

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

3
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17

18 **Abstract**

19 Zero-valent iron (ZVI) was tested for the removal of 150 $\mu\text{g L}^{-1}$ As(V) and 350 $\mu\text{g L}^{-1}$ Se(VI) in
20 high-salinity (ionic strength 0.35-4.10 M) flowback water of hydraulic fracturing. Over 90%
21 As(V) and Se(VI) was removed by 2.5 g L^{-1} ZVI in Day-14 flowback water up to 96-h reaction,
22 with the remaining concentration below the maximum contaminant level for As(V) and criterion
23 continuous concentration for Se(VI) recommended by US EPA. The kinetics of As(V) and
24 Se(VI) removal followed a pseudo-second-order rate expression with the observed rates of
25 4.51×10^{-2} - 4.91×10^{-1} and 3.48×10^{-2} - 6.58×10^{-1} h^{-1} (with 0.5-10 g L^{-1} ZVI), respectively. The
26 results showed that Se(VI) removal significantly decreased with increasing ionic strength, while
27 As(V) removal showed little variation. Common competing anions (nitrate, bicarbonate, silicate,
28 and phosphate), present in shallow groundwater and stormwater, caused marginal Se(VI)
29 desorption ($2.42 \pm 0.13\%$) and undetectable As(V) desorption from ZVI. The competition
30 between As(V) and Se(VI) for ZVI removal depended on the initial molar ratio and surface sites,
31 which occurred when the Se(VI) concentration was higher than the As(V) concentration in this
32 study. The characterization of As(V)- and Se(VI)-loaded ZVI by X-ray diffraction and Raman
33 analysis revealed that ZVI gradually converted to magnetite/maghemite corrosion products with
34 lepidocrocite in flowback water over 30 days. Similar corrosion compositions were confirmed in
35 aerobic and anaerobic conditions regardless of the molar ratio of As(V) to Se(VI). The high
36 reactivity and stability of ZVI showed its suitability for *in-situ* prevention of As(V) and Se(VI)
37 migration due to accidental leakage, spillage, or overflow of flowback water.

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

40

41 **1. Introduction**

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

51

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

63

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

74

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

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

89
90 In addition, typical anions such as phosphate, silicate, bicarbonate, and nitrate in shallow ground
91 water and stormwater may re-mobilize As(V) and Se(VI) from ZVI surfaces due to competitive
92 adsorption (Yin et al., 2012). It has been reported that As(V) (initial concentration, 1 mg L⁻¹)
93 removal by 0.1 g L⁻¹ nano-scale ZVI was reduced by 90.9%, 84.8%, 20.9% and 9.9% in the
94 presence of PO₄³⁻, SiO₄⁴⁻, HCO₃⁻, and NO₃⁻, respectively (Kanel et al., 2006). Therefore, the
95 influence of high ionic strength and competitive anions may cause concern about the
96 effectiveness and stability of ZVI.

97
98 In order to investigate the uncertainties described above, the objectives of this study were to: (i)
99 determine the kinetics and extent of As(V) and Se(VI) immobilization by ZVI in synthetic
100 flowback water of different compositions; (ii) describe the interaction between flowback water
101 chemistry (ionic strength and competing anions/cations) and As(V) and Se(VI) immobilization
102 by ZVI; and (iii) identify the nature of the surface-formed precipitates on the As(V)- and Se(VI)-
103 treated ZVI in flowback water using spectroscopic analysis.

104

105 **2. Methods and Materials**

106 ***2.1 ZVI and Flowback Water Constituents***

107 The ZVI filings (ETC-CC-1200) were obtained from Connelly GPM Inc., in which their grain
108 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,

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

124

125 ***2.2 Kinetics and Extent of As(V) and Se(VI) Removal from Flowback Water by ZVI***

