On the solubility of technetium in geochemical systems

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SUMMARY

The solubility of technetium under groundwater conditions has been calculated from hydrolysis and redox data.

Under reducing conditions (Eh < 0.27-0.06pH, V) a formation of elementary Tc(s) is feasible. Total concentrations in solution may go down to the 10^{-9} M-level or below.

Under mildly reducing conditions (Eh between 0.27-0.06pH and 0.45-0.06pH) a constant solubility of the order 10^{-5} M would be achieved, limited by $TcO_2(s)$ and with $TcO(OH)_2$ as dominating species in solution.

At higher redox potentials (Eh > 0.5-0.06pH) the heptavalent TcO_4^- dominates entirely, and no solubility limiting phase would be expected in most natural waters.

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1   INTRODUCTION

Technetium (as ^{99}Tc, half-life 2.14×10^5y) is one of the fission products in spent nuclear fuel that may contribute significantly to the long-term biological hazards from reprocessing waste and spent fuel.

Some calculations on technetium speciation and solubilities in environmental waters are given in this report.

2   TECHNETIUM CHEMISTRY IN AQUEOUS SOLUTIONS

Technetium can exist at least in the oxidation states II, III, IV and VII in aqueous solutions. The corresponding ions Tc^{2+}, TcO^+, TcO^{2+} and TcO_4^-, respectively, have been suggested in the absence of complexing agents. The lower oxidation states (II and III) would only exist under highly reducing conditions, and any intermediate oxidation state that could possibly exist (V and VI) are prone to disproportionation. Thus, the oxidation states of prime importance for natural water systems are IV and VII. The data on hydrolysis and redox chemistry given below are taken from recent papers or reviews on technetium chemistry (1-7).

2.1   HYDROLYSIS AND COMPLEX FORMATION

The only complexing reactions of importance in environmental waters appear to be hydrolysis processes. Technetium forms strong hydroxide complexes in the tetravalent state, Table 1. The corresponding neutral hydroxide, $TcO(OH)_2(s)$, has a low solubility and tends to dehydrate, forming the even more sparingly soluble oxide phase $TcO_2(s)$.

No information is available concerning the hydrolysis of Tc(II) and Tc(III).

Table 1   Hydrolysis and solubility limiting reactions.

Oxidation state	Reaction	log K
7	$TcO_4^- + M^+ = MTcO_4(s)$	-2^a
4	$TcO^{2+} + OH^- = TcOOH^+$	12.6
4	$TcO^{2+} + 2OH^- = TcO(OH)_2$	24.6
4	$TcO^{2+} + 2OH^- = TcO_2(s) + H_2O$	-28.9^a
3	$TcO^+ + OH^- = TcOOH$	?
2	$Tc^{2+} + OH^- = TcOH^+$	?

[a] Solubility product.

The only sparingly soluble compounds of environmental interest, besides the tetravalent oxide, are $MTcO_4(s)$, where M is a monovalent cation (K^+, possibly Na^+?), and $Tc_2S_7(s)$. None of these two compounds would be expected to act as solubility limiting species under the conditions normally encountered in e.g. deep groundwaters, since the concentrations of both monovalent cations and S^{2-} are far too low.

2.2   REDOX REACTIONS

Measured standard potentials for technetium redox reactions are collected in Table 2.

From these potentials and the hydrolysis constants for Tc(IV) in Table 1, the standard potentials in Table 3 for non-hydrolysed species in solution have been calculated (using the Nernst equation $E = E^o + (RT/nF)\ln([Ox] / [Red])$).

3   CALCULATED TECHNETIUM SOLUBILITIES

Speciation and concentrations of the various technetium species have been calculated under the following assumptions:

o pH in the range 5-11 (often 7-9 in deep groundwaters

o Eh$>$0.2-0.06pH, V

(cf. Eh = 0.21-0.06pH in the $Fe_2O_3(s)/Fe_3O_4(s)$-system, and Eh $\approx$ 0.8-0.06pH in aerated systems).

No other complexing reactions than the formation of hydrolysis products have been considered.

Table 2   Redox reaction and standard potentials.

Oxidation states	Reaction	Standard potential, V
7-4	$TcO_4^- + 4H^+ + 3e^- = TcO_2(s) + 2H_2O$	0.738
7-0	$TcO_4^- + 8H^+ + 7e^- = Tc(s) + 4H_2O$	0.472
4-3	$TcO_2(s) + 2H^+ + e^- = TcO^+ + H_2O$	0.319
4-2	$TcO_2(s) + 4H^+ + 2e^- = Tc^{2+} + 2H_2O$	0.144
4-0	$TcO_2(s) + 4H^+ + 4e^- = Tc(s) + 2H_2O$	0.272
3-2	$TcO^+ + 2H^+ + e^- = Tc^{2+} + H_2O$	-0.031
3-0	$TcO^+ + 2H^+ + 3e^- = Tc(s) + H_2O$	0.256
2-0	$Tc^{2+} + 2e^- = Tc(s)$	0.400

Table 3   Calculated standard potentials assuming log K_s = -28.9 for $TcO_2(s)$ and potentials according to Table 2.

