Heterogeneous selenite reduction by zero valent iron steel wool

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ABSTRACT

Mine drainage from the low-sulfur surface coal mines in southern West Virginia, USA, is circumneutral (pH > 6) but contains elevated selenium (Se) concentrations. Removal of selenite ions from aqueous solutions under anoxic condition at pH 6–8.5 by zero valent iron steel wool (ZVI-SW) was investigated in bench-scale kinetic experiments using wet chemical, microscopic and spectroscopic techniques (X-ray photoelectron spectroscopy). ZVI-SW could effectively and efficiently remove Se\(^{IV}\) from solution with pH 6–8.5. A two-step removal mechanism was identified for Se\(^{IV}\) reduction by ZVI-SW. The proposed mechanism was electrochemical reduction of Se\(^{IV}\) by Fe\(^0\) in an initial lag stage, followed by a faster heterogeneous reduction, mediated by an Fe\(^{II}\)-bearing phase (hydroxide or green rust). Solution pH was a critical factor for the kinetic rate in the lag stage (0.33 h\(^{-1}\) for pH > 8 and 0.10 h\(^{-1}\) for pH 6–8). The length of lag stage was 20–30 min as determined by the time for dissolved Fe\(^{II}\) concentration to reach 0.30 ± 0.04 mg L\(^{-1}\) which was critical for induction of the faster stage. About 65% of the initial Se\(^{IV}\) was reduced to Se\(^{0}\), the primary reductive product in both stages.

Key words | green rust, iron hydroxides, kinetics, mechanism, selenite, treatment

INTRODUCTION

Elevated selenium (Se) levels in the environment can be attributed to both natural and anthropogenic sources including seleniferous parent material, volcanic activities, agricultural irrigation, petroleum production, coal mining and combustion (Lemly 2004). The toxicity and mobility of Se in the environment depends on redox conditions (Masscheleyn et al. 1990; Tokunaga et al. 1997) and the presence of adsorbents and microbes (Balistrieri & Chao 1987; Zhang & Moore 1997). The oxidized forms of selenium, Se\(^{IV}\) and Se\(^{VI}\) are soluble, bioavailable and problematic, for they can bioaccumulate through the food chain. The acute toxicity of Se\(^{IV}\) is two to four times larger than that of Se\(^{VI}\) to aquatic organisms (Somogyi et al. 2007). The primary species in the leachates from coal mine and combustion byproducts is typically Se\(^{IV}\) (Committee on Mine Placement of Coal Combustion Wastes 2006; Wang et al. 2007; Ziemkiewicz et al. 2011).

Various iron-containing materials including Fe\(^{II}\) hydroxide (Murphy 1988; Zingaro et al. 1997), green rust (GR) (Myneni et al. 1997; Hayashi et al. 2009), Fe\(^{II}\)-containing minerals (Charlet et al. 2007; Scheinost & Charlet 2008; Chen et al. 2009), Fe\(^{0}\) powder (Twidwell et al. 2005; Zhang et al. 2005; Gibson et al. 2012) and foil (Qiu et al. 2000; Scheidegger et al. 2005), Fe-bearing and Fe\(^{0}\) nanoparticles (Lopez de Arroyabe Loyo et al. 2008; Scheinost & Charlet 2008; Olegario et al. 2010; Ling et al. 2015) have been shown to remove selenium oxyanions from solution. Because of the reducing capacity (−0.44 V), environmentally benign redox products and high removal efficiency, Fe\(^{0}\) has been widely used in in situ Se treatment technologies, including permeable reactive barriers (Morrison et al. 2002; Frankenberger et al. 2004). However, the drawback of Fe\(^{0}\) when used as powders or filings, is its propensity for corrosion and cementation which has limited its long-term field application (Frankenberger et al. 2004; Yoon et al. 2011). The adaption of Fe\(^{0}\) nanoparticles for treating Se has attracted interest (Olegario et al. 2010; Ling et al. 2015); however, their small particle size and the aggregation effect make them difficult to apply in continuous flow systems. Steel wool is an inexpensive source of Fe\(^{0}\). It has inherent resistance to corrosion, which decreases passivation during treatment processes, making it a good ZVI candidate material for Se treatment.

