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Electrosorption and Reduction of Pertechnetate by Anodically Polarized Magnetite

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The radionuclide technetium is a common surface and groundwater contaminant at many nuclear fuels processing facilities. This research investigated a new method for removing pertechnetate from contaminated waters based on the low aqueous solubility of reduced technetium species. The removal method involved electrostatic adsorption of pertechnetate at an anodically polarized magnetite electrode, followed by reduction of the adsorbed Tc(VII). This method was capable of reducing technetium associated β activity below the 900 pCi/L drinking water maximum contaminant level set by the US EPA for manmade β activity. Upon termination of the applied polarization, the reduced technetium species remained adhered to the magnetite electrode under anaerobic conditions. Under aerobic conditions, the technetium was slowly released back into solution, indicating that the reduced technetium is afforded a degree of cathodic protection due to preferential oxidation of the magnetite. The advantages of this electrosorption/reduction technique over direct cathodic reduction are an increase in the stability of the reduced technetium, removal to lower aqueous concentrations, and greatly increased removal kinetics.

Introduction

Former site activities and disposal practices at nuclear fuels processing facilities have resulted in groundwaters contaminated by the radioisotope technetium-99. Technetium-99 is a low-energy (0.29 MeV) β-emitting radionuclide produced as a byproduct of uranium fission. Its long half-life and high environmental mobility make it an environmental concern at many uranium processing facilities (*1*). In surface waters and shallow groundwaters, technetium is normally found as Tc(VII) in the form of the pertechnetate anion, TcO_4^-. Presently, there is no suitable technology for remediation of technetium from contaminated groundwaters. Because pertechnetate is a weakly adsorbing species (*2*), the high relative concentrations of background electrolytes commonly present in contaminated groundwaters makes its removal by adsorption and ion exchange processes economically impractical. A number of laboratory investigations have found that technetium may be removed from aqueous solution via reduction of pertechnetate to less soluble technetium species (*3*, *4*). Technetium is similar in its redox behavior to manganese and rhenium and may exist in one of four aqueous oxidation states Tc(III), Tc(IV), Tc(V), and Tc(VII) (*5*). The highly soluble pertechnetate anion may be removed from solution via reduction to Tc(IV), followed by precipitation of $TcO_2 \cdot nH_2O$, which may also be written as $Tc(OH)_4$ (*6*). In the absence of potentially complexing ligands, the solubility of Tc(IV) may be more than 3 orders of magnitude less than that of Tc(VII) (*7*, *8*).

Several studies have investigated the removal of pertechnetate from solution using zerovalent iron and Fe(II)-containing minerals (*5*, *2*, *9*−*11*). The results from these studies indicate that under anoxic conditions, Tc(VII) may be reduced by zerovalent iron and ferrous iron containing minerals and precipitates. However, in the presence of dissolved oxygen, ferrous iron bearing minerals are preferentially oxidized by dissolved oxygen, and little or no reduction of Tc(VII) occurs (*12*). Reduction of Tc(VII) by ferrous ions in solution may also occur, but recent evidence indicates that rates of Tc(IV) formation are too slow to be of any practical significance (*13*).

A recent investigation of pertechnetate reduction by Fe(II)-bearing minerals indicated that reduction by magnetite was more than an order of magnitude faster than reduction by the Fe(II)-containing minerals, hornblende and chlorite (*14*). After accounting for differences in mineral surface area and Fe(II) content, the increased rate of reduction by magnetite was attributed to the low band gap between its valence and conduction bands and its ability to adsorb pertechnetate via a ligand exchange mechanism.