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

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

139
140 The investigation of As(V) and Se(VI) removal was conducted with 2.5 g L^{-1} ZVI in 50 mL of
141 Day-14 flowback water for 48 h, which was adequate to reach apparent equilibrium as indicated
142 by preliminary experiments. The concentrations of As(V) (50-1500 $\mu\text{g L}^{-1}$) and Se(VI) (50-3500
143 $\mu\text{g L}^{-1}$) ranging from median to 10-times maximum concentrations were based on the reported
144 values in Marcellus flowback water, and were analysed by VGA-AAS at the end of the reaction.
145 All experiments were performed in duplicate. The maximum contaminant level (MCL, US EPA)
146 of As(V) in drinking water is 10 $\mu\text{g L}^{-1}$ and the criterion continuous concentration (CCC, US
147 EPA) of Se(VI) in surface water is 50 $\mu\text{g L}^{-1}$. The maximum allowable concentrations of As(V)
148 and Se(VI) in surface waters (Class I to III) in China are 50 $\mu\text{g L}^{-1}$ and 10 $\mu\text{g L}^{-1}$, respectively
149 (GB3838-2002). The MCL for As(V) and CCC for Se(VI) were adopted as benchmark values in
150 this study.

151
152 ***2.3 Significance of Flowback Water Chemistry for As(V) and Se(VI) Removal by ZVI***

153 The significance of ionic strength (I) on As(V) and Se(VI) removal by ZVI was investigated by
154 comparing the 48-h removal of 150 $\mu\text{g L}^{-1}$ As(V) and/or 350 $\mu\text{g L}^{-1}$ Se(VI) by 2.5 g L^{-1} ZVI in 50

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

163
164 As NaCl was the major constituent in flowback water, sodium and chloride compounds were
165 selected. The composition of SSW was: NaCl (5.1 mM), CaCl₂ (0.75 mM), MgCl₂ (0.075 mM),
166 Na₂SO₄ (0.33 mM), NaHCO₃ (1 mM), NaNO₃ (0.072 mM), NH₄Cl (0.072 mM), and Na₂HPO₄
167 (0.016 mM) (Mohanty et al., 2013). The concentrations of competing anions in shallow
168 groundwater were: phosphate (10-132 μM), silicate (137-463 μM), and bicarbonate (3-30 mM),
169 representing the ranges from minimum to maximum reported values (Guo et al., 2005).
170 Furthermore, competitive removal between maximum concentration of As(V) (150 μg L⁻¹; 2 μM)
171 and median to maximum concentration of Se(VI) (53-351 μg L⁻¹; 0.67-4.45 μM), based on the
172 reported Marcellus flowback water, was investigated by using ZVI (2.5 g L⁻¹) in 50 mL of Day-
173 14 fracturing flowback water for 48 h.

174
175 ***2.4 Solid-phase Characterization of As(V)- and Se(VI)-loaded ZVI***

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

178 reported in Marcellus flowback water) at molar ratios of 1:0.33, 1:1, 1:2.22 in Day-14 fracturing
179 flowback water for 1-day shaking, followed by 1-min shaking by hand for another 29 days. The
180 solutions were either used as is (i.e., aerobic) or nitrogen-purged before the experiments in order
181 to determine the effect of redox potential on iron oxides/hydroxides formation on ZVI. The
182 As(V)- and Se(VI)-loaded ZVI samples were separated by centrifugation and freeze-dried prior
183 to X-ray diffraction (XRD) and Raman analysis along with indigenous ZVI. The ZVI dosage and
184 As(V)/Se(VI) concentrations were selected to ensure a sufficiently high surface loading of 1000
185 mg kg⁻¹ As(V) and Se(VI) for subsequent spectroscopic analysis. The structure of the surface
186 precipitates was determined by using a high-resolution powdered X-ray diffractometer (XRD,
187 Rigaku SmartLab). The scanning degrees were from 5° to 85° 2θ with 5° min⁻¹ speed duration at
188 45 kV and 200 mA. The type of the surface precipitates formed was evaluated by using Raman
189 spectroscope (RM 3000).

