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Technetium Removal Using Tc-Goethite Coprecipitation

W Um
G Wang
HB Jung
RA Peterson

November 2013



Pacific Northwest
NATIONAL LABORATORY

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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

This report describes the results from laboratory tests performed at Pacific Northwest National Laboratory for the U.S. Department of Energy (DOE) EM-31 Support Program (EMSP) subtask, “Low temperature waste forms coupled with technetium removal using an alternative immobilization process such as Fe(II) treated-goethite precipitation” to increase our understanding of ^{99}Tc long-term stability in goethite mineral form and the process that controls the $^{99}\text{Tc(VII)}$ reduction and removal by the final Fe (oxy)hydroxide mineral forms.

The overall objectives of this task were to 1) evaluate the transformation process of Fe (oxy)hydroxide minerals to more crystalline goethite ($\alpha\text{-FeOOH}$) mineral for ^{99}Tc removal and 2) determine a scientific mechanism for limiting $^{99}\text{Tc(IV)}$ reoxidation in Fe(II)-treated ^{99}Tc -goethite mineral and the long-term $^{99}\text{Tc(IV)}$ oxidation state change.

The results of mineral transformation tests using three synthesized Fe(oxy)hydroxide minerals [ferrihydrite, magnetite, and $\text{Fe(OH)}_2(\text{s})$] showed that $\text{Fe(OH)}_2(\text{s})$ transformed easily to a mixture of magnetite, maghemite, and goethite even at room temperature (RT) and circumneutral pH conditions. Even though the most transformation products were found at high pH (~ 12) and temperature ($75\text{--}80^\circ\text{C}$) conditions, $\text{Fe(OH)}_2(\text{s})$ can be used as an initial substrate for ^{99}Tc removal due to its high reactivity. Removal of ^{99}Tc from solution by $\text{Fe(OH)}_2(\text{s})$ was fast and more than 95% of the initial ^{99}Tc (10^{-5} M) was removed from solution containing $\text{Fe(OH)}_2(\text{s})$, even without aqueous Fe(II) addition. Since $\text{Fe(OH)}_2(\text{s})$ can be oxidized to form magnetite (Fe_3O_4) by reacting with H_2O even in anaerobic conditions, the presence of $\text{Fe(OH)}_2(\text{s})$ can provide aqueous Fe(II) to reduce $^{99}\text{Tc(VII)}$ to $^{99}\text{Tc(IV)}$. In addition, because the final pH of a slurry mixed with ^{99}Tc and $\text{Fe(OH)}_2(\text{s})$ was fairly alkaline ($\text{pH} = 9\text{--}11.5$), ^{99}Tc removal was not considered to be from surface adsorption, but incorporation into transformed mineral product. Although a further analysis is essential to confirm ^{99}Tc speciation in the final transformed product from $\text{Fe(OH)}_2(\text{s})$, mineral transformation from $\text{Fe(OH)}_2(\text{s})$ can be used to effectively remove $^{99}\text{Tc(VII)}$ in alkaline pH conditions germane to off-gas scrubber secondary waste and low-activity waste streams. Slightly more transformation products were also found from $\text{Fe(OH)}_2(\text{s})$ with a solution-to-solid ratio of 100 than with a ratio of 1000. The transformation product from ferrihydrite was similar, and solely goethite mineral was produced in most of the conditions. It is clear that comparison results from both $\text{Fe(OH)}_2(\text{s})$ and ferrihydrite substrates show that high slurry pH and high temperature conditions favor more goethite formation from the transformation reaction. Unfortunately, we could not conduct ^{99}Tc removal using ferrihydrite as an initial substrate in this task, but based on previous results (Um et al. 2010), ferrihydrite can also be used to remove ^{99}Tc with additional aqueous Fe(II). Transformation product from magnetite was very limited and there were only small amounts of maghemite and goethite formed from magnetite reacted as initial substrate under high pH and temperature conditions. In addition, negligible ^{99}Tc removal ($<5\%$) from solution was also found in magnetite slurry without aqueous Fe(II) addition.

Even after long-term leaching in the Integrated Disposal Facility (IDF) pore water solution for two years, very limited amounts of ^{99}Tc and Fe(total) were detected in the IDF leachates. The limited ^{99}Tc release was attributed to more stabilized $^{99}\text{Tc(IV)}$ present in ^{99}Tc -goethite lattice even after long-term exposure to oxygen, while zero detected Fe(total) concentration in the IDF leachate indicated that the

structure of the final goethite mineral was stable in a circumneutral pH condition similar to the IDF pore water. Reduced $^{99}\text{Tc(IV)}$ incorporated in the goethite was unlikely to be reoxidized to $^{99}\text{Tc(VII)}$, even when the final ^{99}Tc -goethite product (sample 2-5) was exposed to oxidizing conditions for three years (two years in IDF solution plus one year in air). In addition, the measured reductive capacity of both ^{99}Tc -goethite 2-2 sample (prepared without additional armoring process) and 2-5 sample (with additional Fe(III) armoring) before leaching showed that a higher reductive capacity of 0.744 meq/g was found in ^{99}Tc -goethite 2-2 sample, which was not prepared with an additional armoring process, while a lower reductive capacity of 0.140 meq/g was found in the ^{99}Tc -goethite 2-5 sample, which was prepared with the additional armoring process. However, more ^{99}Tc leaching was found in sample 2-2 than sample 2-5, which also indicates that a higher chemical reducing factor (e.g., higher reductive capacity in sample 2-2) is not the main controlling process in ^{99}Tc reoxidation and release. The limited reoxidation and release of ^{99}Tc is attributed to $^{99}\text{Tc(IV)}$ coprecipitated within goethite lattices and subsequently armored with additional goethite layers as well as to the chemical and structural stability of goethite in the circumneutral Hanford pore water solution.

Since mineral transformation from $\text{Fe(OH)}_2(\text{s})$ to a more stable Fe (oxy)hydroxide mineral such as goethite can be used to remove ^{99}Tc from alkaline waste streams, ^{99}Tc reduction and incorporation into a goethite mineral lattice is an effective solidifying method for long-term ^{99}Tc sequestration even after exposure to oxygen, suggesting potential use of goethite as a low-temperature Fe oxide solid waste form.

Although additional analysis of ^{99}Tc speciation in the final transformed product and more detailed Fe(II) analysis to identify the pathway of transformation are still required to confirm ^{99}Tc incorporation within the mineral structure of the transformed product from $\text{Fe(OH)}_2(\text{s})$, the results of this testing are expected to provide more credible indication of the possibility of goethite precipitation as an alternative immobilization process for ^{99}Tc removal from alkaline Hanford waste streams.

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Acronyms and Abbreviations

DI	deionized
DOE	U.S. Department of Energy
EDS	energy dispersive x-ray spectroscopy
EMSP	DOE EM-21 Support Program
EQL	estimated quantitation limit
FESEM	field emission scanning electron microscopy
HAW	high-activity waste
ICP-MS	inductively coupled plasma mass spectroscopy
ICP-OES	inductively coupled plasma optical emission spectroscopy
IDF	Integrated Disposal Facility
LAW	low-activity waste
RT	room temperature
PNNL	Pacific Northwest National Laboratory
SEM	scanning electron microscopy
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XAFS	x-ray absorption fine structure
XANES	x-ray absorption near-edge structure
XRD	x-ray diffraction

Units of Measure

θ	angle of incidence (Bragg angle)
Å	Angstrom (10^{-10} m or 10^{-1} nm)
°C	temperature in degrees Celsius [$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$]
eV	electron volt(s)
g	gram(s)
Hz	hertz
keV	kiloelectron volt(s)
kV	kilovolt(s)
kW	kilowatt(s)
μ	micro (prefix, 10^{-6})
μm	micrometer(s)
L	liter(s)
M	molarity, mol/L
mA	milliampere(s)
mCi	millicurie(s)
meq	milliequivalent(s)
mL	milliliter(s)
mm	millimeter(s)
mM	millimole(s)
ppm	parts per million

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1.0 Introduction

About 1900 kg of ^{99}Tc has been produced as fission product of ^{239}Pu at the U.S. Department of Energy's (DOE's) Hanford Site in southeastern Washington State (Darab and Smith 1996) during the Cold War era and most of the radioactive ^{99}Tc waste is presently stored in 177 underground Hanford storage tanks. Even with careful engineering controls, volatilization of a fraction of the ^{99}Tc during vitrification of both the high-activity waste (HAW) and low-activity waste (LAW) streams is expected. Because of the extremely complex chemical behavior of technetium, novel methods for controlling it in vitrification systems are critical to the safe and cost-effective treatment of ^{99}Tc -containing nuclear waste. In the high temperatures ($\sim 1000\text{--}1200^\circ\text{C}$) of the melters used in vitrification, a significant fraction of the ^{99}Tc volatilizes and is collected in an off-gas scrubber system. Although scrubber solutions can be recycled back to the melters, some or most of this captured ^{99}Tc ultimately can leave the vitrification facilities at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) as a secondary waste stream, which requires additional treatment and immobilization processes in a low-temperature environment. Risk assessments indicate that ^{99}Tc is a significant contributor to the environmental impact from the disposal of secondary wastes in low-activity disposal facilities like the Integrated Disposal Facility (IDF) at Hanford, because of the long half-life and high mobility of ^{99}Tc in oxidizing subsurface environments (Bondietti and Francis 1979). Under reducing conditions, ^{99}Tc can precipitate as $^{99}\text{Tc(IV)O}_2 \cdot 2\text{H}_2\text{O}$ (Lee and Bondietti 1983; Lukens et al. 2002), sorb to mineral phases (Bondietti and Francis 1979) more strongly, and be retained in various natural environments (Keith-Roach et al. 2003; Fredrickson et al. 2004; Burke et al. 2006) and engineered waste forms (Gilliam et al. 1990; Lukens et al. 2005). However, the reoxidation of $^{99}\text{Tc(IV)}$ by changing background to oxic conditions, such as contact with atmospheric oxygen and infiltrating fresh pore water solution, can result in an enhanced release of ^{99}Tc into the environment right after reoxidation of $^{99}\text{Tc(IV)}$ to $^{99}\text{Tc(VII)}$ (Burke et al. 2006), leading to the prediction of high ^{99}Tc release risk in many performance assessments (Smith and Walton 1993; Lukens et al. 2005). There are, therefore, incentives to decrease the impacts of ^{99}Tc both within the low-temperature waste form and at the waste disposal facility with a sustaining reduction environment.

Goethite, an iron-bearing oxyhydroxide mineral found in nature, could be a key to stabilize ^{99}Tc . Through a coprecipitation process with respect to goethite, this mineral has proven effective in capturing and sequestering ^{99}Tc from simulated off-gas scrubber solutions (Um et al. 2010). Tests have shown that over 90 percent of ^{99}Tc in highly alkaline waste streams was captured into the goethite mineral structure as reduced $^{99}\text{Tc(IV)}$ species. Most of the ^{99}Tc sequestering agents studied to date remove pertechnetate $^{99}\text{Tc(VII)O}_4^-$, the stable technetium oxidation state under oxidizing conditions, from the waste stream using redox processes where pertechnetate is ultimately reduced to $^{99}\text{Tc(IV)}$ prior to being immobilized in a solid matrix. Because $^{99}\text{Tc(IV)}$ and Fe^{3+} have similar ionic radii, $^{99}\text{Tc(IV)}$ tends to have a full compatibility with the goethite and hematite lattice (Um et al. 2011; Geckeis et al. 2012) and quantum chemistry calculations predict energetically more favorable incorporation of $^{99}\text{Tc(IV)}$ in the hematite lattice than $^{99}\text{Tc(VII)}$ (Skomurski et al. 2010). However, upon contact with O_2 , reduced $^{99}\text{Tc(IV)}$ species generally reoxidizes rapidly, and reoxidation leads to formation of the soluble $^{99}\text{Tc(VII)}$ oxyanion (Lukens et al. 2005) in cementitious waste form. Thus, both the stability of the waste form material and its ability to prevent reoxidation of $^{99}\text{Tc(IV)}$ to $^{99}\text{Tc(VII)}$ to limit the ^{99}Tc leachability are key to the success of any proposed immobilization strategy for waste form development. While many of the proposed disposal options rely on isolating $^{99}\text{Tc(IV)}$ from oxidizing components in gas or aqueous fluid,

the reductive capacity of the material hosting $^{99}\text{Tc(IV)}$ and the mechanism preventing the reoxidation of $^{99}\text{Tc(IV)}$ that affect ^{99}Tc remobilization from the waste forms have not been clearly demonstrated.

Pacific Northwest National Laboratory (PNNL) has conducted the laboratory testing for the DOE EM-21 Support Program (EMSP) subtask, “Low temperature waste forms coupled with technetium removal using an alternative immobilization process such as Fe(II) treated-goethite precipitation.” Recent tests have shown that ^{99}Tc can be removed from caustic off-gas scrubber simulants by a process that reduces pertechnetate, $^{99}\text{Tc(VII)}$ to $^{99}\text{Tc(IV)}$, which then coprecipitates with the goethite-dominant iron (oxy)hydroxide mineral phase (Um et al. 2010). The final product also exhibits very slow weathering and low ^{99}Tc leachability rates in subsurface environment conditions (Um et al. 2011, 2012). Despite the positive results for ^{99}Tc removal and long-term sequestration in a solidifying goethite waste form, more fundamental understanding of the processes that control the $^{99}\text{Tc(VII)}$ reduction and the location of $^{99}\text{Tc(IV)}$ in the final Fe (oxy)hydroxide mineral lattice is needed. In addition, the long-term stability and the mechanism of reoxidation of $^{99}\text{Tc(IV)}$ in the final Fe (oxy)hydroxide mineral lattice needs to be determined so that this ^{99}Tc sequestration process will be sustained for the thousands of years required in shallow land burial environments such as the Hanford IDF.

The goal for this task in FY 2013 was to obtain additional fundamental understanding of the ^{99}Tc -goethite coprecipitation process. The data and results generated by the laboratory tests described in this report provide both empirical and more fundamental scientific information to increase our understanding of the ^{99}Tc removal process in Fe (oxy) hydroxide products. In addition, the new understanding will aid development of a large-scale process design to sequester ^{99}Tc in various waste streams at the Hanford Site. The overall objectives of this task were to

- Evaluate the Fe (oxy)hydroxide solids’ transformation process to goethite for ^{99}Tc removal
- Determine the long-term ^{99}Tc oxidation state change and determine a scientific mechanism for limiting ^{99}Tc reoxidation in a final ^{99}Tc -goethite product.

It is expected that the results of this task will provide a more credible basis for the goethite precipitation process as an alternative immobilization process for ^{99}Tc removal from WTP secondary waste and LAW streams.

2.0 Materials and Methods

2.1 Materials

2.1.1 Synthesis of Fe (Oxy)hydroxide Minerals

Three different Fe (oxy) hydroxide minerals, $\text{Fe(OH)}_2(\text{s})$, ferrihydrite [Fe(OH)_3], and magnetite [Fe_3O_4], were synthesized as initial Fe (oxy)hydroxide substrate and used for testing to formulate $^{99}\text{Tc(IV)}$ -goethite final solid product under different reaction conditions. All three minerals were synthesized in the laboratory using well-known recipes (Schwertmann and Cornell 1991). In brief, $\text{Fe(OH)}_2(\text{s})$ was prepared using 0.07 M of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with a pH increasing to near 7.5 using NaOH solution (1 M) inside an anaerobic chamber (Coy Laboratory Products) equipped with a H_2/O_2 gas analyzer and palladium-coated alumina catalyst. A mixture of N_2 (97%) and H_2 (3%) was used as the

anaerobic gas in the chamber. Because $\text{Fe}(\text{OH})_2(\text{s})$ is very unstable, the entire process was conducted inside the anaerobic chamber and the final powder sample after filtration and drying was also stored inside the anaerobic chamber before any analysis and use. Two-line ferrihydrite was synthesized using dissolved ferric nitrate [8.0 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] in NANOpure® water (100 mL) in a polyethylene bottle (250 mL) with addition of 1 M NaOH dropwise while stirring the slurry, until a pH of 6 was obtained. To obtain a pH of 7 to 8, additional low-concentration NaOH (i.e., 0.01 M) was added while continuously stirring. The final product was filtered from solution by vacuum filtration and dried in air before use. Magnetite synthesis was carried out using 80 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in 560 mL of previously N_2 -flushed deionized (DI) water inside the anaerobic chamber. After preparing 240 mL of an oxygen-free solution containing 6.64 g KNO_3 and 44.9 g KOH, this solution was mixed with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution stepwise at 90°C for 30–60 minutes. The black precipitates was filtered out, washed with DI water several times, and dried before use. All the synthesized Fe (oxy) hydroxide minerals were confirmed by x-ray diffraction (XRD) analysis right after synthesis and before use.

