Sulfide Limited Technetium Immobilization in Cementitious Waste Forms

YUJI ARAI[1], BRIAN POWELL[2], DANIEL I KAPLAN[3]

[1]Department of Natural Resources and Environmental Sciences, Urbana, IL 61801

[2]1Department of Environmental Engineering and Earth Science, Clemson University, Anderson, SC 29625

[3]2Environmental Sciences and Biotechnology Division, Savannah River National Laboratory, Aiken, SC 29808

The United States Department of Energy is currently considering the cement technology to immobilize technetium-99 (^{99}Tc) ($t_{1/2}$: 2.1 x 10^5 yr) in low level radioactive waste (LLW). Because of mobile pertechnetate ($Tc(VII)O_4^-$) species in the aquatic and terrestrial environment, it is critical to reduce Tc(VII) to Tc(IV) in cementitious waste forms (CWF) to facilitate the formation of insoluble Tc(IV) oxides and Tc(IV) sulfides species. The objective of this study was to examine the solubility and the chemical speciation of Tc within aged (over 300 d) CWFs (45 wt% blast furnace slag (BFS), 45 wt% fly ash, and 10 wt% cement) under the oxic condition. Samples were analysed for Tc solid state speciation as well as S and Fe speciation using X-ray absorption spectroscopy (XAS). Leaching tests for S and Tc were also performed to better understand the Tc-S chemistry in CWFs. The XAS analysis shows which reduced Tc/S/Fe species in solid phase contribute to the labile Tc/S/Fe in the leaching test. Although both Fe(II) and sulfide initially remained in the CWFs, most of sulfide and ferrous ion were oxidized after several days in the CWFs. Both reduced Tc(IV) and unreduced Tc(VII) were observed after 29 days. However, after 117 days, no Tc(VII) remained in the CWFs. Some of Tc(VII) in CWFs were lost during the cement dewatering process, leaving only Tc(IV) in CWFs The concentration of Tc within the water increased over time up to 35% ± 5% of the total Tc added after 453 days. The leaching of Tc from the CWFs into the pooled water reduced the fraction of Tc(VII) within the CWFs. Based on the Extended X-ray absorption Fine Structure spectroscopy analysis, it appears that Tc(VII) was reduced to form soluble Tc(IV) species, and then was slowly sulfidized to form Tc(IV) sulfide aqueous species. However, there was no evidence of Tc(IV) sulphide precipitates. The activity of sulfidein seemed to be critical in stabilizing Tc(IV) in the CWFs. The results of XAS analysis and leaching experiments will be combined to discuss the future direction of the cement technology to immobilize LLW.