Low-temperature magnetite oxidation most often produces maghemite through a topotactic reaction which maintains the inverse spinel structure of the original magnetite crystals (*15*). The half-cell redox reactions for Tc(VII) reduction coupled with magnetite oxidation may be expressed as (*16*)

$$TcO_2 \cdot nH_2O = TcO_4^- + 4H^+ + 3e^- \qquad (1)$$

$$3[Fe^{2+}Fe_2^{3+}]O_{4(\mathrm{magnetite})} \rightarrow 4\gamma[Fe_2^{3+}]O_{3(\mathrm{maghemite})} + Fe^{2+} + 2e^- \qquad (2)$$

The net cell reaction is given by

$$TcO_4^- + 4.5[Fe^{2+}Fe_2^{3+}]O_{4(\mathrm{magnetite})} + 4\,H^+ \rightarrow TcO_2 \cdot nH_2O + 6\gamma[Fe_2^{3+}]O_{3(\mathrm{maghemite})} + 1.5Fe^{2+} \qquad (3)$$

with an equilibrium cell potential at 25 °C of (*15*)

$$E = 0.835\ \mathrm{V} + 0.020 \log[TcO_4^-] - 0.079\ \mathrm{pH} - 0.03 \log[Fe^{2+}] \qquad (4)$$

For pH and pertechnetate concentrations of practical interest, the cell potential for this reaction is positive, and thus reduction of pertechnetate by magnetite is thermodynamically favorable. The effect of pH on the cell potential indicates that the thermodynamic favorability for pertechnetate reduction decreases with increasing pH.

Cui and Eriksen (*14*) recently reported that the rate-limiting mechanism for reduction of pertechnetate by magnetite is adsorption of the pertechnetate anion to the magnetite surface via a ligand exchange mechanism. In the ligand exchange process, a pertechnetate anion replaces a

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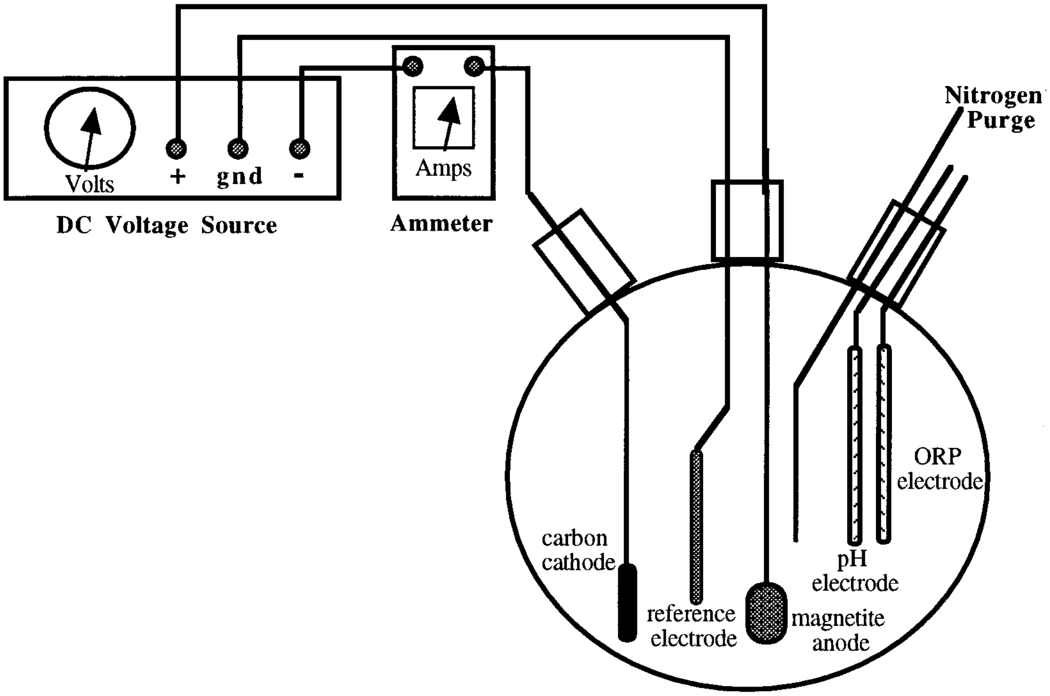

FIGURE 1. Apparatus for electrochemical removal of technetium from solution by a porous magnetite foam anode.

surface hydroxyl group (>SOH) as illustrated by (*14*)

$$>\mathrm{SOH} + \mathrm{TcO_4}^- = \mathrm{S} - \mathrm{OTcO_3} + \mathrm{OH}^- \qquad (5)$$

Adsorption of TcO_4^- by this ligand exchange mechanism requires an uncharged, hydroxylated surface and is thus sensitive to pH. The pH at which there is no net charge on the magnetite surface is in the range of 6.5 ± 0.2 (*1*), and therefore, this ligand exchange mechanism will contribute to pertechnetate adsorption only under near neutral pH conditions. However, at pH values below the magnetite point of zero charge (pzc), the positively charged magnetite surface may adsorb TcO_4^- by an electrostatic mechanism.