2.1.2 ^{99}Tc -Goethite 2-2 and 2-5 Samples

A previously well-developed method was used to prepare ^{99}Tc -goethite samples designated 2-2 (prepared without additional armoring process) and 2-5 (with additional Fe(III) armoring) according to the method in Um et al. (2010, 2011). Between 2.75 and 3.5 g of synthesized goethite powder were resuspended in 250 mL of DI water in the anaerobic chamber to minimize the oxidation of the ferrous solution prior to its use. The pH was adjusted to pH ~2.0 by adding nitric acid (2 M HNO_3), and an aliquot of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.48 g) solid was directly added to the goethite slurry as the Fe(II) source to make 0.07 M of dissolved Fe(II) concentration, while the suspension was continuously mixed at low pH (~2.0) in the anaerobic chamber. After one day of mixing, 0.25 mL of $^{99}\text{Tc}(\text{VII})$ from a NaTcO_4 solution (2.2×10^{-2} M) was added to make a total 2.2×10^{-5} M of ^{99}Tc in the Fe(II)-goethite slurry (250 mL). As soon as the $^{99}\text{Tc}(\text{VII})$ was added, the bottle was immediately capped and mixed in a platform shaker for one to two days. After reaction, 2 M NaOH was added and the bottle was placed in an oven at 80°C for seven days to promote additional precipitation of a ^{99}Tc -goethite solid. After seven days reaction, the final ^{99}Tc -goethite solids were separated by filtration, washed using DI water, air dried, and used for additional analysis. In selected experiments, the ^{99}Tc -goethite solids were further modified to armor the ^{99}Tc -goethite solids with additional goethite precipitates using separately prepared $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (11.4g/100 mL) and 2 M NaOH (150 mL) solutions. These two solutions were added sequentially to the ^{99}Tc -goethite slurry in a series of additional experiments. After one to two days of reaction with sodium hydroxide solution, the bottle containing the final slurry was placed inside an oven at 80°C for seven days. The final slurry was subsequently filtered and both the solution and solid samples were used for further analyses. Both the ^{99}Tc -goethite 2-2 sample prepared without the additional armoring process and the ^{99}Tc -goethite 2-5 sample with additional Fe(III) armoring performed were used for long-term ^{99}Tc oxidation state change in ^{99}Tc -goethite solid sample and reductive capacity measurement.

2.2 Methods

2.2.1 Solid-Phase Characterizations

The morphology and crystallinity of three different synthesized iron oxides (or hydroxides) [$\text{Fe}(\text{OH})_2(\text{s})$, ferrihydrite, and magnetite] and their related final product (goethite) after mineral

transformation reaction under different conditions were tested using a scanning electron microscope (SEM) and a powder [or capillary sample for Fe(OH)₂(s)] X-ray diffractometer, respectively. Characterizations of morphology and chemical composition were made by field emission scanning electron microscopy (FESEM) and energy dispersive x-ray spectroscopy (EDS) using a LEO982 FESEM system (JEOL, Peabody, Massachusetts) with an Oxford ISIS energy dispersive x-ray detector. The dried powder specimens were carefully mounted with double-sided carbon tape attached to an aluminum stud without either polishing or carbon-coating. X-ray diffractograms were collected using a Phillips X'Pert x-ray diffractometer with a Cu-K α radiation x-ray tube ($\lambda = 1.5418 \text{ \AA}$) and a graphite monochromator. Normal operating power is 40 kV and 50 mA (2.0 kW). Data were collected from 10 to 80 degrees 2 θ with a scanning step size of 0.05 degree and dwell time of 1.5 seconds. Additional micro-XRD using a Rigaku MicroMax diffractometer was used for Fe(OH)₂(s) analysis. The Fe(OH)₂(s) powder was loaded into a glass capillary tube (0.5 mm in diameter and 80 mm high) and the top opening was sealed with grease. A rotating anode source at 875 W was used to generate Cr K α x-rays and the beam was collimated to 300 μm in diameter for the sample. The diffraction patterns were recorded on a two-dimensional image plate detector by integrating between 10 and 150 degrees 2 theta. Mineral identification was conducted using JADE[®] software (Materials Data Inc., Livermore, California) with a database published by the Joint Committee on Powder Diffraction Standards (International Center for Diffraction Data, Newtown Square, Pennsylvania).

The initial synthesized Fe(OH)₂(s) and its final mineral products after 30 days reaction at pH 12 were characterized using Mössbauer spectroscopy. The Mössbauer sample was prepared by mixing a dried sample with Vaseline[®] in a Cu holder sealed at one end with Kapton tape. After mixing the sample in the holder, the open end of the holder was sealed with Kapton tape. Then both the ends of the sample holder were secured with rings made of carbonized polyethyletherketone (PEEK) to ensure tightness. All sample preparation was carried out in an anaerobic environmental chamber (<0 ppm oxygen). The Mössbauer spectra were collected using a 50-mCi (initial strength) ⁵⁷Co/Rh single-line thin source, and the velocity transducer, MVT-1000 (WissEL), was operated in a constant acceleration mode (23 Hz) in the velocity range of ± 5 or ± 12 mm/s. An Ar-Kr proportional counter was used to detect the radiation transmitted through the holder, and the counts were stored in a multichannel scalar as a function of energy (transducer velocity) using a 1024-channel analyzer. Data were folded to 512 channels to give a flat background and a zero-velocity position corresponding to the center shift (CS) of a metal Fe foil at room temperature (RT). Calibration spectra were obtained with a 25- μm -thick metal Fe foil (Amersham, England) placed in the same position as the samples to minimize any errors due to changes in geometry. The Mössbauer data were modeled with Recoil software (University of Ottawa, Canada) using a Voigt-based structural fitting routine. The coefficient of variation of the spectral areas of the individual sites generally ranged between 1% and 2% of the fitted values.

2.2.2 Mineral Transformation Effects on ⁹⁹Tc Removal

Three sets of experiments were conducted to investigate the mineral transformation effects on ⁹⁹Tc removal in solution. First, screening tests of pure mineral transformations without ⁹⁹Tc spiking were designed to identify the suitable Fe (oxy)hydroxide mineral candidates as the substrates being used and to determine the optimal conditions for mineral transformation (temperature and pH). Secondly, the tested minerals showing possible mineral transformation to goethite (or other crystalline Fe oxide or oxyhydroxide minerals) were tested spiked with a constant ⁹⁹Tc concentration (10⁻⁵ M) under conditions with or without ferrous Fe²⁺ ion addition because surface-sorbed Fe(II) is expected to behave as a catalyst

and dramatically enhance the ^{99}Tc removal from solutions after reduction of $^{99}\text{Tc(VII)}$ to $^{99}\text{Tc(IV)}$. Finally, the mineral transformation was tested with varied spiked ^{99}Tc concentrations in slurry to investigate the maximum ^{99}Tc loadings that can be retained by the final product using the selected minerals and conditions. Table 1 lists the experimental matrix in this testing, and examples of the mineral transformation reactors (50-mL polyethylene centrifuge tubes) are shown in Figure 1.

Table 1. Experimental Setup for ^{99}Tc Removal Through Mineral Transformation

Initial Mineral Types	Solution to Solid Ratio (mL/g)	Temperature (°C)	Contact Times	Final pH	Fe ²⁺ Addition (M)	^{99}Tc Spike (M)		
Fe(OH) ₂ (s), Ferrihydrite, or Magnetite	100	21°C	3 d, 14 d, 30 d	~7	0	No		
			3 d, 14 d, 30 d	~12	0	No		
		80°C	3 d, 14 d, 30 d	~7	0	No		
			3 d, 14 d, 30 d	~12	0	No		
		21°C	3 d, 14 d, 30 d	~7	0	No		
			3 d, 14 d, 30 d	~12	0	No		
	1,000	21°C	3 d, 14 d, 30 d	~7	0	No		
			3 d, 14 d, 30 d	~12	0	No		
		80°C	3 d, 14 d, 30 d	~7	0	No		
			3 d, 14 d, 30 d	~12	0	No		
		Fe(OH) ₂ (s)	1,000	21°C	7 d	~12	0 7E-06 2E-05 2E-04 0	1E-05
						~12	7E-06 2E-05 2E-04	1E-05
75°C	7 d			~12	0 0	1E-04 1E-03		
				~12	0 0	1E-04 1E-03		
21°C	7 d			~12	0	1E-04		
				~12	0	1E-03		
75°C	7 d	~12	0	1E-04				
		~12	0	1E-03				
Oxidized Fe(OH) ₂ (s) with predominant magnetite ^(a)	1,000	21°C	14 d, 42 d	~12	0	1E-05 1E-04 1E-03		
				~12	0	1E-05 1E-04		
		75°C	14 d, 42 d	~12	0	1E-05 1E-04		

(a) Initial Fe(OH)₂(s) that was oxidized by air contact showed predominantly magnetite mineral based on Mössbauer analysis.

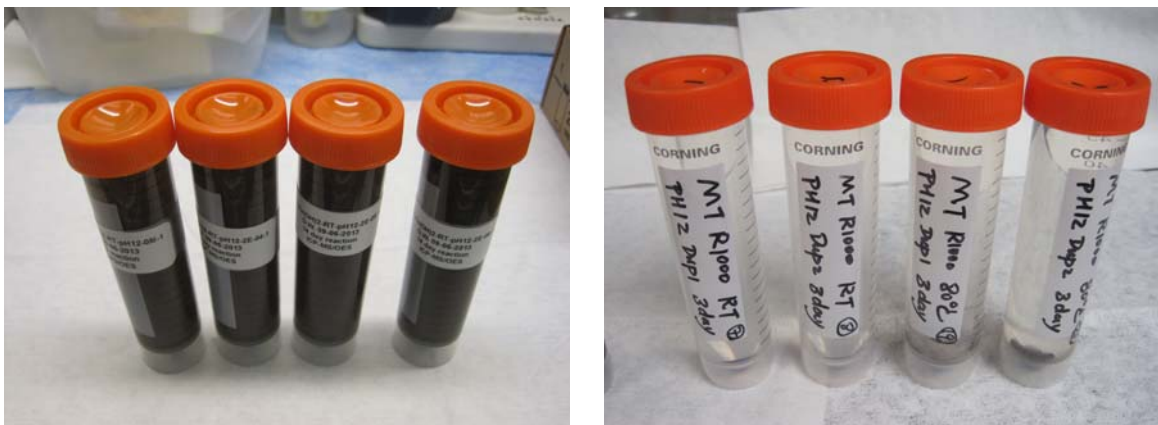


Figure 1. Centrifuge Tube Reactors Used for Mineral Transformation Tests and Tc Removal. Left: ^{99}Tc -spiked $\text{Fe}(\text{OH})_2(\text{s})$ slurries prepared at pH ~ 12 with various ferrous Fe concentration additions at room temperature (RT) after 18 hours reaction; right: pure magnetite used for mineral transformation screening tests at pH ~ 12 and RT conditions after reacting for three days.

Mineral transformation of three synthesized initial Fe (oxy)hydroxide minerals [ferrihydrite, magnetite, and $\text{Fe}(\text{OH})_2(\text{s})$] to a more crystalline Fe (oxy)hydroxide such as goethite was tested under various experimental conditions. The mineral transformation was conducted at two different temperatures (21°C and $75\text{--}80^\circ\text{C}$) under two pH conditions (circumneutral pH of $6\text{--}7.5$ and basic pH of 12). About 0.05 g or 0.1 g of the synthesized individual mineral solid was resuspended in 50 mL or 10 mL DI water in centrifuge tubes to achieve two solution-to-solid ratios of 1000 and 100 , respectively. The initial solution pHs (~ 7 and 12) in the reactors were adjusted by addition of 1 M HNO_3 or NaOH . Duplicate parallel reaction tubes for each testing condition were set up with varying reaction times of 3 , 14 , and 30 days to observe the mineral transformation kinetics. High-temperature-condition samples were reacted inside an oven. The reaction tubes were hand shaken at least once per day during the entire testing period. At the designed time intervals, the reaction tubes were moved out of the sample batches, and both 21°C and 80°C reaction tubes were kept right side up overnight to enable the solid particles to separate from solution through settlement. Then the supernatant was carefully decanted out of the reaction tubes, and the remaining mineral slurry was filtered using a $0.02\text{-}\mu\text{m}$ syringe filter and dried in air. The final solid samples were used for the solid characterization by XRD and SEM analysis to confirm the mineral transformation if there was any. For the experiment using $\text{Fe}(\text{OH})_2(\text{s})$, the solid was initially resuspended in deoxygenated DI water and the solution pH was adjusted inside an anaerobic chamber, then the reaction tubes containing $\text{Fe}(\text{OH})_2(\text{s})$ were completely sealed and moved outside of the chamber to react at 21°C and 80°C conditions. The supernatant pH was measured with a solid-state pH electrode and a pH meter (Hanna, Model HI 4521). Before taking the measurement, the pH probe was calibrated with National Bureau of Standards buffers (pH = 7.0 , 10.0 , and/or 13.0 at 25°C).

The mineral transformation screening test results showed that both ferrihydrite and $\text{Fe}(\text{OH})_2(\text{s})$ could be successfully transformed into goethite, especially under high temperature (80°C) and high pH (~ 12) conditions at a solution-to-solid ratio of 1000 . More details can be found in Section 3.0. Therefore, further ^{99}Tc removal experiments were prepared using $\text{Fe}(\text{OH})_2(\text{s})$ as an initial Fe mineral substrate with varying ferrous Fe solution concentrations. Inside an anaerobic chamber, 0.0 , 0.0006 , 0.0017 , and 0.0166 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 210 mL DI water to achieve ferrous Fe solutions of about 0.0 ,

14×10^{-6} , 4×10^{-5} , and 4×10^{-4} M, respectively. The 0.0 M ferrous Fe solution (i.e., pure DI water) was used as a control condition to illustrate the ferrous Fe effects on the ^{99}Tc removal by mineral transformation. All the solution pHs were initially adjusted to \sim pH 3.3 using 2 M HNO_3 to avoid any ferrous Fe precipitating from the solution at higher pH conditions. Then 0.05 g of the synthesized $\text{Fe}(\text{OH})_2(\text{s})$ was resuspended in 25 mL of each of the four different ferrous Fe solutions in 50-mL-size centrifuge tubes, and kept inside the chamber overnight. The solution with a ^{99}Tc spike of 2×10^{-5} M was prepared outside the anaerobic chamber with DI water in which the solution pH was adjusted to pH \sim 12 using 1 M NaOH. The 25 mL of $\text{Fe}(\text{OH})_2$ slurries with different ferrous Fe concentrations were mixed with 25 mL of ^{99}Tc -spiked solution outside the anaerobic chamber, leading to a final solution-to-solid ratio of 1,000 with a final pH value ranging 9 to 11.5 immediately after each solution was mixed. Because of 1:2 dilution with mixing two 25-mL solutions, the final concentrations of Fe(II) and ^{99}Tc as shown in Table 1 are half of those initially prepared in each 25-mL solution. The reaction tubes were immediately sealed after mixing the two solutions and the initial slurry still had a greenish color like that of green rust. The reaction lasted for seven days at both 21°C and 75°C temperatures with hand shaking at least once per day. After the reaction, about 4 mL of supernatant was collected and filtered using a 0.02- μm syringe filter, and the concentrations of ^{99}Tc and total Fe were determined using inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, respectively.

In addition, the ^{99}Tc removal capacity by the dominant mineral for transformation, $\text{Fe}(\text{OH})_2(\text{s})$, was tested with varying ^{99}Tc concentrations and no ferrous Fe addition. Although the original plan was to determine the maximum ^{99}Tc removal capacity by only pure $\text{Fe}(\text{OH})_2(\text{s})$, practically an extra ^{99}Tc -removal-capacity experiment was also conducted by using oxidized $\text{Fe}(\text{OH})_2(\text{s})$, i.e., the former synthesized $\text{Fe}(\text{OH})_2(\text{s})$ had been identified as oxidized and become a magnetite-dominated Fe mineral, which was confirmed by Mössbauer analysis later. Because $\text{O}_2(\text{g})$ contamination of 1 ppm $\text{O}_2(\text{g})$ concentration was detected inside the anaerobic chamber, the formerly synthesized $\text{Fe}(\text{OH})_2(\text{s})$ that had been stored in the same chamber, even in a capped vial, for more than six months could have contacted $\text{O}_2(\text{g})$ and oxidized to become the magnetite-dominant solid sample. Therefore, in this experiment, the ^{99}Tc -removal capacity experiments were carried out by using both new-synthesized fresh $\text{Fe}(\text{OH})_2(\text{s})$ and the oxidized one. About 0.05 g of the fresh or oxidized $\text{Fe}(\text{OH})_2(\text{s})$ solid was directly resuspended in 50 mL of ^{99}Tc -spiked solutions with three different ^{99}Tc concentrations of 10^{-5} , 10^{-4} , and 10^{-3} M at adjusted pH values of \sim 12. No ferrous Fe was added in these slurries to investigate the effect of ferrous Fe from $\text{Fe}(\text{OH})_2(\text{s})$ itself on ^{99}Tc removal. Similar to the conditions of the above $\text{Fe}(\text{OH})_2(\text{s})$ -ferrous Fe- ^{99}Tc experiments, these tests were also conducted at both 21°C and 75°C temperature conditions, whereas the reaction time intervals of seven days for the fresh-synthesized $\text{Fe}(\text{OH})_2(\text{s})$, and 14 and 42 days for the oxidized $\text{Fe}(\text{OH})_2(\text{s})$ were adopted. For the experiments using oxidized $\text{Fe}(\text{OH})_2(\text{s})$, after the 14-day reaction, about 2 mL of supernatant was collected for ^{99}Tc analysis and the reaction was continued with the remaining 48-mL solution until the next sampling time of 42 days. The influence of withdrawing 2 mL supernatant from the reactor system was ignored due to its small volume reduction (4% of the initial total solution volume).

