

Removal of Pertechnetate from Simulated Nuclear Waste Streams Using Supported Zerovalent Iron

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The application of nanoparticles of predominantly zerovalent iron (nanosiron), 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 research discussed here was 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, nanocrystalline zirconia was used as a support for nanosiron 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 h of contact time, the high surface area zirconia supported nanosiron 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 h of contact time, the silica-supported nanosiron 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, nanosiron reduced the Tc(VII) to Tc(IV), or possibly to 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-supported nanosiron 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 h sintered into an easily handled glass composite waste form.

Introduction

During the approximately 30 years since the world's first full-scale nuclear reactors and processing plants needed for the production and isolation of plutonium-239 began operating at the Hanford Site River in southeastern Washington, a vast amount of solid and liquid radioactive waste has been generated. One reference¹ indicates that these wastes consist of approximately 208 000 m^3 of mixed waste in 177 underground storage tanks. Current emphasis at U.S. Depart-

ment 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, that is, sludge containing insoluble high-activity waste (HAW) species as well as nonradioactive 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 $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$, would be further separated using previously demonstrated methods and would be added to the HAW portion, leaving an aqueous solution containing both low-activity waste (LAW) species and a host of other nonradioactive species such as Na^+ , K^+ , $\text{Al}(\text{OH})_4^-$, Cl^- , F^- , NO_3^- , NO_2^- , OH^- , CO_3^{2-} , and organics.² The LAW and HAW fractions resulting from these pretreatment steps would then be separately mixed with glass precursor additives or glass

(2) Westinghouse Hanford Co. Report WHC-SD-WM-RD-044; p A3.

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(1) Stewart, T. L.; Frey, J. A.; Geiser, D. W.; Manke, K. L. In *Science and Technology for Disposal of Radioactive Tank Wastes*; Schulz, W.W., Lombardo, N. J., Eds.; Plenum Press: New York, 1998; p 3.

frit and then would be vitrified for long-term storage. However, one potentially troublesome radionuclide remaining in the LAW after pretreatment is technetium-99 (^{99}Tc), a considerable fraction of which occurs as pertechnetate, TcO_4^- .

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. On the basis of this, one plan to address the technetium problem is to remove pertechnetate from the waste using commercially available polymeric ion-exchange resins, to elute the pertechnetate off the resins, to concentrate the eluate, and then to add the eluate to the HAW fraction.

However, there are some inherent difficulties to this approach to dealing with the potential pertechnetate problem. First, at the time this manuscript was prepared, it was still unclear as to whether or not technetium would need to be removed prior to LAW vitrification. Second, if removing pertechnetate from LAW is required, several operations will be needed for the approach: 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. Last, on the basis of plans described above, the ultimate fate of the pertechnetate would be vitrification, either as part of the LAW or as separated pertechnetate that would be vitrified along with the rest of the HAW melter feed, 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 because of volatilization of Tc(VII) compounds under even modest thermal processing conditions³ 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 cleanup 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 nanoscale zerovalent iron (nanoscale iron) supported on high surface area substrates^{4,5} are viable candidates for the proposed technetium removal scheme. Such materials have previously been referred to as "Ferragels".^{4,5} Additionally, unsupported nanoscale zerovalent iron alone may also exhibit some degree of usefulness.

The support material used in making supported nanoscale iron provides, in principle, a medium on which the individual,

nanoscale, zerovalent 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 then is similar to that for use in many other heterogeneous catalytic applications involving, for example, supported PGMs (platinum group metals) and other metals. Thus, the high surface area materials often used in such heterogeneous catalyst applications—alumina (i.e., various aluminum hydroxides, oxyhydroxides, and oxides), silica (including silica gels), and zirconia (i.e., zirconium oxyhydroxides and oxides)—may also prove useful for supporting nanoscale iron for the application investigated here. While high surface area alumina, silica, or zirconia may work well as supports for nanoscale iron in near-neutral pH solutions, at very high pH, typical of what might be 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 nanoscale iron that needs to be considered, but is often not well delineated, is their contribution to the overall chemistry involved with depositing metal onto their surfaces: for the same support material, for example, zirconia, with the same surface areas, how well the metal can ultimately be dispersed onto the support often depends on how the material was made.

