THE REMOVAL OF INORGANIC GROUNDWATER CONTAMINANTS USING A NOVEL POROUS IRON COMPOSITE MATERIAL

by

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(Under the Direction of John C. Seaman)

## ABSTRACT

Zero valent iron (ZVI) is a promising method of remediation for a variety of groundwater contaminants. However, several limitations to its capabilities exist, including decreased efficacy at non-acidic pH, in oxic environments, and in the presence of multiple contaminants or complexing ligands. This study assessed the ability of a novel porous iron composite (PIC) material to immobilize redox-sensitive groundwater contaminants. Batch experiments were performed to assess PIC performance at removing uranium, arsenic, and nitrate in a complex groundwater surrogate solution with high contaminant load and alkalinity. The PIC successfully removed all contaminants to levels below drinking water standards in both oxic and anoxic environments. Another set of batch experiments were carried out to assess PIC removal of Cr at environmentally relevant concentrations. The PIC showed at least 75% Cr removal, with slightly better performance in the oxic environment. Overall, PIC provides a promising alternative to conventional ZVI materials.

INDEX WORDS: Contaminant immobilization, Zero valent iron, Uranium, Chromium, Nitrate, Batch

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# Introduction

## 1.1 Groundwater Contamination

Groundwater is an important source of drinking water globally. In the United States (U.S.) in 2015, approximately 87% of the population received potable water from groundwater withdrawals (Dieter et al., 2018). In other countries, such as China or India, groundwater supplies over two-thirds of drinking water in certain regions (Nath et al., 2018; Jia et al., 2019). However, aquifers may accumulate high concentrations of contaminants that reach or exceed safe drinking water standards (DWS). Chronic exposure through drinking water to various common contaminants, such as heavy metals, nitrates, and radionuclides, is associated with a variety of health risks. Therefore, groundwater contamination is a serious concern for its potential impact to drinking water supplies and public health.

Potential toxins may be released into an aquifer by both anthropogenic and natural means. Manmade groundwater contamination sources, such as improper storage or disposal of contaminated material or industrial wastewater release, are often sources of metals like arsenic (Baragaño et al., 2019), chromium (Kotaś and Stasicka, 2000), and in nuclear industries, uranium plus associated fission and decay products (Shi et al., 2012). Intensive agriculture is linked to increased groundwater nitrate ($NO_3^-$) concentrations (Keeny 1989).

In some instances, the local geology may present an inherent health risk. Potentially toxic elements such as uranium (U) and chromium (Cr) occur naturally in minerals in many parts of the U.S. (Nriagu 1988; Palmer and Wittbrodt, 1991; Testa et al., 2004; Jurgens et al., 2010; Cumberland et al., 2016). Changes in the concentrations of complexing ions such as carbonate ($CO_3^{2-}$), bicarbonate ($HCO_3^-$), sulfate ($SO_4^{2-}$), and iron (Fe), may mobilize local contaminants.

Further changes in aquifer conditions, such as a shift in pH or dissolved oxygen (DO) levels, may also result in the enhanced leaching of toxic elements from the local geology (Oze et al., 2007; Jurgens et al., 2010; Nath et al., 2018).

## 1.2 Remediation Methods

Challenges of groundwater remediation include costs, the temporal and spatial variability of contaminants (often prompted by changing environmental conditions), and the tendency of many contaminants to accumulate in groundwater under typical aquifer conditions (Blowes et al., 2000; Ayotte et al., 2015). Many conventional remediation methods fail to effectively address these challenges, including the class of methods known as “pump-and-treat.” This approach involves the removal of contaminated water from the system for above-surface treatment before disposal or replacement (Mackay and Cherry, 1989). Pump-and-treat methods tend to be expensive and even quite inefficient, as they fail to address the larger residual contaminant source associated with the aquifer solids (Cantrell, Kaplan, and Wietsma, 1995; Blowes et al., 2000).

As an alternative to pump-and-treat methods, *in situ* remediation methods are of increasing interest for removing heavy metals and chlorinated solvents. In situ (lit. “in the original place”) remediation does not require water to be removed aboveground; instead, remediation occurs within the aquifer itself. A variety of *in situ* remediation methods have been studied, including the addition of soil amendments, soil flushing, injection (of dithionites, colloids, or other restorative materials, directly into groundwater), and permeable reactive barriers (PRBs) (Hashim et al., 2011).

Many of these methods have significant drawbacks. The addition of soil amendments and/or soil flushing are expensive and require significant disturbance of the contaminated soil system, which may actually lead to greater worker exposure and the enhanced mobilization of contaminants if proper containment measures are not taken (Moore et al.,1993; US EPA,1997).

For example, subsurface injection into groundwater can create hazardous gases or intermediate species (Amonette et al.,1994; Fruchter et al., 2000). The use of chelating agents is effective, but potentially hazardous itself and time-consuming to deploy and recover (Arwidsson et al., 2010).

However, PRBs show great potential for aquifer remediation, when engineered to take advantage of a site's inherent chemical, physical, or biological properties. A PRB is a wall installed within the path of groundwater flow such that it interacts with the migrating contaminant plume (Blowes et al., 2000; Hashim et al., 2011) (Figure 1). The barrier is filled with a media which reacts with the contaminant while allowing groundwater to pass through the other side under the natural flow gradient. As a passive treatment method, PRBs have a number of potential advantages over other remediation methods. Although PRBs are associated with high initial costs (Blowes et al., 2000), they become relatively inexpensive to operate after installation, as they require only limited monitoring and maintenance (Zolla et al., 2007; Obiri-Nyarko, Grajales-Mesa, and Malina, 2014). However, questions remain about their long-term effectiveness as the target contaminants remain in place with the potential to be remobilized if condition change. Barrier failure may occur for a variety of reasons, including inadequate characterization of the contaminated aquifer system, poor barrier design and installation, a reduction in the barrier permeability that alters groundwater flow, and loss of media reactivity over time (Henderson and Demond, 2007; Hashim et al., 2011). The choice of media in a PRB is clearly essential for its viability as a long-term solution to groundwater contamination.

Various reactive substrates have been studied with attention to potential use in a PRB. Media used in laboratory tests and field-scale demonstrations include zero valent metals, zeolites, activated carbon, and other materials which chemically reduce and/or sorb contaminants (Scherer et al., 2000; Hashim et al., 2011). Of these, zero valent iron (ZVI) is one of the most widely studied materials. Field-scale ZVI PRBs have successfully demonstrated removal of chlorinated solvents (Wilkin et al., 2005; Xui et al., 2010; Zingaretti et al., 2019), nickel (Ni) (Zhang et al., 2016), $NO_3^-$ (Grau-Martinez et al., 2019), and U (Naftz et al., 2003; Sihn et al., 2019). ZVI is generally inexpensive to produce (Bower et al., 2008) and mimics natural redox processes.

