Some Aspects of Near Field Chemistry in a Nuclear Waste Repository

By

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Abstract

The groundwater chemistry of technetium is dominated by Tc(VII), as TcO_4^-, in aerobic waters and Tc(IV), as TcO_2 precipitate, in anaerobic waters. What is not known is, what happens to Tc when it migrates from an aerobic water to an anaerobic water which contains possible complexants, e.g. ethylenediaminetetraacetic acid (EDTA). The production of ^{99m}Tc pharmaceuticals in nuclear medicine is based on reacting TcO_4^- with a pharmaceutical in the presence of a reducing agent. During the reaction, Tc(VII) is reduced to a lower oxidation state (possibly (V)) and, in the process, reacts with the pharmaceutical. Thus the transition from Tc(VII) to Tc(IV) does not occur in these reactions. With this in mind, it is essential to investigate the possibility of similar reactions that might occur in the near-field of a nuclear waste repository i.e. reactions of Tc(VII) with possible complexants in a reducing aquatic environment.

The thesis begins with an investigation into the chemistry of technetium under reducing conditions. It includes investigating and developing methods for the reduction of pertechnetate, TcO_4^-, and measurement of the solubility of TcO_2 in the presence of EDTA, NTA, ISA, gluconic acid and picolinic acid, which are organic complexing agents expected to be found in the near field of a nuclear waste repository. To produce technetium(IV) the preferred method was the reduction of technetium(VII) by either reduction with $SnCl_2$ or an electrochemical method that was developed during this project. Using both methods the solubility of technetium(IV) was measure and found to be in agreement with the solubilities in the literature. However, it was shown that in the presence of the low molecular weight organics, EDTA, NTA, ISA, gluconic acid and picolinic acid, the solubility of technetium(IV) is increased due the formation of complexes. It was also shown that the solubility of preformed $TcO_2(s)$ is increased by the presence of the ligands, through the formation of technetium complexes. The initial results indicate that the complexes formed are not the same, it is thought that technetium(V) complexes are formed when TcO_4^- is reduced in the presence of ligands but technetium(IV) complexes are formed when the ligands are contacted with $TcO_2(s)$. Using solubility data the stability constants for the technetium complexes were determined using the solubility product approach. The log of the conditional stability constants calculated for technetium(IV) and the ligands of interest are all within the range 13.8 – 14.9 assuming that the stoichiometry is 1:1.

The second part of this study examines the degradation of tetraphenylphosphonium bromide (TPPB), which is being considered for use in reducing the concentration of pertechnetate in some nuclear waste streams. Under the conditions expected in a nuclear waste repository TPPB is likely to degrade by 2 different mechanisms to triphenylphosphonium oxide (TPPO) and triphenylphosphine (TPP). The degradation of TPPB by alkaline hydrolysis and the effect these degradation products have on radionuclides under near-field conditions has been studied. Analysis of the products from the alkaline hydrolysis of TPPB showed that the only identifiable product formed was TPPO. The alkaline hydrolysis was shown to follow first order kinetics with respect to the concentration of TPPB however the reaction follows third order kinetics overall. From kinetics data an Arrhenius expression was derived for the degradation of TPPB and the activation energy for the reaction estimated to be 105.20 ± 3.21 kJ mol^{-1}. At high pH the TcO_4TPP solid is unstable and over time the concentration of technetium in solution increases. This increase was shown to be as a direct result of the degradation of TPPB only. The presence of TPPB and it degradation products, TPP and TPPO, have no significant effect on the solubility of europium, iodine, nickel, technetium, and uranium and therefore this work was used to help in the acceptance of TPPB as a method for the removal of pertechnetate from technetium waste streams.

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"…..You say you got a real solution
Well, you know
We'd all love to see the plan,
You ask me for a contribution
Well, you know
We're doing what we can….."

Revolution
John Lennon and Paul McCartney

Abbreviations

BFS	Blast Furnace Slag
CDTA	1,2-Cyclohexylenedinitrilotetraacetic acid
DPPO	Diphenylphosphine oxide
EARP	Enhanced Actinide Removal Plant
EA	Environment Agency
EDTA	Ethylenediaminetetraacetic acid
Gluc	Gluconic acid
HLW	High Level Waste
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ILW	Intermediate Level Waste
ISA	Isosaccharinic acid
LLW	Low Level Waste
LSC	Liquid Scintillation Counting
MAC	Medium Active Concentrate
NTA	Nitrilotriacetic acid
Pic	Picolinic acid
PMT	Photomultiplier Tube
TBP	Tributylphosphate
TPP	Triphenylphosphine
TPPB	Tetraphenylphosphonium bromide
TPPCl	Tetraphenylphosphonium Chloride
TPPO	Triphenylphosphonium oxide
wt %	Percentage by Weight
XAFS	X-ray absorption fine structure spectroscopy
XANES	X-ray absorption near-edge spectroscopy

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Chapter 1 –

Introduction

1.0 Introduction to this thesis

1.1 Chemistry of technetium under reducing conditions

Technetium-99 (Tc), a fission product of uranium-238, is important when considering a safety case for nuclear waste disposal because of its high yield in radioactive waste (6% of all fission products consists of ^{99}Tc) and long half-life (2.14×10^5 yr). Technetium is redox sensitive and the near and far-field chemistry of technetium is currently dominated by Tc(VII), as TcO_4^-, in aerobic waters and Tc(IV), as TcO_2 precipitate, in anaerobic waters. However, the heterogeneous nature of the near field of the repository means that areas of oxidising and reducing potentials will co-exist.

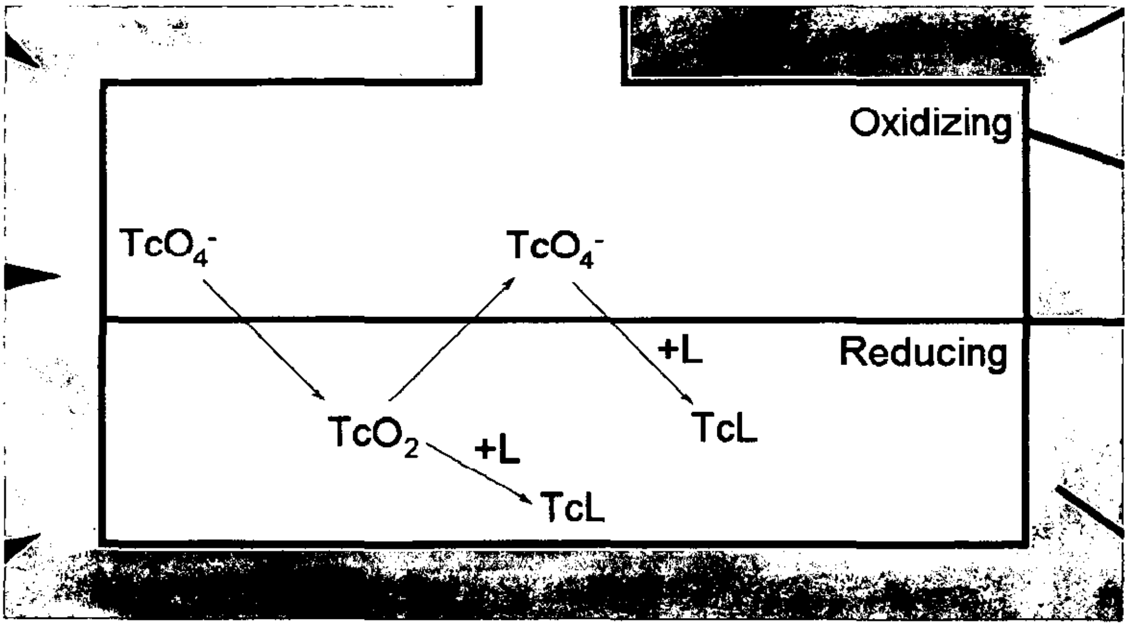


Fig. 1.1: Schematic of the possible fates of pertechnetate in the near field of a nuclear waste repository

This thesis is concerned with the behaviour of technetium under reducing conditions in the presence of low molecular weight organic complexants. In particular what effects do the complexants have on the solubility of reduced technetium, $TcO_2(s)$ and what happens when technetium migrates from an aerobic water to an anaerobic water which contains possible complexants (Fig. 1.1).

1.1.1 Schedule

The schedule for this project is as follows:

1.1.1.1 Literature review

- On the chemistry of technetium

1.1.1.2 Experimental

- Find a suitable method of reduction of TcO_4^- at high pH
- Investigate the speciation of Tc(IV) in alkaline conditions
- Measure any changes in the solubility as TcO_4^- is placed in a reducing environment at high pH in the absence and presence of EDTA, nitriliotriacetic acid (NTA), isosaccharinic acid (ISA), gluconic acid and picolinic acid;
- Measure the changes in the solubility of TcO_2 at high pH in the absence and presence of EDTA, NTA, ISA, gluconic acid and picolinic acid;
- Determine the stability constants of any Tc(IV) complexes formed

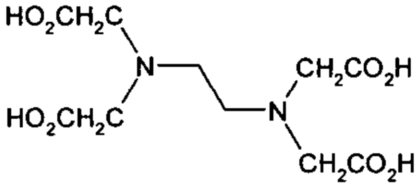
1.1.2 Organic complexing agents of interest

In the ILW/LLW repository there will be a number of organic complexing agents. Some will have ingressed into the repository with the groundwater, others will form part of the waste and some will be formed as decomposition products of the materials in the waste, e.g. cellulose [1]. The organics investigated in this project are:

- Ethylenediaminetetraacetic acid (EDTA),
- Nitrilotriacetic acid (NTA),
- Picolinic acid
- α - Isosaccharinic acid (ISA)
- Gluconic acid

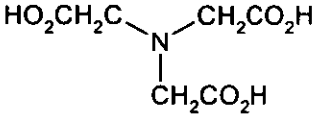
EDTA, NTA, and picolinic acid will be contained in the waste because they are used as decontamination agents in the nuclear industry.

Large amounts of cellulose will be contained in the waste, which under the alkaline conditions expected in the near field of the repository will degrade. ISA appears to be the most important of the cellulose degradation products due to its complexing abilities and yields. Gluconic acid is of interest because it is often used as an analogue for ISA and other polyhydroxylates.



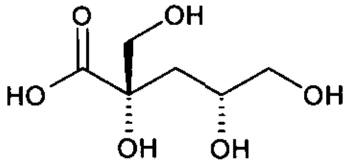
Ethylenediaminetetraacetic acid

(EDTA)



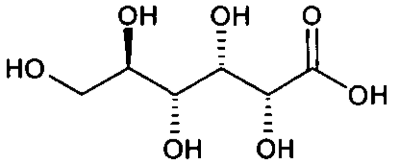
Nitrilotriacetic acid

(NTA)

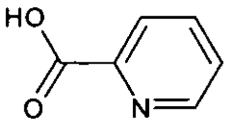


α - Isosaccharinic acid

(ISA)



Gluconic acid



Picolinic acid

Fig. 1.2: Structures of the organics of interest

1.2 Degradation of tetraphenylphosphonium bromide (TPPB) at high pH and the solubility of various radionuclides in its degradation products

During the reprocessing of nuclear waste streams in the past technetium was not removed and was discharged into the sea in the permeate. However, this discharging of technetium into the sea was no longer deemed acceptable and therefore a method for the removal of technetium from some nuclear waste streams has been developed.

Tetraphenylphosphonium bromide (TPPB) is now used to reduce the concentration of pertechnetate in some nuclear waste streams. Therefore, as a result TPPB, pertechnetate and various other radionuclides will be present in certain waste streams which will be placed in a nuclear waste repository. TPPB is known to be stable at neutral pH, but is prone to degradation by alkaline hydrolysis at high pH and also by radiolytic degradation, conditions expected in the near field of a nuclear waste repository. Part B of this thesis is concerned with the investigation of the solubility of europium, iodine, nickel, technetium(VII), uranium(VI) and uranium(IV) in solutions of TPPB, and its major degradation products. Also described in this thesis are the kinetics of the alkaline hydrolysis degradation process of TPPB.

1.2.1 Schedule

The schedule for this project is as follows:

1.2.1.1 Experimental

- Determine the effects of tetraphenylphosphonium bromide, and its degradation products, on the solubility of various radionuclides
- Investigate the degradation products of TPPB at high pH

- Investigate the effect of competing ligands on the pertechnetate-TPPB complex (TcO_4TPP)

Part A –

The chemistry of technetium under reducing conditions

Chapter 2 –

Literature Review

2.0 Literature review

2.1 History and discovery of technetium

Mendeleev's most recognised work is the organisation of 63 elements into the Mendeleev table, or periodic table as it is now known. At the time this table contained a great many gaps and Mendeleev made many predictions about the missing elements. One of these missing elements was element number 43 and in 1869 Mendeleev predicted some of the properties of this unknown 43rd element. Due to the position of this predicted element Mendeleev decided to give it the name Eka-Manganese [1]. These predictions inspired many people to try and find the missing elements. Many reports claimed to have found or produced the 43rd element including Walter Noddack, Ida Tacke (later Ida Noddack) and Otto Berg, who in 1925 claimed to have discovered the missing element by X-ray spectroscopy in concentrates of the minerals sperrylire ($PtAs_2$), gadolinite [$Be_2Y_2Fe(SiO_4)_2O_2$] and columbite [$(Fe,Mn)(NbO_3)_2$] [2]. This discovery was made at the same time and in the same way that Noddack *et al*, discovered element 75. Element 75 was named rhenium (from the Greek word "*Rhenus*" meaning river "*Rhine*") and element 43 was masreium (after Masuria in eastern Prussia). However, they were able to isolate a small quantity of rhenium (2 mg) but were not able to isolate any maserium and so, because they could not produce any further evidence, the discovery was discredited.

In 1937 Perrier and Segrè [3, 4] were credited with the discovery of Technetium (meaning "artificial" in Greek) the missing element number 43. At Berkeley, the home of the cyclotron, a molybdenum plate was bombarded with deuterons in the cyclotron. This molybdenum plate was then given to Segrè who took it back to Italy and analysed it. After his analysis he found that the plate was radioactive and the radiation was identified as that of the missing element 43. In the initial experiment ^{95m}Tc and ^{97m}Tc were produced by the following nuclear reactions.

$$^{94}_{42}Mo(d,n)^{95m}_{43}Tc \qquad t_{\frac{1}{2}} = 61d$$

$$^{96}_{42}Mo(d,n)^{97m}_{43}Tc \qquad t_{\frac{1}{2}} = 91d$$

Fig. 2.1: Nuclear reactions for the production of ^{95m}Tc and ^{97m}Tc

2.2 Occurrence, production and isolation of technetium

2.2.1 Natural occurrence of technetium

In 1955, Alperovitch and Miller [5], reported the presence of naturally occurring technetium in columbite. This technetium was isolated and after irradiation, the γ radiation of ^{99m}Tc was identified for several samples. Soon after these results were published, it was shown by Boyd and Larson [6] that the half life of ^{98}Tc was of the order 1×10^5 years. This finding eliminated the possibility of there being any primordial technetium remaining in the earths crust as the accepted age of the earth is approximately 4.55 billion years (plus or minus about 1%). They also carefully examined the minerals which were claimed to contain technetium and gained negative results for each sample. However its was discovered that an extremely small amount of technetium was created naturally in sustained underground nuclear reactions estimated to have occurred about 1.9 billion years ago. The relics of a nuclear reactor were found in a uranium mine in Oklo, Gabon, Africa. These reactors must have operated and generated ^{99}Tc as a high yield fission product by induced fission of ^{235}U with slow neutrons. The phenomenon occurred because much higher concentrations of ^{235}U were present at that time; the current ^{235}U concentration, about 0.72%, will not sustain such natural reactions. However since the half-life of ^{99}Tc is 2.13×10^5 years the isotope has completely decayed to ^{99}Ru.

2.2.2 Artificial production of technetium

The first weighable amount of technetium was produced by irradiating molybdenum metal powder (5.7 kg) with neutrons in a nuclear reactor [7]. The synthesis is shown in Fig. 2.2.

$$^{98}Mo(n,\gamma)^{99}Mo \xrightarrow[\beta^-]{67h} {}^{99m}Tc \xrightarrow[IT]{6.0h} {}^{99g}Tc$$

Fig. 2.2: The nuclear reaction involved in the synthesis of technetium

The technetium was then separated from the bulk rhenium and precipitated as the sulphide, which was then dissolved in hydrogen peroxide and the sequence of distillation and sulphide precipitation repeated several times. This method is unsuitable for the production of gram and kilogram amounts of technetium as from 5.7 kg of molybdenum metal powder only 2 mg of technetium were produced, giving a yield of *ca.* 3.51×10^{-5} %.

However, large amounts of technetium can be obtained from the fission of ^{235}U with thermal neutrons. This process produces technetium in a 6.13% yield, therefore 1 kg of technetium is produced from approximately 1 ton of uranium (3% enriched in ^{235}U) after burn up in a nuclear reactor [8]. Approximately 2.5g of ^{99}Tc can be produced per day in a reactor with a power of 100 MW. Table 2.1 shows the other possible methods of producing ^{99}Tc by fission.

Radionuclide	Type of Fission	Percentage yield of ^{99}Tc (atom %)
^{233}U	Thermal neutron	4.8
^{239}Pu	Thermal neutron	5.9
^{239}Pu	Fast Neutron	5.9
^{238}U	Fast Neutron	6.3
^{232}Th	Fast Neutron	2.7

Table 2.1: Methods of production of ^{99}Tc

2.3 Properties of technetium

2.3.1 Isotopes and isomers of technetium

There are 22 isotopes and 9 isomers known at the present day, Table 2.2 lists all the know isotopes and isomers along with their methods of production, half-life and method and energy (keV) of decay[1].

Nuclide	Production	Atomic Mass (A.M.U.)	Half-life	Mode and Energy (keV) of Decay
^{90}Tc	^{92}Mo(p,3n)	89.983810	8.7 s	β^+7900; 6950; γ948
^{90m}Tc	^{92}Mo(p,3n)		49.2 s	β^+; γ1054; 948; 945;...
^{91}Tc	^{92}Mo(p,2n)	90.918430	3.14 min	β^+;γ2451;1639; 1605;...
^{91m}Tc	^{92}Mo(p,2n)		3.3 min	β^+; γ653; 503; 928;...
^{92}Tc	^{92}Mo(d,2n)	91.915257	4.23 min	β^+4300; 4100; γ1510; 773;329;...
	^{92}Mo(p,n)			
^{93}Tc	^{92}Mo(d,n)	92.910246	2.75 h	β^+807; ε; γ1363; 1522; 1478;...
	^{92}Mo(p,γ)			
^{93m}Tc	^{92}Mo(d,n)		43.5 min	IT 392; ε;γ2645; 3129; 3221;...
	^{92}Mo(p,γ)			
	^{93}Nb(α,4n)			
^{94}Tc	^{93}Nb(α,3n)	93.909654	4.883 h	ε; β^+800; γ871; 850; 916;...
	^{94}Mo(d,2n)			
	^{94}Mo(p,n)			
	^{93}Nb(^{3}He,3n)			
^{94m}Tc	^{93}Nb(α,3n)		52.0 min	β^+2420; γ871; 1869;1522;...
	^{94}Mo(d,2n)			
	^{94}Mo(p,n)			
^{95}Tc	^{95}Mo(p,n)	94.907657	20.0 h	ε; γ766; 1074; 948;...
	^{94}Mo(d,n)			
	^{95}Mo(d,2n)			
^{95m}Tc	^{95}Mo(p,n)		61 d	ε; β^+700;492; IT; γ204; 582;835;...
	^{94}Mo(d,n)			
	^{95}Mo(d,2n)			
^{96}Tc	^{93}Nb(α,n)	95.907870	4.28 d	ε; γ778; 850;813;...
	^{96}Mo(p,n)			
	^{96}Mo(d,2n)			
^{96m}Tc	^{93}Nb(α,n)		51.5 min	IT 34; ε; γ778;1200; 481;...
	^{96}Mo(p,n)			
	^{96}Mo(d,2n)			
^{97}Tc	Daughter ^{97}Ru	96.906364	2.6×10^6 a	ε
	^{97}Mo(d,2n)		(4.0×10^6 a)	
^{97m}Tc	^{96}Mo(d,n)		90.1 d	IT 97
	^{97}Mo(p,n)			
	^{97}Mo(d,2n)			
^{98}Tc	^{98}Mo(p,n)	97.907215	4.2×10^6 a	β^-397; γ745; 652
^{99}Tc	Fission	98.906254	2.13×10^5 a	β^-292; 203
	Daughter ^{99}Mo			
^{99m}Tc	Daughter ^{99}Mo		6.006 h	IT 140;143;β^-, e^-, γ322; 233
^{100}Tc	^{99}Tc(n,γ)	99.907657	15.8 s	β^-3380; 2880; γ540;591;1512;...
	^{100}Mo(p,n)			
	^{103}Mo(n,α)			
^{101}Tc	Daughter ^{101}Mo	100.907327	14.22 min	β^-1320;1070; γ307; 545;127;...
^{102}Tc	Daughter ^{102}Mo	101.909208	5.28 s	β^-4150;3400;2200;γ475;105;628;...
^{102m}Tc	^{102}Ru(n,p)		4.35 min	β^-1600; 3200; γ475;628;630;... IT
	Fission			
^{103}Tc	Fission	102.909172	54.2 s	β^-2200; 2000; γ136;346;210;...
	^{104}Ru(n,np)			
	^{104}Ru(γ,p)			
^{104}Tc	Fission	103.911460	18.3 min	β^-5100;...;γ358; 531; 535;...
	^{104}Ru(n,p)			
^{105}Tc	Fission	104.911820	7.7 min	β^-3400; γ143; 108; 159;...
^{106}Tc	Fission	105.914510	36 s	β^-;γ270; 2239;1969;...
^{107}Tc	Fission	106.915230	21.2 s	β;γ103;106; 177;...

Table 2.2 continued on page 12

^{108}Tc	Fission	107.918420	5.17 s	β^-;γ242; 732;708;...
^{109}Tc	Fission	108.919580	0.86 s	β^-
^{110}Tc	Fission		0.92 s	β^-;γ241
^{111}Tc			0.30 s	β^-

Table 2.2: Isotopes and isomers of technetium [1]

The table shows that the mass numbers range from 90 – 111, and the half-lifes range from 0.3 s to 4.2 $\times 10^6$ (4.2 million) years. The isotopes with the long half-lifes are associated with the region of mass numbers where the electron capture turns to β^- emission, in this region there are stable isobars of the neighbouring elements molybdenum and ruthenium.

As ^{99}Tc is produced in large amounts by the the fission of ^{235}U in nuclear reactors it is the isotope of technetium that has major relevance to post-closure performance of a nuclear waste repository.

2.3.2 Nuclear properties of ^{99}Tc

The nuclear properties of the different isotopes of technetium are all different. However, ^{99}Tc is the only isotope that is achievable in weighable amounts, and therefore the majority of work has been completed using this isotope. Table 2.3 shows a summary of the properties of ^{99}Tc.

Atomic Mass	98.906254 amu
Decay Mode	β^-, no γ
β^--Energy	292.203 (1.2 $\times 10^{-5}$ %) keV
Half-life	2.13 $\times 10^{-5}$ years
Spec. Activity	17.0 mCi (629M Bq)/g
Cross-Section	20 barn [9]
Nuclear Spin	9/2 h/2π
Nuclear Magnetic Moment	+5.6847 nucl. Magneton [9]
Elect. Quadrupole Moment	-0.129 barn [9]

Table 2.3: Nuclear data of ^{99}Tc

^{99}Tc is a β^- emitter with a maximum β^--energy of 292 keV which decays to stable ^{99}Ru . The β^-emission is not accompanied by γ-radiation.

In addition the nuclide emits a β^- particle at 203 keV, however, the probability of this secondary β^- particle emission is 1.2 × 10^{-5} %. The secondary emission gives a daughter product with 89 keV level 3/2+ of ^{99}Ru (Fig. 2.3) which has a half-life of 18.9 ns which then decays to stable ^{99}Ru. Therefore, with such a low probablilty of occurrence and such a short lived daughter, the secondary emission is said to be negligible.

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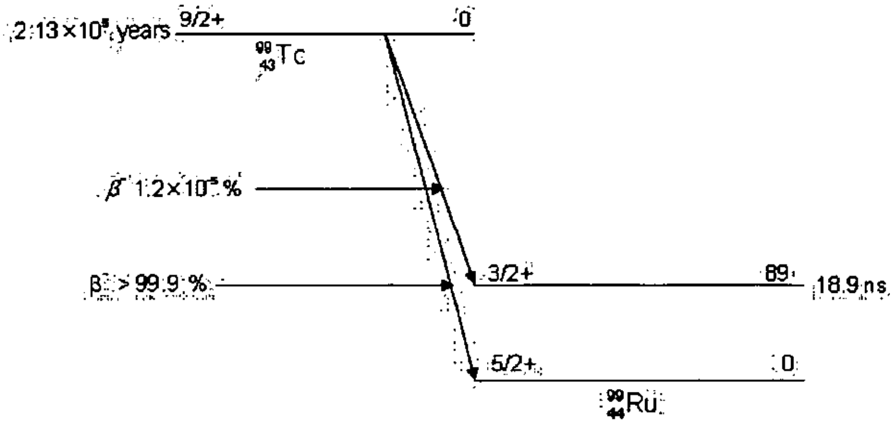


Fig. 2.3: Decay scheme of ^{99}Tc (Energies in keV)

2.3.3 Chemical properties of technetium

Table 2.4 summarises some of the properties of the group 7 elements for comparison of technetium against manganese and rhenium.

Property		Mn	Tc	Re
Atomic Number		25	43	75
Number of naturally occurring isotopes		1	-	2
Atomic Weight		54.938049(9)	98.9063^a	186.207(1)
Electronic Configuration		[Ar]3d^{5}4s^2	[Kr]4d^{6}5s^1	[Xe]4f^{14}5d^{5}6s^2
Electronegativity		1.5	1.9	1.9
Metal Radius (12-coordinate) (pm)		127	136	137
Ionic Radius (pm) (4-coordinate if marked *; otherwise 6-coordinate	VII	46	56	53
	VI	25.5*	-	55
	V	33*	60	58
	IV	53	64.5	63
	III	58 (1s), 64.5 (hs)	-	-
	II	67	-	-
MP (°C)		1244	2200	3180
BP (°C)		2060	4567	(5650)
ΔH_{fus} (kJ mol^{-1})		(13.4)	23.8	34(±4)
ΔH_{vap} (kJ mol^{-1})		221(±8)	585	704

Table 2.4 continues on page 14

ΔH_f (monatomic gas) (kJ mol^{-1})	281(±6)	-	779(±8)
Density (25 °C) (g cm^{-3})	7.43	11.5	21.0
Electrical resistivity (20 °C) (μohm cm)	185.0	-	19.3

[a] – This refers to ^{99}Tc

Table 2.4: Some of the properties of the group 7 elements [10, 11]

The chemistry of technetium is very similar to that of the third row element of group 7, rhenium. This is due to the prolonged effects of the steady contraction caused by the filling of the 4*f* orbitals, known as the lanthanide contraction [11]. As a consequence of lanthanide contraction, the atomic radius of technetium is 1.358 Å (136 pm) (Table 2.4) only 0.015 Å smaller than that of rhenium, whereas the difference between the atomic radii of technetium and manganese is nearly 0.1 Å.

Like rhenium, ruthenium and osmium, technetium crystallises in the hexagonal system with dense packing, the lattice constants are a = 2.7404 Å, c = 4.3980 Å at 298 K (Table 2.5). The unit cell of the technetium consists of 2 atoms which gives the atomic radius 1.358 Å (136 pm). The crystal structure of technetium can withstand pressures of up to 60,000 kg cm^{-2} [12]. Technetium is a type II superconductor at low temperatures and has a transition temperature of 11.2 K the highest for a hexagonal metal and the second highest after niobium of any element [1, 12].

Property	**Value**
Crystal structure	Hexagonal close-packed
Lattice dimensions (298 K)	a = 2.7404 Å, c = 4.3980 Å
Superconducting Transition Temperature	7.73 ± 0.02 K
Debye Temperature (zero-degree)	454 ± 4 K
Entropy (298.15 K)	33.0 ± 0.3 J.mole^{-1}.K^{-1}
Magnetic susceptibility	2.7 ×10^{-6} cm^3 g^{-1}
Specific heat Cp (1000 K)	0.29 J.g^{-1}.K^{-1}
Work function	4.88 ± 0.05 eV

Table 2.5: more physical properties of technetium [1]

2.4 ^{99m}Tc

^{99m}Tc is obtained as the radioactive decay product of ^{99}Mo (Fig. 2.4), $t_{1/2}$ = 66 hours, which is produced by irradiating natural molybdenum or uranium with neutrons in nuclear reactors. ^{99m}Tc is an isomer of ^{99}Tc and is said to be in the metastable state, i.e. the nucleus has a slight excess of energy, this excess of energy, in the case of ^{99m}Tc, is released as γ radiation with an energy of 140 keV. ^{99m}Tc decays, almost quantitatively to ^{99}Tc by isomeric transition.

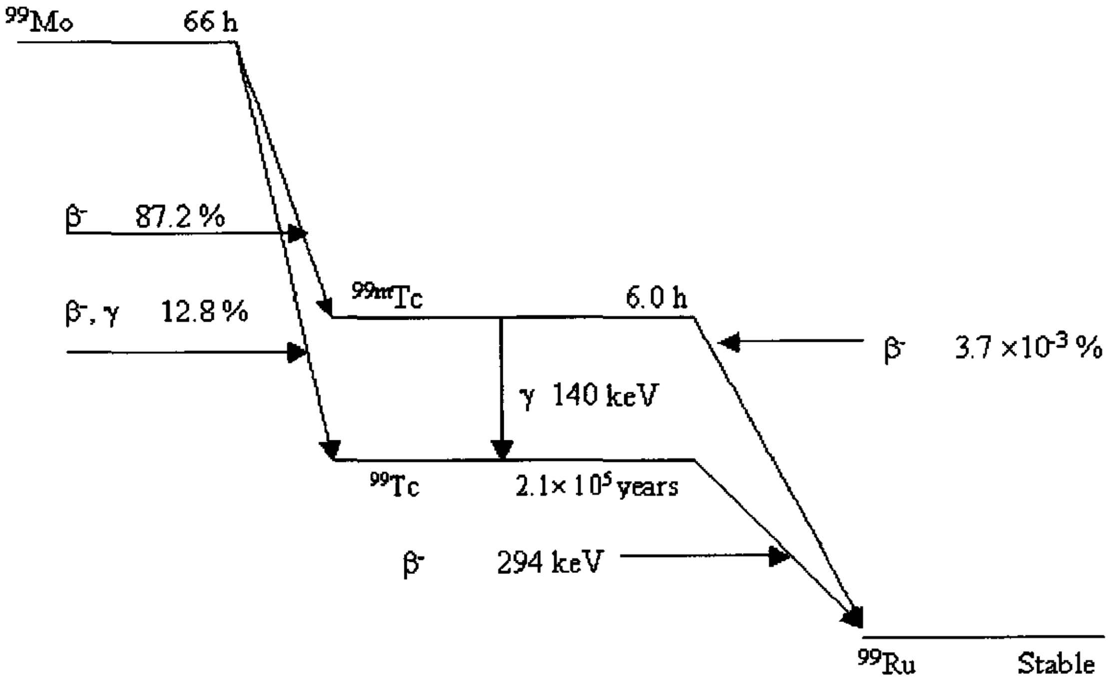


Fig. 2.4: Generation and decay of ^{99m}Tc and ^{99}Tc

^{99m}Tc is the most widely used radioisotope in medicine, employed in over half of all nuclear medicine procedures. This is because ^{99m}Tc possesses all of the necessary properties of an ideal diagnostic radiopharmaceutical; decay via gamma emission and the release of low energy electrons. The gamma rays are low energy and so the dose to the patient is minimized but they are still strong enough to be able to penetrate the crystal on the gamma camera. The short half-life, 6 hours, is long enough to prepare the radiopharmaceutical and run the diagnostic test, yet short enough to minimize the radiation dose to the patient. The chemistry of technetium is also versatile. It can form tracers by being incorporated into a range of biologically-active substances to ensure that it concentrates in the tissue or organ of interest.

2.5 Mechanisms of technetium complex formation

Due to the widespread use of ^{99m}Tc for radiopharmaceuticals the chemistry of technetium is well known and therefore the mechanisms by which complexes are formed is also well known.

The synthesis of ^{99m}Tc complexes usually involves three components: Pertechnetate, TcO_4^-; a reducing agent (R); and a ligand (L). In the case of radiopharmaceuticals the ligand is the pharmaceutical itself. Common reducing agents include metal species like Sn(II), Fe(II), Cu(I) as well as common non-metallic reducing agents such as borohydride, formamidine sulfinic acid and dithionite. These reducing agents are all 1- or 2-electron reductants.

The first step in the formation of technetium complexes is the reduction of the TcO_4^- to a form TcO_4^{2-}, which is a metastable species. (Eq. 1, Fig. 2.5). This reduced species is then captured by the ligand to form the complex. However if the ligand does not form a strong enough complex with technetium or the rate of complexation is slow compared to the rate of reduction, there is a possibility that the reduced form of technetium will degrade to the thermodynamically stable and relatively unreactive TcO_2. This formation of TcO_2 proceeds through a disproportionation reaction of the reduced intermediate to TcO_2 (Tc(IV)) and TcO_4^- (Tc(VII)).

1.
$$\begin{tikzcd}
\mathrm{TcO_4^-} + \mathrm{R} \arrow[r] & \mathrm{TcO_4^{2-}} \arrow[r, "+\mathrm{L}"] \arrow[d] & \mathrm{TcL} \\
 & \mathrm{TcO_2(s)} &
\end{tikzcd}$$

2.
$$\mathrm{TcO_4^-} + \mathrm{R} + \mathrm{L'} \longrightarrow \mathrm{TcL'} \xrightarrow{+\mathrm{L}} \mathrm{TcL}$$

3.
$$\mathrm{TcO_4^-} + \mathrm{R} + n\mathrm{L'} \longrightarrow [\mathrm{TcL}_n]^{m} + \mathrm{R} \longrightarrow [\mathrm{TcL}_n]^{m-p}$$

Fig. 2.5: 3 different mechanisms of technetium complex formation

It is sometimes possible to form an intermediate complex with a weak ligand, L', if the ligand doesn't react fast enough with the reduced metastable species. The weak ligand can then be displaced by the ligand of choice, L, by a straightforward ligand displacement (Eq. 2, Fig. 2.5). The weak ligand, L', is generally referred to as a transfer ligand. Examples of transfer ligands include carbohydrates such as glucoheptonate [13] and tartrate [14] and simple oxygen donors such as ethylene glycol.

In a number of cases the reduction probably proceeds in several steps (Eq. 3, Fig. 2.5). This is because most of the reductants can only reduce technetium(VII) by 1 or 2 oxidation states at a time. This case usually applies when technetium(VII) is being reduced to oxidation states lower than Tc(V) [15].

2.6 Repository conditions

One possible option for the management of intermediate-level radioactive waste (ILW) in the UK is to dispose of it in an underground cementitious repository (Fig. 2.6).

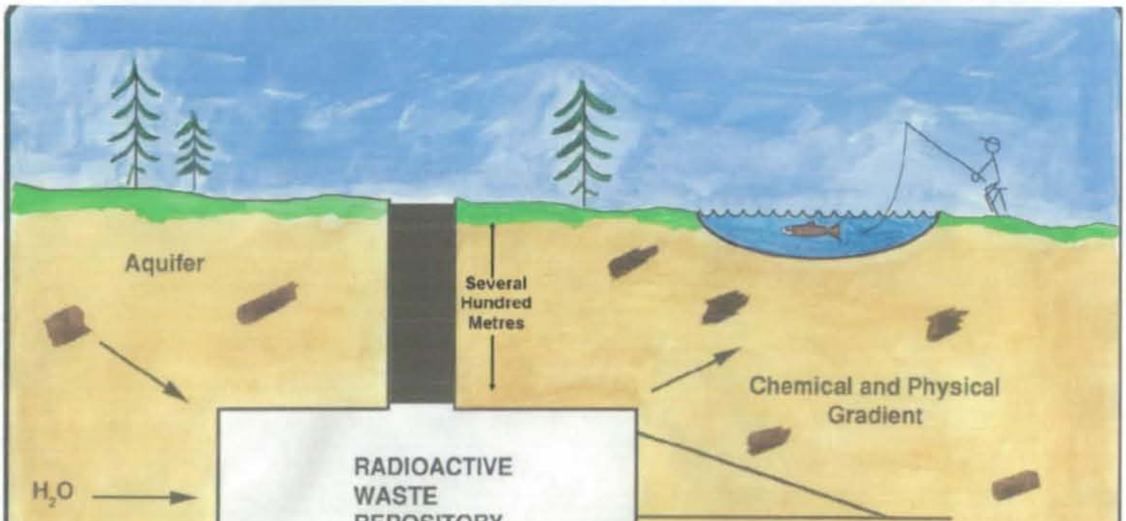


Fig. 2.6: Cartoon schematic of repository

This option for the management of radioactive waste uses a combination of engineered and natural barriers to produce a multi-barrier system, with the following elements:

- Physical containment provided by the waste packages
- Chemical conditioning provided by a cement-based backfill material and waste encapsulant
- Geological isolation provided by locating the disposal vaults deep underground in a suitable geological environment.

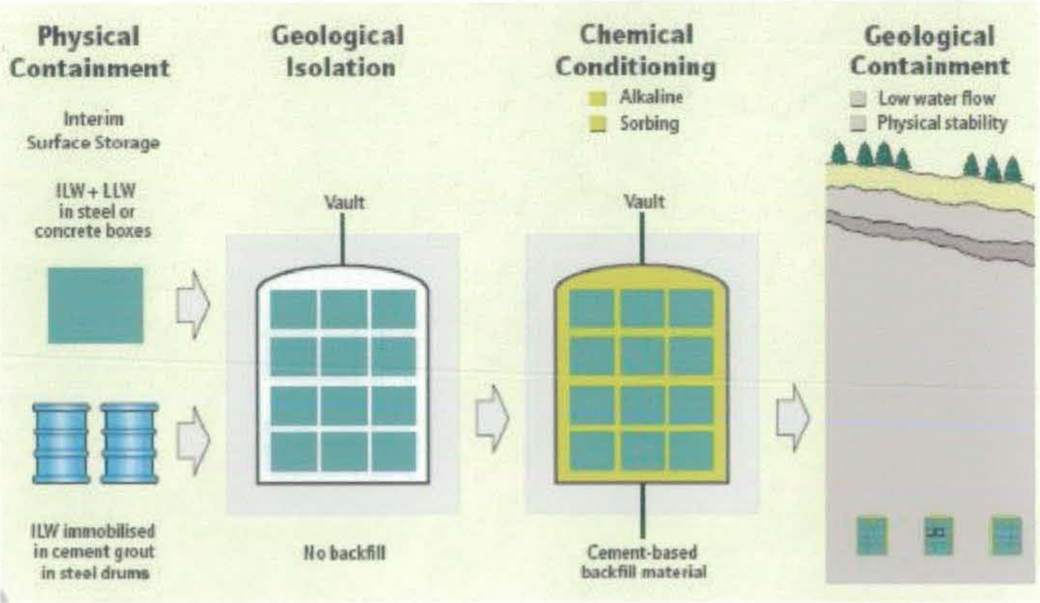


Fig. 2.7: Nirex multi - barrier containment system © United Kingdom Nirex Limited [16]

At a time determined by future generations the repository will be sealed using Nirex Reference Vault Backfill (NRVB) leading to geological containment. NRVB has three main purposes: to provide abundant surfaces for sorption (through its relatively high porosity) and low strength to facilitate retrievability should this be required. However, its primary purpose is to create a long lasting, high pH environment throughout the near-field [17]. NRVB was chosen because of it properties, it has an extensively documented history of use and draws upon readily available technology.

Once closed the repository will become saturated with groundwater, and then highly alkaline pore water will develop. The initial pH of this pore water will be approximately 13.3 - 13.4. This value will decrease to *ca.* 12.5 as the ground water flow dissolves and removes any sodium and potassium hydroxides present. Modelling completed by Nirex shows that the mineral phases in the cement will act as a buffer and maintain the pH at that level for approximately 10^5 years (Fig. 2.8) [18].

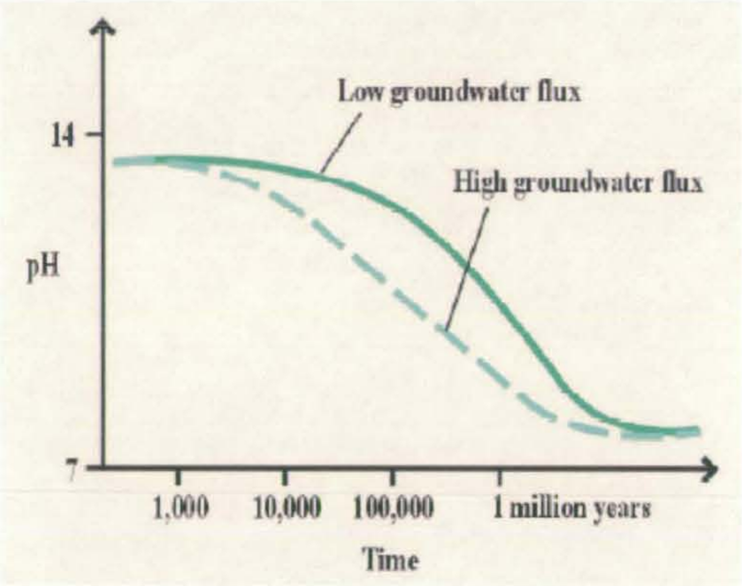


Fig. 2.8 - pH evolution of the engineered system (schematic) © United Kingdom Nirex Limited [18]

In this highly alkaline cement pore water, many radioelements and other hazardous species will show limited solubility and sorption can also take place on the cementitious surfaces.

2.6.1 Contents of the repository

An underground cementitious repository may contain:

- Nirex Reference Vault Backfill (NRVB)
- The waste container
- Groundwater (following resaturation)
- Radionuclides
- Conditioned wastes

2.6.1.1 Nirex reference vault backfill (NRVB)

NRVB is a mixture of calcium hydroxide, ordinary Portland cement, limestone flour and water. After hydration in the repository the principal mineralogical components will be:

- Sodium and potassium hydroxides
- Calcium hydroxide
- Calcium silicate hydrate (CSH) gels
- Calcium carbonate
- Hydrated calcium aluminates

Once the initial pore water has been replaced by ingressing groundwater, calcium hydroxide and CSH gels will dominate the near-field chemistry of a nuclear waste repository.

2.6.1.2 Calcium hydroxide (lime)

Calcium hydroxide has a solubility of *ca.* 1.2 g dm^{-3} at 18 °C and produces a pH of approximately 12.5. In the presence of moisture and carbon dioxide, lime will re-carbonate slowly to form calcium carbonate although without significant dimensional change.

2.6.1.3 Portland cement

Mineralogically, Portland cement clinker consists of four principal phases. These have idealised compositions close to Ca_3SiO_5, Ca_2SiO_4, $Ca_3Al_2O_6$ and $Ca_2(Al,Fe)O_5$. Free lime CaO, normally comprises less than 2 – 3% of the clinker. Modern Clinkers contain 40 – 60% Ca_3SiO_5 and as a consequence the resulting finely-ground product reacts rapidly with water and stiffens. In order to allow a period of plasticity for mixing, transportation and handling, several wt % gypsum, $CaSO_4.2H_2O$, is normally ground with the clinker. This retards the initial set. The amount of gypsum added is usually adjusted so as to achieve retardation of initial set for several hours.

The use of cement will bring with it pore water, which is the excess water not required for hydration. Although there is only a small amount of Na_2O and K_2O (0.5 – 1.0 wt%) the alkali concentrates in the pore water and the result is that they dominate the pore water alkalinity. The pore water pH frequently exceeds that of saturated $Ca(OH)_2$ ($\approx$ 12.4 at 18 °C), reaching 13 to 14. The exact pH is dependent on the cement alkali content, the water/cement ratio and the content of added alkali in activators, amounts of mix water and waste and also the presence of soluble waste components. However, the cement will not set except at high pH. The most immediate consequence of the high alkalinity is that the high hydroxyl concentrations suppresses the solubility of calcium. However once Na_2O and K_2O are washed away, solid $Ca(OH)_2$ and other lime-rich solids combine with waste components and remain to buffer the pH.

Another aspect of cement behaviour is the oxidation-reduction potential they produce in the aqueous phase, and hence waste components. Portland cements are normally produced under oxidising conditions and therefore most of their iron content is present as Fe(III). Not surprisingly, therefore, its associated pore fluids are slightly oxidising, having potentials of up to +200mV vs. SHE [19]. However, both lime-based and Portland cements lack any redox couples, so the Eh, is readily affected by the presence of active redox couples.

This can cause the cement chemistry of individual radionuclides to be complex. However if the solubility limiting phase of the element is known then the performance within a cement system can be anticipated. But for many radioelements, although solubility data exists it is difficult to anticipate what performance is to be expected from cement systems due to the uncertainties in the following:

- Radioelement oxidation state
- Crystallinity/evolution of the solubility limiting phase
- The effects of organic compexants

2.6.1.3.1 Ageing and environmentally-conditioned reactions of cement

Once wastes have been cement conditioned and disposed, usually into the natural environment, further reactions may occur. Two types of reaction between cement-conditioned waste and their disposal environment may occur, one characterised by closed system behaviour and the other, by open system behaviour. In reality the situation may approximate closely to closed system behaviour over long periods, hydrated calcium silicates have been observed to persist for $>10^6$ years [16].

The cement matrix may, however, react with waste constituents. Degradation of organic materials could lead to the formation of carbon dioxide (or CO_3^{2-}). The consequential reaction, carbonation of the cement, leads to a reduction in the pH buffering capacity and the potential resolubilisation of waste species. Generation of "inert" gases, e.g. CH_4, H_2 O_2, etc. could lead to cracking and physical deterioration of the matrix. These and other mechanisms have been suggested to occur but there is little hard evidence that they will be important in practice. One reason for the formation of CO_2 and CH_4 is microbial action on organic waste. The importance of gas generation from the decomposition of organic components is, by and large, unresolved. Moreover, many hazardous species form poorly soluble carbonates.

The most important reactions encountered in open systems are with groundwater and its components. Leaching by initially pure water remains a possibility, although in practice, even low levels of dissolved matter present in groundwater are likely to prove important. Sensitivity studies show that the important groundwater components are Na^+, Ca^{2+}, $Mg^{2+}$and Cl^-, CO_3^{2-} and SO_4^{2-}. Given the complexity of the system, empirical studies of the impact of groundwater constituents, especially anions, may also affect waste constituent solubilities by complexation. Much empirical experience can be applied to predict the general reaction(s) and consequence(s) of specific groundwater components. Table 2.6 shows selected examples

Ion	Characteristic Reactions
Na^+, K^+, Ca^{2+}	Very Slight
Mg^{2+}	Replaces Ca in $Ca(OH)_2$, C-S-H. etc. with decrease in pH
Cl^-	Partially replaces OH^- in cement phases. Consequences slight at low Cl^- concentrations
SO_4^{2-}	Increases stability of solid sulphates. Reaction may be expansive Converts cement phases to monosulphate and ettringite
CO_3^{2-}	Converts cement phases to $CaCO_3$ with decrease in pH

Table 2.6: Reactions of groundwater components with cement [19]

Organic complexants may also influence the resolubilisation of waste species. A large amount of work has been carried out on the effects on solubility and sorption of cellulose degradation products and other organics on radioelements. Table 2.7 shows a few examples. Many organics are precipitated in cement environment, e.g. oxalate as its calcium salt, so high aqueous concentrations cannot be realistically achieved. The long term consequences of CO_2 production and of cellulose degradation products, continues to be assessed with respect to impact on radioelement complexation and solubilisation mechanisms, but straightforward reduction of cement pH appears to be the most immediate problem. However, this can (and is) taken into account in calculating the amount of NRVB required to give a suitable longevity in pH.

Type of Organic	Reaction with Cement
High M.W. soluble dispersible polymers, e.g. plasticisers	Hydrolysis of functional groups and precipitation
High M.W. insoluble polymers, e.g. cellulose	Possible development of lower molecular weight soluble products. Products variable depending oil prescence or absence of oxygen. ISA formed shown to be important complexant.
Microbiological degradation of natural and synthetic polymers, etc.	Possible production of CO_2, CH_4 (reducing conditions) or organic acids (oxidising conditions)
Low molecular weight complexants, e.g. citric acid, oxalic acid , EDTA	Probably destroyed or precipitated, with solubility controls, at high cement pH

Table 2.7: Reactions between cement and selected organics [19]

2.6.1.4 Packaging

316 stainless steel is used for the physical containment of many of the wastes [17]. One of the purposes of the waste container is to be a physical barrier to stop the groundwater reaching the more soluble radionuclides until they have substantially decayed. However 316 stainless steel is purposely used to help control the near-field chemical environment. Together the use of 316 stainless steel and NRVB in the waste inventory would condition the near-field environment to high pH and low Eh for at least a million years [17].

The non-uniformity of the surface of iron results in areas of low electrode potential which function as anodes and the other areas on the iron surface function as cathodes. It can therefore be said that the iron acts as a short-circuited cell when moist. The reactions that occur at the anode and cathode are shown in Fig. 2.9.

At the Anode $Fe - 2e^- \rightarrow Fe^{2+}$

At the Cathode $H_2O \rightarrow H^+ + OH^-$

$2e^- + 2H^+ \rightarrow H_2$

In the presence of O_2 $2H_2 + O_2 \rightarrow 2H_2O$

Fig. 2.9: Reactions occurring on surface of Fe

This depletion of O_2 and production of H_2 produces a reducing environment and therefore the groundwater has a low Eh. Once anaerobic conditions are established, corrosion is uniform and slow. The iron(II) produced at the anode then reacts further as shown in Fig 2.10. The basic ferric carbonate produced in reaction 3 is then hydrolyzed to $Fe(OH)_3$. Dehyrdation of $Fe(OH)_3$ then occurs which produces $Fe_2O_3.xH_2O$. These solid iron oxides present a surface that radionuclides can sorb on to, therefore producing another method by which radionuclide migration is retarded.

1 $Fe^{2+} + OH^- \rightarrow Fe(OH)_2$

2 $Fe(OH)_2 + CO_2 \rightarrow FeCO_3 + H_2O$

3 $FeCO_3 + O_2 + H_2O \rightarrow Fe(OH)_2(HCO_3)$

Fig. 2.10: Reaction of Iron(II) from 316 stainless steel containers in reducing conditions

2.6.1.5 Groundwater

The groundwater that will flow into the repository will contain many substances. Table 2.8 shows the analysis and identification of organics present in several trench leachates. The samples were collected from commercially operated low-level radioactive waste disposal sites at Maxley Flats, Kentucky and at West Valley, New York [20].

Acids
Benzoic Acid
Butanoic Acid
Decanoic Acid
2-Ethylhexanoic Acid
Hexanoic Acid
Hydroxybenzoic Acid
3-Methyl-4-hydroxybenzoic Acid
2-Methylbutyric Acid
3-Methylbutyric Acid
2-Methylhexanoic Acid
2-Methylpentanoic Acid
2-Methylpropionic Acid
Nonanoic Acid
Octanoic Acid

Alcohols
Borneol
2-Butanol
Cyclohexanol
2-Ethylhexanol
3-Ethylhexanol
2-Hexanol
3-Hexanol
2-Methyl-2-butanol
Methylcyclohexanol
Octanol
2-Phenylcyclohexanol
(propylene glycol)$_n$
3,3,5-Trimethylcyclohexanol

Acids(Cont'd)
Pentanoic Acid
Phenylacetic Acid
Phenylbutyric Acid
Phenylhexanoic Acid
Phenylpropionic Acid
Toluic Acid (isomers)

Phenols
Cresol (isomers)
Octylphenol
Phenol
4-*t*-Butylphenol
Tetramethylbutylphenol

Aromatic Hydrocarbons
Benzene
Biphenyl
Dimethylnapthalene
Napthalene
Toluene
Xylene (isomers)

Esters
Butyl Phthalate
Dimethyl Phthalate
Several Unidentified phthalates
Tributyl Phosphate
Triethyl Phosphate
Triphenyl Phosphate

Aldehydes and Ketones
p-Hydroxybenzaldehyde
Paraldehyde
Vanillin
Acetovanillion
Camphor
Diacetone Alcohol
Dibutyl Ketone
Fenchone
Methyl Ethyl Ketone
Methyl Isobutyl Ketone

Ethers
Anisole
Bis(2-chloroethyl) Ethyl
Bis(2-chloroethoxy) Methane
Bis(2-ethoxyethyl) Ethyl
1,1-Diethoxyethane
1,1-Diethoxy-2-chloroethane
1,4-Dioxane
Tetrahydronfuran
Tripropylene Glycol Methyl Ester

Amines
Aniline
Cyclohexylamine
Dicyclohexylamine
Methyldicyclohexylamine

Table 2.8: Compounds identified in trench leachates from Maxey Flats and West Valley disposal sites [20]

In fresh waters, the dissolved organic content (DOC) varies considerably, reaching a possible 50 mg dm^{-3} in swamp waters. 100 Samples of water were taken from different sites in USA and the DOC was measured. The values obtained for the DOC ranged from 0.1 to 15 mg dm^{-3} however 85% of the samples had a DOC below 2 mg dm^{-3} [21].

In Sweden, water samples were taken from 25 different sites from a depth of approximately 100 – 700 m in crystalline rock. The DOC was measured at 0.1 – 8 mg dm^{-3}. In Nevada, USA the DOC was reported at 0.2 – 0.9 mg dm^{-3} from depths of 340 – 1100 m in limestone and tuff [21]. A survey of the DOC in several sites in southern Manitoba, Canada was also performed to assess their potential role in radionuclide transport. The results of the survey showed that the range of DOC was <0.1 – 19.5 ppm at depths of 0 – 1100 m in plutonic rock [22].

The concentration of the majority of the simpler organic compounds are too low to affect the speciation of any of the radionuclides present in the waste. This is particularly true for deep repositories where they will be filtered out of the water to a large extent by the time the water reaches the depth at which the waste is buried.

The monocarboxylic fatty acids are the most abundant organic found in groundwater. However, the formation constants for metal monocarboxylic fatty acid complexes are low. The dicarboxylate ligands such as oxalate and malonate are stronger complexants but appear in the DOC at very low concentrations. As a result dicarboxylate ligands can not compete with hydrolysis or with complexation by carbonate, or in some waters, by sulphate, phosphate, fluoride or humates. Monosaccharides can complex metals, including the actinides, but not with sufficient strength to overcome their low concentrations [23].

Carbonate, either as carbonic acid, bicarbonate or carbonate ion is a major component of groundwater systems. Various carbonate species form aqueous complexes with several aqueous actinide species including Am^{3+}, UO_2^{2+}, NpO_2^{+}, Th^{4+} and U^{4+}. Complexation between tetravalent actinides and carbonate can be strong, which may increase the solubility of the oxides and hydrous oxides of tetravalent actinides present in nuclear waste repositories [23]. Carbonate has also been shown to inhibit the reduction of Tc(VII) to Tc(IV) by gamma irradiation. This is due to the formation of $CO_3^{\cdot-}$ radicals which can cause reoxidisation of the immobile Tc(IV) to the mobile Tc(VII) species [24].

2.6.1.6 Waste

The total volume of the waste is likely to be 263,000 m^3, the break down of the waste types and the upper and lower bounds can be seen in Table 2.9 [16].

Waste type	**Reference case (m^3)**	**Upper bound (m^3)**	**Lower bound (m^3)**
ILW	248,238	498,456	133,569
LLW	15,072	15,072	15,072
Total	**263,311**	**513,529**	**148,641**

Table 2.9: Estimation of the total volume (m^3) and upper and lower bounds of the waste

Nirex have also specified a number of materials for which the total mass disposed will be of key importance in post-closure radiological assessment studies. Table 2.10 presents the quantities of bulk metal and Table 2.11 the quantities of organic material. In each case, the data are given for operational and decommissioning ILW and LLW (high and low scenarios).

	Total mass of materials (tonnes)						
	Stainless Steel	Other Steel	Magnox/ Magnesium	Aluminium	Zircalloy	Other Metals	Other Materials
ILW							
Operational	90254	47514	15447	4788	15746	6827	197500
Decommissioning	24439	32791	327	274	0.0	11889	101944
LLW (High Scenario)							
Operational	56940	222957	0.2	3521	58	7972	220151
Decommissioning	116225	231107	0.0	1396	0.0	95311	787696
LLW (Low Scenario)							
Operational	2072	15652	0.0	791	5	1482	103120
Decommissioning	432	6581	0.0	1834	0.0	999	1499
Total ILW	114692	80305	15774	5062	15746	18717	299444
Total LLW (High Scenario)	173164	454064	0.0	4917	58	103283	1007847
Total Waste (High LLW Scenario)	287857	534370	15774	9979	15804	122000	1307291

Table 2.10: Total quantities of bulk materials in ILW and LLW [16]

	Total Mass of Materials (tonnes)						
	Cellulose	**Halogenated Plastics**	**Non - Halogenated Plastics**	**Ion - Exchange Materials**	**Halogenated Rubber**	**Non Halogenated Rubber**	**Other Organics**
ILW							
Operational	6225.6	9481.5	1785.1	12601.3	2443.6	714.3	1055.5
Decommissioning	183.8	781.4	716.9	412.2	49.8	80.1	65.0
LLW (High Scenario)							
Operational	41160.2	19640.3	17895.3	3404.6	5992.9	5873.4	1021.4
Decommissioning	1118.7	2792.1	1603.1	220.2	221.8	188.3	0.0
LLW (Low Scenario)							
Operational	8936.7	854.2	370.8	46.2	386.4	441.1	2.4
Decommissioning	124.1	346.3	143.0	0.0	43.2	0.0	0.0
Total ILW	6409	10263	2502	13013	2493	794	1120
LLW (High Scenario)	42279	22432	19498	3625	6215	6062	1021
LLW (Low Scenario)	48688	32695	22000	16638	8708	6856	2142

Table 2.11: Total quantities of organic materials in ILW and LLW [16]

The organic material has been classified into the following catergories [25]:

- Cellulosics – includes materials composed of polysaccharide cellulose, for example paper, cloth and wood.
- Halogenated Plastics – e.g. PVC
- Non-Halogenated Plastics – including condensation polymers, for example polyesters, Bakelite, nylon, epoxy and other polymers including polyethylene, polypropylene and polystyrene
- Organic ion exchange resins
- Rubber compounds – both Halogenated (e.g. neoprene (polychloroprene), Hypalon (chlorosulphonated polyethylene)) and non-halogenated (e.g. latex (polyisoproprene), styrene butadiene).
- Complexing agents – e.g. EDTA, citric acid, oxalic acid
- Other organics – including organic material not included under the above heading (e.g. oils and other organic liquids)

Table 2.12 shows the proportions of each of these components in ILW in the UK.

Material	**Stocks at 1 April 1994 (tonnes)**		**Committed arisings (tonnes)**	
	Operational	**Decommissioning**	**Operational**	**Decommissioning**
Cellulosics	1030	34	763	104
Halogenated plastics	2630	53	3580	84
Non-halogenated plastics	836	23	638	225
Ion exchange materials	483	1.4	568	77
Rubber compounds	885	11	1210	78
Complexing agents	274	0.1	297	2.8
Other organics	8.6	0	17	0.1

Table 2.12: Organic material in UK intermediate level waste [25]

2.6.1.6.1 Cellulose degradation

Cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units (often loosely called glucose units) linked by β-1,4-glycosidic bonds (Fig. 2.11).

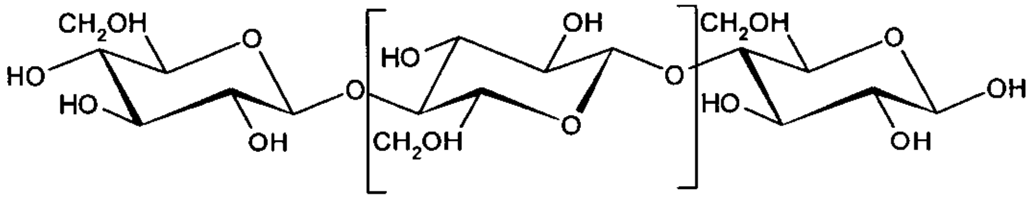


Fig. 2.11: The structure of cellulose

Under alkaline, anaerobic conditions at temperatures below approximately 170 °C, the likely conditions in the near field, the main degradation mechanism is by beta-alkoxycarbonyl elimination which ruptures the 1,4-glycosidic linkage and takes place from the reducing group at the end of the chain. This is known as the peeling reaction (Fig. 2.12).

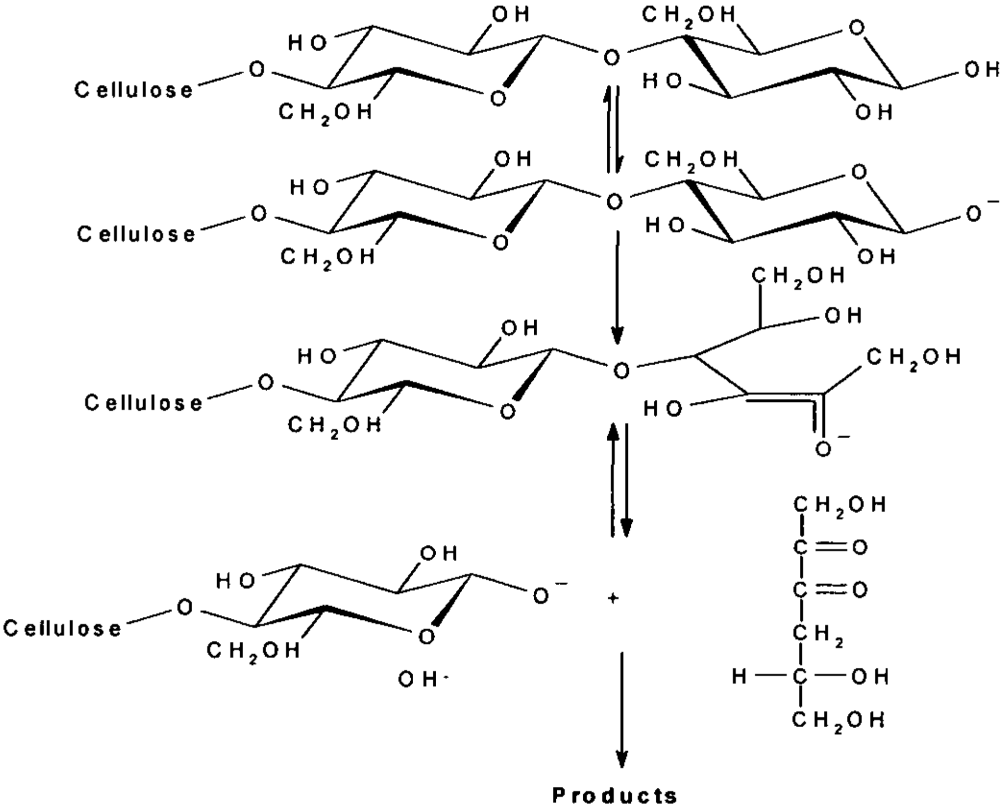


Fig. 2.12: The peeling reaction of cellulose

The reactive end of the cellulose chain is regenerated and a small water-soluble organic molecule is released which undergoes further reaction or rearrangement to give several possible products. If no other reactions occur then cellulose will degrade completely by this reaction; however, there are competing reactions at the reducing end groups. Reactions which form end groups stable to alkaline attack (e.g. 3-deoxyhexonic acid units) are called stopping reactions. The short-term degradation of isolated cellulose chains in anaerobic, alkaline solution in the presence of calcium is determined principally by competition between the peeling and stopping reactions. The general scheme of the reaction is shown in Fig. 2.13.

Initiation a) $HGO(-GO)_n\text{-}GOH \leftrightarrow HGO(-GO)_n\text{-}GO^- + H^+$
b) $HGO(-GO)_n\text{-}GO^- \rightarrow HGO(-GO)_{n-1}\text{-}GO^- + \text{Products}$
Propagation c) $HGO(-GO)_{n-1}\text{-}GO^- \rightarrow HGO(-GO)_{n-2}\text{-}GO^- + \text{Products}$
Termination d) $HGO^- \rightarrow \text{Products}$
e) $HGO(-GO)_n\text{-}GO^- \rightarrow HGO(-GO)_n$ – 3-deoxyhexonic acid residue

G = glucose unit

Fig. 2.13: General reaction scheme of the degradation of cellulose

In Fig. 2.13 the peeling reaction is reaction b) and the stopping reactions are reactions c) and e). This mechanism also accounts for chain termination by complete unzipping of the chain, reaction d) [26].

The products formed by the degradation of cellulose under alkaline conditions are important compounds within the repository. This is because many of them are strong complexing agents and can affect the speciation and therefore the solubility and sorption characteristics of the radionuclides if complexes are formed . Table 2.13 lists some of the products formed by the degradation of cellulose.

Formic acid	Succinic acid
Acetic acid	Butyric acid
Glycolic acid	Threonic acid
Pyruvic acid	Adipic acid
Glyceric acid	Isosaccharinic acid
Lactic acid	2-Hydroxyvaleric acid
Propionic acid	

Table 2.13: Products from the degradation of cellulose under alkaline conditions [26 - 28]

2.6.1.7 Radionuclides

In 1995, Nirex conducted a preliminary analysis of the groundwater pathway for a deep repository at Sellafield [29]. Table 2.14 shows which radionuclides were included in the waste for this assessment.

^{3}H	^{60}Co	^{94}Nb	^{147}Pm	^{233}U	^{241}Am
^{10}Be	^{59}Ni	^{95}Nb	^{151}Sm	^{234}U	^{242m}Am
^{14}C	^{63}Ni	^{93}Mo	^{154}Eu	^{235}U	^{243}Am
^{35}S	^{65}Zn	^{99}Tc	^{182}Ta	^{236}U	^{242}Cm
^{36}Cl	^{79}Se	^{103}Ru	^{210}Pb	^{238}U	^{243}Cm
^{41}Ca	^{89}Sr	^{106}Ru	^{210}Po	^{237}Np	^{244}Cm
^{45}Ca	^{90}Sr	^{107}Pd	^{226}Ra	^{238}Pu	^{245}Cm
^{51}Cr	^{91}Y	^{134}Cs	^{229}Tb	^{239}Pu	^{246}Cm
^{54}Mn	^{93}Zr	^{135}Cs	^{230}Th	^{240}Pu	
^{55}Fe	^{95}Zr	^{137}Cs	^{232}Th	^{241}Pu	
^{58}Co	^{93m}Nb	^{144}Ce	^{231}Pa	^{242}Pu	

Table 2.14: List of radionuclides from Sellafield preliminary assessment [23]

The radionuclides in the waste will suffer a number of different fates, from decay in the repository to escape into the environment. These procedures are summarised in Table 2.15 for the radionuclides found in the repository.

Decayed in the packages	Decayed in the near field	Decayed in the Geosphere	Escape into the Environment
^{3}H	^{14}C	^{59}Ni	^{36}Cl
^{63}Ni	^{94}Nb	^{79}Se	^{226}Ra
^{90}Sr	^{128}Sn	^{93}Zr	^{238}U
^{137}Cs	^{239}Pu	^{93m}Zr	
^{238}Pu	^{240}Pu	^{135}Cs	
^{241}Pu		^{242}Pu	

Table 2.15: Fate of the radionuclides in the waste repository [23]

The radionuclides that are predicted to escape into the environment are ^{36}Cl, ^{238}U and ^{226}Ra. ^{36}Cl will be present in the repository environment as anion and therefore as anions are generally mobile in the aquatic environment it is likely that Cl species will escape into the environment. ^{226}Ra is a daughter of ^{238}U and so the fate of both radionuclides are connected. The conditions of the repository will cause uranium to reduced to the insoluble U(IV), however, the half life of ^{238}U is *ca.* 4 billion years. It is likely therefore that uranium will out live the conditions expected in the repository and will therefore escpae into the environment. Table 2.16 shows the inventories of long-lived (> 30 years) radionuclides found in low level waste, shielded and unshielded intermediate level waste for the Nirex reference case waste volume.

Radionuclide	Unshielded ILW (TBq)	Shielded ILW (TBq)	LLW (TBq)
^{3}H	9.4×10^{3}	6.7×10^{3}	8.0×10^{-1}
^{10}Be	3.2×10^{-2}	7.1×10^{-5}	0.0
^{14}C	3.5×10^{3}	1.1×10^{3}	1.7
^{36}Cl	9.5	1.9	1.8×10^{-1}
^{59}Ni	7.7×10^{3}	2.5×10^{2}	0.0
^{63}Ni	5.7×10^{5}	1.9×10^{4}	3.7
^{79}Se	2.5	6.5×10^{-4}	2.3×10^{-7}
^{90}Sr	8.6×10^{4}	2.5×10^{2}	7.6×10^{-2}
^{93}Zr	2.9×10^{2}	6.5×10^{1}	1.5×10^{-6}
^{93m}Nb	2.3×10^{2}	4.4×10^{1}	1.2×10^{-6}
^{94}Nb	1.7×10^{2}	5.7	2.9×10^{-3}
^{99}Tc	4.0×10^{2}	2.5×10^{1}	6.5×10^{-7}
^{126}Sn	5.2	6.7×10^{-4}	2.2×10^{-7}
^{129}I	1.6	3.9×10^{-5}	2.1×10^{-7}
^{135}Cs	6.4	4.7×10^{-3}	0.0
^{137}Cs	3.8×10^{5}	8.2×10^{2}	9.5×10^{-2}
^{210}Pb	8.4	4.7×10^{-7}	9.7×10^{-5}
^{226}Ra	9.0	1.1×10^{-6}	1.1×10^{-4}
^{229}Th	1.6×10^{-2}	3.5×10^{-9}	1.1×10^{-7}
^{230}Th	1.3×10^{-1}	8.7×10^{-5}	9.6×10^{-4}
^{232}Th	2.1×10^{-1}	9.4×10^{-13}	7.3×10^{-5}
^{231}Pa	7.1×10^{-1}	6.6×10^{-6}	8.5×10^{-5}
^{233}U	9.7×10^{-1}	7.9×10^{-7}	1.6×10^{-5}
^{234}U	7.8×10^{-1}	1.7×10^{1}	1.4
^{235}U	1.6	5.8×10^{-3}	5.2×10^{-2}
^{236}U	1.1×10^{1}	4.7×10^{-4}	5.0×10^{-3}
^{238}U	3.7×10^{1}	1.7×10^{-1}	1.1×10^{-1}
^{237}Np	8.6×10^{1}	1.7×10^{-3}	3.8×10^{-5}
^{238}Pu	6.5×10^{3}	1.6×10^{1}	3.0×10^{-2}
^{239}Pu	1.4×10^{4}	6.2×10^{1}	8.3×10^{-1}
^{240}Pu	1.4×10^{4}	6.0×10^{1}	2.5×10^{-1}
^{241}Pu	3.0×10^{4}	2.1×10^{3}	1.2×10^{-1}
^{242}Pu	1.7×10^{-1}	5.0×10^{-2}	3.3×10^{-4}
^{241}Am	4.3×10^{4}	6.2×10^{1}	2.0×10^{-1}
^{242m}Am	5.0×10^{1}	8.5	2.3×10^{-4}
^{243}Am	2.0×10^{1}	7.9×10^{-2}	6.5×10^{-5}

Table 2.16: Inventories of long-lived (> 30 years) radionuclides for the Nirex reference case waste volume [16]

2.6.2 Technetium in the repository

2.6.2.1 Speciation of technetium

The Eh vs pH behavior of technetium species in aqueous noncomplexing environments has been summarized in the predominance diagram (Fig. 2.14) The data used to construct the solid lines were based on experimentally determined standard potentials [30] and hydrolysis constants [31]. The dashed line represents equilibrium between TcO_4^- and Tc^{2+} solution species discussed by Pourbaix [30]. No mention of Tc(IV) solution species were given in the study by Pourbaix [30] but were incorporated in the more recent work [32]. The species which predominates over the entire pH range of 0-14 for Eh values which are not strongly reducing is the pertechnetate anion, TcO_4^-, which corresponds to the stable +7 oxidation state. The TcO_2 predominance domain represents both solution and precipitated species. The line representing the $TcO_4^-(aq)/TcO_2(aq)$ equilibrium in Fig. 2.14 falls very close to that of the $TcO_4^-(aq)/TcO_2(s)$ equilibrium summarized by Pourbaix

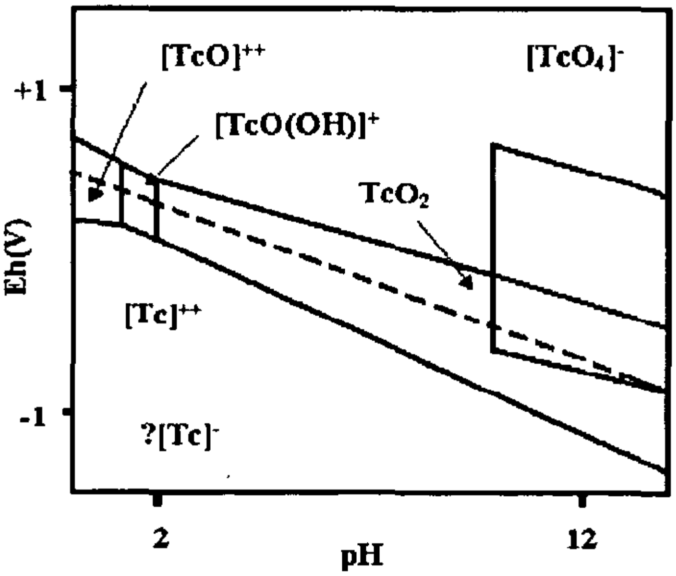


Fig. 2.14: Predominance diagram of technetium

Under reducing conditions, most studies indicate that TcO_4^- in noncomplexing aqueous solutions initially undergoes a 1e⁻ reduction to form the unstable $Tc^{VI}O_4^{2-}$. Subsequent 2e⁻ or 3e⁻ reductions to Tc(V) or Tc(IV) species then readily occur. It has also been suggested that $HTcO_4$ can even be reduced to H_2TcO_4 by H_2O or dust particles [33]. However, as stated above, the Tc(V) and Tc(VI) species are unstable and disproportionate into the more stable Tc(IV) and Tc(VII) species. Owunwanne *et al* [34] discussed the formation of a hydrolyzed Tc(IV) species with an overall charge of +2, most likely TcO^{2+}[35] by reduction of TcO_4^- with Sn^{2+} in perchlorate solutions of pH between 1.1 and 2.0. Further hydrolysis of TcO^{2+} to $TcO(OH)^+$ and $TcO(OH)_2^0$ is possible at a pH between 1.3 and 2.2. Dimerization of the $TcO(OH)_2^0$ species to $[TcO(OH)_2^0]_2$ is reported to occur at a pH of 2.7 [34]. The equilibrium constants for the hydrolysis and dimerization of various Tc(IV) species are summarized in Fig. 2.15:

$$TcO^{2+} + H_2O \rightleftharpoons TcO(OH)^+ + H^+ \qquad K_{h1} = (4.3 \pm 0.4) \times 10^{-3}\ \text{mol dm}^{-3}$$

$$TcO(OH)^+ \rightleftharpoons TcO(OH)_2 + H^+ \qquad K_{h2} = (3.7 \pm 0.4) \times 10^{-3}\ \text{mol dm}^{-3}$$

$$2TcO(OH)_2 \rightleftharpoons \left[TcO(OH)_2\right]_2 \qquad K_D = (3.14 \pm 0.28) \times 10^{-6}\ \text{mol dm}^{-3}$$

Fig. 2.15: The equilibrium constants for the hydrolysis and dimerization of various Tc(IV)

The stability ranges of hydrolyzed Tc(IV) species under reducing conditions have been summarised [34]: pH < 1.5, TcO^{2+}; 1.5 < pH < 2.2, $TcO(OH)^+$ and $TcO(OH)_2^0$; pH > 2.2, $TcO(OH)_2^0$ and $[TcO(OH)_2^0]_2$; pH > 3, precipitation of $TcO_2{\cdot}2H_2O$. One summary by Vida *et al* [36] indicated that precipitates of $TcO(OH)_2$, i.e., $TcO_2{\cdot}2H_2O$, formed above a pH of 2 under reducing conditions. The shaded box in Fig. 2.13 represents the presumed working range for solutions of pH equivalent to those expected in Hanford LLW. The lower Eh limiting line of the box has its traditional meaning, representing the reduction of water.

Compounds containing technetium with oxidation states less than +4 are generally realized only through stabilization with complexants, including those already found in, (e.g., EDTA, oxalic acid, etc.) and those that are being considered as additives to (e.g., citric, glycolic, formic acids, etc.) the LLW stream.

2.6.2.2 Solubility of technetium

Under reducing conditions the speciation of technetium is expected to be dominated by technetium(IV) which is highly insoluble [37]. TcO_4^-, the expected oxidised form of technetium, is highly soluble if formed.

There are only a small number of papers concerned with the solubility of technetium in the conditions expected in the near-field of a nuclear waste repository. In one of the studies [38] the solubility of technetium was determined by contacting technetium hydrous oxide with blast furnace slag/ordinary portland cement-, pulverised fuel ash/ordinary portland cement- and limestone/ordinary portland cement-equilibrated water for seven weeks. The technetium hydrous oxide was formed by the reduction of pertechnetate with zinc in hydrochloric acid followed by the addition of concentrated ammonia solution to precipitate the oxide. No dependence of technetium solubility on pH over a range from about pH 7 to pH 13 was observed and the average solubility was approximately 1×10^{-7} mol dm^{-3}. Sodium dithionite was used as a holding reductant in these experiments which were carried out in a nitrogen atmosphere glovebox. The total technetium in solution was determined after sampling by filtration through 30,000 and/or 25,000 NMWCO filters; some samples were also filtered through 0.45 μm filters [38].

Another study [39] that has also been carried out on the solubility of technetium gave lower concentrations for the solubility of technetium(IV) in the pH range 7 to 10 in sodium chloride solutions. The solubility was approached from undersaturation, as in the work discussed above [38], but the solid phases used were electrodeposited oxide and oxide precipitated onto sand particles from the reduction of TcO_4^- with hydrazine. Average solubilities above electrodeposited oxide were 1.7×10^{-8} mol dm^{-3} (pH 9.0 to 9.7) for oxide deposited from acidic solution and 3.2×10^{-9} mol dm^{-3} (pH 7.46 to 9.43) for oxide deposited from basic solution. The experiments lasted from two weeks to three weeks and were carried out in an argon atmosphere glovebox with an oxygen content of < 1 ppm [39]. Solid:liquid separation was by centrifugation. No holding reductant was used and the concentration of technetium(IV) was determined after solvent extraction to remove technetium(VII). Samples were rejected if the ratio of technetium(VII) to technetium(IV) was greater than 200. A slight trend of increased technetium solubility with increasing pH was observed in some of the studies. The increase was thought to be due to the existence of anionic hydroxy species, however, this was not investigated further. [39].

A further study over the pH range 6.05 to 12.1 has also been reported [40]. The investigation used electrodeposited technetium(IV) oxide and the methodology was similar to that employed by Meyer *et al* [39]. However, no holding reductant was used and the concentration of technetium(IV) was determined after solvent extraction to remove any TcO_4^- still present. One difference between the Meyer *et al* [39] study was that the samples may not have been centrifuged (or filtered) prior to solvent extraction. Solution samples were taken daily until a constant ^{99}Tc concentration was achieved; the equilibration time is not stated in the paper. All operations were carried out in an argon atmosphere glovebox. The solubility of technetium(IV) was found to be independent of pH over the range 6 to 9.5 (at about 7×10^{-9} mol dm^{-3}) [40]. Above pH 9.5 the solubility increased, and in the range pH 11 to 12 the log of concentration of technetium(IV) versus pH was linear with a slope of 1. This was interpreted as arising through the formation of an anionic species, $TcO(OH)_3^-$, at high pH (Fig. 2.16).

$$TcO_2.nH_2O \rightleftharpoons TcO(OH)_3^- + H^+ + (n-2)H_2O \qquad \text{Log K} = -19.06 \pm 0.24$$

Fig. 2.16: Formation of $TcO(OH)_3^-$ [39]

However, the highest pH in the experiments was 12.1, and a solubility of about 8×10^{-8} mol dm^{-3} was measured at this pH [40]. This appears to be the only study that has provided evidence for the existence of the anionic species, $TcO(OH)_3^-$.

In a recent study [41] the aqueous solubility of technetium was measured. The solubility was measured by contacting electrodeposited technetium(IV) oxides with NRVB-equilibrated water containing sodium dithionite as a holding reductant. Samples were taken after 28, 59 and 95 days for the determination of the technetium-99 concentration by liquid scintillation counting. After 28 days equilibration most of the concentrations were at or below the detection limit of 2×10^{-9} mol dm^{-3} for this series of measurements. After 59 days, the technetium concentrations had increased and were in the range $\leq 5\times10^{-10}$ to 9×10^{-9} mol dm^{-3}. But with no evidence for a trend of increasing solubility with increasing pH, suggesting that the samples had not reached equilibration after 28 days. However, samples taken after 95 days had much lower concentrations of technetium in solution with most of the concentrations below the detection limit of 5×10^{-10} mol dm^{-3} [41]. Data reported in this study were for total technetium concentration in solution, whereas the studies by Meyer *et al* [39] and Eriksen *et al* [40] measured the technetium(IV) concentration after solvent extraction. The concentrations measured in this study are consistently below those measured for the other two studies. It is also not clear why the concentrations measured after 95 days equilibration should be less than those measured after 59 days. The typical equilibration times are not given in the study by Eriksen [40] but Meyer *et al*'s [39] was obtained after two and three weeks from experiments that had reached equilibriuim. At pH 13 there was an indication of a slight increase in solubility, as the four experiments gave concentrations in the range $\leq 5\times10^{-10}$ to 9×10^{-9} mol dm^{-3}. However, this result was considered tentative. Thus, the results do not confirm the existence of the anionic technetium species $TcO(OH)_3^-(aq)$ but neither do they rule it out [41].

2.6.2.3 Interactions within the repository

As discussed above the repository will contain many different substances. Each of these substances has the chance to interact with the technetium in the near field of the repository. The following section discusses some of the work that has been completed on the interaction between technetium and substances expected to be found in the near field of the repository.

2.6.2.3.1 Cement

A range of commercial products can be added to cements and concretes in order to modify their properties. These admixtures may be used in cementitious materials employed in the construction and back filling of a radioactive waste repository vault. Many of these admixtures contain organic materials and it is known that some organic compounds can alter the solubility and sorption behaviour of radionuclides in a repository.

One study [42], measured the effect of two Japanese cement additives (HS-100 and HS-700 (Fig. 2.17)) on the solubilities of technetium, plutonium and americium at pH 12.

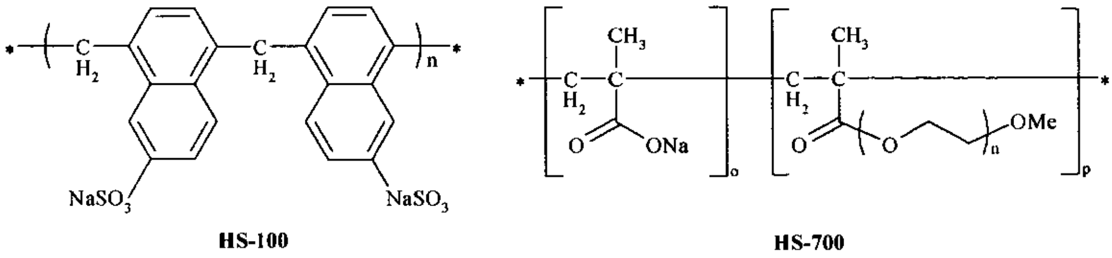


Fig. 2.17: Structures of two cement additives HS-100 and HS-700

The effects of the cement additives were studied at the typical concentration that would be used in water when mixing concrete ('mix water" concentration) and a dilution of this concentration by a factor of 100. For HS-100 these concentrations were 30 g HS-100 per kg water and 0.3 g kg^{-1} water respectively, and for HS-700, 50 g kg^{-1} water and 0.5 g kg^{-1} water [42].

The solubility of technetium in concrete-equilibrated water is 7×10^{-9} mol dm^{-3}. The addition of the two cement additives were found to have very different effects on the solubility of technetium. The mix water concentration of HS-100 results in a technetium solubility of 5×10^{-6} mol dm^{-3} which decreases to 2×10^{-8} mol dm^{-3} in the diluted solution. However, the technetium solubility in the HS-700 solution at the mix water concentration is only 9×10^{-8} mol dm^{-3} and 3×10^{-8} mol dm^{-3} in diluted HS-700. These experiments showed that both cement additives can cause significant solubility enhancements of technetium. Reported stability constants for complexes involving only the radionuclide and model ligands were far too small to explain these solubility enhancements. From observations in other studies, on the evidence for the formation of mixed complexes of metal ions with humic acid and small inorganic ligands, including hydroxyl ions [43], it was concluded that the formation of mixed complexes with the radionuclides and the additives and hydroxyl ions, is responsible for the increase in solubility. However, it was not possible to predict radionuclide solubilities in typical porewaters from concretes containing these additives because the additives present in the mix water may be bound in the cement phases, and not released completely into solution. The ultimate long-term fate of these additives has not been demonstrated, but they are likely to undergo reaction, thus reducing the soluble ligand concentration. Therefore the enhancements observed for the diluted solutions of the two cement additives may be more typical in concrete porewater [42].

A study was also completed on the chemistry of technetium in cement waste forms using X-ray absorption fine structure spectroscopy (XAFS) and X-ray absorption near-edge spectroscopy (XANES), the aim of this study was to identify the reductive components of blast furnace slag (BFS) [44]. From this work it was shown that XANES and XAFS can be utilized to quantitatively determine changes in the oxidation state and local structure of Tc in cement waste forms. While the addition of BFS achieves only a partial reduction, however, the addition of the pure Na_2S and FeS reduced the TcO_4^- completely. These observations, combined with the absence of reduction by FeO, Fe_3O_4 and Mn_3O_4 suggest that a sufide containing species is the active reducing agent in BFS. These results are consistent with the results of previous work completed in this area [45]. In all the cases where the sulfide has been utilized the reduced Tc species has Tc-S bonds. For Na_2S and FeS additives, Tc-Tc interactions are observed giving rise to an oligomeric structure such as found in TcS_2. other reducing agents such as NaH_2PO_2 are also effective in reducing TcO_4^-, where the reduced species formed resembles TcO_2.

