Perrhenate Sorption Kinetics in Zerovalent Iron in high pH and Nitrate Media

Brian A. Lenell and Yuji Arai*

Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana-Champaign, Urbana, IL 61801

*Correspondence: Yuji Arai
E-mail: yarai@illinois.edu, office: (217)244-3602

Keywords: Perrhenate, Sorption, Zerovalent iron, reduction, technetium

Abstract

Technetium(Tc)-99 is one of major risk drivers in low level radioactive liquid waste at the U.S. Department of Energy sites. Cementitious waste technology (CWT) has been considered immobilizing pertechnetate, Tc(VII)O_4^- , in brine and alkaline waste solutions, as Tc(IV) oxides and/or sulfides with the use of reducing agents like slag. In this study, zero valent iron (ZVI) was evaluated as a potential reducing agent in CWT as a function of pH and [nitrate] (0-0.1M) using perrhenate, Re(VII)O_4^- , as an analogue for Tc(VII)O_4^- . Batch Re(VII)O_4^- sorption experiments in conjunction with X-ray absorption spectroscopic analysis showed that the Re(VII) sorption occurred via the reductive precipitation of $\text{Re(IV)O}_2(\text{s})$ and the extent of sorption decreased with increasing pH from 8 to 10. Interestingly, pseudo 2nd order kinetic rates increased with increasing [nitrate] which was attributed to co-adsorption of NH_4^+ (i.e., a reaction product of reduced nitrate by ZVI), facilitating electrostatic attraction towards ReO_4^- under alkaline conditions. Considering the thermodynamically favorable reduction of Tc(VII) over Re(VII) , ZVI might have potential for improving the reduction capacity of the current CWT.

1. Introduction

Radioactive waste is of growing concern in the United States and around the world. Environmental contamination of radionuclides is a serious issue with use of nuclear power sources. Technetium-99 (^{99}Tc) ($t_{1/2}$: 2.1×10^5 yr) is produced from induced fission of ^{235}U . A common nuclear reactor operating at normal conditions can produce approximately 1 MBq per year [1]. Prior to being banned, nuclear weapon testing also released ^{99}Tc into the environment. Levels of ^{99}Tc from these types of tests are estimated between 100 and 160 TBq across the world [2,3].

Currently, the United States Department of Energy (DOE) considers the immobilization of ^{99}Tc in low level radioactive waste (LLW) using cement technology. Since pertechnetate (Tc(VII)O_4^-) is highly mobile in the environment, reduction of Tc(VII) to Tc(IV) is the key to form insoluble Tc(IV) oxides and sulfides species.

At the Savannah River site (SRS), saltstone formulation (slag, fly ash, and portland cement) has been demonstrated since 1990 [4]. Blast furnace slag (BFS) and fly ash are major ingredients in the saltstone cement formulation that create a reducing environment within the cement in order to immobilize ^{99}Tc . At the Hanford site, a cast stone project is currently considered as a future project.

The critical process/element of CWF technology is to have the effective electron donor to reduce Tc(VII) to Tc(IV) . In alkaline conditions, sulfide rich slag present in CWF solutions can rapidly oxidize to sulfate in solutions containing Ca(OH)_2 and NaOH , therefore possibly compromising its reductive capacity in such environments [5]. Many researchers are currently seeking better electron donors to effectively reduce Tc(VII) .

Zero Valent Iron (ZVI), which is a byproduct of the reduction of FeCl_3 or FeSO_4 with borohydride and also is a byproduct of the steel manufacturing industry, which can possibly make it economically feasible to use as a reducing agent on larger scales. It has been shown to effectively reduce various metals (e.g., Cr, Pb, U, and Mo) and trichloroethylene [6,7,8]. Especially, metal contaminants are commonly immobilized to induce the formation of less soluble precipitates. Several researchers recently reported the reduction of rhenium (Re), a chemical analogue of Tc (e.g., +4 and +7 common valence states and coordination chemistry), by ZVI [9,10]. They found that Re(VII) can be reduced by ZVI to form $\text{Re(IV)O}_2(\text{s})$, most rapidly at pH 8. In the case of CWT, the system is highly alkaline ($\text{pH} > 8$), leaving uncertainties in effectively reduce Re(VII) by ZVI. There is little information on the reduction capacity of ZVI in alkaline cementitious materials. The objective of this study is to evaluate the reduction of Re(VII) using synthetic ZVI in simulated environmental conditions (e.g., $\text{pH} > 8$, presence of bicarbonate and nitrate anions) of LLW [11]. Results gained from this study should give insight to the practicality of using ZVI to create a reducing environment for Tc(VII) within CWFs and document any interferences caused by bicarbonate and nitrate present in LLW.

