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**Reduction of Tc(VII) and Np(V) in
solution by ferrous iron**

**A laboratory study of homogeneous
and heterogeneous redox processes**

Daqing Cui, Trygve E Eriksen

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March 1996

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ABSTRACT

The redox chemistry of technetium and neptunium in deep groundwater systems has been studied under well controlled conditions in laboratory experiments. The measured redox potentials in anoxic deep groundwater systems are consistent with redox reactions between Fe(II) in solution and hydrous Fe(III)-oxide phases.

The fracture filling material and groundwater in transmissive fractures in bedrock constitute two different compartments in the groundwater system and experiments were therefore carried out in homogeneous Fe(II) containing solutions and in heterogeneous mixtures of solution with Fe(II) containing solid mineral phases.

Reduction of the strongly sorbing neptunyl cation (NpO_2^+) and the slightly sorbing pertechnetate anion (TcO_4^-) by Fe(II) in solution was found to proceed very slowly, if at all, in reaction vessels with hydrophobic inner surfaces. However, in the heterogeneous systems we observed surface mediated reduction to the slightly soluble ($< 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$) tetravalent (hydr)oxides $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ ($=\text{Tc}(\text{OH})_4$) and $\text{NpO}_2 \cdot n\text{H}_2\text{O}$ ($=\text{Np}(\text{OH})_4$). by Fe(II) sorbed on quartz, precipitated $\text{Fe}(\text{OH})_2(\text{s})$, $\text{Fe}(\text{II})\text{CO}_3(\text{s})$ and Fe(II) bearing minerals such as magnetite, hornblende and Fe(II)-chlorite.

It is concluded that surface mediated redox-reactions will be the most effective pathway for the reduction of Tc(VII) and Np(V) in deep groundwater systems. On exposure of the surface-precipitated tetravalent (hydr)oxides to air saturated groundwater solutions the oxidative dissolution was found to be a very slow process and high concentration of hydrogen peroxide was required for oxidative dissolution. The slow rate of oxidative dissolution is most probably due to kinetic suppression of the reactions between dissolved oxygen and the precipitated (hydr)oxides. The kinetic suppression is caused by competing redox reactions at the surface of the Fe(II)-bearing minerals which consumes the dissolved oxygen.

SAMMANFATTNING

Redoxkemin för teknetium och neptunium i djupa grundvattensystem har studerats i väl kontrollerade laboratorieförsök. Under oxiska betingelser förekommer teknetium som den svagt sorberande anjonen TcO_4^- och neptunium som den starkt sorberande katjonen NpO_2^+ . Uppmätta redoxpotentialer i djupa grundvatten överensstämmer med antagandet om redoxjämvikt mellan Fe(II) i lösning och Fe(III) oxider. Under dessa förhållanden förväntas teknetium och neptunium förekomma som de svårslösliga ($<10^{-8}$ mol \cdot dm $^{-3}$) fyrvärda (hydr)oxiderna $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ ($=\text{Tc}(\text{OH})_4$) och $\text{NpO}_2 \cdot n\text{H}_2\text{O}$ ($=\text{Np}(\text{OH})_4$).

I vattenförande sprickor i granitiskt berg kan vattennfasen och den fasta fasen betraktas som två separata delar av redoxsystemet. Vi har därför genomfört försök med Fe(II)-lösningar och heterogena blandningar av fast fas och lösning, där den fasta fasen bestod av granit, sprickfyllnadsmaterial och Fe(II) mineral. Försöken visar att TcO_4^- och NpO_2^+ , reduceras och fälls ut som fyrvärda (hydr)oxider av Fe(II) sorberat på mineralytor och fällningar av Fe(II)-hydroxid och karbonat. Även Fe(II) haltiga mineral, reagerar på detta sätt men reduktionen sker endast mycket långsamt, om än alls, med Fe(II) i grundvatten.

De på ytor utfällda oxiderna oxideras mycket långsamt av löst syre i grundvattnet och höga koncentrationer av väteperoxid krävdes för att få oxidativ upplösning av fällningarna. Fällningarnas stabilitet förklaras av att det lösta syrets förbrukning i redoxreaktioner på Fe(II) mineralens våta ytor är snabbare än syrets reaktioner med de utfällda fyrvärda oxiderna.

1. INTRODUCTION

Migration of radionuclides by groundwater flowing through fractures in the bedrock is controlled by their solubility and sorption on the fracture filling material .

The oxidation state may have a dramatic effect on the speciation, solubility and sorption behaviour of multivalent radionuclides. Examples of redox sensitive radionuclides are the fission product ^{99}Tc and the actinide ^{237}Np which constitute a long term potential hazard in nuclear wastes due to their long half life and relatively high abundance. Heptavalent technetium Tc(VII) is present as the highly soluble and mobile TcO_4^- anion in oxic groundwater. Pentavalent neptunium Np(V) occurs in the form of NpO_2^+ and the hydroxy and carbonate complexes of NpO_2^+ with a strong, pH dependent sorption behaviour. The redox potentials in deep groundwater systems have been found to be consistent with redox reactions involving Fe(II) in solution and hydrous Fe(III)-oxide phases [1]. Therefore, reducing conditions are expected to prevail in a deep repository for high level nuclear wastes and the solubility of Tc and Np will be controlled by precipitation of the tetravalent hydrous oxides $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ ($= \text{Tc}(\text{OH})_4(\text{s})$), and $\text{Np}_2 \cdot n\text{H}_2\text{O}$ ($= \text{Np}(\text{OH})_4(\text{s})$). The solubility of these oxides is of the order $10^{-8} \text{ mol} \cdot \text{dm}^{-3}$ [2].

Several research groups have reported the reduction of TcO_4^- by Fe(II) in solution [3-6], but the interpretation of the experimental data is far from straightforward. The reason for this is the presence of added or unintentionally formed Fe(II)-containing solid phases which may have caused surface mediated reduction of TcO_4^- in several of the systems studied. Sorption of technetium from solutions initially containing TcO_4^- onto granite under reducing conditions or in the absence of oxygen has been reported by several researchers [7-11]. According to Vandergraaf et al [11] technetium is removed from anoxic solutions, and in some cases in the presence of air, by iron oxides but not by minerals containing ferrous iron as an integral part of their crystal lattice. Haines et al [12] demonstrated in a Fourier Transform Infrared (FTIR) study that the reaction between TcO_4^- and magnetite occurs via surface mediated reduction to Tc(IV) and precipitation of TcO_2 on the Fe_3O_4 surface.

Reduction of Np(V) under simulated anaerobic groundwater conditions has recently been studied by Hakanen and Lindberg [6]. Reduction to Np(IV) was observed both in reaction systems containing water only and in systems containing water and rock coupons. The groundwater was rich in sulphide ($10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) and correspondingly poor in Fe(II) ($10^{-7} \text{ mol} \cdot \text{dm}^{-3}$). The active redox couple was assumed to be $\text{HS}^- / \text{S}(\text{s})$.

The aim of the present work is to study the reduction of Tc(VII) and Np(V) in solution by Fe(II) and to demonstrate the importance of surface mediated reduction by heterogeneous electron transfer from redox active Fe(II)-bearing fissure fillings. The focus is on technetium but the results from some neptunium experiments are also discussed.

2. EXPERIMENTAL

All experiments were carried out at ambient temperature ($22 \pm 2^\circ\text{C}$) in a controlled atmosphere box flushed with argon to minimise intrusion of oxygen into the reaction vessel.

2.1 Materials

Dark green, black and light green coloured, henceforth denoted A, B and C, fracture fillings and granite were collected from drillcores containing natural fractures taken 360m below ground level in Stripa mine. Hornblende and magnetite were used as pure reference minerals.

The solids were crushed in argon atmosphere using an agate mortar and pestle, sieved to 60-90, 90-125, 125-250 and 250-500 μm size fractions and washed with acetone in a ultra-sonic bath.

The 125-250 μm size fraction of the light green fracture filling material was separated into nine fractions with respect to iron content using a Frantz Model L-1 isodynamic separator. The mineral composition of the various crushed fractions were characterised by qualitative or semiquantitative X-ray diffraction and the BET surface areas measured using a Micro-meritics Flow Sorb II 2300 apparatus with N_2 as sorbing gas. The mineral composition of the solids used are given in. tables 1 and 2.

All chemicals were of analytical grade and used as received. The water used to prepare perchlorate and ground water solutions was deionized, triple distilled in quartz and purged with argon (AGA 5.7 quality) containing less than 0.5 ppm oxygen. The composition of the synthetic ground water is given in Table 3. ^{99}Tc was purchased from Amersham as TcO_4^- in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ NH_4OH solution. A stock solution of $^{237}\text{Np(V)}$ was obtained by dissolving $2.8 \text{ mg } ^{237}\text{NpO}_2(\text{cr})$ in 4 cm^3 concentrated HNO_3 solution. TcO_4^- and NpO_2^- solutions were prepared by diluting aliquots of the stock solutions.

2.2 Analyses

The Fe(II) content of the fracture filling material was determined as FeO by the method described by Graff [13]. The pH measurements were made by a Radiometer model pHM84 pH meter and a GK 202C glass electrode and the redox potentials were monitored by a Metrohm Pt electrode connected to a Metrohm 632 pH meter. A Yokogawa SR 20/AR 24 (Ag/AgCl) electrode was used as reference. The electrodes were standardised using saturated quinhydrone buffers at pH 4 and 7. Samples drawn from the solutions with a syringe were weighed on an electronic balance with 10^{-2} accuracy and analysed for ^{99}Tc or ^{237}Np in a Beckman model 5801 Liquid Scintillation System using Ready Safe as scintillation cocktail. The counter was calibrated with standard solutions containing known ^{99}Tc and ^{237}Np concentrations.

Table 1. Qualitative mineral composition according to x-ray diffraction analysis.

Granite	quartz	microcline	albite	muscovite	chlorite	calcite
Fracture filling(A)	quartz	epidote	calcite	chlorite	microcline	muscovite
Fracture filling(B)	quartz	muscovite	chlorite	pyroxeme	albite	

Table 2. Mineral composition of the magnetically separated fractions of crushed light green coloured fracture filling material (C)

Fraction No.	orig.	1#	2#	3#	4#	5#	6#	7#	8#	9#
Weight %	100	0.82	2.67	6.68	18.9	7.92	7.83	5.56	18.45	31.18
Surface (m ² /g)	1.02	1.8	3.93	4.29	2.44	0.97	0.65	0.47	0.46	0.3
CEC (μquiv/g)	22.7	61.3	55.9	53.2	30.0	21.4	17.6	13.4	9.1	3.6
Fe(II) %(titrat.)	0.96	16.45	6.01	2.58	1.37	0.86	0.63	0.43	0.28	0.11
Fe total %(INAA)	1.25	17.34	6.81	3.62	1.93	1.14	0.77	0.59	0.38	0.14
Quartz %	22	17	23	19	18	19	19	19	22	26
Microcline %	23	17	22	23	22	21	26	24	25	23
Albite %	37	20	42	38	41	38	40	38	35	37
Plagioclase %	15	-	-	18	17	16	16	15	13	16
Fe-chlorite %	0.8	37	5	2	0.7	0.5	0.7	0.5	-	-
Muscovite mica %	1.7	9	8	7	4	2	-	0.1	0.1	-

Ideal chemical composition of minerals in Tables 1 and 2

Quartz: SiO_2
 Microcline: KAlSi_3O_8
 Albite: $\text{NaAlSi}_3\text{O}_8$
 Intermediate plagioclase: $\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$
 Muscovite: $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})$
 Fe-Chlorite: $\text{Fe}_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot \text{Fe}_3(\text{OH})_6$

Table 3. Composition of synthetic groundwater

Species	HCO_3^-	SO_4^{2-}	Cl^-	SiO_2	Ca^{2+}	Mg^{2+}	K^+	Na^+
Conc. (mg·dm ⁻³)	123	9.6	70	12	18	4.3	3.9	65

The Tc(IV)/T(VII) speciation was determined by solvent extraction of TcO_4^- into chloroform containing 0.1 M tetraphenyl arsonium chloride. Np(IV) and Np(V) were separated by solvent extraction using a 0.5 mol·dm⁻³ 2-theonyl trifluoroacetone solution in xylene (2). Samples from the different phases were analysed for ⁹⁹Tc or ²³⁷Np as described above.

2.3 Experimental procedures

2.3.1 Technetium

Fe(II)-solutions: The first experiment was carried out in a 500 cm³ glass bottle with untreated inner surface. The inner surface of the reaction vessel used in all other experiments was coated with hexadimethyldisilazane at 120-130°C [14] and the treated surface thoroughly washed with methanol.

The reaction vessel, containing the ⁹⁹TcO₄⁻ solution, was flushed continuously for four days with a Ar(1% H₂) mixture (AGA 5.7 quality) to reach stable reducing conditions (approximately -250 mV vs. NHE). The gas stream was fed through alkaline pyrogallol solution to remove traces of oxygen [15]. The gas purging was then stopped and the reaction vessel was kept under a slight overpressure of the Ar/H₂ gas mixture. The solutions were stirred gently by a teflon covered magnetic stirrer throughout the experiments.