2.2.3 Reductive Capacity Measurement

The Ce(IV) method was used to determine the reductive capacity of the previous ^{99}Tc -goethite powder samples (2-2 and 2-5) as synthesized. The ^{99}Tc -goethite powder samples, sample 2-2 that was prepared without an additional armoring process and sample 2-5 that was prepared with an armoring

process (Um et al. 2011) were ground to a homogeneous powder and used to determine reductive capacity. In the Ce(IV) method, a Ce(IV) stock solution $[(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}]$ was prepared in 10% H_2SO_4 with a concentration of 30–60 mM depending on the reductive capacity of the specimen. Approximately 0.1 g of each sample was mixed with 15 mL of the Ce(IV) stock solution in a 20-mL quartz vial. Immediately after mixing, the vial was tightly closed and placed on a platform shaker. The sample was reacted at RT for seven days. After the seven-day reaction, the supernatant solution was filtered through a 0.45- μm syringe filter and 0.05 mL of ferroine solution $[0.025 \text{ M Fe}(\text{o-phenanthroline})_3^{2+}]$ was added to 5 mL of the filtrate. The final solution was titrated using 20 mM ammonium ferrous sulfate prepared in 4% H_2SO_4 solution until the solution developed and retained a lilac color. The reductive capacity was calculated by determining the difference between the oxidizing equivalent in Ce(IV) solution [meq Ce(IV)] and the reducing equivalent of Fe(II) needed to neutralize excess Ce(IV) after reaction with the sample [meq Fe(II)]. The final reductive capacity per gram of sample was determined by dividing the reductive capacity (meq) by the mass of the sample (g).

2.2.4 Long-Term Leaching Experiment

A long-term batch leaching experiment was conducted using a homogeneously ground ^{99}Tc -goethite powder sample, sample 2-5 that was prepared with further armoring process, at a solid concentration of 1 g/L ($\sim 0.1 \text{ g}/100 \text{ mL}$) with synthetic Hanford vadose zone pore water solution. The synthetic Hanford pore water with pH = 7.2 and ionic strength = 0.05 M was prepared to simulate the IDF pore water condition in the Hanford Site 200 East Area using the chemicals, CaSO_4 ($1.2 \times 10^{-2} \text{ M}$), NaNO_3 ($3.4 \times 10^{-3} \text{ M}$), NaHCO_3 ($3.0 \times 10^{-4} \text{ M}$), NaCl ($2.1 \times 10^{-3} \text{ M}$), MgSO_4 ($2.6 \times 10^{-3} \text{ M}$), MgCl_2 ($2.4 \times 10^{-3} \text{ M}$), and KCl ($7.0 \times 10^{-4} \text{ M}$). Independent leaching solutions were prepared as duplicates for different leaching times. For each ^{99}Tc -goethite leaching test, a subsample (2 mL) of supernate was collected from samples leached for three months, six months, one year, and two years after the test commenced using a 0.45- μm Nalgene® syringe filter and submitted for analyses of dissolved Fe(total) and ^{99}Tc concentrations. The pH was directly measured in the slurry leaching solution, and concentrations of Fe(total) and ^{99}Tc were determined using ICP-OES and ICP-MS, respectively. For the three-year reacted sample, the filtered solid powder sample that had been leached two years in the IDF solution was exposed to atmosphere for one more year. After the sample collection at the designated leaching and reaction times was completed, the powder ^{99}Tc -goethite sample 2-5 was separated by filtration and used to determine ^{99}Tc oxidation state change using x-ray absorption fine structure (XAFS) spectroscopy.

2.2.5 X-Ray Absorption Fine Structure Spectroscopy

The XAFS spectra were collected on Beamline 4-1 at the Stanford Synchrotron Radiation Laboratory. The ^{99}Tc -goethite solid samples were mounted on Teflon® sample holders and sealed with Kapton tape. A Si(220) double-flat crystal monochromator was used and the energy was calibrated by using the first inflection point of the ^{99}Tc K edge spectrum of the ^{99}Tc (VII) standard (KTcO_4) defined as 21.044 keV. The XAFS spectra of ^{99}Tc -standards and ^{99}Tc -goethite samples were collected in transmission and fluorescence mode, respectively, at RT using a 13-element germanium detector. Data reduction and analysis were performed using the software IFEFFIT (Newville 2001) and Athena/Artemis (Ravel and Newville 2005) after correction for detector dead-time. The x-ray absorption near-edge structure (XANES) spectra for the ^{99}Tc -goethite 2-5 samples were fit using a linear combination of the XANES

spectra of KTcO_4 as the Tc(VII) standard spectrum and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ as the Tc(IV) standard spectrum, respectively (Lukens et al. 2002).

3.0 Results and Discussion

3.1 Synthesis of Fe (Oxy)hydroxide Substrates

The XRD and SEM analysis results on the synthesized ferrihydrite, $\text{Fe}(\text{OH})_2(\text{s})$, and magnetite, as well as the potential transformed product, goethite, are shown in Figure 2. The two broad XRD patterns are typical for amorphous 2-line ferrihydrite, while the other three crystalline iron oxides showed sharp XRD patterns that matched well with the JADE reference peaks of each mineral. In the case of the synthesized $\text{Fe}(\text{OH})_2(\text{s})$, more than 90% of the synthesized minerals can be roughly identified as $\text{Fe}(\text{OH})_2(\text{s})$, while less than 10% of the minerals were identified to be a mixture of fougérite [$\text{Fe}(\text{OH},\text{Cl})$] and magnetite. A naturally occurring green rust mineral, fougérite forms a layered double hydroxide structure containing Fe(II) and Fe(III) in cation sites and OH^- , Cl^- , or CO_3^{2-} in anion sites. It is bluish-green in color with hexagonal platelets of submicron diameter (Figure 2 and Figure 3) and the ideal formula is $[\text{Fe}(\text{II})_4\text{Fe}(\text{III})_2(\text{OH})_{12}][\text{CO}_3] \cdot 3\text{H}_2\text{O}$, where OH^- and CO_3^{2-} can be replaced by Cl^- . For $\text{Fe}(\text{OH})_2(\text{s})$ XRD analysis, more magnetite content was detected in an oxidized darker grain sample. The amorphous morphology of ferrihydrite and the well-crystallized shapes of goethite, magnetite, and $\text{Fe}(\text{OH})_2(\text{s})$ were also detected in the SEM images (Figure 4). Amorphous shapes of ferrihydrite and $\text{Fe}(\text{OH})_2(\text{s})$ were clearly detected, while needle and hexagonal shapes typical of goethite and magnetite, respectively, were also found.

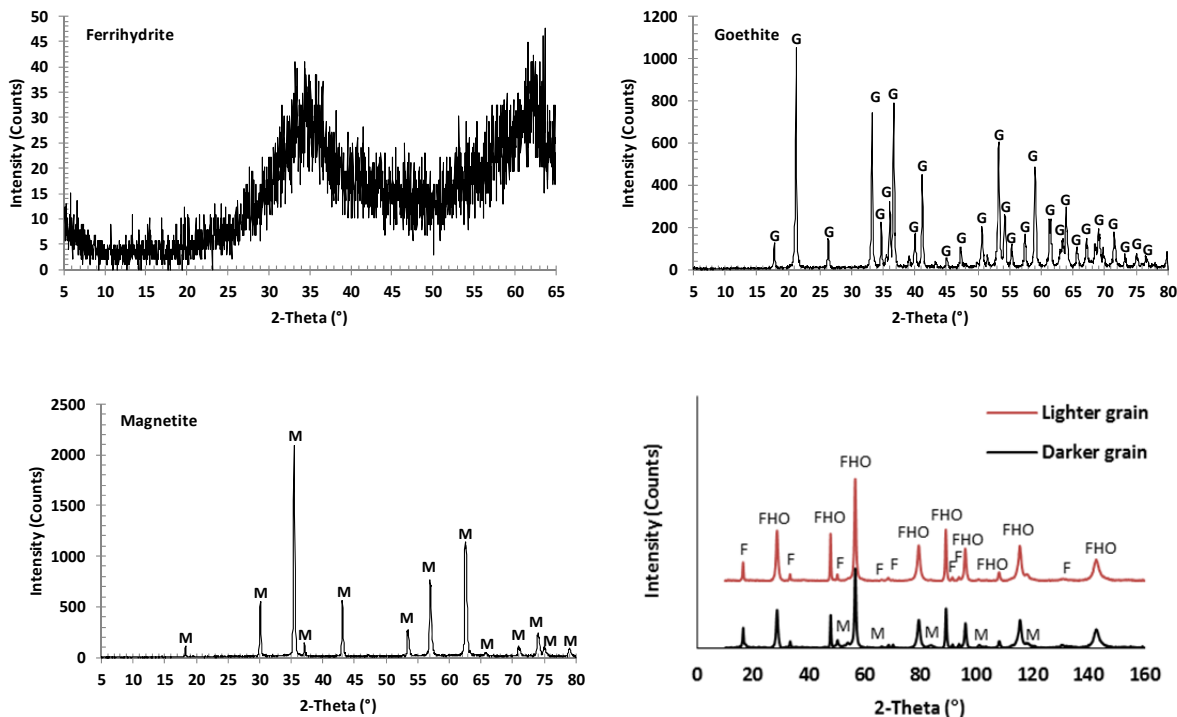


Figure 2. XRD Patterns of Synthesized 2-line Ferrihydrite, Goethite, Magnetite, and $\text{Fe}(\text{OH})_2(\text{s})$: G = goethite, M = magnetite, FHO = $\text{Fe}(\text{OH})_2(\text{s})$, F = Fougérite.



Figure 3. Photographs of Synthesized $\text{Fe}(\text{OH})_2(\text{s})$. Left: $\text{Fe}(\text{OH})_2(\text{s})$ with more fougurite; right: oxidized $\text{Fe}(\text{OH})_2(\text{s})$ showing darker color due to the presence of magnetite

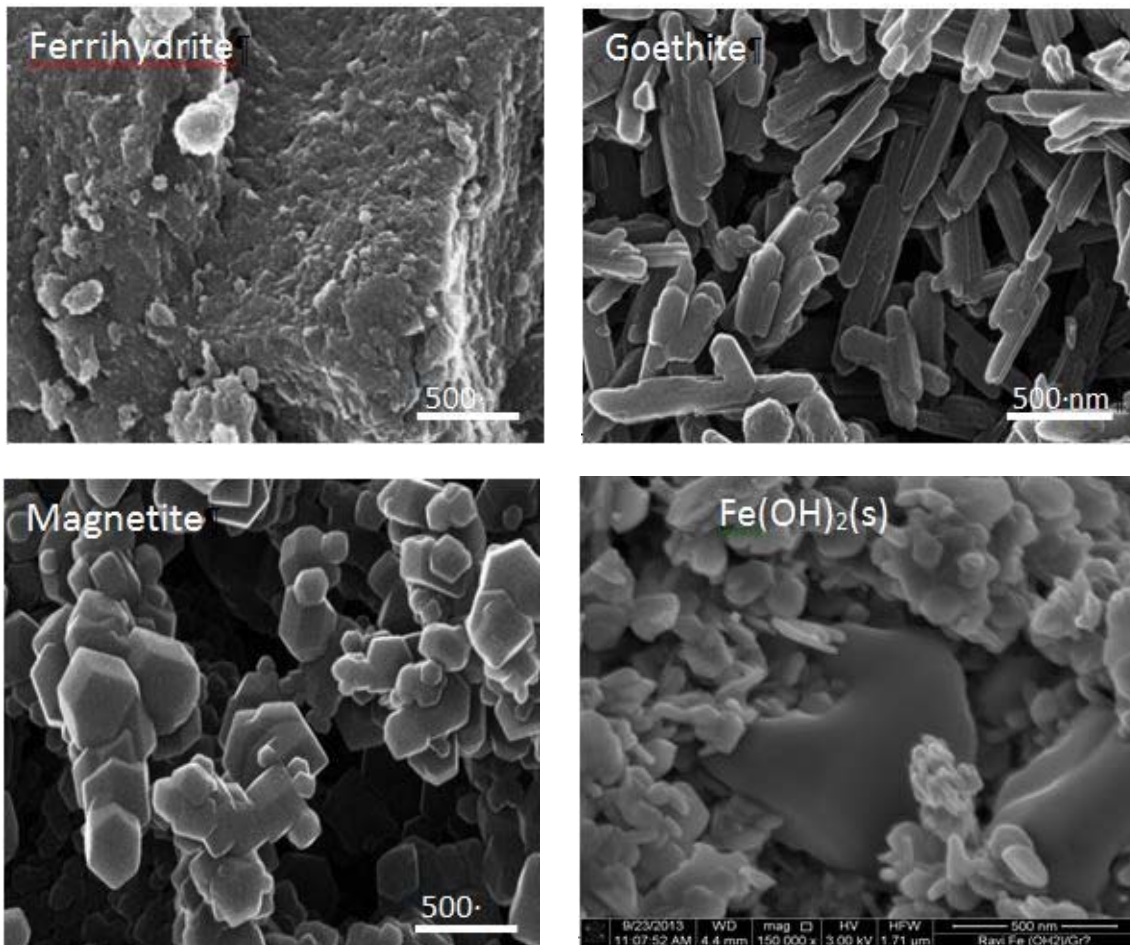


Figure 4. SEM Images and Morphology of Synthesized Ferrihydrite, Goethite, Magnetite, and $\text{Fe}(\text{OH})_2(\text{s})$

The freshly synthesized Fe(OH)₂(s) and the oxidized Fe(OH)₂(s) due to oxygen contact, as well as the final mineral product of Fe(OH)₂(s) reacted for 30 days at 80°C and pH 12 were characterized using Mössbauer spectroscopy. The Mössbauer spectra of these three Fe(OH)₂(s) samples are shown in Figure 5. The freshly synthesized Fe(OH)₂(s) Mössbauer spectrum indicates that besides Fe(OH)₂(s), other iron oxides containing Fe(II) and Fe(III) are also present. This agrees well with the XRD pattern of Fe(OH)₂(s) (Figure 2), which shows that less than 10% of the minerals are identified to be a mixture of fougérite and magnetite. This is not surprising since the pure white colored Fe(OH)₂(s) is amorphous and quite unstable, and thus even a trace amount of oxygen contact can lead to oxidation of part of the Fe(OH)₂(s) materials, resulting in greenish colored green rust like fougérite (Figure 3). Figure 5 also shows that after reacting at pH 12 and 80°C for 30 days, the initial Fe(OH)₂(s)-fougérite green rust mixture was transformed into maghemite, goethite, and other small-particle iron oxides (Figure 5-middle). This is expected since Fe(OH)₂(s) is very reactive, and a mixture of Fe(OH)₂(s) and fougérite green rust can be easily transformed to more stable and crystalline iron oxides, such as maghemite/magnetite and goethite. The Mössbauer spectrum fit of the former Fe(OH)₂(s) oxidized due to the anaerobic chamber failure (Figure 5-bottom) also indicates that the initial Fe(OH)₂(s) has been transformed to non-stoichiometric (NS) magnetite (>90%), i.e., partially oxidized magnetite (a mixture of maghemite and magnetite).

3.2 Mineral Transformation

Mineral transformation without ferrous Fe addition and ⁹⁹Tc spiking was tested under various conditions for all three synthesized Fe (oxy) hydroxide minerals [ferrihydrite, magnetite, and Fe(OH)₂(s)]. The fate and transformed final products differed from the initial mineral substrates depending on the transformation reaction conditions.

