

Dissolution of Tc(IV) Oxides in Aqueous Solutions

LIU De-jun* and FAN Xian-hua

China Institute of Atomic Energy, P. O. Box 275(93), Beijing 102413, China

Abstract

The long-lived fission product ^{99}Tc is present in large quantities in nuclear wastes and its chemical behavior in aqueous solution is of considerable interest. Under oxidizing conditions technetium exists as the anionic species TcO_4^- whereas under the reducing conditions it is generally predicted that technetium will be present as $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. Technetium oxide was prepared by reduction of a technetate solution with Sn^{2+} . The concentration 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. The experimental results show that the rate of oxidation of Tc(IV) in simulated groundwater and redistilled water is about $(1.49\sim 1.86) \times 10^{-9}$ mol/(L·d) under aerobic conditions, but Tc(IV) in simulated groundwater and redistilled water is not oxidized under anaerobic conditions. Under aerobic or anaerobic conditions the solubility of Tc(IV) oxide in simulated groundwater and redistilled water is equal on the whole.

Key words: Tc(IV) oxide; solubility; rate of oxidation

Introduction

The deep geological disposal of the high level radioactive wastes is expected to be a safer disposal method in most countries.¹ The long-lived fission product ^{99}Tc is

present in large quantities in nuclear wastes and its chemical behavior in aqueous solution is of considerable interest. It is not known whether in nuclear waste Tc is present as Tc(VII) or Tc(IV).² Under oxidizing conditions technetium exists as the anionic species TcO_4^- whereas under the reducing conditions, expected to exist in a deep geological repository, it is generally predicted that technetium will be present as $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. Overseas the solubility of Tc(IV) oxide in deep geological repository has been discussed³⁻⁵, whereas at home it was not reported on literatures. Many investigations have been carried out with respect to the reduction of TcO_4^- , but only little information is available about the oxidation of Tc(IV).^{2, 6} The information about the rate of oxidation of Tc(IV) is important under aerobic and anaerobic conditions for safety assessment of repository.

Experimental

Preparation and composition of simulated ground water can be seen from our previous paper⁷. Experiments were carried out under aerobic and anaerobic conditions. Anaerobic conditions were established in inert gas boxes ($\text{O}_2 < 5\text{ppm}$), filled with pure argon. pH value or CO_3^{2-} concentration of the simulated ground water or redistilled water was adjusted with 0.1mol/L NaOH and HCl or 0.01mol/L Na_2CO_3 in the experiment. pH value was measured by use of calibrated electrode (HI 2930, HANNA Ltd.). Stock solution of ^{99}Tc was prepared by adding $\text{NH}_4^{99}\text{TcO}_4$ (Radiochemical Centre, Amersham, England, kept in 0.1M NH_4OH solution) to the simulated ground water or redistilled water to obtain the tracer concentration of $3 \times 10^{-6}\text{mol/L}$.

The mixed solutions of TcO_4^- and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were shaken by a rotation machine, which rotated at time intervals in room temperature. After certain periods of time the phases were separated by centrifugation (TOMY RD-20III) at 20,000 rpm for 30minutes. 1 ml of the aqueous solution was mixed with 8 ml liquid cocktail, shaken for a while and measured for 60 minutes in an ultra low level liquid scintillation

spectrometer (Wallac Ltd.). An aliquot samples were removed from the aqueous solution and added to equivalent volumes of chloroform containing 0.05 mol/L tetraphenylarsonium chloride. The organic phase removes TcO_4^- very efficiently leaving Tc(IV)-species in the aqueous phase. Two to three consecutive extractions were carried out to secure complete removal of TcO_4^- from the solution before determining the concentration of Tc(IV) in the aqueous phase, if the $\text{TcO}_4^- / \text{Tc(IV)}$ ratio was less than 20. After extraction, 1 ml of the aqueous phase was measured in the liquid scintillation spectrometer as above. The concentration of Tc(IV) in the aqueous phase is the solubility of Tc(IV). The concentration of different Tc-species in aqueous solutions was measured as a function of time.