Although pertechnetate can be removed from solution by magnetite, its weak electrostatic adsorption and the slow kinetics of the ligand exchange mechanism, result in an overall removal rate which is too slow to implement in a practical remediation scheme. However, if the amount and rate of pertechnetate adsorption could be sufficiently increased, pertechnetate reduction by magnetite could be implemented in a canister-type treatment system.

Electrochemical enhancement of the adsorption process may provide a means to increase the rate of pertechnetate reduction by magnetite. Increased electrostatic adsorption, as well as increased transport rates to the magnetite surface, can be achieved by anodically polarizing the magnetite. This technique is called electrosorption and has been used to remove pertechnetate from solution using electrodes coated with anion-exchange resins (*17*). However, electrosorption using ion-exchange resins is inefficient due to competition for exchange sites by background electrolytes (*17*). In contrast to ion-exchange resins, anodically polarized magnetite has the ability to reduce adsorbed pertechnetate and, thus, does not suffer from the site saturation effects associated with anion-exchange resins. Using anodically polarized magnetite, the pertechnetate removal mechanism is analogous to cementation reactions in which a metal ion is removed from solution via reduction and precipitation at the surface of a more readily oxidized metal (*18*).

This research investigates the kinetics of electrosorption and reduction of aqueous pertechnetate by anodically polarized magnetite. The research objectives were to determine the ability of magnetite for reducing Tc(VII) when anodically polarized, and to assess the stability of the resulting technetium−magnetite precipitate.

Materials and Methods

Experiments investigating the electrochemical removal of technetium from solution by a porous magnetite electrode were performed using the apparatus depicted in Figure 1. The reaction vessel consisted of a 3-L, three-necked, Pyrex flask. Openings in the flask were sealed with rubber stoppers containing perforations to accommodate electrode wires and tubing for the purge gas. Anaerobic conditions were maintained by purging the solution with 50 mL/min of nitrogen gas through 16-mm o.d., stainless steel tubing. The purge gas was vented through a second piece of 16-mm stainless steel tubing. A silver/silver chloride electrode (Orion) with a reference potential of +222 mV with respect to the standard hydrogen electrode (SHE) was used to set the potential of the ground terminal. The reference electrode was placed midway between the anode and cathode in the test solution. This placement resulted in anode potentials of 0.49 times the applied polarization above the reference electrode potential. The solution pH was monitored with an Orion gel-filled pH electrode. A regulated DC voltage source with a maximum output rating of 10 amps was used to polarize the electrodes between 0 and 3.5 V. Although a potentiostat was not used to control the potential of the working electrode, the small current drain on the voltage source was insufficient to cause any observable voltage drift from the set potentials.

A 1.5-cm-diameter by 2-cm-long cylinder composed of porous magnetite foam was used as the anode. The magnetite foam electrode was produced by Cercona of America (Dayton, OH) from scrap iron powder and an aluminosilicate binder. Gassing agents and surfactants were added to the iron/aluminate/silicate slurry to produce porosity upon heating. The iron was then converted to magnetite by heating under a carbon dioxide atmosphere at 800 °C. The resulting magnetite foam contained 7 wt % aluminosilicate binder and 93% magnetite and had a bulk density of 1.24 g/mL. The electrode had an internal pore volume of 2.6 mL and a specific

