Zero-Valent Iron for the Abatement of Arsenate and Selenate from Flowback Water of Hydraulic Fracturing

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Graphical Abstract:

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Abstract

Zero-valent iron (ZVI) was tested for the removal of $150\text{ }\mu\text{g L}^{-1}$ As(V) and $350\text{ }\mu\text{g L}^{-1}$ Se(VI) in high-salinity (ionic strength 0.35-4.10 M) flowback water of hydraulic fracturing. Over 90% As(V) and Se(VI) was removed by 2.5 g L^{-1} ZVI in Day-14 flowback water up to 96-h reaction, with the remaining concentration below the maximum contaminant level for As(V) and criterion continuous concentration for Se(VI) recommended by US EPA. The kinetics of As(V) and Se(VI) removal followed a pseudo-second-order rate expression with the observed rates of 4.51×10^{-2} - 4.91×10^{-1} and 3.48×10^{-2} - $6.58\times 10^{-1}\text{ h}^{-1}$ (with 0.5 - 10 g L^{-1} ZVI), respectively. The results showed that Se(VI) removal significantly decreased with increasing ionic strength, while As(V) removal showed little variation. Common competing anions (nitrate, bicarbonate, silicate, and phosphate), present in shallow groundwater and stormwater, caused marginal Se(VI) desorption ($2.42\pm 0.13\%$) and undetectable As(V) desorption from ZVI. The competition between As(V) and Se(VI) for ZVI removal depended on the initial molar ratio and surface sites, which occurred when the Se(VI) concentration was higher than the As(V) concentration in this study. The characterization of As(V)- and Se(VI)-loaded ZVI by X-ray diffraction and Raman analysis revealed that ZVI gradually converted to magnetite/maghemite corrosion products with lepidocrocite in flowback water over 30 days. Similar corrosion compositions were confirmed in aerobic and anaerobic conditions regardless of the molar ratio of As(V) to Se(VI). The high reactivity and stability of ZVI showed its suitability for *in-situ* prevention of As(V) and Se(VI) migration due to accidental leakage, spillage, or overflow of flowback water.

Keywords: zero-valent iron; hydraulic fracturing; ionic strength; arsenic; selenium; permeable reactive barrier.

1. Introduction

Natural gas is a leading source of clean energy compared to coal and petroleum, and its presence in organic-rich shale formations has been identified around the world. China is believed to have one of the largest shale gas reserves, which have been estimated to be about 35 trillion m³ (Tollefson, 2013). According to the current plans (Shale Gas Development in the National 12th Five-Year Plan), shale gas will account for 8-12% of all natural gas production by 2020, as recent advances in hydraulic fracturing have made shale gas extraction economical. Typically for each operation, hydraulic fracturing requires an injection of nearly 2-5 million gallons of water with various chemical additives, known as hydraulic fracturing fluids, in order to create a network of fissures and enable gas extraction (Clark et al., 2013).

Prior to gas production, 10-70% of the hydraulic fracturing fluids is recovered as flowback water, which is enriched with shale formation constituents including chloride (5,000-8,000 mg L⁻¹), sodium (50-4,000 mg L⁻¹), calcium (500-12,000 mg L⁻¹), barium (50-9,000 mg L⁻¹), magnesium (50-2,000 mg L⁻¹), and iron (50-160 mg L⁻¹). Various chemical additives used in the fracturing fluids may also contribute to the high level of total dissolved solids (up to 350,000 mg L⁻¹). In general, the later the flowback water reaches the ground surface, the higher the ionic strength (Vengosh et al., 2013), which may influence the reactivity of the contaminants in the flowback water. In addition, toxic metals such as arsenic (As) and selenium (Se) have also been identified in flowback water in Marcellus shale, ranging from 1.5 to 151 and 2.5 to 350 µg L⁻¹ (Abualfaraj et al., 2014), respectively, which was selected as the target concentration range in this research.

This may draw particular concerns regarding pollution by flowback water, because deep well injection is not feasible for wastewater disposal in China due to geology challenges and water shortage (Warner et al., 2013). It has been estimated that arsenic-contaminated groundwater is prevalent in areas of Northwest and Northeast China (Rodriguez-Lado et al., 2013), which probably overlap with some shale regions and arouse risk concerns. Although selenium availability plays an important role in plants and animals, livestock health may be of concern due to selenium enrichment in the underlying shales (Parnell et al., 2016). In particular, As(V) and Se(VI) would be the predominant form and susceptible to mobilization under acidic and oxidizing conditions (Goldberg et al., 2008; Phan et al., 2015), so this study investigated their removal from the synthetic flowback solution.

