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Thermodynamics of Technetium Related to Nuclear Waste Disposal

Solubilities of Tc(IV) Oxides and the Electrode Potential of the Tc(VII)/Tc(IV)–Oxide Couple

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Oak Ridge National Laboratory

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Thermodynamics of Technetium Related to Nuclear Waste Disposal

Solubilities of Tc(IV) Oxides and the Electrode Potential of the Tc(VII)/Tc(IV)–Oxide Couple

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May 1988	Thermodynamic Properties of Tc(IV) Oxides: Solubilities and the Electrode Potential of the Tc(VII)/Tc(IV)-Oxide Couple, NUREG/CR-5108

ABSTRACT

Solubilities of Tc(IV) oxides have been determined in a number of solutions in the pH range 1 to 10. Technetium oxide was prepared by precipitation upon purified sand with a 30% excess of hydrazine and by electrodeposition. The oxide-covered sand was transferred to a small column, and the solutions to be studied were continuously cycled through the column. The electrodeposited oxide was formed on a platinum mesh electrode, and after careful rinsing, the solution to be studied was added to the electrolytic cell. The concentrations of total technetium and Tc(IV) species in the solutions were periodically determined by separating the oxidized and reduced technetium species using a solvent extraction procedure and counting the beta activity of the ^{99}Tc with a liquid scintillation counter. In basic solutions, the concentrations of Tc(IV) species in equilibrium with the oxide were in the range of 10^{-8} to 10^{-9} mol/L and tended to increase slightly with pH. In acid solutions the concentrations were much higher and were consistent with literature data on the hydrolytic species of Tc(IV). Solubilities appeared to reach a minimum in the intermediate pH range, and they were generally a factor of three or four lower for oxides electrodeposited in basic solutions compared to those for oxides electrodeposited from acid solution. The oxides were hydrated, and assuming a formula of $TcO_2 \cdot nH_2O$, the value of n was found to be 1.63 $\pm$ 0.28. These data can be used to estimate Tc(IV) solubilities for cases where solubility limits transport of technetium in reducing environments of high-level waste repositories.

Because there is some disagreement among published values of E° for the Tc(VII) - Tc(IV) redox couple, a redetermination of the standard potential was completed. The slopes of plots of electrode potential vs pH and electrode potential vs concentration were confirmed, and the value of E° was determined to be 0.747 $\pm$ 0.004 V. Within the limits of error, this agrees most closely with the value E° = 0.741 $\pm$ 0.004 V reported by Cartledge and Smith (1955), the value generally used.

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THERMODYNAMICS OF TECHNETIUM RELATED TO NUCLEAR WASTE DISPOSAL: 1. SOLUBILITIES OF Tc(IV) OXIDES 2. THE ELECTRODE POTENTIAL OF THE Tc(VII)/Tc(IV)-OXIDE COUPLE

R. E. Meyer
W. D. Arnold
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G. D. O'Kelley

1. EXECUTIVE SUMMARY

The fission product ^{99}Tc is expected to occur in oxidizing environments as the anion TcO_4^- and in reducing environments as Tc(IV) oxide ($TcO_2 \cdot nH_2O$) plus the aqueous species in equilibrium with the oxide. The transport of technetium in reducing geologic environments may be limited to low levels by the solubility of $TcO_2 \cdot nH_2O$. Studies of the solubility of the oxide have been reported in solutions of low ionic strength (Meyer et al. 1986, 1987) and in solutions of higher ionic strength (Meyer et al. 1988). Additional solubility measurements have now been made in 0.05- to 2.6-mol/L NaCl solutions, and the results of these and the previously determined solubilities are compiled and discussed here.

Technetium oxide was prepared in a controlled-atmosphere box containing argon with < 1 ppm oxygen either by electrodeposition or by precipitation upon purified sand with a 30% excess of hydrazine. The oxide-covered sand was transferred to a small column, and test solutions were continuously recirculated through the column. The electrodeposited oxide was formed either from acidic or basic solutions; solutions to be tested were then added to the electrolytic cell after careful rinsing of the cell to remove the solution used for the electroreduction. The concentrations of total technetium and Tc(IV) species in the test solutions were periodically determined by separating the oxidized and reduced technetium species using a solvent extraction procedure and counting the beta particles of ^{99}Tc with a liquid scintillation counter.

In basic solutions, the concentrations of Tc(IV) species in equilibrium with the oxide were in the range of 10^{-8} to 10^{-9} mol/L and tended to increase with pH. In acidic solutions the concentrations were much higher and were consistent with literature data on the hydrolytic species of Tc(IV). Solubilities appeared to reach a minimum in the intermediate pH range, and they were generally a factor of three or four lower for oxides electrodeposited in basic solutions compared to those electrodeposited from acid solution. The oxides were hydrated, and assuming a formula of $TcO_2 \cdot nH_2O$, the value of n was found to be 1.63 ± 0.28. These data can be used to estimate Tc(IV) solubilities for cases where solubility limits transport of technetium in reducing environments.

The total concentration of technetium in the tested solutions includes Tc(IV) species, which are in equilibrium with the oxide, and TcO_4^-. The concentration of TcO_4^- in contact with the oxide is dependent on the redox conditions in the system. For some determinations with the electrodeposited technetium oxide, the potential was controlled with a potentiostat. In these experiments, the concentration of TcO_4^- was controlled by the potential imposed by the potentiostat. However, for most experiments, the potentiostat was not used, and no other method was used to establish a redox potential. Generally, the concentrations of TcO_4^- in these solutions varied considerably and were probably controlled by rates of reaction of the technetium(IV) in the solution or solid with the very small amounts of residual oxygen remaining in the solution or with redox-active products of radiolysis.

Because there is some disagreement among published values of E^o for the Tc(VII) - Tc(IV) redox couple, a redetermination of the standard potential was completed using electrodeposited technetium oxide. The slopes of the graphs of electrode potential vs pH and concentration were measured to be 0.0773 $\pm$ 0.0023 V/(pH unit) and 0.0211 $\pm$ 0.0050 V/(log $[TcO_4^-]$ unit). These values agree with the theoretical values of 0.0788 V/(pH unit) and 0.0197 V/(log $[TcO_4^-]$ unit) within the standard deviations of our measurements. The value of E^o was determined to be 0.747 $\pm$ 0.004 V. Within the limits of error, this agrees with the value E^o = 0.741 $\pm$ 0.004 V determined by Cartledge and Smith (1955). Cartledge and Smith reported their value as 0.738 V using a value 0.242 V for the potential of the saturated calomel electrode (SCE). We have used the value 0.244_5 V for the potential of the SCE (Hills and Ives 1961), and we have converted Cartledge and Smith's data using this value.

2. SOLUBILITIES OF Tc(IV) OXIDES

2.1 INTRODUCTION

The nuclide ^{99}Tc ($t_{1/2}$ = 213,000 years, fission yield ~ 6%) is present in large quantities in nuclear waste, and properties related to its migration in geological environments are therefore of considerable interest. Under oxidizing conditions, technetium is expected to exist in the oxidation state (VII) as the anion TcO_4^-. Technetium released into the groundwater surrounding a geologic high-level waste repository in the form of TcO_4^- is not expected to be sorbed significantly on the minerals and rocks present because of its negative charge. A number of studies have confirmed that little or no sorption occurs under oxic conditions (Salter et al. 1981, Barney 1982, Barney 1983, Palmer and Meyer 1981). Furthermore, compounds of TcO_4^- are generally soluble so that the concentration would not be expected to be limited to low values by solubility. However, if technetium is reduced to a lower valence state, then it is possible that species may be formed that either are more highly sorbed or are insoluble enough to limit the maximum concentration of technetium in the groundwaters surrounding the repository. This solubility-limited concentration enters into the calculation of the release rate of technetium to the environment if the repository should be breached by groundwater. Based upon current knowledge of technetium chemistry, it is generally predicted that some form of Tc(IV) oxide will be formed if reducing conditions exist in a repository geological environment. However, technetium has an unusually complicated redox chemistry, and little is known about the chemistry of its lower valence states. In particular, little is known about the solubilities of Tc(IV) oxides and the hydrolytic chemistry of Tc(IV), and for that reason, we report here a study of the solubilities of Tc(IV) oxides precipitated from aqueous solutions.

