

Chemistry of Technetium in the Near Field of a Cementitious Waste Repository

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In the UK, tetraphenylphosphonium bromide (TPPB) has been used to remove technetium prior to disposal from some waste-streams by forming TPPBTc floc. If this floc is placed in a cementitious ILW repository the TPPB will degrade by alkaline hydrolysis to triphenylphosphonium oxide, or by radiolysis to triphenylphosphine. On the degradation of TPPBTc, technetium will be released into solution, where its chemistry will be dominated by the pertechnetate anion, TcO_4^- , in aerobic waters and the sparingly soluble $\text{TcO}_2(\text{s})$ in anaerobic.

The aqueous concentration of Tc(IV) was measured from pH 11.5 to 14.5 to determine its solubility, and to investigate the possible existence of $\text{TcO}(\text{OH})_3$. Between pH 11 and 13.5 the Tc concentration was independent of pH at ca. $4.6 \times 10^{-10} \text{ mol dm}^{-3}$. The solubility product for the dissolution of $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ was $\log K_{\text{sp}} = -33.6 \pm 0.32$ at pH 13.4. However, at pH >13.5, the Tc concentration increased. The $\log K_2$ value for $\text{TcO}(\text{OH})_3^-$ was determined to be -14.2.

Repository heterogeneity could mean that both Tc(VII) and Tc(IV) are present simultaneously. If pertechnetate migrates into reducing conditions, ligands in the waste may complex with Tc during reduction to form water-soluble complexes. Also possible, is increased Tc solubility when organic ligands react with $\text{TcO}_2(\text{s})$. Stability constants for Tc(IV) with EDTA, NTA, ISA Na gluconic acid have been measured by the solubility product approach.

Comparison of Tc solubilities at high pH starting from TcO_2 and from TcO_4^- reduced in the presence of ligands was made. With EDTA and NTA no difference was observed, suggesting that Tc(IV)-ligand complexes were formed. For ISA and gluconic acid the Tc solubility starting from pertechnetate was higher than in systems with TcO_2 as the starting point. This suggests that the TcO_4^- was not reduced to Tc(IV), but an intermediate oxidation state complex was formed, possibly Tc(V).