Zero-valent iron (ZVI) has been widely employed as a permeable reactive barrier that can form strong complexes between iron oxides and dissolved ions (Manning et al., 2002), and therefore is potentially suitable for preventing As(V) and Se(VI) migration due to accidental leakage, spillage, or overflow of flowback water. However, while there have been promising indications of the removal of As(V) and Se(VI) compounds by ZVI in low ionic strength waters, this is uncertain for flowback water where the high-salinity may interfere with metal adsorption onto the ZVI. Increasing ionic strength has been shown to enhance particle aggregation due to compressed double layers, which consequently reduce available surface sites and inhibit ZVI reactivity for contaminant removal (Sato et al., 2005). Moreover, anions such as chloride and phosphate with a lone pair of electrons could be adsorbed either specifically or non-specifically on surface iron oxide, and shift the isoelectric point of ZVI to a lower pH value. Therefore, the elevated chloride concentration in flowback water may reduce electrostatic attraction, or increase

electrostatic repulsion, between ZVI and targeted contaminants, such as As(V) and Se(VI), which will be present as oxyanions in aqueous conditions (Xiao et al., 2011).

In addition, typical anions such as phosphate, silicate, bicarbonate, and nitrate in shallow ground water and stormwater may re-mobilize As(V) and Se(VI) from ZVI surfaces due to competitive adsorption (Yin et al., 2012). It has been reported that As(V) (initial concentration, 1 mg L⁻¹) removal by 0.1 g L⁻¹ nano-scale ZVI was reduced by 90.9%, 84.8%, 20.9% and 9.9% in the presence of PO₄³⁻, SiO₄⁴⁻, HCO₃⁻, and NO₃⁻, respectively (Kanel et al., 2006). Therefore, the influence of high ionic strength and competitive anions may cause concern about the effectiveness and stability of ZVI.

In order to investigate the uncertainties described above, the objectives of this study were to: (i) determine the kinetics and extent of As(V) and Se(VI) immobilization by ZVI in synthetic flowback water of different compositions; (ii) describe the interaction between flowback water chemistry (ionic strength and competing anions/cations) and As(V) and Se(VI) immobilization by ZVI; and (iii) identify the nature of the surface-formed precipitates on the As(V)- and Se(VI)-treated ZVI in flowback water using spectroscopic analysis.

2. Methods and Materials

2.1 ZVI and Flowback Water Constituents

The ZVI filings (ETC-CC-1200) were obtained from Connelly GPM Inc., in which their grain size, specific surface area, and particle density were 0.25 to 2.0 mm, 1.8 m² g⁻¹, and 6.43 g cm⁻³,

respectively. The chemicals used in the experiments (viz. NaOH, HCl, KCl, NaBr, BaCl₂·2H₂O, CaCl₂·2H₂O, Fe(NO₃)₃·9H₂O, SrCl₂·6H₂O, MgCl₂·6H₂O, NaCl, H₃BO₃, Na₂HPO₄, Na₄SiO₄, NaHCO₃, NaNO₃, polyacrylamide, ethylene glycol, glutaraldehyde) were reagent grade from Sigma Aldrich. Model flowback waters (corresponding to Day-1, Day-14, or Day-90, i.e., the fluids returning to the ground surface in 1, 14, or 90 days after well creation) were synthesized according to a comprehensive report of “Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas” (Hayes, 2009), in which a total of 17 shale gas companies enabled the sampling of 19 locations across the Marcellus Shale Region, including 3 locations in West Virginia and 16 locations in Pennsylvania. The concentrations of major inorganic compounds in Table 1 represented the median values of the 19 locations. Three representative organic chemicals in flowback waters were also selected in this study, yet it should be noted that flowback water in the field comprised over 200 organic chemicals with concentrations and compositions dependent on proprietary fracturing fluids and shale formations. The speciation of As(V) and Se(VI) in model flowback waters were calculated using Visual MINTEQ ver. 3.0 program and shown in Table S1.

2.2 Kinetics and Extent of As(V) and Se(VI) Removal from Flowback Water by ZVI

Varying dosages of ZVI (0.5, 1, 2.5, 5, and 10 g L⁻¹) were used for treating 50 mL of Day-14 flowback water with 150 µg L⁻¹ As(V) and/or 350 µg L⁻¹ Se(VI) (which represent the maximum concentrations reported in Marcellus flowback water) in 50-mL polypropylene copolymer centrifuge. Standard solutions of sodium arsenate and sodium selenate (Assurance grade, Spex Certiprep) were used and the initial pH values of the model flowback waters were adjusted by using 0.1 M HCl or NaOH. The initial pH value of flowback water was in the range of 5.9-7.2,

which does not affect the ZVI activity for As(V) and Se(VI) removal. The samples were shaken on a rotary shaker (30 rpm) at room temperature for 0.5, 2, 4, 8, 12, 24, 36, 48, 72, and 96 h, and then centrifuged at 4000 rpm for 5 min. The supernatants were filtered through a 0.45- μ m membrane filter (Millipore) and analysed for As(V) and Se(VI) by atomic absorption spectrometry with vapour generation accessory (VGA-AAS, Agilent VGA77, limits of detection at 1 μ g L⁻¹). The selective-reduction-VGA-AAS technique was employed for measuring the speciation of As(V) and Se(VI) based on Shraim et al. (1999).

