Capture and Immobilization of Technetium from Liquid Radioactive Waste Streams into a Stable Goethite Mineral Form—11351

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ABSTRACT

Technetium-99 (Tc-99), a long-lived fission product, presents a challenge in managing legacy wastes from the production of nuclear materials. In the thermal processes used to convert radioactive tank wastes to a glass waste form, much of the Tc-99 volatilizes in the high temperatures of the glass melters and is collected in off-gas scrubber systems within the vitrification plants. Although the off-gas scrubber solutions containing the Tc-99 are recycled back to the melters, some Tc ultimately leaves the vitrification facilities as a secondary waste stream requiring treatment and immobilization. The off-gas scrubber solutions also capture S, Cl, F, and Cr that, when recycled to the melter, reduce the waste loading in the glass. For the secondary wastes, risk assessments indicate that Tc-99 is a significant contributor to the environmental impact from the disposal of these wastes in low-activity waste disposal facilities. There are, therefore, incentives to reduce the impacts of Tc-99 within the vitrification and waste disposal facilities.

Goethite is a stable iron oxyhydroxide mineral, FeOOH, that is showing the potential to effectively sequester Tc from radioactive waste liquids. Testing to date has shown that Tc-99 can be removed from an aqueous simulant of a caustic off-gas scrubber solution by a process that reduces Tc-99 from Tc(VII) to Tc(IV) and co-precipitates the Tc(IV) with iron to form a goethite-dominant iron oxy-hydroxide material [(Tc,Fe)OOH]. The process involves reducing the pertechnetate, Tc(VII), to Tc(IV) with the reductant Fe(II); the Tc(IV) then co-precipitates with the iron to form the goethite. Goethite appears to be effective in sequestering Tc because the Tc(IV) and Fe(III) are similar in cation size, metal-oxygen bond lengths, and number of coordinating oxygen atoms. In tests with both deionized water and a caustic off-gas scrubber simulant solution containing Tc(VII), between 93 and 99 percent of the Tc was removed from the liquids and captured in the goethite. X-ray diffraction and transmission electron microscopy confirm goethite as the primary product with some magnetite also present. X-ray absorption spectroscopy (XAS) confirmed that the Tc was in the +4 oxidation state and that the bond distances were consistent with substitution of Tc(IV) for Fe(III) in the goethite mineral structure. The final Tc-goethite product was also tested for Tc leachability in various leachants for up to 180 days. Further, XAS showed no reoxidation of Tc(IV) to Tc(VII) in the leaching solutions nor the dried Tc-goethite solid exposed to air, even after 180 days of leaching or air exposure. There was minimal dissolution of the goethite and subsequent release of Tc at the expected conditions (pH=7.2) of pore waters in the Hanford Integrated Disposal Facility.

Testing is currently underway to demonstrate the capture of Tc in goethite from more complex waste solutions. Rhenium is also being evaluated as a surrogate for Tc in the goethite process, leading to a bench-scale demonstration of the preparation of Re- and/or Tc- goethite.

INTRODUCTION

Technetium (Tc) is produced in large quantities as a fission product during the irradiation of ^{235}U-enriched fuel for commercial power production and plutonium genesis for nuclear weapons. The most abundant isotope of Tc present in wastes is Tc-99 because of its high fission yield (~6%) and long half-life (2.13×10^5 years) [1, 2]. During the Cold War era, generating fissile ^{239}Pu for use in America's atomic

weapons arsenal yielded nearly 1900 kg of Tc-99 at the Hanford Site in Washington State, USA [3]. The bulk of the Tc-99 is present in radioactive wastes temporarily stored in underground tanks awaiting retrieval, treatment, immobilization, and permanent disposal. After the wastes are retrieved from the storage tanks, current treatment plans call for separating the waste into a low-volume, high-level waste (HLW) stream and a larger volume, low-activity waste (LAW) stream, both which will be vitrified and disposed of separately. The bulk of the LAW stream will be converted into a borosilicate glass waste form that will be disposed of in the Integrated Disposal Facility (IDF) at the Hanford Site [4]. The HLW will also be vitrified and stored until a deep-geologic repository is available. Even with careful engineering controls, it is expected that a fraction of the Tc-99 will be volatilized during the vitrification of both the HLW and LAW streams. Although this volatilized Tc will be captured in melter off-gas scrubbers and returned to the melter, some of the Tc is expected to become part of the secondary waste stream from the vitrification process. This secondary waste stream will be treated and immobilized in the Effluent Treatment Facility for disposal.

Although a variety of Tc-99 waste forms have been proposed [5-7], data bearing on the permanent disposal of this radioisotope have not yet been adequately presented. There are experimental results, however, which hint at a long-term immobilization strategy for Tc-99. Several investigations into the interaction of pertechnetate with Fe (oxy) hydroxide and sulfide minerals have shown that once Tc(VII) is reduced, the association of Tc(IV) with ferric iron [Fe(III)] solid phases is strong [8-11]. The Fe phase most commonly reported in these studies is goethite [α-FeO(III)OH]. The similarity in inter-atomic distance between Fe(III)—O and Tc(IV)—O (2.06 and 2.01 Å, respectively) [12] suggests that direct substitution of Tc(IV) for Fe(III) in the goethite lattice is possible, provided that a charge-balancing cation is part of a coupled substitution in the goethite structure. Alternatively, trace Tc(IV) may substitute for Fe(III) if a defect-bearing solid is stable. Goethite is also easily synthesized in the laboratory with particle sizes and surface areas that can readily be manipulated [13]. In addition, goethite is resistant to chemical weathering because the hydrogen and oxygen atoms in the goethite structure are resistant to exchange with the environment for up to 50 Myr [14]. Further, iron in goethite is Fe(III) so that in oxidizing environments, which will likely prevail in the disposal setting, there will be minimal chemical potential for oxidation-reduction reactions that would cause a greater mobility of Tc(IV). Therefore, a waste form based on goethite appears to be a simple, durable, cost-efficient, and effective candidate for disposing of Tc from secondary wastes.

The experiments described herein evaluate the immobilization of Tc in goethite with the addition of Fe(II) and attempt to elucidate the association of Tc with Fe in the final Tc-goethite product by various microscopic and spectroscopic analyses.

EXPERIMENTAL SECTION

Synthesis of Goethite

Goethite was synthesized based on a scaled-down procedure of Schwertmann and Cornell [15]. In summary, ferric nitrate [11.4 g of $Fe(NO_3)_3 \cdot 9H_2O$] was dissolved into deionized (DI) water (100 mL) and reacted with 2 M sodium hydroxide (150 mL). The slurry was heated in an oven (80^oC) for 7–10 days. The solid product was filtered from solution by vacuum filtration, washed with fresh DI water two times, and air dried overnight. The air-dried solid was gently crushed to a powder form and used for Tc removal.