2.6.2.3.2 Radiolysis

Radiolysis effects on the stability of the oxidation state of radioelements and diffusion within the framework of nuclear waste repositories are often neglected, although it may influence physicochemical processes and thus transfer of radionuclides to the biosphere and geosphere. This knowledge is essential to model transport phenomena. For example due to radiolytic effects, the oxidation state of Tc can change. Under reducing conditions, technetium is mainly present as Tc(IV) but γ-radiation might perturb the equilibrium of the Tc(VII)/Tc(IV) system. In fact, under gamma irradiation in alkaline media Tc(IV), as TcO_2, is oxidised to Tc(VII),as TcO_4^-, while in alkaline and neutral media Tc(VII) has been shown to be reduced to Tc(VI) by pulse radiolysis. There have been a small number of studies on the radiolysis effects of technetium. One such study reported on the effects of gamma irradiation on technetium in carbonate media, which is representative of natural systems [25]. It was shown that in the presence of carbonate ions, TcO_4^- may be reduced by free radicals from water radiolysis into technetium dioxide. Technetium intermediates may be re-oxidised by dissolved O_2 and carbonate radicals. These results may account for the absence of any radiolytical changes on pertechnetate ions in carbonate media. In nuclear waste repository conditions where reducing conditions prevail, reduction of Tc(VII) into Tc(IV) is expected. Data from [25] shows that γ-radiation effects in carbonate media may prevent this reduction and stabilise Tc(VII). However, the radiolytical reducing conditions used in this study are close to the reducing conditions in the environment but still differ slightly from the actual expected conditions. This study shows that gamma radiolysis can lead to the stabilisation of soluble valencies and as such may influence the mobility of technetium. Therefore these processes should be seriously taken into account [25].

In another study [46], the radiolytic reduction of TcO_4^- in alkaline solutions containing selected organic compounds, approximating the conditions in HLW, was investigated to determine the classes of compounds that can be formed under these conditions. From this study it was found that insoluble $TcO_2.xH_2O$ is the primary radiolysis product with the majority of organic compounds investigated, including citrate, dibutyl phosphate, and aminopolycarboxylates. Using XAFS measurements it was also shown that $TcO_2.x$H2O has a one-dimensional chain structure consisting of edge-sharing TcO_6 octahedra with bridging oxide and trans water ligands (Fig. 2.18).

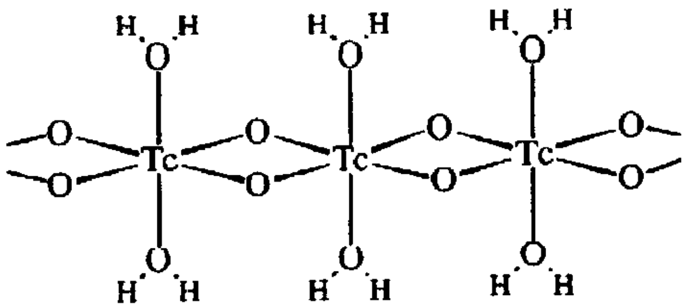


Fig. 2.18: Proposed structure of the $TcO_2.xH_2O$ product

However, when diols, such as ethylene glycol, are present, only soluble, Tc(IV) alkoxide compounds are produced. The XAFS and UV-visible spectra of these compounds provide evidence for a binuclear structure similar to $(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$ (Fig. 2.19).

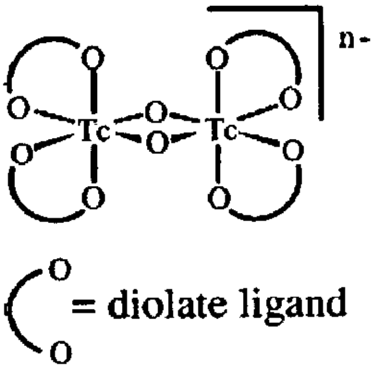


Fig. 2.19: Proposed structure of the soluble radiolysis product

The properties of the Tc(IV) alkoxide complexes were determined and are consistent with those observed for the soluble, lower valent technetium complexes that complicate the treatment of HLW at the Hanford site [46].

Chapter 3 –

Experimental

3.0 Experimental

3.1 Introduction

This chapter describes the experimental work completed for part A of the thesis, i.e. an investigation of the chemistry of technetium in reducing conditions..

The starting point for this project was an investigation into the various chemical methods for the reduction of pertechnetate at high pH. From this it was found that $SnCl_2$ was the best reducing agent for pertechnetate.

Using the preferred method for TcO_4^- reduction, $SnCl_2$ reduction, the following was investigated:

- The solubility of technetium(IV) at high pH
- Reduction of TcO_4^- at high pH in presence of EDTA, nitriliotriacetic acid (NTA), ISA, gluconic acid and picolinic acid;
- Solubility of pre reduced technetium(IV) at high pH in the presence of EDTA, NTA, ISA, gluconic acid and picolinic acid;

From the results the stability constants of technetium(IV) complexes formed during the investigation were determined using the solubility product approach method. However, using $SnCl_2$ as a reducing agent introduced the possible problems of competition for the ligands between the technetium and tin ions in solution. Therefore, the possibility of complexation between $SnCl_2$ and the ligands, EDTA, NTA, ISA, gluconic acid and picolinic acid, was investigated and the stability constants were determined for any tin(II) complexes formed during the investigation.

To overcome the problem of competition between the technetium and tin for the ligands a clean electrochemical reduction method was developed and the stability constants for any technetium(IV) ligand complexes were then determined.

3.2 Materials and equipment

A Canberra Packard Tricarb 2750 TR/LL Liquid Scintillation Analyser (Packard) was used for the liquid scintillation counting for all the experiments. For all experiments the activity was measured over a time period that provided at least 10000 counts per sample. As radioactive decay is a random event the probability is more accurately described by the Poisson distribution. From the Poisson distribution the standard deviation is given by the square root of the mean of all measurements.

$$\text{Standard deviaiton} = \sqrt{\mu} = (\mu)^{\frac{1}{2}}$$

A total of 10000 counts per sample gives a standard deviation of 100. Therefore the error due to counting is ±1%.

The pH was measured using an Orion 720A pH meter with an Orion Combination Redox Electrode number 2 electrode. The electrode was calibrated using an Aldrich volumetric standard sodium hydroxide solution.

Deionised water produced by a Barnstead NANOpure ultrapure water purification system, and AR reagents, were used throughout. Sodium ISA was prepared using the procedure described by Whistler and BeMiller (Section 2.3.9) [51]. Sodium gluconate, disodium EDTA, sodium nitrate, disodium NTA and picolinic acid were purchased from Aldrich. Technetium was purchased from Amersham.

All experiments were completed in an MBraun Unilab nitrogen atmosphere glovebox with an oxygen content of < 1 ppm.

3.3 Experimental

3.3.1 Production of a calibration curve of activity against the concentration of technetium in solution

Ammonium pertechnetate (NH_4TcO_4) solutions were made in the concentration range 1.76×10^{-6} to 1.04×10^{-10} mol dm^{-3} in NaOH (0.3 mol dm^{-3}) to give a pH of *ca.* 13.3. The solution was shaken vigorously and a 1 cm^3 sample was extracted and added to goldstar multipurpose liquid scintillation cocktail (10 cm^3) in a liquid scintillation counting vial. HCl (6 mol dm^{-3}) was added, to neutralise the sample in order to minimize any chemiluminescence caused by the hydroxide ions. The sample was shaken vigorously and counted by liquid scintillation counting (LSC).

3.3.2 Reduction of ammonium pertechnetate at high pH

The most stable forms of technetium are pertechnetate, TcO_4^-, under aerobic conditions and the sparingly soluble technetium dioxide under anaerobic conditions. Technetium present in some of the nuclear waste streams will be present as TcO_4^-. However, the conditions expected in the near field of a nuclear waste repository will be reducing therefore the following reduction will take place.

$$TcO_4^-(aq) \rightarrow TcO_2(s)$$

Therefore for this project it is important to be able to produce technetium in the reduced form. A number of a reducing agents were investigated for their suitability for the reduction of pertechnetate.

Ammonium pertechnetate (NH_4TcO_4) (*ca.* 1 kBq, *ca.* 4 $\times 10^{-7}$ mol dm^{-3}) was added to 10 cm^3 of the sodium hydroxide (0.3 mol dm^{-3}). The pH was measured. The solution was shaken vigorously and a 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

To the remaining solution iron granules (0.1 g) were added, this was then left for 1 week. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

The procedure was repeated for 5 replicates.

The procedure was then repeated for the following reducing agents:

- 0.1 g Tin Metal
- Tin (II) Chloride
- Iron (II) Sulphate
- Sodium Borohyride
- Sodium Dithionite
- Sodium Hypophosphite

Reducing agents were added as solids to give a concentrations *ca.* 0.1 mol dm^{-3}.

3.3.3 Reduction of ammonium pertechnetate at high pH using hydrazine hydrate

Ammonium pertechnetate (NH_4TcO_4) (ca. 1 kBq) was added to deionised water (20 cm^3). The pH of the solution was adjusted to between 12.5 – 13 by the addition of 1 cm^3 NaOH (1 mol dm^{-3}). The pH was measured. The solution was shaken vigorously and a 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

To the remaining solution, 1 cm^3 of the hydrazine hydrate (11.4 mol dm^{-3}) was added, this was then left for 1 week. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

3.3.4 Measurement of possible quenching effects on technetium counts from added ligands by the sample channels ratio method

The number of photons emitted from a scintillation solution by a given energy beta particle can be reduced by the presence of species in the sample which produce an effect known as quenching.

One method used for the correction of quenching is known as the sample channels ratio method. In this method, two counting channels are set (Fig. 3.1).

For example:

Channel A - The full counting channel

Channel B – One third of channel A

Each standard containing a known activity but varying amounts of quench chemical, is counted in the two channels and the ratio of the count rates in each channel is calculated (the "sample channels ratio"). Since the absolute activity of each standard is known, the counting efficiency of each standard in the full counting channel can be calculated.

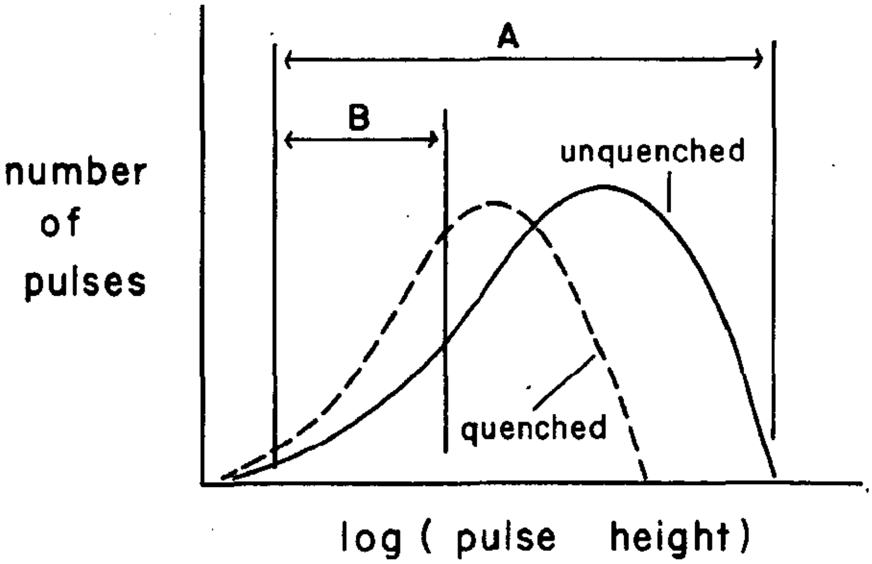


Fig. 3.1: Samples channel ratio method

A correlation graph can then be plotted of counting efficiency in channel A against the sample channel ratio.. From this graph the correct counting efficiency can then be determined for the corresponding sample channel ratio.

To 20 cm^3 EDTA (0.3 mol dm^{-3}) 0.2 cm^3 NH_4TcO_4 (*ca.* 1 kBq) were added. The solution was then shaken for a period of 24 h. After this time a 1 cm^3 sample was extracted and neutralised. The activity in solution was measured in the following channels of the liquid scintillation counter.

Channel A – 15 – 300 keV
Channel B – 0 – 15 keV

The ratio of B:A was calculated. This was repeated for the following EDTA concentrations of 0.01, 0.05, 0.1 and 0.2 mol dm^{-3}. A graph of EDTA concentration (mol dm^{-3}) against the sample channels ratio (B/A) was plotted.

This experiment was repeated for the following ligands; NTA, ISA, gluconic acid and picolinic acid.

3.3.5 Solubility of TcO_2 at pH 13.3

The solubility of technetium(IV) at high pH was measured to provide a baseline for the rest of the work completed for part A of this thesis. This baseline solubility of technetium(IV) can then be used for two purposes;

- Comparison of the solubility of technetium(IV) measured in this project to that found in the literature [36 – 40] gives an indication of whether the reduction of TcO_4^- has gone to completion

- Comparison of the solubility of technetium(IV) in the absence of organic ligands to the concentration of technetium in the presence of organic ligands gives a measure of the effects that the complexants have upon the solubility of technetium.

Ammonium pertechnetate (NH_4TcO_4) (*ca.* 1 kBq) was added to 20 cm^3 NaOH solution (0.3 mol dm^{-3}), to give a pH of 13.3. To the solution 0.7 g of tin(II) chloride powder were added. The solution was left for 1 week.

After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

3.3.6 Solubility of TcO_2 between pH 11.5 and pH 14.5

In a study by Meyer *et al* [39] the solubility of technetium(IV) was found to be independent of pH over the range 6 to 9.5 (at about 7×10^{-9} mol dm^{-3}). However, above pH 9.5 the solubility increased, and in the range pH 11 to 12 a plot of the log of the concentration of technetium(IV) against pH was linear with a slope of 1. This was interpreted as arising through the formation of an anionic species, $TcO(OH)_3^-$, at high pH. At present this is the only study that indicates the existence of $TcO(OH)_3^-$.

The solubility of technetium(IV) measured in this thesis does not agree with the results in the study by Meyer *et al* [39]. Therefore the solubility of technetium(IV) was measured between pH 11.5 and pH 14.5 to investigate the existence of $TcO(OH)_3^-$.

Ammonium pertechnetate (NH_4TcO_4) (*ca.* 1 kBq) was added to 20 cm^3 NaOH solution (1 mol dm^{-3}), to give a pH of 13.3. To the solution 0.7 g of tin(II) chloride powder were added. The solution was left for 1 week.

After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

The procedure was repeated for several pH's in the range 11.5 – 14.5.

3.3.7 Ion exchange method for the determination of Tc(IV) speciation

The overall charge of the aqueous phase technetium(IV) was investigated using ion exchange resins. In an attempt to support the existence of $TcO(OH)_3^-$.

3.3.7.1 Cation ion exchange resin

Ammonium pertechnetate (NH_4TcO_4) (*ca.* 1 kBq) was added to 20 cm^3 NaOH solution (0.3 mol dm^{-3}), to give a pH of 14. To the solution 0.7 g of tin(II) chloride powder were added. The solution was left for 1 week. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

This procedure was repeated as in section 3.3.6.

After sampling BioRad AG50W X2, 100-200 mesh cation exchange resin was added to each vial. The solutions were left for 3days. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

3.3.7.2 Anion ion exchange resin

The procedure described in section 3.3.7.1 was repeated but the cationic exchange resin was replaced with an Amberlite IRA-400 anion exchange resin

3.3.8 Reduction of ammonium pertechnetate in the presence of organic complexing agents at high pH

Technetium will enter the nuclear waste repository as TcO_4^-, where under the reducing conditions that prevail it will be reduced to TcO_2(s). However, as discussed in section 2.6.1.6 organic material will form part of the waste and so low molecular weight organics, such as the ligands under investigation in this project (EDTA, NTA, ISA, gluconic acid and picolinic acid) will be present. Therefore, as discussed in section 2.5 the reduction from TcO_4^- to TcO_2(s) may not occur and as in the radiopharmaceutical industry soluble technetium complexes may be formed.

EDTA was added to 20 cm^3 sodium hydroxide (0.3 mol dm^{-3}). To give a final EDTA concentration of 0.2 mol dm^{-3}. Ammonium pertechnetate (NH_4TcO_4) (0.2 cm^3, *ca.* 1 kBq) was added and the pH was measured. To the solution 0.7 g of tin(II) chloride were added, this was left for 3 days. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

This was repeated for the following EDTA concentrations 0.1, 0.05 and 0.01 mol dm^{-3}. This was repeated for 5 times for each concentration.

This experiment was repeated using NTA, ISA, gluconic acid and picolinic acid instead of EDTA.

3.3.9 Solubility of TcO_2 in the presence of organic complexing agents at high pH

Ammonium pertechnetate (NH_4TcO_4) (ca. 1 kBq) was added to 20 cm^3 of the sodium hydroxide (0.3 mol dm^{-3}). The pH was measured. The solution was shaken vigorously and a 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

To the solution 0.7 g of tin(II) chloride were added, this was left for 1 week. After this time, EDTA, was added as a solid, to give a concentration of 0.2 mol dm^{-3}. This was shaken for 3 days. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

This was repeated for the following EDTA concentrations 0.005, 0.01, 0.05 and 0.1 mol dm^{-3}.

This experiment was repeated using NTA, ISA, gluconic acid and picolinic acid instead of EDTA.

From the results the stability constants were calculated using the solubility product approach method.

3.3.10 Solubility product approach for the calculation of stability constants

The solubility product approach for determining metal complex stability constants, developed at Loughborough University [47], is used when a metal with an inherent insolubility, complexes with a ligand to form a more soluble metal-ligand complex.

Dissolution of a sparingly soluble salt (M_mX_x) may be represented as:

$$M_mX_x \rightleftharpoons mM^{a+} + xX^{b-} \qquad (3.1)$$

The equilibrium constant (K) for the dissolution is given by:

$$K = \frac{\left[M^{a+}\right]^m \left[X^{b-}\right]^x}{\left[M_mX_x\right]} \qquad (3.2)$$

The solid phase has a constant activity, so the solubility product is obtained, i.e.

$$K_{SP} = \left[M^{a+}\right]^{m} \left[X^{b-}\right]^{x} \tag{3.3}$$

Hence at equilibrium:

$$\left[M^{a+}\right] = \left(\frac{K_{sp}}{\left[X^{b-}\right]^{x}} \right)^{\frac{1}{m}} \tag{3.4}$$

If a ligand (L) is added, complexation may occur which can be represented as (charges omitted):

$$pM + qL \rightleftharpoons M_pL_q \tag{3.5}$$

The stability constant of the complex is given by:

$$\beta = \frac{\left[M_pL_q\right]}{[M]^{p}[L]^{q}} \tag{3.6}$$

hence using equation (3.4):

$$\beta = \frac{\left[M_pL_q\right]}{\left(\frac{K_{SP}}{[X]^{x}} \right)^{\frac{p}{m}} \left\{ [L]_{total} - q\left[M_pL_q\right] \right\}^{q}} \tag{3.7}$$

Therefore, to calculate the stability constant, values for the concentration of the complex, the ligand, and the associated anion in solution are required, as is the stoichiometry of the complex formed, and the solubility product for the solid phase present.

3.3.10.1 An example of the solubility product approach for the determination of the stability constant for the reaction between TcO_2 with NTA at high pH

Under reducing conditions the dissolution of sparingly soluble technetium (IV) oxide may be represented as:

$$TcO_2.2H_2O\,(am) \rightleftharpoons TcO(OH)^+\,(aq) + OH^-\,(aq) + H_2O \qquad (3.8)$$

The equilibrium constant (K) for the dissolution is given by:

$$K_{SP} = \frac{\left[TcO(OH)^+\right]\left[OH^-\right][H_2O]}{[TcO_2.2H_2O]} \qquad (3.9)$$

The solid reactant and the water may be regarded as having constant activities, so a pseudo solubility constant is obtained:

$$K_{sp} = \left[TcO(OH)^+\right]\left[OH^-\right] \qquad (3.10)$$

In the absence of any complexing ligand, the dissolved technetium(IV) will consist of the $TcO(OH)^+$ ion and its major hydrolysis product [48], i.e.

$$[Tc]_{solution} = \left[TcO(OH)^+\right] + [TcO(OH)_2] + \mathit{etc} \qquad (3.11)$$

$$[Tc]_{solution} = \left[TcO(OH)^+\right] + \sum\left[TcO(OH)_x^{\,z+}\right] \qquad (3.12)$$

$$[Tc]_{solution} = \left[TcO(OH)^+\right]\left\{1 + \sum\beta_x\left[OH^-\right]^x\right\} \qquad (3.13)$$

$$[Tc]_{solution} = \left[TcO(OH)^+\right]A \qquad (3.14)$$

where $A = 1 + \sum \beta_x \left[OH^-\right]^x$ (the side reaction coefficient) [48]. This is constant at any given pH. In this particular case the NIST database of critical stability constants gives the following hydrolysis reactions and constants:[49]

$$TcO^{2+} + OH^- \rightleftharpoons TcO(OH)^+ \qquad \text{Log } K_1 = 12.6 \tag{3.15}$$

$$TcO^{2+} + 2OH^- \rightleftharpoons TcO(OH)_2 \qquad \text{Log } K_2 = 24.2 \tag{3.16}$$

However the base species that is of interest in this report is $TcO(OH)^+$, the first hydrolysis product, and the hydrolysis reaction that is of interest is:

$$TcO(OH)^+ + OH^- \rightleftharpoons TcO(OH)_2 \tag{3.17}$$

For which the equilibrium constant is given as:

$$\text{Log } K_3 = \frac{\left[TcO(OH)_2\right]}{\left[TcO(OH)^+\right]\left[OH^-\right]} \tag{3.18}$$

Log K_3 can be calculated by using log K_1 and log K_2.

This gives a value for log K_3 = 11.6 or $K_3 = 3.972 \times 10^{11}$. The A term for this particular case is thus:

$$A = 1 + \left(K_3\left[OH^-\right]\right) \tag{3.19}$$

In the absence of NTA, at pH = 13.3, i.e. $[OH^-] = 0.2$ mol dm^{-3}, $[Tc]_{solution}$ was found to be 3.99×10^{-9} mol dm^{-3}.

Therefore:

$$A = 1 + (3.97 \times 10^{11} \times 0.2)$$
$$A = 7.96 \times 10^{10}$$

As $K_{sp} = \left[TcO(OH)^+\right]\left[OH^-\right]$ (3.20)

It follows that:

$$K_{sp} = \frac{[Tc]_{solution}\left[OH^{-}\right]}{A}$$

$$K_{sp} = \frac{3.99 \times 10^{-9} \times 0.2}{7.96 \times 10^{10}} \qquad (3.21)$$

$K_{sp} = 1.0 \times 10^{-20}$

or $\log K_{sp} = 20.0$

By comparing the solubility product or $TcO_2.nH_2O(s)$ determined above to the solubility product determined by Meyer *et al* [39], it can be seen that they are in excellent agreement.

Log $K_{SP} = -19.72$ or $K_{SP} = 1.92 \times 10^{-20}$

It is necessary to know the stoichiometry of the complex in order to obtain the correct algebraic expression for the next step of the calculation of the stability constant. However, to give an example of the solubility product approach the reaction between Tc(IV) and NTA (equation 3.30) is used and a 1:1 stoichiometry will be assumed for the complex. The reaction may be represented as:

$$TcO(OH)^{+} + NTA^{y-} \rightleftharpoons TcO(NTA)^{(1-y)+} \qquad (3.30)$$

The concentration of the dissolved technetium(IV) will be increased by the formation of the complex, therefore:

$$[Tc]_{solution} = \left[TcO(OH)^{+}\right]A + \left[TcO(OH)(NTA)^{(1-y)+}\right] \qquad (3.31)$$

$$\left[TcO(OH)(NTA)^{(1-y)+}\right] = [Tc]_{solution} - \left[TcO(OH)^{+}\right]A \qquad (3.32)$$

Hence, using equation (3.10) above:

$$\left[\mathrm{TcO(OH)(NTA)}^{(1\text{-}y)+}\right] = [\mathrm{Tc}]_{\mathrm{solution}} - \left(\frac{K'_{sp}}{\left[\mathrm{OH}^-\right]}\right)A \tag{3.33}$$

The stability constant of the complex is given by:

$$\beta = \frac{\left[\mathrm{TcO(OH)(NTA)}^{(1\text{-}y)+}\right]}{\left[\mathrm{TcO(OH)}^+\right]\left[\mathrm{(NTA)}^{y-}\right]} \tag{3.34}$$

Therefore, substituting equations (3.10) and (3.33) in (3.34) gives β as:

$$\beta = \frac{[\mathrm{Tc}]_{\mathrm{solution}} - \left(\frac{K'_{SP}}{\left[\mathrm{OH}^-\right]}\right)A}{\left(\frac{K'_{SP}}{\left[\mathrm{OH}^-\right]}\right)\left(\left[\mathrm{(NTA)}^{y-}\right]_{\mathrm{total}} - \left\{[\mathrm{Tc}]_{\mathrm{solution}} - \left(\frac{K'_{SP}}{\left[\mathrm{OH}^-\right]}\right)A\right\}\right)} \tag{3.35}$$

Using the specimen data (Table 3.1) and equation (3.35) it is possible to calculate the stability constant for the 1:1 $\mathrm{TcO(OH)NTA}^{2-}$ complex.

[NTA] (mol dm^{-3})	pH	dpm	A term	$[\mathrm{Tc}]_{\mathrm{solution}}$ (mol dm^{-3})	$[\mathrm{TcO(OH)}^+]$ (mol dm^{-3})	[TcO(NTA)] (mol dm^{-3})	Log β
2.00E-01	13.3	300.03	1.19E+11	4.35E-08	5.91E-21	4.28E-08	13.6

Table 3.1: Calculation of TcO(OH)NTA conditional stability constant

3.3.11 Solubility of $SnCl_2$ in the presence and absence of organic complexing agents at high pH

As described in section 3.1 the use of $SnCl_2$ as a reducing agent introduces the possibility of competition between the technetium and tin for the organic ligands under investigation. Therefore, the behaviour of $SnCl_2$ in solutions of EDTA, NTA, ISA, gluconic acid and picolinic acid were investigated. The results from this investigation were used to predict how much free ligand was actually available in solution for complexation with technetium.

0.7 g of tin(II) chloride were added to 20 cm^3 of the sodium hydroxide (0.3 mol dm^{-3}). The pH was measured. To the solution EDTA, was added as a solid, to give a concentration of 0.2 mol dm^{-3}. This was shaken for 3 days. After this time a 2 cm^3 sample was extracted from the filtrate, neutralised and diluted by a factor of 10, the the concentration of Sn in solution was measured by ICP-AES.

From the results the stability constant was calculated.

This was repeated for the following EDTA concentrations 0.005, 0.01, 0.05 and 0.1 mol dm^{-3}.

The experiment was repeated using NTA, ISA, gluconic acid and picolinic acid instead of EDTA.

3.3.12 Development of an electrochemical method for the reduction of ammonium pertechnetate at high pH

As described in section 3.1 and section 3.3.10 the use of $SnCl_2$ as a reducing agent introduces the possibility of competition between the technetium and tin for the organic ligands under investigation. To eliminate the competition between the technetium and tin for the ligand in solution a new "clean" method of reduction was developed. As described below an electrochemical reduction was developed for the reduction of pertechnetate.

3.3.12.1 Electrochemical cell 1

An electrochemical cell was set up as shown in the Fig. 3.4 consisting of:

- 100 cm^3 pear shaped flask with a side arm
- 1 platinum electrode (Fig. 3.2)
- 1 reticulated vitreous carbon electrode (Fig. 3.3)

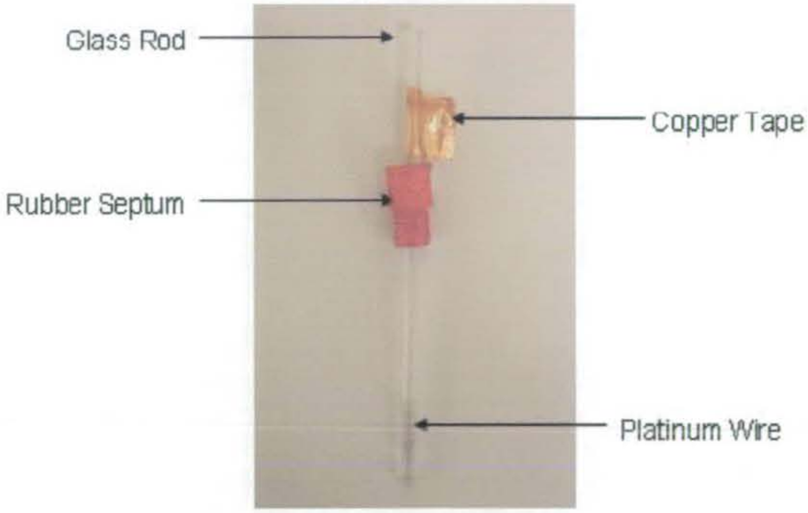


Fig. 3.2: A platinum electrode

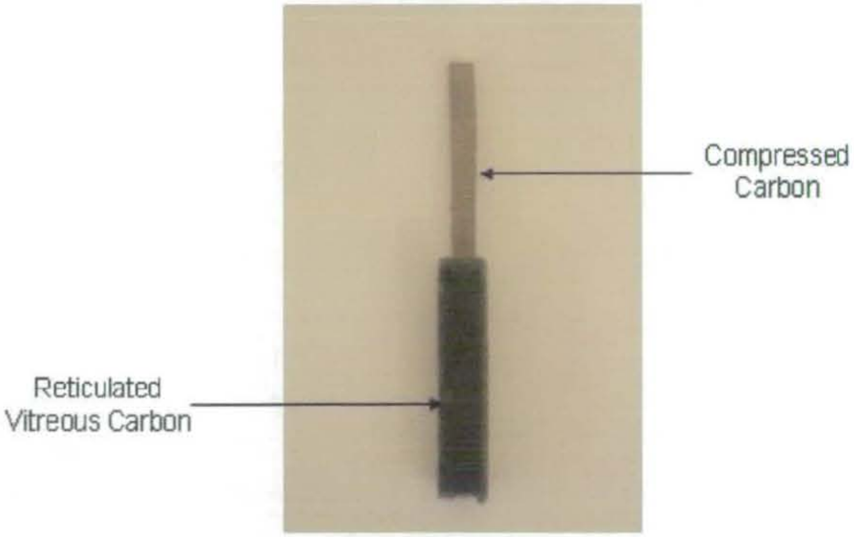


Fig. 3.3: Reticulated vitreous carbon electrode

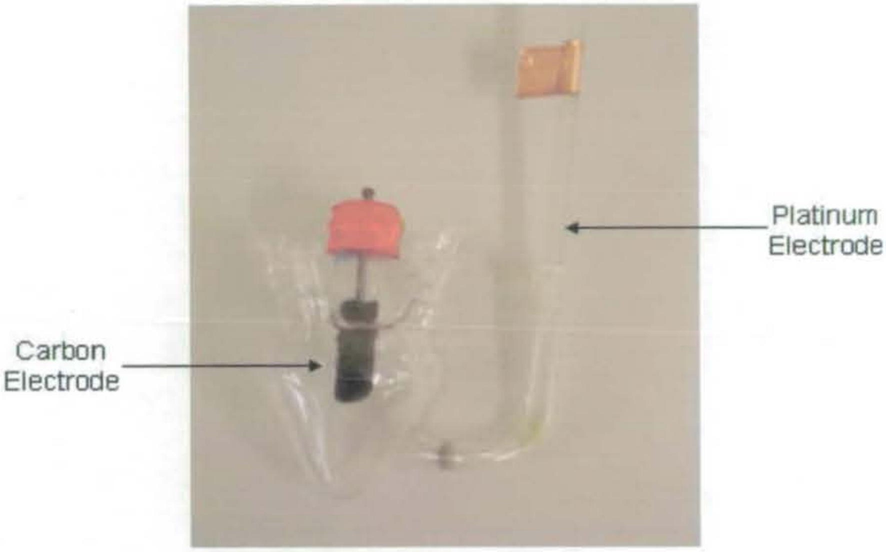


Fig. 3.4: Electrochemical cell 1

To the electrochemical cell (Fig. 3.4) ammonium pertechnetate (NH_4TcO_4) (ca. 10 kBq) was added and made up to 100 cm^3 using deionised water. To this NaOH (s) was added to give a concentration of 0.3 mol dm^{-3}. The cell was placed in a nitrogen atmosphere glovebox to reduce the risk of reoxidation after the current was turned off. A potential difference of 2 V was passed across the cell, which was left for the reaction to reach completion over 3 days or until the solubility of technetium(IV) was reached. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

3.3.12.2 Electrochemical cell 2

The cell was set up as described in Section 3.3.12.1. However a 3 necked 250 cm^3 flask was used instead of the 100 cm^3 pear shaped flask. Ammonium pertechnetate (NH_4TcO_4) (ca. 10 kBq) was added and made up to 200 cm^3 using deionised water. To this NaOH (s) was added to give a concentration of 0.3 mol dm^{-3}. The cell was placed in a nitrogen atmosphere glovebox to reduce the risk of reoxidation. A potential difference of 6 V was used across the cell, in the hope of speeding up the reaction time, this was left for 1 day or until the solubility of technetium(IV) was reached. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

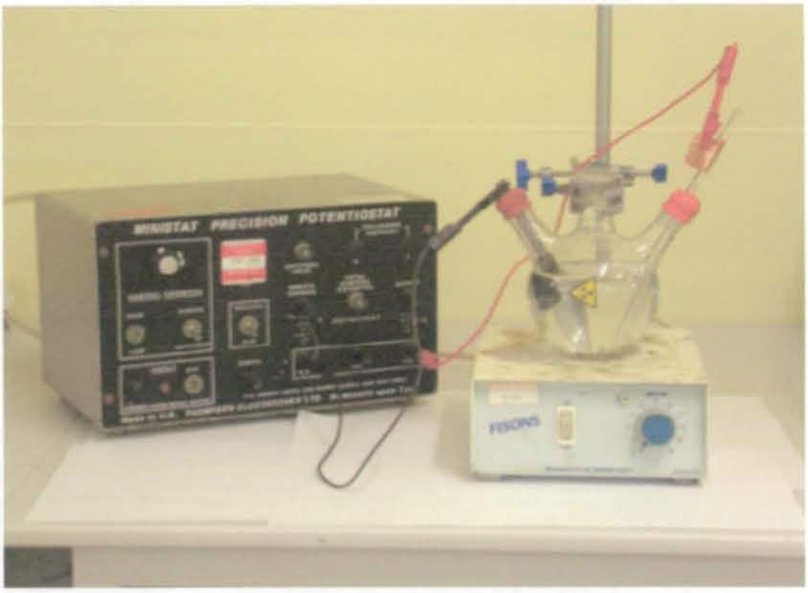


Fig. 3.5: Electrochemical reduction apparatus

3.3.12.3 Electrochemical cell 3

The cell was set up as described in Section 3.3.12.2. The platinum electrode however was placed in a glass tube with a frit at one end (Fig. 3.6). Any oxygen that was produced at the platinum electrode via hydrolysis escaped to atmosphere and not into the reaction mixture. Ammonium pertechnetate (NH_4TcO_4) (ca. 10 kBq) was added and made up to 200 cm^3 using deionised water. To this NaOH(s) was added to give a concentration of 0.3 mol dm^{-3}. The cell was placed in a nitrogen atmosphere glovebox to reduce the risk of reoxidation. A potential difference of 6 V was then used across the cell, in the hope of speeding up the reaction time, this was left for 1 day or until the solubility of technetium(IV) was reached. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

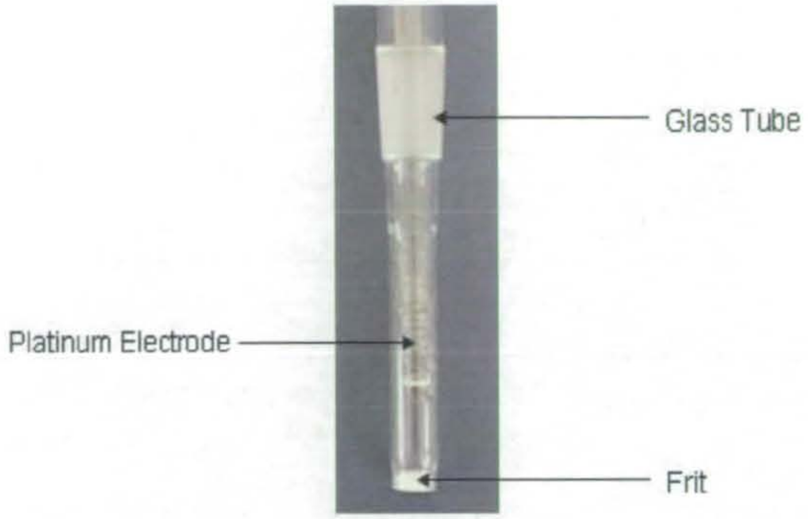


Fig. 3.6: Glass housing for platinum electrode

3.3.12.4 Electrochemical cell 4

The experiment above was repeated but this time a much coarser frit was used on the end of the glass housing to increase the mass transport of the electrochemical cell.

3.3.13 Determination of Tc(IV) conditional stability constants using the Schubert (ion exchange) method and TcO_2 (aq) formed from electrochemical reduction

The electrochemical method for the reduction of pertechnetate described in section 3.3.11 produces solutions of technetium(IV) at low concentrations (i.e. the solubility of technetium(IV)). Using the Schubert method and the technetium(IV) solutions, separated from solid TcO_2, an attempt was made to determine the stability constants of technetium(IV) and the ligands under investigation.

A strong cation exchange resin in the sodium form was prepared. The resin needed to be stable at up to pH 14. The resin used was BioRad AG50W X2, 100-200 mesh cation exchange resin. It was washed, in a column, successively with 2 times the bed volume of sodium hydroxide (1 mol dm^{-3}), at a flow rate of *ca.* 2 cm^3 min^{-1} cm^{-2}, and four times the bed volume with deionised water. It was dried in a desiccator for at least one week to a constant mass. The air-dried resin (*ca.* 50 mg) was weighed into 2 vials. To one of the vials 1 cm^3 of 0.1 mol dm^{-3} EDTA was added. 9 cm^3 of the TcO_2 supernatant, prepared by following section 3.3.12.4 were added to both vials. To a third vial 0.1 g of sodium dithionite and 9 cm^3 of the TcO_2 supernatant was added. These vials were then left for 3 days to equilibrate. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

The stability constant was calculated for the complex formed.

Each measurement was repeated three times.

This method was also repeated for the NTA, ISA, gluconic acid and picolinic acid instead of EDTA and at different pH's.

3.3.14 Calculation of Tc(IV) conditional stability constants using the solubility product approach method and TcO_2 formed from electrochemical reduction

The attempt to determine the stability constants for the reaction of technetium(IV) and the individual ligands by the Schubert method was unsuccessful. Therefore, the solubility product approach method was used to determine the stability constants of technetium(IV) and the individual ligands under investigation

TcO_2 was produced as described in section 3.3.12.4. To the electrochemical cell, EDTA was added as solids, to give a concentration of 0.01 mol dm^{-3}.

The cell was stirred constantly for 3 days. During this time the potential difference was left on, to reduce the possibility of technetium reoxidation. After this time the mixture was filtered using a 0.22 μm cellulose membrane syringe filter. A 1 cm^3 sample was taken and the activity measured by LSC as described in section 3.3.1.

The solubility product and stability constant were calculated.

This was then repeated for [EDTA] = 0.1 mol dm^{-3}.

This method was also repeated for the NTA, ISA, gluconic acid and picolinic acid instead of EDTA

3.3.15 Preparation of isosaccharinic acid (2-C-(hydroxymethyl)-3-deoxy-D-erythro-pentonic acid) (ISA)[51]

In a repository cellulose will be degraded by the mechanism described in the literature review [1]. However, in the laboratory it was necessary to prepare pure *erythro*-ISA, since this compound is not commercially available. The following approach was used, using α-lactose hydrate. Initially the calcium salt was made, which was converted to the sodium salt. This method is the standard method of ISA production used at Loughborough University. The production of ISA via this method has been confirmed by characterisation of the products by FT-IR, X-Ray, melting points and ICP-MS [23].

3.3.15.1 Calcium isosaccharinic acid

The preparation of erythro isosaccharinic acid was performed as follows. α-lactose monohydrate (500 g) (Fig. 3.7) was dissolved in 5 dm^3 of distilled water. Calcium hydroxide (135 g) was added and the flask was flushed with oxygen-free nitrogen for six hours, whereupon it was stoppered, and left at room temperature for 3 days. The resulting brown solution was refluxed for 10 hours and filtered whilst hot. It was evaporated in a stream of moving air until the volume was down to about 1500 cm^3. The mixture was refrigerated overnight and the white solid removed by filtration. The solid was washed with cold water, ethanol and propanone.

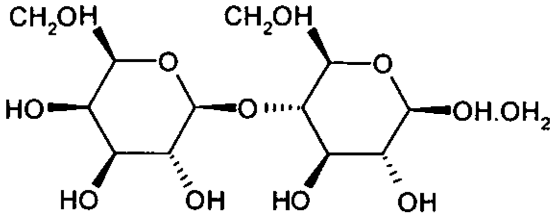


Fig. 3.7: Structure of α-lactose hydrate

3.3.15.2 Recrystallisation of the calcium salt

The salt is soluble in hot water to the extent of 1.19 g in 100 g of hot water and so was dissolved in the required quantity of hot deionised water and filtered free of calcium carbonate. Next the solution was evaporated under reduced pressure in a Büchi RE11 Rotavapor until crystallisation began, and stored for several days in a refrigerator. The crystals or amorphous powder were reclaimed by filtration, washed and dried.

3.3.15.3 Preparation of the sodium salt

The $Ca(ISA)_2$ was mixed with Chelex-100 (BioRad) resin in the ratio of 1:25 by mass in deionised water and mixed for three hours. The resin was filtered off with a Millipore 0.2 μm membrane filter, and the solution concentrated by boiling down to about 500 cm^3. It was evaporated on a rotary evaporator until a thick syrup was obtained. This was allowed to cool and was then triturated in the presence of water-free diethyl ether.

Chapter 4 –

Results and Discussion

4.0 Results and discussion

4.1 Production of a calibration curve of activity against the concentration of technetium in solution

Table 4.1 shows the results for the production of the calibration curve of activity against the concentration of technetium in solution at high pH. For each different concentration 3 replicate solutions were produced and counted.

Calibration curve 1 (Fig. 4.1)		Calibration curve 2 (Fig. 4.2)		Calibration curve 3 (Fig. 4.3)	
[Tc] (mol dm^{-3})	**dpm**	**[Tc] (mol dm^{-3})**	**dpm**	**[Tc] (mol dm^{-3})**	**dpm**
1.76×10^{-6}	11624.9	5.31×10^{-8}	382.1	1.66×10^{-9}	13.8
1.76×10^{-6}	11231.3	5.31×10^{-8}	357.4	1.66×10^{-9}	11.9
1.76×10^{-6}	11217.8	5.31×10^{-8}	352.6	1.66×10^{-9}	19.5
8.50×10^{-7}	5769.8	2.66×10^{-8}	199.0	8.30×10^{-9}	8.1
8.50×10^{-7}	5426.3	2.66×10^{-8}	186.4	8.30×10^{-9}	6.1
8.50×10^{-7}	5575.1	2.66×10^{-8}	174.7	8.30×10^{-9}	11.8
4.25×10^{-7}	2865.8	1.33×10^{-8}	99.4	4.15×10^{-10}	8.9
4.25×10^{-7}	2831.7	1.33×10^{-8}	2.0^*	4.15×10^{-10}	4.4
4.25×10^{-7}	2839.9	1.33×10^{-8}	1.7^*	4.15×10^{-10}	5.8
2.13×10^{-7}	1477.1	6.64×10^{-9}	50.1	2.08×10^{-10}	2.0
2.13×10^{-7}	1702.7	6.64×10^{-9}	43.9	2.08×10^{-10}	5.8
2.13×10^{-7}	1424.2	6.64×10^{-9}	45.3	2.08×10^{-10}	3.0
1.06×10^{-7}	750.8	3.32×10^{-9}	26.0	1.04×10^{-10}	1.1
1.06×10^{-7}	710.8	3.32×10^{-9}	22.7	1.04×10^{-10}	1.4
1.06×10^{-7}	714.5	3.32×10^{-9}	23.2	1.04×10^{-10}	1.2

Table 4.1: Data for calibration curve

If all the data in Table 4.1 were plotted in a single calibration curve the weight of the points at the higher concentrations would be far greater than those at the lower concentrations. With this in mind the data were split into three sets and individual calibration curves were plotted for three different concentration ranges (Fig. 4.1 – 4.3).

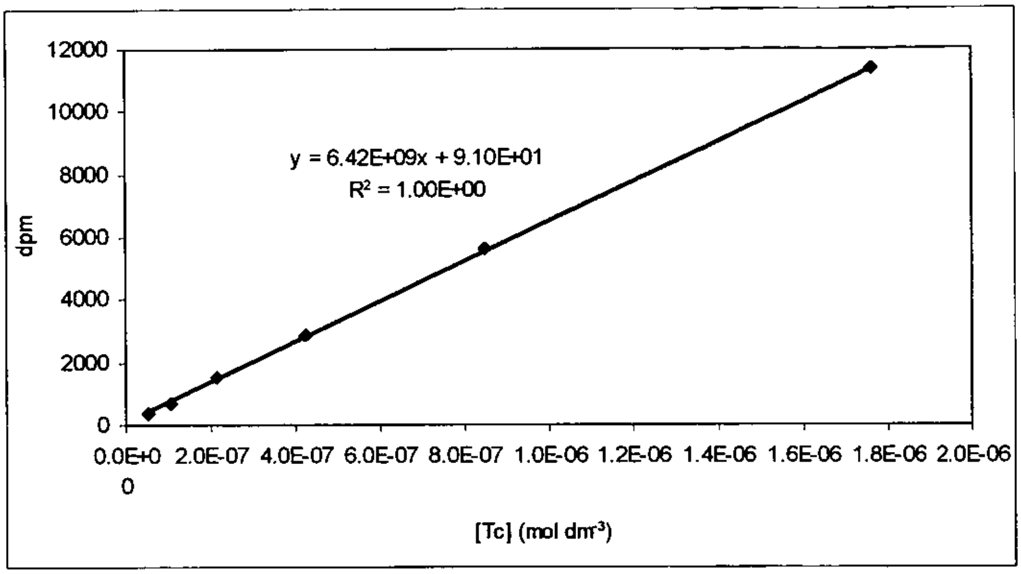


Fig. 4.1: Calibration of activity (dpm) against the technetium concentration range 1.76 $\times 10^{-6}$ – 5.31 $\times 10^{-8}$ mol dm^{-3}

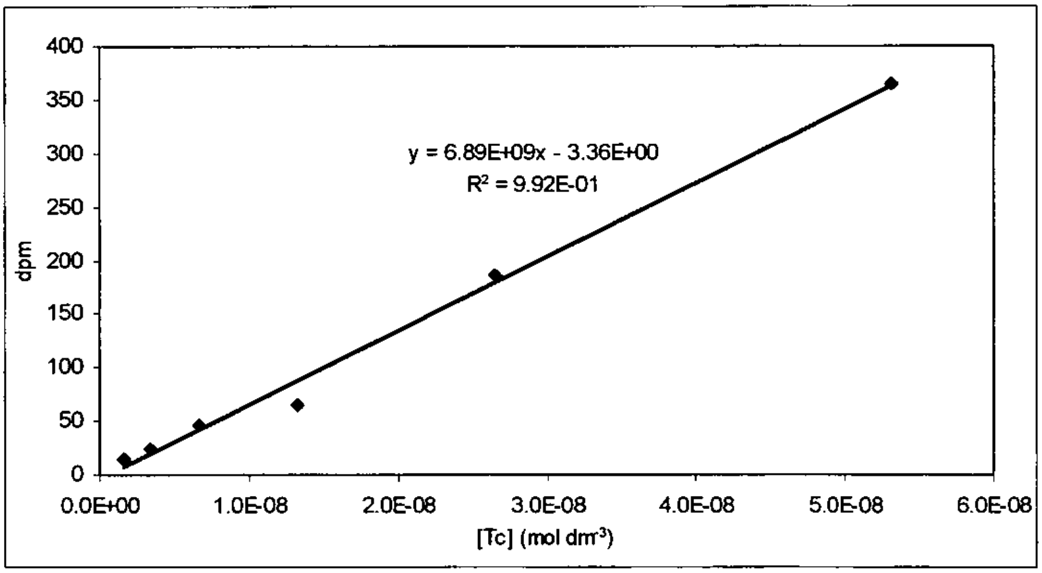


Fig. 4.2: Calibration of activity (dpm) against the technetium concentration range 5.31 $\times 10^{-8}$ – 1.66 $\times 10^{-9}$ mol dm^{-3}

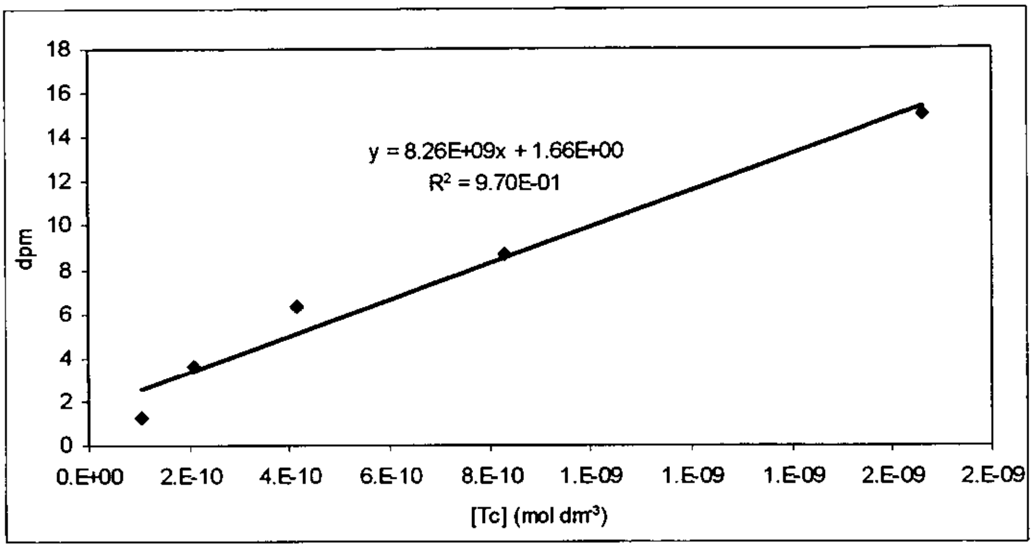


Fig. 4.3: Calibration of activity (dpm) against the technetium concentration range 1.66 ×10^{-9}- 1.04 ×10^{-10} mol dm^{-3}

The calibrations curves (Fig. 4.1 – 4.3) show good linear relationships.

4.2 Reduction of ammonium pertechnetate (NH_4TcO_4) at high pH

$$TcO_4^- + 3e^- + 4H^+ \rightleftharpoons TcO_2 + 2H_2O \qquad E^\theta = +0.738\ V$$

The reduction of TcO_4^- to $TcO_2.nH_2O(s)$ is a three-electron process. Standard potentials of the possible reactions paths leading from TcO_4^- to $TcO_2.nH_2O$ [35, 52] are given in Fig. 4.4

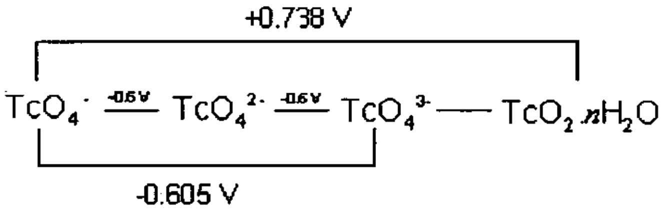


Fig. 4.4: Reduction potentials (V versus NHE) of Tc(VII) – Tc(IV) system

The one-electron reduction of TcO_4^- has been studied by electrochemical [54] and radiochemical [55 - 58] methods. The results of these two studies provide clear evidence for the formation of the Tc(VI) species TcO_4^{2-}. This species, which is known to protonate and form $HTcO_4^-$ and H_2TcO_4 with pK_1 0.3 ± 0.8 and pK_2 8.7 ± 0.5, respectively [59], is unstable and rapidly disproportionates. Although different disproportionation reactions have been suggested [54, 60], the most probable one electron reduction path in alkaline solution seems to be

$$TcO_4^- + e^- \rightleftharpoons TcO_4^{2-}$$
$$HTcO_4^- \rightleftharpoons TcO_4^{2-} + H^+$$
$$2TcO_4^{2-} \rightleftharpoons TcO_4^- + TcO_4^{3-}$$

The results of the reduction of TcO_4^- with a variety of reducing agents are presented and discussed below.

From Section 2.6.2.2 it can be seen that $TcO_2.nH_2O(s)$ has a low solubility of approximately *ca.* ≤ 1 × 10^{-8} mol dm^{-3}. Therefore reducing agents will be measured on their ability to reduce technetium solubility to this level or below.

4.2.1 Iron

$$Fe(0) \rightleftharpoons Fe^{2+} + 2e- \quad E^{\theta} = +0.409\ V$$

$$2TcO_4^- + 3Fe + 8H^+ \rightleftharpoons 2TcO_2 + 3Fe^{2+} + 4H_2O \quad E_{Tc(VII)/Fe} = +0.249\ V$$

Using thermodynamics it is possible to estimate whether this reduction is spontaneous. Using the following equation

$$\Delta G = -nF\Delta E$$

Using the values for the E^{θ} and the half cell reactions above it can be seen that the Gibbs free energy for this reaction is -144.15 kJ mol^{-1}. Therefore the reaction should be spontaneous.

Table 4.2 shows the results of the reduction of ammonium pertechnetate with iron at high pH.

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.21	5701.6	8.72E-07	5824.5	8.91E-07
2	13.11	6196.0	9.49E-07	5956.3	9.12E-07
3	13.36	5741.4	8.78E-07	5741.5	8.78E-07
4	13.40	6125.3	9.38E-07	6103.9	9.35E-07
5	13.31	5834.4	8.93E-07	5793.7	8.87E-07

Table 4.2: Reduction of ammonium pertechnetate at high pH using Fe(0)

The results in Table 4.2 show that very little or no technetium has been removed from the solution. As the Gibbs free energy for this reaction indicated that the reaction should be spontaneous it must therefore be kinetically controlled not thermodynamically controlled. The reducing power of iron metal is dependent on the corrosion of the metal. These results show that the corrosion must be inhibited by the high pH of the solution that the iron is in contact with.

This is because the anodic reaction (shown below) which yields the unprotected soluble Fe^{2+} ion as the primary anodic product is not favored at high pH. The formation of the free Fe^{2+} ions gives way to the formation of a thin, dense, insoluble and protective film. This phenomenon is know as passivity.

At the Anode $3Fe - 8OH^- \rightarrow Fe_3O_4 + 4H_2O + 8e^-$

At the Cathode $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

The Pourbaix diagram below shows the regions where passivity occurs.

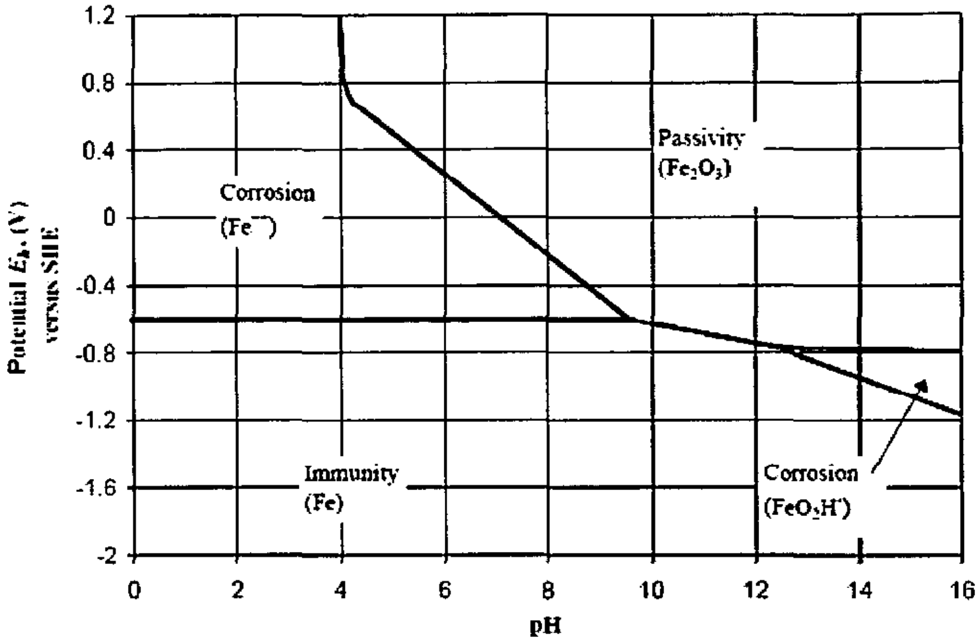


Fig. 4.5: A simiplified Pourbaix diagram for iron [60]

Due to passivity the rate of corrosion is very dependent on the pH of the solution. The effect on the rate can be seen below.

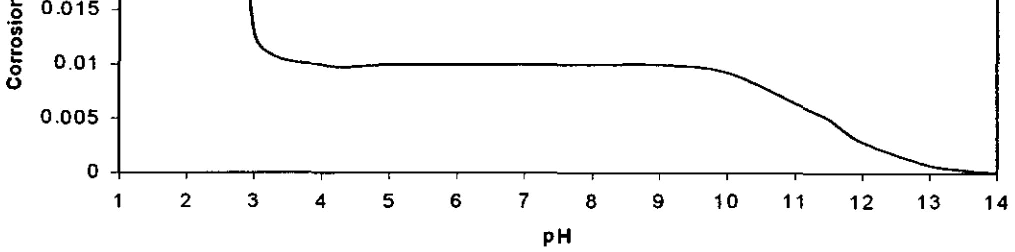


Fig. 4.6: Rate of corrosion of a piece of iron metal(inches/year) against pH [60]

Table 4.3 shows the results of the reduction of ammonium pertechnetate with iron at near neutral pH

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	7.12	7008.2	1.08E-06	55.5	7.74E-09
2	6.77	6931.1	1.06E-06	41.3	5.66E-09
3	7.06	6394.9	9.80E-07	61.6	8.63E-09
4	6.69	6103.9	9.35E-07	63.2	8.87E-09
5	6.91	5958.2	9.12E-07	77.6	1.10E-08

Table 4.3: Reduction of ammonium pertechnetate at neutral pH using Fe(0)

From these results it can be seen that the reaction, as predicted above, is spontaneous at near neutral conditions, as there is very little technetium left in solution. The use of iron metal as reducing agent is effective, however, one disadvantage of using this method is the time it takes for the reaction to occur. These samples had to be left for 1 month.

4.2.2 Tin

$$Sn(0) \rightleftharpoons Sn^{2+} + 2e- \qquad E^{\theta} = +0.136\ V$$

$$2TcO_4^- + 3Sn(0) + 8H^+ \rightleftharpoons 2TcO_2 + 3Sn^{2+} + 4H_2O \qquad E_{Tc(VII)/Sn} = +1.067\ V$$

Using the values for the E^{θ} and the half cell reactions above it is possible to calculate the Gibbs free energy for this reaction. ΔG = -617.58 kJ mol^{-1}. Therefore the reaction should be spontaneous.

From Table 4.4 it can be seen that no reduction has taken place. The reason for this is that the tin metal forms a tin oxide coating at the surface when exposed to the air. This tin oxide layer retards the reducing power of the metal.

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.17	5391.3	8.24E-07	5293.2	8.08E-07
2	13.32	6014.5	9.21E-07	4970.8	7.58E-07
3	13.43	5937.2	9.09E-07	4804.1	7.32E-07
4	13.37	5963.8	9.13E-07	5070.9	7.74E-07
5	13.34	5434.7	8.30E-07	4905.8	7.48E-07

Table 4.4: Reduction of ammonium pertechnetate with tin at high pH

The reduction was repeated, this time the tin surface was cleaned with emery paper to remove any oxide layer before being introduced to the reaction mixture.

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.37	5382.3	8.22E-07	1308.2	1.86E-07
2	13.28	6423.5	9.85E-07	1148.4	1.61E-07
3	13.37	5431.2	8.30E-07	1256.1	1.78E-07
4	13.24	5898.8	9.03E-07	1247.4	1.76E-07
5	13.63	5637.7	8.62E-07	1206.6	1.70E-07

Table 4.5: Reduction of ammonium pertechnetate at high pH using Sn(0)

From Table 4.5 it can be seen that the tin metal does reduce the pertechnetate to a certain degree, when the coating of tin oxide has been removed from the surface. However, the cleaned tin metal does not completely reduce TcO_4^- since the measured solubility is not comparable to the reported solubility of technetium(IV).

4.2.3 Tin (II) chloride

$$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e- \quad E^{\theta} = -0.070\,V$$

$$2TcO_4^- + 3Sn^{2+} + 8H^+ \rightleftharpoons 2TcO_2 + 3Sn^{4+} + 4H_2O \quad E_{Tc(VII)/Sn(II)} = +1.686\,V$$

Using the values for the E^{θ} and the half cell reactions above it is possible to calculate the Gibbs free energy for this reaction. ΔG = -976.05 kJ mol^{-1}. Therefore the reaction should be spontaneous.

Table 4.6 shows the results of the reduction of ammonium pertechnetate with $SnCl_2$ at high pH.

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.33	5629.9	8.61E-07	141.5	9.01E-09
2	13.32	5568.2	8.51E-07	79.0	1.12E-08
3	13.34	5449.0	8.33E-07	89.9	1.28E-08
4	13.38	5433.2	8.30E-07	102.6	9.78E-09
5	13.31	5669.4	8.67E-07	100.0	1.31E-08

Table 4.6: Reduction of ammonium pertechnetate at high pH using $SnCl_2$

From Table 4.6 it can be seen that as predicted by the Gibbs free energy $SnCl_2$ is an excellent reductant for the reduction of TcO_4^- to TcO_2. This was to be expected as $SnCl_2$ is the most commonly used reductant in the preparation of ^{99m}Tc-labelled radiopharmaceuticals.

4.2.4 Iron (II) sulphate

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e- \qquad E^{\theta} = -0.770\ V$$

$$TcO_4^- + 3Fe^{2+} + 4H^+ \rightleftharpoons TcO_2 + 3Fe^{3+} + 2H_2O \qquad E_{Tc(VII)/Fe(II)} = +3.048\ V$$

Using the values for the E^{θ} and the half cell reactions above it is possible to calculate the Gibbs free energy for this reaction. ΔG = -882.26 kJ mol^{-1}. Therefore the reaction should be spontaneous.

Table 4.7 shows the results of the reduction of ammonium pertechnetate with $FeSO_4$ at high pH

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.34	5731.8	8.77E-07	88.2	1.25E-08
2	13.40	5453.7	8.33E-07	93.1	1.32E-08
3	13.30	5752.2	8.80E-07	61.8	8.66E-09
4	13.30	5407.8	8.26E-07	72.3	1.02E-08
5	13.31	5460.4	8.34E-07	64.8	9.10E-09

Table 4.7: Reduction of ammonium pertechnetate at high pH using $FeSO_4$

From Table 4.7 it can be seen that $FeSO_4$ has reduced the majority of the technetium resulting in a small amount of technetium remaining in solution.

4.2.5 Sodium borohyride

Table 4.8 shows the results of the reduction of ammonium pertechnetate with $NaBH_4$ at high pH

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.30	4767.9	7.26E-07	3674.3	5.55E-07
2	13.36	5004.6	7.63E-07	3746.5	5.67E-07
3	13.30	4850.4	7.39E-07	3757.7	5.68E-07
4	13.36	4910.2	7.48E-07	3793.9	5.74E-07
5	13.30	4813.8	7.33E-07	3691.3	5.58E-07

Table 4.8: Reduction of ammonium pertechnetate at high pH using $NaBH_4$

While $NaBH_4$ is a good selective reductant in organic chemistry, the results show that it is not powerful enough to reduce the technetium effectively.

4.2.6 Sodium dithionite

Table 4.9 shows the results of the reduction of ammonium pertechnetate with sodium dithionite at high pH

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.31	5664.4	8.66E-07	549.0	6.70E-08
2	13.30	5875.8	8.99E-07	726.4	9.48E-08
3	13.36	5732.2	8.77E-07	676.1	8.69E-08
4	13.32	5611.9	8.58E-07	696.2	9.00E-08
5	13.37	5446.7	8.32E-07	611.0	7.67E-08

Table 4.9: Reduction of ammonium pertechnetate at high pH using sodium dithionite

The results show that the sodium dithionite has reduced the majority of the technetium in solution. The extent of reduction is not as great as when using $FeSO_4$, $SnCl_2$ or Fe(0) at near neutral pH.

4.2.7 Sodium hypophosphite

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.37	3184.2	4.79E-07	2337.1	3.46E-07
2	13.08	3127.6	4.70E-07	2361.2	3.50E-07
3	13.36	3132.0	4.71E-07	2533.1	3.77E-07
4	13.36	3058.4	4.59E-07	2530.0	3.77E-07
5	13.40	3068.6	4.61E-07	2748.1	4.11E-07

Table 4.10: Reduction of ammonium pertechnetate using Sodium Hypophosphite

From Table 4.10 it can be seen that sodium hypophosphite was a poor reducing agent for TcO_4^-, as after an equilibration of 1 week the concentration of technetium has only been reduced by *ca.* 25 %.

4.2.8 Hydrazine hydrate

Table 4.11 shows the results of the reduction of ammonium pertechnetate with hydrazine at high pH

Sample Number	pH	Initial		Final	
		dpm	[Tc] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.11	5733.4	8.77E-07	1545.4	2.23E-07
2	13.20	5491.3	8.39E-07	1566.9	2.26E-07
3	13.30	5791.9	8.86E-07	1580.8	2.28E-07
4	13.34	5281.7	8.07E-07	1610.4	2.33E-07
5	13.20	5455.7	8.34E-07	1530.4	2.20E-07

Table 4.11: Reduction of ammonium pertechnetate at high pH using hydrazine

From Table 4.11 it can be seen that hydrazine hydrate was a poor reducing agent for TcO_4^-, as after an equilibration of 1 week the concentration of technetium has only been reduced by *ca.* 50 %.

4.2.9 Summary of the reduction of TcO_4

The equation below expresses the extent of reduction as a percentage of the technetium reduced.

$$\text{Reduction}\,(\%) = 100 - \left(\left(\frac{[\text{Tc}]_{\text{Final}}}{[\text{Tc}]_{\text{Initial}}}\right)\times 100\right)$$

Its is therefore possible to compare all the reducing agents

From Table 4.12 it can be seen that the reducing agents that achieve the solubility of Tc(IV) (highlighted in red in Table 4.12) due to the reduction of TcO_4^- to TcO_2 are:

- Iron metal at near neutral pH
- Tin(II) chloride
- Iron(II) sulphate

Reductant	Average Reduction (%)	±
Fe(0) (pH ~ 13.3)	0.5	2.2*
Fe(0) (pH ~ 7)	99.1	0.3
Sn(0) (untreated)	12.8	7.1
Sn(0)	80.1	2.4
$SnCl_2$	98.7	0.2
$FeSO_4$	98.7	0.2
$NaBH_4$	23.9	1.0
Sodium Dithionite	90.4	1.2
Sodium Hypophosphite	20.4	6.7
Hydrazine Hydrate	73.3	1.4

Table 4.12: Average reductions (%) for each reductant used

The large amount of iron excepted in the near field of the repository make it the obvious choice for achieving the conditions expected in the repository. However, because the reduction of TcO_4^- with iron at high pH is kinetically slow due to the passivity of the iron metal it is impractical to use as the reducing agent for these experiments.

As tin(II) chloride gave the best reduction of TcO_4^- and it is used throughout the radiopharmceutical industry as the reducing agent for pertechnetate it was decided that it would be used for these experiments.

4.3 Solubility of TcO_2(s) at pH 13.3

The solubility of technetium(IV) was discussed in section 2.6.2.2, from this it can be seen that at high pH TcO_2 is sparingly soluble, with a solubility of $<1 \times 10^{-8}$ mol dm^{-3}. By measuring the solubility of technetium(IV) a baseline is provided that can be used as an indication of whether the reduction of TcO_4^- has gone to completion. The solubility of technetium(IV) can also be used to measure the effect the ligands, under investigation, have on the solubility of technetium when they are introduced into the system.

From Table 4.13 it can be seen that the mean solubility of TcO_2 in the absence of any ligand is $3.6 \pm 2.4 \times 10^{-10}$ mol dm^{-3}. This value is in good agreement with the literature value for solubility of TcO_2 [38, 40].

Sample number	dpm	[Tc] (mol dm^{-3})
1	7.7	7.33E-10
2	5.1	4.18E-10
3	4.4	3.34E-10
4	2.7	1.28E-10
5	3.2	1.88E-10

Table 4.13: Solubility of Tc(IV)

Using the mean measured solubility of technetium(IV) (Table 4.13) and equation 3.21 (section 3.3.10.1) the solubility product can be calculated for the reaction:

$$TcO_2.2H_2O\,(am) \rightleftharpoons TcO(OH)^+\,(aq) + OH^-\,(aq) + H_2O$$

Therefore the log of the solubility product (log K_{sp}) of $TcO_2.2H_2O$ is -21.1 ± 0.3.

The solubility of Tc(IV) measured experimentally agrees with data reported by Baker *et al* [40]. However, these data, like data from the study by Eriksen *et* al [39] show a solubility increase with increasing pH. However, these data are not in agreement with the pH at which this solubility increase begins. In the study by Eriksen *et al* it was found that the solubility of $TcO_2.nH_2O$ (s) was independent of pH in the range $6 < pH < 9.5$. This is in agreement with other solubility studies and with data measured in this study. This can be explained by the following equilibrium.

$$TcO_2.nH_2O \rightleftharpoons TcO(OH)_2 + (n-1)H_2O$$

$$k_1 = \left[TcO(OH)_2\right] = -8.22 \pm 0.06$$

However, in the pH range 9.5 – 12 Eriksen *et al* found that there was a solubility increase with increasing pH (Fig. 4.7).

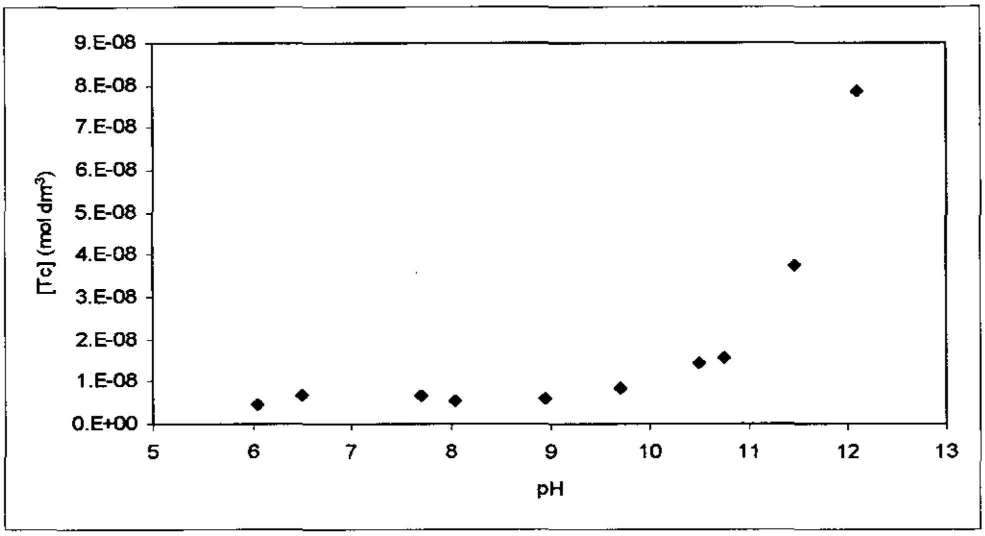


Fig. 4.7: Solubility increase of Tc(IV) against pH measured by Eriksen *et al* [39]

This increase in solubility was explained by the following equilibrium:

$$TcO_2.nH_2O \rightleftharpoons TcO(OH)_3^- + H^+ + (n-2)H_2O$$

$$k_2 = \left[TcO(OH)_3^-\right]\left[H^+\right]$$

Therefore, the total technetium in solution will be equal to the sum of the concentrations of $TcO(OH)_2$ and $TcO(OH)_3^-$.

$$\left[Tc(IV)\right]_{Total} = \left[TcO(OH)_2\right] + \left[TcO(OH)_3^-\right]$$

$$\therefore \left[Tc(IV)\right]_{Total} = k_1 + \frac{k_2}{\left[H^+\right]}$$

Plotting data measured by Eriksen *et al* [39] (Fig. 4.8) and, using the equations above log k_2 is approximately equal to -19.2.

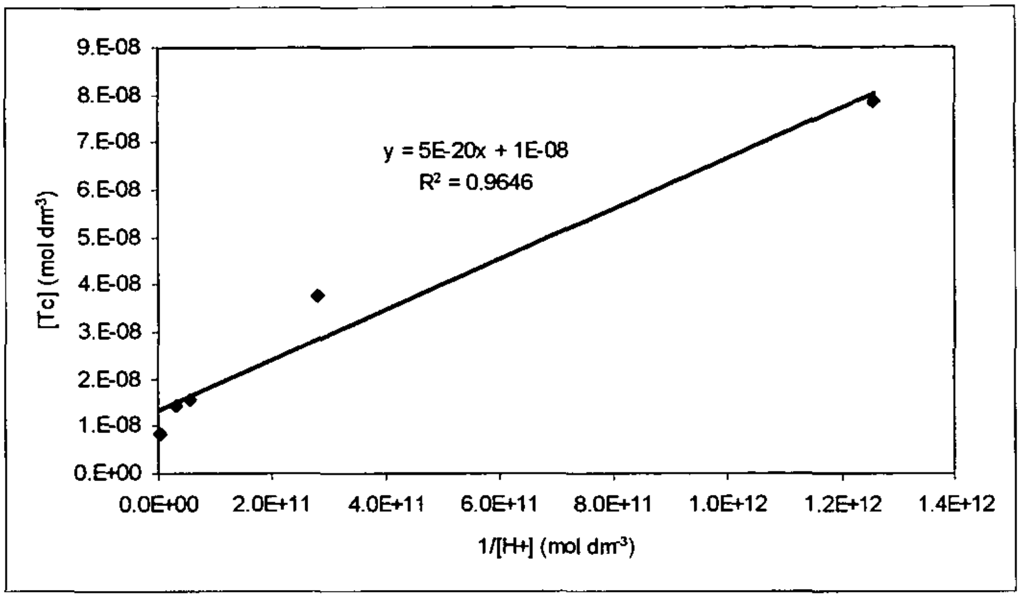


Fig. 4.8: Solubility increase of Tc(IV) against 1/[H$^+$] measured by Eriksen et al [39]

The results obtained in this study do not agree with the results obtained by Eriksen *et al* [39]. From the study by Baker *et al* [40] there was an indication of a slight increase in the solubility of technetium(IV) with increasing pH, as the four experiments gave concentrations in the range ≤ 5×10^{-10} to 9×10^{-9} mol dm^{-3}. However, this result was not seen in the experiments reported in this thesis and Baker *et al* [40] considered the results tentative. Thus, the results do not confirm the existence of the anionic technetium species $TcO(OH)_3^-$ but neither do they rule it out. However, it is thought that the anionic species, $TcO(OH)_3^-$, may exist at higher pH.

4.3.1 Solubility of Tc(IV) between pH 11 and pH 14

As shown above in section 4.3 the solubility reported in this project and that reported by Eriksen *et al* [39] are not in agreement. Therefore the solubility of technetium(IV) was measured between pH 11.5 and pH 14.5 to investigate the existence of $TcO(OH)_3^-$.

From Fig. 4.9 and Table 9.2 (section 9.1) it can be seen that between pH 11 – 13.5 the concentration of Tc in solution appears to be independent of pH. However at pH's greater than 13.5 the concentration of technetium in solution increases.

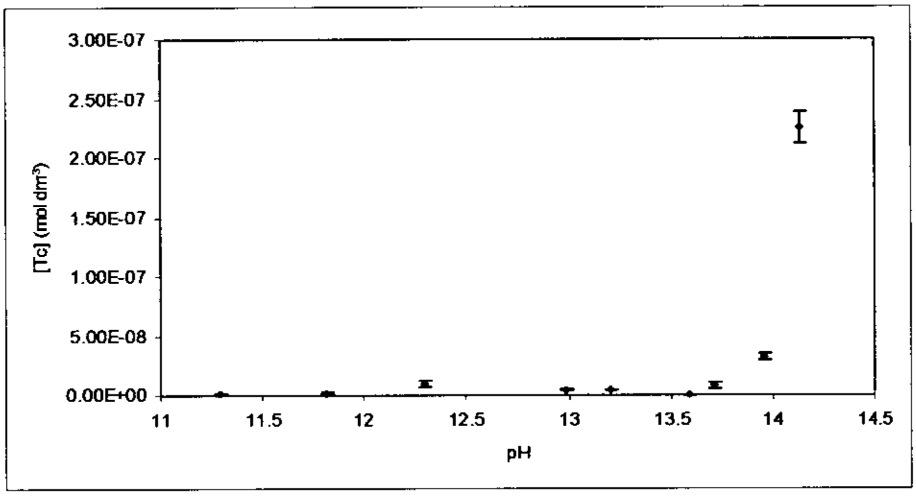


Fig. 4.9: Concentration of technetium (mol dm^{-3}) against pH

Assuming that the increase in solubility can be explained by the equilibrium suggested by Eriksen *et al* [39] and plotting a graph of Tc(IV) solubility against 1/[H$^+$] (Fig. 4.10) the log k_2 is estimated to be -20.6. Fig. 4.10 is clearly not linear but in order to calculate k_2 from the gradient a straight line has been put throught the datum points. Clearly this creates an error in the calculation.

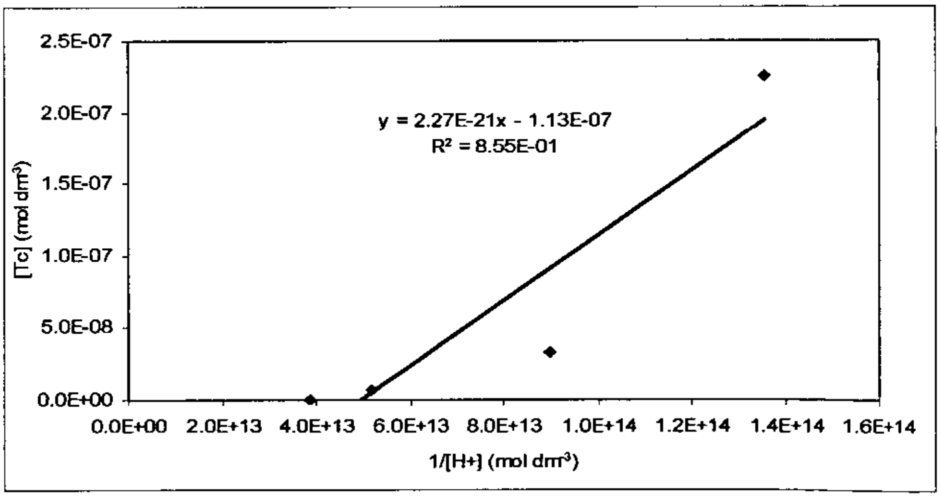


Fig. 4.10: Solubility increase of Tc(IV) against 1/[H$^+$]

To check that the increase in the technetium solubility in solution was not due to reoxidation the E$_h$ was measured for the 5 highest pH solutions, i.e. where the increase in solubility begins. The maximum and minium E$_h$ values were recorded as there was considerable variation in the measurement and the meter never stabilised on a specific value.

Sample	$[OH^-]$ (mol dm^{-3})	E$_{h\ (max)}$ (mV)	E$_{h\ (min)}$ (mV)	Sample	$[OH^-]$ (mol dm^{-3})	E$_{h\ (max)}$ (mV)	E$_{h\ (min)}$ (mV)
1	0.1	-395	-408	**13**	0.5	-408	-410
2	0.1	-392	-407	**14**	1.0	-460	-469
3	0.1	-394	-410	**15**	1.0	-431	-437
4	0.1	-394	-411	**16**	1.0	-392	-399
5	0.1	-395	-411	**17**	1.0	-418	-430
6	0.3	-391	-410	**18**	1.0	-289	-400
7	0.3	-399	-407	**19**	2.0	-1000	-1021
8	0.3	-391	-409	**20**	2.0	-1009	-1013
9	0.5	-391	-408	**21**	2.0	-1010	-1018
10	0.5	-409	-414	**22**	2.0	-962	-971
11	0.5	-396	-408	**23**	2.0	-984	-992
12	0.5	-404	-411				

Table 4.14: Eh values for the reduction of technetium(VII) at high pH

As can be seen from the E$_h$ values measured for the reduction of technetium(VII) the technetium is not reoxidised in solution.

The results from this section suggest that the anionic technetium(IV) species, $TcO(OH)_3^-$ exists. The stability constant for the formation of $TcO(OH)_3^-$ (below) has also been determined to be -20.6.

$$TcO_2.nH_2O \rightleftharpoons TcO(OH)_3^- + H^+ + (n-2)H_2O$$

4.3.1.1 Ion exchange method for the determination of Tc(IV) speciation

To determine whether the increase in solubility above pH 13.5 was due to the formation of $TcO(OH)_3^-$ ion exchange resins were added to solutions containing reduced technetium between pH 12.5 and pH 14.0.

4.3.1.1.1 Cationic exchange resin

From Fig. 4.11 and Table 9.3 (section 9.1) it can be seen that the solubility of technetium in solution does not change when the BioRad AG50W X2, 100 – 200 mesh cation exchange resin is contacted with the solution. This indicates that the technetium species is not cationic.

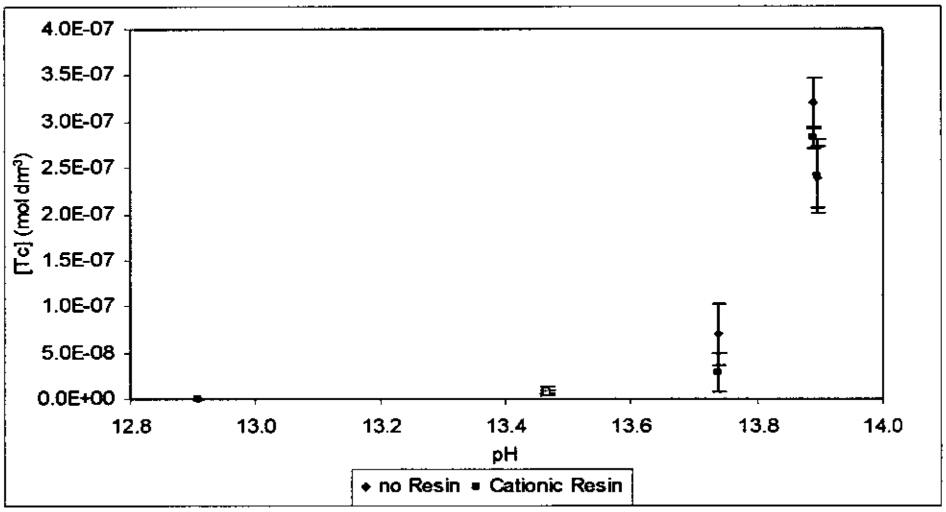


Fig. 4.11: Technetium solubility against pH in the presence of a cationic exchange resin

4.3.1.1.2 Anionic exchange resin

From Fig. 4.12 and Table 9.4 (section 9.1) it can be seen that the solubility of technetium in solution does not change when the Amberlite IRA-400 anion exchange resin is contacted with the solution. This indicates that the technetium species is not anionic.

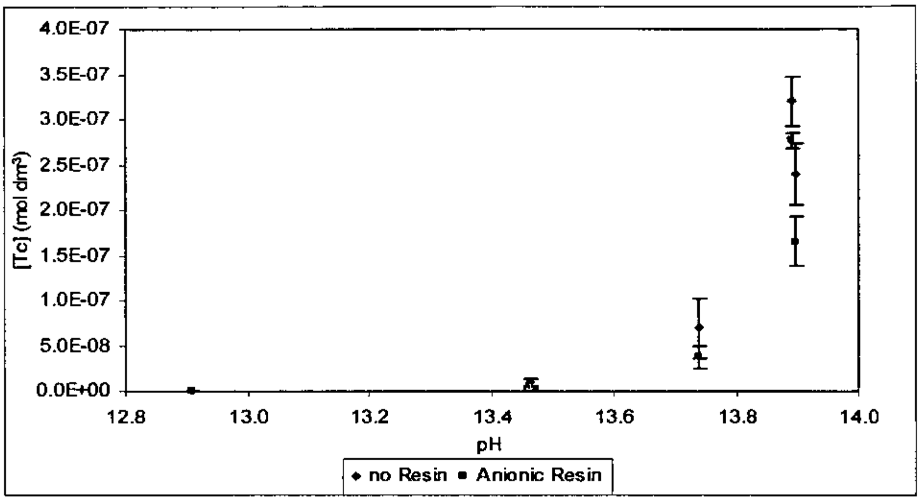


Fig. 4.12: Technetium solubility against pH in the presence of an anionic exchange resin

4.3.1.1.3 Summary

From section 4.4.1.1.1 and 4.4.1.1.2 it can be seen that the solubility of reduced technetium does not change in the presence of either cationic or anionic exchange resins. There are 2 possible reasons for this:

- It is possible that other ions in solution are filling the sites on the ion exchange resins.
- The species of technetium(IV) in solution is neutral

4.4 Measurement of possible quenching effects on the technetium from the ligands by the sample channels ratio method

Quenching is a reduction in counting efficiency as a result of light loss in the liquid scintillation solution (Fig. 4.13). If quenching takes place then the pulse height spectrum detected from the radionuclide appears to shift toward a lower energy.

The two major types of quenching are as follows:

- **Chemical quenching (Impurity quenching)** causes losses in the transfer of energy from solvent to solute.
- **Colour quenching (Optical quenching)** causes the attenuation of photons produced by the solution.