The investigation of As(V) and Se(VI) removal was conducted with 2.5 g L⁻¹ ZVI in 50 mL of Day-14 flowback water for 48 h, which was adequate to reach apparent equilibrium as indicated by preliminary experiments. The concentrations of As(V) (50-1500 μ g L⁻¹) and Se(VI) (50-3500 μ g L⁻¹) ranging from median to 10-times maximum concentrations were based on the reported values in Marcellus flowback water, and were analysed by VGA-AAS at the end of the reaction. All experiments were performed in duplicate. The maximum contaminant level (MCL, US EPA) of As(V) in drinking water is 10 μ g L⁻¹ and the criterion continuous concentration (CCC, US EPA) of Se(VI) in surface water is 50 μ g L⁻¹. The maximum allowable concentrations of As(V) and Se(VI) in surface waters (Class I to III) in China are 50 μ g L⁻¹ and 10 μ g L⁻¹, respectively (GB3838-2002). The MCL for As(V) and CCC for Se(VI) were adopted as benchmark values in this study.

2.3 Significance of Flowback Water Chemistry for As(V) and Se(VI) Removal by ZVI

The significance of ionic strength (*I*) on As(V) and Se(VI) removal by ZVI was investigated by comparing the 48-h removal of 150 μ g L⁻¹ As(V) and/or 350 μ g L⁻¹ Se(VI) by 2.5 g L⁻¹ ZVI in 50

mL of Day-1 ($I = 0.35$ M), Day-14 ($I = 2.49$ M), and Day-90 ($I = 4.10$ M) flowback waters, respectively. After reaction, the concentrations of As(V) and Se(VI) in the supernatants were analysed by VGA-AAS, while the treated ZVI were recovered and gently washed with de-ionized water (DIW) to remove loosely entrapped As(V) and Se(VI). The As(V)-/Se-loaded ZVI was then leached for 48 h by each of the following: 50 mL of de-ionized (DI) water, background solution (BS, 10 mM NaNO₃), synthetic stormwater (SSW), and competing anions present in shallow groundwater, respectively. These leaching solutions based on the literature are described as follows.

As NaCl was the major constituent in flowback water, sodium and chloride compounds were selected. The composition of SSW was: NaCl (5.1 mM), CaCl₂ (0.75 mM), MgCl₂ (0.075 mM), Na₂SO₄ (0.33 mM), NaHCO₃ (1 mM), NaNO₃ (0.072 mM), NH₄Cl (0.072 mM), and Na₂HPO₄ (0.016 mM) (Mohanty et al., 2013). The concentrations of competing anions in shallow groundwater were: phosphate (10-132 µM), silicate (137-463 µM), and bicarbonate (3-30 mM), representing the ranges from minimum to maximum reported values (Guo et al., 2005). Furthermore, competitive removal between maximum concentration of As(V) (150 µg L⁻¹; 2 µM) and median to maximum concentration of Se(VI) (53-351 µg L⁻¹; 0.67-4.45 µM), based on the reported Marcellus flowback water, was investigated by using ZVI (2.5 g L⁻¹) in 50 mL of Day-14 fracturing flowback water for 48 h.

2.4 Solid-phase Characterization of As(V)- and Se(VI)-loaded ZVI

The ZVI was mixed at 1.0 g L⁻¹ with 3 mg L⁻¹ As(V) (20-times maximum concentration reported in Marcellus flowback water) and 1.06, 3.16, 7 mg L⁻¹ Se(VI) (20-times maximum concentration

reported in Marcellus flowback water) at molar ratios of 1:0.33, 1:1, 1:2.22 in Day-14 fracturing flowback water for 1-day shaking, followed by 1-min shaking by hand for another 29 days. The solutions were either used as is (i.e., aerobic) or nitrogen-purged before the experiments in order to determine the effect of redox potential on iron oxides/hydroxides formation on ZVI. The As(V)- and Se(VI)-loaded ZVI samples were separated by centrifugation and freeze-dried prior to X-ray diffraction (XRD) and Raman analysis along with indigenous ZVI. The ZVI dosage and As(V)/Se(VI) concentrations were selected to ensure a sufficiently high surface loading of 1000 mg kg⁻¹ As(V) and Se(VI) for subsequent spectroscopic analysis. The structure of the surface precipitates was determined by using a high-resolution powdered X-ray diffractometer (XRD, Rigaku SmartLab). The scanning degrees were from 5° to 85° 2θ with 5° min⁻¹ speed duration at 45 kV and 200 mA. The type of the surface precipitates formed was evaluated by using Raman spectroscope (RM 3000).

