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Title

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Journal

Lawrence Berkeley National Laboratory

Author

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Publication Date

2008-11-18

Removal of Pertechetate from Simulated Nuclear Waste Streams Using Supported Zero-Valent Iron

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The application of zero-valent iron nanoparticles or “Ferragels,” either unsupported or supported, to the separation and reduction of pertechnetate anions (TcO_4^-) from complex waste mixtures was investigated as an alternative approach to current waste processing schemes. Although applicable to pertechnetate-containing waste streams in general, the tests reviewed here were directed at two specific potential applications at the U.S. Department of Energy’s Hanford Site: (1) the direct removal of pertechnetate from highly alkaline solutions, typical of those found in Hanford tank waste; and (2) the removal of dilute pertechnetate from near neutral solutions, typical of the eluate streams from commercial organic ion-exchange resins that may be used to remediate Hanford tank wastes. It was envisioned that both applications would involve the subsequent encapsulation of the loaded sorbent material into a separate waste form. A high surface area ($>200 \text{ m}^2/\text{g}$) base-stable, nano-crystalline zirconia was used as a support for Ferragel for tests with highly alkaline solutions, while a silica gel support was used for tests with near neutral solutions. It was shown that after 24 hours of contact time, the high surface area zirconia supported Ferragel sorbent removed about 50% ($K_d = 370 \text{ L/kg}$) of the pertechnetate from a pH 14 tank waste simulant containing 0.51 mM TcO_4^- and large concentrations of Na^+ , OH^- , NO_3^- , and CO_3^{2-} for a phase ratio of 360 L simulant per kg of sorbent. It was also shown that after 18 hours of contact time, the silica supported Ferragel removed $>95\%$ pertechnetate from a neutral pH eluate simulant containing 0.076 mM TcO_4^- for a phase ratio of 290 L/kg. It was determined that in all cases, Ferragels reduced the Tc(VII) to Tc(IV), or possibly Tc(V), through a redox reaction. Finally, it was demonstrated that a mixture of 20 mass % of the solid reaction products obtained from contacting zirconia support Ferragel with an alkaline waste solution containing Re(VII) - a surrogate for Tc(VII) - with 80 mass % alkali borosilicate based frit heat treated at 700°C for 4 hours sintered into a handleable waste form.

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INTRODUCTION

A vast amount of solid and liquid radioactive waste had been generated during the approximately thirty years since the world's first full-scale nuclear reactors and processing plants needed for the production and isolation of plutonium-239 began operating in 1944 at the Hanford Site River in southeastern Washington,. One reference [1] indicates that these wastes consist of approximately 208,000 m³ of mixed waste in 177 underground storage tanks. Current emphasis at U.S. Department of Energy (DOE) and commercial sites has been directed at remediation of such radioactive wastes.

One plan for Hanford Site tank wastes, for example, has been to separate the waste into primarily solid, i.e., sludge containing insoluble high-activity waste (HAW) species as well as non-radioactive solids, and aqueous liquid portions that will contain tank supernatant and water-soluble species derived from HAW sludge washings. Water-soluble, high-activity species contained in the liquid portion, such as ¹³⁷Cs and ⁹⁰Sr, would be further separated using previously demonstrated methods and added to the HAW portion, leaving an aqueous solution containing both low-activity waste (LAW) species and a host of other non-radioactive species such as Na⁺, K⁺, Al(OH)₄⁻, Cl⁻, F⁻, NO₃⁻, NO₂⁻, OH⁻, CO₃²⁻, and organic compounds [2]. The LAW and HAW fractions resulting from these pre-treatment steps would then be mixed with glass precursors or glass frit and vitrified for long term storage. However, one potentially troublesome radionuclide remaining in the LAW after pre-treatment is ⁹⁹Tc a considerable fraction of which occurs as pertechnetate, TcO₄⁻.

Previous estimates of Hanford tank waste inventories indicated that the amount of technetium in the waste needed to be reduced substantially to prepare immobilized low-activity waste (ILAW) glass that meets performance assessment requirements [3]. Based on this, one plan to address the technetium problem is to remove pertechnetate from the waste using commercially available polymeric ion exchange resins, elute the pertechnetate off the resins, concentrate the eluate, then add the eluate to the HAW fraction.

However, there are some inherent difficulties in this approach to dealing with the potential pertechnetate problem. First, at the time this manuscript was written, it was still unclear whether or not technetium would need to be removed prior to LAW vitrification. Secondly, if removing pertechnetate from LAW is required, several operations will be needed for ion-exchange, elution, and eluate concentration. Although these operations may be taken into account in the design of the treatment plant, a simpler approach, provided one could be developed, could result in considerable cost savings in both plant construction and plant operation. Lastly, based on plans described above, the ultimate fate of the pertechnetate would be vitrification using glass formulations and melter systems that will most likely not be tailored to handle the inherently great volatility typical of Tc(VII) compounds. Significant technetium loss may thus occur due to volatilization of Tc(VII) compounds under even modest thermal processing conditions, [4] and commercial polymeric ion exchange resins do not reduce Tc(VII) to much less volatile Tc(IV) species (see below).

To help address this and other concerns for the clean up of these sites by providing the means by which research could be performed on, for example, alternative process chemistry schemes, the DOE initiated the Environmental Management Science Program (EMSP) beginning in 1996. One such alternative approach that was proposed would be to use a technetium ion-exchange or sorbent material that did not require the sorbed technetium to be subsequently removed and could also be directly stabilized, not necessarily through high temperature vitrification, into a separate technetium waste form. Composite materials consisting of nano-scale zero valent iron supported on high surface area substrates, which have been termed

“Ferragels” [5], are viable candidates for the proposed technetium removal scheme. Additionally, unsupported, nano-scale, zero-valent iron alone may also exhibit some degree of usefulness.

The support material used in making supported Ferragels provides, in theory, a medium on which the individual, nano-scale, zero-valent iron particles can be kept in a highly dispersed, and hence more active state, as opposed to an agglomerated, less active state. The role of the support material for use in Ferragel applications then is similar to that for use in many other heterogeneous catalytic applications involving supported PGMs (platinum group metals) and other metals. Thus, the high surface area materials often used in such heterogeneous catalyst applications – alumina, silica, and zirconia - may also prove useful for supporting Ferragels for the application investigated here. While high surface area alumina, silica, or zirconia may work well as supports for Ferragels in near neutral pH solutions, at the very high pH encountered in caustic waste streams, zirconia may be the best choice owing to its extremely low solubility at high pH compared to alumina and especially silica. One additional property of potential support materials for Ferragels that needs to be considered, but often can not be very well delineated, is their contribution to the overall chemistry involved with putting metal down onto their surfaces; for the same support material, e.g., zirconia, with the same surface area, how well the metal can ultimately be dispersed onto the support often depends on how the material was made.

Ferragel materials are powerful reductants for aqueous metal ions [5]. These materials consist ostensibly of particles of iron, 10-30 nm in diameter, immobilized on a support material via borohydride reduction of an aqueous iron salt. Typically, Ferragels contain about 20-25% iron by weight, approximately 40-85% of which is in the zero-valent state, and the balance is oxidized to di- and/or tri-valent iron oxides/oxyhydroxides [6 and this work]. Ferragels are relatively stable in air once dried but are highly active reductants when wet. They can be made using a wide variety of support materials, including zirconia and silica. When Ferragel encounters aqueous Tc(VII) species, the technetium is reduced to immobilized Tc(IV) species, most likely $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and the iron is oxidized to Fe(III) species such as FeOOH(s) (see below).

Under the aegis of the EMSP initiative, we began studying the use of Ferragels in removing pertechnetate from caustic aqueous waste streams then stabilizing the loaded composite material into a separate waste form. Here, Ferragels consisting of nano-scale zero-valent iron on base-stable supports, especially zirconia-based materials, were tested and shown to be effective for the removal and reduction of TcO_4^- from simplified DSSF tank-waste simulants. In addition to testing base-stable Ferragels, an iron-on-silica gel Ferragel was tested on Tc(VII) solutions at near-neutral pH. A dilute, near-neutral pertechnetate solution would be the typical result of eluting the sorbed Tc(VII) from the commercial ion exchange resins. While it is not stable in strong base, silica gel-supported Ferragel was effective in removing and reducing TcO_4^- from these near-neutral prototypical eluate solutions. Unsupported Ferragels were also tested and were found to efficiently remove pertechnetate from both simplified DSSF tank waste and near-neutral eluate simulants.

