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The complexation of Tc(IV) with organic ligands in radioactive waste

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The preferred option in the UK for the management of higher-activity radioactive wastes is to store it in a deep Geological Disposal Facility (GDF). This may then be backfilled with a cementitious material. Once closed, the GDF will become saturated with groundwater and highly alkaline porewater will develop with an initial pH of ca. 13.4. This will decrease to 12.5 as groundwater flow removes the NaOH and KOH present. Mineral phases in the cement will then act as a buffer and maintain the pH at 12.5 for ca. 105 years. Corrosion of waste-containing steel canisters will lead to the gradual formation of reducing conditions. Thus, the behaviour of radionuclides in the waste must be understood in the context of this chemistry.

Organic complexing agents will be present as inherent components of the waste, especially isosaccharinic acid (ISA) and other polyhydroxylated carboxylic acids which will be formed by the degradation of cellulose. These are highly complexing and can cause significant increases in radionuclide solubility at high pH. The GDF will not be homogenous, there are likely to be areas of reducing and oxidising potential. This heterogeneity could mean that both Tc(VII) and Tc(IV) are present within the GDF. If TcO₄⁻ migrates into an area in which reducing conditions exist, the organics may complex with technetium during reduction to form water-soluble complexes. Also of relevance is the possibility of increased solubility when organics are in contact with reduced technetium (TcO₂(am)). In other words, do organics affect the reduction of Tc(VII) to Tc(IV)? Therefore, studies have been undertaken in which TcO₄⁻ was reduced electrochemically, and by Sn(II) and Fe(II), in the presence and absence of ISA, gluconic acid, EDTA, NTA and picolinic acid, to determine whether they caused an increase in Tc solubility when TcO₂(am) was contacted with them.

In the presence of ISA and gluconic acid a lowering of [Tc(aq)] took place on reduction, showing such ligands did not prevent some reduction occurring. If this reduction was to Tc(IV), then the final aqueous concentration should be the same as that produced by the addition of the same ligands to Tc(IV) solution at steady state, i.e. the Tc(IV) complexes would again be formed, but by 2 different routes. However, the final Tc in the system where reduction took place in the presence of ISA and gluconate was higher than when starting from TcO₂(am). This indicates that Tc(VII) may not have been reduced to Tc(IV) but an intermediate oxidation state complex such as Tc(V) may have formed. This concept is well known in ^{99m}Tc radiopharmaceuticals, where polyhydric complexes of Tc(V) can be formed by the reduction of pertechnetate in aqueous solution of excess O-donor ligand, although in pharmaceuticals this is not carried out at high pH.

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