

The fate of Tc in a UK intermediate-level nuclear waste repository

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Abstract

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 were to be disposed of in a cementitious repository the TPPBTc would degrade by alkaline hydrolysis to triphenylphosphonium oxide, or by radiolysis to triphenylphosphine, releasing the Tc into solution. Its chemistry would be dominated by TcO_4^- in aerobic waters and sparingly soluble $\text{TcO}_2(\text{s})$ in anaerobic. Repository heterogeneity could mean that both $\text{Tc}(\text{VII})$ and $\text{Tc}(\text{IV})$ are present simultaneously. If TcO_4^- 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 $\text{TcO}_2(\text{s})$. Comparisons of Tc solubilities at high pH starting from TcO_2 and from TcO_4^- reduced in the presence of ligands were made. With EDTA and NTA no difference was observed, suggesting that $\text{Tc}(\text{IV})$ -ligand complexes were formed. For ISA and gluconic acid the Tc solubility starting from TcO_4^- was higher than in systems with TcO_2 as the starting point. This suggests that the TcO_4^- was not reduced to TcO_2 , but an intermediate oxidation state complex was formed, e.g. $\text{Tc}(\text{V})$. The conditional stability constant for the $\text{Tc}(\text{IV})$ -gluconic acid complex has been determined to be $\log \beta = 26.6 \pm 0.2$.

Keywords: technetium, redox, high pH, nuclear waste repository, EDTA, ISA, gluconic acid.

1 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 would develop with an initial pH of around 13.4. However, 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 *ca.* 10^5 years. Corrosion of waste-containing steel canisters will lead to the gradual formation of reducing conditions. Thus, the behaviour of radionuclides likely to be in the waste must be understood in the context of this chemistry [1].

1.1 Technetium

^{99}Tc , a low energy β emitter, present in some nuclear waste streams as TcO_4^- , is an important species for performance assessment of any proposed repository, due to its high yield (6% of fission products) and long half-life (2.1×10^5 years). 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 $\text{TcO}_2(\text{am})$ solid, in anaerobic [2]. Under reducing conditions, TcO_4^- in non-complexing aqueous solutions initially undergoes a one-electron reduction to the unstable $\text{Tc}^{\text{VI}}\text{O}_4^{2-}$ species [3-5]. Subsequent two- or three-electron reductions to Tc(V) or Tc(IV) species then readily occur. However, the Tc(V) and Tc(VI) species are unstable and disproportionate into more stable Tc(IV) and Tc(VII) species. This leads to the formation of four significant technetium aqueous species (figure 1), although in a repository only $\text{TcO}_2(\text{s})$ and TcO_4^- are likely to be present.

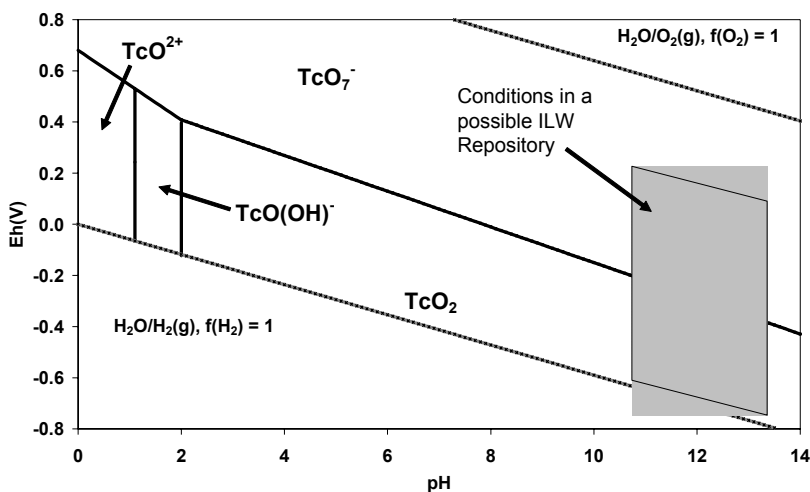


Figure 1: Predominance diagram for technetium.

