

The complexation of Tc(IV) with EDTA and picolinic acid at high pH

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ABSTRACT

In the UK, technetium may be disposed of in a high pH, low Eh cementitious repository. In such a scenario, its chemistry would be dominated by TcO_4^- , in aerobic conditions and the sparingly soluble $\text{TcO}_{2(s)}$ in anaerobic conditions. Repository heterogeneity could mean that both Tc(VII) and Tc(IV) are present simultaneously. The anthropogenic ligands EDTA and picolinic acid are commonly used as decontamination agents and are likely to be present in intermediate-level waste (ILW). They could complex with Tc(IV) increasing its aqueous concentration and mobility in the cement porewaters and beyond. The conditional stability constants (measured in 0.3 mol dm^{-3} NaOH) for the Tc(IV)–EDTA and Tc(IV)–picolinic acid complexes have been determined to be: $\beta_{\text{Tc(IV)-EDTA}} = 1.6 \times 10^{26}$, which corresponds to $\log \beta = 25.2 \pm 0.6$; and $\beta_{\text{Tc(IV)-PA}} = 8.65 \times 10^{26}$, which corresponds to $\log \beta = 26.9 \pm 0.1$, respectively.

KEYWORDS: complexation modelling, EDTA, engineered barrier system, picolinic acid, radionuclide transport, technetium.

Introduction

THE currently preferred UK option for the management of intermediate-level radioactive waste (ILW) is to store it in a deep underground repository. This may then be backfilled with a cementitious material. Once closed, the repository will become saturated with groundwater and highly alkaline porewater will develop with an initial pH of around 13.4. This will decrease to 12.5 as the groundwater flow dissolves and removes any NaOH and KOH present. The mineral phases in the cement will act as a buffer and maintain the pH at 12.5 for $\sim 10^5$ years. Corrosion of waste-containing steel canisters will lead to the gradual formation of reducing conditions. The behaviour of the radionuclides present in the waste must be understood in the context of this chemistry (Warwick *et al.*, 2003).

Technetium-99 is an important species in the performance assessment of any proposed geological disposal facility (GDF), due to its high yield and long half-life. The aqueous chemistry of technetium is likely to be dominated by the highly mobile pertechnetate anion (TcO_4^-) in aerobic waters, and by Tc(IV), as solid $\text{TcO}_{2(am)}$, in anaerobic waters (Cui and Eriksen, 1996). The solubility of Tc(IV) in anoxic conditions at high pH above $\text{TcO}_{2(am)}$, the phase that will most probably be present in a GDF, is independent of pH from circum-neutral to pH 13.5 (Warwick *et al.*, 2007). The species $\text{TcO}(\text{OH})_3^-$ is only likely to be formed in significant quantities above the highest pH likely to be found in a cementitious GDF, and hence is of little interest to performance assessment.

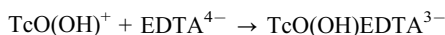
The small amounts of waste technetium that have been produced in the UK have in the past been discharged into the Irish Sea. It was originally thought that the waste technetium dispersed widely, but was found to accumulate in seaweed (Copplestone *et al.*, 2004). Treatment

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with tetraphenylphosphonium bromide (TPPB) is now used to precipitate out the technetium as TPPTc, to reduce marine discharges to an acceptable level. This leads to the possibility that the floc may be sent to a cementitious repository for disposal. However, TPPB degrades by alkaline hydrolysis at high pH. It is also prone to radiolytic degradation.

Organic complexing agents will be present as inherent components of the waste, especially EDTA and picolinic acid, which are heavily used as decontamination agents. These are highly complexing and can cause significant increases in radionuclide solubility at high pH. The GDF will not be homogenous and there are likely to be areas of reducing and oxidizing potential. The possibility of increased solubility when such organics are in contact with reduced technetium ($\text{TcO}_{2(\text{s})}$) is of relevance to technetium mobility. Therefore, studies were undertaken in which TcO_4^- was reduced electrochemically, and by use of Sn(II) and Fe(II), to determine whether there was an increase in technetium solubility when TcO_2 was contacted with the organic ligands. It can be assumed that these ligands will have been washed out by the time the pH of the GDF decreases to 12.5.