3. Results and Discussion

3.1 Kinetics and Extent of As(V) and Se(VI) Removal from Flowback Water by ZVI

The results summarized in Figure 1 show that 95.4±1.6% As(V) (from 150 µg L⁻¹) and 87.1±0.9% Se(VI) (from 350 µg L⁻¹) were removed after 96-h and 48-h reaction, respectively, with 2.5 g L⁻¹ ZVI in Day-14 flowback water. The solution pH in Day-14 flow water increased from 6.5 to 7.9 in 8 h and then gradually to 8.8 in 96 h (Figure S1), while the pH values similarly increased from 7.2 to 8.5 in Day-1 flowback water and from 5.9 to 8.2 in Day-90 flowback water, which was indicative of iron corrosion. The E_h values varied little and ranged between 226 and 235 mV in all individual and binary-metal solutions during the 96-h reaction. The remaining concentrations of As(V) and Se(VI) in solution were 6.9±2.4 µg L⁻¹ and 45.2±3.1 µg

L⁻¹, respectively, which were lower than the MCL for As(V) (10 µg L⁻¹) in drinking water and CCC for Se(VI) (50 µg L⁻¹) in surface water suggested by US EPA. The results demonstrated the applicability of ZVI to remove As(V) and Se(VI) from high-salinity flowback water.

The removal of As(V) and Se(VI) from flowback water by ZVI conformed to pseudo-second-order kinetics (details can be found in the Supplementary Information and Table S2), except for the case of Se(VI) with 0.5 g L⁻¹ ZVI, which corresponded to zero-order kinetics, implying insufficient surface sites for 350 µg L⁻¹ Se(VI). The observed pseudo-second-order rate coefficients (k_{obs} , h⁻¹) for As(V) (4.51×10^{-2} - 4.91×10^{-1} h⁻¹) and Se(VI) (3.48×10^{-2} - 6.58×10^{-1} h⁻¹) increased with increasing ZVI dosages (0.5-10 g L⁻¹), and the magnitude of the increase with ZVI dose was greater for Se(VI) than As(V). This could be attributed to the different mechanisms involved in As(V) and Se(VI) removal by ZVI. Selenate could be first reduced to Se(IV) and adsorbed rapidly onto Fe oxyhydroxides, or removed in a reverse sequence (Myneni et al., 1997), while arsenate may not be reduced to As(III) after the reaction with ZVI (Farrell et al., 2001). The reduction rate of Se(VI) by ZVI could be accelerated in the presence of mineral surfaces, such as goethite, hematite, ferrihydrite and maghemite identified on the ZVI by XRD and Raman analysis (Figure S2), as Fe(II) is an important electron donor and reduced Se(IV) could be readily adsorbed onto hydrous ferric oxides (Zhang et al., 2005). Due to interference of high salinity in fracking water, no As(V)/As(III) and Se(IV)/Se(VI) was identified on As(V)- and Se(VI)-loaded ZVI solid samples in XPS tests.

Nevertheless, the surface-size normalized rate coefficients (k_{sa} , L m⁻² h⁻¹) (see SI for definition) for As(V) firstly increased from 5.01×10^{-2} L m⁻² h⁻¹ at 0.5 g L⁻¹ to a maximum of 9.95×10^{-2} L m⁻²

h⁻¹ at 1 g L⁻¹ ZVI, and then decreased with increasing ZVI dosages (1-10 g L⁻¹). Likewise, the k_{sa} for Se(VI) increased from 3.87×10^{-2} L m⁻² h⁻¹ at 0.5 g L⁻¹ ZVI to a maximum of 5.29×10^{-2} L m⁻² h⁻¹ at 2.5 g L⁻¹ ZVI, and then decreased with ZVI dosage (Figure 2 and Table S2). It was noted that the k_{obs} and k_{sa} values in this study were 2-10 times lower than those reported in previous studies for As(III) and Cr(VI) removal (Su and Puls, 2001; Liu et al., 2008). Su and Suarez (2000) noted that Se(VI) removal by amorphous iron hydroxides was dramatically decreased in 1 M NaCl solution compared to deionized water, and the high ionic strength was found to hinder the activity of metal ions (Reddad et al., 2002). The comparatively lower rate coefficients were believed to partly result from the high-salinity solution ($I = 2.49$ M).

It can be seen in Figure 2 that at low ZVI dosages (0.5-1 g L⁻¹), the values for As(V)- k_{sa} (5.01×10^{-2} - 9.95×10^{-2} L m⁻² h⁻¹) are greater than Se(VI)- k_{sa} (3.87×10^{-2} - 4.86×10^{-2} L m⁻² h⁻¹) (similar for As(V)- k_{obs} and Se(VI)- k_{obs}). It has been reported that As(V) displayed a stronger adsorption affinity than Se(VI), e.g., As(V)>Se(IV)>As(III)>Se(VI) on soil (Goh and Lime, 2004) and As(V)>Se(IV)>Se(VI) on hydrous ferric oxide (Ryden et al., 1987). In this study, the ratio of occupied site density to total site density ($ZVI_{occupied}/ZVI_{total}$) was estimated to be 0.24-0.46 at 0.5-1 g L⁻¹ ZVI (Table S2; see SI for calculation). A relatively high occupation of surface sites probably rendered the difference in adsorption affinity more important. Accordingly, the kinetics and extent of As(V) removal was greater than that of Se(VI) removal by ZVI at lower dosages.