The solubility of Tc(IV) in anaerobic conditions at high pH above amorphous $\text{TcO}_2(\text{s})$, the phase most likely to be present in a repository, has been a matter of debate for some time. A recent study by Warwick *et al.* [6] showed that, from pH 11 to 13.5, the aqueous Tc concentration appeared to be independent of pH. However, at pH values greater than 13.5, the aqueous concentration of

technetium increased with increasing pH (figure 2). The increase in solubility can be explained by the equilibrium in eqn. 1. Log K for the species $\text{TcO}(\text{OH})_3^-$ was determined to be $\log K_2 = -14.2$ [7], but this anionic Tc(IV) species is only likely to be formed in significant quantities above the highest pH likely to be found in a cementitious repository, and hence should be of little interest to performance assessment.

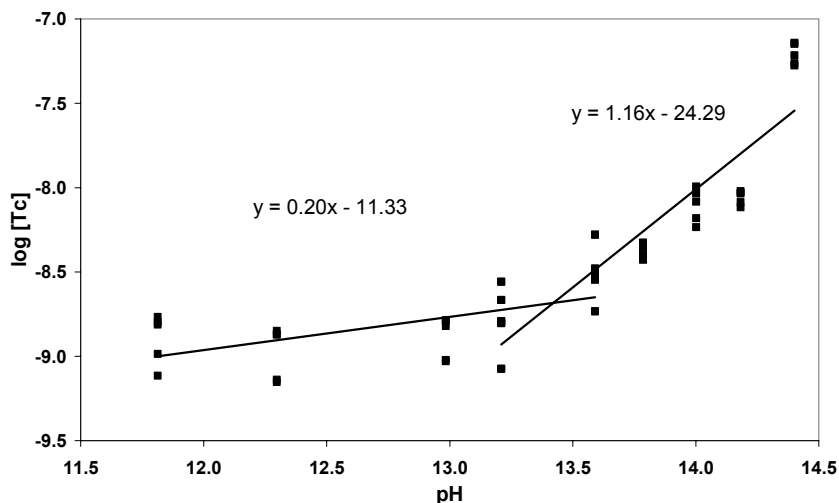
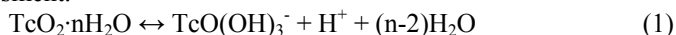


Figure 2: Solubility increase of Tc(IV) against pH.

1.2 Management of technetium waste before disposal

During the reprocessing of Magnox fuel, the uranium fuel rods are dissolved in nitric acid. One of the waste streams is an aqueous acidic Tc-containing medium-active liquor. This is concentrated by evaporation to produce a medium active concentrate (MAC) at Sellafield [8]. Sodium hydroxide and a flocculating agent are added to the MAC. An insoluble floc is formed which contains the main α -emitters and plutonium species. An ion exchange reagent is incorporated into the floc and removes additional species, mainly caesium. The floc is then dewatered by ultrafiltration prior to encapsulation in steel drums. The permeate, which contains a very small fraction of the radioactivity in the MAC, is discharged to sea [9]. In the past, technetium was not removed from the permeate into the floc and was, therefore, discharged into the Irish Sea. It was originally thought to disperse widely, but was discovered to concentrate in seaweed [10]. Hence, the MAC floc may now be treated with tetraphenylphosphonium bromide (TPPB) to precipitate out the technetium as TPPTc, to prevent more marine discharges.

Before being accepted for use an investigation on TPPB and its degradation products had to be undertaken to show that they would not have a significant detrimental impact on post-closure performance of the repository [7], which has been shown to be the case. 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, when the products are generally phenylphosphine compounds [11]. The mechanism for the alkaline hydrolysis of quaternary phosphonium salts has been suggested by Khalil and Aksnes [12] to produce, principally, triphenylphosphine oxide. The rate of reaction was found to be third order, first order with respect to TPPB, and second order with respect to the hydroxide ions [12]. The mean activation energy was calculated to be $105.2 \pm 3.2 \text{ kJ mol}^{-1}$ [7].

