Behavior of Reduced ^{99}Tc and ^{99}Tc Organic Complexes on Hanford Soil

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February 1982

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

3 3679 00048 6516

BEHAVIOR OF REDUCED ^{99}Tc AND ^{99}Tc
ORGANIC COMPLEXES ON HANFORD SOIL

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SUMMARY

Both synthetically and naturally derived organic complexing agents in soil have been found in other studies to accelerate the rate of migration of specific radionuclides. In an effort to aid in the development of comprehensive plans for the disposal of low-level waste, the effect of organic complexing agents on the transport properties of ^{99}Tc , a long-lived constituent of radioactive waste, was examined.

The effect of ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and sodium citrate on the mobility of reduced Tc species was examined from two aspects: first, by techniques of desorption from soil in which reduced, sorbed Tc was exposed to solutions of organic ligands; and second, by exposure of synthetic Tc-organic complexes to soils. Only a slight desorption of reduced Tc from Hanford soil by EDTA was found to occur in 10-day desorption tests.

However, when synthetic EDTA and DTPA complexes of reduced Tc were exposed to soil under similar conditions, only a slight amount of Tc was sorbed by the soil. This comparison clearly shows that at least one type of test did not reach equilibrium in the 10-day time period allowed. Although the effects of these complexants at equilibrium cannot be quantified from these data, it is obvious that they can have large effects on the mobility of reduced Tc.

Desorption tests of reduced Tc from Hanford soil by citrate solutions showed definite indications of desorption only at a relatively high (0.01 M) citrate concentrations. Results with synthetic Tc(IV) and Tc(V) citrate complexes indicate the Tc(V) citrate complex to be strongly sorbed, while the Tc(IV) citrate complex was sorbed only slightly.

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INTRODUCTION

Technetium is among several of the long-lived radioisotopes generated by fission reactors for which adequate geochemical histories are lacking. Technetium-99 is present in significant quantities in existing nuclear waste inventories.⁽¹⁻⁴⁾ The practice of burial of low-level waste, which may include Tc, in shallow-land burial sites has renewed interest in the mobility of Tc and other nuclides in soil.

Technetium exhibits several oxidation states, depending on the chemical environment. In aqueous solution the IV and VII oxidation states predominate in the absence of organic ligands which stabilize oxidation states (such as III or V). In an oxidizing environment (such as air-saturated water) in the absence of strong complexing agents, all lower oxidation states are converted to the highly soluble pertechnetate (TcO_4^-) anion. Technetium as pertechnetate is known to move rapidly through saturated soil systems, to pass readily through animals, to be absorbed by plants,⁽⁵⁾ and as a result of microbial activity, to be immobilized in soil.⁽⁶⁾ However, the role of organic complexing agents in stabilizing the oxidation states III, IV, and V of Tc, and the resulting properties of complexed Tc, has not been examined.

A reducing environment in the absence of organic complexing agents converts TcO_4^- to insoluble, hydrated TcO_2 . The anion TcO_4^- does not react directly with organic ligands to form Tc(VII) complexes. Thus, when TcO_4^- enters the soil or bedrock environment and encounters reducing species (such as Fe^{2+}), it is converted to insoluble TcO_2 , resulting in a substantial reduction in its migration potential. Recent studies under conditions of deep geologic media^(7,8) have led to the conclusion that the potential hazard to man posed by Tc has been over estimated due to a reducing environment found in ground water and deep geologic formations. However, very little is known about the effect of organic complexing agents on the transport properties of Tc in the III, IV, and V oxidation states, and data are lacking from which the kinetics of complex formation and equilibrium stabilities can be predicted in pH ranges encountered in soils. The lower oxidation states of Tc, unlike TcO_4^- , can react with organic complexants. This area warrants further

examination in light of studies^(9,10) which have linked both synthetically and naturally derived organic complexing agents in the soil to the accelerated rate of migration of several radionuclides.

Organic complexation is likely to be a facile pathway for the transport of radioisotopes, especially where synthetic chelating agents occur with buried low-level waste and the soil is subject to aqueous saturation and flow conditions. Means and Hastings⁽¹¹⁾ have pointed out that the presence of organic matter does not necessarily lead to mobilization; fixation may occur instead (e.g., by stable complex formation with insoluble fulvic acids). Whether fixation or mobilization occurs will depend on the types of organic agents present, the oxidizing or reducing nature of the medium, the competition between various metals for organic ligands, the pH dependence of that competition, the kinetic and thermodynamic parameters of the various complexes, and the charged or uncharged character of the complex. No information of this type regarding the soil behavior of reduced Tc complexes exists.

