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Reduction of Pertechnetate from Off-gas Condensate using Aged Zero-valent Iron as a Reducing Agent

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

REDUCTION OF PERTECHNETATE FROM OFF-GAS CONDENSATE USING
AGED ZERO-VALENT IRON AS A REDUCING AGENT

A thesis submitted in partial fulfillment of the

requirements for the degree of

MASTER OF SCIENCE

in

CIVIL ENGINEERING

By

Abraham Tadesse Gebru

2019

To: Dean John Volakis
College of Engineering and Computing

This thesis, written by Abraham Tadesse Gebru, and entitled Reduction of Pertechnetate From Off-gas Condensate Using Aged Zero-Valent Iron as a Reducing Agent, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

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Florida International University, 2019

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ABSTRACT OF THE THESIS

REDUCTION OF PERTECHNETATE FROM OFF-GAS CONDENSATE USING
AGED ZERO-VALENT IRON AS A REDUCING AGENT

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Abraham Tadesse Gebru

Florida International University, 2019

Miami, Florida

Professor Shonali Laha, Major Professor

The Hanford site located in Washington State was one of the major nuclear processing facilities in the U.S. where plutonium was produced between the 1940s and the 1980's. As a result of this forty yearlong production, approximately 53 million gallons of radioactive waste was generated and currently stored in 177 single and double shelled underground tanks. There were around 60 major and minor leaking incidents in the tanks through the years. These leaking incidents were wakeup calls to a search for an effective long term disposal solution. This paper will concentrate on the low activity waste (LAW), specifically the radioactive element technetium (Tc). Tc-99 is radioactive with a half-life of 211,000 years, formed during nuclear fission of Uranium-235. Tc-99 can be found in different oxidation states. However, Tc(VII), as pertechnetate anion (TcO_4^-), is the most abundant in Hanford low activity aqueous waste due to its high solubility.

Currently there is no operational treatment plant at the site, but, once the treatment plant starts operation, the planned technique for the LAW is vitrification. Because of the higher volatility of technetium, this method can be challenging to accomplish. Here, we investigate another way of dealing with this highly volatile Tc(VII) via zero valent iron

(ZVI). This material could be used to reduce Tc(VII) into a less volatile isotope Tc(IV) followed by possible precipitation.

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Introduction

Between World War II and the 1980's, production of nuclear elements for both military and power consumption purposes was common practice among developed countries. The Hanford processing site located in Washington State was one of the major nuclear processing facilities for plutonium production in the United States. Construction of the Hanford site began in 1943 along the Colombia River, where its first full scale nuclear activity was the production and isolation of plutonium-239 beginning in December 1944 [1].

According to a previous report, approximately 208,000 m³ of solid and liquid waste (both radioactive and non-radioactive) were generated at the Hanford site [2]. At the Hanford site, approximately 53 million gallons of radioactive waste is currently stored in 149 single and 28 double-shell underground tanks. According to a Washington state Department of Ecology report [1], all 177 tanks have passed their design lifetime of 25 years, and at least 67 tanks have leaked. These leaking incidents have allowed the waste stream to enter the subsurface environment and groundwater, thus, an effective solution is needed. The waste in these tanks is categorized as two main groups, high-activity waste (HAW) and low-activity waste (LAW). Among these two waste groups, the LAW comprises around 90% of the total waste volume in the tanks. Based on the Westinghouse Hanford Company (WHC) inventory, the LAW is estimated to contain around 88 tons of solid and 180 million gallons of aqueous solution waste across the site (both radioactive and nonradioactive waste) [3]. The LAW consists of salts [Na⁺, K⁺, Al(OH)₄⁻, Cl⁻, F⁻, NO₃⁻, NO₂⁻, OH⁻, CO₃²⁻], organics, and radioactive elements like Tc-99 [4], which is the element of concern for this study.

Plutonium and uranium yield other radioactive elements during thermal nuclear fission processes in the reactors, including Tc-99. Production of this nuclear element has ceased since the 1980's at Hanford site [1], but removing the by-products of nearly forty years of operation is not an easy task for the Department of Energy (DOE). It is estimated that a total of 1990 kg Tc was produced in the 40 years of operation of the nuclear processors [5]. Of the total Tc-99 produced on the site, 510 ± 210 kg was shipped off site or co-extracted with uranium oxide product, another 80 ± 10 kg was released to the environment, and the remaining amount in the storage tanks is approximately 1310 ± 220 kg [5].

Currently, there is no operating treatment plant for LAW waste stream, but, once the Waste Treatment and Immobilization Plant (WTP) is built by 2024 at the Hanford nuclear reservation, the planned treatment technique for LAW is vitrification. It is a process which involves addition of liquid waste to borosilicate glass at high temperatures (around 1150 °C). It involves frequent heating of the aqueous waste with glass-forming materials. However, it is estimated that as little as 35% of Tc(VII) will be incorporated with borosilicate due to its high volatility at melter temperatures. Therefore, recovery of Tc-99 from the off-gas condensate is required [6]. The current plan is to recycle Tc-99 recovered in the off-gas condensate back into the vitrification facility.