Tc(VII) Removal from Solution in the Fe(II)-Goethite System

Between 2.75 and 3.5 g of goethite powder was re-suspended in 250 mL of deaerated DI water in an anoxic chamber with a mixture of N_2 (97%) and H_2 (3%) to minimize oxidation of the ferrous solution before its use in treating the goethite-Tc slurry. The initially measured pH for the goethite-DI water slurry

was 10.4, and it was adjusted to pH ~2.0 by adding nitric acid (2 M HNO_3). A powder of $FeCl_2 \cdot 4H_2O$ (3.48 g) was directly added to the goethite slurry as the Fe(II) source while the suspension was continuously mixed at low pH (~2.0) in the anoxic chamber. After 1 day, 0.25 mL of Tc(VII) from a $NaTcO_4$ solution (2.2×10^{-2} M) was added to the Fe(II)-goethite slurry. During the Tc addition, the headspace of the bottle was purged with N_2 gas to prevent oxygen contact, and the bottle was immediately capped after adding Tc(VII) and taking the subsample for the initial Tc(VII) concentration. After 1–2 days of mixing in a platform shaker, a subsample was collected to determine the residual Tc(VII) concentration in solution using a syringe filter. After subsampling, 2 M sodium hydroxide (NaOH) was added to prepare Tc-goethite samples (Samples 2-2 and 2-3) without an Fe(III) armoring process. Several other batches of the caustic slurry were inoculated with additional ferric nitrate solution to promote more ferric oxide precipitation, some as coatings that would "armor" the initial Tc-goethite product. The final suspensions were placed inside an oven at 80°C for 7 days. The final Tc-goethite solids were separated by filtration, dried in air, and used for additional analysis. A summary of the conditions used to produce different batches of Tc-goethite specimens used in this study is provided in Table I.

Table I. Summary of Tc-Goethite Preparation Methods and Tc Removal Efficiencies.

Test Description and Tc Removal	Samples						
	2	2-1	2-2	2-3	2-3*[a]	2-4	2-5
Additional Fe(III) armoring[a]	Yes	Yes	No	No	No	Yes	Yes
Initial solution[c]	DIW	DIW	DIW	CS-1	CS-2	CS-1	DIW
Initial goethite mass (g)	3.47	2.75	2.75	2.75	2.0	2.75	2.75
pH after 1 day reaction with Fe(II)	2.25	2.06	2.04	2.04	1.98	2.03	3.54
pH after Tc spike	2.01	2.06	2.04	13.0	13.5	13.0	3.03
Initial spiked-Tc mass (μg)	597	551	501	522	5547	546	615
pH after mixing Fe(III) and NaOH	13.0	13.3	13.3[d]	13.0[d]	13.4	13.0[d]	13.3
Final solid mass (g)	6.53	6.05	3.24	3.51	5.10	6.43	6.41
Tc in final solid (μg/g)[e]	85.7	84.4	149.1	143.1	1020	78.9	96.0
Tc uptake in goethite (%)	93.7	92.7	96.5	96.3	93.8	92.9	100.0

[a] Additional Tc-goethite sample, Sample 2-3*, was prepared in a different caustic scrubber simulant (CS-2) with a high Tc concentration, 4.2×10^{-4} M and 0.1 M of Fe(II).
[b] "No" indicates no armoring process was conducted with additional Fe(III) for Samples 2-2 and 2-3.
[c] The initial solution was either DI water (DIW) or synthetic caustic scrubber solution (CS-1 or CS-2).
[d] The pH values were measured after adding NaOH in Samples 2-2.
[e] The concentration of Tc in the final Tc-goethite was determined by acid digestion.

A small aliquot of filtered solution was used to measure the pH and the concentrations of Tc(VII), Fe(II), and total Fe at each subsampling step during the entire experiment. Concentrations of Tc(VII) and total Fe in the supernatants were determined using inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectrometry (ICP-OES), respectively. The dissolved ferrous [Fe(II)] concentration was determined using the ferrozine colorimetric method [16]. The removal of Tc(VII) and Fe(II) from the aqueous phase was determined by comparing the aqueous Tc(VII) and Fe(II) concentration in the collected subsamples with the initial concentrations of Tc(VII) and Fe(II).

The synthesis process was also modified to armor the Tc-goethite solid with additional goethite precipitates using separately prepared $Fe(NO_3)_3 \cdot 9H_2O$ (11.4g/100 mL) and 2 M NaOH (150 mL) solutions

(Table I). These two solutions were added sequentially into the Tc-goethite slurry in a series of additional experiments. After 1–2 days of reaction with added ferric nitrate and sodium hydroxide solutions, the bottle containing the final slurry was placed inside an oven at 80°C for 7 days. The final slurry was subsequently filtered, and both the solution and solid samples were subjected to further analyses. For Sample 2-5, the order in which the ferric nitrate and sodium hydroxide was added was reversed so that NaOH was added before the $Fe(NO_3)_3 \cdot 9H_2O$ was introduced (Table I). The order of adding reagents to generate additional goethite to armor the Tc-goethite solid was reversed to evaluate the efficacy of the armoring process.

Samples 2-2, 2-3, and 2-3* were Tc-goethite solids that had no further Fe(III) armoring performed, whereas Samples 2, 2-1, 2-4, and 2-5 were subjected to the additional Fe(III) armoring. Two samples, 2-3 and 2-4, were prepared with the Tc(VII) present in a caustic scrubber solution (CS-1) [17]. One sample, 2-3*, was prepared with higher total Tc(VII) concentration (4.2×10^{-4} M) and 0.1 M of Fe(II) reductant in a different caustic scrubber simulant [18]. The caustic scrubber simulants (CS-1 and CS-2) were spiked with Tc(VII), and similar sequestration tests were performed for Tc removal using the Fe(II)-goethite system. Simulant compositions are given in Table II. After the caustic scrubber simulants spiked with Tc(VII) were prepared, similar Tc sequestration tests were performed. Because the caustic scrubber waste stream that captures volatilized species from the proposed vitrification process is both highly alkaline and saline, each caustic scrubber solution was designed to be highly alkaline.

Table II. Composition of Hanford Tank Waste Treatment and Immobilization Plant Secondary Waste Simulants (moles/L).

Component	Simulant CS-1 Caustic Scrubber [17]	Simulant CS-2 Caustic Scrubber Median from [18]	Simulant SBS Submerged Bed Scrubber Condensate [18]
Na	1.8	2.0	2.0
Al	NI	1.88E-01	9.88E-03
Cr	NI	4.06E-04	3.46E-03
Ag	NI	1.25E-05	7.2E-05
Cd	NI	3.14E-06	7.24E-05
I	NI	9.14E-06	2.10E-04
Hg	NI	2.26E-05	1.84E-06
Pb	NI	1.80E-05	1.55E-05
NH_4^+	1.84	NI	2.08
CO_3^{2-}	8.10E-01	4.56E-02	3.32E-03
NO_3^-	1.60E-02	6.56E-01	3.44
OH^-	1.92	7.96E-01	6.66E-08
PO_4^{3-}	NI	1.37E-02	7.62E-03
SO_4^{2-}	NI	8.82E-03	1.44E-01
TOC (as acetate)	7.80E-02	NI	NI
TOC (as oxalate)	NI	1.88E-01	9.88E-03
NI = not included; TOC = total organic carbon.			

Solid Phase Characterization

The initial goethite substrate and the final solid product were first characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM)/transmission electron microscopy (TEM) with energy dispersive X-ray (EDX) spectroscopy. X-ray absorption near-edge (XANES) and fine structure (XAFS) spectroscopy were used to characterize the Tc oxidation state in the goethite and to determine the local atomic environment for the Tc within the iron oxide matrix, respectively. The XANEs and XAFS spectra were collected either on beam line X10C at the National Synchrotron Light Source (NSLS) or on beam line 4-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). Acid extraction using 8 M HNO_3 at $90^{o}C$ was used to determine the total Tc(VII) concentration in the final Tc-goethite solid.

