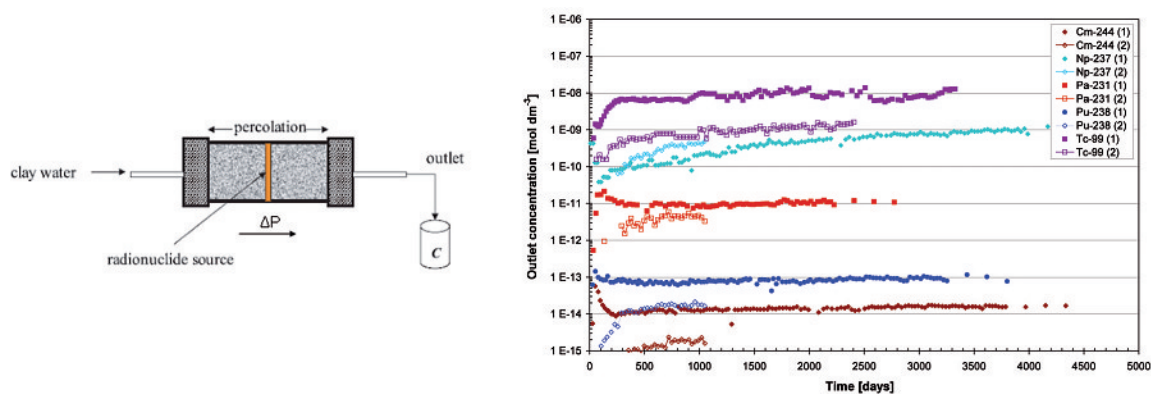


Figure 1: Experimental set-up (left side) and data (right side, evolution with time of the concentrations measured in the water collected at the outlet of the diffusion experiments for clay core 1 (1) and core 2 (2)).

As the concentration in the percolate remained constant for many years, the RN-species eluting from the core are assumed to be well in equilibrium with the Boom Clay geochemical conditions. Therefore, they were used as input source (constant concentration boundary condition) for a migration experiment through a fresh clay core (i.e. the outlet of a first cell was coupled to the inlet of a second cell). The measured concentrations at the outlet of the second clay core also reached a constant value, but this value is about one order of magnitude lower than for the first cell (Figure 1). This indicates that the species that is transported is not a conservative tracer as otherwise the outlet concentration should equal the inlet concentration.

Recently, Bruggeman and Maes (2009) put forward a phenomenological model which describes the Tc retention and transport mechanisms in Boom Clay. They hypothesise that Tc is transported as a Tc-NOM

colloidal species exhibiting slow dissociation kinetics. This phenomenological model was now tested to describe the NOM related transport of Cm, Pu, Np, Tc and Pa in these “sequential” migration experiments. All these RNs are known to form strong complexes with NOM in batch experiments.

To describe the RN elution profiles from the second clay core, we used the migration parameters (diffusion coefficient, porosity and retardation factor) of NOM derived from small-scale lab experiments (Put *et al.*, 1998) and validated by large-scale (long-term) in-situ tests (Martens and Maes, 2009) in combination with a first order kinetic dissociation reaction.

The transport feature of the geochemical code PhreeqC-2 (Parkhurst and Appelo, 1999) was used for the simulations.

Based on the original NOM transport parameters, and a narrow range for the parameter in the kinetic dissociation equation ($2.4-8.5 \times 10^{-8} \text{s}^{-1}$), a good match with the experimental data could be achieved for all RNs considered in this study (Figure 2). This supports our hypothesis that for a large array of RNs (Tc, Pa, Np, Pu and Cm in this study), the transport behaviour observed in the experiments is indeed linked to NOM, irrespective of their dominant valence state (tri-, tetra-, pentavalent). Their overall transport potential (at longer times and distances) remains limited due to dissociation and subsequent sorption on the Boom Clay.

The results presented in this study form an important step forward for safety assessments analysis: (i) the model is easy to implement, (ii) there is a link with a phenomenological description, and (iii) elements with a similar NOM association behaviour can be described in the same way with more or less the same parameters.

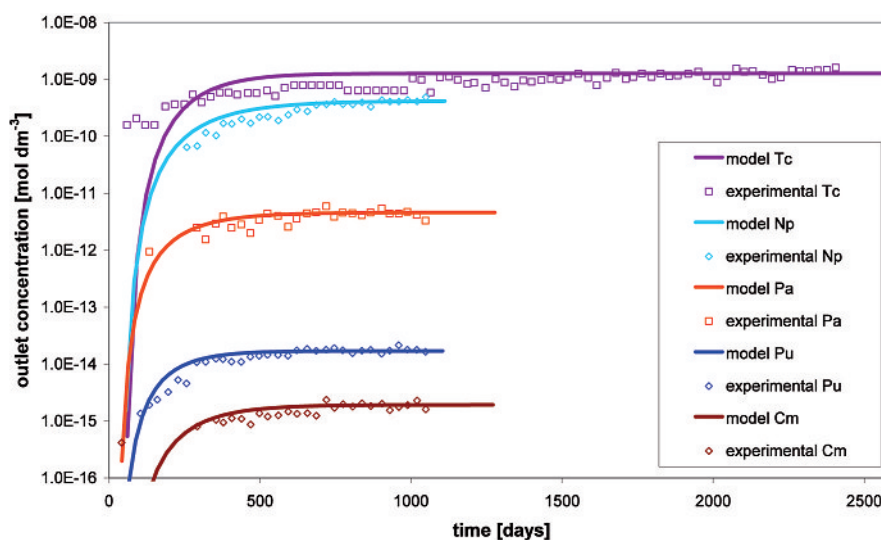


Figure 2: Experimental and modelled outlet concentrations (Tc, Pa, Np, Pu and Cm) for the second clay core.

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