One important aspect of this EMSP work is the potential advantage of avoiding the relatively high-temperature vitrification process, where volatilization of Tc(VII) species can be expected to be great, as a means of stabilizing the separated technetium. The use of completely inorganic Ferragels may allow the conversion of the loaded Ferragel material into a stable waste form through an encapsulation process, for example, by mixing the loaded Ferragel with glass powder then sintering the composite using a relatively low temperature process [see for example 7]. At the time this work had been conducted, such a low temperature sintering process and a glass formulation had already been developed, demonstrated, then ultimately relegated to be

subordinate to a yet-to-be developed alternative technology for the encapsulation of Rocky Flats plutonium-containing incinerator ash. The alkali boro-aluminosilicate glass developed for the Rocky Flats ash encapsulation was specifically designed to sinter at temperature of between 600°C and 800°C [7]. This sintering temperature range is also ideal for encapsulating our loaded Ferragel material and thus was implemented in this work.

One last aspect of Ferragels that was not explored here is their use in rendering any unremoved technetium in waste streams innocuous during the vitrification process. Tc(IV) compounds are typically much less volatile than Tc(VII) compounds. Ideally then, the addition of Ferragels, either supported or not, to a Tc(VII)-containing waste stream would act to reduce the Tc(VII) to Tc(IV) and provide for less technetium volatilization during vitrification. This concept would be a useful one to explore in the future.

EXPERIMENTAL PROCEDURE

Preparation of Ferragel Sorbent Materials

The composite Ferragel (FG) sorbent materials studied in this work are ideally zero-valent iron nano-particles dispersed onto inorganic support materials. The support materials were chosen depending on the application: removal of pertechnetate from either caustic tank wastes (in which case, support stability under high pH conditions was required) or organic ion-exchanger eluate (in which case a broader range of materials could be examined due to the near-neutral solution pH).

Support materials included both commercially available zirconium-, tin-, and zinc-oxide powders (Aldrich), as well as high surface area “RTDS” zirconias that were prepared at Pacific Northwest National Laboratory (PNNL) (see [Appendix A](#)).

Application of the zero-valent iron nano-particles to the support materials to form Ferragels was conducted at Penn State University (PSU) and is described previously in the literature [5,6]. Unsupported Fe⁰ nano-particles were also prepared in a similar manner by simply leaving out the support material [Table 1](#) summarizes the characteristics of the Ferragel sorbent materials investigated.

Typical Ferragel sorbent materials have been characterized using a variety of techniques that confirmed the presence of Fe⁰ with the balance being oxidized species [6]. An oxidized rind on the zero-valent iron is certainly expected, yet the portion of un-reacted Fe⁰ still provides for sufficient reactivity towards TcO₄⁻, as is demonstrated from the results presented here.

Control Materials

In addition to the Ferragel sorbents studied in this work, two control samples were also evaluated. One sample was the RTDS cubic zirconia material (RTDS-6) by itself with no zero-valent iron applied to it. The other sample was a ferrihydrite, FeOOH, prepared using the method of Schwartman [8]. These materials were studied to determine to what extent the pertechnetate would sorb to typical support materials alone and to typical corrosion products from iron. Iron powder was APS 6-10 micron, reduced iron powder from Alfa/Aesar and had a measured specific surface area of 0.17 m²g⁻¹ by the BET method.

Simulants

In previous Hanford tank waste processing work performed at PNNL [9], a DSSF (double shell slurry feed) LAW simulant of fairly complex chemistry was employed. This DSSF simulant composition is summarized in Table 2. The original plan for this work was to use a graded approach to testing Ferragel sorbent efficacy with simulants, beginning with simplified versions of DSSF or other waste stream simulants and becoming more complex in chemistry with each succeeding set of experiments and material modifications. We began with a caustic supernatant simulant containing only NaOH, Na₂CO₃, and NaNO₃ (simulant S1). This was followed by using related caustic supernatant simulants containing other species, such as NaNO₂ (simulant S3), or other components that influence corrosion behavior (simulant S2).

We had planned to use a full caustic DSSF simulant and also had made arrangements to test Ferragel sorbents in actual DSSF waste. During the course of this EMSP work, however, Hanford Site contractors decided to select a commercially available organic ion-exchange resin for removing pertechnetate from LAW. Since testing Ferragel sorbents in more complex simulants and actual LAW was no longer meaningful to the end-user (Hanford Site contractors), which is something EMSP research is supposed to reflect, the development of more complex simulants and actual LAW was discontinued. Discussions with Hanford Site contractors at that time, however, indicated that there was an interest in evaluating Ferragel sorbents in the treatment of the large volumes of technetium-containing eluate that would be generated in removing pertechnetate from the commercial ion-exchange resin. The anticipated composition for this eluate consisted of essentially water, with relatively low concentrations ($< 10^{-3}$ M) of only a few components: B, Na and Si species as well as nitrate, nitrate, and chloride. Thus, in addition to the base supernatant simulants, distilled and deionized water was also used as an initial base eluate simulant (E1).

Simulants S1, S2, and S3 were prepared by mixing appropriate amounts of NaNO₃, NaNO₂, NaOH, Na₂CO₃, KNO₃, Al(NO₃)₃·9H₂O, Cr(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O, Co(NO₃)₃·6H₂O, Ca(NO₃)₃·4H₂O, Pb(NO₃)₂, MnSO₄·xH₂O, MgSO₄, Zn(SO₄)₂·7H₂O, CuSO₄·5H₂O, Na₂MoO₄·2H₂O, NaNO₃, and CrO₃, and sufficient de-ionized water in a pyrex volumetric flask. The pH of each simulant was estimated using color fixed indicator sticks (Baker). Densities were calculated from the measured mass of a known volume of solution. Polypropylene bottles were used to store freshly prepared stimulant. Other than simulant E1 (D.I. water), Table 2 summarizes the composition, pH, and density of each of the simulants considered here.

Aliquots of simulants S1 and S2 were spiked at PNNL with an appropriate amount of a stock Na⁹⁹TcO₄ solution of known approximate concentration. The actual concentration of pertechnetate in the simulants was determined using counting methods (see below) and varied from 0.51mM to 12mM. An aliquot of simulant S1 was also spiked with 17mM NH₄ReO₄ for use in initial loaded Ferragel encapsulation experiments (see below). Simulants S3 and E1 were left un-spiked until they were tested with sorbent material at Lawrence Berkeley National Laboratory (LBNL) (see below).

Batch Contact Measurements Using Pertechnetate-Spiked Simulants S1 and S2

For each sorbent material to be evaluated, between 0.03-g and 0.06-g of the material was weighed, placed in a 50-mL conical bottom polypropylene centrifuge tube of known mass, and the final mass of the centrifuge tube and sorbent material determined. Between 5-mL and 20-mL of the appropriate pertechnetate-spiked simulant (S1 or S2) was then added using a plastic

syringe and the centrifuge tube was weighed again. An electronic scale (Mettler AE 240) was used to measure these masses to ± 0.0001 g. For each sorbent material, a duplicate tube was prepared in an identical manner. A blank spike consisting of the appropriate Tc-spiked simulant with no sorbent (to determine the starting concentration of TcO_4^-) and a blank consisting of an adsorbent material with deionized water were also prepared and evaluated along with the sorbent samples.

The target sorbent sample mass and the simulant volume were determined based on a target phase ratio, which is equal to the volume of simulant divided by the mass of sorbent. The goal was to sufficiently vary the phase ratio and pertechnetate concentration to determine the limits for these Ferragel composite sorbent materials.

All centrifuge tubes were placed on an Orbit® Shaker at ≈ 100 rpm. After 24 hours, each tube was weighed, then centrifuged (Damon IEC HN-SII Centrifuge) at 1500 rpm for 10 minutes. Using individual plastic 5-mL syringes, a portion of each sample was removed and approximately 4 drops filtered through a $0.2\ \mu\text{m}$ filter (Millipore Co.) into a pre-weighed glass scintillation vial and weighed again to determine the aliquot mass. Again, an electronic scale (Mettler AE 240) was used to measure these masses to ± 0.0001 -g. To each tube was added ~ 20 -mL of Optifluor® Liquid Scintillation Cocktail (Packard Co.) after which each tube was hand shaken for approximately ten seconds.

The sample aliquots were then analyzed for disintegrations per minute (dpm) using two standard methods at PNNL. Method A involved liquid scintillation counting (LSC) using an LSC instrument (Wallac 1415 Liquid Scintillation Counter). Method B employed a Bremsstrahlung secondary photon emission instrument (Autogamma Wallac 1411). The measured dpm values were converted to curies (Ci) which, combined with the known specific activity for ^{99}Tc of $0.017\ \text{Ci/g}$ and the measured aliquot and sample masses, enabled the concentration of technetium in the solutions to be determined.

Batch Contact Measurements Using Pertechnetate-Spiked Simulants S3 and E1

Approximately 35-mg of a given Ferragel sorbent was weighed into each of three 15 ml plastic centrifuge cones. To this, 10 ml of simulant S3 or E1 was added by volumetric pipette. The samples were shaken vigorously. To each tube was added $20\ \mu\text{L}$ of $0.045\text{M Na}^{99}\text{TcO}_4$ stock solution. Each sample was inverted several times then placed on an orbital shaker for 18 hours at 150 rpm. Each sample was allowed to stand for 18 hours to settle. The precipitate was then removed by pipette and placed in a 2 mL centrifuge cone. The cones were centrifuged and the supernatant removed using a pipette. The efficacy of the Ferragel sorbents on removing pertechnetate from these particular simulants were estimated by obtaining UV-Vis spectra of the final supernatant solutions and comparing them to those obtained from the starting simulants. The remaining precipitate was used in the preparation of samples for XAS (see below).