In an effort to aid in the development of more comprehensive plans for the terminal storage of low-level waste, the following study addresses the effects of organic chelating agents on the mobility of reduced Tc.

The effect of ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and sodium citrate on the sorption/migration of Tc was examined using two approaches. In one approach, desorption techniques were applied to remove sorbed and/or precipitated reduced Tc from soil by exposure to organic ligands. In the other approach, synthetic Tc organic complexes were exposed to soil. Naturally occurring organic materials, such as humic and fulvic acids, were not selected for the studies due to their complex, multicomponent nature, which would make complex characterization very difficult. The synthetic organic ligands selected for the study are some of those which are commonly associated with decontamination and clinical and laboratory research activities.

EXPERIMENTAL

The materials and procedures used in this study are described in this section.

REAGENTS

$\text{NH}_4^{99}\text{TcO}_4$, as the solid, supplied by Oak Ridge was used in preparing stock solutions. The stock solutions were standardized against a standard $\text{NH}_4^{99}\text{TcO}_4$ aqueous solution supplied by Amersham. A few drops of 30% H_2O_2 were added to the stock solutions and the standard solution to ensure that all of the ^{99}Tc was present as TcO_4^- . The disodium salt of EDTA ($\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$), trisodium salt of citric acid ($\text{Na}_3\text{citrate} \cdot 2\text{H}_2\text{O}$), and DTPA were used without further purification. Hydrazine (N_2H_4) as an aqueous 64% solution was diluted to 32% in water for use as a reducing agent. ACS II liquid scintillant, used in counting, was obtained from Amersham.

DESORPTION STUDIES

Unless otherwise indicated below, all operations were performed under an atmosphere of argon in a glove box. The distilled water used in these experiments was boiled and degassed with argon. Five tenths of a gram of soil was weighed into 30-ml polypropylene Oak Ridge-type tubes, which were evacuated and then repressurized with argon in a vacuum desiccator several times throughout a 2-day period. A calcareous, sandy loam Hanford soil (pH ~8.2) was examined in this study.

Solution/soil ratios were 30:1 (15 ml of solution, 0.5 g soil). Solution pH was not controlled but was measured after a 3-day equilibrium period following TcO_4^- reduction and again at the end of the ligand desorption study. Samples of 7.5 ml of NH_4TcO_4 (10^{-5} to 10^{-9} M in Tc after dilution of the aqueous phase to the final volume, 15 ml) were reduced with hydrazine in the presence of 0.5 g soil. The samples were equilibrated for 3 days in a shaker container designed to maintain a continuous argon purge. After this 3-day period, pH readings were taken, and 7.5 ml of either EDTA or citrate solutions

were added to the reaction tubes. The contents were again equilibrated under argon in the shaker for 10 days for EDTA and 10 and 45 days for citrate. Ligand-to-metal ratios were varied over the Tc concentration range of 10^{-5} to 10^{-9} M to determine the effect of ligand concentration on the desorption of reduced Tc via complex formation. The following ligand/technetium concentrations ratios were employed: for EDTA, 1:1, 5:1, and 10:1, and for citrate, 1:1, 10:1, 100:1 and 10,000:1. The effect of time on the desorption of reduced Tc was examined in the citrate system by extending the desorption period to 45 days. Duplicates were run on each Tc sample investigated for both desorbing ligand systems. At the end of the final equilibration period, the samples were filtered through 0.45- μ m Millipore filters, and 1-ml samples were analyzed by scintillation counting. The EDTA-treated samples were counted for 20 min. The citrate-treated samples were counted for 100 min.

PREPARATION OF Na[TcO(HEDTA)] $4H_2O$

To a solution of NH_4TcO_4 (0.065 g, 0.36 mmol) in 25 ml water, $Na_2EDTA \cdot 2H_2O$ (0.67 g, 1.8 mmol) was added. The mixture was warmed to dissolve the EDTA, and a solution of 0.2 g (5.4 mmol) of $NaBH_4$ in 20 ml water was added from a dropping funnel over a 40-min period. The color of the reaction mixture changed from orange to reddish-orange to purple-red to blue and finally to purple-red during the course of the reaction. The reaction mixture was warmed and stirred for an additional 2 h, at which time the pH was adjusted to seven with 6 N HCl and the reaction volume concentrated to 15 ml by gentle boiling. Approximately 15 ml of methanol was added, followed by sufficient ethyl ether to reach a cloud point. After the solution stood overnight, a purple powder separated, which was recrystallized twice from water/methanol/ethyl ether as above to give 0.94 g (0.19 mmol) of product, 54% yield based on M.W. 483. Elemental analyses were carried out by Schwarztzoff Microanalytical Laboratories, Woodside, New York. Scintillation counting was accomplished using scintillation standards (NH_4TcO_4) provided by Amersham, Inc., to determine β -particle detection efficiencies.