2. Materials and Methods

2.1. ZVI Synthesis

All chemicals are ACS grade, and mili-Q water was boiled and purged with N_2 prior to the use. The synthesis of ZVI was performed using a modified method described by Ponder and co-

workers [7]. Instead of $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 was used to eliminate the S contamination during the ZVI synthesis. 16 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 150 mL of degassed mili-Q water, and then NaBH_4 was added incrementally in 1.6 times the molar amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. NaBH_4 was slowly added allowing H_2 gas formed to subside between increments. The solution mixture was then shaken for 20 min. and then filtered using a 0.45 μm Millipore type HA gridded membrane filter paper (Millipore, Billerica, MA). The remaining solids were washed liberally with 15 mL of degassed Mili-Q water and then washed with 100% ethanol. Washing with freshly synthesized ZVI with degassed Mili-Q prior to redox experiments has been commonly performed by other researchers [12-16]. This fresh ZVI was immediately used for each redox kinetic experiment. The Point of Zero Charge (PZC) of the ZVI particles was measured using the method described by Ferris and Jepson (1975) [17]. The PZC was about 8.4 (± 0.2) (Fig S1). Five points Brunauer, Emmett and Teller (BET) N_2 adsorption isotherm showed that surface area analysis is 43.3(± 0.5) m^2/g . Scanning electron microscope image shows spherical particles is about 600-700nm, and platy like structure is $\sim 100\text{nm}$ (Fig S2). The ZVI seems to be a mixture of micro and nano ZVI.

2.2. Bulk X-ray Diffraction Analyses

Powder XRD data were collected from 10 to 90° 2 θ using a Siemens-Bruker D5000 diffractometer (Siemens Corp., Washington, D.C.) (graphite monochromatized Cu K α radiation, 0.02° 2 θ step size, scanning speed of 1 deg/min). All samples were analyzed as random mounts using the back-packed procedure [18]. The detection limit for crystalline phases by bulk XRD analyses is approximately 2 % by wt. Mineral identifications were conducted using the JCPDS reference files.

2.3. Re(VII)O_4^- Sorption in ZVI as a Function of pH

The pseudo-equilibrium sorption experiments of ReO_4^- in ZVI were conducted as a function of pH (4 to 12) (ZVI: solution ratio: approximately 2.5 g/L, an initial $[\text{ReO}_4^-]$: 0.27 mM, and 0.3M NaCl electrolyte) under the atmospheric condition ($\text{pCO}_2 = 10^{-3.4}$ atm). This was to simulate the mixing condition of the current CWT. Freshly synthesized ZVI was washed with

ethanol-milli-Q water-ethanol, dried in N₂ atm. for 2 hrs, and immediately weighed right before the experiments. The dry mass was calculated after correcting for residual moisture using subsamples. The 0.3M electrolyte concentration was used to maintain similar ionic strength conditions required in the kinetic studies described below. For example, the pH 8.3 kinetic test conditions required high amounts of NaHCO₃⁻ (0.2M) to provide adequate buffering and high NaNO₃ concentrations (0.1M). The freshly synthesized ZVI was added to the NaCl solution to allow for pH equilibration for several hrs and then the suspensions were spiked with the ReO₄⁻ stock solution. The reaction vessels were shaken on an end-over shaker at 18 rpm overnight. After the equilibration, pH was measured. ZVI suspensions were then filtered through 0.2 µm PVDF filters, and aliquots were analyzed for ReO₄⁻ concentration using the spectrophotometric method [19,20].

2.4. Kinetic Experiments

Rhenium sorption kinetic experiments in ZVI (0.27 mM and a 10 g/L ZVI concentration) were carried out at pH 8.3 (± 0.1), 9.2 (± 0.16), and 10.2 (± 0.12) controlled by carbonate buffer solutions (pH 8.3: 0.2M NaHCO₃, pH 9.2: 0.09M NaHCO₃ and 0.01M Na₂CO₃ and pH 10.2: 0.04M NaHCO₃ and 0.06M Na₂CO₃). Samples were also prepared with increasing amounts of nitrate at 0.001M, 0.01M, and 0.1M in order to evaluate the effects of nitrate on Re sorption. Ionic strength of the all samples was adjusted to 0.3M with addition of NaCl. Duplicate bottles were sacrificially sampled at 10, 30 min, 1, 3, 6, 12, and 24 hrs. The aliquot samples were then filtered through a 0.2 µm PVDF syringe filter. Samples were then analyzed for aqueous Re using the spectrophotometric analysis method [19,20]. Ferrous ion and total Fe analysis were also performed by using the 1, 10-phenanthroline method [21]. Our preliminary experiments using different [Re(VII)] suggested that the rate was not independent of [Re(VII)] and was not directly proportional to [Re(VII)]. Assuming that the concentration of Fe remains relatively constant in comparison to [Re(VII)] because it is supplied in great excess, the following pseudo second order rate kinetic model (Eq. 1) by Ho and McKay (1998) [22] was used to estimate the rate.

$$\frac{t}{q_t} = \frac{1}{kq_c^2} + \frac{1}{q_c}t \quad (\text{Eq. 1})$$

Where q_t is the amount of Re sorbed onto ZVI at a unit time in mg/g. The q_c term is the modeled amount of Re sorbed onto ZVI at equilibrium, and is determined in equation (1) by plotting t/q_t vs. t where the slope of the fit line is equal to $1/q_c$. The rate constant k (g/mg hr) is determined from equation (1) by the same linear plot and using the intercept value to solve for k .