Goethite Leach Tests

Batch leaching experiments were conducted in which ground Tc-goethite powder was exposed to 1) pH 4, 7, and 10 buffer solutions; 2) a synthetic pore water simulating that expected at the IDF at Hanford; and 3) a simulated low-activity waste glass leachate that might be observed in the IDF for the LAW glass waste form. The makeup for the pore water and glass leachates is shown in Table III. A goethite solid-to-leachant ratio of 1 g/L was used for each leaching test.

Table III.   Chemicals Used to Prepare the IDF Pore Water and Hanford WTP[a] Glass Leachate Solutions

Chemical	IDF Pore Water, M	Glass Leachate, M
$CaSO_4$	1.2×10^{-2}	NI
$NaNO_3$	3.4×10^{-3}	NI
$NaHCO_3$	3.0×10^{-4}	2.3×10^{-1}
Na_2CO_3	NI	4.6×10^{-1}
NaCl	2.1×10^{-3}	NI
$Na_2SiO_3 \cdot 9H_2O$	NI	1.9×10^{-2}
NaOH	NI	2.5×10^{-3}
$MgSO_4$	2.6×10^{-3}	NI
$MgCl_2$	2.4×10^{-3}	NI
KCl	7.0×10^{-4}	NI
KOH	NI	5.2×10^{-4}
H_3BO_3	NI	1.3×10^{-2}
$MgSO_4$	2.6×10^{-3}	NI
pH	7.2	9.7

(a) WTP = Hanford Tank Waste Treatment and Immobilization Plant
NI = not included.

RESULTS AND DISCUSSION

Tc(VII) Removal by Fe(II)-Goethite

The total amount of Tc present in the final Tc-goethite solid as determined by acid digestion showed a high degree of Tc removal, 93 to 100% (Table I). The greatest magnitude of Tc removal, 100%, was found in Sample 2-5 (Table I), which was prepared with the addition of NaOH before the armoring Fe(III). In Sample 2-5, most of the dissolved Fe(II) and Tc(VII) added to the goethite suspension was

removed from solution immediately after adding the NaOH and before adding the Fe(III) armoring solution. Similar rapid and near-complete removal of Tc was also observed in Samples 2-2 and 2-3 prepared with DI water and synthetic scrubber solution (pH~13), respectively, even without the additional Fe(III) armoring process [19]. Sample 2-3 prepared with the caustic scrubber simulant CS-1 showed almost 100% Tc removal in solution before adding NaOH because of the initially high pH of the caustic scrubber simulant. This suggests that the key step in Tc sequestration is producing a high-pH condition after mixing Tc with the Fe(II)-goethite slurry prepared at low pH. In addition, the 100% Tc removal observed in Sample 2-5 was found to occur right after adding NaOH and before adding additional Fe(III), indicating that the amount of additional Tc removed from solution during the Fe(III) armoring process was not significant.

Solid Phase Characterization

The XRD pattern of Tc-goethite solids confirmed the formation of goethite in the synthesis process (Fig. 1). Goethite was not necessarily the only mineral in the final Tc-goethite products because noticeable amounts of magnetite (arrows in Fig. 1) were identified in Samples 2, 2-1, 2-2, and 2-3. A sharp peak at 35.6 degrees 2-theta indicated the presence of magnetite, and this peak was more discernable in Samples 2-2 and 2-3, which were prepared in a system without Fe(III) addition for armoring. A much darker, greenish-black color was observed, and more fine particles were attached on a magnetic stirring bar in the slurry during preparation of Samples 2-2 and 2-3, indicative of the presence of magnetic phases (i.e., magnetite). Semi-quantitative analysis using standard magnetite and goethite XRD patterns showed approximately 70% and 60% magnetite content for Samples 2-2 and 2-3, respectively, with the remainder being goethite [19].

Increased XRD peak intensities in the 21 degrees 2-theta region, indicative of the presence of goethite, were also found in Samples 2-4 and 2-5, which were prepared with additional Fe(III) armoring, compared to Samples 2-2 and 2-3 that were prepared without additional Fe(III). There was no magnetite found in Samples 2-4 and 2-5. Even though synthetic off-gas scrubber solution, which contains 0.8 M of carbonate, was used to prepare Tc-goethite Samples 2-3 and 2-4, siderite ($FeCO_3$) was not found in the final Tc-goethite samples (Fig. 1).

The SEM images of final Tc-goethite products exhibited the acicular shape typical of goethite (Fig. 2). The presence of small cubes or pseudo-cubic crystals, likely magnetite, attached to acicular goethite was found in Samples 2-2, 2-3, and 2-3*, which is consistent with XRD analysis. No cubic-shaped magnetite was found in Sample 2-5 [19]. The Tc EDX peak was found in a cubic-shaped particle (magnetite) in Sample 2-3*, which was prepared with a higher Tc concentration.

TEM revealed similar acicular goethite in Samples 2-2 and 2-5 with the selected area electron diffraction (SAED) pattern taken along the B[001] direction of goethite (Fig. 3). Because Sample 2-2 contained a relatively higher Tc concentration per gram of goethite (Table I), Tc was detected in Sample 2-2 by TEM/EDX [19]. However, the exact location of the Tc was not clear because the Tc EDX peak was found in the mixture of magnetite and goethite in Sample 2-2. An additional Tc TEM/EDX peak was found in an acicular-shaped particle (goethite) in Sample 2-3*, which was prepared with high Tc concentration. In addition, for the same Sample 2-3*, a similar Tc SEM/EDX peak was also detected in a separated cubic-shaped mineral particle, the typical shape of magnetite (Fig. 2b and 2c).
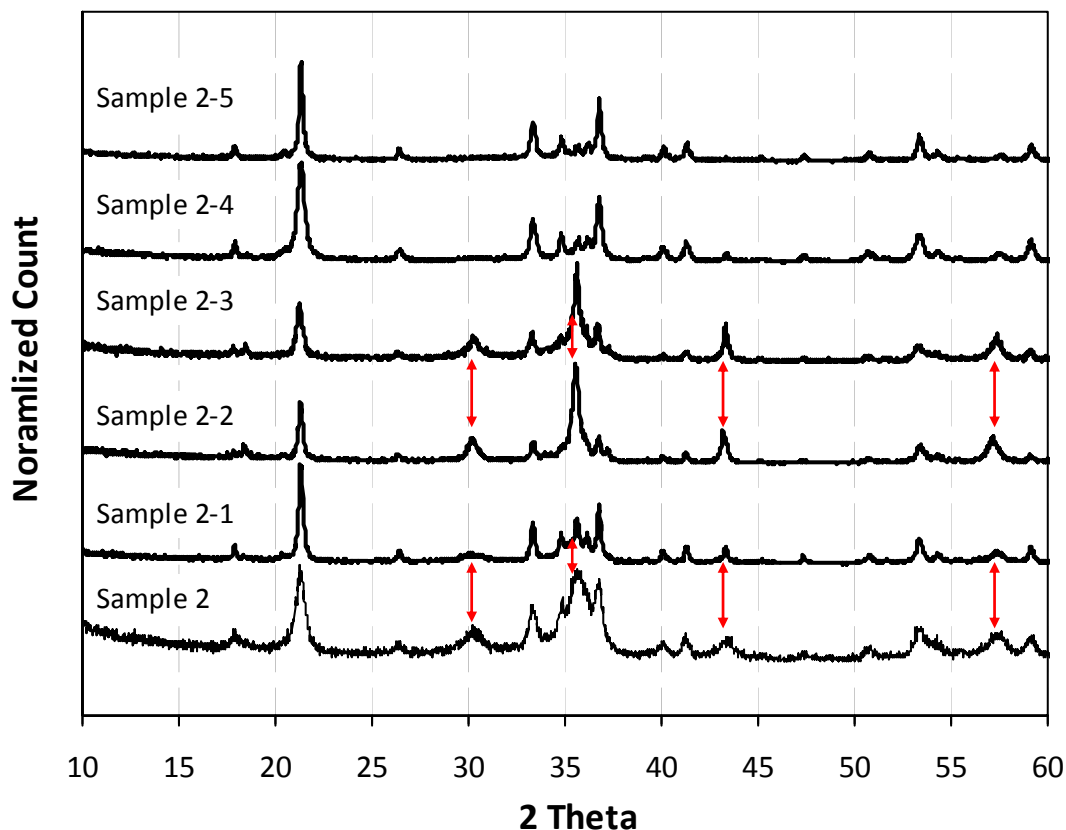
Fig. 1. XRD patterns for final Tc-goethite solids. Arrows (red) indicate the presence of magnetite. Samples 2-4 and 2-5 showed 100% goethite as found in initial goethite.