The results of these analyses and other tests were:

Elemental Analysis: Calculated for--Na C₁₀ H₂₁ O₁₂ N₂ Tc [NaH(TcOEDTA) 4H₂O] C, 24.0; H, 4.21; N, 5.61; Tc, 19.84.

Found--C, 23.77; H, 3.75; N, 6.21; Tc, 19.29 (Tc by scintillation counting).

IR Spectrum (KBr pellet): 3400, 3200 cm⁻¹ (OH), 1735 to 1740 cm⁻¹ (shoulder, uncoordinated carboxyl), 1655, 1613 cm⁻¹ (coordinated carboxyls, relative intensities 1:2), 930 cm⁻¹ [TcO stretch (tentative)].

UV-Visible Spectrum (H₂O) λ_{max} (ϵ , m⁻¹cm⁻¹): 600 (180), 505 (1307), 280 (shoulder).

Conductivity in water: (Sample concentration 2.06×10^{-3} M based on assigned M.W.), $\kappa_M = 126.4$ cm²ohm⁻¹mole⁻¹ (value for 1:1 electrolyte). For a discussion of conductivity determinations, see References 12 and 13.

PREPARATION OF Tc(V) DTPA

To a solution of 0.078 g (0.43 mmol) of NH₄TcO₄ in 25 ml water, 0.846 g (2.15 mmol) of DTPA was added, and the mixture was warmed until dissolution of the DTPA was complete. To this solution was added a solution of 0.251 g (6.63 mmol) of NaBH₄ in 20 ml of water over a 30-min period. The color became successively orange-yellow, orange, and finally orange brown. Isolation was accomplished in a manner identical to that of the EDTA complex. The yield was 0.14 g, 62%.

Characterizational results with this material were:

Elemental Analysis: Calculated for--C₁₄ H₂₂ O₁₂ N₃ Tc C, 32.12; H, 4.21; N, 8.03; Tc, 18.93. Found--C, 32.01; H, 4.23; N, 8.45; Tc 19.2 (Tc analysis by scintillation counting).

IR Spectrum (KBr pellet): 3400 cm⁻¹ (OH), 1645 cm⁻¹ (coordinated carboxyls).

UV-Visible Spectrum (H₂O) [λ_{max} (ϵ , m⁻¹cm⁻¹)]: 430 (3222), 343 (4236), and 485 (shoulder).

Conductivity: Behaves as nonelectrolyte: $\Omega_m = 11 \text{ cm}^2\text{ohm}^{-1}\text{mole}^{-1}$ (see References 12 and 13.)

EXPOSURE OF SYNTHETIC Tc(IV)EDTA AND Tc(V)DTPA COMPLEXES TO SOIL

Aqueous solutions of the Tc(IV)EDTA and Tc(V)DTPA complexes were exposed to Hanford soil by shaking 0.5 g of soil with 30 ml of aqueous solution containing 7.2×10^{-5} to 7.2×10^{-7} M of Tc(V)DTPA, or 6.6×10^{-5} to 6.6×10^{-7} M of Tc(IV)EDTA. Initial and final pH readings were determined. The stability of the Tc complexes to air oxidation enabled the 10-day equilibration in the shaker to be conducted in the air. The stability of Tc(V)DTPA and Tc(IV)EDTA complexes to air oxidation was determined by recording the UV-visible spectra of stock solutions (exposed to air) of 10^{-4} M and 10^{-5} M concentrations of each of the two complexes over the period of study. The distinct UV-visible spectra of the two complexes remained unchanged, with no appearance of the resolved absorption of TcO_4^- . It is assumed that the 10^{-6} and 10^{-7} M solutions were also inert to air oxidation. Filtration procedures were identical to those described earlier for desorption experiments. The samples were analyzed by scintillation counting.

PREPARATION OF Tc(IV) AND Tc(V) CITRATE COMPLEXES

Several preliminary experiments were carried out with Tc(IV) and Tc(V) citrates. Both Tc(IV) and Tc(V) citrates were prepared according to Munze⁽¹⁴⁾ by reduction of NH_4TcO_4 with Sn(II). The complexes were isolated by gel filtration chromatography on a 625 M Sephadex column as described by Eckelman.⁽¹⁵⁾ The complexes were used directly as aqueous solutions without further characterization. Thus, the structural assignments of Münze are tentatively accepted until a more complete characterization is possible. However, the stability of both complexes to air oxidation and hydrolysis was examined by rechromatographing the complexes after 60 days to determine the formation of resolved TcO_4^- . None was observed.