Oxidation states	Reaction	Standard potential, V
7-4	$TcO_4^- + 6H^+ + 3e^- = TcO^{2+} + 3H_2O$	0.72
7-3	$TcO_4^- + 6H^+ + 4e^- = TcO^+ + 3H_2O$	0.633
7-2	$TcO_4^- + 8H^+ + 5e^- = Tc^{2+} + H_2O$	0.500
4-3	$TcO^{2+} + e^- = TcO^+$	0.37
4-2	$TcO^{2+} + 2H^+ + 2e^- = Tc^{2+} + H_2O$	0.17
4-0	$TcO^{2+} + 2H^+ + 4e^- = Tc(s) + H_2O$	0.28

Under reducing conditions (up to Eh = 0.27-0.06pH), a reduction to metallic Tc(s) is feasible. Dominating species in solution would be $TcO(OH)_2$, and possibly also TcO^+ at low pH and highly reducing conditions (Eh < 0.2-0.06pH), Fig. 1a.

Under mildly reducing conditions (Eh > 0.27-0.06pH) the solubility limiting phase would be $TcO_2(s)$, with $TcO(OH)_2$ as dominating soluble species up to Eh = 0.5-0.06pH, Fig. 1b.

The heptavalent state (TcO_4^-) would dominate at Eh > 0.5-0.06pH, still with $TcO_2(s)$ as solubility limiting phase.

The total solubility under highly reducing conditions would be as low as 10^{-9} M or below (less than μg/l) and would increase to 10^{-4}-10^{-5} M (mg/l-level) with increasing Eh (cf. Fig. 2). This concentration, which would be constant at Eh between 0.27 and 0.45 V, is related to the choice of solubility product for $TcO_2(s)$ and should be considered as a maximum value. By using log K_s = -31, which was previously suggested (2), instead of log K_s = -28.9 (Table 1) which is an assessed maximum value, the resulting total technetium solubility at Eh between 0.27 and 0.45 V would be less than 10^{-6} M.

At Eh above 0.45-0.50 V the solubility is increasing up to at least 10^{-1}-10^{-2} M, which would be the solubility limit set by a $MTcO_4(s)$-species, assuming a concentration of monovalent cations M^+ of 0.1 M (g/l-level). This could possibly be achieved in very saline waters, but rarely under groundwater conditions.

4   CONCLUSIONS

The following conclusions can be made concerning the solubility of technetium in natural waters, particularly deep groundwaters.

