

MOBILE SPECIES OF Pu, Np, Cm, Am AND Tc IN THE ENVIRONMENT*

E. A. BONDIETTI
Oak Ridge National Laboratory**, Oak Ridge, TN 37830

MASTER

This paper will describe field and laboratory findings on the nature of soluble species of plutonium, neptunium, curium, americium, and technetium and demonstrate the importance of oxidation state and complexing ligands on migration potential. Both of these geochemically-influenced variables are difficult to incorporate into "models", yet significantly influence actual migration if it occurs.

Field research on several former waste disposal sites has demonstrated that the dominant migrating species of Pu in alkaline, aerated solutions was Pu(V). The evaluation of Pu(V) was conducted by chemical separations and selective sorption techniques [1]. Both Am and Cm as well as Pu(IV) have been found in solution associated with organic ligands. For Pu, a most unusual case exists where two distinctly different species [Pu(V) and Pu(IV)] exist in solution simultaneously, are not in equilibrium with each other (as "predicted" by models), and which respond to entirely different environmental variables.

When coral soils from the Marshall Islands have been dissolved, Pu(V+VI) species have been found at depth, but not at the surface. However, more typical soils and sediments contain Pu in reduced states, indicating that the more mobile Pu(V) specie is exceptional. The presence of this unique specie will be discussed in terms of thermodynamic considerations (it is the stable oxidation state in aerobic environments) and also from a kinetic perspective (air oxidation of Pu(IV) may be very slow).

In contrast to plutonium, neptunium and technetium are far more likely to exist in mobile forms (i.e., NpO_2^+ , TcO_4^-) and considerable laboratory work has been devoted to establishing "redox boundaries" for

*Research supported by The Office of Health and Environmental Research, and The Office of Nuclear Waste Isolation, U.S. Department of Energy.

**Operated by Union Carbide Corporation for the U.S. Department of Energy under contract W-7405-eng-26.

these elements. The concept of a redox boundary will be advanced to overcome the inherent weakness of equilibrium constants in modeling migration of long-lived, redox sensitive elements. Experimentally, the redox potential [or Fe(II)/Fe(III) activity ratio] is measured along with the reduction of Tc(VII) to Tc(IV) and Np(V) to Np(IV). These studies, conducted under environmentally realistic conditions (ionic environment, nuclide concentration) will provide experimental justification for geochemical models which predict chemical forms of nuclides migrating from repositories. For example, it has been demonstrated that the model: $\log[\text{TcO}_4^-] = (\text{Eh} - 0.710 + 0.0788)/\text{pH}$ is appropriate for inclusion in master geochemical models. By predicting the groundwater chemistry during rock/water interactions, it is possible to predict if Tc will be present as TcO_4^- , which is very mobile [2]. This work is the only known attempt to experimentally determine the geochemical conditions necessary to reduce mobile Np and Tc species to less mobile forms.

Based on the above perspectives, it is concluded that laboratory studies on plutonium generally ignore the environmentally-important chemical species, and that redox chemistry is extremely important in developing proper models for the migration of Pu, Tc, and Np.

REFERENCES

- [1] BONDIETTI, E.A., TRABALKA, J.R., Radiochem. Radioanal. Lett. 42 (1980) 169.
- [2] BONDIETTI, E.A., FRANCIS, C.W., Science 203 (1979) 1337.