

## Background

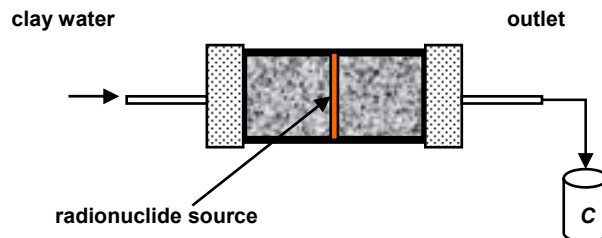
For the disposal of high-level radioactive waste (HLW) in a deep geological formation such as the Boom Clay, safety assessment studies have shown that the long-lived  $^{79}\text{Se}$  ( $T_{1/2}$  presently reassessed to  $\sim 295$  ka) is one of the more critical fission products. Therefore, the understanding of its migration properties (diffusion, retention, sorption, solubility) through the geological barrier is of prime importance. The migration behaviour of selenium strongly depends on its chemical speciation. Under the reducing conditions prevailing in Boom Clay, selenide,  $[\text{Se}(-\text{II})]$ , is the thermodynamically stable species, and  $\text{HSe}^-$  is expected to be the dominant selenium species in solution. The selenium migration should mainly be controlled by the low solubility of iron selenide such as  $\text{FeSe}$  or  $\text{FeSe}_2$ , or solid solutions with seleniferous pyrite. However Se species are often found in redox disequilibrium and more soluble higher oxidation state [selenite:  $\text{Se}(+\text{IV})$ , and selenate:  $\text{Se}(+\text{VI})$ ] might also coexist if their reduction is kinetically hindered. Due to the unknown oxidation state of selenium in the waste form and the uncertainties related to the redox disequilibrium it is important to study the behaviour of selenium in all its oxidation states.

## Objectives

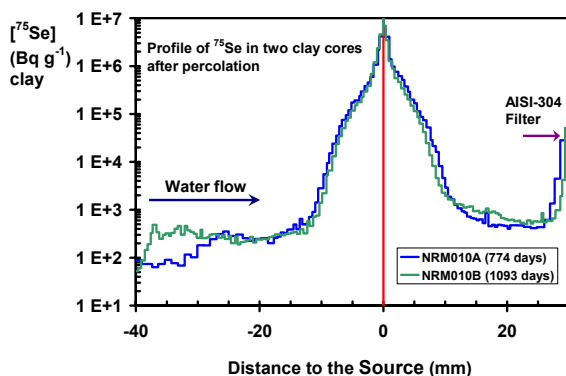
The aim of the study on the behaviour of selenium in Boom Clay is to understand its chemical speciation under *in situ* conditions and especially the “*redox stability*” of selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ) whose reduction kinetics can be extremely slow. Then, to determine for the various selenium species present in solution, their solubility, their sorption distribution coefficient ( $K_d$  approach), and their diffusion coefficient in Boom Clay to provide relevant conceptual models and associated transport parameters for safety assessment purposes. To achieve this objective, an interdisciplinary study was undertaken by SCK·CEN for ONDRAF/NIRAS in close collaboration with KULeuven and AEA Technology.

## Principal results

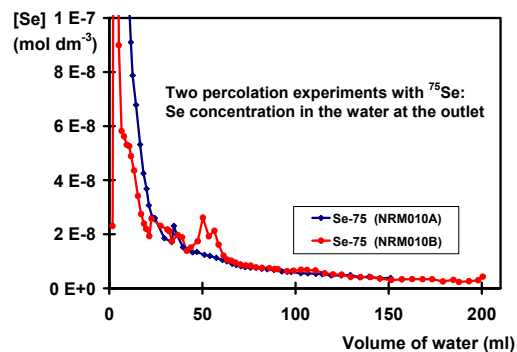
Diffusion and percolation experiments on small clay cores with selenite ( $\text{SeO}_3^{2-}$ ) have been affected by the effects of reactive transport. The obtained diffusion patterns are intricate and cannot be used to determine migration parameters. It indicates that precipitation reactions due to reduction have occurred. A slow reduction of  $\text{SeO}_3^{2-}$ , followed by precipitation of phases, such as, e.g.,  $\text{Se}(0)$  or  $\text{FeSe}$ , likely arises, but, no information could be obtained on the exact nature of the precipitate and its solubility.