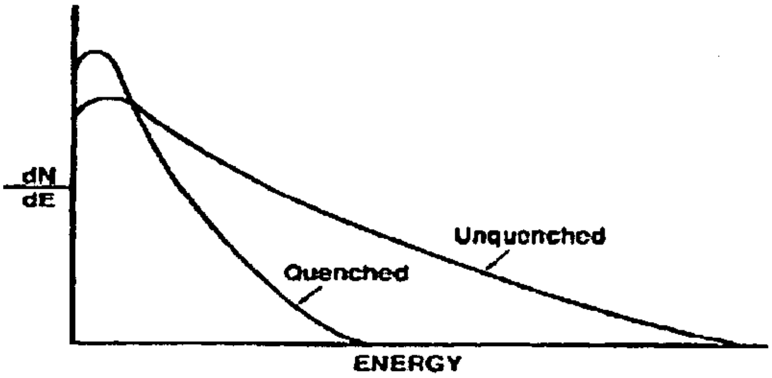


Fig. 4.13: Quenched and unquenched pulse height spectrum

Chemical quenching absorbs beta energy before it is converted to photons while colour quenching results from the passage of photons through the medium. Colour quenching depends on the colour of the interfering chemical and path length that the photon must travel. In a chemically quenched sample, all energy radiations appear to be equally affected whereas, for a coloured sample, events that take place close to one photomultiplier tube (PMT) will give rise to a large pulse and a smaller pulse in the other PMT. The pulses are added together so the resultant pulse height may be as large as the pulse height from an unquenched sample, only the number of events will be significantly reduced. Thus, at equal quench levels, the pulse height of coloured samples are spread over a wider range than chemical quench samples.

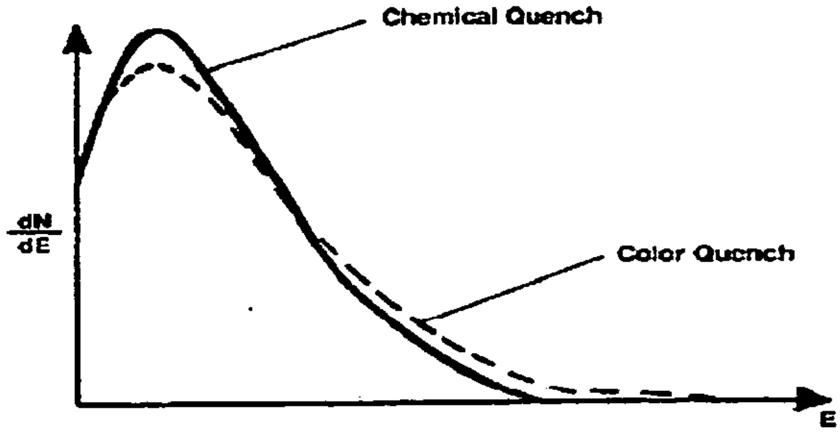


Fig. 4.14: Comparison of the effects on a pulse height spectrum by chemical and colour quenching

The additions of the organic complexing ligands to the solutions of technetium may cause quenching to occur. In particular the addition of ISA to the technetium solutions as this produces coloured solutions.

4.4.1 EDTA

From Fig. 4.15 and Table 9.6 (section 9.1) it can be seen that the sample channels ratio is approximately 0.29 at all concentrations of EDTA. This indicates that EDTA is having no quenching effect on the liquid scintillation counting of technetium.

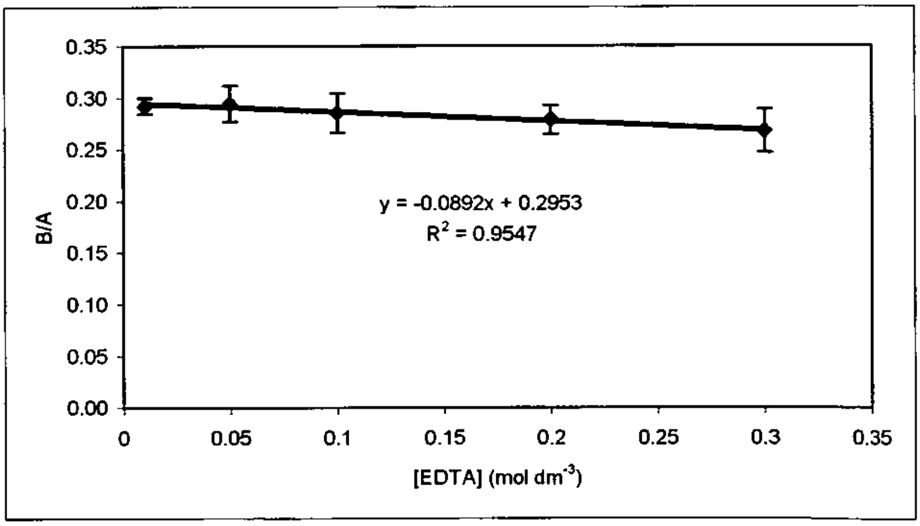


Fig. 4.15: Concentration of EDTA against channels ratio

4.4.2 NTA

From Fig. 4.16 and Table 9.7 (section 9.1) it can be seen that the sample channels ratio is approximately 0.29 at all concentrations of NTA. This indicates that NTA is having no quenching effect on the liquid scintillation counting of technetium.

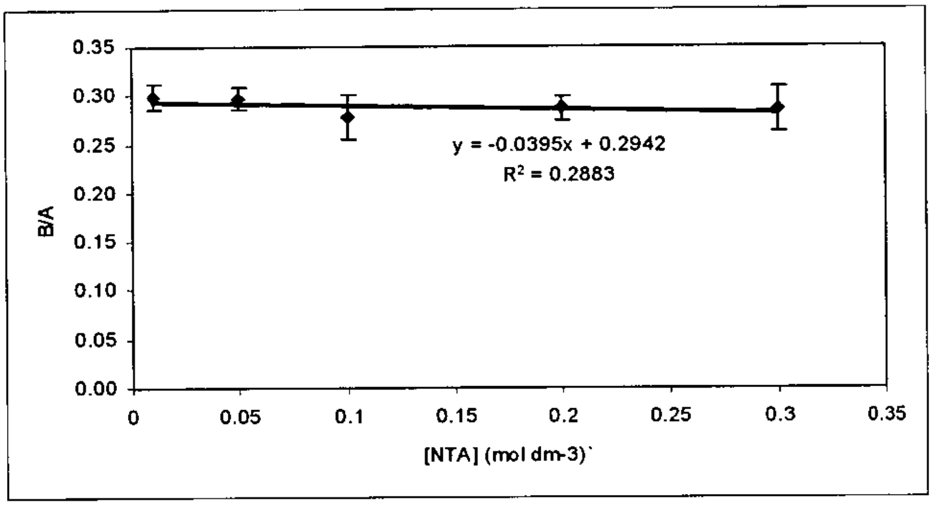


Fig. 4.16: Concentration of NTA against channels ratio

4.4.3 ISA

From Fig. 4.17 and Table 9.8 (section 9.1) it can be seen that as the concentration of ISA is increased the sample channels ratio (B/A) increases. This is because of colour quenching. ISA becomes increasingly yellowy brown with increased concentration.

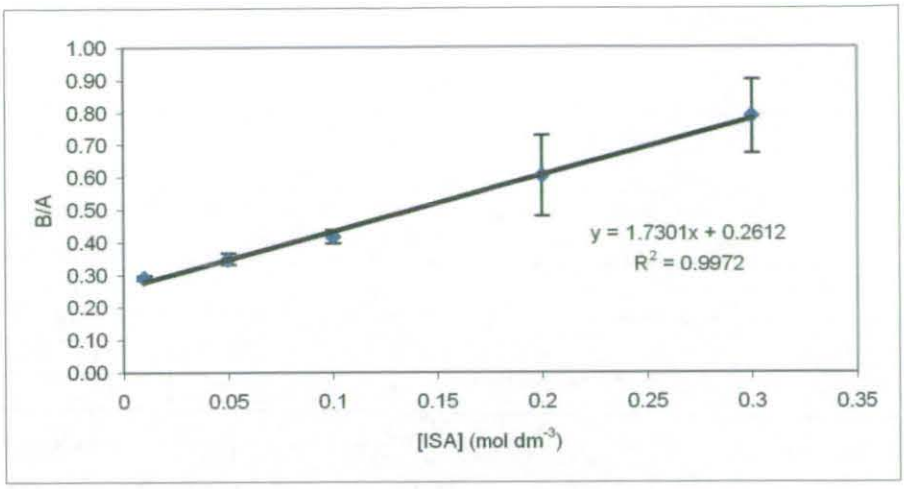


Fig. 4.17: Concentration of ISA against channels ratio

By calculating the counting efficiency in channel A for each sample (Table 9.9) it is possible to construct a plot of sample channels ratio against counting efficiency. From this plot the correct counting efficiency can now be determined for each sample.

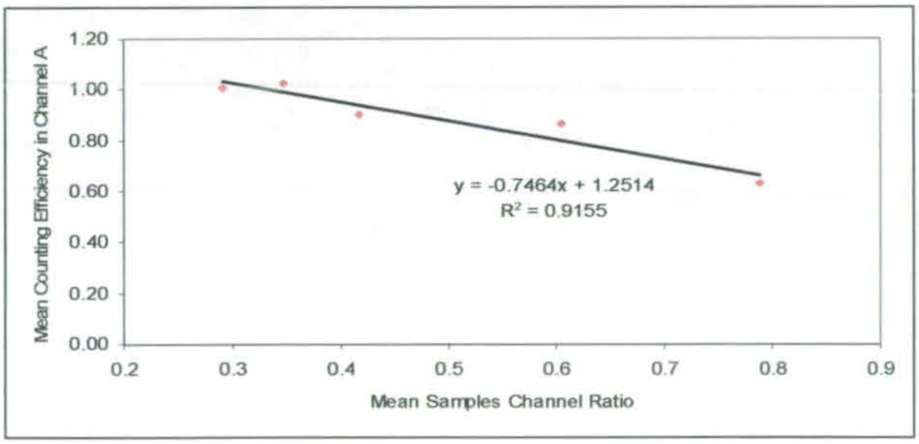


Fig. 4.18: Mean sample channels ratio against the mean counting efficiency in channel A

4.4.4 Gluconic acid

From Fig. 4.19 and Table 9.10 (section 9.1) it can be seen that the sample channels ratio is approximately 0.29 at all concentrations of gluconic acid. This indicates that gluconic acid is having no quenching effect on the liquid scintillation counting of technetium.

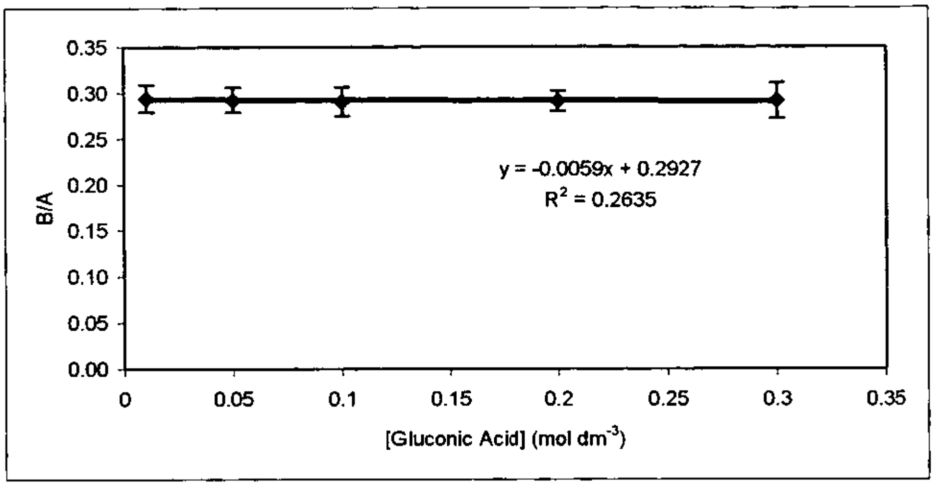


Fig. 4.19: Concentration of gluconic acid against channels ratio

4.4.5 Picolinic Acid

Fig. 4.20 shows the samples channel ratio against the concentration of picolinic acid (mol dm^{-3}) added.

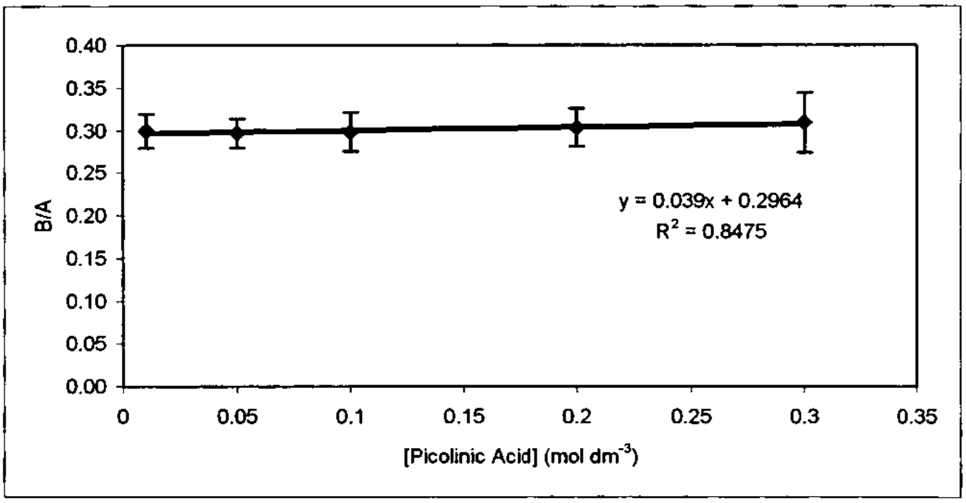


Fig. 4.20: Concentration of picolinic acid against channels ratio

From Fig. 4.20 and Table 9.11 (section 9.1) it can be seen that the sample channels ratio is approximately 0.29 at all concentrations of picolinic acid. This indicates that picolinic acid is having no quenching effect on the liquid scintillation counting of technetium.

4.5 Reduction of ammonium pertechnetate in the presence of organics complexing agents at high pH

The formation of technetium complexes are discussed in section 2.5. It can be seen from section 2.5 that the most common pathway used for the formation of technetium complexes is the reduction of pertechnetate in the presence of a ligand (Eq. 1, Fig. 2.5). This mechanism is especially used for the synthesis of diagnostic radiopharmaceuticals, where the ^{99m}Tc is used instead of ^{99}Tc as a tracer and the ligand is the actual pharmaceutical designed for the target of a specific organ.

Technetium will enter the nuclear waste repository as TcO_4^-, where under the reducing conditions that prevail it will be reduced to TcO_2(s). However, as discussed in section 2.6.1.6 organic material will form part of the waste and so low molecular weight organics, such as the ligands under investigation in this project (EDTA, NTA, ISA, gluconic acid and picolinic acid) will be present. Therefore, as discussed in section 2.5, the reduction from TcO_4^- to TcO_2(s) may not occur and as in the radiopharmaceutical industry soluble technetium complexes may be formed.

As discussed in section 4.2.9 Sn(II) is used as the reducing agent for TcO_4^-.

4.5.1 EDTA

The results for reduction of pertechnetate in the presence of EDTA are shown below in Fig. 4.21 and Table 9.12 (section 9.1).

From Fig. 4.21 it can be seen that at low concentrations of EDTA there is little effect on the solubility of technetium. However as the concentration of EDTA is increased there is an increase in the solubility of technetium. At [EDTA] = 0.2 mol dm^{-3} the concentration of technetium in solution is approximately equal to the technetium inventory of *ca.* 4 $\times 10^{-7}$ mol dm^{-3}.

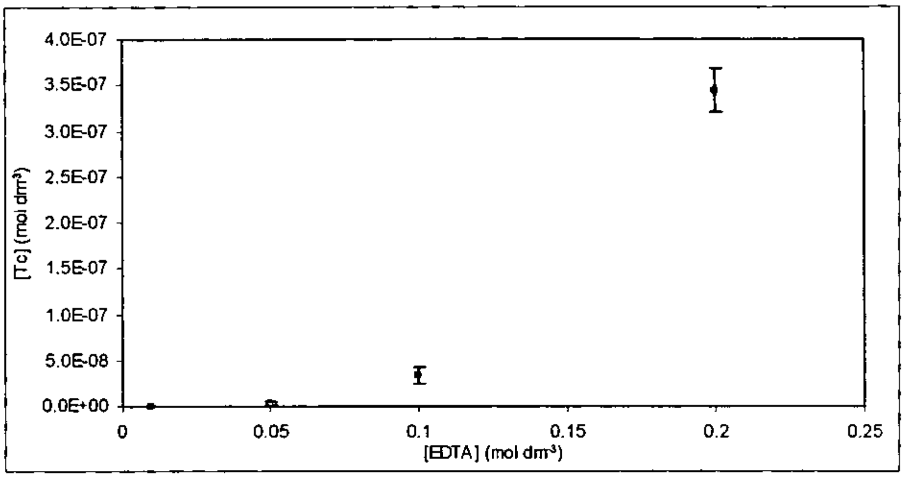


Fig. 4.21: Solubility of technetium (mol dm^{-3}) against the concentration of EDTA (mol dm^{-3})

By using the equation below the solubility enhancement factor (SEF) can be calculated and the increases in solubility be compared relative to the measured solubility of Tc(IV) in the absence of a complexing ligand.

$$\text{Solubility Enhancement Factor (SEF)} = \frac{\text{Tc}(\text{IV})\ \text{solubility in presence of organic}}{\text{Tc}(\text{IV})\ \text{solubility in the absence of organic}}$$

For Tc(IV) in the presence of EDTA the mean solubility enhancement factors (5 replicates) are shown below (Table 4.15), where the solubility of Tc(IV) in the absence of ligand is 3.6×10^{-10} mol dm^{-3}.

[EDTA] (mol dm^{-3})	SEF	±
0.2	925.2	63.7
0.1	92.2	24.4
0.05	9.9	5.3
0.01	1.0	0.7

Table 4.15: Solubility enhancement factors (SEF) for the solubility of technetium in EDTA

From the Fig. 4.21, Table 4.15 and Table 9.12 (section 9.1) it can be seen that as the concentration of the EDTA increases the solubility of technetium increases. As discussed in section 2.5, technetium complexes, especially technetium radiopharmaceuticals, are produced by reducing pertechnetate in the presence of a ligand. It is therefore likely that a soluble technetium EDTA complex is being formed.

$$TcO_4^- + R + EDTA^{y-} \rightleftharpoons Tc-(EDTA)^{(y-1)-}$$

4.5.2 NTA

From Fig. 4.22 and Table 9.13 (section 9.1) it can be seen that at low concentrations of NTA there is little effect on the solubility of technetium. However as the concentration of NTA is increased there is an increase in the solubility of technetium. At [NTA] = 0.2 mol dm^{-3} approximately all the technetium is in solution.

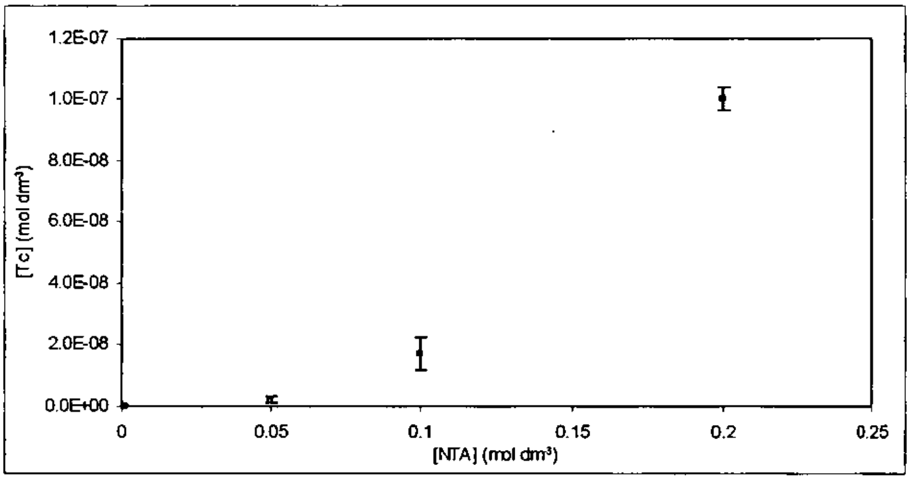


Fig. 4.22: Solubility of technetium (mol dm^{-3}) against the concentration of NTA (mol dm^{-3})

The solubility enhancement factors for the reduction of TcO_4^- in the presence of NTA are shown below (Table 4.16)

[NTA] (mol dm^{-3})	SEF	±
0.2	269.5	9.9
0.1	46.1	14.7
0.05	5.3	2.9
0.01	0.5	0.1

Table 4.16: Solubility enhancement factors (SEF) for the solubility of technetium in NTA

From Fig. 4.22, Table 4.16 and Table 9.13 (section 9.1) it can be seen that as the concentration of the NTA increases the solubility of technetium increases. As discussed in section 4.5.1, this is most like due to the formation of soluble technetium NTA complexes.

$$TcO_4^- + R + NTA^{y-} \rightleftharpoons Tc\text{-}(NTA)^{(y-1)}$$

4.5.3 ISA

The results for reduction of pertechnetate in the presence of ISA are shown below in Fig. 4.23 and Table 9.14 (section 9.1).

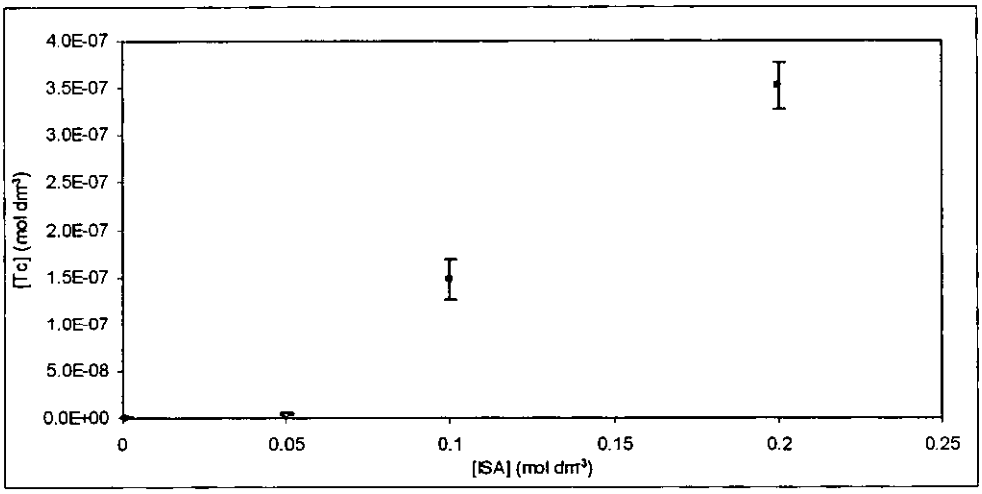


Fig. 4.23: Solubility of technetium (mol dm^{-3}) against the concentration of ISA (mol dm^{-3})

From Fig 4.23 it can be seen that at low concentrations of ISA there is little effect on the solubility of technetium. However as the concentration of ISA is increased there is an increase in the solubility of technetium. At [ISA] = 0.2 mol dm^{-3} approximately all the technetium is in solution.

The solubility enhancement factors for the reduction of TcO_4^- in the presence of ISA are shown below (Table 4.17)

[ISA] (mol dm^{-3})	SEF	±
0.2	946.9	65.7
0.1	397.5	58.9
0.05	13.2	5.1
0.01	1.4	1.5

Table 4.17: Solubility enhancement factors (SEF) for the solubility of technetium in ISA

From Fig. 4.23, Table 4.17 and Table 9.14 it can be seen that as the concentration of the ISA increases the solubility of technetium increases. As discussed in section 4.5.1, this is most like due to the formation of soluble technetium ISA complexes.

$$TcO_4^- + R + ISA^{y-} \rightleftharpoons Tc-(ISA)^{(y-1)}$$

4.5.4 Gluconic acid

From Fig. 4.24 and Table 9.15 (section 9.1) it can be seen that at low concentrations of gluconic acid there is little effect on the solubility of technetium. However as the concentration of gluconic acid is increased there is an increase in the solubility of technetium. At [Gluconate] = 0.2 mol dm^{-3} approximately all the technetium is in solution.

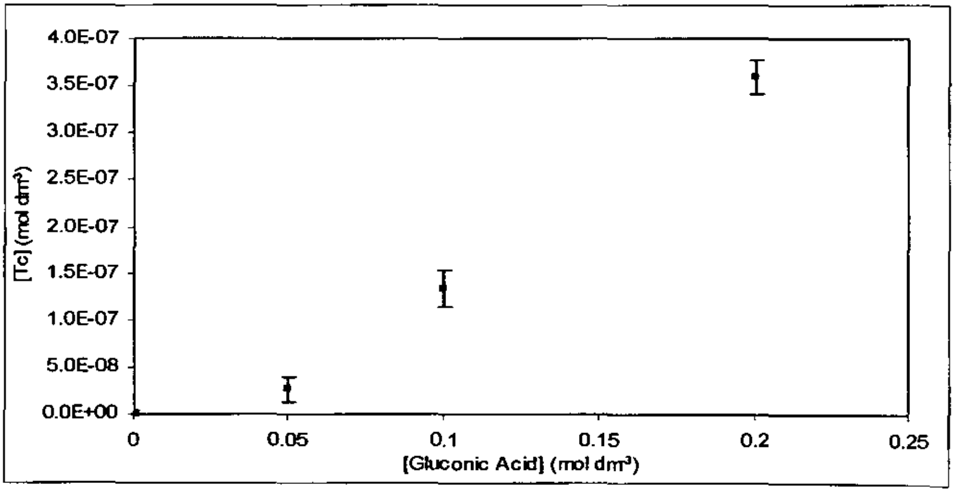


Fig. 4.24: Solubility of technetium (mol dm^{-3}) against the concentration of gluconic acid (mol dm^{-3})

The solubility enhancement factors for the reduction of TcO_4^- in the presence of gluconic acid are shown below (Table 4.18)

[Gluconate] (mol dm^{-3})	SEF	±
0.2	965.4	46.35
0.1	357.7	51.9
0.05	70.0	35.6
0.01	0.9	0.5

Table 4.18: Solubility enhancement factors (SEF) for the solubility of technetium in gluconic acid

From the Fig. 4.24, Table 4.18 and Table 9.15 it can be seen that as the concentration of the gluconic acid increase the solubility of technetium increases. As discussed in section 4.5.1, this is most like due to the formation of soluble technetium gluconate complexes.

$$TcO_4^- + R + Gluc^{y-} \rightleftharpoons Tc-(Gluc)^{(y-1)}$$

4.5.5 Picolinic acid

Fig. 4.25 shows the concentration of technetium (mol dm^{-3}) against concentration of picolinic acid (mol dm^{-3}).

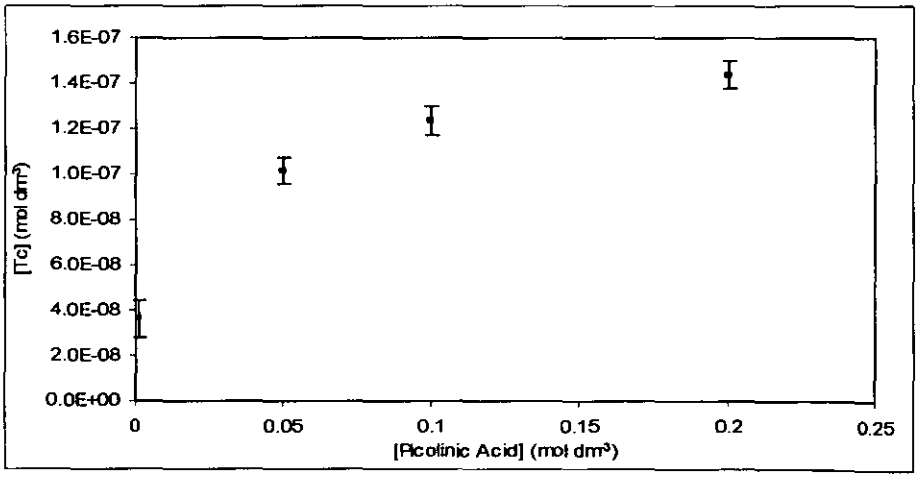


Fig. 4.25: Solubility of technetium (mol dm^{-3}) against the concentration of picolinic acid (mol dm^{-3})

From Fig. 4.25 it can be seen that as the concentration of picolinic acid is increased there is an increase in the solubility of technetium. At [picolinate] = 0.2 mol dm^{-3} approximately all the technetium is in solution.

The solubility enhancement factors for the reduction of TcO_4^- in the presence of picolinic acid are shown below (Table 4.19)

[Picolinate] (mol dm^{-3})	SEF	±
0.2	386.7	16.6
0.1	331.8	17.4
0.05	273.3	15.3
0.01	97.3	22.5

Table 4.19: Solubility enhancement factors (SEF) for the solubility of technetium in picolinic acid

From Fig. 4.25, Table 4.19 and Table 9.15 (section 9.1) it can be seen that as the concentration of the gluconic acid increase the solubility of technetium increases. As discussed in section 4.5.1, this is most like due to the formation of soluble technetium picolinate complexes.

$$TcO_4^- + R + Pic^{y-} \rightleftharpoons Tc\text{-}(Pic)^{(y-1)}$$

4.5.6 Summary

From Fig. 4.26 it can be seen that for all the ligands there is a solubility increase with increasing organic concentration. From Fig. 4.25 it can also be seen that, as expected, ISA and gluconic acid have almost the same behaviour. This is likely due to the similarity of the structures of the 2 organics.

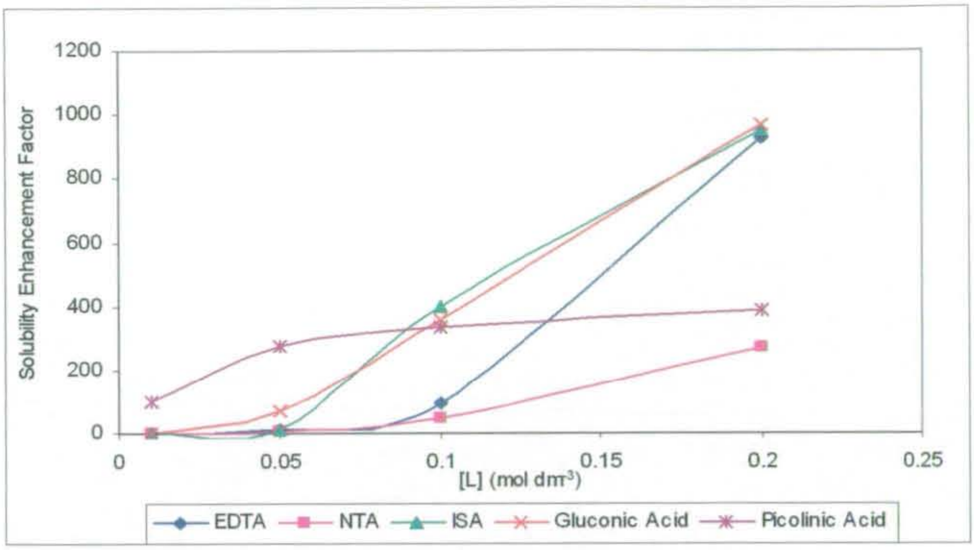


Fig 4.26: Solubility enhancement factors for the reduction of pertechnetate in the presence of organic complexing agents

In section 2.5, it can be seen that the major route for forming technetium complexes is by reducing pertechnetate in the presence of a ligand. From data in this section it appears that the the results above can be explained by the formation of technetium complexes via the mechanism discussed in section 2.5 [15].

At the lowest concentration of the organic the concentration of technetium in solution is low, in some case only slightly above the solubility of Tc(IV) therefore demonstrating that low levels of added organic have no effect on the solubility of reduced technetium. For all the organics investigated, except picolinic acid, it can also be seen that an organic concentration of $>10^{-2}$ mol dm^{-2} is required to give a significant increase in solubility. This is important in terms of repository performance assessment as such high concentrations of organic ligand are not expected to be present on the vault scale.

From the literature it appears that most complexes formed by this mechanism have a technetium oxidation state of +5. It is therefore likely that the complexes formed in this work are Tc(V) complexes.

4.6 Solubility of TcO_2 in the presence and absence of organic complexing agents at high pH

The results obtained in section 4.5 show that as pertechnetate is placed into a reducing environment, in the presence of low molecular weight organics, the reduction to TcO_2(s) does not occur. Instead the results show that, as described in section 2.5, soluble technetium complexes are formed.

In this section the solubility of pre-reduced technetium(IV) is measured in the presence of EDTA, NTA, ISA, gluconic acid and picolinic acid separately. The results from this experiment will give the following information:

1. The effect that the organic ligands under investigation have on the solubility of technetium(IV).
2. If Tc(IV) ligand complexes are formed, are they the same complexes that are formed in section 4.5. i.e. in section 4.5 is TcO_2 produced before complexation with the ligand occurs?

4.6.1 EDTA

From Fig. 4.27 it can be seen that in the presence of EDTA there is an increase in solubility of the Tc(IV). EDTA is therefore complexing with the Tc(IV) and forming a more soluble Tc(IV)-EDTA complex.

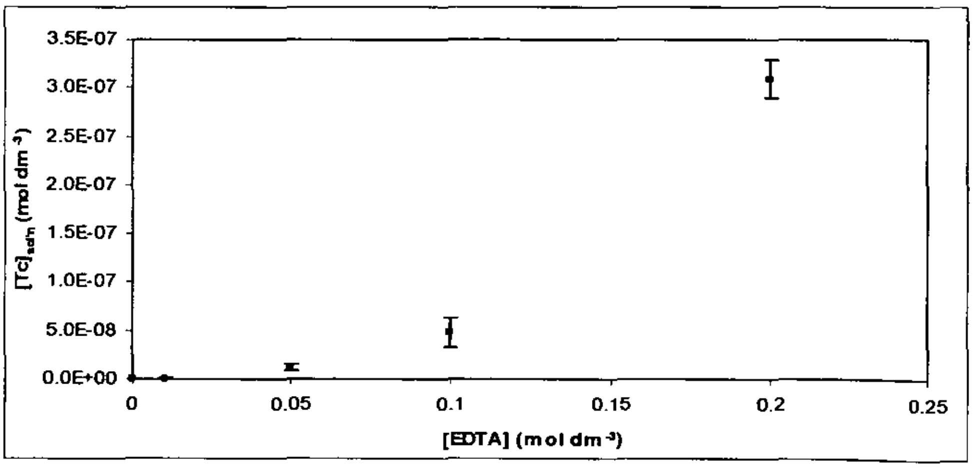


Fig. 4.27: Solubility of technetium(IV) (mol dm^{-3}) against the concentration of EDTA (mol dm^{-3})

$$TcO_2 + EDTA^{y-} \rightleftharpoons Tc(IV)(EDTA)^{(y-1)}$$

The solubility enhancement factors for the solubility of TcO_2 in the presence of EDTA are shown below (Table 4.20)

[EDTA] (mol dm^{-3})	SEF	±
0.2	832.5	53.3
0.1	127.9	40.3
0.05	32.0	10.2
0.01	2.3	0.4

Table 4.20: Solubility enhancement factors (SEF) for the solubility of TcO_2 in EDTA

4.6.2 NTA

Fig. 4.28 and Table 9.18 shows the solubility of Tc(IV) in the presence of different concentrations of NTA.

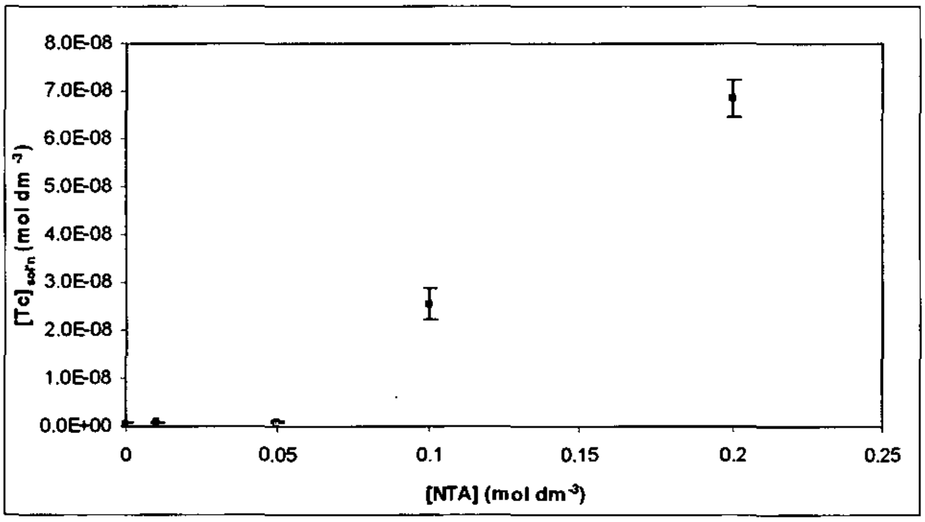


Fig. 4.28: Solubility of technetium(IV) (mol dm^{-3}) against the concentration of NTA (mol dm^{-3})

From Fig. 4.28 it can be seen that in the presence of NTA there is an increase in solubility of Tc(IV). NTA is therefore complexing with the Tc(IV) and forming a more soluble Tc(IV)-NTA complex.

$$TcO_2 + NTA^{y-} \rightleftharpoons Tc(IV)(NTA)^{(y-1)}$$

The solubility enhancement factors for the solubility of TcO_2 in the presence of NTA are shown below (Table 4.21)

[NTA] (mol dm^{-3})	SEF	±
0.2	184.1	10.4
0.1	67.8	9.0
0.05	1.6	0.2
0.01	1.1	0.1

Table 4.21: Solubility enhancement factors (SEF) for the solubility of TcO_2 in NTA

4.6.3 ISA

From Fig. 4.29 and Table 9.19 it can be seen that in the presence of ISA there is an increase in solubility of technetium(IV). ISA is therefore complexing with the Tc(IV) and forming a more soluble Tc(IV)-ISA complex.

$$TcO_2 + ISA^{y-} \rightleftharpoons Tc(IV)(ISA)^{(y-1)}$$

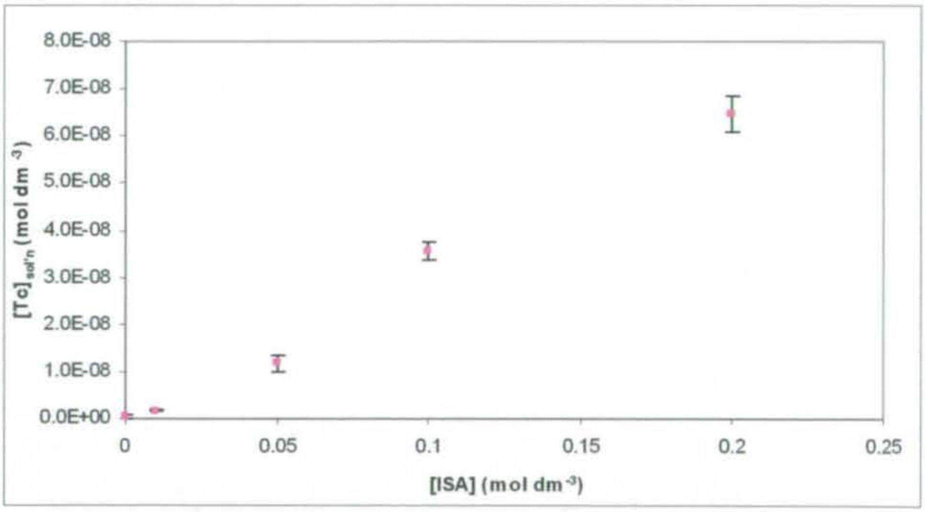


Fig. 4.29: Solubility of technetium(IV) (mol dm^{-3}) against the concentration of ISA (mol dm^{-3})

The solubility enhancement factors for the solubility of TcO_2 in the presence of ISA are shown below (Table 4.22)

[ISA] (mol dm^{-3})	SEF	±
0.2	173.8	10.5
0.1	95.9	5.2
0.05	31.8	4.6
0.01	3.5	0.7

Table 4.22: Solubility enhancement factors (SEF) for the solubility of TcO_2 in ISA

4.6.4 Gluconic acid

Fig. 4.30 and Table 9.20 shows the solubility of Tc(IV) in the presence of different concentrations of NTA.

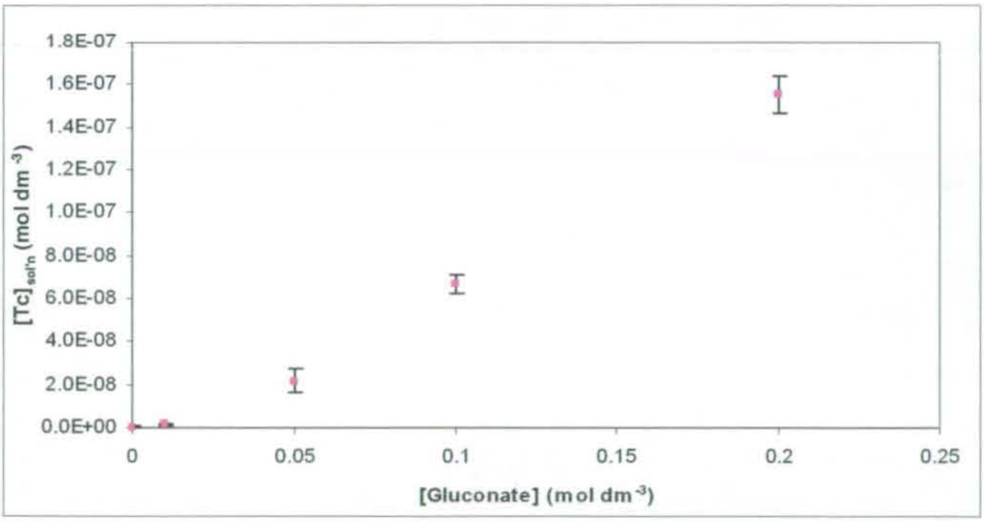


Fig. 4.30: Solubility of technetium(IV) (mol dm^{-3}) against the concentration of gluconic acid (mol dm^{-3})

From Fig. 4.30 it can be seen that in the presence of gluconic acid there is an increase in solubility of the Tc(IV). Gluconic acid is complexing with Tc(IV) and forming a more soluble Tc(IV)-Gluconate complex.

$$TcO_2 + Gluc^{y-} \rightleftharpoons Tc(IV)(Gluc)^{(y-1)}$$

The solubility enhancement factors for the solubility of TcO_2 in the presence of gluconic acid are shown below (Table 4.23)

[Gluconate] (mol dm^{-3})	SEF	±
0.2	417.2	24.1
0.1	178.8	11.7
0.05	58.4	15.1
0.01	4.2	1.5

Table 4.23: Solubility enhancement factors (SEF) for the solubility of TcO_2 in gluconic acid

4.6.5 Picolinic acid

From Fig. 4.31 and Table 9.21 it can be seen that in the presence of picolinic acid there is an increase in solubility of the Tc(IV). Picolinic acid is therefore complexing with the Tc(IV) and forming a more soluble Tc(IV)-Picolinate complex.

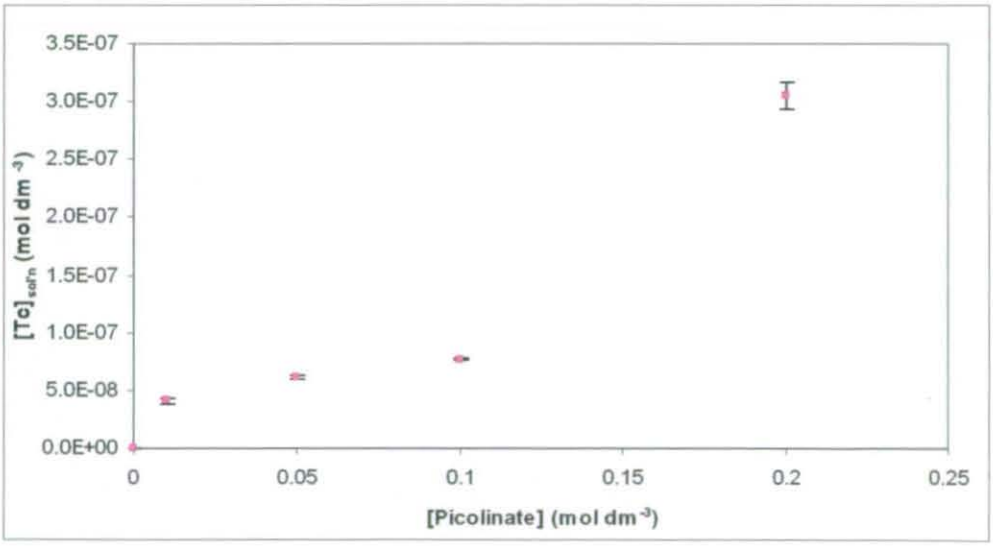


Fig. 4.31: Solubility of technetium(IV) (mol dm^{-3}) against the concentration of picolinic acid (mol dm^{-3})

$$TcO_2 + Pic^{y-} \rightleftharpoons Tc(IV)(Pic)^{(y-1)}$$

The solubility enhancement factors for the solubility of TcO_2 in the presence of picolinic acid are shown below (Table 4.24)

[Picolinate] (mol dm^{-3})	SEF	±
0.2	821.2	30.5
0.1	207.1	2.5
0.05	164.1	5.7
0.01	110.4	5.9

Table 4.24: Solubility enhancement factors (SEF) for the solubility of TcO_2 in picolinic acid

4.6.6 Summary

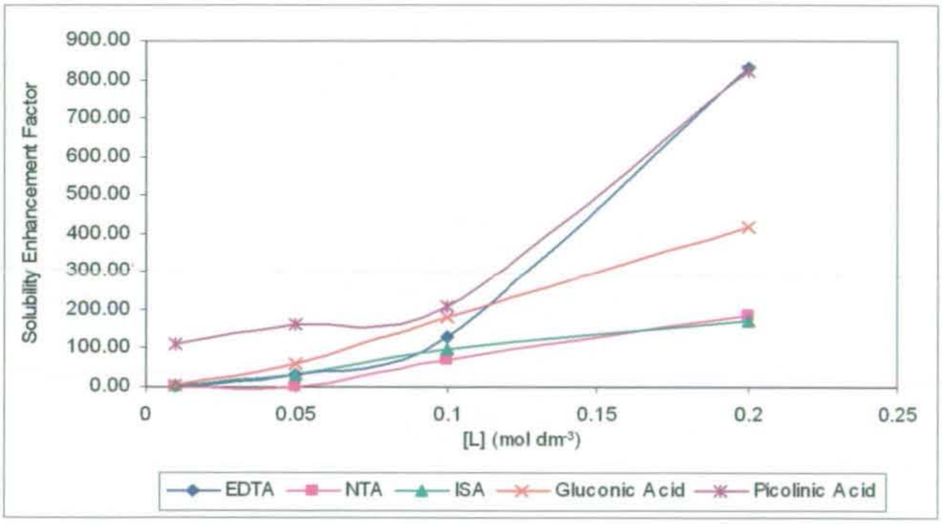


Fig. 4.32: Solubility enhancement factors for the solubility of Tc(IV) in the presence of organic complexing agents

From Fig. 4.32 it can be seen that for all the ligands there is a solubility increase with increasing organic concentration, this is due to the formation of technetium complexes. The complexes formed are likely to be technetium(IV) complexes, as the ligands do not have any oxidising potential to reoxidise Tc(IV) back upto another oxidation state of technetium.

As shown in section 4.5 at the lowest concentration of the organic the concentration of technetium in solution is low, in some case only slightly above the solubility of Tc(IV) therefore demonstrating that low levels of added organic have no effect on the solubility of reduced technetium. For all the organics investigated, except picolinic acid, it can also be seen that an organic concentration of $>10^{-2}$ mol dm^{-2} is required to give a significant increase in solubility. This is important in terms of repository performance assessment as such high concentrations of organic ligand are not expected to be present on the vault scale.

4.7 Comparison of the 2 reaction pathways

Data in sections 4.5 and 4.6 show that EDTA, NTA, ISA, gluconic acid and picolinic acid have a significant effect on the solubility of technetium under reducing conditions. Data from section 4.5 suggests that as the pertechnetate is reduced the ligand present stabilises the reduced intermediate of technetium producing technetium(V) complexes [15]. This is the standard method for synthesis technetium complexes.

Data in section 4.6 suggests that the ligand present reacts with the sparingly soluble $TcO_2(s)$ and increases the solubility of technetium by producing technetium(IV) complexes. The presence of the reducing agent rules out the possibility of reoxidisation of the $TcO_2(s)$ and as stated in section 4.6 the ligands present do not have oxidising potential and therefore can not reoxidise the $TcO_2(s)$.

The following section compares the results of the different reaction pathways with the same ligand.

4.7.1 EDTA

From Fig. 4.33 it can be seen that there is no difference between the solubility enhancement factors for the 2 different reaction pathways. This suggests that in both cases Tc(IV) complexes are being formed.

$$TcO_2 + EDTA^{y-} \rightleftharpoons (Tc(IV)EDTA)^{(1+y)-}$$

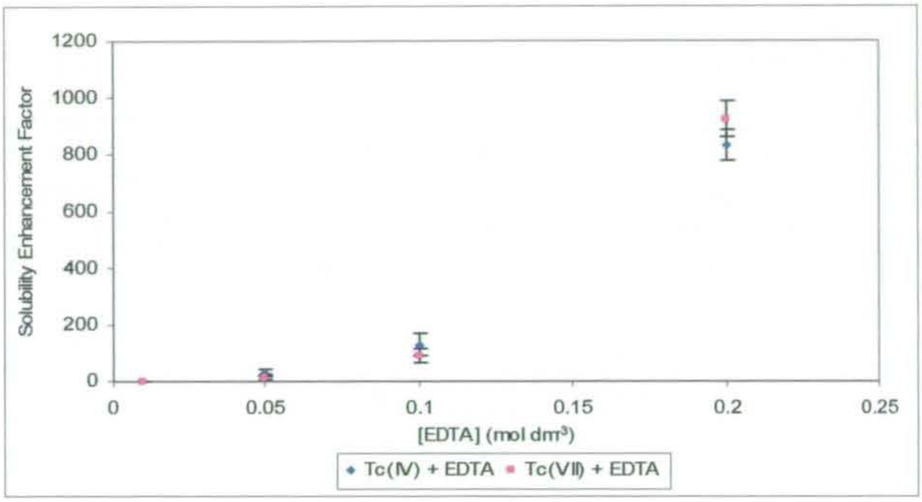


Fig. 4.33: Comparison of the solubility enhancement factors for the effects of EDTA on the 2 different reaction pathways

4.7.2 NTA

From Fig. 4.34 it can be seen that solubility enhancement factors for the effects of NTA on the 2 different reaction pathways are different.

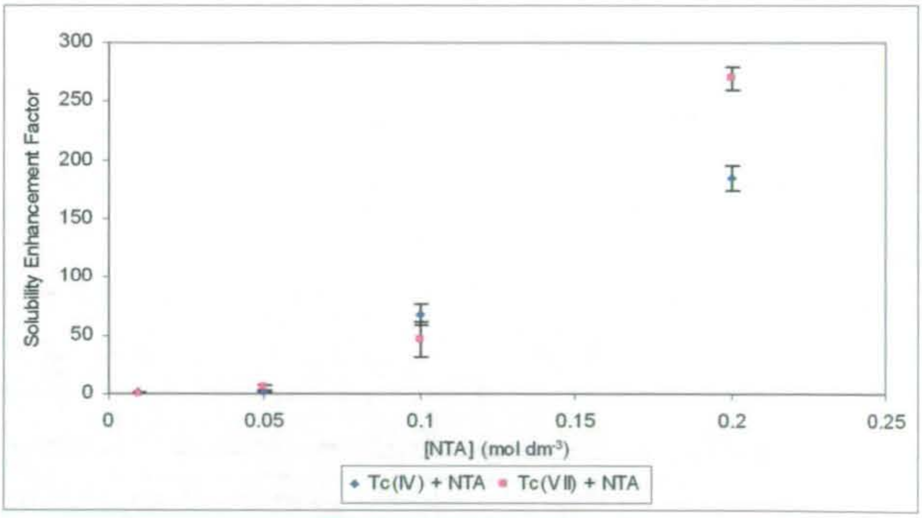


Fig. 4.34: Comparison of the solubility enhancement factors for the effects of NTA on the 2 different reaction pathways

This suggests that 2 different complexes are being formed. As discussed above in section 4.6 when TcO_4^- is reduced in the presence of NTA a soluble complex is formed and TcO_2 is not formed. When TcO_2 is produced and then contacted with NTA soluble complexes are formed.

$$TcO_4^- + R + NTA^{y-} \rightleftharpoons (Tc(x)NTA)^{(-1+y)-} \quad (\text{where } x > 4)$$

$$TcO_2 + NTA^{y-} \rightleftharpoons (Tc(IV)NTA)^{(1+y)-}$$

Where x represents the oxidation state of technetium.

4.7.3 ISA

From Fig. 4.35 it can be seen that the solubility enhancement factors for the effects of ISA on the 2 different reaction pathways are different.

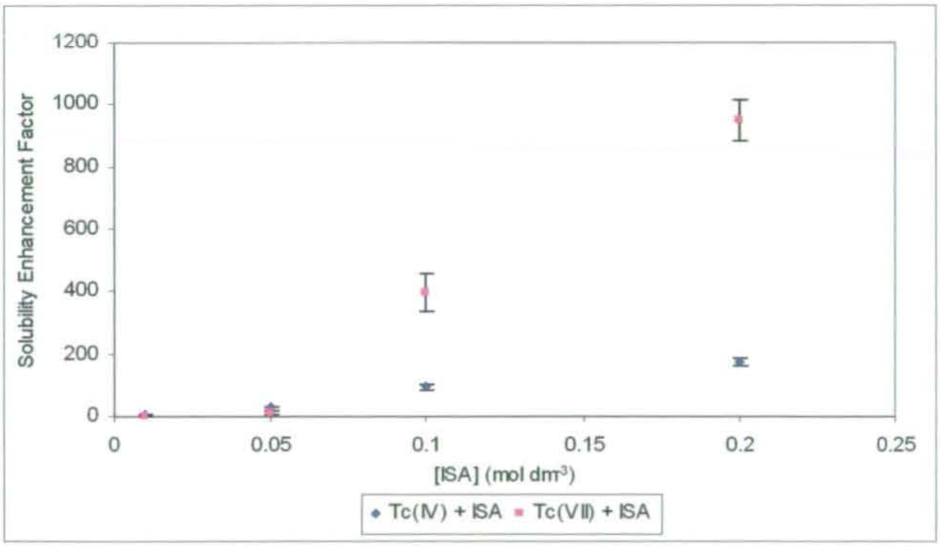


Fig. 4.35: Comparison of the solubility enhancement factors for the effects of ISA on the 2 different reaction pathways

From Fig. 4.35 it can be seen that solubility enhancement factors for the effects of ISA on the 2 different reaction pathways are different. This suggests that 2 different complexes are being formed. As discussed above in section 4.6 it appears that when TcO_4^- is reduced in the presence of ISA a soluble complex is formed and TcO_2 is not formed. When TcO_2 is produced and then contacted with ISA soluble technetium(IV) - ISA complexes are formed.

$$TcO_4^- + R + ISA^{y-} \rightleftharpoons (Tc(x)ISA)^{(-1+y)-} \quad (\text{where } x > 4)$$

$$TcO_2 + ISA^{y-} \rightleftharpoons (Tc(IV)ISA)^{(1+y)-}$$

Where x represents the oxidation state of technetium.

4.7.4 Gluconic acid

From Fig. 4.36 it can be seen that the solubility enhancement factors for the effects of gluconic acid on the 2 different reaction pathways are different.

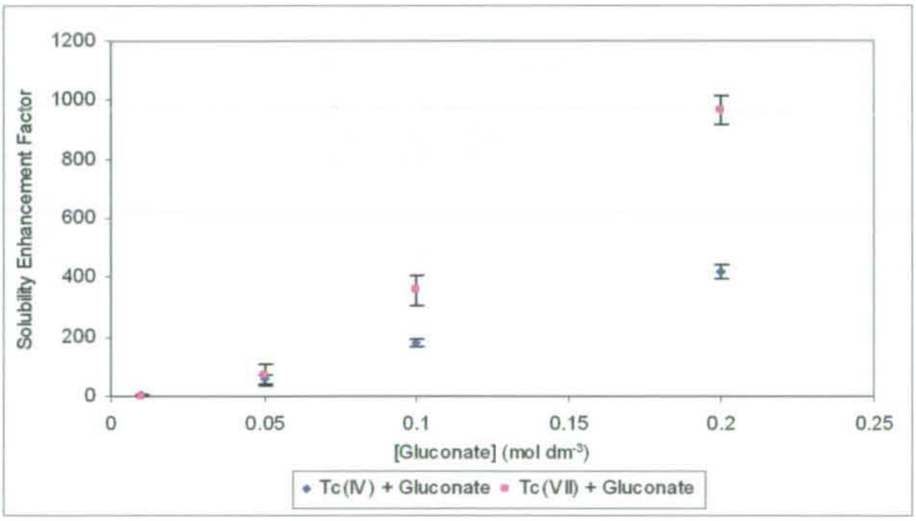


Fig. 4.36: Comparison of the solubility enhancement factors for the effects of gluconic acid on the 2 different reaction pathways

From Fig. 4.36 it can be seen that solubility enhancement factors for the effects of gluconate on the 2 different reaction pathways are different. This suggests that 2 different complexes are being formed. As discussed above in section 4.6 when TcO_4^- is reduced in the presence of gluconate a soluble complex is formed and TcO_2 is not formed. When TcO_2 is produced and then contacted with gluconate a soluble complex is formed.

$$TcO_4^- + R + Glu^{y-} \rightleftharpoons (Tc(x)Glu)^{(-1+y)-} \quad (\text{where } x > 4)$$

$$TcO_2 + Glu^{y-} \rightleftharpoons (Tc(IV)Glu)^{(1+y)-}$$

Where x represents the oxidation state of technetium.

4.7.5 Picolinic acid

From Fig. 4.37 it can be seen that the solubility enhancement factors for the effects of picolinic acid on the 2 different reaction pathways are different.

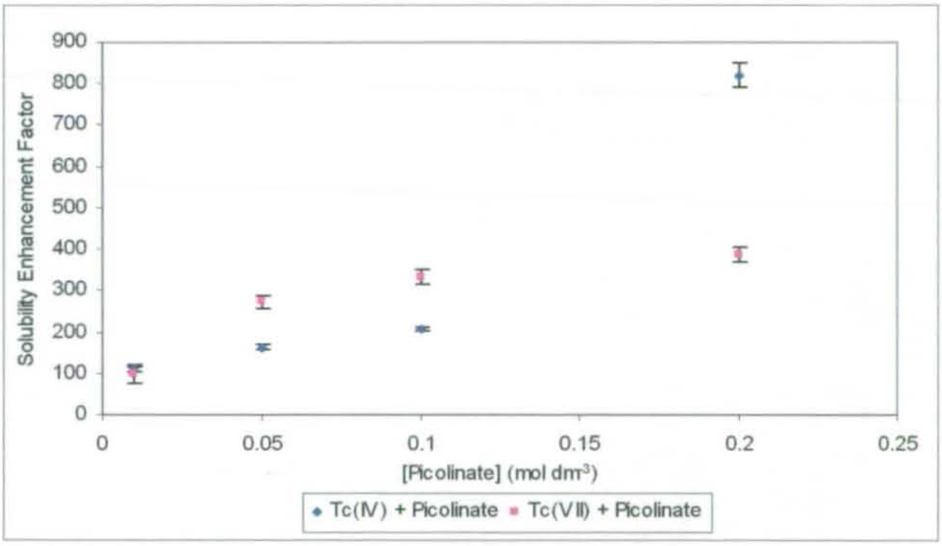


Fig. 4.37: Comparison of the solubility enhancement factors for the effects of picolinic acid on the 2 different reaction pathways

From Fig. 4.37 it can be seen that solubility enhancement factors for the effects of picolinate on the 2 different reaction pathways are different. This suggests that 2 different complexes are being formed. As discussed above in section 4.6 when TcO_4^- is reduced in the presence of picolinate a soluble complex is formed and TcO_2 is not formed. When TcO_2 is produced and then contacted with picolinate a soluble complex is formed.

$$TcO_4^- + R + Pic^{y-} \rightleftharpoons (Tc(x)Pic)^{(-1+y)-} \quad (\text{where } x > 4)$$

$$TcO_2 + Pic^{y-} \rightleftharpoons (Tc(IV)Pic)^{(1+y)-}$$

Where x represents the oxidation state of technetium.

4.7.6 Summary and other evidence

From section 4.5 and 4.6 it can be seen that the presence of individual ligands has an effect on the behaviour of technetium in reducing conditions. When TcO_4^- is reduced in the presence of the ligands it can be seen that the solubility of technetium(IV) is not reached suggesting that complexation occurs as described in section 2.5 and section 4.5. When TcO_4^- is reduced to TcO_2 and is then contacted with the individual ligands there is an increase in the solubility of the technetium. A recent study completed at the Los Alamos National Laboratory, USA [61] supports the findings of this thesis.

In this work completed by Berning *et al* [61] an attempt was made to recreate the work by Lukens *et al* [45]. However, a ^{137}Cs source (37 MBq) was used for irradiation of the pertechnetate samples instead of the 2.22 ×10^7 MBq ^{60}Co source used by Lukens *et al* [45]. Despite the use of this weak radiation source the solutions turned pink within 24 hours, indicating formation of the ^{99}Tc-gluconate complex. As a control, an identical sample was allowed to react in the absence of ^{137}Cs radiation but exposed to standard laboratory lighting, and a third sample was kept in the dark for 24 hours. Both of the controls and the irradiated sample contained the ^{99}Tc-gluconate complex in approximately equal chemical yields, indicating that spontaneous reduction and complexation of TcO_4^- is possible without applying an external radiation source. Work was then carried out using several different ligands and it was observed that complexation occurred for most ligands investigated during the "autoreduction" of pertechnetate. After analysis by UV-vis spectroscopy it was shown that the complexes formed were either Tc(IV) or Tc(V) complexes.

4.8 Calculation of Tc(IV) conditional stability constants using the solubility product approach method

By using data measured in section 4.6 and the solubility product (section 4.2) it is possible to determine the stability constants for the complexes formed between technetium(IV) and the ligands under investigation.

4.8.1 EDTA

By measuring the solubility increase of Tc(IV), in the presence of different concentrations of EDTA (Table 9.17), it is possible to calculate the conditional stability constant of Tc(IV) and EDTA using the solubility product approach method (section 3.3.10).

Sample	pH	[EDTA] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.42	0.2	2197.6	3.25E-07	2.23E-21	3.24E-07	14.9
2	13.33	0.2	2031.4	2.99E-07	2.75E-21	2.98E-07	14.7
3	13.31	0.2	2157.3	3.18E-07	2.87E-21	3.18E-07	14.7
4	13.32	0.2	2207.0	3.26E-07	2.82E-21	3.26E-07	14.8
5	13.23	0.2	1911.7	2.80E-07	3.45E-21	2.80E-07	14.6
6	13.46	0.1	328.9	4.70E-08	2.03E-21	4.66E-08	14.4
7	13.41	0.1	259.7	3.71E-08	2.28E-21	3.67E-08	14.2
8	13.32	0.1	291.6	4.16E-08	2.82E-21	4.13E-08	14.2
9	13.53	0.1	513.3	7.35E-08	1.74E-21	7.31E-08	14.6
10	13.36	0.1	270.2	3.86E-08	2.55E-21	3.82E-08	14.2
11	13.32	0.05	119.5	1.70E-08	2.86E-21	1.66E-08	14.1
12	13.21	0.05	52.6	7.36E-09	3.63E-21	6.99E-09	13.6
13	13.12	0.05	94.3	1.33E-08	4.43E-21	1.30E-08	13.8
14	13.40	0.05	91.3	1.29E-08	2.35E-21	1.25E-08	14.0
15	13.30	0.05	63.7	8.96E-09	2.95E-21	8.58E-09	13.8

Table 4.25: Calculation of Tc(IV)-EDTA stability constants

From Table 4.25 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and EDTA are within the range 13.6 – 14.9. The mean log of the stability constant is 14.3 ± 0.6.

The stoichiometry of the complexes has been assumed to be 1:1 and, therefore, the algebra used could be incorrect for the calculation of the individual constants if the complex isn't 1:1.

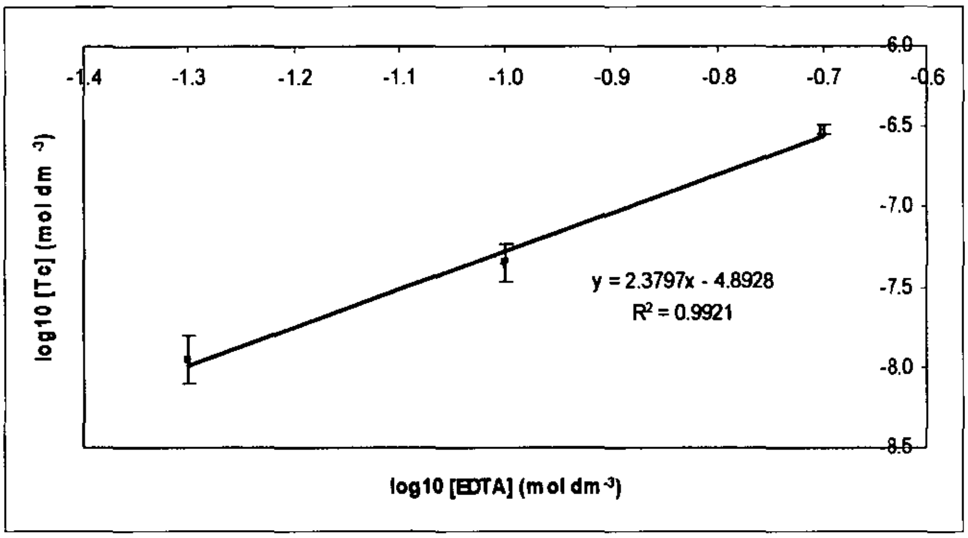


Fig. 4.38: $\log_{10}$ [EDTA] (mol dm^{-3}) against $\log_{10}$ [Tc] (mol dm^{-3})

By plotting the log of the EDTA concentration against the log of the technetium concentration in solution (Fig. 4.38) it can be seen that the plot is linear. It can, therefore, be stated that there is complexation occurring between EDTA and technetium(IV) in solution, because the increase in the complex concentration is dependent on the concentration of EDTA.

4.8.2 NTA

By measuring the solubility increase of Tc(IV), in the presence of different concentrations of NTA (Table 9.18), it is possible to calculate the conditional stability constant of Tc(IV) and NTA using the solubility product approach method (section 2.1.2).

Sample	pH	[NTA] (mol dm^{-3})	dpm	$[Tc]_{solution}$ (mol dm^{-3})	$[Tc^{4+}]$ (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.43	0.2	436.0	6.34E-08	2.18E-21	6.31E-08	14.2
2	13.26	0.2	507.0	7.38E-08	3.22E-21	7.35E-08	14.1
3	13.33	0.2	476.0	6.93E-08	2.75E-21	6.89E-08	14.1
4	13.36	0.2	456.5	6.65E-08	2.56E-21	6.61E-08	14.1
5	13.36	0.2	474.9	6.91E-08	2.56E-21	6.88E-08	14.1
6	13.33	0.1	157.7	2.27E-08	2.74E-21	2.23E-08	13.9
7	13.03	0.1	158.6	2.28E-08	5.47E-21	2.25E-08	13.6
8	13.37	0.1	162.9	2.35E-08	2.54E-21	2.31E-08	14.0
9	13.34	0.1	210.8	3.05E-08	2.67E-21	3.01E-08	14.1
10	13.37	0.1	184.5	2.66E-08	2.54E-21	2.62E-08	14.0
11	13.36	0.05	6.2	5.55E-10	2.56E-21	1.83E-10	12.2
12	13.43	0.05	5.8	5.06E-10	2.18E-21	1.33E-10	12.1
13	13.24	0.05	7.2	6.72E-10	3.42E-21	3.00E-10	12.2

Table 4.26: Calculation of Tc(IV)-NTA stability constants

From Table 4.26 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and NTA are within the range 12.1 – 14.2. The mean log of the stability constant is 13.8 ± 1.0.

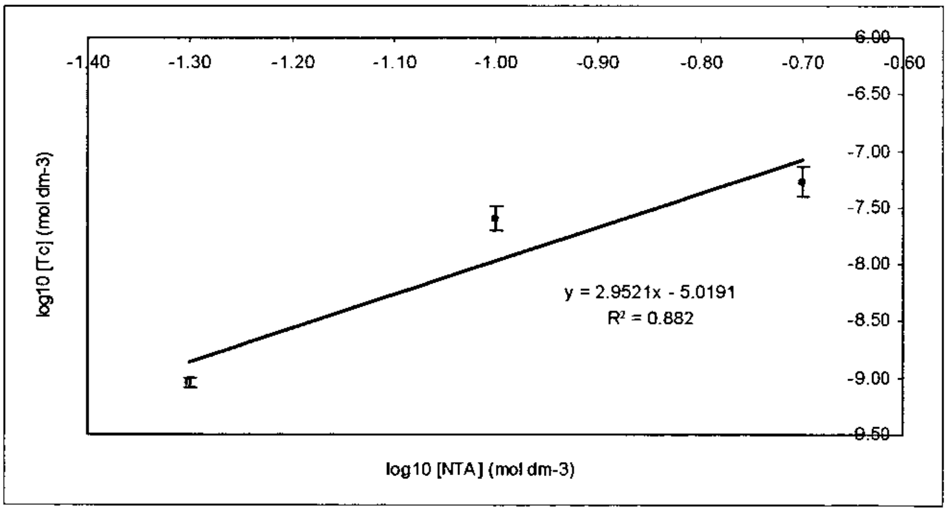


Fig. 4.39: $\log_{10}$ [NTA] (mol dm^{-3}) against $\log_{10}$ [Tc] (mol dm^{-3})

Fig. 4.39 shows a linear graph. As in section 4.8.1, the graph shows that the complex concentration is dependent on the concentration of NTA, indicating that complexation occurs between the technetium and NTA.

4.8.3 ISA

By measuring the solubility increase of Tc(IV), in the presence of different concentrations of ISA (Table 9.19), it is possible to calculate the conditional stability constant of Tc(IV) and ISA using the solubility product approach method (section 2.1.2).

Sample	pH	[ISA] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.37	0.2	477.3	6.95E-08	3.20E-21	6.91E-08	14.0
2	13.33	0.2	429.7	6.25E-08	3.45E-21	6.21E-08	14.0
3	13.46	0.2	435.6	6.34E-08	2.56E-21	6.30E-08	14.1
4	13.42	0.2	465.5	6.78E-08	2.80E-21	6.74E-08	14.1
5	13.37	0.2	412.1	5.99E-08	3.20E-21	5.96E-08	14.0
6	13.37	0.1	244.9	3.55E-08	3.17E-21	3.51E-08	14.0
7	13.27	0.1	232.0	3.36E-08	4.03E-21	3.32E-08	13.9
8	13.14	0.1	256.0	3.71E-08	5.43E-21	3.67E-08	13.8
9	13.53	0.1	262.9	3.81E-08	2.18E-21	3.77E-08	14.2
10	13.26	0.1	235.6	3.41E-08	4.05E-21	3.37E-08	13.9
11	13.69	0.05	96.8	1.38E-08	1.51E-21	1.34E-08	14.3
12	13.32	0.05	72.0	1.02E-08	3.53E-21	9.79E-09	13.7
13	13.33	0.05	85.0	1.21E-08	3.45E-21	1.17E-08	13.8
14	13.33	0.05	71.0	1.00E-08	3.45E-21	9.64E-09	13.7
15	13.13	0.05	92.5	1.32E-08	5.47E-21	1.28E-08	13.7

Table 4.27: Calculation of Tc(IV)-ISA stability constants

From Table 4.27 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and ISA are within the range 13.7 – 14.1. The mean log of the stability constant is 13.9 ± 0.3.

Fig. 4.40 shows a linear graph. As in section 4.8.1, the graph shows that the complex concentration is dependent on the concentration of ISA, indicating that complexation occurs between the technetium and ISA.

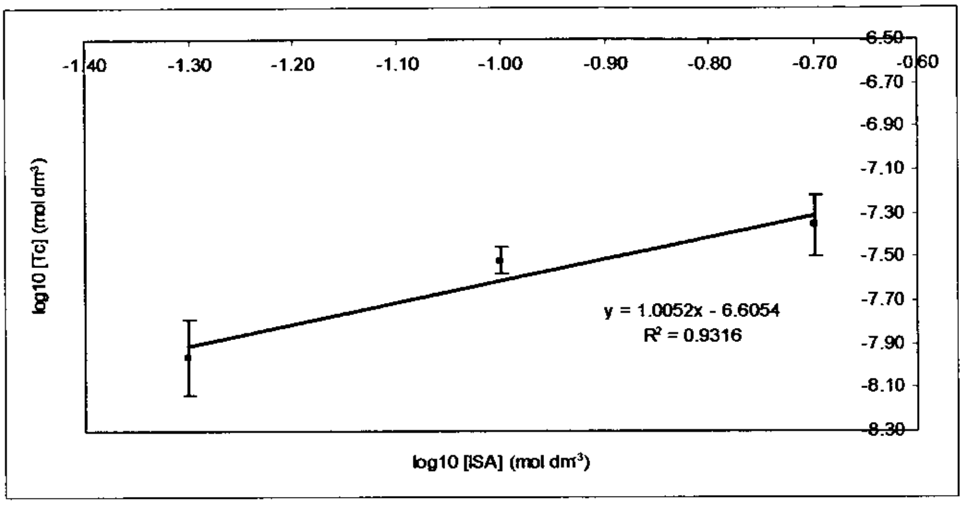


Fig. 4.40: Log_{10} [ISA] (mol dm^{-3}) against Log_{10} [Tc] (mol dm^{-3})

4.8.4 Gluconic acid

By measuring the solubility increase of Tc(IV), in the presence of different concentrations of gluconic acid (Table 9.20), it is possible to calculate the conditional stability constant of Tc(IV) and gluconic acid using the solubility product approach method (section 2.1.2).

Sample	pH	[Gluc] (mol dm^{-3})	dpm	$[Tc]_{solution}$ (mol dm^{-3})	$[Tc^{4+}]$ (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.26	0.2	1090.2	1.52E-07	4.05E-21	1.51E-07	14.3
2	13.37	0.2	1211.7	1.71E-07	3.20E-21	1.70E-07	14.4
3	13.36	0.2	1110.3	1.55E-07	3.21E-21	1.54E-07	14.4
4	13.30	0.2	1083.6	1.51E-07	3.75E-21	1.50E-07	14.3
5	13.36	0.2	1067.8	1.48E-07	3.23E-21	1.48E-07	14.4
6	13.26	0.1	420.0	6.11E-08	4.05E-21	6.07E-08	14.2
7	13.25	0.1	461.7	6.72E-08	4.17E-21	6.68E-08	14.2
8	13.33	0.1	434.9	6.33E-08	3.45E-21	6.29E-08	14.3
9	13.55	0.1	493.8	7.19E-08	2.08E-21	7.15E-08	14.5
10	13.37	0.1	473.4	6.89E-08	3.20E-21	6.86E-08	14.3
11	13.33	0.05	106.2	1.52E-08	3.50E-21	1.48E-08	13.9
12	13.35	0.05	135.7	1.95E-08	3.33E-21	1.91E-08	14.1
13	13.36	0.05	130.3	1.87E-08	3.25E-21	1.83E-08	14.1
14	13.26	0.05	191.9	2.77E-08	4.04E-21	2.73E-08	14.1
15	13.62	0.05	190.3	2.75E-08	1.80E-21	2.71E-08	14.5

Table 4.28: Calculation of Tc(IV)-gluconate stability constants

From Table 4.28 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and gluconic acid are within the range 13.9 – 14.5. The mean log of the stability constant is 14.2 ± 0.4.

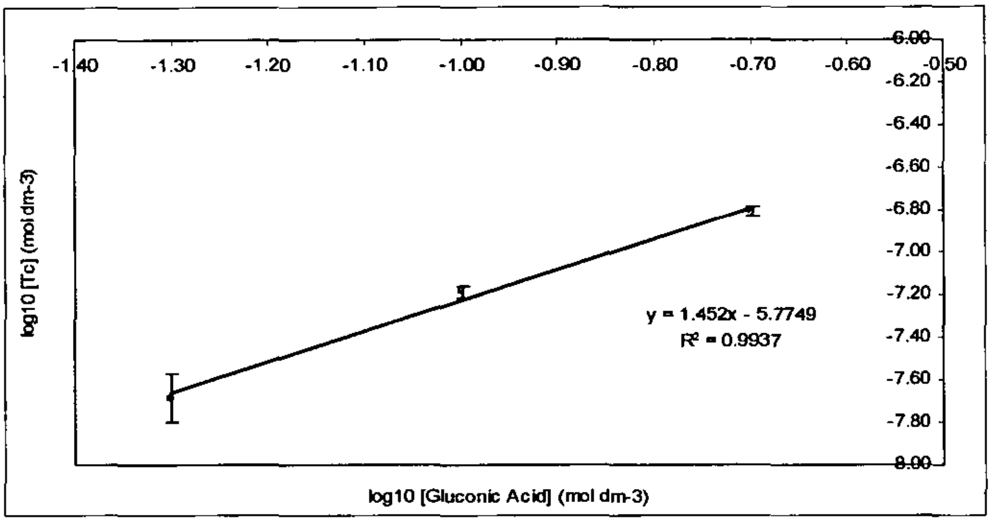


Fig. 4.41: Log$_{10}$ [Gluconic Acid] (mol dm^{-3}) against Log$_{10}$ [Tc] (mol dm^{-3})

Fig. 4.41 shows a linear graph. As in section 4.8.1, it can be seen that the complex concentration is dependent on the concentration of gluconic acid, indicating that complexation occurs between the technetium and gluconic acid.

4.8.5 Picolinic acid

By measuring the solubility increase of Tc(IV), in the presence of different concentrations of picolinic acid (Table 9.21), it is possible to calculate the conditional stability constant of Tc(IV) and picolinic acid using the solubility product approach method (section 2.1.2).

Sample	pH	[Pic] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.32	0.2	2044.4	2.99E-07	2.85E-21	2.99E-07	14.7
2	13.43	0.2	2211.6	3.23E-07	2.19E-21	3.23E-07	14.9
3	13.40	0.2	2015.0	2.95E-07	2.37E-21	2.94E-07	14.8
4	13.04	0.2	2057.7	3.01E-07	5.34E-21	3.01E-07	14.4
5	13.35	0.2	2112.4	3.09E-07	2.63E-21	3.09E-07	14.8

Table 4.29 continues on page 119

6	13.40	0.1	524.8	7.65E-08	2.37E-21	7.61E-08	14.5
7	13.33	0.1	525.0	7.65E-08	2.76E-21	7.61E-08	14.4
8	13.10	0.1	523.6	7.63E-08	4.65E-21	7.59E-08	14.2
9	13.24	0.1	530.8	7.73E-08	3.40E-21	7.70E-08	14.4
10	13.32	0.1	539.0	7.85E-08	2.84E-21	7.82E-08	14.4
11	13.30	0.05	430.5	6.26E-08	2.96E-21	6.23E-08	14.6
12	13.25	0.05	405.1	5.89E-08	3.33E-21	5.86E-08	14.5
13	13.13	0.05	403.0	5.86E-08	4.41E-21	5.82E-08	14.4
14	13.37	0.05	424.0	6.17E-08	2.54E-21	6.13E-08	14.7
15	13.33	0.05	434.3	6.32E-08	2.74E-21	6.28E-08	14.7
16	13.30	0.01	260.5	3.78E-08	2.94E-21	3.74E-08	15.1
17	13.14	0.01	292.7	4.25E-08	4.30E-21	4.21E-08	15.0
18	13.30	0.01	287.9	4.18E-08	2.98E-21	4.14E-08	15.1
19	13.28	0.01	298.0	4.32E-08	3.07E-21	4.29E-08	15.1
20	13.36	0.01	276.4	4.01E-08	2.57E-21	3.97E-08	15.2

Table 4.29: Calculation of Tc(IV)-Picolinate stability constants

From Table 4.29 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and picolinic acid are within the range 14.2 – 15.2. The mean log of the stability constant is 14.9 ± 0.3.

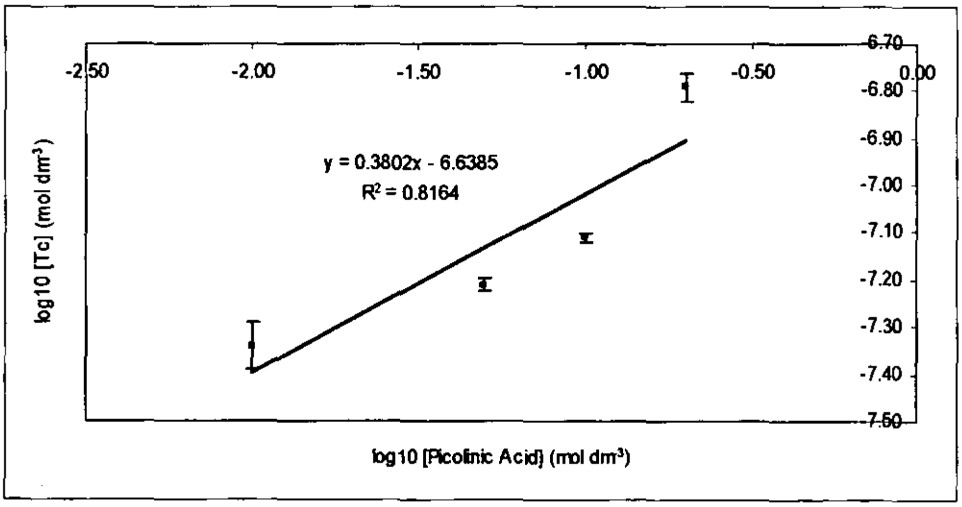


Fig. 4.42: Log$_{10}$ [Picolinic Acid] (mol dm^{-3}) against Log$_{10}$ [Tc] (mol dm^{-3})

Fig. 4.42 shows a linear graph. As in section 4.8.1 it can be seen that the complex concentration is dependent on the concentration of picolinic acid, indicating that complexation occurs between the technetium and picolinic acid.

4.8.6 Summary

Reaction	β	$\log_{10} \beta$	±
$TcO(OH)^{+} + EDTA^{y-} \rightleftharpoons (Tc(IV)EDTA)^{(1+y)-}$	2.19E+14	14.3	0.6
$TcO(OH)^{+} + NTA^{y-} \rightleftharpoons (Tc(IV)NTA)^{(1+y)-}$	6.05E+13	13.8	1.0
$TcO(OH)^{+} + ISA^{y-} \rightleftharpoons (Tc(IV)ISA)^{(1+y)-}$	8.17E+13	13.9	0.3
$TcO(OH)^{+} + Gluc^{y-} \rightleftharpoons (Tc(IV)Gluc)^{(1+y)-}$	1.57E+14	14.2	0.4
$TcO(OH)^{+} + Pic^{y-} \rightleftharpoons (Tc(IV)Pic)^{(1+y)-}$	7.06E+14	14.9	0.3

Table 4.30: Conditional stability constants of Tc(IV)

From Table 4.30 it can be seen that the log of the stability constants calculated for the reactions of Tc(IV) and the individual ligands are within the range 13.8 – 14.9. The stability constants calculated for the technetium ligand complexes are very similar, this is due to the similar nature of the ligands investigated.

At present there are only literature stability constants for Tc(IV)-EDTA and Tc(IV)-NTA [62, 63]. These values are shown in Table 4.31.

Complex	Stoichiometry	Log K [61, 62]
Tc(IV) - EDTA	ML	19.1
Tc(IV) - NTA	ML	13.8
Tc(IV) - NTA	ML_2	25.7

Table 4.31: Literature stability constants [62, 63]

The difference in the stability constants presented from work reported in this thesis and those given in the literature are due to the different conditions used in the two different sets of experiments. Therefore, it is possible that the complexes formed are not the same. The work completed by Gorski and Koch [62, 63] was carried out at pH 1-2 the work completed for this study was carried out at pH 12.5-13.3. In a paper by Geraedts *et al*, [64] speciation calculations with the CHESS speciation programme (using EQ3/6 database) were completed, and from this it was shown that the Tc^{3+} species is dominant at low pH. At higher pH (>4) Tc(IV) becomes the dominant species. Therefore, it is possible that the complexes formed in the report by Gorski and Koch are Tc(III) complexes and the complexes formed in this work are Tc(IV) complexes.

The report by Gorski and Koch [62, 63] states that when NTA was in large excess, in the conditions used throughout their experimental work, the complex formed was an ML_2 and not ML.

However, as well as the difference in the technetium speciation there is also a large difference in the NTA speciation. Using JChess [50] it is possible to speciate NTA in solution when 1 g is placed into 1 dm^3 at the pH's of 1.5 and 13.3 (Table 4.32)

	Concentration (mol dm^{-3})	
	pH 1.5	**pH 13.3**
NTA[3-]	3.99E-13	5.20E-03
NTAH[2-]	1.35E-04	1.41E-06
NTAH2[-]	2.42E-03	2.65E-17
NTAH3(aq)	4.70E-04	7.13E-30
NTAH4[+]	2.17E-03	5.99E-41

Table 4.32: Speciation of NTA at different pH's

From Table 4.32 it can be seen that at pH 1.5 the dominant NTA species is $NTAH_2^-$ whereas at pH 13.3 the dominant NTA species is NTA^{3-}. Therefore at pH 13.3 an ML_2 complex will have a charge of 5-, which is very unlikely to be stable.

4.9 Solubility of $SnCl_2$ in the presence and absence of organics complexing agents at high pH

The use of $SnCl_2$ as a reducing agent introduces the possibility of competition between the technetium and tin for the organic under investigation. Therefore, the behaviour of $SnCl_2$ in solutions of EDTA, NTA, ISA, gluconic acid and picolinic acid was investigated to determine;

1. If $SnCl_2$ complexes with the organic ligands under investigation
2. If complexation does occur between the tin ions and ligands of interest, what concentration of ligand, if any, is free for complexation with the reduced technetium?

4.9.1 Sn(II)

Table 4.33 shows the solubility of Sn(II) in the absence of any ligands.