2.5. Characterization Reaction Products

Reaction products from 24hr kinetic samples were selectively analyzed using X-ray diffraction (described above) and Re L_3 -edge X-ray absorption spectroscopy. Rhenium L_3 -edge XAS measurements were performed at DND-CAT 5BM-D at Advanced Photon Source, Argonne, IL. All measurements of sorption sampled were performed in fluorescence mode at room temperature using a 4 element vortex detector with several layers of Al foils. Two Re standards (Re(IV)O₂ and NH₄ReO₄) were measured in transmission mode. 30mg of Re standards were mixed with 40 mg of boron nitride (BN). The energy calibration was performed at 10,535 eV using the Re(VI)O₂ standard. Spectra were recorded in two regions: 0.6 eV steps from -200 eV to -30 eV with a base count time of 1 sec. and 0.05 eV steps from -30 eV to 14 Å⁻¹ at a final K count time of 20 sec. dwell. XAS spectra were processed using Sixpack software [23] according to the method described by Arai [24]. A fixed value of 0.9 was used for the amplitude reduction factor (S_0^2). Errors of R for the Re-O/Re shells were estimated by comparison of the EXAFS fit results of α -ReO₂ to the values given by Ferreria et al. [25]. The accuracies were 3.3% for $R_{\text{Re-O}}$ and 14% for $R_{\text{Re-Re}}$. Debye Waller factor for Re-O was fixed 0.029 which is average value for the Re-O shell of α -ReO₂ [25]. The coordination number (CN) and interatomic distance (R) of Re-O/Re shells were not fixed during the fit.

3. Results and Discussion

3.1. Effect of pH on ReO₄⁻ Sorption in ZVI

Fig 1A shows the results of ReO_4^- sorption in ZVI after 24 hrs. The Re(VI) sorption was highest at near neutral pH. And the sorption decreases with decreasing pH from near neutral pH to 3. At low pH, the activity of protons is high. Protons readily accept electrons from ZVI, resulting in the formation of corrosion products at the ZVI surface. This reaction, in turn, would cause less electron donor, ZVI, to be available for Re(VII)O_4^- . The production of H_2 gas was observed during the experiments. The reduction of H^+ by ZVI at acidic pH is shown below [10]. Gibbs free energy of the oxidation of ZVI by protons is negative, indicating that the reaction is spontaneous [26].

It is also apparent that ReO_4^- sorption was inhibited in alkaline conditions. The reduction in Re sorption is attributed to 1) auto oxidation of ZVI and 2) surface charge property. The ZVI surface becomes more passive towards Re(VII) reduction due to the formation of Fe-hydroxides at the surface [27-29]. Yoon and co-workers state that when dissolved iron species are formed during oxidation reactions of ZVI in water [30]. Two oxidation reactions of ZVI are suggested by Furukawa and co-workers [31].

and

The newly dissolved ferrous species can further react with OH^- that is present in solution to form ferrous hydroxide species. This can further oxidized to form $\text{Fe}^{\text{III, II}}$ (oxyhydr)oxide compounds such as magnetite, lepidocrocite, ferrihydrite, and goethite, which in turn pacifies the ZVI surface towards further reduction reactions [30-32]. The XRD analysis showed that the major

peak for the fresh ZVI has a 2θ value of about 45° (Fig 2A). With increasing pH in the presence of Re(VII) (Fig 2A), magnetite and iron hydroxide minerals begin to form, and the most prominent being Fe_3O_4 . No peaks of Re(IV)O_2 or Re(OH)_2 species were observed. It is likely that it is below the detection limit of XRD and or amorphous nature of reaction products. Perrhenate reduction can also be inhibited due to a higher negative surface charge of the ZVI particles in alkaline solution. Since the ReO_4^- anions are not attracted to the negatively charged surface under these conditions ($\text{pH} > \text{PZC}$), electron transfer reactions are suppressed [10,33].

3.2. XAS Analysis of ReO_4^- Reacted ZVI at alkaline pH

Under such favorable alkaline conditions, the reduction of Re(VII) was observed. X-ray absorption near edge structure spectroscopy (XANES) analysis revealed the formation of Re(IV) reaction products. At pH 8.29-10.43 in the absence of nitrate, Re(VII) was readily reduced to Re(IV) (Fig 3). The whiteline peak of these sorption samples are at the whiteline peak of $\text{Re(IV)O}_2(\text{s})$. Extended X-ray absorption fine structure spectroscopy (EXAFS) analysis (Fig 4 and Table-1) also support the presence of Re(IV). In the absence of nitrate, all products are similar to the structural parameter of $\text{Re(IV)O}_2(\text{s})$ that were reported by Ferreria et al. [25]. The interatomic distance of Re-O is $\sim 2\text{\AA}$ and coordination number (CN) is approximately 6, indicating the Re(IV) octahedral environment. If Re(VII) is present, CN should be ~ 4 . Because of distorted ReO_6 environment in Re(IV)O_2 [25], we attempted to fit the Re-O shell with three different distances between 1.8 and $2.01\text{\AA}$. However, these close distances were not successfully separated in the fit. For this reason, the Re-O was treated as an average interatomic distance. The presence of Re-Re can be observed at $\sim 2.53\text{\AA}$ in the samples without nitrate. The large CN of Re-Re (~ 7 -15) indicates the presence of amorphous ReO_2 precipitates. Calculated solubility of ReO_2 ($K_{\text{sp}}: 6.77 \cdot 10^{-43}$) indicates that it is very insoluble. A study by Kim et al. (2003) showed that dissolution of $\text{ReO}_2(\text{s})$ was not effected by pH or presence of dissolved oxygen in solution [34]. This supports the stability of $\text{ReO}_2(\text{s})$ under the oxic and alkaline conditions we studied.

Interestingly, when 0.1M NaNO_3 is present, different surface species are observed. At pH 8.36-10.51, we only report the presence of Re-O first shell. When Re-Re shell was incorporated in the fit, R-factor only improved less than few %. If there is any, Re-Re scatters are very weak in these samples. It is probably due to much smaller loading level in the samples with nitrate.