However, at higher ZVI dosages (5-10 g L⁻¹) the values for Se(VI)- k_{sa} (4.85×10^{-2} - 3.36×10^{-2} L m⁻² h⁻¹) were greater than those for As(V)- k_{sa} (3.94×10^{-2} - 2.73×10^{-2} L m⁻² h⁻¹) (similar for Se(VI)-

k_{obs} and As(V)- k_{obs}). As the $ZVI_{occupied}/ZVI_{total}$ was estimated to be 0.03-0.06 only (Table S2), abundant amount of surface sites were available for As(V) and Se(VI) removal while mass transfer from bulk solution to surface sites may be the rate limiting step. According to the Fick's law of diffusion, the mass transfer rate is proportional to the product of diffusion coefficient and concentration gradient. The reported diffusion coefficient of As(V) compounds in water is in the range of 6.40×10^{-6} - 8.75×10^{-6} $\text{cm}^2 \text{ s}^{-1}$ (Tanaka et al., 2013), and that of Se(VI) compounds in water is 7.14×10^{-6} - 9.46×10^{-6} $\text{cm}^2 \text{ s}^{-1}$ (Sato et al., 1996). With similar diffusion coefficients, the mass transfer rates of As(V) and Se(VI) were therefore dependent on the concentration gradient. Since the initial concentration of Se(VI) ($350 \mu\text{g L}^{-1}$, $4.45 \mu\text{M}$) was greater than As(V) ($150 \mu\text{g L}^{-1}$, $2 \mu\text{M}$), the kinetics (and therefore removal) of Se(VI) was greater than As(V). In comparison, at 2.5 g L^{-1} ZVI dosage, the value of As(V)- k_{sa} ($5.81 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$) was similar to that of Se(VI)- k_{sa} ($5.29 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$) (similar for As(V)- k_{obs} and Se(VI)- k_{obs}), hence this dosage was chosen for the subsequent experiments as corresponding to the lowest ZVI dosage with sufficient surface sites for As(V) and Se(VI) removal.

3.2 Significance of Solution Chemistry of Flowback Water on As(V) and Se(VI) Removal

The results in Figure 3 summarise the impact of solution chemistry, principally the ionic strength, of the flowback water on As(V) and Se(VI) removal. The data show that the remaining concentrations of As(V) after 48-h reaction with ZVI were $10.4 \pm 0.1 \mu\text{g L}^{-1}$ in Day-1 ($I = 0.35 \text{ M}$), $15.9 \pm 1.8 \mu\text{g L}^{-1}$ in Day-14 ($I = 2.49 \text{ M}$), and $11.5 \pm 0.4 \mu\text{g L}^{-1}$ in Day-90 ($I = 4.10 \text{ M}$) flowback waters, respectively. The similar values suggest that arsenate removal was only slightly affected by ionic strength, which implied that inner-sphere surface complexes were formed with ZVI (McBride, 1997). This is consistent with observations of As(V) interactions with amorphous

Fe oxide (Hsia et al., 1994). Evidence from previous studies using EXAFS, FTIR, and Raman spectroscopy has revealed that As(V) was adsorbed via an inner-sphere adsorption mechanism, forming bi-dentate surface complexes on goethite, ferrihydrite, gibbsite, and hematite (Catalano et al., 2007). A recent study of the diffusion and reaction steps of As(V) with ZVI nanoparticles presented direct evidence that As(V) was attracted to the solid surface by electrostatic interactions and replaced a surface-bonded –OH group via ligand exchange (Ling and Zhang, 2014).

In contrast to As(V) removal, Se(VI) removal was significantly inhibited by the increase of ionic strength, with the remaining concentrations increasing from $21.5 \pm 0.5 \mu\text{g L}^{-1}$ in Day-1, $45.2 \pm 3.1 \mu\text{g L}^{-1}$ in Day-14, to $145 \pm 2.8 \mu\text{g L}^{-1}$ in Day-90 solutions (Figure 3). Such dependence on ionic strength corresponded to the formation of outer-sphere surface complexes (McBride, 1997). Similar results were obtained for Se(VI) adsorption on amorphous Fe oxide (Su and Suarez, 2000), which was demonstrated to be a mono-dentate outer-sphere complex formation on goethite (Zhang and Sparks, 1990). Increasing ionic strength from deionized water to 0.1 M NaCl also resulted in a rapid decrease of the rate coefficient for hexavalent chromium reduction with metallic iron (Gould, 1982), which is controlled by a surface electron transfer process. Similarly, Se(VI) removal by ZVI could be inhibited by the temporal increase of ionic strength in flowback water due to hindered electron transfer on ZVI surface. However, direct spectroscopic evidence of adsorption mechanism was not available due to the technical difficulties resulting from high-salinity interference in the As(V)- and Se(VI)-loaded ZVI samples.