Because of its long half-life (specifically Tc-99) and high solubility, Tc-99 is considered to be the main risk-contributing radionuclide during low activity waste (LAW) vitrification at the proposed Hanford WTP [7]. Although the proposed off-gas recycling method increases Tc loading in LAW glass, it also disproportionately increases concentrations of chromate, sulfate, halides, and other salts that impede overall LAW processing. These

increased loadings significantly complicate the process and affect the quality of the glass wasteform [7, 8].

This research investigates an alternative treatment for the risk-driving Tc in the waste stream. This method involves using zero valent iron (ZVI) as a reducing agent to transform aqueous Tc(VII) into a less soluble Tc(IV). ZVI is a powder form of iron with zero oxidation state. It is often used as a permeable reactive barrier (PRB) to remove reducible contaminants in groundwater [9]. It can also be used for treatment of reducible contaminants in industrial waste streams. In this research, ZVI is expected to reduce Tc(VII) to Tc(IV) and potentially incorporate Tc into Fe oxidation products to prevent re-oxidation of Tc(IV) over time. This research proposes ZVI as the reducing agent because it is relatively cheaper than Sn(II) and simpler to incorporate into the treatment scheme [8]. It is estimated that applying ZVI for treatment of Tc-99 from the LAW stream can save more than \$4 billion throughout the life time of the waste treatment plant compared to the base line vitrification and recycling process [unpublished estimate by DOE ORP]. In addition to observing how effective ZVI may be in reducing Tc(VII) to Tc(IV), we will determine the useful life time of ZVI (period that ZVI can effectively reduce Tc-99). ZVI aging experiments will be conducted to quantify how long the ZVI can effectively remove Tc from the aqueous phase.

Technetium Chemistry

Technetium (Tc) is a synthetic element, which was first produced by Emilio Segre and Carlo Perrier in a laboratory located in Berkeley, California in 1937 [10]. There are sixteen known isotopes of Tc with atomic mass ranging from 92 to 107. All of these isotopes are not stable. These isotopes have varying life span with the short-lived being as short as few

hours while long-lived Tc-99 has a half-life of 211,000 years [11]. Tc has the lowest atomic number among all synthetic radioactive elements (with atomic number 43) and has an electronic configuration of [Kr] 4d⁵ 5s².

Among the 16 isotopes of Tc, Tc-99 is the most significant due to its risk to the public health because of its long half-life, significant production in the reactors, and large historical releases to the environment. Tc-99 is produced by thermal neutron fission of other radioactive elements like uranium-235 and plutonium-239 in fission reactors, it can also be formed by spontaneous fission of uranium-238 in the earth's crust [12, 13]. Tc-99 is a beta emitting element with a maximum energy of 0.292 MeV. Uranium fission produces not only Tc-99, it also can produce Tc-101, Tc-102, Tc-103, Tc-104, Tc-105, and Tc-107 with different yield percentage for each isotope [11]. Table 1, shows the yield percentage of uranium fission for the above mentioned Tc isotopes.

Table 1. Yield of technetium isotopes for uranium-235 fission (John E. Till source terms for technetium-99 from nuclear fuel cycle facilities) [11].

Isotope	Tc-99	Tc-101	Tc-102	Tc-103	Tc-104	Tc-105	Tc-107
Yield (%)	6.06	5.6	4.3	3.0	1.8	0.9	0.19

Tc can be found in various oxidation states ranging from –I to +VII, but, in the case of aqueous systems, the most dominant oxidation states are +IV and +VII [11]. Among the two most dominant oxidation states in aqueous solution (+IV and +VII), +VII is the most dominant in oxidizing environments where it exists as the highly soluble pertechnetate (TcO₄[–]) anion. On the other hand, when the environment is reducing with little oxygen present, TcO₄[–] will be reduced to Tc⁺⁴ which exhibits poor solubility and low aqueous

mobility and often precipitates as TcO₂. Some of the chemical properties of Tc are similar to rhenium as it exhibits similar behavior as the perrhenate anion [ReO₄⁻] under oxidizing conditions in water. However, it is inadequate as a chemical analog in this research due to its significantly greater redox couple and the importance of redox chemistry in this Tc removal process.

Zero Valent Iron (ZVI)

ZVI is a powder form of iron with zero oxidation state. Significant research has been conducted on removal of various contaminants using ZVI materials. Treatment techniques that involve ZVI have proven favorable as it is non-toxic, abundant, cheap, easily producible, and having admirable reduction capacity. Trichloroethylene (TCE), nitrate, arsenic, chromium, phenol, and nitrobenzene are among the major contaminants treated by ZVI in the last decade or so [14]. Besides these contaminants, ZVI has been investigated for its removal capacity of the radioactive element technetium (specifically Tc-99) [15, 16, 19].

Various iron oxides and hydroxides might be formed upon contact of the ZVI with water and other constituents. Among the iron oxides that might be formed Fe(II) oxides are expected to help in the reduction of Tc(VII) to Tc(IV). ZVI can react further with water to produce H₂, OH⁻, or H₂O₂ depending on the pH and presence of O₂ (Eqns. 1-3) [15].