There is little literature on the hydrolytic chemistry of Tc(IV) and on the solubility of technetium oxides. Gorski and Koch (1969) have reported electromobility measurements from which they calculated equilibrium quotients for hydrolysis reactions, which they write as follows:

$$TcO^{2+} + H_2O = TcO(OH)^+ + H^+ \qquad Q_{h1} = (4.3 \pm 0.4) \times 10^{-2} \qquad (2.1)$$

$$TcO(OH)^+ + H_2O = TcO(OH)_2 + H^+ \qquad Q_{h2} = (3.7 \pm 0.4) \times 10^{-3} \qquad (2.2)$$

Their experiments were done by measuring the ionic mobility of Tc(IV) in columns composed of sea sand using solutions of pH 1 to 2.5 at an ionic strength of 0.1 mol/L. Their data showed sharp decreases in mobility at about pH 1.3 and 2.2. At pH values above about 2.3, the mobility was approximately zero, which indicated an uncharged species. The height of the first step (pH 1 to 1.3) of the mobility vs pH curve was twice that of the second step (pH 1.3 to 2.2). This was taken as evidence of the migration of a doubly charged species in the first step and a singly charged species in the second step, and the hydrolysis quotients were

calculated from the mobilities. Since the hydrolysis studies of Gorski and Koch were reported, two reports of unsuccessful attempts to repeat them have appeared (Sundrehagen 1979, Noll et al. 1975). A critical discussion of these experiments is given in Meyer et al. (1986). It appears that an important factor in these experiments is the initial concentration of technetium. If the concentration is too high, polymeric and/or colloidal forms of technetium may be present. Support for Gorski and Koch's results comes from the work of Owunwanne et al. (1977), who worked with carrier-free ^{99m}Tc at low concentrations (10^{-7} to 10^{-9} mol/L). Using standard ion exchange techniques, they determined a charge of plus two for the Tc(IV) species at pH values < 2. Owunwanne et al. suggest, on the basis of correlations with the formal charge of the metal and the pH, that the species in their experiment was actually $Tc(OH)_2^{2+}$ or possibly a mixture of $Tc(OH)_2^{2+}$ and TcO^{2+}. Sundrehagen (1979) reports hydrolysis quotients from spectrophotometric measurements in the ultraviolet spectrum region for the reaction given in Eq. 2.2 and a quotient for a dimerization reaction.

$$2TcO(OH)_2 = [TcO(OH)_2]_2 \qquad (2.3)$$

The values for the quotients, $Q_{h2} = (9.3 \pm 2.0) \times 10^{-3}$ and $Q_{dim} = 3.14 \pm 0.28) \times 10^{6}$ were obtained by a computer fit of a plot of molar absorptivity as a function of concentration of Tc(IV). The data were collected at 210 nm, a region in the ultraviolet spectrum where it is difficult to obtain reliable data. The dimerization reaction, Eq. 2.3, was postulated to account for the observation that the molar absorptivity was constant above about 10^{-5} mol/L Tc(IV) but increased rapidly below this concentration. If the assumption is valid that the dimerization reaction occurs, then the change of molar absorptivity with concentration implies that above this concentration (10^{-5} mol/L) dimerization is essentially complete, but below this concentration the monomer is formed. In addition, it was assumed that a singly charged species hydrolyzed (as in Eq. 2.2) to form the monomer. The value of $Q_{h2} = (9.3 \pm 2.0) \times 10^{-3}$ obtained by Sundrehagen agrees within a factor of 2.5 with the value $(3.7 \pm 0.4) \times 10^{-3}$ obtained by Gorkski and Koch. These experiments were done in 0.028-mol/L $HClO_4$ with added $NaClO_4$, and 0.05-mol/L $HClO_4$ with enough $NaClO_4$ to maintain the same ionic strength. The computer program did not produce a better fit when the first hydrolysis reaction (Eq. 2.1) was included. We have not seen any other spectroscopic study of this type or any confirmation of the spectrum at these wavelengths.

On the basis of a single determination of solubility by Lefort (1963) and the data reported by Gorski and Koch (1969) and by Sundrehagen (1979), Rard (1983) calculated the solubility product for $TcO_2 \cdot H_2O$; the value of $K_s = 3.55 \times 10^{-34}$, or $\log_{10} K_s = -33.45 \pm 1.0$ at infinite dilution.

2.2 EXPERIMENTAL

Two methods of preparing Tc(IV) oxides were used. In the first of these, Tc(IV) oxide was formed by reduction with hydrazine from a

solution containing TcO_4^- and purified sand; the resulting precipitate coated the particles of sand to form a product of high surface area. Reduction by hydrazine was the method used by Gorski and Koch (1979) and by Sundrehagen (1979) to prepare Tc(IV) oxides. The second procedure was electroreduction and precipitation of Tc(IV) oxide from a solution of TcO_4^- (Cartledge and Smith 1955).

The sand used in the column was prepared from Ottawa Sand that had been washed sequentially in 0.1 mol/L NaOH, 0.1 mol/L HCl, and water and then dried at 110°C. To 1.2 g of this sand in a small test tube containing a magnetic stirrer bar, 4 mL of water was added, along with 0.1 mL of a stock solution of ^{99}Tc which was approximately 0.5 mol/L ammonium pertechnetate, and a 30% excess of hydrazine (2.9 microliters of 85% $N_2H_4 \cdot H_2O$). The tube was stirred about 1 hr and the contents transferred to a column. The columns were made of 3 mm ID tubing and were about 15 cm long. The bed was 7 cm long and had a volume of about 0.5 cm^3. A polyethylene reservoir was included in the circuit for use in pH measurements and sampling. The precipitation occurred with the evolution of nitrogen formed by the reaction, assumed to be that given in Eq. 2.4.

$$3N_2H_5^+ + 4TcO_4^- + H^+ = 4TcO_2 + 3N_2 + 8H_2O \qquad (2.4)$$

The oxide-covered sand in the column was then washed with water. Before each determination, it was thoroughly washed with the solution to be studied.

For the preparation of electrodeposited technetium, a large platinum mesh electrode was constructed and placed into an electrolytic cell with a capacity of about 100 mL. The electrode has a cross-sectional area of about 6 cm^2. It is difficult to estimate the actual geometrical area of a mesh electrode; we estimate that the actual area is 3 to 4 cm^2. Enough of our stock solution was added to produce a solution of about 0.005 mol/L Tc, and the pH was adjusted to about 2 with HCl. The potential imposed on the electrode by the potentiostat was gradually made more reducing, and significant electrolysis began at -200 mV vs the saturated calomel electrode (SCE). The current density was approximately 1.0 mA/cm^2. A black solid gradually formed on the electrode, and after about two and a half hours, deposition was stopped. For some experiments, the oxide was electrodeposited from 0.01 mol/L NH_4OH. In this alkaline solution, significant electrolysis did not occur until the potential was lowered to about -850 mV vs SCE. However, these deposits did not adhere as well to the platinum electrode as those deposited from acid solution.

To determine the stoichiometric formula of Tc(IV) oxide, oxides were formed by electrodeposition onto a large platinum mesh electrode. To avoid oxidation of the technetium all operations were done within a controlled atmosphere box containing argon. Before electrodeposition, the electrode was carefully cleaned, dried, and weighed (ca. 4 gm). It was placed into an electrodeposition cell containing ca. 5 x 10^{-3} mol/L-NH_4TcO_4 and either 0.01 mol/L-HCl or 0.01 mol/L-NH_4OH, and a deposit of

from 10 to 25 mg was formed by electrodeposition. The electrode was then removed from the solution, rinsed carefully with distilled water, and allowed to dry. The moisture in the controlled-atmosphere box was continuously removed by circulation of the argon over molecular sieves. Thus the drying conditions were effectively 0% humidity at the temperature of the interior of the box, approximately 30°C. After a drying period of up to 7 days, the electrode was carefully wrapped in a weighed piece of aluminum foil. This was done to avoid any loss of oxide when the oxide-covered electrode was taken out of the box and weighed. The weight of the oxide was determined by difference. The amount of technetium in the oxide was then determined by dissolving the oxide with concentrated HNO_3, diluting the HNO_3 solution, and determining the technetium content of the diluted HNO_3 solution by liquid scintillation counting of the ^{99}Tc.

The solubility experiments lasted from two to three weeks. In the column experiments with the oxide-covered sand, 25 mL of the solution to be studied was added and samples were taken from a reservoir in the circuit of the continuously circulating solution. For experiments with electrodeposited oxide, the oxide-covered electrode was left in the cell and 100 mL of the solution to be studied was added to the cell after the electrode and cell had been carefully washed to remove traces of technetium. Typically, 1.0-mL samples were removed daily immediately after the pH was measured. The solution was then centrifuged at 14,000 rcf for 15 minutes. A 0.2-mL portion was saved as a head solution, and a 0.5-mL portion was treated by the solvent extraction process described below to distinguish between Tc(VII) and lower valence states, which we assume to be Tc(IV). The concentrations of ^{99}Tc were then determined in the 0.2-mL head solution and in the aqueous and organic phases from the valence state determination.

The solutions resulting from these experiments were analyzed by liquid scintillation counting after the extractions to determine the distribution of technetium between Tc(VII) and reduced technetium. In practice, for our apparatus this technique has a concentration limit (sensitivity) in the range of 10^{-9} mol/L Tc. At this concentration level, the counts due to the technetium were of the same order of magnitude as the background count. Consequently, in our reported concentrations, we report higher standard deviations for concentrations in this range. The concentration levels are determined by averaging the last five determinations before the experiment was ended. The efficiency of the counter was determined with a standard solution of known technetium concentration obtained from Amersham.

The procedure to determine the relative amounts of Tc(IV) and Tc(VII) in the solutions consisted of solvent extraction of the solution with 0.05-mol/L tetraphenyl arsonium chloride dissolved in chloroform. The organic phase removed the TcO_4^- very efficiently, leaving reduced species in the solution. If the ratio of Tc(VII) to Tc(IV) was high, two extractions were done to help insure that all of the Tc(VII) was removed before determining the concentration of Tc(IV) in the aqueous solution. When the ratio of Tc(VII) to Tc(IV) was greater than 200, the

results for that experiment were discarded, because the efficiency of removal of Tc(VII) from the solution was not great enough to insure that all of the Tc(VII) had been removed. The results of some experiments reported earlier (Meyer et al. 1987) were discarded by use of this criterion.

Because Tc(IV) is so easily oxidized, all operations were carried out in a controlled atmosphere box filled with high purity argon. The oxygen level in the argon was constantly monitored and was maintained at < 1 ppm. Sampling, centrifugation, and solvent extraction were carried out within the box. Exposure to air occurred only when the final samples were removed for counting.

The standard deviations (SD) associated with the values for the solubilities were calculated from Eq. 2.5.

$$SD = [(1/n)*\text{Summation}(x_i - AVG)^2]^{1/2}, \qquad (2.5)$$

where n is the number of determinations, always 5, AVG is the average of the solubilities, and x_i are the individual solubilities.