XANES and EXAFS Characterization of Technetium Sorbed to Ferragel Sorbents

One benefit to using Ferragel sorbents to remove pertechnetate from waste streams is its reduction of pertechnetate to Tc(IV) species, which will aid in later stabilization efforts. To evaluate the reduction, technetium sorbed onto various Ferragel materials was characterized using X-ray absorption spectroscopy (XAS), which includes both the near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). Technetium was sorbed onto

Ferragel sorbent materials in experiments conducted at LBNL. Samples for XAS were then prepared at LBNL and shipped to the Stanford Synchrotron Radiation Laboratory (SSRL).

XAS samples were prepared by mixing the precipitate that remained after the batch contact measurements in pertechnetate-spiked simulants S3 and E1 as described above with 50 mg boron nitride and placing the mixture in the sealed off tip of a plastic pipette, which was then flame sealed. All the technetium-containing samples were triply contained in accordance with LBNL safety procedures.

X-ray absorption spectra were recorded at SSRL on beam line 4-1 by collaborators from LBNL, PNNL, and PSU. The beam was monochromated using Si (220) crystals detuned by 50% to decrease the contribution from higher harmonics. Data were recorded in fluorescence mode using a Ge solid state fluorescence detector developed at LBNL [10,11]. X-ray energies were calibrated using an aqueous pertechnetate solution as a reference that was simultaneously measured in transmission mode using a standard ionization detector. A hydrated TcO_2 reference as well as pertechnetate sorbed onto the commercial organic ion-exchange resin Reillex-HPQTM were also measured. Between two and five scans were taken for each sample, depending on the signal to background ratio, and then averaged together. Data was treated by the usual method [12] using the EXAFSPAK suite of programs [13]. Theoretical phases and amplitudes were calculated for a model complex using the program FEFF6 [14]. Energies were referenced to the pre-edge feature in the pertechnetate spectrum.

Encapsulation of Rhenium-Loaded Ferragel Sorbents

As indicated above, another benefit to using inorganic composite Ferragel sorbents to remove pertechnetate from waste streams is its compatibility with low-temperature encapsulation processes. To initially evaluate this, several experiments were performed in which FG RTDS-10 sorbent material was contacted with perrhenate-spiked simulants for 24 hours then treated (see below) to yield a rhenium-loaded Ferragel feed stock for a model encapsulation process. The rhenium-loaded Ferragel feed stock was then mixed with glass frit, referred to as NBS frit [7], and heat-treated to temperatures at or below 800°C (see below). The composition of the NBS frit was as follows: 60 mass % SiO_2 , 10 mass % B_2O_3 , 15 mass % Na_2O , 5 mass % Li_2O , 5 mass % Al_2O_3 , and 5 mass % ZrO_2 [7].

This encapsulation work was intended to be a significant portion of work. We had planned on beginning the work using perrhenate as a surrogate for pertechnetate to work out any process-related problems before actually using pertechnetate-containing simulants. In spite of support from EMSP, however, during the course of this work, end users were understandably not very supportive of a separate waste form for technetium due to the added costs this would incur. Thus, additional work on encapsulating Ferragel materials, with the concatenate expenditure of resources, was discontinued. Although incomplete, we present the experimental details, and later the results as such, solely for demonstrating the completed processes for removing and stabilizing pertechnetate from waste streams as we envisioned it.

Into a 50-mL conical bottom polypropylene centrifuge tube was added 0.50-g of FG RTDS-10 sorbent material and 40.0-mL of perrhenate-spiked simulant S1. The centrifuge tube was closed, shaken by hand, and then placed in a near vertical position in a beaker. After 24 hours, the tube was centrifuged then washed with de-ionized water and re-centrifuged three times to remove the majority of residual simulant. The resulting rhenium-loaded FG RTDS-10 was dried at 80°C in a vacuum oven then ground into a fine powder using an agate mortar and pestle and mixed with NBS frit at a loading of 20 mass % Ferragel feed to 80 mass % NBS frit. Approximately 1.5-g of this mixture was put in a cylindrical alumina crucible as a loose powder

which was then placed uncovered in a box furnace equilibrated at 700°C. After four hours, the crucible was removed from the furnace and allowed to cool to room temperature.

RESULTS

Batch Contact Results

Tables 3a and 3b summarize the pertechnetate concentrations in solution before and after batch contact with the more relevant Ferragel sorbent materials. The sorbent mass and simulant volume used are also included for each entry.

XANES and EXAFS Characterization

Figure 1 shows the Tc K-edge XANES spectra obtained from representative sorbent and reference materials. Table 4 summarizes the absorption edge energy shifts with respect to that of pertechnetate. Table 5 summarizes the Tc EXAFS results from technetium species sorbed onto different Ferragels under different conditions. The corresponding measured and fitted $\chi(k)$ and $\chi(R)$ data obtained from this system are shown in Figure 2. In all cases, technetium exists as Tc(IV) surrounded by 6 oxygen neighbors forming an octahedral coordination environment. With the exception of Tc sorbed on iron powder, scattering from other nearby metal atoms is apparent and is best fit with Fe neighbors, although the Tc-Fe distances vary with sorbent and solution composition. For Tc sorbed on iron powder scattering from nearby metal atoms is best fit with Tc neighbors.

In addition to the Tc K edges, the Fe K edge XANES spectra of the Ferragels were examined; they are shown in Figure 3 along with the spectra of relevant reference materials. Figure 3 also shows the results of fitting the Ferragel XANES spectra using the reference materials. The resulting contributions of the different iron species are given in Table 6.

Encapsulation of Rhenium-Loaded Ferragel Sorbents

As stated above, washed, dried, and ground rhenium-loaded FG RTDS-10 Ferragel sorbent material was mixed with NBS frit [7] at a loading of 20 mass t% Ferragel feed to 80 mass % NBS frit and heat-treated as a loose powder for four hours in a cylindrical alumina crucible at 700°C. After the heat-treated material was allowed to cool to room temperature, it was easily removed from the crucible as a single monolithic pellet. Figure 4 shows a photograph of this pellet, which was mechanically stable and readily handle able.

DISCUSSION

Batch Contact Results

From the concentration data, examples of which are summarized in Table 3, the percentage of pertechnetate removed from simulants S1 and S2 during these batch contact measurements have been calculated and are indicated in Table 7. With the exception of the RTDS-6 alone without zero-valent iron, all the entries in Table 7 indicate that RTDS-6 supported zero-valent iron sorbent materials remove significant concentrations of pertechnetate from the caustic supernatant simulants.

Based on the UV-Vis absorption data collected before and after contacting FG SG10 or unsupported FG with simulant E1, it is observed that <5% of the original pertechnetate remains after the batch contact experiments (see Table 7). As was the case above, the support material alone (silica gel) without zero-valent iron removes very little pertechnetate (see Table 7). This demonstrates that Ferragels, even in an unsupported state, can remove greater than approximately 95% of the pertechnetate in the neutral pH ion-exchange resin eluate simulant containing typical concentrations of pertechnetate.

Distribution Coefficients

Another way of visualizing the results obtained from batch contact measurements is through the distribution or partition coefficient, K_d . For the systems being studied here, K_d represents a quantitative measure of the concentration of technetium species that is sorbed by the Ferragels with respect to the concentration of technetium species remaining in the simulant solutions after contact. Although the results obtained here most likely do not represent equilibrium conditions, a necessity for true K_d determinations, the K_d construct is still a useful evaluation tool and has been implemented here and elsewhere [15].

Batch K_d values (L/kg) were calculated from the experimental data using the following equation:

$$K_d = S_f/C_f = [(C_o - C_f)V/M_{FG}]/C_f \quad (1),$$

where S_f is the concentration (mg/kg) of technetium species sorbed to the Ferragel after contact, C_f is the concentration (mg/L) of technetium species in the final simulant solution after contact with the Ferragel, C_o is the concentration (mg/L) of technetium species in the starting simulant solution prior to contact with the Ferragel (determined from the blank spike), V is the volume (L) of simulant solution, and M_{FG} is the mass (kg) of Ferragel. Typically, K_d ($= S_f/C_f$) is determined from the practical form of equation (1), i.e., the far right part, and assumes that the species in solution at “equilibrium”, pertechnetate in this case, is the same as that sorbed to the sorbent. One then experimentally measures the amount of species removed from solution due to the action of the sorbent to calculate K_d . This is not the case here, since the most probable form of technetium sorbed to the Ferragels is $TcO_2 \cdot H_2O$, (see below). However, again, this method of calculating the K_d values is still a useful evaluation tool as it does not require precise knowledge concerning the final state of the sorbed technetium a priori and has been implemented here. Table 7 summarizes the batch K_d values determined in this way for various Ferragel sorbents, as well as for the control samples, in different simulants.