3.2.1 Transformation from Fe(OH)₂(s)

The mineral transformation from Fe(OH)₂(s) to a mixture of maghemite/magnetite and goethite was confirmed by XRD analysis. Figure 6 and Figure 7, respectively, show the mineral transformation of Fe(OH)₂(s) to a maghemite/magnetite and goethite mixture at pH 7 or pH 12 at both 80°C and RT (21°C) conditions after reacting for 30 days. Similar XRD patterns were found in the final product of maghemite/magnetite and goethite mixture generated from transformation of Fe(OH)₂(s) with solution-to-solid ratio of 1000 or 100 at RT and pH 7 or pH 12 after reacting for 30 days (Figure 8). However, much higher XRD peak intensity was found with the low solution-to-solid ratio of 100 under the same transformation conditions, because more solid content was used in the lower solution-to-solid ratio of 100 than 1000. The well-crystallized magnetite or goethite is thermodynamically more stable than the ferrous hydroxide, Fe(OH)₂(s). Even under anaerobic conditions, the ferrous hydroxide [Fe(OH)₂(s)] can be oxidized by protons of the water present to form magnetite by the Schikorr reaction (Schikorr 1933; Ardizzone and Formaro 1983):



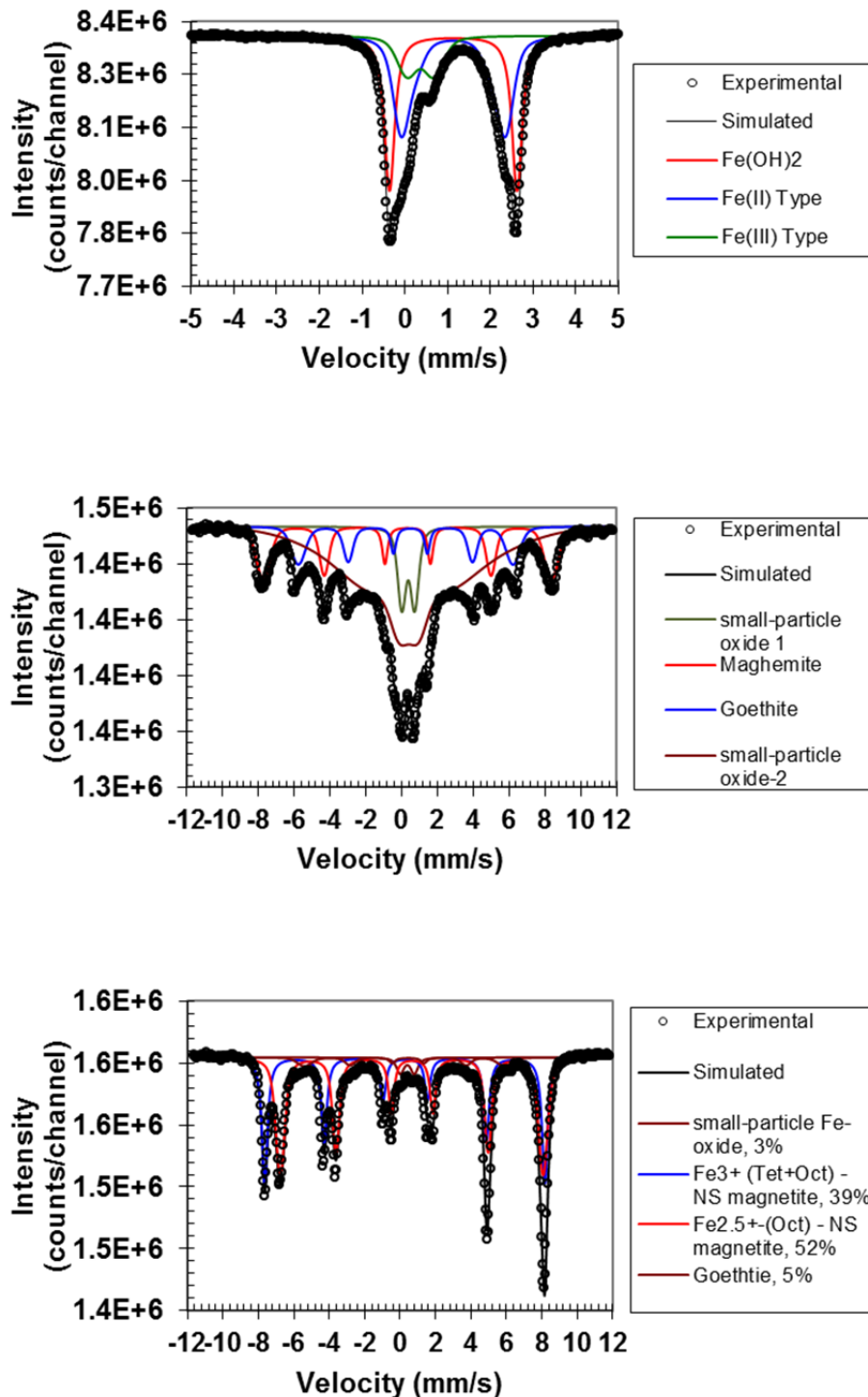


Figure 5. Mössbauer Spectra of the Fresh Fe(OH)₂(s) (top), Transformed Fe(OH)₂(s) Minerals Product after Fe(OH)₂(s) Reacted at pH 12 and 80°C (middle), and the Former Fe(OH)₂(s) Oxidized due to Oxygen Contact (bottom)

Compared with the XRD patterns of pure synthesized magnetite and goethite (Figure 2), the XRD intensity peaks in the regions of about 21.24 and 35.60 two-theta degree can be identified as goethite and

magnetite/maghemite “fingerprints” in this study. With the help of these “fingerprint” intensity counts, the mineral transformations under different transformation reaction conditions were compared. Figure 9 shows comparisons of mineral transformation products from $\text{Fe}(\text{OH})_2(\text{s})$ to maghemite/magnetite and goethite using goethite and maghemite/magnetite “fingerprint peaks” under different pHs, temperatures, and reaction durations under transformation conditions.

The results of comparison graphs show that pH 12 slurries under high temperature (80°C) led to the most goethite products whereas less goethite was observed under pH 7 and RT reaction conditions. Under the same temperature condition, either RT or 80°C , more goethite was produced from $\text{Fe}(\text{OH})_2(\text{s})$ at the higher pH condition of 12 than at pH 7. Even though the higher temperature and high pH condition produces more goethite from $\text{Fe}(\text{OH})_2(\text{s})$, certain amounts of goethite can be still produced even at pH = 7 and RT, which can allow a much easier operating process in a field site. Regarding the products with maghemite/magnetite mineral mixture, no significant differences were observed among different $\text{Fe}(\text{OH})_2(\text{s})$ transformation reaction conditions. This result implies that higher pH and heating condition favors the formation of more goethite product, while transformation from $\text{Fe}(\text{OH})_2(\text{s})$ to a maghemite/magnetite mixture does not depend on a specific condition and will be possible even in natural environmental geochemical conditions. This observation is also supported by the different XRD intensity counts for goethite (~60 to 125 counts) and for maghemite/magnetite (~250 counts). Regarding the mineral transformation kinetics, the mineral transformation was relatively fast in most of $\text{Fe}(\text{OH})_2(\text{s})$ reaction conditions based on the results in Figure 9. It seems that three–seven days could be long enough to produce goethite and maghemite/magnetite mixtures from $\text{Fe}(\text{OH})_2(\text{s})$ substrate.

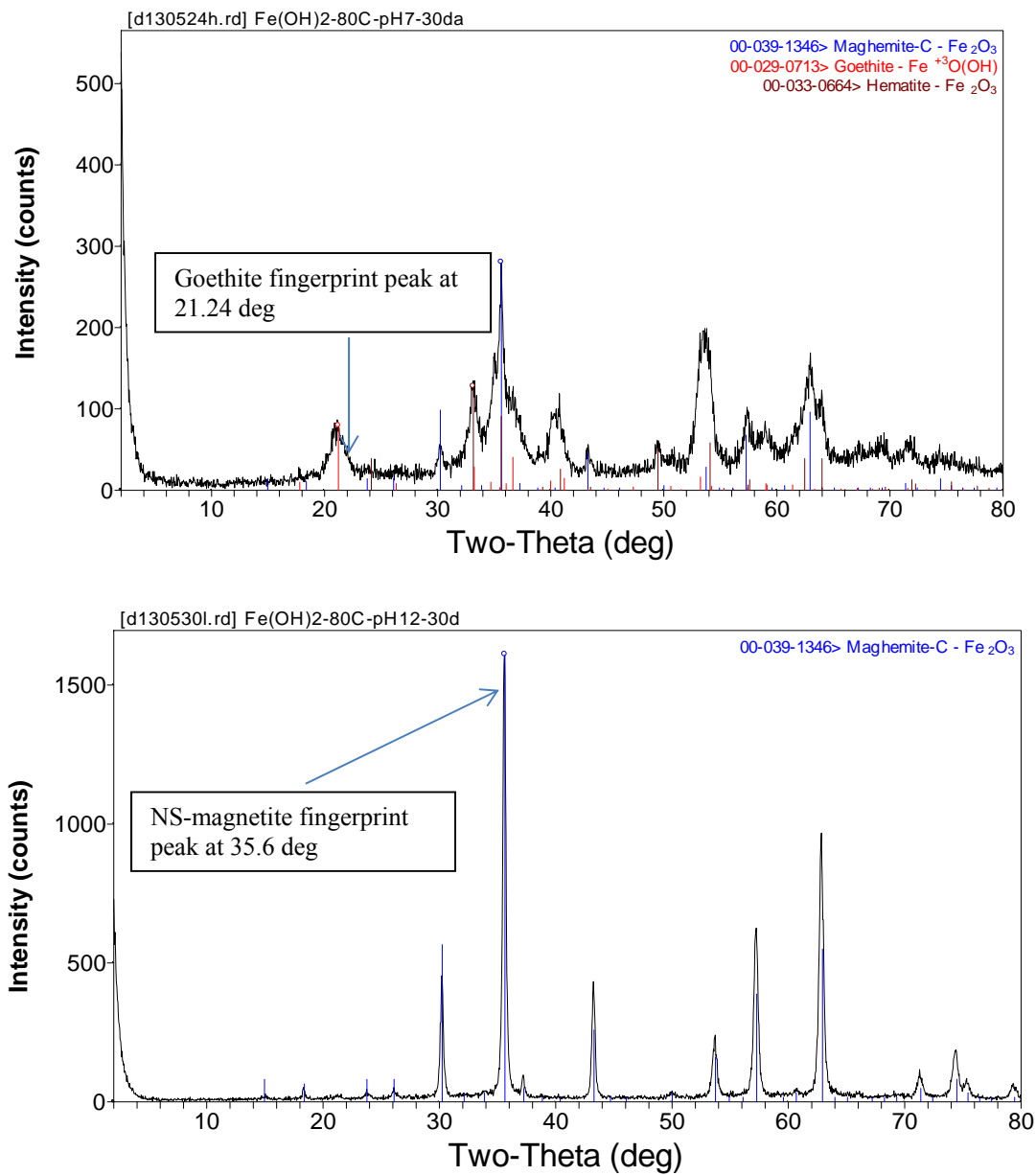


Figure 6. XRD Pattern of Maghemite/Magnetite and Goethite Mixture Transformed from Fe(OH)₂(s) Reacted Under pH 7 (top) and pH 12 (bottom) at 80°C with a Solution-to-Solid Ratio of 1000 for 30 Days

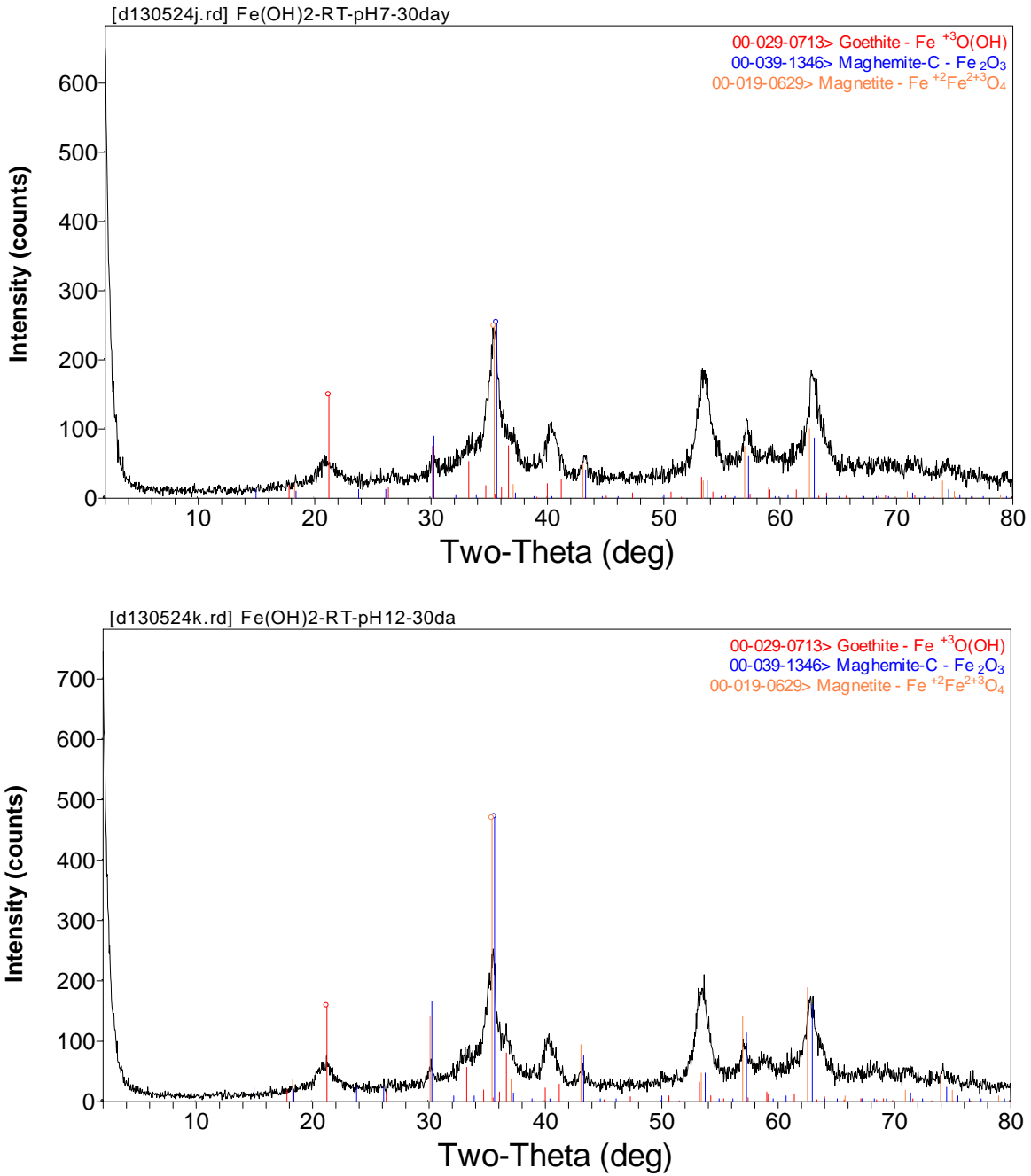


Figure 7. XRD Pattern of Maghemite/Magnetite and Goethite Mixture Transformed from Fe(OH)₂(s) Reacted at pH 7 (top) and pH 12 (bottom) at 21°C with a Solution-to-Solid Ratio of 1000 for 30 Days

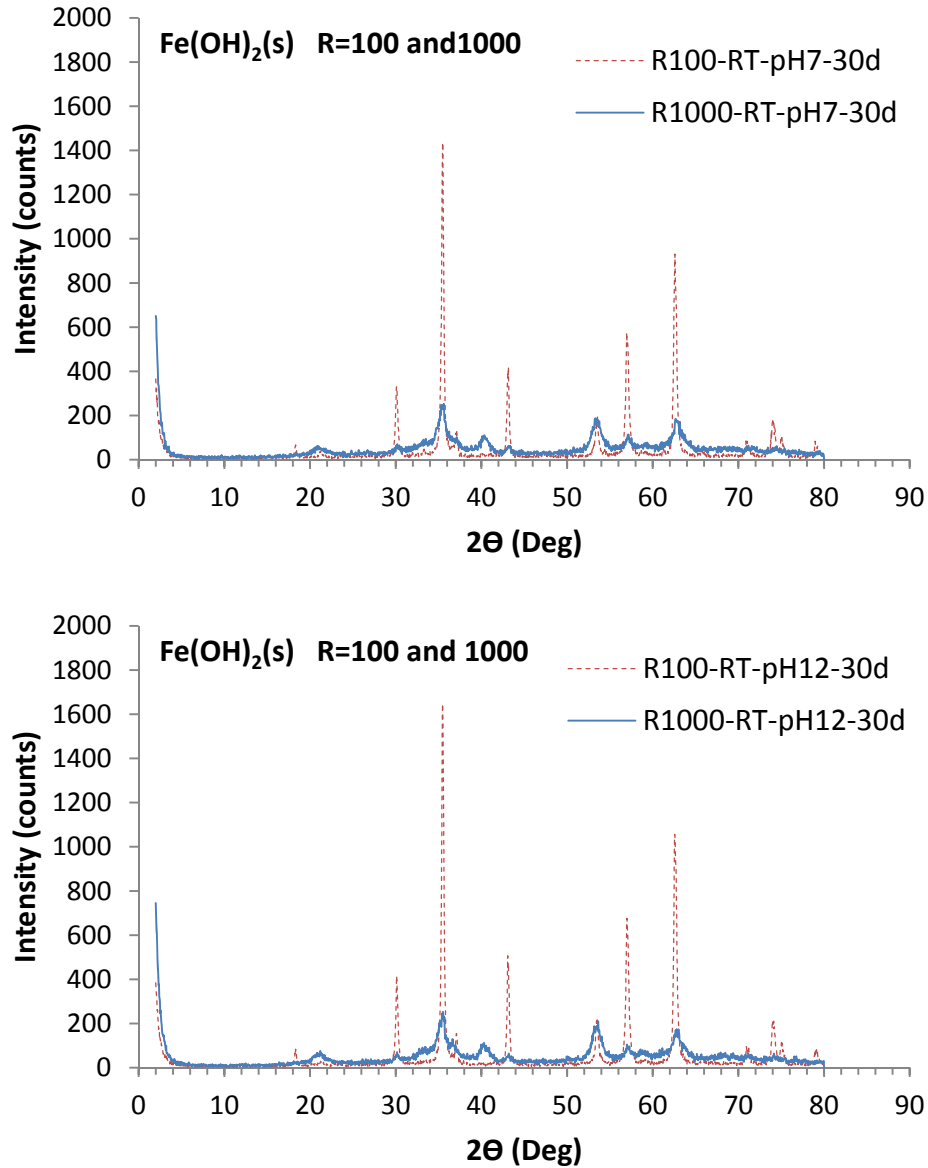


Figure 8. XRD Patterns of Transformed $\text{Fe(OH)}_2(\text{s})$ Product Reacted at pH 7 (top) and pH 12 (bottom) at 21°C with Different Solution-to-Solid Ratios of 1000 or 100 for 30 Days. The higher intensity of XRD peaks was found with the ratio of 100 because more $\text{Fe(OH)}_2(\text{s})$ was used at the low solution-to-solid ratio of 100 [0.1 g of $\text{Fe(OH)}_2(\text{s})$ for ratio 100 vs. 0.05 g of $\text{Fe(OH)}_2(\text{s})$ for ratio 1000].