EXPOSURE OF Tc(IV) AND Tc(V) CITRATES TO HANFORD SOIL

Ten milliliters of the Sephadex column eluent containing 1×10^{-6} M of Tc for each Tc(IV) and Tc(V) citrates were analyzed by scintillation counting and shaken with exposure to air for 1 h with 5.0 g of Hanford soil in duplicate experiments. The aqueous phases were analyzed for Tc as in the desorption experiments discussed above.

CONTROL EXPERIMENT FOR OXIDATION OF TcO_2

To determine the rate of reoxidation of TcO_2 to TcO_4^- under conditions of air saturation, a sample of NH_4TcO_4 was reduced in the presence of Hanford soil by SnCl_2 (1.5 eq. per eq. NH_4TcO_4) with a 10-ml total aqueous volume and 5 g of soil. After the reduction, the sample was exposed to air and shaken for 1 h. Scintillation counting revealed 85% of the Tc to be in the aqueous phase, indicating that extensive reoxidation to TcO_4^- occurred.

CALCULATION OF DISTRIBUTION COEFFICIENT, K_d , AND PERCENT Tc SORBED

The batch equilibration techniques described above were used to determine the distribution coefficients, K_d . K_d is defined as the ratio, at equilibrium, of the quantity of solute sorbed per gram of soil to the quantity of solute per milliliter of equilibrating solution. The following equation was used for this calculation:

$$K_d = \frac{A_{\text{soil}}}{A_{\text{soln}}} \frac{\text{ml soln}}{\text{g of soil}}$$

where

A_{soil} = activity of ^{99}Tc in the soil = $A_{\text{initial}} - A_{\text{soln}}$;

A_{initial} = activity of ^{99}Tc control (oxidized form) containing no soil;

A_{soln} = activity of ^{99}Tc remaining in solution.

The experimental results are also expressed as percent ^{99}Tc sorbed obtained by

$$\frac{A_{\text{soil}}}{A_{\text{initial}}} \times 100 = \frac{A_{\text{initial}} - A_{\text{soln}}}{A_{\text{initial}}} \times 100$$

Strictly applied, K_d measurements refer to solutes which are entirely soluble in the concentration range of interest. This condition holds for TcO_4^- , Tc(V)DTPA and Tc(IV)EDTA , and Tc citrate complexes. However, TcO_2 is expected to display a solubility product, K_{sp} , of perhaps 10^{-25} . Thus, the K_d values measured in this study do not account for precipitation of TcO_2 . True K_d values for Tc(IV) must await studies at significantly lower concentrations. Although an experimental value for the K_{sp} of TcO_2 is not available, Srivastava⁽¹⁶⁾ et al. calculated a solubility product constant, $[\text{TcO}^{2+}][\text{OH}^-]^2$, of 6.29×10^{-25} based on the following hydrolysis reactions:⁽¹⁷⁾

$$(K_1 = 4.3 \times 10^{-2})$$

$$(K_2 = 3.7 \times 10^{-3})$$

At pH 10 (the region where most of the desorption experiments here were carried out), a concentration of uncomplexed Tc(IV) exceeding approximately 6×10^{-17} M would result in precipitation.

RESULTS AND DISCUSSION

The experimental results are presented and discussed in this section. Tables are used to present the data for the soil used in the study and the results obtained in the sorption and desorption experiments.

HANFORD SOIL

Analytical data for the Hanford soil used in this study are presented in Table 1. This soil is a sandy, calcareous soil which contains negligible organic matter. The saturation paste pH value, 8.23, reflects the carbonate content in the soil. The lack of humus content indicates that humate or fulvate interaction with nuclides can be neglected, and, lacking external sources of organic matter, nuclide/soil interaction will be limited to inorganic interactions.

DESORPTION STUDIES WITH EDTA--EFFECT OF EDTA ON SORBED (OR PRECIPITATED) REDUCED Tc

The results of the 10-day desorption of reduced Tc by EDTA are presented in Table 2, as are the results of the sorption of NH_4TcO_4 , the oxidized (ox) form of Tc. At all concentrations studied (4×10^{-7} , 2×10^{-6} , 10^{-5} M), NH_4TcO_4 underwent negligible sorption by Hanford soil. When NH_4TcO_4 was reduced with hydrazine, 99 and 97% from 10^{-5} M and 2×10^{-6} M NH_4TcO_4 solutions became sorbed on the soil or precipitated from solution. The

