CHEMICAL APPROACHES TO UNDERSTANDING THE ENVIRONMENTAL BEHAVIOR OF Pu, Np, AND Tc[1]

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Several long-lived radioelements produced by fission reactors are essentially extinct geologically. In particular, the lack of geochemical histories for Pu, Np, and Tc (all of which can theoretically exhibit multiple oxidation states under the various chemical regimes encountered in the environment) requires that their respective speciation behavior be examined before long-term predictions of transport and bioavailability are made. While it is possible to predict speciation using chemical thermodynamics, such calculations are most useful if supported experimentally since, at the very low concentrations encountered in the real world, the equilibrium conditions assumed in thermodynamic calculations may not exist. By combining our knowledge of the thermodynamic and radiochemical behavior of Pu, Np, and Tc with field and laboratory investigations on speciation, our understanding of the potential geochemical behavior of these elements is being expanded. This presentation will discuss such research aimed at understanding the environmental chemistry of these elements.

Because Pu is chemically a very complex element, care must be taken in evaluating its long-term environmental behavior, particularly if the results of laboratory experiments are used to project environmental

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behavior. While macro-concentration concepts like polymerization and disproportionation have little practical meaning under environmental conditions, they may influence the results observed in laboratory experiments. An example of this is sorption studies with soils where a small amount of Pu(V) formed during tracer addition can influence the interpretation of the results if only total Pu distribution is followed. Radiolysis of water at neutral to alkaline pHs can lead to Pu(V) formation from Pu(IV), an example being the dissolution of crystalline PuO_2 in water. In this instance, classical solubility studies are confounded by H_2O_2-generated Pu(V) dominating the soluble Pu species present in neutral to alkaline solutions contacting PuO_2 microspheres. Radiochemical separations of Pu(III + IV) from Pu(V + VI) are used to study Pu oxidation states at tracer levels in these types of experiments.

Understanding Pu speciation in the real world is more difficult, but has been attempted. Examples include the evaluation of Pu oxidation states in fresh water by selective precipitation (bismuth phosphate) of Pu(III + IV) coupled with laboratory studies on the stability of Pu(III) in the same water samples. Results indicated that Pu(IV) dominates the soluble Pu (10^{-15} M) in the lake water examined. Separate studies have indicated that although O_2 can theoretically oxidize Pu(IV) to Pu(V or VI) under alkaline conditions the rate appears to be slow and difficult to measure over periods of several months (at $\leq 10^{-11}$ M Pu concentrations).

Neptunium has the same basic oxidation state chemistry as Pu but the relative stability of each oxidation state differs. Thus Pu(V) is reduced more readily than Np(V) in environmental-type experiments.

Neptunium(V) tends to be more stable in alkaline soils than acid soils presumably because ferrous iron is more abundant in the latter. Neptunium(V) was also reduced to Np(IV) by unweathered igneous and sedimentary rocks which were examined in a generic study of radionuclide migration in geologic media. These results in particular emphasize the extreme care that must be taken in evaluating radionuclide chemistry in the environment since experiments conducted in the presence of O_2 gave different results than experiments conducted in the absence of O_2. The differences are related to Fe(II) stability. Thus sorption coefficients used in long-term migration models must be determined under redox conditions comparable to the actual migration environment.

Technetium may represent the best example of how the oxidation state affects environmental transport predictions. Under oxygenated conditions, the very soluble oxyanion, TcO_4^-, dominates the solution behavior of this element. However, there are several environmental situations where reduction to insoluble TcO_2 radically alters the migration potential or biological availability of this element. For example, equilibration experiments with unweathered igneous rocks have demonstrated that reduction of TcO_4^- to TcO_2 readily occurs. It has been possible to demonstrate that the redox potentials measured using Pt electrodes can predict when TcO_4^- will be unstable with respect to reduction. Previous waste disposal studies with Tc have not indicated that reduction occurs because O_2-free conditions were not adhered to (O_2-free simulating deep geological storage in unweathered media). It is thus possible to integrate thermodynamic calculations of Tc speciation with experimental measurements and establish

sound predictions on Tc migration potentials. Our perceptions of the migration potential of this long-lived fission product must therefore be radically modified.

These examples illustrate how chemically complex elements like Pu, Np, and Tc may be studied in order to strengthen long-term predictions of environmental behavior.