It was recognized at the outset that a determination of the solubility of reduced technetium would be difficult because the sample counting rates due to the ^{99}Tc beta particles would be relatively close to the background counting rate of the liquid scintillation counter. Counting times were 120 minutes, which was estimated to yield reasonable statistical accuracy for the samples of low counting rate, but short enough to be practical when as many as 39 samples needed to be counted for one experiment over a period of 3.25 days.

An analysis of the errors due to counting statistics was carried out for a measurement of technetium solubility, taking into account the certified error of $\leq$ 1.2% in the Amersham technetium standard solution used, together with statistical counting errors in the background, standard, and sample counts. Details are given in Meyer et al. (1988). In the case for which a detailed analysis was made (Table 2.2, 1.78 mol/L NaCl), the standard deviation in the solubility of reduced technetium was 11.1%, but for counting errors alone was 2.30%. Thus, it appears that counting errors account only for a small part of the errors in measuring technetium solubility. Although counting errors can be estimated with considerable accuracy, the magnitude of other types of errors, such as incomplete extraction, errors associated with pipetting the small volumes used, and variations in experimental conditions from one determination to another, are more difficult to estimate.

2.3. RESULTS

In Figs. 1 and 2, concentration vs time plots for two experiments are shown, one at relatively high concentrations and one near the lower limit of our ability to assay the solution. The lines shown on Fig. 1 are second order regression fits to the data and are intended only to guide the eye. In the experiment shown in Fig. 1, the potential of the

electrode on which the oxide was deposited was controlled to +325 mV vs SCE, and the final concentration of Tc(VII) was controlled by the Tc(IV)-Tc(VII) electrochemical equilibrium (Eq. 3.1). The amount of Tc(IV) and Tc(VII) smoothly increased with time until a steady value was attained after about 12 days. For the other experiment, the electrode potential was not controlled. A relatively steady value was obtained after a few days, but because the values are so low there is more scatter in the data. These experiments emphasize the importance of distinguishing between the Tc(IV) and the Tc(VII) valence states because for these conditions the Tc(VII) concentrations were much greater than the Tc(IV) concentrations.

The results of the solubility measurements are given in Tables 2.1 to 2.3 and in Figs. 3 to 5. During the experiments, the pH generally drifted somewhat, often to less basic values. The range of the pH and average value for the last five determinations are given in Tables 2.1 to 2.3. The lines in Fig. 3 were obtained from calculations discussed below.

In Table 2.4, the degree of hydration of the oxide is shown. Values are given for n in the formula $TcO_2 \cdot nH_2O$ as determined by the weight of the electrodeposited oxide. The average value of n for determinations with oxides dried at least four days is 1.63 ± 0.28.

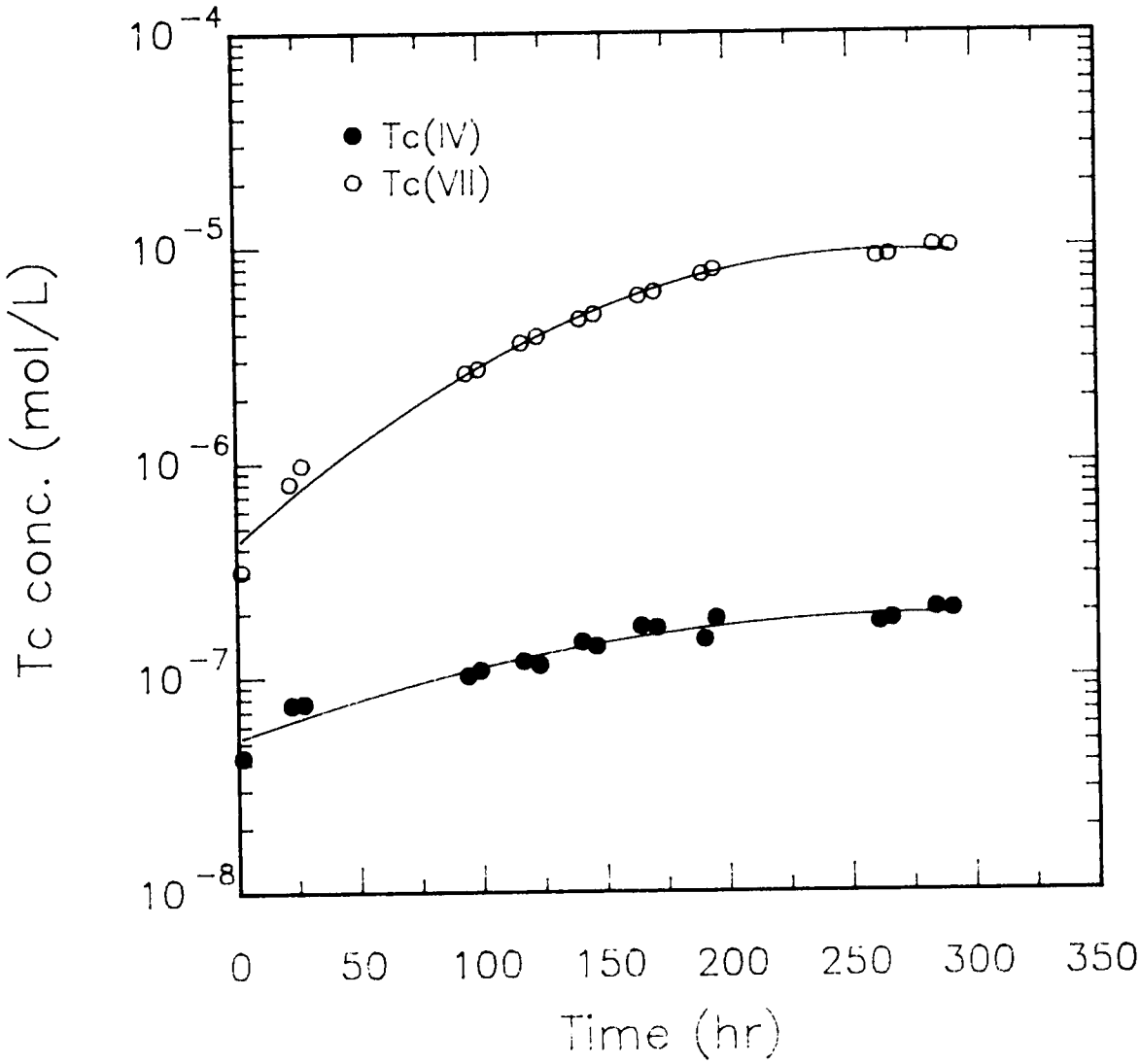

Fig. 1. Concentrations of Tc(VII) and Tc(IV) vs time. Samples were electrodeposited oxide in 0.1 mol/L HCl, 25°C. The electrode potential was controlled to +325 mV vs SCE.

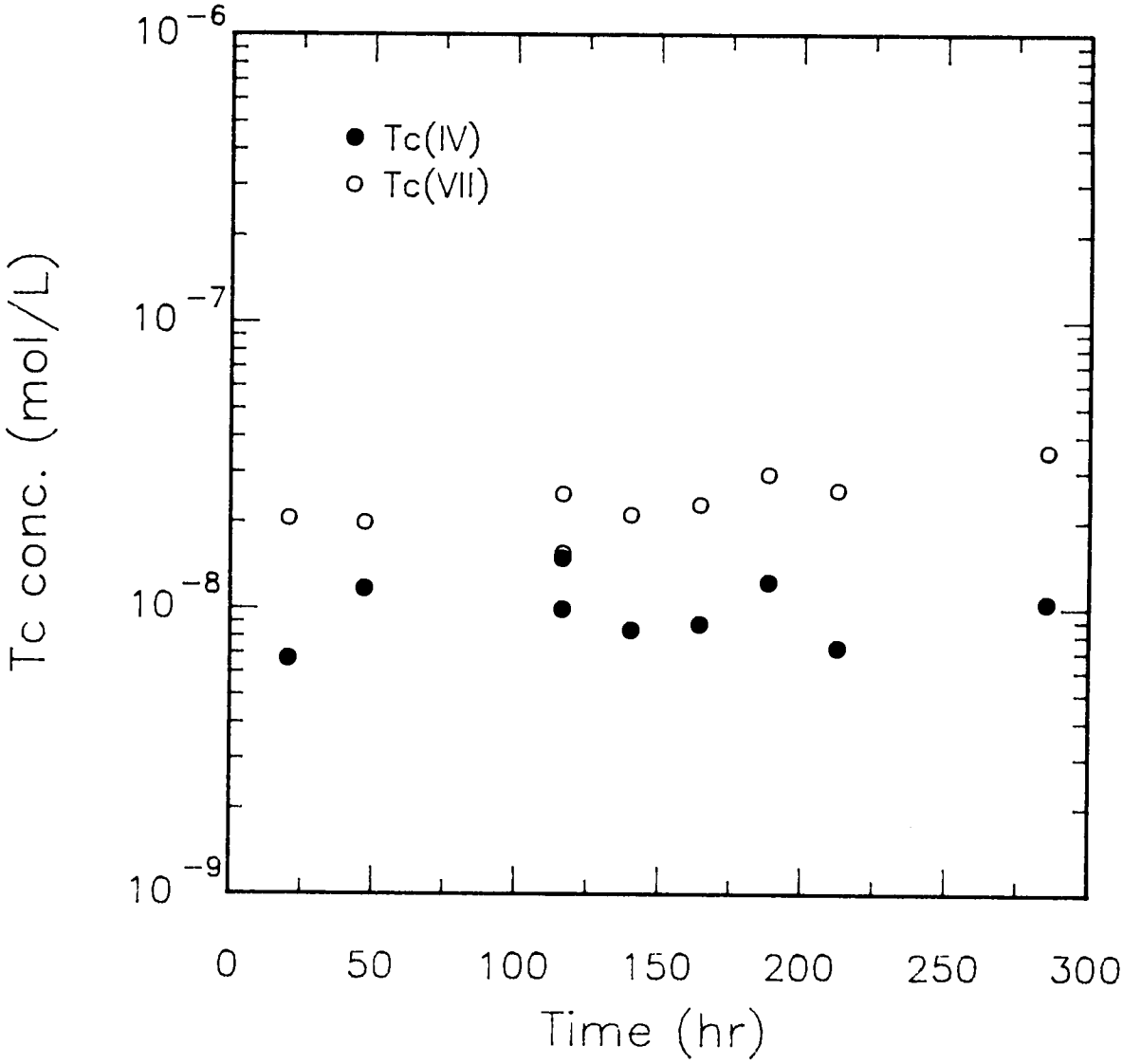

Fig. 2. Concentrations of Tc(VII) and Tc(IV) vs time. Samples were electrodeposited oxide in basalt groundwater GR-4 (composition given in Table 2.1), pH 9.27, 25°C. The electrode potential was not controlled.