Small volumes of a argon flushed 0.1 M FeCl₂ solution at pH 4 was added by syringe through a rubber/teflon septum. Solution samples, drawn with a syringe, were weighed on an electrical balance with 10⁻⁵ g accuracy and analysed for Fe(II) and Tc. The Fe(II) concentration was determined by the o-phenanthroline method [16] and the Tc concentration measured by ⁹⁹Tc counting as described above.

The experimental conditions for the different experiments are summarised in Table 4.

Table 4 Experimental conditions

Series No	1	2	3	4	5	6	7
Surface	glass	hyd	quartz	hyd	hyd	hyd	hyd
Bulk solution	NaClO ₄	NaClO ₄	NaClO ₄	NaClO ₄	NaClO ₄	NaClO ₄	SGW
[Fe ²⁺] ₀ , 10 ⁻⁵ M	5.8	4.43	4.64	12	0.35	0.64	4.6
glass:	untreated inner surface of the reaction vessel						
hyd:	inner surface of the reaction vessel was coated to be hydrophobic with hexadimethyldisilazane at 120-130°C and washed with methanol						
quartz:	hydrophobic inner surface of reaction vessel, 2 g HCl washed quartz (0.068 m ² · g ⁻¹) added to the solution.						
NaClO ₄ : 0.1	M aqueous solution						
SGW:	synthetic ground water with the composition given in Table 3.						

Heterogeneous systems: The batch experiments were carried out as shown schematically in Figure 1. Small polypropene reaction vials containing the solids were placed inside the receptacle. The system was flushed with Ar or Ar(1% H_2) for three days before adding oxygenfree ground water or perchlorate solution to the vials. Two different methods were used to prepare solutions with low redox potential; ground water was equilibrated with granitic rock in a closed all glass system [17,18] or ground water/perchlorate solutions were purged with Ar containing 1% H_2 . An overview of the experimental conditions is given in Table 5. The TcO_4^- concentration was in the range $1 \cdot 10^{-6}$ to $2 \cdot 10^{-6}$ moles $\cdot dm^{-3}$ in all experiments. Solution samples were taken at time intervals and analysed for ^{99}Tc . At the end of the reduction/sorption experiment with the electromagnetically separated fractions of light green coloured fracture filling material we removed the solution and washed each solid fraction with Ar purged water. The desorption of technetium into air saturated ground water and $3 \text{ mol} \cdot dm^{-3} H_2O_2$ by analysing the solution for ^{99}Tc as described above. The effect of ionic strength and pH on the reduction of TcO_4^- by magnetite was studied in perchlorate solutions.

2.3.2 Neptunium

Fe(II) solution: The polypropene reaction vessel containing a solution of $5 \cdot 10^{-7}$ mol $\cdot dm^{-3}$ Np(V) in $0.1 \text{ mol} \cdot dm^{-3} NaClO_4$ was flushed with a 1% H_2 / Ar mixture. On addition of $FeCl_2$ solution to a Fe(II) concentration of $1.6 \cdot 10^{-4}$ mol $\cdot dm^{-3}$ the pH decreased from 7.6 to 4.9. Solution samples, drawn with a syringe, were weighed and analysed for ^{237}Np . Three sampling techniques were tested; direct sampling, using a $0.45 \mu m$ filter and Np(V)/Np(IV) separation by liquid extraction.

Heterogeneous systems: Three experimental series of batch sorption experiments were carried out with electromagnetically separated fractions of fracture filling material, Al_2O_3 and magnetite (Fe_3O_4). 0.2 of fractions 2, 5 and 9 of fracture filling C (see Table 2) were added to air saturated ground water solutions containing $5 \cdot 10^{-6}$ mol $\cdot dm^{-3}$ Np(V).

Experiments with magnetite (specific surface area $6.6 \text{ m}^2 \cdot g^{-1}$) and Al_2O_3 ($102 \text{ m}^2 \cdot g^{-1}$) were carried out under oxic and anoxic conditions using 0.1 g solid and 4 cm^3 $0.1 \text{ mol} \cdot dm^{-3} ClO_4^-$ solution containing $5.5 \cdot 10^{-6}$ mol $\cdot dm^{-3}$ Np(V).

Solution samples were analysed for ^{237}Np as described above.

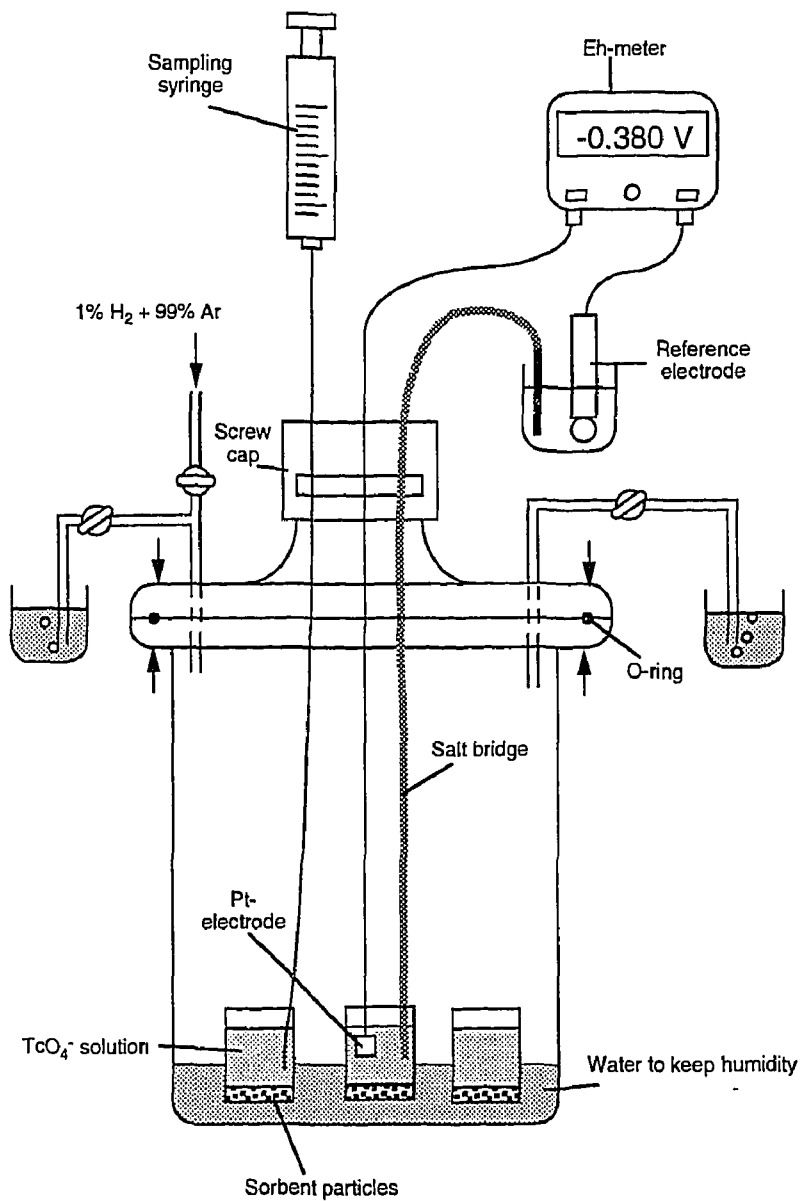


Figure 1

Equipment used for reduction of TcO_4^- by heterogeneous electron transfer from Fe(II) bearing solids.

Table 5. Experimental conditions.

exp.	solution	C_{Tc} $10^{-6}(M)$	inner atm.	sorbent	m/V (g/cm^3)	comments
1	SGW*	2.0	Ar	FCGM	1/10.5	S.-R.
2	SGW	1.6	Ar-H ₂	none	-	R.
3(1)	SGW	1.5	Ar-1%H ₂	MSSFF	1/7.5	S.-R.
3(2)	SGW	-	Ar	MSSFF	1/3.75	D.-O.
3(3)	SGW	-	Ar+air	MSSFF	1/3.75	D.-O.
3(4)	SGW	-	air	MSSFF	1/3.75	D.-O.
3(5)	SGW,H ₂ O ₂	-	air	MSSFF	1/3.75	D.-O.
4 (1)	NaClO ₄ , pH 9 0.1-10 ⁻⁴ M	1.2	Ar-1%H ₂	magnetite	1/1	S.-R. different ionic strength
4(2)	NaClO ₄ ,10 ⁻³ M pH 7.8-9.5	1.2	Ar-1%H ₂	magnetite	1/1	S.-R. different pH
4(3)	SGW	2.0	Ar+1%H ₂	magnetite	1/7	S.-R.

Note:

inner atm.: atmosphere in reaction vessels

SGW: synthetic groundwater

SGW*: synthetic groundwater equilibrated with Stripa granite

FCGM: Fe(II) containing geological material: granite, fracture fillings (A, B) from Stripa mine, and hornblende

MSSFF: magnetically separated Stripa fracture filling (C)

S.-R.: sorption-reduction process

D.-O. desorption-oxidation process

3 RESULTS AND DISCUSSION

In a study of the redox couple $TcO_4^-/TcO(OH)_2$ in aqueous solution saturated with a 30% H₂/70% N₂ mixture Guppy et al [4] observed that the reduction of TcO_4^- by H₂ is kinetically hindered. The possibility of using a H₂/Ar mixture as purging gas to prepare stable TcO_4^- solutions in oxygen free groundwater with low redox potential was therefore tested. The experimental data from this pretest are shown in Figure 2. The plot clearly demonstrates the stability of the TcO_4^- solution purged with 1%H₂/Ar and this gas composition was therefore used in most of the experiments.

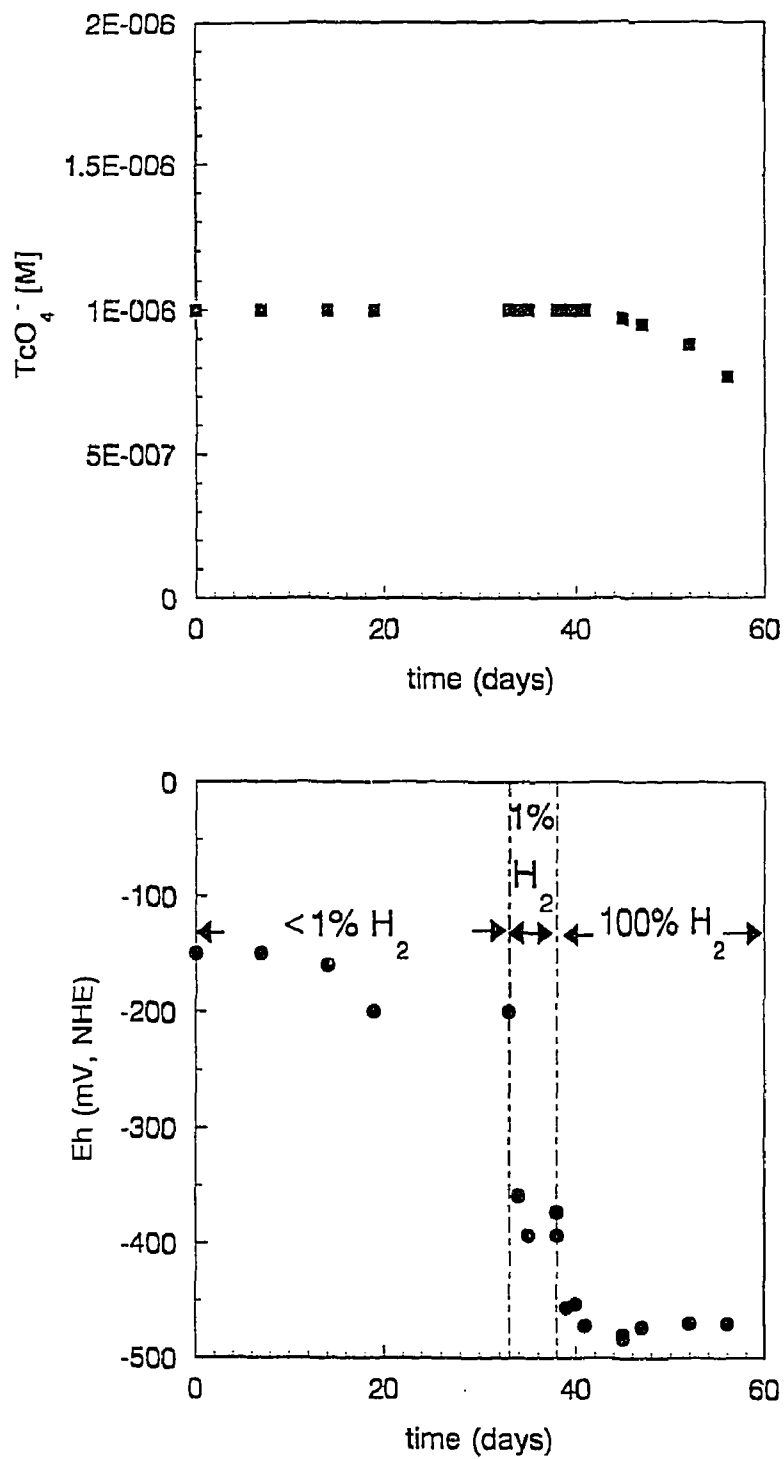


Figure 2

Pretest of TcO_4^- stability in solution purged with H_2 -Ar mixtures.