Sample number	[Sn] (ppm) (w.v)	[Sn] (mol dm^{-3})
1	125.4	1.06E-03
2	163.0	1.37E-03
3	273.8	2.31E-03
4	867.2	7.31E-03
5	278.8	2.35E-03

Table 4.33: Solubility of Sn(II)

From the results it can be seen that the mean solubility of $SnCl_2$ in the absence of any ligand is 2.88×10^{-3} mol dm^{-3}.

4.9.2 EDTA

From Table 4.34 it can be seen that in the presence of EDTA there is an increase in solubility of Sn(II), due to complexation between the EDTA and the Sn(II) to form a soluble complex.

Sample number	[EDTA] (mol dm^{-3})	[Sn] (ppm) (w.v)	[Sn] (mol dm^{-3})
1	0.01	1482.4	1.30E-02
2	0.01	1415.1	1.20E-02
3	0.01	1212.8	1.00E-02
4	0.1	5596.0	4.70E-02
5	0.1	4184.0	3.50E-02
6	0.1	4006.0	3.40E-02
7	0.2	11313.6	9.50E-02
8	0.2	11705.5	9.90E-02
9	0.2	10435.8	8.80E-02

Table 4.34: Solubility of Sn(II) in the presence of EDTA

The solubility enhancement factors for the solubility of Sn(II) in the presence of EDTA are shown below (Table 4.35)

[EDTA] (mol dm^{-3})	SEF	±
0.2	32.6	1.9
0.1	13.4	2.6
0.01	4.0	0.4

Table 4.35: Solubility enhancement factors for the solubility of Sn(II) in the presence of EDTA

4.9.3 NTA

Table 4.36 shows the solubility of Sn(II) in the presence of different concentrations of NTA.

Sample number	[NTA] (mol dm^{-3})	[Sn] (ppm) (w.v)	[Sn] (mol dm^{-3})
1	0.01	349.4	2.94E-03
2	0.01	908.8	7.66E-03
3	0.01	1079.2	9.09E-03
4	0.1	2158.0	1.82E-02
5	0.1	5488.0	4.62E-02
6	0.1	2792.0	2.35E-02
7	0.2	10766.7	9.07E-02
8	0.2	20437.4	1.72E-01
9	0.2	11124.3	9.37E-02

Table 4.36: Solubility of Sn(II) in the presence of NTA

From Table 4.36 it can be seen that in the presence of NTA there is an increase in solubility of the Sn(II), due to complexation between the NTA and the Sn(II) to form a soluble complex.

The solubility enhancement factors for the solubility of Sn(II) in the presence of NTA are shown below (Table 4.37)

[NTA] (mol dm^{-3})	SEF	±
0.2	41.3	16.0
0.1	10.2	5.2
0.01	2.3	1.1

Table 4.37: Solubility enhancement factors for the solubility of Sn(II) in the presence of NTA

4.9.4 ISA

From Table 4.38 it can be seen that in the presence of ISA there is an increase in solubility of the Sn(II). ISA is therefore complexing with the Sn(II) and forming a more soluble Sn(II)-ISA complex.

Sample number	[ISA] (mol dm^{-3})	[Sn] (ppm) (w.v)	[Sn] (mol dm^{-3})
1	0.01	1267.0	1.07E-02
2	0.01	223.6	1.88E-03
3	0.01	720.0	6.07E-03
4	0.1	7472.0	6.30E-02
5	0.1	7102.2	5.98E-02
6	0.1	6964.0	5.87E-02
7	0.2	11711.6	9.87E-02
8	0.2	10524.7	8.87E-02
9	0.2	11711.6	9.87E-02

Table 4.38: Solubility of Sn(II) in the presence of ISA

The solubility enhancement factors for the solubility of Sn(II) in the presence of ISA are shown below (Table 4.39)

[ISA] (mol dm^{-3})	SEF	±
0.2	33.1	2.0
0.1	21.0	0.8
0.01	2.2	1.5

Table 4.39: Solubility enhancement factors for the solubility of Sn(II) in the presence of ISA

4.9.5 Gluconic acid

Table 4.40 shows data for the solubility of Sn(II) in the presence of gluconic acid

Sample number	[Gluconic acid] (mol dm^{-3})	[Sn] (ppm) (w.v)	[Sn] (mol dm^{-3})
1	0.01	1045.2	8.81E-03
2	0.01	478.7	4.03E-03
3	0.01	892.2	7.52E-03
4	0.1	2566.0	2.16E-02
5	0.1	2902.4	2.45E-02
6	0.1	2733.3	2.30E-02
7	0.2	11279.0	9.50E-02
8	0.2	10566.8	8.90E-02
9	0.2	11041.6	9.30E-02

Table 4.40: Solubility of Sn(II) in the presence of gluconic acid

From Table 4.40 it can be seen that in the presence of gluconic acid there is an increase in solubility of the Sn(II). Gluconic acid is therefore complexing with the Sn(II) and forming a soluble Sn(II)-gluconate complex.

The solubility enhancement factors for the solubility of Sn(II) in the presence of gluconic acid are shown below (Table 4.41)

[Gluconate] (mol dm^{-3})	SEF	±
0.2	32.1	1.1
0.1	8.0	0.5
0.01	2.4	0.9

Table 4.41: Solubility enhancement factors for the solubility of Sn(II) in the presence of gluconic acid

4.9.6 Picolinic acid

From Table 4.42 it can be seen that in the presence of picolinic acid there is an increase in solubility of the Tc(IV). Picolinic acid is therefore complexing with the Tc(IV) and forming a more soluble Tc(IV)-picolinate complex.

Sample number	[Picolinic Acid] (mol dm^{-3})	[Sn] (ppm) (w.v)	[Sn] (mol dm^{-3})
1	0.01	416.8	3.51E-03
2	0.01	467.4	3.94E-03
3	0.01	474.4	4.00E-03
4	0.1	1563.4	1.32E-02
5	0.1	793.6	6.69E-03
6	0.1	1674.6	1.41E-02
7	0.2	7494.0	6.31E-02
8	0.2	16196.0	1.36E-01
9	0.2	12824.0	1.08E-01

Table 4.42: Solubility of Sn(II) in the presence of picolinic acid

The solubility enhancement factors for the solubility of Sn(II) in the presence of picolinic acid are shown below (Table 4.43)

[Picolinate] (mol dm^{-3})	SEF	±
0.2	35.6	12.8
0.1	3.9	1.4
0.01	1.3	0.1

Table 4.43: Solubility enhancement factors for the solubility of Sn(II) in the presence of picolinic acid

4.9.7 Summary

From data shown above it can be seen that the organic complexing agents do complex with the tin to produce more soluble tin species.

From Fig. 4.43 it can be seen that as the concentration of the organics in solution increases the solubility of tin in solution also increases. This result shows that the metal reducing agent, used for the reduction of pertechnetate, introduces competition for the organics between the reducing agent and the technetium.

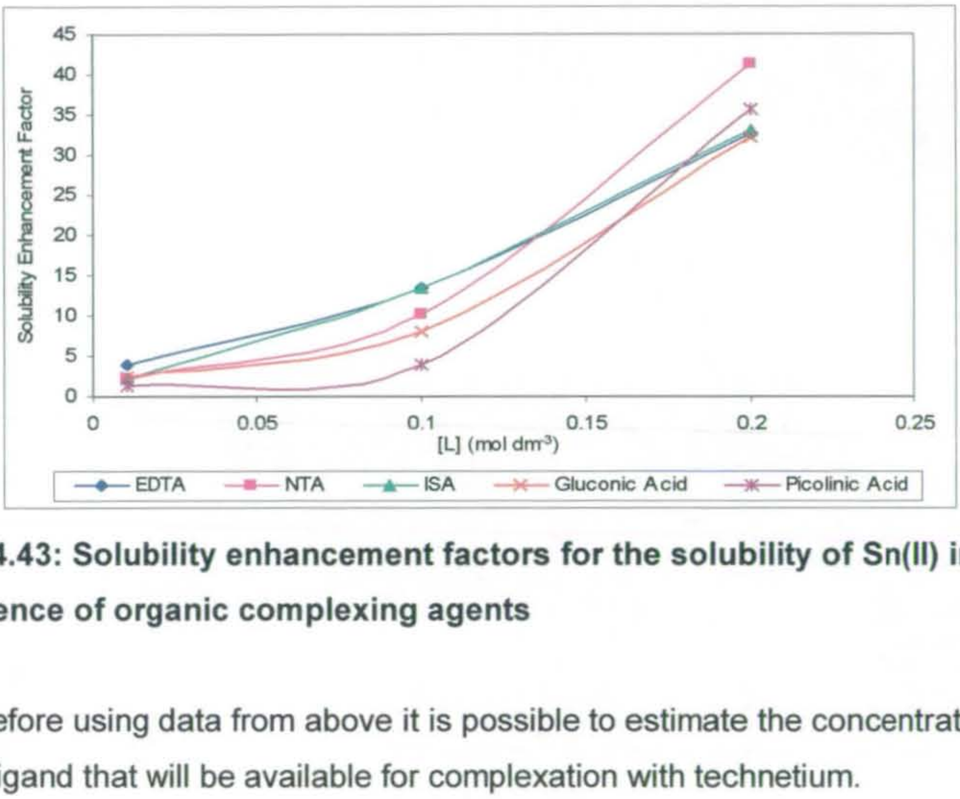


Fig. 4.43: Solubility enhancement factors for the solubility of Sn(II) in the presence of organic complexing agents

Therefore using data from above it is possible to estimate the concentration of free ligand that will be available for complexation with technetium.

	Estimated concentration of free ligand (mol dm^{-3})				
Starting [L] (mol dm^{-3})	**EDTA**	**NTA**	**ISA**	**Gluconic acid**	**Picolinic acid**
0.2	6.60E-02	6.14E-02	7.20E-02	5.99E-02	7.16E-02
0.1	3.77E-02	3.17E-02	4.35E-02	2.96E-02	2.93E-02
0.05	2.35E-02	1.69E-02	2.93E-02	1.44E-02	8.22E-03

Table 4.44: Estimation of concentration of the organics free for complexation with technetium

Using data from Table 4.44 the technetium stability constants can be recalculated using a more accurate ligand concentration by taking into account the amount of ligand bound to tin.

4.10 Calculation of the solubility product for $Sn(OH)_2(s)$ at high pH

By measuring the solubility of the Sn(II) (Table 4.45) it is possible to calculate the solubility product of $Sn(OH)_2$.

Sample	pH	A Term	$[Sn]_{solution}$ (mol dm^{-3})	K_{SP}	log K_{SP}
1	13.43	7.89E+22	1.06E-03	2.47E-27	-26.6
2	13.63	3.14E+23	1.37E-03	2.02E-27	-26.7
3	13.23	1.99E+22	2.31E-03	8.52E-27	-26.1
4	13.26	2.45E+22	7.31E-03	2.52E-26	-25.6
5	13.33	3.89E+22	2.35E-03	6.93E-27	-26.2
			Mean Log K_{SP} =		-26.0

Table 4.45: Calculation of the solubility product (K_{SP}) for $Sn(OH)_2$

From Table 4.45 it can be seen that the mean solubility product for $Sn(OH)_2$ is -26.0 ± 0.44.

4.11 Calculation of Sn(II) conditional stability constants using the solubility product approach method

The derivation for the solubility product for Sn(II) with the complexing ligands can be found in section 9.2.

4.11.1 EDTA

By measuring the solubility increase of Sn(II), in the presence of different concentrations of EDTA (Table 4.46), it is possible to calculate the conditional stability constant of Sn(II) and EDTA using the solubility product approach method (section 9.2).

Sample	pH	[EDTA] (mol dm^{-3})	[Sn]$_{solution}$ (mol dm^{-3})	[Sn^{2+}] (mol dm^{-3})	[SnL] (mol dm^{-3})	log β
1	13.33	0.01	1.25E-02	7.99E-26	9.46E-03	26.3
2	13.24	0.01	1.19E-02	1.17E-25	9.42E-03	26.1
3	13.37	0.01	1.02E-02	6.68E-26	6.90E-03	25.5
4	13.29	0.1	4.71E-02	9.30E-26	4.43E-02	24.9
5	13.37	0.1	3.53E-02	6.66E-26	3.19E-02	24.8
6	13.41	0.1	3.38E-02	5.36E-26	3.01E-02	24.9
7	13.40	0.3	9.53E-02	5.63E-26	9.17E-02	25.2
8	13.40	0.3	9.86E-02	5.79E-26	9.51E-02	25.2
9	13.26	0.3	8.79E-02	1.07E-25	8.53E-02	24.8

Table 4.46: Calculation of Sn(II)-EDTA stability constants

From Table 4.46 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Sn(II) and EDTA are within the range 24.8 – 26.3. The mean log of the stability constant is 25.5 ± 0.5.

4.11.2 NTA

By measuring the solubility increase of Sn(II), in the presence of different concentrations of NTA (Table 4.47), it is possible to calculate the conditional stability constant of Sn(II) and NTA using the solubility product approach method (section 9.2).

Sample	pH	[NTA] (mol dm^{-3})	[Sn]$_{solution}$ (mol dm^{-3})	[Sn^{2+}] (mol dm^{-3})	[SnL] (mol dm^{-3})	log β
1	13.32	0.01	7.66E-03	8.17E-26	4.66E-03	25.0
2	13.26	0.01	9.09E-03	1.06E-25	6.47E-03	25.2
3	13.26	0.1	1.82E-02	1.07E-25	1.56E-02	24.2
4	13.45	0.1	4.62E-02	4.52E-26	4.22E-02	25.2
5	13.40	0.1	2.35E-02	5.61E-26	1.99E-02	24.6
6	13.20	0.3	9.07E-02	1.41E-25	8.84E-02	24.8
7	13.30	0.3	1.72E-01	9.02E-26	1.69E-01	25.8
8	13.33	0.3	9.37E-02	7.85E-26	9.07E-02	25.0

Table 4.47: Calculation of Sn(II)-NTA stability constants

From Table 4.47 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Sn(II) and NTA are within the range 24.2 – 25.8. The mean log of the stability constant is 25.1 ± 0.5.

4.11.3 ISA

By measuring the solubility increase of Sn(II), in the presence of different concentrations of ISA (Table 4.48), it is possible to calculate the conditional stability constant of Sn(II) and ISA using the solubility product approach method (section 9.2).

Sample	pH	[ISA] (mol dm^{-3})	[Sn]$_{solution}$ (mol dm^{-3})	[Sn^{2+}] (mol dm^{-3})	[SnL] (mol dm^{-3})	log β
1	13.37	0.01	1.07E-02	6.54E-26	7.32E-03	25.6
2	13.32	0.01	6.07E-03	8.17E-26	3.07E-03	24.7
3	13.36	0.1	6.30E-02	6.75E-26	5.97E-02	25.3
4	13.38	0.1	5.98E-02	6.35E-26	5.64E-02	25.3
5	13.44	0.1	5.87E-02	4.74E-26	5.47E-02	25.4
6	13.33	0.2	9.87E-02	7.74E-26	9.56E-02	25.1
7	13.36	0.2	8.87E-02	6.85E-26	8.54E-02	25.0
8	13.49	0.2	9.87E-02	3.71E-26	9.42E-02	25.4

Table 4.48: Calculation of Sn(II)-ISA stability constants

From Table 4.48 it can be seen that the stability constants calculated, using the solubility product approach method, for Sn(II) and ISA are within the range 23.5 – 25.3. The mean stability constant is therefore 25.2 ± 0.3.

4.11.4 Gluconic acid

By measuring the solubility increase of Sn(II), in the presence of different concentrations of gluconic acid (Table 4.49), it is possible to calculate the conditional stability constant of Sn(II) and gluconic acid using the solubility product approach method (section 9.2).

Sample	pH	[Gluc] (mol dm^{-3})	[Sn]$_{solution}$ (mol dm^{-3})	[Sn^{2+}] (mol dm^{-3})	[SnL] (mol dm^{-3})	log β
1	13.30	0.01	8.81E-03	8.87E-26	5.93E-03	25.2
2	13.35	0.01	4.03E-03	7.24E-26	8.50E-04	24.1
3	13.36	0.01	7.52E-03	6.98E-26	4.27E-03	25.0
4	13.40	0.1	2.16E-02	5.59E-26	1.80E-02	24.6
5	13.35	0.1	2.45E-02	7.29E-26	2.13E-02	24.6
6	13.50	0.1	2.30E-02	3.55E-26	1.85E-02	24.8
7	13.10	0.2	9.50E-02	2.24E-25	9.32E-02	24.6
8	13.21	0.2	8.90E-02	1.38E-25	8.67E-02	24.7
9	13.30	0.2	9.30E-02	5.68E-26	8.94E-02	25.2

Table 4.49: Calculation of Sn(IV)-gluconate stability constants

From Table 4.49 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Sn(II) and gluconic acid are within the range 24.1 – 25.2. The mean log of the stability constant is 24.9 ± 0.4.

4.11.5 Picolinic acid

By measuring the solubility increase of Sn(II), in the presence of different concentrations of picolinic acid (Table 4.50), it is possible to calculate the conditional stability constant of Sn(II) and picolinic acid using the solubility product approach method (section 2.1.2).

Sample	pH	[P. A.] (mol dm^{-3})	[Sn]$_{solution}$ (mol dm^{-3})	[Sn^{2+}] (mol dm^{-3})	[SnL] (mol dm^{-3})	Log β
1	13.34	0.01	3.51E-03	7.48E-26	3.79E-04	23.7
2	13.37	0.01	3.94E-03	6.69E-26	6.26E-04	24.0
3	13.44	0.01	4.00E-03	4.82E-26	9.40E-05	23.3
4	13.40	0.1	1.32E-02	5.69E-26	9.58E-03	24.3
5	13.36	0.1	6.69E-03	6.81E-26	3.40E-03	23.7
6	13.36	0.1	1.41E-02	6.80E-26	1.08E-02	24.3
7	13.36	0.2	6.31E-02	6.71E-26	5.98E-02	24.6
8	13.33	0.2	1.36E-01	7.73E-26	1.33E-01	25.0
9	13.37	0.2	1.08E-01	6.56E-26	1.05E-01	24.9

Table 4.50: Calculation of Sn(II)-picolinate stability constants

From Table 4.50 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Sn(II) and picolinic acid are within the range 23.3 – 25.0. The mean log of the stability constant is 24.6 ± 0.5.

4.11.6 Summary

The Sn(II) ligand stability constants are summarised in Table 4.51.

Complex	β	Log β	±
Sn(II) - EDTA	2.92E+25	25.5	0.5
Sn(II) - NTA	1.39E+25	25.1	0.5
Sn(II) - ISA	1.73E+25	25.2	0.3
Sn(II) - Gluc	7.35E+24	24.9	0.4
Sn(II) - Pic	3.85E+24	24.6	0.5

Table 4.51: Sn(II) ligand stability constants

From Table 4.51 it can be seen that corrected log of the stability constants calculated for Sn(II) ligand complexes are within the range 24.6 – 25.5. The stability constants for the Sn(II)-ligand complexes are all very similar. As discussed in above (Section 4.8.6) this is due to the similar nature of the ligands investigated.

4.12 Corrected conditional stability constants

From section 4.10 and 4.11 it can be seen that tin does form soluble complexes with the organic complexing ligands EDTA, NTA, ISA, gluconic acid and picolinic acid. Therefore, due to this complexation between the tin and ligands of interest, the amount of free ligand available for complexation with the technetium is less than the orginal starting ligand concentration. The stability constants that were calculated in section 4.9 do not take this complexation between tin and ligand into consideration. Therefore using the free ligand concentration estimated in section 4.9.7 (Table 4.44) the stability constants for technetium(IV) and ligands under investigation were recalculated.

4.12.1 EDTA

Sample	pH	[EDTA] (mol dm^{-3})	dpm	$[Tc]_{solution}$ (mol dm^{-3})	$[Tc^{4+}]$ (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.42	6.60E-02	2197.6	3.25E-07	2.23E-21	3.24E-07	15.3
2	13.33	6.60E-02	2031.4	2.99E-07	2.75E-21	2.98E-07	15.2
3	13.31	6.60E-02	2157.3	3.18E-07	2.87E-21	3.18E-07	15.2
4	13.32	6.60E-02	2207.0	3.26E-07	2.82E-21	3.26E-07	15.2
5	13.23	6.60E-02	1911.7	2.80E-07	3.45E-21	2.80E-07	15.1
6	13.46	3.77E-02	328.9	4.70E-08	2.03E-21	4.66E-08	14.8
7	13.41	3.77E-02	259.7	3.71E-08	2.28E-21	3.67E-08	14.6
8	13.32	3.77E-02	291.6	4.16E-08	2.82E-21	4.13E-08	14.6
9	13.53	3.77E-02	513.3	7.35E-08	1.74E-21	7.31E-08	15.0
10	13.36	3.77E-02	270.2	3.86E-08	2.55E-21	3.82E-08	14.6
11	13.32	2.35E-02	119.5	1.70E-08	2.86E-21	1.66E-08	14.4
12	13.21	2.35E-02	52.6	7.36E-09	3.63E-21	6.99E-09	13.9
13	13.12	2.35E-02	94.3	1.33E-08	4.43E-21	1.30E-08	14.1
14	13.40	2.35E-02	91.3	1.29E-08	2.35E-21	1.25E-08	14.4
15	13.30	2.35E-02	63.7	8.96E-09	2.95E-21	8.58E-09	14.1

Table 4.52: Calculation of corrected Tc(IV)-EDTA stability constants

From Table 4.52 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and EDTA are within the range 13.9 – 15.3. The mean log of the stability constant is therefore 14.9 ± 0.47. Therefore, stability constants for the Tc(IV)-EDTA complex increase as the free EDTA concentration is decreased due to Sn(II) complexation.

4.12.2 NTA

From Table 4.53 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and NTA are within the range 12.6 – 14.7. The mean log of the stability constant is 14.4 ± 0.84. Therefore, stability constants for the Tc(IV)-NTA complex increase as the free NTA concentration is decreased due to Sn(II) complexation.

Sample	pH	[NTA] (mol dm^{-3})	dpm	$[Tc]_{solution}$ (mol dm^{-3})	$[Tc^{4+}]$ (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.43	6.14E-02	436.0	6.34E-08	2.18E-21	6.31E-08	14.7
2	13.26	6.14E-02	507.0	7.38E-08	3.22E-21	7.35E-08	14.6
3	13.33	6.14E-02	476.0	6.93E-08	2.75E-21	6.89E-08	14.6
4	13.36	6.14E-02	456.5	6.65E-08	2.56E-21	6.61E-08	14.6
5	13.36	6.14E-02	474.9	6.91E-08	2.56E-21	6.88E-08	14.6
6	13.33	3.17E-02	157.7	2.27E-08	2.74E-21	2.23E-08	14.4
7	13.03	3.17E-02	158.6	2.28E-08	5.47E-21	2.25E-08	14.1
8	13.37	3.17E-02	162.9	2.35E-08	2.54E-21	2.31E-08	14.5
9	13.34	3.17E-02	210.8	3.05E-08	2.67E-21	3.01E-08	14.6
10	13.37	3.17E-02	184.5	2.66E-08	2.54E-21	2.62E-08	14.5
11	13.36	1.69E-02	6.2	5.55E-10	2.56E-21	1.83E-10	12.6
12	13.43	1.69E-02	5.8	5.06E-10	2.18E-21	1.33E-10	12.6
13	13.236	1.69E-02	7.2	6.72E-10	3.42E-21	3.00E-10	12.7

Table 4.53: Calculation of corrected Tc(IV)-NTA stability constants

4.12.3 ISA

From Table 4.54 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and ISA are within the range 13.9 – 14.6. The mean log of the stability constant is 14.3 ± 0.21. Therefore, stability constants for the Tc(IV)-ISA complex increase as the free ISA concentration is decreased due to Sn(II) complexation.

Sample	pH	[ISA] (mol dm^{-3})	dpm	$[Tc]_{solution}$ (mol dm^{-3})	$[Tc^{4+}]$ (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.37	7.20E-02	395.5	5.75E-08	3.20E-21	5.71E-08	14.4
2	13.33	7.20E-02	356.0	5.17E-08	3.45E-21	5.14E-08	14.3
3	13.46	7.20E-02	361.0	5.25E-08	2.56E-21	5.21E-08	14.5
4	13.42	7.20E-02	385.7	5.61E-08	2.80E-21	5.57E-08	14.4
5	13.37	7.20E-02	341.5	4.96E-08	3.20E-21	4.92E-08	14.3
6	13.37	4.35E-02	227.0	3.29E-08	3.17E-21	3.25E-08	14.4
7	13.27	4.35E-02	215.1	3.11E-08	4.03E-21	3.07E-08	14.2
8	13.14	4.35E-02	237.4	3.44E-08	5.43E-21	3.40E-08	14.2
9	13.53	4.35E-02	243.7	3.53E-08	2.18E-21	3.49E-08	14.6
10	13.26	4.35E-02	218.4	3.16E-08	4.05E-21	3.12E-08	14.2
11	13.69	2.93E-02	94.3	1.34E-08	1.51E-21	1.30E-08	14.5
12	13.32	2.93E-02	70.1	9.88E-09	3.53E-21	9.51E-09	14.0
13	13.33	2.93E-02	82.7	1.17E-08	3.45E-21	1.14E-08	14.1
14	13.33	2.93E-02	69.2	9.74E-09	3.45E-21	9.37E-09	14.0
15	13.13	2.93E-02	90.1	1.28E-08	5.47E-21	1.24E-08	13.9

Table 4.54: Calculation of corrected Tc(IV)-ISA stability constants

4.12.4 Gluconic acid

From Table 4.55 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and gluconic acid are within the range 14.5 – 15.1. The mean log of the stability constant is 14.8 ± 0.17. Therefore, stability constants for the Tc(IV)-gluconate complex increase as the free gluconic acid concentration is decreased due to Sn(II) complexation.

Sample	pH	[Gluc] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.26	5.99E-02	1090.2	1.52E-07	4.05E-21	1.51E-07	14.8
2	13.37	5.99E-02	1211.7	1.71E-07	3.20E-21	1.70E-07	14.9
3	13.36	5.99E-02	1110.3	1.55E-07	3.21E-21	1.54E-07	14.9
4	13.30	5.99E-02	1083.6	1.51E-07	3.75E-21	1.50E-07	14.8
5	13.36	5.99E-02	1067.8	1.48E-07	3.23E-21	1.48E-07	14.9
6	13.26	2.96E-02	420.0	6.11E-08	4.05E-21	6.07E-08	14.7
7	13.25	2.96E-02	461.7	6.72E-08	4.17E-21	6.68E-08	14.7
8	13.33	2.96E-02	434.9	6.33E-08	3.45E-21	6.29E-08	14.8
9	13.55	2.96E-02	493.8	7.19E-08	2.08E-21	7.15E-08	15.1
10	13.37	2.96E-02	473.4	6.89E-08	3.20E-21	6.86E-08	14.9
11	13.33	1.44E-02	106.2	1.52E-08	3.50E-21	1.48E-08	14.5
12	13.35	1.44E-02	135.7	1.95E-08	3.33E-21	1.91E-08	14.6
13	13.36	1.44E-02	130.3	1.87E-08	3.25E-21	1.83E-08	14.6
14	13.26	1.44E-02	191.9	2.77E-08	4.04E-21	2.73E-08	14.7
15	13.62	1.44E-02	190.3	2.75E-08	1.80E-21	2.71E-08	15.0

Table 4.55: Calculation of corrected Tc(IV)-gluconate stability constants

4.12.5 Picolinic acid

From Table 4.56 it can be seen that the log of the stability constants calculated, using the solubility product approach method, for Tc(IV) and picolinic acid are within the range 14.7 – 15.4. The mean log of the stability constant is 15.2 ± 0.22. Therefore, stability constants for the Tc(IV)-picolinate complex increase as the free picolinic acid concentration is decreased due to Sn(II) complexation.

Sample	pH	[Pic] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.32	7.16E-02	2044.4	2.99E-07	2.85E-21	2.99E-07	15.2
2	13.43	7.16E-02	2211.6	3.23E-07	2.19E-21	3.23E-07	15.3
3	13.40	7.16E-02	2015.0	2.95E-07	2.37E-21	2.94E-07	15.2
4	13.04	7.16E-02	2057.7	3.01E-07	5.34E-21	3.01E-07	14.9
5	13.35	7.16E-02	2112.4	3.09E-07	2.63E-21	3.09E-07	15.2
6	13.40	2.93E-02	524.8	7.65E-08	2.37E-21	7.61E-08	15.0
7	13.33	2.93E-02	525.0	7.65E-08	2.76E-21	7.61E-08	15.0
8	13.10	2.93E-02	523.6	7.63E-08	4.65E-21	7.59E-08	14.7
9	13.24	2.93E-02	530.8	7.73E-08	3.40E-21	7.70E-08	14.9
10	13.32	2.93E-02	539.0	7.85E-08	2.84E-21	7.82E-08	15.0
11	13.30	8.22E-03	430.5	6.26E-08	2.96E-21	6.23E-08	15.4
12	13.25	8.22E-03	405.1	5.89E-08	3.33E-21	5.86E-08	15.3
13	13.13	8.22E-03	403.0	5.86E-08	4.41E-21	5.82E-08	15.2
14	13.37	8.22E-03	424.0	6.17E-08	2.54E-21	6.13E-08	15.5
15	13.33	8.22E-03	434.3	6.32E-08	2.74E-21	6.28E-08	15.4

Table 4.56: Calculation of corrected Tc(IV)-picolinate stability constants

4.12.6 Summary

From section 4.10 and 4.11 it can be seen that the tin in solution complexes with the ligands under investigation. This reduces the amount of free ligand that is available for complexation with technetium. In section 4.10 an estimate was made for the free ligand concentration available for complexation with technetium taking into account the tin complexation. Using the new equilibrium ligand concentration the stability constants for techetnium(IV) ligand complexes were recalculated.

	Orginal stability constants			Corrected stability constants		
Complex	β	Log β	±	β	Log β	±
Tc(IV) - EDTA	2.19E+14	14.3	0.6	8.17E+14	14.9	0.5
Tc(IV) - NTA	6.05E+13	13.8	1.0	2.67E+14	14.4	0.8
Tc(IV) - ISA	8.17E+13	13.9	0.3	2.00E+14	14.3	0.2
Tc(IV) - Gluc	1.57E+14	14.2	0.4	6.60E+14	14.8	0.2
Tc(IV) - Pic	7.06E+14	14.9	0.3	1.60E+15	15.2	0.2

Table 4.57: Corrected Tc(IV)-ligand stability constants

From Table 4.57 it can be seen that corrected log of the stability constants calculated for Tc(IV) ligand complexes are within the range 14.3 – 15.2.

Comparing the new stability constants for technetium(IV) ligand complexes to the stability constants calculated in section 4.9 (Table 4.57), it can be see that the corrected stability constants have increased. This increase in the stability constants of technetium(IV) ligand complexes is expected as the stability constant is inversely proportional to the equilibrium ligand concentration and the amount of complexation remains unchanged. Therefore, as the ligand concentration decreases the stability constant increases.

4.13 Development of an electrochemical method for the reduction of ammonium pertechnetate at high pH

As described in section 4.8 – 4.12 the use of $SnCl_2$ as a reducing agent introduces the possibility of competition between the technetium and tin for the organic ligand under investigation. Therefore to eliminate the competition between the technetium and tin for the ligand a new method of pertechnetate reduction was developed. The aim of this new method of reduction was to produce solutions of technetium(IV) that were "clean" i.e. free from competiting metal ions for the organic ligands under invesitigation.

4.13.1 Electrochemical cell 1

Table 4.58 shows that after 3 days the final concentration of technetium was *ca.* 4.5×10^{-8} mol dm^{-3}. This value is higher than the literature value for TcO_2 of $\leq 9 \times 10^{-9}$ mol dm^{-3} [38, 40]. The reaction was therefore left for another day to see if the reduction went to completion. However no change in the solubility was observed.

Sample	dpm	[Tc] (mol dm^{-3})
1	317.9	4.62E-08
2	324.1	4.71E-08
3	299.7	4.35E-08

Table 4.58: Electrochemical cell 1

It is possible that due to the placement of the platinum electrode the mass transport, a controlling factor in the kinetics of electrochemistry, is reduced and therefore hindering the reduction of TcO_4^-.

4.13.2 Electrochemical cell 2

On the advice of Dr Frank Marken the cell was redesigned (Section 3.3.12.2). By placing the electrodes directly into the same flask it was hoped that the mass transport would be increased. The potential difference was also increased to speed the reaction up. As the voltage was increased to 6 V, the reduction of the water occurred producing oxygen, therefore the possibility of the reoxidation of Tc(IV) was increased.

Sample	dpm	[Tc] (mol dm^{-3})
1	1497.3	2.15E-07
2	1461.7	2.10E-07
3	1484.9	2.13E-07

Table 4.59: Electrochemical cell 2

Table 4.59 shows that the final concentration of technetium is much higher than the literature value for TcO_2 of $\leq 9 \times 10^{-9}$ mol dm^{-3} [38, 40]. Therefore the electrochemical reduction using cell 2 was unsuccessful.

4.13.3 Electrochemical cell 3

Glass housing was introduced around the platinum electrode (Fig. 3.6). The introduction of this was to give the oxygen formed at the platinum electrode a route to escape to the atmosphere instead of into the reaction vessel.

Sample	dpm	[Tc] (mol dm^{-3})
1	357.6	5.20E-08
2	286.4	4.15E-08
3	308.4	4.48E-08

Table 4.60: Electrochemical cell 3

From the results it can be seen that a reduction had taken place. However after 3 days on 6 V the solubility of the Tc in solution had not reached that expected from reduced Tc(IV). It is thought that the frit at the end of the glass housing was reducing the mass transport of the system and therefore impeding the reaction.

4.13.4 Electrochemical cell 4

New glass housing was placed around the platinum electrode. This time the frit was much coarser.

Sample	dpm	[Tc] (mol dm^{-3})
1	33.8	4.66E-09
2	32.8	4.52E-09
3	32.8	4.52E-09

Table 4.61: Electrochemical cell 4

Table 4.61 shows that the final concentration of technetium in solution is close to the literature value for TcO_2 of $\leq 9 \times 10^{-9}$ mol dm^{-3} [38, 40], which lends support to the view that pertechnetate has been completely reduced to $TcO_2(s)$.

4.14 Calculation of Tc(IV) stability constants using the Schubert (ion exchange) method

The electrochemical method for the reduction of pertechnetate developed in in section 4.13 produces solutions of technetium(IV) at low concentrations (i.e. the solubility of technetium(IV)). Using the Schubert method and the technetium(IV) solutions an attempt was made to determine the stability constants of technetium(IV) and the EDTA.

From the results shown in Table 4.62 it can been seen that the concentration of technetium in solution is approximately equal regardless of the presence of the resin or the presence of the resin and the organic ligand. It therefore follows that none of the technetium has sorbed to the resin. One possible reason for this is that the TcO_2 has been reoxidised back to TcO_4^- and, therefore, as an anion it will not sorb to a cation exchange resin. Another possible explanation for this is that the aqueous species formed by the dissolution of TcO_2 at high pH is itself anionic or neutral and therefore the concentration of the cationic species is very low.

Sample number	Contents of Vial	cpm	dpm	[Tc] (mol dm^{-3})
1	Resin	76.3	58.0	6.82E-09
2	Resin	70.6	52.3	6.13E-09
3	Resin	73.1	54.8	6.44E-09
4	Resin	72.9	54.6	6.40E-09
5	Resin	73.2	54.9	6.44E-09
6	-	73.1	54.8	6.43E-09
7	-	75.9	57.6	6.77E-09
8	-	74.2	55.9	6.57E-09
9	-	73.6	55.3	6.49E-09
10	-	72.3	54.0	6.34E-09
11	Resin + 0.05 mol dm^{-3} EDTA	73.6	55.3	6.49E-09
12	Resin + 0.05 mol dm^{-3} EDTA	79.0	60.7	7.15E-09
13	Resin + 0.05 mol dm^{-3} EDTA	73.9	55.6	6.53E-09
14	Resin + 0.05 mol dm^{-3} EDTA	72.5	54.2	6.36E-09
15	Resin + 0.05 mol dm^{-3} EDTA	75.1	56.8	6.67E-09

Table 4.62: Schubert method results

To reduce the chances of the TcO_2 reoxidising back to TcO_4^-, 4 different holding reductants were tried. These were sodium dithionite, ascorbic acid, sodium hypophosphite and hydrazine. The reductants were chosen because they were all non metallic reducing agents and therefore wouldn't compete for the organic ligand under investigation in solution and also limit the competition for the sites on the resin. From the results of the vials which only contain the resin (Table 4.63) it appears that the technetium has sorbed to the resin. However the results for the rest of the vials contain approximately the same concentration of technetium.

It was therefore concluded that technetium(IV) had reoxidised without the presence of a holding reductant. However, when the holding reductant was present, keeping the Tc(IV) reduced, sorption occurred to the walls of the vials. Therefore the Schubert method was not a suitable method for measuring Tc(IV) stability constants at high pH.

	Reductant	**Resin**	**EDTA (0.05 mol dm^{-3})**	**dpm**	**[Tc] (mol dm^{-3})**
1	Dithionite	Yes	No	6.5	5.86E-10
2	Dithionite	Yes	No	5.8	5.00E-10
3	Dithionite	Yes	No	5.3	4.41E-10
4	Dithionite	Yes	No	5.3	4.46E-10
5	Dithionite	Yes	No	5.6	4.77E-10
6	Dithionite	No	No	5.8	5.00E-10
7	Dithionite	No	No	5.2	4.24E-10
8	Dithionite	No	No	5.4	4.49E-10
9	Dithionite	No	No	4.5	3.46E-10
10	Dithionite	No	No	4.6	3.50E-10
11	Dithionite	Yes	Yes	4.8	3.78E-10
12	Dithionite	Yes	Yes	5.3	4.41E-10
13	Dithionite	Yes	Yes	5.6	4.76E-10
14	Dithionite	Yes	Yes	4.9	3.87E-10
15	Dithionite	Yes	Yes	5.0	4.09E-10
16	Ascorbic Acid	Yes	No	6.2	5.45E-10
17	Ascorbic Acid	Yes	No	4.8	3.74E-10
18	Ascorbic Acid	Yes	No	4.9	3.92E-10
19	Ascorbic Acid	No	No	4.9	3.87E-10
20	Ascorbic Acid	No	No	4.8	3.80E-10
21	Ascorbic Acid	No	No	5.5	4.65E-10
22	Ascorbic Acid	Yes	Yes	5.8	4.96E-10
23	Ascorbic Acid	Yes	Yes	5.4	4.56E-10

Table 4.63 continues on page 142

24	Ascorbic Acid	Yes	Yes	4.8	3.80E-10
25	Sodium Hypophosphite	Yes	No	5.6	4.78E-10
26	Sodium Hypophosphite	Yes	No	4.8	3.74E-10
27	Sodium Hypophosphite	Yes	No	5.0	4.06E-10
28	Sodium Hypophosphite	No	No	5.1	4.21E-10
29	Sodium Hypophosphite	No	No	5.5	4.66E-10
30	Sodium Hypophosphite	No	No	6.1	5.41E-10
31	Sodium Hypophosphite	Yes	Yes	5.6	4.72E-10
32	Sodium Hypophosphite	Yes	Yes	5.4	4.54E-10
33	Sodium Hypophosphite	Yes	Yes	5.3	4.42E-10
34	Hydrazine	Yes	No	5.4	4.48E-10
35	Hydrazine	Yes	No	4.8	3.79E-10
36	Hydrazine	Yes	No	4.9	3.97E-10
37	Hydrazine	No	No	5.7	4.90E-10
38	Hydrazine	No	No	5.7	4.87E-10
39	Hydrazine	No	No	5.4	4.48E-10
40	Hydrazine	Yes	Yes	4.9	3.87E-10
41	Hydrazine	Yes	Yes	6.0	5.27E-10
42	Hydrazine	Yes	Yes	7.5	7.05E-10

Table 4.63: Schubert method results holding reductants

4.15 Calculation of the solubility product for TcO_2

From section 4.14 it can be seen that it is not possible to use the Schubert method for the determination of the technetium(IV) ligand stability constants. Therefore, the solubility product approach method for the determination of stability constants is used in the following section to determine the stability constants for technetium(IV) complexes which were formed using the electrochemical reduction of TcO_4^-.

By measuring the solubility of the TcO_2 (Table 4.64) and using equation 3.21 it is possible to calculate the solubility product for the dissolution of technetium(IV) (shown below).

$$TcO_2.2H_2O\,(am) \rightleftharpoons TcO(OH)^+\,(aq) + OH^-\,(aq) + H_2O$$

The log K_{SP} calculated has a value –19.8 ± 0.4 which is in good agreement with the literature value –19.5 [50].

Sample	pH	dpm	A Term	$[Tc]_{solution}$	K_{SP}	Log K_{SP}
1	13.45	128.2	1.12E+11	1.84E-08	4.62E-20	-19.3
2	13.37	33.8	9.35E+10	3.89E-09	9.77E-21	-20.0
3	13.30	32.8	7.94E+10	3.77E-09	9.48E-21	-20.0
4	13.26	21.7	7.19E+10	2.42E-09	6.08E-21	-20.2
5	13.23	32.8	6.73E+10	3.77E-09	9.47E-21	-20.0
6	13.23	141.0	6.76E+10	2.03E-08	5.09E-20	-19.3
					Mean Log K_{SP} =	-19.8 ± 0.4

Table 4.64: Calculation of the solubility product (K_{SP}) for $TcO_2.2H_2O$

4.16 Calculation of Tc(IV) conditional stability constants using the solubility product approach method

4.16.1 EDTA

From Table 4.65 it can be seen that the calculated Tc(IV)EDTA constant is 14.1 ± 1.03 at [EDTA] = 0.01 mol dm^{-3} and 13.0 ± 0.07 at [EDTA] = 0.1 mol dm^{-3}. In using the electrochemical method the problems associated with the reduction of TcO_4^- by a metallic reducing agent (discussed in Section 4) are no longer a concern as this method does not produce competing metal.

	pH	[EDTA] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.45	0.01	127.7	1.83E-08	8.41E-20	2.60E-09	12.5
2	13.37	0.01	130.9	1.88E-08	1.72E-20	1.65E-08	14.0
3	13.30	0.01	165.5	2.38E-08	7.71E-21	2.29E-08	14.1
4	13.26	0.1	523.1	7.62E-08	5.93E-20	6.91E-08	13.1
5	13.23	0.1	253.6	3.68E-08	3.82E-20	3.25E-08	12.9
6	13.23	0.1	360.3	5.24E-08	5.25E-20	4.65E-08	12.9

Table 4.65: Calculation of Tc(IV)-EDTA stability constants

4.16.2 NTA

Table 4.66 shows the stability constants calculated for the reaction between technetium(IV) and NTA using the electrochemical reduction to reduce TcO_4^-.

	pH	[NTA] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.35	0.01	107.7	1.5E-08	3.7E-20	1.0E-08	13.4
2	13.32	0.01	160.4	2.3E-08	3.9E-20	1.8E-08	13.7
3	13.23	0.01	61.1	8.6E-09	4.8E-20	3.2E-09	12.8
4	13.35	0.1	199.8	2.9E-08	1.6E-20	2.7E-08	13.2
5	13.40	0.1	161.5	2.3E-08	1.6E-20	2.1E-08	13.1
6	13.29	0.1	82.1	1.2E-08	2.8E-20	8.0E-09	12.5

Table 4.66: Calculation of TcO(OH)-NTA stability constants

From Table 4.66 it can be seen that the calculated Tc(IV)NTA constant is 13.4 ± 0.43 at [NTA] = 0.01 mol dm^{-3} and 13.0 ± 0.42 at [NTA] = 0.1 mol dm^{-3}.

4.16.3 ISA

Table 4.67 shows the stability constants calculated for the reaction between technetium(IV) and ISA using the electrochemical reduction to reduce TcO_4^-.

	pH	[ISA] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.34	0.01	40.4	3.01E-09	8.69E-21	1.77E-09	13.3
2	13.43	0.01	70.5	7.90E-09	7.18E-21	6.63E-09	14.0
3	13.61	0.01	53.0	5.34E-09	1.58E-20	1.10E-09	12.8
4	13.30	0.1	130.5	1.67E-08	5.70E-20	9.24E-09	12.2
5	13.43	0.1	106.2	1.31E-08	4.84E-20	4.61E-09	12.0
6	13.31	0.1	110.8	1.38E-08	5.94E-20	5.87E-09	12.0

Table 4.67: Calculation of TcO(OH)-ISA stability constants

From Table 4.67 it can be seen that the calculated Tc(IV)ISA constant is 13.6 ± 0.56 at [ISA] = 0.01 mol dm^{-3} and 12.1 ± 0.13 at [ISA] = 0.1 mol dm^{-3}.

4.16.4 Gluconic acid

Table 4.68 shows the stability constants calculated for the reaction between technetium(IV) and gluconate using the electrochemical reduction to reduce TcO_4^-.

	pH	[Gluconate] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.45	0.01	24.1	2.72E-09	2.95E-21	2.16E-09	13.9
2	13.20	0.01	84.3	1.20E-08	6.54E-20	5.06E-09	12.9
3	13.31	0.01	40.2	5.50E-09	2.85E-20	1.66E-09	12.8
4	13.32	0.1	95.1	1.35E-08	5.70E-20	5.67E-09	12.0
5	13.27	0.1	96.2	1.37E-08	8.21E-20	3.62E-09	11.6
6	13.40	0.1	95.8	1.36E-08	5.22E-20	4.92E-09	12.0

Table 4.68: Calculation of TcO(OH)-gluconate stability constants

From Table 4.68 it can be seen that the calculated Tc(IV)-Gluconate constant is 13.5 ± 0.60 at [Gluconate] = 0.01 mol dm^{-3} and 11.9 ± 0.20 at [Gluconate] = 0.1 mol dm^{-3}.

4.16.5 Picolinic acid

Table 4.69 shows the stability constants calculated for the reaction between technetium(IV) and picolinate using the electrochemical reduction to reduce TcO_4^-.

	pH	[Picolinate] (mol dm^{-3})	dpm	[Tc]$_{solution}$ (mol dm^{-3})	[Tc^{4+}] (mol dm^{-3})	[TcL] (mol dm^{-3})	Log β
1	13.36	0.01	61.5	5.74E-09	2.73E-20	1.65E-09	12.8
2	13.26	0.01	73.6	8.57E-09	3.40E-20	4.48E-09	13.1
3	13.32	0.01	68.4	7.81E-09	2.96E-20	3.72E-09	13.1
4	13.26	0.1	94.2	1.12E-08	6.75E-21	1.04E-08	13.2
5	13.40	0.1	122.1	1.75E-08	1.34E-20	1.53E-08	13.1
6	13.40	0.1	186.3	2.69E-08	5.61E-20	1.77E-08	12.5

Table 4.69: Calculation of TcO(OH)-picolinate stability constants

From Table 4.69 it can be seen that the calculated Tc(IV)-Picolinate constant is 13.0 ± 0.19 at [Picolinate] = 0.01 mol dm^{-3} and 13.0 ± 0.37 at [Picolinate] = 0.1 mol dm^{-3}.

4.16.6 Summary

Reaction	β	Log β	±
$TcO(OH)^+ + EDTA^{y-} \rightleftharpoons (Tc(IV)EDTA)^{(1+y)-}$	7.16E+13	13.9	0.7
$TcO(OH)^+ + NTA^{y-} \rightleftharpoons (Tc(IV)NTA)^{(1+y)-}$	1.74E+13	13.2	0.4
$TcO(OH)^+ + ISA^{y-} \rightleftharpoons (Tc(IV)ISA)^{(1+y)-}$	2.05E+13	13.3	0.8
$TcO(OH)^+ + Gluc^{y-} \rightleftharpoons (Tc(IV)Gluc)^{(1+y)-}$	1.49E+13	13.2	0.8
$TcO(OH)^+ + Pic^{y-} \rightleftharpoons (Tc(IV)Pic)^{(1+y)-}$	1.03E+13	13.0	0.3

Table 4.70: Tc(IV) stability constants calculated using electrochemical reduction

4.17 Comparison of stability constants measured using different reduction methods

From Table 4.71 above it can be seen that the stability constants are in good agreement with each other if the errors are taken into account. The presence of the tin ions in solution therefore does not make a difference to the overall amount of complexation between the technetium(IV) and the ligands.

	Sn(II) Reduction			Electrochemical Reduction		
Ligand	**β**	**log β**	**±**	**β**	**log β**	**±**
EDTA	2.19E+14	14.3	0.6	7.16E+13	13.9	0.7
NTA	6.05E+13	13.8	1.0	1.74E+13	13.2	0.4
ISA	8.17E+13	13.9	0.3	2.05E+13	13.3	0.8
Gluconate	1.57E+14	14.2	0.4	1.49E+13	13.2	0.8
Picolinate	7.06E+14	14.9	0.3	1.03E+13	13.0	0.3

Table 4.71: Tc(IV) stability constants calculated using different reduction methods

4.18 Prediction of stability constants

A number of methods have been used to predict stability constants, from simple extrapolations and linear free energy relationships, if relevant data exist, to more complex methods including acid-base methods and complex methods such as the Brown – Silva – Ellis equations [65]. However, no single approach is applicable to every chemical system.

Stablity constants prediction can generally be used for two reasons:

- Where the experimental determination is deemed too dangerous or difficult and/or
- as a useful tool for checking stability constants that have been measured experimentally.

The following section describes how linear free energy relationships were employed as a tool for checking the stability constants determined in this project.

4.18.1 The computer program STAB [66]

The computer program, STAB, was developed by Warwick *et al* at Loughborough University to predict stability constants for metal ligand complexes [66]. The program was originally designed for the two reasons stated in section 4.18. Three different approaches are used within the software, Linear Free Energy Relationships (LFERs), Brown – Silva – Ellis equations (BSE) and Hancock equations. The use of STAB in this work was restricted to the use of LFERs.

4.18.1.1 Linear free energy relationships (LFERs)

The IUPAC definition of a Linear free energy relationships (LFERs) is: "A linear correlation between the logarithm of a rate constant or equilibrium constant for one series of reactions and the logarithm of the rate constant or equilibrium constant for a related series of reactions."

The aim of LFERs is to convert qualitative ideas into quantitative theories of reactivity. The validity of such correlations has been examined both experimentally and theoretically, and is well accepted. The basis for most LFERs is that the free energies of similar reactions often exhibit a linear relationship to each other.

$\Delta G(ML) = a\,\Delta G(ML') + b$

It is, however, more common to express these relationships in terms directly related to those that can be experimentally determined, such as the logarithm of the rate (log k) or equilibrium constant (log K). Where a is the gradient and b is the y-intercept of the graphical representation.

Relationship	Class
$\log K = a_1 \log K_S + b_1$	II
$\log k = a_2 \log K_S + b_2$	I
$\log k = a_3 \log k_S + b_3$	II

Table 4.72: Classification of linear free energy relationships

Class I free energy relationships compare the rate constants to the equilibrium constant of the same process. Brønsted - Leffler equations are examples of this class of free energy relationship.

Class II free energy relationships compare the rate or equilibrium constants of a process to the rate or equilibrium constants of an unconnected but similar process. For example, when the free energies for a series of complexes between various metals and one ligand (ML) are plotted against the free energies of complexes with the same metals but a different ligand (ML'), a linear relationship is obtained.

The following use of liner free energy relationships (section 4.18.1.2) is concerned only with thermodynamic (equilibrium consntant) relationships.

4.18.1.2 Prediction of Tc(IV) EDTA stability constants using STAB

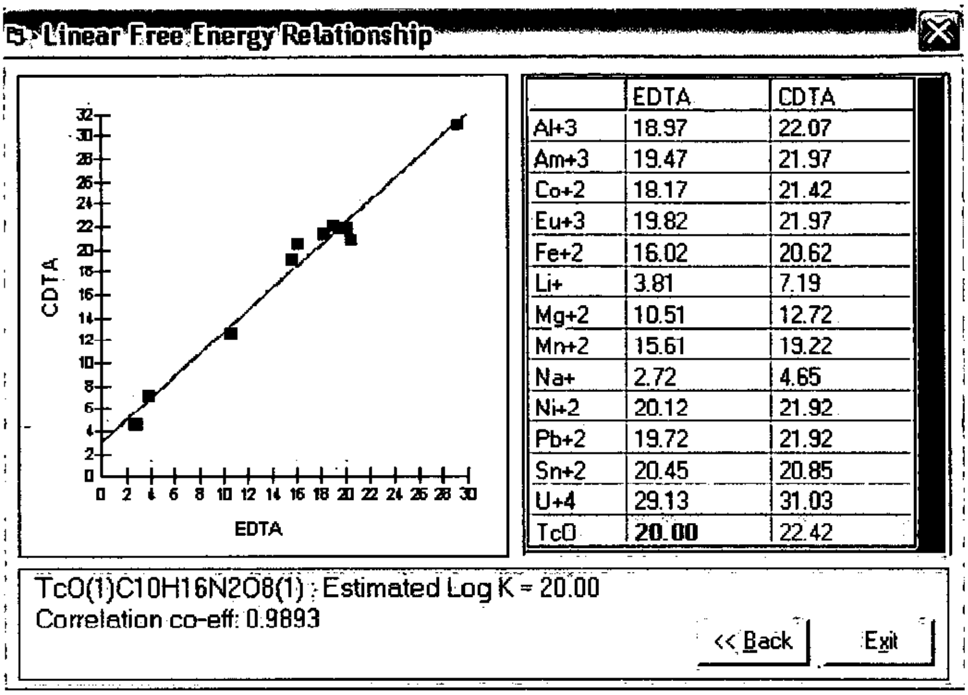
As described in section 4.18.1 a LFER plot can be obtained when the stability constants of a series of complexes between various metals and one ligand (ML) are plotted against the stability constants of complexes with the same metals but a different ligand (ML'). The NIST standard reference database [53] contains the stability constants for the complexes of the series of metals with EDTA, NTA and 1,2-Cyclohexylenedinitrilotetraacetic acid (CDTA).. These are shown in Table 4.73.

Stability constants found in the NIST database [48] for the following metals and organic ligands:		
EDTA	**NTA**	**CDTA**
Li [+]	Li [+]	Li [+]
Na [+]	Na [+]	Na [+]
Eu [3+]	Eu [3+]	Eu [3+]
Am [3+]	Am [3+]	Am [3+]
U [4+]		U [4+]
Np [4+]	Np [4+]	
Mn [2+]	Mn [2+]	Mn [2+]
Fe [2+]	Fe [2+]	Fe [2+]
Co [2+]	Co [2+]	Co [2+]
Ni [2+]	Ni [2+]	Ni [2+]
Sn [2+]		Sn [2+]
Pb [2+]	Pb [2+]	Pb [2+]
Al [3+]	Al [3+]	Al [3+]
Cr [2+]	Cr [2+]	
Mg [2+]	Mg [2+]	Mg [2+]

Table 4.73: Stability constants found in the NIST database complexes of the series of metals and EDTA, NTA and CDTA

The log of the stability constants for the series of complexes are given in Table 9.22. As discussed, in section 4.8.6, Gorski and Koch [61, 62] determined the stability constant for technetium(IV) NTA, in the same study the stability constant for technetium(IV) CDTA was detemined (Table 9.22). Therefore, using the series of stability constants for EDTA, NTA and CDTA it is possible to plot 2 LFERs;

1. log of the stability constants for M-EDTA against log of the stability constants for M-CDTA (Fig. 4.44) referred to as LFER 1 in the following text.
2. log of the stability constants for M-EDTA against log of the stability constants for M-NTA (Fig. 4.45) referred to as LFER 2 in the following text.



	EDTA	CDTA
Al+3	18.97	22.07
Am+3	19.47	21.97
Co+2	18.17	21.42
Eu+3	19.82	21.97
Fe+2	16.02	20.62
Li+	3.81	7.19
Mg+2	10.51	12.72
Mn+2	15.61	19.22
Na+	2.72	4.65
Ni+2	20.12	21.92
Pb+2	19.72	21.92
Sn+2	20.45	20.85
U+4	29.13	31.03
TcO	**20.00**	22.42

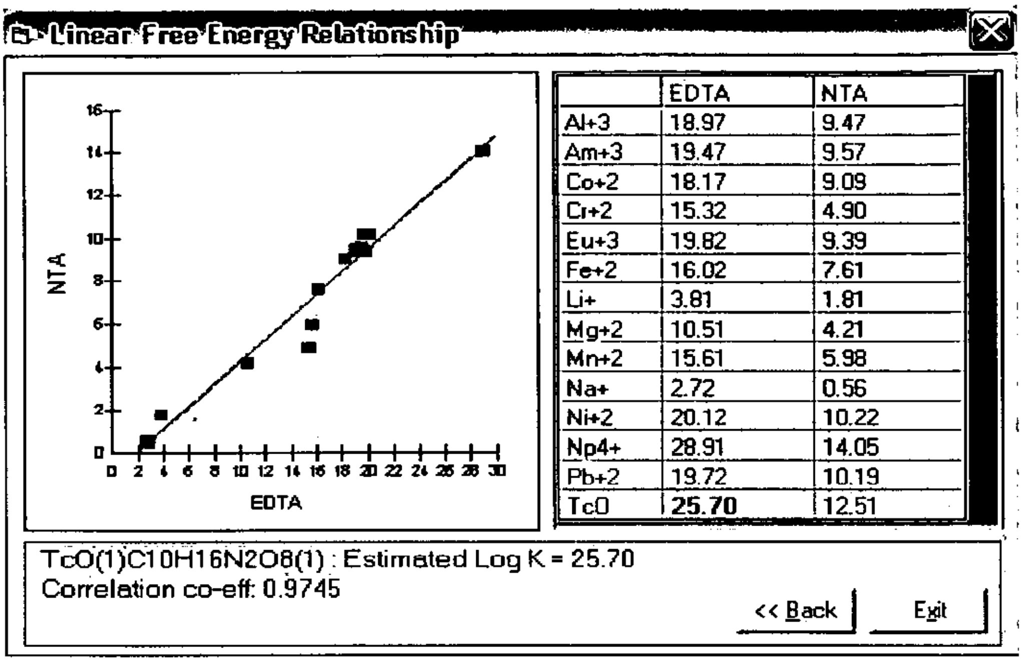
TcO(1)C10H16N2O8(1) : Estimated Log K = 20.00
Correlation co-eff: 0.9893

Fig. 4.44: Linear free energy relationship between stability constants for M-EDTA and M-CDTA

Using the STAB computer programme and LFER 1 the log of the stability constants for technetium(IV) EDTA (log $\beta_{\text{Pred - (CDTA)}}$) was predicted to be 20.00 (Fig. 4.44). The linear free energy relationship between the log of the stability constants for M-EDTA and M-CDTA complexes had a good linear relationship and gave an $r^2 = 0.9893$.

Fig. 4.45 shows the LFER for the log of the stability constants for M-EDTA against log of the stability constants for M-NTA (Fig. 4.45)

Using the STAB computer programme and LFER 2 the log of the stability constant for technetium(IV) EDTA (log $\beta_{\text{Pred - (NTA)}}$) was predicted to be 25.70 (Fig. 4.40). The linear free energy relationship between the log of the stability constants for M-EDTA and M-NTA complexes had a good linear relationship and gave an $r^2 = 0.9745$



Linear Free Energy Relationship

	EDTA	NTA
Al+3	18.97	9.47
Am+3	19.47	9.57
Co+2	18.17	9.09
Cr+2	15.32	4.90
Eu+3	19.82	9.39
Fe+2	16.02	7.61
Li+	3.81	1.81
Mg+2	10.51	4.21
Mn+2	15.61	5.98
Na+	2.72	0.56
Ni+2	20.12	10.22
Np4+	28.91	14.05
Pb+2	19.72	10.19
TcO	**25.70**	12.51

TcO(1)C10H16N2O8(1) : Estimated Log K = 25.70
Correlation co-eff: 0.9745

Fig. 4.45: Linear free energy relationship between stability constants for M-EDTA and M-NTA

From Table 4.74 it can be seen that the value for the predicted stability constant for the Tc(IV)-EDTA complex is not in agreement with the stability constants determined in this thesis.

	Experimentally determined log β		Predicted log β	
[L] (mol dm^{-3})	log $\beta_{Exp't(SnCl2)}$	log $\beta_{Exp't(electrochem)}$	log $\beta_{Pred-(CDTA)}$	log $\beta_{Pred-(NTA)}$
0.2	15.2 ± 0.1		20.0	25.7
0.1	14.7 ± 0.2	14.2 ± 0.6		
0.05	14.2 ± 0.2	13.1 ± 0.1		

Table 4.74: Measured and predicted Tc(IV)EDTA complex stability constants

Small differences between the measured and linear free energy relationship predicted stability constants can be explained due to the empirical nature of the prediction because the error on the prediction is not calculated as this would have to take into account the individual errors on each stability constant. However as it can be seen the differences are very large. The reason for this could be that the constants entered into the STAB computer program database were for the technetium species TcO^{2+}, however, the technetium species $TcO(OH)^+$ was assumed for the calculation of the stability constants in this project.

The Tc(IV)-EDTA complex stability constants were recalculated assuming that TcO^{2+} was the technetium species present (Table 4.75) and not $TcO(OH)^+$ (Section 9.2).

	Experimentally determined log β		**Predicted log β**	
[L] (mol dm^{-3})	**log $\beta_{Exp't(SnCl2)}$**	**log $\beta_{Exp't(electrochem)}$**	**log $\beta_{Pred - (CDTA)}$**	**log $\beta_{Pred - (NTA)}$**
0.2	26.5 ± 0.2	[redacted]	20.0	25.7
0.1	25.6 ± 0.3	26.6 ± 0.8		
0.05	24.5 ± 0.9	26.2 ± 0.3		

Table 4.75: Measured and predicted Tc(IV)EDTA complex stability constants

From Table 4.75 it can now be seen that there is good agreement between the technetium(IV)-EDTA stability constants determined experimentally in this thesis and the technetium(IV)-EDTA stability constant predicted using LFER 2 (log $\beta_{Pred - (NTA)}$). However, there is still a large difference (10^4 – 10^6) between the experimentally determined technetium(IV)-EDTA stability constants and the technetium(IV) EDTA log of the stability constant predicted using LFER 1 (log $\beta_{Pred - (CDTA)}$). This maybe be due to the conditions under which the experiments were performed when the technetium CDTA stability constant was determined.

4.19 Errors analysis for stability constants

4.19.1 Assumptions

The error analysis was performed to give an approximation of the errors in the stability constants due to the counting statistics only. All other errors were assumed to be neiglible.

4.19.2 Estimated error for the stability constant for Tc(IV)EDTA

The error was estimated for a stability constant calculated for the formation of Tc(IV)EDTA complex.

4.19.2.1 Estimated error in $\Delta[\mathrm{Tc}]_{\mathrm{Sol}}$

To calculate the concentration of technetium solution the following equation is used:

$$[\mathrm{Tc}]_{\mathrm{Sol}} = \frac{\left(\left(\frac{(\mathrm{cpm} - \mathrm{BKG})}{0.98}\right) - 1.66\right)}{6.4 \times 10^{9}}$$

This equation is derived from calibration curves calculated in section 4.1. Using the rules for the propagation of error (section 9.3) the error in the calculated concentration can be estimated.

Therefore when Tc(IV) is placed in a solution of 0.2 mol dm^{-3} EDTA the following count rates were measured:

cpm = 2166.0 ± 21.7

BKG = 12.4 ± 0.1 cpm

Therefore, the concentration of technetium in solution is 3.25 $\times 10^{-7}$ mol dm^{-3}. The error in this is given as:

$$[\mathrm{Tc}]_{\mathrm{Sol}} \pm \Delta[\mathrm{Tc}]_{\mathrm{Sol}} = 3.25 \pm 0.03 \times 10^{-7}\ \mathrm{mol\,dm^{-3}}$$

For the calculation of the solubility product and the concentration of the Tc(IV) ion the concentration of technetium in solution in the absence of any ligand needs to calculated. Therefore using the following count rates:

cpm = 22.9 ± 0.2

BKG = 12.4 ± 0.1 cpm

Therefore, the concentration of technetium in solution is 1.41 $\times10^{-9}$ mol dm^{-3}, the error in this is given as:

$$[\mathrm{Tc}]_{\mathrm{Sol}} \pm \Delta[\mathrm{Tc}]_{\mathrm{Sol}} = 1.41 \pm 0.20 \times 10^{-9}\ \mathrm{mol\,dm^{-3}}$$

4.19.2.2 Estimated error in the solubility product, K_{sp}

To calculate the solubility product the following equation is used.

$$K_{sp} = \frac{[\mathrm{Tc}]_{\mathrm{sol}}\left[\mathrm{OH^-}\right]}{A}$$

The solubility product is calculated using the concentration of technetium in solution in the absence of ligands. Therefore using the rules for the propagation of error and the estimated error in section 4.19.2.1 and the follwing data:

$[\mathrm{OH^-}]$ = 0.36 mol dm^{-3}
A = 1.43 $\times10^{11}$

The error in the solubility product is estimated at:

$$K_{sp} = 3.55 \pm 0.5 \times 10^{-21}$$

4.19.2.3 Estimated error in $\left[\mathrm{TcO(OH)^+}\right]$

To calculate the concentration of the $\left[\mathrm{TcO(OH)^+}\right]$ the following equation is used.

$$\left[\mathrm{TcO(OH)^+}\right]=\frac{K_{sp}}{\left[\mathrm{OH^-}\right]}$$

Therefore using the error estimated in section 4.19.2.2 the estimated error for $\left[\mathrm{TcO(OH)^+}\right]$ is:

$$\left[\mathrm{TcO(OH)^+}\right]=9.87\pm1.39\times10^{-21}\ \mathrm{mol\,dm^{-3}}$$

4.19.2.4 Estimated error in $\left[\mathrm{TcO(OH)EDTA^{y-1}}\right]$

To calculate the concentration of Tc(IV) – EDTA complex in solution, $\left[\mathrm{TcO(OH)EDTA^{y-1}}\right]$, the following equation is used.

$$\left[\mathrm{TcO(OH)EDTA^{y-1}}\right]=[\mathrm{Tc}]_{\mathrm{Sol}}-\left[\mathrm{TcO(OH)^+}\right]\mathrm{A}$$

Using the estimated errors for $[\mathrm{Tc}]_{\mathrm{Sol}}$, in the presence of 0.2 mol dm^{-3} EDTA, and $\left[\mathrm{TcO(OH)^+}\right]$, the error in $\left[\mathrm{TcO(OH)EDTA^{y-1}}\right]$ is estimated to be.

$$\left[\mathrm{TcO(OH)EDTA^{y-1}}\right]=3.41\pm0.032\times10^{-7}\ \mathrm{mol\,dm^{-3}}$$

4.19.2.5 Estimated error in β

To calculate the stability constant (β) for the Tc(IV) EDTA complex the following equation is used.

$$\beta=\frac{\left[\mathrm{TcO(OH)EDTA^{y-1}}\right]}{\left[\mathrm{TcO(OH)^+}\right]\left[\mathrm{EDTA^{y-}}\right]}$$

Therefore using the errors estimated in sections 4.19.2.1 to 4.19.2.4 and the rules for the propagation of errors (section 9.3) the error in β is:

$$\beta = 1.73 \pm 0.25 \times 10^{14}$$

4.19.3 Estimation of the errors for all stability constants calculated

The method desribed in section 4.19.3 was applied to all the solubility products and the stability constants caulated for Tc(IV) complex with the following ligands, EDTA, NTA, ISA, Gluconic acid and Picolinic.

4.19.3.1 Estimation of errors for stability constants using $SnCl_2$ for the reduction of pertechnetate

4.19.3.1.1 Solubility product, K_{sp}

Sample	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	A Term	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	K_{SP}	± K_{SP}
1	0.36	22.9	0.2	7.9	0.4	1.43E+11	7.52E-10	1.97E-10	1.89E-21	4.95E-22
2	0.29	20.3	0.2	5.2	0.4	1.14E+11	4.31E-10	2.01E-10	1.08E-21	5.05E-22
3	0.32	19.6	0.2	4.5	0.4	1.26E+11	3.45E-10	2.02E-10	8.66E-22	5.08E-22
4	0.23	17.9	0.2	2.8	0.3	9.20E+10	1.35E-10	2.05E-10	3.38E-22	5.14E-22
5	0.37	18.4	0.2	3.3	0.3	1.48E+11	1.96E-10	2.04E-10	4.93E-22	5.13E-22

Table 4.76: Estimated errors for the solubility product, K_{sp}

The mean error in the solubility product, K_{sp}, was calculated and used in subsequent calculations of the error in the stability constants. The mean error was found to be 5.07×10^{-22}.

4.19.3.1.2 Tc(IV) - EDTA complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.42	2166.0	21.7	2197.6	21.8	3.25E-07	3.14E-09	2.23E-21	1.21E-21	3.24E-07	3.35E-09	2.21E+15	1.20E+15
2	0.34	2003.2	20.0	2031.4	20.2	2.99E-07	2.89E-09	2.75E-21	1.49E-21	2.98E-07	3.09E-09	1.64E+15	8.93E+14
3	0.33	2126.5	21.3	2157.3	21.4	3.18E-07	3.08E-09	2.87E-21	1.56E-21	3.18E-07	3.28E-09	1.68E+15	9.11E+14
4	0.33	2175.2	21.8	2207.0	21.9	3.26E-07	3.16E-09	2.82E-21	1.53E-21	3.26E-07	3.36E-09	1.75E+15	9.50E+14
5	0.27	1885.9	18.9	1911.7	19.0	2.80E-07	2.71E-09	3.45E-21	1.88E-21	2.80E-07	2.91E-09	1.23E+15	6.66E+14
6	0.46	334.7	3.4	328.9	3.5	4.70E-08	2.83E-10	2.03E-21	1.10E-21	4.66E-08	4.85E-10	6.09E+14	3.31E+14
7	0.41	267.0	2.7	259.7	2.8	3.71E-08	1.77E-10	2.28E-21	1.24E-21	3.67E-08	3.79E-10	4.28E+14	2.32E+14
8	0.33	298.1	3.0	291.6	3.1	4.16E-08	2.26E-10	2.82E-21	1.53E-21	4.13E-08	4.28E-10	3.88E+14	2.11E+14
9	0.54	515.5	5.2	513.3	5.3	7.35E-08	5.65E-10	1.74E-21	9.44E-22	7.31E-08	7.67E-10	1.12E+15	6.06E+14
10	0.37	277.2	2.8	270.2	2.9	3.86E-08	1.93E-10	2.55E-21	1.39E-21	3.82E-08	3.95E-10	3.97E+14	2.15E+14
11	0.33	129.5	1.3	119.5	1.4	1.70E-08	3.77E-11	2.86E-21	1.55E-21	1.66E-08	2.40E-10	2.47E+14	1.34E+14
12	0.26	64.0	0.6	52.6	0.8	7.36E-09	1.40E-10	3.63E-21	1.97E-21	6.99E-09	3.42E-10	8.17E+13	4.45E+13
13	0.21	104.8	1.1	94.3	1.2	1.33E-08	7.63E-11	4.43E-21	2.41E-21	1.30E-08	2.78E-10	1.24E+14	6.75E+13
14	0.40	101.8	1.0	91.3	1.1	1.29E-08	8.09E-11	2.35E-21	1.27E-21	1.25E-08	2.83E-10	2.27E+14	1.23E+14
15	0.32	74.9	0.8	63.7	0.9	8.96E-09	1.23E-10	2.95E-21	1.60E-21	8.58E-09	3.25E-10	1.24E+14	6.72E+13

Table 4.77: Estimated errors for Tc(IV) - EDTA complex stability constants

4.19.3.1.3 Tc(IV) - NTA complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.43	442.4	4.4	436.0	4.6	6.34E-08	4.56E-10	2.18E-21	1.20E-21	6.31E-08	6.60E-10	4.71E+14	2.59E+14
2	0.29	512.0	5.1	507.0	5.3	7.38E-08	5.64E-10	3.22E-21	1.77E-21	7.35E-08	7.69E-10	3.72E+14	2.04E+14
3	0.34	481.6	4.8	476.0	5.0	6.93E-08	5.17E-10	2.75E-21	1.51E-21	6.89E-08	7.22E-10	4.09E+14	2.25E+14
4	0.37	462.5	4.6	456.5	4.8	6.65E-08	4.87E-10	2.56E-21	1.41E-21	6.61E-08	6.92E-10	4.21E+14	2.31E+14
5	0.37	480.5	4.8	474.9	5.0	6.91E-08	5.15E-10	2.56E-21	1.41E-21	6.88E-08	7.20E-10	4.37E+14	2.40E+14
6	0.34	169.8	1.7	157.7	1.9	2.27E-08	2.96E-11	2.74E-21	1.51E-21	2.23E-08	2.34E-10	2.57E+14	1.41E+14
7	0.17	170.6	1.7	158.6	1.9	2.28E-08	3.08E-11	5.47E-21	3.01E-21	2.25E-08	2.36E-10	1.30E+14	7.12E+13
8	0.37	174.8	1.8	162.9	1.9	2.35E-08	3.75E-11	2.54E-21	1.40E-21	2.31E-08	2.42E-10	2.86E+14	1.57E+14
9	0.35	221.8	2.2	210.8	2.4	3.05E-08	1.11E-10	2.67E-21	1.47E-21	3.01E-08	3.16E-10	3.55E+14	1.95E+14
10	0.37	195.9	2.0	184.5	2.1	2.66E-08	7.05E-11	2.54E-21	1.40E-21	2.62E-08	2.75E-10	3.25E+14	1.79E+14
11	0.37	21.3	0.2	6.2	0.4	5.55E-10	2.02E-10	2.56E-21	1.41E-21	1.83E-10	4.07E-10	4.23E+12	9.70E+12
12	0.43	20.9	0.2	5.8	0.4	5.06E-10	2.03E-10	2.18E-21	1.20E-21	1.33E-10	4.08E-10	3.63E+12	1.13E+13
13	0.27	22.3	0.2	7.2	0.4	6.72E-10	2.01E-10	3.42E-21	1.88E-21	3.00E-10	4.06E-10	5.20E+12	7.59E+12

Table 4.78: Estimated errors for Tc(IV) - NTA complex stability constants

4.19.3.1.4 Tc(IV) - ISA complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.29	388.5	3.9	395.5	4.3	5.75E-08	4.09E-10	3.20E-21	1.76E-21	5.71E-08	6.14E-10	2.48E+14	1.36E+14
2	0.27	351.3	3.5	356.0	3.9	5.17E-08	3.47E-10	3.45E-21	1.90E-21	5.14E-08	5.52E-10	2.06E+14	1.14E+14
3	0.37	356.0	3.6	361.0	3.9	5.25E-08	3.55E-10	2.56E-21	1.41E-21	5.21E-08	5.60E-10	2.82E+14	1.55E+14
4	0.33	379.3	3.8	385.7	4.2	5.61E-08	3.94E-10	2.80E-21	1.54E-21	5.57E-08	5.98E-10	2.76E+14	1.52E+14
5	0.29	337.5	3.4	341.5	3.7	4.96E-08	3.24E-10	3.20E-21	1.76E-21	4.92E-08	5.29E-10	2.13E+14	1.17E+14
6	0.30	237.7	2.4	227.0	2.6	3.29E-08	1.44E-10	3.17E-21	1.74E-21	3.25E-08	3.48E-10	2.35E+14	1.29E+14
7	0.23	226.0	2.3	215.1	2.5	3.11E-08	1.25E-10	4.03E-21	2.22E-21	3.07E-08	3.30E-10	1.75E+14	9.63E+13
8	0.17	247.8	2.5	237.4	2.7	3.44E-08	1.60E-10	5.43E-21	2.98E-21	3.40E-08	3.65E-10	1.44E+14	7.92E+13
9	0.43	254.0	2.5	243.7	2.8	3.53E-08	1.70E-10	2.18E-21	1.20E-21	3.49E-08	3.75E-10	3.68E+14	2.02E+14
10	0.23	229.2	2.3	218.4	2.5	3.16E-08	1.30E-10	4.05E-21	2.23E-21	3.12E-08	3.35E-10	1.77E+14	9.74E+13
11	0.62	109.3	1.1	94.3	1.3	1.34E-08	6.45E-11	1.51E-21	8.28E-22	1.30E-08	2.69E-10	2.96E+14	1.63E+14
12	0.27	85.2	0.9	70.1	1.0	9.88E-09	1.02E-10	3.53E-21	1.94E-21	9.51E-09	3.07E-10	9.22E+13	5.08E+13
13	0.27	97.8	1.0	82.7	1.1	1.17E-08	8.26E-11	3.45E-21	1.90E-21	1.14E-08	2.87E-10	1.13E+14	6.20E+13
14	0.27	84.2	0.8	69.2	1.0	9.74E-09	1.04E-10	3.45E-21	1.90E-21	9.37E-09	3.08E-10	9.27E+13	5.11E+13
15	0.17	105.1	1.1	90.1	1.2	1.28E-08	7.11E-11	5.47E-21	3.01E-21	1.24E-08	2.76E-10	7.77E+13	4.28E+13

Table 4.79: Estimated errors for Tc(IV) - ISA complex stability constants

4.19.3.1.5 Tc(IV) - gluconate complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.23	1080.8	10.8	1090.2	11.2	1.52E-07	1.48E-09	4.05E-21	2.43E-21	1.51E-07	1.71E-09	6.23E+14	3.73E+14
2	0.29	1199.9	12.0	1211.7	12.4	1.71E-07	1.67E-09	3.20E-21	1.92E-21	1.70E-07	1.90E-09	8.87E+14	5.31E+14
3	0.29	1100.5	11.0	1110.3	11.4	1.55E-07	1.51E-09	3.21E-21	1.92E-21	1.54E-07	1.74E-09	8.02E+14	4.80E+14
4	0.25	1074.3	10.7	1083.6	11.1	1.51E-07	1.47E-09	3.75E-21	2.25E-21	1.50E-07	1.70E-09	6.67E+14	4.00E+14
5	0.29	1058.9	10.6	1067.8	10.9	1.48E-07	1.45E-09	3.23E-21	1.93E-21	1.48E-07	1.67E-09	7.64E+14	4.58E+14
6	0.23	424.0	4.2	420.0	4.5	6.11E-08	4.36E-10	4.05E-21	2.42E-21	6.07E-08	6.59E-10	5.07E+14	3.04E+14
7	0.22	464.8	4.7	461.7	4.9	6.72E-08	5.01E-10	4.17E-21	2.49E-21	6.68E-08	7.24E-10	5.43E+14	3.25E+14
8	0.27	438.6	4.4	434.9	4.6	6.33E-08	4.60E-10	3.45E-21	2.06E-21	6.29E-08	6.83E-10	6.17E+14	3.70E+14
9	0.45	496.3	5.0	493.8	5.2	7.19E-08	5.52E-10	2.08E-21	1.24E-21	7.15E-08	7.75E-10	1.16E+15	6.97E+14
10	0.29	476.4	4.8	473.4	5.0	6.89E-08	5.20E-10	3.20E-21	1.92E-21	6.86E-08	7.43E-10	7.24E+14	4.33E+14
11	0.27	116.5	1.2	106.2	1.3	1.52E-08	5.39E-11	3.50E-21	2.10E-21	1.48E-08	2.77E-10	2.94E+14	1.76E+14
12	0.28	145.4	1.5	135.7	1.6	1.95E-08	7.73E-12	3.33E-21	2.00E-21	1.91E-08	2.31E-10	3.99E+14	2.39E+14
13	0.29	140.1	1.4	130.3	1.6	1.87E-08	1.62E-11	3.25E-21	1.95E-21	1.83E-08	2.39E-10	3.92E+14	2.35E+14
14	0.23	200.5	2.0	191.9	2.2	2.77E-08	8.00E-11	4.04E-21	2.42E-21	2.73E-08	3.03E-10	4.70E+14	2.82E+14
15	0.52	198.9	2.0	190.3	2.2	2.75E-08	7.75E-11	1.80E-21	1.08E-21	2.71E-08	3.00E-10	1.05E+15	6.28E+14

Table 4.80: Estimated errors for Tc(IV) - gluconate complex stability constants

4.19.3.1.6 Tc(IV) - picolinate complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.33	2018.4	20.2	2044.4	20.7	2.99E-07	2.98E-09	2.85E-21	1.57E-21	2.99E-07	3.18E-09	1.46E+15	8.04E+14
2	0.43	2182.2	21.8	2211.6	22.4	3.23E-07	3.24E-09	2.19E-21	1.20E-21	3.23E-07	3.44E-09	2.06E+15	1.13E+15
3	0.40	1989.5	19.9	2015.0	20.4	2.95E-07	2.93E-09	2.37E-21	1.30E-21	2.94E-07	3.14E-09	1.74E+15	9.54E+14
4	0.18	2031.3	20.3	2057.7	20.9	3.01E-07	3.00E-09	5.34E-21	2.94E-21	3.01E-07	3.20E-09	7.86E+14	4.32E+14
5	0.36	2084.9	20.9	2112.4	21.4	3.09E-07	3.08E-09	2.63E-21	1.45E-21	3.09E-07	3.29E-09	1.64E+15	9.02E+14
6	0.40	529.1	5.3	524.8	5.5	7.65E-08	6.04E-10	2.37E-21	1.30E-21	7.61E-08	8.09E-10	1.09E+15	6.02E+14
7	0.34	529.3	5.3	525.0	5.5	7.65E-08	6.04E-10	2.76E-21	1.52E-21	7.61E-08	8.09E-10	9.41E+14	5.18E+14
8	0.20	527.9	5.3	523.6	5.5	7.63E-08	6.02E-10	4.65E-21	2.56E-21	7.59E-08	8.07E-10	5.56E+14	3.06E+14
9	0.28	535.0	5.4	530.8	5.6	7.73E-08	6.13E-10	3.40E-21	1.87E-21	7.70E-08	8.18E-10	7.72E+14	4.25E+14
10	0.33	543.0	5.4	539.0	5.7	7.85E-08	6.26E-10	2.84E-21	1.56E-21	7.82E-08	8.31E-10	9.37E+14	5.15E+14
11	0.32	436.7	4.4	430.5	4.6	6.26E-08	4.57E-10	2.96E-21	1.63E-21	6.23E-08	6.61E-10	2.56E+15	1.41E+15
12	0.28	411.8	4.1	405.1	4.3	5.89E-08	4.17E-10	3.33E-21	1.83E-21	5.86E-08	6.22E-10	2.14E+15	1.18E+15
13	0.21	409.8	4.1	403.0	4.3	5.86E-08	4.14E-10	4.41E-21	2.43E-21	5.82E-08	6.18E-10	1.61E+15	8.84E+14
14	0.37	430.3	4.3	424.0	4.5	6.17E-08	4.46E-10	2.54E-21	1.40E-21	6.13E-08	6.51E-10	2.94E+15	1.62E+15
15	0.34	440.4	4.4	434.3	4.6	6.32E-08	4.63E-10	2.74E-21	1.50E-21	6.28E-08	6.67E-10	2.79E+15	1.54E+15

Table 4.81: Estimated errors for Tc(IV) - picolinate complex stability constants

4.19.3.2 Estimation of errors for stability constants using electrochemical reduction of pertechnetate

4.19.3.2.1 Solubility product, K_{sp}

Sample	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	A Term	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	K_{SP}	± K_{SP}
1	0.47	143.8	1.4	134.1	1.6	1.87E+11	1.60E-08	1.04E-11	4.03E-20	2.60E-23
2	0.39	33.8	0.3	21.8	0.3	1.55E+11	2.44E-09	2.06E-10	6.13E-21	5.16E-22
3	0.33	32.8	0.3	20.9	0.3	1.32E+11	2.32E-09	2.07E-10	5.83E-21	5.20E-22
4	0.30	21.7	0.2	9.5	0.2	1.19E+11	9.43E-10	2.25E-10	2.37E-21	5.65E-22
5	0.28	32.8	0.3	20.8	0.3	1.12E+11	2.32E-09	2.07E-10	5.83E-21	5.20E-22
6	0.28	141.0	1.4	131.2	1.4	1.12E+11	1.57E-08	3.46E-11	3.94E-20	8.68E-23
7	0.37	72.6	0.7	61.4	0.7	1.32E+11	7.23E-09	1.44E-10	1.82E-20	3.61E-22
8	0.33	49.3	0.5	37.7	0.5	1.32E+11	4.36E-09	1.81E-10	1.09E-20	4.54E-22
9	0.42	62.7	0.6	51.3	0.6	1.32E+11	6.01E-09	1.59E-10	1.51E-20	4.00E-22

Table 4.82: Estimated Errors for the solubility product, K_{sp}

The mean error in the solubility product, K_{sp}, was calculated and used in subsequent calculations of the error in the stability constants. The mean error was found to be 3.82×10^{-22}.