Because mineral transformation from magnetite to goethite is possible at alkaline pH conditions [20], the Tc EDX peak found in the goethite particle may have been from the mineral-transformation of Tc-magnetite as found in SEM/EDX (Fig. 2c). The presence of Tc in the final Tc-goethite product in Samples 2-2 and 2-3* indicates the possibility that Tc is associated as coprecipitates with Fe oxide, either magnetite or goethite.

XAFS Analysis of Tc in Tc-Goethite

The XANES spectra for Tc standards $KTcO_4$, $NaTcO_4$, TcO_4^- adsorbed on Reillex-HPQ resin, and $TcO_2 \cdot 2H_2O$, along with the Tc-goethite Samples 2, 2-2, 2-3*, and 2-5, are shown in Fig. 4-left. The spectra for $NaTcO_4$, $KTcO_4$, and TcO_4^- adsorbed on ion-exchange resin are very similar and characterized by a strong pre-edge feature because of the 1s to 4d transition, which is allowed for the tetrahedral TcO_4^- anion. The XANES spectrum of $TcO_2 \cdot 2H_2O$ is very different and characteristic of Tc(IV) coordinated by six oxygen atoms in an octahedral geometry. In addition, the absorption edge of $TcO_2 \cdot 2H_2O$ is 5.5 eV lower in energy than the absorption edge of TcO_4^-. The oxidation states of Tc in the Tc-goethite samples were determined by fitting their XANES spectra using the spectra of TcO_4^- adsorbed on Reillex-HPQ resin and $TcO_2 \cdot 2H_2O$ as the Tc standards (Fig. 4-left). In all cases, the results of fitting indicated that only Tc(IV) was present in Samples 2, 2-2, 2-3*, and 2-5.
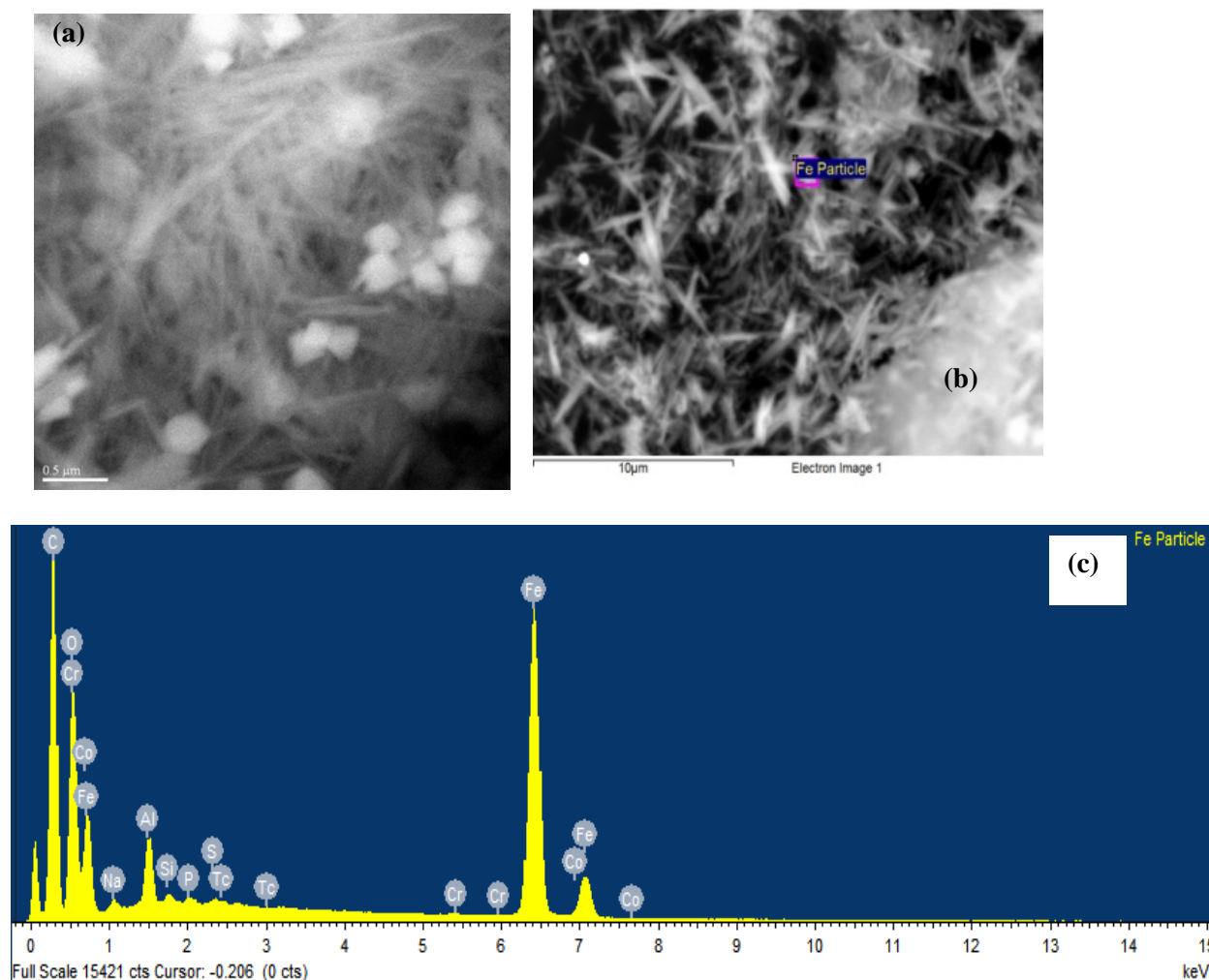
Fig. 2. SEM images for Tc-goethite samples (a) final Tc-goethite Sample 2-2; (b) final Tc-goethite Sample 2-3*; (c) EDX for Tc-goethite Sample 2-3* prepared using caustic scrubber simulant CS-2 with high Tc concentration and 0.1 M of Fe(II) without additional armoring. A beam location is a cubic-shaped particle described as a pink rectangle denoted as "Fe particle" in Fig. 2b.