Mine drainage from low-sulfur southern West Virginia surface coal mines is neutral to slightly alkaline in pH but contains selenium concentration above 5 μg L\(^{-1}\). A small
In acidic solutions, both SeIV and SeVI oxyanions were reduced by Fe0, primarily to Se0, under either oxic or anoxic conditions (Scheidegger et al. 2003; Liang et al. 2013, 2015). In acidic solutions, both SeIV and SeVI oxyanions were reduced by Fe0, primarily to Se0, under either oxic or anoxic conditions (Scheidegger et al. 2003; Liang et al. 2013, 2015). But the Se oxyanions removal by Fe0 were negligible under anoxic condition when pH was >6 (Yoon et al. 2011; Klas & Kirk 2013; Liang et al. 2015).

The reaction processes between granular Fe0 and SeIV when pH < 6 has been thoroughly explored by previous studies (Yoon et al. 2011; Klas & Kirk 2013; Liang et al. 2013, 2015); when pH > 6 granular Fe0 didn’t work for SeIV removal. However, ZVI-SW in the in situ Se treatment cell worked efficiently and effectively (Lovett 2008). The processes by which SeIV was removed by ZVI-SW under O2 limited conditions and what physical–chemical processes were involved during treatment are still unknown. The objectives of the present study were to: (1) quantify the removal rate of SeIV by ZVI-SW under anoxic condition at pH 6–8.5; (2) identify the oxidation status of products in the SeIV reduction / ZVI-SW oxidation system; and (3) propose the mechanisms for these reactions.

**MATERIAL AND METHODS**

**Materials**

All experiments were conducted with at least analytical grade chemicals and distilled-deionized water (DIW). Sodium selenite (Na2SeO3) was purchased from Sigma (MO, USA). Calcium chloride (CaCl2) was purchased from Fisher Scientific, Inc. (NJ, USA). The FeII source was Fe3(NH4)2(SO4)2·6H2O (Hach Co., USA). Steel wool was #0-Grade (Homax Products Inc., WA, USA) and purchased at a local paint supply store. A primary selenite stock solution (1,000 mg L−1) was prepared by dissolving Na2SeO3 in DIW. Working solutions were prepared daily by dilution from the primary standard. High purity nitrogen was obtained from Mountain State Air Gas (Morgantown, WV, USA). All experiments were conducted in water-jacketed, glass reaction flasks designed to allow for control of gas partial pressures, pH measurement and periodic sample collection. A constant mixing speed (300 rpm) was maintained with a digital overhead stirrer (Heidolph RZR-2000) with a Teflon-coated paddle.

Reference Fe-oxyhydroxide for microscopic and spectroscopic analysis was prepared from FeCl3 (Fisher Scientific, NJ, USA) and NaOH (1 M, Fisher Scientific, NJ, USA), FeIII oxyhydroxides were collected and air dried before analysis (Huang 2010).

**Selenite removal kinetics**

Initial selenite concentrations were 0.0, 1.0, 2.0 and 4.0 mg L−1 at two different CaCl2 concentrations (2.5 and 25 mM). Other experimental parameters investigated were the presence or absence of external FeII (20 mg L−1) and initial solution pH (pH 6–8.5). Selenium-containing solutions (1.0 L) were pre-equilibrated via N2-sparging. The Fe0 ZVI-SW loading rate was 0.5 g L−1. Batch experiments were conducted in free pH drift mode, with continuous pH measurement. Subsamples (9 mL) were withdrawn from the reactor periodically throughout the reactions and filtered immediately with a 0.45-μm pore diameter membrane for chemical analysis. Se speciation was determined by difference (Huang 2010). Briefly, each subsample was divided into three aliquots: aliquot 1 was acidified with 6 M HCl to a final acid concentration of 4 M, and SeIV determined by hydride generation–inductively coupled plasma spectroscopy (HG-ICP) (Perkin Elmer DV2100, Perkin-Elmer, Norwalk, CT, USA); aliquot 2 was digested with concentrated HCl at 90 °C for 15 min and then determined on HG-ICP (SeIV + SeVI); aliquot 3 was oxidized with 70% HNO3 at 90 °C for 15 min to fully oxidize SeIV and Se0 and then reduced following the procedure of aliquot 2 to determine Se0 + SeVI + SeIV. The limit of detection of the HG-ICP method is 0.097 μg kg−1. Ferrous iron was determined colorimetrically with the ferrozine method (Cary 50, Varian Inc. Palo Alto, CA, USA). At the end of each reaction, all residuals were collected and selenite, selenate and elemental selenium determined, as described above. All experiments were conducted at 30 °C at least in triplicate.