Results and discussion

Reduction stoichiometry of TcO_4^- and Sn(II)

Certain quantities of TcO_4^- and Sn^{2+} were mixed in redistilled water in a test tuber. The test tuber had been shaken on a rotation machine in room temperature for twenty days before the phases were separated by centrifugation. The relationship of the reduced mol amount of TcO_4^- and the added mol amount of Sn(II) was shown in Fig. 1. As seen from Fig. 1, the resulted curve from the reduced mol amount of TcO_4^- plotted against the added mol amount of Sn(II) is linear ($r = 0.988$) and the slope of the curve is about 2/3. TcO_4^- is reduced to Tc(IV) by Sn(II), since Sn(II) is oxidized to Sn(IV) in the reaction. The result in agreement with published data⁸ indicates that TcO_4^- is reduced to the IV state by stannous ion. The stoichiometry of the reduction can be expressed as: $3\text{Sn(II)} + 2\text{Tc(VII)} \rightarrow 3\text{Sn(IV)} + 2\text{Tc(IV)}$.

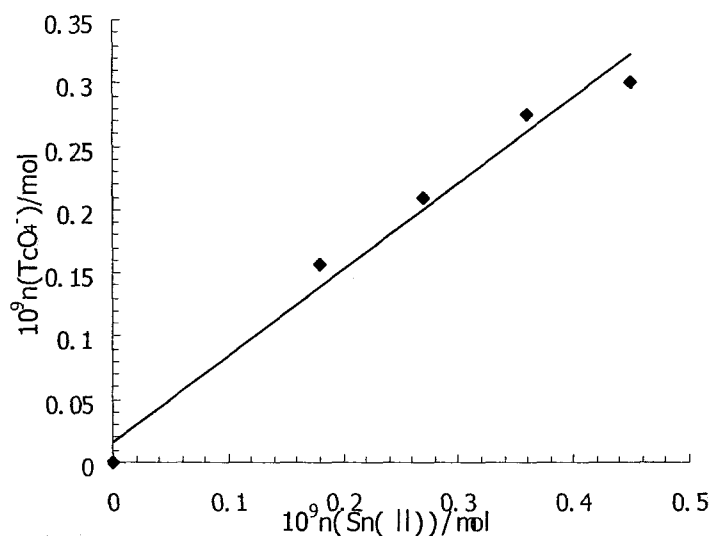


Figure 1 The relationship of the reacted mol amount of TcO_4^- and the added mol amount of Sn(II)

Effect of pH on solubility of Tc(IV) oxide

To 30 ml of TcO_4^- in simulated ground water or redistilled water is added 0.5 ml of 0.01 mol/L $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to help insure that all of the Tc(VII) was reduced by Sn^{2+} . The concentrations of Tc were determined by averaging all determinations in redistilled water and simulated groundwater with different pH before the experiment was ended. The effects of pH on solubility of Tc(IV) oxide under various conditions are shown in Fig. 2. Under aerobic or anaerobic conditions the solubility of Tc(IV) oxide in simulated groundwater and redistilled water is equal on the whole at the same pH values, as seen in Fig. 2. It decreases with increasing pH at $\text{pH} < 2$ and increases with increasing pH at $\text{pH} > 10$. The solubility proves to be pH independent in the range $2 < \text{pH} < 10$. The technetium species produced in the reduction of TcO_4^- by Sn^{2+} at $\text{pH} \leq 2$ is either the soluble dihydroxy technetate (Tc(OH)_2^{2+}) ion or the soluble oxotechnetate (TcO^{2+}) ion, and is hydrolyzed to the insoluble technetium oxide dihydrate ($\text{TcO}_2 \cdot 2\text{H}_2\text{O}$) at $2 < \text{pH} < 10$.⁹ Although no evidence of negative species has been found in the literature, it is possible that species such as Tc(OH)_5^- might be formed which tend to increase the solubility at $\text{pH} > 10$. So the solubility of Tc(IV) oxide is the least at $2 < \text{pH} < 10$.

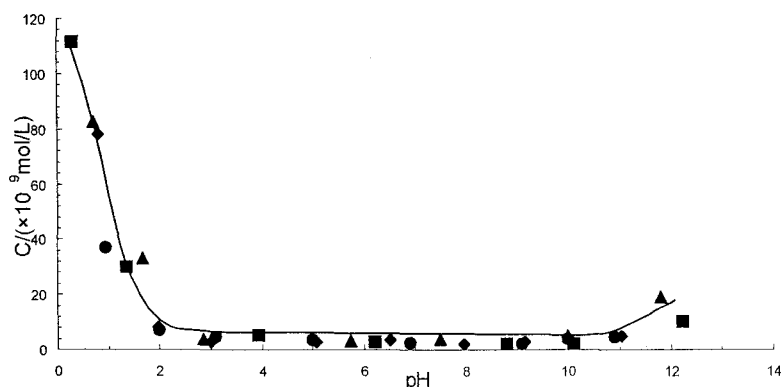


Figure 2 Effects of pH on Solubility of Tc(IV) oxide

■ simulated groundwater, anaerobic conditions; ◆ simulated groundwater, aerobic conditions; ▲ redistilled water, anaerobic conditions; ● redistilled water, aerobic conditions