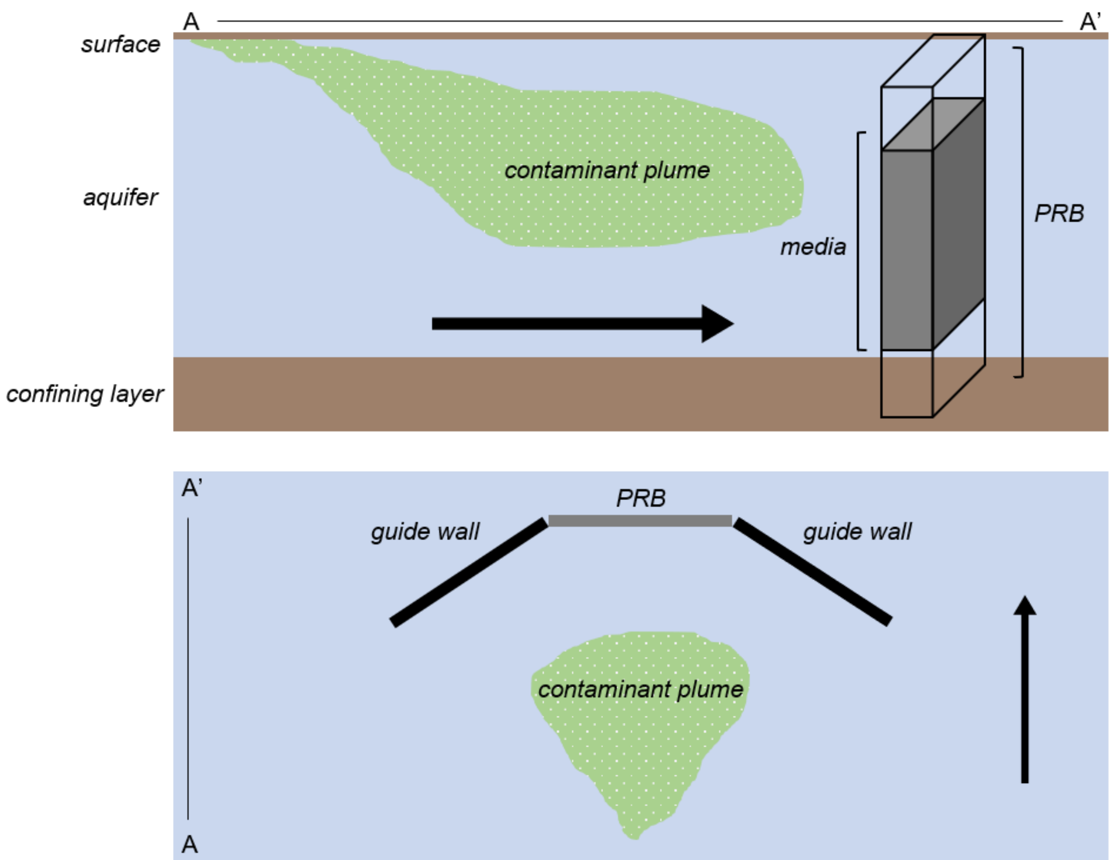


Figure 1.1. A schematic of a potential PRB design, with side (top) and overhead (bottom) views. Arrows indicate direction of groundwater flow.

## 1.3 Zero Valent Iron

Zero valent iron (ZVI) is iron (Fe) with a valence state of zero, or $Fe^0$. This $Fe^0$ can be oxidized to $Fe^{2+}$ or $Fe^{3+}$, and those electrons become available to reduce contaminants. For most contaminants treated with ZVI, removal appears to be accomplished by a combination of reduction and sorption mechanisms (i.e., adsorption, precipitation, etc.). The source of electrons available for transfer in a ZVI system is the $Fe^0$ core of the particles (O'Carroll et al., 2013). The resulting Fe oxides form a passive "shell" around the core (Crane et al., 2011; Zhang et al., 2017).

Table 1.1 lists several redox potentials for Fe species under standard conditions. These equations are written in the direction of reduction by convention; when reversed, they describe oxidation, and the sign of $E^0$ reverses as well. Thus, an element or compound with an unfavorable reduction potential will be more likely to oxidize. Under standard conditions, the oxidation of $Fe^0$ to $Fe^{2+}$ has a potential of 0.44 V, indicating the favorability of the donation of those electrons to the contaminant of interest.

Table 1.1. Standard redox potentials ($E^0$) for various Fe species in aqueous solution at 25 °C. [a] = from Pang et al. (2007); all others from Bard et al. (1985).

| Half reaction | $E^0$ (V) |
|---|---|
| $Fe_3O_{4(s)} + 8H^+ \leftrightarrow 3Fe^{2+} + 4H_2O$ | 0.98[a] |
| $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ | 0.77 |
| $3Fe_2O_{3(s)} + 2H^+ + 2e^- \leftrightarrow 2Fe_3O_{4(s)} + H_2O$ | 0.22[a] |
| $Fe^{3+} + 3e^- \leftrightarrow Fe_{(s)}$ | -0.04 |
| $Fe_3O_{4(s)} + 8H^+ + 8e^- \leftrightarrow 3Fe_{(s)} + 4H_2O$ | -0.085 |
| $Fe^{2+} + 2e^- \leftrightarrow Fe$ | -0.44 |
| $Fe_2O_{3(s)} + 3H_2O + 2e^- \leftrightarrow 2Fe(OH)_{2(s)} + 2OH^-$ | -0.86 |
| $Fe(OH)_{2(s)} + 2e^- \leftrightarrow Fe_{(s)} + 2OH^-$ | -0.89 |

However, the contaminant of interest is not necessarily the most favorable electron recipient within a system. Electron transfer also occurs via corrosion of $Fe^0$ material in an oxygenated water system (Tosco et al., 2014):

$$Fe^0_{(s)} + 2H^+_{(aq)} + 1/2O_{2\,(g)} \rightarrow 2Fe^{2+}_{(aq)} + H_2O_{(l)} \quad \text{(Eq. 1)}$$

$$2Fe^{2+}_{(aq)} + 2H^+_{(aq)} + 1/2O_{2\,(g)} \rightarrow 2Fe^{3+}_{(aq)} + H_2O_{(l)} \quad \text{(Eq. 2)}$$

$$Fe^{0}_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2\,(g)} + 2OH^{-}_{(aq)} \quad \text{(Eq. 3)}$$

The removal of electrons from Fe by oxygen gas ($O_2$) is noteworthy because it indicates that $O_2$ functions as an electron acceptor in oxygenated systems, which is likely the case when addressing oxidized contaminant species, i.e., Cr(VI), U(VI). ZVI is rapidly oxidized by $O_2$ when exposed to the atmosphere and when dissolved oxygen (DO) is present in aqueous systems (Fu et al., 2014; Tosco et al., 2014). In fact, contaminant removal by ZVI is typically slower or less effective under oxic conditions (Crane and Scott, 2014; Li et al., 2015). Oxygen is consumed first in natural water systems (Stumm and Morgan, 1995), which leaves fewer electrons available for the target contaminant(s).