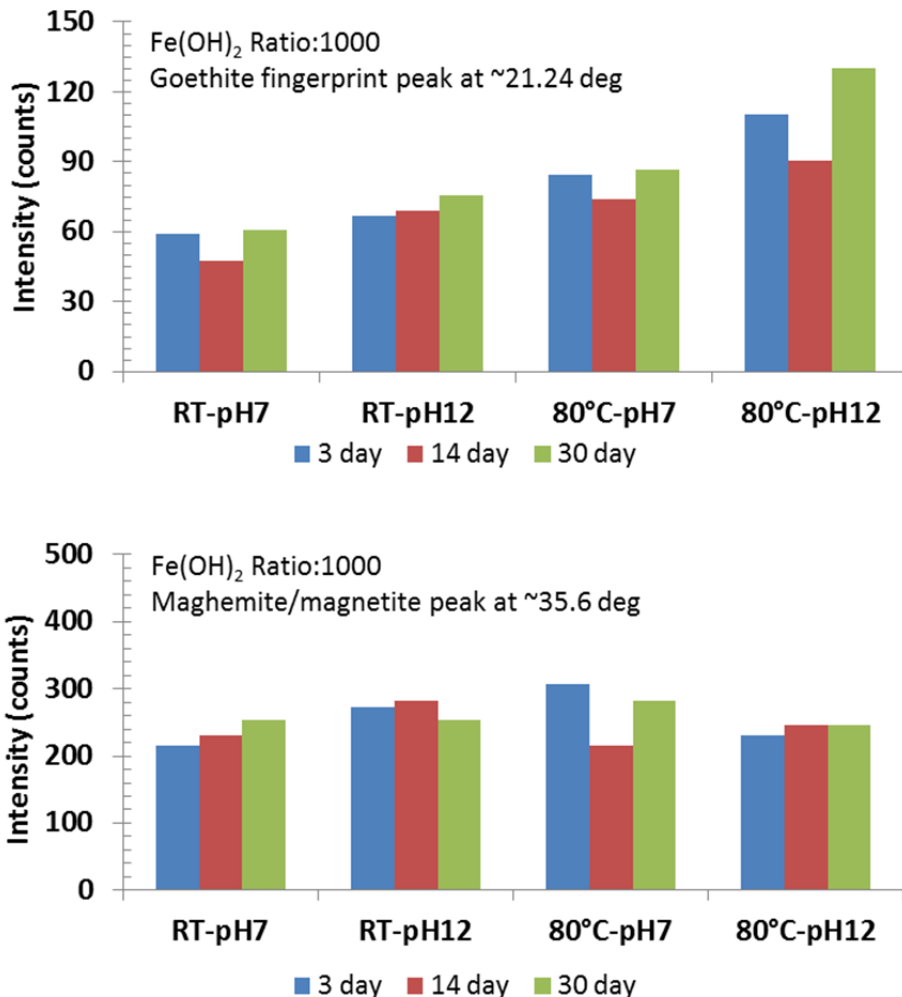


Figure 9. Comparison of Mineral Transformation Products from $\text{Fe}(\text{OH})_2(\text{s})$ to Goethite (top) and Maghemite/Magnetite (bottom) Using Goethite and Maghemite/Magnetite “Fingerprint XRD Peak” Under Different Slurry pHs, Temperatures, and Reaction Days

3.2.2 Transformation from Ferrihydrite

The difference in XRD patterns before and after the transformation reactions from ferrihydrite that was used as initial substrate illustrated the potential of ferrihydrite transformation to solely goethite. The XRD patterns of the goethite produced from ferrihydrite transformation under pH 7 or pH 12 at both 80°C and RT (21°C) conditions after reacting for 30 days are shown in Figure 10 and Figure 11, respectively. The XRD patterns for ferrihydrite transformation reactions were similar for solution-to-solid ratios of 100 and 1000 (Figure 12). Using the same comparison method previously applied for $\text{Fe}(\text{OH})_2(\text{s})$ transformation products, the goethite “fingerprint” peak at $\sim 21.24^\circ$ two-theta, the products of transformation from ferrihydrite under different reaction conditions were evaluated. Figure 13 compares results of mineral transformation product from ferrihydrite among different pHs, temperatures, and reaction durations. Figure 14 shows the complete XRD patterns for both pH 7 and 12 and temperature 21°C and 80°C conditions after reacting for 30 days with a solution-to-solid ratio of 1000. Except at conditions of high pH (=12) and temperature (80°C) for 14 and 30 days reaction, most of the ferrihydrite

transformation product seems to be similar to goethite with the same intensity no matter what pH and temperature condition was used. It is clear that both comparison results from $\text{Fe}(\text{OH})_2(\text{s})$ and ferrihydrite substrates imply that a high slurry pH and high temperature condition favors more goethite formation from ferrihydrite transformation. Regarding the mineral transformation kinetics, since no great intensity difference was observed for different reaction durations (Figure 13), it appears that three–seven days could be long enough for most of the experimental setup to complete mineral transformation.

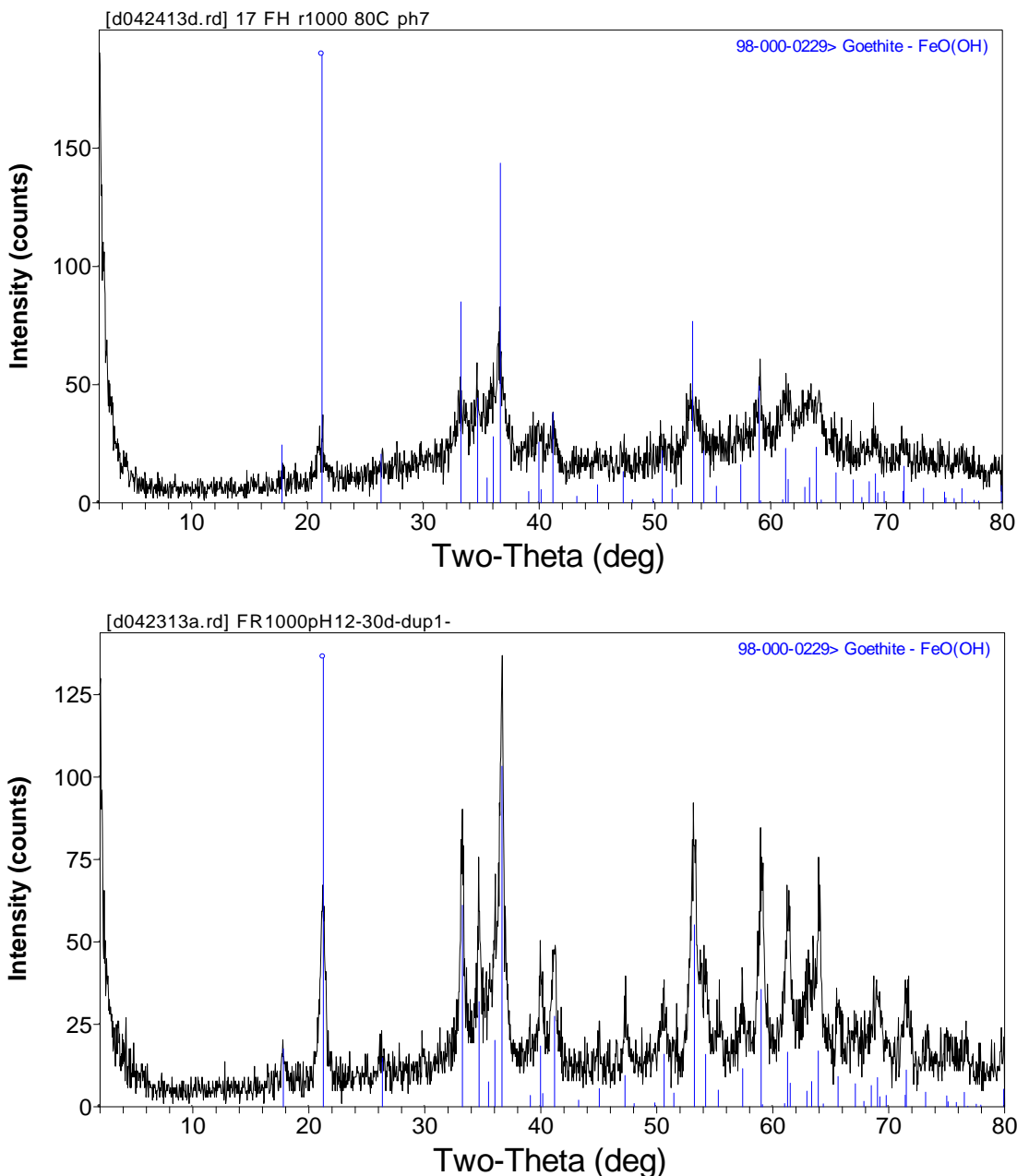


Figure 10. XRD Patterns of Goethite Transformed from Ferrihydrite under pH 7 (top) and pH 12 (bottom) at 80°C with a Solution-to-Solid Ratio of 1000 After Reacting for 30 Days

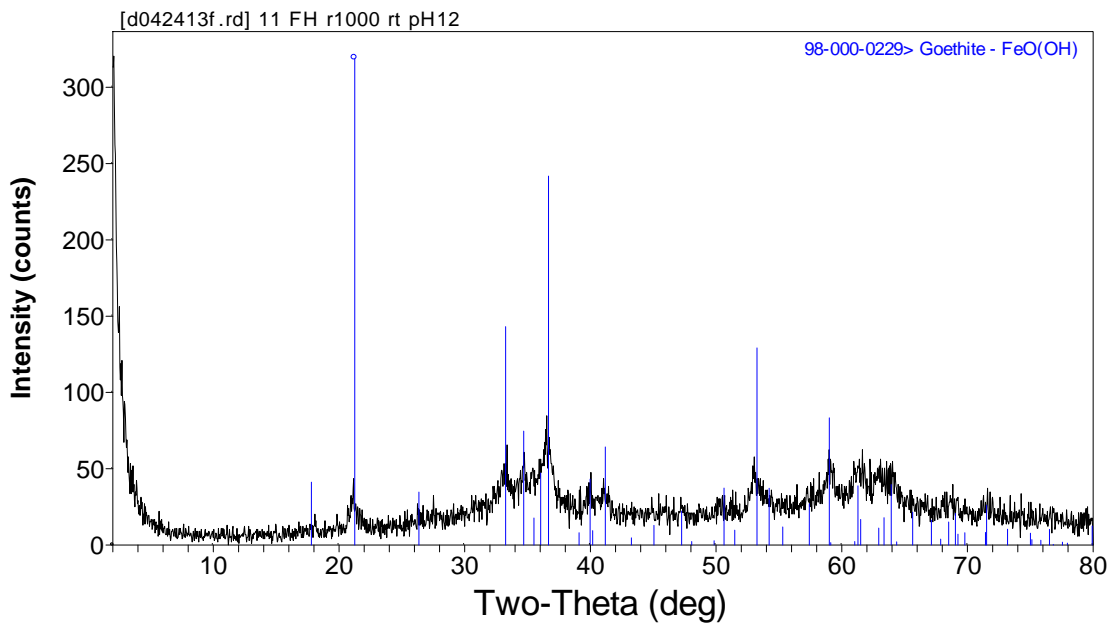
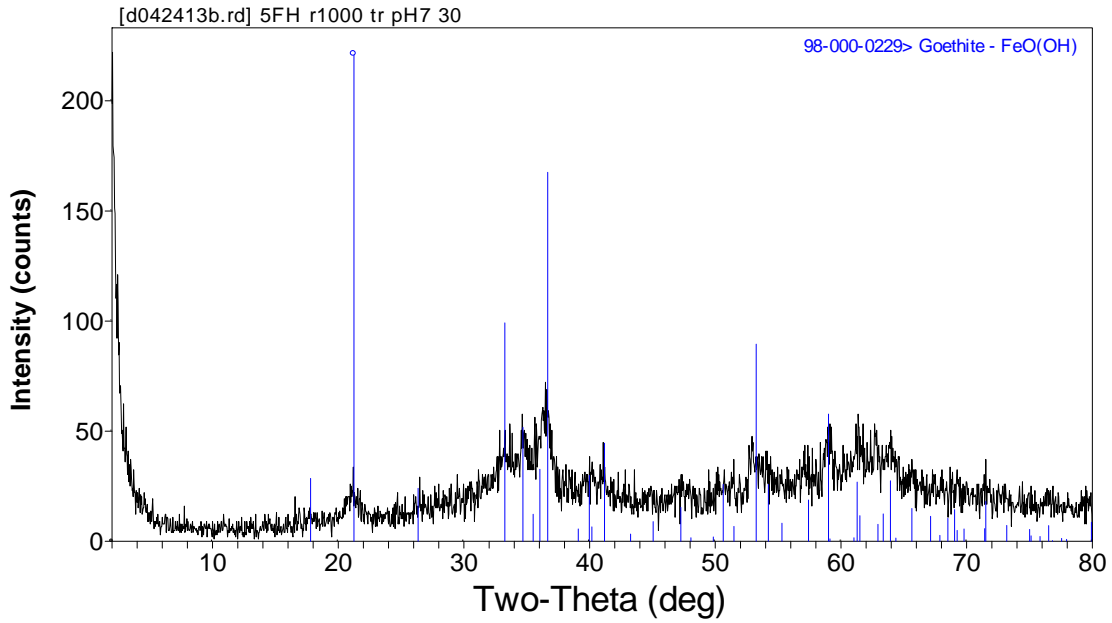


Figure 11. XRD Patterns of Goethite Transformed from Ferrihydrite at pH 7 (top) and pH 12 (bottom) at RT (21°C) with a Solution-to-Solid Ratio of 1000 After Reacting for 30 Days

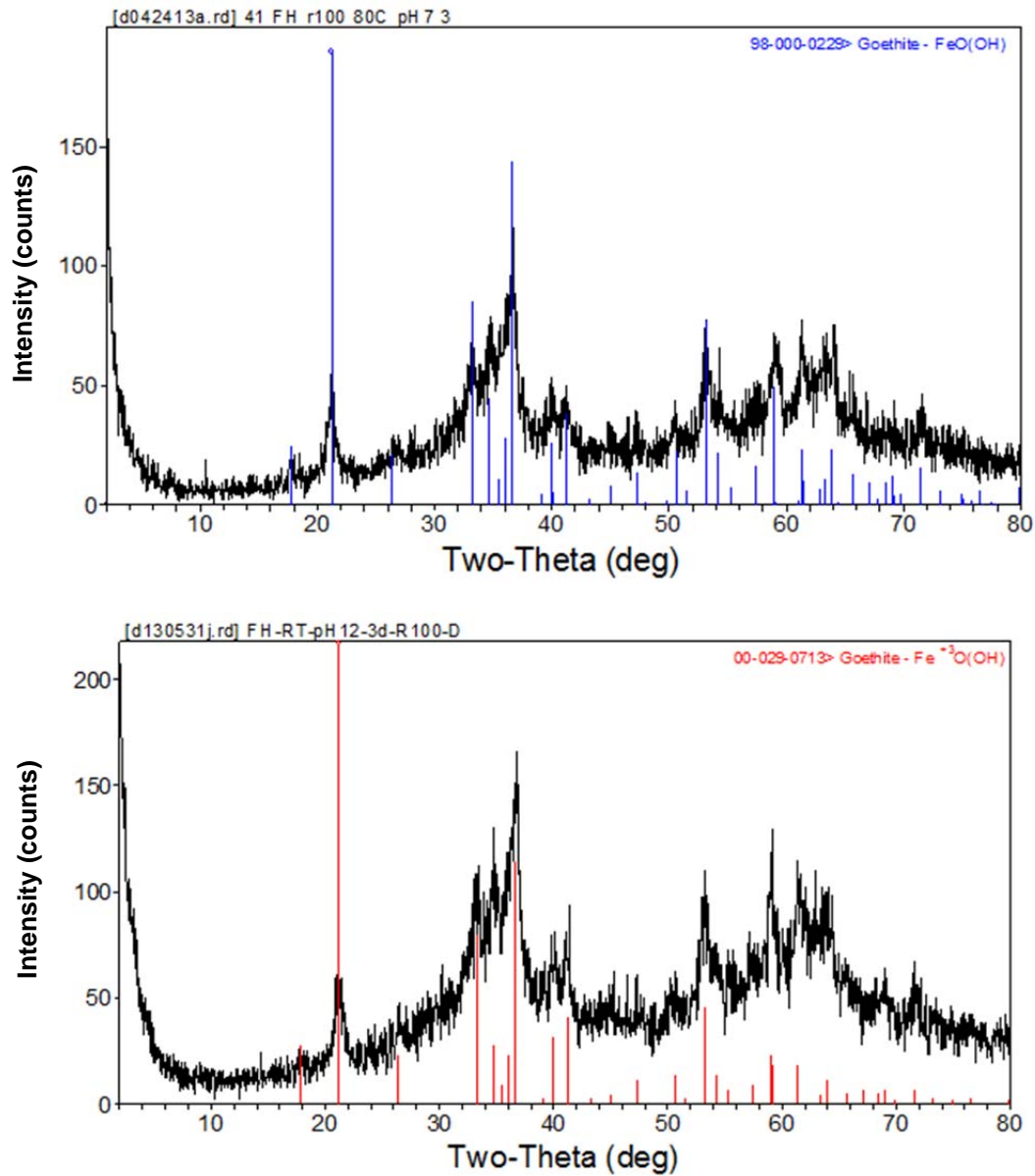


Figure 12. XRD Patterns of Goethite Transformed from Ferrihydrite at pH 7 and 80°C (top) and at pH 12 and RT (21°C) (bottom) with a Solution-to-Solid Ratio of 100 After Reacting for Three Days