Because nitrate competitively oxidize Fe(0) (see discussion in 3.3), the amount of Re(VII) reduction was suppressed (Table-1). There was a negligible contribution from a Fe backscatterer, suggesting that the presence of Re(IV) inner-sphere surface species is unlikely. The presence of outer-sphere Re(IV) surface species might be more appropriate in addition to ReO₂ surface precipitates.

3.3. The Extent of Re(VII) Sorption in ZVI

Figs 1B-1D show the removal of Re(VII) from the solution that is expressed in a ratio of $[Re]_i:[Re]_0$ as a function of time, pH and $[NO_3^-]$. $[Re]_i$ is the concentration of Re(VII) at given time, $[Re]_0$ is the initial Re(VII) concentration. Table-2 summarizes the results of % Re(VII) sorbed in ZVI after 24 hrs. It is important to note that $[nitrate]$ was greater than $[Re(VII)]$ except for the control systems (i.e., no nitrate).

At all pH values tested, the addition of nitrate decreases the total amount of Re(VII) sorbed. After 24hrs, $[Re(VII)]$ remaining in the solution increases with increasing $[NO_3^-]$. The same trend is observed in at all pH values. Nitrate is a competitive electron acceptor for ZVI, since nitrate is more favorably reduced by ZVI than perrhenate. Thus lowering the reduction capacity of ZVI for Re(VII) when nitrate is added. XRD analysis (Fig 2B) supports the interpretation. Upon addition of NaNO₃ at respective pH, a Fe(0) peak disappeared while many additional iron (oxyhydr)oxide peaks appeared. The primary phase of these iron species is goethite.

Thermodynamic calculations of the NO_3^- and Re(VII) reduction by ZVI are shown below at standard state.

$$\Delta G^0 = -620 \text{ kJ} \quad [35]$$

$$\Delta G^0 = -136 \text{ kJ} \quad [36,37]$$

Several researchers documented NH_4^+ as the product of nitrate reduction when nitrate was reacted with ZVI [38-40]. The reaction is further inhibited as the surface of ZVI gets oxidized by Re(VII) and nitrate, and thus preventing the reduction of Re(VII) at the surface.

The effect of pH was also observed under the respective $[\text{NO}_3^-]$. At pH 8.3, 9.2 and 10.2, Re(VII) sorption decreased from 91% to 39% , 88.35% to 35.50%, 29.34% to 9.70%, respectively. The highest amount of Re(VII) sorption was observed at pH 8.2. Comparing to the control systems without any nitrate, little Re(VII) sorption occurs at pH 10.2. Although the effect of pH was small from 8.3 to 9.2, it is clear that the reaction extent decreases with increasing pH. At lower pH (e.g., $8.2 < \text{PZC}$) without nitrate, surface charge density is less negative than that at higher pH ($10.2 > \text{PZC}$). This is a preferred condition for Re(VII) to approach the ZVI surfaces. One can expect more reduction of Re(VII) to occur at pH 8.2 than at pH 10.2. As Re(VII) gets reduced, more Fe(0) gets oxidized. This will increase solubility of Fe(II) as well as Fe(III) as long as the system is undersaturated with respect to Fe(II)/Fe(III) oxyhydroxides at given pH. The release of Fe(III) for the kinetic samples is shown in Figs S3-S5. Most of dissolved Fe(II) was below detection limit of the phenanthroline method ($<0.19 \mu\text{M}$), the majority of dissolved iron shown in the figures is present as Fe(III). At pH 8.3, $[\text{Fe(III)}]$ generally peaked after several hours, and gradually decreases with increasing time (Fig S3). The same kinetic trend in the Fe(III) release was observed at pH 9.2 and 10.2 (Figs S4 and S5). At a fixed $[\text{NO}_3^-]$ in Figs S2-S4, the quantity of $[\text{Fe(III)}]$ decreases with increasing pH. In the pH 8.3 system, $[\text{Fe(III)}]$ remained less than 0.08mM (Fig S3). In the pH 9.2 system, the release of Fe(III) is no more than 0.025mM (Fig S4). At pH 10.2, the amount of Fe(III) release further decreases to $<0.02\text{mM}$ in all conditions (Fig S5). The Fe dissolution data support the pH dependent Re(VII) sorption data. A decrease in the extent of Re(VI) sorption at alkaline pH can also be described by the formation of reaction products by auto oxidation of ZVI. At high pH, auto oxidation of the ZVI surface is also expected, forming iron hydroxide coatings [10]. This iron hydroxide layer can suppress the electron transfer reactions between ZVI and Re(VII), which in turn less reductive capacity of the ZVI particles at alkaline pH [10].