190

191 **3. Results and Discussion**

192 ***3.1 Kinetics and Extent of As(V) and Se(VI) Removal from Flowback Water by ZVI***

193 The results summarized in Figure 1 show that 95.4±1.6% As(V) (from 150 µg L⁻¹) and
194 87.1±0.9% Se(VI) (from 350 µg L⁻¹) were removed after 96-h and 48-h reaction, respectively,
195 with 2.5 g L⁻¹ ZVI in Day-14 flowback water. The solution pH in Day-14 flow water increased
196 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
197 increased from 7.2 to 8.5 in Day-1 flowback water and from 5.9 to 8.2 in Day-90 flowback
198 water, which was indicative of iron corrosion. The E_h values varied little and ranged between
199 226 and 235 mV in all individual and binary-metal solutions during the 96-h reaction. The
200 remaining concentrations of As(V) and Se(VI) in solution were 6.9±2.4 µg L⁻¹ and 45.2±3.1 µg

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

204
205 The removal of As(V) and Se(VI) from flowback water by ZVI conformed to pseudo-second-
206 order kinetics (details can be found in the Supplementary Information and Table S2), except for
207 the case of Se(VI) with 0.5 g L⁻¹ ZVI, which corresponded to zero-order kinetics, implying
208 insufficient surface sites for 350 µg L⁻¹ Se(VI). The observed pseudo-second-order rate
209 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)
210 increased with increasing ZVI dosages (0.5-10 g L⁻¹), and the magnitude of the increase with
211 ZVI dose was greater for Se(VI) than As(V). This could be attributed to the different
212 mechanisms involved in As(V) and Se(VI) removal by ZVI. Selenate could be first reduced to
213 Se(IV) and adsorbed rapidly onto Fe oxyhydroxides, or removed in a reverse sequence (Myneni
214 et al., 1997), while arsenate may not be reduced to As(III) after the reaction with ZVI (Farrell et
215 al., 2001). The reduction rate of Se(VI) by ZVI could be accelerated in the presence of mineral
216 surfaces, such as goethite, hematite, ferrihydrite and maghemite identified on the ZVI by XRD
217 and Raman analysis (Figure S2), as Fe(II) is an important electron donor and reduced Se(IV)
218 could be readily adsorbed onto hydrous ferric oxides (Zhang et al., 2005). Due to interference of
219 high salinity in fracking water, no As(V)/As(III) and Se(IV)/Se(VI) was identified on As(V)- and
220 Se(VI)-loaded ZVI solid samples in XPS tests.

221
222 Nevertheless, the surface-size normalized rate coefficients (k_{sa} , L m⁻² h⁻¹) (see SI for definition)
223 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

224 h^{-1} at 1 g L^{-1} ZVI, and then decreased with increasing ZVI dosages ($1\text{-}10 \text{ g L}^{-1}$). Likewise, the k_{sa}
225 for Se(VI) increased from $3.87 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$ at 0.5 g L^{-1} ZVI to a maximum of $5.29 \times 10^{-2} \text{ L m}^{-2}$
226 h^{-1} at 2.5 g L^{-1} ZVI, and then decreased with ZVI dosage (Figure 2 and Table S2). It was noted
227 that the k_{obs} and k_{sa} values in this study were 2-10 times lower than those reported in previous
228 studies for As(III) and Cr(VI) removal (Su and Puls, 2001; Liu et al., 2008). Su and Suarez
229 (2000) noted that Se(VI) removal by amorphous iron hydroxides was dramatically decreased in 1
230 M NaCl solution compared to deionized water, and the high ionic strength was found to hinder
231 the activity of metal ions (Reddad et al., 2002). The comparatively lower rate coefficients were
232 believed to partly result from the high-salinity solution ($I = 2.49 \text{ M}$).