Supported nanoscale iron, typical of what we will be discussing here, is a powerful reductant for aqueous metal ions.^{4,5} These materials contain particles of iron, 10–30 nm in diameter, immobilized on a support material by reduction of an aqueous iron salt, for example. Typically, supported nanoscale iron made by the borohydride reduction method contains about 20–25% iron by weight, approximately 40–85% of which is in the zerovalent state, and the balance is oxidized to di- or trivalent iron oxides/oxyhydroxides (ref 6 and this work). These materials are relatively stable in air once dried but are highly active reductants when wet. They can be made with a wide variety of support materials, including zirconia and silica. When nanoscale iron encounters aqueous Tc(VII) species, the technetium is reduced to immobilized Tc(IV) species, most likely TcO_2 , and the iron is oxidized to Fe(III) species such as FeOOH (see below).

We report here the use of supported nanoscale iron in removing pertechnetate from caustic aqueous waste streams and then stabilizing the loaded composite material into a separate waste form. Materials consisting of nanoscale zerovalent iron on base-stable supports, especially zirconia-based supports, were tested and shown to be effective for the removal and reduction of TcO_4^- from simplified tank-waste simulants. In addition to testing base-stable-supported nanoscale iron, an iron-on-silica gel material 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 nanoscale iron was effective in removing and reducing TcO_4^- from these near-neutral solutions. Unsupported nanoscale iron was also tested and was

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found to efficiently remove pertechnetate from both simplified tank waste and near-neutral eluate simulants.

One important aspect of separating Tc species by reduction to an insoluble form is the potential to avoid the relatively high-temperature vitrification process, in which volatilization of Tc(VII) species can be expected to be a serious problem. The use of completely inorganic supports for nanoiron may allow the conversion of the loaded material into a stable waste form through an encapsulation process, for example, by mixing the loaded material with glass powder and then by sintering the composite using a relatively low-temperature process [see, e.g., ref 7]. At the time this work was conducted, such a low-temperature sintering process and a glass formulation had already been developed and demonstrated as one technology option 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 was also ideal for encapsulating the loaded nanoiron material and thus was implemented in this work.

One final aspect of nanoiron that was not explored here is its 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 nanoiron, either supported or not, to a Tc(VII)-containing waste stream would act to reduce the Tc(VII) to Tc(IV) and would provide for less technetium volatilization during vitrification. This concept would be a useful one to explore in the future.

Experimental Procedures

Preparation of Nanoiron Sorbent Materials. The composite sorbent materials studied in this work are ideally zerovalent iron nanoparticles 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 because of 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 zerovalent iron nanoparticles to the support materials was conducted at The Pennsylvania State University as described previously.⁴⁻⁶ Unsupported Fe⁰ nanoparticles were prepared in a similar manner by simply leaving out the support material. Table 1 summarizes the characteristics of the nanoiron sorbent materials investigated.

Typical nanoiron 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 zerovalent iron is certainly expected, yet the portion of unreacted Fe⁰ still provides for sufficient reactivity toward TcO₄⁻, as is demonstrated from the results presented here.

Table 1. Summary of Unsupported Nanoiron and Supported Nanoiron Sorbent Materials, Previously Referred to as Ferragels (FG), Studied in This Work

sorbent	description	target mg Fe ⁰ /g sorbent
nanoiron	unsupported Fe nanoparticles	1000
FG SnO ₂	Fe on commercial tin oxide	20
FG ZnO ₂	Fe on commercial zinc oxide	20
FG ZrO ₂	Fe on commercial zirconia	20
FG SG10	Fe on commercial silica gel	280
FG RTDS-10	Fe on RTDS monoclinic zirconia	80
FG RTDS-6	Fe on RTDS cubic zirconia	80
RTDS-6	RTDS cubic zirconia (no Fe)	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 ^b
density (g/cm ³)	1.42	1.31	1.19	nm

^a Total organic carbon (TOC) from EDTA. ^b nm, not measured.

Control Materials. In addition to the nanoiron 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 zerovalent iron applied to it. The other sample was a ferrihydrite, FeOOH, prepared using the method of Schwartman and Cornell.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.

Simulants. In previous Hanford tank waste-processing work performed at PNNL (see, e.g., ref 9), a double shell slurry feed (DSSF) 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 test nanoiron 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).

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(9) Darab, J. G.; Meiers, E. M.; Smith, P. A. *Mater. Res. Soc. Proc.* **1999**, 556, 215–222.

(7) Vienna, J. D.; Luey, L.; Hrma, P.; Li, H.; Smith, D. E.; Scheele, R. D.; Wigent, H. L.; Crum, J. V. *Ceram. Trans.* **1999**, 93, 399–408.