Zero valent iron has been applied to the removal of a large variety of contaminants. The reductive dechlorination of organic solvents by ZVI has been extensively studied (see reviews O'Carroll et al., 2013; Fu et al., 2014). The reaction of $Fe^0$ and $O_2$ additionally produces hydroxyl radicals in what is known as a Fenton reaction, which are responsible for the high rate of removal seen when ZVI is applied to organic contaminants (Fu et al., 2014):

$$Fe^{0}_{(s)} + O_{2\,(g)} + 2H^{+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_2O_{2\,(l)} \quad \text{(Eq. 4)}$$

$$Fe^{0}_{(s)} + H_2O_{2\,(l)} + 2H^{+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2H_2O_{(l)} \quad \text{(Eq. 5)}$$

$$Fe^{2+}_{(aq)} + H_2O_{2\,(l)} \rightarrow Fe^{3+}_{(aq)} + \cdot OH + OH^{-}_{(aq)} \quad \text{(Eq. 6)}$$

Zero valent iron has also demonstrated effective removal of a large variety of heavy metals, including As (Ludwig et al., 2009; Mak, Rao, and Lo, 2009; Neumann et al., 2013); Cr (discussed in chapter 3); cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn) (Li and Zhang, 2007); and mercury (Hg) (Weisener et al., 2005), as well as radionuclides, including U (as discussed in chapter 2); rhenium (Re) (Lenell and Arai, 2017); and technetium-99 ($^{99}$Tc) (Coutelot et al. 2019; Cantrell, Kaplan, and Wietsma, 1995; Liang, Gu, and Yin, 1996).

For most ZVI-treated contaminants, a few general patterns emerge in removal experiments. Removal is higher and more efficient under anoxic conditions, due to the influence of DO as discussed previously. Generally, contaminant removal also increases with decreasing pH (Riba et al., 2008; Yan et al., 2014; Song et al., 2017). While the removal of many contaminants proceeds rapidly at low pH, removal may be limited or even absent at high pH (Jurgens et al., 2010; Yoshino and Kawase, 2013; Guo et al., 2015). At acidic pH levels, extensive corrosion of the ZVI surface occurs. Corrosion is understood to increase available reactive surface area and limit direct precipitation at the ZVI surface (Liu et al., 2005; Liu and Lowry, 2006; Crane et al., 2015a).

However, corrosion also encourages the formation of ferrous/ferric oxy-hydroxides (Fu et al., 2014):

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2\,(s)} \quad \text{(Eq. 7)}$$

$$4Fe(OH)_{2\,(s)} + 2H_2O_{(l)} + O_{2\,(g)} \rightarrow 4Fe(OH)_{3\,(s)} \quad \text{(Eq. 8)}$$

Other potential Fe oxides formed may include hematite ($Fe_2O_3$), magnetite ($Fe_3O_4$) and goethite (FeO(OH)) (Puls, Paul, and Powell, 1999). These oxides accumulate on the surface of the ZVI particles, and may also encourage the precipitation of certain contaminants (Fu et al., 2014). However, the accumulation of crystalline precipitates may limit the available ZVI surface area (Dixit and Hering, 2003) and therefore its effective removal capacity.

Equations 1 and 2 also illustrate another consistent observation of ZVI removal: over experimental time, the solution pH increases (Riba et al., 2008). This pH increase is observed irrespective of other pH-influencing ions in solution (Crane et al., 2015b), which indicates that the consumption of protons via Fe corrosion is the primary control on solution pH.

If no DO is present, $Fe^0$ corrosion may still occur through direct reaction with $H_2O$ (Crane and Scott, 2011):

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2\,(g)} + 2OH^-_{(aq)} \quad \text{(Eq. 9)}$$

$$2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow 2Fe^{3+}_{(aq)} + H_{2\,(g)} + 2OH^-_{(aq)} \quad \text{(Eq. 10)}$$

However, these reactions are thermodynamically unfavorable ($E^0$ = -0.39 V for eq. 9, $E^0$ = -1.60 V for eq. 10), and thus the production of $OH^-$ is less likely to be an observed feature of ZVI systems.

When considering its use in a PRB, the long-term loss of reactivity is a major problem for widespread use of ZVI. A frequent observation in ZVI experiments is a high initial rate of removal, followed by re-release of contaminants as the system ages. This may occur due to the typically observed increase in system pH, as alkaline pH tends to mobilize contaminants (Jurgens et al., 2010; O'Carroll et al., 2013), or it may occur in the presence of complexing ligands (Crane and Scott, 2014).

To increase reactivity, many previous studies have amended ZVI material by (1) anchoring the ZVI to a substrate, such as illite (Jing et al., 2017), bentonite, or various zeolites (Chen et al., 2016); or (2) creating a bimetallic particle, where the ZVI is paired with another metal, such as copper, silver, or palladium (O'Carroll et al., 2012).

A commonly used subtype of ZVI in nano-scale ZVI (nZVI). Compared to conventional ZVI, nZVI has an increased surface area to volume ratio and smaller particle size (Fu et al., 2014). This means that nZVI has a higher initial reactivity (O'Carroll et al., 2013) and has the potential to disperse farther through aquifer pores (Varadhi et al., 2005) than millimeter-scale particles when injected into a contaminated aquifer to form a PRB. However, particle aggregation is frequently observed with nZVI, which decreases available surface area and surface reactivity (O'Carroll et al., 2013; Crane and Scott, 2014; Li et al., 2015). Aggregation can also result in a decrease in the saturated hydraulic conductivity ($K_{sat}$) of the PRB system, which limits continued exposure to the contaminant. (Sun et al., 2006). Because the loss of ZVI reactivity is a major concern in PRB failure, the material used in this study was specifically formulated with the intent of increasing and maintaining the reactivity and $K_{sat}$ of the PRB system without decreasing particle size.

## 1.4 Uranium

The radioactive element uranium (U) occurs naturally in geologic formations. Natural U consists of the isotopes $^{238}U$, $^{235}U$, and $^{234}U$ at ratios of approximately 99%, 0.75%, and 0.01%, respectively. Uranium-238 also has the longest half-life of these isotopes at of ~$4.5 \times 10^9$ years (Andersen, Stirling, and Weyer, 2017). Uranium occurs in valence states of +4, +5, or +6, with U(IV) and U(VI) being most common in natural environments (Crane et al., 2015b; Cumberland et al., 2016). Under typical circumneutral aquifer conditions, U is highly mobile, while U(IV) is typically considered immobile due to solubility limitations (McKinley et al., 2007). Uranium poses a health risk to humans because of its radiological and chemical toxicity (World Health Organization, 2004), although the long half-life of $^{238}U$, the predominant isotope, makes its chemical toxicity more of a concern. The Environmental Protection Agency has set DWS for U at 30 μg $L^{-1}$ (USEPA, 2000).

