Sorption Kinetics of Plutonium (V) to Three Montmorillonite Clays

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The sorption of Pu(V) to montmorillonite clay leads to the reduction of Pu(V) to Pu(IV) on the clay surface. In this project, the role of structural Fe on this reaction was investigated by quantifying Pu(V) sorption rates under atmospheric (oxic) conditions to three different montmorillonites with variable Fe content (SWy-1: 2.6 Wt % Fe; STx-1: 0.6 Wt % Fe; Barasym SSM: 0.01 Wt % Fe) at pH 4, pH 6, and pH 8. At all pH values, the sorption rate was positively correlated with structural Fe content. However, by 360 d, the extent of sorption was independent of Fe. Moreover, in the case of SSM (lowest Fe content) it was not apparent that sorption equilibrium had been achieved by the end of the experiment. The results indicate that at circumneutral pH, structural Fe will affect the kinetics of Pu(V) surface mediated reduction on montmorillonite but not necessarily the equilibrium Pu sorption affinity at environmentally relevant timescales. The differences in sorption rates and sorption extent on the three clays emphasize the need to perform long-term sorption experiments (> 1 year) to adequately capture the equilibrium processes controlling the uptake of Pu under oxic conditions. Comparison to other minerals indicates that surface mediated reduction rates of Pu(V) to Pu(IV) can vary by as much as five orders of magnitude depending on the structure and composition of the surface. The results highlight the confounding effect of Pu redox transformation kinetics on its observed behavior and the difficulties this causes for determining equilibrium values.