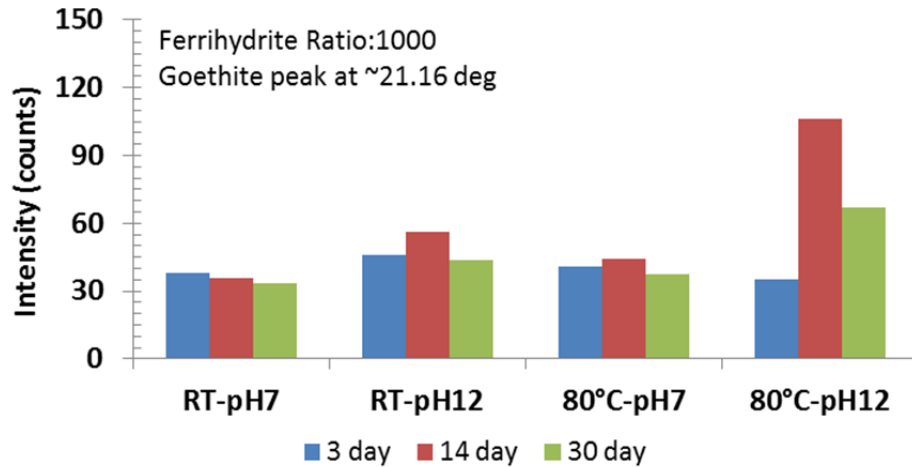


Figure 13. Comparison of Mineral Transformation Products from Ferrihydrite to Goethite Using Goethite “Fingerprint XRD Peak” Among Different Slurry pHs, Temperatures, and Reaction Days

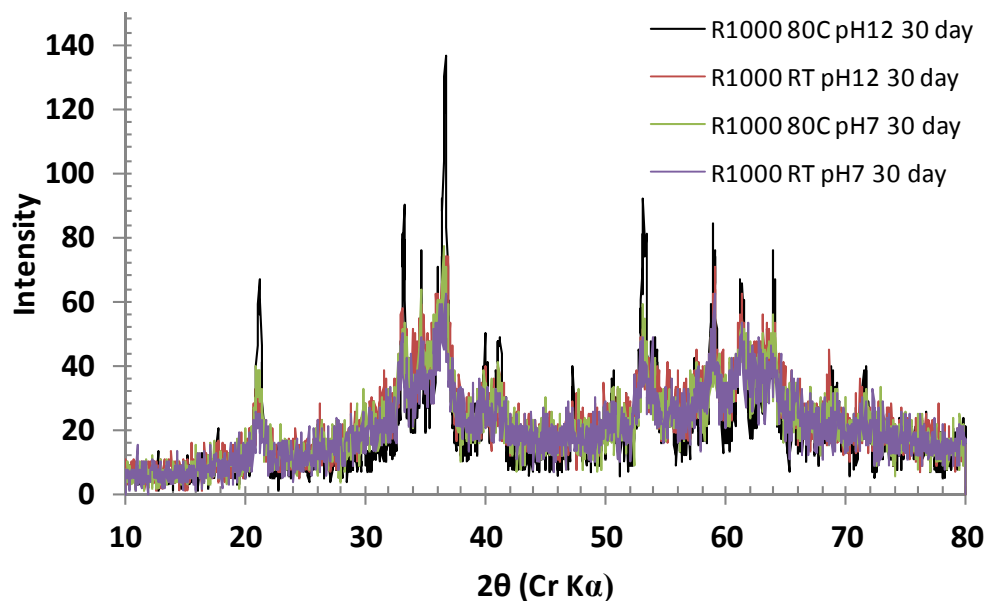


Figure 14. XRD Patterns of Goethite Transformed from Ferrihydrite Under Different pHs (7 and 12), and RT and 80°C Conditions after Reacting for 30 Days. R1000 indicates the solution-to-solid ratio of 1000.

3.2.3 Transformation from Magnetite

The XRD patterns before and after the reactions of magnetite illustrated that the transformation of magnetite was quite limited, implying that magnetite is stable in most of the experimental conditions. No obviously new transformed mineral product was created after slurry with a solution-to-solid ratio of 1000 reacted for three days at 80°C and pH 7 (Figure 15). Only a limited amount of the magnetite was

transformed to maghemite, goethite, and hematite while the majority of the magnetite remained unchanged even at pH 12 and 80°C conditions with a solution-to-solid ratio of 1000 after reacting for 30 days (Figure 16).

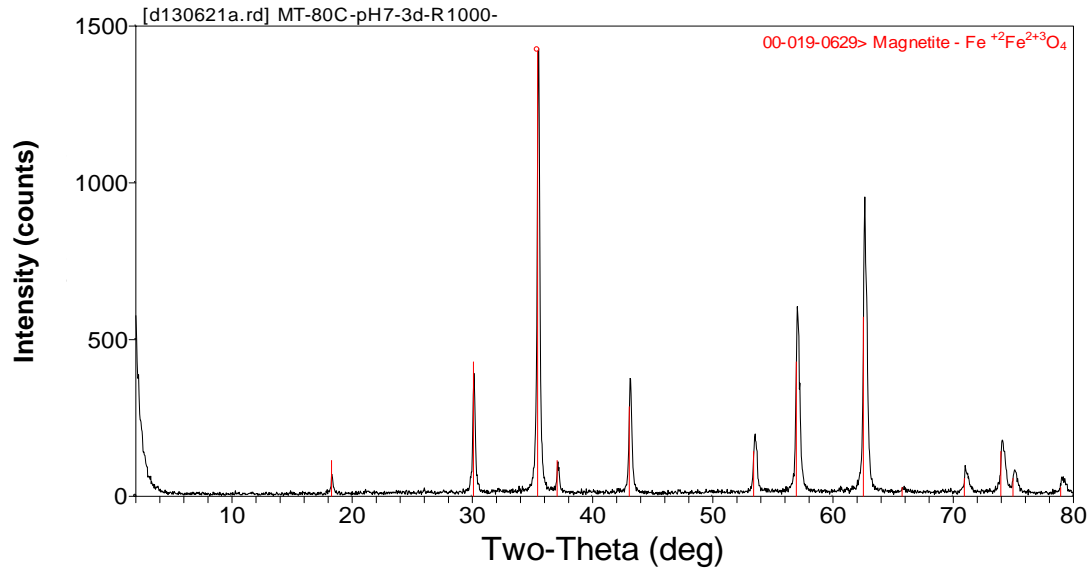


Figure 15. XRD Patterns of Transformed Magnetite at pH 7 and 80°C Conditions with a Solution-to-Solid Ratio of 1000 after Reacting for Three Days. No changes were observed.

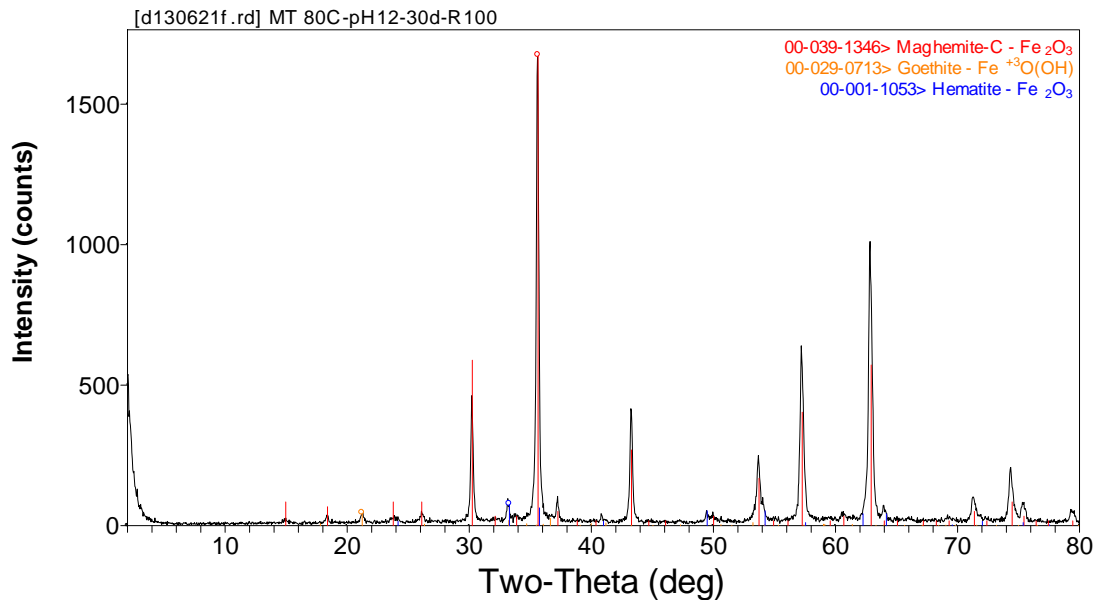


Figure 16. XRD Patterns of Transformed Magnetite at pH 12 and 80°C Conditions with a Solution-to-Solid Ratio of 1000 after Reacting for 30 Days. Limited mineral transformation of magnetite to maghemite was observed, with the major content of magnetite unchanged.

3.3 Tc Removal by Fe Oxy (hydroxide) Mineral Transformation

3.3.1 Tc Removal by Fe(OH)₂(s) Transformation

Removal of ⁹⁹Tc(VII) from ⁹⁹Tc-spiked solution at pH ~12 by Fe(OH)₂(s) transformation reaction at both room (21°C) and elevated (75°C) temperatures was tested with or without addition of aqueous ferrous iron, Fe(II). A ⁹⁹Tc-spiked solution with a high pH of 12 was prepared to mimic the alkaline pH value of the off-gas scrubber secondary waste stream. Comparisons of the final ⁹⁹Tc concentrations to that of the control solution [⁹⁹Tc-spiked solution without Fe(OH)₂(s) addition] and the reaction solutions [⁹⁹Tc-spiked solution with Fe(OH)₂(s)] after reacting for seven days with varied aqueous Fe(II) concentrations added in the system are shown in Figure 17. In all the cases, the ⁹⁹Tc concentration in the reaction solutions was completely removed from the initial 10⁻⁵ M concentration, indicating that most of the ⁹⁹Tc originally in solution was sequestered into the solid phases due to the presence of Fe(OH)₂(s) in the reaction system. In terms of ⁹⁹Tc mass, Figure 18 illustrates that about only 2–4% of the spiked ⁹⁹Tc still remained in the aqueous phase, which means that 96–98% of the ⁹⁹Tc was removed from solution within seven days of reaction.

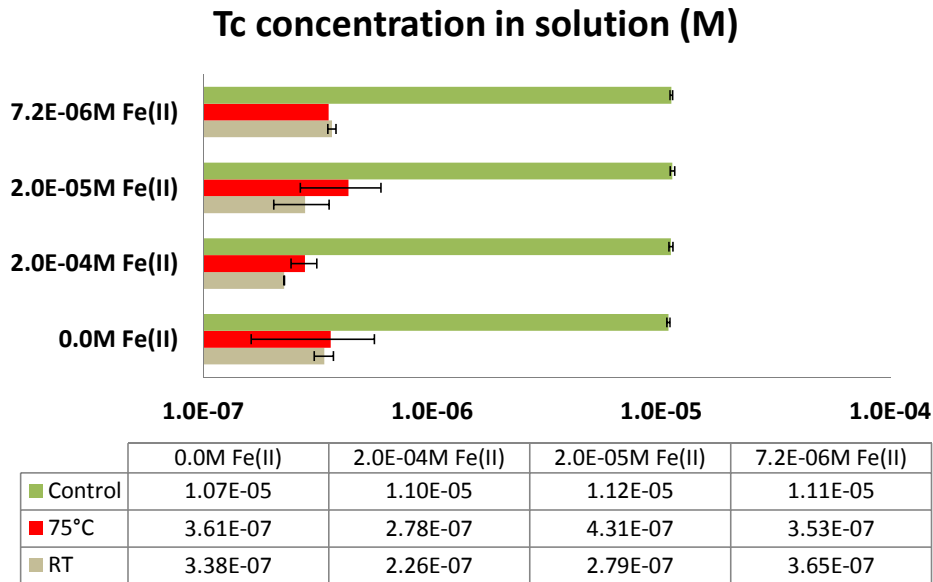


Figure 17. Comparisons of the Final ⁹⁹Tc Concentrations Between the Control Solution [⁹⁹Tc-spiked solution without Fe(OH)₂(s)] and the Solutions in the Reactors [⁹⁹Tc-spiked solution with Fe(OH)₂(s)] After Seven Days Reacting at Both Room (21°C) and High (75°C) Temperatures with Various Ferrous Iron Concentrations Added in the System. The solution-to-solid ratio in the reactors was 1000.

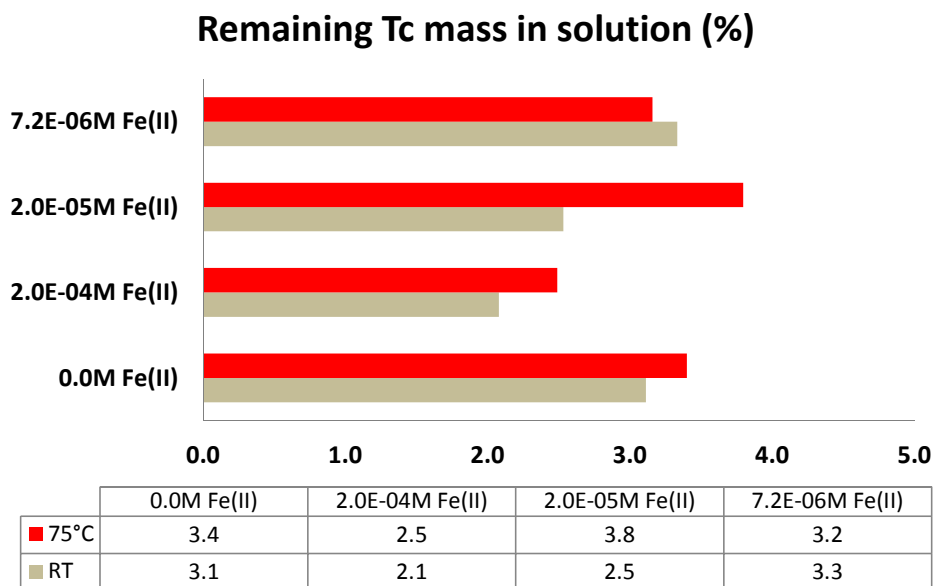


Figure 18. The Remaining ^{99}Tc Concentration (in percentage) in the $\text{Fe}(\text{OH})_2(\text{s})$ Reactors after Reacting for Seven Days at Both Room (21°C) and 75°C Temperatures with Different Ferrous Iron Concentrations Added in the System. The solution-to-solid ratio in the reactors was 1000.

Figure 17 and Figure 18 illustrate that the ^{99}Tc removal from solution was almost independent of the aqueous $\text{Fe}(\text{II})$ concentrations added in the reactor solutions, at least as long as $\text{Fe}(\text{OH})_2(\text{s})$ was present. In all the cases, the remaining ^{99}Tc concentration percentages in the final reacted solutions showed similar values of 2.1–3.3% and 2.5–3.8% for the experiments conducted at 21°C and 75°C , respectively. The remaining ^{99}Tc concentration in percentage at 75°C (2.5–3.8%) was a little bit higher than the values (2.1–3.3%) of ^{99}Tc concentration at RT. However, this difference is negligible since it is considered within the analytical uncertainty range ($\pm 5\%$), and also might be from potential evaporation of the solutions at high temperature. There was no ^{99}Tc removal found in any of the control solution samples under different conditions, and the final pHs of reaction solutions were between 9 and 11.5. There is also no significant difference in ^{99}Tc removal (2.5–3.3% and 3.2–3.8% of remaining ^{99}Tc for 21°C and 75°C , respectively) among the reaction solutions with different aqueous $\text{Fe}(\text{II})$ concentrations even without $\text{Fe}(\text{II})$ addition. However, carefully comparing the ^{99}Tc removal percentages in the solution with 10^{-4} M $\text{Fe}(\text{II})$ added with results of the other experiments shows clearly that the solution with 10^{-4} M $\text{Fe}(\text{II})$ added showed the highest ^{99}Tc removal, resulting in the minimum ^{99}Tc concentration remaining in the solution, with values of 2.1 and 2.5% for 21°C and 75°C temperatures, respectively. This indicates that $\text{Fe}(\text{II})$ addition still helps the ^{99}Tc removal from solution, but the main ^{99}Tc removal is considered to result from the mineral transformation, i.e., from $\text{Fe}(\text{OH})_2(\text{s})$ transformed to maghemite, magnetite, and goethite (Figure 9). During this mineral transformation process, $\text{Fe}(\text{II})$ in the $\text{Fe}(\text{OH})_2(\text{s})$ solid structure can oxidize to $\text{Fe}(\text{III})$ by releasing electrons, resulting in the formation of magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which is considered an $\text{Fe}(\text{II})$ -deficient magnetite with the same structure as magnetite, or goethite ($\alpha\text{-FeOOH}$), while $^{99}\text{Tc}(\text{VII})$ is reduced to $^{99}\text{Tc}(\text{IV})$ by electron acceptance before being incorporated within the final transformed mineral structure. The mineral transformation could be confirmed by the color change of $\text{Fe}(\text{OH})_2(\text{s})$ in the solutions. The initial blue-greenish color of $\text{Fe}(\text{OH})_2(\text{s})$ turned to black after one day reacting under this condition. Removal of ^{99}Tc is also possible through a coprecipitation process with respect to maghemite or magnetite as reduced $\text{Tc}(\text{IV})$ species.

Geckeis et al. (2012) found that $^{99}\text{Tc(IV)}$ tends to be fully compatible with the hematite lattice, and Um et al. (2012) reported removal of Tc(IV) using goethite through coprecipitation. However, further tests for solid characterization, with ^{99}Tc speciation analysis as well as Fe(II) concentration changes in solutions, should be conducted to confirm ^{99}Tc incorporation into the $\text{Fe(OH)}_2(\text{s})$ transformed minerals.

