
Technetium-Iron Oxide Reactions Under Anaerobic Conditions: A Fourier Transform Infrared, FTIR Study

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Abstract

The behaviour of technetium in the geosphere is important in nuclear fuel waste management studies because this man-made element has a long half-life and, under ambient conditions in the laboratory, is not readily sorbed on geological materials. Fourier transform infrared spectroscopy studies have shown conclusively that the reaction between TcO_4^- and Fe_3O_4 at room temperature occurs via a surface reduction of TcO_4^- to TcO_2 , the latter being precipitated at the Fe_3O_4 surface. These results confirm that technetium can be contained effectively by magnetite in the geosphere, provided reducing conditions can be maintained.

Résumé

Le comportement du technetium dans la géosphère est d'une importance particulière dans les études de gestion des déchets de combustible nucléaire du fait que cet élément artificiel a une longue période radioactive et que, dans les conditions ambiantes du laboratoire, il ne sorbe pas facilement sur les matériaux géologiques. Les études de spectroscopie de l'infra-rouge à transformation de Fourier ont montré d'une manière concluante que la réaction entre TcO_4^- et Fe_3O_4 se produit à la température ambiante par une réduction de surface de TcO_4^- à TcO_2 , ce dernier précipitant à la surface de Fe_3O_4 . Ces résultats confirment que la magnetite de la géosphère peut confiner efficacement le technetium à condition de pouvoir maintenir les conditions de réduction.

Introduction

The fission of ^{235}U and ^{239}Pu in a nuclear reactor

produces a large number of radioactive products. Most of these decay to stable isotopes within a few years after the fuel has been discharged from the reactor and, therefore, pose no problem in the long-term management of nuclear fuel wastes. There are, however, a number of long-lived radionuclides that must be considered in assessing the environmental impact of any nuclear fuel waste disposal vault in the geosphere. For example, the fission products technetium and promethium are unique in that they do not have any stable isotopes and are expected to occur in nature only in minute amounts as a result of spontaneous fission of uranium. While promethium has a number of chemical analogues in the other rare earth elements, this is not the case for technetium, and therefore it is difficult to predict its behaviour in the geosphere.

The technetium isotope of interest for nuclear fuel waste disposal is ^{99}Tc . It is a pure β -emitter ($E = 0.293 \text{ MeV}$) with a half-life of $2.13 \times 10^5 \text{ a}$. Its high fission yield of 6% accounts for the relatively high concentration (approx. 0.02% by weight) [9] in fuel discharged from a CANDU reactor (burnup = approx. 650 g/kg U).

Technetium is a Group VII B element. Its chemical behaviour is not well known, but it is expected to fall between that of manganese and rhenium. Figure 1 [25] summarizes the aqueous technetium species possible at 298 K under a wide range of redox potential (E_h) and pH values. Under oxidizing conditions, technetium exists in solution in the +7 oxidation state as the anionic species TcO_4^- , and shows little sorption by geological materials [3, 14, 18, 23]. For this reason, in previous safety and environmental assessments of geological disposal of nuclear fuel wastes, technetium had been assumed to travel at the same rate as moving groundwater [28].

Under reducing conditions, or in the absence of oxygen, sorption of technetium has been noted in some cases. Bondietti and Francis [4] reported the removal of technetium from a nitrogen-sparged solution by basalt and granite, and Allard *et al.* [3] reported

Keywords: technetium, FTIR, sorption, redox, radionuclide, magnetite, hematite, anaerobic.

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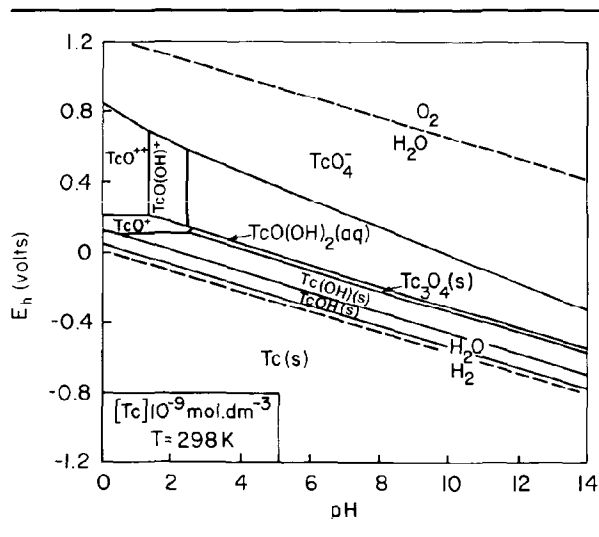