Groundwater U contamination in the U.S. has been part of the legacy of the industries of nuclear energy and nuclear weapons production. Various Department of Energy sites record elevated U groundwater levels as a result of these activities (Zachara et al., 2007; Dong et al., 2012). Uranium may also enter groundwater through the natural weathering of rocks and minerals, as in California's eastern San Joaquin Valley, where groundwater U concentrations are higher than average as a result of the local U-rich geology (Jurgens et al., 2010; Cumberland et al., 2016). Increased groundwater withdrawal for irrigation, combined with $NO_3^-$ application for agriculture, serve to mobilize U by changing the oxidation level within the local strata. Groundwater pumping also pulls U deeper into an aquifer (Jurgens et al., 2010), with the end result that municipal wells in this area have reported increased U concentrations, sometimes violating the DWS, 30 μg $L^{-1}$ (Burow et al., 2017).

Uranium oxidation state and mobility is dependent on a number of environmental factors. Mobility is strongly controlled by pH (Crawford et al., 2017; Markich 2002), with U(VI) sorption decreasing with increasing pH (Jurgens et al., 2010). Under oxic conditions, U(VI) predominately exists as the mobile uranyl ion ($UO_2^{2+}$) and associated complexes, while the less soluble U(IV) predominates in anoxic conditions (Yan et al., 2010; Crawford et al., 2017). Bicarbonate and calcium ($Ca^{2+}$) ions also play a significant role in U mobility, with the complexation of each in the aqueous phase decreasing U sorption (Ragnarsdottir and Charlet, 2000; Stewart et al., 2010; Yan et al., 2010; Crane et al., 2015b; Banning et al., 2017). Nitrate has also been observed to remobilize U(IV) (Banning et al., 2017).

## 1.5 Chromium

Chromium (Cr) is a common metallic element, the 21st most abundant element in the Earth's crust (Barnhart 1997). It may have oxidation states ranging from -2 to +6 (Testa et al., 2004), but in the environment, Cr occurs primarily in two oxidation states: hexavalent (Cr(VI)) and trivalent (Cr(III)) (Krishnamurthy and Wilkens, 1994). Chromium mobility and redox behavior depends on a number of factors, including the pH and redox status of the environment, and the concentrations of other chemical species.

The two Cr species have radically different toxicities. Cr(III) is the most common form, and is considered an essential trace element for humans and other organisms (Kotaś and Stasicka, 2000). Cr(VI), on the other hand, is harmful to human health. Hexavalent Cr may have a variety of adverse health effects, depending on the route of exposure: contact with skin and inhalation may cause dermal and lung effects, respectively. Chromium (VI) is an oxidizing agent and coordinates easily with cell enzymes, potentially disrupting cell function; this risk is present in exposure to Cr(VI) through contaminated drinking water (Kotaś and Stasicka, 2000). The Environmental Protection Agency (EPA) has set a maximum contaminant level for total Cr at 100 μg $L^{-1}$ (0.1 mg $L^{-1}$).

When groundwater contamination of Cr occurs, Cr primarily originates from industries such as leather tanning and pigment production, although Cr(VI) may also be oxidized from Cr(III)-bearing minerals (such as chromite, $FeCr_2O_4$) through natural processes (Oze et al., 2007). The speciation of Cr may vary depending upon the industry from which the wastewater originates: metallurgic industry wastewater generally contains high Cr(VI), while Cr(III) dominates in tannery wastewater.

In addition to being more toxic than its trivalent state, Cr(VI) is more mobile in the environment. Trivalent Cr has low solubility in water, so it readily precipitates as Cr(III) hydroxide or mixed Fe(III)-Cr(III) hydroxides/oxyhydroxides; hexavalent Cr, on the other hand, mostly exists in soluble forms (e.g. $Na_2CrO_4$), and easily leaches, causing contamination (Gheju et al., 2008). The dominant Cr(III) species within the pH range of natural waters (pH 5 to 12) are $Cr(OH)^{2+}$ and $Cr(OH)_{3(s)}$ (Kotaś and Stasicka, 2000; Markiewicz et al., 2015). The dominant Cr(VI) species are $CrO_4^{2-}$, $HCrO_4^-$, and $Cr_2O_7^{2-}$; at acidic pH (1-6), $HCrO_4^-$ is dominant, with dichromate appearing when Cr(VI) concentration reaches $10^{-2}$ M (Gheju et al., 2008).

The reduction of Cr(VI) to Cr(III) in acidic solution (Kotaś and Stasicka, 2000) occurs as follows:

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$$

Hexavalent Cr has a very high redox potential in acidic solutions (E0 = 1.33 - 1.38 V) and is unlikely to be reduced at alkaline pH. Thus, Cr(VI) reduction to Cr(III) may be quite reversible under certain environmental conditions, and an effective method of sequestration alongside reduction may be necessary (Han et al., 2000).

## 1.6 Objectives

The objective of this study was to assess the efficacy of a novel porous iron composite (PIC) material at removing various inorganic groundwater contaminants under both oxic and anoxic conditions in the presence and absence of other redox sensitive groundwater species (i.e., $NO_3^-$). This objective was achieved through a series of batch reaction experiments.

# CHAPTER 2

## Porous Iron Composite Material for Remediating a Complex Surrogate Groundwater Solution

The contamination of groundwater sources of drinking water is a concern in the United States. Uranium (U) may contaminate groundwater as a result of nuclear industry activity, but it can also be mobilized through changes in local geology, particularly as a result of groundwater withdrawal and agricultural nitrate ($NO_3^-$) application. Zero valent iron has been demonstrated to effectively immobilize U, but its effectiveness is highly limited in alkaline environments and those with high levels of $NO_3^-$ and carbonate. Batch reaction experiments using a surrogate groundwater solution containing 100 µg $L^{-1}$ U, 23 mg $L^{-1}$ $NO_3^-$ (as N), and 200 mg $L^{-1}$ alkalinity (as $CaCO_3$), as well as 100 µg $L^{-1}$ each rhenium, strontium, and thorium, and 55 µg $L^{-1}$ arsenic (As) were conducted to assess the performance of a novel porous iron composite material (PIC). The concentrations of all contaminants except for strontium were successfully lowered below respective drinking water standards in both oxic and anoxic environments.

### 2.1 Introduction

#### 2.1.1 Uranium

Uranium (U) is a naturally occurring radioactive element. The most abundant U isotope, $^{238}U$, accounts for approximately 99% of natural U and has a half-life of ~4.5 x $10^9$ years; the other isotopes, $^{235}U$ and $^{234}U$, account for approximately 0.75% and 0.01%, and have half-lives of ~2.7 x $10^5$ and ~7.13 x $10^8$ years, respectively (Andersen, Stirling, and Weyer, 2017). Natural U is primarily found in granitic formations (Langmuir 1978) and their derivative sedimentary rocks (Burow et al., 2017). Much of the radiation risk associated with natural U is derived from the decay products, radium-226 ($^{226}Ra$) and gaseous radon (Rn). Because of its long half-life, the risks natural U poses to human health are similar to those of other heavy metals in the absence of its decay products, and include renal toxicity, as well as cardiovascular, muscular, and neurological effects (Taylor and Taylor, 1997).