From Table 7, note that the mean pertechnetate K_d values for the FG RTDS-6 sample in contact with simulant S2 and in contact with simulant S1 are 350-390 L/kg and 130-180 L/kg, respectively. These pertechnetate K_d values are similar to those obtained by Blanchard et al. [16] for the commercial organic ion-exchange resins Reillex™-HPQ and ABEC 5000 in contact with actual caustic DSSF waste using a phase ratio of 100 L/kg. It should be noted that these sets of data are not directly comparable, due to the fact that simplified simulants as opposed to real waste, different starting pertechnetate concentrations, and different phase ratios were used. With these caveats in mind, however, the similarity between the data still indicates that the inorganic Ferragel sorbent materials are, to a first approximation, reasonable alternatives to commercial organic ion-exchange resins.

Additional Analyses

Refining the data further, [Table 8](#) represents the estimated pertechnetate distribution coefficients in terms of only the targeted mass of Fe^0 in the sorbents, K_d' (L/kg Fe^0), as opposed to the total mass of the sorbents presented earlier, K_d (L/kg sorbent). The phase ratios in [Table 8](#) have been left uncorrected with respect to the targeted mass of Fe^0 in the sorbents for ease in keeping track of the individual experimental conditions and to avoid confusion.

Consider FG RTDS-6 and FG ZrO_2 in contact with simulant S1 with 12 mM pertechnetate and nearly the same average phase ratios. For these particular experiments the amount of Fe^0 is limited with respect to TcO_4^- (i.e., the molar ratio of $\text{TcO}_4^-:\text{Fe}^0$ is greater than unity). Under these iron-limited caustic conditions the average K_d' values are within experimental error of each other. This indicates that under these conditions it is to a large extent the amount of nano-scale zero-valent iron loaded onto a given support that helps dictate the overall FG performance. Support materials that provide greater loadings of zero-valent iron, RTDS-6 zirconia in contrast to lesser grades of zirconia, for example, would thus provide for greater pertechnetate extraction efficiencies. Furthermore, note that the control samples, RTDS-6 (without zero-valent iron) and $\text{Fe}(\text{OH})_3$, exhibited relatively low pertechnetate K_d values compared to the FG RTDS-6 samples. See [Table 7](#). The percentage of pertechnetate removed by these control samples, which should contain no Fe^0 , was insignificant.

To normalize the results with respect to the different starting concentrations of pertechnetate in the simulants and different phase ratios, we introduce the additional term R_0 , which we define as the total mass of TcO_4^- in the starting solution per mass of sorbent. [Figure 5](#) shows a plot of S_f (grams of TcO_4^- removed per kg of sorbent) vs R_0 (grams of TcO_4^- in the starting solution per kg of sorbent). [Figure 5](#) represents a working “engineering” curve, so to speak, that enables one to calculate the amount of a particular Ferragel material required to remove a known amount of TcO_4^- from a particular media to a particular level of extraction. The curve indicated in [Figure 5](#), defined by the equation, $S_f = (R_0)$, is the best fit to the data obtained from FG RTDS-6 in simulant S1 only. It is interesting to note that by taking the data obtained from FG ZrO_2 in stimulant S1 and normalizing them to the same amount of Fe^0 present in the Ferragel as that in FG RTDS-6 by multiplying the FG ZrO_2 data by four, the normalized FG ZrO_2 data lies close to the curve for the FG RTDS-6 data. This once again demonstrates the importance of the amount of iron that can be loaded onto a particular support material.

XANES and EXAFS Characterization

To better understand the mechanism of pertechnetate adsorption by Ferragels, both the Fe K-edge and Tc K-edge XAS spectra were investigated. The Tc K-edge EXAFS spectra of the Ferragels after treatment with pertechnetate clearly show that the inner coordination environment of the sorbed technetium species consists of six oxygen ligands with a Tc-O bond distance of 2.0 Å. This bond distance and the Tc K-edge shifts given in [Table 5](#) clearly establish the oxidation state of Tc as Tc(IV) [17,18]. The presence of the Tc-O multiple scattering is consistent with the octahedral coordination environment expected for a d^3 transition metal center. In addition to the inner shell of oxygen neighbors, the EXAFS spectra reveal additional neighboring metal atoms that can be assigned as Fe, with the exception of Tc sorbed on iron powder in which the neighboring metal atoms are best assigned as Tc.

Fitting the spectra of Tc(IV) sorbed to FG and FG SG10 in distilled water reveals very similar environments for the sorbed Tc(IV) species: one Fe neighbor at 2.7 Å and two at 3.3 Å.

The spectra can be fit using a Tc neighbor in place of the nearer Fe neighbor; however, the quality of the fit is not as good, and the Tc-Tc distance of 2.44(1) Å is too short for a pair of Tc(IV) atoms with only oxygen ligands. For comparison, the Tc-Tc distance in $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ is 2.57 Å [18].

The spectra of Tc(IV) sorbed to iron metal at pH 5 and to FG in simulant S3 are similar to each other in that the Tc(IV) center has two Fe neighbors at 3.1 Å. The spectrum of Tc(IV) adsorbed to iron metal shows an additional scattering atom that can be fit using either one Tc at 3.7 Å or one Fe at 3.6 Å, but a better fit is obtained with Tc as the scattering atom.

The Fe K-edge XANES spectra reveal the changes in the bulk composition of the Ferragels upon treatment with pertechnetate solution. Prior to reaction with solution containing pertechnetate, Ferragels consist primarily of iron metal and hematite, presumably a core of iron metal with a protective “rind” of insulating Fe(III) oxides/hydroxides [6,8]. Upon exposure to pertechnetate in distilled water, the Ferragel is oxidized, primarily to hematite with smaller amounts of goethite and magnetite. At high pH, oxidation of Ferragel produces mainly magnetite, presumably from the reduction of the hematite skin upon exposure to the solution.

Because six coordinate Tc(IV) and high spin Fe(III) are the same size [19], the results of the EXAFS studies can be interpreted using the polyhedral approach of Manceau and coworkers [20,21]. A number of potential mechanisms could describe the sorption of Tc(IV) onto the surface of the Ferragel particles [21]. Tc(IV) could substitute for Fe(III) isomorphically at the surface of the iron oxide. Tc(IV) could form $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ oligomers at surface of the particles. $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ could precipitate as a separate phase. Finally, Tc(IV) could be adsorbed as isolated complex on the surface of the iron oxide phase. Although interpretation of the results is complicated by tendency of Tc(IV) to form metal-metal bonds [17,18,22,23] and the fact that isomorphic substitution of Tc(IV) into an Fe(III) structure requires charge compensation, the final mechanism, surface sorption, best explains the EXAFS results.

Bulk or surface precipitation of $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ was not observed at these pertechnetate concentrations and fraction surface coverage. The spectra are clearly not due to $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ since the required scattering from a Tc neighbor at 2.6 Å is not observed in any of these experiments. Although the spectra of Tc(IV) adsorbed on Ferragel from distilled water require a short distance to a neighboring metal atom, the spectra are better fit using Fe rather than Tc as the scattering atom, and the Tc-Tc distance of 2.4 Å obtained using technetium as the scattering atom does not agree with the Tc-Tc distance in $\text{TcO}_2 \cdot x\text{H}_2\text{O}$.

Isomorphic substitution of Tc(IV) into the lattice of an iron oxide also does not occur in these experiments. In all of these experiments, the Tc absorbing atom has very few metal neighbors, which is not consistent with isomorphic substitution. Moreover, the Tc-Fe distances do not agree well with the Fe-Fe distances in the common iron oxides [8] with the possible exception of green rusts in which the iron centers are separated by 3.1 Å [8,24]. However, the Fe XANES results show that after exposure to pertechnetate solution, the ferragels consist primarily of more highly oxidized iron oxides, which is not consistent with the presence of green rusts on the surface of these samples [8,25].

Surface sorption of isolated TcO_6 octahedra is the mechanism most consistent with the EXAFS results since it explains both the lack of short Tc-Tc distances and the small number of metal atoms neighboring the Tc(IV) center. This result is not surprising for the ferragel absorption experiments since the less than a monolayer of Tc(IV) ions is present. However, for sorption of Tc(IV) on iron filings, sufficient pertechnetate was present to form ~15 monolayers, and only 4 monolayers of TcO_6 are found on the surface. It is worth noting that Tc-Tc scattering is observed only for Tc adsorbed on iron filings, but even in this case, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ is not present. These observations suggest that, in these cases, sorption of pertechnetate on Ferragels occurs

through simultaneous reduction and adsorption of a pertechnetate ion at the surface of the metal rather than reduction of pertechnetate in solution followed by sorption of Tc(IV) from solution. If the latter were occurring, a detectable amount of $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ should form.