The Fourier transforms of extended X-ray absorption fine structure (EXAFS) spectra for Samples 2, 2-2, 2-3*, and 2-5 solids before leaching are presented in Fig. 4-right. Three different models were examined, and the distances were allowed to vary in the fitting process. Therefore, if the distances to neighboring atoms did not correspond to the model, the structure was free to relax. In all cases, the local environment of Tc is consistent with Tc replacing Fe in the goethite lattice. The main difference between the local environment of Tc in the Tc-goethite and that of Fe in "pure" goethite is that in "pure" goethite, there are two sets of two iron atoms at 3.01 and 3.28 Å, while in the structure determined by EXAFS for the Tc-goethite solids, there are four iron atoms at an intermediate distance, 3.1 Å. This difference could be either an inability to resolve the two sets of iron neighbors in the EXAFS analysis of the Tc-goethite solids, or a disorder in the local environment of Tc-goethite caused by the Tc substituting for Fe. In addition to this slightly changed distance, Sample 2 also displays additional scattering due to a Tc
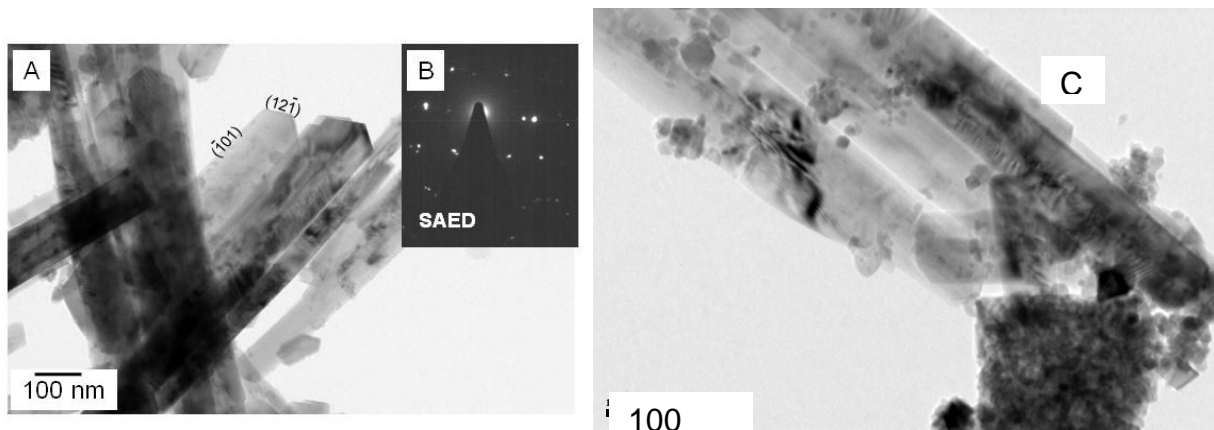
Fig. 3. TEM images for Tc-goethite samples: (A) high magnification image of Tc-goethite Sample 2-5; (B) presence of visible magnetite with goethite in agreement with XRD in Sample 2-5; (C) TEM image of Sample 2-2 showing mixture of magnetite and goethite.
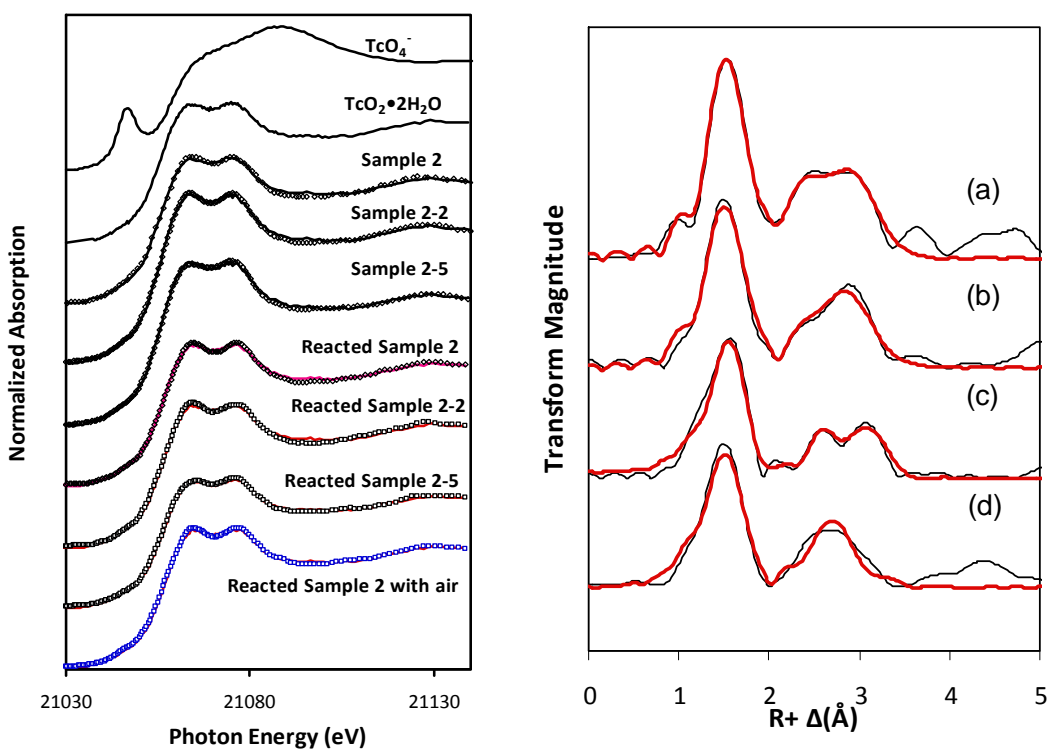

Fig. 4. The X-ray absorption spectrometry (XAS) spectra for Tc-goethite samples: (left) normalized XANES spectra for Tc(VII) and Tc(IV) standards, and Tc-goethite samples before and after leaching. The black symbol (rectangular) and the solid line in Tc-goethite spectra indicate the measured data and a linear combination fit, respectively, for Tc-goethite samples; (right) Fourier transforms of EXAFS spectra for Tc-goethite samples (a) Sample 2; (b) Sample 2-2; (c) Sample 2-3*; and (d) Sample 2-5 before leaching test. The fits are shown on the bold red line, and the measured data are shown as the black lines.

neighbor at 2.51 Å, which is not consistent with a neighboring Tc in the goethite lattice. This distance, however, is consistent with the presence of $TcO_2 \cdot 2H_2O$ and is attributed to the presence of residual Tc(IV) not incorporated into the goethite lattice in Sample 2.

The local environment of Tc in goethite is distinctly different from that of Tc adsorbed on the surfaces of iron oxides. Peretyazhko et al. [21] examined Tc(IV) adsorbed on both goethite and hematite. In both cases, a complex coordination geometry was observed with a first shell consisting of six oxygen atoms at 2 Å, a neighboring metal atom (either Tc or Fe) at 2.6 A, three oxygen atoms at 3 Å, and two iron atoms at 3.5 Å. A similar local environment was also observed for Tc adsorbed on ferrihydrite [22]. In comparison to these previous reports, it is unlikely that Tc in our Tc-goethite samples is adsorbed onto the iron oxide mineral surfaces.