One route of U exposure is through contaminated drinking water obtained from groundwater supplies with high concentrations of U (Taylor and Taylor, 1997; Jurgens et al., 2010). Uranium contamination in groundwater may be the result of anthropogenic contamination associated with the nuclear fuel or weapons industries (Shi et al., 2012). It may also occur naturally, as the result of leaching from minerals (Jurgens et al., 2010; Burow et al., 2017). In the eastern San Joaquin Valley of California, overuse of groundwater for irrigation has led to increases in pH, alkalinity, and nitrate ($NO_3^-$) concentrations in groundwater (Jurgens et al., 2008). These environmental changes altered the redox status and caused natural U to be released from the region's granitic bedrock into the aquifer, resulting in elevated concentrations in many drinking water wells (Table 2.1) (Jurgens et al., 2008). The average U concentration approaches the drinking water standard (DWS) of 30 μg $L^{-1}$ U set by the United States Environmental Protection Agency (US EPA), and exceeded this standard in at least 23 wells measured between 1988-2008 (Jurgens et al., 2010).

Table 2.1. United States Geological Survey (USG) average data collected from California groundwater wells (Jurgens et al., 2008). US EPA Drinking Water Standards included where applicable. Parameters of the water, including pH, dissolved oxygen (D.O), and alkalinity, are also included.

| **Parameter** | **Units** | **USGS Report** | **DWS** |
|---|---|---|---|
| pH | | 7.2 | |
| D.O. | mg/L | 5 | |
| Alkalinity | mg/L $CaCO_3$ | 358 | |
| | | | |
| Uranium | µg/L | 24.2 | 30 |
| Arsenic | µg/L | 7.7 | 10 |
| Nitrate | mg/L (as N) | 8.1 | 10 |
| | - | - | |
| Sodium | mg/L | 56.8 | |
| Potassium | mg/L | 3 | |
| Calcium | mg/L | 82.1 | |
| Magnesium | mg/L | 36.5 | |
| Sulfate | mg/L | 40.5 | |
| Phosphate | mg/L | 0.78 | |

Aqueous U is found in valence states ranging from +1 to +6, but the most common forms in natural waters are U(IV) and U(VI). Hexavalent U is the more mobile form, and its associated complexes are more soluble (Crane and Scott, 2014). The oxidation state of U is strongly pH dependent (Markich 2002; Crawford et al., 2017). Uranium(VI), as uranyl ($UO_2^{2+}$), is the predominant form of U in the circumneutral, oxic waters typical of aquifers (Langmuir 1978; McKinley et al., 2007).

Redox manipulation has proved a useful way to remediate or limit U mobility. Uranium reduction to enhance immobilization has been achieved through both biotic and abiotic means, including the use of metal-reducing bacteria species, organic compounds (e.g., acetate), and inorganic compounds (e.g., sulfur species) (Dullies et al., 2010; Sitte et al., 2010; Chen et al, 2016). More specifically, Fe-bearing minerals and Fe oxides have been investigated extensively, due to the important effect concentrations of sorptive iron (oxy)hydroxides have on environmental U (Langmuir 1978).

### 2.1.2 Arsenic

Arsenic (As) is a common inorganic contaminant, often found in soil and groundwater as a result of industrial activity (Baragaño et al., 2019), pesticide use, or natural weathering processes (Foster et al., 2019). Severe As contamination occurs in India, where the accelerated weathering of naturally As-rich soils threatens regional drinking water supplies (Nath et al., 2018). Chronic exposure to As is associated with a variety of negative health effects, including skin lesions, neuropathy, and cancer development (Kapaj et al., 2006). The US EPA DWS for As is 10 μg $L^{-1}$ (US EPA 2001), which is approached by As concentrations in some regions of California (Table 1).

The primary As valence states found in groundwater are As(V) and As(III) (Aide, Beighley, and Dunn, 2016), with As(III) being more mobile and toxic than As(V). Because of this, As(III) is more difficult to remove than As(V) (Fu et al., 2014). As an example, Dixit and Hering (2003) concluded that the reduction of As(V) in the presence of the mineral goethite only slightly affects As mobility at circumneutral pH. Remediation plans which involve manipulating As redox state therefore should include further immobilization steps. Methods such as soil washing and phytoremediation have conventionally been used to remove As (Hasegawa et al., 2016). Additionally, the in situ immobilization of As using Fe-containing species for adsorption and surface complexation has been extensively investigated (Baragaño et al., 2019). Dixit and Hering (2003) found that the sorption of As(V) onto goethite and amorphous iron oxides was favored at acidic pH, whereas the sorption of As(III) was favored at alkaline pH. Arsenic has also been successfully removed in field-scale filtration using an Fe matrix (Neumann et al., 2013).

### 2.1.3 Nitrate

Nitrate ($NO_3^-$) is an extremely common groundwater contaminant due to its importance in agriculture. Sources of $NO_3^-$ contamination include nitrogenous fertilizers, animal waste (e.g., poultry or livestock farms), and industrial wastewater (Keeny 1989; Jung et al., 2011). Nitrate reduces to nitrite ($NO_2^-$) readily under standard conditions (Table 2). A buildup of $NO_2^-$ in the blood, especially in children, can result in the dangerous methemoglobinemia or "blue baby syndrome" (Kapoor and Viraraghavan, 1997; Kay et al., 2004). Thus, the US EPA has instated a DWS of 10 mg $L^{-1}$ $NO_3^-$ and 1 mg $L^{-1}$ $NO_2^-$, both measured as N. However, in 2011, 32% of domestic wells had $NO_3^-$ concentrations above the DWS, and in areas of intensive agriculture, groundwater quality is still degraded by high $NO_3^-$ concentrations (Table 1) (Jurgens et al., 2011).

Nitrate also acts as a ligand for many toxic heavy metals, including U and As, and can increase their mobility in otherwise reducing conditions (Jurgens et al., 2010; Crane et al., 2015b; Banning et al., 2017). Conversely, $NO_3^-$ may initially promote contaminant removal, later followed by re-release from the complexes formed (Su et al., 2014). For this reason, contaminated groundwater with high $NO_3^-$ concentrations can prove more difficult to remediate. Studied methods of $NO_3^-$ removal include biological denitrification, ion exchange technologies, reverse osmosis, and chemical reduction (i.e., using Fe and Fe-based materials), including within a permeable reactive barrier (Robertson et al., 2000; Soares, 2000; Clauwaert et al., 2007; Su et al., 2014; Zhang et al., 2017).