4.19.3.2.2 Tc(IV) – EDTA complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.47	137.5	1.4	127.7	1.5	1.83E-08	2.04E-11	8.59E-20	8.18E-22	2.28E-09	1.73E-10	2.65E+12	2.03E+11
2	0.33	140.7	1.4	130.9	1.4	1.88E-08	3.51E-11	1.76E-20	1.16E-21	1.65E-08	1.88E-10	9.34E+13	6.23E+12
3	0.30	174.6	1.8	165.5	1.8	2.38E-08	1.90E-11	7.90E-21	1.28E-21	2.29E-08	1.72E-10	2.90E+14	4.70E+13
4	0.37	525.0	5.3	523.1	5.4	7.62E-08	5.78E-10	4.93E-20	1.04E-21	6.90E-08	7.30E-10	1.40E+13	3.30E+11
5	0.33	261.0	2.6	253.6	2.7	3.68E-08	1.57E-10	3.32E-20	1.16E-21	3.24E-08	3.09E-10	9.77E+12	3.55E+11
6	0.42	365.5	3.7	360.3	3.7	5.24E-08	3.23E-10	3.61E-20	9.17E-22	4.64E-08	4.76E-10	1.28E+13	3.51E+11

Table 4.83: Estimated errors for Tc(IV) - EDTA complex stability constants

4.19.3.2.3 Tc(IV) – NTA complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.34	117.9	1.2	107.7	1.3	1.54E-08	5.16E-11	3.94E-20	1.17E-21	1.00E-08	2.11E-10	2.54E+13	5.36E+11
2	0.38	169.6	1.7	160.4	1.9	2.31E-08	3.08E-11	3.54E-20	1.05E-21	1.77E-08	1.90E-10	5.00E+13	5.37E+11
3	0.39	72.3	0.7	61.1	0.9	8.56E-09	1.24E-10	3.49E-20	1.04E-21	3.18E-09	2.84E-10	9.10E+12	8.14E+11
4	0.33	208.2	2.1	199.8	2.3	2.89E-08	9.23E-11	1.75E-20	1.22E-21	2.66E-08	2.52E-10	1.52E+13	1.44E+11
5	0.42	170.6	1.7	161.5	1.9	2.33E-08	3.25E-11	1.54E-20	9.49E-22	2.07E-08	1.92E-10	1.34E+13	1.25E+11
6	0.36	92.9	0.9	82.1	1.1	1.16E-08	9.15E-11	2.53E-20	1.11E-21	7.99E-09	2.51E-10	3.16E+12	9.92E+10

Table 4.84: Estimated errors for Tc(IV) - NTA complex stability constants

4.19.3.2.4 Tc(IV) – ISA complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.36	40.4	0.4	28.6	0.5	3.80E-09	1.75E-10	1.05E-20	1.04E-21	2.30E-09	3.24E-10	2.19E+13	3.09E+12
2	0.45	70.5	0.7	59.3	0.9	8.30E-09	-1.27E-10	8.39E-21	8.37E-22	6.80E-09	2.17E-11	8.11E+13	2.59E+11
3	0.68	53.0	0.5	41.5	0.7	5.68E-09	1.55E-10	1.68E-20	5.53E-22	1.16E-09	3.04E-10	6.93E+12	1.81E+12
4	0.33	130.5	1.3	120.5	1.5	1.73E-08	-3.15E-11	5.82E-20	1.14E-21	9.65E-09	1.17E-10	1.66E+12	2.02E+10
5	0.44	106.2	1.1	95.8	1.2	1.36E-08	-7.02E-11	4.94E-20	8.45E-22	4.93E-09	7.87E-11	9.98E+11	1.59E+10
6	0.34	110.8	1.1	100.4	1.3	1.43E-08	6.30E-11	7.23E-20	1.12E-21	4.67E-09	2.12E-10	6.46E+11	2.93E+10

Table 4.85: Estimated errors for Tc(IV) - ISA complex stability constants

4.19.3.2.5 Tc(IV) - gluconate complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.47	38.0	0.4	24.1	0.5	2.72E-09	1.77E-10	3.05E-21	7.97E-22	2.15E-09	3.26E-10	7.03E+13	2.12E+13
2	0.27	98.2	1.0	84.3	1.0	1.20E-08	1.03E-10	6.68E-20	1.41E-21	4.92E-09	2.52E-10	7.37E+12	4.08E+11
3	0.34	54.1	0.5	40.2	0.6	5.50E-09	1.73E-10	2.91E-20	1.11E-21	1.58E-09	3.22E-10	5.41E+12	1.13E+12
4	0.35	109.0	1.1	95.1	1.1	1.35E-08	8.56E-11	5.68E-20	1.08E-21	5.69E-09	2.35E-10	1.00E+12	4.55E+10
5	0.31	110.1	1.1	96.2	1.1	1.37E-08	8.38E-11	8.23E-20	1.21E-21	3.60E-09	2.33E-10	4.37E+11	2.90E+10
6	0.42	109.7	1.1	95.8	1.1	1.36E-08	8.45E-11	5.21E-20	8.92E-22	4.92E-09	2.34E-10	9.44E+11	4.76E+10

Table 4.86: Estimated errors for Tc(IV) - gluconate complex stability constants

4.19.3.2.6 Tc(IV) - picolinate complex stability constants

	$[OH^-]$ (mol dm^{-3})	cpm	± cpm	dpm	± dpm	$[Tc]_{sol}$ (mol dm^{-3})	± $[Tc]_{sol}$ (mol dm^{-3})	$[TcO(OH)^+]$ (mol dm^{-3})	±[TcO(OH)+] (mol dm^{-3})	[TcL] (mol dm^{-3})	± [TcL] (mol dm^{-3})	β	± β
1	0.31	106.6	1.1	94.2	1.2	1.12E-08	6.97E-11	6.95E-21	1.31E-21	1.04E-08	2.28E-10	1.49E+13	2.82E+12
2	0.42	134.5	1.3	122.1	1.5	1.75E-08	2.52E-11	1.37E-20	9.51E-22	1.52E-08	1.84E-10	1.11E+13	7.86E+11
3	0.41	198.7	2.0	186.3	2.2	2.69E-08	7.72E-11	5.73E-20	9.65E-22	1.75E-08	2.36E-10	3.05E+12	6.58E+10
4	0.38	61.5	0.6	49.1	0.8	5.74E-09	1.42E-10	2.73E-20	1.06E-21	1.65E-09	3.00E-10	6.05E+12	1.13E+12
5	0.30	73.6	0.7	61.2	0.9	8.57E-09	1.22E-10	3.40E-20	1.32E-21	4.48E-09	2.81E-10	1.32E+13	9.73E+11
6	0.35	68.4	0.7	56.0	0.8	7.81E-09	1.31E-10	2.96E-20	1.15E-21	3.72E-09	2.89E-10	1.26E+13	1.09E+12

Table 4.87: Estimated errors for Tc(IV) - picolinate complex stability constants

4.20 Summary

The reduction of pertechnetate was investigated and it was found that the best reducing agents, i.e. the reducing agents that reduce technetium to the solubility levels expected of technetium(IV) are Fe(II) and Sn(II). It was also found that at near neutral pH Fe(0) is an excellent reducing agent for technetium(VII), however, at high pH Fe(0) becomes passive and the kinetics of the reduction are severely hindered.

Using the Sn(II) as the reducing agent for technetium(VII) the solubility of technetium(IV) was investigated in increasingly alkaline conditions. It was found that between the pH 11 and 13 the concentration of technetium in solution was in agreement with the expected solubility of technetium(IV) from the literature. However, above pH 13 it was observed that the solubility of technetium(IV) increased. Eriksen *et al* [39] observed a similar solubility increase at a lower pH (pH *ca.* 10.5). The explanation for this increase was due to the formation of an anionic technetium(IV) species, $TcO(OH)_3^-$. Although this study does not agree with the pH at which the solubility increase occurs the formation of $TcO(OH)_3^-$ is the most likely explanation. The formation constant was estimated with data from this study and was found to be log k_{sp}= -20.6. The log of the constant for the formation of $TcO(OH)_3^-$ was determined by Eriksen *et al* [39] to be -19.2.

The effect that low molecular weight organics have upon the reduction of technetium(VII) to technetium(IV) was investigated. In the absence of ligands, technetium(VII), in the form of TcO_4^-, is reduced to the insoluble TcO_2(s). However, the insoluble TcO_2(s) is not produced when the complexing ligands, EDTA, NTA, ISA, gluconic acid and picolinic acid, are present during the reduction of pertechnetate. The results in this project show, through solubility studies, that complexation occurs during the reduction. For NTA, ISA, gluconic acid and picolinic acid it is thought that technetium(V) complexes are formed. However, it is thought that for EDTA technetium(IV) complexes are formed.

The solubility of the solid TcO_2 was also measured in the presence of the low molecular weight organics and it was shown that there was a solubility increase with increasing ligand concentration. This is due to the formation of soluble technetium complexes. These data show that when TcO_4^- is reduced in the presence of ligands technetium(V) complexes are formed, however, when the ligands are contacted with TcO_2(s), technetium(IV) complexes are formed. Using these data from the solubility studies the stability constants for the technetium(IV) complexes were determined and are within the range, 13.8 – 14.9. The use a $SnCl_2$ as a reducing agent introduces the possibility of competition for the ligands and changes the free concentration of the ligand available for complexation with the technetium. By measuring the solubility increases due to complexation of Sn(II) with the individual ligands the stability constants for the Sn(II) – ligand complexes were determined, and found to be in the range 24.6 – 25.5. These data where then used to estimate the actual free ligand concentration available for complexation with technetium. Taking the competition effect into account the technetium(IV) stability constants were determined again, using the estimated free ligand concentration and the log of the stability constants were found to be in the range 14.3 – 15.2.

To remove any competition effect introduced into the system, by the use of a metallic reducing agent, a clean electrochemical method of reduction was developed for the reduction of TcO_4^- to TcO_2(s). The electrochemical cell consists of a reticulated vitreous carbon electrode (cathode) and platinum wire electrode (anode). The reduction of technetium(VII) using this technique gives a solubility of technetium(IV) well within the limits of the literature solubility for TcO_2(s) [38, 40]. Using this method of reduction the solubility of TcO_2(s) was measured in the presence of the ligands and it was shown that the solubility of technetium(IV) increased with increasing ligand concentration, due to the formation of technetium complexes. The conditional stability constants calculated for technetium(IV) and the ligands of interest were determined using the solubility product approach and are within the range 13.0 – 14.0 assuming that the stoichiometry is 1:1.

Using data from the literature and the computer program STAB, developed at Loughborough University [66], it was possible to predict the stability constants for the technetium(IV)-EDTA complex using a linear free energy relationship (LFER). The predicted constant for the technetium(IV) – EDTA complex, using the M-EDTA and M'-NTA linear free energy relationship, was in good agreement. However, as the speciation of technetium(IV) differed between this project and the literature the derivation of technetium(IV) – EDTA complex stability constant was changed (Section 9.2.1) to fit the literature.

Chapter 5 –

Modelling

5.0 Modelling

Moving from the near field to the far field of a nuclear waste repository several gradients are produced (Fig. 2.6). For example, a pH gradient is produced, the near field of a nuclear waste repository will initially be at *ca.* pH 13.3 (section 2.6.1.3) and the natural pH of the environment is *ca.* pH 5 - 8. If a radionuclide escapes from the near field of a nuclear waste repository and is exposed to a pH gradient it is important to know how that radionuclide behaves. Using a speciation code (CHESS [50]) and the stability constants determined in this work for each complex the behaviour of these technetium(IV) complexes can be estimated in terms of the solubility and speciation of technetium(IV) over a given pH gradient.

All the following speciation curves are calculated using the constants measured in section 4 and under the assumption that all complexes have a 1:1 metal – ligand stoichiometry.

5.1 Correcting for Ionic Strength

The stability constants in the Chess database [50] are thermodynamic stability constants which have been corrected to zero ionic strength. Therefore, to be able to compare the stability constants for technetium(IV) complexes, determined in chapter 4, they have to be corrected to zero ionic strength.

For the reaction:

$$M + L \rightleftharpoons ML \qquad (5.1)$$

The thermodynamic constant is given as:

$$\mathrm{Log}\ K_{\mathrm{Therm}} = \mathrm{Log}\ \beta \left(\frac{\gamma_{[ML\}}}{\gamma_{[M]}\gamma_{[L]}} \right) \qquad (5.2)$$

Where the β is the experimentally calculated stability constant and γ is the activity coefficient of the corresponding species. The activity coefficients can be using the ionic strength of a solution, defined as:

$$I = \frac{1}{2}\sum c_i z_i^2 \qquad (5.3)$$

Where c_i and z_i are the concentration and charge of ion, i, respectively. There have been several attempts have been made to produce a generalised ionic strength correction. To date, however, no universally accepted and practical procedure for solutions with an ionic strength >0.3 has been found. The major approaches are discussed below. In the work that follows the Davies equation (section 5.1.3) and the truncated Davies equation (section 5.1.3.1) were used to correct for ionic strength. These methods were used because the technetium-ligand complexes were determined at ionic strengths in the range $1 \times 10^{-4} < I < 1$ and the Davies equation is the most popular method of correction for geochemical equiliubrium codes.

5.1.1 The Debye – Hückel equation

The Debye – Hückel equation [67] was developed for very dilute solutions of electrolytes ($I < 0.001$). The activity coefficient is given by:

$$\log \gamma = -Az_i^2 \sqrt{I} \qquad (5.4)$$

Or in its extended form [68]

$$\log \gamma = -Az_i^2 \frac{\sqrt{I}}{1 + B.a_i \sqrt{I}} \qquad (5.5)$$

Where A and B are constantswith values of respectively 0.5085 and 0.3281 at 25°C in water and a_i is the is the size or effective diameter of the ion (Å).

5.1.2 The Guggenheim equation

The introduction of an extra parameter into equation 5.5 was proposed by Guggenheim in 1935 [69]. This extra parameter was termed the "thermodynamic potential", G^{int} (or the interionic energy) and is given by the sum of contribution of the standard solution and the contribution of specific interactions

$$G^{int} = G^{stand} + G^{spec} \tag{5.6}$$

G^{spec} is a complex function dependent on size, shape, electron configuration, polarizability and relative position (distance) of ions, There the activity coefficient is given by a combination of γ^{stand}, the Debye – Hückel term, and γ^{spec} which take specific interactions effects into account.

$$\log \gamma = \log \gamma^{stand} + \log \gamma^{spec} \tag{5.7}$$

Guggenheim evaluated many experimental data then proposed an equation for the calculation for the determination of the activity coefficient. This equation has now been modified into the form below:

$$\log \gamma = -Az_i^2 \left(\frac{\sqrt{I}}{1 + B.a_i\sqrt{I}} - B^* I \right) \tag{5.8}$$

Where B^* is an adjustable parameter.

5.1.3 The Davies equation

Davies modified the Guggenheim equation by suggesting that the adjustable parameter B* should be equal 0.3 to make it applicable for use in low ionic strength soluions [70].

$$\mathrm{Log}\gamma_\pm = -Az_i^2 \left[\frac{\sqrt{I}}{1 + B.a_i\sqrt{I}} - 0.3.I \right] \tag{5.9}$$

This is the most commonly used ionic strength correction in geochemical speciation codes and gives a good approximation for ionic strengths up to 0.3.

5.1.3.1 The truncated Davies equation

However the Davies equation is compromised at ionic strengths > 0.3. Therefore the Truncated Davies equation was developed [71] to minimise the errors of the Davies equation at ionic strength > 0.3 .

$$\mathrm{Log}\gamma = -A\left(0.3539z^2 - 0.09\right) \tag{5.10}$$

5.1.4 The SIT equation

Emphasising the specific interaction of ions the activity coefficient of a single ion, j, with charge z_j in a solution with ionic strength I_m is given by the equation [72]:

$$\log \gamma_j = -Az_j^2\left(\frac{\sqrt{I_m}}{1+Ba_i\sqrt{I_m}}\right)+\sum \in \left(j,k,I_m\right)m_k \tag{5.11}$$

Where m_k is the molality of all ions k present in solution. Equation 5.11 is also a modified form of the Guggenheim equation enhanced by adding specific coeffients dexcribing the interactions of an ion with the counter ion present.

5.1.5 The Pitzer equations

At high ionic strengths, I > 2, the interdependency of activity coefficients and ionic strength can not be described using a simple parameter as in the SIT equation. This led Pitzer [73] to try and take into account the interactions of a given ion with cations, anions and solvent molecules in solution, by developing equations whose parameters have physical meaning as far as possible. The equation below shows the calculation of the activity coefficient of a single electrolyte, MX, where v_m and v_x are the numbers of cations and anions respectively and z_m and z_x their respective charges.

$$\log\gamma = \left|z_m z_x\right|.f^y + m\left(\frac{2v_m v_x}{v}\right)B^y_{MX} + m^2\frac{2\left(v_m v_x\right)^{\frac{3}{2}}}{v}C^y_{MX} \tag{5.12}$$

With

$$f^y = -A\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln\left(1+b\sqrt{I}\right)\right] \tag{5.13}$$

$$B^y_{MX} = 2\beta^{(0)}_{MX} + \frac{2\beta^{(1)}_{MX}}{a^2 I}\left[1 - e^{-\alpha\sqrt{I}}\left(1+\alpha\sqrt{I} - \left(\frac{1}{2}\right)\alpha^2 I\right)\right] \tag{5.14}$$

$$C^y_{MX} = \left(\frac{3}{2}\right)C^{\varphi}_{MX} \tag{5.15}$$

Where b and α are constant for all solutes, values of 1.2 and 2.0 have been proposed, v is the sum of the number of anions and cations , n_w is a kilogram of solvent and m is the molality.

5.1.6 Ion Pairing, Complexation [74]

Many organic and inorganic chemical substances form combinations or dissolved complexes and there cannot be assumed to be totally dissociated in real aqueous solutions. For the reaction shown in equation 5.1 the equilibrium constant is given as:

$$K = \frac{[MX]}{\left[M^+\right]\left[X^-\right]} \tag{5.16}$$

However, the formation of dissolved complexes exerts a strong influence on the ionic strength and therefore at high concentrations the activity must be used instead of the concentration:

$$K = \frac{\{MX\}}{\{M^+\}\{X^-\}} \tag{5.17}$$

Or by using the activity coefficients:

$$K = \frac{\gamma_{MX}[MX]}{\gamma_M[M^+]\gamma_X[X^-]} \tag{5.18}$$

Therefore the an ionic strength corrected complex stability constant (K^*) can be written in the form:

$$K^* = K.\frac{\gamma_{MX}}{\gamma_M\gamma_X} \tag{5.19}$$

As the non-dissociated complex has no charge its activity coefficient is usually assumed to be unity.

5.2 Modelling

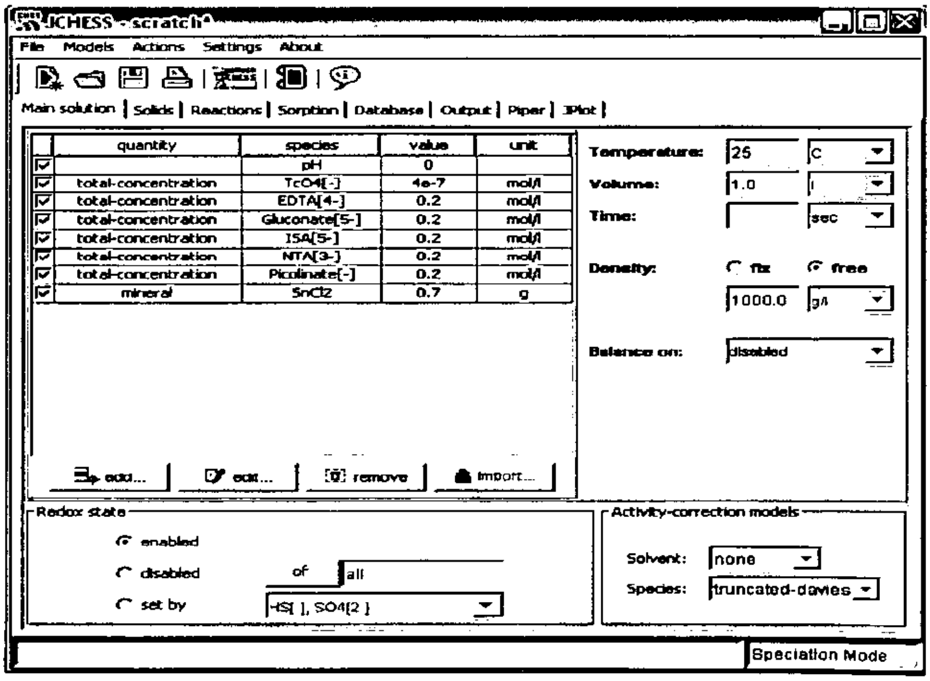
All the speciation curves determined in this project for technetium(IV) and its complexes were over the pH range 0 – 14. The concentrations of the various species were representative of the amounts used in the actual experimental work. It was assumed for simplicity that the lowest oxidation state that the technetium could be present in was technetium(IV) this was because there has been no evidence in the experiments completed that the any species of technetium with an oxidation state less than +4 was formed. Also without stability constants for technetium complexes at lower oxidation states the modelling would become increasingly difficult.

5.2.1 Stability constants calculated using $SnCl_2$ for the reduction of $TcO4^-$

The technetium(IV) complex stability constants entered into the Chess database are shown in Table 5.1. Before the constants can be added to the Chess database they are corrected, this is to allow for the difference in technetium species used for the determination of the stability constants. Chess uses the technetium(IV) species TcO^{2+} for technetium stability constants. However, the stability constants determined in this project use the technetium(IV) species $TcO(OH)^+$.

Complex	Calculated Stability Constant (Log β)	Corrected Stability Constant (Log K_{therm})	Corrected for JChess Database
$TcO(OH)EDTA^{3-}$	14.3	15.4	16.9
$TcO(OH)NTA^{2-}$	13.8	14.6	16.1
$TcO(OH)ISA^{4-}$	13.9	15.3	16.8
$TcO(OH)Gluc^{4-}$	14.2	15.6	17.1
TcO(OH)Pic	14.9	15.1	16.6

Table 5.1: Stability constants and ionic strength corrected stability constants of TcO(OH)-ligands



	quantity	species	value	unit
☑		pH	0	
☑	total-concentration	TcO4[-]	4e-7	mol/l
☑	total-concentration	EDTA[4-]	0.2	mol/l
☑	total-concentration	Gluconate[5-]	0.2	mol/l
☑	total-concentration	ISA[5-]	0.2	mol/l
☑	total-concentration	NTA[3-]	0.2	mol/l
☑	total-concentration	Picolinate[-]	0.2	mol/l
☑	mineral	SnCl2	0.7	g

Temperature: 25 C
Volume: 1.0 l
Time: sec
Density: ○ fix ● free
1000.0 g/l
Balance on: disabled

Redox state
● enabled
○ disabled of all
○ set by HS[ ], SO4[2]

Activity-correction models
Solvent: none
Species: truncated-davies

Fig. 5.1: Data entered into CHESS

5.2.1.1 Technetium(IV)

Fig. 5.2 shows the speciation diagram for technetium(IV)

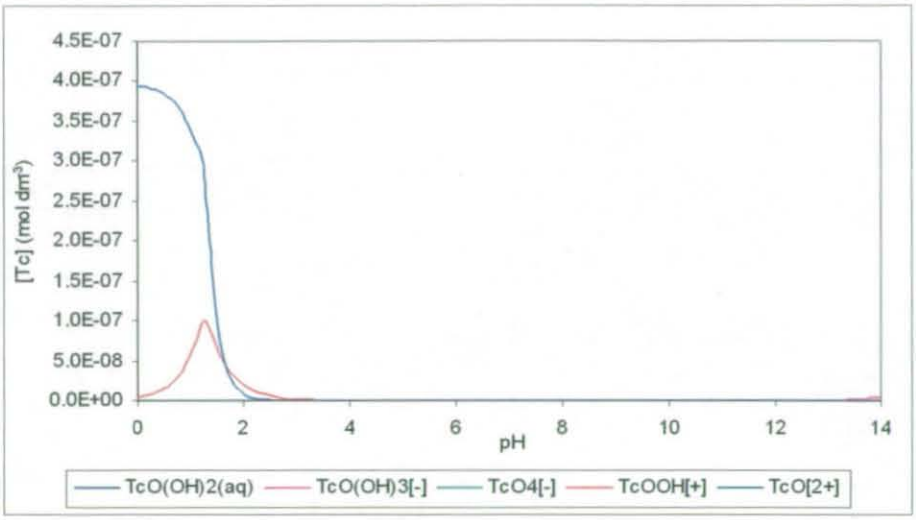


Fig. 5.2: Speciation curve for technetium(IV) over the pH range 0 – 14

From Fig. 5.2 it can be seen that the majority of the technetium that is in solution at pH = 0 is in the form of TcO^{2+}. As the pH is increased from 0 to approximately 2 the concentration of this species decreases in solution as the concentration of $TcO(OH)^+$ in solution increases. When the pH is increased further still the concentration of $TcO(OH)^+$ falls until at approximately pH = 2 there is very little technetium in solution. However at very high pH a small increase in technetium solubility can be seen. Fig. 5.3 shows that after pH 12.5 there is a solubility increase as the technetium(IV) species $TcO(OH)_3^-$ is formed. It can also be seen that the speciation curve predicts the concentration of technetium(IV) at pH 13.3 higher than the actual measured solubility. However, the difference is small and both the predicted and measured concentrations of technetium(IV) within the accepted solubility limits in the literature.

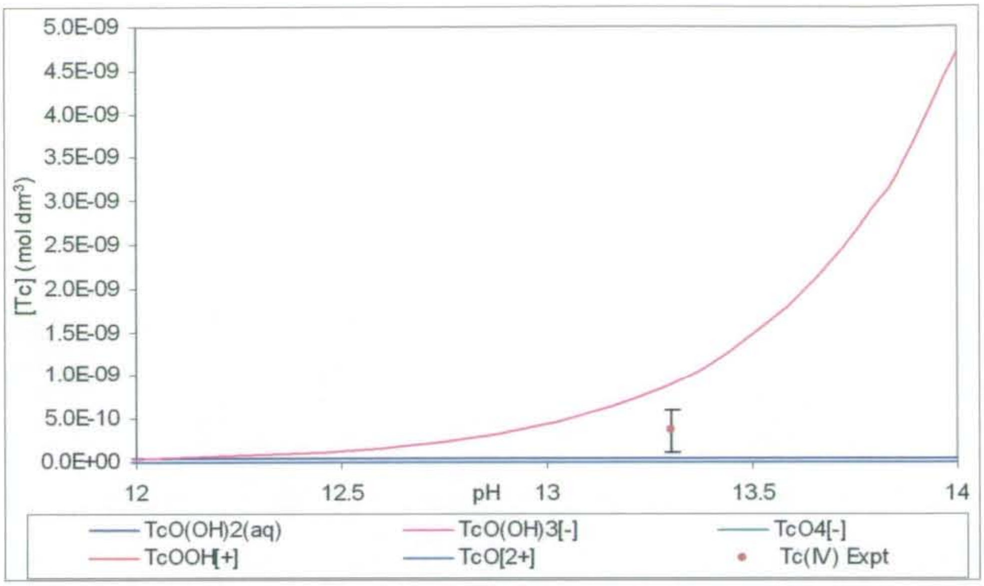


Fig. 5.3: Speciation curve for technetium(IV) over the pH range 12 – 14

5.2.1.2 Technetium(IV) + EDTA

From Fig. 5.4 it can be seen that there is strong complexation between the technetium(IV) and EDTA between pH 2 – 14. This has a significant effect on the concentration of technetium in solution, as all the technetium is in solution between the pH 2 – 14.

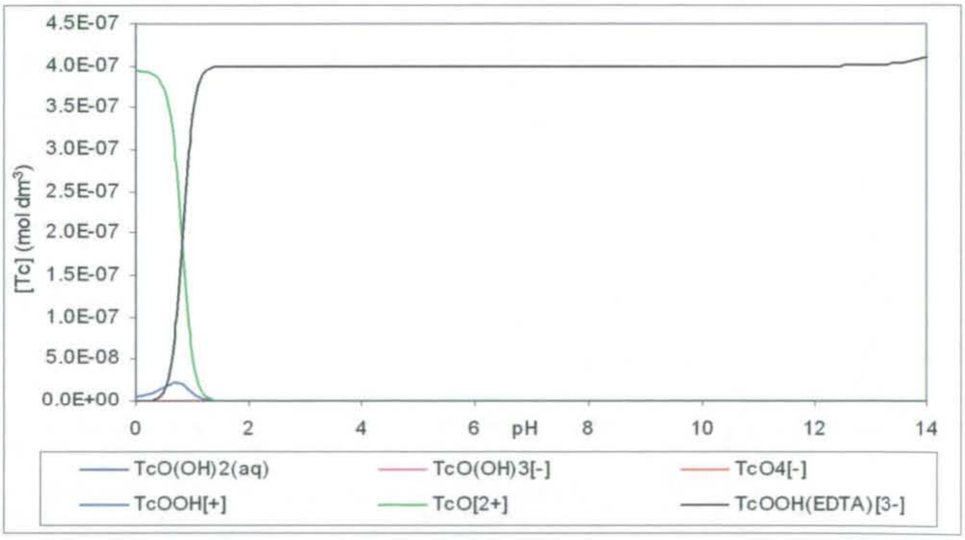


Fig. 5.4: Speciation curve for technetium(IV)in the presence of EDTA over the pH range 0 – 14

5.2.1.3 Technetium(IV) + NTA

From Fig. 5.5 it can be seen that there is strong complexation between the technetium(IV) and NTA between pH 1 – 14. This has a significant effect on the concentration of technetium in solution, as all the technetium is in solution between the pH 1 – 14.

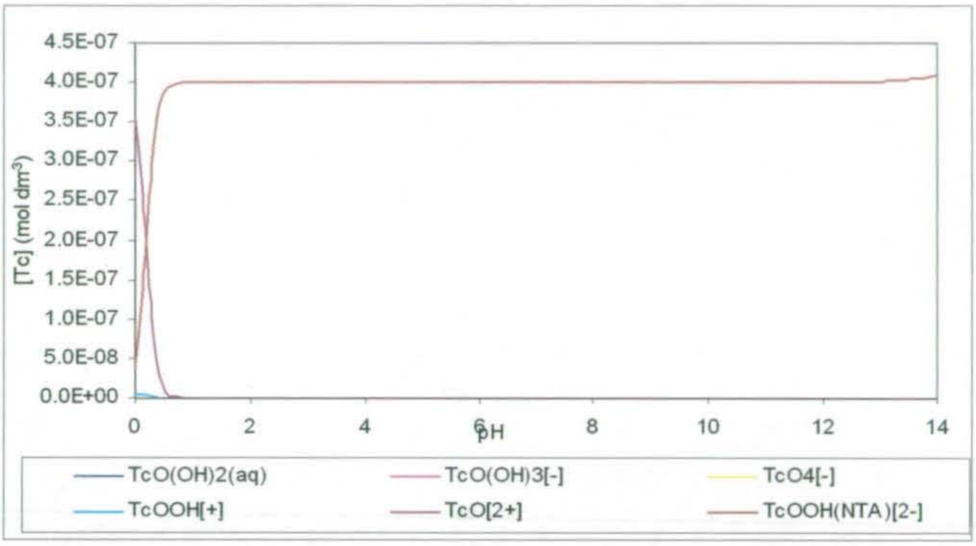


Fig. 5.5: Speciation curve for technetium(IV)in the presence of NTA over the pH range 0 – 14

5.2.1.4 Technetium(IV) + ISA

From Fig. 5.6 it appears that the behaviour of technetium(IV) in the presence of ISA is almost identical to the behaviour of Tc(IV) in the absence of all ligands (Fig. 5.2). However after pH 13 the solubility increases as there is complexation between the technetium(IV) and ISA^{5-}.

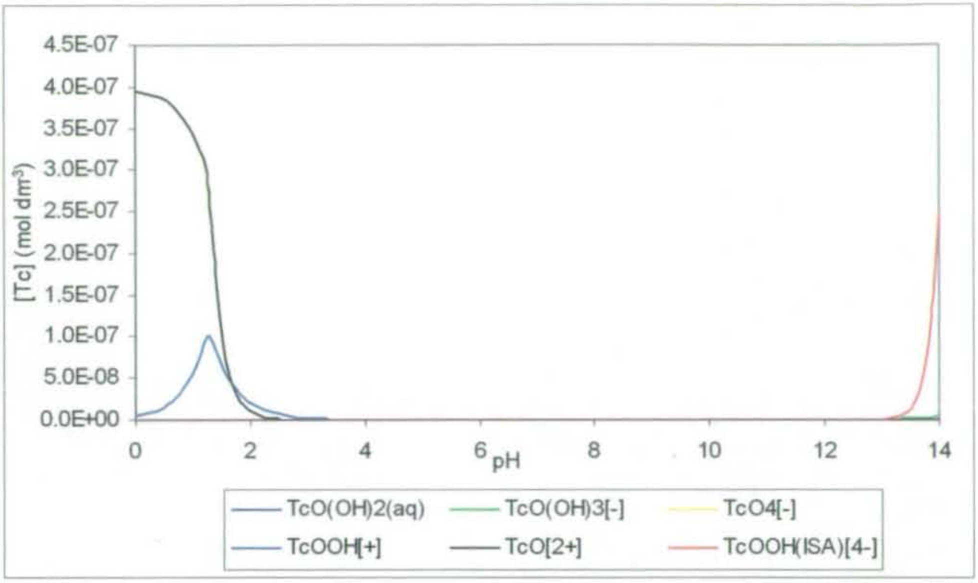


Fig. 5.6: Speciation curve for technetium(IV)in the presence of ISA over the pH range 0 - 14

5.2.1.5 Tc(IV) + Gluconic acid

From Fig. 5.7 it can be seen that gluconic acid appears to have a significant effect on the solubility of Tc(IV) after *ca.* pH 12. This is due to the formation of the Tc(IV) – Gluconate complex.

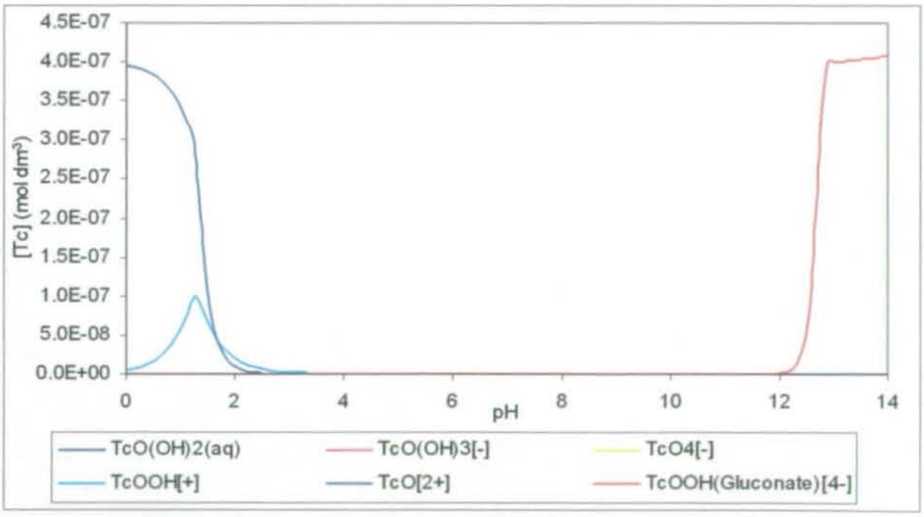


Fig. 5.7: Speciation curve for technetium(IV)in the presence of gluconic acid over the pH range 0 – 14

5.2.1.6 Tc(IV) + Picolinic acid

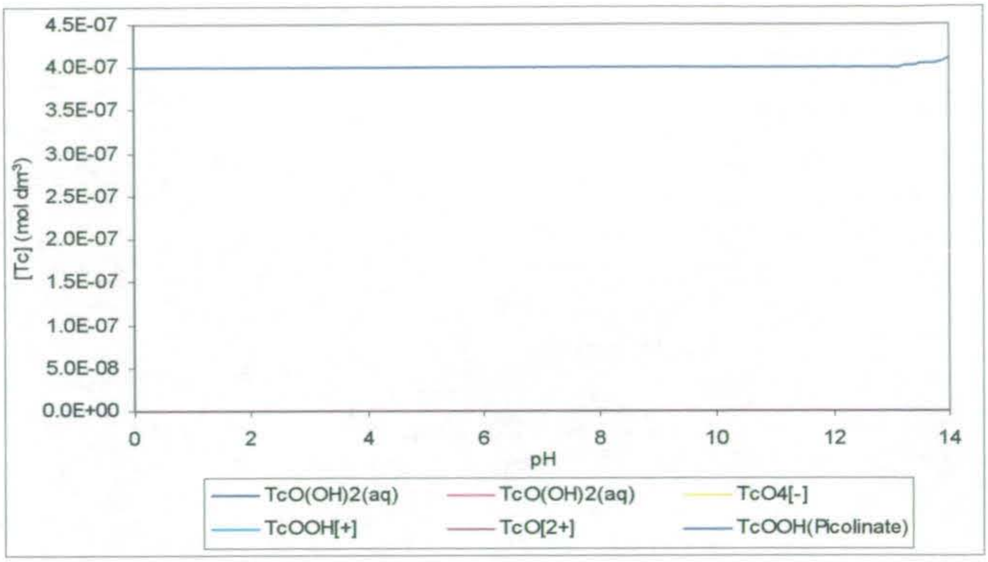


Fig. 5.8: Speciation curve for technetium(IV)in the presence of picolinic acid over the pH range 0 – 14

From Fig. 5.8 it can be seen that picolinic acid has a significant effect on the solubility of Tc(IV). The technetium(IV) complex appears to be soluble across the whole pH range.

5.2.1.7 Tc(IV) + All Ligands

Fig 5.9 shows the speciation diagram for technetium(IV) in the presence of all the ligands under investigation.

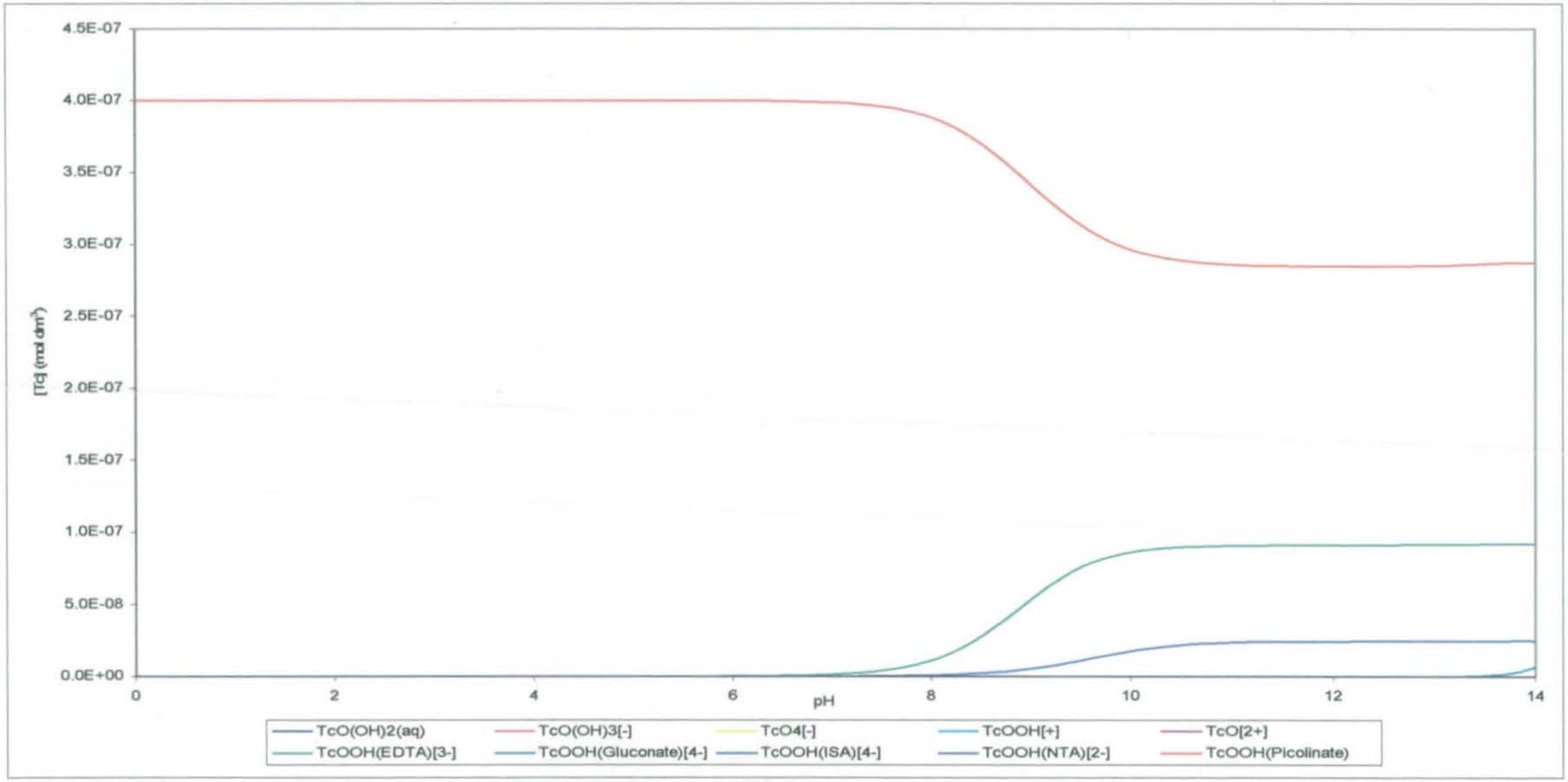


Fig. 5.9: Speciation curve for technetium(IV)in the presence of all the ligands under investigation over the pH range 0 - 14

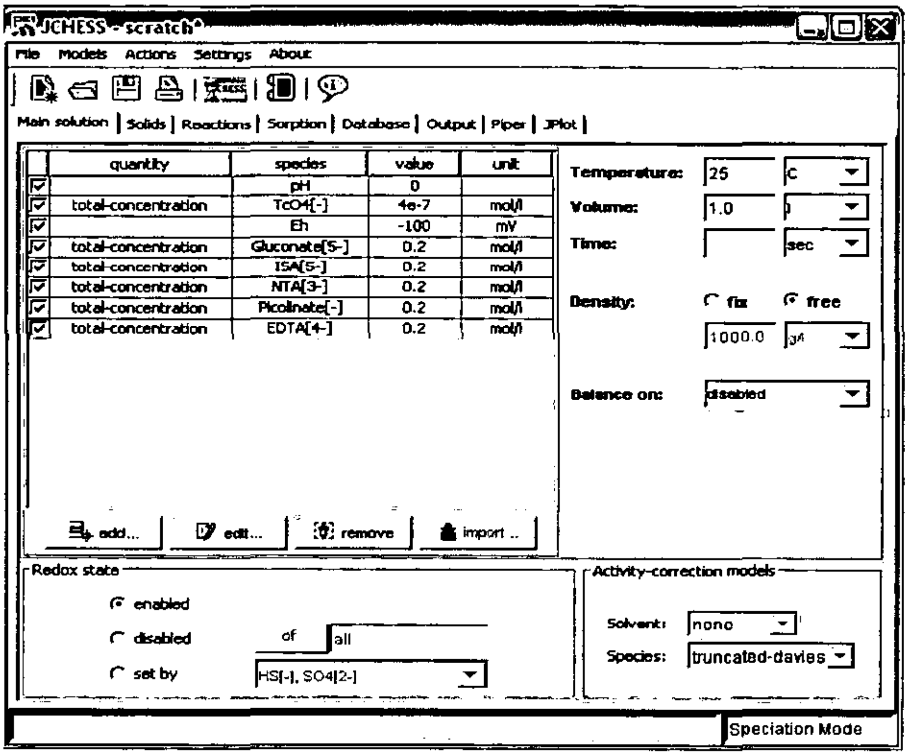
From Fig. 5.9 it can be seen that the ligands have a significant effect on the solubility of technetium(IV). The technetium is completely soluble over the pH range 0 – 14 due to the formation of technetium(IV) complexes. Technetium(IV) picolinate is formed and has the most significant effect on the solubility of technetium. In the pH range 0 – 8 all the technetium is soluble as the picolinate complex. Above pH *ca.* 8 the concentration of the picolinate complex drops as the technetium(IV) - EDTA complex is formed, this complex is soluble in the range 8 – 14. At even higher pH the formation of technetium(IV) NTA (pH *ca.* 10) and technetium(IV) ISA (pH *ca.* 13.5) becomes significant to the solubility of technetium.

5.2.2 Stability constants calculated using electrochemical reduction of TcO_4^-

The constants entered into the Chess database are shown in the table below. As discussed in section 5.2.1 the technetium(IV) constants have to be corrected from the base species $TcO(OH)^+$ to TcO^{2+}.

Complex	Calculated Stability Constant (Log β)	Corrected Stability Constant (Log K_{therm})	Corrected for JChess Database
$TcO(OH)EDTA^{3-}$	13.9	15.0	16.5
$TcO(OH)NTA^{2-}$	13.2	14.0	15.5
$TcO(OH)ISA^{4-}$	13.3	14.7	16.2
$TcO(OH)Gluc^{4-}$	13.2	14.6	16.1
TcO(OH)Pic	13.0	13.2	14.7

Table 5.2: Stability constants and ionic strength corrected stability constants of TcO(OH)-organics



	quantity	species	value	unit
☑		pH	0	
☑	total-concentration	TcO4[-]	4e-7	mol/l
☑		Eh	-100	mV
☑	total-concentration	Gluconate[5-]	0.2	mol/l
☑	total-concentration	ISA[5-]	0.2	mol/l
☑	total-concentration	NTA[3-]	0.2	mol/l
☑	total-concentration	Picolinate[-]	0.2	mol/l
☑	total-concentration	EDTA[4-]	0.2	mol/l

Temperature: 25 C
Volume: 1.0 l
Time: sec
Density: ○ fix ● free
1000.0 g/l
Balance on: disabled

Redox state
● enabled
○ disabled of all
○ set by HS[-], SO4[2-]

Activity-correction models
Solvent: none
Species: truncated-davies

Speciation Mode

Fig. 5.10: Data entered into CHESS

5.2.2.1 Technetium(IV) + EDTA

From Fig. 5.11 it can be seen that there is strong complexation between technetium(IV) and EDTA between pH 2 – 14. This has a significant effect on the concentration of technetium in solution, as all the technetium is in solution between the pH 2 – 14.

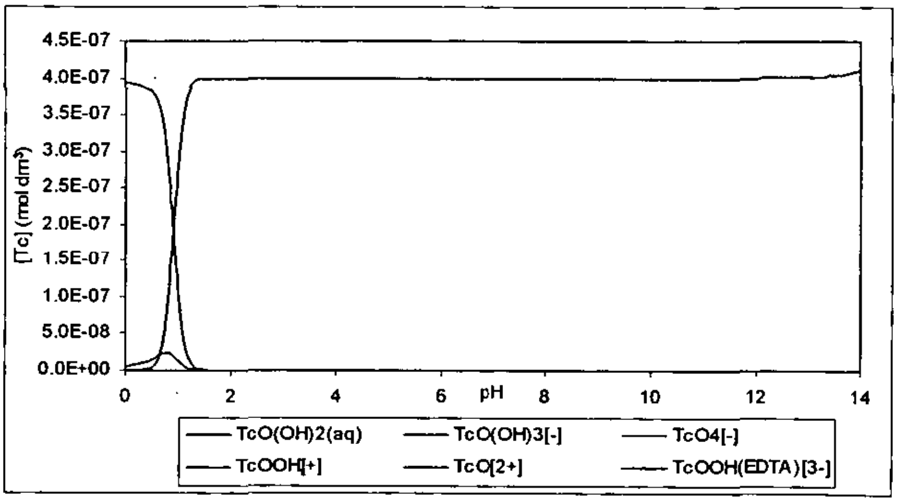


Fig. 5.11: Speciation curve for technetium(IV)in the presence of EDTA over the pH range 0 - 14

5.2.2.2 Technetium(IV) + NTA

Fig 5.12 shows a speciation curve for the technetium(IV) in the presence of NTA

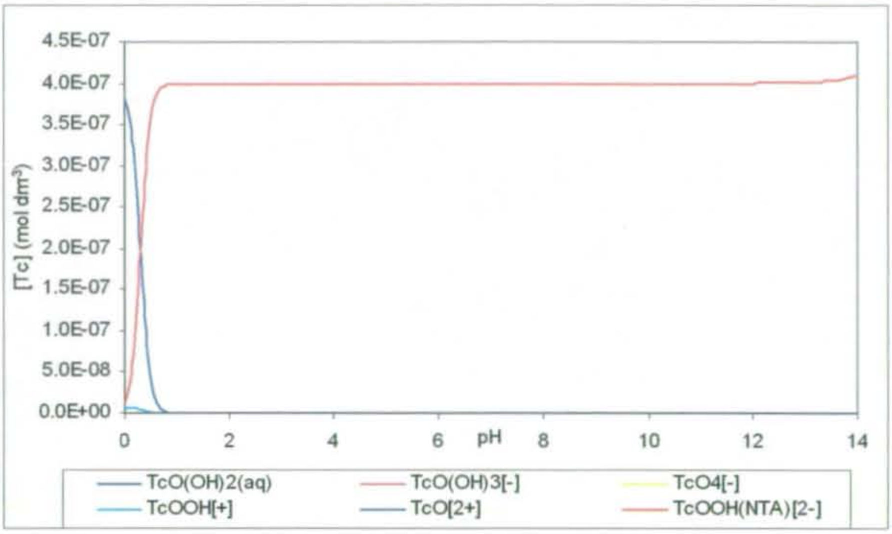


Fig. 5.12: Speciation curve for technetium(IV)in the presence of NTA over the pH range 0 - 14

From Fig. 5.12 it can be seen that there is strong complexation between the technetium(IV) and NTA between pH 1 – 14. This has a significant effect on the concentration of technetium in solution, as all the technetium is in solution between the pH 1 – 14.

5.2.2.3 Technetium(IV) + ISA

From Fig. 5.13 it appears that the behaviour of technetium(IV) in the presence of ISA is almost identical to the behaviour of Tc(IV) in the absence of all ligands (Fig. 5.2). However above pH 13 the solubility increases due to complexation between the technetium(IV) and ISA^{5-}.

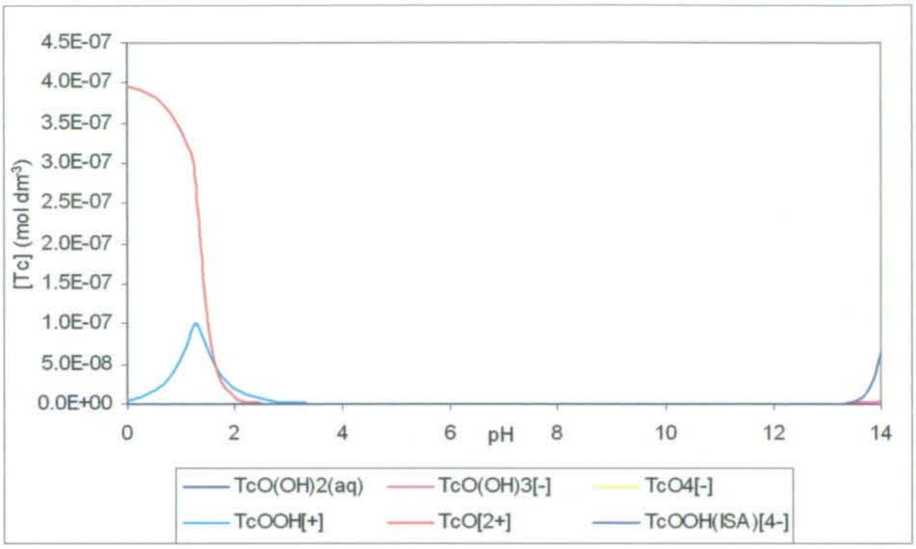


Fig. 5.13: Speciation curve for technetium(IV)in the presence of ISA over the pH range 0 – 14

5.2.2.4 Technetium(IV) + Gluconic acid

From Fig. 5.14 it can be seen that gluconic acid appears to have a significant effect on the solubility of Tc(IV) above *ca.* pH 12. This is due to the formation of the Tc(IV) – gluconate complex.

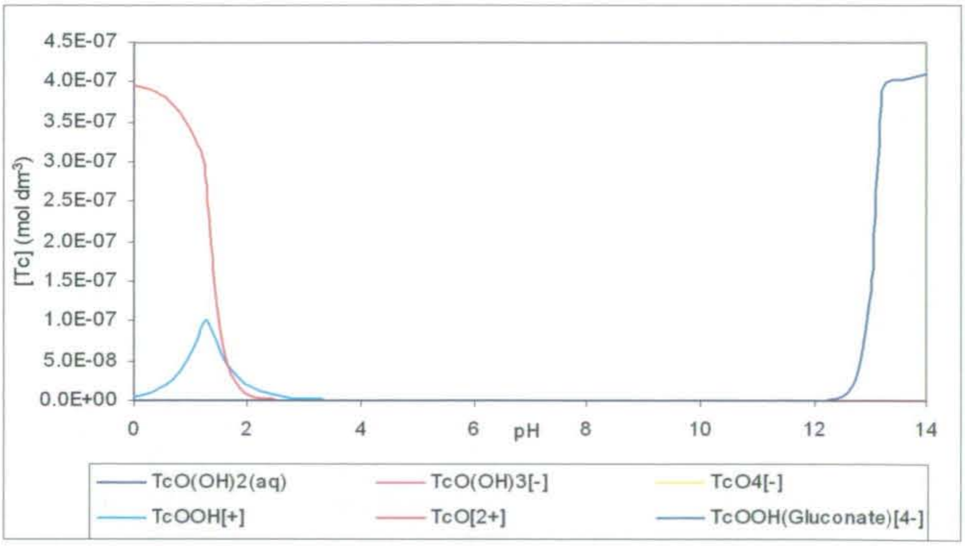


Fig. 5.14: Speciation curve for technetium(IV)in the presence of gluconic acid over the pH range 0 – 14

5.2.2.5 Technetium(IV) + Picolinic acid

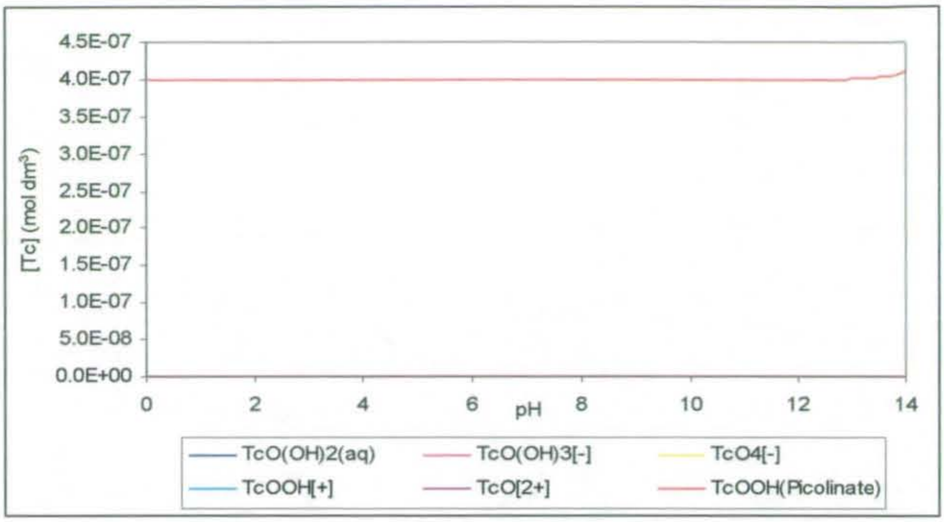


Fig. 5.15: Speciation curve for technetium(IV)in the presence of picolinic acid over the pH range 0 – 14

From Fig. 5.15 it can be seen that picolinic acid has a significant effect on the solubility of Tc(IV). The technetium(IV) complex appears to be soluble at all pHs.

5.2.2.6 Technetium(IV) + All ligands

Fig 5.9 shows the speciation diagram for technetium(IV) in the presence of all the ligands under investigation.

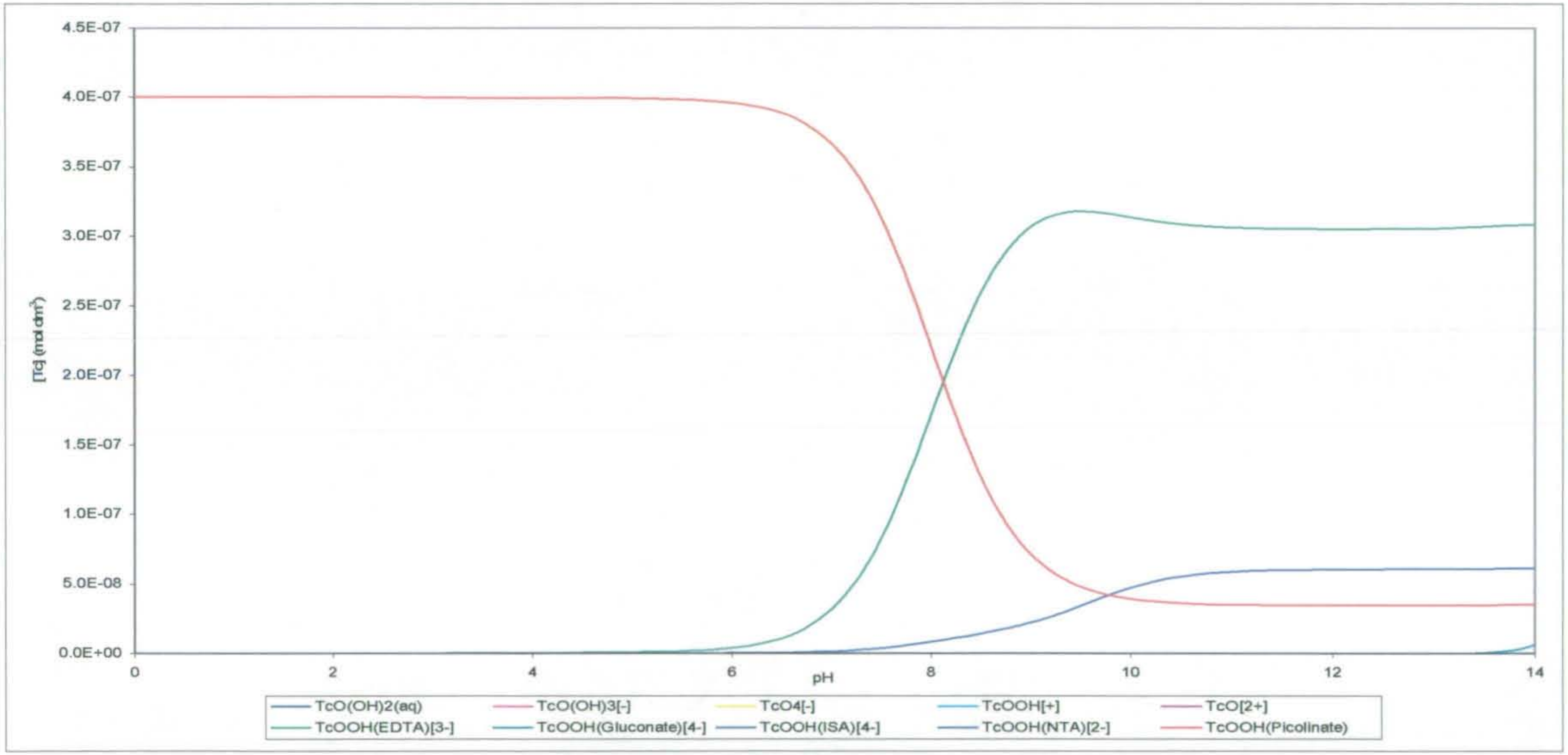


Fig. 5.16: Speciation curve for technetium(IV)in the presence of all the ligands under investigation over the pH range 0 - 14

From Fig. 5.16 it can be seen that the ligands have a significant effect on the solubility of technetium(IV), the technetium is completely soluble over the pH range 0 – 14 due to the formation of technetium(IV) complexes. Technetium(IV) - picolinate is formed and has the most significant effect on the solubility of technetium. In the pH range 0 –7 all the technetium is soluble as the picolinate complex. After pH *ca.* 7 the concentration of the picolinate complex decreases as the technetium EDTA complex is formed This complex is soluble in the range 8 – 14. At even higher pH the formation of technetium(IV) NTA (pH *ca.* 9) and technetium(IV) ISA (pH *ca.* 13.5) becomes significant to the solubility of technetium.

5.3 Comparison between the stability constants determined using data from the $SnCl_2$ and electrochemical reductions

The speciation curves for the reactions between technetium(IV) and the ligands of interest are shown in sections 5.1 and 5.2. The stability constants used in sections 5.2.1 and 5.2.2 are determined from different sets of data, the stability constants in section 5.1 were calculated using the solubility data achieved from the reduction of TcO_4^- using stannous chloride and the stability constants in section 5.2 were calculated using the solubility data achieved from the reduction of TcO_4^- using electrochemical techniques. In the following section the speciation curves, for each individual organic ligand, from section 5.1 and 5.2 are compared.

5.3.1.1 Technetium(IV)-EDTA

Fig. 5.17 shows the comparison of the speciation curves from the two different stability constants calculated for technetium(IV) - EDTA.

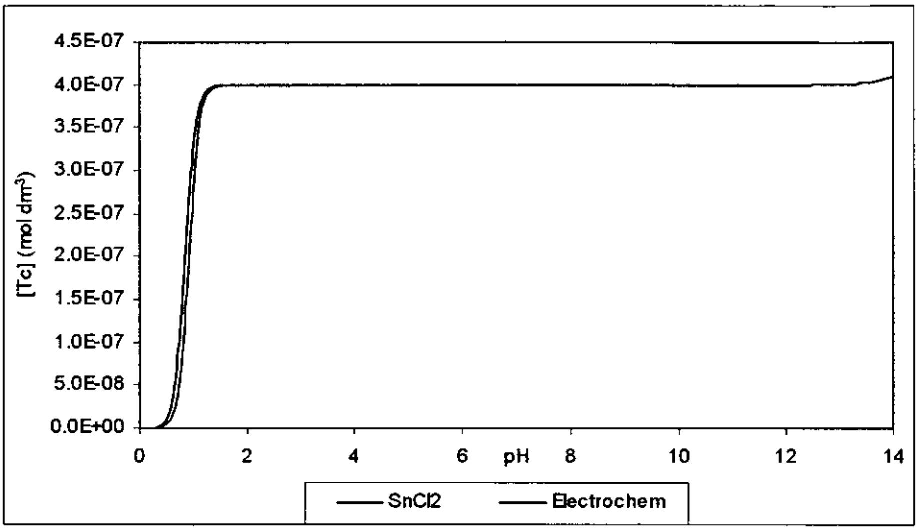


Fig. 5.17: Comparison of speciation curves for technetium(IV) in the presence of EDTA over the pH range 0 – 14

From Fig. 5.17 it can be seen that the two speciation curves are in good agreement.

5.3.1.2 Technetium(IV)-NTA

From Fig. 5.18 it can be seen that the two speciation curves are in good agreement.

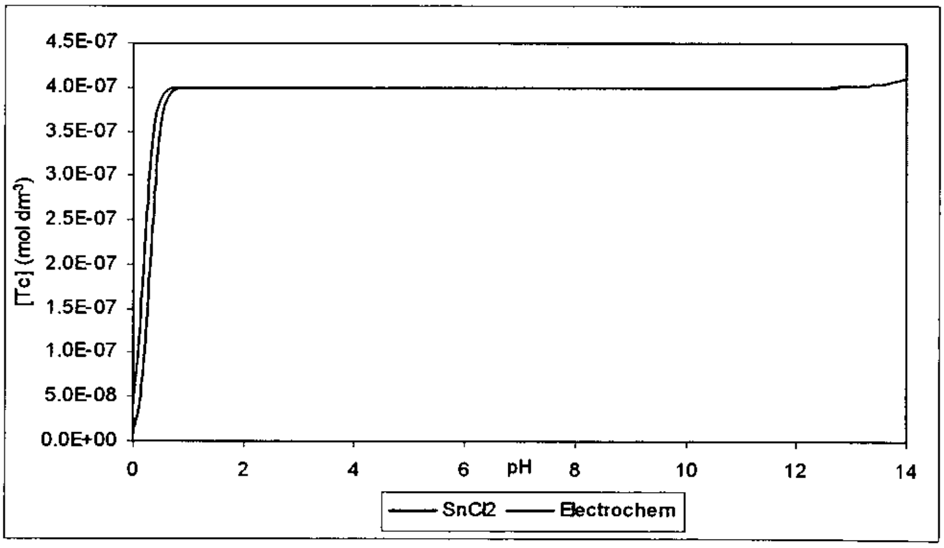


Fig. 5.18: Comparison of speciation curves for technetium(IV)in the presence of NTA over the pH range 0 – 14

5.3.1.3 Technetium(IV)-ISA

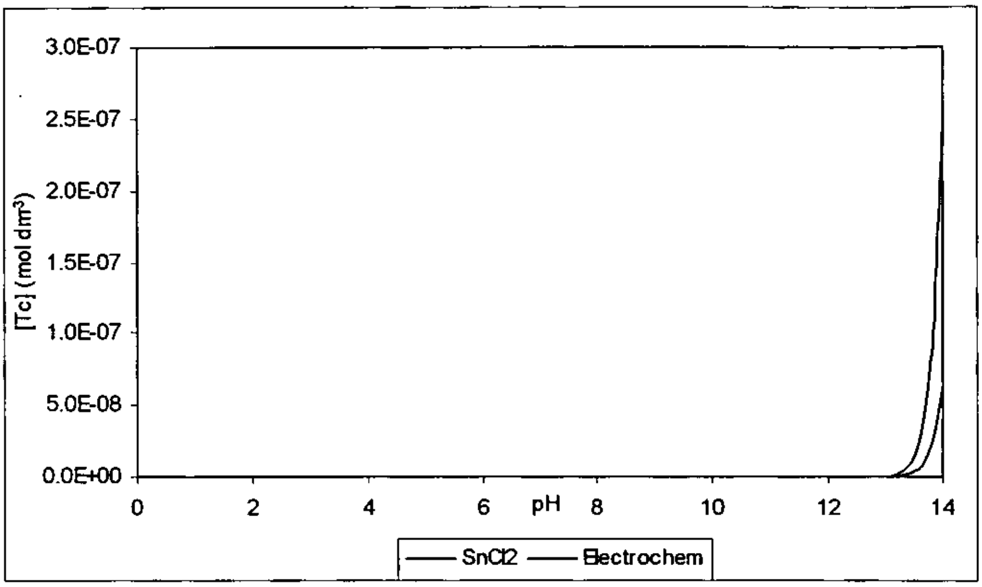


Fig. 5.19: Comparison of speciation curves for technetium(IV)in the presence of ISA over the pH range 0 – 14

From Fig 5.19 it can be seen that the shapes of the speciation curves are in good agreement. However, the speciation curve for the $SnCl_2$ reduction predicts that the technetium(IV) ISA complex will form at a lower pH.

5.3.1.4 Technetium(IV)-Gluconate

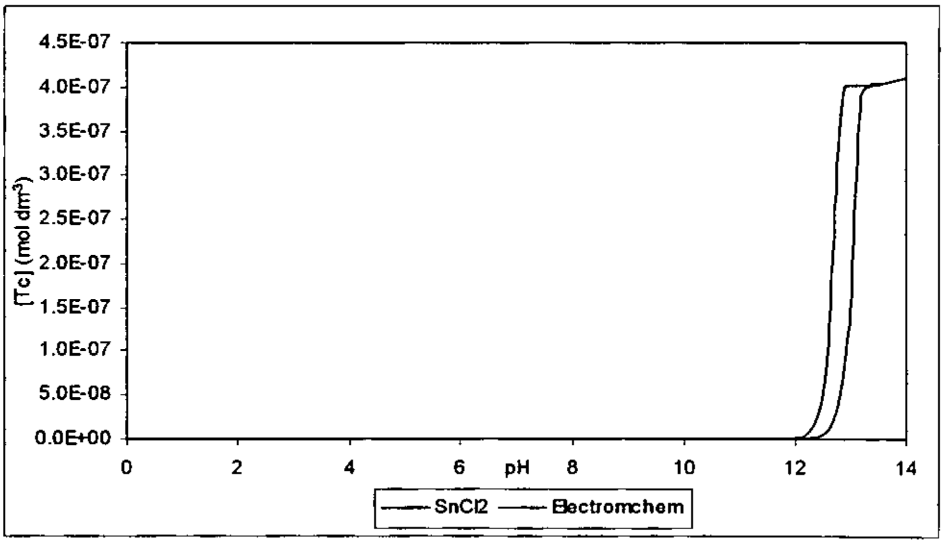


Fig. 5.20: Comparison of speciation curves for technetium(IV)in the presence of gluconic acid over the pH range 0 – 14

From Fig 5.20 it can be seen that the speciation curves are in good agreement. However, the speciation curve for the $SnCl_2$ reduction predicts that the formation of the technetium(IV) gluconate complex will start at pH *ca.* 12, whereas the speciation curve for the electrochemical reduction predicts the formation of the complex at approximately pH 12.5

5.3.1.5 Technetium(IV)-Picolinate

From Fig. 5.21 it can be seen that the two speciation curves are in excellent agreement.

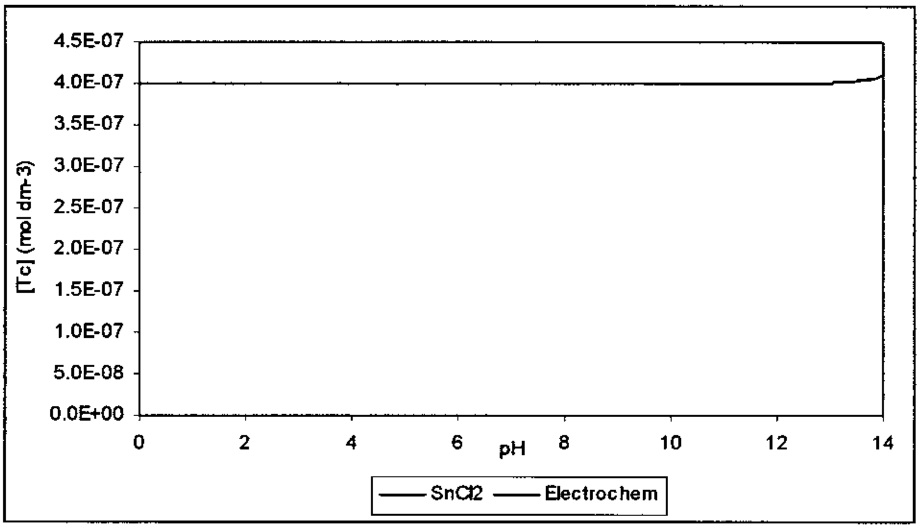


Fig. 5.21: Comparison of speciation curves for technetium(IV)in the presence of picolinic acid over the pH range 0 – 14

5.4 Summary

The importance of correcting for ionic strength and calculating the activity coefficients were discussed as well as the major approaches for correcting stability constants for ionic strength. As the ionic strength at which the technetium(IV)–ligand stability constants were determined ranged from 1×10^{-4} to 1 it was decided that the Davies equation and the truncated Davies equation were the appropriate methods for correcting for ionic strength.

Speciation curves were obtained using the Chess speciation code for each individual technetium-ligand complex. From the speciation curves the following can be seen:

- Technetium(IV)-EDTA complex is the dominant species formed in the pH range 1 – 14.
- Technetium(IV)-NTA complex is the dominant species formed in the pH range 0.5 – 14.
- Technetium(IV)-picolinate complex is the dominant species formed across the entire pH range.
- Technetium(IV)-ISA complex is not formed until pH 13 but as the pH is increased the complex becomes more important.
- Technetium(IV)-gluconate complex is not formed until pH 12.5 but as the pH is increased the complex becomes more important and at pH 13 all the technetium is soluble as the complex.

These speciation curves give a very simplistic view of the solubility and speciation of technetium(IV) in the presence of the individual ligands. However, to get a more realistic view of the speciation and solubility more technetium(IV) data under different conditions are needed. For example at lower pH ISA and gluconate (Fig. 5.22) will be less deprotonated but technetium(IV) will still complex with these species. However, without data for these complexes they can not be added to the model.

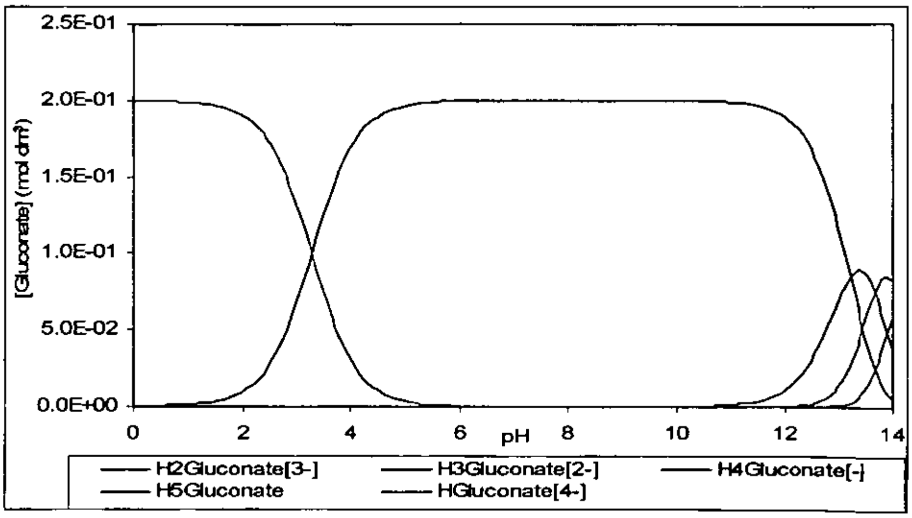


Fig. 5.22: Speciation curve of gluconic acid

Part B – Degradation of TPPB at high pH and the solubility of various radionuclides in its degradation products

6.0 Degradation of tetraphenylphosphonium bromide (TPPB) at high pH and the solubility of various radionuclides in its degradation products

6.1 Introduction

During reprocessing of MAGNOX fuel at Sellafield the irradiated and decanned uranium fuel rods are dissolved in nitric acid. Plutonium and uranium are separated from the resulting solution by liquid extraction using a mixture of 30% tributylphosphate (TBP) solution in odourless kerosene. One of the waste streams from this chemical separation process is an aqueous, acidic, medium active liquor. The liquor contains a range of radioactive species in solution such as caesium, strontium, plutonium and other alpha and beta emitters, including technetium. The medium active liquor is concentrated by evaporation to produce a concentrate known as the medium active concentrate (MAC). [75]

MAC is collected and stored in 1200 m^3 tanks prior to treatment in the Enhanced Actinide Removal Plant (EARP). Sodium hydroxide and an ion exchange material are added to the MAC within the EARP. Iron in the MAC produces an insoluble floc, which contains the main alpha and plutonium species.

The ion exchange reagent is incorporated into the floc and removes additional species, mainly caesium. Therefore the most soluble radioactive species are separated into a solid floc. The floc is then dewatered by ultrafiltration prior to encapsulation in 500 litre steel drums with cement. The permeate which contains a tiny fraction of the radioactivity in the MAC is discharged to sea [76].

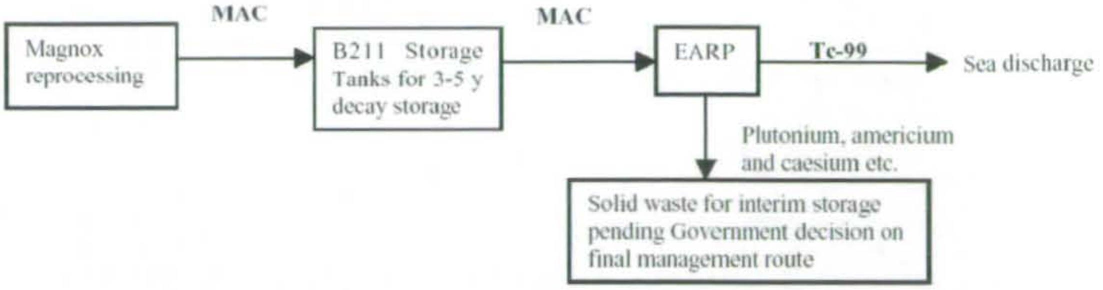


Fig. 6.1: Schematic of nuclear waste reprocessing and management [76]

Technetium was not removed into the floc by either of the processes described above and as a result was discharged to the sea in the permeate. Technetium was thought to disperse widely and although it does disperse to a certain extent, it is carried from the Irish sea by the gulf stream which flows past the British Isles to the Arctic and the Barents sea. En route, ^{99}Tc accumulates in seaweed [78 - 80] and lobsters [81, 82] along the Norwegian coastline. Although ^{99}Tc is not specifically harmful to human health, it is a radioactive material and therefore, linked to increased chances of developing cancer if exposed. Concentrations of ^{99}Tc released into the Irish sea by BNFL had increased 18-fold since 1996 from 50 to 900 Bq kg^{-1} [77]. This lead to the UK Environment Agency (EA) deciding that the current levels of technetium discharge to the sea, 90 terabecquerels (TBq) per year, was no longer acceptable and due to new legislation BNFL had to reduce the discharges of technetium to 10 TBq per year [75 – 77]. Extensive development and assessment work was therefore carried out on the abatement of ^{99}Tc, the technically feasible methods identified for reducing technetium releases into the sea were:

- Removal of ^{99}Tc by ion exchange columns within a new treatment plant. This plant would treat the permeate from the EARP process to remove ^{99}Tc before discharge to the sea
- Removal of ^{99}Tc by electrolysis using a new plant to treat the EARP permeate. Electrolytic cells would be used to deposit ^{99}Tc on one of the electrodes for retention and long-term storage.

- Precipitation of the ^{99}Tc in the EARP permeate by formation of an insoluble salt within a new treatment plant. The precipitate would then be removed by filtration for retention.
- Addition of tetraphenylphosphonium bromide (TPPB) to the MAC feed to precipitate the ^{99}Tc into the EARP floc. This could be performed in EARP and would require no new plant and equipment.

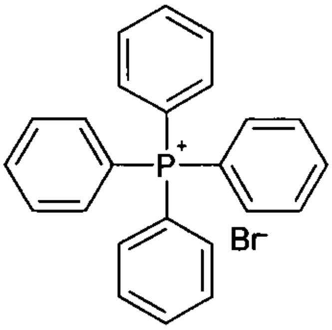


Fig.6.2: Structure of tetraphenylphosphonium bromide (TPPB)

As the first three methods required additional plant and equipment they would be expensive to implement making the fourth method much more attractive.

A three month trial was then carried out by treating *ca.* 250 m^3 of MAC floc with TPPB. From the trial it was found that >95% of the ^{99}Tc in the MAC feed was removed and retained in the final encapsulated waste product. It was also found that the TPPB had no detrimental effects on the removal of other radioactive species by the EARP process [76].

Therefore, the use of TPPB was seen as an ideal method for the abatement of technetium. However, TPPB is known to be stable at neutral pH, but it is prone to degradation by alkaline hydrolysis at high pH, it can also degrade via radiolytic degradation under conditions expected in the near field of a nuclear waste repository.

The study of the degradation and the effect of the by-products on radionuclides under conditions expected in the near field of a nuclear waste repository is an important issue when considering a post closeure safety assessment for a repository.

6.2 Mechanisms of the degradation of TPPB

As discussed in section 6.1 TPPB can degrade via two mechanisms:

- Radiolytic degradation
- Alkaline hydrolysis

6.2.1 Radiolytic degradation

A basic mechanism for radiolytic degradation of tetraphenylphosphonium chloride is thought to be as shown below [83].

$$Ph_4P^+ + Cl^+ \rightarrow Ph_4P\bullet + Cl$$

$$Ph_4P\bullet \rightarrow Ph\bullet + Ph_3P$$

$$Ph\bullet + Ph\bullet \rightarrow Ph_2$$

The products are generally phenyl phosphine compounds. The structure of triphenylphosphine is shown in Fig. 6.3.

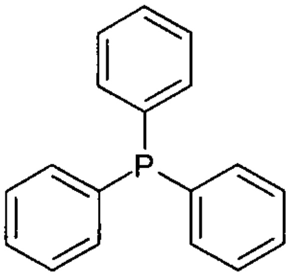


Fig. 6.3: Structure of triphenylphosphine (TPP)

6.2.2 Alkaline hydrolysis

The mechanism for the alkaline hydrolysis of quaternary phosphonium salts has been suggested to be as follows [84, 85]:

$$R_4P^+ + 2OH^- \rightleftharpoons R_4POH + OH^- \rightleftharpoons R_4PO^- + H_2O$$

$$R_4PO^- + H_2O \xrightarrow{\text{High pH}} R_3PO + R^+ + H_2O \longrightarrow R_3PO + RH + OH^-$$

Or in detail for TPPB:

$$Ph_3P^{\oplus} - -Ph + OH^- \rightleftharpoons OH - -P(Ph_3) - -Ph + OH^-$$

$$OH - -P(Ph_3) - -Ph + OH^- \rightleftharpoons Ph - -P(Ph_3) - -O^- \text{ SLOW}$$

$$Ph_3 = O + Ph^- + H_2O \longrightarrow Ph_3 = O + PhH + OH^-$$

The alkaline hydrolysis of TPPB is thus thought to produce triphenylphosphine oxide. Although further degradation by the loss of a second phenyl group seems possible there is no evidence in the literature to suggest the formation of further degradation products, i.e. diphenylphosphine oxide (DPPO).

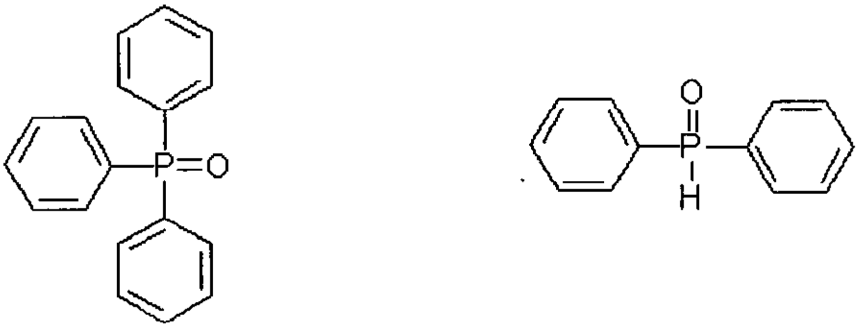


Fig. 6.4: Structures of triphenylphosphine oxide (TPPO) and diphenylphosphine oxide (DPPO)

6.3 Aims

The aims of the experimental work described here are to

- determine the effects of tetraphenylphosphonium bromide, and its degradation products, on the solubility of various radionuclides,
- investigate the degradation products of TPPB at high pH,
- investigate the effect of the organic complexing ligands, EDTA, NTA, ISA, gluconic acid and picolinic acid, on the pertechnetate-tetraphenylphosphonium complex (TcO_4TPP).

To avoid confusion the phosphonium compounds involved in this study will be given initials in the following way, see Table 6.1.

Phosphonium compounds	Initials
Tetraphenylphosphonium bromide	TPPB
Triphenylphosphine oxide	TPPO
Triphenylphosphine	TPP
Diphenylphosphine	DPP

Table 6.1: Abbreviations of the phosphonium compounds used in this report

6.4 Previous studies

The decomposition of TPPB in water was studied by Khalil and Aksnes in 1973 [84] and 1974 [85]. This was part of a study of the decomposition of quaternary phosphonium salts in dioxane-water mixtures, and acetone-water mixtures, respectively. The main findings were that under strongly alkaline conditions the decomposition of phosphonium compounds may start at room temperature; and that the type of phosphonium compound, and the solvent, influence the stability in an alkaline system.

Whilst investigating the effects of organic solvents on the rate of degradation, Khalil *et al.* [83, 84] also ran an investigation of the kinetics of the degradation of TPPB in pure water at pH 11.2. This led to the production of the Arrhenius expression for the rate constant given below:

$$k = 19.6e^{\frac{(-33.5\,[\text{kcal/mole}])}{RT}}\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

The major finding in the kinetics was that rate is vastly increased by the presence of organics, by up to a factor of 2 x 10^7. The suggested explanation was that this was due to differences in the dielectric constants of the solvents, organic and water.

It was also suggested that the production of TPPO by degradation causes co-precipitation of TPPB. However, there is no evidence of this from this study. The authors followed the degradation by measuring the reduction in hydroxide ion concentration. This method was not practical at pH values of 13 and above in this study, as any change would be too small to detect. The rate of reaction was found to be third order overall; first order with respect to TPPB, and second order with respect to the hydroxide ion concentration. This means that the degradation is very sensitive to changes in pH. The rate equation was quoted as:

$$\text{Rate} = k[\text{TPPB}][\text{OH}]^2$$

The expression for the rate constant was quoted as:

$$k = 5.3 \times 10^{-4}\ \text{dm}^6\ \text{mol}^{-2}\ \text{min}^{-1}\ (25\ °\text{C})$$

The work by Khalil et al. [84, 85] can also be expressed in S.I. units as:

$$k = 3.27 \times 10^{19} e^{\left(\frac{-140.17[\text{kJ/mole}]}{RT}\right)} \text{dm}^6\text{mol}^{-2}\text{s}^{-1}$$

From this, the initial rate of reaction at pH 13 was calculated to be 8.55×10^{-12} mols s^{-1}, for a starting concentration of 1×10^{-4} mol dm^{-3}. The 'time for complete destruction' was quoted as 31800 years at 25 °C and pH 13. This is for a case when the half life of TPPB is 91 days.

6.5 Materials and equipment

Deionised water produced by a Barnstead NANOpure ultrapure water purification system, and AR reagents, were used throughout. Sodium ISA was prepared using the procedure described by Whistler and BeMiller (Section3.3.15) [51]. Sodium gluconate, disodium EDTA, sodium nitrate, NTA and picolinic acid were purchased from Aldrich. The radionuclides were purchased from Amersham or, in the case of ^{233}U, www.isotopes.com. pH was measured using an Orion 720A glass electrode. The electrode was calibrated using an Aldrich volumetric standard sodium hydroxide solution.

Spectrophotometric absorbances were measured using 1 cm silica cells in a Varian Cary 50 UV/Vis spectrophotometer. The radionuclides were counted by liquid scintillation counting in a Canberra Packard TRI-Carb 2750TR/LL, using Goldstar multipurpose liquid scintillation cocktail, or by gamma scintillation counting on a Packard Cobra II Autogamma.

6.6 Experimental

6.6.1 TPP and TPPO solubility

TPPO (1 g) was placed into 100 cm^3 of water and left for 1 month. The samples were filtered through a 0.2 μm syringe filter and measured using a ICP-MS method developed for measuring phosphorous by Dr. B. Sharp and P. Winship [87].
This procedure was then repeated for TPP.

This procedure was the repeated in NaOH (0.3 mol dm^{-3})

6.6.2 Kinetic studies by UV/Vis spectroscopy

Solutions of TPPB (0.02 mol dm^{-3}, 250 cm^3) and sodium hydroxide (0.6 mol dm^{-3}, 250 cm^3) were prepared. The temperatures of the individual solutions were then adjusted to 298 K using a water bath. The two solutions were then mixed together and held at the respective temperatures.

Samples were taken at certain time intervals, and placed immediately into 10 cm^3 of hydrochloric acid (5 mol dm^{-3}) to prevent the alkaline hydrolysis reaction continuing during measurement. The samples were then filtered through a 0.2 μm syringe filter before being measured by UV/Vis spectroscopy at a wavelength of 268 nm.

This procedure was then repeated at 313, 333 or 353 K.

This procedure was then repeated for [NaOH] = 0.1, 0.3 and 1 mol dm^{-3}.

6.6.3 Solubility studies

Once technetium has been precipitated by TPPB, the sparingly soluble TcO_4TPP complex will be placed in the nuclear waste repository along with the rest of the ILW nuclear waste. As described in section 2.6.1.3 the near field of the nuclear waste repository will initially reach a pH of *ca.* 13.3. Under these porewater conditions TPPB will start to degrade and produce TPPO and TPP (section 6.2.2). The effect that the degradation products of TPPB has on the other insoluble radionuclides in the near field of the repository is an important issue when considering the repository safety assessment. In particular, any increases in the solubility of radionuclides due to effects of TPPB and its degradation products could increase the mobility of the species and therefore, the possibility of escape from the repository.