Table 2.1. Column determinations of solubilities of $TcO_2 \cdot nH_2O$ as a function of pH

Solution	Reduced Tc (mol/L)	pH range	Average pH
1.0 mol/L HCl	$(5.41 \pm 1.16) \times 10^{-5}$	-0.04 - 0.21	0.09
0.1 mol/L HCl	$(1.05 \pm 0.03) \times 10^{-6}$	1.04 - 1.06	1.05
0.1 mol/L HCl and 0.01 mol/L NaCl	$(1.92 \pm 0.24) \times 10^{-7}$	1.23 - 1.34	1.27
0.01 mol/L HCl and 0.01 mol/L NaCl	$(2.51 \pm 0.29) \times 10^{-8}$	2.15 - 2.17	2.16
0.001 mol/L HCl and 0.01 mol/L NaCl	$(9.08 \pm 2.82) \times 10^{-9}$	2.99 - 3.04	3.01
0.01 mol/L NaCl	$(7.45 \pm 2.83) \times 10^{-9}$	4.82 - 5.22	4.95
0.01 mol/L NaCl	$(1.01 \pm 0.41) \times 10^{-8}$	8.21 - 8.37	8.23
0.01 mol/L NaCl	$(5.47 \pm 2.20) \times 10^{-6}$	9.51 - 9.66	9.63
0.01 mol/L Na^+ $NaHCO_3$ and Na_2CO_3	$(1.77 \pm 0.24) \times 10^{-8}$	9.44 - 9.63	9.54
GR-4*	$(1.47 \pm 0.36) \times 10^{-8}$	9.24 - 9.36	9.29

* Basalt groundwater:
334 mg/L Na^+, 405 mg/L Cl^-, 13.8 mg/L K^+, 2.2 mg/L Ca^{2+}, 96.3 mg/L SiO_2, 92 mg/L HCO_3^-, 19.9 mg/L F^-, 4.0 mg/L SO_4^{2-}.

Table 2.2. Column determinations of solubilities of $TcO_2 \cdot nH_2O$ as a function of NaCl concentration

Solution	Reduced Tc (mol/L)	pH range	Average pH
0.05 mol/L NaCl	$(3.84 \pm 0.26) \times 10^{-9}$	8.01 - 7.44	7.71
0.1 mol/L NaCl	$(2.52 \pm 0.84) \times 10^{-9}$	7.20 - 6.57	6.90
0.5 mol/L NaCl	$(1.20 \pm 0.58) \times 10^{-9}$	7.93 - 7.51	7.67
1.0 mol/L NaCl	$(3.71 \pm 0.98) \times 10^{-9}$	9.10 - 8.75	8.89
1.0 mol/L NaCl	$(2.45 \pm 0.87) \times 10^{-9}$	8.66 - 8.42	8.59
1.2 mol/L NaCl	$(3.93 \pm 0.20) \times 10^{-9}$	9.33 - 9.01	9.22
1.6 mol/L NaCl	$(3.57 \pm 0.25) \times 10^{-9}$	9.28 - 9.07	9.15
1.78 mol/L NaCl	$(4.76 \pm 0.53) \times 10^{-9}$	9.44 - 9.18	9.33
2.0 mol/L NaCl	$(1.47 \pm 0.41) \times 10^{-9}$	9.22 - 9.12	9.18
2.2 mol/L NaCl	$(4.63 \pm 0.37) \times 10^{-9}$	9.02 - 8.90	8.95
2.6 mol/L NaCl	$(2.24 \pm 0.14) \times 10^{-9}$	9.08 - 8.90	9.04
2.6 mol/L NaCl	$(2.60 \pm 0.16) \times 10^{-9}$	8.46 - 8.05	8.25

Table 2.3. Solubilities of electrodeposited $TcO_2 \cdot nH_2O$[a]

Solution	Reduced Tc (mol/L)	pH range	Average pH
DEPOSITED FROM ACID SOLUTION:			
0.1 mol/L HCl[b]	$(1.93 \pm 0.12) \times 10^{-7}$	0.93 - 1.01	0.96
0.1 mol/L HCl[b]	$(3.31 \pm 0.25) \times 10^{-7}$	0.84 - 0.90	0.88
0.01 mol/L HCl[b]	$(8.85 \pm 2.31) \times 10^{-9}$	1.94 - 1.94	1.94
0.01 mol/L NaCl	$(3.78 \pm 1.23) \times 10^{-9}$	2.65 - 2.74	2.67
0.01 mol/L NaCL	$(2.90 \pm 1.90) \times 10^{-9}$	3.31 - 3.39	3.37
0.01 mol/L NaCl	$(1.07 \pm 0.74) \times 10^{-8}$	3.60 - 3.75	3.67
0.01 mol/L NaCl[b]	$(2.50 \pm 0.48) \times 10^{-8}$	8.96 - 9.05	9.00
GR-4[c]	$(9.43 \pm 1.75) \times 10^{-9}$	9.27 - 9.36	9.32
0.01 M Na^+ $NaHCO_3$ and Na_2CO_3	$(1.77 \pm 0.32) \times 10^{-8}$	9.60 - 9.77	9.70
0.01 mol/L NaCl 0.001 mol/L HCl	$(2.70 \pm 1.49) \times 10^{-9}$	2.98 - 3.04	3.01
0.01 mol/L NaCl 0.01 mol/L HCl	$(2.55 \pm 1.65) \times 10^{-9}$	2.06 - 2.12	2.09
0.01 mol/L NaCl 0.1 mol/L HCl	$(1.20 \pm 0.24) \times 10^{-8}$	1.08 - 1.27	1.14
1 mol/L HCl	$(9.58 \pm 0.57) \times 10^{-8}$	-0.14 - -0.02	-0.06

(continued next page)

(Table 2.3, continued)

DEPOSITED FROM BASIC SOLUTION:

GR-4[c]	$(2.94 \pm 2.80) \times 10^{-9}$	9.31 - 9.49	9.43
0.01 mol/L NaCL	$(3.14 \pm 1.54) \times 10^{-9}$	8.71 - 8.74	8.73
0.01 mol/L NaCl	$(3.20 \pm 1.69) \times 10^{-9}$	7.37 - 7.50	7.46
0.01 mol/L NaCl	$(1.70 \pm 1.29) \times 10^{-9}$	5.41 - 5.62	5.56
0.01 mol/L NaCl	$(2.20 \pm 0.78) \times 10^{-9}$	5.27 - 5.38	5.33

[a]The experiments are listed in the order that they were done.
[b]Freshly electrodeposited sample.
[c]Composition of GR-4 is given in Table 2.1.

Table 2.4. Determination of stoichiometry of $TcO_2 \cdot nH_2O$ (values of n)

Drying time	n
Deposited from acid solution:	
2 hr	4.22
1 d	2.87
2 d	0.44
7 d	2.10
7 d	1.50
Deposited from basic solution:	
7 d	1.38
4 d	1.81
4 d	1.38
Average for drying times of 4 and 7 d:	1.63 ± 0.28