**Steel wool and reaction residual characterization**

Microscopic (Nikon SMZ-U plus Nikon digital camera DXM1200 Nikon, Japan) and scanning electron microscopy (SEM) (JEOL 7600F, JEOL, USA) images were collected. Chemical composition of the steel wool was determined after acid digestion with HCl (5 M) and HNO3 (10%). Iron, Mn, Cu, Zn and Cr were determined by inductively coupled plasma optical emission spectroscopy.
X-ray photoelectron spectroscopy (XPS) (Physical Electronics PHI 5000 VersaProbe) was employed to identify SeIV reaction products with the ZVI-SW sample described above. Monochromatic Al Kα (1,486.6 eV) was used as the X-ray source and an Ar neutralizer was applied for all samples. The analysis passing energy of 117.4 eV was used for survey scans, and 23.5 eV for high resolution scans of individual element peak regions; the takeoff angle was fixed at 45°. Spectra binding energies were calibrated by referencing adventitious carbon C(1 s) signal to binding energy 284.8 eV. XPS spectra peaks were fit using Gauss-Lorenz mode and Shirley background with PHI Multipack software.

RESULTS AND DISCUSSION

Steel wool characterization

Steel wool used in this study contained >99% iron, 0.43% manganese, 0.135% copper, 0.022% zinc, and 0.017% chromium. Optical and SEM images of ZVI-SW indicated a rough surface (Figure 1). These surface features increase surface area, potentially increasing reaction rates (Murphy 1988; Ling et al. 2015), and provide sites for the accumulation of reaction products.

Selenite removal in N₂ purged systems

When the initial solution pH was 6–8 the reaction between SeIV and ZVI-SW proceeded in two stages (Figure 2(a)). There was a lag stage of about 0.5 hour followed by a much faster removal stage lasting up to 4 hours. During the lag stage, pH increased from near 6 and plateaued just above pH 8, where it remained. There was a simultaneous increase in FeII from zero to 0.30 mg L⁻¹. Near the end of the lag stage, Se⁰ concentration began to increase, and increased for the remainder of the experiment. In previous studies on granular iron reduction-based treatment, this lag stage was not present under oxic condition (Rangsivek & Jekel 2005; Liang et al. 2013). The presence of the lag stage is attributed to the resistance of the steel wool to rapid oxidation to ferric iron. At the end of reaction, less than 3% of the initial SeIV was associated with the residual solids (Table 1), indicating that co-precipitation and/or adsorption of SeIV by ferric oxyhydroxide contributed very little to SeIV removal. Nearly 100% of the initial selenite in solution was removed in 4 hours. This is considerably faster removal than has been observed in other iron-mediated Se removal studies (Myneni et al. 1997; Zhang et al. 2005; Charlet et al. 2007; Scheinost & Charlet 2008; Tang et al. 2014).

When initial solution pH was >8, the overall reaction was shorter (2 h), solution pH remained near 8 and the increase in Se⁰ concentration began when the FeII concentration was near 0.30 mg L⁻¹ (Figure 2(b)). If the length of the lag stage is taken as the time to reach [FeII] = 0.30 ± 0.04 mg L⁻¹ or for Se⁰ to appear, then it was the length of the lag stage that determined the time needed to remove SeIV. When initial solution pH was greater than 8, lag stage, k, was larger than when solution pH was less than 8 (0.33 vs 0.10 h⁻¹, Table 2), assuming that the lag-stage reaction was pseudo-first-order (Su & Puls 1999),

\[
\frac{d[Se]}{dt} = -k[Se]
\]

(Supplemental Material Figure S1, Table 2).

