Surface complexation and oxidation of ferrous iron on montmorillonites

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Ferrous iron (Fe^{II}) is involved in many environmental geochemical processes and has a widespread occurrence in anaerobic conditions and in radioactive waste repositories. Through the corrosion process of steel canisters large amounts of Fe^{II} will be produced and released into the engineered barrier system. With respect to reduction reactions of redox sensitive contaminats, Fe^{II} bound to solid phases is much more reactive than dissolved Fe^{II}. Hence, the presence of high Fe^{II} concentrations could have a significant influence on the retention of redox-sensitive contaminants by clay minerals. In this study the uptake of Fe^{II} by several montmorillonites with low and high structural ferric iron (Fe^{III}) was investigated by batch sorption experiments, surface complexation modelling, Mössbauer and X-ray absorption spectroscopy (XAS) under anoxic and electrochemically controlled reducing conditions [1,2]. Under anoxic conditions Fe^{II} sorption on Fe^{III}-poor montmorillonites followed well the uptake of other divalent metals and could be successfully modelled with a non-electrostatic surface complexation model. In contrast, the reaction of Fe^{II} with Fe^{III}-rich montmorillonite yielded considerably higher sorption values, and the Fe^{II} uptake could be reproduced only after introducing an additional surface reaction involving an electron transfer to the surface-bound Fe^{II}. Sorption experiments under electrochemically reducing conditions were in agreement with the sorption on the Fe^{III}-poor montmorillonite. The oxidation state of sorbed and structural iron was probed by Mössbauer spectroscopy on samples prepared under anoxic conditions. Iron was mainly sorbed as Fe^{II} on Fe^{III}-poor clays whereas on Fe^{III}-rich clays, iron is predominantly oxidized to surface-bound Fe^{III} and Fe^{III}-oxides. Upon sorption of Fe^{II}, part of structural iron in Fe^{III}-rich montmorillonite is reduced to Fe^{II}, which unambiguously evidences the role of structural Fe^{III} as an e^- acceptor. These results were supported by XAS measurements. This study highlights the importance of structural iron (*i.e.* oxidation state and availability) on the uptake of ferrous iron on clay minerals.

[1] Soltermann et al. 2014, *Environ. Sci. & Technol.* **48**, 8698-705. [2] Soltermann et al. 2014, *Environ. Sci. & Technol.* **48**, 8688-97.