How do redox alterations of Boom Clay change its interactions with selenite?

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Selenium-79 (^{79}Se), a fission product present in spent nuclear fuel, is a radionuclide of concern in radioactive waste disposal due to its long half-life and relatively high mobility. Boom Clay (BC), a clay-rich formation and potential host rock for radioactive waste in the Netherlands and Belgium, has been shown to be able to retard migration of Se by reduction of Se^{IV} to Se^0 and by adsorption of Se^{IV} to clay minerals. However, the capability of BC to reduce Se^{IV} may be affected by oxidation of BC during construction and operation of the repository.

To examine the effect of BC redox transformations on interactions with Se^{IV}, batch experiments were performed. BC was separated in different size fractions (clay, silt, total sample) to distinguish the influence of redox alterations on the interactions with clay minerals from those of other reactive minerals such as pyrite. The redox state of the different size fractions was chemically altered using BH_4^- and H_2O_2 as a reducing or oxidizing agent, respectively. Upon this treatment, materials with four different levels of redox modification were obtained: reduced, unaltered, partially-oxidized and fully-oxidized. The redox modification of BC changed the kinetics of the Se partitioning between solids and solution. Initially, oxidation of BC led to a faster removal of dissolved Se. However, after one month, concentrations of dissolved Se were higher in oxidized compared to unaltered BC. X-ray absorption spectroscopy (XAS) was used to determine the oxidation state of solid-bound Se. Analyses of the XAS spectra indicate that, after 30 days, Se in partially-oxidized and fully-oxidized clay fractions was predominately present in the form of adsorbed SeO_3^{2-}. This was also the case in the fully-oxidized silt fraction but not in the experiments containing all size fractions. It is remarkable that this material retains reductive potential even after rigorous treatment with H_2O_2. Reduction of SeO_3^{2-} to Se^0 was detected in all other materials where only unaltered and reduced materials displayed complete reduction after 30 days. This shows that the contribution of adsorption and reduction to the removal of dissolved Se is altered upon reduction or oxidation of the BC material.