The contributions of various species of As(V) and Se(VI) in Day-1, Day-14, Day-90 flowback

waters was listed in Table S1. In a neutral pH range (5.9-7.2) and aerobic condition, As(V) existed in the form of H_2AsO_4^- and HAsO_4^{2-} oxyanions. Increasing ionic strength and decreasing pH from Day-1 ($I = 0.35 \text{ M}$, $\text{pH} = 7.2$) to Day-90 ($I = 4.0 \text{ M}$, $\text{pH} = 5.9$) significantly promoted the contribution of H_2AsO_4^- (Day-1: 19.4%, Day-14: 83.3%, Day-90: 96.6%) to the total dissolved As(V) in flowback waters. In comparison, although the predominant form of Se(VI) in flowback waters was soluble selenate (SeO_4^{2-}), an increasing proportion of CaSeO_4 was formed in Day-1 (29.2%), Day-14 (97.3%), Day-90 (99.2%) flowback waters. Thus, the increasing formation of stable Ca-Se complex could also inhibit Se(VI) removal by ZVI in flowback waters with increasing ionic strength.

3.3 Surface Characteristics of As(V)- and Se(VI)-loaded ZVI

The zero valency state and crystalline structure of as-received ZVI were confirmed by XRD analysis (Figure S2a) and the Raman spectrum demonstrated that the ZVI surface was fully oxidized (Figure S2b). The Fe(II)/Fe(III) and Fe(III) corrosion products on ZVI were a mixture of ferroxhyte ($\delta\text{-FeOOH}$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), amorphous graphite, goethite ($\alpha\text{-FeOOH}$), and/or hematite ($\alpha\text{-Fe}_2\text{O}_3$), which were identified with relevant information from the literature (Table S3). The XRD analysis of As(V)- and Se(VI)-loaded ZVI samples showed the peaks of magnetite/maghemite ($\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$), lepidocrocite ($\gamma\text{-FeOOH}$), and predominant Fe^0 (Figure 4), which are in agreement with the previous results (Manning et al., 2002; Richmond et al., 2004). After 30-day reaction, the major component of the ZVI corrosion layers was lepidocrocite ($\gamma\text{-FeOOH}$), which resulted from the oxidation of the Fe(II) formed on the corroding Fe^0 surface.

Of particular note is that similar types of the iron precipitates were formed in aerobic and

anaerobic feed solutions regardless of the various molar ratios of As(V) to Se(VI) (i.e., 1:0.33, 1:1, and 1:2.22), representing possible conditions in the reported flowback water. Anaerobic conditions resulted in higher XRD peak intensities and more crystalline iron oxides than aerobic conditions. The insignificant effect of dissolved oxygen and molar ratio of As(V) to Se(VI) probably suggested the presence of mature corrosion products formed on the ZVI surface during As(V) and Se(VI) removal from flowback water. Hence, the effectiveness of As(V) and Se(VI) removal by adsorption onto ZVI corrosion layers is less likely to be compromised after long-term application, while the reduction performance of ZVI may be inhibited due to hindered electron transfer through thicker shell of iron(hydro)oxides.

3.4 Desorption of As(V) and Se(VI) from ZVI due to Competing Anions and Cations

After 48-h reaction with ZVI in Day-14 flowback water, 1.79 μM As(V) or 3.86 μM Se(VI) was loaded on 2.5 g L⁻¹ ZVI. The results of Figure 5 show that no detectable amount of As(V) was desorbed by leaching with DIW, BS, or common competing anions in shallow groundwater (i.e., bicarbonate, silicate, and phosphate), which supported the hypothesis that As(V) may form strongly bonded inner-sphere surface complexes with ZVI. In comparison, the desorption of Se(VI) was also undetectable by leaching with DIW, BS, and 3 mM HCO₃⁻, and there was little desorption (0.08±0.07%) at the higher HCO₃⁻ concentration (30 mM). Both SiO₄⁴⁻ and HPO₄²⁻ were relatively more effective in causing Se(VI) desorption, though the greatest desorption was only about 2.5%.

The magnitude of the effect of competing anions on Se(VI) desorption was in the order phosphate > silicate > bicarbonate > nitrate, which is consistent with the findings reported for

Se(VI) desorption in a soil environment (Goh and Lim, 2004). The desorption tendency of an anion is partly attributed to its valency and the capacity to form outer- or inner- sphere complexes with ZVI (Caporale et al., 2013). Phosphate, which has a similar ionic structure as As(V), can associate with surface functional groups and form strong inner-sphere complexes with ZVI (Zhu et al., 2013), and is thus able to cause the largest Se(VI) desorption from ZVI due to competition for active surface sites. Both silicate and bicarbonate can form outer-sphere complexes with ZVI (Ramesh et al., 2007) and lower surface potential (Feng et al., 2013). Therefore, it is possible that the electrostatic repulsion increased between Se(VI) and the negatively charged surface and contributed to Se(VI) desorption. Since silicate is tetravalent and bicarbonate is monovalent, silicate could lead to larger electrostatic repulsion between Se(VI) and the ZVI surface, therefore causing more Se(VI) desorption than with bicarbonate. Nitrate is a redox-sensitive anion and could be reduced by Fe^0 to form predominantly NH_4^+ and smaller amounts of NO_2^- (Till et al., 1998). Desorption by nitrate in BS was not observed.