Figure 1 E_h -pH diagram for technetium speciation in aqueous solution at 298 K. (E_h = equilibrium redox potential, in volts).

k_d values (defined as the ratio of sorbed to nonsorbed concentrations) well above zero, indicating sorption on Fe(II)-containing minerals in contact with deaerated solutions, and on granite in a deaerated solution containing Fe(II) ions. Vandergraaf *et al.* [25] showed that iron oxide fracture infilling materials in altered granite and iron oxide inclusions in biotite are responsible for the removal of technetium from solution under reducing conditions. Walton *et al.* [26] have reported that sorption of a reduced technetium carbonate complex occurs on iron oxyhydroxides. Meyer *et al.* [15] showed sorption of technetium under anoxic conditions from a $0.1 \text{ mol} \cdot \text{dm}^{-3}$ NaCl solution on hematite, ilmenite, and iron-containing microcline. The same authors [16] also reported sorption of technetium in recirculation column experiments using basalt, hematite, ilmenite, and mordenite, and stated that the reduction of TcO_4^- to Tc(IV) or other oxidation states is a complex process. Additional studies [19] have shown that Tc(IV) forms a complex in carbonate solution under reducing conditions, which has a much higher solubility than the sparingly soluble technetium(IV) oxide. Walton *et al.* [26] show that this technetium(IV)-carbonate complex is in turn strongly adsorbed by iron oxides. Allard [2] has suggested that under strongly reducing conditions, the formation of Tc(O) is possible.

In this paper, we describe a study of the interaction of pertechnetate ion with magnetite and hematite surfaces in aqueous anaerobic solution, using Fourier transform infrared spectroscopy to characterize the nature of the interactions of the radionuclide with the iron oxide surfaces. Evidence is presented for the formation of technetium(IV) oxide in the reaction of pertechnetate ion with magnetite, and a possible mechanism is discussed.

Experimental

Solutions of ammonium pertechnetate were prepared by dilution from a stock solution (Amersham-Searle) with doubly distilled de-ionized water. Technetium(IV) oxide ($\text{TcO}_2 \cdot 2\text{H}_2\text{O}$) was prepared by electrochemical reduction of the pertechnetate anion. Magnetite powder was synthesized under ambient conditions from ferrous solutions at pH 9 [10]. Hematite was prepared by the hydrothermal decomposition of ferric chloride [8].

Analysis for the TcO_4^- anion was performed by UV/visible spectrophotometry ($\lambda_{\text{max}}(\text{TcO}_4^-) = 244 \text{ nm}$; $\epsilon_{\text{max}} = 6190 \text{ mol}^{-1} \text{ dm}^{-3} \text{ cm}^{-1}$) using a Hewlett-Packard model 8450A diode-array spectrophotometer. Trace concentrations were determined with a Tennelec LB-5100 β -counter, calibrated with a u.s. National Bureau of Standards ^{99}Tc standard source. The purity of the iron oxides was confirmed by X-ray diffraction analysis.

Fourier transform infrared, FTIR spectra were measured using a Nicolet 10 MX single-beam spectrometer under nitrogen purge, using a 0.2-g-KBr disc as a reference. A Globar (Reg. trademark) source, a room temperature deuterated triglycine sulphonate, DTGS, detector and CsI optics were used to collect data from 300 to 1500 cm^{-1} at 2 cm^{-1} resolution. Thirty-two scans were signal-averaged for most spectra, with no smoothing of data.

Because of the tendency of technetium(IV) oxide to build up static charge in the dry state, the infrared spectrum of the electrochemically reduced technetium was measured using a nujol mull between KBr plates. Transmission FTIR spectra of the TcO_4^- anion were measured using the KBr disc method. Since preliminary measurements of spectra of KTcO_4 using pressed CsI discs showed changes in the far infrared (300 to 400 cm^{-1}) lattice vibrations, which indicated the solid state metathesis of CsTcO_4 , KBr discs were used for subsequent measurements. Aliquots of stock pertechnetate solution were added to accurately weighed, 0.2 g portions of anhydrous spectroscopic-grade potassium bromide (Aldrich). The resulting solutions were evaporated in an oven at 363 K overnight and desiccated over phosphorus pentoxide at room temperature for 72 hours. The crystalline residues were ground in an agate mortar and pestle and pressed into 1-cm-diameter discs in a stainless steel die at 280 MPa for 2 minutes at room temperature.