Table 3. (a) Pertechnetate Concentrations in Waste Simulant Solutions (Simulants S1 and S2) before and after 24 h of Contact with the More Relevant Sorbent Materials.^a (b) Pertechnetate Concentrations in Waste Simulant Solutions (Simulant S3) before and after 18 h of Contact with the More Relevant Sorbent Materials^b

(a) Simulants S1 and S2							
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	
(b) Simulant S3							
sorbent	mass sorbent (g)	simulant volume (mL)	phase ratio (L/kg)	[TcO ₄ ⁻] ₀ (μM)	[TcO ₄ ⁻] _f (μM)	K _d (L/kg)	
nanoiron	0.033	10	303	90 ± 5	3.3 ± 0.5	8100 ± 1000	
FG SG-10	0.033	10	303	90 ± 5	3.7 ± 0.6	7100 ± 900	
iron powder	0.050	10	200	90 ± 5	63 ± 2	87 ± 27	
silica	0.033	10	303	90 ± 5	89 ± 2	5 ± 24	

^a Concentrations were determined using liquid scintillation counting and Bremsstrahlung secondary photon emission. ^b Concentrations were determined using UV-vis spectroscopy.

The use of a full caustic DSSF simulant was planned, and arrangements had been made to test nanoiron 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 nanoiron sorbents in more complex simulants and actual LAW was no longer meaningful from an end-user (i.e., Hanford Site contractors) perspective, 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 nanoiron 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)₂·4H₂O, Pb(NO₃)₂, MnSO₄·xH₂O, MgSO₄, Zn(SO₄)₂·7H₂O, CuSO₄·5H₂O, Na₂MoO₄·2H₂O, NaNO₃, and CrO₃ and sufficient deionized 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 0.51 mM to 12 mM. An aliquot of simulant S1 was also spiked with 17 mM NH₄ReO₄ for use in initial loaded nanoiron encapsulation experiments (see below). Simulants S3 and E1 were left unspiked 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 30 mg and 60 mg of the material was weighed and placed in a 50 mL conical bottom polypropylene centrifuge tube of known mass, and the final mass of the centrifuge tube and sorbent material was 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 TcO₄⁻) 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 on the basis of 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 nanoiron composite sorbent materials.

All centrifuge tubes were placed on an Orbit Shaker at ≈100 rpm. After 24 h, each tube was weighed and then was centrifuged (Damon IEC HN-SII Centrifuge) at 1500 rpm (approximately 2600g) for 10 min. Using individual plastic 5 mL syringes, a portion of each sample was removed, and approximately four drops were filtered through a 0.2 μm filter (Millipore Co.) into a preweighed glass scintillation vial and were weighed again to determine the aliquot mass. To each tube was added ~20 mL of Optifluor Liquid Scintillation Cocktail (Packard Co.) after which each tube was hand shaken for approximately 10 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 ⁹⁹Tc of 0.017 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 nanoiron

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 pipet. The samples were shaken vigorously. To each tube was added 20 μ L of 0.045M Na⁹⁹TcO₄ stock solution. Each sample was inverted several times and then was placed on an orbital shaker for 18 h at 150 rpm. Each sample was allowed to stand for 18 h to settle. For the 15 mL plastic centrifuge cones used here, the settling depth was approximately 4 cm. The precipitate was then removed by pipet and was placed in a 2 mL centrifuge cone. The cones were centrifuged and the supernatant was removed using a pipet. The efficacy of the nanoiron sorbents in removing pertechnetate from these particular simulants was estimated by obtaining UV-vis spectra on the final supernatant solutions and by comparing to the starting simulants. The remaining precipitate was used in the preparation of samples for X-ray absorption spectroscopy (XAS) (see below).

XAS Characterization of Technetium Sorbed to Nanoiron Sorbents. One benefit to using nanoiron sorbents to remove pertechnetate from waste streams is its potential to render the sorbed technetium species in a reduced state, which will aid in later stabilization efforts. To evaluate the reduction, technetium sorbed onto various nanoiron materials was characterized using XAS, which includes both the near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). Technetium was sorbed onto nanoiron sorbent materials in experiments conducted at LBNL. Samples for XAS were then prepared at LBNL and were 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 by placing the mixture in the sealed-off tip of a plastic pipet, 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. The beam was monochromatized 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 TcO₂ reference as well as pertechnetate sorbed onto the commercial organic ion-exchange resin Reillex-HPQ was also measured. Between two and five scans were taken for each sample, depending on the signal-to-background ratio, and then were averaged together. Data was treated by the usual method¹² 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 Nanoiron Sorbents. As indicated above, another benefit to using inorganic composite nanoiron sorbents to remove pertechnetate from waste streams is