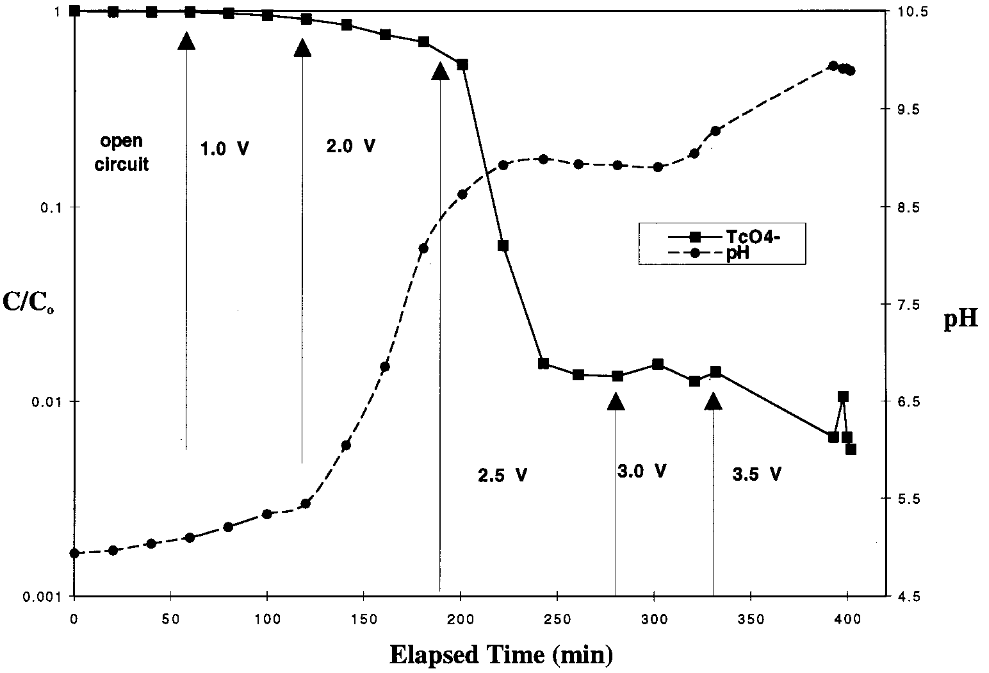

FIGURE 2. Technetium removal from 2 L of 4.2×10^{-8} M solution of ammonium pertechnetate in 0.1 M NaCl as a function of applied voltage and elapsed time.

surface area of 0.11 m^2/g, measured using BET analysis of nitrogen adsorption (*19*). The end-to-end electrical resistance of the dry magnetite foam electrode was ~100 Ω. A 10-cm-long by 1-cm-diameter carbon rod was used as the cathode.

The solution in the reaction vessel consisted of 2000 mL of 4.2×10^{-8} M TcO_4^- in 0.1 M NaCl. The solution was prepared from dilution of an ammonium pertechnetate solution obtained from USDOE Isotope Distribution, Oak Ridge National Laboratories, TN. A Teflon-coated, magnetic stir bar was used to agitate the solution. Aqueous pertechnetate concentrations were determined by withdrawing 2-mL samples using 0.45-μm polypropylene syringe filters (Nalgene). Sample masses were determined gravimetrically with an electronic balance. Ten milliliters of Ecolume scintillation cocktail were added to each sample. A Packard 2550 TR/AB analyzer was used for α/β scintillation counting, with counting times of 100 min. Background levels of β activity were subtracted from all sample counts and were determined from counts of deionized water samples.

Prior to placing the magnetite electrode in the reaction vessel, the test solution was deaerated for 2 h and then sampled to determine the initial pertechnetate concentration. The reaction vessel was then sampled at ~15 min intervals until 330 min elapsed. At 400 min elapsed, four final samples were taken and the applied polarization was terminated.

Results and Discussion

Pertechnetate removal from solution has been previously observed to follow first-order removal kinetics (*14*). Surface-mediated reactions following first-order kinetics can be described in terms of an observed first-order rate constant (k_{obs}), defined as

$$k_{obs} = -\left[\frac{d(\ln C/C_0)}{dt}\right]\left[\frac{V_s}{S}\right] \qquad (6)$$

where C_0 is the initial reactant concentration, C is the reactant concentration as a function of time (t), V_s is the solution volume, and S is the reactive surface area. The rate constant defined in this manner is normalized to a surface area to solution volume ratio of 1 cm^2/mL and can be easily compared to rate constants determined under other experimental conditions. Since the observed first-order rate constant may be affected by mass-transfer limitations, it is often convenient to define an intrinsic rate constant, k, which expresses the kinetics of the electron-transfer reaction at the electrode surface.