In previous studies of complex formation between Tc and EDTA, Gorski and Koch (1969, 1970) dissolved freshly prepared hydrous oxide of Tc(IV) in HClO_4 and obtained an aqueous solution containing an unknown trace concentration of technetium(IV). In the pH range from 1 to 2.5, they investigated the ionic mobility by electrophoresis and studied the formation of complexes in the presence of complexing ligands by cation exchange and by electrophoresis, as quoted in Hummel *et al.* (2005). The results were interpreted by assuming the presence of TcO^{2+} at pH 1, reacting to form $\text{TcO}(\text{OH})^+$ and $\text{TcO}(\text{OH})_{2(\text{aq})}$ at higher pH, and the concomitant formation of $\text{TcO}(\text{OH})\text{EDTA}^{3-}$. The authors quoted a value of $\log K = 19.1$ for the reaction shown below in acidic conditions:



Experimental

All experiments were conducted in a Unilab MBraun nitrogen glove box with O_2 levels kept below 1 ppm. All solutions were boiled and N_2 sparged. Solid sodium EDTA and sodium picolinate were added to carbonate-free $\text{NaOH}_{(\text{aq})}$ (2 mol dm^{-3}) to give concentrations

between 0.3 and 0.01 mol dm^{-3} at pH 13.3, with sodium dithionite added as a holding reductant. Ammonium pertechnetate was added and reduction was achieved using a potential difference of 5 V across the solution for at least 12 h. The activity in solution was measured by liquid scintillation counting using Canberra Packard TRI-Carb 2750TR/LL, indicating an aqueous concentration of Tc(IV) of $\sim 4 \times 10^{-9} \text{ mol dm}^{-3}$. Five replicates were used. Control experiments without ligands showed no increase in aqueous technetium concentration, indicating that reducing conditions were maintained for the requisite periods of time. To measure the stability constants for the reaction of Tc(IV) with EDTA and picolinic acid, the solubility product approach was used (Warwick *et al.*, 2004). The solids were aged for 14 days before ligand addition and the solutions left for at least 10 days to reach a steady state, following the procedure reported by Maes *et al.* (1988). The pH was measured using a high-pH solution Orion 720A glass electrode. The electrode was calibrated using Aldrich volumetric standard sodium hydroxide solutions. Experiments were performed at ambient laboratory temperature.

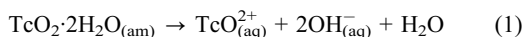
Results and discussion

The solubility product for the $\text{TcO}_{2(\text{am})}$ phase formed in these experiments was determined by Warwick *et al.* (2004) to be $\log K_{\text{sp}} = -33.6 \pm 0.32$.

Complexation of Tc(IV)

Figure 1 shows the effect of increasing the concentration of EDTA on technetium(IV) solubility, the aqueous concentration of Tc(IV) rising from $\sim 10^{-9} \text{ mol dm}^{-3}$ to $\sim 10^{-7} \text{ mol dm}^{-3}$, albeit at high EDTA concentrations. The slope of close to unity in the log-log plot (1.18) indicates that the increase in solubility of Tc is being controlled by the formation of a 1:1 Tc(IV)-EDTA complex. This relationship allows the calculation of a conditional stability constant for this complex using the solubility product approach described in Warwick *et al.* (2004).

In the absence of ligands, dissolved Tc(IV) will consist of the $\text{TcO}(\text{OH})^+$ ion and its major hydrolysis products. The dissolution of TcO_2 can be written as:



COMPLEXATION OF Tc(IV)

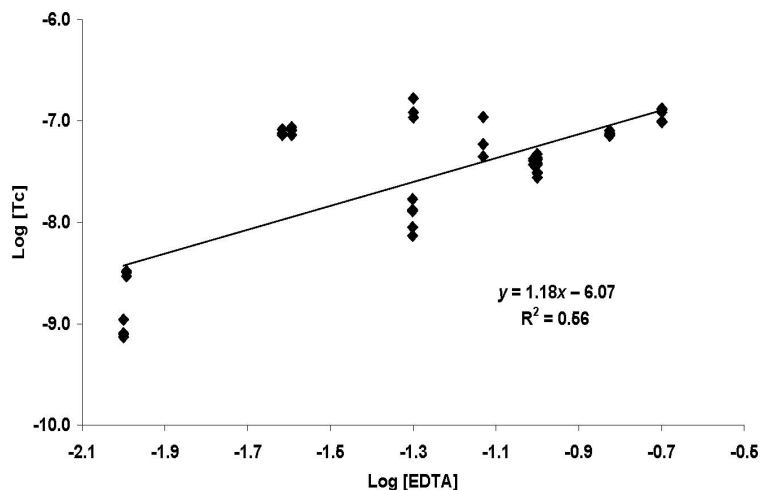
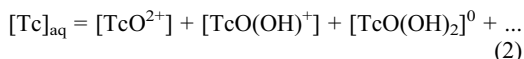


FIG. 1. Effect of concentration of EDTA on aqueous technetium concentration above $\text{TcO}_{2(\text{am})}$ at pH 13.3.