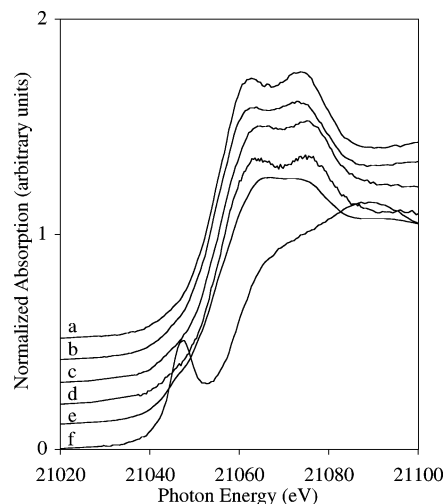


Figure 1. Tc K edge XANES spectra of (a) Tc on nanoiron, (b) Tc on FG SG10, (c) Tc on iron powder, (d) Tc on nanoiron, pH 14, (e) TcO₂·xH₂O, (f) TcO₄⁻ on Reillex-HPQ^h resin. For samples a–c and f, TcO₄⁻ was in DI water, for sample d, TcO₄⁻ was in simulant S3.

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 h and then was treated (see below) to yield a rhenium-loaded nanoiron feed stock for a model encapsulation process. The rhenium-loaded nanoiron feed stock was then mixed with glass frit, referred to as NBS frit,⁷ and was heat-treated to temperatures at or below 800 °C (see below). The composition of the NBS frit was as follows: 60 mass % SiO₂, 10 mass % B₂O₃, 15 mass % Na₂O, 5 mass % Li₂O, 5 mass % Al₂O₃, and 5 mass % ZrO₂.⁷

This encapsulation work was intended to be a significant portion of the overall project. It was planned to use perrhenate as a surrogate for pertechnetate in the initial work. This was to be done to ascertain any process-related problems before actually using radioactive pertechnetate-containing simulants. Because of the changes in project priorities during the course of this EMSP work, as previously discussed, only encapsulation work involving perrhenate was undertaken for proof of concept purposes. Presented here are the experimental details, and later the results as such, that demonstrate the completed processes for removing and stabilizing pertechnetate from waste streams as we originally envisioned them.

A 0.50 g portion of the FG RTDS-10 sorbent material was added to a 50 mL conical bottom polypropylene centrifuge tube. To this, 40.0 mL of perrhenate-spiked simulant S1 was added. The centrifuge tube was closed, was shaken by hand, and then was placed in a near-vertical position in a beaker. After 24 h, the tube was centrifuged at ~2600g for 10 min and then was washed with deionized water and was recentrifuged (~2600g for 10 min) 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 and then was ground into a fine powder using an agate mortar and pestle and was mixed with NBS frit at a loading of 20 mass % supported nanoiron 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 4 h, the crucible was removed from the furnace and was allowed to cool to room temperature.

Results

Batch Contact Results. Table 3a and 3b summarizes the pertechnetate concentrations in solution before and after batch

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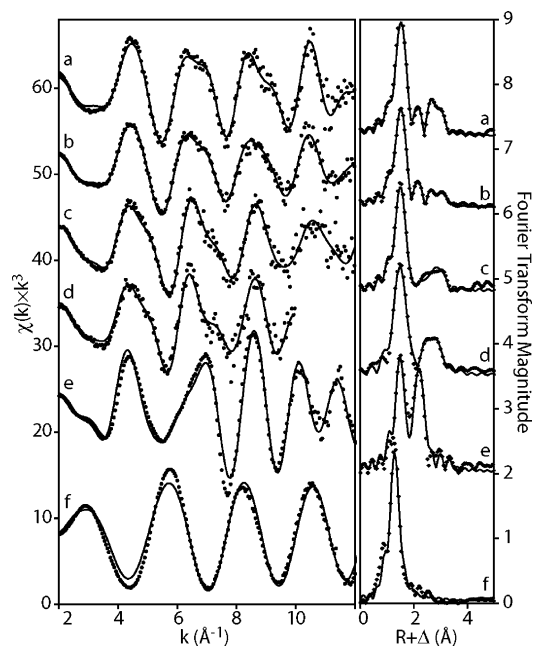


Figure 2. (a–d) EXAFS spectra (left) and Fourier transforms (right) of Tc sorbed onto (a) unsupported nanoiron, (b) FG SG10, (c) iron powder, and (d) unsupported nanoiron, pH 14. For a–c, TcO_4^- in simulant E1 was used; for d, TcO_4^- in simulant S3 was used. (e) and (f) Reference EXAFS spectra (left) and Fourier transforms (right) of e $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ and f TcO_4^- . Data are indicated by dots and the least-squares fits by lines.