TABLE 1. Normalized Observed Removal Rate Constants, Regression Correlation Coefficients, and Anode Potentials at Each Applied Polarization

applied polarization (V)	k_{obs} (cm/min)	correlation R^2	anode potential (mV/SHE)
0	7.7×10^{-5}	0.55	–
1	6.8×10^{-4}	0.95	712
2	2.1×10^{-3}	0.99	1202
2.5	3.5×10^{-2}	0.99	1447
3	–		1692
3.5	–		1937

Data showing technetium solution concentrations as a function of elapsed time and applied polarization are shown in Figure 2. At each polarization, a removal rate constant was determined from the slope of the ln(C/C_0) versus time plot for the three or four data points taken at each polarization. For removal at 2.5-V polarization, only the first three points were used to determine the rate constant, since there was essentially no more removal after 230 min elapsed. Table 1 lists the observed removal rate constants, normalized for the electrode surface area to solution volume ratio of 2.4 cm^2/mL. Also listed in Table 1 is the linear regression correlation coefficient for each rate constant and the anode potential at each applied polarization, referenced to the standard hydrogen electrode. The high correlation coefficients at 1, 2, and 2.5 V indicate that pertechnetate removal by anodically polarized magnetite is reasonably well described as a first-order process. For mass transfer limited removal, first-order kinetics are expected, since the electrophoretic flux of pertechnetate toward the electrode is directly proportional to its solution concentration.

During the first hour elapsed under open circuit conditions, 1.5% of the pertechnetate was removed from solution at a pH of 5. This corresponds to an observed removal rate constant of 7.7 × 10^{-5} cm/min. This rate constant is more than 2 orders of magnitude greater than the normalized rate constant of 6.9 × 10^{-7} cm/min reported by Cui and Eriksen for pertechnetate removal by magnetite at pH 8.3 (*14*). The faster removal in this study can be attributed enhanced electrostatic adsorption, since the initial solution pH was below the magnetite pzc of ~6.5. The increase in pH over the course of the experiment is due to magnetite dissolution, which proceeds according to (*15*)

$$[\mathrm{Fe}^{2+}\mathrm{Fe}_2{}^{3+}]\mathrm{O}_{4(\mathrm{magnetite})} + 2\mathrm{H}^+ \rightarrow \gamma[\ \mathrm{Fe}_2{}^{3+}]\mathrm{O}_{3(\mathrm{maghemite})} + \mathrm{Fe}^{2+} + \mathrm{H_2O} \quad (7)$$

The data in Figure 2 show that as the polarization is increased, the rate of pertechnetate removal also increases. The observed rate constants in Table 1 indicate that the pertechnetate removal rate at 2.5 V polarization was more than 450 times the open circuit removal rate. Increasing removal rates at greater polarizations can be attributed to both increased electrostatic adsorption capacity, and increased mass-transfer rates. In the absence of applied polarization, pertechnetate transport to the electrode is limited by diffusion through the film boundary layer at the electrode surface. However, under the applied electric field, pertechnetate transport through the hydrodynamic boundary layer is governed by its electrophoretic mobility, which is a function of the applied polarization.