Solid phase characterization of precipitates formed in other research has suggested incorporation of Tc(IV) into Fe(III) and Fe(II) solid phases created during oxidation of Fe^0 [16]. Incorporation of Tc into Fe precipitates decreases the likelihood of oxidation and release of Tc in the long-term as compared to precipitation as TcO_2 [17]. Other observations also suggest that Fe(II) oxides on the surface of ZVI facilitate reduction of Tc(VII) more effectively than aqueous Fe(II) [18]. Thus, identification of the solid phase species present is important in order to demonstrate long-term containment of Tc and to develop a final waste form for its disposal.

The potential for reductive separation of Tc-99 by ZVI or iron oxides/oxyhydroxides has not been adequately investigated for treatment of Hanford's radioactive waste stream. According to batch experiments conducted by Pacific North National Laboratory (PNNL), ZVI reduced the concentration of TcO_4^- in the groundwater by almost 75% in the first half hour of contact [9]. ZVI is expected to reduce TcO_4^- to Tc^{+4} , where the reduced Tc(IV) will be removed from the waste stream by precipitation, co-precipitation, and/or adsorption processes [19]. The goal of this study is to consider ZVI for treatment of the off-gas condensate that will be produced during vitrification of LAW at the Hanford site. This research focuses on how ZVI can help in reducing Tc-99 to its less soluble oxidation state with an emphasis on the ZVI longevity; or, how long it can be used without losing its reducing power.

Objectives

The main objective of this research is to analyze the effect of ZVI aging on the reductive removal of Tc-99 from the LAW off-gas condensate of Hanford's processing facility. Under the main objective this research will strive to answer the following questions:

1. How effective is ZVI in reducing Tc(VII) to Tc(IV)?
2. How does aging of ZVI affect its reductive capacity?
3. What are the factors (if any) that cause ZVI to lose its reductive capacity with time?

Hypothesis

The research hypothesis is that reductive removal of Tc-99 via ZVI will be more efficient and cheaper than the baseline case for recycling back to vitrification. We hypothesize that oxidation reactions that will occur upon interaction of ZVI and solutions will cause the material to lose its reducing capacity both before and after contact with technetium. In the long term, due to the formation of different iron oxides, we are expecting to see a decrease in the reducing capacity of ZVI. We are expecting this might be as a result of formation of iron oxide coatings surrounding the ZVI core, which might result in a reduction of transfer of electrons between the ZVI and Tc-99.

Methodology

Batch Experimental Protocol

Batch experiments were conducted for this research in order to investigate the kinetics of reductive removal of Tc-99 in the presence of ZVI. These experiments were conducted in triplicate with a 40 mL volume of 0.5 g/L ZVI, 0.08 M NaCl, and 500 µg/L of Tc-99 at pH 7. The general protocol for these experiments is expanded below.

First, a background solution was prepared, which is composed of ultrapure water (>18 MΩ-cm) and 0.08 M sodium chloride (ACS reagent grade, Fisher Chemical), in an aerobic environment to resemble the conditions for treatment of off-gas condensate in an industrial facility.

Next, the pH was adjusted with 0.01 and 0.1 M solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH). The pH electrode was calibrated daily using three buffer solutions (pH 4.01, 7.00, and 10.01). The pH of the solution was adjusted to 7.0 ± 0.1 prior to addition of ZVI or Tc-99.

The supernatant solution was used to prepare suspensions of 0.5 g/L ZVI (99% vendor listed purity, 200 mesh, Fisher Scientific). Vendor provided specifications of the ZVI used are listed in Table 2 below.

Table 2 . Vendor provided characteristics of ZVI (Fisher Scientific)

Molecular weight	55.845 g/mol
Mean Size	-200 mesh (<75 μ m)
Physical Form	Powder
Percent Purity	≥ 99 %
Assay Percent Range	99+ % (metal basis)

Samples were prepared in triplicates for variable ZVI oxidation times (0 hour, 1 hour, 8 hours, 1 day, 2 days, 1 week, 10 days, 2 weeks, and 1 month). Each set of samples was prepared in triplicate with an additional control sample containing only the supernatant (0.08 M NaCl) and Tc-99. One milliliter of a KTcO_4 stock solution (0.2 mM) was added to all samples after the completion of the designated ZVI aging time to reach a concentration of approximately 500 $\mu\text{g/L}$. During reaction times, samples were placed on an end over end rotator with a speed of 25 rpm (ThermoFisher Scientific).

Samples were collected at variable time points to monitor reductive removal of technetium (10 mins, 30 mins, 1 hour, 3 hours, 1 day, 2 days, 5 days, 8 days, and 30 days). A wide range of both ZVI oxidation and Tc-99 reaction times were chosen to investigate

the effect of aging ZVI on its reduction efficiency for technetium. Upon sampling, the aqueous phase was filtered through 0.2 μm syringe filters (PTFE, Fisher Scientific).

