



Zero-valent iron for the abatement of arsenate and selenate from flowback water of hydraulic fracturing



Yuqing Sun^{a, b}, Season S. Chen^b, Daniel C.W. Tsang^{b, *}, Nigel J.D. Graham^c, Yong Sik Ok^d, Yujie Feng^{a, **}, Xiang-Dong Li^b

^a State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, 150090, China

^b Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

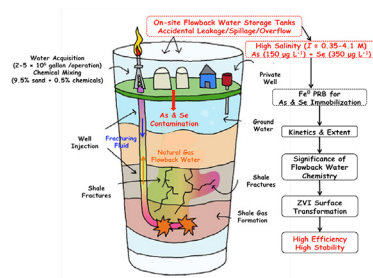
^c Environmental and Water Resources Engineering, Department of Civil and Environmental Engineering, Imperial College London, South Kensington, London, SW7 2AZ, UK

^d Korea Biochar Research Center & School of Natural Resources and Environmental Science, Kangwon National University, Chuncheon, 24341, South Korea

HIGHLIGHTS

- As(V) and Se(VI) in high-salinity flowback water was effectively removed by ZVI.
- As(V) removal was less susceptible to ionic strength variations than Se(V).
- Competing anions in groundwater and stormwater caused insignificant desorption.
- As(V) and Se(VI) competition depended on their molar ratio and ZVI surface sites.
- Surface characteristics of ZVI were unaffected by molar ratio and dissolved oxygen.

GRAPHICAL ABSTRACT



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ABSTRACT

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 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

* Corresponding author.

** Corresponding author.

E-mail addresses: dan.tsang@polyu.edu.hk (D.C.W. Tsang), yujief@hit.edu.cn (Y. Feng).

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.

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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 (5000–8000 mg L⁻¹), sodium (50–4000 mg L⁻¹), calcium (500–12,000 mg L⁻¹), barium (50–9000 mg L⁻¹), magnesium (50–2000 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 2.5–350 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 (Rodríguez-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; Tsang et al., 2009), 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 Connolly GPM Inc., in which their grain size, specific surface area, and particle density were 0.25–2.0 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.

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