Migration case study: transport of radionuclides in a reducing clay sediment

Fact Sheet

Project Information

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Objective

For deep geological disposal of radioactive waste in clay, it is essential to consider the mobility of radionuclides. This proposal addresses the migration behaviour of radionuclides (U, Pu, Se and Am), identified as critical by Performance Assessment, in a reducing clay environment, with special emphasis on the role of the organic matter. Considerable attention is devoted to developing and demonstrating concepts describing radionuclide migration and the acquisition of the model parameters. An equal amount of effort is devoted to batch experiments, aimed at understanding the mechanisms behind the migration.

Batch experiments revealed that the solubility of amorphous UO2 is \( \sim 10^{-8} \text{ mol dm}^{-3} \) with no effect of NOM complexation. However, it was evidenced that the presence of NOM facilitated the formation of uranium colloids upon dissolution of UO2. The formation of colloids, with molecular size between 2 nm and 0.45 µm, accounts for a total uranium concentration, three orders of magnitude higher than the solubility of the amorphous UO2. These colloids, only evidenced in batch experiments, are
unlikely to be mobile in the compact natural Boom Clay. Electromigration experiments showed that U(VI) reduces to U(IV) and precipitates. This U(IV) precipitated phase constantly releases positive or neutral charged U-species. Furthermore, classical migration experiments with U(IV) mixed with 14C-labelled NOM showed that U(IV) migrates independently of the NOM through the Boom Clay. The migration of uranium in the Boom Clay is governed by strong retention due to precipitation (solubility limit) and sorption and is not enhanced by the mobile organic matter. Oxidised selenium species, as might be present in the waste forms, undergo a slow reduction in the Boom Clay. SeO42-, although thermodynamically not stable under the Boom Clay conditions, remains fairly stable, and migrates unretarded through the Boom Clay. SeO32-, showes a more complex behaviour which is described as a kinetically controlled sorption-reduction process ending in a constant Se concentration of ~ 3 10-9 mol dm-3 similar to the concentration in equilibrium with a prepared Se(0) phase.

Part of the Se in solution is found to be associated with OM as a colloid and not as a complex and did not have a pronounced effect on the Se(0) solubility. Solubility experiments of Pu(IV) in absence and presence of Boom Clay organic matter were not conclusive: Pu concentrations (< 30 000 MWCO) of 4 10-8 mol dm-3 up to 8 10-7 mol dm-3 were measured with increasing Pu concentration as a function of NOM concentration suggesting that NOM may increase the Pu(IV) solubility by an order of magnitude. Migration experiments with Pu(IV) showed that the spiking solution contains Pu-OM complexes. But no enhanced transport of Pu by OM, in terms of mobile Pu-OM species (complexes or colloids) was noticed. These are either filtered or instable with respect to the clay phase. The Pu transport mechanism can be described by an immobilisation (solubility or quasi irreversible interaction with the solid phase) followed by a constant release of Pu and resembles the behaviour of the trivalent Am. Am-OM complexes dissociate, almost instantaneously, when contacted with Boom Clay and only a small portion persists as "stabilised" Am-OM complex leading to a constant bleeding of Am. These "stabilised" Am-OM complexes also dissociate upon travelling through the clay but this dissociation is controlled by slow kinetics. The constant bleeding of Am, [Am]~10-13 - 10-12 mol dm-3, is caused by an Am "source" which is not associated to OM (inorganic Am-"solid phases") acting as a continuous source of Am to form "stabilised" Am-OM complexes which results in a constant release of Am. This immobilisation/constant release resembles a solubility like process. The experimentally observed constant concentration of mobile Americium is treated in PA as a constant concentration source released from immobilised Am, which diffuses through the Boom Clay with a similar migration parameters as the mobile OM. A transport model, POPCORN, is developed to describe and evaluate the influence of OM on radionuclide transport in clay.

It accounts for attachement/detachment rates of OM to clay surfaces, the kinetics of RN complexation to, and destabilisation from, OM. The model described well the Am-OM transport behaviour and offers potential means of extrapolating parameter
values for application of the model to larger-scale. Methodologies were developed to identify the source of mobile NOM: leaching, discrete porewater sampling & OM isolation, characterisation of the kerogen. Solving the question on the source of mobile NOM was however beyond the scope of the project, but the methodologies are proven to be useful and will be further explored. The transport mechanism for the studied radionuclides (except for SeO42) is dominated by an immobilisation (precipitation or strong, quasi irreversible interaction with the solid phase) process with a constant release of RN. The transport of the released RN is only in case of the trivalent Am (possibly also Pu) correlated with NOM. PA calculations are therefore performed with a limited set of parameters: concentration limit (or solubility limit), Dpore, R and diffusion accessible porosity. The values are taken from experimental observations and interpretations. Examples of PA calculations for U and Se in BC are performed with selected data and compared to former used datasets. Special attention is given to selenate as possible species and the presence of inactive Se in the waste.

Programme(s)

Topic(s)

Funding Scheme

CSC - Cost-sharing contracts

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