Studies [7] have shown that initially, at high pH, TPPB causes a large reduction in the aqueous technetium concentration, by precipitating out the pertechnetate anion, but after 8 weeks the TcO_4^- solubility reached the inventory concentration of technetium. The increase in aqueous technetium was caused by the alkaline degradation of TPPTc, releasing TcO_4^- into solution. So, if TPPTc floc is introduced to a high pH environment, TcO_4^- will be re-released. Therefore, the reduction of Tc(VII) to Tc(IV) will be crucial in restricting technetium escape to the far-field of the repository.

Organic complexing agents, e.g. EDTA and nitrilotriacetic acid (NTA) will be present as inherent components of the waste. Also, isosaccharinic acid (ISA) and similar polyhydroxylated carboxylic acids, will be formed by the anaerobic, alkaline degradation of cellulose. ISA is highly complexing and can cause significant increases in radionuclide solubility at high pH [1]. The repository will not be homogenous and 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 repository. If TcO_4^- migrates into an area in which reducing conditions exist, the organics may complex with technetium during reduction to form water-soluble complexes. This approach to complex formation, i.e. reduction in the presence of complexing ligands, is widely used to produce $^{99\text{m}}\text{Tc}$ radiopharmaceuticals. However, such investigations have been carried out at near-neutral pH and little has been reported on technetium complexation in the highly alkaline conditions to be expected in a cementitious repository.

Also of relevance to technetium mobility, is the possibility of increased solubility when organics are in contact with reduced technetium ($\text{TcO}_2(\text{s})$). In other words, does the presence of organics affect the reduction of Tc(VII) to Tc(IV)? With these considerations in mind, studies were undertaken in which TcO_4^- was reduced electrochemically, and by use of Sn(II), in the presence and absence of EDTA, NTA, picolinic acid, ISA and gluconic acid, to determine whether there was an increase in technetium solubility when TcO_2 was contacted with the organic ligands, TcO_2 was prepared by the reduction of TcO_4^- and then contacted with anaerobic solutions of the ligands.

2 Experimental

All experiments were conducted in a Unilab MBraun Nitrogen Glove Box with oxygen levels kept below 1 ppm. All solutions were boiled, sparged with nitrogen and kept in the presence of iron filings to maintain reducing conditions. Solid EDTA was added to sodium hydroxide solution at pH 13.3, to give

concentrations between 0.4 and 0.001 mol dm⁻³. Ammonium pertechnetate (NH₄TcO₄) was added and the pH and Eh measured. Reduction was achieved by the addition of 0.7 g of SnCl₂ and the solutions were left for 14 days. Alternatively the reduction was achieved electrochemically. The activity in solution was measured by liquid scintillation counting using Canberra Packard TRI-Carb 2750TR/LL. 5 replicates were used. This was repeated using NTA, picolinic acid, ISA and gluconic acid. Control experiments without the ligands present showed that reducing conditions were maintained for the requisite periods of time. Control experiments with the ligands present showed that 14 days was sufficient for equilibrium to be established. For the solubility of TcO₂ at high pH in the presence of complexing agents, the same procedure was used except that the electrochemical reduction, or the addition of SnCl₂, was performed prior to the addition of the ligands. To measure the stability constant for the reactions of sparingly soluble Tc(IV) with gluconic acid, the solubility product approach was used, as discussed by Warwick *et al.* [13].

3 Results and discussion

3.1 Solubility of Tc(IV) and the calculation of the solubility product of TcO₂

The solubility product for the TcO₂(am) phase formed in these experiments was determined to be $\log K_{sp} = -33.6 \pm 0.32$. The data are shown in table 1.