3.4. Effects of Nitrate Concentration on Kinetic Rates

As described in the method section, the pseudo 2nd order models used to estimate the rate of Re(VII) sorption per unit mass of solid ZVI surface in the solution. Although the data are not presented, pseudo 1st order model was also attempted. However, the pseudo 2nd order model yielded in a better fit in all data. Linear fits for these 2nd order models are displayed in Figs 5-7, in the four panels of each figure for each tested reaction condition. A summary of rate constants along with the goodness of fit values are shown in Table-1. Increasing [NO₃⁻] within each pH value results in an increase in kinetic rate, the rate was increased from 0.023 g mg⁻¹ hr⁻¹ to 1.43 g mg⁻¹ hr⁻¹ at pH 8.2, from 0.03 to 1.81 at pH 9.2 and from 0.115 to 3.34 g mg⁻¹ hr⁻¹ at pH 10.2, respectively. A t-test was performed at an alpha value of 0.1 for duplicate kinetic experiments. The results are shown in Table S9. It shows that within each fixed pH range, increasing nitrate concentration results in a significant increase in kinetic rate values. Which further supports the fact that nitrate has an effect on the system. This process is explained by the charge neutrality effect by the adsorption of NH₄⁺ on the ZVI surfaces. Ammonium ions were generated during the reduction of nitrate by ZVI according to the reaction mentioned earlier in the sorption extent discussion.

The release of [NH₄⁺] in each kinetic system is shown in Figs S6-S8. Adding more nitrate has yielded in greater production of ammonium (Figs S6 and S7), though there is a slight decrease in [NH₄⁺] from pH 9.2 (Fig S7) to pH 10.2 (Fig S8). This can be explained by the adsorption of ammonium at pH > PZC (~8.4), but it might also be attributed to the change in aqueous speciation of ammonium at pH > pKa of ammonium (~9.25). Fig S1 clearly showed that ammonium adsorption was enhanced at alkaline pH values. The adsorption of ammonium on the ZVI surface makes the surface charge of ZVI less negative. This in turn, causes an electrostatic attraction of perrhenate anions to the NH₄⁺ adsorbed ZVI surfaces. Fig 8 illustrates how NH₄⁺ can facilitate attraction of perrhenate anions in these alkaline conditions.

3.5. Effects of pH on Kinetic Rates

Observing the data in Table-2, at a fixed nitrate concentration, there is an apparent increase in kinetic rates with increasing pH. For example, in the 0.1M NaNO₃ systems, there is a rate increase from 1.41 at pH 8.3 to 4.75 at pH 10.2. A t-test was also performed at an alpha value of 0.1 for duplicate kinetic experiments for each fixed nitrate value with increasing pH (8.3-10.2) (Table S10). Results show a significant increase in kinetic rates when increasing pH up to 10.2 under all reaction conditions. This may be due to an increase in NH₄⁺ affinity towards the surface under more alkaline conditions. As the results of NH₄⁺ adsorption, the surface charge becomes less negative comparing to the surface without NH₄⁺. This charge neutrality effect in turn facilitates more attraction of ReO₄⁻. However, this may not occur in the system without nitrate. The rate in no nitrate increases from 0.023 to 0.2154 g mg⁻¹ hr⁻¹ with increasing pH (Table-2). This trend could be the difference in corrosion products of the ZVI surface (i.e., oxidation of ZVI). More corrosion products are expected at lower pH values than higher pH values.

4. Conclusions

The results of this study provide insight towards the use of ZVI particles in cementitious waste technology to immobilize Tc⁹⁹. Using ReO₄⁻ as a chemical surrogate of Tc(VII)O₄⁻, effects of reaction conditions (i.e., pH and nitrate concentration) on the ReO₄⁻ sorption in synthetic ZVI particles was investigated. Over a broad pH range from pH 4-12, ReO₄⁻ shows highest sorption over a 24 hr period at near neutral pH conditions. Sorption onto ZVI is shown to decrease in both acidic and alkaline conditions. More surface corrosion of ZVI is expected to occur at within acidic conditions due to surface oxidation by H⁺, and preventing further donation of electrons to Re(VII)O₄⁻. In alkaline conditions, the formation of Fe-hydroxides at the surface likely causes the ZVI particles to become more passive towards Re(VII)O₄⁻. The surface charge of ZVI also becomes increasingly more negative in alkaline solution, causing less charge attraction between perhenate anions and the ZVI surfaces. Overall, these factors contribute to slow down the electron transfer reactions. Kinetic experiments exhibited less reaction extent both with increasing pH from 8.3 to 10.2 and [NO₃⁻] concentration from 0M to 0.1M. Interestingly, the kinetic rate increased with increasing [NO₃⁻]. Addition of [NO₃⁻] facilitates the production of

NH_4^+ , which adsorb strongly to the ZVI surface under alkaline conditions. This charge neutrality facilitates an electrostatic attraction of perrhenate anions, resulting in an increase of the rate of Re(VII) reduction.

Although the Re(VII) sorption was limited at high pH and high nitrate conditions, the reduction of Re(VII) occurred and formed Re(IV)O_2 precipitates. Because the Tc(VII) reduction is thermodynamically favorable than Re(VII), the results of this study is promising to improve the current cement waste form formulation such as saltstone. If one can suppress the auto oxidation of ZVI with chemical coatings, it may be possible to incorporate the ZVI as a potential reducing agent in highly alkaline LLW solutions. Some studies have involved the use of starches during the synthesis process [9,41,42]. This improves particle stability by making them less susceptible to surface oxidation, and prevents agglomeration of particles in solution in order to maintain higher surface area, thereby improving overall treatment effectiveness [43]. Additionally, some methods of treatment have looked into incorporating additional electron donors, specifically sulfide, in order to improve reducing capacity of ZVI towards TcO_4^- , and to facilitate formation of insoluble Tc(IV) sulfide species in addition to Tc(IV) oxides [44].