The sample preparation for iron oxide-pertechnetate interactions followed that described above, except that, prior to the disc-pressing step, 1-mg amounts of magnetite or hematite were intimately mixed with the dry $\text{TcO}_4^-/\text{KBr}$ mixture. Spectra of these samples represent physically admixed reagents. To study the interaction of TcO_4^- with the oxide surfaces in aqueous solution, the discs were taken up in 2 cm^3 of nitrogen purged water in an anaerobic chamber

(Vacuum Atmospheres DL 002-SP). The oxygen level in the atmosphere in the chamber was maintained below 2×10^{-5} % by volume, as determined with a Teledyne model 317-X trace oxygen analyzer. The resulting solutions were allowed to stand, with periodic agitation, for up to 14 days at room temperature. The solutions were centrifuged, and the iron oxide residues collected, dried and pressed with approx. 0.2 g KBr. To remove residual excess non-sorbed technetium from the samples, these discs were redissolved in distilled, deionised water, and three centrifugation/washing cycles were performed. The final residues, which contained only technetium species that were irreversibly adsorbed on the iron oxide surfaces, were pressed with a further 0.2 g KBr.

Results and Discussion

Figure 2 shows a typical FTIR spectrum of potassium pertechnetate (KBr disc) in the 1200 to 300 cm^{-1} range. The three bands between 300 and 400 cm^{-1} are due to lattice vibrations in the KTcO_4 crystals [21]. The absorbance at 912 cm^{-1} is a composite of ν_1 and ν_2 vibrations of the tetrahedral TcO_4^- anion of T_d symmetry [6]. This peak is indicative of the Tc(VII)-O stretching vibration, and may be used as a qualitative indicator of the presence of Tc(VII) adsorbed onto the iron oxides. Quantitative measurement of adsorbed technetium is not feasible, since interaction of the tetrahedral anion with the hydrous oxide surfaces (e.g. of hematite) would lower the symmetry. The resulting C_{3v} (for monodentate co-ordination) or C_{2v} system (for bidentate co-ordination) would show greater multiplicity in the Tc-O band [17], with different extinction coefficients [11, 13] from the original composite peak centred at 912 cm^{-1} . The electrochemically-reduced technetium(IV) oxide gave a spectrum with a Tc-O stretching vibration band at 896 cm^{-1}

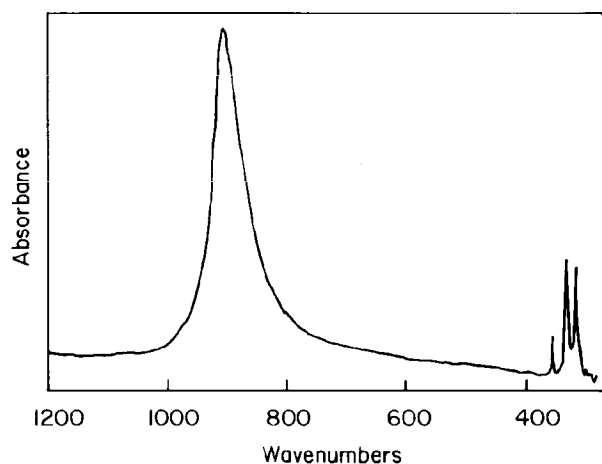


Figure 2 Typical FTIR spectrum of KTcO_4 (KBr disc).

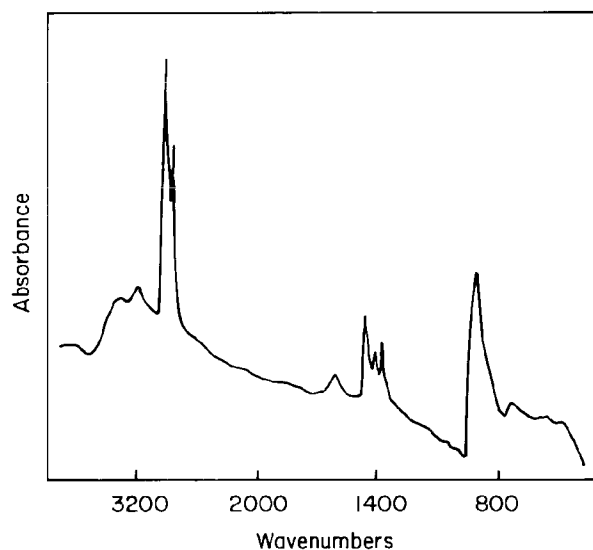


Figure 3 FTIR spectrum of technetium(IV) oxide (nujol mull).

(Figure 3). The mid-infrared spectrum of this oxide has not been reported previously.