233
234 It can be seen in Figure 2 that at low ZVI dosages ($0.5\text{-}1 \text{ g L}^{-1}$), the values for As(V)- k_{sa}
235 ($5.01 \times 10^{-2}\text{-}9.95 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$) are greater than Se(VI)- k_{sa} ($3.87 \times 10^{-2}\text{-}4.86 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$)
236 (similar for As(V)- k_{obs} and Se(VI)- k_{obs}). It has been reported that As(V) displayed a stronger
237 adsorption affinity than Se(VI), e.g., As(V)>Se(IV)>As(III)>Se(VI) on soil (Goh and Lime,
238 2004) and As(V)>Se(IV)>Se(VI) on hydrous ferric oxide (Ryden et al., 1987). In this study, the
239 ratio of occupied site density to total site density ($ZVI_{occupied}/ZVI_{total}$) was estimated to be 0.24-
240 0.46 at $0.5\text{-}1 \text{ g L}^{-1}$ ZVI (Table S2; see SI for calculation). A relatively high occupation of surface
241 sites probably rendered the difference in adsorption affinity more important. Accordingly, the
242 kinetics and extent of As(V) removal was greater than that of Se(VI) removal by ZVI at lower
243 dosages.

244
245 However, at higher ZVI dosages ($5\text{-}10 \text{ g L}^{-1}$) the values for Se(VI)- k_{sa} ($4.85 \times 10^{-2}\text{-}3.36 \times 10^{-2} \text{ L m}^{-2}$
246 h^{-1}) were greater than those for As(V)- k_{sa} ($3.94 \times 10^{-2}\text{-}2.73 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$) (similar for Se(VI)-

247 k_{obs} and As(V)- k_{obs}). As the $ZVI_{occupied}/ZVI_{total}$ was estimated to be 0.03-0.06 only (Table S2),
248 abundant amount of surface sites were available for As(V) and Se(VI) removal while mass
249 transfer from bulk solution to surface sites may be the rate limiting step. According to the Fick's
250 law of diffusion, the mass transfer rate is proportional to the product of diffusion coefficient and
251 concentration gradient. The reported diffusion coefficient of As(V) compounds in water is in the
252 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
253 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
254 mass transfer rates of As(V) and Se(VI) were therefore dependent on the concentration gradient.
255 Since the initial concentration of Se(VI) ($350 \mu\text{g L}^{-1}$, $4.45 \mu\text{M}$) was greater than As(V) ($150 \mu\text{g}$
256 L^{-1} , $2 \mu\text{M}$), the kinetics (and therefore removal) of Se(VI) was greater than As(V). In
257 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
258 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
259 was chosen for the subsequent experiments as corresponding to the lowest ZVI dosage with
260 sufficient surface sites for As(V) and Se(VI) removal.

261

262 ***3.2 Significance of Solution Chemistry of Flowback Water on As(V) and Se(VI) Removal***

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

270 Fe oxide (Hsia et al., 1994). Evidence from previous studies using EXAFS, FTIR, and Raman
271 spectroscopy has revealed that As(V) was adsorbed via an inner-sphere adsorption mechanism,
272 forming bi-dentate surface complexes on goethite, ferrihydrite, gibbsite, and hematite (Catalano
273 et al., 2007). A recent study of the diffusion and reaction steps of As(V) with ZVI nanoparticles
274 presented direct evidence that As(V) was attracted to the solid surface by electrostatic
275 interactions and replaced a surface-bonded -OH group via ligand exchange (Ling and Zhang,
276 2014).

277
278 In contrast to As(V) removal, Se(VI) removal was significantly inhibited by the increase of ionic
279 strength, with the remaining concentrations increasing from $21.5 \pm 0.5 \mu\text{g L}^{-1}$ in Day-1, 45.2 ± 3.1
280 $\mu\text{g L}^{-1}$ in Day-14, to $145 \pm 2.8 \mu\text{g L}^{-1}$ in Day-90 solutions (Figure 3). Such dependence on ionic
281 strength corresponded to the formation of outer-sphere surface complexes (McBride, 1997).
282 Similar results were obtained for Se(VI) adsorption on amorphous Fe oxide (Su and Suarez,
283 2000), which was demonstrated to be a mono-dentate outer-sphere complex formation on
284 goethite (Zhang and Sparks, 1990). Increasing ionic strength from deionized water to 0.1 M
285 NaCl also resulted in a rapid decrease of the rate coefficient for hexavalent chromium reduction
286 with metallic iron (Gould, 1982), which is controlled by a surface electron transfer process.
287 Similarly, Se(VI) removal by ZVI could be inhibited by the temporal increase of ionic strength in
288 flowback water due to hindered electron transfer on ZVI surface. However, direct spectroscopic
289 evidence of adsorption mechanism was not available due to the technical difficulties resulting
290 from high-salinity interference in the As(V)- and Se(VI)-loaded ZVI samples.