Effect of CO_3^{2-} concentration on solubility of Tc(IV) oxide

The solubility of Tc(IV) oxide were also influenced by CO_3^{2-} concentration, as seen from Fig. 3. A look to the experimental data indicates a sizeable effect of CO_3^{2-} on the solubility of Tc(IV) oxide under various conditions. This would suggest the formation of aqueous Tc(IV)-hydroxo-carbonato complexes which are responsible for the increase in solubility of Tc(IV) oxide in carbonate containing solutions. The increase of the solubility is due to the formation of the complexes $\text{TcOCO}_3(\text{aq})$ and TcOOHCO_3^- .¹⁰ The presence of CO_3^{2-} in groundwater increases the concentration of Tc released from waste repository.

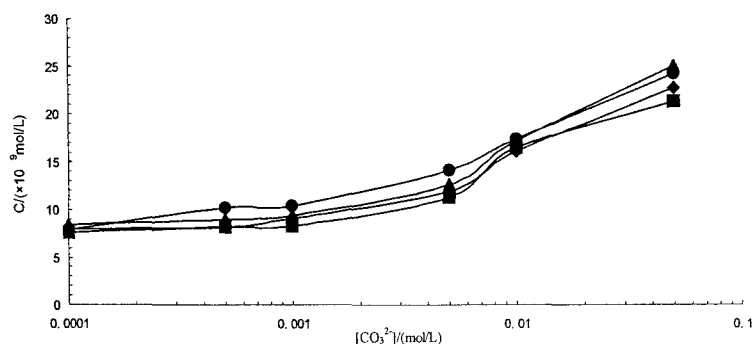


Figure 3 Effects of CO_3^{2-} concentrations on solubility of Tc(IV)

◆ simulated groundwater, aerobic conditions; ■ redistilled water, aerobic conditions; ▲ simulated groundwater, anaerobic conditions; ● redistilled water, anaerobic conditions

Oxidation curves of Tc(IV) in different water samples

Under aerobic conditions the concentration of TcO_4^- in aqueous solution increased with the storage time linearly after certain periods of time, as shown in Figs. 4 and 5. The increase is caused by oxidation of Tc(IV) by oxygen in air. The slope of the line is the rate of oxidation of Tc(IV). Whereas under anaerobic conditions the concentration of TcO_4^- is independent with the storage time as seen in Figs. 6 and 7, which indicates that Tc(IV) is not oxidized under anaerobic conditions. It is derived from the calculation that the rate of oxidation of Tc(IV) in simulated groundwater and redistilled water is about $(1.49\sim 1.86)\times 10^{-9}$ mol/(L·d) under aerobic conditions.

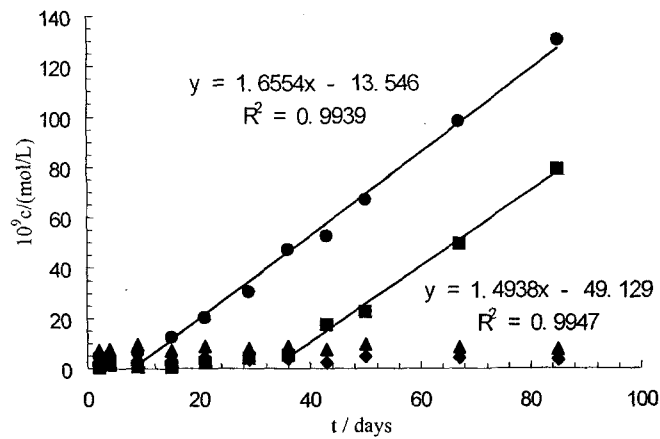


Figure 4 Oxidation curve of Tc(IV) in redistilled water under aerobic conditions

◆、Tc(IV) (pH=5.00); ■、Tc(VII) (pH=5.00); ▲、Tc(IV) (5×10^{-4} mol/L CO_3^{2-}); ●、Tc(VII) (5×10^{-4} mol/L CO_3^{2-})