Although SSW contained $16\ \mu\text{M}\ \text{HPO}_4^{2-}$ and $1\ \text{mM}\ \text{HCO}_3^-$, there was much less Se(VI) desorption than the individual addition of HPO_4^{2-} anion (Figure 4). It is possible that the adsorption of these two anions affected the surface charge and solution pH in different ways, so that the adsorption environment for the mixed anions changed compared to their individual addition (Ryden et al., 1987). Also, it is possible that the divalent cations (Ca^{2+} and Mg^{2+}) in the SSW neutralized some of the negative surface charges on ZVI (Tanboonchuy et al., 2013), which alleviated the electrostatic repulsion and accounted for less Se(VI) desorption in the SSW than in the presence of a single competing anion.

3.5 Competitive Removal of As(V) and Se(VI) by ZVI in Flowback Water

The results summarized in Figure 5a show the effect of the initial Se(VI) concentration (53-350 $\mu\text{g L}^{-1}$, 0.67-4.45 μM) on the removal of As(V) at a constant concentration (150 $\mu\text{g L}^{-1}$ or 2 μM), corresponding to a change in molar ratio of As(V) to Se(VI) from 1:0.33 to 1:2.22. When the initial concentration of Se(VI) (53-158 $\mu\text{g L}^{-1}$, 0.67-2 μM) was less than, or equal to, that of As(V), the removal of As(V) was approximately constant at 75% with 2.5 g L^{-1} ZVI (Figure 6a). With increasing Se(VI) concentrations (158-350 $\mu\text{g L}^{-1}$, 2-4.45 μM) the As(V) removal significantly reduced to $34.6 \pm 5.5\%$ at a As(V):Se(VI) molar ratio of 1:2.22. In contrast, the Se(VI) removal increased from $54.8 \pm 9.8\%$ to $86.7 \pm 0.3\%$ with increasing initial Se(VI) concentration, although the greater removal did not vary substantially for As(V) to Se(VI) molar ratios ≥ 1 . These results indicate that As(V) was only sensitive to Se(VI) competition when the Se(VI) initial concentration was greater than As(V), and vice versa, under the experimental conditions.

It was also evident that the Se(VI) removal (0.15 ± 0.03 to $1.54 \pm 0.01 \mu\text{mol g}^{-1}$ ZVI) was approximately linear-correlated with the Se(VI) initial concentration. Also, the removal of As(V) ($0.60 \pm 0.01 \mu\text{mol g}^{-1}$ ZVI) and Se(VI) ($0.63 \pm 0.02 \mu\text{mol g}^{-1}$ ZVI) was similar at 1:1 molar ratio. It is possible that As(V) and Se(VI) preferentially react with different sites on the ZVI when sufficient sites are available. As depicted in Figure 6b, the ZVI surface can be empirically described in terms of different sites. Fraction s1 indicates active adsorption sites, and fraction s2 represents sites that could provide electron donors for reduction by ZVI and Fe hydroxides. It is known that Se(VI) reduction by ZVI to Se(IV) is an important mechanism for Se(VI), while the competition of As(V) at these sites is unlikely as the much lower redox potential of As(V)

reduction to As(III), compared to the Se(VI) reduction to Se(IV), makes such competition thermodynamically unfavourable (Farrell et al., 2001; Zhang et al., 2005).

Therefore, when the Se(VI) concentration was lower than that of As(V) in this case, the Se(VI) first occupied the s2 sites whereas the As(V) was adsorbed at the s1 sites; this was reflected by the minor impact of Se(VI) on As(V) removal. With greater Se(VI) concentrations, there was competition between As(V) and Se(VI) for the s1 sites, which is similar to the observed competition for adsorption sites of Fe hydroxides (Goh and Lim, 2004; Zhang et al., 2005). This result implies that, in addition to inner-sphere surface complexes, As(V) may also form outer-sphere surface complexes with ZVI that are subject to Se(VI) competition. In contrast, if present individually, the 48-h removals were consistently high (As(V): 75.8 ± 0.2 to $86.1 \pm 0.1\%$; Se(VI): 77.1 ± 1.8 to $92.5 \pm 0.4\%$, as indicated in Figure S3) over a wide range of As(V) (250 - $3000 \mu\text{g L}^{-1}$) and Se(VI) (500 - $7000 \mu\text{g L}^{-1}$) concentrations, corresponding to 20-times the maximum concentration reported in Marcellus flowback water.