TABLE 1. Characterization of Hanford Soil

Exchangeable Cations, meq/100 g		Soluble Components, ppm		pH	Composition, wt%				
					Carbonate	Organic Carbon	Sand	Silt	Clay
Ca^{+2}	3.5	37 Ca^{+2}	133.1 HCO_3^-	8.23	0.07	0.097	87	9.3	3.7
Mg^{+2}	1.0	5.6 Mg^{+2}	7.5 SO_4^{2-}						
K^+	0.4	5.6 K^+	6.4 NO_3^-						
Na^+	0.1	9 Na^+	5.0 CO_3^{2-}						
		0.8 Cl^-							

TABLE 2. Desorption of Reduced ^{99}Tc by Na_2EDTA (a)

^{99}Tc Concentration	Form of ^{99}Tc (ox or red)	EDTA/Tc Molar Ratio	Initial Counts/min	Final Counts/min	K_d	% ^{99}Tc Sorbed/Pptd	pH	
							Initial (b)	Final
$1 \times 10^{-5} \text{ M}$ ($3 \times 10^{-7} \text{ mEq Tc/g soil}$)	ox	0	39,939	39,755	0.14	0.46	7.8	7.8
	red(c)	0	39,939	400	2947	99	10.4	10.2
	red(c)	1:1	39,939	1,136	1022	98	10.4	10.1
	red(c)	5:1	39,939	2,904	375	93	10.3	10.1
	red(c)	10:1	39,939	3,809	281	91	10.2	10.0
$2 \times 10^{-6} \text{ M}$ ($6 \times 10^{-8} \text{ mEq Tc/g soil}$)	ox	0	8,406	8,385	0.07	0.25	7.9	7.6
	red(d)	0	8,406	283	847	97	10.4	9.4
	red(d)	1:1	8,406	207	1217	98	9.6	9.3
	red(d)	5:1	8,406	364	648	96	9.6	9.4
	red(d)	10:1	8,406	706	317	92	9.5	9.4
$4 \times 10^{-7} \text{ M}$ ($1.2 \times 10^{-8} \text{ mEq Tc/g soil}$)	ox	0	1,613	1,587	0.48	1.6	7.8	7.5
	red(e)	0	1,613	635	46	61	8.7	8.1
	red(e)	1:1	1,613	441	79	73	8.7	8.3
	red(e)	5:1	1,613	497	67	69	8.7	8.2
	red(e)	10:1	1,613	637	46	61	8.7	8.2

(a) Data presented is average of duplicate runs.

(b) After 3-day equilibration of reduced Tc.

(c) 0.07 M hydrazine used based on final 15 ml aqueous contacting solution volume.

(d) 0.007 M hydrazine used based on final 15 ml aqueous contacting solution volume.

(e) 0.0007 M hydrazine used based on final 15 ml aqueous contacting solution volume.

hydrazine concentrations used for the three Tc concentrations mentioned above were 7×10^{-4} M, 7×10^{-3} M, and 7×10^{-2} M. This variation caused the pH values to vary from about 10 to 8.2 (Table 2). As the mole ratio EDTA/Tc was increased from 1 to 10, the percent Tc sorbed or precipitated decreased from 98 (± 1) to 91 (± 1) for the 10^{-5} M and 2×10^{-6} M experiments. The magnitudes of the observed effects are greater than the error limits of the method and indicate that EDTA is desorbing Tc. These results reveal that relatively modest concentrations of EDTA (2×10^{-5} M to 10^{-4} M) lead to desorption of reduced Tc in the saturated soil environment.

The observation of a 7 to 8% decrease in sorbed Tc in 10 days may mean that a significant fraction of Tc would become desorbed on the time scale of several months in a saturated, reducing medium containing EDTA. At Tc concentrations of 4×10^{-7} M (Table 2), the control experiment in which NH_4TcO_4 is reduced in the absence of EDTA shows only 61% sorption of Tc. At the low concentrations of Tc and hydrazine used in this series, reduction of Tc was probably incomplete after 3 days. In the absence of data longer than 10-day desorption tests, the effect of EDTA cannot be separated from the effects of apparent partial reduction at these lower concentrations.