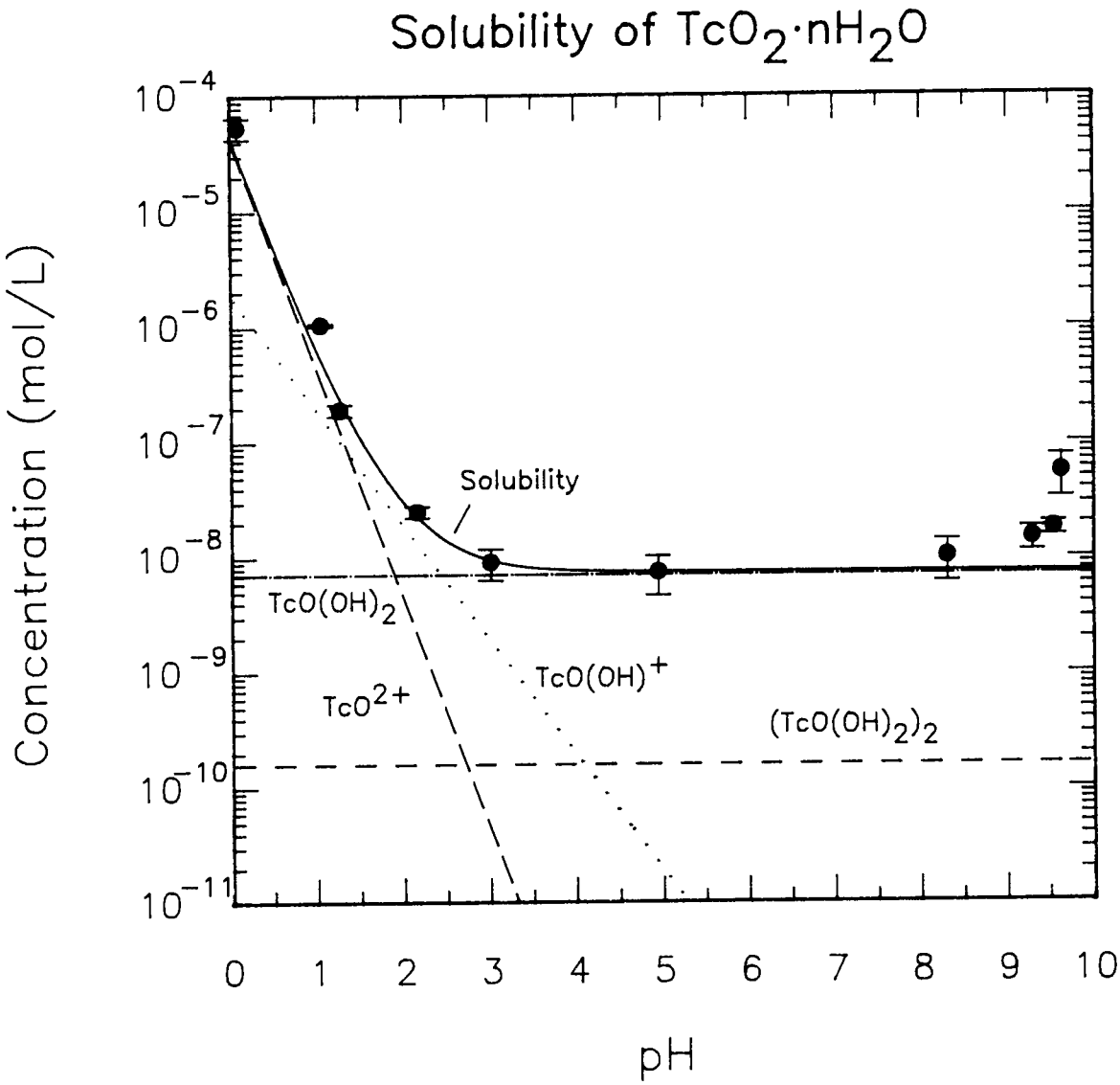

Fig. 3. Column determinations of the solubility of $TcO_2 \cdot nH_2O$ as a function of pH. Calculated solubility of $TcO_2 \cdot nH_2O$ and concentrations of aqueous species in equilibrium with the oxide for $K_s = 4.47 \times 10^{-33}$.

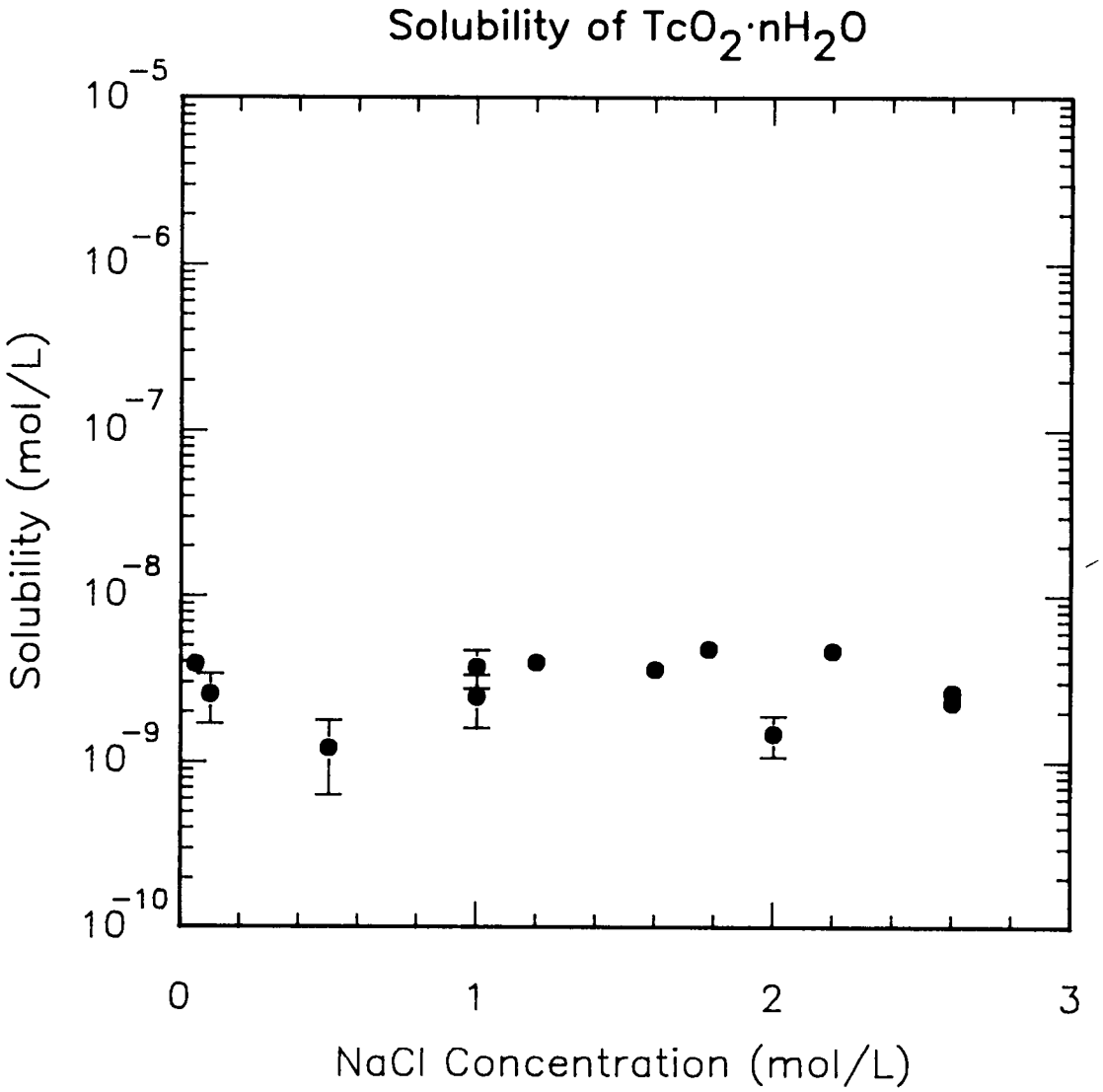

Fig. 4. Column determinations of solubilities of $TcO_2 \cdot nH_2O$ as a function of NaCl concentration. (For the points where no error bars are shown, the errors are small and are therefore contained within the symbols.)

