# TECHNETIUM MIGRATION IN BOOM CLAY – ASSESSING THE ROLE OF COLLOID-FACILITATED TRANSPORT IN A DEEP CLAY FORMATION

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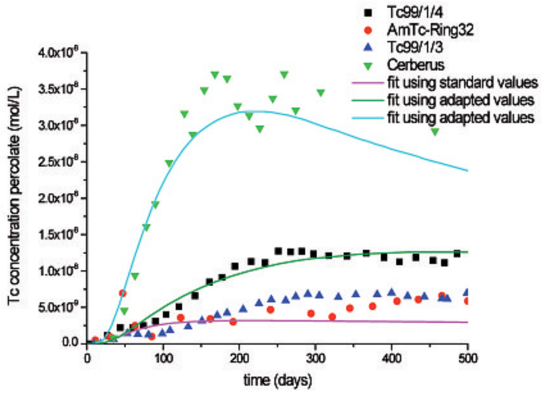
The role of colloids – mainly dissolved natural organic matter (NOM, 50-150 mg/l) - in the transport of radionuclides in the Boom Clay formation (Mol, Belgium), has long since been a matter of (heavy) debate. For more than 20 years, batch experiments with Boom Clay suspensions showed a pronounced influence of the dissolved organic carbon concentration on the aqueous concentrations of different radionuclides like Tc, Np, Am and U (Henrion *et al*., 1988). Moreover, small fractions of these radionuclides were also observed to elute almost unretarded out of confined clay cores in percolation experiments (Maes *et al*., 2006).

In the past years, a new conceptual model for the speciation of the long-lived fission product Technetium-99 ($^{99}$Tc) under Boom Clay conditions has been drafted. In brief, the stable oxidation state of $^{99}$Tc in these conditions is +IV (Geraedts *et al*., 2002; Baston *et al*., 2002), and, therefore, Tc solution concentrations are limited by the solubility of $TcO_2.nH_2O(s)$ (Rard *et al*., 1999; Baston *et al*., 2002; Rard, 2005). However, during reduction of $Tc^{VII}$ (in the $TcO_4^-$ form) to $Tc^{IV}$, precursor $TcO_2.nH_2O$ colloids are formed, which are stabilised by the dissolved organic matter present in Boom Clay interstitial porewater, and in supernatants of Boom Clay batch suspensions (Maes *et al*., 2004). Moreover, this stabilisation process occurs in such a systematic way, that (conditional) interaction constants could be established, and the behaviour was described as a "hydrophobic sorption", or, more accurately, a "colloid-colloid" interaction (Maes *et al*., 2003).

This conceptual model was implemented into PhreeqC geochemical and Hydrus transport code to come to a reactive transport model that was used to simulate both the outflow and the tracer profile in several long-term running percolation experiments (both in lab and under *in situ* conditions). To account for slow dissociation kinetics of Tc from the NOM colloid, a first-order kinetic rate equation was also added to the model. In order to describe the migration of colloidal particles (NOM), an independent study on the migration of natural organic matter was used to extract migration parameters (Martens *et al*., 2009). This independent study relied on both lab-scale and *in situ* large-scale migration experiments with $^{14}$C-labelled NOM which were performed over a period of 15 years. A classic diffusion-advection equation, including a colloid filtration term and/or non-linear sorption, simulated the experimental data quite well and could also account for the anisotropy of the Boom Clay formation.

By using information from independent experiments on processes that were assumed to occur upon transport of Tc through the Boom Clay formation, the degree of freedom of the model was seriously constrained. All parameters used in the reactive transport model (Tc solubility, complexation with inorganic ligands, stability constant for the "colloid-colloid" interaction process, solid-solution distribution coefficient of aqueous inorganic Tc species) were either taken from established thermodynamic data sources, or from published data of batch experiments. Only the first-order kinetic rate that accounted for slow decoupling of the Tc colloid and the organic matter colloids was fitted. An accurate model simulation could be obtained both for the Tc concentration in the outflowing solution, and the Tc tracer profile across the clay cores used in the setup.

The good accuracy between the reactive transport model, batch experimental data and the experimental percolation data shows that the conceptual model is strong enough to handle different types of experimental



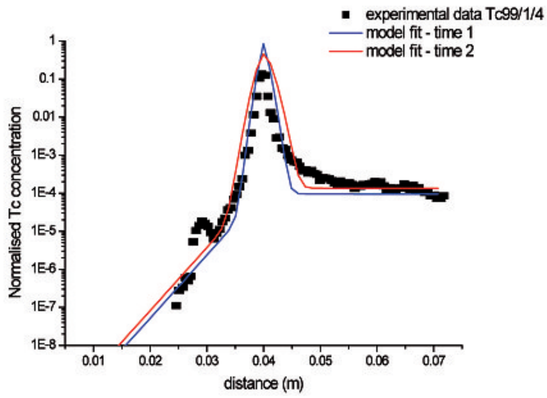




**Figure 1:** (left) Tc concentration in the percolate of four different migration experiments performed under lab (Tc99/1/4 and Tc99/1/3) or *in situ* conditions (Am-Tc-Ring32 and Cerberus). Model fits are continuous lines.
(right) normalised Tc concentration profile in a clay core cut after ~ 10 years since start of percolation experiments under lab conditions. Model fits are continuous lines.

setups, and allows to make interpolations for different geochemical conditions. Moreover, the model was adapted to make predictions of Tc migration as a NOM-associated colloid over the entire height of the overlying formation. Based on these predictions, we are now able to assess the potential for colloid-facilitated transport of radionuclides by dissolved NOM in Boom Clay.

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