4. Conclusions

This study has demonstrated that ZVI can sufficiently remove As(V) and Se(VI) from high-salinity flowback water. The removal of Se(VI) was more susceptible to ionic strength variations than As(V), which suggested different removal mechanisms by ZVI in flowback water. The results also showed that desorption of As(V) and Se(VI) by common competing anions present in shallow aquifer and stormwater was negligible. It is suggested that Se(VI) and As(V) preferentially occupied different surface sites on ZVI when sufficient sites were available relative to the total solute concentration, while competition for the adsorption sites occurred with

increasing molar ratio of Se(VI) to As(V). The spectroscopic results revealed that ZVI corrosion products formed in flowback water were less affected by the molar ratio of As(V) to Se(VI) and dissolved oxygen content. Therefore, ZVI represents a potential candidate as a reactive material for the *in-situ* prevention of As(V) and Se(VI) migration arising from the accidental leakage, spillage, or overflow of flowback water.

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Figure 1. Time-dependent removal of (a) As(V) ($150 \mu\text{g L}^{-1}$) and (b) Se(VI) ($350 \mu\text{g L}^{-1}$) from Day-14 flowback water at pH 6.5 by $0.5\text{-}10 \text{ g L}^{-1}$ ZVI.

Figure 2. Pseudo-second-order rates (k_{obs} and k_{sa}) for removal of As(V) ($150 \mu\text{g L}^{-1}$) and Se(VI) ($350 \mu\text{g L}^{-1}$) from Day-14 flowback water at pH 6.5 by $0.5\text{-}10 \text{ g L}^{-1}$ ZVI.

Figure 3. Significance of ionic strength on the 48-h removal of (a) As(V) ($150 \mu\text{g L}^{-1}$) and (b) Se(VI) ($350 \mu\text{g L}^{-1}$) from Day-1 ($I = 0.35 \text{ M}$), Day-14 ($I = 2.49 \text{ M}$), Day-90 ($I = 4.10 \text{ M}$) flowback water at pH 6.5 by 2.5 g L^{-1} ZVI.

Figure 4. XRD (a) and Raman (b) analysis of As(V)- and Se(VI)-loaded ZVI in Day-14 flowback water for 30 days at different molar ratios under aerobic and anaerobic conditions (remarks: major peaks correspond to magnetite/maghemite ($\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$) (M), lepidocrocite ($\gamma\text{-FeOOH}$) (L), goethite/hematite ($\alpha\text{-FeOOH}/\alpha\text{-Fe}_2\text{O}_3$) (G/H), amorphous graphite (AG), and Fe^0).

Figure 5. Desorption of Se(VI) and As(V) by deionized water (DIW), background solution (BS), competitive anions, and synthetic stormwater (SSW) after 48-h removal by ZVI (remarks: $150 \mu\text{g L}^{-1}$ ($2 \mu\text{M}$) As(V) or $350 \mu\text{g L}^{-1}$ ($4.45 \mu\text{M}$) Se(VI) in Day-14 flowback water at pH 6.5 was first removed by 2.5 g L^{-1} ZVI; in all desorption experiments, As(V) was undetectable in the leaching solutions).

Figure 6. Competition between As(V) ($150 \mu\text{g L}^{-1}$, or $2 \mu\text{M}$) and Se(VI) ($53\text{-}351 \mu\text{g L}^{-1}$, or $0.67\text{-}4.45 \mu\text{M}$) at varying molar ratio in Day-14 flowback water at pH 6.5 by 2.5 g L^{-1} ZVI: (a) 48-h removal and (b) occupied site density (remarks: fraction s1 indicates adsorption sites whereas fraction s2 indicates reduction sites).

Table 1. Chemical compositions of synthetic fracturing flowback water

Constituents	Units	Day 1	Day 14	Day 90
KCl	g L ⁻¹	0	0	31.9
NaBr	g L ⁻¹	0.113	0.911	1.51
BaCl ₂ ·2H ₂ O	g L ⁻¹	0.689	3.26	3.80
CaCl ₂ ·2H ₂ O	g L ⁻¹	2.48	40.6	67.8
Fe(NO ₃) ₃ ·9H ₂ O	g L ⁻¹	0.140	0.540	0.844
MgCl ₂ ·6H ₂ O	g L ⁻¹	1.02	7.85	14.2
SrCl ₂ ·6H ₂ O	g L ⁻¹	0.476	10.1	9.56
NaCl	g L ⁻¹	15.2	80.7	111
H ₃ BO ₃	g L ⁻¹	0.046	0.094	0.102
polyacrylamide	g L ⁻¹	0.8	0.8	0.8
ethylene glycol	g L ⁻¹	0.43	0.43	0.43
glutaraldehyde	g L ⁻¹	0.1	0.1	0.1
pH	—	7.2	6.5	5.9
Ionic strength	M	0.35	2.49	4.10