In the absence of ligands, aqueous phase Tc(IV) will also consist of the $\text{TcO}(\text{OH})^+$ ion and its major hydrolysis products:



Or $[\text{Tc}]_{\text{aq}} = [\text{TcO}^{2+}]A$, where $A = 1 + \sum \beta_x [\text{OH}]^x$ [the side reaction coefficient, as described by Maes *et al.* (1988)], which is constant at a given pH. Addition of EDTA causes the following reaction to occur:



The concentration of dissolved Tc(IV) will be increased by the formation of a complex:



Following the derivation in Warwick *et al.* (2004), the conditional stability constant of the complex is given by expression 5 below.

The conditional stability constant for the Tc(IV)–EDTA complex was calculated using equation 5, and determined to be $\beta_{\text{Tc(IV)-EDTA}} = 1.6 \times 10^{26}$ which corresponds to $\log \beta_{\text{Tc(IV)-EDTA}} = 25.2 \pm 0.6$ (1 SD).

Figure 2 shows the effect of increasing the concentration of picolinic acid on technetium(IV)

solubility, the aqueous concentration of Tc(IV) rising from $\sim 10^{-9} \text{ mol dm}^{-3}$ to $\sim 10^{-6} \text{ mol dm}^{-3}$ at high picolinate concentrations. The slope of close to unity in the log–log plot (1.05) indicates that the increase in solubility of technetium is being controlled by the formation of a 1:1 Tc(IV)–PA complex. This relationship allows the calculation of a conditional stability constant for this complex using the solubility product approach.

The conditional stability constant for the Tc(IV)–picolinic acid complex was calculated using equation 5, and was determined to be $\beta_{\text{Tc(IV)-PA}} = 8.65 \times 10^{26}$, which corresponds to $\log \beta_{\text{Tc(IV)-PA}} = 26.9 \pm 0.1$.

Conclusions

The presence of EDTA and picolinic acid caused some increase in Tc(IV) solubility, indicating the formation of Tc(IV)–EDTA and Tc(IV)–PA complexes with 1:1 stoichiometries. The conditional stability constants were calculated and determined to be $\log \beta = 25.2 \pm 0.6$ and $\log \beta = 26.9 \pm 0.1$ for EDTA and picolinate, respectively. However, the overall effect of EDTA and picolinic acid on the solubility of technetium is

$$\beta = \frac{[\text{Tc}]_{\text{aq}} - \left(\frac{K'_{\text{SP}}}{[\text{OH}^-]} \right) A}{\left(\frac{K'_{\text{SP}}}{[\text{OH}^-]} \right) \left([\text{EDTA}^{y-}]_{\text{total}} - \left\{ [\text{Tc}]_{\text{aq}} - \left(\frac{K'_{\text{SP}}}{[\text{OH}^-]} \right) A \right\} \right)} \quad (5)$$

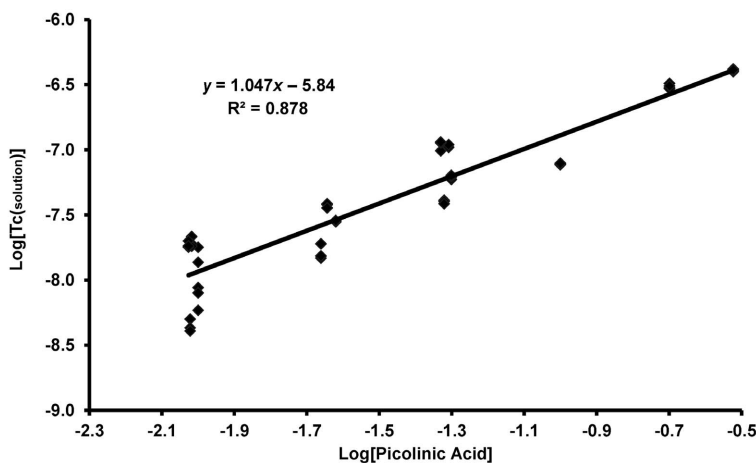


FIG. 2. Effect of concentration of picolinic acid on aqueous technetium concentration above $\text{TcO}_{2(\text{am})}$ at pH 13.3.

quite low in such high pH environments. Although it is possible that such high concentrations of EDTA and picolinic acid ($10^{-2} \text{ mol dm}^{-3}$) could be found in some waste containers, the concentration of technetium is only increased from 10^{-8} to $10^{-6} \text{ mol dm}^{-3}$. This means, for example, that only 0.001% of the picolinic acid would be bound in complexes with Tc(IV) under these conditions. These results indicate that a detailed understanding of the effect of such organic ligands on Tc(IV) may be required for performance assessment if technetium is to be safely disposed of in a GDF, but that such ligands may not outcompete the hydroxide ion for technetium complexation and therefore, have no significant effect on technetium behaviour in cementitious environments.

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