3.1 Technetium

Fe(II)-solution: The data from the first experiment, carried out in a reaction vessel with untreated inner surface are shown in $[\text{Fe(II)}]$, $[\text{Tc}]_{\text{tot}}$ and pH vs. time plots in Figure 3.

The initial Fe(II) concentration ($5.8 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$) decreased within a few hours to approximately $4.6 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$. The decrease in $[\text{Fe(II)}]$ was concurrent with a decrease in pH. The decrease in pH is too small to be explained by oxidation of Fe(II) followed by precipitation of Fe(III) as $\text{Fe(OH)}_3 (\text{s})$. The Fe(II) concentration was, following the initial decrease, found to be stable for at least one week. During this period the technetium - concentration slowly decreased from $3.3 \cdot 10^{-7}$ to $2.7 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$. On addition of NaOH, Fe(II) was precipitated as $\text{Fe(OH)}_2 (\text{s})$, the Fe(II) concentration in solution decreased to $3.4 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ at pH 8.6 and the technetium concentration decreased within two days to $< 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$

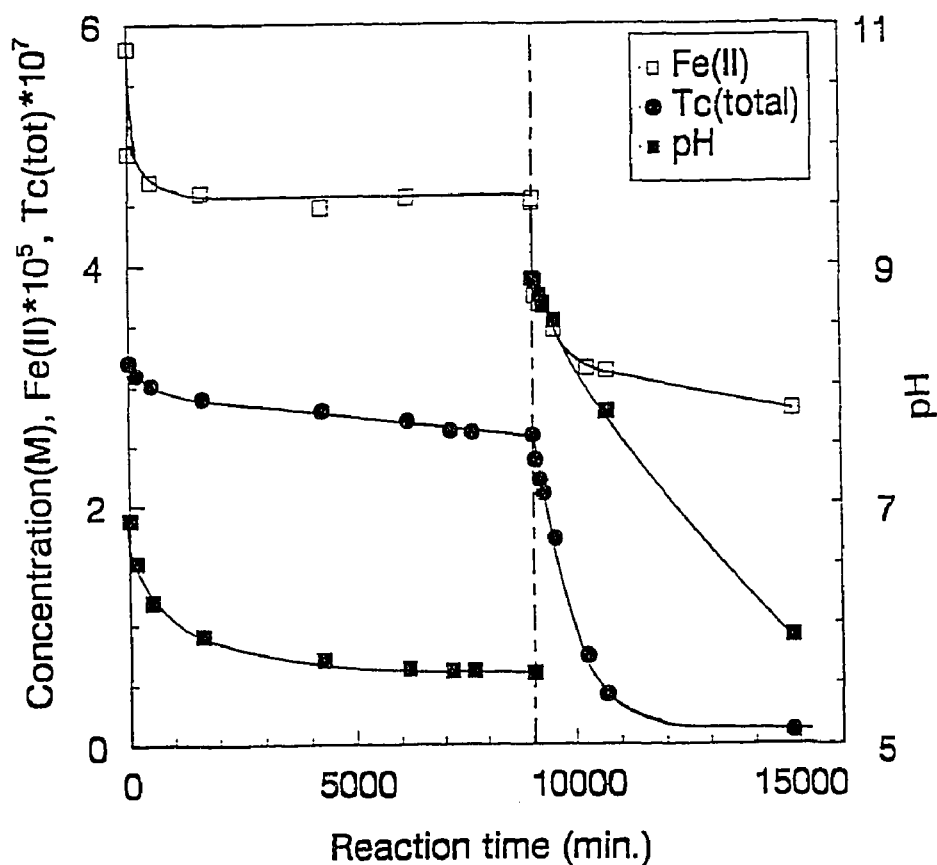


Figure 3.

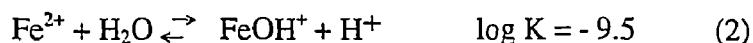
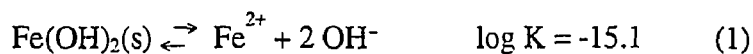
Concentration of Fe(II), Tc(tot) and pH of solution plotted against reaction time. Reaction vessel with untreated inner surface. Dotted line marks addition of NaOH.

The data from the experiment carried out in a reaction vessel with hydrophobic inner surface are plotted in Figure 4. In this experiment the initial decrease in the Fe(II)-concentration was smaller, $4.4 \cdot 10^{-5}$ to $4.2 \cdot 10^{-5}$ mol·dm⁻³, and no decrease in the Tc-concentration was observed. On addition of NaOH the Fe(II)-concentration decreased from 4.0 to $3.7 \cdot 10^{-5}$ mol·dm⁻³ and the Tc concentration decreased within 4 days from $2.2 \cdot 10^{-7}$ to $<10^{-8}$ mol·dm⁻³.

The data from the experiment with hydrophobic vessel surface and 2 g crushed quartz, with surface area $0.043\text{m}^2 \cdot \text{g}^{-1}$ added to the solution are plotted in Figure 5.

The initial Fe(II)-concentration decreased quickly from $4.64 \cdot 10^{-5}$ to $3.7 \cdot 10^{-5}$ mol·dm⁻³ and the Tc-concentration decreased from $5.2 \cdot 10^{-7}$ to $4.7 \cdot 10^{-7}$ mol·dm⁻³ within six days. On addition of NaOH the Fe(II)-concentration decreased quickly to $3 \cdot 10^{-5}$ mol·dm⁻³ and the Tc-concentration decreased from $4.7 \cdot 10^{-7}$ to $<10^{-8}$ mol·dm⁻³ within seven days.

The data from the three experiments can be explained as follows. Fe(II) in solution is reacting very slowly, if at all, with the pertechnetate anion. Fe(II) sorbed on the untreated vessel surface and quartz, presumably as the surface complex $>\text{SOFe}^+$, reacts slowly with TcO_4^- . Silylation of the vessel surface blocked the adsorptive hydroxyl groups and hence the Fe(II)-sorption, thereby decreasing the surface mediated reaction between sorbed Fe(II) and TcO_4^- . On addition of NaOH, Fe(II) was precipitated, the solubility of the "active" $\text{Fe}(\text{OH})_2(\text{s})$ precipitate is according to Stumm et al [14] given by the following hydrolysis reactions and equilibrium constants



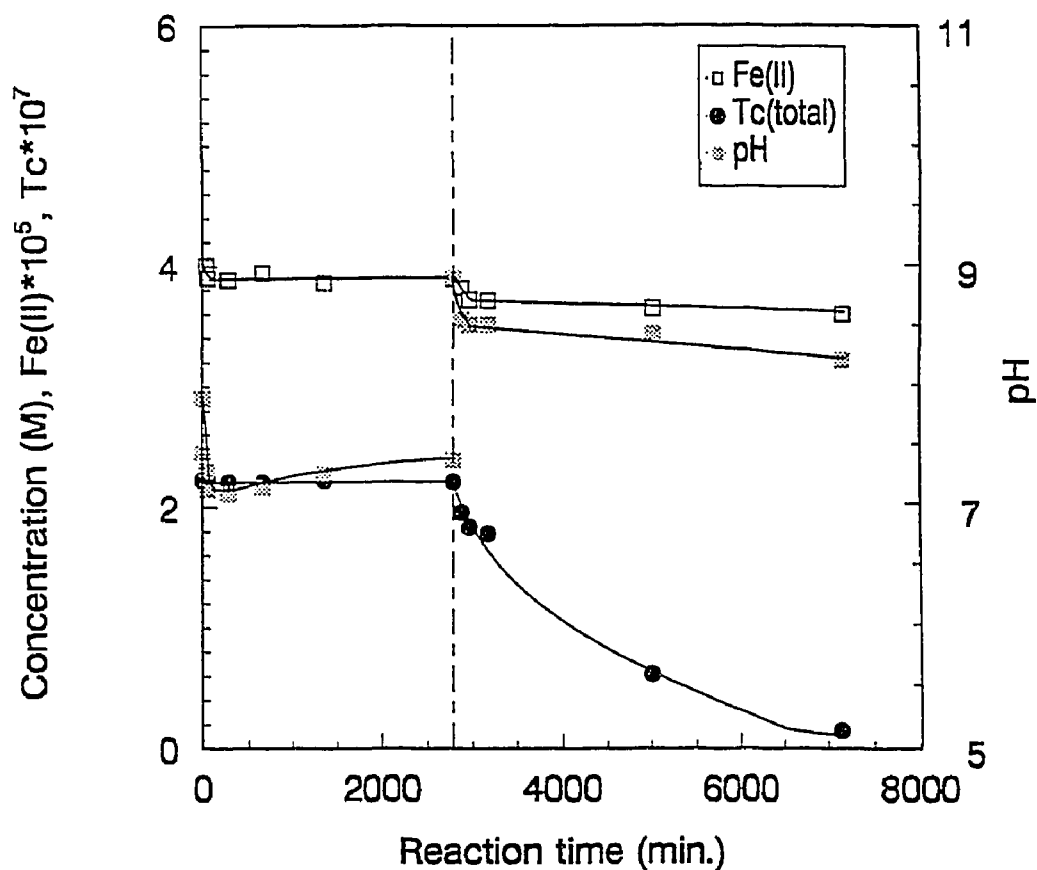


Figure 4.

Concentrations of Fe(II), Tc(tot) and pH of solution plotted against reaction time. Reaction vessel with treated hydrophobic surface. Dotted line marks addition of NaOH.

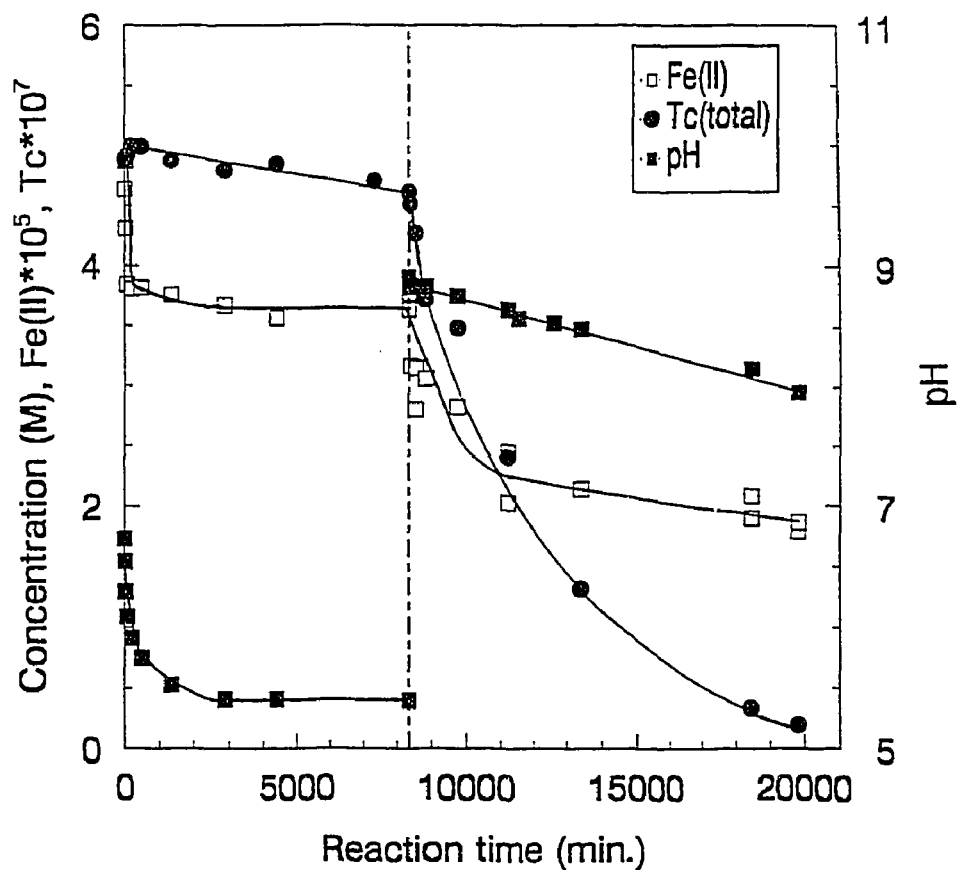


Figure 5

Concentration of Fe(II), Tc(tot) and pH of solution plotted against reaction time. The reaction vessel has treated, hydrophobic inner surface and 2g quartz ($0.043 \text{ m}^2 \cdot \text{g}^{-1}$) is added to the solution. Dotted line marks addition of NaOH.