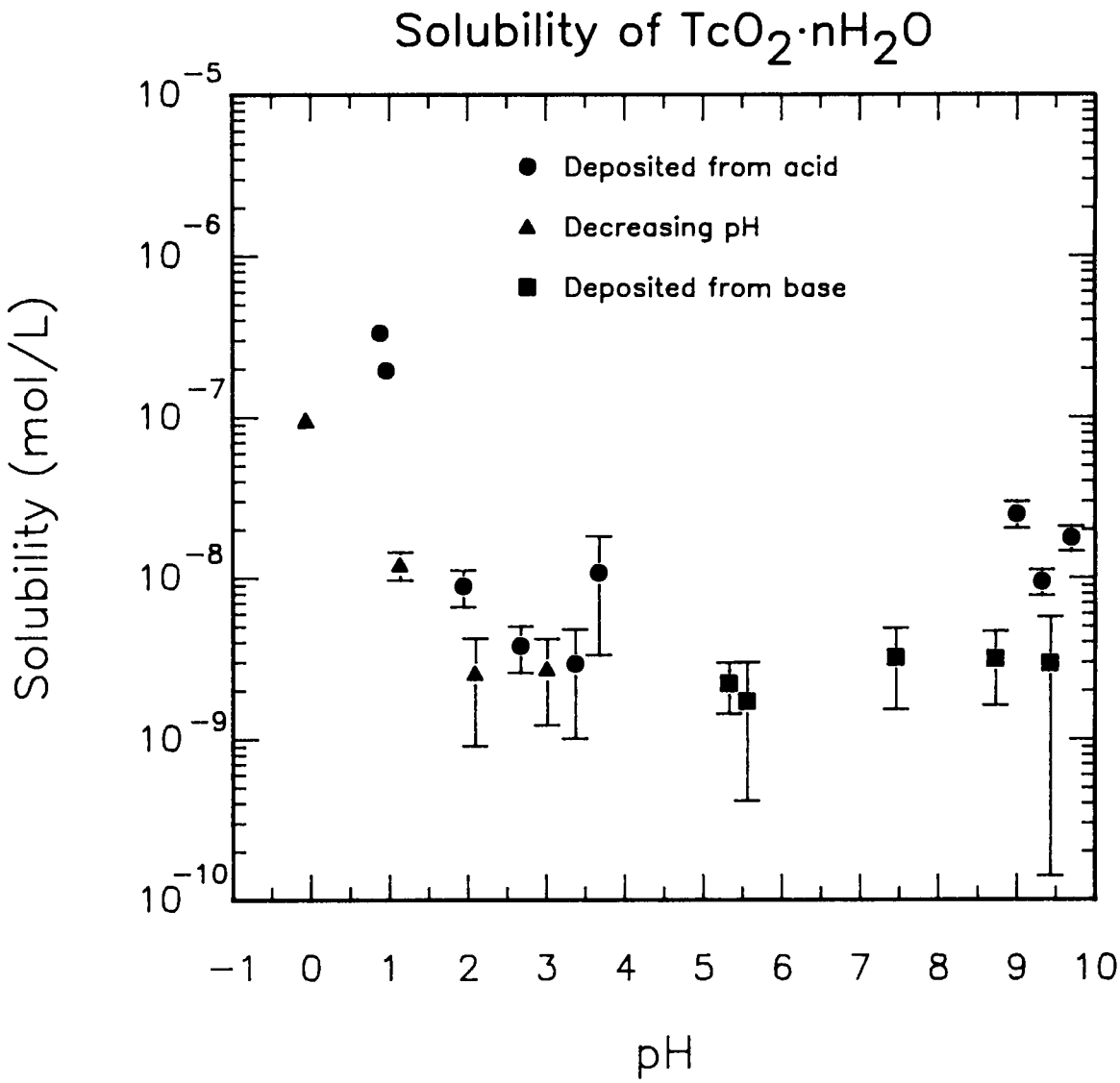

Fig. 5. Solubilities of electrodeposited $TcO_2 \cdot nH_2O$ as a function of pH. (For the points where no error bars are shown, the errors are small and are therefore contained within the symbols.)

2.4 DISCUSSION OF SOLUBILITY RESULTS

The results of the solubility experiments shown in Tables 2.1 to 2.3 are plotted in Figs. 3 to 5. The solubilities measured by the column method and the solubilities measured with electrodeposited oxides show similar trends in that the values are highest in acid solutions, decrease to a minimum, and rise somewhat in the pH region 5 to 10. In Table 2.3, the experiments are listed in the order in which they were done, and the experiments done with freshly deposited oxide are indicated. The last four experiments shown in Table 2.3 for acid-deposited oxides, which were done in solutions from pH 3.01 to -0.06, were carried out with one sample of oxide that had been extensively studied in alkaline solution. The data from these four experiments are not consistent with those in acid solutions shown at the top of the table, which were done after a sample was first prepared. It is possible that the exposure to basic solutions tended to lower the solubility of this sample or perhaps lowered the rate of dissolution in acid solution. The samples deposited from basic solution showed very low solubilities.

The solubilities in Table 2.2 and Fig. 4 for NaCl solutions are approximately the same for all concentrations except that the solubility values may be low at NaCl concentrations of 0.5 and 2.0 mol/L. These data show that there is no effect of NaCl concentration on the solubility, and all of the measured solubilties are quite low. These experiments were not done in the order shown in Table 2.2; they were done in arbitrary order with respect to the concentration of NaCl.

The column data were taken with oxide-coated sand with a high surface area, and less solution (25 mL) was used in the column experiments than in the experiments with electrodeposited oxides (100 mL). The more favorable surface-to-volume ratio helped establish equilibrium more rapidly, thus insuring that the technetium(IV) was in true thermodynamic equilibrium with the oxide.

These experiments used solutions that were initially free of technetium, and as the solubility product equilibrium was established, the concentration of Tc(IV) increased to the equilibrium value, as shown in Figs. 1 and 2. However, Tc(VII) also appeared in solution, possibly from several sources. In the case of the oxides on electrodes whose potential was controlled by a potentiostat, the concentration was controlled by the Tc(IV)/Tc(VII) redox equilibrium. Most of the experiments were done without control of the potential, and the concentration of the TcO_4^- appearing in solution seemed to vary in a random manner. Residual Tc(VII) from the original precipitation solution could contribute to the Tc(VII) present. Another possible source of technetium(VII) is oxidation of Tc(IV) either by residual oxygen or by products of radiolysis of ^{99}Tc. To reduce the residual oxygen to a low level the entire apparatus was kept in an anoxic box filled with argon with < 1 ppm of oxygen. Assuming equilibrium, 1 ppm of oxygen in the gas phase corresponds to approximately 10^{-10} mol/L of oxygen. Considerable effort was used to eliminate all possible sources of oxygen in the cell. For example, all apparatus was deoxygenated by

placing the apparatus in a vacuum chamber; this procedure was especially necessary for plastics which have considerable capacity for dissolved molecular oxygen. Thus, unless oxygen was accidentally introduced, not much Tc(VII) could be produced by residual oxygen. At these very low concentrations of oxygen, the reaction of oxygen with Tc(IV) species would be very slow. A more likely source of oxidizing agents is radiolysis, which can produce both oxidizing and reducing agents.

In experiments with solutions which were prepared from the original stock solution of ammonium pertechnetate, small concentrations of technetium(IV) were always found. Stock solutions of ammonium pertechnetate, if allowed to stand for long periods of time, will gradually form a dark precipitate of technetium(IV) oxide. Thus, if any appreciable amount of technetium(VII) was present at the conclusion of the solubility experiment, some of the Tc(IV) could have been formed from radiolysis and would have led to high results if the rate of attainment of equilibrium between $TcO_2 \cdot nH_2O$ and the aqueous Tc(IV) species was not large enough. It is for this reason that we rejected determinations in which the ratio of technetium(VII) to technetium(IV) was greater than 200.

In Fig. 3, theoretical lines are drawn which represent total solubility and the concentrations of the species assumed to be present. The lines were calculated using Eqs. 2.6 to 2.9; activity coefficients are assumed to be one. The values of K_{h1} and K_{h2} are those given by Gorski and Koch (1969), and the value of K_{dim} is that given by Sundrehagen (1979). These equations follow the solubility discussion given by Rard (1982). In Rard's discussion the solid is assumed to be $TcO(OH)_2$ which corresponds to $TcO_2 \cdot H_2O$. We have modified Rard's equations slightly to show the oxide as $TcO_2 \cdot nH_2O$; in our experiments, n has an average value of 1.63 $\pm$ 0.28 (Table 2.4). The solubility product was calculated from the value of the solubility at pH 4.95, the minimum solubility observed in these experiments.

$$TcO_2 \cdot nH_2O(solid) + (1-n)H_2O = TcO^{2+} + 2(OH)^- \qquad K_s = 4.47 \times 10^{-33} \qquad (2.6)$$

$$TcO^{2+} + H_2O = TcO(OH)^+ + H^+ \qquad K_{h1} = 4.3 \times 10^{-2} \qquad (2.7)$$

$$TcO(OH)^+ + H_2O = TcO(OH)_2(aqueous) + H^+ \qquad K_{h2} = 3.7 \times 10^{-3} \qquad (2.8)$$

$$2TcO(OH)_2(aq.) = [TcO(OH)_2]_2(aq.) \qquad K_{dim} = 3.14 \times 10^{6} \qquad (2.9)$$

This scheme assumes the existence in solution of neutral monomers and dimers of $TcO(OH)_2$.

Because the solubility product was calculated from the total solubility at pH 4.95, the line representing the total solubility necessarily goes through this point. If the total solubility is accurately given by Eqs. 2.6 to 2.9, then the solubility should be constant with pH in basic solutions. However, the solubilities in solutions more basic than pH 4.95 are above the line, suggesting that other species may be present

which increase the solubility. Although we have found no evidence of negative species in the literature, it is possible that species such as $Tc(OH)_5^-$ might be formed which tend to increase the solubility in basic solutions.

The average value of the solubilities in NaCl solutions given in Table 2.2 is 3.08 x 10^{-9} mol/L, and the average pH is 8.6. The solubility product K_s calculated from these averages is (1.89 $\pm$ 0.71) x 10^{-33} ($\log_{10} K_s$ = -32.7). The solubilities of reduced technetium shown in Table 2.2 are similar in magnitude to those that we found for oxides electrodeposited from basic solution (Table 2.3); the solubility product calculated from the average of these data is (1.63 $\pm$ 0.40) x 10^{-33} ($\log_{10} K_s$ = -32.8). These are within the estimate $\log_{10} K_s$ = -33.45 $\pm$ 1.0 given by Rard (1982).

As shown in Table 2.4, the oxides are hydrated, and the average value of n for $TcO_2 \cdot nH_2O$ is 1.63 $\pm$ 0.28 for those dried for 4 or more days. It is possible that the formula is $TcO_2 \cdot 2H_2O$ as Cartledge and others have suggested. Whether the variation in the measured value of n is due to experimental error or actual differences in n is difficult to determine. Because the measurement is made by weighing from 10 to 20 mg of oxide on an electrode that weighed approximately 4 g, small weighing errors can lead to large errors in n. There are also possible sources of error in the determination of the amount of technetium in the deposit.

It is interesting that the solubilities of oxides formed in basic solutions are lower than the solubilities of oxides formed in acid solutions. Also, we observed that the oxides electrodeposited from basic solution were less adherent to the platinum electrode than those electrodeposited from acid solutions. These observations suggest that there may be differences in hydration leading to differences in structure, depending on the conditions of the reduction in aqueous solutions, and this could account for the observed differences in solubility. Similarly, the differences in electrode potential observed by different investigators (Section 3 of this report) may also be the results of differences in structure and composition. Anhydrous technetium oxide, TcO_2, can be prepared by high temperature preparative techniques; however, attempts to measure the electrode potential (Cobble et al. 1953) and Tc(IV) solubility (Lieser et al. 1987) of this material have not been successful. Apparently it is a much less soluble form of Tc(IV) oxide, and the only observed dissolution was the formation of Tc(VII), which depended upon the amount of dissolved oxygen (Lieser at al., 1987). However, this material may be the only oxide of Tc(IV) prepared so far that has a well-defined structure. In terms of applicability to thermodynamic calculations relative to the formation of oxides in groundwaters, the oxides formed by reduction in aqueous solutions are probably more relevant, but their thermodynamic properties may vary somewhat depending on the method and conditions of formation. To obtain conservative results in calculations of transport rates from high-level nuclear waste repositories, solubilities considerably greater than the highest we have measured at the pH of interest should be used in the calculations, and thermodynamic

properties dependent on solubilities should be calculated from these conservatively selected solubilities.

