

Surface-mediated reduction in plutonium surface complexation modelling

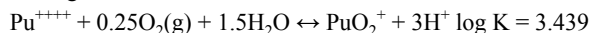
FANNY COUPELOT AND BRIAN POWELL

Clemson University

Presenting Author: fcoutel@clemson.edu

Plutonium, with its particularly complex redox chemistry, may be thermodynamically stable in the states + III to + VI, depending on the redox conditions in the environment. Mineral surfaces can also affect Pu redox speciation. While Pu(IV) is generally assumed to be immobile in the subsurface environment due to sorption or precipitation, Pu(V) tends to be mobile due to its relatively low effective charge and weak complex formation. One particularly important aspect of plutonium behavior at the mineral–water interface—is the concept of surface-mediated reduction, which describes the reduction of plutonium on a mineral surface. The redox cycling between Pu(IV) and Pu(V) further complicates this modeling approach, with various Pu oxidation states exhibiting drastically different sorption behavior. Therefore, a model capable of predicting not only the partitioning of Pu but also the oxidation state speciation would provide a more robust, mechanistic description of Pu geochemical behavior.

Due to their abundance, aluminosilicate minerals and iron oxides are proposed to play an essential role in retarding actinide subsurface migration. A surface complexation model was developed focusing on Pu(IV) and Pu(V) interactions with silica, gibbsite, Na-montmorillonite and iron oxides using literature sorption data. were examined as a function of time and pH, including the Pu(IV)/Pu(V) redox couple was based upon the following reaction:



to demonstrate a possible technique for incorporation of the Pu(IV)/Pu(V) redox couple into modeling efforts in an effort to provide a more technically accurate model.