### 2.1.4 Zero Valent Iron

Zero valent iron (ZVI) has been extensively investigated for use in redox manipulation of a variety of contaminants, including organic solvents (O'Carroll et al., 2013; Fu et al., 2014), toxic heavy metals such as uranium (O'Carroll et al., 2013; Fu et al., 2014; Tosco et al., 2014), chromium (Gould, 1982; Lai and Lo, 2008; Wilkin et al., 2005), and mercury (Weisener et al., 2005), and other common inorganic groundwater contaminants like As (Gil-Díaz et al., 2017; Baragaño et al., 2019), and $NO_3^-$ (Ren et al., 2015; Zhang et al., 2017). The efficacy of ZVI in this use can be explained by examining its half-reactions and those of each contaminant of interest (Table 2.2) (Bard et al., 1985). Redox potential ($E^0$) indicates the tendency of electron transfer in the indicated direction of the equation. The more positive the value of $E^0$, the more likely the reaction is to occur; reactions in the environment proceed in order of decreasing redox potential. These half-reactions are written in the direction of reduction by convention, and reversing their direction also changes the sign of their $E^0$. Thus, under standard conditions, U, As, and $NO_3^-$ are favored to undergo reduction, while $Fe^0$ is favored to oxidize. Furthermore, $Fe^0$ is more likely to react with the contaminants, rather than being oxidized by the water directly. Together, these sets of equations describe the favorable conditions that lead to ZVI being a useful material for the remediation of redox-sensitive contaminants.

Table 2.2. Standard redox potentials ($E^0$) for $NO_3^-$, As, U (as uranyl) and Fe in aqueous solution at 25 °C.

| | Half reaction | $E^0$ (V) |
|---|---|---|
| Nitrate (to nitrite) | $NO_{3\ (aq)}^- + 2H^+ + e^- \leftrightarrow NO_{2(g)} + H_2O$ | 0.80 |
| Iron | $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ | 0.77 |
| Arsenic | $H_3AsO_4 + 2H^+ + 2e^- \leftrightarrow HAsO_2 + 4H_2O$ | 0.56 |
| Uranium | $UO_2^{2+} + 4H^+ + 2e^- \leftrightarrow U^{4+} + 2H_2O$ | 0.27 |
| Iron | $Fe^{3+} + 3e^- \leftrightarrow Fe_{(s)}$ | -0.04 |
| Iron | $Fe^{2+} + 2e^- \leftrightarrow Fe$ | -0.44 |

For example, under acidic conditions, the reduction of U by ZVI can be written as follows (Fiedor et al., 1998; Riba et al., 2008):

$$Fe^0 + 1.5UO_2^{2+} + 6H^+ \rightarrow Fe^{3+} + 1.5U(IV) + 3H_2O \qquad \text{(Eq. 1)}$$

With a potential of $E^0$ = +0.17 V, this reaction is favored over its reverse. In other words, ZVI will consistently reduce U under acidic conditions.

However, reduction is not the only mechanism of immobilization observed when using ZVI. A combination of reduction, adsorption, and precipitation is known to occur, with some uncertainty as to the specifics of the kinetics involved. In denitrification experiments, ZVI generally removes $NO_3^-$ via adsorption followed by redox reactions. This has been reported as a pseudo first-order kinetic equation, although there are indications this may be an insufficient to explain the removal relationship (Zhang et al., 2017). Yan et al. (2010) postulate that U(VI) reduction occurs in a two-step process of sorption followed by reduction at the particle surface:

$$\equiv Fe + U^{6+}_{(aq)} \rightarrow \equiv FeU^{6+} \qquad \text{(Eq. 2)}$$

$$\equiv FeU^{6+} \rightarrow \equiv FeU^{4+} + [iron\ (hydr)oxides] \qquad \text{(Eq. 3)}$$

The final U(IV) species formed is generally the solid precipitate similar to uranite, $UO_2$ (Riba et al., 2008; Dickinson and Scott, 2010). A minor amount of $UO_3 \cdot 2H_2O$ may also precipitate (O'Carroll et al., 2013).

Several notable limitations of ZVI have been observed regardless of the contaminant involved. First, pH is highly influential in ZVI removal kinetics. Acidic conditions favor reduction by ZVI (Eq. 1; Table 2.2), due in part to the corrosive effect of protons (O'Carroll et al., 2013; Guo et al., 2015). Uranium sorption decreases with increasing pH (Jurgens et al., 2010), as does $NO_3^-$ reduction (Guo et al., 2015). Yoshino and Kawase (2013) found that millimeter-scale ZVI was only capable of removing $NO_3^-$ under strongly acidic conditions, despite the expectation of removal at a wider pH range (see Table 2.2 and previous discussion of redox potential). However, while lowering pH increases corrosion of the ZVI particle surface and heightens initial reactivity, it may reduce the material's reactive longevity (O'Carroll et al., 2013). Zhang et al. (2017) found that $NO_3^-$ reduction to $NH_3$ was the lowest and least efficient at the low pH of 1.22, compared to pH 1.62 and 1.92. The buildup of Fe oxides on the surface of ZVI particles creates a passive surface layer (O'Carroll et al., 2013) which, combined with the formation of crystalline phases, decreases contaminant removal (Dixit and Hering, 2003).

Carbonate ($CO_3^{2-}$) and bicarbonate ($HCO_3^-$) ions have a particularly strong effect on ZVI effectiveness, especially when associated with calcium ($Ca^{2+}$) cations. Carbonates increase U solubility even at alkaline pH (Langmuir 1978). Aquifer U concentrations are positively correlated with $HCO_3^-$ concentrations (Jurgens et al., 2010; Burow et al., 2017). Crane et al. (2015b) observed that while $Ca^{2+}$ in solution with $HCO_3^-$ did not inhibit initial U sorption to ZVI, it did encourage U(VI) desorption after >48 hours. Additionally, U immobilization was proportional to $HCO_3^-$ concentration when no $Ca^{2+}$ was present. Yan et al. (2010) showed that at circumneutral pH, ZVI immobilization of U dramatically decreases with increasing $HCO_3^-$ and $Ca^{2+}$ concentrations. Similarly to $NO_3^-$, $HCO_3^-$ may initially increase contaminant removal: $Ca^{2+}$ and $HCO_3^-$ have been found to increase As removal by promoting Fe (oxy)hydroxide formation, which As binds to (Mak, Rao, and Lo, 2009).

Another environmental factor important to ZVI-based remediation strategies is dissolved oxygen (DO). The presence of DO indicates oxic water conditions, as also evident from oxidation-reduction potential readings (ORP), and is quite common in aquifers (McKinley et al., 2007; see also Table 1). Under these conditions, U tends to remain in the mobile U(VI) form (Langmuir 1978); reduction of U is less favorable, and remobilization via desorption is a greater concern (Fiedor et al., 1998). Fiedor et al. (1998) further found that at constant U speciation (maintained by controlling pH), U(VI) sorption was favored under oxic condition, while U(VI) reduction to U(IV) was favored under anoxic conditions. Additionally, DO interacts with the surfaces of ZVI particles to form a new surface layer of oxidized Fe precipitates (Liu and Lowry, 2006), thus potentially aging the particles faster and consuming electrons that might otherwise have been donated to the desired contaminant. However, Tanboonchuy et al. (2011) found that high DO favored As removal at low pH, and Guo et al. (2015) found that at pH 5 and 7, the presence of $O_2$ facilitated $NO_3^-$ removal. These findings are likely due to an enhancing effect of oxidation on initial reactivity, i.e., the effects of corrosion.