Although most samples were prepared with a 40 mL volume, select samples were prepared with a 1 L volume as described below for additional solid phase characterization. Additionally, to consider the effect of dissolved Fe in the reduction kinetics of Tc-99, another set of experiment was conducted, which involves removing the old solution, which contains the supernatant solution and dissolved Fe(II/III) ions from ZVI oxidation, and replacing it with a fresh supernatant solution prior contacting with Tc. Removal of the old solution was conducted after centrifuging the samples at 4500 rpm for 10 mins in order to retain the Fe solids.

Aqueous Phase Analysis

Ultra violet visible spectroscopy for Fe (II/III)

UV spectrometer (Genesys 10S UV–Vis) was used to measure the Fe(II) and Fe(III) concentrations in the supernatant mix solution prior to spike with Tc. The materials used in this analysis were ferrozine (Arcos Organics, 98% purity) (pH = 6.6), hydroxylamine ($\text{NH}_2\text{OH}\cdot\text{HCl}$), 0.15 M HCl, and Ultrapure water. Standard solutions were prepared with a range of concentrations for calibration: 0.1, 0.25, 0.5, 1, 5, 10, 20, and 30 mg/L. Aqueous Fe(II) was measured by reaction with ferrozine and measurement of absorption at 562 nm. Additionally, ferric iron was measured by the difference following reduction with the hydroxylamine solution (after obtaining ferrous iron results) [20]. HCl (0.15 M) was used to lower the pH in the samples as final color development in the samples can only be observed in pH range between 2.5 and 4.7. This method measured aqueous Fe(II) and Fe(III) produced after Fe oxidation when it reacted with Tc.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) for total Fe

The filtered supernatant solution was diluted with 2% nitric acid (HNO₃) for further analysis under the inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer, Optima 7300 DV) or inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific, iCAP RQ).

Liquid Scintillation Counting (LSC)

Ten milliliters of liquid scintillation cocktail was mixed in 20 mL plastic vials with 0.2 mL of the aqueous phase recovered from 0.2 µm syringe filters during sampling of batch experiments. A liquid scintillation counter, LSC (Tricarb 2910 TR), was used to count the total beta radioactivity in the vials. The minimum detectable for Tc-99 for this study was approximately 1 µg/L (38.5 dpm/mL) based on equations 4-6 below.

$$MDA = \frac{LLD}{T * \eta} \quad \text{Eqn. 4}$$

$$LLD = (4.66 * \delta_A) + 3 \quad \text{Eqn. 5}$$

$$\delta_A = \frac{\sqrt{CPM_A * T}}{T} \quad \text{Eqn. 6}$$

Where MDA is minimum detectable radioactivity, calculated based on Cember and Johnson, 2009;

δ_A - the standard deviation of background measurements in total counts;

CPM_A - total technetium counts in the vials per minute;

LLD is the lower limit of detection;

η - Detector efficiency;

T - Time.

The reductive removal rate in Table 3 is calculated using the first order rate equation with the analytical solution of the differential equation in Eqn.7;

$$\ln\left(\frac{[C]_t}{[C]_0}\right) = -Kt \quad \text{Eqn. 7}$$

Solid Phase Characterization

Select samples were prepared as described for batch experiments but with a total volume of one liter. At variable time points, the solid phase ZVI was centrifuged (at 4500 rpm for 10 mins) and isolated from the aqueous phase for further analysis of the crystallinity, morphology, and chemical composition utilizing various characterization tools and application. Prior to characterization the solids were washed with pH adjusted ultrapure water, dried at 30°C, and stored in an anaerobic glovebox until analysis.

Brunauer–Emmett–Teller analysis (BET)

ZVI samples were analyzed for the surface area and pore size distribution. The analysis was conducted using TriStar II surface area and porosity measuring instrument at 80 K, which is the boiling temperature of nitrogen (N₂) and is the most commonly used gaseous adsorbate for surface probing in BET analysis [13]. Solid phase of our samples was dried at 30°C in anaerobic glove box until analysis, in addition the samples were dried for 24 hours at 80 K (using FlowPrep 060 sample degas system) prior to measuring surface area per gram of ZVI and the pore size.

Attenuated total reflectance Fourier-transform infrared spectroscopy

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) was conducted via Agilent Cary 670 with a PIKE diamond/ZnSe ATR optical crystal to

determine if different iron oxides were forming on the surface as a result of ZVI oxidation from water and atmospheric oxygen. Because each of the iron oxides absorbs light at different wavelengths creating different characteristic spectra, this method allows for a qualitative determination of the presence of different Fe oxidation products. Approximately 100 mg of the powder ZVI was placed under the stage on the diamond ATR-FTIR crystal.

Scanning electron microscopy (SEM)

SEM was used as a tool to acquire the surface characteristics of aged ZVI. This analysis was conducted using Jeol JSM – 5900LV at operating conditions of 30 KeV, 24 spot size, beam size 1, and 11 mm working distance. SEM was used to visualize changes due to agglomeration or precipitation of iron oxidation products as well as to determine the average particle size of the ZVI powder before and after reaction with suspensions. Energy dispersive spectroscopy (EDS) was conducted in conjunction with SEM to determine samples' elemental composition, most notably weight percentages of Fe and O.