The solubility of Fe(II), calculated from these equilibria are plotted in Figure 6 together with the Fe(II)-concentration in solution measured shortly after addition of NaOH. The disappearance of TcO_4^- from the solutions is most probably caused by reactions with the precipitated $\text{Fe(OH)}_2(\text{s})$. In an experiment with synthetic groundwater (Fig 7), with the composition given in Table 2, the solution was neutralised to pH 7.0. Following addition of FeSO_4 to an initial Fe^{2+} concentration of $4.6 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, the pH was gradually increased by purging the solution with $\text{Ar}(1\% \text{ H}_2)$ thereby removing CO_2 from the solution. No changes in Fe(II) or TcO_4^- concentration were observed before reaching pH 7.5. At $\text{pH} > 7.5$ Fe(II) was gradually precipitated, initially as $\text{FeCO}_3(\text{s})$ and with increasing pH probably as a mixture of $\text{FeCO}_3(\text{s})$ and $\text{Fe(OH)}_2(\text{s})$ (see Fig 6). The Fe(II)-precipitation was paralleled by a decrease in the technetium concentration to $< 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$, corresponding to the solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ obtained by Eriksen et al [1] in an earlier solubility study. Assuming pseudo first order kinetics for the disappearance of technetium from solution the rate constants obtained in the various experiments are plotted against the amount of precipitated Fe(II) in (Figure 8). A plausible mechanism for the disappearance of technetium from the solution is sorption of TcO_4^- on precipitated Fe(II) followed by surface mediated three electron reduction of TcO_4^- to $\text{TcO}_2 \cdot n\text{H}_2\text{O}$.

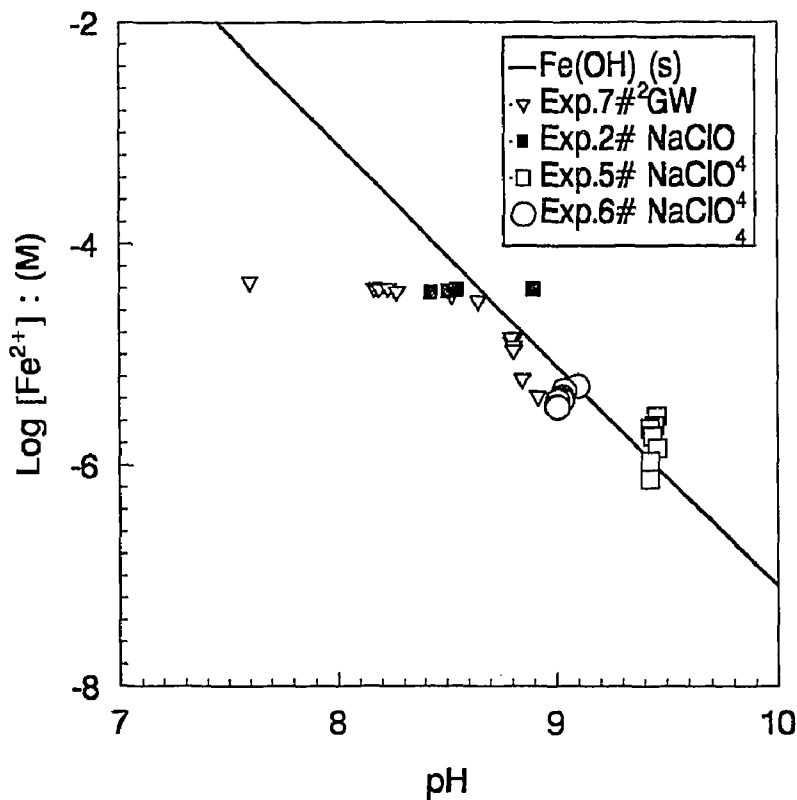


Figure 6.

Fe(II) concentration in solution after addition of NaOH plotted against pH. Full line gives solubility of "active" $\text{Fe(OH)}_2(\text{s})$ [19].

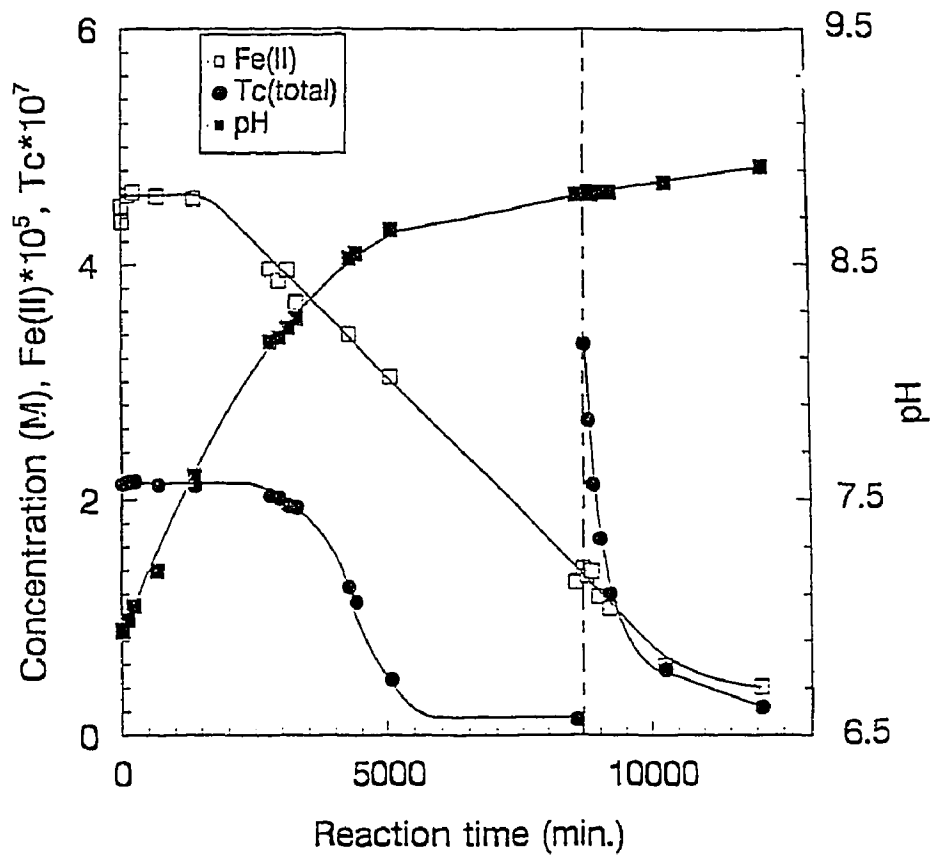


Figure 7

Concentrations of Fe(II), Tc(tot) and pH in a groundwater solution where the pH is changed by removal of CO₂. Dotted line marks addition of TcO₄.

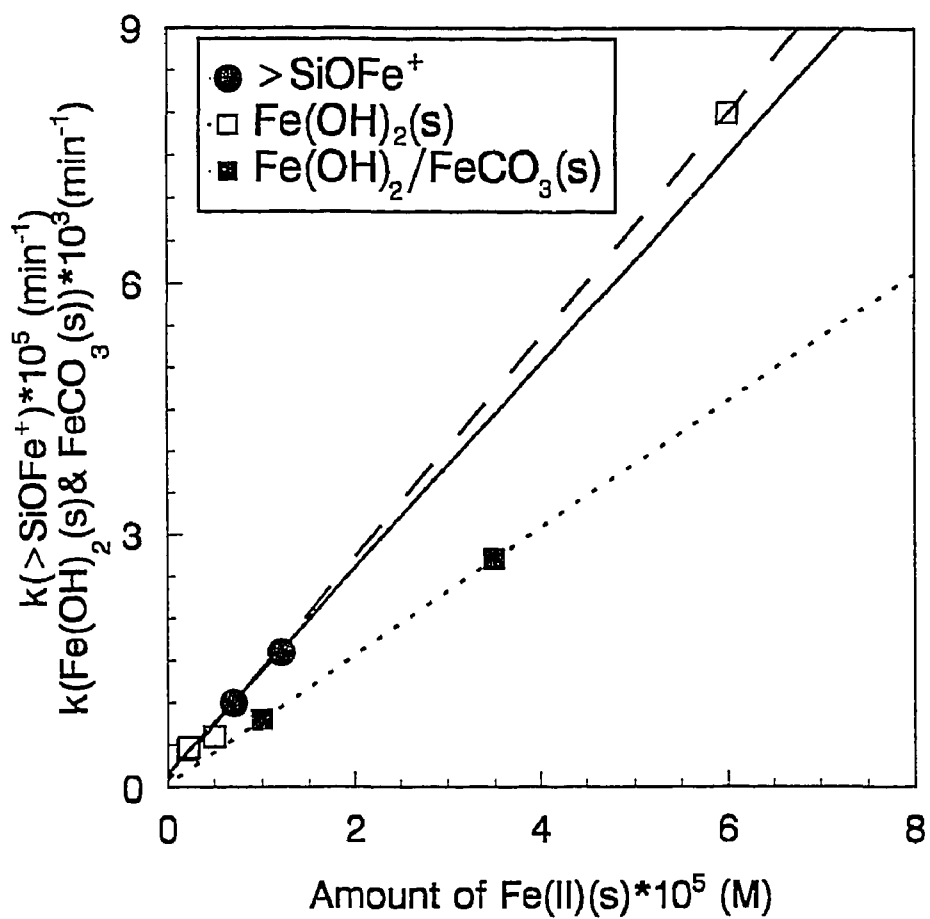
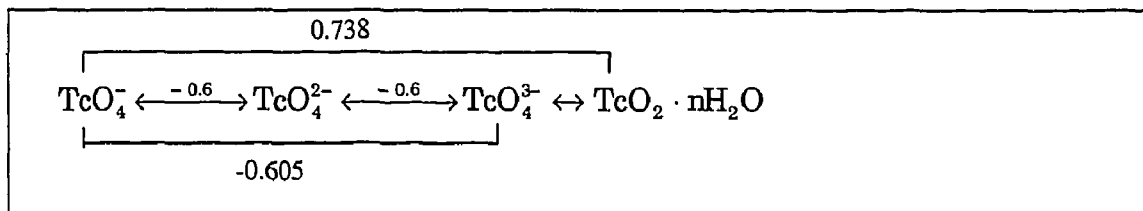


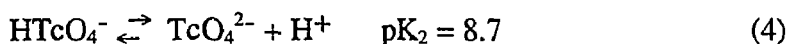
Figure 8

Rate constants for disappearance of Tc from solution obtained by regression analysis assuming the reaction to be pseudo first order, plotted against amount of sorbed/precipitated Fe(II). The amount of Fe(II) is given as concentration in solution.

Standard potentials (V,NHE) of the possible reaction paths leading from TcO_4^- to $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ [20,21] are given by



The one electron reduction of TcO_4^- has been studied by electrochemical [21] and radiation chemical [23-26] methods. Taken together these 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 $\text{pK}_1 = 0.3 (\pm 0.8)$ and $\text{pK}_2 = 8.7 (\pm 0.5)$ respectively [27] is unstable and disproportionates rapidly. Although different disproportionation reactions have been suggested [22, 28] the most probable one electron reduction path in alkaline solution seems to be



$$k_5 = 1.5 \cdot 10^5 \text{ (M}^{-1}\text{s}^{-1}\text{)}$$

The redox potential for the Fe(III)/Fe(II) couple is according to Grenthe et al [29] given by the equation

$$E = 0.707 - 2.303 (RT/F) (3 \text{ pH} + \log \text{Fe}^{2+}) \quad (6)$$

Assuming equilibrium to prevail between the redox couples $\text{TcO}_4^{2-}(\text{TcO}_4\text{H}^-)/\text{TcO}_4^-$ and Fe(II)/Fe(III) under the experimental conditions in this work we estimate the ratio

$$\text{TcO}_4^{2-}(\text{TcO}_4\text{H}^-)/\text{TcO}_4^- \text{ to be } < 10^{-5}.$$

The one electron transfer pathway may thus be expected to be very slow, which is indeed what is observed in this work.

Heterogeneous systems: The potentials measured in a series of experiments with granite, natural and electromagnetic separated fissure filling material from Stripa mine and hornblende as solid phases and Ar purged water from the reservoir with rock equilibrated groundwater are plotted in Figure 9. The potentials in the various systems studied varied within the range -150 to -60 mV vs. NHE as the experiments progressed. The rate of disappearance (k) of technetium from the solution was found to follow first order kinetics and in Figures 10a, b the experimental data are shown in $\ln[(\text{Tc})/(\text{Tc})_0]$ versus time plots. We observed no influence of the gradually changing Eh on the kinetics. By linear regression analysis we obtained rates of disappearance of technetium from the solution for a given solid to volume ratio. The calculated pseudo first order rate constants are given in Table 6. The reduction/sorption of TcO_4^- by magnetite was measured in ground water and in perchlorate solutions with different ionic strength and pH. Rates were calculated by regression analysis of $\ln[(\text{Tc})/(\text{Tc})_0]$ vs. time plots.