One of the primary factors that controls ZVI contaminant removal ability is available surface area (O'Carroll et al., 2013). Dixit and Hering (2003) postulated that As mobility could be increased by the formation of crystalline phases (and the associated loss of surface area). Nano-scale ZVI (nZVI) has been investigated extensively for its larger surface area and increased surface reactivity, compared to larger ZVI particles. However, nZVI presents unique challenges, including an observed tendency to aggregate, which reduces available surface area (Nurmi et al., 2005). The material used in these experiments has a novel porous surface, which is intended to increase available surface area at a particle size large enough to avoid aggregation.

The objective of this study was to evaluate the ability of a novel porous iron composite material to immobilize U under complex aqueous conditions in the presence of other redox sensitive species, as might be found in an aquifer. This objective was achieved through a series of laboratory batch tests.

## 2.2 Materials and Methods

### 2.2.1 Solutions

A solution of artificial groundwater containing ionic concentrations similar to those of the California eastern San Joaquin Valley was created (CAGW) (Table 2.3). Although not an exact match, this solution was created with the intention of mimicking the complexity of natural aquifer chemistry. However, the concentrations of contaminants were increased to levels much higher than those found in the aquifer, as a comparison of Table 2.1 to Table 2.3 will show. Specifically, concentrations of U were increased from 24 to 100 μg $L^{-1}$, As from 7.7 to 55 μg $L^{-1}$, and $NO_3^-$ from 8.1 to 23 mg $L^{-1}$ (as N).

Because U contamination may occur as a result of nuclear fuel or weapons industries, the possibility exists of the release of other radionuclides at the same time. Several other contaminants were added to the CAGW solution to investigate this possibility. Thorium (Th) exists as part of the U decay chain (Andersen, Stirling, and Weyer, 2017). Technetrium-99 ($^{99}Tc$) is a highly unstable radioisotope and a nuclear fission product found in waste material from both nuclear power and weapons production. Rhenium (Re) has previously been used as a non-radioactive chemical surrogate for $^{99}Tc$ (Lenell and Arai, 2016). Strontium-90 ($^{90}Sr$) is a fission product, although not one that occurs in the natural U decay chain. To limit the hazards of this experiment, Re was used as an analogue for $^{99}Tc$, and stable Sr was used as an analogue for $^{90}Sr$.

Table 2.3. Composition of the surrogate groundwater solution, CAGW.

| **Parameter** | **Units** | **Surrogate Solution** |
|---|---|---|
| Uranium | µg/L | 100 |
| Rhenium | µg/L | 100 |
| Strontium | µg/L | 100 |
| Thorium | µg/L | 100 |
| | | |
| Arsenic | µg/L | 55 |
| Nitrate | mg/L (as N) | 23 |
| | | |
| Alkalinity | mg/L $CaCO_3$ | 200 |
| | | |
| Sodium | mg/L | 93 |
| Potassium | mg/L | - |
| Calcium | mg/L | 80 |
| Magnesium | mg/L | 36 |
| Sulfate | mg/L | 60 |
| Phosphate | mg/L | - |

### 2.2.2 Iron Material

A novel porous iron composite (PIC) material developed by Höganäs North America LLC was used in these experiments (Hu 2011). The PIC material consists primarily of Fe(0) and Fe oxides and has a specific surface area of 10 $m^2$ $g^{-1}$ (Hu 2011; Seaman et al., 2018). It has been suggested that the material's complex, large reactive surface area may facilitate the removal of contaminants at concentrations or under environmental conditions which typically hinder ZVI effectiveness, with encouraging results demonstrated in preliminary experiments (Seaman 2015).

2.2.3 Batch Tests

A series of batch tests to evaluate the ability of PIC to remove U in the presence of other contaminants and complexing ions was conducted. Two-hundred mL of the CAGW solution was added to 5 g of PIC in 250-mL plastic bottles. The test setup was repeated in either an oxic environment (laboratory bench) or an anoxic environment (glove bag maintained at 2% $H_2$ via addition of 95% $N_2$/5% $H_2$ gas mixture; Coy Vinyl Anaerobic Chambers, Grass Lake, MI). Inside the anaerobic chamber, $H_2$ reacts with a palladium catalyst to consume $O_2$ and form $H_2O$. Batch vessels were agitated on an orbital shaker (~100 rpm) for the duration of each test to facilitate equilibration and particle dispersal.

Each batch vessel was sampled at regular intervals, at 4, 24, 48, 72, and 96 hours, at which times 1-2 mL was removed and separated into two aliquots. One was reserved for measurement of the primary contaminants (i.e., U, As, Sr, Re, Th), and preserved for analysis by filtering (0.2 μm pore size) and acidification to 2% $HNO_3$. The remaining aliquot was immediately analyzed for the other compounds in solution (i.e., $NO_3^-$, $NO_2^-$, $NH_4^+/NH_3$, $S^{2-}$, Fe(II)) by their respective methods. The amount removed from the solution was small in order to minimize the effects of destructive sampling. The pH and oxidation-reduction potential (ORP) of the remaining suspension were also measured at the time of sampling, and continued until 240 hours.

### 2.2.4 Analysis

Concentrations of U, Re, Sr, Th, and As were determined by inductively coupled plasma-mass spectrometry (ICP-MS) on a NexIon 300 (Perkin Elmer, Inc.), in accordance with the quality assurance (QA) and quality control (QC) protocols of EPA method 6020A (USEPA, 2007).

Concentrations of $NO_3^-$, $NO_2^-$, $NH_4^+/NH_3$, $S^{2-}$, and Fe(II) were determined by Chromotropic Acid, Diazotization (APHA, 1997a), Phenate (APHA, 1997b), Methylene Blue (APHA, 1997c), and phenanthroline methods, respectively.