Figure 1 | Microscopic (a) and SEM images (b) of steel wool surface.
available with the online version of this paper), and the final FeII/SeIV molar ratio was smaller (2.68 vs 5.23) than when initial solution pH was less than 8 (Table 2). Then, when the reaction was above pH 8, the molar ratio of FeII/SeIV was 2.68 (Table 2), similar to the stoichiometric ratio of Fe0 and SeIV in Equation (1). Both the increment of pH and the presence of Se0 support this hypothesis (Figure 2(a) and 2(b)). The FeII/SeIV ratio was larger (5.23) when the initial pH was 6–8 indicating that when Fe0 was the electron donor the potential for \( \text{H}^+ \rightarrow \text{H}_2(\text{g}) \) to occur increased when the initial \([\text{H}^+]\) was larger. Increased competition for electrons slowed SeIV removal. Although Se0 was detected, more FeII had been oxidized by \( \text{H}^+ \) (FeII/SeIV = 5.23). Note also the larger pH change (Figure 2(a) and 2(b)). Neither initial SeIV concentration nor ionic strength had a significant effect on SeIV removal in any stage. Precipitation as Fe2(SeO3)3 or FeSeO3 is an unlikely explanation for SeIV removal. All experimental solutions were undersaturated with respect to FeSeO3 (solubility product constant \( K_{sp} \) of \( 10^{-10} \) (Seby et al. 2001). Fe2(SeO3)3 precipitation starts when SeIV concentration exceeds \( 10^{-10} \) M and \( \text{pH} < 5 \) (Missana et al. 2009). In addition, very little SeIV was detected in acidified reaction residuals (Table 1).

![Figure 2](image-url) | SeIV removal kinetics with initial pH 6–8 (a), SeIV removal with initial pH > 8 (b); (♦) SeIV; (▴) FeII; (○) elemental selenium; (△) pH. Initial conditions: 2 mg L\(^{-1}\) SeIV, 2.5 mmol L\(^{-1}\) CaCl\(_2\). Arrows indicate when the FeII reached 0.30 ± 0.04 mg L\(^{-1}\).

Table 1 | Selenium fate in the reaction of SeIV and ZVI-SW

<table>
<thead>
<tr>
<th>Source</th>
<th>Selenium species</th>
<th>Portions %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliquot withdrawn for analysis</td>
<td>SeIV</td>
<td>9.5 ± 3.3</td>
</tr>
<tr>
<td></td>
<td>Se0</td>
<td>4.5 ± 1.8</td>
</tr>
<tr>
<td>Residual(^a)</td>
<td>SeIV</td>
<td>3.0 ± 2.2</td>
</tr>
<tr>
<td></td>
<td>Se0</td>
<td>60.9 ± 9.7</td>
</tr>
<tr>
<td>Recovery</td>
<td></td>
<td>77.9</td>
</tr>
</tbody>
</table>

\(^a\)Residual: Se speciation of the reaction residuals after acid digestion with HCl at the end of each experiment.

\(2\text{Fe}^0 + \text{HSeO}_3^- + 5\text{H}^+ \rightarrow \text{Se}^0 + 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \) (1)

The change in solution pH when ZVI reacted with SeIV was much slower than the control without SeIV (Supplemental Material Figure S2, available online), especially over the first 0.5 h indicating that \( \text{H}^+ \) competes with SeIV for electrons supplied by Fe0 (Kirby 1979). Thus, initial \( \text{H}^+ \) concentration was critical for SeIV removal rate in the lag stage and that it was the length of the lag stage that determined the time required to completely remove SeIV (Figure 2(a) and 2(b)). Additional evidence for an initial pH effect was the molar ratio of FeII in the solution and SeIV removed at the end of lag stage. When the reaction was above pH 8, the molar ratio of FeII/SeIV was 2.68 (Table 2), similar to the stoichiometric ratio of Fe0 and SeIV in Equation (1). Both the increment of pH and the presence of Se0 support this hypothesis (Figure 2(a) and 2(b)). The FeII/SeIV ratio was larger (5.23) when the initial pH was 6–8 indicating that when Fe0 was the electron donor the potential for \( \text{H}^+ \rightarrow \text{H}_2(\text{g}) \) to occur increased when the initial \([\text{H}^+]\) was larger. Increased competition for electrons slowed SeIV removal. Although Se0 was detected, more FeII had been oxidized by \( \text{H}^+ \) (FeII/SeIV = 5.23). Note also the larger pH change (Figure 2(a) and 2(b)). Neither initial SeIV concentration nor ionic strength had a significant effect on SeIV removal in any stage. Precipitation as Fe2(SeO3)3 or FeSeO3 is an unlikely explanation for SeIV removal. All experimental solutions were undersaturated with respect to FeSeO3 (solubility product constant \( K_{sp} \) of \( 10^{-10} \) (Seby et al. 2001). Fe2(SeO3)3 precipitation starts when SeIV concentration exceeds \( 10^{-10} \) M and \( \text{pH} < 5 \) (Missana et al. 2009). In addition, very little SeIV was detected in acidified reaction residuals (Table 1).