Acknowledgements

We thank for C. Mitchell from UIUC for the chloride and ammonium analysis. Portions of this work were performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) located at Sector 5 of the Advanced Photon Source (APS). DND-CAT is supported by Northwestern University, E.I. DuPont de Nemours & Co., and The Dow Chemical Company. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

References

- [1] K. Schwochau, Technetium: chemistry and radiopharmaceutical applications, Wiley-VCH, Weinheim, 2000.
- [2] E.H. Schulte, P. Scoppa, Sources and behavior of technetium in the environment, Sci. Total Environ. 64 (1987) 163–179.
- [3] K. Yoshihara, Technetium and rhenium: their chemistry and its applications, in: K.

- Yoshihara, T. Omori (Eds.), *Technetium Rhenium Their Chem. Its Appl.*, Springer, Berlin, 1996 17–35.
- [4] D.I. Kaplan, T. Hang, Estimated duration of the subsurface reduction environment produced by the salt-stone disposal facility on the Savannah River Site, Washington Savannah River Company WSRC-STI-2007-00046 (2007).
- [5] A. Roy, Sulfur speciation in granulated blast furnace slag: An X-ray absorption spectroscopic investigation, *Cem. Concr. Res.* 39 (2009) 659–663.
- [6] K.J. Cantrell, D.I. Kaplan, T.W. Wietsma, Zero-valent iron for the in situ remediation of selected metals in groundwater, *J. Hazard. Mater.* 42 (1995) 201–212.
- [7] S.M. Ponder, J.G. Darab, T.E. Mallouk, Remediation of Cr (VI) and Pb (II) aqueous solutions using supported nanoscale zero-valent iron, *Environ. Sci. Technol.* 34 (2000) 2564–2569.
- [8] J. Xin, X. Zheng, J. Han, H. Shao, O. Kolditz, Remediation of trichloroethylene by xanthan gum-coated microscale zero valent iron (XG-mZVI) in groundwater: Effects of geochemical constituents, *Chem. Eng. J.* 271 (2015) 164–172.
- [9] Q. Ding, T. Qian, F. Yang, H. Liu, L. Wang, D. Zhao, et al., Kinetics of reductive immobilization of rhenium in soil and groundwater using zero valent iron nanoparticles, *Environ. Eng. Sci.* 30 (2013) 713–718.
- [10] H. Liu, T. Qian, D. Zhao, Reductive immobilization of perrhenate in soil and groundwater using starch-stabilized ZVI nanoparticles, *Chinese Sci. Bull.* 58 (2013) 275–281.
- [11] P.M. Almond, D.I. Kaplan, C.A. Langton, D.B. Stefanko, W.A. Spencer, Method evaluation and field sample measurements for the rate of movement of the oxidation front in saltstone, (2012). SRNL-STI-2012-00468. The U.S. Department of Energy Savannah River National Laboratory. Aiken, SC
- [12] L. Garcell, M. Morales, M. Andres-Vergés, P. Tartaj, C. Serna, Interfacial and rheological characteristics of maghemite aqueous suspensions, *J. Colloid Interface Sci.* 205 (1998) 470–475.
- [13] Y. Hwang, D. Kim, H.-S. Shin, Inhibition of nitrate reduction by nacl adsorption on a nano-zero-valent iron surface during a concentrate treatment for water reuse, *Environ. Technol.* 3330 (2014) 1–31.
- [14] M. Mallet, K. Barthélémy, C. Ruby, A. Renard, S. Naille, Investigation of phosphate adsorption onto ferrihydrite by X-ray photoelectron spectroscopy, *J. Colloid Interface Sci.* 407 (2013) 95–101.
- [15] A.M. Moore, T.M. Young, Chloride interactions with iron surfaces: implications for perchlorate and nitrate remediation using permeable reactive barriers, *J. Environ. Eng.* 131 (2005) 924–933.
- [16] T. Rennert, T. Mansfeldt, Sorption of iron-cyanide complexes on goethite in the presence

