Conf-811278--1

CONF-811278--1

DE83 010631

RADIOLYTIC OXIDATION OF TECHNETIUM DIOXIDE*

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Abstract

Samples of the insoluble technetium dioxide (TcO_2) were slurried in distilled water and in seawater and allowed to oxidize under the influence of their own radiation

Under these conditions only about 10-15% of the Tc was oxidized. When the technetium solutions were subjected to greater radiation fields by addition of ^{244}Cm the oxidation of the technetium to pertechnetate was virtually complete.

In the case of TcO_2 slurries without added radioactivity it was found that the concentration of pertechnetate ion, TcO_4^- , reached a maximum and then declined to about one-half of that maximum value.

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*Work performed under the auspices of Sandia National Laboratory under contract number 74-1160.

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Introduction

Design of an effective radioactive-waste repository requires considerable knowledge of the solution chemistry and sorptive behavior of the radioactive species to be isolated. Many fission products and the important actinide elements exhibit multiple oxidation states in environmental media necessitating knowledge of the behavior of each of the potential terms. One aspect of the environment surrounding a repository shown to be important to the speciation of actinide elements is radiolysis of the water surrounding the repository.

In a continuation of studies of the effect of radiolysis on the speciation of important radioactive species, the present report outlines the results of a study of the radiolytic oxidation of TcO_2 by alpha radiation from ^{244}Cm . Previous results^{1,2} on the effect of radiolysis on plutonium and neptunium speciation indicated that both oxidation and reduction occurred in those systems. Plutonium was stabilized primarily in the tetravalent state in distilled water and seawater, though small amounts of the higher oxidation states were also present. Neptunium was stabilized in the pentavalent state and was quite soluble in both media. In a saturated brine, both plutonium and neptunium were present primarily in the hexavalent state.

Among the long-lived fission products, technetium and iodine are of great concern, because they exist in aqueous solutions as anionic species and as such, exhibit high mobility through most rocks. In the case of technetium, the two most stable forms are $\text{Tc(IV)} - (\text{TcO}_2 \text{ solid})$ and $\text{Tc(VII)} (\text{TcO}_4^- - \text{pertechnetate anion})$. In this investigation, the effect of radiolysis on a solution contacting solid TcO_2 was determined.

Experimental

A 0.15 M stock solution of NH_4TcO_4 was analyzed spectrophotometrically using spectral bands at 246 nm ($\epsilon=6220$) and 289 nm ($\epsilon=2360$). Technetium dioxide $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ was prepared by reduction of NH_4TcO_4 using granulated zinc and concentrated HCl ³. Black solid $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ was washed with dilute ammonium hydroxide to remove traces of zinc then centrifuged and air dried. The quantity of $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ prepared in each of four test tubes was inferred by using measured aliquots of the stock solutions. Eight milliliters of distilled water were introduced into each of two tubes while eight milliliters of Copenhagen seawater were added to each of the other two. The amount of Tc in each test tube was

calculated to be 535 μg in the case of the distilled water sample and 840 μg in the case of the seawater sample. Into one each of the distilled water and the seawater samples sufficient ^{244}Cm was introduced to give an alpha radiation dose of 1.39×10 d/min/ml. Each test tube was equipped with a micromagnet, sealed with a serum cap and stirred on a specially modified magnetic stirrer. The pH changes were insignificant. Periodic samples were withdrawn to allow determination of soluble technetium by radiochemical techniques. The experiments were allowed to continue for five months.

Technetium was assayed radiometrically using liquid scintillation methods. A calibration curve was prepared by making dilutions of a spectrophotometrically assayed solution of NH_4TcO_4 , sampling these dilutions, and counting. The counting efficiency via this method was found to be greater than 96% in the concentration range 2×10^{-7} to 2×10^{-4} M.

In the experiments containing ^{244}Cm , the amount of activity in the periodic samples attributable to ^{244}Cm alpha particles saturated the counting system. This problem was solved by preextracting the sample with a ten-fold volume excess of 10% Aliquat 336 in toluene after first acidifying the sample with a small amount of concentrated HClO_4 . This method gave 99% TcO_4^- extracted while only 0.04% ^{244}Cm was extracted. Any extracted ^{244}Cm was at a sufficiently low concentration to allow discrimination against the high energy alpha radiation in the counting system. Aliquat 336 caused no quenching of the scintillations.

Results and Discussion

In each of the unirradiated experiments, an increase in the soluble technetium concentration (to 5.3×10^{-5} M in distilled water and 6.3×10^{-5} M in seawater) was observed in the 30-50 day interval of the experiment. After 50 days, the concentration of technetium in solution declined and leveled off at about 3.0×10^{-6} M in both media. The unexpected rise and decline in soluble technetium may be attributable to the normal solubilization of TcO_2 (with some radiation-induced oxidation to TcO_4^- included) to an equilibrium level, followed by co-precipitation with silica leached from the glass vessel by radiolysis products of water.

The addition of ^{244}Cm has a dramatic effect on the speciation of technetium. At equilibrium, technetium was found completely oxidized to TcO_4^- and achieved the molarity calculated from the amount of solid TcO_2 . As shown in

figures, technetium grows into the solution primarily via a two component first order rate process in both distilled water and seawater. In seawater, a third fast rate process is also indicated in the first two days. Analysis of the $[\text{TcO}_4^-]$ vs time plots give the first order rate constants for the linear components in each of the experiments (Table 1). The similarity of the rate constants in the two media imply that the radiolytic oxidation of TcO_2 occurs via a complex process whose rate is independent of the medium in which the oxidation occurs. Further experiments are required to derive any mechanistic information in this system.

The practical significance of these results is that technetium does exist in the oxidized form (as soluble pertechnetate) in a radiation field. Repository design, therefore, must include a backfill material which will adsorb or reduce the TcO_4^- anion to ensure its isolation from the surrounding environment.

TABLE 1. First Order Rate Constants for the Radiolytic Oxidation of TcO_2 .

Experiment	k_1 (days ⁻¹)	k_1 (days ⁻¹)
$\text{TcO}_2 + \text{Cm}$ in seawater	$1.730(\pm 0.047) \times 10^{-1}$	$8.438(\pm 0.165) \times 10^{-2}$
$\text{TcO}_2 + \text{Cm}$ in distilled water	$1.862(\pm 0.060) \times 10^{-1}$	$7.794(\pm 0.140) \times 10^{-2}$

References

1. K. L. Nash, S. Fried, A. Friedman, "The Effect of Radiolysis on the Oxidation State of Neptunium in Environmental Solutions", to be published in Nuclear Technology.
2. K. L. Nash, S. Fried, A. Friedman, "Radiolytic Oxidation and Reduction of Plutonium in Environmental Solutions", to be published in Nuclear Technology.
3. R. D. Peacock, "The Chemistry of Technetium and Rhenium", Elsevier Publishing Company, Amsterdam, 1966.

Figure Captions

- Figure 1a. First order plot of technetium solubilized by alpha radiolysis of $\text{TcO}_2(\text{s})$ in distilled water ($\text{pH} = 6.77(\pm 0.12)$).
- Figure 1b. First order plot of technetium solubilized by alpha radiolysis of $\text{TcO}_2(\text{s})$ in seawater ($\text{pH} = 8.27(\pm 0.041)$).