Table 1: Calculation of the solubility product of TcO₂(am).

pH	[OH ⁻]	[Tc] _{solution}	K _{sp}	Log K _{sp}
13.46	0.29	7.5 x 10 ⁻¹⁰	4.75 x 10 ⁻³⁴	-33.3
13.36	0.23	4.3 x 10 ⁻¹⁰	2.72 x 10 ⁻³⁴	-33.6
13.40	0.25	3.5 x 10 ⁻¹⁰	2.17 x 10 ⁻³⁴	-33.7
13.26	0.18	1.4 x 10 ⁻¹⁰	8.50 x 10 ⁻³⁵	-34.1
13.47	0.29	2.0 x 10 ⁻¹⁰	1.24 x 10 ⁻³⁴	-33.9
13.26	0.30	9.2 x 10 ⁻¹⁰	5.81 x 10 ⁻³⁴	-33.2
	Mean	4.6 x 10 ⁻¹⁰	2.92 x 10 ⁻³⁴	-33.6
	S.D.	3.1 x 10 ⁻¹⁰	1.97 x 10 ⁻³⁴	0.32

3.2 Complexation of Tc(IV)

All five ligands caused an increase in the solubility of technetium. Figure 3 shows the effect of increasing gluconic acid concentration on technetium(IV) solubility. The slope of close to unity indicates that the increase in solubility of Tc is being controlled by the formation of a 1:1 Tc(IV)-gluconate complex. This relationship allows the calculation of a conditional stability constant for this complex using the solubility product approach as detailed in the following section. Data for ISA, EDTA and NTA can be seen in figures 5 and 6. The results for picolinic acid were inconclusive.



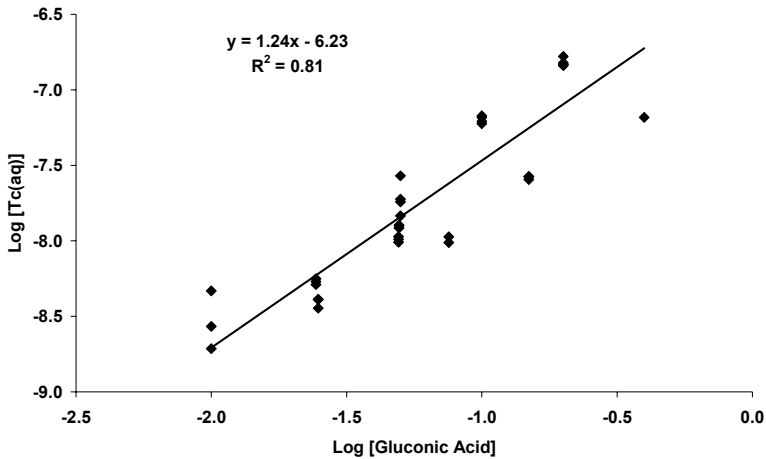


Figure 3: Effect of concentration of gluconic acid on aqueous technetium concentration above $\text{TcO}_2(\text{am})$ at pH 13.3.

3.3 Determination of Tc(IV)-gluconate conditional stability constant

The dissolution of TcO_2 can be written as:



Therefore, the solubility product $K_{\text{sp}} = [\text{TcO}^{2+}][\text{OH}^-]^2$. In the absence of added ligand, dissolved Tc(IV) will consist of the $\text{TcO}(\text{OH})^+$ ion and its major hydrolysis products, eqn. 3.

$$[\text{Tc}]_{\text{solution}} = [\text{TcO}^{2+}] + [\text{TcO}(\text{OH})^+] + [\text{TcO}(\text{OH})_2]^0 + \text{etc} \quad (3)$$

Or $[\text{Tc}]_{\text{solution}} = [\text{TcO}^{2+}]A$, where $A = 1 + \sum \beta_x [\text{OH}^-]^x$ (the side reaction coefficient) [14], which is a constant at any given pH. Addition of gluconic acid caused the following reaction to occur, eqn. 4.