Schematic principle of a percolation experiment with a  $^{75}\text{Se}$  source sandwiched between two clay cores.



The complicated  $^{75}\text{Se}$  profiles obtained after slicing two Boom Clay cores indicate chemical-coupled transport.



Concentration of  $^{75}\text{Se}$  measured in the water percolated through two different clay cores.

Electromigration tests made by Beauwens *et al.* (2005) with selenate ( $\text{SeO}_4^{2-}$ ) have indicated that selenate did not sorb and did not undergo any reduction, nor precipitation in the conditions and time scale of the experiments. So, selenate migrates as a non-retarded and soluble divalent anion ( $D_{\text{app}} = 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ). Similar electromigration experiments performed with selenite ( $\text{SeO}_3^{2-}$ ), revealed that, at the contrary of selenate, selenite was sorbed and underwent a slow reduction to finally precipitate as  $\text{Se}(0)$  or  $\text{FeSe}$ .

Complementary to the migration tests, batch experiments were performed with different synthetic selenium solid phases. The solubility of  $\text{Se}(0)$  and  $\text{FeSe}$  was investigated. Furthermore, the interaction of the Se-oxyanions with pyrite and Boom Clay was studied to elucidate the interaction mechanism: sorption, reduction, and precipitation. Solubility tests were carried out with initial selenium concentrations respectively higher and lower than the value expected at saturation. Results indicate no reduction or sorption of selenate after one year equilibration time with pyrite or Boom Clay suspensions.

The interaction of  $\text{SeO}_3^{2-}$  with  $\text{FeS}_2$ , can be described by sorption followed by a slow reduction and precipitation of a Se-solid phase with a solubility of  $10^{-9} \text{ M}$  which corresponds to the solubility of the prepared crystalline  $\text{Se}(0)$  phase. The reduction kinetics were slow but the rate was faster for suspensions with low concentration of dissolved selenite and high amount of pyrite. In Boom Clay, a competition also likely exists between two different sorption sites: selenite can sorb onto clay minerals (60 wt. %), or onto pyrite (2 wt. %). The affinity and the extent of sorption of  $\text{SeO}_3^{2-}$  for clay minerals appears to be stronger than for pyrite. So, before that reduction can take place onto the pyrite reactive surface, a desorption of selenite from the clay sites must first occur. As a consequence, the reduction kinetics at the pyrite surface were slowed down but resulted in a Se concentration close to the solubility value. An interaction between Se and organic matter colloids was also observed.

So, experiments in reducing environments starting from selenium oxyanions proceed only very slowly to thermodynamical equilibrium. If selenium is released as selenate from spent nuclear fuel and if selenate reduction is exceedingly slow under Boom Clay conditions because of redox-disequilibrium,  $^{79}\text{Se}$  is presently expected to migrate as an unretarded species without solubility limit. Then, it would be one of the main contributors to the dose.

Noticeable progresses, resulting in a higher degree of confidence in the system, have been achieved thanks to a better understanding of the geochemical behaviour of selenium in Boom Clay. On the basis of the present results safety assessment calculations can now be updated to reduce the remaining uncertainties.

### Future works

In order to unravel the intricate sorption mechanism of selenite, a more detailed study of its chemisorption onto clay minerals frayed edges is needed and currently under study by our partners of KULeuven. Now that the transport parameters of Se-oxyanions are available, new migration experiments dedicated to selenide ( $\text{HSe}^-$ ) must be performed again with freshly prepared sources of reduced selenium ( $\text{Se}^0$  or  $\text{FeSe}$ ).

Recent publications indicate that selenate reduction can be catalysed by "green rust" a corrosion product of iron (from canisters and overpacks). Other works in the field of geo-microbiology also suggest that bacterially-mediated reduction of selenate should not be excluded in the near-field environment. Because of the redox-disequilibrium of selenate under *in situ* Boom Clay conditions, these unusual, but possible, reduction mechanisms and their kinetics certainly deserve further attention.

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