o Under highly reducing conditions the solubility can be as low as 10^{-9} M or below; a reduction to elementary technetium is feasible.
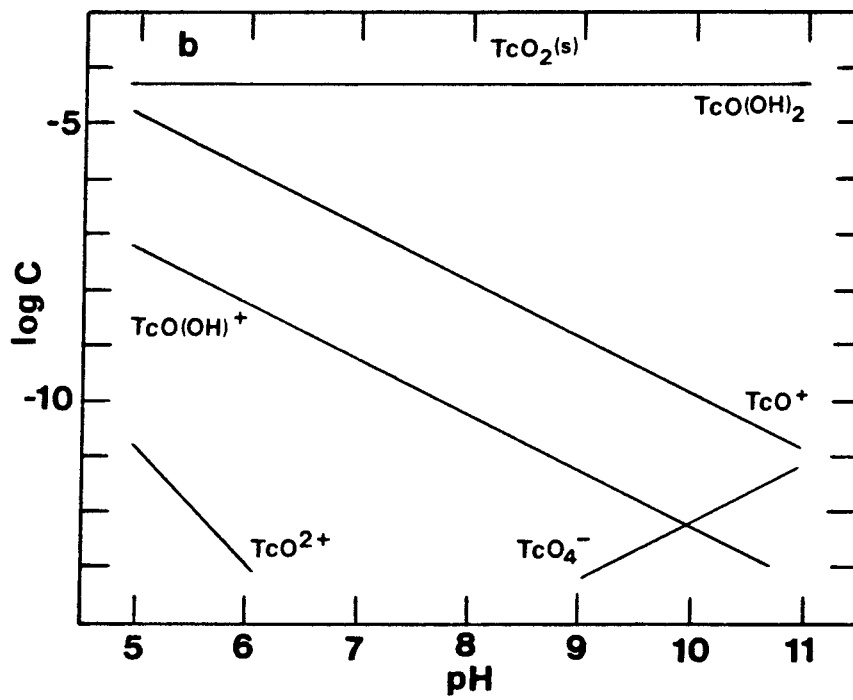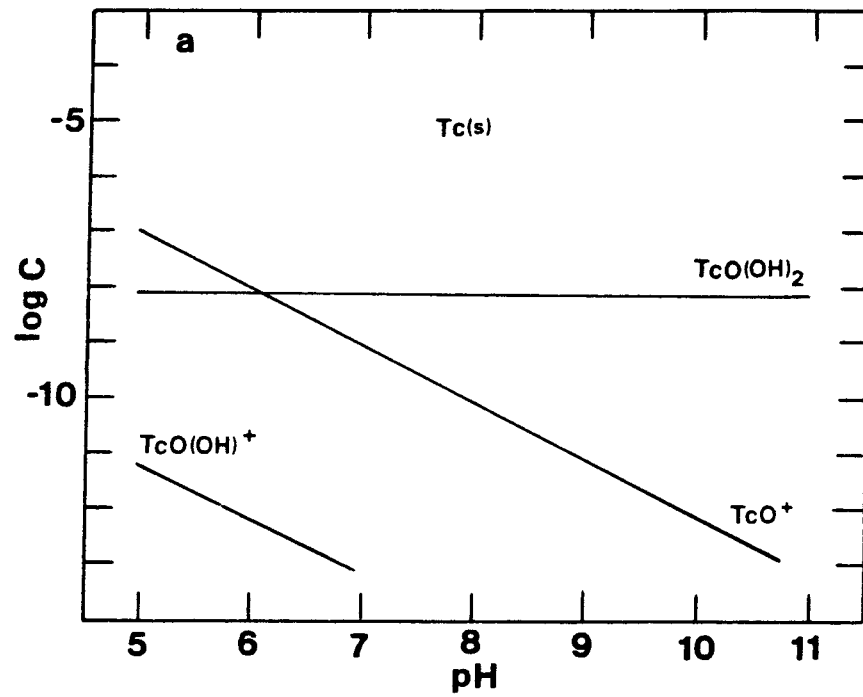
Figure 1 Calculated technetium solubility and speciation.
  a. Eh = 0.21-0.06pH
  b. Eh = 0.30-0.06pH
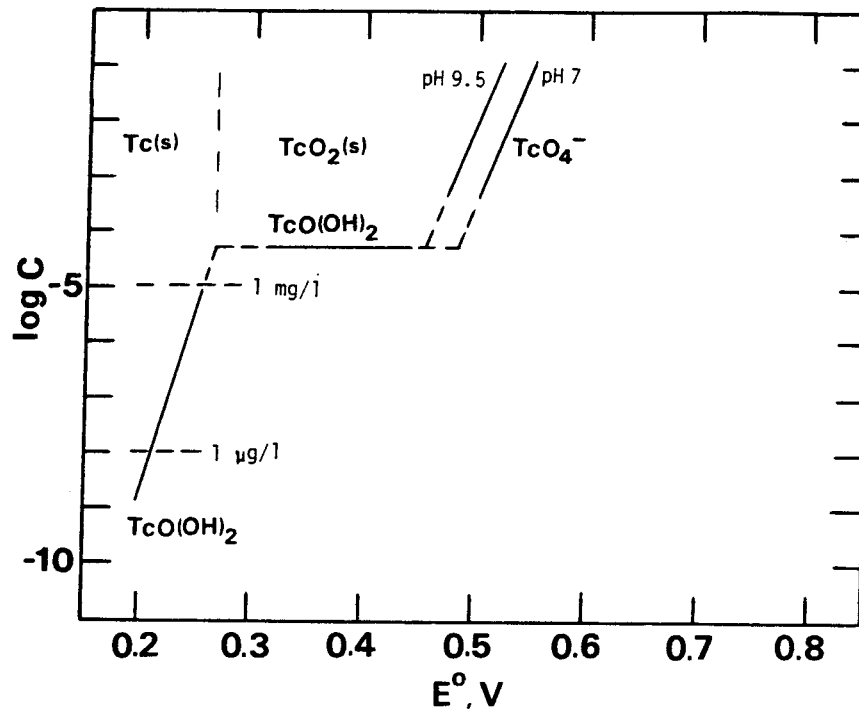
Figure 2 Calculated technetium solubilities vs the standard potential
(E = E^o-0.06pH) for pH 7 and 9.5.

o Under mildly reducing conditions (Eh in the range 0.27-0.06pH
to 0.45-0.06pH) the solubility is limited by TcO_2(s) to about
10^{-4}-10^{-5} M, probably somewhat lower.

o Under oxidizing conditions TcO_4^- dominates in solution and the
maximum concentration is high.

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