- of sulfate and desorption with phosphate and chloride, *J. Environ. Qual.* 31 (2002) 745–751.
- [17] A.P. Ferris, W.B. Jepson, The exchange capacities of kaolinite and the preparation of homoionic clays, *J. Colloid Interface Sci.* 51 (1975) 245–259.
- [18] Moore, D. M.; R. C. Reynolds, J. X-ray diffraction and the identification and analysis of clay minerals; Second ed.; Oxford University Press: New York, 1997.
- [19] G. Dutta, B. Sur, Spectrophotometric determination of rhenium using 2-pyridyl thiourea, *Mikrochim. Acta.* (1987) 359–369.
- [20] B.A. Lenell, Y. Arai, Evaluation of perrhenate spectrophotometric methods in bicarbonate and nitrate media, *Talanta.* 150 (2016) 690–698.
- [21] J.W. Stucki, Quantitative assay of minerals Fe²⁺ and Fe³⁺ using 1,10 phenanthroline: III a rapid photochemical method, *Clays Clay Miner.* 36 (1988) 379–381.
- [22] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [23] S.M. Webb. A graphical user interface for XAS analysis using IFEFFIT. *Physica Scripta.* T115 (2005)1011–1014.
- [24] Y. Arai. X-ray Absorption Spectroscopic investigation of molybdenum multi-nuclear sorption mechanism at the goethite-water interface. *Environ. Sci. Technol.* 44(2010) 8491-8496.
- [25] F.F. Ferreira, H.P.S. Corrêa, M.T.D. Orlando, J. L. Passamai Jr, C.G.P. Orlando, I.P. Cavalcante, F. Garcia, E. Tamura, L. G. Martinez, J. L. Rossi and F. C. L. de Meloe. Pressure study of monoclinic ReO₂ up to 1.2 GPa using X-ray absorption spectroscopy and X-ray diffraction. *J. Synch. Rad.*16 (2009) 48–56.
- [26] M.M. Benjamin, *Water Chemistry*, 2nd ed., Waveland Press, Inc, Long Grove, IL, 2015.
- [27] J.L. Chen, S.R. Al-Abed, J.A. Ryan, Z. Li, Effects of pH on dechlorination of trichloroethylene by zero-valent iron, *J. Hazard. Mater.* 83 (2001) 243–254.
- [28] H. Tian, J. Li, Z. Mu, L. Li, Z. Hao, Effect of pH on DDT degradation in aqueous solution using bimetallic Ni/Fe nanoparticles, *Sep. Purif. Technol.* 66 (2009) 84–89.
- [29] G.C.C. Yang, H.L. Lee, Chemical reduction of nitrate by nanosized iron: kinetics and pathways, *Water Res.* 39 (2005) 884–894.
- [30] I.H. Yoon, S. Bang, J.S. Chang, M. Gyu Kim, K.W. Kim, Effects of pH and dissolved oxygen on Cr(VI) removal in Fe(0)/H₂O systems, *J. Hazard. Mater.* 186 (2011) 855–862.

- [31] Y. Furukawa, J.W. Kim, J. Watkins, R.T. Wilkin, Formation of ferrihydrite and associated iron corrosion products in permeable reactive barriers of zero valent iron, *Env. Sci. Tech.* 36 (2002) 5469-5475.
- [32] H. Li, J. Wan, Y. Ma, M. Huang, Y. Wang, Y. Chen, New insights into the role of zero-valent iron surface oxidation layers in persulfate oxidation of dibutyl phthalate solutions, *Chem. Eng. J.* 250 (2014) 137–147.
- [33] P. Yuan, D. Liu, M. Fan, D. Yang, R. Zhu, F. Ge, Removal of hexavalent chromium [Cr(VI)] from aqueous solutions by the diatomite-supported/unsupported magnetite nanoparticles, *J. Hazard. Mater.* 173 (2010) 614–621.
- [34] E. Kim, J. Boulègue, Chemistry of rhenium as an analogue of technetium: Experimental studies of the dissolution of rhenium oxides in aqueous solutions, *Radiochim. Acta.* 91 (2003) 211–216.
- [35] I. Kielemoes, P. De Boever, W. Verstraete, Influence of denitrification on the corrosion of iron and stainless steel powder, *Environ. Sci. Technol.* 34 (2000) 663–671.
- [36] A.J. Bard, R. Parsons, J. Jordan, Standard potentials in aqueous solution, 1st ed., M. Dekker, New York, 1985.
- [37] D.D. Ebbing, General Chemistry, 4th ed., Houghton Mifflin, Boston, 1993.
- [38] S.C. Ahn, S.Y. Oh, D.K. Cha, Enhanced reduction of nitrate by zero-valent iron at elevated temperatures, *J. Hazard. Mater.* 156 (2008) 17–22.
- [39] D. Cho, H. Song, F.W. Schwartz, B. Kim, B. Jeon, Chemosphere The role of magnetite nanoparticles in the reduction of nitrate in groundwater by zero-valent iron, *Chemosphere.* 125 (2015) 41–49.
- [40] J.M. Rodríguez-Maroto, F. García-Herruzo, A. García-Rubio, C. Gómez-Lahoz, C. Vereda-Alonso, Kinetics of the chemical reduction of nitrate by zero-valent iron, *Chemosphere.* 74 (2009) 804–809.
- [41] H. Dong, I.M.C. Lo, Influence of humic acid on the colloidal stability of surface-modified nano zero-valent iron, *Water Res.* 47 (2013) 419–427.
- [42] F. He, D. Zhao, Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water, *Environ. Sci. Technol.* 39 (2005) 3314–3320.
- [43] N. Saleh, K. Sirk, Y. Liu, T. Phenrat, B. Dufour, K. Matyjaszewski, Surface modifications enhance nanoiron transport and npl targeting in saturated porous media, *Environ. Eng. Sci.* 24 (2007) 45–57.
- [44] D. Fan, R.P. Anitori, B.M. Tebo, P.G. Tratnyek, J.S.L. Pacheco, R.K. Kukkadapu,

Reductive sequestration of pertechnetate ($^{99}\text{TcO}_4^-$) by nano zerovalent iron (nZVI) transformed by abiotic sulfide, *Environ. Sci. Technol.* 47 (2013) 5302–5310.

Table-1: Least-squares analyses of Re L₃-edge XAS spectra.