Results

Tc-99 Reductive Removal by ZVI without aging

For 0 hours of ZVI aging (oxidation), where the Tc-99 solution was added to the supernatant as soon as the ZVI was added to the solution, the reductive removal of aqueous Tc-99 is shown in Figure 1. Removal of Tc-99 from the aqueous phase was initially fast (Table 3) with Tc measurements of the aqueous phase reaching detection limits (1 ppb) within three hours with > 99% removed. Then, slow re-oxidation of Tc-99 occurred with nearly 20% dissolving back into the aqueous phase after ten days. Further, it is notable that < 15% of Tc-99 was in the aqueous phase after 30 days of reaction.

Figure 1. Reductive removal of Tc-99 over time from batch suspensions of 0.08 M NaCl without aging of ZVI at $\text{pH}_i=7.0$ [500 $\mu\text{g/L}$ Tc-99, 0.5 g/L ZVI], Note: error bars are based on analysis of triplicate samples.

Tc-99 Reductive Removal by aged ZVI

As indicated in Figure 1, ZVI was effective in removing Tc-99 from solutions within three hours without aging. For samples with variable ZVI aging (oxidation) periods, the reduction trend in the aqueous Tc-99 phase is described in Figure 2. Figure 2 depicts Tc-99 reductive removal from the aqueous phase over time following exposure to ZVI suspensions aged for variable periods with 0.08 M NaCl. These results show that the aging of ZVI significantly affects trends in removal of Tc-99. Tc-99 was removed from solutions in the presence of ZVI for aging times up to 10 days with similar trends in Tc-99 removal. Further, there was a visible trend of increasing Tc-99 re-oxidation with ZVI aging based upon measurements at 24 hours and 30 days. The Tc-99 measured in the aqueous phase after 24 hours of exposure to ZVI increased from 2.7% after one hour of ZVI aging to 25% with 10 days of ZVI aging ($\pm 11\%$). Oxidation and dissolution of Tc-99 back into the aqueous phase as Tc(VII) is likely occurring as oxygen slowly diffuses into the system.

For ZVI aging of one hour, a similar trend is observed to results in the absence of aging. However, there are some important differences in removal for the eight-hour aging period. In the first hour of reaction of Tc-99 with ZVI, the eight-hour aging period exhibited the greatest removal of Tc-99 as compared to all aging periods of ZVI. Reductive removal of Tc in the first 10 minutes of contact with ZVI is more efficient for eight hours of aging than in the case of both zero and one hour aged ZVI samples with 21% ($\pm 7\%$) of Tc-99 remaining in solution for eight hours of ZVI aging versus $> 40\%$ for zero and one hour of ZVI aging. Despite Tc re-oxidation after three hours of reaction time, aqueous Tc remained below 20% ($\pm 18\%$) of the initial Tc.

For the next ZVI aging periods from 24 hours to one week, Tc reductive removal kinetics slowed with respect to shorter aging periods (Table 3). For example, aqueous Tc at the first sampling time (10 mins) was 80% ($\pm 6\%$) of the initial in the sample solution for 24 hours of ZVI aging. Although it appears that the reductive removal rate for Tc-99 increases for two and seven days of ZVI aging, the measurements are not statistically different based on the error on the linear regressions. However, the ten-day ZVI aging period shows a significantly lower trend which falls between the one-week and two-week series. For one-month aged ZVI samples, there was no substantial reduction in Tc concentration throughout the sampling periods. The minimum Tc concentration observed in this case was 80% ($\pm 2\%$), which is recorded at 30 days oxidation time. These results lead to the conclusion that ZVI aging for two-weeks or more will not allow for reductive removal of Tc-99 to occur under these batch conditions.

We hypothesize that this loss of reactivity after two weeks occurred because of the ZVI oxidation with time in the solution leading to a loss of reducing capacity. The oxidation reactions for ZVI under aerobic conditions are as follows: [21]

Figure 2. Reductive removal of Tc-99 from batch suspensions of 0.08 M NaCl at $\text{pH}_i=7.0$ with variable aging periods up to 30 days for ZVI, [500 $\mu\text{g/L}$ Tc-99, 0.5 g/L ZVI], Note: error bars are based on analysis of triplicate samples.

Table 3. Tc-99 reductive removal rate for variable aging times of ZVI based on a pseudo first order model for the first four data points (up to three hours).