Table 6. Fe(II) content, surface area (BET) of Fe(II) containing materials and rate of TcO_4^- reduction in synthetic groundwater

geological material	exp.	Fe(II) cont. as FeO	surface $A(\text{m}^2 \cdot \text{g}^{-1})$	solid/solution $(\text{g} \cdot \text{cm}^{-3})$	rate of TcO_4^- reduction day^{-1}
fracture(A)	1	0.021	1.51	1/10.5	0.00348 ± 0.00014
fracture(B)	1	0.036	1.80	1/10.5	0.00398 ± 0.00025
granite	1	0.0082	0.65	1/10.5	0.00118 ± 0.00014
hornblende	1	0.079	0.44	1/10.5	0.00057 ± 0.00009
fracture(C)	3(1)	0.0123	1.02	1/7.5	0.00130 ± 0.00046
MSSFF(C).1	3(1)	0.212	1.80	1/7.5	0.00692 ± 0.00036
MSSFF(C).2	3(1)	0.0773	3.93	1/7.5	0.00544 ± 0.00016
MSSFF(C).3	3(1)	0.0332	4.29	1/7.5	0.00370 ± 0.00027
MSSFF(C).4	3(1)	0.0176	2.44	1/7.5	0.00150 ± 0.00040
MSSFF(C).5	3(1)	0.0111	0.97	1/7.5	0.00081 ± 0.00024
magnetite	4(3)	0.295	0.045	1/7.0	0.0639 ± 0.0041

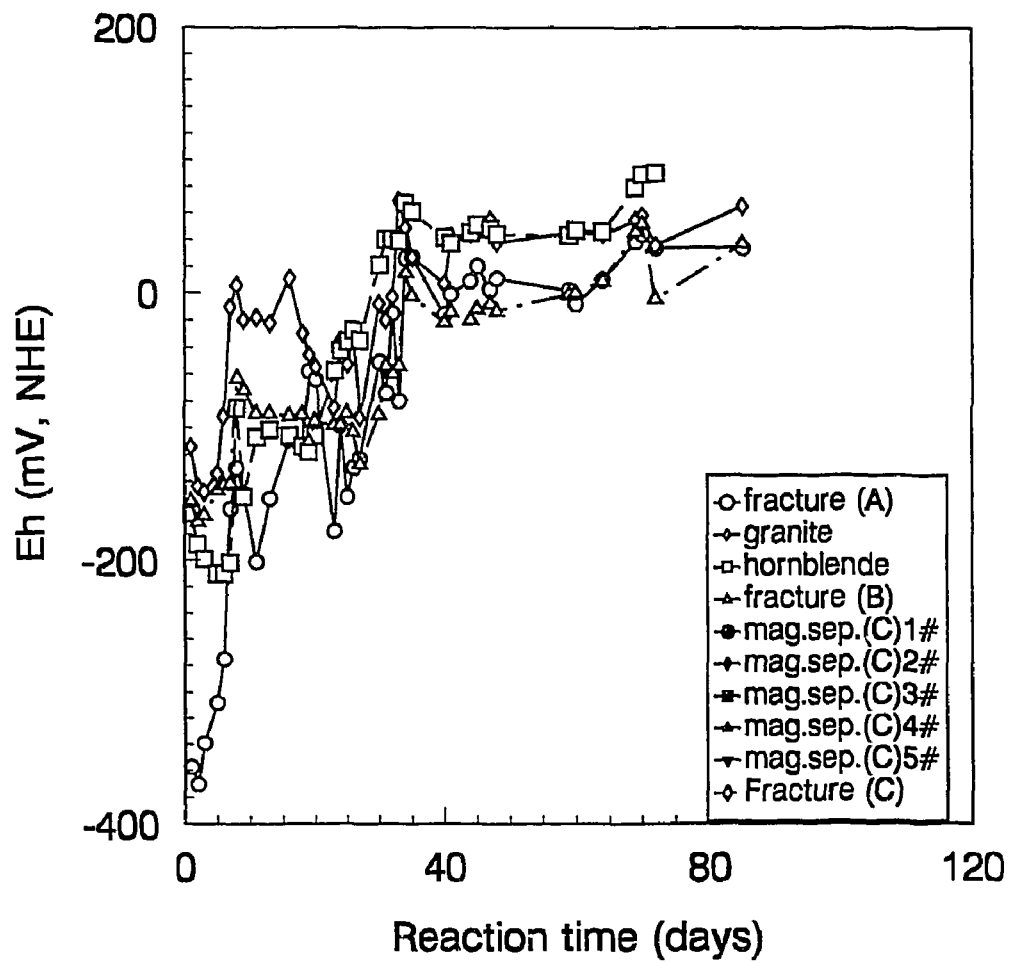


Figure 9

Measured redox potentials plotted versus reaction time for experiments (1 and 3 (1) see table 5).

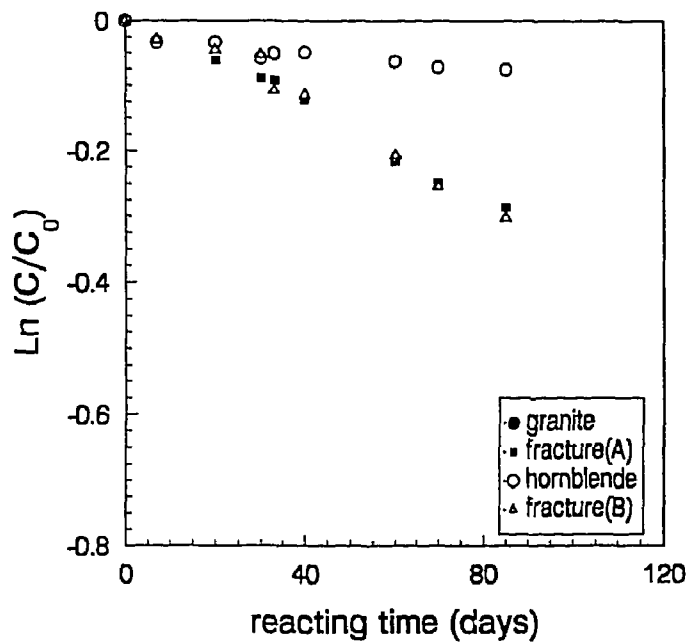
The electromagnetically separated fractions of the light green fracture filling material displayed great variation in specific surface area and Fe(II) content. From the mineral composition given in Table 2 it is evident that Fe-chlorite was the major Fe(II) bearing mineral in all fractions. Based on the assumption that the rate of reduction is controlled by a reaction step at the solid surface involving Fe(II) as reductant we have chosen to plot the rate constants (k) against $A \cdot f_{\text{FeO}}$ where A is the BET-area and f_{FeO} the Fe(II) content of the solid. As can be seen from Figure 11 the reaction rate is clearly correlated to the surface area and Fe(II) content of the solid.

When comparing the rates of disappearance of technetium from ground water solutions in contact with the different solids studied we have normalised the rates to 1:7 ($\text{g} \cdot \text{cm}^{-3}$) solid to volume ratio. The normalised rate constants are plotted against $A \cdot f_{\text{FeO}}$ in Figure 12. The plot clearly demonstrates the major influence of the Fe(II) content on the reduction/sorption of TcO_4^- on granite and fracture filling material.

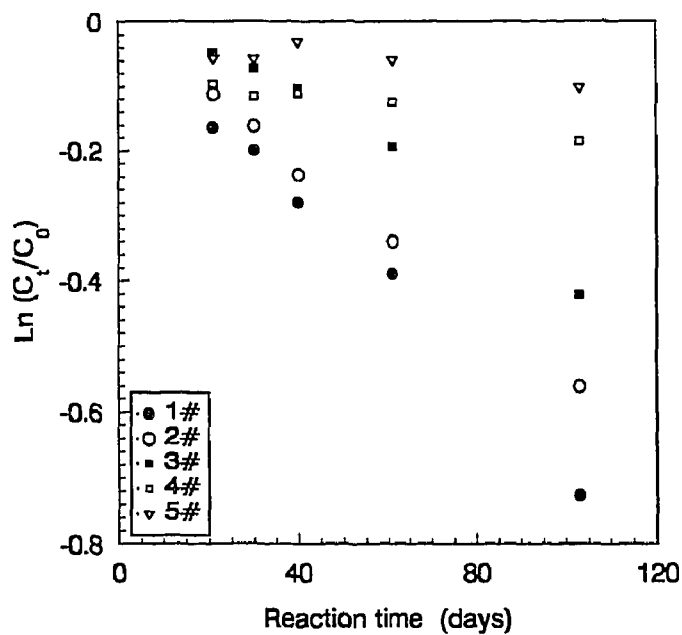
The two minerals hornblende and magnetite display very different reductive properties. Whereas hornblende, on the $A \cdot f_{\text{FeO}}$ scale, is reducing TcO_4^- somewhat less efficiently than the granite and fracture filling materials studied, magnetite is at least one order of magnitude more efficient. The influence of ionic strength on the reduction of TcO_4^- by magnetite in neutral to basic solution is demonstrated in Figure 13 where the rate constants for TcO_4^- disappearance from solution are plotted against $\log(I)$. Reduction of TcO_4^- by magnetite in different ground waters has been studied by Vandergraaf et al [12] and Byegård et al [3]. By regression analysis of the experimental concentration-time data given in their publications we have calculated the rates of TcO_4^- disappearance from solution. For comparison the calculated rate constants are plotted in Figure 14.

The rate constants obtained from analysis of the experimental data of Vandergraaf and co-workers are higher than the constants found in our work, but the plot indicates similar pH dependence. When comparing the experimental results the following differences in experimental conditions should be considered; our experiments were carried out at pH 8.2 with 125-250 μm particles and the rates are normalised to 1:7 ($\text{g} \cdot \text{cm}^{-3}$) solid to solution ratio whereas Vandergraaf et al [4] carried out their experiments at pH 7 with 1:10 solid to solution ratio and 100-180 μm particles.

Vandergraaf et al [4] give no information on the surface area of the solid phase so we make the simple assumption of spherical particles. The particle surface area to solution volume ratio is proportional to $(w/V) \cdot (1/d)$ where V is the solution volume, w is the weight of the solid and d the mean diameter of the particles. This ratio differs by less than 10% between the experiments carried out by Vandergraaf et al and in our work, clearly pointing at pH as an important parameter. In Figure 13 the rate constants for TcO_4^- reduction by magnetite in $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ perchlorate solution are plotted against pH. For comparison we have, based on the ionic strength dependence obtained from Figure 13, also plotted the ionic strength normalised rate constants for TcO_4^- reduction by magnetite in different ground waters. The regression analysis demonstrates a linear decrease in the rate of TcO_4^- reduction with increasing pH by more than one order of magnitude in the pH range 7 to 9.5.



a)



b)

Figure 10

Techneium concentration in solution samples, given as $\ln(C_t/C_0)$, from reduction experiments with TcO_4^- solutions and Fe(II)-bearing solids plotted versus time.
 a) Natural fissure filling material and minerals. b) Fractions of light green coloured fissure filling separated with respect to iron content.

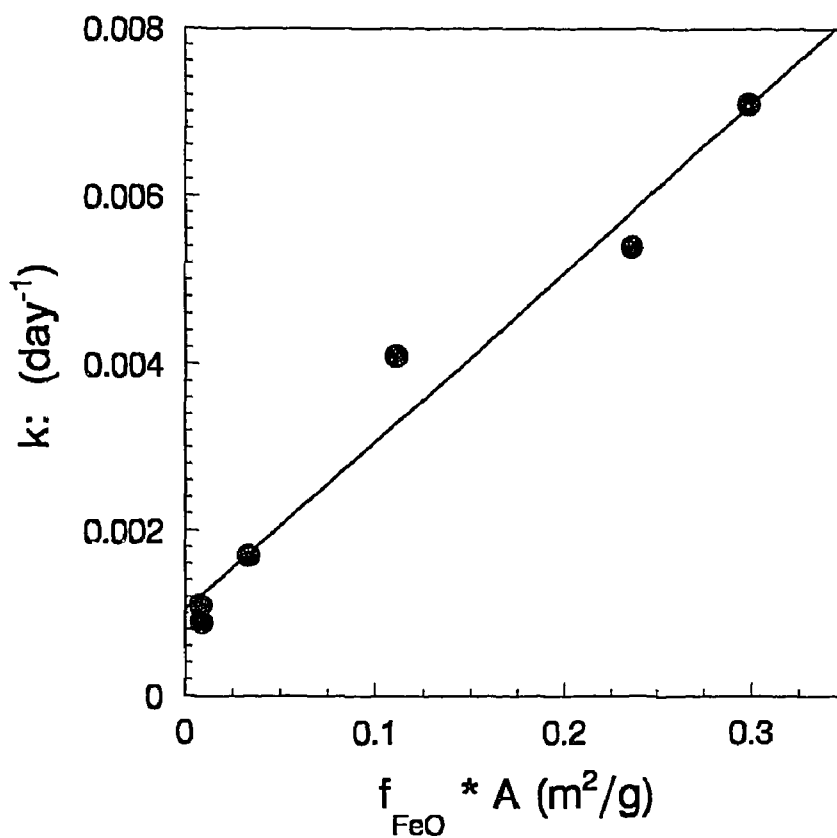


Figure 11

Pseudo first order rate constants for the disappearance of technetium from solution by reduction of TcO_4^- on electromagnetically separated fractions of the light green-coloured fissure filling (C) plotted against $f_{\text{FeO}} \cdot A$. A = BET surface area ($\text{m}^2 \cdot \text{g}^{-1}$) and f_{FeO} = iron content given as the mass ratio of FeO.