The concentration of dissolved Tc(IV) will be increased by the formation of the gluconate complex, eqn. 5:

$$[\text{Tc}]_{\text{solution}} = [\text{TcO}^{2+}]A + [\text{TcO}(\text{Gl})^{(2-y)+}] \quad \text{OR} \quad [\text{TcO}(\text{Gl})^{(2-y)+}] = [\text{Tc}]_{\text{solution}} - [\text{TcO}^{2+}]A \quad (5)$$

Hence:

$$[\text{TcO}(\text{Gl})^{(2-y)+}] = [\text{Tc}]_{\text{solution}} - \left(\frac{K'_{\text{sp}}}{[\text{OH}^-]} \right) A \quad (6)$$

The conditional stability constant of the complex is given by:

$$\beta = [\text{TcO}(\text{Gl})^{(2-y)+}] / [\text{TcO}^{2+}][\text{Gl}^{y-}] \quad \text{or:} \quad (7)$$

$$\beta = \frac{[\text{Tc}]_{\text{solution}} - \left(\frac{K'_{\text{sp}}}{[\text{OH}^-]} \right) A}{\left(\frac{K'_{\text{sp}}}{[\text{OH}^-]} \right) \left([\text{Gl}^{y-}]_{\text{total}} - \left\{ [\text{Tc}]_{\text{solution}} - \left(\frac{K'_{\text{sp}}}{[\text{OH}^-]} \right) A \right\} \right)} \quad (8)$$

The conditional stability constant was calculated using eqn. (8) and was determined to be; $\beta = 4.0 \times 10^{26}$ or $\log \beta = 26.6 \pm 0.2$.

3.4 Reduction of Tc(VII) in the presence of ligands

In the presence of all five ligands a lowering of the aqueous technetium concentration took place upon reduction, showing that the ligands did not prevent reduction taking place. If this reduction was to Tc(IV), then the final aqueous concentration of technetium should be the same as that produced by the addition of the same ligands to Tc(IV) solution, i.e. the Tc(IV)-ligand complexes would again be formed, but by two different routes.

3.5 Comparison of final technetium solubilities

For EDTA and NTA no difference in final technetium concentration was observed (figure 4), leading to the conclusion that Tc(IV) complexes are formed with these two ligands, whether or not Tc(VII) or Tc(IV) are used as the starting point. For ISA and gluconic acid (figure 5) the final equilibrium solubility of technetium in the systems where reduction took place in the presence of the ligands is higher than when TcO₂ was the starting point. This indicates that the Tc(VII) was not reduced to Tc(IV) but an intermediate oxidation state such as Tc(V) complex was formed. This idea is well known in the formation of ^{99m}Tc radiopharmaceuticals [13]. Tc(V) chemistry is governed by oxotechnetium species, TcO³⁺. The coordination character of TcO³⁺ with multidentate oxygen donor ligands is controlled by the square pyramidal geometry of TcO³⁺ complexes. Complexes of TcO³⁺ with polyhydric alcohols and 2-hydroxy carboxylates are stable in aqueous solution due to chelating effects [15].

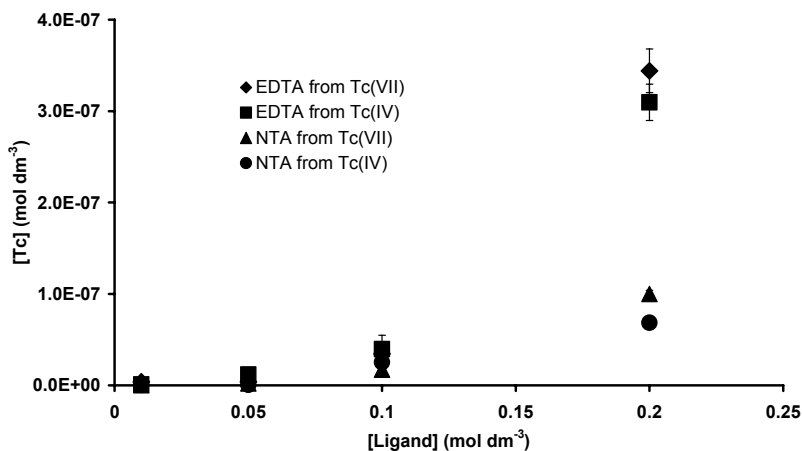


Figure 4: Comparison of final Tc concentrations in the presence of EDTA and NTA, starting from TcO₄⁻ and Tc(IV) at pH 13.3.