Sample		Re-O	Re-Re	R-factor	Loading level (mg/kg)/reference
pH 8.29 kinetics 0M nitrate	CN	4.3(8)	15(9)	0.147	10961.5
	R(Å)	2.04(6)	2.53(3)		
	σ ² (Å ²)	0.0029*	0.008(5)		
pH 8.36 kinetics 0.1 M nitrate	CN	7.3(8)	-----	0.156	7384.6
	R(Å)	2.04(1)			
	σ ² (Å ²)	0.0029*			
pH 9.42 kinetics 0M nitrate	CN	5.2(7)	11(6)	0.098	8076.9
	R(Å)	2.00(2)	2.53(2)		
	σ ² (Å ²)	0.0029*	0.005(3)		
pH 9.51 kinetics 0.1 M nitrate	CN	7.5(8)	-----	0.136	7442.3
	R(Å)	2.04(1)			
	σ ² (Å ²)	0.0029*			
pH 10.43 kinetics 0M nitrate	CN	6.6(9)	7 (5)	0.115	5769.2
	R(Å)	2.02(1)	2.53(2)		
	σ ² (Å ²)	0.0029*	0.005		
pH 10.51 kinetics 0.1 M nitrate	CN	7.5(9)	-----	0.177	5192.3
	R(Å)	2.05(1)			
	σ ² (Å ²)	0.0029*			
α-ReO ₂ (s)	CN	6	-----	-----	[25]
	R(Å)	1.93-2.10			
	σ ² (Å ²)	0.0027-0.0032			

The number in parentheses is the standard deviation of the parameter obtained by EXAFS fit. *Fixed parameter. CN: coordination number, R(Å): interatomic distance, σ² (Å²): Debye-Waller factor. S_o² of 0.9 was used in the fit.

Table 2: Summary of reaction extents and pseudo 2nd order rates for Re(VII) sorption in ZVI as a function of reaction conditions. Values in parenthesis indicate goodness of fit from kinetic model fit.

Reaction Conditions	% Re(VII) sorbed after 24 hours	Pseudo 2 nd order model, g mg ⁻¹ hr ⁻¹	
pH 8.3, 0 M NaNO ₃	90.44	0.023	(0.9714)
pH 8.3, 0.001 M NaNO ₃	59.41	0.10293	(0.9984)
pH 8.3, 0.01 M NaNO ₃	48.93	0.643	(0.9993)
pH 8.3, 0.1 M NaNO ₃	39.05	1.412	(0.9997)
pH 9.2, 0 M NaNO ₃	88.35	0.030	(0.9684)
pH 9.2, 0.001 M NaNO ₃	75.28	0.1183	(0.9793)
pH 9.2, 0.01 M NaNO ₃	51.07	0.261	(0.9935)
pH 9.2, 0.1 M NaNO ₃	35.50	1.8099	(0.9997)
pH 10.2, 0 M NaNO ₃	29.34	0.2154	(0.984)
pH 10.2, 0.001 M NaNO ₃	19.91	1.2633	(0.9896)
pH 10.2, 0.01 M NaNO ₃	19.65	2.34	(0.9918)
pH 10.2, 0.1 M NaNO ₃	9.70	4.745	(0.9997)

Figure 1: (A) Re(VII) sorption in ZVI as a function of pH (suspension density: 2.5 g/L, reaction time:24 hrs., background electrolyte: 0.3M NaCl, and initial [Re(VII)]:0.27 mM). The extent of Re(VII) sorption in ZVI at [NaNO₃]: 0-0.1M.. $[Re]_i/[Re]_0$ is plotted against time in hrs, for pH 8.3 (B), 9.2 (C), and 10.2 (D) respectively. All error bars (<2%) are hidden within symbols.

Figure 2: XRD patterns of fresh ZVI and equilibrium reaction samples after 24 hr reaction time (ZVI suspension = 5 g/L, [ReO₄⁻] = 150 mg/L) (A) and kinetic samples after 24 hr reaction time at 0M and 0.1M NaNO₃ (ZVI suspension = 10 g/L, [ReO₄⁻] = 50 mg/L) (B).

Figure 3: Re L₃-edge XANES spectra of Re reference compounds (Re(IV)O₂ and NH₄Re(VII)O₄) and Re(VII) reacted ZVI at alkaline pH in 0 and 0.1M NaNO₃. A vertical dashed line is at the whiteline peak of Re(IV)O₂(s).

Figure 4: A) Non-linear least-squares fit of normalized k^3 -weighted Re L_3 -edge EXAFS spectra of Re(VII) reacted ZVI. B) respective Fourier Transformed radial structural function (uncorrected for phase shift of backscattering atom) of EXAFS spectra. Solid lines and dashed lines represent normalized raw data and fit, respectively.

Figure 5: Results of pseudo 2nd order kinetic model fit in the Re(VII) sorption data in ZVI at pH 8.3 with increasing NaNO₃. A) 0M NaNO₃, B) 0.001M NaNO₃, C) 0.01M NaNO₃, and D) 0.1M NaNO₃.

Figure 6: Results of pseudo 2nd order kinetic model fit in the Re(VII) sorption data in ZVI at pH 9.2 with increasing NaNO₃. A) 0M NaNO₃, B) 0.001M NaNO₃, C) 0.01M NaNO₃, and D) 0.1M NaNO₃.

Figure 7: Results of pseudo 2nd order kinetic model fit in the Re(VII) sorption data in ZVI at pH 10.2 with increasing NaNO₃. A) 0M NaNO₃, B) 0.001M NaNO₃, C) 0.01M NaNO₃, and D) 0.1M NaNO₃.

Figure 8: Ammonium adsorption enhanced ReO_4^- adsorption in ZVI under alkaline conditions (modified from Cho et al., 2015).

Ammonium adsorption enhanced ReO_4^- adsorption in ZVI under alkaline conditions (modified from Cho et al., 2015)