SORPTION CHARACTERISTICS OF SYNTHETIC Tc(IV)EDTA AND Tc(V)DTPA COMPLEXES

The sorption characteristics of synthetic Tc(IV)EDTA and Tc(V)DTPA were examined to determine the behavior of Tc(IV) or Tc(V) under circumstances where the equilibrium between complexed and uncomplexed, sorbed Tc is approached from the complexed species. Table 3 shows the results of exposing 10^{-5} to 10^{-7} M Tc(IV)EDTA and Tc(V)DTPA to Hanford soil. For Tc(IV)EDTA, an average of 3% at 10^{-5} M and 1% at 10^{-6} or 10^{-7} M of the total Tc was sorbed by the soil. For Tc(V)DTPA, $4 \pm 1\%$ of the total Tc was associated with the soil after 10 days. The soil was exposed to aqueous solutions of the complexes in the presence of air. The complexes were found to be inert to air oxidation at 10^{-4} M and 10^{-5} M in the absence of soil, and similar stability is assumed in these sorption experiments.

TABLE 3. $^{99}\text{Tc(V)}$ DTPA and $^{99}\text{Tc(IV)}$ EDTA Interaction with Hanford Soil (a)

^{99}Tc Complex Concentration (b)		K_d	% ^{99}Tc Sorbed/Pptd
Tc(V)DTPA	10^{-5} M	1.19	4
		1.63	5
		0.64	2
	10^{-6}	1.74	6
		1.34	4
		1.30	4
	10^{-7}	1.00	3
		1.04	3
		3.66	11
Tc(IV)EDTA	10^{-5}	0.42	1
		0.85	4
		1.27	3
	10^{-6}	0.34	1
		0.19	1
		0.45	1
	10^{-7}	0.24	1
		0.09	0.3
		0.41	1

(a) Shaken 10 days in air, pH remained unchanged throughout investigation (9.6).

(b) Ligand/Metal ratios are 1:1.

The great discrepancy between the results obtained on 10-day desorption of reduced Tc and on 10-day sorption experiments with the synthetic Tc(IV)EDTA complex appears, therefore to be caused by slow rates of attainment of equilibrium. The effect of EDTA at equilibrium cannot be quantified from these data, but it is obvious that EDTA can have a large effect on the mobility of reduced Tc.

DESORPTION OF REDUCED Tc BY CITRATE

Results of desorption experiments with sodium citrate solutions at Tc concentrations of 10^{-6} to 5×10^{-9} M and citrate concentrations from 5×10^{-9} to 10^{-2} M are given in Tables 4, 5, and 6. These data appear to be of questionable value because of incomplete reduction of Tc by hydrazine (0.07 M) during the 3-day period before the citrate was added to desorb the Tc. With 10^{-6} M NH_4TcO_4 , 94% of the Tc was reduced and removed from solution during this period, but less reduction evidently occurred at lower Tc concentrations. This indicates that the rate reduction of TcO_4^- by hydrazine varies with the TcO_4^- concentration raised to a power greater than one (the reaction is greater than first order in TcO_4^- concentration).

The fact that more Tc was sorbed/precipitated after the 10-day desorption period than before the citrate was added, indicates that additional reduction occurred after the citrate was added. Comparison of 45-day and 10-day desorption results indicates that, at Tc concentrations $<10^{-8}$ M, reduction continued even beyond the 10-day time period.

Ignoring the experiments of $<10^{-8}$ M Tc to avoid kinetic complications, there was only one experiment (with 10^{-6} M Tc and a 10,000:1 Cit/Tc molar ratio) in which the citrate appeared to give a definite decrease in the sorption/precipitation of the reduced Tc. These results thus indicate that a relatively high concentration (0.01 M) of citrate was required to give a detectable decrease in sorbed/precipitated Tc in these experiments.

SORPTION CHARACTERISTICS OF SYNTHETIC Tc(IV) AND Tc(V) CITRATES

Sorption tests with the synthetic citrate complexes produced the important observation that, unlike the Tc(V)DTPA complex, the Tc(V) citrate complex is sorbed/precipitated quite extensively when the solution is contacted with Hanford soil. The Tc(IV) citrate complex, however, was not extensively sorbed, analogous to the behavior of the Tc(IV) EDTA complex. These synthetic citrate complex results are presented in Table 7.

TABLE 4. Ten-Day Desorption of Reduced ^{99}Tc by Na_3 Citrate^(a)