The final aqueous pertechnetate concentration after 400 min elapsed corresponds to 2.4 × 10^{-10} M. This concentration is more than an order of magnitude lower than the average reported solubility of Tc(IV) in NaCl solutions of 3.08 × 10^{-9} M (*8*). The final soluble technetium concentration is also an order of magnitude lower than the solubility of cathodically deposited Tc(IV), reported by Meyer et al. to be 2.6 ± 0.5 × 10^{-9} M (*20*). Electrosorption of aqueous Tc(IV) species also cannot explain the high level of removal, since dissolution of $\mathrm{TcO_2{\cdot}}n\mathrm{H_2O}$ produces an uncharged species, as seen by (*7*)

$$\mathrm{TcO_2{\cdot}}n\mathrm{H_2O_{(s)}} = \mathrm{TcO(OH)_{2(aq)}} + (n-1)\mathrm{H_2O} \quad (8)$$

The low final concentration achieved in this investigation indicates that the pertechnetate removal mechanism is not simply precipitation of $\mathrm{TcO_2{\cdot}}n\mathrm{H_2O}$ at the surface of the magnetite.

Formation of a solid solution between technetium and the iron oxides in magnetite may account for the low final aqueous concentrations. Technetium incorporated into a solid solution would have a lower solubility than a pure technetium compound, since the technetium activity in the solid solution would be less than unity. Previous investigations have found that Tc(IV) may be incorporated into iron oxide minerals upon reduction of aqueous pertechnetate. Walton et al. (*5*) reported that Tc(IV) may be incorporated into hematite upon aging of hydrous ferric oxide ($\mathrm{Fe(OH)_3}$). Additionally, Lee and Bondietti (*21*) found that technetium may be incorporated into ferrous- and sulfide-containing minerals. There is also evidence that Tc(IV) may be reduced to form an oxide with the stoichiometry of $\mathrm{Tc_3O_4}$ (*6*). The final solution redox potential of −435 mV (SHE) does indicate that oxidation states lower than Tc(IV) were thermodynamically favorable (*16*). The overall reaction for magnetite oxidation coupled with Tc(VII) reduction to $\mathrm{Tc_3O_4}$ is described by (*6*)

$$3\mathrm{TcO_4}^- + 19.5[\mathrm{Fe}^{2+}\mathrm{Fe}^{3+}]\mathrm{O}_{4(\mathrm{magnetite})} + 16\mathrm{H}^+ \rightarrow \mathrm{Tc_3O_4} + 26\gamma[\ \mathrm{Fe}_2{}^{3+}]\mathrm{O}_{3(\mathrm{maghemite})} + 6.5\mathrm{Fe}^{2+} + 8\mathrm{H_2O} \quad (9)$$

with a cell potential of

$$E = 0.792\ \mathrm{V} - 0.073\ \mathrm{pH} + 0.014 \log [\mathrm{TcO_4}^-] - 0.030 \log [\mathrm{Fe}^{2+}] \quad (10)$$

For pH, Fe^{2+}, and pertechnetate concentrations of practical interest, the overall cell potential for reaction 9 is positive. Therefore, reduction of $\mathrm{TcO_4}^-{}_{(\mathrm{aq})}$ to $\mathrm{Tc_3O_4}$ coupled with magnetite oxidation is thermodynamically favorable.

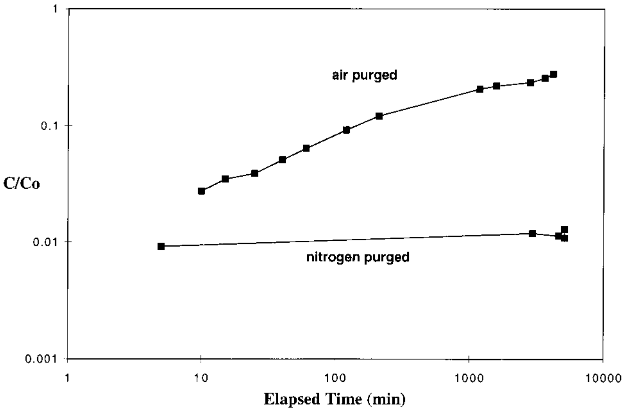

FIGURE 3. Release of technetium from unpolarized magnetite electrode as a function of elapsed time under oxic and anoxic conditions.