Comparisons between the FTIR spectra of physical admixtures of pertechnetate and the iron oxides, and the oxides themselves are illustrated in Figures 4a and 4b. The spectral bands of the iron oxides do not mask those due to Tc-O stretching vibrations between 890 and 920 cm^{-1} . Subtraction of normalized digital spectra

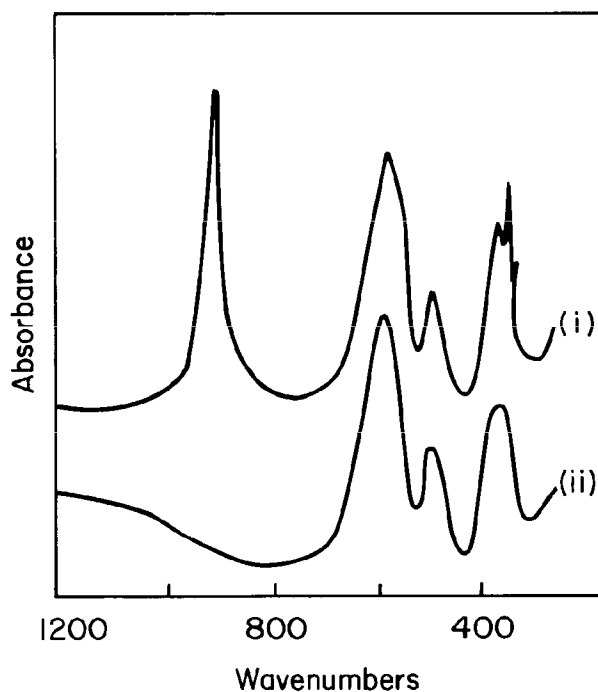


Figure 4a FTIR spectra of hematite (i) with and (ii) without 0.1 cm^3 of stock NH_4TcO_4 solution (see text).

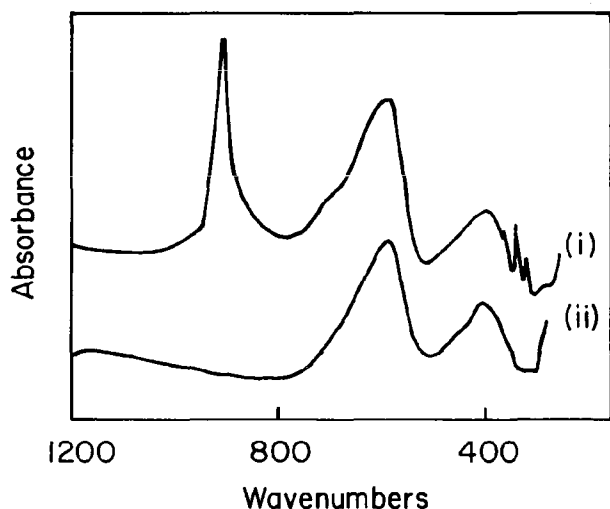


Figure 4b FTIR spectra of magnetite (i) with and (ii) without 0.05 cm³ of stock NH₄TcO₄ solution (see text).

of the separate components from the mixtures show additive behaviour, indicating no chemical interaction between the reagents in the dry state.

To study the interaction of aqueous pertechnetate anion with the iron oxide surfaces, nitrogen-purged water was added to the physical admixtures, producing a technetium concentration of 10⁻³ mol.dm⁻³. Infrared spectra of magnetite and hematite showed the presence of significant amounts of residual TcO₄⁻, by the presence of the Tc-O vibration at 912 cm⁻¹ (Figure 5a). Copious washing of the hematite residues completely removed the band at 912 cm⁻¹ from the spectra. Hence, if physisorption of the pertechnetate ion onto hematite occurs, the process is readily reversible. Anions are known to adsorb onto hydrous oxide surfaces [12, 27]; here a ligand exchange mechanism occurs, with replacement of surface hydroxyl groups by the incoming anion. The pertechnetate anion appears to behave as a simple non-co-ordinating species. The development of surface charge on the iron oxides stems from surface hydration in aqueous suspension, followed by dissociation of the surface hydroxyls [20]. At the zero point of charge (zpc), the surface is neutral. At a pH < zpc, the surface becomes protonated, resulting in positively-charged particles. A negative charge is generated at pH > zpc, by acidic dissociation of surface hydroxyl groups [22]. The mean zpc of hematite samples with varying histories has been determined as 8.5 ± 0.5 [5]. The sorption experiments were performed using neutral water containing 10⁻³ mol.dm⁻³ NH₄⁺ (as the pertechnetate salt). This will result in a solution buffered to a pH of 6. Under these conditions, the hematite suspension is expected to have a positive charge, facilitating reversible physisorption of the TcO₄⁻ anion.

