Incorporation of Technetium-99 into nanoparticulate magnetite

S. SHAW[1*], T. A. MARSHALL[1], K. MORRIS[1],
G. T. W. LAW[2], P. BOTS[1] AND
J. F. W. MOSSELMANS[3]

[1]SEAES, Univ. of Manchester, M13 9PL, UK.
(*Correspondence: sam.shaw@manchester.ac.uk)
[2]School of Chemistry, Univ. of Manchester, M13 9PL, UK.
[3]Diamond Light Source Ltd., Didcot, OX11 0DE, UK.

Technetium-99 (Tc-99) is a long-lived radioactive fission product (half-life 2.1 × 105 years) present in many spent fuel and reprocessing derived wastes. Under oxidizing conditions, Tc(VII) is highly soluble and mobile, in contrast, under reducing conditions, sparingly soluble Tc(IV) is dominant. Fe(II)-bearing nanoparticulate iron oxides (e.g. magnetite) have been shown to remove Tc(VII) from solution via reductive adsorption or precipitation. However, Tc(VII) may be remobilised during reoxidation. The aim of this study was to determine whether Tc-99 could be incorporated into magnetite and to explore the effects of oxidative perturbations on Tc-99 speciation and solubility.

Ferrihydrite was crystallised to magnetite (via addition of $Fe^{2+}_{(aq)}$) under CO_2-free, anoxic conditions in three synthetic cement leachates spiked with Tc(VII). The leachates represent early (pH 13.1), middle (pH 12.5) and late (pH 10.5) stage cement evolution for a cementitious radioactive waste geodisposal facility. After aging, the systems were reoxidised with CO_2-free air for 152 days. Solution samples were taken to determine the partitioning of Tc between the solid and solution, and X-ray Absorption Spectroscopy was used to characterise Tc associations with the solid phases.

All Tc(VII) was removed from solution rapidly (minutes) upon addition of the $Fe^{2+}_{(aq)}$, with some oxidative remobilisation after 152 days [1]. Analysis of both X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data indicated that Tc(IV) was predominantly incorporated into the magnetite octahedral site in all systems studied. On reoxidation in air, the incorporated Tc(IV) was recalcitrant to oxidative dissolution with less than 40% remobilization to solution despite significant oxidation of the magnetite to maghemite/goethite: All solid associated Tc remained as Tc(IV). Immobilization of Tc(VII) by reduction and incorporation into magnetite at high pH and with significant stability upon reoxidation has clear and important implications for limiting technetium migration under conditions where magnetite is formed, including in geological disposal of radioactive wastes.

[1] Marshall et al., *Environ. Sci. Technol.* **48**, 11853–11862 (2014).