6.6.3.1 Europium, iodine and nickel

To sodium hydroxide (20 cm^3, 0.30 mol dm^{-3}) TPPB was added as a solid to give a concentration of 0.001 mol dm^{-3}. Non-active nickel chloride was then added as a solid to give a concentration of 0.001 mol dm^{-3}. The solutions were then spiked with the ^{63}Ni (3.7 kBq). The samples were then left for two weeks. After this time, a 5 cm^3 sample was taken and filtered through a 0.22 μm syringe filter. 1 cm^3 sample was taken of the filtrate and added to goldstar multipurpose liquid scintillation cocktail (10 cm^3) in a liquid scintillation counting vial. HCl (6 mol dm^{-3}) was added, to neutralise the sample in order to minimize any chemiluminescence caused by the hydroxide ions. The sample was shaken vigorously and counted by LSC.

Samples for all three radionuclides were taken for measurement again after 4 and 8 weeks.

This procedure was then repeated for TPPO and TPP.

This experiment was then repeated for europium (^{152}Eu – 1.5 kBq) and iodine (^{125}I – 4.2 kBq), which are γ-emitters. The counting was performed on a 2 cm^3 sample, after filtration, in a gamma scintillation counter.

6.6.3.2 Technetium

To sodium hydroxide (20 cm^3, 0.30 mol dm^{-3}) TPPB was added as a solid to give a concentration of 0.001 mol dm^{-3}. *ca.* 1 kBq of technetium (*ca.* 4×10^{-7} mol dm^{-3}) was then added.

The sample was then left for two weeks. After this time, a sample was taken and filtered through a 0.22 μm syringe filter. 1 cm^3 of the filtrate was then neutralised and the activity in solution was measured by LSC.

Samples for all three radionuclides were taken for measurement again after 4 and 8 weeks.

This was then repeated for TPPO and TPP.

6.6.3.3 Uranium(VI)

To a solution of sodium hydroxide (10 cm^{-3}, 0.3 mol dm^{-3}) uranyl nitrate (0.001 mol dm^{-3}), spiked with ^{233}U (*ca.* 3.7 kBq) TPPB was added as a solid to give a concentration of 0.001 mol dm^{-3}.

The sample was left for two weeks. After this time, a sample was taken and filtered through a 0.22 μm syringe filter. 1 cm^3 of the filtrate was then neutralised and the activity in solution was measured by LSC.

Samples for all three radionuclides were taken for measurement again after 4 weeks.

This was then repeated for TPPO and TPP.

6.6.3.4 Uranium(IV)

To a solution of carbonate free sodium hydroxide solution (100 cm^3, 1 mol dm^{-3}) uranyl nitrate (40 cm^3, .01 mol dm^{-3}) containing ^{233}U spike (*ca.* 600 kBq) was added. To this solution sodium dithionite solution (100 cm^3, 0.10 mol dm^{-3}) was added. This was then left for 2 weeks to equilibrate. After this time a sample was taken, filtered, neutralised and the activity in solution measured by LSC. The solubility was then compared with the literature range [79] to ensure that the solubility of $UO_2.2H_2O$ (am) had been achieved.

Once $UO_2.2H_2O$ (am) had been produced the solution was shaken thoroughly and 5 cm^3 aliquots were removed and placed in polyethylene vials unfiltered. TPPB was then added as a solid to give a concentration of 0.001 mol dm^{-3}.

The sample was then left for two weeks. After this time, a sample was taken and filtered through a 0.22 μm syringe filter. 1 cm^3 of the filtrate was then neutralised and the activity in solution was measured by LSC.

This was then repeated for TPPO and TPP.

6.6.3.5 Solubility studies in the presence of 3 mol dm^{-3} NaNO$_3$

All the solubility experiments described above, except uranium(IV), (section 6.5.4.1 – 6.5.4.3) were repeated with the same reagents and, in addition, sodium nitrate was added to give a concentration of 3 mol dm^{-3}, in order to mimic waste streams in the nuclear industry.

6.6.3.6 Alkaline hydrolysis tetraphenylphosphonium bromide (TPPB) degradation mixture experiments

To investigate the actual effects of the degradation of TPPB in the presence of various radionuclides instead of the pure degradation products, TPPB was degraded and then Ni, Eu, I, Tc and U were placed in the degraded mixture. The pH of a 1 dm^3 TPPB (0.4 mol dm^{-3}) solution was increased to 13.3 by the addition of NaOH pellets. The solution was then left to degrade for 1 week. After this time the solution was shaken and aliquots of 20 cm^3 were taken and placed into vials. To these vials the metals were added to give concentrations of 0.01 mol dm^{-3}, except in the case of technetium where *ca.* 1 kBq, giving a concentration of 2 x 10^{-7} mol dm^{-3} were added. The solutions were then spiked with the appropriate tracer. The vials were then left for 2 weeks to equilibrate before being filtered and counted.

This experiment was then repeated for TPPB that had been degraded for 2 and 4 weeks.

6.6.3.7 Solubility of TcO$_4$TPP

100 kBq of TcO$_4^-$ were added to a solution of TPPB solution (100 cm^3, 0.01 mol dm^{-3}) giving a technetium concentration in the vials of 1.74 x 10^{-5} mol dm^{-3}. These were left for one week. After this time, a 5 cm^3 sample was taken and filtered through a 0.22 μm syringe filter. 1 cm^3 sample

was taken of the filtrate and added to goldstar multipurpose liquid scintillation cocktail (10 cm^3) in a liquid scintillation counting vial. HCl (6 mol dm^{-3}) was added, to neutralise the sample in order to minimize any chemiluminescence caused by the hydroxide ions. The sample was shaken vigorously and counted by LSC.

6.6.3.8 Solution studies involving organic complexing ligands

100 kBq of TcO_4^- were added to a solution of TPPB solution (100 cm^3, 0.01 mol dm^{-3}) giving a technetium concentration in the vials of 1.74 x 10^{-5} mol dm^{-3}. These were left for one week. The pH was then adjusted to 13.3 with sodium hydroxide and left for 1 month. After this time, a 5 cm^3 sample was taken and filtered through a 0.22 μm syringe filter. 1 cm^3 sample was taken of the filtrate and added to goldstar multipurpose liquid scintillation cocktail (10 cm^3) in a liquid scintillation counting vial. HCl (6 mol dm^{-3}) was added, to neutralise the sample in order to minimize any chemiluminescence caused by the hydroxide ions. The sample was shaken vigorously and counted by LSC.

Sampling and counting the activity in solution was then repeated every month for 7 months.

This procedure was then repeated in the presence of 0.01 mol dm^{-3} EDTA, NTA, ISA, gluconic acid and picolinic acid separately.

6.7 Results and discussion

6.7.1 TPPO and TPP solubility

From Table 6.2 it can be seen that the TPP and TPPO samples were counted as ^{31}P and ^{47}Ti. This is because ^{31}P suffers from several interferences, including those from molecular gases. To overcome this Dr Barry Sharp and Peter Winship, at Loughborough University, developed a modified method based on the work by Bandura *et al* [87] where the phosphorous sample is atomised and then reacted with oxygen in a collision cell to form PO, which is then counted as ^{47}Ti.

Concentration (ppb)	^{31}P	^{47}Ti
0	49218.3	2595.2
19	60241.1	6734.9
38	69045.2	10686.0
75	84560.6	17375.9
125	112332.4	28078.9
250	177683.7	52697.4
500	310341.1	105327.9

Table 6.2: Results for ICP-MS calibration curve

Table 6.2 shows data used in the calibration curve (Fig. 6.5).

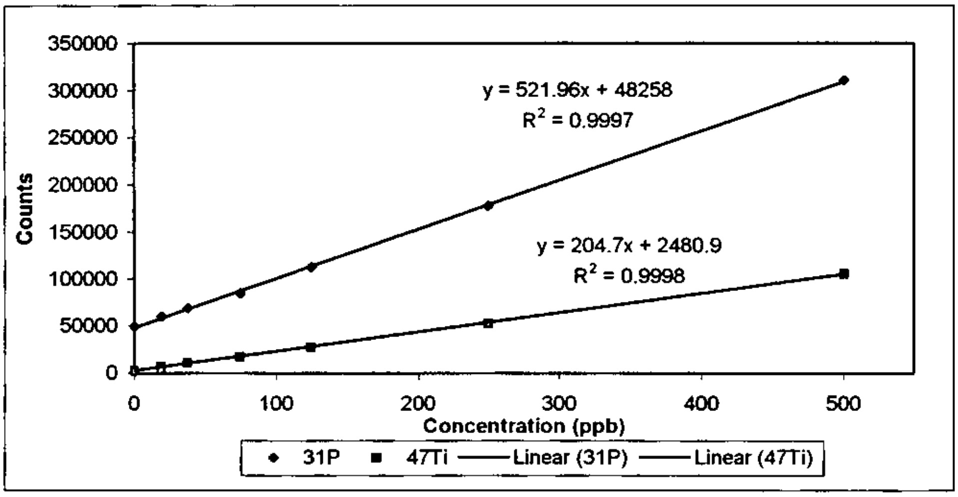


Fig. 6.5: Calibration curve for phosphorous using ICP-MS

From Fig. 6.5 it can been seen that the calibration curves give good linearity with R^2 values of 0.9997 and 0.9998 respectively.

	pH 7			pH 13.3		
	Counts	ppb	[P] (mol dm^{-3})	Counts	ppb	[P] (mol dm^{-3})
1	7292846	13879.6	4.48E-04	1371876	2535.9	8.18E-05
2	7722550	14702.8	4.74E-04	1478884	2740.9	8.84E-05
3	7701859	14663.2	4.73E-04	1475331	2734.1	8.82E-05
	Mean =	4.65E-04 ± 1.50E-05		Mean =	8.61E-05 ± 3.76E-06	

Table 6.3: Solubility results for TPPO

From Table 6.3 it can be seen that the solubility of TPPO at pH 7 is *ca.* 4.65 $\times 10^{-4}$ mol dm^{-3}. It can also be seen that as the pH is increased from pH 7 to pH 13.3 the solubility of TPPO decreases to 8.61 $\times 10^{-5}$ mol dm^{-3}.

	pH 7			**pH 13.3**		
	Counts	**ppb**	**[P] (mol dm^{-3})**	**Counts**	**ppb**	**[P] (mol dm^{-3})**
1	574334.3	1007.9	3.25E-05	70875.7	43.3	1.40E-06
2	376208.4	628.3	2.03E-05	65877.9	33.8	1.09E-06
3	291099.0	465.3	1.50E-05	59882.3	22.3	7.18E-07
	Mean =	2.26E-05 ± 8.98E-06		**Mean =**	1.07E-06 ± 3.40E-07	

Table 6.4: Solubility results for TPP

From Table 6.4 it can be seen that the solubilities of TPP at pH 7 and 13.3 are 2.26 $\times 10^{-5}$ mol dm^{-3} and 1.07 $\times 10^{-6}$ mol dm^{-3} respectively.

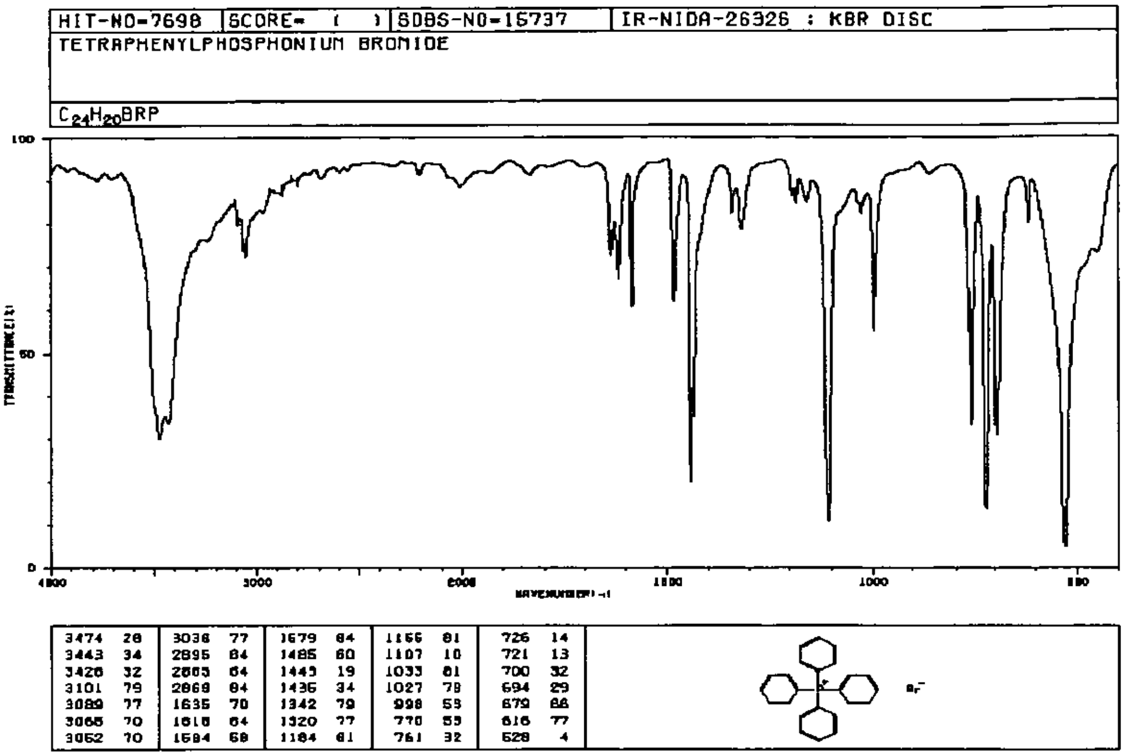
6.7.2 Degradation studies

As discussed in section 6.2.2 under alkaline conditions TPPB degrades via a mechanism of alkaline hydrolysis to form TPPO. The possibility of further degradation to DPPO looks possible however there is no evidence to suggest that this occurs. Also in section 6.4 past studies performed by Khalil *et* al [84, 85] showed evidence of co-precipitation of TPPB as TPPO was formed. The following study of the alkaline degradation of TPPB by FT-IR was performed to investigate;

- possibility of further degradation to produce DPPO,
- possibility of co-precipitation of TPPB during the degradation

6.7.2.1 Analysis of products

The spectra shown below in Fig. 6.6 – 6.9 are for TPPB, TPP, TPPO and DPP respectively. They were obtained from reference [88] and were used to analyse the degradation products of TPPB in this study.



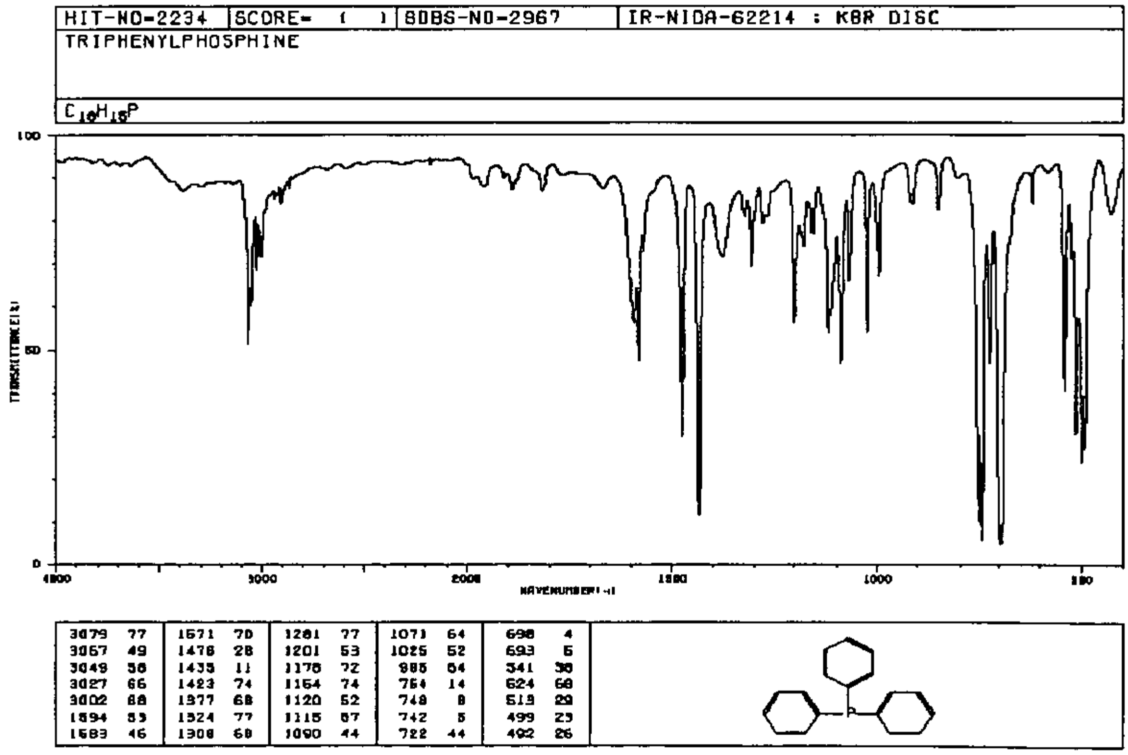
HIT-NO=7698 | SCORE= ( ) | SDBS-NO=15737 | IR-NIDA-26326 : KBR DISC

TETRAPHENYLPHOSPHONIUM BROMIDE

$C_{24}H_{20}BRP$

3474	28	3036	77	1679	84	1166	81	726	14
3443	34	2895	84	1485	60	1107	10	721	13
3426	32	2885	64	1443	19	1033	81	700	32
3101	79	2869	84	1436	34	1027	78	694	29
3089	77	1635	70	1342	79	998	59	679	88
3065	70	1618	64	1320	77	770	55	616	77
3052	70	1584	68	1184	81	761	32	528	4

Fig. 6.6: Literature IR spectrum of TPPB [88]



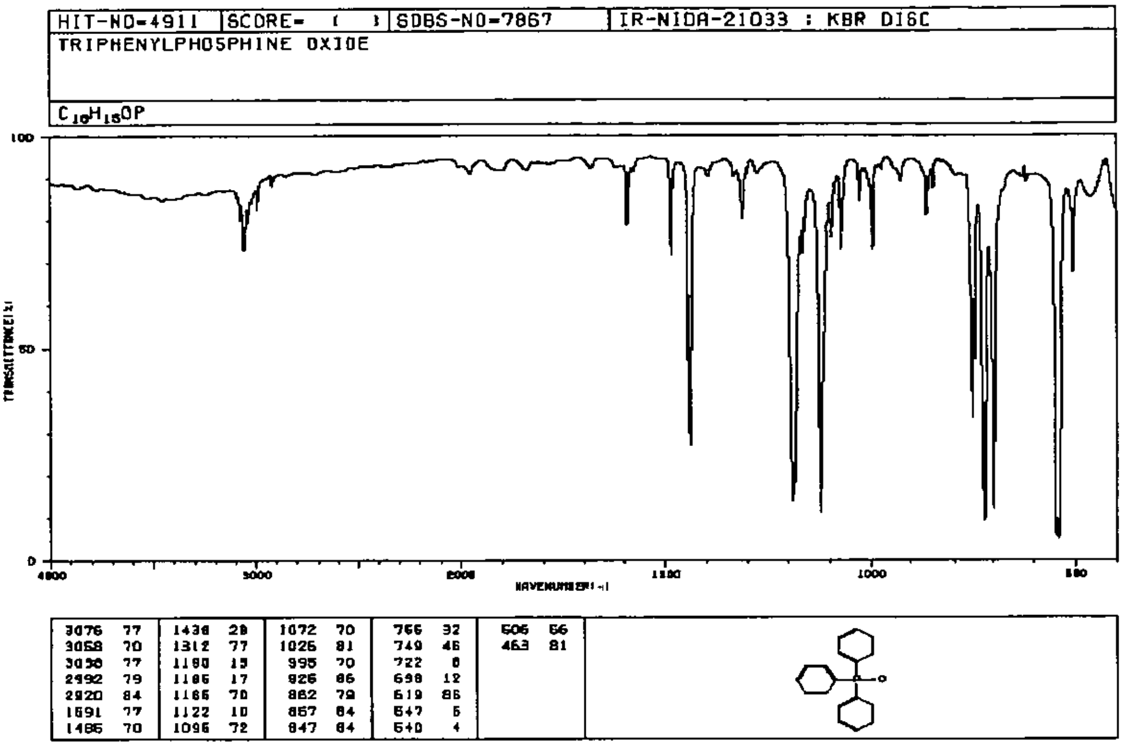
HIT-NO=2234 | SCORE= ( ) | SDBS-NO=2967 | IR-NIDA-62214 : KBR DISC

TRIPHENYLPHOSPHINE

$C_{18}H_{15}P$

3079	77	1571	70	1281	77	1071	64	698	4
3067	49	1478	28	1201	53	1025	52	693	6
3049	56	1435	11	1178	72	985	64	541	38
3027	66	1423	74	1164	74	754	14	624	68
3002	88	1377	68	1120	52	748	8	519	29
1594	83	1324	77	1115	87	742	5	499	23
1583	46	1308	68	1090	44	722	44	492	26

Fig. 6.7: Literature IR spectrum of TPP [88]



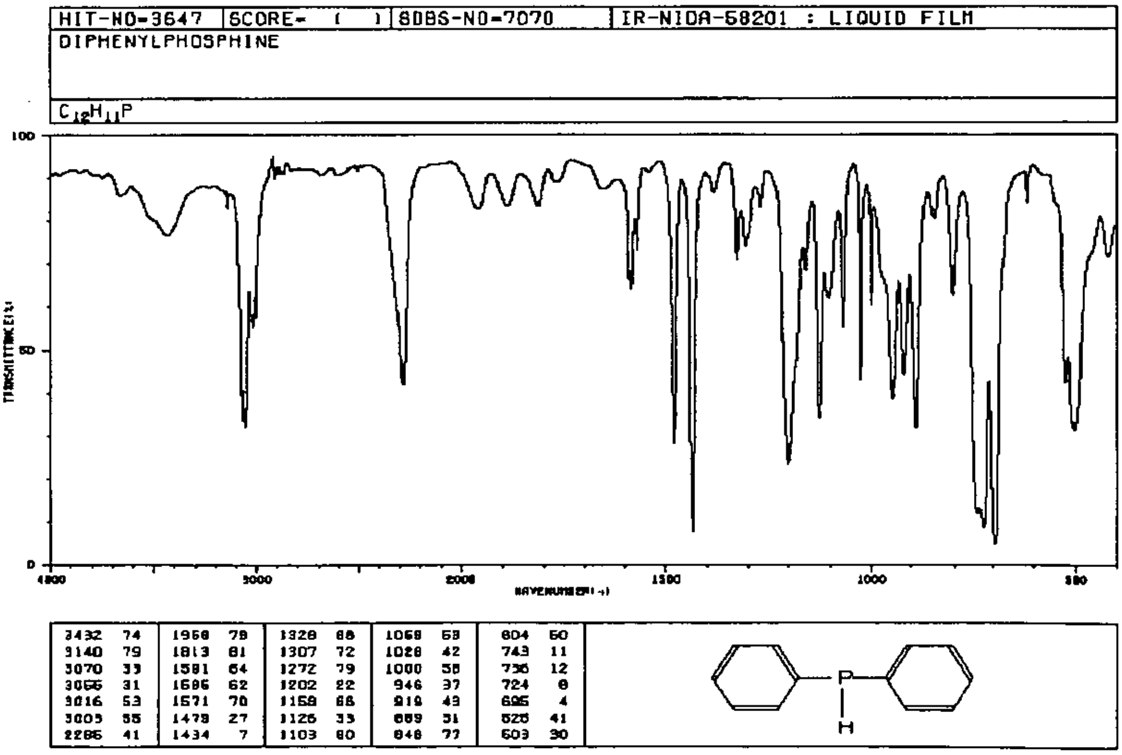
HIT-NO=4911 | SCORE= ( ) | SDBS-NO=7867 | IR-NIDA-21033 : KBR DISC

TRIPHENYLPHOSPHINE OXIDE

$C_{18}H_{15}OP$

3076	77	1438	28	1072	70	766	32	506	56
3058	70	1312	77	1026	81	749	46	463	81
3050	77	1190	15	995	70	722	8		
2992	79	1186	17	926	86	698	12		
2920	84	1166	70	862	79	619	86		
1591	77	1122	10	857	84	547	5		
1485	70	1096	72	847	64	540	4		

Fig. 6.8: Literature IR spectrum of TPPO [88]



HIT-NO=3647 | SCORE= ( ) | SDBS-NO=7070 | IR-NIDA-68201 : LIQUID FILM

DIPHENYLPHOSPHINE

$C_{12}H_{11}P$

3432	74	1958	78	1328	88	1068	58	804	50
3140	79	1813	81	1307	72	1028	42	743	11
3070	33	1581	64	1272	79	1000	58	736	12
3056	31	1586	62	1202	22	946	37	724	8
3016	53	1571	70	1158	88	918	43	695	4
3005	55	1478	27	1126	33	889	31	526	41
2286	41	1434	7	1103	80	848	77	503	30

Fig. 6.9: Literature IR spectrum of DPP [88]

It appears that no studies have been performed on the degradation of TPPB at pH > 12. Therefore to rule out the possibility of further degradation of TPPB resulting in the formation of DPPO the products of the degradation were analysed after 1 month and 6 months. The precipates were analysed by FT-IR spectroscopy. Sample 1, shown in Fig. 6.10, was the precipitate after 1 month of degradation and sample 2, shown in Fig. 6.11, was the precipate after 6 months of degradation .

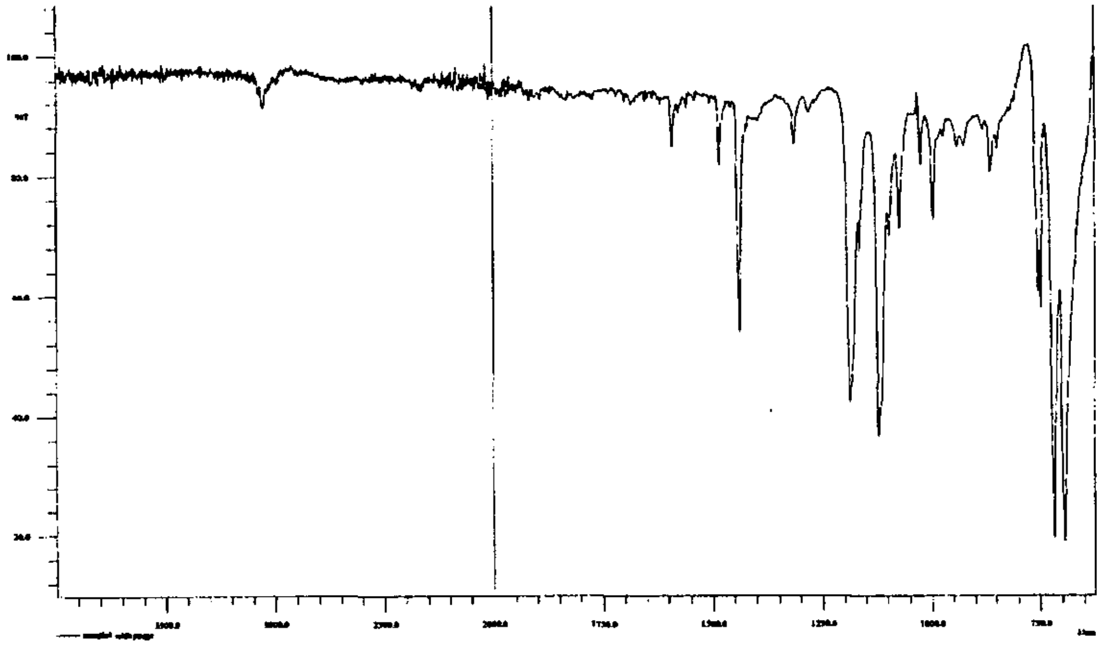


Fig. 6.10 IR spectrum on KBR disc of sample 1

Comparison with the spectra of sample 1 and Aldrich TPPB (Fig. 6.12) and TPPO (Fig. 6.13) shows that sample 1 is TPPO. Therefore it can be seen that after 1 month there has been no co-precipitation of TPPB. It can also be seen that there has been no further degradation to DPPO.

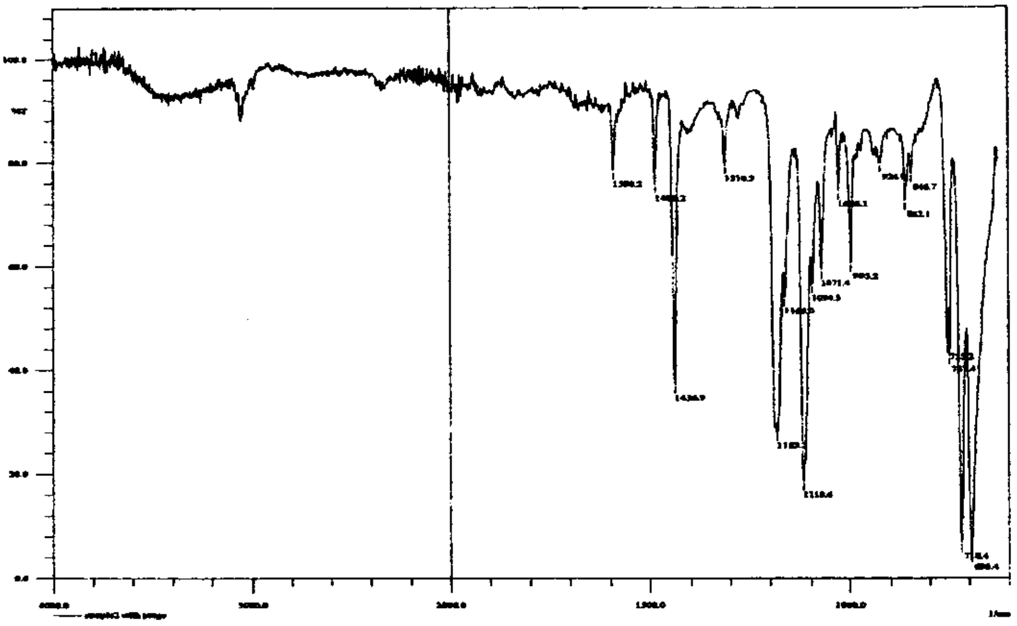


Fig. 6.11: IR spectrum on KBR disc of sample 2

Comparison with the spectra of sample 2 and Aldrich TPPB (Fig. 6.12) and TPPO (Fig. 6.13) shows that sample 2 is TPPO. Therefore it can be seen that after a significant amount of time there has been no co-precipitation of TPPB and no further degradation to DPPO.

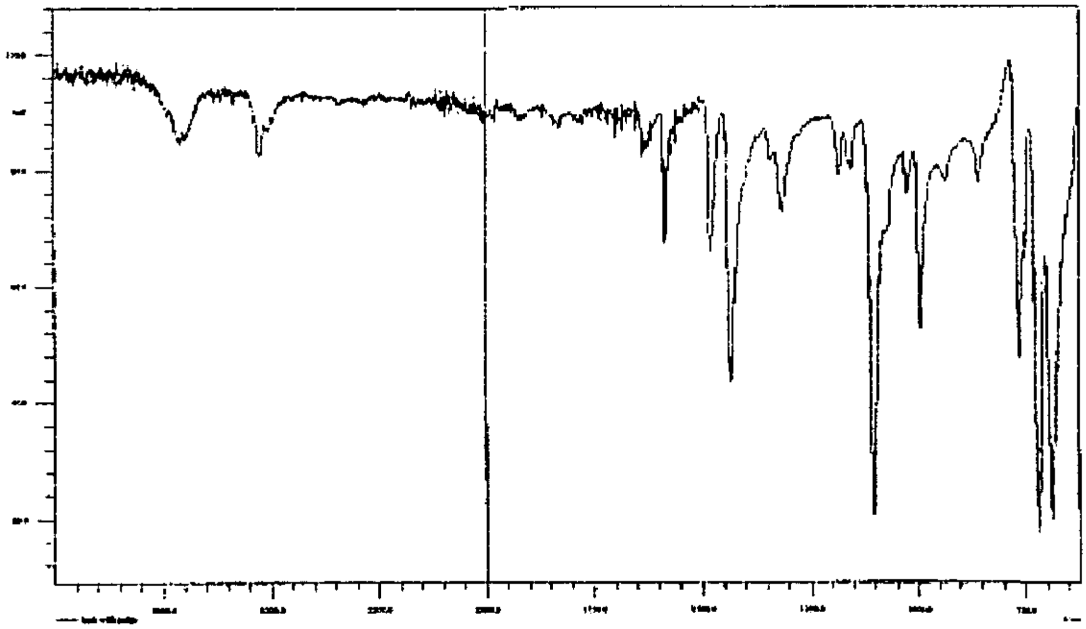


Fig. 6.12: IR spectrum on KBr disc of Aldrich TPPB

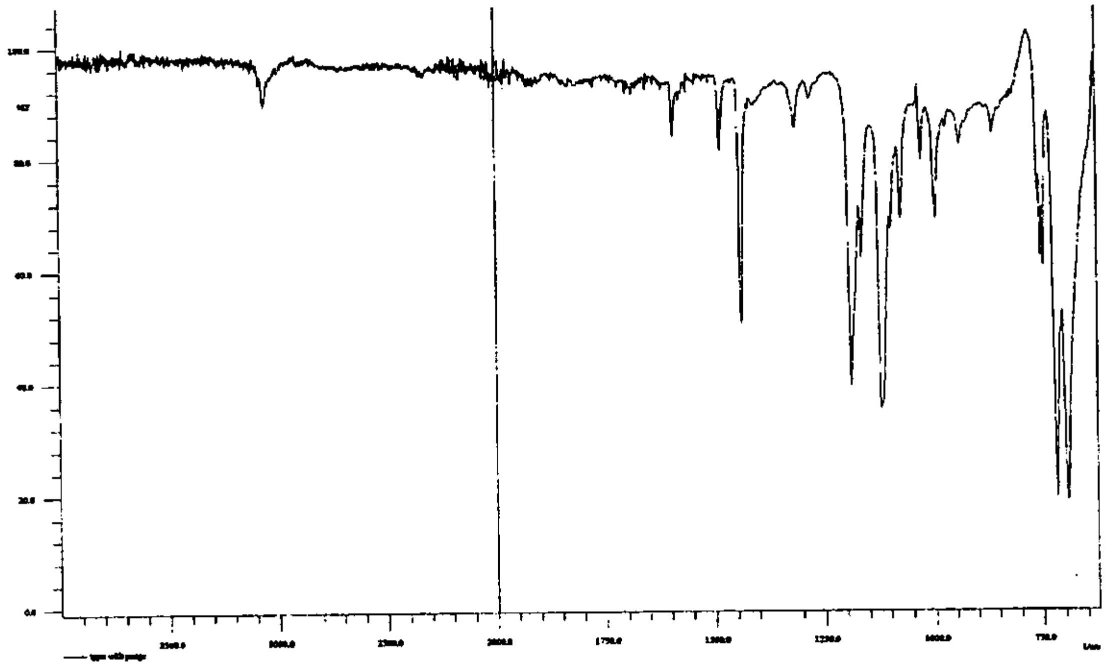


Fig. 6.13: IR spectrum on KBr disc of Aldrich TPPO

6.7.3 Kinetics

As discussed in section 6.4 the kinetics of the degradation on tetraphenylphosphonium ion due to alkaline hydrolysis have been studied before [84, 85]. However, these studies were completed using tetraphenylphosphonium chloride (TPPCl) and not TPPB. The studies completed by Khalil *et al* [84, 85] were also completed at pH 12.2 and not 13.3. Therefore, the kinetics of the degradation of TPPB, via alkaline hydrolysis, at pH 13.3 were investigated to give a better understanding of however TPPB will degrade under the near field conditions initially expected in a nuclear waste repository.

6.7.3.1 Calibration of UV/Vis spectroscopy for TPPB concentration

The measurements for the calibration curves were performed at neutral pH as in the actual experiments the high pH samples were neutralised before measurement. From Fig. 6.14 it can be seen that there are 3 peaks associated with TPPB, the calibration curve was measured using peak 2, which has a corresponding λ = 268.5 nm. Absorbances for the calibration curves were measured in the presence of NaCl. This is to account for any NaCl formed during the neutralisation of the samples.

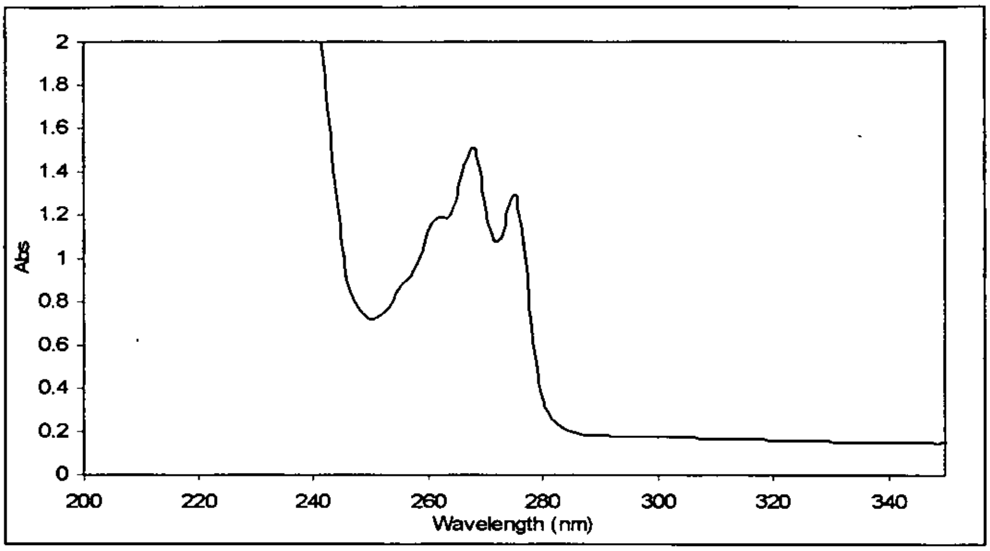


Fig. 6.14: UV spectra of TPPB in 0.03 mol dm^{-3} NaCl

To quench the alkaline degradation of TPPB HCl was added. This quenching step produces NaCl in the reaction solutions, therefore, the calibration curves (Fig. 6.15 – 6.17) were measured in the presence of 0.3, 0.1 and 0.03 mol dm^{-3} NaCl.

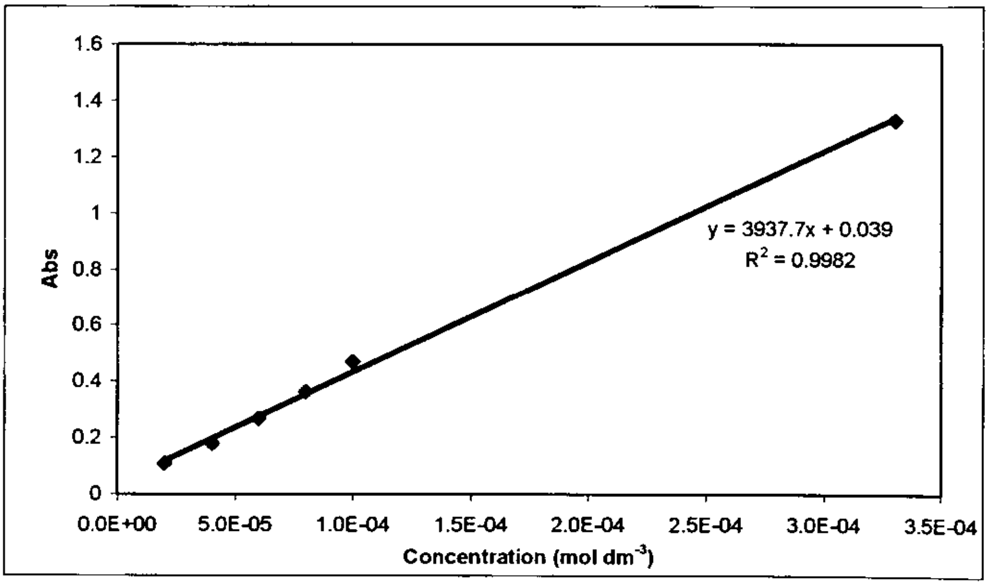


Fig. 6.15: Calibration curve for 0.3 mol dm^{-3} sodium chloride

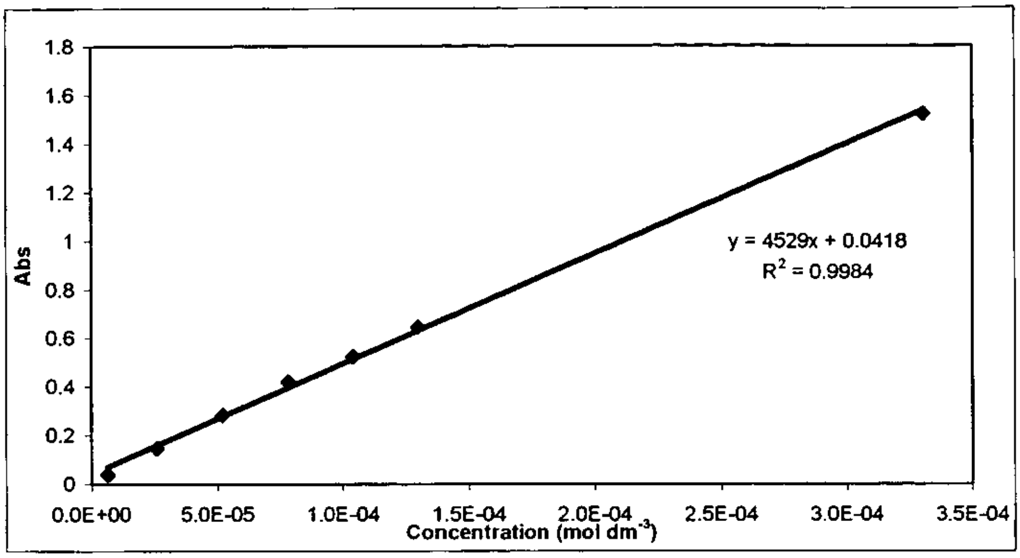


Fig. 6.16: Calibration curve for 0.1 mol dm^{-3} sodium chloride

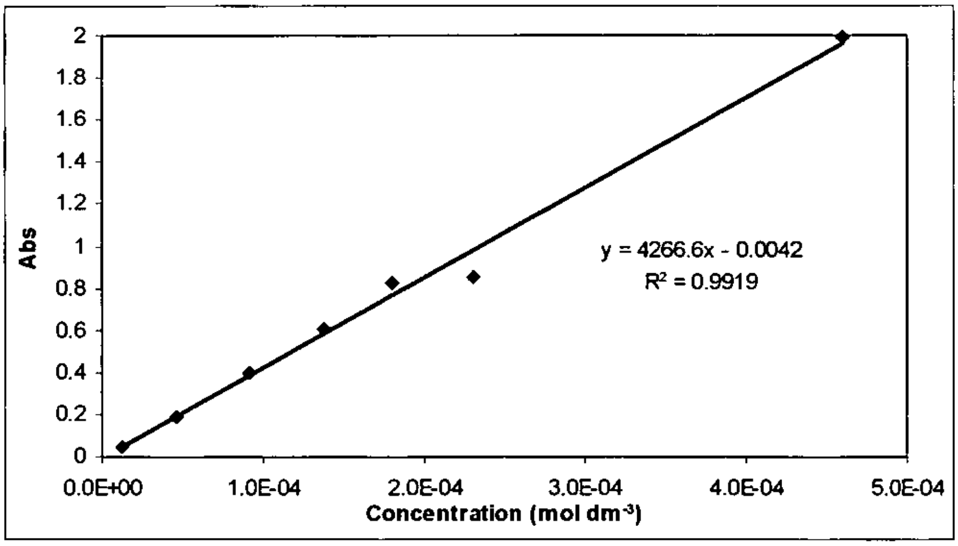


Fig. 6.17: Calibration curve for 0.03 mol dm^{-3} sodium chloride

6.7.3.2 Variation of room temperature

The tempertuare was recorded for the period of 1 month (Fig. 6.18 and Table 9.23) to give a more realistic idea of what the room temperature was during the kinetic experiments. This allows more accurate predictions of the degradation of TPPB at room temperature using the rate equation determined by Khalil *et al* [84, 85]

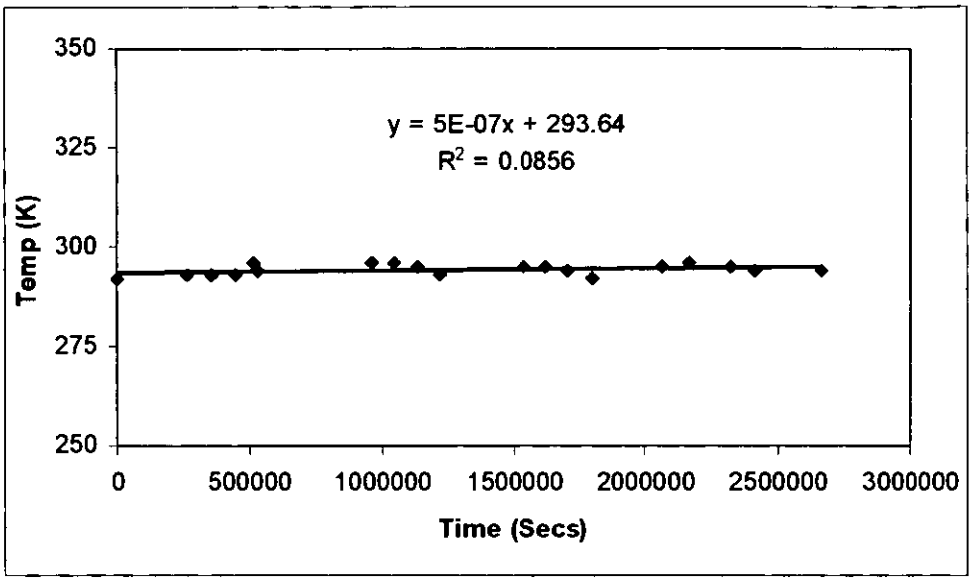


Fig. 6.18: Variation of room temperature with time

The average room temperature measured to be 294 ± 1.33 K. Therefore all degradation studied at room temperature will be compared to the rate of degradation of TPPB at 294 K.

6.7.3.3 Example of calculation of the predicted degradation of TPPB at 294 K and pH 14

From section 6.4 it can be seen that the rate constant for the degradation of the tetratphenylphosphonium ion is given by:

$$k = 3.27\times10^{19} e^{\left(\frac{-140.17\left[kJ mol^{-1}\right]}{RT}\right)} dm^6 mol^{-2} s^{-1}$$

Therefore at T = 294 k, k = 4.07 ×10^{-6} dm^6 mol^{-2} s^{-1}

$$k = 3.27\times10^{19} e^{\left(\frac{-140.17\left[kJ mol^{-1}\right]}{RT}\right)} dm^6 mol^{-2} s^{-1}$$

$$k = 4.07\times10^{-6}\ dm^6 mol^{-2} s^{-1}$$

It can also be seen from section 6.4 that the rate of reaction is given by:

Rate = $k[TPPB][OH]^2$

Therefore,

$$[TPPB] = [TPPB]_0\, e^{-k[OH^-]^2.t}$$

Therefore if $[TPPB]_0$ = 0.01 mol dm^{-3} and t = 7200 s. The remaining concentration of TPPB is given by:

$$[TPPB] = (0.01)e^{-(4.07\times10^{-6}\times(1^2)\times7200)}$$

$$[TPPB] = 0.099\,\text{mol}\,\text{dm}^{-3}$$

The method described above was used to draw graphs of predicted concentration of TPPB remaining in solution against time.

6.7.3.4 Degradation at 294 K and pH 14

The results for the degradation of TPPB, via alkaline hydrolysis, at pH 14 and 294 K are shown in Fig. 6.19 and Table 9.24. The experimental results compared favourably with the calculated values for the kinetics of the degradation.

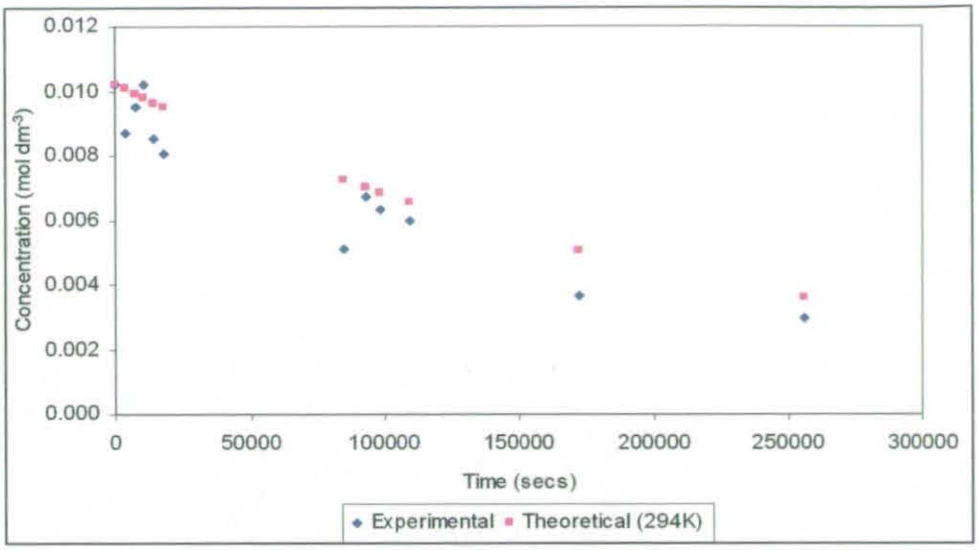


Fig. 6.19: TPPB degradation at 294 K and pH 14.

6.7.3.5 Degradation at 313 K and pH 14

The results for the degradation of TPPB at pH 14 and 313 K are shown in Fig. 6.20 and Table 9.25. The experimental results showed that the degradation occurred more quickly than the prediction would have suggested.

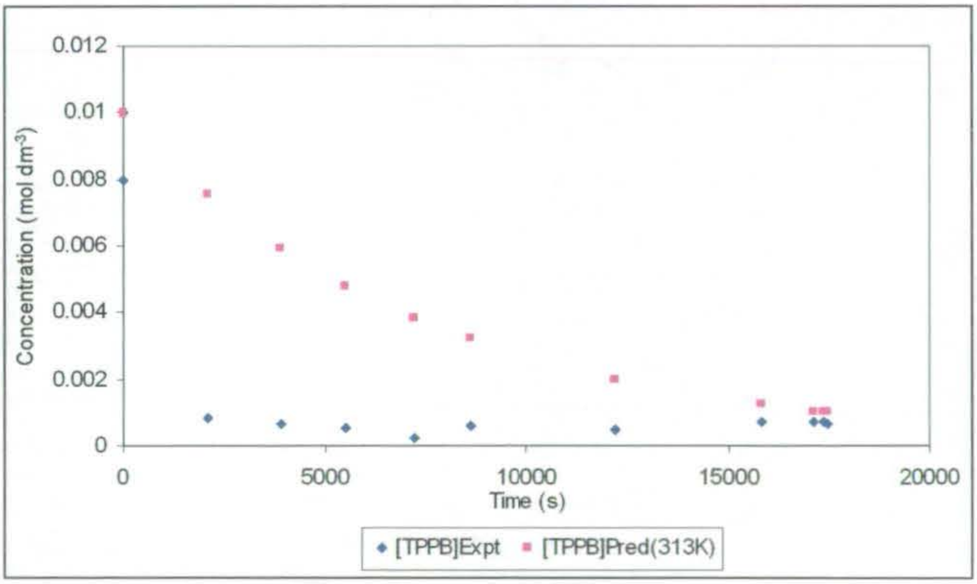


Fig. 6.20: TPPB degradation at 313 K and pH 14

6.7.3.6 Degradation at 333 K and pH 14

The results for the degradation at pH 14 and 333 K are shown in Fig. 6.21 and Table 9.26. The experimental results showed the degradation to be slightly slower than predicted. This might have been due to insufficient mixing at the start of the experiment, the temperature not being controlled exactly, and/or the fact that hydroxide ions are consumed in the reaction, causing a fall in pH, the possible effect of which is not included in the prediction.

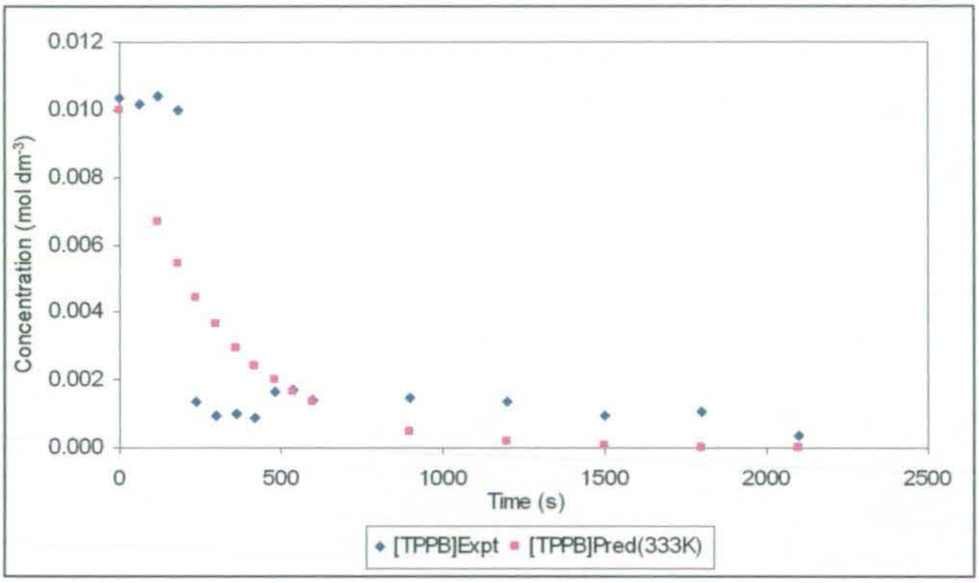


Fig. 6.21: TPPB degradation at 333 K and pH 14

6.7.3.7 Degradation at 353 K and pH 14

This reaction proceeded too quickly for measurements to be made.

6.7.3.8 Degradation at 294 K and pH 13.3

The results for the degradation at pH 13.3 and 294 K are shown in Fig. 6.22 and Table 9.27. The experimental results compared favourably with the calculated values for the kinetics of the degradation.

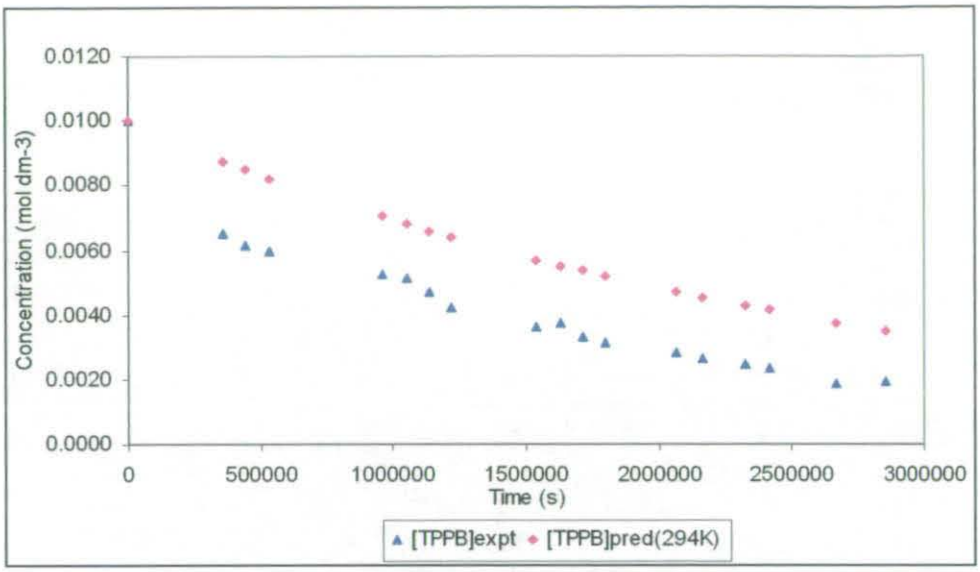


Fig. 6.22: TPPB degradation at 294 K and pH 13.3

6.7.3.9 Degradation at 313 K and pH 13.3

The results for the degradation at pH 13.3 and 313 K are shown in Fig. 6.23 and Table 9.28. The experimental results compared favourably with the calculated values for the kinetics of the degradation.

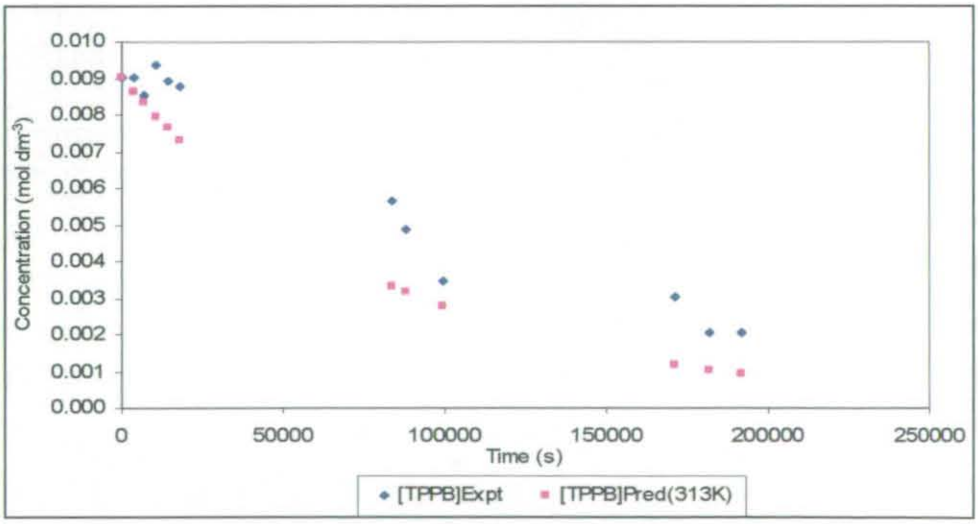


Fig. 6.23: TPPB degradation at 313 K and pH 13.3

6.7.3.10 Degradation at 333 K and pH 13.3

Fig. 6.24 shows the degradation of TPPB at 333 K and pH 13.3.

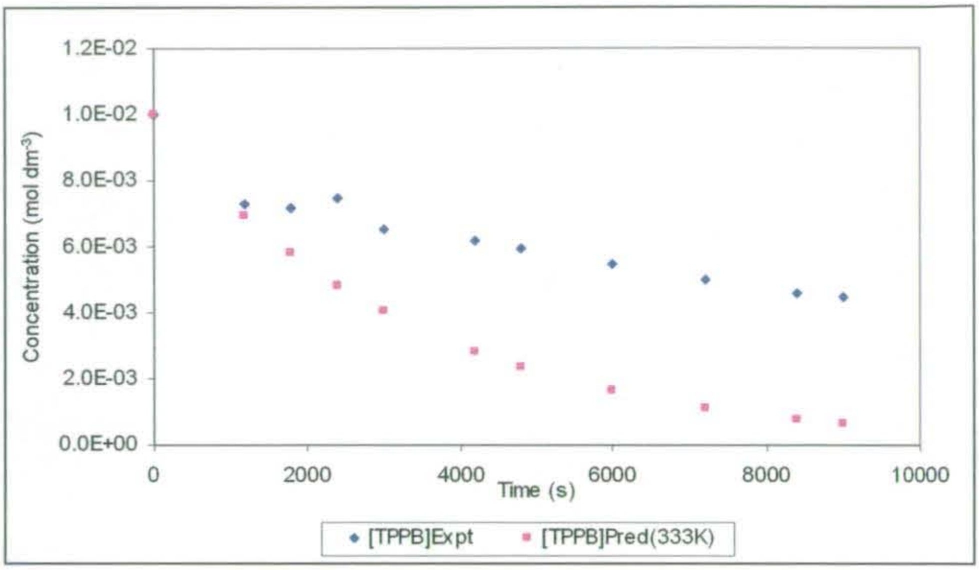


Fig. 6.24: TPPB degradation at 333 K and pH 13.3

The results for the degradation at pH 13.3 and 333 K are shown in Fig. 6.24 and Table 9.29. The experimental results showed the degradation to be slightly slower than predicted. This might have been due to insufficient mixing at the start of the experiment, the temperature not being controlled exactly, and/or the fact that hydroxide ions are consumed in the reaction, causing a fall in pH, the possible effect of which is not included in the prediction.

6.7.3.11 Degradation at 353 K and pH 13.3

This reaction proceeded too quickly for measurements to be made.

6.7.3.12 Degradation at 294 K and pH 13

The results for the degradation at pH 13 and 294 K are shown in Fig. 6.25 and Table 9.30. The experimental results compared favourably with the calculated values for the kinetics of the degradation.

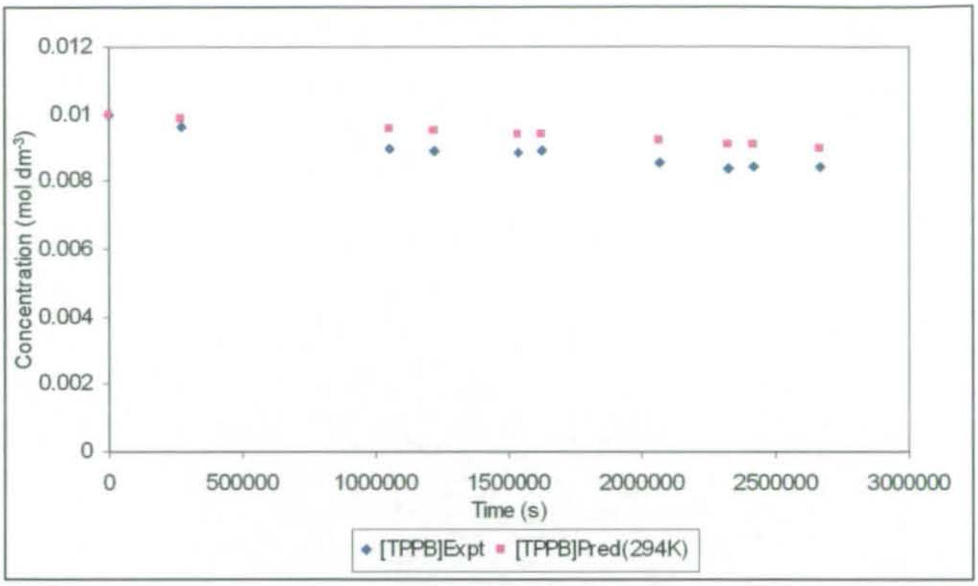


Fig. 6.25: TPPB degradation at 294 K and pH 13

6.7.3.13 Degradation at 313 K and pH 13

The results for the degradation at pH 13 and 313 K are shown in Fig. 6.26 and Table 9.31. The experimental results compared favourably with the calculated values for the kinetics of the degradation.

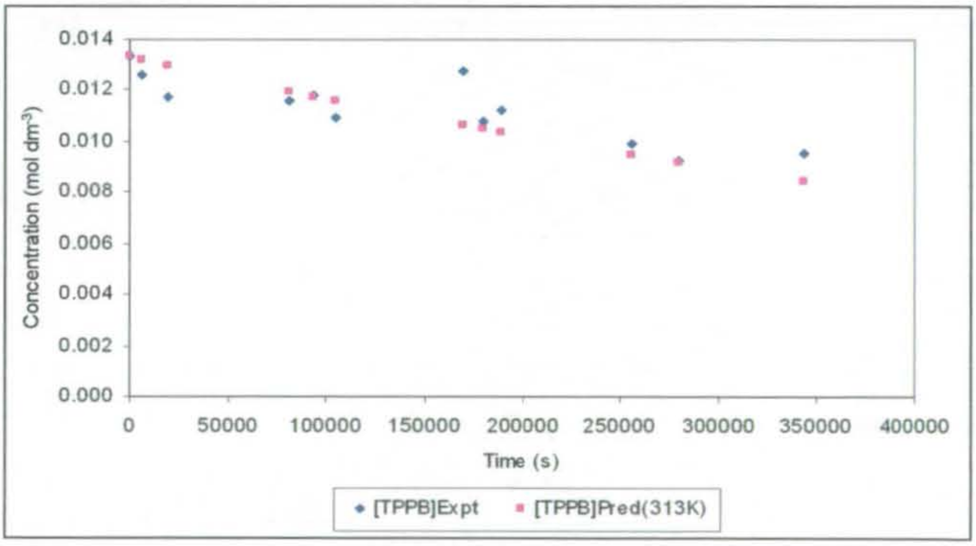


Fig. 6.26: TPPB degradation at 313 K and pH 13.3

6.7.3.14 Degradation at 333 K and pH 13

The results for the degradation at pH 13 and 333 K are shown in Fig. 6.27 and Table 9.32. The experimental results showed the degradation to be slightly slower than predicted. This might have been due to insufficient mixing at the start of the experiment, the temperature not being controlled exactly, and/or the fact that hydroxide ions are consumed in the reaction, causing a fall in pH, the possible effect of which is not included in the prediction.

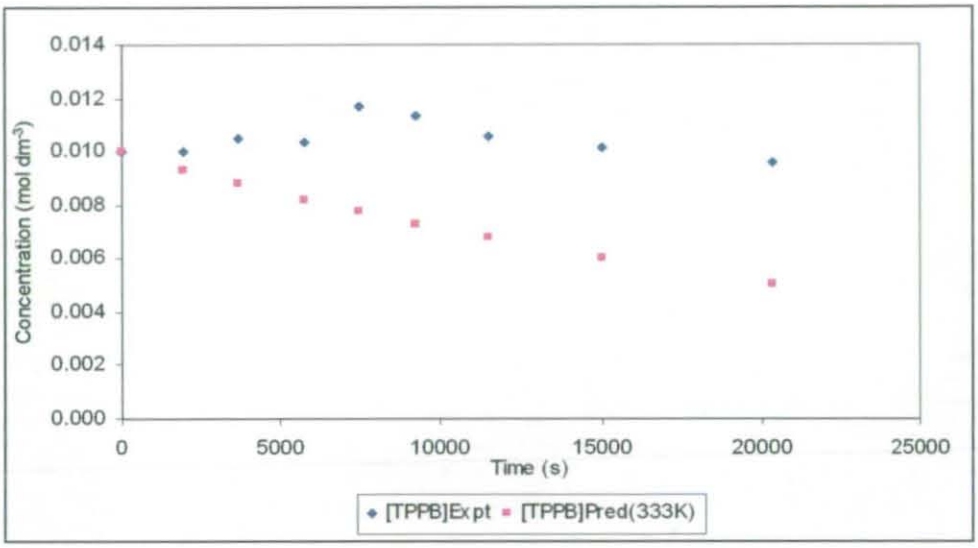


Fig. 6.27: TPPB degradation at 333 K and pH 13.3

6.7.4 Estimation of the activation energy of the degradation of TPPB

Using data obtained by Khalil and Aksnes [84, 85] (Table 6.5), it is possible to derive an Arrhenius equation, by plotting a graph of 1/T against ln k. (Fig. 6.28)

T (°C)	25	35	40	45	50	55
T (K)	298	308	313	318	323	328
1/T (K)	3.36E-03	3.25E-03	3.19E-03	3.14E-03	3.10E-03	3.05E-03
k ($dm^6 mol^{-2} min^{-1}$)	5.30E-04	3.30E-03	7.90E-03	1.80E-02	4.30E-02	9.60E-02
ln k	-7.5	-5.7	-4.8	-4.0	-3.2	-2.3

Table 6.5: Data obtained from Khalil and Aksnes [84, 85]

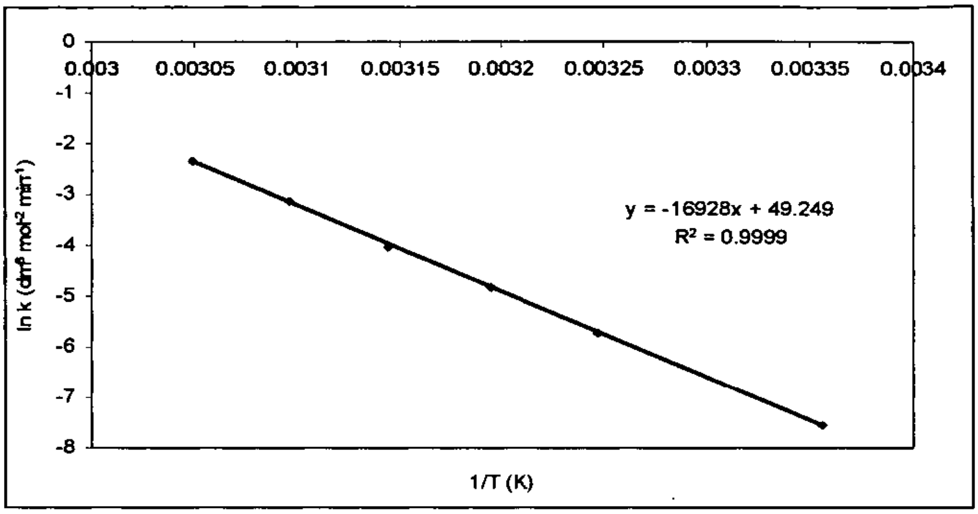


Fig. 6.28: Plot of 1/T (K) against ln k ($dm^6\ mol^{-2}\ min^{-1}$)

From this plot it is possible to calculate the activation energy of the degradation of TPPB. As shown in section 6.3 the activation energy is therefore 140 kJ mol^{-1} and the pre exponential term or A factor is 2.45×10^{21} (ln A = 49.2).

Using data from section 6.6.3 it is possible to estimate the activation energy and obtain an Arrhenius expression for the degradation of TPPB at the different hydroxide concentrations used, i.e. [NaOH] = 0.1, 0.3 and 1 mol dm^{-3}.

6.7.4.1 [NaOH] = 0.1 mol dm^{-3}

From Fig. 6.29 it can be seen that the activation energy is 103 kJ mol^{-1} and the A factor is 1.59×10^{13} (ln A = 30.4).

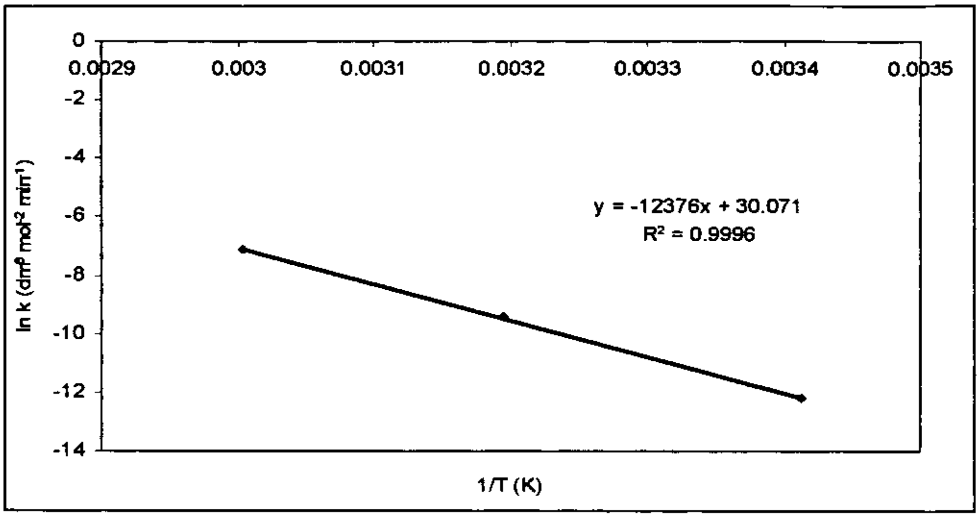


Fig. 6.29: Plot of 1/T (K) against ln k for the degradation of TPPB at [NaOH] = 0.1 mol dm^{-3}

6.7.4.2 [NaOH] = 0.3 mol dm^{-3}

From Fig. 6.30 it can be seen that the activation energy is 122 kJ mol^{-1} and the A factor is 1.43 ×10^{16} (ln A = 37.2).

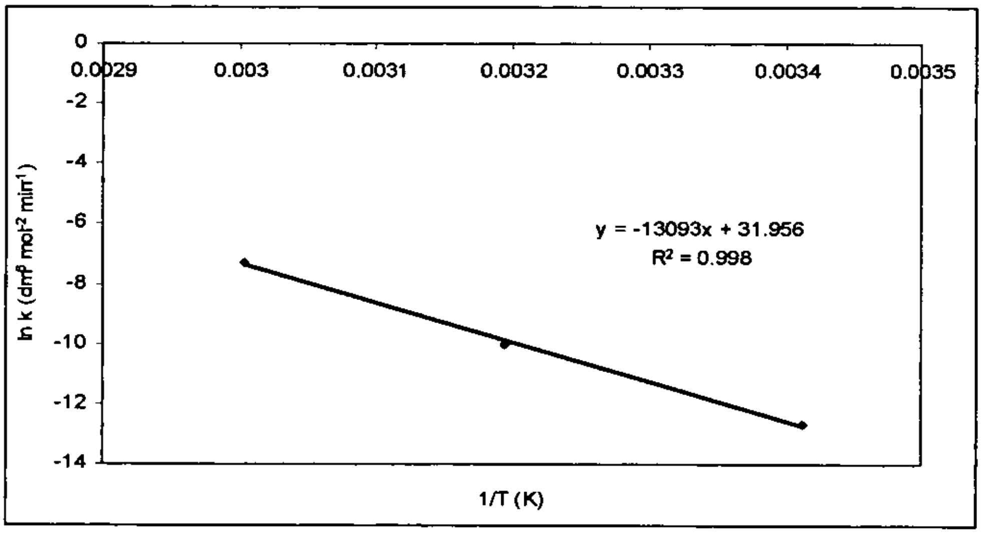


Fig. 6.30: Plot of 1/T (K) against ln k for the degradation of TPPB at [NaOH] = 0.3 mol dm-3

6.7.4.3 [NaOH] = 1 mol dm^{-3}

Fig. 6.31 shows a plot of 1/T (K) against log k for the kinetic studies at pH 14

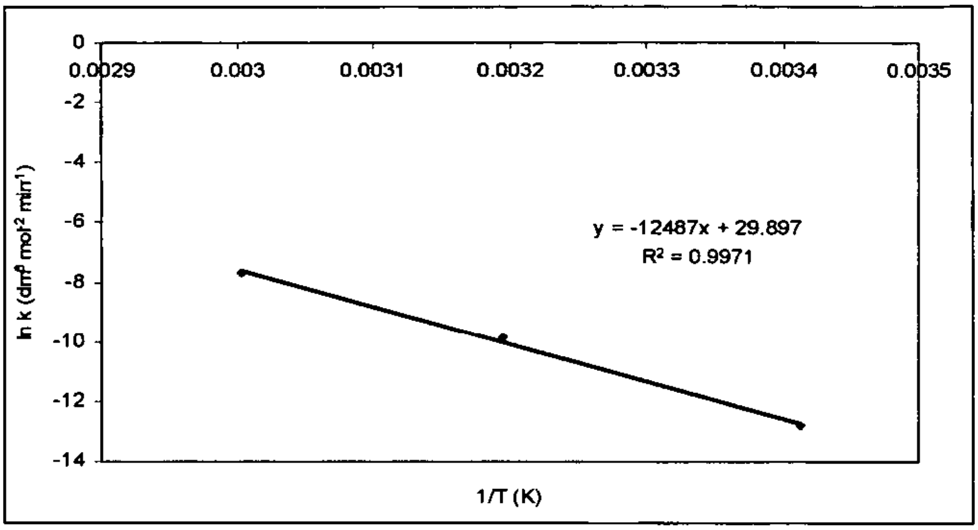


Fig. 6.31: Plot of 1/T (K) against ln k for the degradation of TPPB at [NaOH] = 1 mol dm^{-3}

From Fig. 6.31 it can be seen that the activation energy is 104 kJ mol^{-1} and the A factor is 9.67 ×10^{12} (ln A = 29.9).

6.7.4.4 Summary of estimated activation energies

[OH⁻] (mol dm^{-3})	E_A (kJ mol^{-1})	A	ln A
0.02*	140*	2.45 ×10^{21}*	49.2*
0.1	102.9	1.15 ×10^{13}	30.1
0.3	108.9	7.56 ×10^{13}	32.0
1	103.8	9.64 ×10^{12}	29.9

* - literature vaules [84, 85]

Table 6.6: Estimated activation energies

The mean activation energy is 105.2 ± 3.21 kJ mol^{-1} and the mean pre-expotential term, ln A, is 30.6 ± 1.14. therefore the Arrhenius expression can be expressed as:

$$k = 2.03 \times 10^{13}\, e^{\left(\frac{-105.2\left(\text{kJ mol}^{-1}\right)}{RT}\right)}\ \text{dm}^6\text{mol}^{-2}\text{s}^{-1}$$

By comparing this Arrhenius equation to that of determined by Khalil *et al* [84, 85] it can been seen that activation energy for the degradation of TPPB is lower than that for TPPCl, therefore the degradation of the bromide phosphonium salt is kinetically faster than that of the chloride salt.

6.7.5 Solubility studies

The effects that TPPB and the degradation products of TPPB have on the solubility of other insoluble radionuclides in the near field of the repository is an important issue when considering the repository safety assessment. In particular, any increases in the solubility of radionuclides due to effects of TPPB and its degradation products could increase the mobility of the species and therefore, the possibility of escape from the repository.

6.7.5.1 Europium

Fig. 6.32 shows the log of the europium solubility against time (weeks)

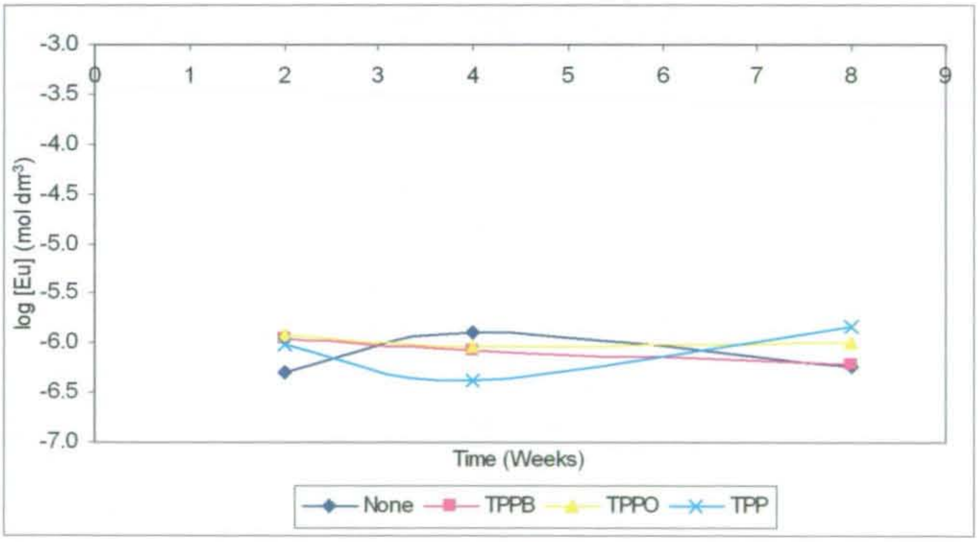


Fig. 6.32: $\log_{10}$ [Eu] (mol dm^{-3}) against time (weeks)

Data from the solubility experiments on europium after 2, 4, and 8 weeks equilibration are shown below in Fig. 6.32 and Table 9.33. The results show that TPPB, TPPO and TPP had no significant effect on the solubility of europium, except for TPP after 8 weeks, where there was a slight rise in solubility from 5.9 x 10^{-7} to 1.44 x 10^{-6} mol dm^{-3}.

6.7.5.2 Iodine

Fig. 6.33 shows the log of the iodine concentration against time.

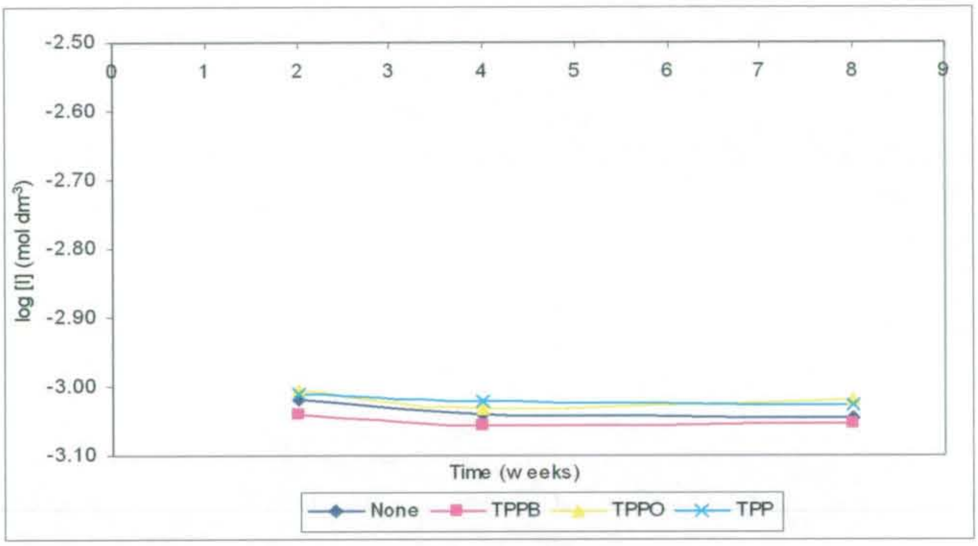


Fig. 6.33: $\log_{10}$ [I] (mol dm^{-3}) against time (weeks)

Data from the solubility experiments on iodine, in the form of iodide, after 2, 4, and 8 weeks equilibration are shown in Fig. 6.33 and Table 9.34. The results show that TPPB, TPPO and TPP had no significant effect on the solubility of iodine. The values for four and eight weeks have been half-life adjusted to be comparable with the values for two weeks.

6.7.5.3 Nickel

Data from the solubility experiments on nickel after 2,4, and 8 weeks equilibration are shown below in Fig. 6.34 and Table 9.35. The results show that TPPB and TPPO had no significant effect on the solubility of nickel. The TPP results show a statistically significant decrease in solubility after 4 weeks but not after 2 and 8. This may be due to the very low levels of nickel being measured, and may not be chemically significant.

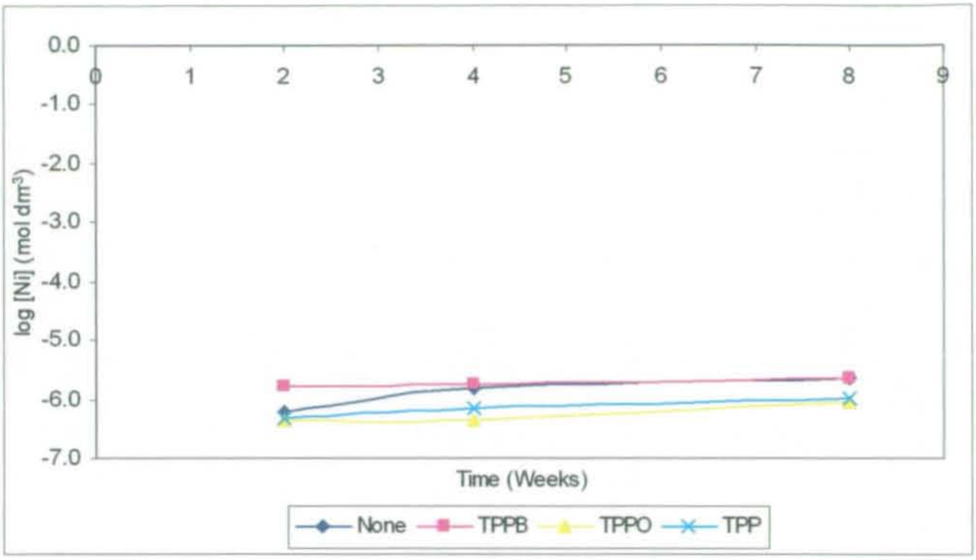


Fig. 6.34: $\log_{10}$ [Ni] (mol dm^{-3}) against time (weeks)

6.7.5.4 Technetium(VII)

Fig. 6.35 shows the log of the technetium concentration against time.

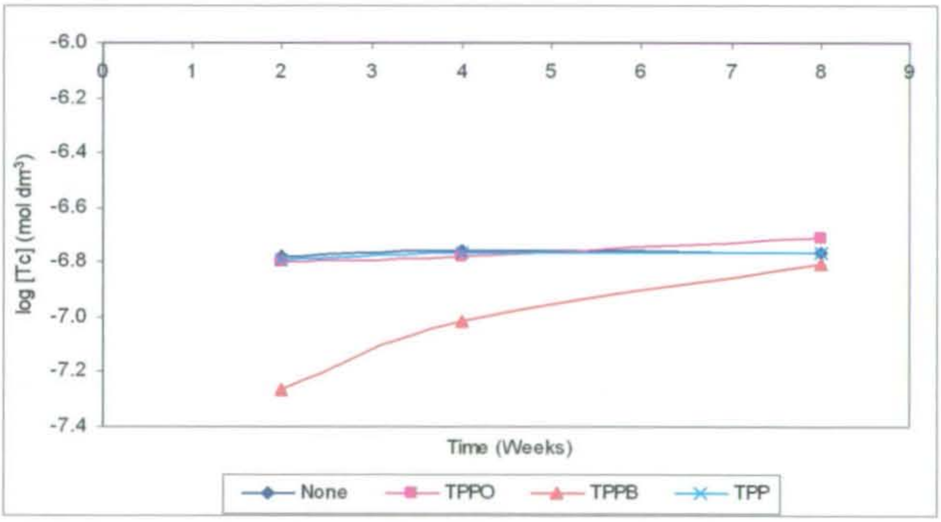


Fig. 6.35: $\log_{10}$ [Tc] (mol dm^{-3}) against time (weeks)

Data from the solubility experiments on technetium after 2, 4 and 8 weeks equilibration are shown below in Fig. 6.35 and Table 9.36. No significant changes in solubility occurred. There is no evidence of TPP or TPPO reducing the solubility of TcO_4^- in the same way that TPPB does.

Using the rate equation and data from this study it is possible to compare the degradation of TPPB with the release of technetium from the TcO_4TPP complex at high pH (Fig. 6.36).