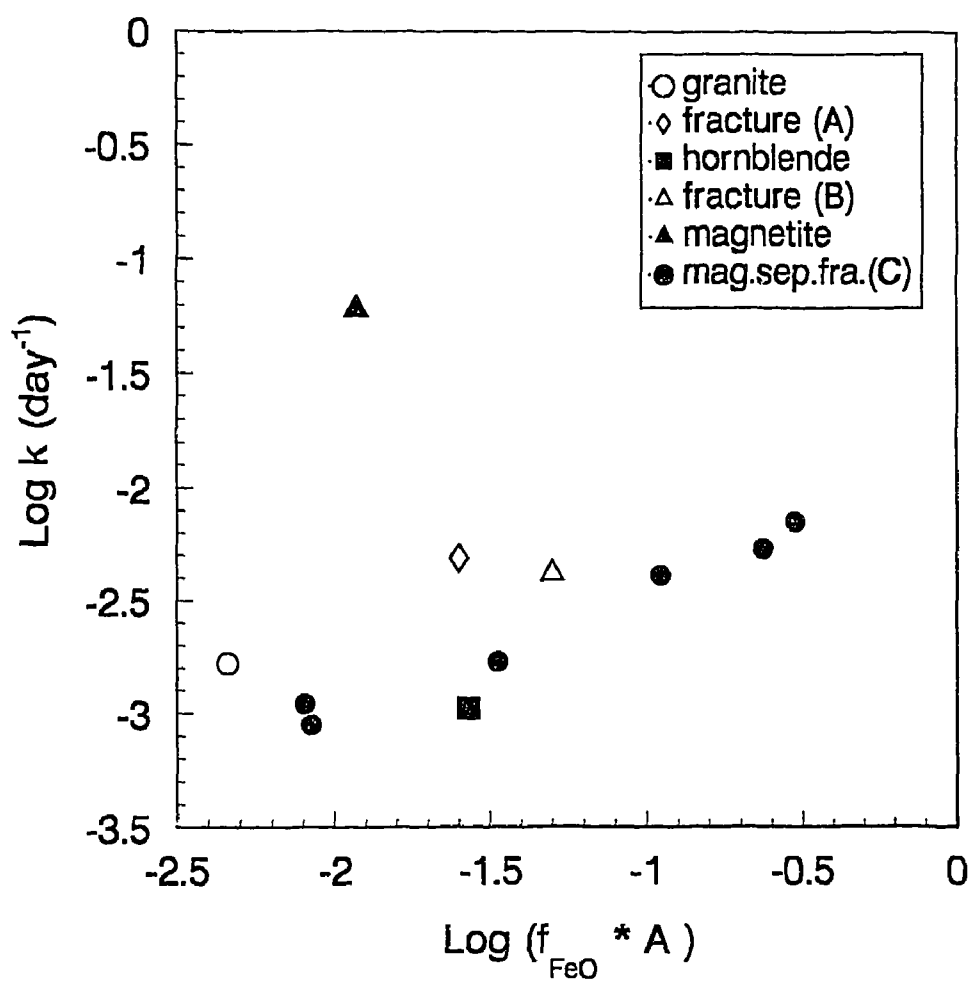


Figure 12

Logarithmic plot of pseudo first order rate constants for the disappearance of Technetium from solution by surface mediated reduction of TcO_4^- on Fe(II)-bearing solids. A = BET surface area ($\text{m}^2 \cdot \text{g}^{-1}$), f_{FeO} = Fe(II) content given as mass ratio of FeO. Solid to solution ratio 1:7 ($\text{g} \cdot \text{cm}^{-3}$).

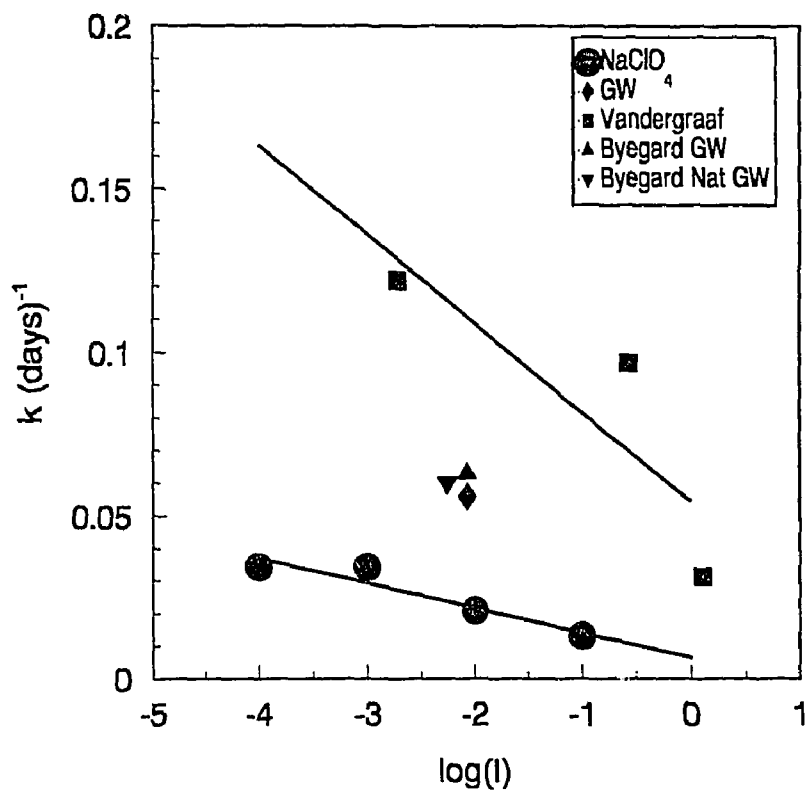


Figure 13

Effect of ionic strength on rate constant for reduction of TcO_4^- by magnetite. Vandergraaf et al : 100 - 180 μm particles, pH 7, solid to volume ratio 1:10 ($\text{g} \cdot \text{cm}^{-3}$); ClO_4^- solutions :125 - 250 μm particles, solid to solution ratio 1:7.

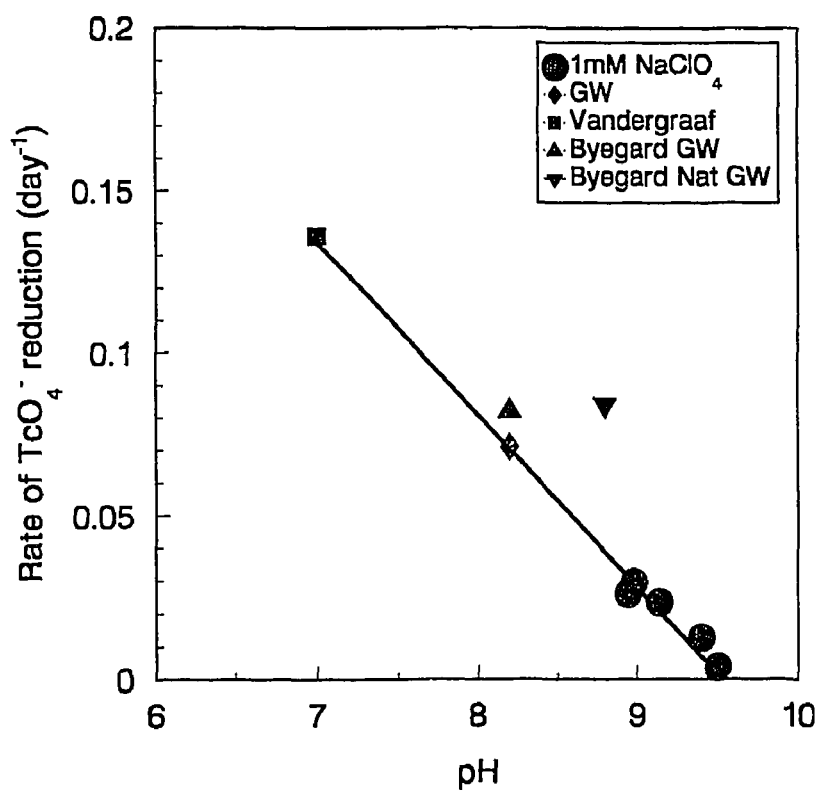


Figure 14

Effect of pH on the rate constant for the reduction of TcO_4^- by magnetite. Data from Figure 13 at ionic strength 0.1.

The pH dependent charge on hydrous oxide surfaces results from proton transfer at the surfaces and the protonation parameters for the equilibria



describing the surface speciation of magnetite are according to Regazzoni et al [30] $\text{pH}_{\text{zpc}} = 6.8$, $\text{p}K_{\text{a1}}^{\text{s}} (\text{int}) = 5.63$. The effect of pH on the surface speciation is shown in Figure 15.

The reduction of an oxidant in solution by heterogeneous electron transfer from structurally bound Fe(II) in minerals is a complex process involving sorption, electron transfer between the solid interface and the adsorbed oxidant, solid state electrochemical reactions and electron transfer. Magnetite has a very low band gap (0.1eV) between the valence and conduction band and fast electron transfer between Fe(II)- and Fe(III)- atoms [31]. The influence of ionic strength and pH on the rate of reduction of TcO_4^- in neutral to alkaline solution by magnetite indicates that sorption by a ligand exchange reaction [32] replacing surface OH group by TcO_4^- according to reaction (2) may be the rate determining step



If this assumption is true the rate of TcO_4^- reduction (r) should be proportional to the surface area of the solid phase and the surface concentration, denoted by brackets, of the species $>\text{SOH}$

$$r \propto A \cdot [>\text{SOH}] \quad (3)$$

In Figure 16 the experimental data are displayed in a $k_{\text{pH}}/k_{\text{pH}} = 7$ versus $[>\text{SOH}]_{\text{pH}} / [>\text{SOH}]_{\text{pH}} = 7$ plot. The slope obtained by linear regression analysis (0.96 ± 0.06) strongly corroborates the assumption that the ligand exchange mechanism is the rate determining step for the TcO_4^- sorption.

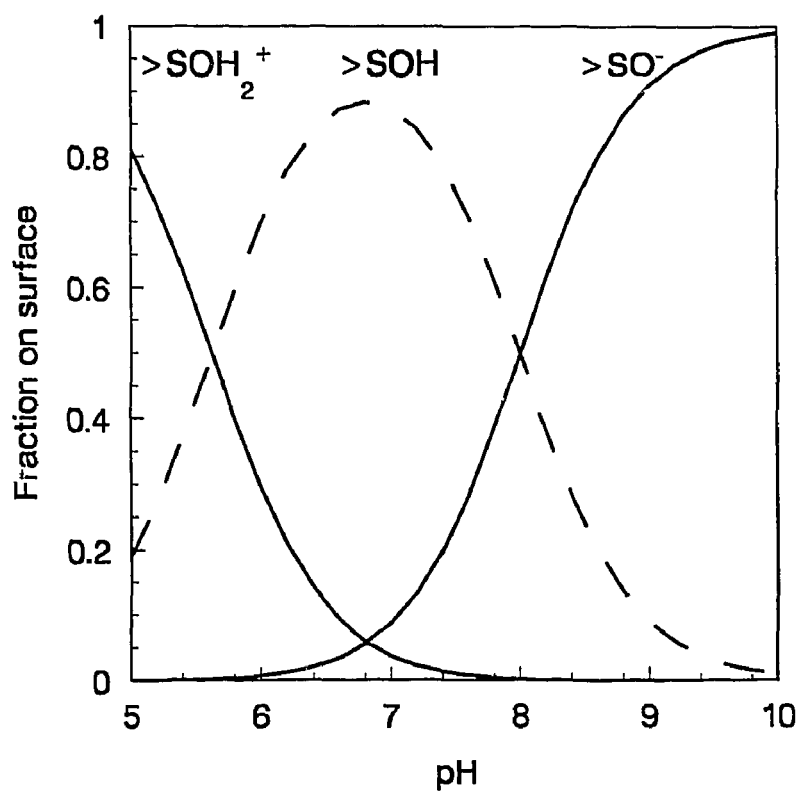


Figure 15

The protonation status of the magnetite surface as a function of pH.

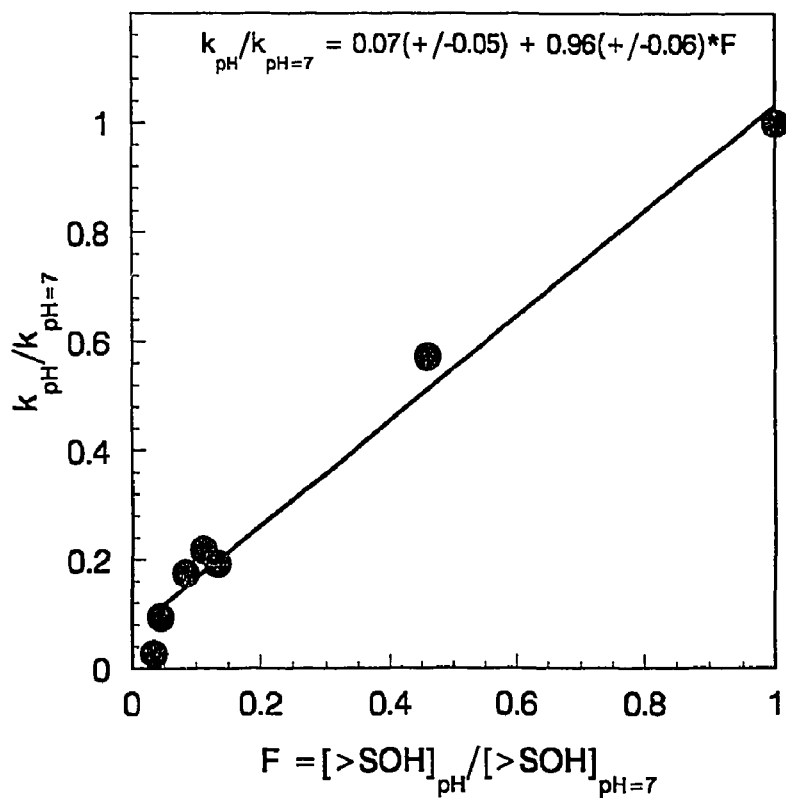


Figure 16

Relative rate constants for the reduction of TcO_4^- by magnetite, given as $k_{\text{pH}}/k_{\text{pH}=7}$, plotted against the fractional concentration of the uncharged surface species $>\text{SOH}$.