Table 2 | Pseudo-first-order rate constant, \( R^2 \) and FeII/SeIV molar ratio in the lag stage

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>( k ) (h(^{-1}))</th>
<th>( R^2 )</th>
<th>FeII/SeIV molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6–8</td>
<td>0.10</td>
<td>0.94</td>
<td>5.23</td>
</tr>
<tr>
<td>pH &gt;8</td>
<td>0.33</td>
<td>0.93</td>
<td>2.68</td>
</tr>
</tbody>
</table>

XPS characterization of products

Previous studies reported spectra of a range of iron oxides and hydroxides that could be fitted using Gupta and Sen multiplet peaks (GS), and satellite and multiplet features (McIntyre & Zetaruk 1977; Grosvenor et al. 2004). The center of gravity (CG) of Fe (2p\(_{1/2}\)) 711.3 eV together with the FeIII characteristic satellite at \( \sim 719.2 \) eV (arrow 2, Supplemental Material Figure S3, available with the online version of this paper) and \( \Delta \text{BE} \) 15.7 eV between CG of Fe (2p\(_{1/2}\)) and Fe (2p\(_{3/2}\)) of 13.7 eV indicated the main Fe species in the sample was FeIII (McIntyre & Zetaruk 1977; Refait et al. 2000; Grosvenor et al. 2004) (Figure S3). Following the procedure and GS parameters of previous studies (McIntyre & Zetaruk 1977; Grosvenor et al. 2004), four
multiep spectra (dashed lines) (full width at half maximum (FWHM) = 1.48 eV) were identified under the Fe (2p3/2) spectra (solid line) envelope of the sample – 709.6 ± 0.2, 710.9 ± 0.2, 712.3 ± 0.2 and 713.7 ± 0.2 eV – in agreement with Fe (2p3/2) found in reference Fe-oxyhydroxides (Supplemental Material Figure S3), again indicating Fe in the end product was mainly ferric oxyhydroxide. The satellite peak (arrow 1) featured at 717.2 eV may indicate trace FeII in the sample, and FeIII (2p3/2) in FeSe or FeSe2 compound was in the region of ~709.2 eV (Grosvenor et al. 2004; Sasaki et al. 2008) and thus may be behind the peaks of FeIII.

Although there was overlap of the two Se (3d) and Fe (5p) binding energy regions, four lines (FWHM = 1.56 eV) could be distinguished with peak fitting software (Figure 3). The peak at 54.1 ± 0.2 eV is uncertain because the Se–II (3d) and FeIII (3p) peaks are both in this region; it could indicate the presence of FeSe or FeSe2 (Shenasa et al. 1986; Koyama et al. 2000). Both are thermodynamically possible, and have been found in other studies of FeII-bearing hydroxides and GRs (Koyama et al. 2000; Sasaki et al. 2008; Scheinost et al. 2008). Peaks 56.7 ± 0.2, 58.2 ± 0.2 eV are assigned to Fe (3p) in FeOOH according to Fe (3p) spectra of reference FeOOH. Both Se0 (3d) and FeIII (3p) have the same peak position of 55.4 eV (Shenasa et al. 1986; Moulder et al. 1995; Sasaki et al. 2008). They may both contribute to the peak of 55.4 ± 0.2 eV. No SeIV peak 59.2 eV (46) was found in the Se 3d region. Selenium Auger line L23M45M45 of the sample is at 180 eV (Figure 3), with agreement of the peak of standard Se0 (dots) indicating Se0 did contribute to peak 55.4 eV. In addition, there was no SeIV Auger peak found. Therefore, Se0 was the main selenium species in the sample, in agreement with the wet chemical analysis described above.