Encapsulation of Rhenium-Loaded Ferragel Sorbents

A mixture of 20 mass % rhenium-loaded FG RTDS-10 Ferragel sorbent material and 80 mass % NBS frit was capable of being sintered in a readily handle able pellet as indicated in **Figure 4**. Although pellets may not be a final waste form candidate, these results clearly demonstrate that concept that Ferragels can be used to directly treat a waste stream, be removed from the waste stream, then directly stabilized into a waste form. Ideally, a series of different frit compositions, additives, and heat-treatment temperatures and times were to be investigated to obtain the optimal means of encapsulating rhenium- (and eventually, technetium-) loaded Ferragel materials into chemically-, as well as mechanically-, stable waste forms. Retention of the rhenium/technetium during the encapsulation was an additional parameter that was to be investigated. Without the support of an end-user for a separate waste form for technetium, however, this exercise would have been a purely academic one, which, again, was not the purpose of EMSP. However, it should be evident from Figure 4 that the strategy presented here has some merit and should be explored further – not only for the treatment of Hanford Site and other nuclear waste streams, but perhaps for other industrial waste streams.

CONCLUSIONS

Nanoparticles of zero-valent iron or “Ferragels,” both unsupported and supported on inorganic materials such as zirconia or silica, were applied to the separation and reduction of pertechnetate anions (TcO_4^-) from complex waste mixtures. was investigated as an alternative approach to current waste processing schemes. Although applicable to pertechnetate-containing waste streams in general, the tests summarized here were directed at two specific potential applications at the U.S. Department of Energy’s Hanford Site: (1) the direct removal of pertechnetate from highly alkaline solutions, typical of those found in Hanford tank waste; and (2) the removal of dilute pertechnetate from near neutral solutions, typical of the eluate streams from commercial organic ion-exchange resins that may be used to remediate Hanford tank wastes. For application (1), a high surface area ($>200 \text{ m}^2/\text{g}$) base-stable, nano-crystalline zirconia was used as a support for Ferragel where the tests were conducted in highly alkaline solutions with large concentrations of Na^+ , OH^- , NO_3^- , and CO_3^{2-} , representative of Hanford tank waste. For application (2), a silica gel support was used as the tests were conducted with near neutral solutions, representative of potential eluate stream from commercial organic ion-exchange resins.. It was shown for application (1) that after 24 hours of contact time, the high surface area zirconia supported Ferragel sorbent removed about 50% ($K_d = 370 \text{ L/kg}$) of the pertechnetate from a pH 14 tank waste simulant containing 0.51 mM TcO_4^- and for a phase ratio of 360 L simulant per kg of sorbent. For application (2) it was shown that after 18 hours of contact time, the silica supported Ferragel removed $>95\%$ pertechnetate from a neutral pH eluate simulant containing 0.076 mM TcO_4^- for a phase ratio of 290 L/kg. From X-ray absorption studies, it was determined that in all cases, Ferragels reduced the Tc(VII) to Tc(IV), or possibly Tc(V), through a redox reaction. Finally, it was demonstrated that a mixture of 20 mass % of the solid reaction products obtained from contacting zirconia support Ferragel with an alkaline waste

solution containing Re(VII) - a surrogate for Tc(VII) - with 80 mass % alkali borosilicate based frit heat treated at 700°C for 4 hours sintered into a handle able waste form.

ACKNOWLEDGEMENTS

Much of the experimental work presented here as well as part of the analyses and write up was supported by the Environmental Management Science Program of the Office of Science and Technology of the U. S. DOE. Part of this work was performed at the following locations: Pacific Northwest National Laboratory (PNNL), which is operated for the U.S. DOE by the Battelle Memorial Institute under Contract DE-AC06-76RLO 1830; the Stanford Synchrotron Radiation Laboratory, which is operated by the Director, U. S. DOE, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences and at Ernest O. Lawrence Berkeley National Laboratory, which is operated by the U. S. DOE under Contract No. DE-AC03-76SF00098. The production of the RTDS zirconia material used as a support material in this work was supported by the Science and Technology for Environmental Processing (STEP) initiative at PNNL.

APPENDIX A

Researchers at PNNL have developed a continuous, hydrothermal process and technology that is capable of generating a variety of ultra-fine, nano-crystalline oxyhydroxide and oxide particulates in large quantities [26,27]. In this process, called the Rapid Thermal Decomposition of precursors in Solution (RTDS), an aqueous solution containing dissolved metal precursor salt(s) and other labile reactants is pumped at high pressures and flow rates through a heated stainless steel or other alloy tube, where precipitation and crystallization reactions occur. The fluid-particle mixture then expands through a pressure-restricting nozzle. Nucleation of nano-crystalline (less than 30 nanometers) metal oxide or oxyhydroxide particles in the RTDS process occurs during the relatively short residence time in the heated hydrothermal region (1-30 seconds) and is then quenched as the particle-fluid mixture is expanded through the nozzle.

PNNL has previously prepared large quantities of monoclinic zirconia and predominantly cubic zirconia having surface areas as high as approximately 200 m²/g for use as catalyst support materials under severe reaction conditions [28]. The cubic zirconia materials (RTDS-6) were good candidates for use in supporting Ferragels under similarly severe environmental conditions.

REFERENCES

1. Stewart, T.L.; Frey, J.A.; Geiser, D.W.; Manke, K.L., in *Science and Technology for Disposal of Radioactive Tank Wastes*, W.W. Schulz, N.J. Lombardo, Eds., Plenum Press, NY, 1998, 3. ?? TM/JD
2. Westinghouse Hanford Co., Report WHC-SD-WM-RD-044, p A3.
3. Pete McGrail ref...? JD
4. Darab, J.G.; Smith, P.A.; *Chem. Mater.*, 1998, **8**,1004-1021.
5. Ponder, S.M.; Darab, J.G.; Mallouk, T.E., *Environ. Sci. Tech.*, 2000, **34**, 2564.
6. Ponder, Darab, J.G.; Bucher, J.M.; Caulder, D.; Craig, I.; Davis, L.; Edelstein, N.; Lukens, W.W.; Nitsche, H.; Rao, L.; Shuh, D.K.; Mallouk, T.E.; *Chem. Mat.*, submitted TM
7. Vienna, J. D., J. Luey, P. Hrma, H. Li, D. E. Smith, R. D. Scheele, H.L. Wigent, and J. V. Crum. 1999. in *Ceramic Transactions*, 1999, **93**, American Ceramic Society, Westerville, OH, pp. 399-408.
8. Schwertmann, U.; Cornell, R.M., *Iron Oxides in the Laboratory: Preparation and Characterization*, 1991, VCH Publishers, Inc., New York.
9. simulant work ref. JD
10. Fabris, L.; Allen, P. G.; Bucher, J. J.; Edelstein, N. M.; Landis, D. A.; Madden, N. W.; Shuh, D. K. *IEEE Trans. Nucl. Sci.* **1999**, *46*, 1891.
11. Fabris, L.; Allen, P. G.; Bucher, J. J.; Edelstein, N. M.; Landis, D. A.; Madden, N. W.; Shuh, D. K. *IEEE Trans. Nucl. Sci.* **1999**, *46*, 417.
12. Koningsberger, D. C.; Prins, R. *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*; John Wiley & Sons: New York, 1988.
13. EXAFSPAK suite of EXAFS analysis programs written by Graham George at SSRL.
14. Rehr, J. J.; Albers, R. C.; Zabinsky, S. I. *Phys. Rev. Lett.* **1992**, *69*, 3397.
15. Kd ref. JD/TM
16. Blanchard ref. JD
17. Almahamid, I.; Bryan, J. C.; Bucher, J. J.; Burrell, A. K.; Edelstein, N. M.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Shuh, D. K.; Nitsche, H.; Reich, T. *Inorg. Chem.* **1995**, *34*, 193.

18. Lukens Jr., W. W.; Bucher, J. J.; Edelstein, N. M.; Shuh, D. K. *Environ. Sci. Technol.* **2002**, *36*, 1124.
19. Shannon, R. D. *Acta Cryst.* **1976**, *A32*, 751.
20. Manceau, A. A.; Combes, J. M. *Phys. Chem. Miner.* **1988**, *15*, 283.
21. Charlet, A.; Manceau, A. A. *J. Colloid Interface Sci.* **1992**, *148*, 443.
22. Bürgi, H. B.; Anderegg, G.; Bläuenstein, P. *Inorg. Chem.* **1981**, *20*, 3829.
23. Linder, K. E.; Dewan, J. C.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3820.
24. McGill, I. R.; McEnaney, B.; Smith, D. C. *Nature* **1976**, *259*, 200.
25. Mishawa, T.; Hashimoto, K.; Shimodaira, S. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4167.
26. Matson, D.W; Fulton, J.L.; Linehan, J.C.; Bean, R.M.; Brewer, T.D.; Werpy, T.A.; Darab, J.G., U.S. Patent Number 5,652,192, 1997.
27. Matson, D.W; Linehan, J.C.; Darab, J.G.; Buehler, M.F.; Phelps, M.R.; Neuenschwander, G.G., in *Advanced Catalysts and Nanostructured Materials*, W.R. Moser, Ed., 1996, Academic Press, New York, pp. 259-283.
28. Darab, J.G.; Neuenschwander, G.G.; Elliott, D.C.; Frye, J.G., in *Mat. Res. Soc. Proc.*, 1999, **549**, Materials Research Society, Pittsburgh, PA, pp. 67-72.