ZVI oxidation time, days	Tc-99 Reduction Rate (hr⁻¹)	R²	Effect
0	-2.01 ± 0.30	0.979	
0.04	-1.30 ± 0.16	0.984	
0.3	-0.96 ± 0.20	0.961	
1	-0.83 ± 0.32	0.879	
2	-0.93 ± 0.09	0.990	
7	-1.00 ± 0.11	0.988	
10	-0.27 ± 0.09	0.907	
14	-0.03 ± 0.03	0.535	
30	0.00 ± 0.01	0.047	

of pH fluctuations on Tc-99 Reductive Removal by aged ZVI

Another set of sampling was conducted to investigate if there are additional factors that may affect Tc-99 reductive removal by ZVI for the 30 days aged samples. For the results shown in previous figures, the pH of samples was adjusted to 7 throughout the 30-day exposure to Tc-99 and during the initial ZVI aging periods. Another set of experiments was conducted following the same procedures for the 30 day aged ZVI samples but without pH adjustment. Figure 3 shows that there was not a significant effect of pH adjustment on Tc-99 reduction kinetics for ZVI aged for 30 days. Further, it should be noted that the pH of the samples that were not adjusted stabilized at high pH values (between 9 and 10).

Figure 3. Reductive removal of Tc-99 over time from batch suspensions of 0.08 M NaCl for 1 month aged ZVI samples at fixed and variable pH conditions [500 $\mu\text{g/L}$ Tc-99, 0.5 g/L ZVI], where orange circles represent natural equilibration from an initial pH of 7 and blue circles represent samples with constant pH adjustment, Note: error bars are based on triplicate samples

Comparison of Tc-99 Reductive Removal by Aged ZVI with Removal of Dissolved Fe(II/III)

In order to assess the impact of dissolved Fe(II/III) on reductive removal of Tc-99 in this system, we also repeated batch experiments with addition of Tc-99 following aging with removal of supernatant solutions and replacement with fresh 0.08 M NaCl. Previous research has shown that both homogeneous (dissolved Fe) and heterogeneous (solid Fe) reduction of Tc-99 may occur [16]. Select aging time points were considered to assess the impacts in comparison to results in Figure 4, Figure 5, and Figure 6. For all four aging times selected (one-hour, one-week, two-week, and one-month) samples showed very similar

reductive removal trends whether they were filled with old (containing dissolved Fe from ZVI oxidation) or freshly replaced supernatant solutions (without dissolved Fe). This coincides with the initial assumption that the majority of Tc reduction is happening on the surface due to Fe(II) on the ZVI surface rather than in the aqueous phase.

Figure 4. Tc remaining in the aqueous phase with respect to time comparing removal with fresh (blue) and old (red) solutions for ZVI aged for 1 hour with 0.08 M NaCl at $pH_i=7.0$, [500 $\mu\text{g/L}$ Tc-99, 0.5 g/L ZVI] Note: error bars are based on triplicate samples

Re-oxidation of Tc is significantly greater for the experiments with fresh 0.08 M NaCl as shown in Figures 4 and 5 representing one hour and one week of aging. It is possible that the higher re-oxidation rate in the samples with fresh supernatant could be due to (1) more dissolved oxygen due to replacement of solution or (2) less co-precipitation of Tc with dissolved Fe due to its removal prior to addition of Tc. Based on Figure 5, for ZVI with

one week of aging, less reduction was observed at three hours when the solution was replaced (aqueous Tc fraction at three hours was 5% and 16%, ($\pm 29\%$ and $\pm 18\%$) respectively, for experiments without and with replacement of 0.08 M NaCl prior to Tc addition.

Figure 5. Tc reductive removal from the aqueous phase with fresh (blue) and old (orange) solutions for 1 week aged ZVI with 0.08 M NaCl at $\text{pH}_i=7.0$, [500 $\mu\text{g/L}$ Tc-99, 0.5 g/L ZVI] Note: error bars are based on triplicate samples

Figure 6 . Tc reductive removal from the aqueous phase with fresh and old solutions for 2 weeks and 1 month aged ZVI with 0.08 M NaCl at $pH_i=7.0$, [500 $\mu\text{g/L}$ Tc-99, 0.5 g/L ZVI]
Note: error bars are based on triplicate samples

Variation in aqueous chemistry with time

Significant variations in oxidation reduction potential (ORP) and dissolved oxygen (DO) were observed throughout the sampling time based on two different experiments (1) one liter of 0.08 M NaCl solution with 0.5 g/L ZVI or (2) 50 mL of 0.08 M NaCl with 0.5 g/L ZVI. Tc-99 was added only to select solutions since the experimental goal at this stage was analyzing pH, ORP, and DO changes in the presence of ZVI.

Figure 7 . DO changes in 0.08 M NaCl with 0.5 g/L of ZVI in Tc- free and Tc- amended solutions with variable solid to liquid including (a) *blue* – No Tc-99, 50 mL, (b) *orange* – 500 μ g/L Tc-99, 50 mL, (c) *grey*- No Tc-99, 1 L, Note: on log scale in the x-axis, initial DO before addition of ZVI was approximately 8.5 mg/L

As described in Figure 7 above, the initial DO level of the supernatant solution before ZVI was added was more than twice levels observed for the samples once the ZVI aging begins. DO level has shown a peak value of 5.14 mg/L for the time zero samples and a lowest value of 0.5 mg/L after 30 days sampling. At 3 hours sampling time, where the highest Tc reduction was observed, the DO level in the samples was around 1.8 mg/L for the 50 mL samples amended with Tc-99. DO level at the same sampling period was recorded to be 2.2 mg/L and 1.6 mg/L for both 1 L and 50 ml samples, respectively, Tc-99-free samples. These results support the theory of the formation of different Fe(II/III) oxides in solution due to the consumption of the oxygen in the supernatant solution by ZVI during oxidation.