Desorption: Desorption of the reduced/sorbed technetium into argon purged and aerated solution was found to be a very slow process in agreement with the results from our previous experiments [10]. During three weeks exposure to air saturated ground water the technetium concentration, initially corresponding to the solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, increased but slightly (Figure 17). On addition of H_2O_2 to a concentration of $3 \text{ mol} \cdot \text{dm}^{-3}$ the leach solution a sudden increase in the technetium concentration was observed. A plausible explanation is that oxidation of the reduced technetium, sorbed or precipitated on the solid, is suppressed by competing reactions between oxygen and the surface of the Fe(II) bearing solid. On addition of H_2O_2 in high concentration the redox active reductant on the solid surface is consumed allowing the oxidation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ to Tc(VII).

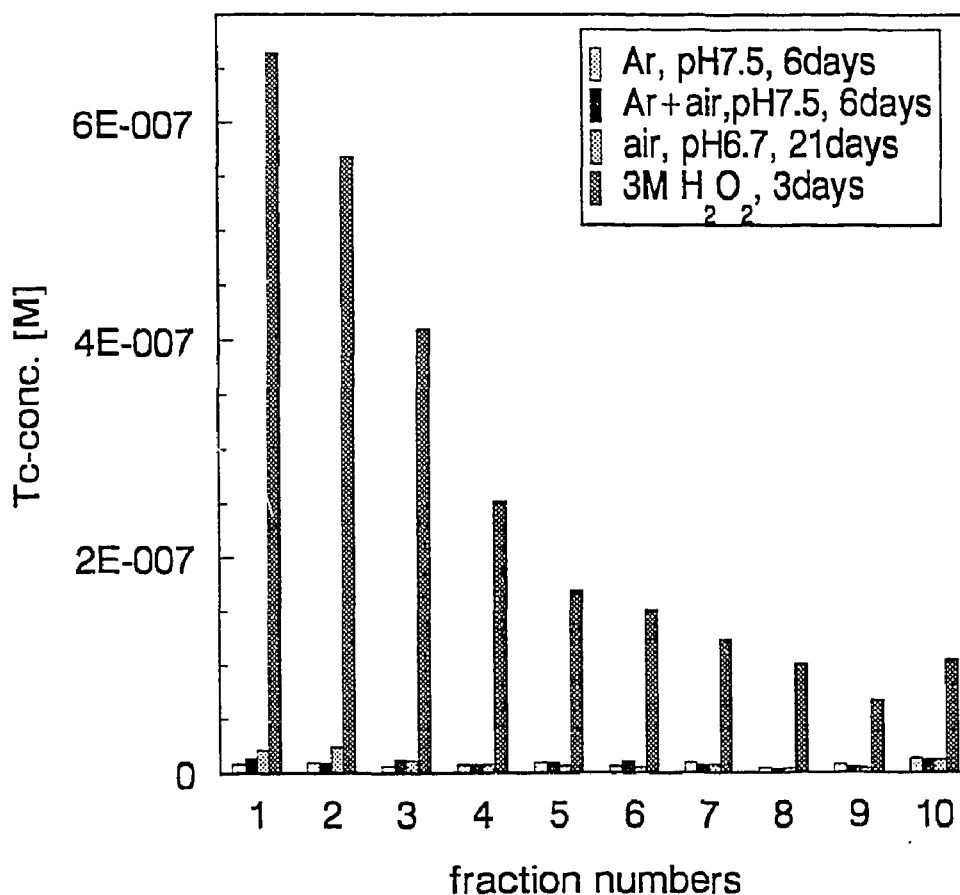


Figure 17

Desorption of technetium from electromagnetically separated fractions (1-9) of the light green coloured fracture filling (C) under different redox conditions. Initial concentration of Tc in the argon purged solutions corresponds to the solubility of $\text{TcO}_2 \cdot n \text{H}_2\text{O}$. Fraction 10 is the original fracture filling C.

3.2 Neptunium

Reactions of neptunyl in Fe^{2+} solution : The data from the solution experiment are shown in Eh and $[\text{Np}]_{\text{tot}}$ versus time plots in Fig. 18. Although reduction of Np(V) by Fe(II) in solution is thermodynamically feasible no reduction of NpO_2^+ was observed in the experiment and the reaction must be considered kinetically hindered.

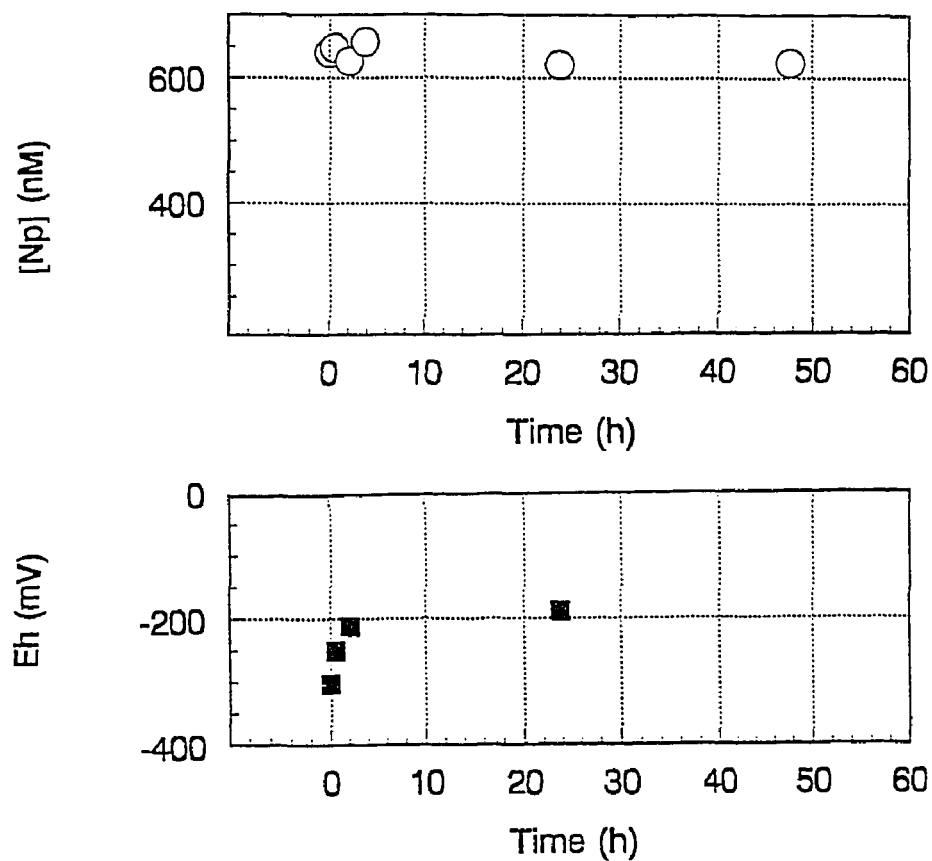


Figure 18

Neptunium concentration in 1% / Ar saturated Fe(II) solution plotted against time. Initial concentrations Fe(II) $1.6 \cdot 10^{-4} \text{ M}$, NpO_2^+ $6.7 \cdot 10^{-7} \text{ M}$.

Reactions of neptunyl in heterogeneous systems: The neptunyl cation NpO_2^+ is strongly sorbed on many minerals and the disappearance of neptunium from solution is not necessarily caused by reduction of Np(V) to Np(IV) .

In Fig. 19 the sorption of NpO_2^+ from air saturated groundwater onto three fractions of fracture filling material containing different amounts of clay material (and Fe(II)) are depicted in a R_d versus cationic exchange capacity (CEC) plot. The sorption is clearly correlated to the CEC of the solid phase.

Magnetite (Fe_3O_4) was found to be the most effective TcO_4^- reductant of the solids studied. A series of neptunium sorption experiments were performed with magnetite and for comparison redox inactive Al_2O_3 .

The data from three parallel experiments with 1% H_2 / Ar and air saturated 0.1 M perchlorate solutions of NpO_4^+ are shown in concentration versus time plots in Figures. 20 and 21.

When comparing the experimental data it should be born in mind that the specific surface area of the Al_2O_3 used was $102 \text{ m}^2 \cdot \text{g}^{-1}$ as compared to $6.6 \text{ m}^2 \cdot \text{g}^{-1}$ for the magnetite.

Whereas the time progress for the removal of neptunium from the solution by sorption of NpO_2^+ onto Al_2O_3 was found to be near identical from argon and (initially) air saturated solutions respectively this is clearly not the case for magnetite. In Fig. 22 we have replotted the magnetite data from in the form $\text{Log } R_d$ versus time. It is evident from the plots that the initial removal of neptunium is at least one order of magnitude faster from the argon saturated than from the air saturated solution. In both experimental series the initial fast removal of neptunium was followed by a slower removal process.

A plausible explanation for the difference in the initial time progress observed in the two experimental series is as follows. The fast initial removal of neptunium from solution is caused by fast surface mediated reduction of NpO_2^+ . The surface of the magnetite in contact with the air saturated solution was probably partly oxidised or covered by sorbed oxygen, thus being less effective than the magnetite in contact with the argon saturated solution. The slowing down of the reduction process with time is probably due to a gradual change from surface reaction to transport (diffusion) as the rate determining step at low NpO_2^+ concentration.

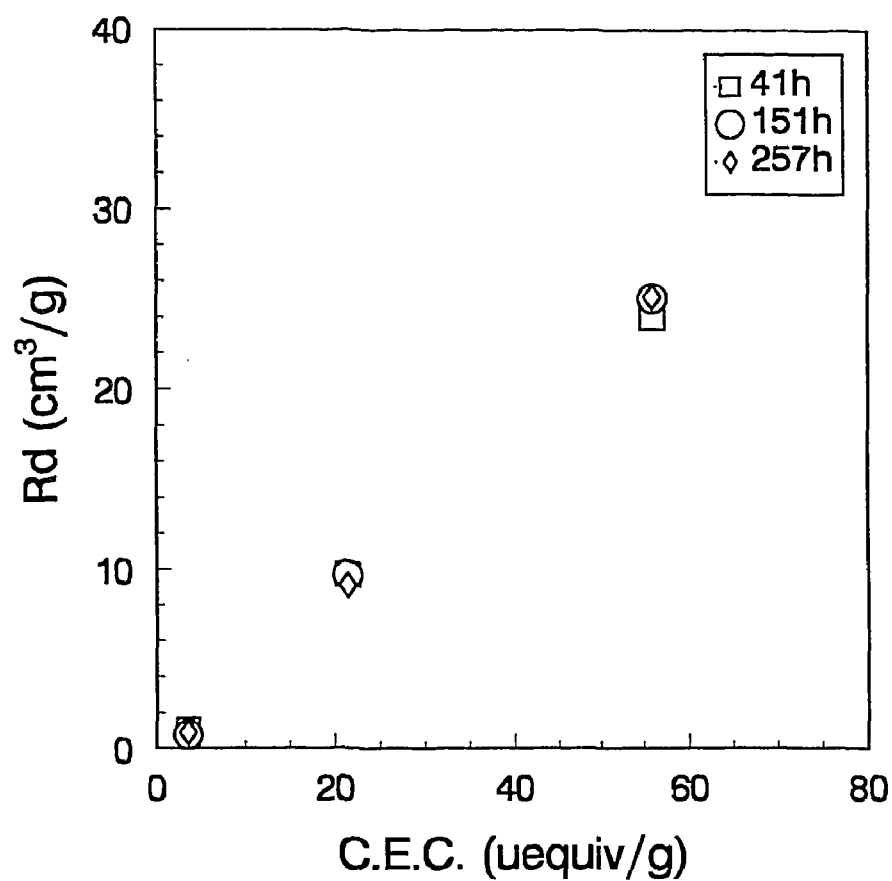


Figure 19

Sorption of NpO_2^+ from air saturated groundwater solution onto electromagnetically separated fractions of light green coloured fracture filling material (C) plotted against the cationic exchange capacity of the solid phase.