^{99}Tc Concentration	Form of ^{99}Tc (ox or red)	Cit/Tc Molar Ratio	Initial(b) Counts/min ^(c)	Final(b) Counts/min	K_d	% ^{99}Tc Sorbed/Pptd	pH	
							Initial ^(d)	Final
$1 \times 10^{-6} \text{ M}$ ($3 \times 10^{-8} \text{ mEq Tc/g soil}$)	ox	0	4078	4033	0.34	1	7.8	7.9
	red	0	4078	241	477	94	10.4	10.1
	red	1:1	4078	197	599	96	10.4	10.1
	red	10:1	4078	281	454	93	10.4	10.1
	red	100:1	4078	288	510	95	10.4	10.1
	red	1000:1	4078	229	511	95	10.3	10.1
	red	10000:1	4078	646	161	85	10.5	10.3
$1 \times 10^{-7} \text{ M}$ ($3 \times 10^{-9} \text{ mEq Tc/g soil}$)	ox	0	440	438	0.14	0.5	8.1	8.3
	red	0	440	59	194	87	10.3	10.1
	red	1:1	440	32	399	93	10.4	10.1
	red	10:1	440	28	446	94	10.4	10.1
	red	100:1	440	40	306	91	10.4	10.2
	red	1000:1	440	47	250	89	10.4	10.3
	red	10000:1	440	47	254	89	10.3	10.1
$1 \times 10^{-8} \text{ M}$ ($3 \times 10^{-10} \text{ mEq Tc/g soil}$)	ox	0	53	52	0.15	0.5	7.8	7.7
	red	0	53	20	52	63	10.0	9.7
	red	1:1	53	4	424	93	10.4	10.1
	red	10:1	53	6	262	89	10.4	10.2
	red	100:1	53	7	200	86	10.3	10.2
	red	1000:1	53	7	222	88	10.1	9.8
	red	10000:1	53	7	208	87	10.2	9.9
$5 \times 10^{-9} \text{ M}$ ($1.5 \times 10^{-10} \text{ mEq Tc/g soil}$)	ox	0	25	25	0.32	1	8.3	8.2
	red	0	25	9	52	64	10.4	10.1
	red	1:1	25	6	110	76	10.4	10.1
	red	10:1	25	6	103	77	10.4	10.1
	red	100:1	25	7	83	73	10.4	10.1
	red	1000:1	25	10	47	61	10.2	9.9
	red	10000:1	25	15	20	39	10.2	9.9

(a) Data presented is average of duplicate runs. In all experiments TcO_4^- was reduced by adding hydrazine (0.07 M in 15 ml final volume).

(b) Less background.

(c) 1×10^{-6} , 10^{-7} M counted 10 min; 10^{-8} and 10^{-9} counted 20 min.

(d) After 3-day equilibration of reduced Tc.

TABLE 5. Forty-Five Day Desorption Study of Reduced ^{99}Tc by Na_3 Citrate^(a)

^{99}Tc Concentration	Form of ^{99}Tc (ox or red)	Cit/Tc ^(d) Molar Ratio	Initial ^(b) Counts/min	Final ^(b) Counts/min	K_d	% ^{99}Tc Sorbed/Pptd	pH	
							Initial ^(c)	Final
$1 \times 10^{-6} \text{ M}$	ox	0	4078	4033	0.34	1	7.0	7.9
	red	0	4078	241	477	94 ^(e)	10.4	10.1
	red	1:1	4078	240	482	94	10.4	10.1
	red	10:1	4078	217	549	95	10.4	10.1
	red	100:1	4078	210	555	95	10.4	10.1
	red	1000:1	4078	213	544	95	10.3	10.1
	red	10000:1	4078	495	218	88	10.5	10.3
$1 \times 10^{-7} \text{ M}$	ox	0	440	438	0.14	0.5	8.1	8.3
	red	0	440	59	194	87 ^(e)	10.3	10.1
	red	1:1	440	39	307	91	10.4	10.1
	red	10:1	440	40	300	91	10.4	10.1
	red	100:1	440	41	297	91	10.4	10.2
	red	1000:1	440	44	275	90	10.4	10.3
	red	10000:1	440	50	236	89	10.3	10.1
$1 \times 10^{-8} \text{ M}$	ox	0	53	52	0.15	0.5	7.8	7.7
	red	0	53	20	52	63 ^(e)	10.0	9.7
	red	1:1	53	3	522	94	10.4	10.1
	red	10:1	53	3	534	95	10.4	10.2
	red	100:1	53	3	573	95	10.3	10.2
	red	1000:1	53	2	687	96	10.1	9.8
	red	10000:1	53	5	339	91	10.2	9.9
$5 \times 10^{-9} \text{ M}$	ox	0	25	25	0.32	1	8.3	8.2
	red	0	25	9	52	64 ^(e)	10.4	10.1
	red	1:1	25	2	388	92	10.4	10.1
	red	10:1	25	3	280	89	10.4	10.1
	red	100:1	25	1	1168	97	10.4	10.1
	red	1000:1	25	8	61	67	10.2	9.9
	red	10000:1	25	11	41	58	10.2	9.9

(a) Data presented is average of duplicate runs; samples counted for 100 min.

(b) Less background.

(c) After 3-day equilibration of reduced Tc.

