

Chemical Factors Controlling Actinide Sorption in
the Environment*

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The fact that the actinides with daughter products dominate the biological hazards of high-level radioactive waste from spent nuclear fuel in the long term perspective has led to an increased interest in basic actinide solution chemistry in order to obtain sufficient understanding to predict the migration behavior of these elements in the environment.

The properties of the chemical two-phase rock-groundwater system in nature involve both the mineral constituents of the rock as well as equilibria with air and contributions from the biosphere. Figure 1 illustrates the complexity and interdependence of these factors in the environment. Of special importance in the natural waters are the bicarbonate-carbonate ions, which directly determine and buffer the pH of the water and indirectly affect the concentrations of calcium, magnesium, sodium, fluoride, and phosphate.

*Research sponsored by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract (W-7405-eng-26) with Union Carbide Corporation.

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The actinides, uranium, neptunium, and plutonium, will vary drastically in their chemical speciation and thus adsorption characteristics depending on their valence. It is thus of prime importance that the valence state of these ions in the environment be known. In Figure 2 calculated equilibrium of potential E vs pH, including effects of hydrolysis, are given for soluble species of uranium, neptunium, and plutonium. The range of natural waters as well as reducing groundwaters (due to the presence of ferrous minerals) are indicated. Thus, uranium would be hexavalent in aerated waters and tetravalent in reducing groundwaters (confirmed from laboratory as well as in situ measurements). While neptunium would be pentavalent and tetravalent, respectively, under similar conditions. Plutonium could exist in tri-, tetra, penta, and possibly hexavalent state in natural water.

The formation of complexes with anions in the water will have a large effect on the actinide sorption behavior. Potential actinide complexing agents in the environment, besides hydroxide, are carbonate, phosphate, and to a lesser extent fluoride and natural organic acids. The effects of pH, carbonate concentration, and ionic strength on sorption of americium on different minerals have been studied in detail. Figure 3 illustrates the effect of pH and ionic strength (NaCl) on the sorption of americium on montmorillonite in equilibrium with air. At low pH (4) the complexation with hydroxide and carbonate could be neglected because of their very low concentrations. The sorption can be considered as an ion exchange process at low sodium concentration and would be expected to follow the slope of -3 expected for americium-sodium exchange. As the chloride concentration increases up to 4M the average charge of the americium ion would decrease from +3 to about +1 due to formation of outer-sphere chloride complexes. Therefore the traditional ion exchange equation

$$d(\log D) = 3d(\log [\text{Na}])$$

does not apply. The lowering of the charge could possibly lower the solvation energy of the actinide thus enhancing the sorption onto the montmorillonite. This effect explains the minimum in sorption at 1 M and then the rise in sorption up to 4 M. The effect of pH on adsorption can be explained in a similar way. As the pH rises the extent of hydrolysis and carbonate complexation will increase, thus lowering the effective charge on the actinide. This would change the mechanism of sorption from predominantly cation exchange at low pH to surface related sorption of actinide complexes of low charge at higher pH's.

For inert solids without appreciable ion exchange capacities the sorption of the actinides would be predicted to increase strongly with increasing pH, which has been confirmed from sorption measurements on several natural oxides. An additional effect observed in these studies is a decreased adsorption at very high pH (> 9), possibly indicating the formation of anionic or neutral complexes.

In conclusion it can be stated that the solid geologic media and the aqueous phase are of equal importance for the retention of actinides in the environment. The composition of the water is largely determined by the mineralogical composition of the rock that it is in equilibrium with. The chemical form of the actinides and their sorption, are highly dependent on the composition of the water with respect to pH, redox potential, and concentration of anions like carbonate, phosphate, fluoride, and organic acids.

- Figure 1. Equilibria and chemical exchange in the igneous rock/groundwater system.
- Figure 2. Potential (E)-pH-diagram for soluble species of uranium, neptunium and plutonium.
- Figure 3. The distribution coefficient ($\log D$) for americium on montmorillonite as a function of pH and salt concentration (NaCl).