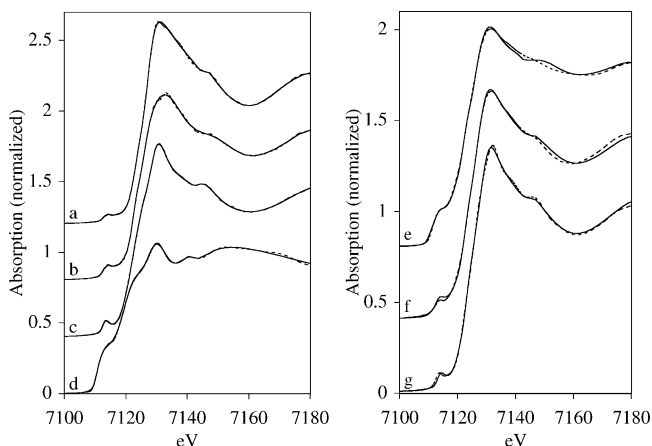


Figure 3. Fe K edge XANES spectra of (a) goethite, (b) hematite, (c) magnetite, (d) iron metal, (e) nanoiron, as made, (f) nanoiron after exposure to TcO_4^- at pH 8, and (g) nanoiron after exposure to TcO_4^- at pH 14. Data are represented by dashed lines, and least-squares fits are given by solid lines.

contact with the more relevant nanoiron sorbent materials. The sorbent mass and simulant volume used are also included for each entry.

XAS 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 obtained from the XANES data. Table 5 summarizes the Tc EXAFS results from technetium species sorbed onto different nanoiron materials under different conditions. The corresponding measured and fitted data obtained from this system are shown in Figure 2. In all cases, technetium exists as Tc(IV) surrounded by six oxygen neighbors forming an octahedral coordination environment. With the exception of Tc sorbed on iron powder, scattering from other nearby metal atoms is

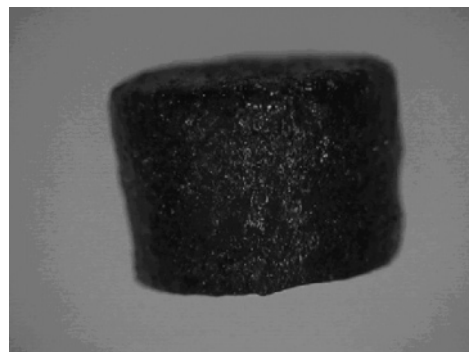


Figure 4. Photograph of a mechanically stable and readily handleable pellet formed by mixing 20 mass % washed, dried, and ground rhenium-loaded FG RTDS-10 nanoiron sorbent material with 80 mass % NBS glass frit and heat-treated as a loose powder for 4 h in a cylindrical alumina crucible at 700 °C. After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

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
nanoiron, contacted with simulant E1	−5.5	+4
FG SG10, contacted with simulant E1	−5.8	+4
iron powder contacted with simulant E1	−5.2	+4
nanoiron, contacted with simulant S3	−5.3	+4
$\text{TcO}_2 \cdot x\text{H}_2\text{O}$ (s) reference	−5.3	+4
Reillex, contacted with simulant E1	+0.4	+7
TcO_4^- (aq), reference	0.0	+7

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 nanoiron samples 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 nanoiron spectra using the reference materials. The resulting contributions of the different iron species are given in Table 6.

Encapsulation of Rhenium-Loaded Nanoiron Sorbents.

As stated above, washed, dried, and ground rhenium-loaded FG RTDS-10 nanoiron sorbent material was mixed with NBS frit⁷ at a loading of 20 mass % supported nanoiron feed to 80 mass % NBS frit. This mixture was then heat-treated as a loose powder for 4 h 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 easy to handle.