291
292 The contributions of various species of As(V) and Se(VI) in Day-1, Day-14, Day-90 flowback

293 waters was listed in Table S1. In a neutral pH range (5.9-7.2) and aerobic condition, As(V)
294 existed in the form of H_2AsO_4^- and HAsO_4^{2-} oxyanions. Increasing ionic strength and decreasing
295 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
296 the contribution of H_2AsO_4^- (Day-1: 19.4%, Day-14: 83.3%, Day-90: 96.6%) to the total
297 dissolved As(V) in flowback waters. In comparison, although the predominant form of Se(VI) in
298 flowback waters was soluble selenate (SeO_4^{2-}), an increasing proportion of CaSeO_4 was formed
299 in Day-1 (29.2%), Day-14 (97.3%), Day-90 (99.2%) flowback waters. Thus, the increasing
300 formation of stable Ca-Se complex could also inhibit Se(VI) removal by ZVI in flowback waters
301 with increasing ionic strength.

302

303 ***3.3 Surface Characteristics of As(V)- and Se(VI)-loaded ZVI***

304 The zero valency state and crystalline structure of as-received ZVI were confirmed by XRD
305 analysis (Figure S2a) and the Raman spectrum demonstrated that the ZVI surface was fully
306 oxidized (Figure S2b). The Fe(II)/Fe(III) and Fe(III) corrosion products on ZVI were a mixture
307 of ferroxhyte ($\delta\text{-FeOOH}$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), amorphous graphite, goethite ($\alpha\text{-FeOOH}$),
308 and/or hematite ($\alpha\text{-Fe}_2\text{O}_3$), which were identified with relevant information from the literature
309 (Table S3). The XRD analysis of As(V)- and Se(VI)-loaded ZVI samples showed the peaks of
310 magnetite/maghemite ($\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$), lepidocrocite ($\gamma\text{-FeOOH}$), and predominant Fe^0 (Figure
311 4), which are in agreement with the previous results (Manning et al., 2002; Richmond et al.,
312 2004). After 30-day reaction, the major component of the ZVI corrosion layers was lepidocrocite
313 ($\gamma\text{-FeOOH}$), which resulted from the oxidation of the Fe(II) formed on the corroding Fe^0 surface.

314

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

316 anaerobic feed solutions regardless of the various molar ratios of As(V) to Se(VI) (i.e., 1:0.33,
317 1:1, and 1:2.22), representing possible conditions in the reported flowback water. Anaerobic
318 conditions resulted in higher XRD peak intensities and more crystalline iron oxides than aerobic
319 conditions. The insignificant effect of dissolved oxygen and molar ratio of As(V) to Se(VI)
320 probably suggested the presence of mature corrosion products formed on the ZVI surface during
321 As(V) and Se(VI) removal from flowback water. Hence, the effectiveness of As(V) and Se(VI)
322 removal by adsorption onto ZVI corrosion layers is less likely to be compromised after long-term
323 application, while the reduction performance of ZVI may be inhibited due to hindered electron
324 transfer through thicker shell of iron(hydro)oxides.

325

326 ***3.4 Desorption of As(V) and Se(VI) from ZVI due to Competing Anions and Cations***

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

336

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

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

352

353 Although SSW contained $16 \mu\text{M HPO}_4^{2-}$ and 1 mM HCO_3^- , there was much less Se(VI)
354 desorption than the individual addition of HPO_4^{2-} anion (Figure 4). It is possible that the
355 adsorption of these two anions affected the surface charge and solution pH in different ways, so
356 that the adsorption environment for the mixed anions changed compared to their individual
357 addition (Ryden et al., 1987). Also, it is possible that the divalent cations (Ca^{2+} and Mg^{2+}) in the
358 SSW neutralized some of the negative surface charges on ZVI (Tanboonchuy et al., 2013), which
359 alleviated the electrostatic repulsion and accounted for less Se(VI) desorption in the SSW than in
360 the presence of a single competing anion.