Thermodynamic data indicate that Fe0 can reduce SeIV to its most reduced form Se–II and XPS data indicate possible evidence of FeSe or FeSe2. Only about 78% of the total Se was recovered, which may indicate that the acidification process used in the residuals analysis released Se–II as H2Se (g). Nevertheless, Se0 was the primary product and SeIV was only 3.0% of the total added selenium (Table 1).

**Proposed mechanism**

The reaction between SeIV and ZVI-SW advanced in two stages. During the lag stage, Fe0 is the electron donor and SeIV is reduced to Se0 as described in Equation (1). As ZVI-SW corrodes in water, ferrous iron is produced at each active site (Fe0/Fc2+) half cell. In the N2-sparged reactor, O2 was limited, and therefore H+ and SeIV were the primary electron competitors. Both the H+ + e– → H2 (g) half reaction and the SeIV half reaction (SeIV/Se0) are H+-consuming reactions, which corresponds to the increase in pH (Figure 2(a) and 2(b)). Once FeII in the solution reached a certain concentration, in the range of 0.50 ± 0.04 mg L−1, and a pH above 8 (Figure 2), an Fe(OH)2/GR coating accumulated (Hansen et al. 1994; Myneni et al. 1997) on the SW surface. A heterogeneous surface mediated reductive reaction by Fe0 is suggested by the relationship between lag-stage length and concentration of FeII, which could explain the catalytic effect on SeIV removal rate in the fast stage. Similar experimental results of pH increasing together with faster Se reduction were also observed in a study of granular Fe0 with SeVI (Gibson et al. 2022), and FeII associated with solid surfaces was believed to facilitate Se oxyanions reduction (Myneni et al. 1997; Charlet et al. 2007; Chen et al. 2009; Gibson et al. 2012; Liang et al. 2013), and Scheiddegger et al. (2005) proved with the solid phase analytical techniques of X-ray diffraction, X-ray fluorescence and X-ray absorption spectroscopy that, under anoxic condition, the reduction of SeIV → Se0 was accompanied by a GR corrosion layer. Additional evidence for this is provided by the decreased length and slope of the lag stage upon external additions of FeII (Supplemental Material Figure S4, available with the online version of this paper).

A heterogeneous Fe(OH)2/GR stage mediated reduction reaction accounts for the second faster stage Equations (2) and (3). At the end of the lag stage, the pH of the reactor
stops increasing, which corresponds to the initiation of Equation (3) (Figure 2(a) and 2(b)). A distinct color change of the ZVI-SW surface occurred, from lustrous metallic silver to a dull gray and finally to a light greenish and yellowish brown patina during the reaction (Supplemental Material Figure S5, available online), which is the characteristic of Fe(OH)₂ and GR (Murphy 1988; Klas & Kirk 2013).

\[
8\text{Fe(OH)}_2(s) + 4\text{Cl}^- + 5\text{H}^+ + \text{HSeO}_3^- \rightarrow 3\text{Se}^0(s) + 2\text{Fe}^{lll}(\text{OH})_3\text{Cl(s)} + 3\text{H}_2\text{O} \tag{2}
\]

\[
4\text{Fe}^{lll}(\text{OH})_3\text{Cl(s)} + 3\text{HSeO}_3^- \rightarrow 3\text{Se}^0(s) + 16\text{FeOOH(s)} + 9\text{H}_2\text{O} + 4\text{Cl}^- + \text{H}^+ \tag{3}
\]