Overall, the EXAFS data are consistent with Tc being incorporated into an iron oxide, most likely magnetite or goethite as a Tc-goethite final product, rather than Tc being adsorbed onto the surface of iron oxide particles. In addition, minor amounts of $TcO_2 \cdot 2H_2O$ solid present in Sample 2 are attributed to residual Tc(IV) not being incorporated into the goethite lattice and forming discrete $TcO_2 \cdot 2H_2O$ upon drying. The $TcO_2 \cdot 2H_2O$ not incorporated into the iron oxide (goethite and magnetite) lattice can be easily reoxidized upon contact with atmospheric oxygen [22,23]. However, the EXAFS result for Sample 2-5 confirmed almost total Tc co-precipitation within the goethite lattice rather than showing Tc adsorbed onto the surfaces of goethite or Tc as a discrete $TcO_2 \cdot 2H_2O$ solid phase. Finding only Tc coprecipitation within goethite lattices in Sample 2-5 is consistent with the Tc leaching results for Sample 2-5 in IDF pore water (see leaching results below) that shows the least Tc release.

Tc Release in Batch Leaching Experiments

Batch-leaching experiments were conducted with a homogeneously ground Tc-goethite powder sample, Sample 2 (see Table I), at a solid concentration of 1 g/L with different leaching solutions. The different leaching solutions were 1) standard Beckman-Coulter® pH buffer solutions of pH 4 (potassium hydrogen phthalate), pH 7 (mixture of potassium and sodium dihydrogen phosphate), and pH 10 (mixture of sodium bicarbonate-carbonate); 2) synthetic pore water (pH = 7.2 and ionic strength=0.05 M) simulating that from the IDF in the Hanford Site 200 East Area; and 3) simulated Hanford Tank Waste Treatment and Immobilization Plant (WTP) glass leachate (GL) with pH = 9.7 and ionic strength=1.67 M, which was developed based on the modeling results of IDF low-level waste glass dissolution [4]. The chemicals used to prepare the latter two Hanford Site-specific leaching solutions are listed in Table III. Additional Tc-goethite powder samples without goethite armoring (Sample 2-2) and with goethite armoring (Sample 2-5) were also leached using only the simulated IDF pore water as the leachant to investigate the effect of the armoring process on Tc release. For each Tc-goethite leach test, a supernatant solution subsample (1 mL) was periodically collected from 30 minutes after the test commenced to 180 days using a 0.45-μm Nalgene syringe filter. It was submitted for analyses of dissolved Fe(tot) and Tc. After the 180-day leach tests were completed, the powder Tc-goethite samples were separated by filtration and used for solids characterization.

Batch-leaching data for Tc and dissolved Fe(tot) as a function of time in different solutions are shown in Fig. 5a and Fig. 5b. Tc concentrations in the leachates even after 180 days of contact were less than 2 μg/L in the pH = 4 and 7 buffer solutions and the IDF pore water (pH = 7.2) solutions. These solution concentrations equate to a Tc release of ~2 μg Tc/g of Tc-goethite solids. The release of Tc was higher when the Tc-goethite solids were immersed in the pH = 10 buffer (up to 7 μg Tc/g of Tc-goethite solid) and glass leachate solutions (up to 2.7 μg Tc/g of Tc-goethite solid). The IDF pore water solution is germane to the expected disposal environment for solidified WTP secondary wastes. The leached Tc
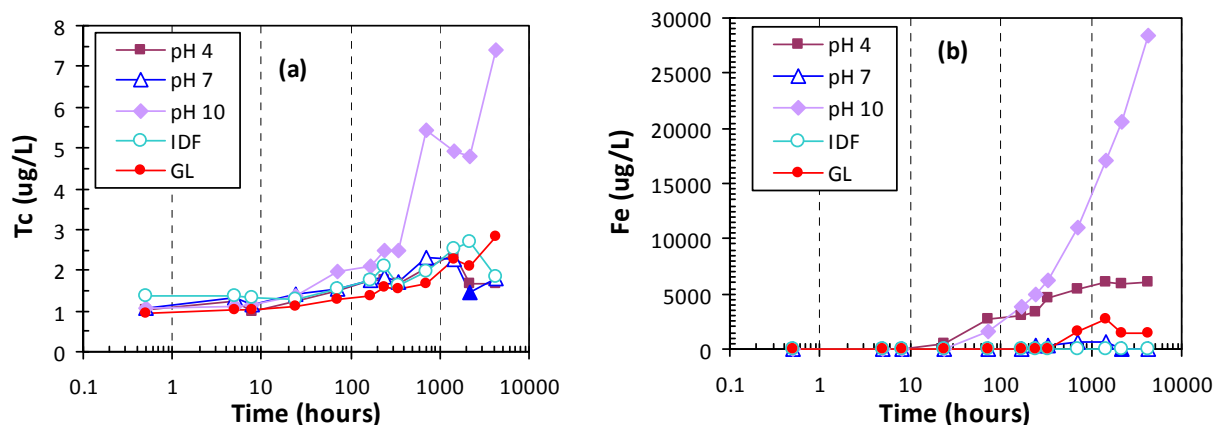
Fig. 5. Batch-leaching results for Tc-goethite samples as a function of reaction time with different pH buffer solutions (4, 7, and 10), IDF pore water, and GL. (a) Tc leaching for Sample 2; (b) dissolved Fe(tot) for Sample 2.

concentrations in the IDF pore water and pH = 7 buffer solution were very similar, and most of the measured Fe(tot) concentrations in these solutions were below the detection limit (< 50 μg/L), suggesting that goethite (Tc-hosting material) dissolution was insignificant in circum-neutral pH conditions.

Because the glass leachate solution has a relatively high pH (~9.7) compared to the IDF pore water, more goethite dissolved such that the leached Tc concentrations in the glass leachate solution were higher than those in the IDF pore water solution.

Leached Fe(tot) in the other leachates, aside from the pH = 10 buffer solution, reached a constant concentration after 30 days of leaching. The comparable trend between the concentrations of dissolved Tc and Fe(tot) in different leaching solutions, except pH = 4 buffer solution, suggests that Tc leaching is closely related to goethite dissolution, especially at high pH. Even though the pH = 4 buffer solution showed the second highest dissolved Fe(tot) concentration, the leached Tc concentration in the pH = 4 buffer solution was not the second highest (Fig. 5a and Fig. 5b). The amount of Tc in the pH = 4 buffer leachate is slightly lower than Tc leached by the IDF pore water and GL solutions, indicating the possibility that released Tc is adsorbing onto the goethite surfaces at low pH [24].

Additional Tc leaching tests using powdered Tc-goethite Samples 2-2 and 2-5 in IDF pore-water solution were conducted to investigate the effect of the additional goethite armoring process. Recall that after sequestering Tc from the waste simulants via the Fe(II) treatment at high pH, an additional treatment with Fe(III) and NaOH solution was performed to promote further ferric oxide precipitation and coating of the Tc-Fe(II)-treated goethite. The results of these additional leach tests on powdered armored (Samples 2 and 2-5) and unarmored (Sample 2-2) samples showed no detectable Fe(tot) in the IDF pore-water leachates for all three Tc-goethite samples even after 180 days of leaching [19]. Especially at early leaching times of less than 10 days, noticeably more Tc was leached from Sample 2-2 [19], which was prepared without additional goethite armoring and showed a more dominant magnetite mineral content, compared to Samples 2 and 2-5 that were prepared with two different armoring processes and in which only goethite mineral was observed in the final product. Although Samples 2 and 2-5 were both prepared with additional goethite armoring, sample 2-5 was the most resistant to Tc leaching (less than 2.0 wt% of Tc removed after 180 days in IDF pore water) and also showed the highest Tc sequestration during the Fe(II)-goethite treatment step (100% Tc uptake in Table I).