361

362 **3.5 Competitive Removal of As(V) and Se(VI) by ZVI in Flowback Water**

363 The results summarized in Figure 5a show the effect of the initial Se(VI) concentration (53-350
364 $\mu\text{g L}^{-1}$, 0.67-4.45 μM) on the removal of As(V) at a constant concentration (150 $\mu\text{g L}^{-1}$ or 2 μM),
365 corresponding to a change in molar ratio of As(V) to Se(VI) from 1:0.33 to 1:2.22. When the
366 initial concentration of Se(VI) (53-158 $\mu\text{g L}^{-1}$, 0.67-2 μM) was less than, or equal to, that of
367 As(V), the removal of As(V) was approximately constant at 75% with 2.5 g L^{-1} ZVI (Figure 6a).
368 With increasing Se(VI) concentrations (158-350 $\mu\text{g L}^{-1}$, 2-4.45 μM) the As(V) removal
369 significantly reduced to $34.6 \pm 5.5\%$ at a As(V):Se(VI) molar ratio of 1:2.22. In contrast, the
370 Se(VI) removal increased from $54.8 \pm 9.8\%$ to $86.7 \pm 0.3\%$ with increasing initial Se(VI)
371 concentration, although the greater removal did not vary substantially for As(V) to Se(VI) molar
372 ratios ≥ 1 . These results indicate that As(V) was only sensitive to Se(VI) competition when the
373 Se(VI) initial concentration was greater than As(V), and vice versa, under the experimental
374 conditions.

375
376 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
377 approximately linear-correlated with the Se(VI) initial concentration. Also, the removal of As(V)
378 ($0.60 \pm 0.01 \mu\text{mol g}^{-1}$ ZVI) and Se(VI) ($0.63 \pm 0.02 \mu\text{mol g}^{-1}$ ZVI) was similar at 1:1 molar ratio. It
379 is possible that As(V) and Se(VI) preferentially react with different sites on the ZVI when
380 sufficient sites are available. As depicted in Figure 6b, the ZVI surface can be empirically
381 described in terms of different sites. Fraction s1 indicates active adsorption sites, and fraction s2
382 represents sites that could provide electron donors for reduction by ZVI and Fe hydroxides. It is
383 known that Se(VI) reduction by ZVI to Se(IV) is an important mechanism for Se(VI), while the
384 competition of As(V) at these sites is unlikely as the much lower redox potential of As(V)

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

387
388 Therefore, when the Se(VI) concentration was lower than that of As(V) in this case, the Se(VI)
389 first occupied the s2 sites whereas the As(V) was adsorbed at the s1 sites; this was reflected by
390 the minor impact of Se(VI) on As(V) removal. With greater Se(VI) concentrations, there was
391 competition between As(V) and Se(VI) for the s1 sites, which is similar to the observed
392 competition for adsorption sites of Fe hydroxides (Goh and Lim, 2004; Zhang et al., 2005). This
393 result implies that, in addition to inner-sphere surface complexes, As(V) may also form outer-
394 sphere surface complexes with ZVI that are subject to Se(VI) competition. In contrast, if present
395 individually, the 48-h removals were consistently high (As(V): 75.8 ± 0.2 to $86.1 \pm 0.1\%$; Se(VI):
396 77.1 ± 1.8 to $92.5 \pm 0.4\%$, as indicated in Figure S3) over a wide range of As(V) (250 - $3000 \mu\text{g L}^{-1}$)
397 and Se(VI) (500 - $7000 \mu\text{g L}^{-1}$) concentrations, corresponding to 20-times the maximum
398 concentration reported in Marcellus flowback water.

399

400 **4. Conclusions**

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

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

413

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419

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