

A very small fraction of the retarded technetium was transported along the column.

About 40 % of total activity of technetium in the sample taken from the column material adjacent to the inlet was associated with Fractions of a and b of the four fractions. Fractions a and b were about 7 % of the total weight of the sample. A mineralogical analysis of the separated fraction showed that Fractions a and b consisted mainly of biotite and other dark or mafic minerals such as hematite, magnetite, and iron oxyhydroxides. The fact that the sorbed technetium was associated predominantly with the mafic minerals suggest that sorption took place via a chemical reaction and not as a result of precipitation in the bulk of the groundwater followed by filtration as particulates.

Under anoxic, anaerobic or reducing conditions, technetium can be sorbed strongly on many minerals and rocks[6-9]. Haines et al.[10] showed that Tc(VII) was reduced to Tc(IV) on the surface of magnetite under anaerobic conditions. Vandergraaf, et al.[6] have pointed out that the reduction of TcO_4^- to a lower oxidation state occurs at or near the surface of the iron oxide such as magnetite and not in the bulk of the solution by dissolved ferrous ions. Eh and pH values obtained for the groundwater used in the migration experiments in the URL are projected on the Eh-pH diagram for technetium speciation in aqueous solution[6]. The projected point was very close to the edge of the TcO_4^- stability field. Lieser and Bauscher[9] have reported irreversible sorption of technetium on sediments under an anoxic condition and suggested the existence of a critical region in which a small shift of Eh in either direction may lead to a dramatic change in technetium mobility. Accordingly, it is suggested that contact of the groundwater with ferrous-containing minerals in the column is sufficient to drive the Eh slightly lower and this would result in the reduction of the technetium very close to the mineral surface. As a result, technetium (IV) sorbed strongly on the iron oxide or iron containing mineral surfaces.

The sorption values (Kd) for technetium batch sorption on the same column material were very low but increased slightly after 52 weeks contact time (from 0 to 2.5). This amount of sorption dose not agree with the strong sorption observed in the column experiment. The disagreement between the results obtained from batch sorption tests under "anoxic" conditions and the results obtained from the column test can be explained by the fact that low oxygen levels (<0.5 ppm in the atmosphere) in the anoxic chamber at the surface laboratory are still sufficiently high to prevent reduction of the technetium by ferrous iron in the geological materials.

The fact that a only small fraction of the injected technetium was transported through the column without retardation suggests that not all of the technetium was reduced to a strongly sorbing species. This is most likely due to an incomplete surface reaction between TcO_4^- and the mafic mineral surfaces. It can be assumed that over longer contact times, the surface reaction would be more complete.

REFERENCES

1. D.A. Palmer and R.E. Meyer, *J. inorg. nucl. Chem.*, **43**, 2979(1981).
2. H. Behrens, D. Klotz, H. Lang, H. Moser, G. Barke, H.Bruehl, S. Gehler and U. Muhlenweg, Material Research Society Symposia Proceedings, **11**, 783(1982).
3. J.C. Balogh and D.F. Grigal, *Soil Science*, **130**, 278(1980).
4. D.R. Champ and D.E. Robertson, In:*Speciation of Fission and Activation Products in the Environment*(R.A.Bulman and J.R.Cooper), UK, 114 (1985).
5. B. Allard, H. Kipatsi and B. Torstenfelt, *Radiochem. Radioanal. Letters*, **37**, 223(1979).
6. T.T. Vandergraaf, K.V. Ticknor and I.M. George, In:*Geochemical Behavior of Disposed Radioactive Waste* (G.S.Barney, J.D.Navratil and W.W.Schulz), USA, 25(1984).
7. F.B. Walton, J. Paquette, J.P.M. Ross and W.E. Lawrence, *Nucl. Chem. Waste Manag.*, **6**, 121(1986).
8. K. Ito and T. Kanno, *J. Nucl. Sci. Technol.*, **25**, 534(1988).
9. K.H. Lieser and Ch. Bauscher, *Radiochimica Acta*, **42**, 205(1987).
10. R.I. Haines, D.G. Owen and T.T. Vandergraaf, *Nucl. J. Canada*, **1**, 32(1987).