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 the batch contact measurements has been calculated and is

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 h. EXAFS Fitting Results for TcO₄⁻ and TcO₂·2H₂O References Are Also Included

parameter	Tc on nanoiron	Tc on FG SG10	Tc on iron powder	Tc on nanoiron	TcO ₄ ⁻	TcO ₂ ·2H ₂ O ^a
simulant	E1	E1	E1	S3	na ^e	na
final pH	8.2	8.0	5.1	>14	na	na
EXAFS Fitting Results:						
first shell ^b	6 O	6 O	6 O	6 O	4 O	6 O
<i>R</i> (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 ^b	1-Fe	1-Fe	2-Fe	2-Fe		2-Tc
<i>R</i> (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 ^b	2-Fe	2-Fe	1-Tc			
<i>R</i> (Å)	3.251 (4)	3.259 (6)	3.69 (1)			
σ^2 (Å ²)	0.0033 (3)	0.0078 (5)	0.0047 (7)			
<i>R</i> (Å), MS ^c	4.02 (2)	4.04 (2)	4.06 (3)	4.07 (2)		4.05 (2)
σ^2 (Å ²), MS ^c	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
surface area of sorbent (m ²)	0.73	0.20		0.73	na	na
area covered by sorbed Tc(IV) (m ²) ^d	0.14	0.14	0.04	not measured	na	na

^a Data from ref 18. ^b The number and identity of the neighboring atoms. ^c MS is the Tc–O–Tc–O multiple 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. ^e na, not applicable.

Table 6. Results from Fitting the Fe K Edge XANES of Nanoiron Using the Spectra of Iron Reference Materials

sample	% Fe metal	% magnetite	% goethite	% hematite
raw nanoiron	41	3	1	54
nanoiron w/TcO ₄ ⁻ , pH 8	13	23	24	41
nanoiron w/TcO ₄ ⁻ , pH 14	1	57	16	27

indicated in Table 7. With the exception of the RTDS-6 alone without zerovalent iron, all the entries in Table 7 indicate that RTDS-6 supported zerovalent iron sorbent materials remove significant concentrations of pertechnetate from the caustic supernatant simulants.

On the basis of the UV–vis absorption data collected before and after contacting FG SG10 or unsupported nanoiron 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 zerovalent iron removes very little pertechnetate (see Table 7). This demonstrates that nanoiron, 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 interpreting the results obtained from batch contact measurements is through the distribution 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 material containing the nanoiron (supported or not) with respect to the concentration of technetium species remaining in the simulant solutions after contact.

The partition ratio (k) is defined as the ratio of the total number of moles of solute in the solid phase (n_{solid}) to that in the liquid phase ($n_{\text{H}_2\text{O}}$) at equilibrium:

$$k = \frac{n_{\text{solid}}}{n_{\text{H}_2\text{O}}} \quad (1)$$

Table 7. Percentage of Pertechnetate Removed from Supernatant Simulants (S1, S2, and E1) and Sorbent-Based Pertechnetate Distribution Coefficient (K_d) Values Determined from Batch Contact Experiments with Various Sorbent Materials^a

sorbent	simulant	[TcO ₄ ⁻] ₀ (mM)	phase ratio (L/kg)	% TcO ₄ ⁻ removed during contact	K_d (L/kg) ^a
FG RTDS-6	S2	0.51	420	49 ± 6	390 ± 140
			300	53 ± 6	350 ± 150
FG RTDS-6	S1	9.1	640	23 ± 4	180 ± 50
			640	18 ± 4	130 ± 40
FG RTDS-6	S1	9.7	80	57 ± 3	100 ± 30
			80	46 ± 3	66 ± 16
FG RTDS-6	S1	12	130	42 ± 4	92 ± 12
			150	31 ± 4	68 ± 10
RTDS-6	S1	9.7	160	<4	3 ± 2
			150	<4	<4
Fe(OH) ₃	S1	9.1	630	<3	<32
			580	<3	<27
FG SnO ₂	S1	9.1	640	<9	<63
			640	<6	<41
FG ZrO ₂	S1	12	150	11 ± 4	19 ± 7
			160	8.1 ± 4.8	14 ± 7
FG ZnO ₂	S1	12	150	<5	<13
			150	<5	<11
nanoiron	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

^a K_d values are based on total mass of sorbent.