The potential oxides that are formed were analyzed using SEM and FTIR analysis and will be discussed in a separate section.

A second set of experiments was conducted in a smaller volume (50 mL) but included samples with and without Tc-99 to investigate whether presence of Tc-99 could impact pH and redox conditions. Figure 8 compares the pH with and without Tc-99 with respect to sampling time.

Figure 8. pH changes in 50 mL solution with 0.08 M NaCl at $pH_i=7.0$ with ZVI aging with time, [500 $\mu\text{g/L}$ Tc-99, 0.5 g/L ZVI]

These results showed that the average pH of triplicate samples amended with Tc-99 was higher than without, although there was little fluctuation with time. Similar trends with DO were also observed for the 50 mL volume as compared to the one liter. However, Figure 7 shows that samples without Tc-99 have less dissolved oxygen than those with Tc-99. For the non Tc-99 samples, DO level reduces to the lower values through aging as the iron is consuming the dissolved oxygen in solution during oxidation.

Figure 9: ORP changes in 0.08 M NaCl in Tc- free and Tc- amended 1 L solution with 0.5 g of aging ZVI as shown on log x-axis scale, Note: prior to addition of ZVI to solutions, the ORP was approximately 542 mV

The ORP measurement of solutions became more negative as Fe(0) was oxidized in the solution during reaction with the supernatant solution due to release of e^- and Fe(II) and consumption of oxygen. Other researchers also found that ORP decreases to negative values due to Fe(0) oxidation (up to -550 mV) [21]. This correlates with the reduction trends observed for the longer ZVI aging periods. The longer the ZVI was aged in the supernatant solution without contact with Tc, the reducing agent became less effective due to formation of a shell of Fe(II/III) oxides on the ZVI surface. Even though a negative ORP value means the system is under a reducing environment, Tc reduction was not possible at the longer aging periods. The lack of Tc reduction at longer periods was likely due to the inability of ZVI to continue to oxidize and release electrons due to formation of the shell

of Fe(III) oxides on the surface which inhibited interaction of Fe(0) with the solutions. Figure 7 and Figure 9 showed that there was a positive correlation between a DO and ORP values. These results are logical due to the fact that the presence of more oxygen will result in higher oxidation potential in the system. Further, it is important to note that the presence of Tc-99 in the system inhibited the DO and ORP levels of the system, potentially due to slower iron oxidation rates due to Tc-99 interacting with the surface.

Solid Phase Characterization of ZVI

SEM analysis was conducted to observe alterations in the surface morphology of ZVI. The remaining ZVI was collected after centrifugation and decanting of the aqueous phase. Samples were dried in anaerobic glove box at 30°C before analysis. Micrographs were collected at four different magnifications to allow for comparison of individual particles and overall morphology. These images show formation of various iron oxides in the solid phase. For images magnified 100x under the SEM, we noticed formation of nano-sized iron oxide phases especially for the 30 day aged samples.

Figure 10. SEM images of solid phase 3 hour aged ZVI samples with 100X (A), 3000x (B), and 40000x (C) magnification respectively

Figure 11 . SEM images of solid phase 24 hour aged ZVI samples with 100X (A), 3000x (B), and 40000x (C) magnification respectively

Figure 12. SEM images of solid phase 10 day aged ZVI samples with 100X (A), 3000x (B), and 40000x (C) magnification, respectively

Figure 13. SEM images of solid phase 1- month aged ZVI samples with 100X (A), 3000x (B), and 40000x (C) magnification respectively

In addition, the visual color change in batch samples during experiments also suggests the formation of Fe oxides in the solid phase.

Figure 14. Visual images of aqueous phase 40 ml samples with 0.08 M NaCl, 1 g/l ZVI, and Tc-99 (A), one-month aged (B) one-hour aged and (C) control samples for 1 hour and 1 month aged samples with 1 g/l ZVI and 0.08 M NaCl only.

All precipitates in samples were colored dark black or brown which is likely due to formation of mixed Fe(II/III) oxides like magnetite or maghemite. This assumption is

consistent with the results found with FTIR analysis, which will be discussed later. In Figure 10 the geometrical shapes of precipitates also indicates the formation of variety of iron oxides. The formation of needle looking crystals for 24 hour aged samples under 3000x magnification indicates the presence of goethite. The hexagonal or prismatic looking crystals seen under 40000x magnification for the 1-month aged samples indicates the presence of green rust or hematite. The fact that most of these shapes formed in the 30 days aged samples suggests that iron forms more oxidized products with longer aging times which is also consistent with aqueous measurements of Tc reduction.