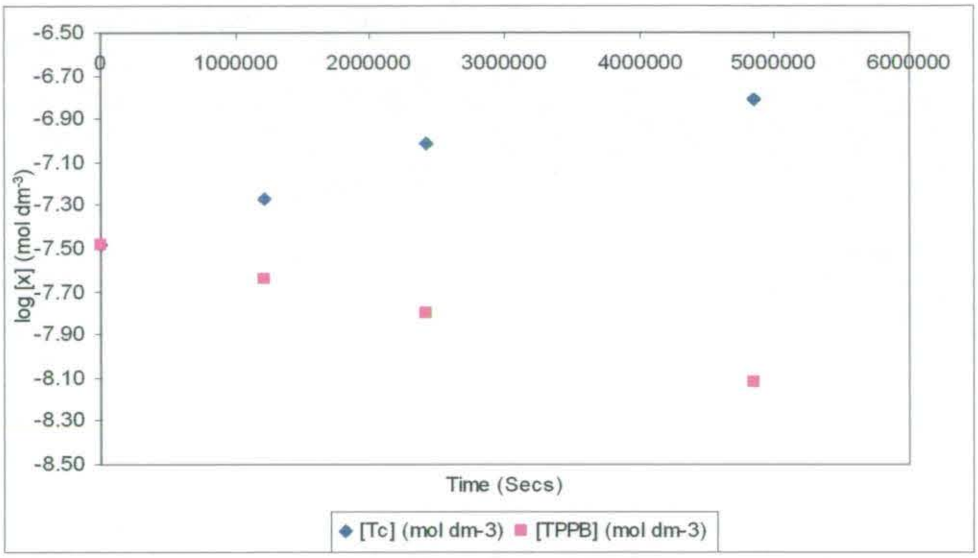


Fig. 6.36: $\log_{10}$ [Tc] (mol dm^{-3}) and $\log_{10}$ [TPPB] (mol dm^{-3}) against time (weeks)

From Fig. 6.36 it can be seen that the release rate of technetium approximately mirrors the degradation of TPPB. The solubility increase of technetium with time is therefore due to the release of technetium as the tetratphenylphosphonium bromide molecule degrades via alkaline hydrolysis.

6.7.5.5 Uranium(VI)

Data from the solubility experiments on uranium(VI) after 1 and 4 weeks equilibration are shown below in Fig. 6.37 and Table 9.37. The results show that there was no significant effect on the solubility of uranium(VI).

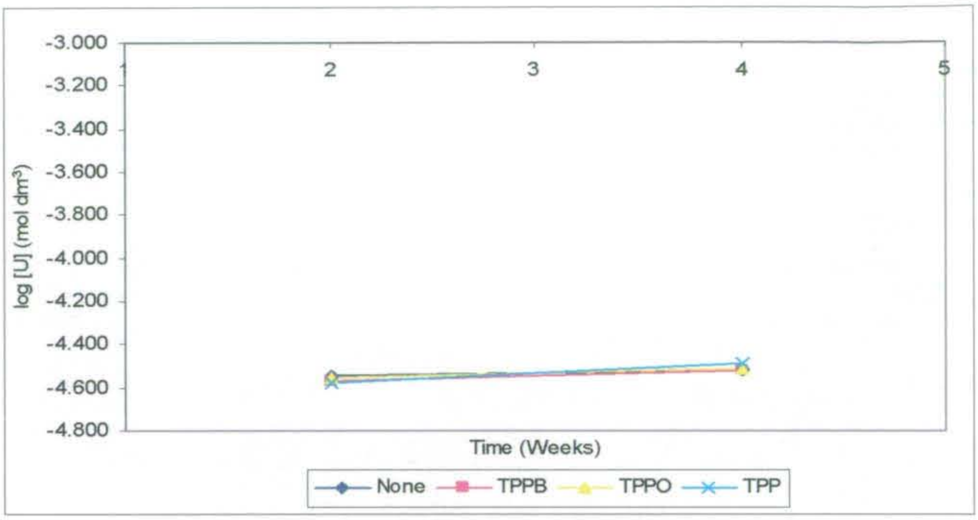


Fig. 6.37: $\log_{10}$ [U] (mol dm^{-3}) against time (weeks)

6.7.5.6 Uranium(IV)

Data from the solubility experiments on uranium(IV) after 2 weeks equilibration are shown below in Table 6.10. TPPB and TPPO had no significant effect on the solubility of uranium(IV), but TPP caused a rise from 1.88 x 10^{-7} to 2.78 x 10^{-6} mol dm^{-3}.

		2 Weeks		
Sample	Organic	[U] (mol dm^{-3})	Mean [U] (mol dm^{-3})	St Dev
1	None	1.23E-07		
2	None	2.46E-07		
3	None	1.53E-06	1.85E-07	8.70E-08
4	TPPB	4.48E-07		
5	TPPB	1.23E-07		
6	TPPB	1.90E-07	3.19E-07	1.82E-07
7	TPPO	1.34E-07		
8	TPPO	4.14E-07		
9	TPPO	2.46E-07	2.65E-07	1.41E-07
10	TPP	3.92E-07		
11	TPP	2.75E-06		
12	TPP	2.81E-06	2.78E-06	3.96E-08

Table 6.7: Data from solubility experiments on U(IV)

6.7.5.7 Summary

Table 6.8 shows the solubility enhancement factors for the solubility studies investigated in section 6.7.5.

	Time (Weeks)	Solubility Enhancement Factors (SEF) TPPB	TPPO	TPP
Eu	2	2.2	2.5	2.0
	4	0.7	0.7	0.3
	8	1.0	1.7	2.5
I	2	1.0	1.0	1.0
	4	1.0	1.0	1.1
	8	1.0	1.1	1.0
Ni	2	2.7	0.7	0.8
	4	1.1	0.3	0.4
	8	1.1	0.4	0.5
Tc	2	0.3	1.0	1.0
	4	0.6	1.0	1.0
	8	0.9	1.1	1.0
U(VI)	2	1.0	1.0	0.9
	4	1.0	1.0	1.1
U(IV)	2	1.7	1.4	15.0

Table 6.8: Solubility enhancement factors for the effects of TPPB, TPPO and TPP on various radionuclides

From Table 6.8 and the results in section 6.7.5 it can be seen that TPPB, TPPO and TPP had no significant effect on the solubility of europium, iodine, nickel and uranium(VI).

TPPB and TPPO were shown to have no effect on the solubility of uranium(IV). However, the solubility of uranium(IV) slightly increased by the presence of TPP. This increase in solubility could be due to the reoxidation of U(IV) to U(VI).

TPPO and TPP were also shown to have no significant effect on the solubility of technetium(VII). However, as expected TPPB reduces the solubility of TcO_4^- as the insoluble TcO_4TPP complex is formed. However, as discussed in section 6.2 under the alkaline conditions used to represent the near field of the nuclear repository TPPB degrades. This degradation can be followed by measuring the concentration of technetium in solution, as TcO_4^- is released during the degradation.

6.7.6 Solubility studies in the presence of 3 mol dm^{-3} sodium nitrate

The MAC floc which will contain technetium, as the TcO_4TPP insoluble complex, will contain a lagre number of other species. One species that will be present in large quantities of nitrate. Therefore, to mimic the conditions of the MAC floc the solublility experiements (section 6.7.5) were repeated in the presence of 3 mol dm^{-3} sodium nitrate.

6.7.6.1 Europium

		2 Weeks		
Sample	Organic	[Eu] (mol dm^{-3})	Mean [Eu] (mol dm^{-3})	St Dev
1	None	4.66E-07		
2	None	9.75E-07		
3	None	7.54E-07		
4	None	6.65E-08		
5	None	1.22E-06	6.96E-07	4.48E-07
6	TPPB	2.44E-07		
7	TPPB	5.10E-07		
8	TPPB	3.33E-07		
9	TPPB	<2.00E-07		
10	TPPB	1.93E-06	7.54E-07	7.91E-07
11	TPPO	<2.00E-07		
12	TPPO	<2.00E-07		
13	TPPO	<2.00E-07		
14	TPPO	6.65E-07		
15	TPPO	5.32E-07	5.99E-07	9.41E-08
16	TPP	2.00E-07		
17	TPP	1.33E-07		
18	TPP	<2.00E-07		
19	TPP	<2.00E-07		
20	TPP	<2.00E-07	1.66E-07	4.70E-08

Table 6.9: Solubility experiments on Eu in 3 mol dm^{-3} sodium nitrate

From Table 6.9 it can be seen that the presence of TPPB or its degradation products has no significant effect on the solubility of europium.

6.7.6.2 Iodine

From Table 6.10 it can be seen that the presence of TPPB or its degradation products has no significant effect on the solubility of iodine

		2 Weeks		
Sample	Organic	[I] (mol dm^{-3})	Mean [I] (mol dm^{-3})	St Dev
1	None	8.17E-04		
2	None	7.68E-04		
3	None	7.86E-04		
4	None	7.87E-04		
5	None	8.28E-04	7.97E-04	2.46E-05
6	TPPB	7.47E-04		
7	TPPB	8.03E-04		
8	TPPB	7.85E-04		
9	TPPB	7.77E-04		
10	TPPB	7.93E-04	7.81E-04	2.13E-05
11	TPPO	8.08E-04		
12	TPPO	7.10E-04		
13	TPPO	7.60E-04		
14	TPPO	8.14E-04		
15	TPPO	7.84E-04	7.75E-04	4.22E-05
16	TPP	7.38E-04		
17	TPP	7.40E-04		
18	TPP	7.41E-04		
19	TPP	7.58E-04		
20	TPP	8.57E-04	7.67E-04	5.13E-05

Table 6.10: Solubility experiments on iodine in 3 mol dm^{-3} sodium nitrate

6.7.6.3 Nickel

From Table 6.13 it can be seen that the presence of TPPB or its degradation products has no significant effect on the solubility of nickel.

		2 Weeks		
Sample	Organic	[Ni] (mol dm^{-3})	Mean [Ni] (mol dm^{-3})	St Dev
1	None	7.82E-07		
2	None	7.88E-07		
3	None	8.39E-07		
4	None	8.14E-07		
5	None	8.03E-07	8.05E-07	2.27E-08
6	TPPB	7.86E-07		
7	TPPB	7.80E-07		
8	TPPB	9.25E-07		
9	TPPB	7.64E-07		
10	TPPB	8.08E-07	8.12E-07	6.49E-08
11	TPPO	8.46E-07		
12	TPPO	8.03E-07		
13	TPPO	8.38E-07		
14	TPPO	8.07E-07		
15	TPPO	7.41E-07	8.07E-07	4.14E-08

Table 6.11 continues on page 238

16	TPP	8.10E-07		
17	TPP	7.50E-07		
18	TPP	7.97E-07		
19	TPP	7.94E-07		
20	TPP	7.86E-07	7.88E-07	2.27E-08

Table 6.11: Solubility experiments on nickel in 3 mol dm^{-3} sodium nitrate

6.7.6.4 Technetium

From Table 6.12 it can be seen that there was no significant effect on the solubility of technetium(VII).

		2 Weeks		
Sample	Organic	[Tc] (mol dm^{-3})	Mean [Tc] (mol dm^{-3})	St Dev
1	None	6.42E-07		
2	None	6.86E-07		
3	None	5.26E-07		
4	None	6.19E-07		
5	None	6.58E-07	6.26E-07	6.11E-08
6	TPPB	2.16E-08		
7	TPPB	1.85E-08		
8	TPPB	2.19E-08		
9	TPPB	1.76E-08		
10	TPPB	2.13E-08	2.02E-08	1.95E-09
11	TPPO	6.29E-07		
12	TPPO	6.11E-07		
13	TPPO	6.20E-07		
14	TPPO	6.12E-07		
15	TPPO	5.56E-07	6.06E-07	2.86E-08
16	TPP	6.10E-07		
17	TPP	6.38E-07		
18	TPP	6.03E-07		
19	TPP	5.41E-07		
20	TPP	5.97E-07	5.98E-07	3.52E-08

Table 6.12: Solubility experiments on Tc in 3 mol dm^{-3} sodium nitrate

6.7.6.5 Uranium(VI)

Data from the solubility experiments on uranium(VI) after 2 weeks equilibration are shown below in Table 6.13. The results show that there was no significant effect on the solubility of uranium(VI).

		2 Weeks		
Sample	Organic	[U] (mol dm^{-3})	Mean [U] (mol dm^{-3})	St Dev
1	None	1.17E-05		
2	None	1.09E-05		
3	None	9.31E-06		
4	None	8.98E-06		
5	None	8.39E-06	9.86E-06	1.39E-06
6	TPPB	1.18E-05		
7	TPPB	1.01E-05		
8	TPPB	7.93E-06		
9	TPPB	9.02E-06		
10	TPPB	8.19E-06	9.41E-06	1.59E-06
11	TPPO	1.09E-05		
12	TPPO	9.64E-06		
13	TPPO	9.96E-06		
14	TPPO	8.44E-06		
15	TPPO	9.18E-06	9.62E-06	8.97E-07
16	TPP	1.14E-05		
17	TPP	1.16E-05		
18	TPP	1.07E-05		
19	TPP	7.87E-06		
20	TPP	8.83E-06	1.01E-05	1.65E-06

Table 6.13: Solubility experiments on U(VI) in 3 mol dm^{-3} sodium nitrate

6.7.6.6 Summary

	Solubility Enhancement Factors (SEF)				
	Eu	**I**	**Ni**	**Tc**	**U(VI)**
TPPB	1.1	1.0	1.0	0.0	1.0
TPPO	0.9	1.0	1.0	1.0	1.0
TPP	0.2	1.0	1.0	1.0	1.0

Table 6.14: Solubility enhancement factors for the effects of TPPB, TPPO and TPP on various radionuclides in the presence of 3 mol dm^{-3} $NaNO_3$

From Table 6.14 and the results in section 6.7.6 it can be seen that the solubility of radionuclides are not effected by the presence of TPPB or its degradation products in solutions containing 3 mol dm^{-3} $NaNO_3$.

6.7.7 Degradation mixtures

6.7.7.1 One week mixture

In the experiments on the degradation mixtures, the radionuclides were added to the mixtures after their stated degradation period, and then allowed to equilibrate for two weeks. During this time the TPPB will have continued to degrade. The results are shown in Table 6.15.

Sample	Metal	dpm	[M] (mol dm^{-3})	Mean (mol dm^{-3})	S.D.
1	^{99}Tc(VII)	344.9	5.08E-08		
2	^{99}Tc(VII)	376.4	5.55E-08		
3	^{99}Tc(VII)	404.3	5.96E-08		
4	^{99}Tc(VII)	481.4	7.10E-08		
5	^{99}Tc(VII)	340.6	5.02E-08	5.74E-08	8.47E-09
6	^{63}Ni	7.51	6.82E-07		
7	^{63}Ni	8.06	7.32E-07		
8	^{63}Ni	6.47	5.87E-07		
9	^{63}Ni	7.37	6.69E-07		
10	^{63}Ni	7.11	6.45E-07	6.63E-07	5.28E-08
11	^{125}I	8745	1.24E-03		
12	^{125}I	7418	1.05E-03		
13	^{125}I	7019	9.98E-04		
14	^{125}I	7050	1.00E-03		
15	^{125}I	6490	9.23E-04	1.04E-03	1.21E-04
16	^{152}Eu	< BG	<2.00E-07		
17	^{152}Eu	2.39	1.05E-06		
18	^{152}Eu	1.06	4.66E-07		
19	^{152}Eu	3.07	1.35E-06		
20	^{152}Eu	6.4	2.81E-06	1.42E-06	9.99E-07
21	^{233}U (VI)	1777	7.78E-05		
22	^{233}U (VI)	1724	7.55E-05		
23	^{233}U (VI)	1851	8.10E-05		
24	^{233}U (VI)	2073	9.08E-05		
25	^{233}U (VI)	1745	7.64E-05	8.03E-05	6.22E-06

Table 6.15: Data from solubility experiments on 1 week degradation mixture

6.7.7.2 Two weeks mixture

In these experiments the radionuclides had been equilibrated with the mixture for two weeks. The TPPB had been degraded for two weeks to produce the mixture. The results are shown in Table 6.16.

Sample	Radionuclide	dpm	[M] (mol dm^{-3})	Mean [M] (mol dm^{-3})	S.D.
1	^{99}Tc(VII)	894.9	1.32E-07		
2	^{99}Tc(VII)	644.4	9.50E-08		
3	^{99}Tc(VII)	728.5	1.07E-07		
4	^{99}Tc(VII)	746.5	1.10E-07		
5	^{99}Tc(VII)	772	1.14E-07	1.12E-07	1.34E-08
6	^{63}Ni	0.77	6.99E-08		
7	^{63}Ni	0.39	3.54E-08		
8	^{63}Ni	0.11	9.99E-09		
9	^{63}Ni	1.37	1.24E-07		
10	^{63}Ni	0.71	6.45E-08	6.08E-08	4.29E-08
11	^{125}I	23490	9.49E-04		
12	^{125}I	25211	1.02E-03		
13	^{125}I	23744	9.59E-04		
14	^{125}I	24844	1.00E-03		
15	^{125}I	24971	1.01E-03	9.88E-04	3.15E-05
16	^{152}Eu	< BG	<2.00E-07		
17	^{152}Eu	2.97	9.62E-07		
18	^{152}Eu	9.03	2.92E-06		
19	^{152}Eu	8.64	2.80E-06		
20	^{152}Eu	11.82	3.83E-06	2.63E-06	1.20E-06
21	^{233}U (VI)	1997	8.74E-05		
22	^{233}U (VI)	1861	8.15E-05		
23	^{233}U (VI)	1738	7.61E-05		
24	^{233}U (VI)	1673	7.32E-05		
25	^{233}U (VI)	1619	7.09E-05	7.78E-05	6.67E-06

Table 6.16: Data from solubility experiments on 2 weeks degradation mixture

6.7.7.3 Four weeks mixture

In these experiments the radionuclides had been equilibrated with the mixture for two weeks. The TPPB had been degraded for four weeks to produce the mixture. The results are shown in Table 6.17 below.

Sample	Radionuclide	dpm	[M] (mol dm^{-3})	Mean [M] (mol dm^{-3})	S.D.
1	^{99}Tc(VII)	811	1.20E-07		
2	^{99}Tc(VII)	907	1.34E-07		
3	^{99}Tc(VII)	780	1.15E-07		
4	^{99}Tc(VII)	819	1.21E-07		
5	^{99}Tc(VII)	862	1.27E-07	1.23E-07	7.28E-09
6	^{63}Ni	2.5	2.27E-07		
7	^{63}Ni	3.5	3.18E-07		

Table 6.17 continues on page 242

8	^{63}Ni	170.2	1.55E-05		
9	^{63}Ni	3.3	3.00E-07		
10	^{63}Ni	3	2.72E-07	2.79E-07	3.95E-08
11	^{125}I	22246	9.15E-04		
12	^{125}I	22188	9.13E-04		
13	^{125}I	21871	9.00E-04		
14	^{125}I	19394	7.98E-04		
15	^{125}I	20994	8.64E-04	8.78E-04	4.92E-05
16	^{152}Eu	4.5	1.10E-06		
17	^{152}Eu	11	2.68E-06		
18	^{152}Eu	29	7.08E-06		
19	^{152}Eu	17.7	4.32E-06		
20	^{152}Eu	17.5	4.27E-06	3.89E-06	2.22E-06
21	^{233}U (VI)	2161	9.46E-05		
22	^{233}U (VI)	2171	9.50E-05		
23	^{233}U (VI)	2036	8.91E-05		
24	^{233}U (VI)	2019	8.84E-05		
25	^{233}U (VI)	2191	9.59E-05	9.26E-05	3.56E-06

Table 6.17: Data from solubility experiments from 4 weeks degradation mixture

Table 6.18 below, shows the results from the Table 6.15 – 6.17 combined, as well as the results from the solubility experiments with TPPB and in the absence of any organics.

	1 Week Mix	2 Week Mix	4 Week Mix	No ligand	TPPB
Metal	**Mean [M] (mol dm^{-3})**	**Mean [M] (mol dm^{-3})**	**Mean [M] (mol dm^{-3})**	**Mean [M] (mol dm^{-3})**	**Mean [M] (mol dm^{-3})**
^{99}Tc	5.58E-08	1.13E-07	1.25E-07	1.72E-07	5.54E-08
^{63}Ni	6.41E-07	6.40E-08	2.67E-07	1.17E-06	2.02E-06
^{125}I	1.04E-03	9.88E-04	8.78E-04	8.48E-04	9.57E-04
^{152}Eu	1.42E-06	2.63E-06	3.88E-06	5.86E-07	5.97E-07
^{233}U	7.91E-05	7.34E-05	9.93E-05	2.99E-05	3.00E-05

Table 6.18: Data from solubility experiments on all mixtures

Using the data from Table 6.18 the solubility enhancement factors were calculated (Table 6.19)

	Solubility Enhancement Factors (SEF)		
Metal	1 Week Mix	2 Week Mix	4 Week Mix
^{99}Tc	0.3	0.7	0.7
^{63}Ni	0.6	0.1	0.2
^{125}I	1.2	1.2	1.0
^{152}Eu	2.4	4.5	6.6
^{233}U	2.7	2.5	3.3

Table 6.19: Solubility enhancement factors for radionuclides in degraded TPPB mixtures

From Table 6.18 and 6.19 it can be seen that for nickel and iodine, the mixtures made no difference to their solubility.

In the case of europium, there was a steady increase in solubility with length of degradation time. Fig. 6.38, below, shows the solubility of europium plotted against the concentration of a hypothetical product being formed from the degradation of TPPB at pH 13.3 and 293 K at a rate of one mole of product to one mole of degraded TPPB.

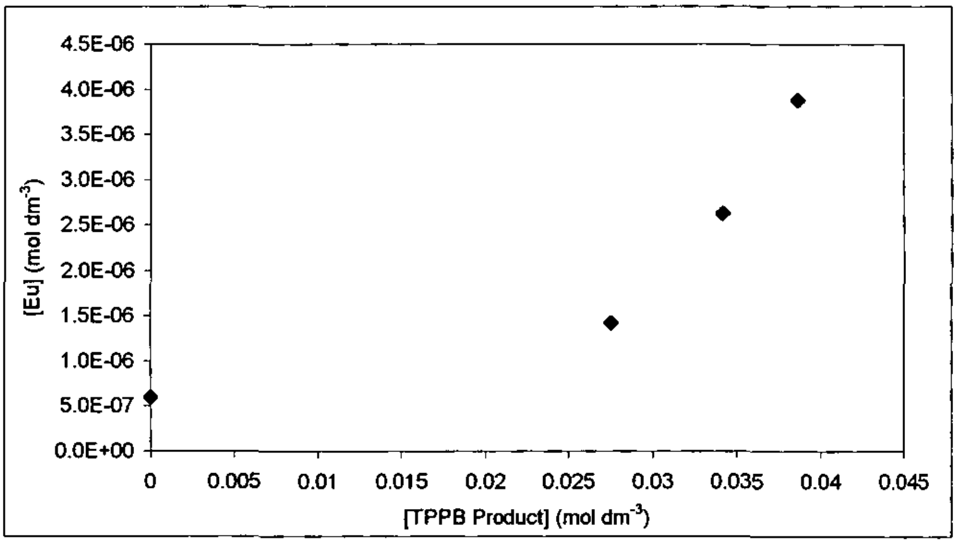


Fig. 6.38: Solubility of europium in mixtures

The europium solubilities measured in these experiments were higher than the solubility of europium in TPPB, TPPO or TPP. This suggests that the degradation in the absence of the metal may be producing a product that is enhancing the solubility of europium.

Technetium shows a gradual increase in solubility with greater degradation time where the concentration of technetium is plotted against the concentration of TPPB remaining in solution. This is to be expected as technetium is being released from the precipitated TcO_4TPP complex as the TPPB degrades.

Uranium(VI) shows a slightly higher solubility in the mixtures than with any of the organics alone, or in sodium hydroxide solution. It is difficult to suggest a reason for this result.

6.7.7.4 Degardation of TcTPPB in alkaline conditions

Table 6.20, shows the results for the release of technetium from TcO_4TPP in near neutral and alkaline conditions. The results show that at high pH technetium is released into solution (Table 6.20 and Fig. 6.39) this is the expected result as the TPPB will still degrade at high pH releasing TcO_4^- into solution.

		4 Weeks		8 Weeks		12 Weeks		16 Weeks	
	pH	DPM	[Tc]	DPM	[Tc]	DPM	[Tc]	DPM	[Tc]
1	7	187.3	2.46E-08	196.0	2.59E-08	180.2	2.35E-08	261.1	3.60E-08
2	7	240.1	3.27E-08	225.9	3.05E-08	204.6	2.72E-08	278.5	3.87E-08
3	7	253.4	3.48E-08	257.2	3.54E-08	217.0	2.92E-08	285.0	3.97E-08
4	7	233.9	3.18E-08	178.6	2.32E-08	220.8	2.97E-08	281.9	3.92E-08
5	7	267.8	3.70E-08	293.9	4.10E-08	244.6	3.34E-08	322.1	4.54E-08
6	13.3	272.4	3.77E-08	2355.3	3.60E-07	822.3	1.23E-07	2855.7	4.37E-07
7	13.3	357.3	5.08E-08	586.7	8.63E-08	931.0	1.40E-07	3443.2	5.28E-07
8	13.3	375.5	5.36E-08	776.2	1.16E-07	1184.6	1.79E-07	4496.1	6.91E-07
9	13.3	384.8	5.51E-08	614.4	9.06E-08	1043.8	1.57E-07	4258.1	6.54E-07
10	13.3	399.8	5.74E-08	643.3	9.50E-08	982.2	1.47E-07	2701.5	4.13E-07

Table 6.20: Concentration of technetium in solution (mol dm^{-3}) released from TcO_4TPP at different pH's

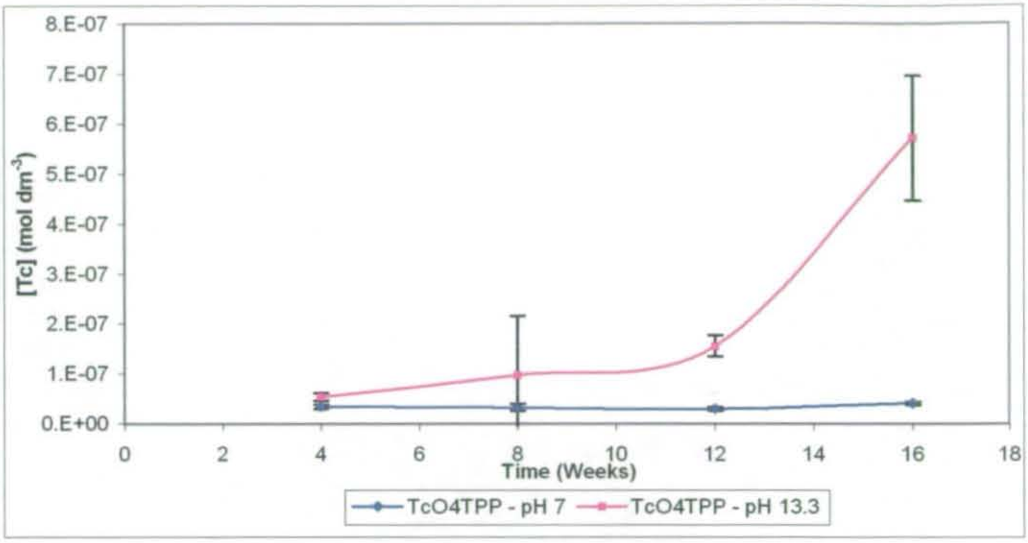


Fig. 6.39: Mean [Tc] in solution (mol dm^{-3}) against time (weeks) for the release of technetium from TcO_4TPP at different pH's

6.7.7.5 Degardation of TcTPPB in alkaline conditions in the presence of other ligands

Table 6.21 shows the mean technetium concentration in solution for the degradation of TcO_4TPP in the presence of organic complexing agents (Table 9.38 – 9.42).

		4 Weeks	8 Weeks	12 Weeks	16 Weeks
	pH	[Tc] (mol dm^{-3})	[Tc] (mol dm^{-3})	[Tc] (mol dm^{-3})	[Tc] (mol dm^{-3})
None	7	3.41E-08	3.25E-08	2.99E-08	4.07E-08
None	13.3	5.42E-08	9.69E-08	1.56E-07	5.71E-07
EDTA	13.3	5.47E-08	1.06E-07	1.21E-07	3.08E-07
NTA	13.3	5.75E-08	1.05E-07	1.24E-07	3.38E-07
ISA	13.3	6.87E-08	2.19E-07	1.99E-07	7.46E-07
Gluconic Acid	13.3	7.66E-08	2.02E-07	2.09E-07	6.65E-07
Picolinic Acid	13.3	6.69E-08	2.58E-07	1.58E-07	5.46E-07

Table 6.21: Mean technetium concentration in solution (mol dm^{-3}) for the different time intervals

6.7.7.5.1 EDTA

Table 6.21, Table 9.38 and Fig. 6.40 shows the effect EDTA on the degradation of TcO_4TPP at high pH.

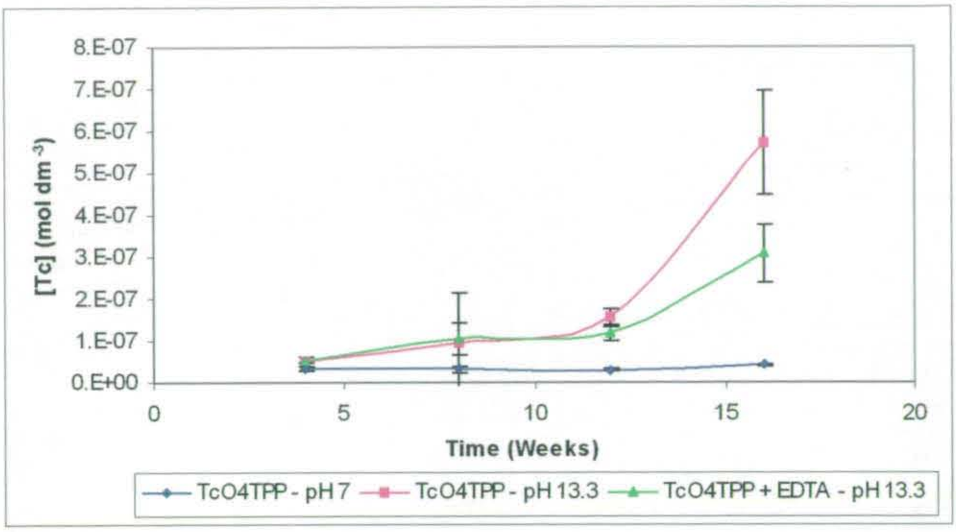


Fig. 6.40: Degradation of TcO_4TPP in the presence and absence of EDTA

From Fig. 6.40 it can be seen that the presence of EDTA is actually retarding the release of technetium as TcO_4TPP solid is degraded. This effect can be seen more clearly by normalising the graph (Fig. 6.41).

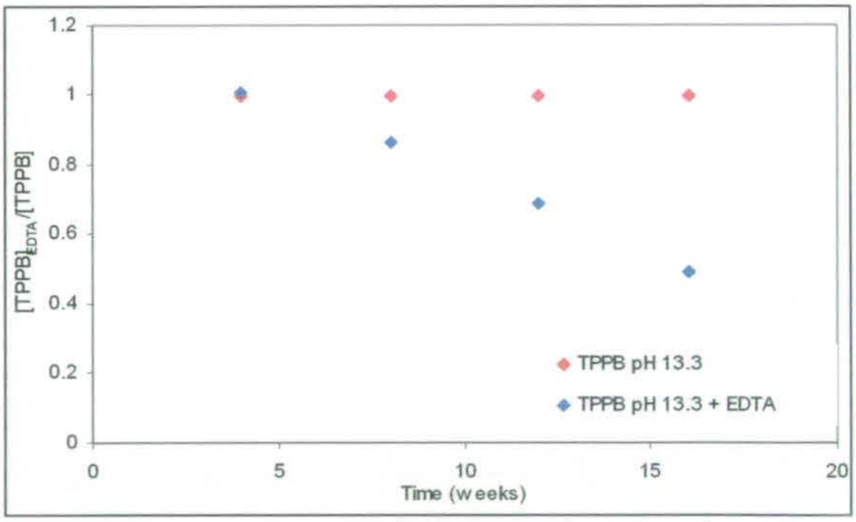


Fig. 6.41: Normalised plot of the degradation of TcO_4TPP in the presence and absence of EDTA

6.7.7.5.2 NTA

Table 6.21, Table 9.39 and Fig. 6.42 shows the effect NTA on the degradation of TcO_4TPP at high pH. From Fig. 6.41 it can be seen that the presence of NTA does not have any effect on the degradation of TcO_4TPP.

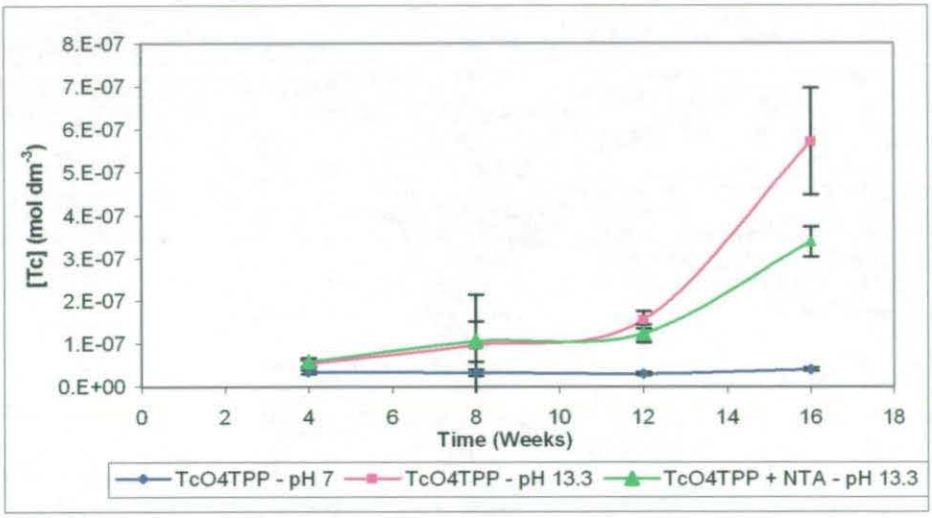


Fig. 6.42: Degradation of TcO_4TPP in the presence and absence of NTA

From Fig. 6.42 it can be seen that the presence of NTA is actually retarding the release of technetium as TcO_4TPP solid is degraded. This effect can be seen more clearly by normalising the graph (Fig. 6.43).

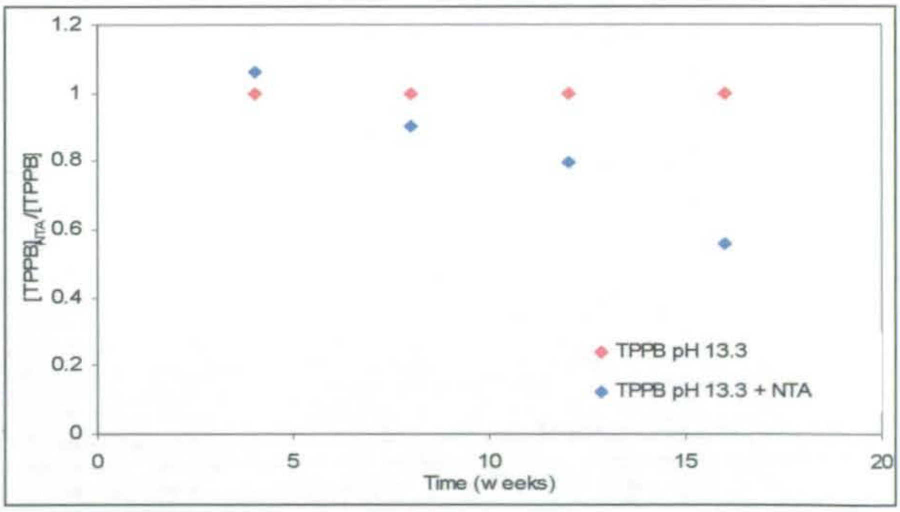


Fig. 6.43: Normalised plot of the degradation of TcO_4TPP in the presence and absence of NTA

6.7.7.5.3 ISA

Table 6.21, Table 9.40 and Fig. 6.44 shows the effect ISA on the degradation of TcO_4TPP at high pH. It can be seen that the presence of ISA has no effect on the degradation of TcO_4TPP.

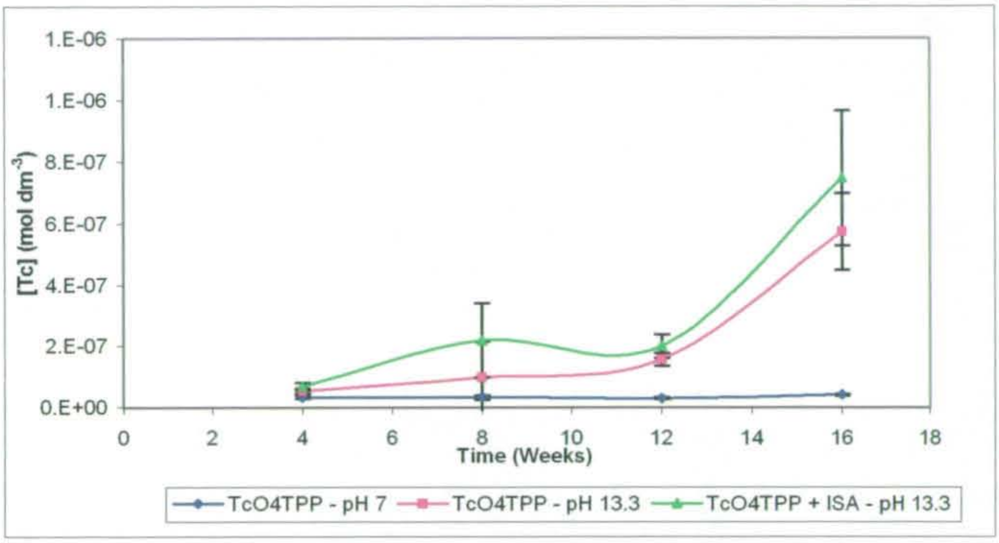


Fig. 6.44: Degradation of TcO_4TPP in the presence and absence of ISA

6.7.7.5.4 Gluconic acid

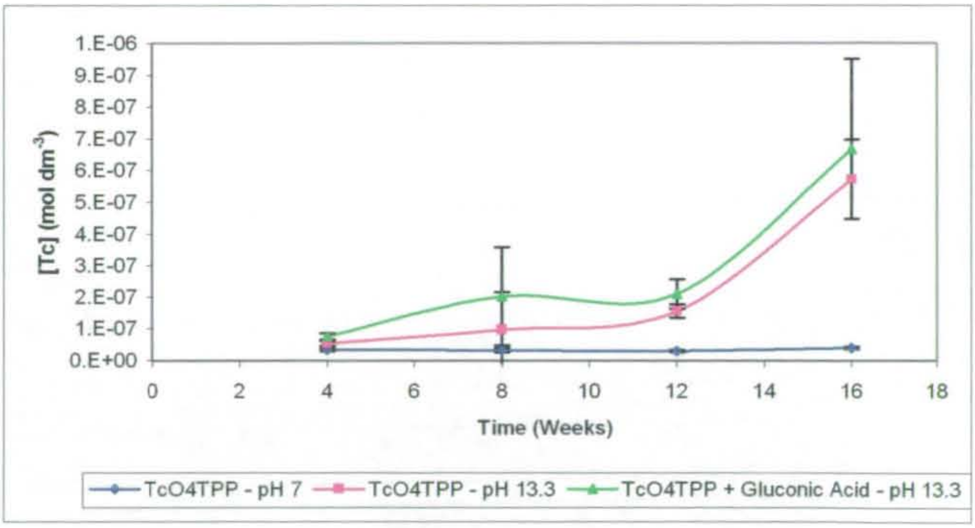


Fig. 6.45: Degradation of TcO_4TPP in the presence and absence of gluconic acid

Table 6.21, Table 9.40 and Fig. 6.45 shows the effect gluconic acid on the degradation of TcO_4TPP at high pH. It can be seen that the presence of gluconic acid has no effect on the degradation of TcO_4TPP.

6.7.7.5.5 Picolinic acid

Table 6.21, Table 9.40 and Fig. 6.46 shows the effect picolinic acid on the degradation of TcO_4TPP at high pH. It can be seen that the presence of picolinic acid has no effect on the degradation of TcO_4TPP.

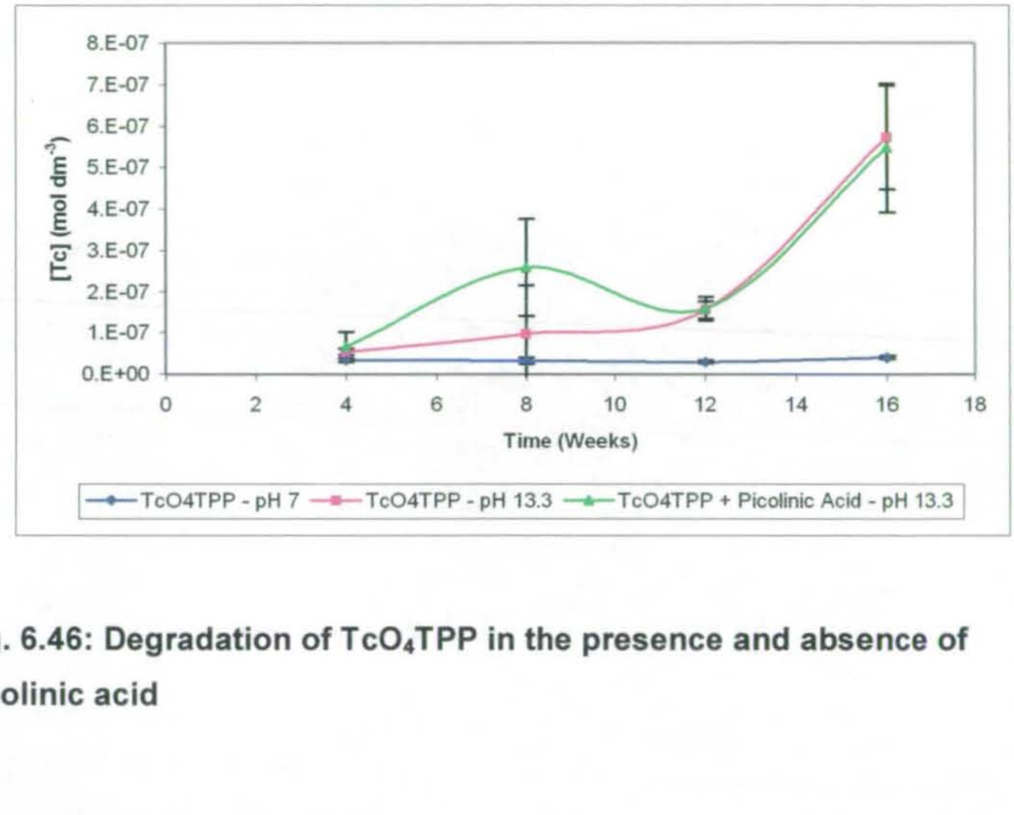


Fig. 6.46: Degradation of TcO_4TPP in the presence and absence of picolinic acid

6.8 Summary

The alkaline hydrolysis of TPPB was studied and it was shown that the only identifiable product formed was TPPO. The alkaline hydrolysis was shown to follow first order kinetics with respect to the concentration of TPPB however the reaction follows third order kinetics overall.

$$\text{Rate} = k[\text{TPPB}][\text{OH}]^2$$

From the kinetics data an Arrhenius expression was derived for the degradation of TPPB and the activation energy for the reaction estimated to be 105.20 ± 3.21 kJ mol^{-1}.

$$k = 2.03 \times 10^{13}\, e^{\left(\frac{-105.2\left(\text{kJ mol}^{-1}\right)}{RT}\right)}\ \text{dm}^{6}\text{mol}^{-2}\text{s}^{-1}$$

The stability of the TcO_4TPP solid was studied at near neutral and high pH. The results show that the solid is unstable at high pH, releasing technetium into solution over time. This increase was shown to be as a direct result of the degradation of TPPB only. However, the presence of EDTA and NTA slows the degradation of the TcO_4TPP and therefore retards the release of technetium into solution.

The presence of TPPB and it degradation products, TPP and TPPO, have no significant effect on the solubility of europium, iodine, nickel, technetium, and uranium and therefore this work was used to help in the acceptance of TPPB as a method for the removal of pertechnetate from technetium waste streams.

Chapter 7 –

Conclusions

7.0 Conclusions and further work

7.1 Section A – The Chemistry of technetium under reducing conditions

7.1.1 Reduction of pertechnetate

From Table 4.12 it can be seen that the best reducing agents, i.e. the reducing agents that reduce technetium to the solubility levels expected of technetium(IV) are Fe(II) and Sn(II). It was also found that at near neutral pH Fe(0) is an excellent reducing agent for technetium(VII), however, at high pH Fe(0) becomes passive and the kinetics of the reduction are severely hindered. Later in the project, electrochemical reduction was developed and this is summarised in Section 7.1.8.

7.1.2 Solubility of technetium(IV) at high pH

Fig. 4.10 shows that the solubility of technetium(IV) increases in alkaline conditions, specifically above pH 13. Erksen *et al* [39] observed a similar solubility increase at a lower pH (pH *ca.* 10.5). The explanation for this increase was due to the formation of an anionic technetium(IV) species, $TcO(OH)_3^-$. Although this study does not agree with the pH at which the solubility increase occurs the formation of $TcO(OH)_3^-$ is the most likely explanation. The formation constant was estimated with data from this study and was found to be log k_{sp}= -20.6. The log of the constant for the formation of $TcO(OH)_3^-$ was determined by Eriksen *et al* [39] to be -19.2.

7.1.3 Reduction of TcO_4^- in the presence of organic complexing agents at high pH

Under reducing conditions and in the absence of ligands, technetium(VII), in the form of TcO_4^-, is reduced to the insoluble $TcO_2(s)$. However, section 4.6

shows that the insoluble TcO_2(s) is not produced when the complexing ligands, EDTA, NTA, ISA, gluconic acid and picolinic acid, are present during the reduction of pertechnetate. The solubility enhancement factors are shown in Table 7.1.

	0.2 mol dm^{-3}	0.1 mol dm^{-3}	0.05 mol dm^{-3}	0.01 mol dm^{-3}
EDTA	925	92	10	1
NTA	270	46	5	1
ISA	947	397	13	1
Gluconic acid	965	358	70	1
Picolinic acid	387	332	273	97

Table 7.1: The solubility enhancement factors (SEF) for the reduction of pertechnetate in the presence of organic complexing agents

The results in this project show, through solubility studies, that complexation occurs during the reduction. For NTA, ISA, gluconic acid and picolinic acid it is thought that technetium(V) complexes are formed. However, it is thought that for EDTA technetium(IV) complexes are formed.

7.1.4 Solubility of TcO_2(s) in the presence of organic complexing agents at high pH

The solubility enhancement factors for the solubility of TcO_2(s) in the presence of organic complexing agents are shown in Table 7.2.

	0.2 mol dm^{-3}	0.1 mol dm^{-3}	0.05 mol dm^{-3}	0.01 mol dm^{-3}
EDTA	832	128	32	2
NTA	184	68	2	1
ISA	174	96	32	4
Gluconic acid	417	179	58	4
Picolinic acid	821	207	164	110

Table 7.2: The solubility enhancement factors (SEF) for the solubility of TcO_2(s) in the presence of organic complexing agents

Section 4.7 shows that when technetium(IV) is formed, by the reduction of TcO_4^- with Sn(II), and then contacted with the organic ligands, EDTA, NTA, ISA, gluconic acid and picolinic acid, a solubility increase of technetium occurs. As the reducing conditions are maintained during the experiments (i.e. the reducing agent is not removed from the samples) this increase in solubility is due to the formation of soluble technetium(IV) complexes.

7.1.5 Determination of conditional stability constants for technetium(IV) and the ligands under investigation

Table 4.30 shows that the log of the conditional stability constants calculated for technetium(IV) and the ligands of interest are all within the range 13.78 – 14.85 assuming that the stoichiometry is 1:1. The constants are all higher than those expected for simple salt formation which shows that complexation has taken place.

7.1.6 Competition between the technetium and the metallic reducing agent for the organic ligands under investigation

From section 4.9 and 4.10 it can be seen that Sn(II), when used as a reducing agent for TcO_4^-, complexes with the organic ligands, EDTA, NTA, ISA, gluconic acid and picolinic acid. However, due to the small starting concentration of technetium, *ca.* 4×10^{-7} mol dm^{-3}, the reducing agent is still massively in excess and a reduction still takes place.

By measuring the solubility increases due to complexation of Sn(II) with the individual ligands the stability constants for the Sn(II) – ligand complexes were determined. Using these data the actual free ligand concentration for complexation with technetium was calculated.

7.1.7 Revised technetium(IV)-ligand stability constants

Taking into account the complexation between the Sn(II) as a reducing agent and the ligands of interest the stability constants for technetium(IV)-ligand complexes were recalculated. Assuming a 1:1 stoichiometry for the technetium(IV)–ligand complexes the log of the stability constants are within the range 14.30 – 15.20.

7.1.8 Development of an electrochemical method for the reduction of ammonium pertechnetate at high pH

A method of reducing TcO_4^- to $TcO_2(s)$ without introducing secondary metal ions in solution has been developed. The electrochemical cell consists of a reticulated vitreous carbon electrode (cathode) and platinum wire electrode (anode). The reduction of technetium(VII) using this technique gives a solubility of technetium(IV) well within the limits of the literature solubility for $TcO_2(s)$ [38, 40].

7.1.9 Determination of conditional stability constants for technetium(IV) and the ligands under investigation (electrochemical reduction)

Table 4.70 shows that the conditional stability constants calculated for technetium(IV) and the ligands of interest are within the range 13.0 – 13.9 assuming that the stoichiometry is 1:1. The constants are higher than those expected for simple salt formation which shows that complexation has taken place.

7.1.10 Prediction of technetium(IV) – ligand stability constants using the computer program STAB [66] and linear free energy relationships

Using the computer program STAB, developed at Loughborough University [66], it was possible to predict the stability constants for the technetium(IV)-EDTA complex using a linear free energy relationship (LFER).

From Table 4.75 it can be seen that the calculated stability constant and the predicted stability constant for the technetium(IV) – EDTA complex, using the M-EDTA and M'-NTA LFER, is in good agreement. However, as the speciation of technetium(IV) differed between this project and the literature the derivation of technetium(IV) – EDTA complex stability constant was changed (Section 9.2.1) to fit the literature.

7.2 Section B - Degradation of TPPB at high pH and the solubility of various radionuclides in its degradation products

7.2.1 Solubility

TPPB, TPPO and TPP had no significant effect on the solubility of europium, except for the case of TPP after 8 weeks when there was a slight rise in the solubility. The presence of sodium nitrate had no significant effect.

TPPB, TPPO and TPP had no significant effect on the solubility of iodine in the absence of sodium nitrate. The presence of sodium nitrate seems to have caused a slight reduction of the iodide solubility with all ligands.

TPPB and TPPO had no significant effect on the solubility of nickel after 8 weeks, with or without sodium nitrate.

No significant changes in the solubility of technetium were seen with or without sodium nitrate. There is no evidence of TPP or TPPO reducing the solubility of pertechnetate in the same way that TPPB does.

There were no significant changes to the solubility of uranium(VI). TPPB and TPPO have also had no significant effect on the solubility of uranium(IV), but TPP caused a slight rise in uranium(IV) solubility.

The degradation mixture experiments showed a number of patterns. For nickel and iodine, the mixtures made no difference to their solubility. In the case of europium, there was a steady increase in solubility with the length of degradation time. The solubilities measured in these experiments were higher than when the solubility of europium was measured in TPPB, TPPO or TPP alone. This suggests that the degradation in the absence of the metal may be producing another product that is enhancing the solubility of europium. Technetium showed a gradual increase in solubility with greater degradation time. This is to be expected as technetium is being released from the precipitated TcTPPB complex as the TPPB degrades. Uranium(VI) showed a slightly higher solubility in the mixtures than with any of the organics alone, or without an organic present. It is difficult to suggest a reason for this result.

When there was competition between ligands, ISA, gluconic acid and picolinic acid raised the technetium concentration by roughly a factor of two, but neither EDTA nor NTA had any impact on the technetium solubility.

For the use of TPPB to be approved as a method of pertechnetate abatement it was important that it could be shown that TPPB and its degradation products would not have a significant detrimental impact on post-closure performance. This work has demonstrated that TPPB and its degradation products do not significantly effect the solubility of other important radioelements. This work therefore directly contributed to the acceptance of TPPB as a method for the removal of pertechnetate from technetium waste streams.

7.2.2 Degradation and kinetics

The only identifiable product formed by the alkaline degradation of TPPB was TPPO. The degradations performed at different temperatures and degrees of alkalinity showed that then literature expression for the kinetics of the reaction gave good predictions for the rate of degradation.

7.3 Future Work

The following is a list of items of possible future work.

7.3.1 Technetium Work

1. The solubility studies performed in this project were completed in deionised water, it would be useful to get a more realistic few and repeat the experiments in cement equilibrated waters.

2. Calculation of stability constants for more relevant organic ligands, e.g. large amounts of ion exchange material will degrade to basic amines under repository conidtions. The calculation of the stability contants between Tc(IV) and basic amines would be important.

3. In this project the stoichiometries of the complexes formed were assumed to 1:1, however, it is important to know the actual stoichiometry of the technetium complex as the stability constants would be different for an ML and ML_2 complex.

4. The possible exsistence of the anionic species of technetium(IV), $TcO(OH)_3^-$, has been shown in this project due to the solubility increase of technetium with increasing pH. Further investigation of the possible $TcO(OH)_3^-$ using techniques like electrophoresis or possibly electromigration would be useful.

5. One of the purposes of NRVB is to provide abundant surfaces for sorption, it would therefore be important to know if Tc(VII) and Tc(IV) sorb to NRVB and how the presence of ligands effects the sorption. It would also be useful to know if the complexes formed between technetium and ligands under reducing conditions sorbed to materials found in the repository

7.3.2 TPPB Work

1. TPPB degrades by 2 mechanisms; alkaline hydrolysis and radiolysis. This focussed on the alkaline hydrolysis of TPPB, it is therefore necessary to study the radiolysis including the kinetics of the degradation.

2. The solubility studies performed in this project were over a time period of 2 months, it would be useful to gather solubility data over a much longer time period.

3. In a nuclear waste repository the products from alkaline hydrolysis will be subjected to radiation from components of the waste. The effects of radiolysis on TPPO should therefore be studied to see if further degradation occurs. If this is the case then solubility studies also need to be performed on radionuclides.

4. The near-field of the nuclear waste repository will be a high pH reducing environment. The effects reducing conditions have upon the TcO_4TPP solid should therefore be studied.

5. The solubility studies performed in this project were completed in deionised water, it would be useful to get a more realistic few and repeat the experiments in cement equilibrated waters.

6. TPPB is at present only used for removal of TcO_4^-, however it is possible that other anions could be removed by precipitation. Therefore, the possible use of TPPB as a method for removing other oxyanions, antimony, arsenic etc, from solution should be investigated.

Chapter 8 –

References

8.0 References

1. Aldridge, S., Literature Review of the Chemistry of Technetium., Loughborough University, **2003**

2. Noddack, W. Tacke, I. Berg, O., Die Ekamangane., *Naturewissensch,* 13, 567, **1925**

3. Perrier, C. Segre, E., Some Chemical Properties of Element 43. *Journal of Chemical Physics*, 5, 712, **1937**

4. Perrier, C. Segre, E., Some Chemical Properties of Element 43 II. *Journal of Chemical Physics*, 7, 155, **1939**

5. Alperovitch, E. A. Miller, J. M., Occurence of technetium-98 in nature. *Nature*, 176, 299, **1955**

6. Boyd, G. E. Larson, Q. V., Report on the Occurence of Technetium on the Earths Crust., *Journal of Physical Chemistry*, 60, 707, **1956**

7. Colton, R., The Chemistry of Rhenium and Technetium, London, Interscience Publishers., 185, **1965**

8. Lieser, K. H., Technetium in the Nuclear-Fuel Cycle, in Medicine and in the Environment. *Radiochimica. Acta*, 63, 5, **1993**

9. CRC Handbook of Chemistry and Physics, D.R. Lide H.P.R. Frederikse, Editors, CRC Press. 60, **1994**

10. Cotton, F. A. Wilkinson, G. Murillo, C. A. Bochmann, M., Chapter 18: The Elements of the Second and Third Transition Series, in Advanced Inorganic Chemistry, Wiley-Interscience, New York. 877, **1999**

11. Greenwood, N. N. Earnshaw, A., Chapter 24: Manganese, Technetium and Rhenium, in *Chemistry of the Elements*, Butterworth-Heinemann, Oxford. 1040, **1997**

12. Lavrukhina, A. K. Pozdnyakov, A. A., Technetium, in *Analytical Chemistry of Technetium, Promethium, Astatine and Francium*, V.I. Spitsyn, Editor, Ann Arbor-Humphrey Science Publishers, London. 1 **1970**

13. Nock, B. A. Maina, T. Yannoukakos, D. Pirmettis, I. C. Papadopoulos, M. S. Chiotellis, E., Glutathione-Mediated Metabolism of technetium-ppm SNS/S mixed ligand complexes: A proposed mechnaism of brain retention. *Journal of Medicinal Chemistry*, 42, 1066, **1999**

14. Pervez, S. Mushtaq, A. Arif, M., Technetium-99m direct radiolabeling of Lanreotide: a Somatostatin analog. *Applied Radiation and Isotopes*, 55, 647, **2001**

15. Nosco, D. L. Beaty-Nosco, J. A., Chemistry of Technetium Radiopharmaceuticals 1: Chemistry behind the development of Technetium-99m compounds to determine kidney function. *Coordination Chemistry Review*, 184, 91, **1999**

16. Generic Repository Studies: Generic Disposal System Specification. Volume 1 – Specification, N/075, UK Nirex Limited **2003**

17. Proceedings of the Royal Society of Chemistry/UK-Nirex Symposium, The chemistry of deep disposal of radioactive waste.Loughborough University. 10th December 1997

18. The scientific foundations of deep geological disposal, N/016, UK Nirex Limited, **2003**

19. Glasser, F. P., Fundamental aspects of cement solidification and stabilisation. *Journal of Hazardous Materials.*, 52(2-3), 151, **1997**

20. Francis, A. J. Iden, C. R. Nine, B. J. Chang, C. K., Characterization of Organics in Leachates from Low-Level Radioactive Waste Disposal Sites. *Nuclear Technology*, 50, 158, **1980**

21. Choppin, G. R. Allard, B., Complexes of Actinides with Naturally Occuring Organic Compounds, in *Handbook on the Physics and Chemistry of the Actinides*, A.J. Freeman C. Keller, Editors, Elsevier Science Publishers. 409, **1985**

22. Vilks, P. Bachinski, D. B., Characterization of organics in Whiteshell research area groundwater and the implications for radionuclide transport. Applied Geochemistry, 11(3), 387, **1996**

23. Evans, N., Literature Survey of Near-Field Radionuclide Solubilities, Loughborough University, Loughborough, **2001**

24. Said, K. B. Seimbille, Y. Fattahi, M. Houee-Lévin, C. Abbé, J. C., Gamma radiation effects on potassium pertechnetate in carbonate media. *Applied Radiation and Isotopes.*, 54, 45, **2001**

25. Ilett, D. J. Pilkington, N. J. Tweed, C. J., Complexation of Radionuclides. in *The chemistry of deep disposal of radioactive waste*. Conference

Proceedings of the Royal Society of Chemistry/UK-Nirex Symposium, Loughborough University, **1997**

26. Greenfield, B. F. Hurdus, M. H. Pilkington, N. J. Spindler, M. W. Williams, S. J. The Degardation of Cellulose in the Near Field of a Radioactive Waste Repository. in *Materials Research Society Symposium*. **1994**

27. Krochta, J. M. Tillin, S. J. Hudson, J. S., Degradation of polysaccharides in alkaline solution to organic acids: Product characterization and identification. *Journal of Polymer Science*, 33, 1413, **1987**

28. Glaus, M. A. Loon, L. R. v. Achatz, S. Chodura, A. Fischer, K., Degradation of Cellulosic Materials Under the Alkaline Conditions of a Cementitious Repository for Low and Intermediate Level Radioactive Waste Part 1: Identification of Degradation Products. *Analytica Chimica Acta*, 398, 111, **1999**

29. UK Nirex 95: A Preliminary Asessment of the Groundwater Pathway for a Repository at Sellafield. UK Nirex Science Report S/95/12, **1995**

30. Pourbaix, M., Atlas of electrochemical equilibria in aqueous solutions, Oxford, Pergamon, **1966**

31. Gorski, B. Koch, H., Chemistry of Technetium in Aqueous Solution. I. State of tetravalent Technetium in Aqueous Solution, *Journal of Inorganic and Nuclear Chemistry*, 31, 3565, **1969**

32. Darab, J. G. Smith, P. A., Chemistry of technetium and rhenium species during low-level radioactive waste vitrification. *Chemistry and Materials*, 8(5), 1004, **1996**

33. Rulfs, C. L. Pacer, R. A. Hirsch, R. F., Technetium Chemistry: Oxidation States and Species, *Journal of Inorganic and Nuclear Chemistry*, 29, 681, **1967**

34. Owunwanne, A. Marinsky, J. Blau, M., Charge and Nature of Technetium Species Produced in Reduction of Pertechnetate by Stannous Ion, *Joumal of Nuclear Medicine.*, 18, 1099, **1977**

35. Rard, J. A., Critical Review Of The Chemistry And Thermodynamics Of Technetium And Some Of Its Inorganic Compounds And Aqueous Species, Lawrence Livermore National Laboratory, University of California, Livermore, California.**1983**

36. Vida, J., The Chemical Behavior of Technetium During the Treatment of High-Level Radioactive Waste. KFK 4642, Translated by J. R. Jewett, PNL-TR-497, Westinghouse Hanford Co., June, 1994.

37. Cui, D. Eriksen, T. E., Reduction of Pertechnetate by Ferrous Iron in Solution: Influence of Sorbed and Precipitated Fe(II). *Environmental Science and Technology*, 30(7), 2259, **1996**

38. Pilkington, N. J., The Solubility of Technetium in the Near-Field Environment of a Radioactive Waste Repository. *Joumal of the Less-Common Metals*, 161, 203, **1990**

39. Meyer, R. E. Arnold, W. D. Case, F. I. O'Kelly, G. D., Solubilities of Tc(IV) Oxides. *Radiochimica Acta*, 55, 11, **1991**

40. Eriksen, T. E. Ndalamba, P. Cui, D. Bruno, J. Caceci, M., Solubility of Redox-sensitive Radionuclides ^{99}Tc and ^{237}Np under reducing conditions in neutral to alkaline solutions: Effect of Carbonate, Royal Institute of Technology, Department of Nuclear Chemsitry, Stockholm. 1 **1993**

41. Baker, S. Baston, G. M. N. Manning, M. C. McCrohon, R. Williams, S. J., The Aqueous Solubility Behaviour of Selenium, Technetium and Tin, AEAT/R/ENV/0233, AEA Technology, Harwell, Didcot, **2000**

42. Greenfield, B. F. Ilett, D. J. Ito, M. McCrohon, R. Heath, T. G. Tweed, C. J. Williams, S. J. Yui, M., The effect of cement additives on radionuclide solubilities. *Radiochimica Acta*, 82, 27, **1998**

43. Maes, A. Dierckx, A. F. M. Vancluysen, J. The formation of mixed complexes between metals, humic acids and small oragnic and inorganic ligands in binding models concerning natural organic substances in performance assessment. in *Proceedings of NEA Workshop*. **1994**

44. Allen, P. G. Siemering, G. S. Shuh, D. K. Bucher, J. J. Edelstein, N. M. Langton, C. A. Clark, S. B. Reich, T. Denecke, M. A., Technetium Speciation in Cement Water Forms Determined by X-ray Absorption Fine Structure Spectroscopy. *Radiochimica Acta*, 76, 77, **1997**

45. Gilliam, T. M. Spence, R. D. Bostick, W. D. Shoemaker, J. L., Solidification Stabilization of Technetium in Cement-Based Grouts. *Journal of. Hazardous. Materials.*, 24(2-3), 189, **1990**

46. Lukens, W. W. Bucher, J. J. Edelstein, N. M. Shuh, D. K., Products of Pertechnetate Radiolysis in Highly Alkaline Solution: Structure of $TcO_2.xH_2O$. *Environmental Science and Technology*, 36, 1124, **2002**

47. Warwick, P. Evans, N. Hall, T. Vines, S., Stability constants of uranium(IV)-alpha-isosaccharinic acid and gluconic acid complexes. *Radiochimica Acta,* 92(12), 897, **2004**

48. Maes, A. Debrabandere, J. Cremers, A., A Modified Schubert Method for the Measurement of the Stability of Europium Humic-Acid Complexes in Alkaline Conditions. *Radiochimica Acta*,. 44-5, 51, **1988**

49. NIST Standard Reference Database 46 version 6.0: NIST Critically Selected Stability Constants of Metal Complexes,

50. Van der Lee, J., A Users Guide to CHESS, Another Speciation and Surface Complexation Code. École des Mines de Paris, Fontainebleau, France, **1998**

51. Whistler, R.L. and J.N. Bemiller, *[115]:* "alpha"- D- Isosaccharino-1, 4-lactone, in Methods in Carbohydrate Chemistry Vol. 2: Reactions of Carbohydrates, M.L. Wolfrom and J.N. Bemiller, Editors., Wiley: New York, 477, **1963**

52. Hughes, M. A. Rossotti, F. J. C., *A Review of Some Aspects of the Solution Chemistry of Technetium, AERE R-1280,* ***1987***

53. Kissel, G. Feldberg, S. W., Disproportionation of Technetate Ion in Aqueous Alkaline Media. An Electrochemical Study, *Journal of Physical Chemistry*, 73, 3082, **1969**

54. Pikaev, A. K. Krchkov, S. V. Kuzina, A. F. Spitsyn, V., Doklady Physical Chemistry, 236, 992, **1977**

55. Deutsch, E. Heineman, W. R. Hurst, R. Sullivan, J. C. Mulac, W. A. Gordon, S., Production, Detection, and Characterization of Transient Hexavalent Technetium in Aqueous Alkaline Media by Pulse-Radiolysis and Very Fast Scan Cyclic Voltammetry, *Journal of the Chemical Society - Chemical Communications*, 1038, **1978**

56. Heller-Grossman, L. Abrashkin, S. Shafferman, A. Davis, M. A. Taube, R. A., Tc-99m Generators. 2. Physicochemical Factors in the Radiolytic Reduction of Pertechnetate, *Applied Radiation and Isotopes,* 32(7), 501, **1981**

57. Libson, K. Sullivan, J. C. Mulac, W. A. Gordon, S. Deutsch, E., Pulse-Radiolysis Studies On Pertechnetate and Perrhenate in Aqueous-Media – Decay of the Technetium(VI) Transient, *Inorganic Chemistry*, 28(2), 375, **1989**

58. Krchkov, S. V. Pikaev, A. K. Kuzina, A. F. Spitsyn, V. I., *Proceedings of the Academy of Sciences of the USSR. Physical Chemistry Section*, 247, 690, **1979**

59. Bratu, C. Bratu, G. Galateanu, I. Roman, M., Study of Lower Valence States of technetium, Journal of Radioanalytical Chemistry, 26 (1), 5, **1975**

60. Hope, B. B., Corrosion of Metals in Concrete, ACI 222R-96., *American Concrete Institute*, **1996**

61. Berning, D. E. Schroeder, N. C. Chamberlin, R. M., The autoreduction of pertechnetate in aqueous, alkaline solutions, *Journal of Radioanalytical and Nuclear Chemistry*, 263(3), 613, **2005**

62. Gorski, B. Koch, H., Zur Chemie des Technetium in wabriger Losung - I. *Journal of Inorganic and Nuclear Chemistry*, **31**, 3565, 1969

63. Gorski, B. Koch, H., Uber Die Komplexbildung von Technetium mit chelatbildenen Liganden - II. *Journal of Inorganic and Nuclear Chemistry*, 32, 3831, **1970**

64. Geraedts, K. Bruggeman, C. Maes, A. Van Loon, L.R. Rossberg, A. Reich, T., Evidence for the existence of Tc(IV)-humic substance species by X-ray absorption near-edge spectroscopy. *Radiochimica Acta*, 90, 879, **2002**

65. Dimmock, P. D. Warwick, P. Robbins, R. A., Approaches to Predicting Stability Constants, *The Analyst*, 120, 2159, **1995.**

66. Warwick, P. Hall, A. King, S., Computer Software (STAB) for Estimating Metal Ligand Stability Constants, Loughborough University, **1999**

67. Debye, P. Hückel, E., Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen. *Physikalische Zeitschrift,* 24, 185, **1923**

68. Hückel, E., Zur Theorie konzentrieter wässriger Lösungen starker Elektrolyte. *Physikalische Zeitschrift,* 26, 93, **1925**

69. Guggenheim, E. A., The specific thermodynamic properties of aqueous solutions of strong electrolytes. *Philosophical Magazine*, 19, 588, **1935**

70. Davies, C., Ion Assocation., London, Butterworths, **1962**

71. Chandratillake, M. R. Robinson, V. J., Application and validadtion of predictive computer programs describing the chemistry of radionuclides in the geosphere. DoE/RW/90.009. Department of Energy, **1990**

72. Grenthe, I. Warner, H., Guidelines for the extrapolation to zero ionic strength. NEA-TDB, TDB-2.1, Nuclear Energy Agency, France. **1989**

73. Pitzer, K. S., Thermodynamics of electrolytes .1. Theoretical basis and general equations. Journal of Physical Chemistry, 77, 268, **1973**

74. Read, D., Nuclear Science and Technology - Chemval-2 project, Report on Stage 1: Status of Six Technical Areas., EUR 15161, WS Atkins Science and Technology: Epsom, UK, **1994**

75. Reed, J., Technetium to go, *Nuclear Engineering International,* 11th May, **2004**.

76. Gordan, J., Where courage is present..., *Nuclear Engineering International,* March **2004**

77. Explanatory document: To assist public consultation on propsals for the future regulation of technetium-99 discharges from British Nuclear Fuels plc Sellafield into the Irish sea, *Environment Agency,* **2000**

78. Mas, J. L. Tagami, K. Uchida, S., Method for the detection of Tc in seaweed samples coupling the use of Re as a chemical tracer and isotope dilution inductively coupled plasma mass spectrometry. *Analytica Chimica Acta*, 509(1), 83, **2004**

79. Webster, S. Salt, C. A. Howard, B. J., Sea-to-land transfer of technetium-99 through the use of contaminated seaweed as an agricultural soil conditioner. *Journal of Environmental Radioactivity*, 70(1-2), 127, **2003**

80. Brown, J. E. Kolstad, A. K. Brungot, A. L. Lind, B. Rudjord, A. L. Strand, P. FØyn, L., Levels of Tc-99 in seawater and biota samples from Norwegian coastal waters and adjacent seas. *Marine Pollution Bulletin*,. 38(7), 560, **1999**

81. Copplestone, D. Jackson, D. Hartnoll, R. G. Johnson, M. S. McDonald, P. Wood, N., Seasonal variations in activity concentrations of Tc-99 and Cs- 137 in the edible meat fraction of crabs and lobsters from the central Irish Sea, *Journal of Environmental Radioactivity*, 73(1), 29, **2004**

82. Olsen, Y.S. Batlle, J. V., A model for the bioaccumulation of Tc-99 in lobsters (Homarus gammarus) from the West Cumbrian coast. *Journal of Environmental Radioactivity*,. 67(3), 219, **2003**

83. Horii, H. Fujita, S. Mori, T. Taniguchi, S. Pulse radiolysis of aqueous solutions of tetraphenylphosphonium ions, *International Journal for Radiation Physics and Chemistry*, 8(4), 521, **1976**

84. Khalil, F.Y. Aksnes, G., Kinetics, Medium and Deuterium Isotope Effects in the Alkaline Decomposition of Quaternary Phosphonium Salts. I. Tetraphenylphosphonium Chloride in Dioxane-Water Mixtures. *Acta Chemica Scandinavica*,. 27, 3832, **1973**

85. Khalil, F.Y. Aksnes, G., Kinetics, Medium and Deuterium Isotope Effects in the Alkaline Decomposition of Quaternary Phosphonium Salts. II.

Tetraphenylphosphonium Chloride in Acetone-Water Mixtures. *Zeitschrift für Physikalische Chemie Neue Folge*, 97, 179, **1974**

86. Neck, V. Kim, J., Solubility and hydrolysis of tetravalent actinides., *Radiochimica Acta,* 89(1), 1, **2001**

87. Bandura, D. R. Baranov, V. I. Tanner, S. D., Detection of ultratrace phosphorus and sulfur by quadrupole ICPMS with dynamic reaction cell, *Analytical Chemistry*, 74(7), 1497, **2002**

88. http://www.aist.go.jp/RIODB/SDBS/menu-e.html, *SDBS - Integrated Spectral Data Base System for Organic Compounds,* National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan, Feburary **2003**
89. Miller, J.C. Miller, J.N., *Statistics and chemometrics for Analytical Chemistry*. 3rd ed., London: Ellis Horwood. **2000**

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Appendix

9.0 Appendix

9.1 Tables of data

9.1.1 Couting efficiency of ammonium pertechnetate

Technetium added (g)	cpm	cpm - Background
0.2021	56605.6	56593.2
0.2040	57650	57637.6
0.2062	58744.4	58732
0.4143	116200	116187.6
0.415	117244	117231.6
0.4164	116267	116254.6
0.6212	170617	170604.6
0.6242	172717	172704.6
0.6216	169633	169620.6
0.8256	226520	226507.6
0.8307	226680	226667.6
0.8308	231040	231027.6

Table 9.1: Data for the counting efficiency experiment

9.1.2 Solubility of reduced technetium against pH

	pH	dpm	[Tc] (mol dm^{-3})		pH	dpm	[Tc] (mol dm^{-3})
1	7	8.8	8.64E-10	**25**	11	8.1	7.80E-10
2	7	10.0	1.01E-09	**26**	11	21.8	2.81E-09
3	7	5.5	4.65E-10	**27**	11	9.8	9.85E-10
4	7	11.2	1.15E-09	**28**	11	9.7	9.73E-10
5	7	4.3	3.20E-10	**29**	11	31.3	4.20E-09
6	7	6.4	5.74E-10	**30**	11	13.1	1.38E-09
7	8	10.3	1.05E-09	**31**	12	90.2	1.28E-08
8	8	8.3	8.04E-10	**32**	12	91.8	1.31E-08
9	8	6.9	6.34E-10	**33**	12	137.7	1.98E-08
10	8	5.8	5.01E-10	**34**	12	89.0	1.26E-08
11	8	10.8	1.11E-09	**35**	12	125.1	1.79E-08
12	8	20.0	2.22E-09	**36**	12	129.7	1.86E-08
13	9	9.2	9.13E-10	**37**	13	42.7	5.87E-09
14	9	8.0	7.68E-10	**38**	13	87.3	1.24E-08
15	9	6.9	6.34E-10	**39**	13	70.2	9.89E-09
16	9	6.2	5.50E-10	**40**	13	65.1	9.15E-09
17	9	7.6	7.19E-10	**41**	13	57.4	8.02E-09
18	9	13.0	1.37E-09	**42**	13	57.3	8.00E-09
19	10	9.5	9.49E-10	**43**	14	359.0	5.22E-08
20	10	10.3	1.05E-09	**44**	14	148.3	2.13E-08
21	10	6.8	6.22E-10	**45**	14	179.2	2.59E-08
22	10	8.8	8.64E-10	**46**	14	172.1	2.48E-08
23	10	38.6	5.27E-09	**47**	14	211.8	3.06E-08
24	10	10.1	1.02E-09	**48**	14	226.6	3.28E-08

Table 9.2: Data for the solubility of Tc(IV) against pH experiment

9.1.2.1 Ion exchange method for the determination of Tc(IV) speciation

9.1.2.1.1 Cationic exchange resin

	pH	dpm	[Tc] (mol dm^{-3})
1	12.50	1.9	2.91E-11
2	12.94	1.5	-1.9E-11
3	12.91	1.5	-2.1E-11
4	13.48	68.6	9.66E-09
5	13.36	48.6	6.78E-09
6	13.48	29.9	4.1E-09
7	13.69	36.9	5.1E-09
8	13.79	296.8	4.24E-08
9	13.62	265.9	3.8E-08
10	13.93	1937.3	2.84E-07
11	13.92	1624.1	2.35E-07
12	13.96	1434.0	2.05E-07
13	13.74	1936.2	2.84E-07
14	13.97	1851.4	2.71E-07
15	13.91	2000.3	2.94E-07
16	13.72	2533.8	3.77E-07
17	13.78	2567.2	3.82E-07
18	13.91	2547.1	3.79E-07

Table 9.3: Data for the solubility of Tc(IV) (mol dm^{-3}) in the presence of an cationic exchange resin

9.1.2.1.2 Anionic exchange resin

	pH	dpm	[Tc] (mol dm^{-3})
1	12.91	2.4	8.84E-11
2	12.86	2.4	8.47E-11
3	12.65	2.9	1.46E-10
4	13.42	20.1	2.70E-09
5	13.54	21.2	2.86E-09
6	13.51	22.8	3.09E-09
7	13.79	343.5	4.91E-08
8	13.74	256.8	3.67E-08
9	13.80	176.1	2.51E-08
10	13.95	1121.2	1.56E-07
11	13.91	1367.6	1.95E-07
12	13.72	1031.6	1.42E-07
13	13.90	1948.2	2.86E-07
14	13.94	1890.8	2.77E-07
15	13.88	1830.1	2.67E-07
16	13.49	2605.9	3.88E-07
17	13.61	2493.5	3.71E-07
18	13.37	2574.6	3.84E-07

Table 9.4: Data for the solubility of Tc(IV) (mol dm^{-3}) in the presence of an anionic exchange resin

9.1.3 Measurement of any quenching effects upon the technetium from the ligands by the multichannels ratio method

9.1.3.1 No Ligand

Sample Number	dpmA	dpmB	Ratio (B/A)
1	2869.5	799.3	0.3
2	2932.5	845.8	0.3
3	2940.2	838.6	0.3
4	2949.0	849.4	0.3
5	2792.1	792.4	0.3
6	2969.1	798.5	0.3
7	3090.7	861.0	0.3
8	3074.1	832.9	0.3
9	2958.8	811.2	0.3
10	2995.2	802.9	0.3

Table 9.5: Data for the queching effect of ligands experiment – no ligand present

9.1.3.2 EDTA

Sample number	[EDTA] (mol dm^{-3})	dpmA	dpmB	ratio (B/A)
1	0.01	3186.6	902.3	0.3
2	0.01	2577.3	767.7	0.3
3	0.01	2616.1	771.7	0.3
4	0.05	2796.6	767.0	0.3
5	0.05	2632.0	794.2	0.3
6	0.05	2149.2	659.4	0.3
7	0.1	2824.3	759.1	0.3
8	0.1	2340.0	675.6	0.3
9	0.1	2153.1	641.6	0.3
10	0.2	2883.8	779.6	0.3
11	0.2	2454.3	692.2	0.3
12	0.2	2934.5	831.6	0.3
13	0.3	3108.6	767.0	0.3
14	0.3	2765.9	784.2	0.3
15	0.3	2211.8	604.0	0.3

Table 9.6: Data for the queching effect of ligands experiment – EDTA

9.1.3.3 NTA

Sample number	[NTA] (mol dm^{-3})	dpmA	dpmB	ratio (B/A)
1	0.01	3171.4	897.3	0.3
2	0.01	2369.4	735.1	0.3
3	0.01	2223.6	672.0	0.3
4	0.05	2826.0	805.6	0.3
5	0.05	2162.4	645.9	0.3
6	0.05	2128.2	652.8	0.3
7	0.1	2857.6	784.4	0.3
8	0.1	3125.9	802.5	0.3
9	0.1	2154.4	649.4	0.3
10	0.2	2956.3	806.4	0.3
11	0.2	2318.5	685.4	0.3
12	0.2	2567.0	749.3	0.3
13	0.3	2876.2	747.7	0.3
14	0.3	2460.5	740.9	0.3
15	0.3	2231.4	658.4	0.3

Table 9.7: Data for the queching effect of ligands experiment – NTA

9.1.3.4 ISA

Sample number	[NTA] (mol dm^{-3})	dpmA	dpmB	ratio (B/A)
1	0.01	2977.9	861.0	0.3
2	0.01	3199.1	952.0	0.3
3	0.01	2765.4	786.4	0.3
4	0.05	2674.9	897.5	0.3
5	0.05	3164.6	1167.7	0.4
6	0.05	3248.2	1104.0	0.3
7	0.1	2686.4	1059.4	0.4
8	0.1	2989.3	1291.5	0.4
9	0.1	2344.2	1001.7	0.4
10	0.2	2590.5	1416.2	0.6
11	0.2	2592.3	1752.3	0.7
12	0.2	2492.0	1473.1	0.6
13	0.3	2203.8	1354.4	0.6
14	0.3	1924.0	1528.0	0.8
15	0.3	1790.5	1396.3	0.8

Table 9.8: Data for the queching effect of ligands experiment – ISA

Ligand	[L] (mol dm-3)	dpmA	CE in channel A	Mean CE in channel A
ISA	0.01	2977.9	1.0	
ISA	0.01	3199.1	1.1	
ISA	0.01	2765.4	0.9	1.0
ISA	0.05	2674.9	0.9	
ISA	0.05	3164.6	1.1	
ISA	0.05	3248.2	1.1	1.0
ISA	0.1	2686.4	0.9	
ISA	0.1	2989.3	1.0	
ISA	0.1	2344.2	0.8	0.9
ISA	0.2	2590.5	0.9	
ISA	0.2	2592.3	0.9	
ISA	0.2	2492.0	0.8	0.9
ISA	0.3	1924.0	0.7	
ISA	0.3	1790.5	0.6	0.6

Table 9.9: Data for the queching effect of ligands experiment – Calculation of the counting efficiency in channel A

9.1.3.5 Gluconic Acid

Sample number	[Gluconic Acid] (mol dm^{-3})	dpmA	dpmB	ratio (B/A)
1	0.01	2977.9	861.0	0.3
2	0.01	3199.1	952.0	0.3
3	0.01	2765.4	786.4	0.3
4	0.05	2674.9	897.5	0.3
5	0.05	3164.6	1167.7	0.4
6	0.05	3248.2	1104.0	0.3
7	0.1	2686.4	1059.4	0.4
8	0.1	2989.3	1291.5	0.4
9	0.1	2344.2	1001.7	0.4
10	0.2	2590.5	1416.2	0.6
11	0.2	2592.3	1752.3	0.7
12	0.2	2492.0	1473.1	0.6
13	0.3	1924.0	1528.0	0.8
14	0.3	1790.5	1396.3	0.8
15	0.3	2977.9	861.0	0.3

Table 9.10: Data for the queching effect of ligands experiment – gluconic acid

9.1.3.6 Picolinic Acid

Sample number	[Picolinic Acid] (mol dm^{-3})	dpmA	dpmB	ratio (B/A)
1	0.01	3073.6	850.6	0.3
2	0.01	2585.9	785.3	0.3
3	0.01	2233.1	672.8	0.3
4	0.05	2929.5	812.2	0.3
5	0.05	2263.2	686.8	0.3
6	0.05	2298.0	681.6	0.3
7	0.1	2969.2	810.0	0.3
8	0.1	2857.1	843.6	0.3
9	0.1	2213.4	671.0	0.3
10	0.2	2927.1	817.2	0.3
11	0.2	2219.7	669.0	0.3
12	0.2	2289.1	669.6	0.3
13	0.3	2879.5	778.3	0.3
14	0.3	2572.3	763.9	0.3
15	0.3	2126.6	654.8	0.3

Table 9.11: Data for the queching effect of ligands experiment – picolinic acid

9.1.4 Reduction of TcO_4^- in the presence of ligands

9.1.4.1 EDTA

Sample	pH	[EDTA] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.33	0.2	2237.0	3.34E-07
2	13.33	0.2	2308.0	3.45E-07
3	13.42	0.2	2503.0	3.76E-07
4	13.40	0.2	2090.6	3.11E-07
5	13.25	0.2	2359.1	3.53E-07
6	13.56	0.1	274.1	3.93E-08
7	13.42	0.1	297.9	4.27E-08
8	13.63	0.1	197.4	2.82E-08
9	13.24	0.1	150.8	2.14E-08
10	13.25	0.1	277.2	3.97E-08
11	13.33	0.05	42.9	5.74E-09
12	13.36	0.05	15.4	1.74E-09
13	13.12	0.05	26.3	3.33E-09
14	13.25	0.05	42.5	5.68E-09
15	13.63	0.05	16.2	1.86E-09
16	13.63	0.01	3.2	1.88E-10
17	13.13	0.01	3.1	1.80E-10
18	13.32	0.01	3.8	2.55E-10
19	13.33	0.01	6.2	5.51E-10
20	13.25	0.01	7.6	7.18E-10

Table 9.12: Data for the reduction of TcO_4^- in the presence of ligands experiment – EDTA

9.1.4.2 NTA

Sample	pH	[NTA] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.62	0.2	663.6	9.58E-08
2	13.20	0.2	687.8	9.93E-08
3	13.36	0.2	733.7	1.06E-07
4	13.04	0.2	692.1	1.00E-07
5	13.30	0.2	692.3	1.00E-07
6	13.26	0.1	97.6	1.37E-08
7	13.39	0.1	75.3	1.04E-08
8	13.42	0.1	148.8	2.11E-08
9	13.62	0.1	168.6	2.40E-08
10	13.30	0.1	116.7	1.65E-08
11	13.05	0.05	19.1	2.17E-09
12	13.61	0.05	11.2	1.21E-09
13	13.06	0.05	5.8	5.56E-10
14	13.33	0.05	24.2	2.78E-09
15	13.42	0.05	27.0	3.12E-09
16	13.61	0.01	2.9	2.13E-10
17	13.06	0.01	2.6	1.76E-10
18	13.33	0.01	3.0	2.25E-10
19	13.32	0.01	2.4	1.47E-10
20	13.30	0.01	3.1	2.4E-10

Table 9.13: Data for the reduction of TcO_4^- in the presence of ligands experiment – NTA