Removal of $^{99}\text{Tc(VII)}$ from ^{99}Tc -spiked solution at $\text{pH} \sim 12$ by $\text{Fe(OH)}_2(\text{s})$ transformation reaction at both room (21°C) and elevated (75°C) temperatures was also tested with varied ^{99}Tc -spiked amount in the system. The initial ^{99}Tc aqueous concentration in the reaction system was of 10^{-5} , 10^{-4} , and 10^{-3} M. Comparisons of the final ^{99}Tc concentrations of the reaction solutions [^{99}Tc -spiked solution with $\text{Fe(OH)}_2(\text{s})$] with varied initial aqueous ^{99}Tc concentrations spiked in the system after reacting for seven days to that of the control solution [^{99}Tc -spiked solution without $\text{Fe(OH)}_2(\text{s})$ addition] for the same seven-day reaction are shown in Figure 19. More ^{99}Tc removal was found at elevated (75°C) temperature than room (21°C) temperature, even though the ^{99}Tc removals at 21°C and 75°C temperatures with initial ^{99}Tc concentration of 10^{-5} M after seven days reaction were similar (or slightly opposite compared to the other results). In terms of ^{99}Tc mass, Figure 20 illustrates that about 3%, 14-23%, and 35-36% of the spiked ^{99}Tc remained in the aqueous phase after seven-day reaction with the initial ^{99}Tc concentrations of 10^{-5} , 10^{-4} , and 10^{-3} M in $\text{Fe(OH)}_2(\text{s})$ slurry, respectively, which means that 97%, 77-86%, and 64-65% of the ^{99}Tc was removed accordingly from solutions within seven days of reaction. Increasing ^{99}Tc removal percentage from $\text{Fe(OH)}_2(\text{s})$ transformation was found with increasing ^{99}Tc initial concentration up to 10^{-3} M as shown a linear relationship between the sequestered ^{99}Tc mass normalized by the initial $\text{Fe(OH)}_2(\text{s})$ mass versus the initial ^{99}Tc aqueous concentrations (Figure 20).

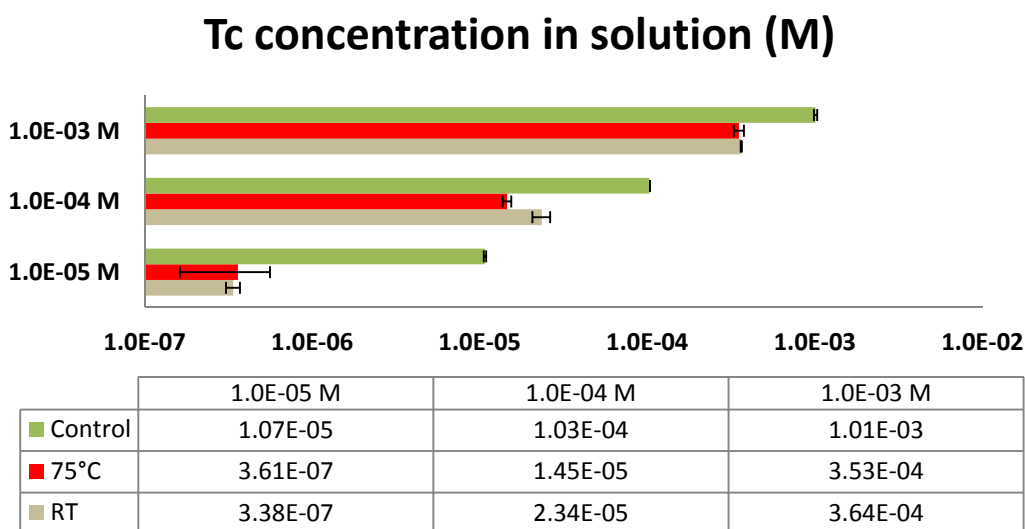


Figure 19. Comparisons of the Final ^{99}Tc Concentrations Between the Control Solution [^{99}Tc -spiked solution without $\text{Fe(OH)}_2(\text{s})$] and the Solutions in the Reactors [^{99}Tc -spiked solution with $\text{Fe(OH)}_2(\text{s})$] After Seven Days Reacting at Both Room (21°C) and High (75°C) Temperatures with Various ^{99}Tc -spiked Concentrations in the System. The solution-to-solid ratio in the reactors was 1000.

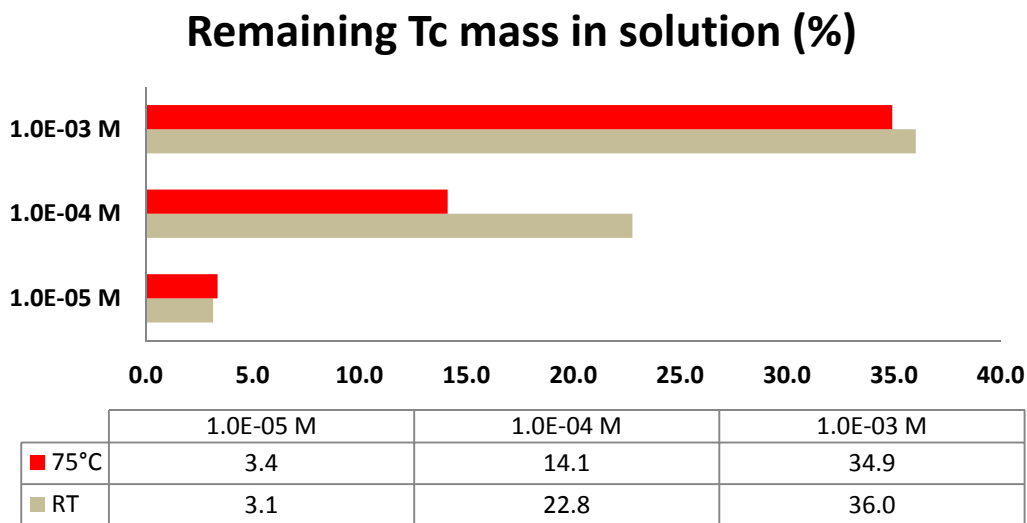


Figure 20. The Remaining ^{99}Tc Aqueous Concentration (%) in the $\text{Fe}(\text{OH})_2(\text{s})$ Reactors after Reacting for Seven Days at Both Room (21°C) and 75°C Temperatures with Different ^{99}Tc -spiked Concentrations of 10^{-5} , 10^{-4} , and 10^{-3} M in the System. The solution-to-solid ratio in the reactors was 1000.

Since the finally measured pHs were close to 11 after seven-day reaction, ^{99}Tc removal was not possible by surface adsorption of $^{99}\text{Tc}(\text{VII})$ on $\text{Fe}(\text{OH})_2(\text{s})$ under this high pH condition. It is clear that the removed ^{99}Tc mass normalized by the initial $\text{Fe}(\text{OH})_2(\text{s})$ mass after seven-day reaction increased with the increasing initial ^{99}Tc aqueous concentrations (Figure 21). Removal of ^{99}Tc is considered to follow $^{99}\text{Tc}(\text{VII})$ reduction to $^{99}\text{Tc}(\text{IV})$ first, which can be further incorporated within the final mixture of $\text{Fe}(\text{OH})_2(\text{s})$ transformation product. However, the presence of independent $^{99}\text{TcO}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ cannot be ruled out in this system, because of a linear relationship between the sequestered ^{99}Tc mass per the initial $\text{Fe}(\text{OH})_2(\text{s})$ and the initial ^{99}Tc aqueous concentrations. Additional XAFS study for the final product containing ^{99}Tc needs to investigate ^{99}Tc oxidation state and ^{99}Tc removal mechanism between $^{99}\text{Tc}(\text{IV})\text{O}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ precipitate and $^{99}\text{Tc}(\text{IV})$ incorporation within a final mixture of $\text{Fe}(\text{OH})_2(\text{s})$ transformation product.

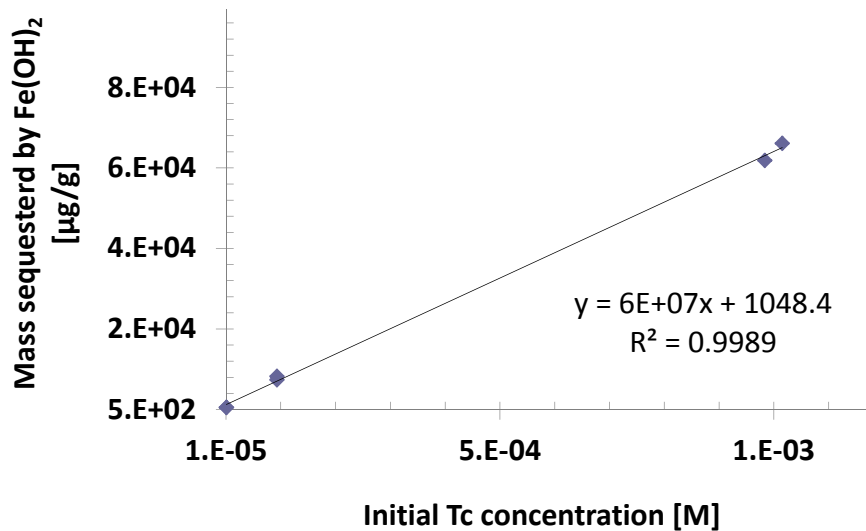
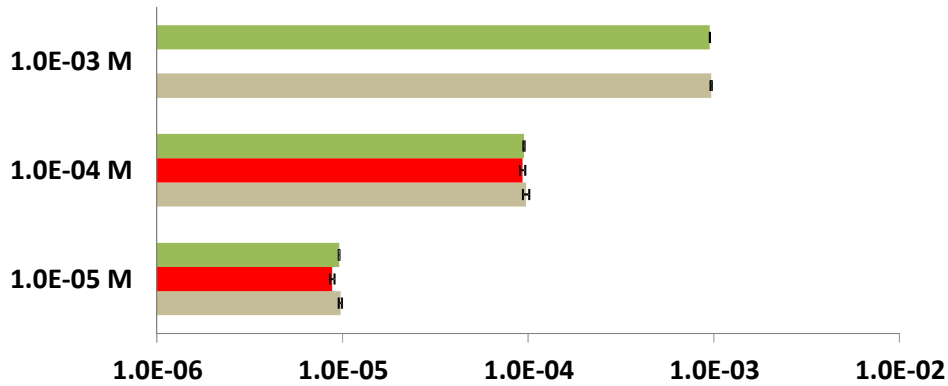


Figure 21. Removed ⁹⁹Tc Mass Normalized by the Initial Fe(OH)₂(s) Mass versus the Initial ⁹⁹Tc Aqueous Concentrations

3.3.2 Tc Removal by Magnetite Transformation

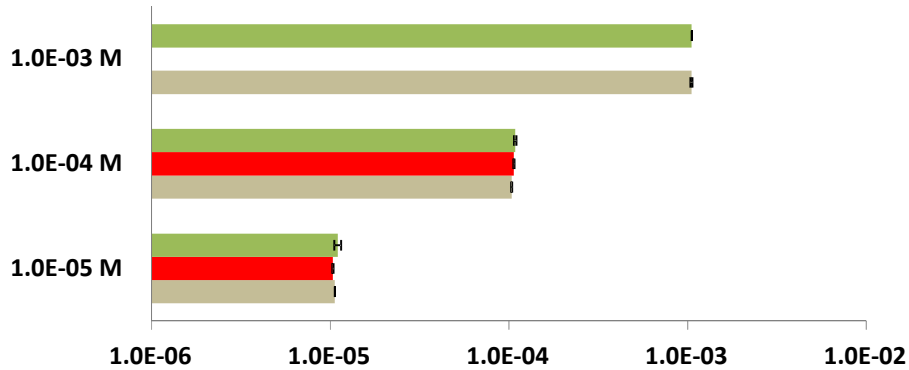
Removal of ⁹⁹Tc(VII) from ⁹⁹Tc-spiked solution of ~pH 12 by magnetite transformation at both room (21°C) and elevated (75°C) temperatures was tested with varied ⁹⁹Tc concentrations. Comparison of the ⁹⁹Tc concentrations between the control solutions (⁹⁹Tc solution without magnetite addition) and the solutions in the reactors (⁹⁹Tc solution with magnetite solid) after reacting with varied spiked ⁹⁹Tc concentrations for 14 days and 42 days are shown in Figure 22. In all the cases, the ⁹⁹Tc concentrations in the reaction solution were unchanged and similar to the values of ⁹⁹Tc concentrations in the control samples, indicating that almost no ⁹⁹Tc was removed from the solutions. In terms of ⁹⁹Tc concentration, Figure 23 illustrates that more than 97% of the spiked ⁹⁹Tc still remained in the aqueous phase. Even considering the analytical uncertainty of ±5%, no ⁹⁹Tc removal from the solution or a very limited amount (<3%) if any, was possible in the reactor solutions with magnetite. Only in the reaction conducted at 75°C combined with the lowest ⁹⁹Tc-spiked concentration of 10⁻⁵ M was measurable ⁹⁹Tc removal (about 9%) observed, where the final ⁹⁹Tc solution concentration in the reactor was 91% of the initial values after the reactions for 14 or 42 days. This phenomenon indicates that very little ⁹⁹Tc could be removed from the tested solutions when magnetite is used. This result agrees well with the mineral transformation results described in Section 3.2. As we observed in the pure mineral transformation experiments, only limited mineral transformation of magnetite to maghemite could occur under conditions of pH 12 and 80°C, where quite limited Fe(II) in magnetite could oxidize to Fe(III). Therefore, a limited amount of ⁹⁹Tc(VII) could be reduced to ⁹⁹Tc(IV) and incorporated into newly formed maghemite structure through coprecipitation. In the experiments with high spiked ⁹⁹Tc concentrations, concentrations of 10⁻⁴ and 10⁻³ M of ⁹⁹Tc in the reactor solutions were too high compared to the releasable electrons resulting from mineral transformation of magnetite; thus no ⁹⁹Tc removal could be observed even if it occurred in very limited amounts after ⁹⁹Tc(IV) reduction.

Tc concentration in solution (M) at 14 days



	1.0E-05 M	1.0E-04 M	1.0E-03 M
Control-14 day	9.60E-06	9.51E-05	9.51E-04
75°C-14 day	8.81E-06	9.34E-05	
RT-14 day	9.76E-06	9.76E-05	9.70E-04

Tc concentration in solution (M) at 42 days



	1.0E-05 M	1.0E-04 M	1.0E-03 M
Control-42 day	1.10E-05	1.08E-04	1.05E-03
75°C-42 day	1.04E-05	1.07E-04	
RT-42 day	1.06E-05	1.04E-04	1.05E-03

Figure 22. Comparisons of ⁹⁹Tc Removal Between the Control Solutions (Tc solution without magnetite) and the Solutions in the Reactors (⁹⁹Tc-spiked solution with magnetite) after Reacting for 14 Days and 42 Days at Both RT (21°C) and 75°C with Varied ⁹⁹Tc Concentrations. The solution-to-solid ratio in the reactors was 1000.

Remaining Tc mass in solution (%) at 42/14 days

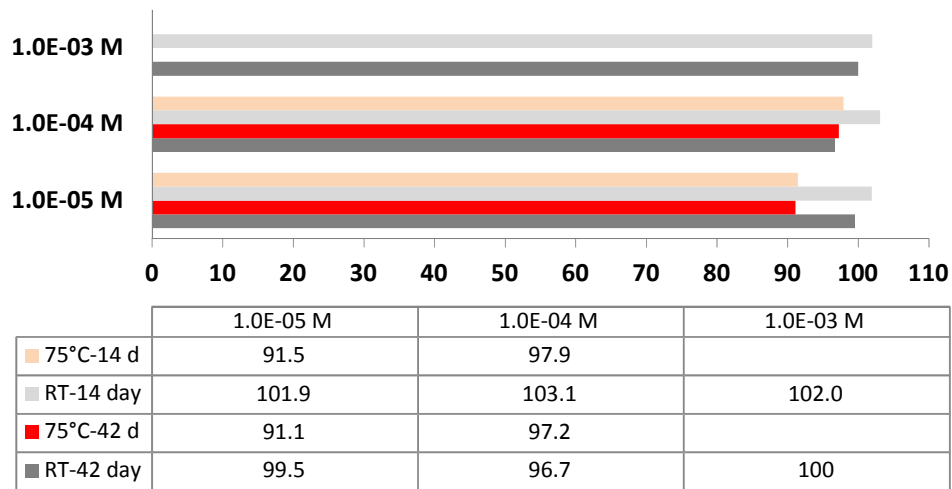


Figure 23. The Remaining Tc Mass (in percentage) in the Magnetite Reactors after Reacting for 14 and 42 Days at Both RT (21°C) and 75°C with Varied Spiked Tc Mass in the System. The solution-to-solid ratio in the reactors was 1000.