Table 1. Summary of Ferragel (FG) sorbent materials studied in this work.

Sorbent	Description	Target mg Fe ⁰ / g sorbent
FG	Unsupported Fe ⁰ nano-particles	1000
FG SnO ₂	FG on commercial tin oxide	20
FG ZnO ₂	FG on commercial zinc oxide	20
FG ZrO ₂	FG on commercial zirconia	20
FG SG10	FG on commercial silica gel	280
FG RTDS-10	FG on RTDS monoclinic zirconia	80
FG RTDS-6	FG on RTDS cubic zirconia	80
RTDS-6	RTDS cubic zirconia (no FG)	0

Table 2. Target compositions of LAW supernatant simulants.

Component	Simulant			
	DSSF	S1	S2	S3
Al ³⁺	1.0		0.0003	
Ca ²⁺	0.0010		0.0018	
Cr ³⁺	0.0087		0.0026	
CrO ₄ ²⁻			0.0002	
Fe ³⁺	0.0008		0.014	
K ⁺	0.50		0.0003	
Mg ²⁺	0.0010		0.0006	
Mn ²⁺	0.0004		0.0002	
MoO ₄ ⁻	0.017		0.0001	
Na ⁺	10.	7.4	3.7	7.7
CO ₃ ²⁻	0.27	0.27		
Cl ⁻	0.16			
F ⁻	0.25			
NO ₃ ⁻	3.1	3.1	0.057	2.7
NO ₂ ⁻	1.7			1.9
OH ⁻	3.8	3.8	3.7	3.1
PO ₄ ³⁻	0.043			
SO ₄ ²⁻	0.043		0.0009	
TOC ^a	1.4			
Cs ⁺	0.017			
IO ₃ ⁻	0.017			
Sr ²⁺	0.017			
pH	14	14	11	nm
density (g/cc)	1.42	1.31	1.19	nm

^a Total Organic Carbon (TOC) from EDTA.

nm = not measured.

Table 3a. Pertechnetate concentrations in waste simulant solutions (simulants S1 and S2) before and after 24 hours of contact with the more relevant Ferragel sorbent materials. Concentrations were determined using liquid scintillation counting and Bremsstrahlung secondary photon emission.

Sorbent	Simulant	Mass sorbent (g)	Simulant volume (mL)	Phase ratio (L/kg)	[TcO ₄ ⁻] ₀ (mM)	[TcO ₄ ⁻] _f (mM)
FG RTDS-6	S2	0.0218	9.14	420	0.51±0.02	0.26±0.02
		0.0299	9.07	300	0.51±0.02	0.24±0.02
FG RTDS-6	S1	0.0308	19.87	640	9.1±0.2	7.0±0.2
		0.0316	20.18	640	9.1±0.2	7.5±0.2
FG RTDS-6	S1	0.0601	4.72	80	9.7±0.2	4.2±0.2
		0.0612	4.77	80	9.7±0.2	5.2±0.2
FG RTDS-6	S1	0.0338	4.36	130	12.4±0.3	7.2±0.3
		0.0318	4.67	150	12.4±0.3	8.5±0.3
RTDS-6	S1	0.0615	9.82	160	9.7±0.2	9.5±0.2
		0.0610	9.35	150	9.7±0.2	9.5±0.2
FG ZrO ₂	S1	0.0317	4.66	150	12.4±0.3	11.0±0.3
		0.0311	4.85	160	12.4±0.3	11.4±0.3

Table 3b: Pertchnetate concentrations in waste simulant solutions (simulant S3) before and after 18 hours of contact with the more relevant Ferragel sorbent materials. Concentrations were determined using UV-Vis spectroscopy.

Sorbent	Mass sorbent (g)	Simulant volume (mL)	Phase ratio (L/kg)	$[\text{TcO}_4^-]_0$ (μM)	$[\text{TcO}_4^-]_f$ (μM)	K_d (g/mL)
FG	0.033	10	303	90 $\pm$ 5	3.3 $\pm$ 0.5	8100 $\pm$ 1000
FG SG-10	0.033	10	303	90 $\pm$ 5	3.7 $\pm$ 0.6	7100 $\pm$ 900
Iron Powder	0.05	10	200	90 $\pm$ 5	63 $\pm$ 2	87 $\pm$ 27
Silica	0.033	10	303	90 $\pm$ 5	89 $\pm$ 2	5 $\pm$ 24

Table 4. Tc K-edge energy shifts of various samples with respect to that of pertechnetate obtained from the XANES data.

Sample	Tc K-edge shift (eV from TcO_4^-)	Most probable oxidation state of Tc
TcO_4^- (aq), reference	0.0	+7
$\text{TcO}_2 \cdot x\text{H}_2\text{O}$ (s) reference	+5.3	+4
Reillex, contacted with simulant E1	+0.4	+7
FG, contacted with simulant E1	-5.5	+4
FG SG10, contacted with simulant E1	-5.8	+4
FG, contacted with simulant S3	-5.3	+4
Iron powder contacted with simulant E1	-5.2	+4

Table 5. Tc K-edge EXAFS fitting results for technetium species sorbed onto iron sorbents after being in contact with pertechnetate in simulant for 18 hours.

Sample	Tc on FG	Tc on FG SG10	Tc on Iron Powder	Tc on FG	TcO ₄ ⁻	TcO ₂ •2H ₂ O ^a
Simulant	E1	E1	E1	S3		
First Shell ^a	6 O	6 O	6 O	6 O	4 O	6 O
R (Å), 6 Tc-O	2.019(2)	2.020(2)	2.008(3)	2.028(3)	1.719(1)	2.005(3)
σ^2 (Å ²), 6 Tc-O	0.0040(1)	0.0053(2)	0.0052(2)	0.0057(3)	0.0019(1)	0.0048(5)
Second Shell ^a	1 Fe	1 Fe	2 Fe	2 Fe		2 Tc
R (Å)	2.66(1)	2.679(7)	3.114(8)	3.137(5)		2.570(2)
σ^2 (Å ²)	0.010(1)	0.0086(7)	0.0087(9)	0.004(1)		0.0059(5)
Third Shell ^a	2 Fe	2 Fe	1 Tc			
R (Å)	3.251(4)	3.259(6)	3.69(1)			
σ^2 (Å ²)	0.0033(3)	0.0078(5)	0.0047(7)			
R (Å), MS ^b	4.02(2)	4.04(2)	4.06(3)	4.07(2)		4.05(2)
σ^2 (Å ²), MS ^b	0.012(4)	0.012(3)	0.001	0.005(4)		0.006(6)
ΔE_0 (eV)	-8.7(6)	-8.6(4)	-6.4(5)	-5.8(4)	-5.7(5)	-9.9
Final pH	8.2	8.0	5.1	>14		
Surface Area	0.73	0.20	0.01	0.73		
Iron Sorbent (m ²)						
Area Covered by Tc(IV) (m ²) ^b	0.14	0.14	0.04	not measured		

a) Data from ref. 18

b) The number and identity of the neighboring atoms.

c) MS is the Tc-O-Tc-O multiples scattering path for *trans* O atoms in the first shell.

d) Assuming TcO₆ octahedra are edge bound to the surface covering 27 Å². Maximum coverage if all technetium in experiment is adsorbed is 0.15 m².

Table 6. Results from fitting the Fe K-edge XANES of Ferragels using the spectra of iron reference materials.

Sample	% Fe Metal	% Magnetite	% Goethite	% Hematite
Raw FG	41	3	1	54
FG w/TcO ₄ ⁻ , pH 8	13	23	24	41
FG w/TcO ₄ ⁻ , pH 14	1	57	16	27

Table 7. Percentage of pertechnetate removed from caustic supernatant simulants (S1, S2, and E1) and sorbent-based pertechnetate distribution coefficient (K_d) values determined from batch contact experiments with various sorbent materials. K_d values are based on total mass of sorbent.