9.1.4.3 ISA

Sample	pH	[ISA] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.33	0.2	2171.0	3.24E-07
2	13.51	0.2	2454.5	3.68E-07
3	13.13	0.2	2428.7	3.64E-07
4	13.33	0.1	1034.8	1.50E-07
5	13.52	0.1	1108.0	1.58E-07
6	13.14	0.1	1232.4	1.78E-07
7	13.62	0.1	906.7	1.27E-07
8	13.36	0.1	899.9	1.26E-07
9	13.24	0.05	34.2	4.47E-09
10	13.34	0.05	27.2	3.46E-09
11	13.30	0.05	30.9	4.00E-09
12	13.20	0.05	56.1	7.66E-09
13	13.62	0.01	13.9	1.48E-09
14	13.24	0.01	4.0	2.80E-10
15	13.36	0.01	3.3	1.93E-10
16	13.37	0.01	4.0	2.77E-10
17	13.26	0.01	4.0	2.88E-10

Table 9.14: Data for the reduction of TcO_4^- in the presence of ligands experiment – ISA

9.1.4.4 Gluconic Acid

Sample	pH	[Gluconate] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.23	0.2	2474.7	3.71E-07
2	13.25	0.2	2506.0	3.76E-07
3	13.31	0.2	2292.8	3.43E-07
4	13.39	0.2	2308.7	3.45E-07
5	13.51	0.1	1075.5	1.53E-07
6	13.15	0.1	829.4	1.15E-07
7	13.61	0.1	929.3	1.31E-07
8	13.35	0.05	127.2	1.80E-08
9	13.39	0.05	101.0	1.42E-08
10	13.47	0.05	247.1	3.54E-08
11	13.65	0.05	310.4	4.46E-08
12	13.28	0.05	127.6	1.80E-08
13	13.60	0.01	3.0	1.66E-10
14	13.21	0.01	4.8	3.80E-10
15	13.44	0.01	3.2	1.86E-10
16	13.31	0.01	6.2	5.55E-10
17	13.30	0.01	5.5	4.66E-10

Table 9.15: Data for the reduction of TcO_4^- in the presence of ligands experiment – gluconic acid

9.1.4.5 Picolinic Acid

Sample	pH	[Picolinate] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.62	0.2	1029.2	1.46E-07
2	13.28	0.2	984.4	1.39E-07
3	13.27	0.2	1077.0	1.54E-07
4	13.18	0.2	991.1	1.40E-07
5	13.31	0.2	988.5	1.40E-07
6	13.46	0.1	847.7	1.18E-07
7	13.61	0.1	917.8	1.29E-07
8	13.34	0.1	832.7	1.16E-07
9	13.42	0.1	926.1	1.30E-07
10	13.33	0.1	891.4	1.25E-07
11	13.68	0.05	789.0	1.09E-07
12	13.26	0.05	736.2	1.00E-07
13	13.27	0.05	690.5	9.97E-08
14	13.30	0.05	693.4	9.38E-08
15	13.36	0.05	728.6	1.05E-07
16	13.56	0.01	212.6	3.04E-08
17	13.20	0.01	189.3	2.70E-08
18	13.24	0.01	234.7	3.36E-08
19	13.39	0.01	314.8	4.52E-08
20	13.44	0.01	311.4	4.47E-08

Table 9.16: Data for the reduction of TcO_4^- in the presence of ligands experiment – picolinic acid

9.1.5 Solubility of TcO_2 in the presence of ligands

9.1.5.1 EDTA

Sample number	pH	[EDTA] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.42	0.2	2197.6	3.25E-07
2	13.33	0.2	2031.4	2.99E-07
3	13.31	0.2	2157.3	3.18E-07
4	13.32	0.2	2207.0	3.26E-07
5	13.23	0.2	1911.7	2.80E-07
6	13.46	0.1	328.9	4.70E-08
7	13.41	0.1	259.7	3.71E-08
8	13.32	0.1	291.6	4.16E-08
9	13.53	0.1	513.3	7.35E-08
10	13.36	0.1	270.2	3.86E-08
11	13.32	0.05	119.5	1.70E-08
12	13.21	0.05	52.6	7.36E-09
13	13.12	0.05	94.3	1.33E-08
14	13.40	0.05	91.3	1.29E-08
15	13.30	0.05	63.7	8.96E-09
16	13.20	0.01	10.8	1.10E-09
17	13.30	0.01	8.3	8.08E-10
18	13.32	0.01	7.8	7.39E-10
19	13.35	0.01	8.2	7.93E-10
20	13.33	0.01	8.2	7.89E-10

Table 9.17: Data for the solubility of TcO_2 in the presence of ligands experiment – EDTA

9.1.5.2 NTA

Sample number	pH	[NTA] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.43	0.2	436.0	6.34E-08
2	13.26	0.2	507.0	7.38E-08
3	13.33	0.2	476.0	6.93E-08
4	13.36	0.2	456.5	6.65E-08
5	13.36	0.2	474.9	6.91E-08
6	13.33	0.1	157.7	2.31E-08
7	13.03	0.1	158.6	2.28E-08
8	13.37	0.1	162.9	2.39E-08
9	13.34	0.1	210.8	3.05E-08
10	13.37	0.1	184.5	2.70E-08
11	13.36	0.05	6.2	8.99E-10
12	13.43	0.05	5.8	8.49E-10
13	13.24	0.05	7.2	1.02E-09
14	13.37	0.01	4.9	7.29E-10
15	13.37	0.01	5.1	7.61E-10
16	13.46	0.01	5.1	7.55E-10
17	13.30	0.01	4.9	7.35E-10
18	13.27	0.01	5.3	7.81E-10

Table 9.18: Data for the solubility of TcO_2 in the presence of ligands experiment – NTA

9.1.5.3 ISA

Sample number	pH	[ISA] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.37	0.2	477.3	6.95E-08
2	13.33	0.2	429.7	6.25E-08
3	13.46	0.2	435.6	6.34E-08
4	13.42	0.2	465.5	6.78E-08
5	13.37	0.2	412.1	5.99E-08
6	13.37	0.1	244.9	3.55E-08
7	13.27	0.1	232.0	3.36E-08
8	13.14	0.1	256.0	3.71E-08
9	13.53	0.1	262.9	3.81E-08
10	13.26	0.1	235.6	3.41E-08
11	13.69	0.05	96.8	1.38E-08
12	13.32	0.05	72.0	1.02E-08
13	13.33	0.05	85.0	1.21E-08
14	13.33	0.05	71.0	1.00E-08
15	13.13	0.05	92.5	1.32E-08
16	13.36	0.01	10.6	1.08E-09
17	13.63	0.01	15.8	1.71E-09
18	13.31	0.01	13.4	1.42E-09
19	13.37	0.01	11.0	1.14E-09
20	13.36	0.01	11.9	1.24E-09

Table 9.19: Data for the solubility of TcO_2 in the presence of ligands experiment – ISA

9.1.5.4 Gluconic acid

Sample number	pH	[Gluconic acid] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.26	0.2	1090.2	1.52E-07
2	13.37	0.2	1211.7	1.71E-07
3	13.36	0.2	1110.3	1.55E-07
4	13.30	0.2	1083.6	1.51E-07
5	13.36	0.2	1067.8	1.48E-07
6	13.26	0.1	420.0	6.11E-08
7	13.25	0.1	461.7	6.72E-08
8	13.33	0.1	434.9	6.33E-08
9	13.55	0.1	493.8	7.19E-08
10	13.37	0.1	473.4	6.89E-08
11	13.33	0.05	106.2	1.52E-08
12	13.35	0.05	135.7	1.95E-08
13	13.36	0.05	130.3	1.87E-08
14	13.26	0.05	191.9	2.77E-08
15	13.62	0.05	190.3	2.75E-08
16	13.27	0.01	19.5	2.16E-09
17	13.64	0.01	19.4	2.15E-09
18	13.69	0.01	10.4	1.06E-09
19	13.03	0.01	11.1	1.14E-09
20	13.10	0.01	12.4	1.30E-09

Table 9.20: Data for the solubility of TcO_2 in the presence of ligands experiment – gluconic acid

9.1.5.5 Picolionic acid

Sample number	pH	[Picolinic Acid] (mol dm^{-3})	dpm	[Tc] (mol dm^{-3})
1	13.32	0.2	2044.4	2.99E-07
2	13.43	0.2	2211.6	3.23E-07
3	13.40	0.2	2015.0	2.95E-07
4	13.04	0.2	2057.7	3.01E-07
5	13.35	0.2	2112.4	3.09E-07
6	13.40	0.1	524.8	7.65E-08
7	13.33	0.1	525.0	7.65E-08
8	13.10	0.1	523.6	7.63E-08
9	13.24	0.1	530.8	7.73E-08
10	13.32	0.1	539.0	7.85E-08
11	13.30	0.05	430.5	6.26E-08
12	13.25	0.05	405.1	5.89E-08
13	13.13	0.05	403.0	5.86E-08
14	13.37	0.05	424.0	6.17E-08
15	13.33	0.05	434.3	6.32E-08
16	13.30	0.01	260.5	3.78E-08
17	13.14	0.01	292.7	4.25E-08
18	13.30	0.01	287.9	4.18E-08
19	13.28	0.01	298.0	4.32E-08
20	13.36	0.01	276.4	4.01E-08

Table 9.21: Data for the solubility of TcO_2 in the presence of ligands experiment – picolinic acid

9.1.6 Prediction of stability constants

	EDTA		CDTA		NTA	
Metal	**I. S.**	**Log K**	**I. S.**	**Log K**	**I. S.**	**Log K**
Li [+]	0.1	3.0	0.5	6.1	0.1	2.5
Na [+]	0.1	1.9	0.1	3.8	0.1	1.2
Eu [3+]	0.1	17.3	0.1	19.4	0.1	11.3
Am [3+]	0.1	16.9	0.1	19.4	0.1	11.5
U [4+]	0.1	25.7	0.1	27.6	[redacted]	[redacted]
Np [4+]	1.0	24.6	[redacted]	[redacted]	1.0	17.3
Mn [2+]	0.1	13.9	0.1	17.5	0.1	7.3
Fe [2+]	0.1	14.3	0.1	18.9	0.1	8.9
Co [2+]	0.1	16.5	0.1	19.7	0.1	10.4
Ni [2+]	0.1	18.4	0.1	20.2	0.1	11.5
Sn [2+]	1.0	18.3	1.0	18.7	[redacted]	[redacted]
Pb [2+]	0.1	18.0	0.1	20.2	0.1	11.5
Al [3+]	0.1	16.4	0.1	19.5	0.1	11.4
Cr [2+]	0.1	13.6	[redacted]	[redacted]	1.0	6.5
Mg [2+]	0.1	8.8	0.1	11.0	0.1	5.5
TcO [2+]	[redacted]	[redacted]	0.1	20.7	0.1	13.8

Table 9.22: Stability constants entered into STAB database for Tc(IV) - EDTA stability constants predictions [53]

9.1.7 Kinetics of the degradation of TPPB

9.1.7.1 Variation of room temperature

Time (Secs)	Temp (°C)	Temp (K)
0	19	292
269400	20	293
359400	20	293
445500	20	293
532800	21	294
518100	23	296
964500	23	296
1051200	23	296
1138200	22	295
1222500	20	293
1541100	22	295
1628700	22	295
1712400	21	294
1800900	19	292
2064900	22	295
2167500	23	296
2325900	22	295
2413200	21	294
2664900	21	294
Mean Temp (K) =		294.26 ± 1.33

Table 9.23: Data for the variation of room tempertuare experiment

9.1.7.2 TPPB degradation at 298 K and pH 14

Time	[TPPB] Expt	[TPPB] Pred'n (298K)	[TPPB] Pred'n (293K)
(s)	(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})
		$K_1 = 3.348 \times 10^{-6}$	$K_1 = 8.792 \times 10^{-6}$
0	1.02E-02	1.02E-02	1.02E-02
3600	8.69E-03	1.01E-02	9.89E-03
7200	9.52E-03	9.97E-03	9.58E-03
10800	1.02E-02	9.85E-03	9.28E-03
14400	8.53E-03	9.73E-03	8.99E-03
18000	8.08E-03	9.61E-03	8.71E-03
84600	5.10E-03	7.69E-03	4.85E-03
92700	6.70E-03	7.48E-03	4.52E-03
98100	6.32E-03	7.35E-03	4.31E-03
109800	5.94E-03	7.07E-03	3.89E-03
172800	3.66E-03	5.72E-03	2.23E-03
255600	2.97E-03	4.34E-03	1.08E-03

Table 9.24: Data for the degradation of TPPB at 298 K and pH 14

9.1.7.3 TPPB degradation at 313 K and pH 14

Time	[TPPB] Expt	[TPPB] Pred'n (313K)
(s)	(mol dm^{-3})	(mol dm^{-3})
		$K_1 = 1.323 \times 10^{-4}$
0	1.00E-02	1.00E-02
10	8.00E-03	9.99E-03
2100	8.38E-04	7.57E-03
3900	6.83E-04	5.97E-03
5520	5.31E-04	4.82E-03
7200	2.46E-04	3.86E-03
8580	6.30E-04	3.21E-03
12180	4.83E-04	2.00E-03
15780	7.24E-04	1.24E-03
17115	7.09E-04	1.04E-03
17370	6.98E-04	1.00E-03
17445	6.79E-04	9.94E-04

Table 9.25: Data for the degradation of TPPB at 313 K and pH 14

9.1.7.4 TPPB degradation at 333 K and pH 14

Time	[TPPB] Expt	[TPPB] Pred'n (333K)
(s)	(mol dm^{-3})	(mol dm^{-3})
		$K_1 = 3.362 \times 10^{-3}$
0	1.00E-02	1.00E-02
300	1.04E-02	3.65E-03
420	1.04E-02	2.44E-03
480	1.02E-02	1.99E-03
540	1.04E-02	1.63E-03
600	1.00E-02	1.33E-03
900	1.33E-03	4.85E-04
1200	9.52E-04	1.77E-04
1500	1.03E-03	6.46E-05
1800	8.76E-04	2.35E-05
2100	1.67E-03	8.59E-06
2820	1.74E-03	7.63E-07
3000	1.45E-03	4.17E-07
3300	1.47E-03	1.52E-07
3600	1.36E-03	5.54E-08
5460	9.22E-04	1.07E-10
7200	1.05E-03	3.07E-13
9000	3.73E-04	7.24E-16

Table 9.26: Data for the degradation of TPPB at 333 K and pH 14

9.1.7.5 TPPB degradation at 298 K and pH 13.3

Time	[TPPB] Expt	[TPPB] Pred'n (298 K)	[TPPB] Pred'n (293 K)
(s)	(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})
		$K_1 = 8.792 \times 10^{-6}$	$K_1 = 3.348 \times 10^{-6}$
0	9.84E-03	9.84E-03	9.84E-03
86400	9.28E-03	9.19E-03	9.59E-03
102000	9.25E-03	9.08E-03	9.55E-03
110100	9.74E-03	9.02E-03	9.52E-03
178500	8.88E-03	8.55E-03	9.33E-03
261900	8.75E-03	8.00E-03	9.10E-03
348300	8.75E-03	7.47E-03	8.86E-03

Table 9.27: Data for the degradation of TPPB at 298 K and pH 13.3

9.1.7.6 TPPB degradation at 313 K and pH 13.3

Time (s)	[TPPB] Expt (mol dm^{-3})	[TPPB] Pred'n (313 K) (mol dm^{-3})
		$K_1 = 1.323 \times 10^{-4}$
0	9.05E-03	9.05E-03
4020	9.05E-03	8.63E-03
7020	8.55E-03	8.32E-03
10680	9.35E-03	7.97E-03
14100	8.92E-03	7.65E-03
17940	8.78E-03	7.31E-03
83700	5.67E-03	3.34E-03
88020	4.88E-03	3.17E-03
99420	3.45E-03	2.77E-03
171420	3.02E-03	1.18E-03
181740	2.06E-03	1.04E-03
191700	2.06E-03	9.23E-04

Table 9.28: Data for the degradation of TPPB at 313 K and pH 13.3

9.1.7.7 TPPB degradation at 333 K and pH 13.3

Time (s)	[TPPB] Expt (mol dm^{-3})	[TPPB] Pred'n (333 K) (mol dm^{-3})
		$K_1 = 3.362 \times 10^{-3}$
0	1.67E-02	1.67E-02
300	1.67E-02	1.53E-02
600	1.04E-02	1.39E-02
900	9.45E-03	1.27E-02
1200	9.11E-03	1.16E-02
1800	8.72E-03	9.69E-03
2400	8.65E-03	8.08E-03
3000	7.82E-03	6.74E-03
3600	7.62E-03	5.62E-03
7260	5.37E-04	1.86E-03
7351	4.04E-04	1.81E-03

Table 9.29: Data for the degradation of TPPB at 333 K and pH 13.3

9.1.7.8 TPPB degradation at 298 K and pH 13

Time	[TPPB] Expt	[TPPB] Pred'n (298 K)	[TPPB] Pred'n (293 K)
(s)	(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})
		$K_1 = 8.792 \times 10^{-6}$	$K_1 = 3.348 \times 10^{-6}$
0	1.17E-02	1.17E-02	1.17E-02
86400	1.17E-02	1.16E-02	1.16E-02
102000		1.16E-02	1.16E-02
178500		1.15E-02	1.16E-02
261900		1.14E-02	1.16E-02
348300		1.13E-02	1.15E-02
434700	1.14E-02	1.12E-02	1.15E-02

Table 9.30: Data for the degradation of TPPB at 298 K and pH 13

9.1.7.9 TPPB degradation at 313 K and pH 13

Time	[TPPB] Expt	[TPPB] Pred'n (313 K)
(s)	(mol dm^{-3})	(mol dm^{-3})
		$K_1 = 1.323 \times 10^{-4}$
0	1.33E-02	1.33E-02
5700	1.26E-02	1.32E-02
19200	1.17E-02	1.30E-02
81720	1.16E-02	1.20E-02
93300	1.18E-02	1.18E-02
104760	1.10E-02	1.16E-02
180180	1.08E-02	1.05E-02
189660	1.12E-02	1.04E-02
255752	9.94E-03	9.49E-03
279452	9.27E-03	9.20E-03
343772	9.56E-03	8.45E-03

Table 9.31: Data for the degradation of TPPB at 313 K and pH 13

9.1.7.10 TPPB degradation at 333 K and pH 13

Time	[TPPB] Expt	[TPPB] Pred'n (333 K)
	(mol dm^{-3})	(mol dm^{-3})
		K_1 = 3.36E-03
0	1.05E-02	1.00E-02
7200	1.05E-02	7.85E-03
14400	8.76E-03	6.16E-03
22500	8.73E-03	4.69E-03
87012	5.14E-03	5.37E-04
94500	4.72E-03	4.17E-04
101412	5.06E-03	3.31E-04
111600	4.50E-03	2.35E-04
173700	2.81E-03	2.91E-05

Table 9.32: Data for the degradation of TPPB at 333 K and pH 13

9.1.8 Solubility studies of various radionuclides in presence of TPPB and its degradation products

9.1.8.1 Europium

		2 Weeks			4 Weeks			8 Weeks		
Sample	Organic	[Eu] (mol dm^{-3})	Mean [Eu] (mol dm^{-3})	St Dev	[Eu] (mol dm^{-3})	Mean [Eu] (mol dm^{-3})	St Dev	[Eu] (mol dm^{-3})	Mean [Eu] (mol dm^{-3})	St Dev
1	None	1.20E-06			9.64E-07			4.45E-07		
2	None	4.94E-06			1.65E-05			<2.00E-07		
3	None	1.78E-08			2.36E-06			3.74E-07		
4	None	3.63E-07			4.85E-07			<2.00E-07		
5	None	4.16E-07	4.98E-07	4.97E-07	<2.00E-07	1.27E-06	9.75E-07	9.42E-07	5.87E-07	3.09E-07
6	TPPB	6.70E-07			6.72E-07			1.08E-06		
7	TPPB	8.77E-07			1.74E-08			5.21E-07		
8	TPPB	1.59E-06			1.69E-06			6.24E-07		
9	TPPB	1.89E-06			1.19E-06			2.63E-07		
10	TPPB	4.23E-07	1.09E-06	6.24E-07	6.57E-07	8.46E-07	6.31E-07	5.03E-07	5.98E-07	2.99E-07
11	TPPO	1.33E-06			<2.00E-07			1.87E-06		
12	TPPO	<2.00E-07			1.10E-06			4.48E-07		
13	TPPO	<2.00E-07			6.93E-07			1.06E-06		
14	TPPO	<2.00E-07			1.91E-06			7.73E-07		
15	TPPO	1.13E-06	1.23E-06	1.42E-07	6.75E-08	9.44E-07	7.73E-07	9.39E-07	1.02E-06	5.28E-07
16	TPP	1.74E-06			4.19E-07			1.84E-06		
17	TPP	9.25E-07			<2.00E-07			1.07E-06		
18	TPP	<2.00E-07			6.87E-07			1.49E-06		
19	TPP	2.89E-07			<2.00E-07			1.36E-06		
20	TPP	<2.00E-07	9.86E-07	7.29E-07	1.71E-07	4.26E-07	2.58E-07	<2.00E-07	1.44E-06	3.20E-07

Table 9.33: Data for the solubility study of europium in solutions TPPB and its degradation prodcts at pH 13.3

9.1.8.2 Iodine

		2 Weeks			4 Weeks			8 Weeks		
Sample	Organic	[I] (mol dm^{-3})	Mean [I] (mol dm^{-3})	St Dev	[I] (mol dm^{-3})	Mean [I] (mol dm^{-3})	St Dev	[I] (mol dm^{-3})	Mean [I] (mol dm^{-3})	St Dev
1	None	8.41E-04			9.36E-04			9.52E-04		
2	None	9.67E-04			9.51E-04			9.30E-04		
3	None	1.01E-03			9.46E-04			8.76E-04		
4	None	9.50E-04			8.95E-04			9.48E-04		
5	None	1.03E-03	9.60E-04	7.38E-05	8.16E-04	9.09E-04	5.64E-05	7.87E-04	8.98E-04	6.94E-05
6	TPPB	1.06E-03			9.53E-04			8.99E-04		
7	TPPB	7.94E-04			8.77E-04			9.11E-04		
8	TPPB	7.55E-04			8.82E-04			9.15E-04		
9	TPPB	9.58E-04			7.43E-04			7.53E-04		
10	TPPB	9.90E-04	9.12E-04	1.32E-04	9.35E-04	8.78E-04	8.22E-05	9.48E-04	8.85E-04	7.60E-05
11	TPPO	1.06E-03			9.85E-04			9.52E-04		
12	TPPO	1.05E-03			7.95E-04			8.01E-04		
13	TPPO	8.77E-04			1.25E-03			1.24E-03		
14	TPPO	9.32E-04			9.16E-04			9.48E-04		
15	TPPO	1.02E-03	9.87E-04	7.87E-05	7.03E-04	9.29E-04	2.08E-04	8.48E-04	9.59E-04	1.72E-04
16	TPP	9.92E-04			9.35E-04			8.81E-04		
17	TPP	9.28E-04			9.74E-04			1.01E-03		
18	TPP	9.89E-04			9.83E-04			9.44E-04		
19	TPP	1.03E-03			9.22E-04			9.33E-04		
20	TPP	9.52E-04	9.78E-04	3.93E-05	9.58E-04	9.55E-04	2.57E-05	9.12E-04	9.37E-04	4.92E-05

Table 9.34: Data for the solubility study of iodine in solutions TPPB and its degradation prodcts at pH 13.3

9.1.8.3 Nickel

		2 Weeks			4 Weeks			8 Weeks		
Sample	Organic	[Ni] (mol dm^{-3})	Mean [Ni] (mol dm^{-3})	St Dev	[Ni] (mol dm^{-3})	Mean [Ni] (mol dm^{-3})	St Dev	[Ni] (mol dm^{-3})	Mean [Ni] (mol dm^{-3})	St Dev
1	None	3.10E-07			1.03E-06			1.08E-06		
2	None	5.48E-07			9.18E-07			9.92E-07		
3	None	6.70E-07			1.80E-06			6.56E-06		
4	None	9.87E-07			2.11E-06			4.11E-07		
5	None	5.32E-07	6.09E-07	2.48E-07	2.08E-06	1.59E-06	5.76E-07	2.21E-06	2.25E-06	2.49E-06
6	TPPB	2.96E-06			1.72E-06			1.71E-06		
7	TPPB	2.12E-06			2.33E-06			3.81E-06		
8	TPPB	1.42E-06			1.85E-06			2.27E-06		
9	TPPB	5.76E-07			1.07E-06			2.06E-06		
10	TPPB	1.08E-06	1.63E-06	9.30E-07	1.96E-06	1.79E-06	4.58E-07	2.04E-06	2.38E-06	8.25E-07
11	TPPO	2.78E-07			4.01E-07			6.56E-07		
12	TPPO	8.52E-07			4.00E-07			6.89E-07		
13	TPPO	2.83E-07			4.22E-07			1.46E-06		
14	TPPO	4.68E-07			5.18E-07			1.12E-06		
15	TPPO	3.60E-07	4.48E-07	2.38E-07	3.92E-07	4.27E-07	5.23E-08	4.79E-07	8.81E-07	4.01E-07
16	TPP	5.86E-07			5.81E-07			2.11E-04		
17	TPP	4.18E-07			7.98E-07			8.69E-07		
18	TPP	4.15E-07			6.08E-07			8.46E-07		
19	TPP	3.89E-07			7.91E-07			1.32E-06		
20	TPP	4.98E-07	4.61E-07	8.06E-08	1.85E-06	6.95E-07	1.16E-07	1.99E-06	1.26E-06	5.34E-07

Table 9.35: Data for the solubility study of nickel in solutions TPPB and its degradation prodcts at pH 13.3

9.1.8.4 Technetium(VII)

		2 Weeks			4 Weeks			8 Weeks		
Sample	Organic	[Tc] (mol dm^{-3})	Mean [Tc] (mol dm^{-3})	St Dev	[Tc] (mol dm^{-3})	Mean [Tc] (mol dm^{-3})	St Dev	[Tc] (mol dm^{-3})	Mean [Tc] (mol dm^{-3})	St Dev
1	None	1.85E-07			1.79E-07			1.97E-07		
2	None	1.55E-07			3.68E-07			3.37E-07		
3	None	1.67E-07			1.80E-07			1.71E-07		
4	None	1.73E-07			1.74E-07			1.62E-07		
5	None	1.70E-07	1.70E-07	1.08E-08	1.78E-07	1.78E-07	2.77E-09	1.74E-07	1.76E-07	1.51E-08
6	TPPB	3.86E-08			3.67E-07			1.25E-07		
7	TPPB	5.20E-08			8.81E-08			1.42E-07		
8	TPPB	5.48E-08			1.18E-07			1.82E-07		
9	TPPB	5.63E-08			9.25E-08			1.60E-07		
10	TPPB	5.87E-08	5.54E-08	7.93E-09	9.70E-08	9.89E-08	1.20E-07	1.50E-07	1.58E-07	2.12E-08
11	TPPO	1.60E-07			1.74E-07			2.21E-07		
12	TPPO	1.63E-07			1.84E-07			1.86E-07		
13	TPPO	1.59E-07			1.58E-07			1.95E-07		
14	TPPO	1.66E-07			1.76E-07			1.87E-07		
15	TPPO	1.63E-07	1.62E-07	2.89E-09	1.58E-07	1.70E-07	1.15E-08	2.09E-07	2.00E-07	1.51E-08
16	TPP	1.55E-07			1.79E-07			1.98E-07		
17	TPP	1.77E-07			1.82E-07			1.68E-07		
18	TPP	1.63E-07			3.24E-07			3.13E-07		
19	TPP	1.68E-07			1.71E-07			1.78E-07		
20	TPP	1.65E-07	1.65E-07	7.80E-09	1.72E-07	1.76E-07	5.33E-09	1.62E-07	1.77E-07	1.58E-08

Table 9.36: Data for the solubility study of technetium(VII) in solutions TPPB and its degradation prodcts at pH 13.3

9.1.8.5 Uranium(VI)

		2 Weeks			4 Weeks		
Sample	Organic	[U] (mol dm^{-3})	Mean [U] (mol dm^{-3})	St Dev	[U] (mol dm^{-3})	Mean [U] (mol dm^{-3})	St Dev
1	None	3.57E-05			3.51E-05		
2	None	2.84E-05			2.68E-05		
3	None	2.51E-05			3.04E-05		
4	None	2.52E-05			2.76E-05		
5	None	2.70E-05	2.83E-05	4.35E-06	2.95E-05	2.99E-05	3.26E-06
6	TPPB	2.74E-05			3.15E-05		
7	TPPB	2.23E-05			2.74E-05		
8	TPPB	2.68E-05			2.84E-05		
9	TPPB	2.61E-05			3.02E-05		
10	TPPB	2.69E-05	2.68E-05	5.03E-07	3.24E-05	3E-05	2.1E-06
11	TPPO	2.92E-05			2.89E-05		
12	TPPO	2.87E-05			2.93E-05		
13	TPPO	2.57E-05			2.90E-05		
14	TPPO	2.78E-05			3.10E-05		
15	TPPO	2.71E-05	2.77E-05	1.37E-06	3.45E-05	3.05E-05	2.38E-06
16	TPP	3.31E-05			3.23E-05		
17	TPP	2.60E-05			3.05E-05		
18	TPP	2.61E-05			3.08E-05		
19	TPP	2.58E-05			3.36E-05		
20	TPP	2.72E-05	2.63E-05	6.22E-07	3.43E-05	3.23E-05	1.69E-06

Table 9.37: Data for the solubility study of uranium(VI) in solutions TPPB and its degradation prodcts at pH 13.3

9.1.9 Degradation of TcO_4TPP in the presence of organic complexing agents

9.1.9.1 EDTA

		4 Weeks		8 Weeks		12 Weeks		16 Weeks	
Organic	**pH**	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})
EDTA	13.3	254.8	3.50E-08	506.6	7.39E-08	EDTA	13.3	254.8	3.50E-08
EDTA	13.3	368.8	5.26E-08	672.1	9.95E-08	EDTA	13.3	368.8	5.26E-08
EDTA	13.3	384.2	5.50E-08	553.0	8.11E-08	EDTA	13.3	384.2	5.50E-08
EDTA	13.3	383.6	5.49E-08	1095.2	1.65E-07	EDTA	13.3	383.6	5.49E-08
EDTA	13.3	393.3	5.64E-08	542.8	7.95E-08	EDTA	13.3	393.3	5.64E-08

Table 9.38: Degradation of TcO_4TPP in the presence of EDTA

9.1.9.2 NTA

		4 Weeks		8 Weeks		12 Weeks		16 Weeks	
Organic	**pH**	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})
NTA	13.3	270.9	3.75E-08	355.4	5.05E-08	551.3	8.08E-08	2135.6	3.26E-07
NTA	13.3	349.2	4.96E-08	1159.8	1.75E-07	756.6	1.13E-07	2303.1	3.52E-07
NTA	13.3	427.4	6.17E-08	499.5	7.28E-08	888.0	1.33E-07	2214.5	3.38E-07
NTA	13.3	410.7	5.91E-08	580.0	8.53E-08	863.4	1.29E-07	2476.2	3.78E-07
NTA	13.3	415.6	5.98E-08	595.0	8.76E-08	807.7	1.20E-07	1859.5	2.83E-07

Table 9.39: Degradation of TcO_4TPP in the presence of NTA

9.1.9.3 ISA

		4 Weeks		8 Weeks		12 Weeks		16 Weeks	
Organic	**pH**	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})
ISA	13.3	280.9	3.90E-08	557.3	8.17E-08	805.1	1.20E-07	2402.3	3.67E-07
ISA	13.3	480.0	6.98E-08	1786.1	2.72E-07	1329.5	2.01E-07	4843.6	7.44E-07
ISA	13.3	465.2	6.75E-08	2362.1	3.61E-07	1299.5	1.96E-07	4734.0	7.27E-07
ISA	13.3	476.1	6.92E-08	628.2	9.27E-08	1189.8	1.79E-07	3639.2	5.58E-07
ISA	13.3	470.3	6.83E-08	992.7	1.49E-07	1455.1	2.21E-07	6199.1	9.54E-07

Table 9.40: Degradation of TcO_4TPP in the presence of ISA

9.1.9.4 Gluconic acid

		4 Weeks		8 Weeks		12 Weeks		16 Weeks	
Organic	**pH**	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})
Gluconic acid	13.3	405.8	5.83E-08	868.6	1.30E-07	1389.4	2.10E-07	6276.6	9.66E-07
Gluconic acid	13.3	557.5	8.18E-08	3017.8	4.62E-07	1445.7	2.19E-07	4417.2	6.78E-07
Gluconic acid	13.3	498.7	7.27E-08	698.1	1.04E-07	1076.4	1.62E-07	2409.2	3.68E-07
Gluconic acid	13.3	579.0	8.51E-08	960.1	1.44E-07	1842.1	2.80E-07	6856.5	1.06E-06
Gluconic acid	13.3	461.9	6.70E-08	678.2	1.00E-07	1159.7	1.75E-07	3629.9	5.57E-07

Table 9.41: Degradation of TcO_4TPP in the presence of gluconic acid

9.1.9.5 Picolinic acid

		4 Weeks		8 Weeks		12 Weeks		16 Weeks	
Organic	**pH**	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})	**dpm**	**[Tc]** (mol dm^{-3})
Picolinic Acid	13.3	347.9	4.94E-08	800.2	1.19E-07	1063.1	1.60E-07	3683.3	5.65E-07
Picolinic Acid	13.3	482.5	7.02E-08	938.0	1.41E-07	1201.7	1.81E-07	4939.1	7.59E-07
Picolinic Acid	13.3	445.3	6.44E-08	2690.8	4.11E-07	749.1	1.11E-07	2226.0	3.40E-07
Picolinic Acid	13.3	455.1	6.59E-08	1471.8	2.23E-07	1208.1	1.82E-07	3519.0	5.40E-07
Picolinic Acid	13.3	934.8	1.40E-07	1132.6	1.71E-07	1114.4	1.68E-07	2946.1	4.51E-07

Table 9.42: Degradation of TcO_4TPP in the presence of picolinic acid

9.2 Derivations of the solubility product approach method

9.2.1 TcO^{2+}

$$TcO_2.2H_2O \rightleftharpoons TcO^{2+} + H_2O + 2OH^-$$

The equilibrium constant (K) for the dissolution is given by:

$$K_{SP} = \frac{\left[TcO^{2+}\right]\left[H_2O\right]\left[OH^-\right]^2}{\left[TcO_2.2H_2O\right]}$$

Therefore,

$$K_{sp} = \left[TcO^{2+}\right]\left[OH^-\right]^2$$

In the absence of any added ligands, the dissolved tin(II) will consist of the Sn^{2+} ion and its major hydrolysis product [46], i.e.

$$[Tc]_{solution} = \left[TcO^{2+}\right] + \left[TcO(OH)^+\right] + \left[TcO(OH)_2\right] + \left[TcO(OH)_3^-\right]$$

$$[Tc]_{sol'n} = \left[TcO^{2+}\right] + \sum\left[TcO(OH)_x^{z+}\right]$$

$$[Tc]_{sol'n} = \left[TcO^{2+}\right]\left\{1 + \sum\beta_x\left[OH^-\right]^x\right\}$$

$$[Tc]_{solution} = \left[TcO^{2+}\right]A$$

where $A = 1 + \sum\beta_x\left[OH^-\right]^x$ (the side reaction coefficient)[46]. This is constant at any given pH. In this particular case the NIST database of critical stability constants gives the following hydrolysis reactions and constants:[47]

$TcO^{2+} + OH^- \rightleftharpoons TcO(OH)^+$	Log K_1 = 12.6	K_1 = 3.98E+12
$TcO^{2+} + 2OH^- \rightleftharpoons TcO(OH)_2$	Log K_2 = 24.2	K_2 = 1.59E+24
$TcO^{2+} + 3OH^- \rightleftharpoons TcO(OH)_2^-$	Log K_3 = 26.2	K_3 = 1.58E+26

Therefore in the absence of a ligand, at pH = 13.3, i.e. $[OH^-] = 0.3$ mol dm^{-3}, $[Tc]_{sol'n}$ was found to be 3.99×10^{-9} mol dm^{-3}.

Therefore:

$$A = 1 + (3.98 \times 10^{12} \times 0.3) + \left(1.59 \times 10^{24} \times \left(0.3^2\right)\right) + \left(1.58 \times 10^{26} \times \left(0.3^3\right)\right)$$
$$A = 4.42 \times 10^{24}$$

As $K_{sp} = \left[TcO^{2+}\right]\left[OH^-\right]^2$

It follows that:

$$K_{sp} = \frac{[Tc]_{sol'n}\left[OH^-\right]^2}{A}$$

$$K_{sp} = \frac{3.99 \times 10^{-9} \times \left(0.3^2\right)}{4.42 \times 10^{24}}$$

$K_{sp} = 8.12 \times 10^{-35}$ mol dm^{-3}

or $\log K_{sp} = -34.1$

In the presence of EDTA the reaction is

$$TcO^{2+} + EDTA^{y-} \rightleftharpoons TcO(EDTA)^{(2-y)+}$$

Therefore;

$$[\mathrm{Tc}]_{\mathrm{sol'n}} = \left[\mathrm{TcO}^{2+}\right]A + \left[\mathrm{TcO(EDTA)}^{(2-y)+}\right]$$

$$\left[\mathrm{TcO(EDTA)}^{(2-y)+}\right] = [\mathrm{Tc}]_{\mathrm{sol'n}} - \left[\mathrm{TcO}^{2+}\right]A$$

Therefore;

$$\left[\mathrm{TcO(EDTA)}^{(2-y)+}\right] = [\mathrm{Tc}]_{\mathrm{sol'n}} - \left(\frac{K_{sp}}{\left[\mathrm{OH}^-\right]^2}\right)A$$

The stability constant of the complex is given by:

$$\beta = \frac{\left[\mathrm{TcO(EDTA)}^{(2-y)+}\right]}{\left[\mathrm{TcO}^{2+}\right]\left[\mathrm{(EDTA)}^{y-}\right]}$$

Therefore

$$\beta = \frac{[\mathrm{Tc}]_{\mathrm{sol'n}} - \left(\frac{K_{SP}}{\left[\mathrm{OH}^-\right]^2}\right)A}{\left(\frac{K_{SP}}{\left[\mathrm{OH}^-\right]^2}\right)\left(\left[\mathrm{(EDTA)}^{y-}\right]_{\mathrm{total}} - \left\{[\mathrm{Tc}]_{\mathrm{sol'n}} - \left(\frac{K_{SP}}{\left[\mathrm{OH}^-\right]^2}\right)A\right\}\right)}$$

9.2.2 Sn(II)

$$Sn(OH)_2 \rightleftharpoons Sn^{2+} + 2OH^-$$

The equilibrium constant (K) for the dissolution is given by:

$$K_{SP} = \frac{\left[Sn^{2+}\right]\left[OH^-\right]^2}{\left[Sn(OH)_2\right]}$$

Therefore,

$$K_{sp} = \left[Sn^{2+}\right]\left[OH^-\right]^2$$

In the absence of any added ligands, the dissolved Tin(II) will consist of the Sn^{2+} ion and its major hydrolysis product [46], i.e.

$$[Sn]_{solution} = \left[Sn^{2+}\right] + \left[Sn(OH)^+\right] + [Sn(OH)_2] + \left[Sn(OH)_3^-\right]$$

$$[Sn]_{sol'n} = \left[Sn^{2+}\right] + \sum\left[Sn(OH)_x^{z+}\right]$$

$$[Sn]_{sol'n} = \left[Sn^{2+}\right]\left\{1 + \sum\beta_x\left[OH^-\right]^x\right\}$$

$$[Sn]_{solution} = \left[Sn^{2+}\right]A$$

where $A = 1 + \sum\beta_x\left[OH^-\right]^x$ (the side reaction coefficient)[46]. This is constant at any given pH. In this particular case the NIST database of critical stability constants gives the following hydrolysis reactions and constants:[47]

$Sn^{2+} + OH^- \rightleftharpoons SnOH^+$	Log K_1 = 10.1	K_1 = 1.26E+10
$Sn^{2+} + 2OH^- \rightleftharpoons Sn(OH)_2$	Log K_2 = 19.9	K_2 = 7.94E+19

$Sn^{2+} + 3OH^- \rightleftharpoons Sn(OH)_3^-$ Log K_3 = 24.0 K_3 = 1.00E+24

Therefore in the absence of a ligand, at pH = 13.3, i.e. $[OH^-] = 0.3$ mol dm^{-3}, $[Sn]_{sol'n}$ was found to be 2.88×10^{-6} mol dm^{-3}.

Therefore:

$$A = 1 + (1.26 \times 10^{10} \times 0.3) + \left(7.94 \times 10^{19} \times \left(0.3^2\right)\right) + \left(1.00 \times 10^{24} \times \left(0.3^3\right)\right)$$
$$A = 2.70 \times 10^{22}$$

As $K_{sp} = \left[Sn^{2+}\right]\left[OH^-\right]^2$

It follows that:

$$K_{sp} = \frac{[Sn]_{sol'n}\left[OH^-\right]^2}{A}$$

$$K_{sp} = \frac{2.88 \times 10^{-6} \times \left(0.3^2\right)}{2.70 \times 10^{22}}$$

$K_{sp} = 9.6 \times 10^{-30}$ mol dm^{-3}

or $\log K_{sp} = -29.02$

If,

$Sn^{2+} + 2OH^- \rightleftharpoons Sn(OH)_2$ Log K_2 = 19.9 K_2 = 7.94E+19

It follows that for

$Sn(OH)_2 \rightleftharpoons Sn^{2+} + 2OH^-$ Log K_{sp} = -19.9

In the presence of EDTA the reaction is

$$Sn^{2+} + EDTA^{y-} \rightleftharpoons Sn(EDTA)^{(2-y)+}$$

Therefore;

$$[Sn]_{sol'n} = \left[Sn^{2+}\right]A + \left[Sn(EDTA)^{(2-y)+}\right]$$

$$\left[Sn(EDTA)^{(2-y)+}\right] = [Sn]_{sol'n} - \left[Sn^{2+}\right]A$$

Therefore;

$$\left[Sn(EDTA)^{(2-y)+}\right] = [Sn]_{sol'n} - \left(\frac{K_{sp}}{\left[OH^{-}\right]^{2}}\right)A$$

The stability constant of the complex is given by:

$$\beta = \frac{\left[Sn(EDTA)^{(2-y)+}\right]}{\left[Sn^{2+}\right]\left[(EDTA)^{y-}\right]}$$

Therefore

$$\beta = \frac{[Sn]_{sol'n} - \left(\frac{K_{SP}}{\left[OH^{-}\right]^{2}}\right)A}{\left(\frac{K_{SP}}{\left[OH^{-}\right]^{2}}\right)\left(\left[(EDTA)^{y-}\right]_{total} - \left\{[Sn]_{sol'n} - \left(\frac{K_{SP}}{\left[OH^{-}\right]^{2}}\right)A\right\}\right)}$$

9.3 Propagation of errors

Value	Standard deviation	Relative standard deviation
A	a	a/A
B	b	b/B
A±B	(a2 + b2)½	$\frac{\sqrt{(a^2 + b^2)}}{A \pm B}$
AB	$AB\left\lvert\frac{a^2}{A^2} + \frac{b^2}{B^2}\right\rvert^{\frac{1}{2}}$	$\left\lvert\frac{a^2}{A^2} + \frac{b^2}{B^2}\right\rvert^{\frac{1}{2}}$
A/B	$\frac{A}{B}\left\lvert\frac{a^2}{A^2} + \frac{b^2}{B^2}\right\rvert^{\frac{1}{2}}$	$\left\lvert\frac{a^2}{A^2} + \frac{b^2}{B^2}\right\rvert^{\frac{1}{2}}$
ln A	a/A	a/A.lnA
ln(A + B)	$\frac{\sqrt{(a^2 + b^2)}}{A + B}$	$\frac{\sqrt{(a^2 + b^2)}}{(A + B)\ln(A + B)}$
ln(A/B)	$\left\lvert\frac{a^2}{A^2} + \frac{b^2}{B^2}\right\rvert^{\frac{1}{2}}$	$\frac{1}{\ln\frac{A}{B}}\left\lvert\frac{a^2}{A^2} + \frac{b^2}{B^2}\right\rvert^{\frac{1}{2}}$
e^x	ae^x	a

Table 9.43: Propagation of errors

9.4 Training record

Date	Title	Speaker	Group
4/11/02	Health and Safety	D. Wilson	Chemistry
11/11/02	Fire Safety		Chemistry
18/10/02	Uranium Diffusion in Boom Clay	G. Walker	Radiochem
25/10/02	Mild Steel Analysis	A. King	Radiochem
1/11/02	Arsenic Interactions with Humic Substances	E. Inam	Radiochem
6/11/02	Sex, Pasta and Molecules	Prof. Jones	RSC Lecture
8/11/02	Technetium Chemistry	S. Aldridge	Radiochem
13/11/02	Molten Salts Chemistry	K. Franklin	RSC Radiochemical Methods Groups AGM
13/11/02	Gross α Determination in Drinking Water using Actinide Resin	M. Langer	RSC Radiochemical Methods Groups AGM
13/11/02	Cancer Therapy with Targeted Radionuclides	P. Blower	RSC Radiochemical Methods Groups AGM
13/11/02	The Importance of Speciation	Prof. P. Warwick	RSC Radiochemical Methods Groups AGM
13/11/02	An Overview of Partitioning and Transmutation Technologies	H. Sims	RSC Radiochemical Methods Groups AGM
13/11/02	New Reactor Design – The Westinghouse AP1000	A. Worrall	RSC Radiochemical Methods Groups AGM
13/11/02	Developments in ICP-MS Analysis of Long-Lived Radioisotopes	M. Keith-Roach	RSC Radiochemical Methods Groups AGM
15/11/02	Uranium Work	G. Walker	Radiochem
15/11/02	Philosophy of Karl Popper	N. van Dyk	Physical Chem
22/11/02	Temperature and Pressure Dependence of the Specific Interaction Free Energies of Some Solid-Solid Interface using an Electrochemical Technique	Prof. Fletcher	Physical Chem
29/11/02	Surfaces and Interfaces	I. Sutherland	Physical Chem
29/11/02	Arsenic Interactions with Humic Substances	E. Inam	Radiochem
03/02/03	Technetium Chemistry	S. Aldridge	UK-Nirex
21/02/03	Electrostatic Bonding	Prof. Fletcher	Physical Chem

7/03/03	Visible-Region Absorption Spectroelectrochemistry	R. Mortimer	Physical Chem
14/03/03	Modelling of Transient Decay Data on Silica Surfaces	I. Kirkpatrick	Physical Chem
21/03/03	Photosynthesis	S. Worral	Physical Chem
25/04/03	Reduction of Tc(VII) and Possible Complexation with EDTA	S. Aldridge	Radiochem
	Technetium Chemistry	S. Aldridge	UK-Nirex
	Further Development of STAB and the Role of ISA in the Complexation of Radionuclides	N.Evans	UK-Nirex
	Behaviour of Technetium(VII) in the Near Field	S. Williams	UK-Nirex
02/05/03	Humic Interaction with Organic Arsenic Species	E. Inam	Radiochem
02/05/03	Pourbaix Diagrams	G. Walker	Physical Chem
09/05/03	Photodynamics of Vision	M. Patel	Physical Chem
30/05/03	Nucleation Growth	Prof. Fletcher	Physical Chem
06/06/03	Impedence (AC)	R. Barton	Physical Chem
16/06/03	Flocculation in Water	M. Biondo	Radiochem
20/06/03	Europa	K. Ryder	Physical Chem
27/06/03	Dendrochronolgy	G. Walker	Physical Chem
11/7/03	The Effects of Thiol Monolayers on Hydrophobicity	Uijal Kumar Sur	Physical Chem
18/07/03	The Chemistry of Soil	N. Evans	Physical Chem
24/07/03	Sour Grapes	A. Buglass	RSC Lecture
25/07/03	The Bionic Ear	D. Patel	Physical Chem
07/08/03	The Anthropic Principle	N. van Dyk	Physical Chem
	Arsenic – Humic Substance interaction	E. Inam	BGS
1909/03	Active Steel Sample Methodology	A. King	Radiochem
19/09/03	Factors affecting Photosensitised Production of Singlet Oxygen in Different Media	A. Abdel Sherfi	Physical Chem
26/09/03	Uranium Diffusion in Boom Clay and U(IV) Solubility	G. Walker	Radiochem
03/10/03	Soil Digestion for Organic Arsenic Separation	E. Inam	Radiochem
08/10/03	A Scientist Loose in the House	B. Iddon (MP)	Science Faculty

10/10/03	The Behaviour of Technetium in the presence of organic complexing ligands under near field conditions	S. Aldridge	Radiochem
10/10/03	Environmental Photochemistry	S. Williams	Physical Chem
17/10/03	Gamma Spectroscopy	A. King	Radiochem
07/11/03	Electrochemical Studies of Redox Chemistry at the Microscale Level	D. R. Rosseinsky	Physical Chem
21/11/03	Nerve Conduction	G. Wyn Jones	Physical Chem
28/11/03	Materials Chemistry of Polymer Light Emitting Devices	J. Palencuela-Conde	Physical Chem
05/12/03	Microwave Enhanced Electrochemistry	U. Kumar Sur	Physical Chem
16/01/04	Chemistry of the Atmosphere	A. Panchall	Physical Chem
30/01/04	Electronic Conduction in the Bulk Surfaces	K. McKenzie	Physical Chem
13/02/04	A Uranium Story	N. Evans	Physical Chem
12/03/04	Acrylamide in Food	D. Patel	Physical Chem
19/03/04	The Fate of Technetium in a Nuclear Waste Repository	S. Aldridge	Physical Chem
26/03/04	Electrodeposition of Metal/CNF Composites	M. Murphy	Physical Chem
02/04/04	DDT	P. Pearson	Physical Chem
30/04/04	20 Years of Humics	Prof. P. Warwick	Physical Chem
07/05/04	Gas Sensors	R. Mayes	Physical Chem
21/06/04	The NEMCA Effect	F. Marken	Physical Chem
28/06/04	Nitric Oxide	G. Wyn Jones	Physical Chem
17/09/04	Radon	N. Evans	Physical Chem
14/10/04	The Catalytic Synthesis of Carbon Nano Structures and Some of Their Uses in Heterogeneous Catalysis	Prof. M. Ledoux	RSC Lecture
05/11/04	The Last Universal Common Ancestor (LUCA)	Prof. S. Fletcher	Physical Chem
12/11/04	Outer Sphere Electron Transfer	Prof. S. Fletcher	Physical Chem
26/11/04	The Electrooxidation of Thiophene-S-Oxides and Tetracyclones	Prof. D. Walton	Physical Chem

June 15-18, 2005	Plutonium – The element of surprise	Prof. G. Choppin	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Exploring the complexity of 5*f*-electron behaviour	F. Wastin	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Aquatic chemistry and thermodynamics of actinides	T. Fanghänel	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Radiation effects in materials	R. Grimes	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Fuel cycle strategies	D. Warin	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Advanced re-processing	J.-P. Glatz	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Actinide fuels and targets	R. Konings	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Actinide waste forms	G. Lumpkin	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Irradiation behaviour of nuclear fuel	C. Ronchi	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Electron microscopy of nuclear fuels	I. Ray	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe

June 15-18, 2005	Evaluation of accidents and risks	A. Birkhofer	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Reactor safety research	D. Bottomley	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Environmental Chemistry of the Actinides	F. Livens	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Environmental aspects of actinides	M. Betti	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Disposal of waste and long-term implications	M. Leroy	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
June 15-18, 2005	Long term stability of spent nuclear fuel	V. Rondinella	The 3rd ACTINET Summer School 2005 focusses on Actinide Science and Applications, Karlsruhe
	The Role of Natural Colloids in the Environmental Transport of Uranium	N. Evans	Radiochemistry Research Meeting
08/11/05	Colloid Structure and Interaction with Trace Metals	M. Hassellov	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	Quantitative Measurement of 2D Colloid and Solute Transport in Porous Media – Time Lapse Fluorescence Imaging	J. Bridge	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	Colloids in Urban Sandstone Groundwaters: Evidence of Groundwater Source and Colloid Transport Distances	J. Tellam	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	Use of Small-Angle Scattering (SANS) for Characterising Natural Aquatic Colloids/ Nanoparticles Dispersions	H. Jarvie S. King	1st International Conference on Aquatic Colloids and Nanoparticles

08/11/05	Origin and Dynamics of Colloids in a Glaciar Flour-Rich Lake	V. Chanudet	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	Collodial Organic Matter in Arctic River Waters as Quantified by Ultrafiltration and Permeate Model	L. Guo	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	Agricultural Colloids as Nanovectors for Diffuse Pollution	P. Haygarth	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	Interaction of Radionuclides with Aquatic Colloids	M. Bouby	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	The Role of Natural Colloids in the Environmental Transport of Uranium	N. Evans	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	Metal Speciation Dynamics in Colloidal Ligand Dispersions	J. P. S. Pinheiro	1st International Conference on Aquatic Colloids and Nanoparticles
08/11/05	Controversial Role of Colloidal Organic Matter in Pb Biouptake by Freshwater Algae	V. Slaveykova	1st International Conference on Aquatic Colloids and Nanoparticles
23/11/05	Postgrduate Research Student Skills Training – Training Record Management	Prof. R. Jones, G. Weaver	Chemistry Department, Loughborough University
18/01/06	The European Political Perspective	Dr. D. Taylor	Materials for Nuclear Waste Management – An RSC Workshop
18/01/06	Overview of the different types of Nuclear Waste and Different Options for their Disposal	Prof, C. Curtis	Materials for Nuclear Waste Management – An RSC Workshop
18/01/06	The Facilities and Scope of Radioactive Work in the UK	Prof, F. Livens	Materials for Nuclear Waste Management – An RSC Workshop
18/01/06	Storage of Radioactive Wastes	Dr. G. Fairhall	Materials for Nuclear Waste Management – An RSC Workshop
18/01/06	Problem Wastes, Wastforms and Knowledge Gaps	Prof. B. Lee	Materials for Nuclear Waste Management – An RSC Workshop

18/01/06	Immobilisation Science - Cements	Dr. N. Milestone	Materials for Nuclear Waste Management – An RSC Workshop
18/01/06	Immobilisation Science - Ceramics	Dr. G. Lumpkin	Materials for Nuclear Waste Management – An RSC Workshop
18/01/06	Nuclear Waste in France: Current and Future Pratice	Prof. E. Vernaz	Materials for Nuclear Waste Management – An RSC Workshop
07/02/06	Development of radionuclide migration modelling in the far field	T. Lewis	Royal Society of Chemistry - Radiochemistry Group, Young Researchers Meeting YR2006
07/02/06	Soluble co-contaminant complexes of long-lived radionuclides by electrospray ionisation mass spectrometry	A. Cartwright	Royal Society of Chemistry - Radiochemistry Group, Young Researchers Meeting YR2006
07/02/06	The fate of ^{99}Tc in a nuclear waste repository (Winning Presentation)	S. Aldridge	Royal Society of Chemistry - Radiochemistry Group, Young Researchers Meeting YR2006
07/02/06	A new strategy for efficient 18F labelling of novel PET tracers	U Choudhry	Royal Society of Chemistry - Radiochemistry Group, Young Researchers Meeting YR2006
07/02/06	Studying Cd fixation by soil minerals using isotopic dilution method	I Ahmed	Royal Society of Chemistry - Radiochemistry Group, Young Researchers Meeting YR2006
07/02/06	Selective tritio-dehalogenations	**P Allen**	Royal Society of Chemistry - Radiochemistry Group, Young Researchers Meeting YR2006
07/02/06	[18F]Fluoridation of iodinium salts: The thiophene mystery	S. Tang	Royal Society of Chemistry - Radiochemistry Group, Young Researchers Meeting YR2006
09/02/06	Nirex Update	Dr. S. Vines	Loughborough University – Nirex Projects Progress Meeting

09/02/06	Competition Effects on Nickel Solubility	Dr. N. Evans	Loughborough University – Nirex Projects Progress Meeting
09/02/06	Isosaccharinic and Gluconic Acid Metal Complexes: A Study using Solid State NMR	C. Heath	Loughborough University – Nirex Projects Progress Meeting
09/02/06	Some Aspects of Near Field Chemistry in a Nuclear Waste Repository	S. Aldridge	Loughborough University – Nirex Projects Progress Meeting
09/02/06	Background/ Update on FUNMIG	Dr. L. Knight	Loughborough University – Nirex Projects Progress Meeting
09/02/06	Development of the Additive Approach for Radionuclide Migration Modelling	T. Lewis	Loughborough University – Nirex Projects Progress Meeting

9.5 Journal Papers

To be published in Chemosphere

Degradation of tetraphenylphosphonium bromide at high pH and its effect on radionuclide solubility

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Abstract

Recently, tetraphenylphosphonium bromide (TPPB) has been used to remove technetium from some radioactive waste streams. However, before TPPB could be approved for use it was necessary to show that TPPB and its degradation products would not have a significant detrimental effect on post-closure performance of a radioactive waste repository. TPPB is known to be stable at neutral pH, however, under alkaline conditions it degrades by an alkaline hydrolysis mechanism to triphenylphosphonium oxide (TPPO). Degradation can also occur by radiolysis to produce triphenylphosphine (TPP). The kinetics of the alkaline hydrolysis degradation of TPPB is described and the solubility of europium, iodine, nickel, technetium(VII) and uranium(VI) in aqueous solutions of TPPB and its degradation products is reported. These results were used to support the use of TPPB in removing technetium from some waste streams.

Keywords: tetraphenylphosphonium bromide (TPPB), alkaline hydrolysis, degradation products, solubility.

Introduction

During reprocessing of Magnox fuel using the PUREX process the irradiated and decanned uranium fuel rods are dissolved in nitric acid. Plutonium and uranium are separated from the resulting solution by liquid extraction using a mixture of 30% tributylphosphate (TBP) solution in odourless kerosene. One of the waste streams from this chemical separation process is an aqueous acidic medium active liquor. The liquor contains a range of radioactive species such as caesium, strontium, plutonium and other alpha and beta emitters, including technetium. The medium active liquor is then concentrated by evaporation to produce a medium active concentrate (MAC) (Reed, 2004).

MAC is collected and stored in tanks prior to treatment in the Enhanced Actinide Removal Plant (EARP). Sodium hydroxide and a flocculating agent are added to the MAC within the EARP and an insoluble floc is then formed which contains the main alpha and plutonium species. The ion exchange reagent is incorporated into the floc and removes additional species, mainly caesium. Therefore soluble radioactive species are made insoluble by the production of the floc. The floc is then dewatered by ultrafiltration prior to encapsulation in 500 litre steel drums with cement. The permeate which contains a small fraction of the radioactivity in the MAC is discharged to sea (Gordan, 2004).

In the past technetium was not removed into the floc by either of the processes described above and was therefore discharged to the sea in the permeate. At the time technetium, present as TcO_4^-, was thought to disperse widely as it is carried from the Irish Sea by the Gulf Stream which flows past the British Isles to the Arctic and the Barents Sea. En route, ^{99}Tc accumulates in seaweed (Brown et al., 1999; Webster et al., 2003; Mas et al., 2004) and lobsters (Olsen, 2003; Copplestone et al., 2004) along the Norwegian coastline. It was therefore preferable to remove technetium from the permeate prior to discharge to sea.

Although a three month trial, in which *ca.* 250 cm^3 of MAC floc was treated with TPPB, showed that TPPB successfully removed most of the technetium before being accepted for use in the plant a further 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 a radioactive waste repository.

Degradation of Tetraphenylphosphonium Bromide

Although tetraphenylphosphonium ion is known to be stable at neutral pH, it is prone to degradation by alkaline hydrolysis at high pH. The tetraphenylphosphonium ion is also prone to radiolytic degradation in a repository environment.

The mechanism for radiolytic degradation of tetraphenylphosphonium chloride is thought to be as shown below (Horii et al., 1976).

$$\mathrm{Ph_4P^+ + Cl^+ \rightarrow Ph_4P\bullet + Cl}$$

$$\mathrm{Ph_4P\bullet \rightarrow Ph\bullet + Ph_3P}$$

$$\mathrm{Ph\bullet + Ph\bullet \rightarrow Ph_2}$$

The products are generally phenylphosphine compounds.

The mechanism for the alkaline hydrolysis of quaternary phosphonium salts has been suggested to be as follows (Khalil, 1973; Khalil, 1974):

$$\mathrm{R_4P^+ + 2OH^- \rightleftharpoons R_4POH + OH^- \rightleftharpoons R_4PO^- + H_2O}$$

$$\mathrm{R_4PO^- + H_2O \xrightarrow{High\ pH} R_3PO + R^- + H_2O \longrightarrow R_3PO + RH + OH^-}$$

Or in detail for TPPB:

$$\mathrm{Ph_3P^+ - -Ph + 2OH^- \rightleftharpoons OH - -P(Ph_3) - -Ph + OH^-}$$

$$\mathrm{OH - -P(Ph_3) - -Ph + OH^- \rightleftharpoons Ph - -P(Ph_3) - -O^- + H_2O \longrightarrow SLOW}$$

$$\mathrm{Ph_4PO^- + H_2O \longrightarrow Ph_3P = O + R^- + H_2O \longrightarrow Ph_3P = O + RH + OH^-}$$

The alkaline hydrolysis of TPPB is thus thought to produce triphenylphosphine oxide.

Experimental

Deionised water produced by a Barnstead NANOpure ultrapure water purification system, and AR reagents, were used throughout. TPPB, TPPO and TPP were purchased from Aldrich and ^{63}Ni, ^{152}Eu, ^{125}I and ^{99}Tc were purchased from Amersham. ^{233}U was purchased from www.isotopes.com. pH was measured using a glass electrode and an Orion 720A pH meter. The electrode was calibrated using a volumetric standard sodium hydroxide solution purchased from Aldrich. ^{63}Ni, ^{99}Tc and ^{233}U were measured by liquid scintillation counting in a Packard Tri Carb 2750 TR/LL counter using Ecoscint cocktail. ^{152}Eu, ^{125}I were counted in a Packard Cobra II Auto Gamma counter. UV/Vis absorption was measured in a Varian 50 Bio UV/Vis spectrophotometer using a 1 cm square cell.

Kinetic Studies

Aqueous solutions of TPPB (0.02 mol dm^{-3}, 250 cm^{3}) and sodium hydroxide (0.6 mol dm^{-3}, 250 cm^{3}) were prepared. The temperatures of the individual solutions were then adjusted to 293 K using a water bath before mixing them together and holding them at 293 K.

Samples were taken at certain time intervals, and placed immediately into 10 cm^{3} of hydrochloric acid (5 mol dm^{-3}) to prevent the alkaline hydrolysis reaction continuing during measurement. The samples were then filtered through a 0.2 μm syringe filter before measuring their absorbance at 268 nm. The concentration of TPPB remaining in solution was determined from a calibration graph of absorbance at 268 nm against TPPB concentration.

This procedure was then repeated at 313, 333 or 353 K.

The investigations were then repeated for sodium hydroxide concentrations of 0.1, 0.3 or 1 mol dm^{-3}.

Solubility Studies

TPPB, TPPO, and TPP were weighed into separate polythene vials in quantities determined to produce 0.001 mol dm^{-3} solutions in 20 cm^3 of 0.30 mol dm^{-3} sodium hydroxide. The elements under investigation were then added in non-active form, again in suitable quantities so as to produce 0.001 mol dm^{-3} solutions. Small quantities of the appropriate radionuclide were then added. However, as there are no inactive technetium isotopes, technetium experiments were conducted using an initial technetium concentration of *ca.* 4 × 10^{-7} mol dm^{-3}. After two weeks, samples were filtered through a 0.22 μm syringe filter and the radioactivity in each solution was measured. The measurements were repeated after 4 and 8 weeks.

Results

Kinetic study of the degradation of tetraphenylphosphonium bromide

In a previous study of the degradation of the tetraphenylphosphonium ion by alkaline hydrolysis, the chloride quaternary salt was used (Khalil, 1973; Khalil, 1974). The rate of reaction was found to follow third order kinetics and the rate of reaction is given as:

$$\mathrm{rate} = k[\mathrm{TPPB}][\mathrm{OH^-}]^2$$

By following the degradation at pH 11.2 the following Arrhenius expression was determined:

$$k = 2.45 \times 10^{21}\, e^{\left(\frac{-140.8\left(\text{kJ mol}^{-1}\right)}{RT}\right)}\ \text{dm}^6\text{mol}^{-2}\text{s}^{-1}$$

Figure 1 shows that the degradation of tetraphenylphosphonium bromide at different sodium hydroxide concentrations and different temperatures. Graphs of ln [TPPB] versus time are straight lines demonstrating that the degradation follows first order kinetics with respect to TPPB concentration.

The rate constants for the alkaline hydrolysis of TPPB at different temperatures can be obtained by measuring the degradation with respect to time. In addition, by plotting the reciprocal of the temperature against the natural log of the rate constant (figure 2), an Arrhenius expression can be obtained for the degradation of tetraphenylphosphonium.

The mean activation energy is 105.20 ± 3.21 kJ mol^{-1} and the mean pre-exponential term, ln A, is 30.64 ± 1.14. Therefore, the Arrhenius expression can be expressed as:

$$k = 2.03 \times 10^{13}\, e^{\left(\frac{-105.2\left(\text{kJ mol}^{-1}\right)}{RT}\right)}\ \text{dm}^6\text{mol}^{-2}\text{s}^{-1}$$

Comparison of this Arrhenius equation with in the literature (Khalil, 1973; Khalil, 1974) shows that the activation energy for the degradation of TPPB is lower than that for TPPCl and therefore the degradation of the bromide phosphonium salt is kinetically faster than that of the chloride salt.

Solubility of $^{99}TcO_4^-$ in solutions of TPPB and its degradation products

The results for the solubility experiments of TcO_4^- in solutions containing either TPPO, TPPB or TPP are shown in figure 3. In the solutions containing TPPO and TPP it can be seen that the concentration of technetium(VII) is the same as in the solution containing only TcO_4^-. However for the solution containing TPPB the solubility of TcO_4^- is much lower as it is precipitated by the phosphonium ion. After 4 weeks it can be seen that the TcO_4^-, solubility increases until, after 8 weeks the solubility of TcO_4^- reaches the inventory concentration of technetium.

The increase in solution phase technetium is most likely because TPPB degrades by alkaline hydrolysis and TcO_4^- is released into solution. Using the rate equation above and data from this study it is possible to compare the degradation of TPPB with the release of technetium from the TcO_4TPP solid at high pH (figure 4).

From figure 4 it can be seen that the release rate of technetium is similar to the rate of degradation of tetraphenylphosphonium bromide. The increase in the

solubility of technetium with time is therefore due to the release of technetium as the tetratphenylphosphonium bromide molecule degrades via alkaline hydrolysis.

Solubility of ^{152}Eu in solutions of TPPB *and its degradation products*

The results for the solubility experiments of ^{152}Eu in solutions containing either tetraphenylphosphonium bromide, triphenylphosphonium oxide or triphenylphosphine are shown in figure 5. At acidic pHs, europium is soluble and a 0.001 mol dm^{-3} $EuCl_3$ solution spiked with ^{152}Eu gave a specific activity of 3630 dpm cm^{-3}. However, at pH 13.3, europium precipitated and the specific activity was reduced to 2.4 dpm cm^{-3}. Measurements showed that in all solutions the solubility of europium was the same as that in the solution containing only ^{152}Eu.

Solubility of ^{125}I in solutions of TPPB and its degradation products

The results for the solubility experiments of ^{125}I in solutions containing either TPPO, TPPB or TPP are shown in figure 5. Iodine is soluble at pH 13.3. However, iodine will be present as an anion and it might be expected to be removed in the same way as TcO_4^-. However, in all solutions the solubility of iodine is the same as that in the solution containing only ^{125}I.

Solubility of ^{63}Ni in solutions of TPPB and its degradation products

The results for the solubility experiments of ^{63}Ni in solutions containing either TPPO, TPPB or TPP are shown in figure 5. At acidic pHs, nickel is soluble and a 0.001 mol dm^{-3} $NiCl_2$ solution spiked with ^{63}Ni gave a specific activity of 11425 dpm cm^{-3}. However, at pH 13.3, nickel precipitated and the specific activity was reduced to 6.8 dpm cm^{-3}. In all solutions the solubility of nickel is the same as that in the solution containing only ^{63}Ni.

Solubility of ^{233}U in solutions of TPPB and its degradation products

The results for the solubility experiments of ^{233}U in solutions containing either TPPO, TPPB or TPP are shown in figure. 5. At acidic pHs, uranium is soluble and a 0.001 mol dm^{-3} $UO_2(NO)I_3$ solution spiked with ^{233}U gave a specific activity of 22000 dpm cm^{-3}. However, at pH 13.3, uranium precipitated and the specific activity was reduced to 625 dpm cm^{-3}. In all solutions the solubility of uranium is the same as that in the solution containing only ^{233}U.

Conclusions

The kinetics of the degradation of TPPB by alkaline hydrolysis were first order with respect to TPPB concentration and were similar to those suggested in the literature (Khalil, 1973; Khalil, 1974). The results of the kinetic experiments were used to calculate an activation energy and develop an Arrhenius expression for the degradation of TPPB.

TPPB and its degradation products appeared to have no significant effect on the solubility of europium, iodine, nickel and uranium(VI). This was also the case for the solubility of technetium(VII) in the presence of TPP or TPPO.

Technetium showed a gradual increase in solubility over time in the presence of tetraphenylphosphonium bromide. The increase in solubility was because TcO_4^- was being released as the TPPB degraded.

As a direct result of this work it was shown that TPPB and its degradation products would not have a significant detrimental effect on post-closure performance of an underground radioactive waste repository. TPPB is now used to remove technetium from some radioactive waste streams.

References

Brown, J. E. Kolstad, A. K. Brungot, A. L. Lind, B. Rudjord, A. L. Strand, P. FØyn, L., 1999. Levels of Tc-99 in seawater and biota samples from Norwegian coastal waters and adjacent seas. Mar. Pollut. Bull. 38, 560-571.

Copplestone, D. Jackson, D. Hartnoll, R. G. Johnson, M. S. McDonald, P. Wood, N., 2004. Seasonal variations in activity concentrations of Tc-99 and Cs- 137 in the edible meat fraction of crabs and lobsters from the central Irish Sea. J. Environ. Radioactiv. 3, 29-48.

Gordan, J., 2004. Where courage is present..., Nucl. Eng. Int. 49, 8-9.

Horii, H. Fujita, S. Mori, T. Taniguchi, S., 1976. Pulse radiolysis of aqueous solutions of tetraphenylphosphonium ions. Int. J. Radiat. Phys. Ch. 8, 521-525.

Khalil, F.Y. Aksnes, G., 1973. Kinetics, Medium and Deuterium Isotope Effects in the Alkaline Decomposition of Quaternary Phosphonium Salts. I. Tetraphenylphosphonium Chloride in Dioxane-Water Mixtures. Acta. Chem. Scand. 27, 3832-3838.

Khalil, F.Y. Aksnes, G., 1974. Kinetics, Medium and Deuterium Isotope Effects in the Alkaline Decomposition of Quaternary Phosphonium Salts. II. Tetraphenylphosphonium Chloride in Acetone-Water Mixtures. Z. Phys. Chem. Neue. Fol. 97, 179-188.

Mas, J. L. Tagami, K. Uchida, S., 2004. Method for the detection of Tc in seaweed samples coupling the use of Re as a chemical tracer and isotope dilution inductively coupled plasma mass spectrometry. Anal. Chim. Acta. 509, 83-88.

Olsen, Y.S. Batlle, J. V., 2003. A model for the bioaccumulation of Tc-99 in lobsters (Homarus gammarus) from the West Cumbrian coast. J. Environ. Radioactiv. 67, 219-233.

Reed, J., 2004. Technetium to go. Nucl. Eng. Int. 49, 14-17.

Webster, S. Salt, C. A. Howard, B. J., 2003. Sea-to-land transfer of technetium-99 through the use of contaminated seaweed as an agricultural soil conditioner. J. Environ. Radioactiv. 70, 127-137.

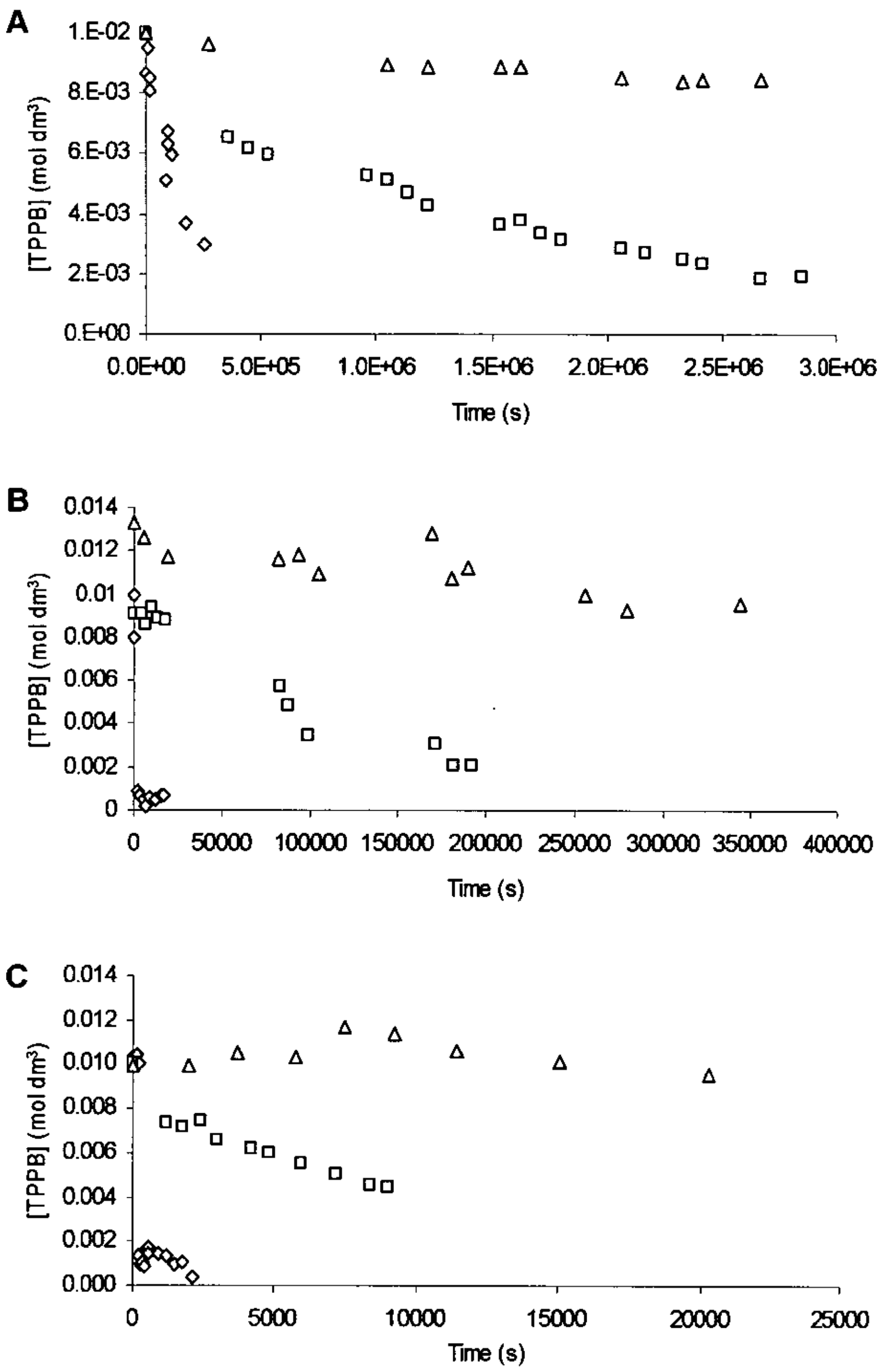

Figure 1: Degradation of tetraphenylphosphonium bromide at different sodium hydroxide concentrations (◇ [NaOH] = 1 mol dm^{-3}; □ [NaOH] = 0.3 mol dm^{-3}; △ [NaOH] = 0.1 mol dm^{-3}) and different temperatures (A. 293 K; B. 313 K; C. 333 K)

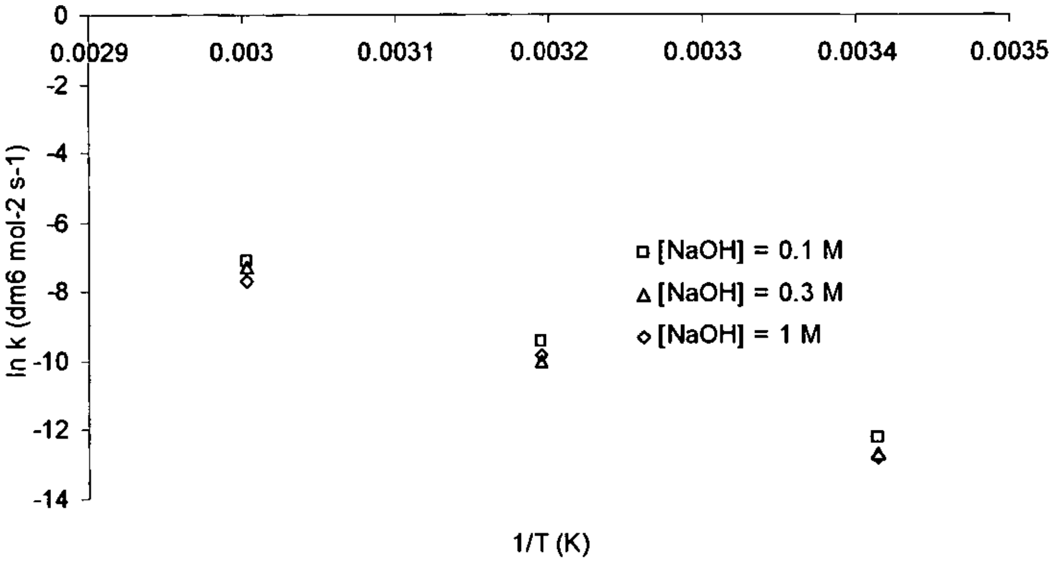

Figure 2: log of the rate constants (k) for the alkaline hydrolysis of TPPB against the reciprocal of the temperature at different hydroxide concentrations.

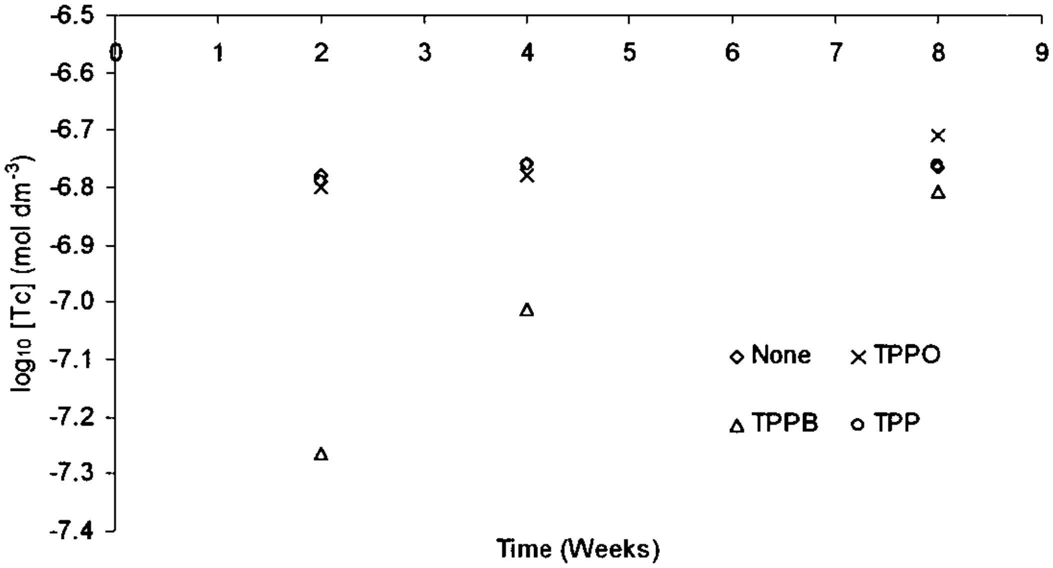

Figure 3: log of the concentration of technetium in solutions of TPPB and its degradation products against time.

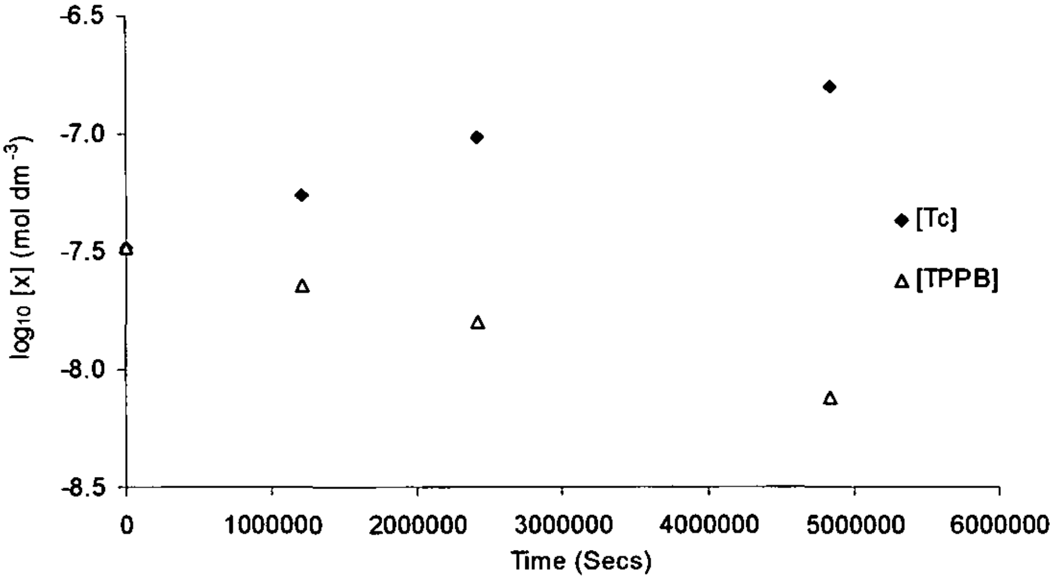

Figure 4: Release rate of TcO_4^- and the degradation of TPPB against time.

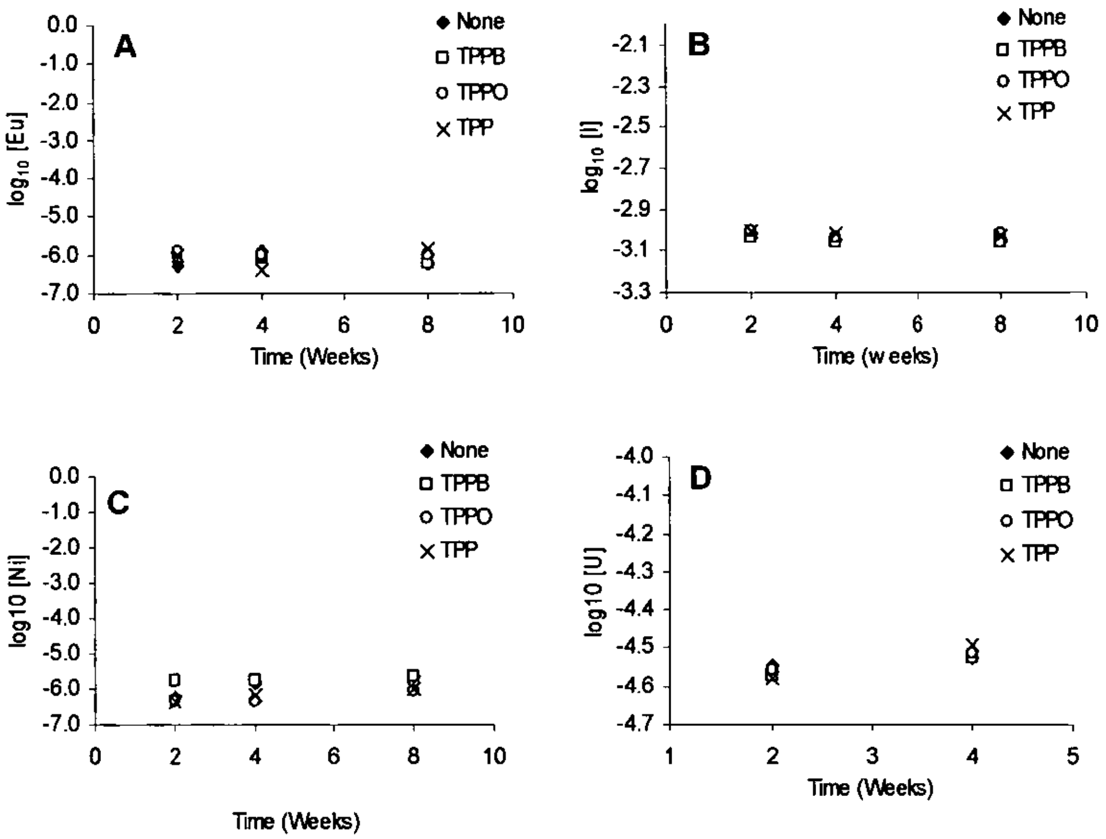

Figure 5: log of the concentration (mol dm^{-3}) of various metals in solutions of TPPB and its degradation products against time. (A. Europium; B. Iodine; C. Nickel; D. Uranium)

Table 1: Rate constants (k) for the alkaline hydrolysis of TPPB at different hydroxide concentrations

	[NaOH] = 0.1 mol dm^{-3}			[NaOH] = 0.3 mol dm^{-3}			[NaOH] = 1 mol dm^{-3}		
T (°C)	20	40	60	20	40	60	20	40	60
T (K)	293	313	333	293	313	333	293	313	333
1/T (K)	0.0034	0.0032	0.0030	0.0034	0.0032	0.0030	0.0034	0.0032	0.0030
k (dm^{6} mol^{-2} s^{-1})	5.1E-06	8.2E-05	8.0E-04	3.2E-06	4.5E-05	6.8E-04	2.8E-06	5.3E-05	4.6E-04
ln k	-12.2	-9.4	-7.1	-12.7	-10.0	-7.3	-12.8	-9.8	-7.7

Table 2: Estimated activation energies for the alkaline hydrolysis of TPPB at different hydroxide concentrations

$[OH^{-}]$ (mol dm^{-3})	E_A (kJ mol^{-1})	A	ln A
0.1	102.89	1.15×10^{13}	30.1
0.3	108.86	7.56×10^{13}	32.0
1	103.82	9.64×10^{12}	29.9