In any calculation of the total technetium concentration in a given geological environment, the possible presence of Tc(VII) must be considered. If the repository environment is sufficiently reducing and there is sufficient reducing capacity, then there may be a negligible amount of Tc(VII). However, in this calculation the possibility of formation of Tc(VII) from oxidizing agents formed by radiolysis must be considered. The problem then may become a question of kinetics, i.e., whether radiolytically induced formation of Tc(VII) is greater than the rate of reduction of Tc(VII) by reducing agents in the geological environment.

3. ELECTRODE POTENTIALS

3.1 INTRODUCTION

A number of measurements have been reported in the literature for the standard potential of the Tc(IV)-Tc(VII) couple, which for acid solutions is represented by Eq. 3.1.

$$TcO_2 + 2H_2O = TcO_4^- + 4H^+ + 3e^- \qquad (3.1)$$

The usual value quoted in the literature for the standard potential, E^o = 0.738 V, is that of Cartledge and Smith (1955). The procedure used to form the oxide was to electrodeposit a "brown adherent deposit" of what was assumed to be TcO_2 from a solution of potassium pertechnetate acidified with sulfuric acid. No further description is given of the solution from which the technetium was deposited. No analysis of the brown deposit is given in this reference. A total of eight measurements were made in mixed solutions of sulfuric acid and potassium pertechnetate. However, seven of the eight solutions were in the pH range 2.49 to 3.10. The only other measurement, taken at pH 6.65, was reported as slowly becoming more positive, and so may not have represented a stable potential. Of the seven measurements between pH 2.49 and 3.10, there was a spread in values from 0.733 to 0.743 V. The average of the measurements was reported to be 0.738 $\pm$ 0.003 V (using 0.242 V for the potential of the saturated calomel reference electrode). The concentration range of the $KTcO_4$ used was 1.00 x 10^{-3} to 1.82 x 10^{-3} mol/L in these solutions. Thus, limited ranges of pH and concentration were investigated, and the ranges were not large enough to determine accurately the slopes of the plots of the potential vs concentration of TcO_4^- and the potential vs pH.

An earlier measurement by Cobble et al. (1953) gives the result E^o = 0.782 $\pm$ 0.011 V. Cartledge and Smith suggested that this result was higher than their value of 0.738 V because the presence of oxygen in the cell used by Cobble et al. tended to polarize the electrode in the positive direction. Although this is a possible explanation, there is also the possibility that the oxides were prepared differently, and differences in composition and/or structure accounted for the difference. A well-defined thermodynamic potential can be obtained only from a well-defined solid and solution, and the methods used to prepare the oxides may differ sufficiently to cause these differences in the standard potential. Spitsyn et al. (1964) calculated a value of 0.71 V from electrodeposition experiments, and the most recent investigation (Liebscher and Münze 1975) gives directly measured values as a function of pH as follows:

pH	1.05	1.85	2.90	3.85	4.50
E^o (V)	0.769	0.766	0.769	0.745	0.728

At the higher pH values, the potential seems to be dropping somewhat, perhaps due to a change in composition or structure of the solid which here is reported to be hydrated $TcO_2 \cdot H_2O$. This work seems to be carefully done with proper consideration to corrections from activity coefficients and junction potentials. The value of 0.769 V at pH 1.05 is closer to the value given by Cobble et al. (0.782 V) than the value 0.738 V.

As pointed out by Isherwood (1985), the potential for the Tc(IV) - Tc(VII) couple (Eq. 3.1) probably refers to a hydrated oxide rather than the anhydrous oxide, TcO_2. In a later publication, Cartledge (1971) refers to oxide electrodeposited by the method used in his 1955 determinations as the hydrated form, $TcO_2 \cdot 2H_2O$ or possibly $Tc(OH)_4$. Thus, thermodynamic calculations based on the 0.738 V potential should probably refer to the hydrated form of Tc(IV) oxide. Some of the differences observed in the standard potential reported in the literature may therefore be due to differences in hydration. Our experiments to determine the stoichiometry of electrodeposited oxides indicated that they had the composition $TcO_2 \cdot nH_2O$, where n is equal to 1.63 $\pm$ 0.28 (Table 2.4).

To reduce uncertainties related to the unavoidable presence of liquid junction potentials and the estimation of activity coefficients which could be significant, electrode potentials were measured in 5×10^{-3} mol/L HCl at relatively low concentrations of the TcO_4^- ion. Despite these precautions there will always be an uncertainty of a few millivolts due to these effects. Calculation of the activity coefficient correction using the Debye-Hückel limiting law at these low concentrations resulted in values no greater than a millivolt in the calculation of E^o.

3.2 EXPERIMENTAL

For the studies of the electrode potential, technetium oxide was electrodeposited onto a platinum mesh electrode. The platinum mesh electrode was placed in a Princeton Applied Research (PAR) electrolytic cell which contained 100 mL of a 0.005-mol/L solution of technetium at pH 2. The electrode had a cross-sectional area of about 6 cm^2 and an estimated actual area of 3 - 4 cm^2. The electrode potential was controlled by a PAR Model 173 Potentiostat/Galvanostat; significant electrolysis occurred at -200 mV vs the saturated calomel electrode (SCE). With respect to the hydrogen scale, the potential was +44.5 mV. The current density was approximately 1.0 mA/cm^2. A black solid gradually formed on the electrode, and deposition was stopped after about five hours.

The electrode measurements were made with a Hewlett Packard 3490A Multimeter capable of reading potentials to within $\pm$ 20 uV. Before use it was calibrated by the Oak Ridge National Laboratory (ORNL) Instrumentation and Controls Division. The PAR cell had a jacket through which water thermostatted at 25 $\pm$ 0.1°C was circulated. Potential measurements were made with respect to a saturated calomel

electrode (SCE) which was checked by periodic comparison to two SCE electrodes maintained as standards. Generally all of the electrodes were within a few tenths of a millivolt of each other. The potential of the SCE is 0.244_5 V with respect to the standard hydrogen electrode. This is the value recommended by Hills and Ives (1961) and Janz and Kelly (1964) for the case where a liquid junction is established with a dilute solution. A value of 0.242 V was used by Cartledge and Smith (1955).

3.3 RESULTS

In Tables 3.1 to 3.3, results are given for the potential as a function of concentration at constant pH for two different electrodeposits of the oxide. Because there were slight variations in pH, the values in the potential column labeled "E pH 2.3" were normalized to a value at pH 2.3 using the coefficient 0.0788 V/(pH unit). The columns labeled "log activ." contain values of the logarithms of the activities obtained by multiplying each concentration by an activity coefficient calculated from the Debye-Hückel limiting law.

Table 3.1. Effect of concentration on potential (sample 1)

E (V)	E pH 2.3 (V)	$[TcO_4^-]$ (mol/L)	pH	E° (V)	log activ.
0.243	0.242	9.66×10^{-5}	2.31	0.749	-4.049
0.258	0.258	2.78×10^{-4}	2.30	0.755	-3.590
0.262	0.265	9.39×10^{-4}	2.27	0.746	-3.063
0.273	0.276	2.88×10^{-3}	2.27	0.748	-2.582
0.274	0.274	2.95×10^{-3}	2.30	0.751	-2.572

Table 3.2. Effect of concentration on potential (repeat sample 1)

E (V)	E pH 2.3 (V)	$[TcO_4^-]$ (mol/L)	pH	E° (V)	log activ.
0.253	0.251	1.01×10^{-4}	2.32	0.760	-4.028
0.258	0.256	2.85×10^{-4}	2.33	0.757	-3.579
0.266	0.265	9.78×10^{-4}	2.32	0.754	-3.046
0.275	0.275	2.93×10^{-3}	2.31	0.753	-2.575

Table 3.3 Effect of concentration on potential (sample 2)

E (V)	E pH 2.3 (V)	$[TcO_4^-]$ (mol/L)	pH	E° (V)	log activ.
0.224	0.224	1.06×10^{-4}	2.31	0.730	-4.007
0.237	0.235	3.15×10^{-4}	2.33	0.735	-3.536
0.252	0.248	1.13×10^{-3}	2.35	0.740	-2.984
0.263	0.262	3.51×10^{-3}	2.32	0.740	-2.497

In Tables 3.4 and 3.5, the effect of pH on potential at constant technetium concentration is shown. The technetium concentrations varied slightly and were normalized using the theoretical coefficient 0.0197 V/log unit of concentration. Experiments were done at TcO_4^- concentrations of approximately 10^{-4} mol/L with sample 1 and 10^{-3} mol/L with a freshly prepared deposit (sample 3).