Sorbent	Simulant	$[\text{TcO}_4^-]_0$ (mM)	Phase ratio (L/kg)	% TcO_4^- removed during contact	K_d (L/kg)
FG RTDS-6	S2	0.51	420 300	49±6 53±6	390±140 350±150
FG RTDS-6	S1	9.1	640 640	23±4 18±4	180±50 130±40
FG RTDS-6	S1	9.7	80 80	57±3 46±3	100±30 66±16
FG RTDS-6	S1	12	130 150	42±4 31±4	92±12 68±10
RTDS-6	S1	9.7	160 150	<4 <4	3±2 <4
$\text{Fe}(\text{OH})_3$	S1	9.1	630 580	<3 <3	<32 <27
FG SnO_2	S1	9.1	640 640	<9 <6	<63 <41
FG ZrO_2	S1	12	150 160	11±4 8.1±4.8	19±7 14±7
FG ZnO_2	S1	12	150 150	<5 <5	<13 <11
FG	E1	0.08	303	>95	7100±900
FG SG10	E1	0.08	303	>95	8100±1000
Iron Powder	E1	0.08	200	30±9	87±27
Silica Gel	E1	0.08	303	<10	<29

Table 8. Estimated iron-based pertechnetate distribution coefficient (K_d') values determined from batch contact experiments with various sorbent materials in simulants S1 and S2. K_d values are based on the mass of iron in the sorbent only.

Sorbent	Simulant	$[\text{TcO}_4^-]_0$ (mM)	Average Phase ratio (L/kg sorbent)	Average K_d (L/kg sorbent)	Average K_d' (L/kg Fe^0)
FG RTDS-6	S2	0.51	360	370±140	4600±1700
FG RTDS-6	S1	9.1	640	160±40	2000±500
FG RTDS-6	S1	9.7	80	83±21	1100±300
$\text{Fe}(\text{OH})_3$	S1	9.1	610	<30	<16
RTDS-6	S1	9.7	160	<4	na
FG RTDS-6	S1	12	140	80±11	1000±100
FG ZrO_2	S1	12	160	16±7	820±360

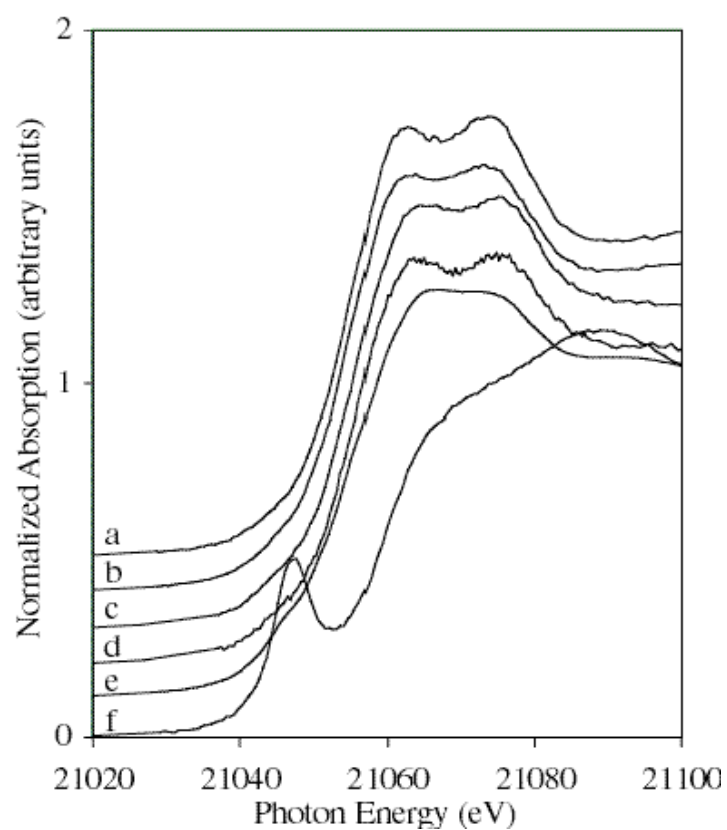


Figure 1. Tc K-shell absorption edges of a) Tc on FG, b) Tc on FG SG10, c) Tc on iron filings, d) Tc on FG, pH 14, e) $\text{TcO}_2 \cdot x\text{H}_2\text{O}$, f) TcO_4^- on Reillex-HPQth resin. For samples a-c, TcO_4^- was in DI water, for sample d, TcO_4^- was in simulant S3.

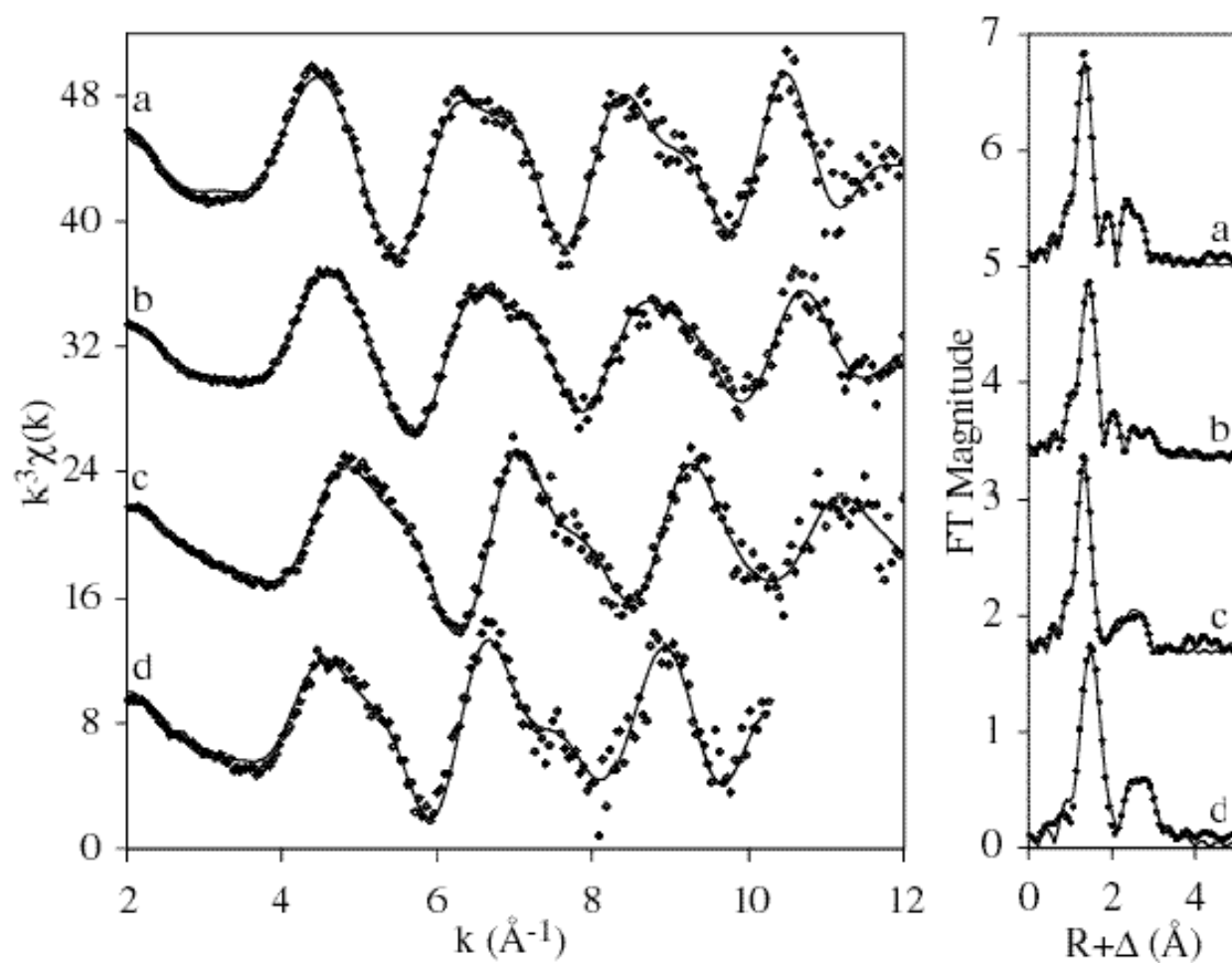


Figure 2. EXAFS spectra (left) and Fourier Transforms (right) for Tc sorbed onto a) FG, b) FG SG10, c) iron powder, and d) FG, pH 14. For a-c, TcO_4^- in simulant E1 was used; for d, TcO_4^- in simulant S3 was used.