In this paper, we report results using a mass- and volume-normalized distribution coefficient K_d , which is related to the partition ratio by

$$K_d = k \frac{V_{\text{H}_2\text{O}}}{M_{\text{solid}}} = \frac{n_{\text{solid}}}{C_{\text{H}_2\text{O}} M_{\text{solid}}} \quad (2)$$

where $V_{\text{H}_2\text{O}}$ and M_{solid} are, respectively, the volume of the solution and the mass of the solid sorbent phase.¹⁵ Here, $C_{\text{H}_2\text{O}}$ is the analytical concentration, that is, the sum of the

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Table 8. Estimated Iron-Based Pertechnetate Distribution Coefficient ($\pm K_d'$) Values Determined from Batch Contact Experiments with Various Sorbent Materials in Simulants S1 and S2^a

sorbent	simulant	[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
Fe(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

^a K_d values are based on the mass of iron in the sorbent only.

concentrations of all species containing the element or compound of interest (in this case is Tc) in aqueous phase at equilibrium

Furthermore, n_{solid} can be represented by the following expression:

$$n_{\text{solid}} = n_0 - n_{\text{H}_2\text{O}} = (C_0 - C_{\text{H}_2\text{O}})V_{\text{H}_2\text{O}} \quad (3)$$

where C_0 and n_0 are the concentration and total number of moles, respectively, of solute in the initial solution prior to being contacted with the sorbent. Upon substituting eq 3 into eq 2, one obtains the following:

$$K_d = \frac{(C_0 - C_{\text{H}_2\text{O}})V_{\text{H}_2\text{O}}}{C_{\text{H}_2\text{O}}M_{\text{solid}}} \quad (4)$$

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. Thus, we represent K_d in the following form:

$$K_d = \frac{(C_0 - C_f)V_{\text{H}_2\text{O}}}{C_fM_{\text{solid}}} \quad (5)$$

where we have replaced $C_{\text{H}_2\text{O}}$, the equilibrium concentration of solute in the liquid phase, with C_f , the final concentration of solute in the liquid phase determined here. Typically, K_d is determined from eq 5 and assumes that the species in solution at "equilibrium", pertechnetate in this case, is the same as that sorbed to the sorbent. This is not the case here, since the most probable form of technetium sorbed to the nanoiron is TcO₂·*x*H₂O, (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.

In this work, batch K_d values (L/kg) were calculated from the experimental data using a simplified form of eq 5:

$$K_d = S_f/C_f \quad (6)$$

where, for ease in communication, we have defined S_f as the following:

$$S_f = \frac{(C_0 - C_f)V_{\text{H}_2\text{O}}}{M_{\text{solid}}} \quad (7)$$

Here, S_f is the concentration (mg/kg) of technetium species sorbed to the nanoiron containing material after contact, C_f

is the concentration (mg/L) of technetium species in the final simulant solution after contact with the material, C_0 is the concentration (mg/L) of technetium species in the starting simulant solution prior to contact with the nanoiron containing material (determined from the blank spike), $V_{\text{H}_2\text{O}}$ is the volume (L) of simulant solution, and M_{solid} is the mass (kg) of material (nanoiron plus support, if used). Table 7 summarizes the batch K_d values determined in this way for various nanoiron 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. These sets of data are not directly comparable because 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 nanoiron 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 Fe⁰ in the sorbents, K_d' (L/kg Fe⁰), 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 Fe⁰ in the sorbents for ease in keeping track of the individual experimental conditions and to avoid confusion.

Consider FG RTDS-6 and FG ZrO₂ in contact with simulant S1 with 12 mM pertechnetate and nearly the same average phase ratios. For these particular experiments, the amount of Fe⁰ is limited with respect to TcO₄⁻ (i.e., the molar ratio of TcO₄⁻:Fe⁰ 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 nanoscale zerovalent iron loaded onto a given support that determines the overall performance of the sorbent material. Support materials that provide greater loadings of zerovalent iron, RTDS-6 zirconia in contrast to lesser grades of zirconia, for

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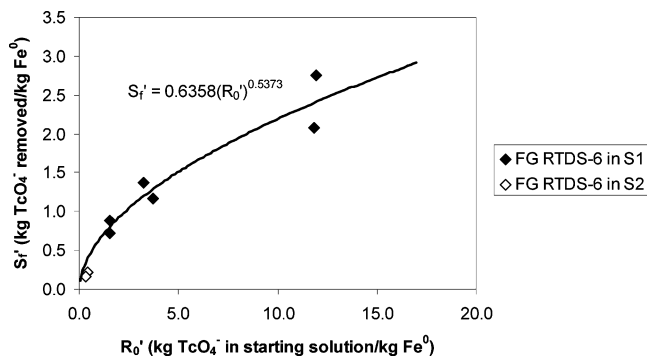


Figure 5. Plot of mass of pertechnetate removed per mass of iron, S_f' , in relation to the mass of starting pertechnetate in solution per mass of iron, R_0' , after 24 h of contact time for samples FG RTDS-6 and FG ZrO_2 in simulants S1 and S2. The curve indicated in the Figure is the best fit to the data obtained from FG RTDS-6 in stimulant S1 only.

