Determining redox capacaties of Boom Clay material by using an electrochemical approach

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Boom Clay (BC) is investigated as a potential host formation for geological disposal of radioactive waste in Belgium and the Netherlands. Knowing the redox properties of BC is important for assessing the speciation and, by this, the migration of radionuclides in the formation. The electron accepting (EAC) and donating capacities (EDC) are relevant for predicting the progression of redox fronts and the potential capacities of the formation to reduce or oxidize redox sensitive radionuclides. A novel electrochemical method, including the addition of mediators, has been successfully applied to characterize redox properties of natural organic matter [1] and clay minerals [2]. Here, we evaluate the applicability of the method to determine redox capacities of BC which contains various potentially redox active constituents such as clay minerals, pyrite and organic matter.

In general, the EAC of BC samples was smaller than the corresponding EDC. The shape of the oxidative current peaks (oxCPs) suggested that more than one component contributed to the EDC. Comparison with measurements of Fe-rich clay minerals and pyrite indicates that the shape of the OCPs can be explained by the different reactivity of these two BC constituents. That is, oxidation of Fe(II) in clay minerals occurs faster than oxidation of pyrite and the measured currents reflect the combination of both kinetics.

Based on the analyses of reference materials, a mathematical procedure was developed which was capable of deconvoluting oxCPs obtained for synthetic mixtures of pyrite and clay minerals and also to reproduce the oxCPs of BC material. Comparison of the determined EDC of pyrite and clay minerals in BC with results from sequential extractions and Mössbauer analyses indicate that only part of the clay-bound Fe is redox active and that the electrochemical method tends to underestimate the EDC of pyrite.

[1] Aeschbacher, et. al. (2010) *ES&T* **44,** 87-93. [2] Gorski,et al. (2012) *ES&T* **46**, 9360-9368