The XANES spectra for the Tc standards (KTcO$_4$, NaTcO$_4$, TcO$_4^-$ adsorbed on Reillex-HPQ resin, and TcO$_2$·2H$_2$O) and the Tc-Fe(II) goethite Samples 2, 2-2, and 2-5 after leaching in IDF pore water solution for 180 days are shown in Fig. 4 (left). The XANES spectrum of the aliquot of Sample 2 contacted with atmospheric oxygen for 180 days is also shown along with the linear combination fit in Fig. 4 (left). Because the XANES spectra for the Tc(VII) standards (NaTcO$_4$, KTcO$_4$, and TcO$_4^-$ adsorbed on ion exchange resin) are very similar and are characterized by a strong pre-edge feature because of the 1s to 4d transition for the tetrahedral TcO$_4^-$ anion, only one XANES spectrum for TcO$_4^-$ is provided in Fig. 4 (left). The XANES spectrum of TcO$_2$·2H$_2$O is very different and characteristic for Tc(IV) coordinated by six oxygen atoms in an octahedral geometry.

The oxidation state of Tc in the leached Tc-Fe(II) goethite samples was determined by fitting their XANES spectra using the spectra for the TcO$_4^-$ adsorbed on Reillex-HPQ resin and the spectra for the TcO$_2$·2H$_2$O standards. In all cases, the fitting results indicated that only Tc(IV) was present in both unleached and leached Tc-Fe(II) goethite Samples 2, 2-2, and 2-5 after they were leached in IDF pore water solution for 180 days. In addition, the unleached Tc-Fe(II) goethite Sample 2 aliquot that was exposed to atmospheric oxygen for 180 days also showed that only the Tc(IV) oxidation state was present. The other Tc-Fe(II) goethite samples that were leached in the different pH buffer and simulated glass leachants also showed no reoxidized Tc(VII) in the XANES spectra.

BENCH-SCALE, RHENIUM-GOETHITE PREPARATION

The initial scale-up of the lab-scale Tc stabilization process into a concept for a full-scale process that can be implemented for Hanford clean-up was planned to be executed in two steps. The first step was to conduct bench-scale testing using 12.5 liters of simulated submerged-bed scrubber effluent (see Table II) and then a 55-gallon scale test. The product from the larger scale test is also to be used in scaled melter tests to determine whether incorporating Tc into goethite has a measurable impact on the volatility of Tc in the HLW melter or whether the precipitated iron-rich solids have a negative impact on the resulting HLW glass. The scaled melter tests will not be conducted in a radioactive environment. Therefore, a substitute for Tc-99 was needed for the test. Rhenium has been used extensively as a substitute for Tc-99 in vitrification studies; its atomic radius is similar to Tc so it is expected to be incorporated similarly into the goethite solid structure and to be incorporated similarly into the vitrified product. The chemistry of rhenium is similar to technetium. It forms a similar oxidized species in the +7 oxidation state (TcO$_4^-$ vs. ReO$_4^-$); and, when reduced, it forms a similar oxide in the +4 oxidation state (TcO$_2$ vs. ReO$_2$). Both +4 oxides have reduced solubility and hence precipitate so they are not readily mobile in the environment.

Although Re is the most similar element to Tc, it is not a perfect substitute for Tc, and their behaviors will not be identical. There are some differences that must be considered. First, the standard oxidation potential of the ReO$_4^-$ anion is significantly less than TcO$_4^-$ (-0.51 V vs. -0.747 V). Secondly, the solubility of the reduced rhenium oxide, ReO$_2$, is greater than the reduced technetium oxide, TcO$_2$, at the process pH($\sim$12)—10^{-6}M for ReO$_2$ vs. 10^{-8}M for TcO$_2$. The basic Tc-99 stabilization process in goethite involves the oxidation of Fe^{2+} to Fe^{3+}, simultaneously reducing the pertechnetate to Tc(IV) and subsequently co-precipitating the Fe oxide and the Tc(IV). Both of these differences between Re and Tc would lead to a lower expected capture efficiency for Re compared to Tc. The bench-scale test and accompanying lab-scale tests were intended to 1) verify that sufficient Re could be incorporated into the solids for use in the melter test, and 2) make the initial modifications that would develop a lab process into a plant process. For example, purged reaction vessels were substituted for working in an oxygen-free glove box, mixers were employed rather than shaking bottles, and concentrated NaOH was used to raise pH rather than 2 M NaOH solution. The lab-scale tests using Re showed a significantly reduced capture efficiency of Re into the solids, but verified that some incorporation was achievable. To compensate for an expected lower capture efficiency, a 20× higher concentration of Re was used in the initial simulant make up.

Table IV shows results of the basic process on Tc, with Re substituted at lab-scale, and with Re substituted at bench-scale.

Table IV. Results of Bench-Scale Demonstration with Re-Goethite Precipitation from SBS Simulant.

	Tc, Lab Scale	Re, Lab Scale	Re, Bench Scale
Final Tc/Re Removal on solid	16.4 µg/g	2.38	13 µg/g
Contaminant (Tc/Re) Uptake	89.2%[a]	17.2%[b]	0.2%[c]

[a] Tc input concentration was 3.2×10^{-6}M, which is much lower than other lab tests reported in Table I.
[b] Re input concentration was 5.4×10^{-6}M.
[c] Re input concentration was 1.0×10^{-3}M.

The results of the bench-scale test indicate that almost no Re was incorporated into the iron oxy-hydroxide solids. The main culprit has been attributed to the high concentrations of nitrate, a strong oxidizer, in the SBS simulant, exacerbating the poorer reduction capacity of ReO_4^- vs. TcO_4^-. The nitrate overwhelmed the reduction of the $ReO4^-$, so ReO_2 could not precipitate.

Initial lab-scale tests indicate that removing nitrate from the reaction mixtures can significantly increase the capture of Re. The next step for engineering-scale tests will be conducted to treat water spiked with sodium perrhenate, $NaReO_4$, and will be scaled to treat 800× more effluent than the initial laboratory tests.

CONCLUSIONS

The observed high-percentage Tc incorporation within the Fe(II)-treated Fe-oxide mineral (magnetite or goethite) structure provides a viable option for treating waste streams containing Tc(VII) and forming stable Tc-bearing solid waste forms. With Fe(II) acting as a catalyst on the surfaces of initially prepared goethite for reducing Tc(VII), the final product of goethite can remove Tc from off-gas secondary waste solutions quickly and efficiently. Because goethite is very stable with respect to other iron oxides or (oxy)hydroxides in both dry and wet environments over a range of particle sizes [25], Tc reduced and incorporated within the goethite is unlikely to be released, even when the final Tc-goethite product is exposed to oxidizing conditions. We also found that the sequestered Tc was slower to reoxidize and exhibited lower leachability compared to the literature data on the leachability/dissolution or release of Tc adsorbed onto ferric oxides or from discrete $TcO_2·2H_2O_{(s)}$ crystals present in mixed solids. The sequestration of Tc within the Fe(II)-treated goethite can be enhanced by using a secondary armoring process where additional goethite coatings or goethite mineral formation from mineral transformation of preexisting magnetite are produced by contacting the Fe(II)-treated goethite with ferric solution at high pH.