Direct spectroscopic evidence for pertechnetate reduction is difficult to obtain due to the problem of detecting small amounts of technetium amide high concentrations of iron oxides. However, indirect information on the technetium removal mechanism can be obtained from the stability of the technetium−magnetite precipitate. Figure 3 illustrates the effect of terminating the applied polarization on release of technetium from the electrode. The data in Figure 3 show that the technetium remained adhered to the magnetite in the absence of applied polarization. In more than 3.5 days of purging the solution with nitrogen gas, only 0.5% of the removed technetium was released back into solution. This indicates that electrostatic adsorption is not the ultimate mechanism for removal of pertechnetate from solution. After purging the solution with nitrogen gas, the final aqueous pertechnetate concentration of 4.5 × 10^{-10} M (750 pCi/L) remained below the 900 pCi/L drinking water maximum contaminant level set by the US EPA for manmade β activity.

The stability of the technetium−magnetite precipitate under oxidizing conditions was investigated by purging the solution with 50 mL/min of air. Purging the solution with air increased the redox potential of the solution from −10 mV to 514 mV (SHE). At this potential, Tc(VII) is the thermodynamically stable oxidation state (*15*). However, over a three-day period of purging the solution with air, only 27% of the technetium was released back into solution, as shown in Figure 3. A similar finding was previously reported by Cui and Eriksen for technetium adsorbed on magnetite (*14*). The faster release rate in the presence of oxygen indicates that the technetium was reduced by the magnetite electrode. The gradual release shown in Figure 3 also indicates that the reduced technetium is resistant to oxidation, and is afforded a degree of cathodic protection by the magnetite. This resistance to oxidation contrasts sharply with the rapid oxidation of $\mathrm{TcO_2{\cdot}}n\mathrm{H_2O}$ electrodeposited on noble metal cathodes as reported by Meyer et al. (*20*).

Mass-Transfer Effects. Although approximately 1 h was required to reduce the technetium concentration by 2 orders of magnitude in the batch reactor, the rate of technetium removal in a flow-through system would be greatly increased, due to reduced mass-transfer limitations, and a greater electrode surface area per volume of solution. Because the magnetite foam is a porous material, the observed pertechnetate removal rates were impacted by both intraelectrode diffusional limitations and film transfer resistance across the hydrodynamic boundary layer at the electrode surface. However, due to the electric field external to the electrode, mass transfer through the boundary layer will be enhanced by electrophoresis. Therefore, the dominant mass-transfer limitation in the batch reactor was the rate of intraelectrode diffusion.

In contrast to film transfer resistance which occurs in series with reaction at the electrode surface, intraelectrode diffusion and surface reaction occur concurrently, and their effects on the observed reaction rate must be simultaneously evaluated. The effect of diffusional limitations on reaction rates in porous particles can be expressed in terms of an effectiveness factor, η (*22*). The effectiveness factor is the ratio of the observed removal rate to the removal rate if diffusion through the intraparticle pores were instantaneous. An effectiveness factor of unity would indicate that the pertechnetate concentration within the electrode pores was uniform, and equal to the bulk solution concentration. Where the effectiveness factor is less than unity, a concentration gradient exists within the electrode, and the observed rate of pertechnetate removal will be less than the rate anticipated based on the intrinsic rate constant (k) and the bulk solution concentration. For reactions limited by intraparticle diffusion, as η approaches one, the observed rate constant (k_{obs}) approaches the intrinsic reaction rate constant.

The effectiveness factor for the approximately cylindrical magnetite electrode of radius R, may be expressed in terms of the intrinsic rate constant normalized to 1 $\mathrm{cm^2/mL}$ of surface area per solution volume, the electrode surface area (S), the internal electrode pore volume (V_{p}), and the effective intraparticle diffusion coefficient of the reacting species (D_{e}) as (*22*)

$$\eta = \frac{1}{\frac{R}{3}\sqrt{\frac{kS}{V_{\mathrm{p}}D_{\mathrm{e}}}}}\left[\frac{1}{\tanh\left(R\sqrt{\frac{kS}{V_{\mathrm{p}}D_{\mathrm{e}}}}\right)} - \frac{1}{R\sqrt{\frac{kS}{V_{\mathrm{p}}D_{\mathrm{e}}}}}\right] \tag{11}$$

The effective diffusion coefficient for pertechnetate can be estimated from its aqueous diffusion coefficient (D_{aq}) of 1.37×10^{-5} $\mathrm{cm^2/s}$ (*23*) and the electrode void fraction (ϵ), as $D_{\mathrm{e}} = \epsilon^2 D_{\mathrm{aq}}$ (*22, 24*). By using this approximation, the effectiveness factor based on k_{obs} is only 2×10^{-4} for the magnetite electrode at 2.5 V polarization. This indicates that the observed rate of pertechnetate removal was mass transfer limited, and thus the intrinsic removal rate is much greater than the observed rate.