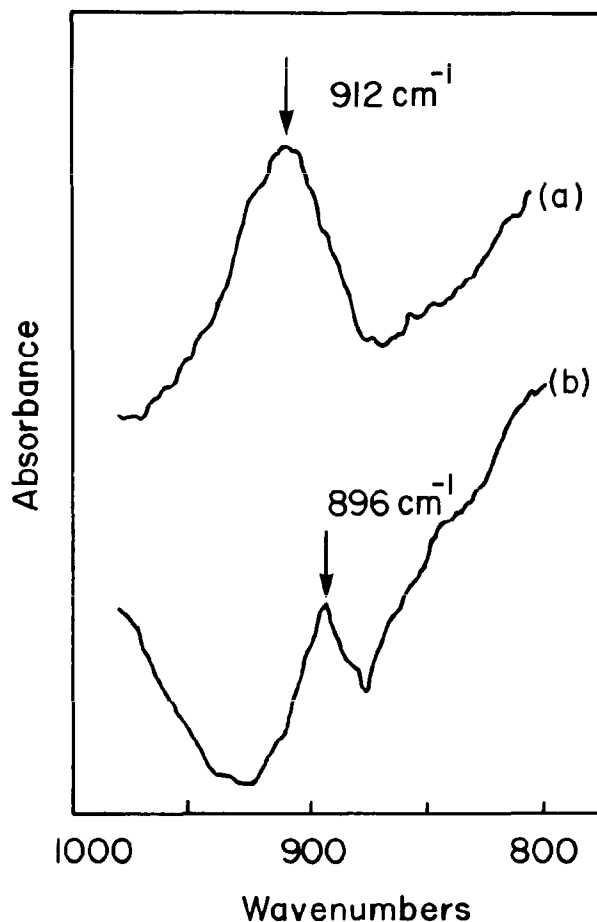


Figure 5 (a) Tc-O vibration region of the infrared spectrum of hematite after reaction with aqueous TcO₄⁻, before removal of the excess NH₄TcO₄. (b) As Figure (a), for a magnetite sample after removal of the excess NH₄TcO₄.

In the reaction between pertechnetate anion and magnetite in aqueous solution under anaerobic conditions, similar residual TcO₄⁻ was found to be present on the centrifuged Fe₃O₄ particles. After repeated washing of the residue, the infrared spectrum of the dried magnetite was measured. Figure 5b shows that no TcO₄⁻ remained (indicated by the absence of a band at 912 cm⁻¹), but a band at 896 cm⁻¹ was observed. This band coincides with that observed for technetium(IV) oxide (Figure 3). Literature values of the zpc for magnetite lie in the range 6.5 ± 0.2 [1, 22, 24]. Thus, the magnetite particles in the sorption experiments are expected to have a slightly positive charge. Some electrostatic attraction between the TcO₄⁻ anions and the magnetite surface is expected.

The relative redox potentials for the Fe(II)/(III) and the TcO₄⁻/TcO₂.2H₂O couples in aqueous solution [7] favour the reduction of Tc(VII) to Tc(IV) by Fe(II). The redox reaction in homogeneous solution is slow, but may be catalysed at the magnetite surface.

Conclusions

The results of this study indicate that under neutral anaerobic conditions, technetium undergoes irreversible adsorption at magnetite surfaces. The infrared observations confirm that the resulting technetium species is no longer the pertechnetate anion, but is, in fact, a Tc(IV) oxide. The mechanism of the reaction is envisaged as proceeding via a positive electrostatic attraction by the magnetite surface for the TcO_4^- anion at pH values below the zpc. A surface redox step between Fe(II) centres at the surface of the oxide and the Tc(VII) species, produced the sparingly soluble Tc(IV) oxide, which is precipitated at the magnetite surface. The buildup of a layer of the Tc(IV) species, coupled with the concomitant oxidation of the Fe_3O_4 surface to Fe_2O_3 serves to inhibit further reduction of TcO_4^- . Thus, the extent of reduction of Tc(VII) by Fe_3O_4 is expected to be dependent upon the surface area of the oxide. This work provides the first known spectroscopic evidence for the reduction of Tc(VII) to Tc(IV) by an Fe(II)-bearing oxide, and indicates that, under the conditions postulated to occur in and around a used-fuel disposal vault, the mobility of technetium may be severely restricted. Further work is in progress to clarify the effects of carbonate on the mobility of technetium in the geosphere.

Acknowledgements

We wish to thank J. Paquette and W.E. Lawrence for spectrophotometric analyses, and I.M. George for some preliminary experimental assistance.

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