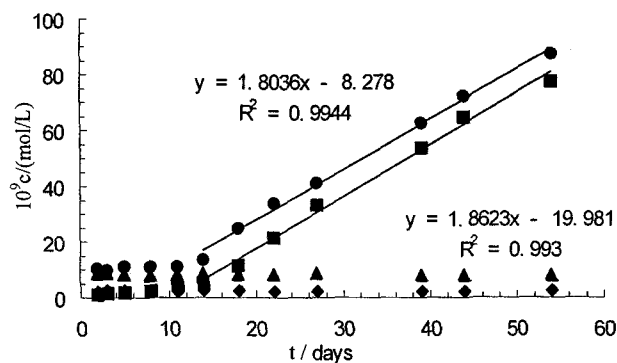


Figure 5 Oxidation curve of Tc(IV) in simulated groundwater under aerobic conditions

◆、Tc(IV) (pH=7.96); ■、Tc(VII) (pH=7.96); ▲、Tc(IV) (5×10^{-4} mol/L CO_3^{2-}); ●、Tc(VII) (5×10^{-4} mol/L CO_3^{2-})

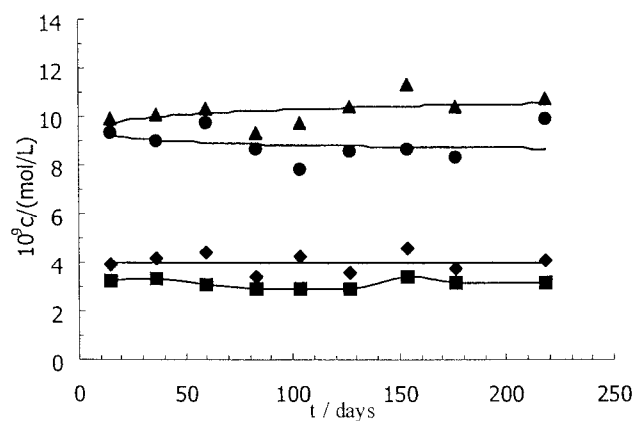


Figure 6 Oxidation curve of Tc(IV) in redistilled water under anaerobic conditions

◆、Tc(IV) (pH=7.50); ■、Tc(VII) (pH=7.50); ▲、Tc(IV) (5×10^{-4} mol/L CO_3^{2-}); ●、Tc(VII) (5×10^{-4} mol/L CO_3^{2-})

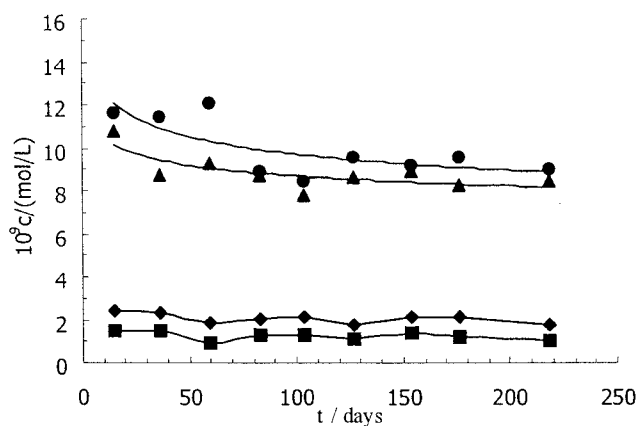


Figure 7 Oxidation curve of Tc(IV) in simulated groundwater under anaerobic conditions

◆、Tc(IV) (pH=8.80); ■、Tc(VII) (pH=8.80); ▲、Tc(IV) (5×10^{-4} mol/L CO_3^{2-}); ●、Tc(VII) (5×10^{-4} mol/L CO_3^{2-})

Conclusions

Tc(IV) oxide was prepared by reduction of TcO_4^- with stannous ion. The effects of pH and CO_3^{2-} concentration of aqueous solution on dissolution of Tc(IV) oxide were studied.

1. Tc(IV) oxide was prepared by reduction of TcO_4^- with Sn(II). The stoichiometry of the reduction can be expressed as: $3\text{Sn}(\text{II}) + 2\text{Tc}(\text{VII}) \rightarrow 3\text{Sn}(\text{IV}) + 2\text{Tc}(\text{IV})$.

2. The solubility of Tc(IV) oxide decreases with the increase of pH at pH < 2, increases with the increase of pH at pH > 10 and is pH independent in the range 2 < pH < 10. The solubility of Tc(IV) increases with the increase of CO₃²⁻ concentration.

3. The rate of oxidation of Tc(IV) in simulated groundwater and redistilled water is about (1.49~1.86)×10⁻⁹ mol/(L·d) under aerobic conditions, but Tc(IV) in simulated groundwater and redistilled water is not oxidized under anaerobic conditions.

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