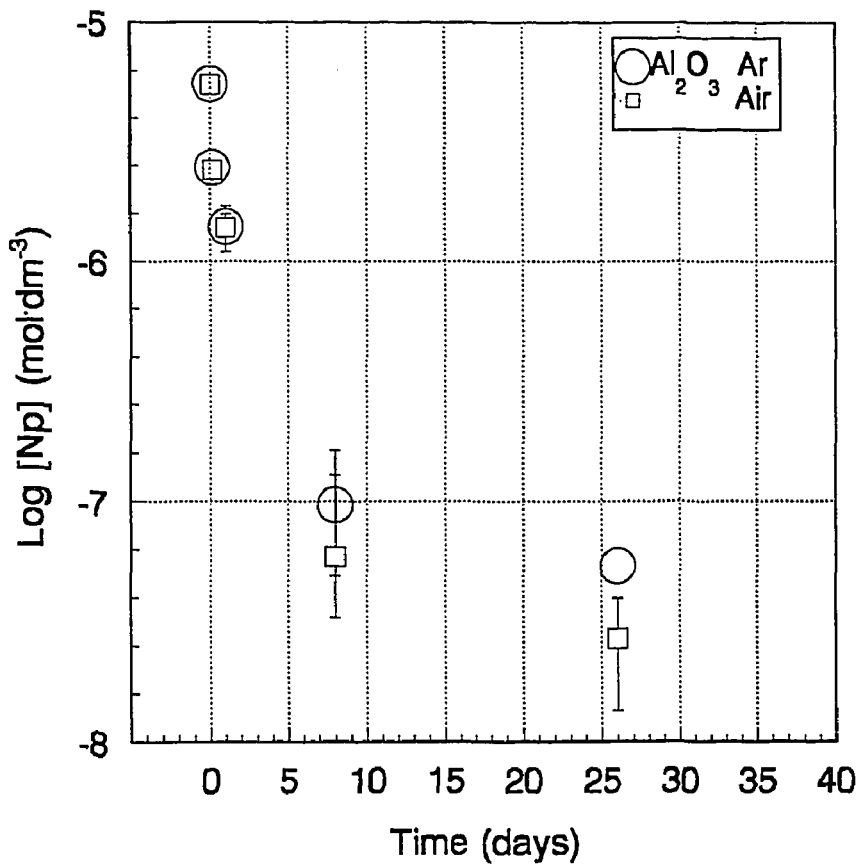


Figure 20

Neptunium concentration in 4 cm³ solution containing 1 g Al₂O₃ plotted against time.

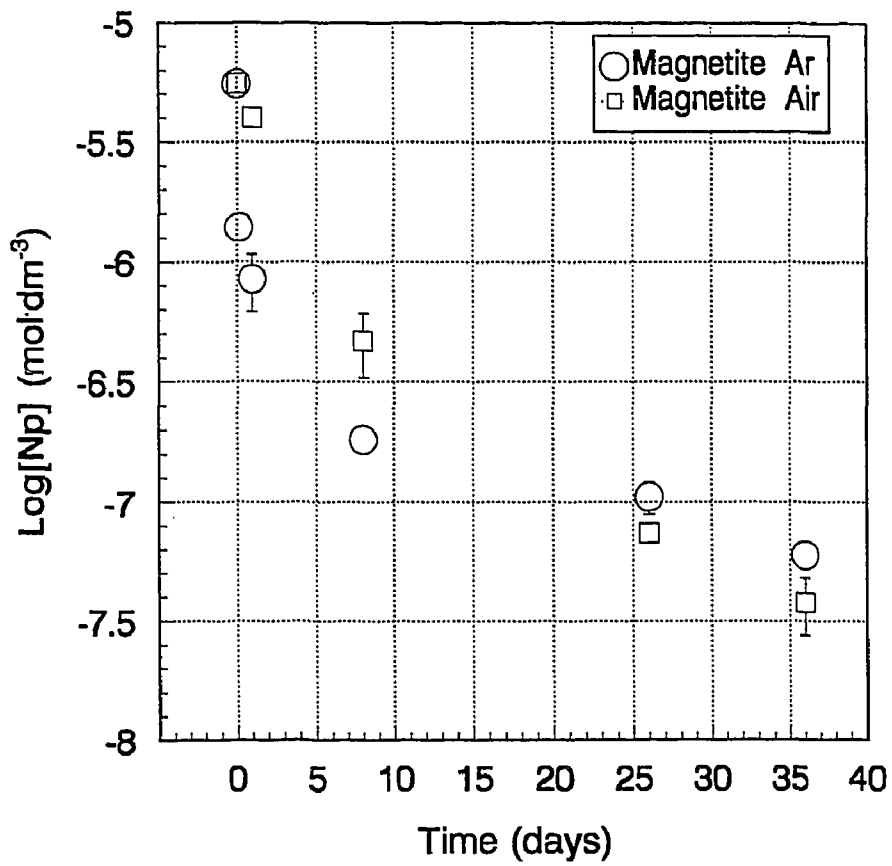


Figure 21

Neptunium concentration in 4 cm³ solution containing 1 g magnetite plotted against time.

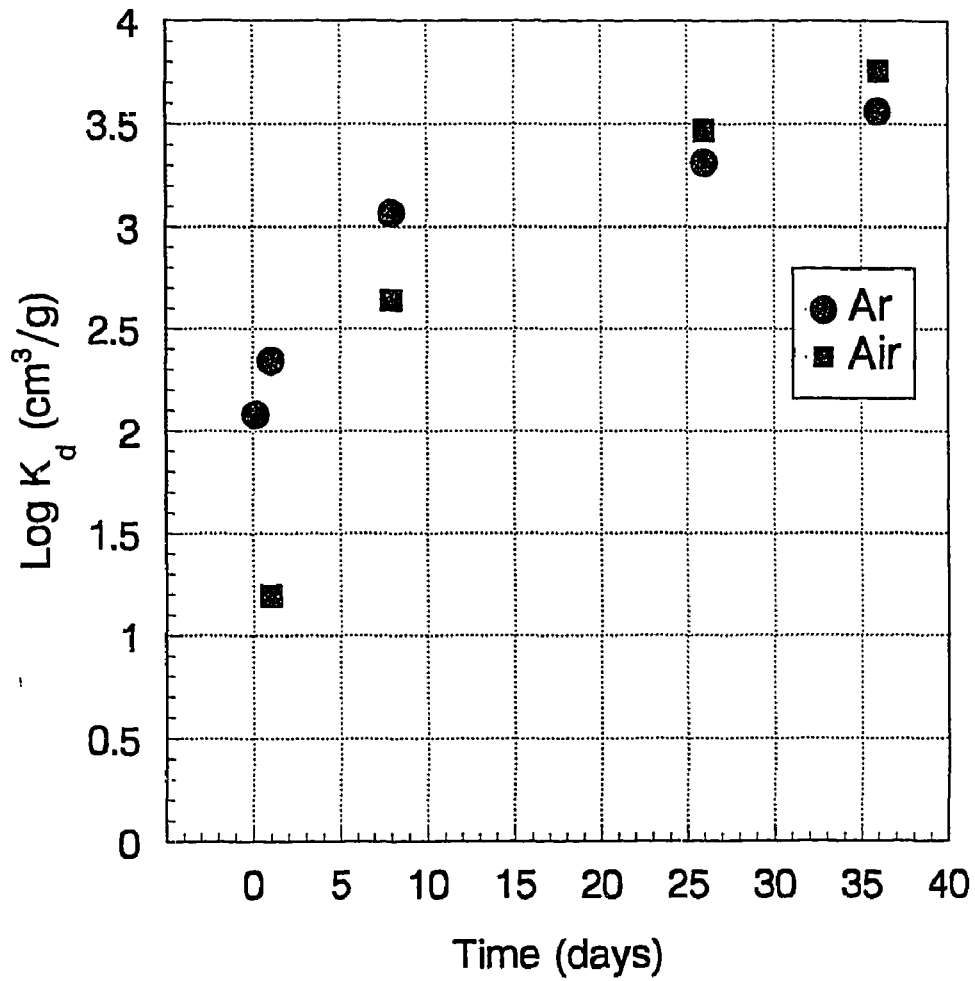


Figure 22

Removal of neptunium from 4 cm^3 solution by 1 g magnetite.

References

1. Eriksen T.E., Ndalamba P., Cui D., Bruno J., Caceci M. and Spahiu K. "Solubility of the redox-sensitive radionuclides ^{99}Tc and ^{237}Np under reducing conditions in neutral to alkaline solution. Effect of carbonate"
SKB-TR 93-18. Swedish Nuclear Fuel and Waste Management Co. Stockholm 1993
2. Grenthe I., Stumm W., Laaksoharju M., Nilsson A.-C. and Wikberg P.
Chemical Geology, 98 (1992) 131-150
3. Byegård J., Albinsson Y., Sharnemark G. and Skålberg M.
Radiochimica Acta 58/59 (1992) 239-244
4. Guppy R. M., Atkinson A. and Valentine T. M.
Studies of the solubility of technetium under a range of redox conditions.
HARWELL ARE-R 13467, DOE/RW/89/102 (1989)
5. Lieser K. H, and Bauscher C.H.
Radiochimica Acta 42 (1987) 205-213
6. Hakanen M., Lindberg A.
Technetium, neptunium and uranium in simulated anaerobic groundwater conditions.
Report YJT-95-02, Nuclear Waste Commission of Finnish Power Companies (1995)
7. Bonedetti E.A., and Francis C.W.
Science 203 (1979) 1337-40
8. Allard B.
Actinide and technetium solubility limitations in groundwater of crystalline rock.
Sci. Basis Nucl. Waste Manag, (VII) (Ed) Mc Vay G.L., 219-226 (1984)
9. Allard B., Kipatsi H. Torstenfelt B
Radiochem. Radioanal. Letters 37 (1979) 223-9
10. Eriksen T.E. and Cui D.
On the interaction of granite with Tc(IV) and Tc(VII) in aqueous solution.
SKB TR, 91-47 Swedish Nuclear Fuel and Waste Management Co. Stockholm 1991.
11. Vandergraff T. T., Ticknor K.V. and George I. M. in "Geological Behaviour of Radioactive Waste G. Scott Barney (Ed)
Am. Chem. Soc. Symp. Ser 246, 24 (1984)
12. Haines R.I., Owen R. I. and Vandergraff T. T.
Nucl. J. Canada 1:1 (1987) 32-37
13. Graff P.R.
Determination of FeO in Geological Materials.
Nor. Geol. Unders., 388 (1983) 2-12

14. Novotny M, Zlatkis A
Chromatogr.Rev.14, 1-14, (1971)
15. Meites L
Handbook of Analytical Chemistry, sect 4,p 3
Mc Graw Hill 1963,
16. Fortune W B, Mellon M G
Ind. and ENG. Chem. 10.2, 60-64,(1938)
17. Wikberg, P.
The chemistry of deep groundwater in crystalline rock. Dissertation, The Royal
Institute of Technology, Stockholm (1987)
18. Eriksen T.E
Radionuclide transport in a single fracture. A laboratory flow system for transport
under reducing conditions.
SKB TR 88-28, Swedish Nuclear Fuel and Waste Management Co. Stockholm (1988)
19. Stumm W, Morgan
Aquatic Chemistry J.Wiley & Sons 1981, p 241
20. Rard J
Critical Review of the Chemistry and Thermodynamics of Technetium and Some of its
Inorganic Compounds and Aqueous Species
UCRL-53440, 1983
21. Hughes M A, Rossotti F J C
A review of some aspects of the solution chemistry of technetium.
AERE R-1280, 1987
22. Kissel G, Feldberg S W
J.Phys Chem 73, 3082-8, 1969
23. Pikaev A K, Krychkov S V, Kuzina A F, Spitsyn V
Dokl.Phys.Chem 236, 992-5, 1977
24. Deutch E, Heineman W R, Hurst R, Sullivan J C, Mulac W A, Gordon S
J.Chem Soc,Chem Commun 1038-40, 1978
25. Heller-Grossman L, Abrashkin S, Schafferman H, Davies M A, Taube R A
Int.J.Appl.Radiat Isot 32, 501-6, 1981
26. Libson K, Sullivan J C, Mulac W A, Gordon S, Deutch E
Inorg.Chem 28, 375-7, 1989
27. Krychkov S V, Pikaev A K,Kuznia A F,Spitsyn V I
Proc.Acad.Sci,USSR, Phys Chem Sect 247,690-2,1979

28. Bratu C, Bratu G U, Galetanu I, Roman M
J. Radioanal. Chem. 26, 5-16, 1975
29. Regazzoni, A. E., Blesa, M. A. and Maroto, A. J. G.
J. Coll. Interf. 91 (1983) 560-570
30. White, A. F.
Heterogeneous electrochemical reactions associated with oxidation of ferrous oxide
and silicate surfaces.
Hochella M. F. and White A. F. (Eds) Reviews in Mineralogy Vol. 23 (1990) p467
31. Stumm W., Sulzberger B.
Geochimica et Cosmochimica Acta 56 (1992) 3233-57

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Bacteria, colloids and organic carbon in groundwater at the Bangombé site in the Oklo area

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February 1996

TR 96-02

Microbial analysis of the buffer/container experiment at AECL's Underground Research Laboratory

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