3.4 Tc-Goethite Long-Term Leaching and XAFS Analysis

Batch-leaching data for ^{99}Tc and dissolved Fe(total) as a function of time in the IDF pore water solution are shown in Table 2. The leachates were analyzed and the average values were determined for ^{99}Tc concentration and pH. Measured pH values in the IDF pore water leaching solution showed no dramatic changes even after two years (Table 2), indicating no significant pH-altering geochemical reaction such as dissolution occurred during the long-term leaching. Detectable ^{99}Tc concentrations in the leachates even after two years were close to or less than 2 $\mu\text{g/L}$ in the IDF pore water solution. No measurable Fe(total) concentrations were detected in the IDF leachates, which were below the estimated quantitation limit (EQL) of ICP-OES (<10 $\mu\text{g/L}$). Because negligible amounts of total Fe concentrations were found in the IDF leachates, the ^{99}Tc -hosting Fe mineral goethite was not dissolved in the circumneutral pH condition, which is related to the low goethite solubility at circumneutral pH values. Gradual increase of the measured ^{99}Tc concentrations from 1.33 $\mu\text{g/L}$ after three months leaching to 2.03 $\mu\text{g/L}$ after two years leaching, but not the 6-month leached ^{99}Tc concentration of 2.16 $\mu\text{g/L}$, was attributed mainly to a slow diffusion process. However, no significantly increased ^{99}Tc concentrations found in the leachates even after two years in the oxidizing condition indicate that ^{99}Tc does not reoxidize much from $^{99}\text{Tc(IV)}$ to pertechnetate, $^{99}\text{Tc(VII)}$, in the ^{99}Tc -goethite solid even during long term leaching and air exposure. Because the powdered ^{99}Tc -goethite sample 2-5 was prepared with additional goethite armoring (Um et al. 2011) and showed the highest $^{99}\text{Tc(IV)}$ contribution (~100%) as prepared (Um et al. 2012), Tc-goethite sample 2-5 is considered to the most resistant to ^{99}Tc reoxidation and leaching, even after less than three years in the oxidizing condition.

Table 2. Measured pH and Concentrations of ^{99}Tc and Fe(total) of Tc-Goethite Sample 2-5 After Long-Term Leaching in IDF Solution

Reaction Conditions	^{99}Tc Concentration ($\mu\text{g/L}$)	Fe(total) Concentration ($\mu\text{g/L}$)	pH	XAFS Sample Preparation
Three months leaching in IDF solution	1.33	ND ^(a)	6.92	No
Six months leaching in IDF solution	2.16	ND	7.20	No
One year leaching in IDF solution	1.68	ND	7.30	Yes
Two years leaching in IDF solution	2.03	ND	7.00	Yes
Three years reaction (two years in IDF solution + one year in air)	-	-	-	Yes

(a) ND = not detected (<10 $\mu\text{g/L}$ of ICP-OES estimated quantitation limit).

The XANES spectra of ^{99}Tc standards ($^{99}\text{TcO}_4^-$ and $^{99}\text{TcO}_2 \cdot 2\text{H}_2\text{O}$) and ^{99}Tc -goethite 2-5 samples reacted in the IDF leaching solution and in air up to three years are shown in Figure 24. The $^{99}\text{Tc(VII)}$ XANES spectrum is characterized by a strong pre-edge feature found at around the 21,046 eV energy region because of the 1s-to-4d transition, which is allowed for the tetrahedral $^{99}\text{TcO}_4^-$ coordination. The XANES spectrum for the $^{99}\text{Tc(IV)}$ standard from $^{99}\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ is very different from the $^{99}\text{Tc(VII)}$ standard spectrum, and is characteristic of $^{99}\text{Tc(IV)}$ coordinated by oxygen atoms in an octahedral geometry without showing the pre-edge feature shown for $^{99}\text{Tc(VII)}$. For comparison, the ^{99}Tc XANES spectra of ^{99}Tc -goethite 2-5 samples as prepared and after 6-month leaching in the IDF pore water solution were obtained from Um et al. (2011, 2012), and are shown together with new XANES results for the ^{99}Tc -goethite 2-5 samples reacted for three years (see Table 2 for XAFS sample information).

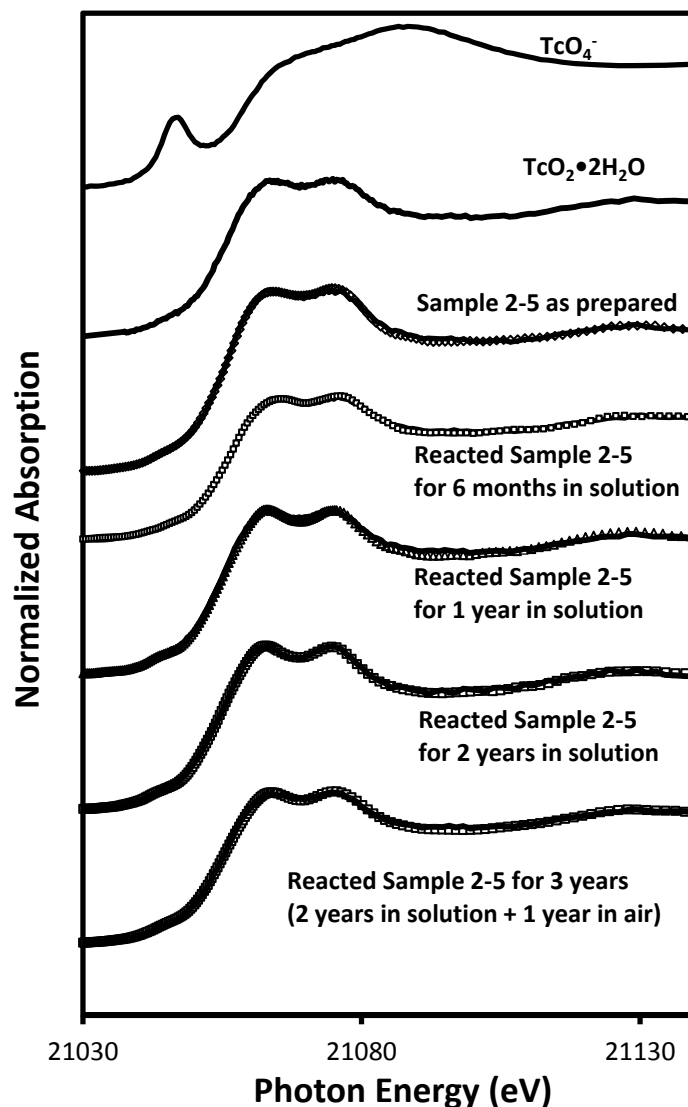


Figure 24. Normalized ^{99}Tc XANES Spectra and Fits for ^{99}Tc -Goethite 2-5 Samples Reacted Under Different Conditions. Data are represented by symbols, and the fits are represented by the solid lines. The contributions of each ^{99}Tc species are from $^{99}\text{TcO}_4^-$ and $^{99}\text{TcO}_2\cdot 2\text{H}_2\text{O}$.

The oxidation state of ^{99}Tc in the reacted ^{99}Tc -goethite 2-5 samples after either leaching in the IDF solution or in air was determined by fitting their XANES spectra using a linear combination model with the spectra for the $^{99}\text{TcO}_4^-$ and the $^{99}\text{TcO}_2\cdot 2\text{H}_2\text{O}$ standards. In all cases, the fitting results indicated that only $^{99}\text{Tc(IV)}$ was present in both reacted and unreacted ^{99}Tc -goethite 2-5 samples. Even though there was two years reaction in the IDF leaching solution and one year exposure in air, the ^{99}Tc speciation and oxidation state was not changed and almost 100% of the $^{99}\text{Tc(IV)}$ was still present in the solid phase. The fraction of $^{99}\text{Tc(VII)}$ present in the reacted ^{99}Tc -goethite samples even after reaction in the leached solution or air condition was less than 1% (Table 3), suggesting that the reoxidation of the $^{99}\text{Tc(IV)}$ initially incorporated within the Fe(II)-treated goethite mineral lattice (sample 2-5) was significantly limited even after being exposed to oxygen both in solution and air. It is not certain why the limited Tc reoxidation is still possible in the three-year reacted Tc-goethite sample 2-5 based on the insufficient data

we have so far. However, it may be attributed to the armoring coating layer of $\text{Fe}(\text{OH})_3$ precipitates in Tc-goethite sample 2-5 that can effectively block oxygen access to $^{99}\text{Tc}(\text{IV})$ present in the goethite lattice. The measured reductive capacities of the ^{99}Tc -goethite 2-5 and 2-2 samples before leaching were 0.140 meq/g and 0.744 meq/g, respectively. Although low reductive capacity was measured in the ^{99}Tc -goethite 2-5 sample, which was prepared with additional armoring, than in the 2-2 sample, which was prepared without additional armoring (Um et al. 2011), more leachable ^{99}Tc concentrations were found in ^{99}Tc -goethite 2-2 sample than in the 2-5 sample under the same leaching solution conditions (Um et al 2012). Therefore, the limited ^{99}Tc reoxidation found in the ^{99}Tc -goethite 2-5 sample may result from a physical barrier effect rather than chemical reductive capacity preserved in the magnetite mineral that was present more in the final ^{99}Tc -goethite 2-2 sample.

Table 3. XANES Fit Results for ^{99}Tc Species in ^{99}Tc -Goethite 2-5 Samples

Samples	Time ^(a) (days)	Tc(IV) ^(b) (%)	Tc(VII) ^(b) (%)	Reaction Conditions
^{99}Tc -goethite sample 2-5 as prepared ^(c)	0	100 ±2	0 ±2	No reaction
^{99}Tc -goethite sample 2-5 after six-month leaching ^(c)	180	100 ±2	0 ±2	Leaching in the IDF solution
^{99}Tc -goethite sample 2-5 after one-year leaching	395	99 ±2	0 ±2	Leaching in the IDF solution
^{99}Tc -goethite sample 2-5 after two-year leaching	670	100 ±2	0 ±2	Leaching in the IDF solution
^{99}Tc -goethite sample 2-5 after three years reacting	1005	100 ±1	0 ±2	Two-year leaching in the IDF solution + one year in air

(a) Time indicates “total time” between sample preparation and XAFS data collection.
(b) These values represent the fraction of the total Tc assumed to be present as the designated species. The sum of all species is 1.0. $\text{Tc}(\text{IV}) = \text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Tc}(\text{VII}) = \text{TcO}_4^-$.
(c) These XANES spectra and information were obtained from Um et al. (2011, 2012).

4.0 Conclusions

Based on the results of this study, the following conclusions were drawn:

1. Mineral transformation of three synthesized Fe (oxy)hydroxide minerals [ferrihydrite, magnetite, and $\text{Fe}(\text{OH})_2(\text{s})$] was tested under various conditions of pH, temperature, and solution-to-solid ratios, and showed that a mixture of magnetite, maghemite, and goethite was obtained from that $\text{Fe}(\text{OH})_2(\text{s})$ transformation, while ferrihydrite transformed to solely goethite and very limited transformation of magnetite to maghemite was found.
2. No matter which Fe (oxy)hydroxide mineral was used as initial substrate material, a high slurry pH and high temperature condition was the best for forming more transformed products, including goethite.
3. ^{99}Tc removal from solution was possible with $\text{Fe}(\text{OH})_2(\text{s})$ presence even without adding aqueous Fe(II) because $\text{Fe}(\text{OH})_2(\text{s})$ could provide aqueous Fe(II) to reduce $^{99}\text{Tc}(\text{VII})$ to $^{99}\text{Tc}(\text{IV})$ before being incorporated within the mineral structure of the transformation product. However, no significant

⁹⁹Tc removal was found in the reactor solution with magnetite used as initial solid substrate because of very limited transformation from magnetite even under high pH and temperature conditions. Due to high pH condition (~9-11.0) in a final reactor solution of transformation from Fe(OH)₂(s), a surface adsorption mechanism cannot account for ⁹⁹Tc removal from this high pH solution, but after ⁹⁹Tc is reduced to ⁹⁹Tc(IV) its incorporation into the mineral structure of the transformed product is possible.

4. Mineral transformation from Fe(OH)₂(s) to more stable Fe (oxy)hydroxide mineral can be used to remove ⁹⁹Tc even from an alkaline solution that is similar in concentration to a secondary or LAW off-gas scrubber waste stream. However, additional analysis of ⁹⁹Tc speciation in the final transformed product is still required to confirm ⁹⁹Tc incorporation within the mineral structure of transformed product.
5. Reductive capacity measurement of both ⁹⁹Tc-goethite 2-2 and 2-5 samples showed that a higher reduction capacity of 0.744 meq/g was found in ⁹⁹Tc-goethite 2-2, which was not prepared with additional armoring process, while the reduction capacity of 0.140 meq/g was found in ⁹⁹Tc-goethite 2-5 sample that was prepared with additional armoring process. The ⁹⁹Tc-goethite 2-2 sample has more magnetite content than the ⁹⁹Tc-goethite 2-5 sample, which is consistent with higher reduction capacity being measured in sample 2-2 than in sample 2-5 before leaching because more Fe(II) is present in magnetite as found in sample 2-2 than in sample 2-5.
6. Even after long-term leaching in the IDF pore water solution for two years, very limited amounts of ⁹⁹Tc and Fe(total) were detected in the leachates. The limited ⁹⁹Tc release was attributed to more stabilized ⁹⁹Tc(IV) present in the ⁹⁹Tc-goethite lattice even after long-term exposure to oxygen, while zero detected Fe(total) concentration indicated that structure of the final goethite mineral was stable at the circumneutral pH condition germane to the IDF pore water.
7. ⁹⁹Tc(IV) that is reduced and incorporated within the goethite lattice is unlikely to be reoxidized to ⁹⁹Tc(VII), even when the final ⁹⁹Tc goethite product (sample 2-5) is exposed to oxidizing conditions for three years. The limited reoxidation and release of ⁹⁹Tc is attributed to ⁹⁹Tc(IV) being coprecipitated within goethite lattices and subsequently armored with additional goethite layers as well as to the chemical and structural stability of goethite in the circumneutral Hanford pore water solution, suggesting potential use of goethite as a low-temperature Fe oxide solid waste form.

5.0 References

- Ardizzone S and L Formaro. 1983. "Temperature induced phase transformation of metastable $\text{Fe}(\text{OH})_3$ in the presence of ferrous ions." *Materials Chemistry and Physics* 8(2):125–133.
- Bondietti EA and CW Francis. 1979. "Geologic migration potential of Tc-99 and Np-237." *Science* 203:1337–1340.
- Burke IT, C Boothman, JR Lloyd, FR Livens, JM Charnock, JM Mcbeth, RJG Mortimer, and K Morris. 2006. "Reoxidation behavior of technetium, iron, and sulfur in estuarine sediments." *Environmental Science and Technology* 40:3529–3535.
- Darab JG and PA Smith. 1996. "Chemistry of technetium and rhenium species during low-level radioactive waste vitrification." *Chemistry of Materials* 9:1004–1021.
- Fredrickson JK, JM Zachara, DW Kennedy, RK Kukkadapu, JP McKinley, SC Heald, C Liu, and AE Plymale. 2004. "Reduction of TcO_4^- by sediment associated biogenic $\text{Fe}(\text{II})$." *Geochimica et Cosmochimica Acta*. 68:3171–3187.
- Geckeis VMH, E González-Robles, A Loida, C Bube, and B Kienzler. 2012. "Radionuclide behavior in the near-field of a geological repository for spent nuclear fuel." *Radiochimica Acta* 100:699–713.
- Gilliam TM, RD Spence, WD Bostick, and JL Shoemaker. 1990. "Solidification/ stabilization of technetium in cement-based grouts." *Journal of Hazardous Materials* 24:189–197.
- Keith-Roach MJ, K Morris, and H Dahlgard. 2003. "An investigation into technetium binding in sediments." *Marine Chemistry* 81:149–162.
- Lee SY and EA Bondietti. 1983. "In technetium behavior in sulfide and ferrous iron solutions." *Materials Research Society Symposium Proceedings* 315–322.
- Lukens WW, JJ Bucher, NM Edelstein, and DK Shuh. 2002. "Products of pertechnetate radiolysis in highly alkaline solution: Structure of $\text{TcO}_2 \cdot x\text{H}_2\text{O}$." *Environmental Science and Technology* 36:1124–1129.
- Lukens WW, JJ Bucher, DK Shuh, and NM Edelstein. 2005. "Evolution of technetium speciation in reducing grout." *Environmental Science and Technology* 39:8064–8070.
- Newville M. 2001. "IFEFFIT: Interactive XAFS analysis and FEFF fitting." *Journal of Synchrotron Radiation* 8:322–324.
- Schikorr G. 1933. "The iron (II) hydroxide and a ferromagnetic iron (III) hydroxide." *Zeitschrift für Anorganische und Allgemeine Chemie* 212 (1): 33–39. doi:10.1002/zaac.19332120105.
- Schwertmann U and RM Cornell. 1991. *Iron Oxides in the Laboratory: Preparation and Characterization*. VCH Publishers, Weinheim, Germany.
- Skomurski FN, KM Rosso, KM Krupka, and BP McGrail. 2010. "Technetium incorporation into hematite ($\alpha\text{-Fe}_2\text{O}_3$)." *Environmental Science and Technology* 44:5855–5861.

Smith RW and JC Walton. 1993. "In the role of oxygen diffusion in the release of technetium from reducing cementitious waste forms." *Materials Research Society Symposium Proceedings* 247–253.

Ravel B and M Newville. 2005. "ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT." *Journal of Synchrotron Radiation* 12:537–541.

Um W, H-S Chang, JP Icenhower, NP Qafoku, SC Smith, RJ Serne, EC Buck, RK Kukkadapu, ME Bowden, JH Westsik, Jr., and WW Lukens. 2010. *Immobilization and Limited Reoxidation of Technetium-99 by Fe(II)-Goethite*. PNNL-19833, Pacific Northwest National Laboratory, Richland, Washington.

Um W, H-S Chang, JP Icenhower, WW Lukens, RJ Serne, NP Qafoku, JH Westsik, Jr., EC Buck, and SC Smith. 2011. "Immobilization of 99-Technetium (VII) by Fe(II)-Goethite and Limited Reoxidation." *Environmental Science and Technology* 45(11):4904–4913.

Um W, HS Chang, JP Icenhower, WW Lukens, RJ Serne, NP Qafoku, RK Kukkadapu, and JH Westsik. 2012. "Iron oxide waste form for stabilizing ⁹⁹Tc." *Journal of Nuclear Materials* 429:201–209.

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