(d) 0.07 M hydrazine in final soil contact solution volume, 15 ml, was used to reduce TcO_4^- in all cases.

(e) From 10-day study.

TABLE 6. Comparison of K_d 's and % ^{99}Tc Sorbed from 10- and 45-day Desorption Study of Reduced ^{99}Tc by $\text{Na}_3\text{Citrate}$

^{99}Tc Concentration(a)	Cit/Tc Molar Ratio	K_d		% Tc Sorbed/Pptd	
		10 Day	45 Day	10 Day	45 Day
$1 \times 10^{-6} \text{ M}$ ($3 \times 10^{-8} \text{ mEq Tc/g soil}$)	0	447 ^(b)	(c)	94 ^(b)	(c)
	1:1	599	482	96	94
	10:1	454	549	93	95
	100:1	510	555	95	95
	1000:1	511	544	95	95
	10000:1	161	218	85	88
$1 \times 10^{-7} \text{ M}$ ($3 \times 10^{-9} \text{ mEq Tc/g soil}$)	0	194 ^(b)	(c)	87 ^(b)	(c)
	1:1	399	307	93	91
	10:1	446	300	94	91
	100:1	306	397	91	91
	1000:1	250	275	89	90
	10000:1	254	236	89	89
$1 \times 10^{-8} \text{ M}$ ($3 \times 10^{-10} \text{ mEq Tc/g soil}$)	0	52 ^(b)	(c)	63 ^(b)	(c)
	1:1	424	522	93	94
	10:1	262	534	89	95
	100:1	200	573	86	95
	1000:1	222	687	88	96
	10000:1	208	339	87	91
$5 \times 10^{-9} \text{ M}$ ($1.5 \times 10^{-10} \text{ mEq Tc/g soil}$)	0	52 ^(b)	(c)	64 ^(b)	(c)
	1:1	110	388	76	92
	10:1	103	280	77	89
	100:1	82	1168	73	97
	1000:1	47	61	61	67
	10000:1	20	41	39	58

(a) Total volume of aqueous phase was 15 ml. The weight of soil was 0.5 g.

(b) These values were determined at the end of 3 days at the time of addition of complexing agent.

(c) Not analyzed.

In our preliminary studies, neither Tc citrate complex underwent hydrolysis of the citrate ligand. Other workers have isolated the Tc(IV) and Tc(V) as well as the Tc(III)⁽¹⁴⁾ citrates in electrophoresis experiments lasting hours, supporting the view that the complexes are probably stable to ligand replacement by water. Thus, our preliminary studies indicate that there is a

TABLE 7. Preliminary Results of $^{99}\text{Tc(IV)}$ Citrate and $^{99}\text{Tc(V)}$ Citrate Interaction with Hanford Soil^(a)

^{99}Tc Complex Concentration		Kd	% ^{99}Tc Sorbed/Pptd
Tc(IV) Citrate ^(b)	1×10^{-6} M	0.026	1
Tc(V) Citrate ^(b)	1×10^{-6} M	204	97.4
TcO ₂	1×10^{-6} M	0.334 ^(c)	14.5

(a) Shaken 1 h in air; pH was 7.5 ± 0.5 . The conditions were 15 ml of aqueous solution and 5 g of Hanford soil

(b) Citrate/Tc ratio is 2 (Reference 14).

(c) Shaken with exposure to air to observe degree of air oxidation in 1 h.

differentiation between Tc(IV) and Tc(V) citrate in affinities with soils. In a related observation, it was observed that Tc is fixed in soil by microbial oxidation as a gluconate complex.⁽¹⁷⁾ Thus, unlike the EDTA-type complexes, Tc complexes of hydroxy-carboxylic acids and polyhydroxylic alcohols^(18,19) would appear to show higher affinity to soils in certain cases. A more complete structural characterization of many of the Tc(III,IV,V) complexes and studies of their hydrolytic stability, stability constants, and oxidation/reduction reactions would be helpful in understanding the organic geochemistry of Tc.

CONCLUSIONS

The data presented here show that EDTA desorbs or dissolves reduced technetium from Hanford soil in a basic reducing medium, and that once formed, Tc(IV)EDTA and Tc(V)DTPA are not sorbed in significant degrees by soil. Significant desorption of reduced Tc occurs in 10 days, but much longer studies, on the order of months, will be necessary to determine the rate of approach to equilibrium and the equilibrium position. The data presented here indicate that citrate complex formation is probably not a potential pathway for mobilizing reduced technetium at technetium concentrations studied, and may in fact lead to the fixation of technetium if Tc(V) complexes are formed.

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