The removal of Tc(VII) by goethite from various waste simulants using the Fe(II) treatment process was tested by varying the synthesis conditions. These variations in synthesis protocol show that the concentration of Fe(II) reductant is the most important factor controlling the removal of Tc(VII) from the simulant solutions, especially when the waste simulants contain relatively high concentrations of Tc. The presence of anions other than hydroxide and carbonate in the waste streams, especially PO_4^{3-} and to a lesser extent SO_4^{2-}, decreases the Tc-removal efficiency slightly. It was also discovered that the mixing time between the waste simulant, the goethite, and the Fe(II) reductant should be less than 1 day to minimize Tc re-release from the solid via Fe oxide dissolution at the high pH condition. The Tc re-release from the Fe(II)-treated solid appears to be caused by the Tc-hosting Fe(II)-treated goethite or magnetite

dissolving in the high-pH slurry. Although more studies are needed, ferrihydrite can be also used as an initial mineral substrate instead of goethite to remove Tc from waste solutions when the slurry is treated with Fe(II).

REFERENCES

1. K.V. KOTEGOV, O.N. PAVLOV, AND V.P. SHVEDOV, *Technetium*. Academic Press: New York, Vol. 2 (1968).
2. F. LUYKX, Technetium Discharges in the Environment. In *Technetium in the Environment*, Desmet, G., Myttenaere, C., Eds. Elsevier: Essex, UK (1986).
3. J.G. DARAB and P.A. SMITH, Chemistry of technetium and rhenium species during low-level radioactive waste vitrification. *Chem. Mat.* 1996, *9*, 1004-1021.
4. B.P. MCGRAIL, D.H. BACON, J.P. ICENHOWER, F.M. MANN, R.J. PUIGH, H.T. SCHAEF, and S.V. MATTIGOD, Near-field performance assessment for a low-activity waste glass disposal system: Laboratory testing to modeling results. *Journal of Nuclear Materials* 2001, *298*, 95-111.
5. Y. BAO, M.W. GRUTZECK, C.M. JANTZEN, Preparation and properties of hydroceramic waste forms made with simulated Hanford Low-Activity Waste. *J. Am. Ceram. Soc.* 2005, *88(12)*, 3287-3302.
6. D.D. SIEMER, Hydroceramics, a "new" cementitious waste form material for U.S. defense-type reprocessing waste. *Mater. Res. Innov.* 2002, *6*, 96-104.
7. D. SINGH, V.R. MANDALIKA, S.J. PARULEKAR, and A.S. WAGH, Magnesium potassium phosphate ceramic for Tc-99 immobilization. *J. Nucl. Mater.* 2006, *348 (3)*, 272-282.
8. F.R LIVENS, M.J. JONES, A. HYNES, J.M. CHARNOCK, F.W. MOSSELMANS, C. HENNIG, H. STEELE, D. COLLISON, D.J. VAUGHN, R.A.D. PATTRICK, W.A. REED, and L.N. MOYES, X-ray absorption spectroscopy studies of reactions of technetium, uranium, and neptunium with mackinawite. *Journal of Environmental Radioactivity* 2004, *74*, 211-219.
9. K. MORRIS, F.R. LIVENS, J.M. CHARNOCK, I.T. BURKE, J.M. MCBETH, J.D.C. BEGG, C. BOOTHMAN, and J.R.LLOYD, An X-ray absorption study of the fate of technetium in reduced and reoxidized sediments and mineral phases. *Applied Geochemistry* 2008, *23*, 603-617.
10. J.H.P. WATSON, I.W. CROUDACE, P.A.B. JAMES, J.M. CHARNOCK, and D. ELLWOOD, Adsorption of radioactive metals by strongly magnetic iron sulfide nanoparticles produced by sulfate-reducing bacteria. *Separations Science and Technology* 2001, *36*, (12), 2571-2607.
11. M.J. WHARTON, B. ATKINS, J.M. CHARNOCK, F.R. LIVENS, R.A.D. PATTRICK, and D. COLLISON, An X-ray absorption spectroscopy study of the coprecipitation of Tc and Re with mackinawite (FeS). *Applied Geochemistry* 2000, *15*, 347-354.
12. H. YANG, R. LU, R.T. DOWNS, and G. COSTIN, Goethite, a-FeO(OH), from single-crystal data. *Acta Crystallographica Section E* 2006, *E62*, 250-252.
13. U. SCHWERTMANN, and R.M. CORNELL, *Iron Oxides in the Laboratory: Preparation and Characterization*. VCH Publishers: Weinheim, Germany (1991).
14. D.L. SHUSTER, P.M. VASCONCELOS, J.A. HEIM, and K.A. FARLEY, Weathering geochronology by (U-Th)/He dating of goethite. *Geochim. Cosmochim. Acta* 2005, *69(3)*, 659-673.
15. U. SCHWERTMANN, and R.M. CORNELL, R. M., *Iron Oxides in the Laboratory. 2nd Edition*. WILEY-VCH Publishers: Weinheim, Germany (2000).
16. C.R. GIBBS, Characterization and application of ferrozine iron reagent as a ferrous indicator. *Anal. Chem.* 1976, *48(8)*, 1197-1201.

17. L.A. MAHONEY, and R.L. RUSSELL, "Vitrification Offgas Caustic Scrubber Secondary Waste Simulant Formulation," PNNL-14582 Rev.1, Pacific Northwest National Laboratory, Richland, Washington (2004).
18. G. JOSEPHSON, G. PIEPEL, and J.H. WESTSIK, *Selection of secondary waste test compositions*, Unpublished, Pacific Northwest National Laboratory, Richland, Washington (2010).
19. W. UM, H. CHANG, J.P. ICENHOWER, N. QAFOKU, R.J. SERNE, S.C. SMITH, E.C. BUCK, R.K. KUKKADAPU, M.E. BOWDEN, J.H. WESTSIK JR., and W.W. LUKENS, "Immobilization and Limited Reoxidation of Technetium-99 by Fe(II)- Goethite," PNNL-19833, Pacific Northwest National Laboratory, Richland, Washington (2010).
20. Y.T. HE, and S.J. TRAINA, Transformation of magnetite to goethite under alkaline pH conditions. *Clay Minerals* 2007, *42(1)*, 13-19.
21. T. PERETYAZHKO, J.M. ZACHARA, S.M. HEALD, B.-H. JEON, R.K. KUKKADAPU, C. LIU, D.A. MOORE, and C.T. RESCH, Heterogeneous reduction of Tc(VII) by Fe(II) at the solid-water interface. *Geochim. Cosmochim. Acta* 2009, *72*, 1521-1539.
22. J.M. ZACHARA, S.M. HEALD, B.-H. JEON, R.K. KUKKADAPU,C. LIU, J.P. MCKINLEY, A.C. DOHNALKOVA, and D.A. MOORE, Reduction of pertechnetate [Tc(VII)] by aqueous Fe(II) and the nature of the solid phase redox products. *Geochim. Cosmochim. Acta* 2007, *71*, 2137-2157.
23. W.W. Lukens, Bucher, J. J., Shuh, D. K., and Edelstein, N. m., 2005. Evolution of Technetium speciation in reducing grout. *Environ. Sci. Technol.* **39**, 8064-8070.
24. D.J. Liu, and X.H. Fan, 2005. Adsorption behavior of Tc-99 on Fe, Fe_2O_3 and Fe_2O_4. *J. Radio. Nuclear Chem.* **264 (3)**, 691-698.
25. A. NAVROTSKY, L. MAZEINA, and J. MAHZLAN, Size-driven structural and thermodynamic complexity in iron oxides. *Science* **319**, 1635-1638.