Table 3.4 Effect of pH on potential (sample 1)

E (V)	E(norm.) (V)	$[TcO_4^-]$ (mol/L)	pH	E° (V)
0.127	0.126	1.14×10^{-4}	3.99	0.764
0.165	0.164	1.20×10^{-4}	3.40	0.755
0.201	0.200	1.12×10^{-4}	2.83	0.747
0.239	0.239	1.07×10^{-4}	2.30	0.744
0.272	0.273	9.11×10^{-5}	1.90	0.747

Table 3.5 Effect of pH on potential (sample 3)

E (V)	E(norm.) (V)	$[TcO_4^-]$ (mol/L)	pH	E° (V)
0.146	0.145	1.14×10^{-3}	3.81	0.749
0.165	0.164	1.15×10^{-3}	3.56	0.748
0.203	0.202	1.16×10^{-3}	3.00	0.743
0.246	0.245	1.15×10^{-3}	2.46	0.743
0.286	0.285	1.13×10^{-3}	2.01	0.748

The data from Tables 3.3 to 3.5 are plotted in Fig. 6. The slope of the line in Fig. 6 is 0.0211 ± 0.005 V/(log unit). The theoretical slope at 25°C is 0.0197 V/(log unit). While the agreement between measured and theoretical slopes seems satisfactory, it appears that one of the electrodes (sample 2) exhibited somewhat lower values of potential than the other two.

The data from Tables 6 and 7 on potential vs pH are plotted in Fig. 7. The straight lines shown were fitted to the respective data sets by the method of least squares. The slope of the line in Fig. 7 for approximately 10^{-4} mol/L TcO_4^- is -0.0700 ± 0.0024 V/pH unit, and the theoretical value is -0.0788 V/pH unit. There appears to be a slight curvature to the data as plotted; in fact, the slope appears to be approaching the theoretical slope at the lower pH values. Initially, at 10^{-4} mol/L TcO_4^-, concentration and pH were adjusted, and the potential was followed with time. However, the potentials tended to drift with time, and it was not possible to determine a steady potential. Therefore, the potential was fixed by a potentiostat; the concentration and pH were then allowed to change with time until a steady state was observed. Because of the difficulty in obtaining steady states at 10^{-4} mol/L Tc, the concentration was increased to 10^{-3} mol/L. In this case the potentials were allowed to change with time after the pH and concentration were adjusted, and they came to a steady state after about 4 hr at the lower pH values and about a day at the highest pH value. The slope of the line at approximately 10^{-3} mol/L TcO_4^- is -0.0773 ± 0.0023 V/pH unit, which is very close to the theoretical slope of -0.0788 V/pH unit. Values of the standard potential in the tables were computed with the assumptions that the theoretical sl s were applicable. Because values of the potential were less reliable at the lower Tc concentrations, we used only measurements at concentrations > 9 x 10^{-4} mol/L to determine the average E^o value of 0.747 ± 0.004 V vs the standard hydrogen electrode from the data in Tables 3 to 6.

3.4 DISCUSSION OF RESULTS

Cartledge and Smith (1955) used techniques similar to ours to measure potentials, and they reported the standard potential as 0.738 ± 0.003 V. Cartedge and Smith measured their potentials with respect to the SCE as we did, but they used a value of 0.242 V for the potential of the SCE, and we used the more recent value 0.244_5 V (Hills and Janz 1961, Janz and Kelly 1964). We recalculated the values for E^o from Cartledge and Smith's data using the same computer program that we used; this resulted in the value 0.741 ± 0.004 V. There appears to be agreement between our value of 0.747 ± 0.004 V and that of Cartledge and Smith (1955), but not with the value 0.782 ± 0.011 V of Cobble et al. (1953) or the more recent values of Liebscher and Münze (1955), which varied with pH.

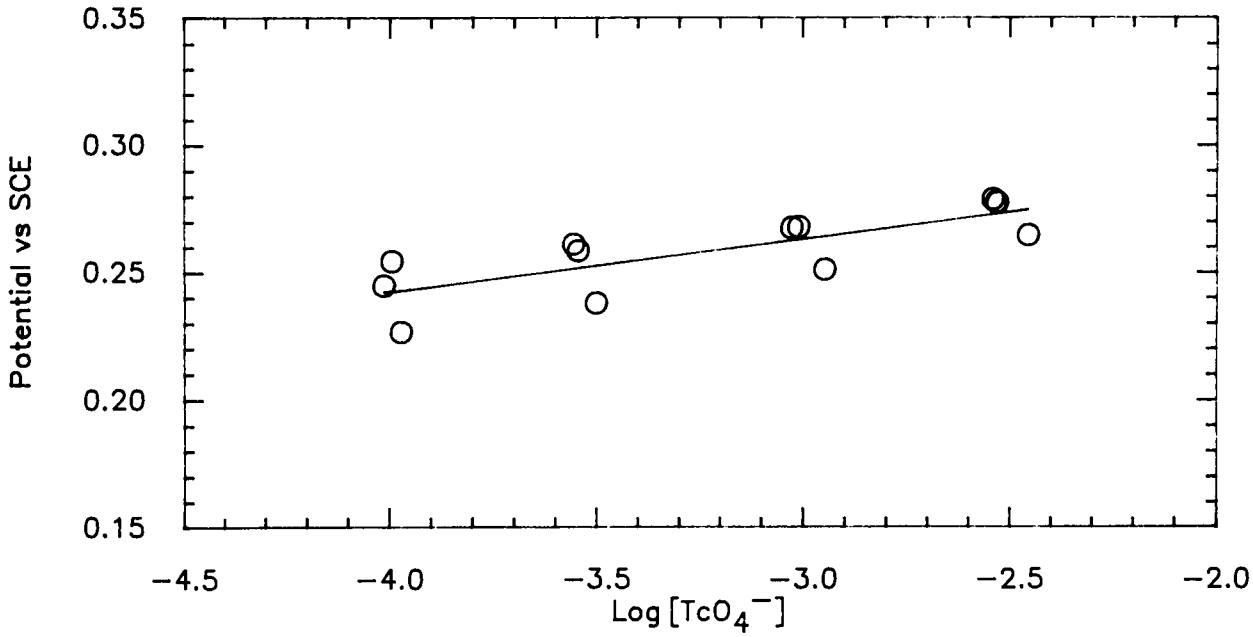

Fig. 6 Potential vs log[TcO_4^-]

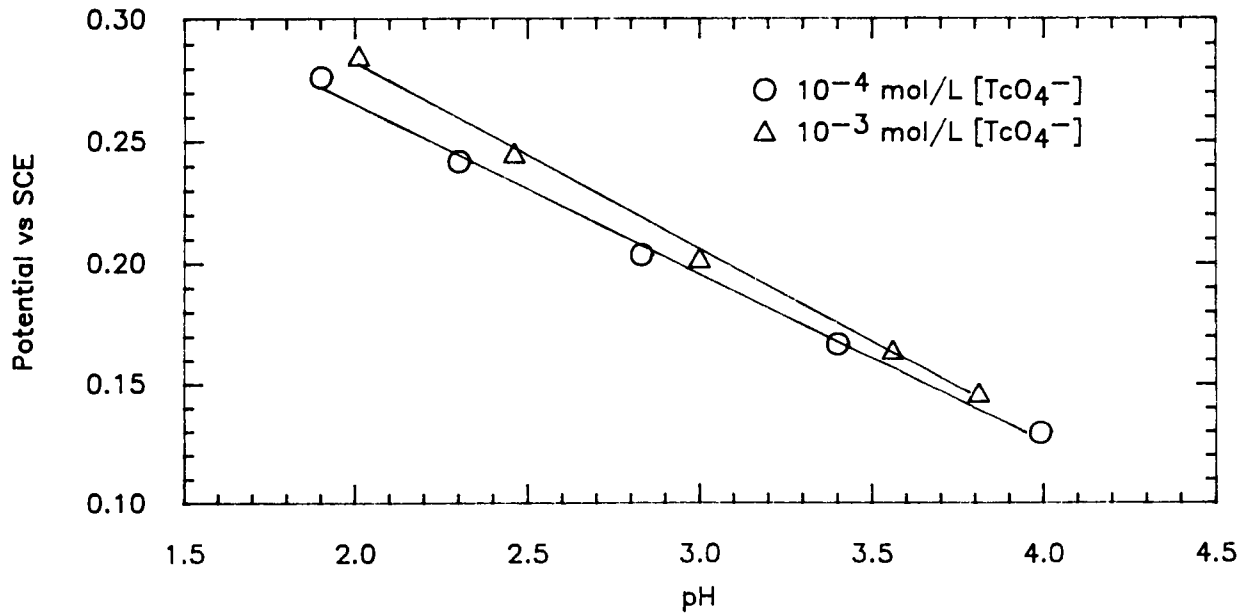

Fig. 7 Potential vs pH

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11. ABSTRACT *(200 words or less)*

Solubilities of Tc(IV) oxides have been determined in a number of solutions in the pH range 1 to 10. Technetium oxide was prepared either by precipitation upon purified sand with a 30% excess of hydrazine or by electrodeposition. The concentrations of total technetium and Tc(IV) species in the solutions were periodically determined by separating the oxidized and reduced technetium species using a solvent extraction procedure and counting the beta activity of the ^{99}Tc with a liquid scintillation counter. In basic solutions, the concentrations of Tc(IV) species in equilibrium with the oxide were in the range of 10^{-8} to 10^{-9} mol/L and tended to increase slightly with pH. In acid solutions the concentrations were much higher and were consistent with literature data on the hydrolytic species of Tc(IV). These data can be used to estimate Tc(IV) solubilities for cases where solubility limits transport of technetium in reducing environments of high-level waste repositories. Because there is some disagreement among published values of E^0 for the Tc(VII)-Tc(IV) redox couple, a redetermination of the standard potential was completed. The value of E^0 was determined to be 0.747 ± 0.004 V. Within the limits of error, this agrees most closely with the value E^0 = 0.741 ± 0.004 V reported by Cartledge and Smith (1955).

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