SORPTION OF ACTINIDES FROM AQUEOUS SOLUTIONS UNDER ENVIRONMENTAL CONDITIONS

G.W. Beall\textsuperscript{1} and B. Allard\textsuperscript{2}
Oak Ridge National Laboratory
Oak Ridge, TN 37830

ABSTRACT

The sorption of americium, neptunium, and plutonium has been studied on a suite of thirty pure minerals and one granite as a function of solution pH, salinity, and redox potential. Three major factors controlling sorption have been identified. These three major factors are pH (for hydrolyzable ions), chemi-sorption reactions at the surface of minerals that contain strong complexing ions, and redox reactions with ferrous iron contained in various minerals. It appears that simple cation exchange does not play a significant role in the pH range of most interest in groundwaters. The implications of these findings for nuclear waste disposal are discussed.

INTRODUCTION

After initial dominance of fission products, the actinides and their daughter products (americium, plutonium, neptunium, thorium, radium) would dominate the biological hazards from high-level reprocessing wastes as well as from unprocessed spent uranium fuel from about 300 years after the discharge from the reactor up to millions of years. Thus, an understanding of the chemical behavior of the actinides in nature is of major importance, e.g. for the design and safety analysis of an underground repository for high-level nuclear wastes.

\textsuperscript{1} Current address: Radian Corporation, 8500 Shoal Creek Blvd.,
Austin, Texas 78766
\textsuperscript{2} Current address: Department of Nuclear Chemistry, Chalmers University of Technology, S-41296 Göteborg, Sweden.

P. H. Tewari (ed.), \textit{Adsorption From Aqueous Solutions}
Most literature data on actinide retention in rock/groundwater systems under environmental conditions indicate high sorption for species in the tri- and tetravalent states (distribution coefficients, mol/kg rock per mol/m$^3$ water, above 1 m$^3$/kg) and generally low values for species in the penta- and hexavalent states (distribution coefficients below 0.1 m$^3$/kg). However, measurements in similar systems have often given contradictory results.\(^1\)

The qualitative and quantitative effects on the retention of actinides by the variation of chemical conditions such as the reduction-oxidation potential, pH, the composition of the groundwater, the mineralogical composition of the ground, etc., are far from well understood. For this study, the sorption of americium, neptunium and plutonium has been measured under simulated environmental conditions to get qualitative information on the relative importance of pertinent chemical parameters on the actinide sorption characteristics in igneous bedrock.

EXPERIMENTAL

The sorption of neptunium,\(^2\) plutonium and americium\(^2-4\) was measured on selected minerals and rocks, using a batch technique.\(^2\) Pure minerals were crushed in a mortar and sieved. The purity of these minerals was primarily determined by X-ray diffraction. Only the size fraction 0.044-0.063 mm was used in the sorption experiments. The cation and anion exchange capacities (with respect to Na\(^+\) and Br\(^-\)) were measured by a batch technique,\(^5\) and the specific surface areas were determined by the ethylene glycol method.\(^6\) The crushed and sieved solid was prewashed and pre-equilibrated with an artificial groundwater solution (see Table 1). Active acidic spike solutions were added, giving a total initial radionuclide concentration of 2.0 x 10^{-11} M for neptunium (\(^{235}\)Np), 1.8 x 10^{-11} M for plutonium (\(^{237}\)Pu), and 2.1 x 10^{-9} M for americium (\(^{241}\)Am). The uptake of the radionuclide on the solid sorbent (solid-liquid ratio of 7-12 g/L) was measured after a contact time of 5 d at ambient temperature. Experimental details concerning spiking, sampling and counting procedures are given elsewhere.\(^2\)

GENERAL DISCUSSION

The Bedrock/Groundwater System

Igneous rocks like granite, basalt etc., are largely composed of a small number of primary, rock-forming minerals (see Figure 1) and some additional accessory minerals, as well as weathering and decomposition products of these constituents. The complicated