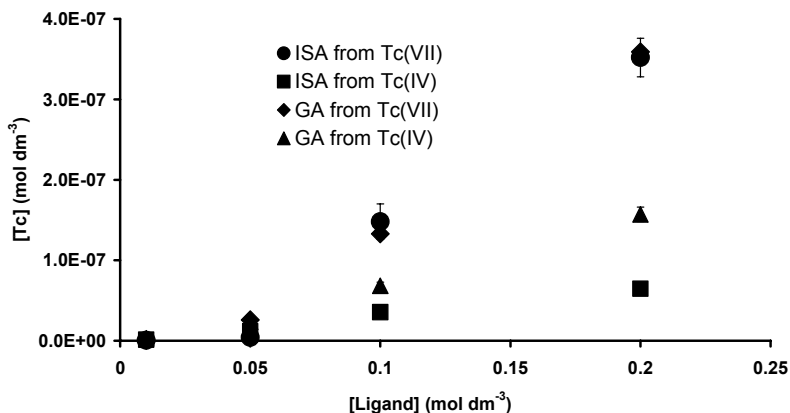


Figure 5: Comparison of final Tc concentrations in presence of ISA and gluconic acid at pH 13.3, starting from TcO_4^- and Tc(IV).

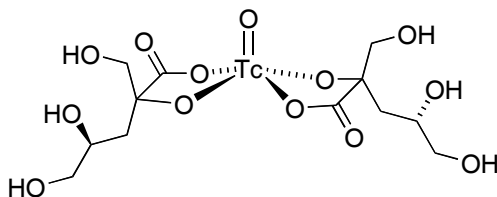


Figure 6: Possible structure of a Tc(V)-ISA complex.

It is known that polyhydric complexes of Tc(V) can be formed by the reduction of pertechnetate in aqueous solution of the excess O-donor ligand [16], although in pharmaceuticals this is not carried out at pH 13.3. Apart from a few cases, the complexes have not been structurally characterised, because of the difficulty of obtaining pure compounds in crystalline form. The Tc-glycolato complex [17-18] has been identified as $[\text{TcO}(\text{OCH}_2\text{CH}_2\text{O})_2]^-$. The anion shows the square-pyramidal arrangement typical of five-coordinated oxotechnetium(V) complexes with the short Tc-O(oxo) bond and longer Tc-O bonds between the metal and the diol oxygen atoms. Hence, it can be assumed that a Tc(V)-ISA complex, such as that shown in figure 5, may have been formed, causing the difference in final solubilities for ISA and gluconic acid.

4 Conclusions

All ligands caused an increase in Tc(IV) solubility. In their presence a lowering of Tc concentration took place upon reduction. For EDTA and NTA no difference in final technetium concentration was observed, leading to the conclusion that Tc(IV) complexes are formed with these two ligands, whether or not Tc(VII) or Tc(IV) are used as the starting point. For ISA and gluconic acid

the Tc solubility in systems starting from Tc(VII) in the presence of the ligands was higher than when TcO₂ was the starting point, suggesting that Tc(VII) was not fully reduced to Tc(IV), but that an intermediate oxidation state complex was formed. By analogy to pharmaceuticals, it may be that a Tc(V)-ISA complex was formed. These results indicate that a detailed understanding of the effect of organic ligands on the reduction of technetium will be required for performance assessment if technetium is to be disposed of in a cementitious repository.

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