SEM-EDS analysis was conducted to estimate the chemical composition of the solid phase ZVI samples at their respective aging times. For each aging time, four locations were randomly selected on the surface to conduct a point analysis. Iron and oxygen content of the samples was determined by using the average value of those four spots (Table 4). The error is large due to the limited number of measurements, therefore, trends will be discussed noting the lack of statistical differences for oxygen. For shorter times (3 or 24 hours), there is more iron in the samples whereas longer aging periods resulted in increased oxygen content as shown by Table 4. These results highlight that more oxygen is detected on the surface of the solid phase with time due to the formation of iron oxides phases which is also confirmed by FTIR results.

Table 4. Iron and Oxygen compositions of the ZVI samples following variable aging periods

ZVI Aging (Days)	Fe (% , Avg $\pm$ Stdev)	Oxygen (% , Avg $\pm$ Stdev)	# of Samples
0.125	75.28 $\pm$ 11.2	24.72 $\pm$ 11.2	4
1	65.58 $\pm$ 25.4	34.42 $\pm$ 25.4	4
10	53.09 $\pm$ 31.6	46.91 $\pm$ 31.6	4
30	46.04 $\pm$ 23.4	53.96 $\pm$ 23.4	4

Table 5. IR bands of iron (hydro) oxides [22]

Iron oxidation species	IR bands, cm ⁻¹
Goethite	892, 795
Lepidocrocite	1018, 750
Ferrihydrite	650, 450
Hematite	548, 471 (spheres) 645, 525, 440 (laths)
Akageneite	650, 490, 420
δ -FeOOH	1124, 890, 810, 580, 480
Maghemite	700, 640-660, 620, 580, 560, 460, 430
Magnetite	580, 400
Wustite	490
Green rust	800, 670

Figure 15. FTIR results of solid phase ZVI samples aged for various time points, Note: y-axis units are % transmittance although each series is offset to allow for simpler differentiation between series

FTIR analysis was conducted to qualitatively observe the iron oxides formed due to oxidation of ZVI in the solutions with time. Different iron oxides show distinct peaks based on absorbance of various wavelengths. Figure 14 describes transmittance between 600 and 700 cm^{-1} . Among the various forms of iron oxides, maghemite and magnetite are known to have a peak near those observed for our samples. The FTIR spectra indicate that there is formation of iron oxides in the solutions whether it is magnetite, maghemite, hematite, or green rust. Table 5 discuss types of iron oxides with their respective transmittance peaks when exposed to light rays. Besides magnetite and maghemite, the transmittance peaks in the samples can also be related with other forms of iron oxides among which is hematite

and green rust, both of these oxides are known for having peaks in this range. In addition, color of the samples (which is dark black to brown) and SEM images of secondary precipitates shows that iron oxides are forming. We suggest that magnetite and maghemite are the two most abundant oxides in the samples. The big peaks seen at a higher wavelength (above 2000 cm^{-1}) are not associated with iron oxides formation since there is no known oxide of iron to have a transmission peak at that wavelength.

Conclusions

ZVI has proven to be an effective reducing agent for the contaminant of concern of this study, Tc-99. Within the first few hours of contact time, ZVI reduced nearly all pertechnetate (TcO_4^-) into the less volatile and less soluble Tc^{+4} . ZVI's reducing capacity decreases with aging time as it oxidizes due to reactions with pertechnetate, atmospheric oxygen, and aqueous solutions. Noticeable re-oxidation of Tc occurs indicating that some precipitated Tc(IV) is re-oxidizing back to the Tc(VII). Further, keeping the ZVI in the solutions for more than 10 days before contact with Tc-99 has resulted in almost zero reduction in pertechnetate. This is due to ZVI being oxidized in the solution and causes the ZVI to lose its reducing capacity prior to contact with Tc-99.

In addition, altering the experimental conditions by replacing existing solutions with a fresh 0.08 M NaCl did not affect the initial Tc-99 reduction. The fluctuation of the pH of the solution did not play a significant role in the reduction kinetics of Tc-99 in the solution as the samples exhibited similar reductions at both neutral and relatively higher pH values. However, it should be noted that both sets of samples started at the same initial pH. In addition, the solid phase characterization results confirmed the formation of different Fe(II/III) oxides as suggested by aqueous measurements. The formation of Fe(II) oxides likely leads to reduction of Tc-99. However, once iron oxidation continues to form Fe(III) phases, Tc-99 reduction is not expected to occur.

This research showed that ZVI can be effectively used as a reducing agent in the process of reducing Tc(VII) to Tc(IV). Applying the ZVI induced reduction process will eliminate the need for constantly recycling the waste into the glass melter as opposed to the case of

vittrification. Since the reduced form of Tc-99 is less volatile and less soluble, it will make either long term storage or disposition of the final waste product easier.

Applying this process also helps in minimizing another major disadvantage of using vittrification, which is the disproportional increase in the concentration of sulfates, halides, and other salts in the LAW. Also, this removal technique will help in minimizing the overall treatment cost over the life time of the treatment facility. The cost that can be saved by choosing this treatment method over the baseline vittrification process is approximately \$4 billion, this is due to the minimal to no need of continuous recycling, which is the basic procedure in vittrification.

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