For this mechanism to be viable, Se⁴⁺ must form an inner-sphere surface complex. Given that the point of zero charge of Fe(OH)₂ is approximately 12 (Parks 1965) and the pKₐ₂ for H₂SeO₃ is 7.3, the threshold pH of near 8 represents the point where the surface has near maximum positive charge, and Se⁴⁺ has maximum negative charge. As pH decreases below pH 8, the Fe(OH)₂/GR surface film becomes increasingly unstable (Ruby et al. 2006). The importance of pH to heterogeneous reduction of Se⁴⁺ by Fe(OH)₂ oxyanions has been reported previously; Se⁴⁺ removal rate, as Se⁰, reached a maximum at pH 8.8, dropping sharply below pH 8 (Murphy 1988). Myneni et al. (1997) found the presence of Se⁰ in Se⁶⁻ reduction by GR experiments performed at pH values of 6.8 and 9.3, and reduction was not observed at pH values of 3.8. Zingaro et al. (1997) observed removal of Se⁶⁻ and Se⁴⁺ by Fe(OH)₂ removal under alkaline conditions (pH 8.8). However, in previous studies of Se⁴⁺ reduction by granular Fe⁰, the removal rate of Se decreased with pH increase, and it was believed that the drop in Se⁴⁺ removal by ZVI with increasing pH was attributable to the decreased adsorption of Se⁴⁺ at higher pH on the ZVI surface, which became more negatively charged with increasing pH (Liang et al. 2013, 2015). Apparently the main Se⁴⁺ removal mechanism with ZVI-SW is different from that with granular Fe⁰ in those studies (Liang et al. 2013, 2015). Additional evidence we found for this was that no Se⁴⁺ was removed from solution when pH was maintained at 4 for 4 hours, and only 10% of the selenium was removed after 6 hours (data not shown). The removal rate of Se by granular ZVI was negligible within 10 h under anoxic condition when pH > 8 (Yoon et al. 2011; Klas 2013; Liang et al. 2015); this might be because granular Fe⁰ is easily covered with a passive layer of corrosion product ferric hydroxide (Yoon et al. 2011), which is inhibiting electron transfer from the Fe⁰ core. The half-reduction reaction (HSeO₄²⁻/Se⁰(s)⁺, E° = 1.89) needs two steps: Se⁶⁻ — Se⁴⁺ and Se⁴⁺ — Se⁰; the lack of a ready source of electrons slows the reduction of Se⁶⁻ to Se⁰, taking 5 to 6 days (Refait et al. 2000; Yoon et al. 2011; Gibson et al. 2012; Tang et al. 2014). Surface-associated Fe⁰ reduction of Se⁴⁺ to Se⁰ has been reported by Scheidegger et al. (2003), the Scheinost and Charlet group (Refait et al. 2000; Charlet et al. 2007; Scheinost & Charlet 2008) and Chen et al. (2009). However, these reductions of Se⁴⁺ by Fe⁰ sorbed clay and iron oxide surface took weeks or months. These results are consistent with our proposed mechanism because the clays, oxides, and Fe⁰-minerals lacked a ready supply of easily transferrable electrons. In our study, ZVI-SW was able to completely reduce Se⁴⁺ to Se⁰ within 2–7 hours.

Previous studies have suggested that passivation of granular Fe⁰ by iron oxyhydroxides eliminates its reductive capacity (Furukawa et al. 2002; Tang et al. 2014). The reduction of Se⁶⁻ by Fe⁰ powder was insignificant under anoxic condition (Yoon et al. 2011; Klas 2013), and Se⁴⁺ removal rate declines with pH increase (Liang et al. 2013, 2015).

Figure 4 | Schematic representation of proposed two-step removal mechanism: (a) lag stage; (b) heterogeneous reduction fast stage.
These did not occur on the surface of ZVI-SW because of its inherent resistance to oxidation. The slower oxidation to Fe(III) allowed surface ferrous phases to form, which act as highly efficient adsorbents and reductants for Se(IV) reduction. Elemental Se was generated in both removal stages.

CONCLUSION

This study demonstrated that ZVI-SW effectively reduced Se(IV) to elemental Se in N2-purged solutions with pH 6–8.5. We propose that the reaction proceeded in two stages, an electrochemical reduction of Se(IV) by Fe0 in an initial lag stage, followed by a faster heterogeneous reduction, mediated by an Fe(II)-bearing phase (hydroxide or GR). The reduction rate increased with increasing initial pH. The length of lag stages and the overall removal process was determined by the time for dissolved Fe(II) concentration to reach 0.30 ± 0.04 mg L⁻¹, which was critical for induction of the faster stage. About 65% of the initial Se(IV) was reduced to Se0, which was the primary reductive product in both stages. The inherent rusting resistance of ZVI-SW slowed the Fe0 → Fe(III) corrosion process and thus inhibited passivation by Fe(III) oxhydroxides. It also allowed the formation of a surface coating of Fe(II)-bearing hydroxides and/or GR providing sites for contaminant adsorption and facilitated the transport of electrons from Fe0 (Figure 4). While our data are consistent with our proposed reaction scheme, additional bulk and surface spectroscopic methods are needed to definitively determine the precise mechanisms by which selenium is reduced to elemental Se by ZVI-SW.

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