example, would thus provide for greater pertechnetate extraction efficiencies. Furthermore, the control samples, RTDS-6 (without zerovalent 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 further normalize the results with respect to the different starting concentrations of pertechnetate in the simulants and different phase ratios, we introduce the additional terms S_f' and R_0' . We define S_f' as the total mass of technetium species sorbed to the sorbent per targeted unit mass of Fe^0 in the sorbent. Likewise, we define R_0' as the total mass of TcO_4^- in the starting solution per targeted unit mass of Fe^0 . Figure 5 shows a plot of S_f' (kg of TcO_4^- removed per kg of iron) versus R_0' (kg of TcO_4^- in the starting solution per kg of iron). The curve indicated in Figure 5, defined by the equation, $S_f' = 0.6358 \cdot (R_0')^{0.5373}$, is the best fit to the data obtained from FG RTDS-6 in simulant S1 only. Figure 5 represents a working “engineering” curve, so to speak, that enables one to calculate the amount of a particular nanoiron material required to remove a known amount of TcO_4^- from a particular medium to a particular level of extraction.

XAS Characterization. To better understand the mechanism of pertechnetate adsorption by nanoiron, both the Fe K edge and Tc K edge XAS spectra were investigated. The Tc K edge EXAFS spectra of the nanoiron 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 distance of 2.0 Å. This distance and the Tc K edge shifts given in Table 5 clearly establish the oxidation state of Tc as $\text{Tc}(\text{IV})$.^{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 $\text{Tc}(\text{IV})$ sorbed to nanoiron and FG SG10 in distilled water reveals similar environments for the sorbed $\text{Tc}(\text{IV})$ 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 Å is too short for a pair of $\text{Tc}(\text{IV})$ 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 $\text{Tc}(\text{IV})$ sorbed to iron powder at pH 5 and to nanoiron in simulant S3 are similar to each other in that the $\text{Tc}(\text{IV})$ center has two Fe neighbors at 3.1 Å. The spectrum of $\text{Tc}(\text{IV})$ 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 nanoiron upon treatment with pertechnetate solution. Prior to reaction with solution containing pertechnetate, nanoiron consists primarily of iron metal and hematite, presumably a core of iron metal with a protective “rind” of insulating $\text{Fe}(\text{III})$ oxides/hydroxides.^{6,8} Upon exposure to pertechnetate in distilled water, the nanoiron is oxidized, primarily to hematite with smaller amounts of goethite and magnetite. At high pH, oxidation of nanoiron produces mainly magnetite, presumably from the reduction of the hematite skin upon exposure to the solution.

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

Bulk or surface precipitation of $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ does not occur 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 $\text{Tc}(\text{IV})$ adsorbed on nanoiron 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

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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 oxides⁸ 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 particles 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 absorption experiments since less than a monolayer of Tc(IV) ions is present. For sorption of Tc(IV) on iron powder, sufficient pertechnetate was present to form ca. 60 monolayers, and about one-third of this amount was found on the surface. These observations suggest that, in these cases, sorption of pertechnetate 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 Nanoiron Sorbents.

A mixture of 20 mass % rhenium-loaded FG RTDS-10 nanoiron sorbent material and 80 mass % NBS frit was capable of being sintered in a readily handleable pellet as indicated in Figure 4. Although pellets may not be a final waste form candidate, these results clearly demonstrate the concept that supported nanoiron can be used to directly treat a waste stream, can be removed from the waste stream, and then can be 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 nanoiron 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 as well as residential water supplies.

Conclusions

Nanoparticles of zerovalent iron, 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 and were evaluated 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, nanocrystalline zirconia was used as a support for nanoiron 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 h of contact time, the high surface area zirconia-supported nanoiron 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 h of contact time, the silica-supported nanoiron 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, nanoiron reduced the Tc(VII) to Tc(IV), or possibly to Tc(V), through a redox reaction resulting in surface adsorption. Finally, it was demonstrated that a mixture of 20 mass % of the solid reaction products obtained from contacting zirconia-supported nanoiron 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 h was sintered into a handleable waste form.

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Appendix A

Researchers at PNNL have developed a continuous, hydrothermal process and technology that is capable of generating a variety of ultrafine, nanocrystalline 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 salts 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 nanocrystalline (less than 30 nm) metal oxide or oxyhydroxide particles in the RTDS process occurs during the relatively short residence time in the heated hydrothermal region (1–30 s) 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 nanoiron under similarly severe environmental conditions.

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