Because k_{obs} is less than the true rate constant, only an upper bound estimate of the removal half-life in a flow-through reactor can be made from the observed rate constants. Adjusting the observed rate constant for the 1800 $\mathrm{cm^2/mL}$ surface area to solution volume ratio that would exist in a flow-through arrangement of this electrode yields a pertechnetate removal half-life of 0.65 s at 2.5 V polarization. Thus, the pertechnetate removal rate is sufficiently fast to be employed in a flow-through remediation scheme, even at polarizations significantly lower than 2.5 V. For example, on the basis of the observed removal rate at 1-V polarization, the removal half-life for a flow-through electrode is estimated to be 33 s.

Electrode Stability. The ultimate feasibility of polarized magnetite for pertechnetate removal is dependent on the stability of the electrode under anodic polarization. Due to the low levels of pertechnetate in solution, wear on the magnetite will be controlled primarily by its rate of oxidation resulting from the anodic polarization. Oxidation of the electrode is undesirable since it will lead to increased electrical resistance and to depletion of the Fe(II) necessary for pertechnetate reduction. Although magnetite is the most oxidation resistant of all the commonly employed metal oxide electrode materials, oxidation of its Fe(II) centers may occur under anodic polarization (*25*). However, due to the high activation energy for magnetite oxidation by anodic polarization (300 kJ/mol (*25*)), oxidation of the electrode will be small compared to oxidation of solution species, such as hydroxyl ions.

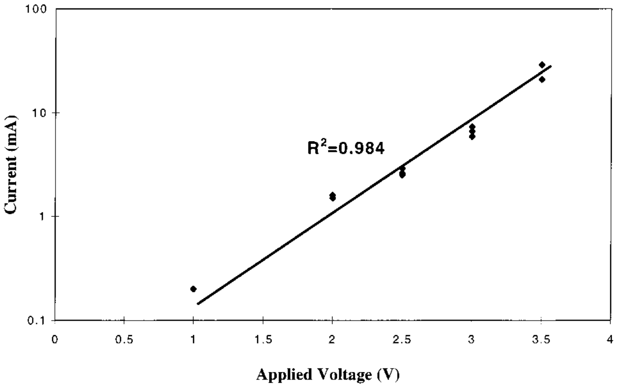

FIGURE 4. Electrode current as a function of applied polarization.

The current–voltage relationship shown in Figure 4 confirms that the rate of magnetite oxidation is small compared to the rate of water oxidation. The current–voltage relationship for a particular redox reaction can often be described by a form of the Taefel equation (*26*):

$$i = a\mathrm{e}^{b\Delta E} \tag{12}$$

where i is the current, ΔE is the potential difference from the equilibrium potential, and a and b are constants characteristic of the particular electrode and redox couple. The slope of the data in Figure 4 is equal to the b parameter in eq 12. As indicated by the high linear regression correlation coefficient of 0.986, the log(i) versus ΔE relationship in Figure 4 is approximately linear. This indicates that a single anode reaction is responsible for the majority of the current. If a second reaction with different a and b parameters were contributing to the measured current, summation of the currents for the two reactions would lead to deviations from linear behavior. This confirms that oxygen evolution is the major anode reaction, and therefore magnetite oxidation is only a minor contributor to the observed current. However, even in a worst case scenario where all the anodic current results from oxidation of the magnetite, the electrode is calculated to last more than 100 days at a polarization of 1 V. Thus, for polarizations suitable in a practical remediation scheme, the wear rate on the electrode is acceptable.

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