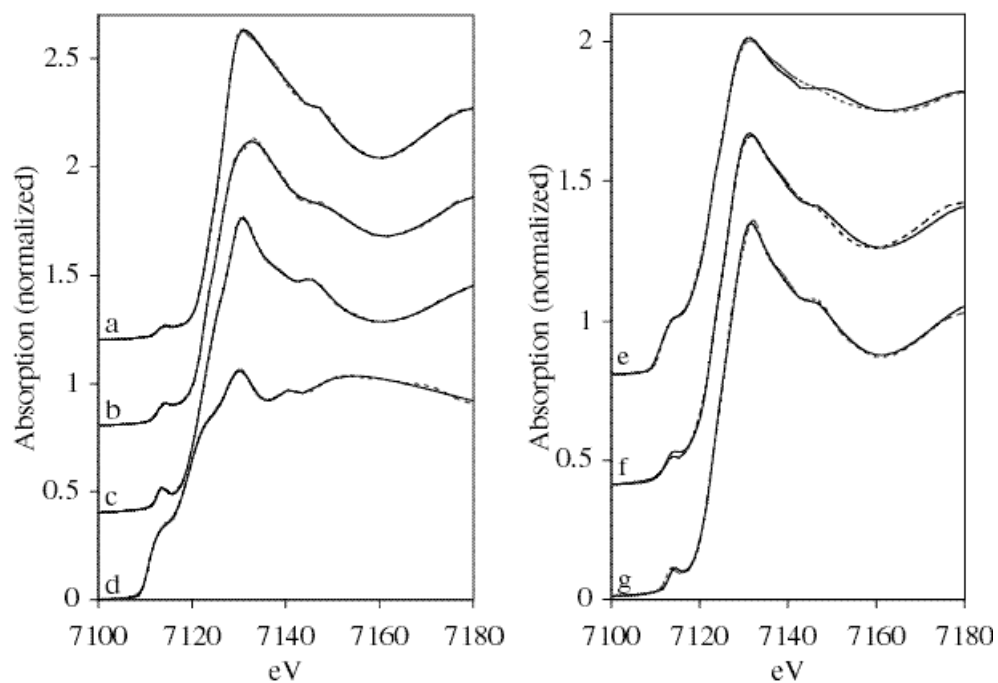


Figure 3. Fe K edge XANES spectra of (a) Goethite, (b) Hematite, (c) Magnetite, (d) Iron metal, (e) FG, as made, (f) FG after exposure to TcO_4^- at pH 8, (g) FG after exposure to TcO_4^- at pH 14. Data are represented by dashed lines, least squares fits are given by solid lines.

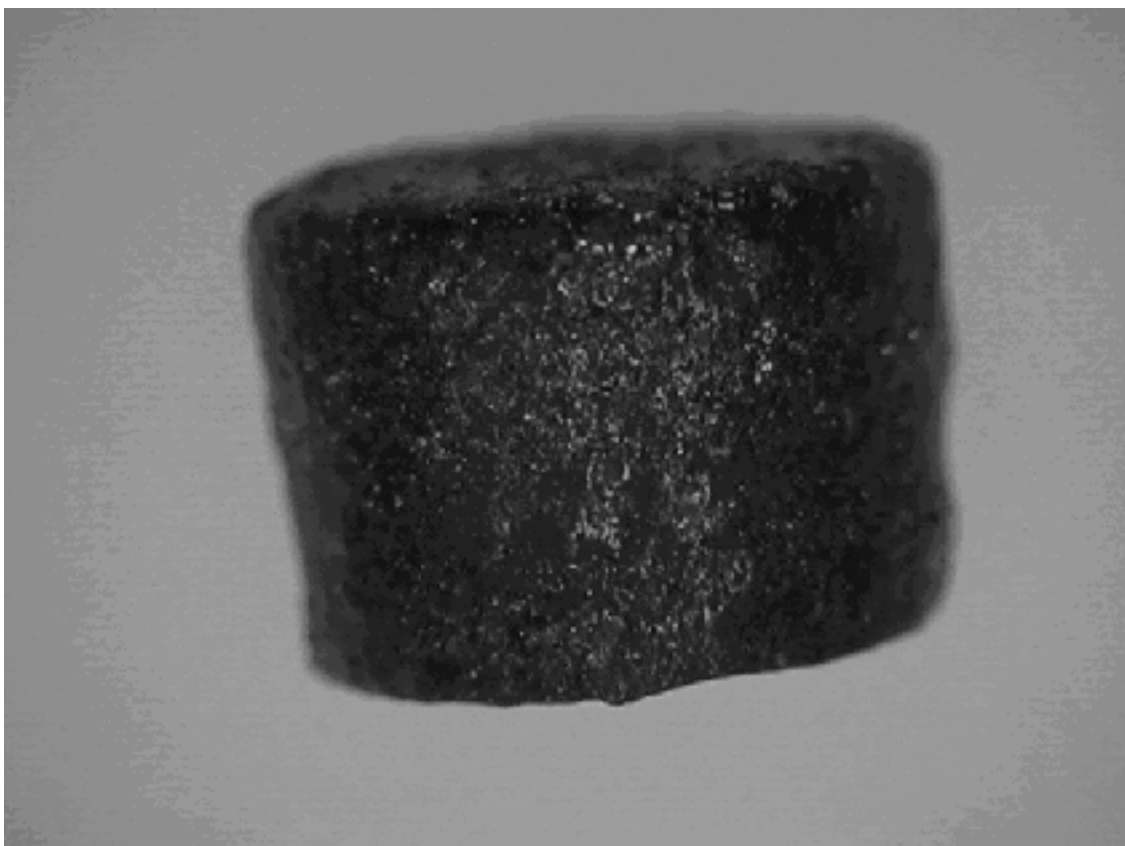


Figure 4. Photograph of a mechanically stable and readily handle able pellet formed by mixing 20 mass % washed, dried, and ground rhenium-loaded FG RTDS-10 Ferragel sorbent material with 80 mass % NBS glass frit and heat-treated as a loose powder for four hours in a cylindrical alumina crucible at 700°C. After the heat-treated material was allowed to cool to room temperature, it was easily removed from the crucible as a single monolithic pellet.

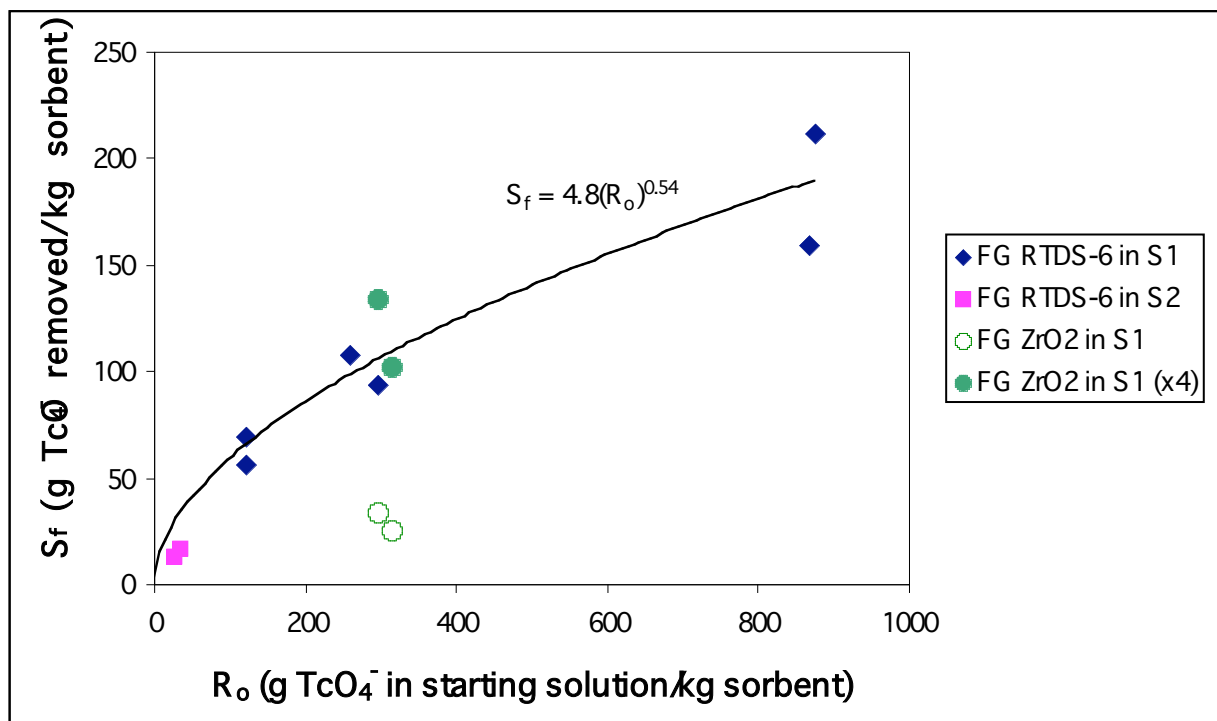


Figure 5. Plot of mass of pertechnetate (g) removed per kg of Ferragel sorbent (kg), S_f , in relation to the mass of starting pertechnetate in solution (g) per mass of Ferragel sorbent (kg), R_o , after 24 hours of contact time for Ferragels FG RTDS-6 and FG ZrO₂ in simulants S1 and S2. The curve indicated in the Figure is the best fit to the data obtained from FG RTDS-6 in stimulant S1 only. Note that by taking the data obtained from FG ZrO₂ in stimulant S1 (open circles) and normalizing them to the same amount of Fe⁰ present in the Ferragel as that in FG RTDS-6 by multiplying the FG ZrO₂ data by four, the normalized FG ZrO₂ data (filled circles) lies close to the curve for the FG RTDS-6 data.