## 2.3 Results

### 2.3.1 pH and ORP

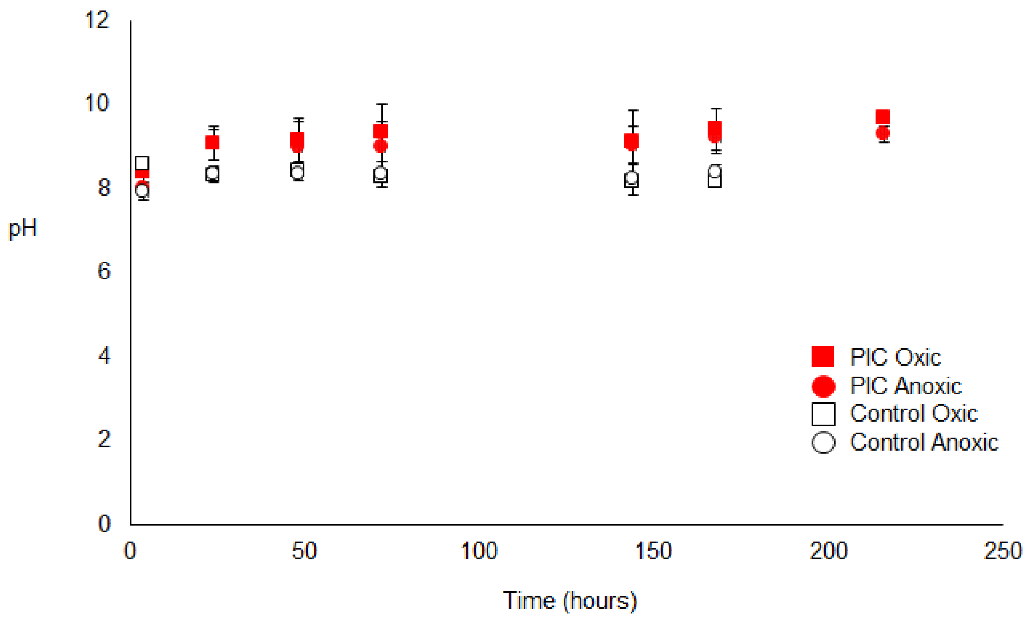


Figure 2.1. Mean measurements of pH over the course of the batch tests. Error bars indicate standard deviation.

The pH in these experiments were not adjusted. The pH of control vessels in all environments remained relatively stable at the same circumneutral pH of the test solution. Without adjustment, the pH of PIC vessels in all environments increased noticeably from the start of the experiment, maintaining a value above 9.0 for the duration of testing. The PIC vessels maintained higher pH than control vessels in both environments.

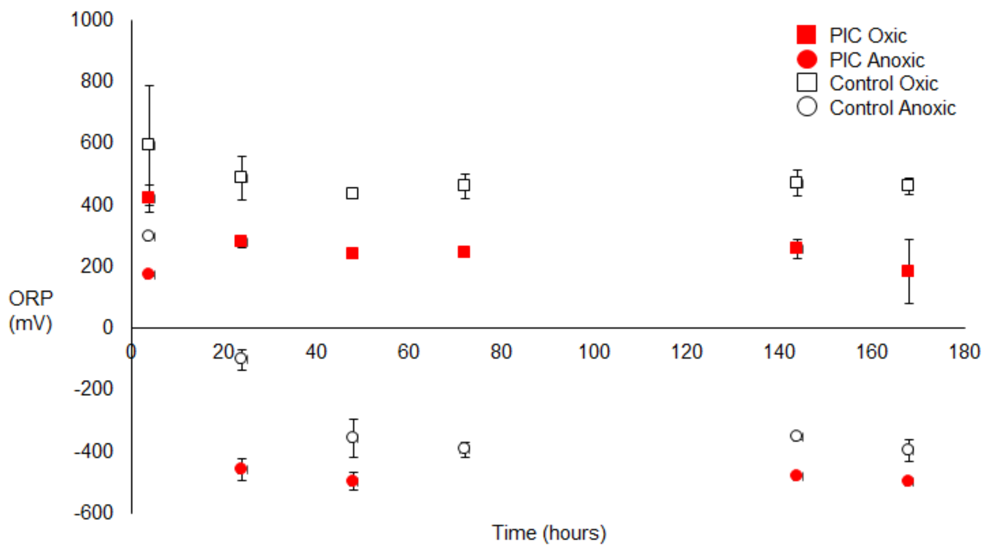


Figure 2.2. Mean measurements of ORP over the course of the batch tests. Error bars indicate standard deviation.

The oxidation-reduction potential (ORP) shows a marked difference between the two test environments. Oxidation-reduction potential is a measurement of whether test conditions (in this case, the aqueous test environment) are likely to oxidize or reduce another material. A more positive value indicates a more oxidizing environment, while a more negative value indicates a reducing environment.

The ORP of the lab bench vessels was positive (i.e., $O_2$ was present), while the ORP of the glovebag vessels was negative (i.e., $O_2$ was absent) (Figure 2). As oxic conditions can promote ZVI aging (Liu et al., 2005; Liu and Lowry, 2006), there is the potential for PIC to show a difference in effectiveness between test environments. While there seemed to be a slight difference in initial rate of U immobilization by PIC between environments, there was not an observable effect on total removal or re-release in these experiments.

2.3.2 Primary Contaminants

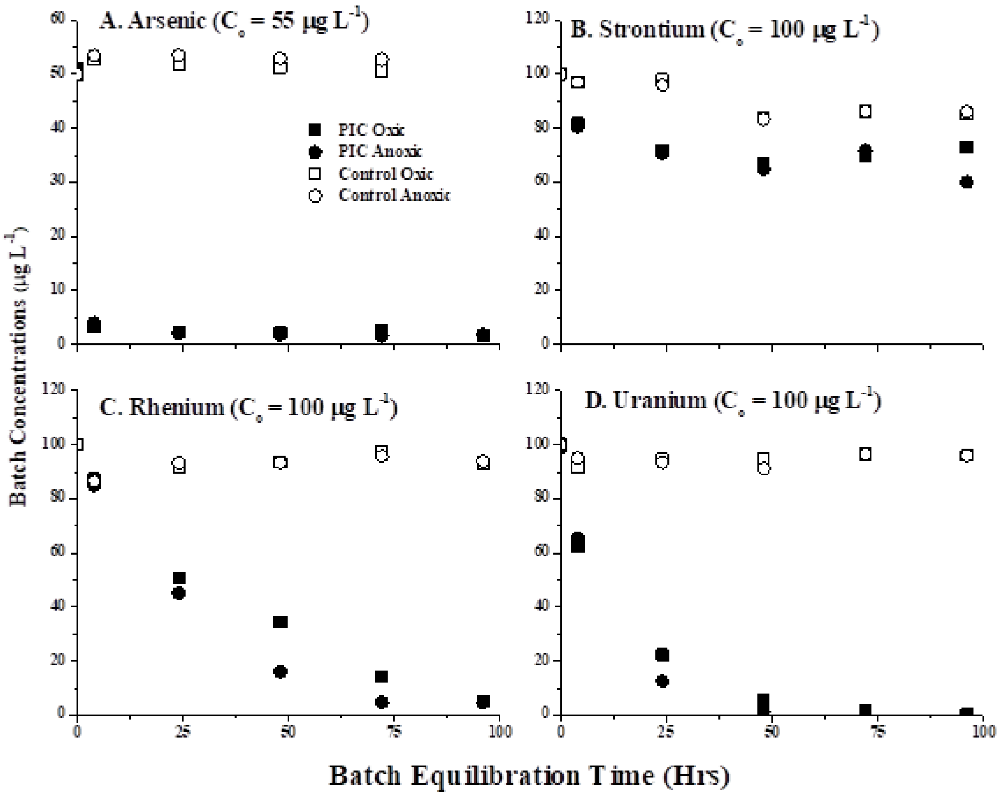


Figure 2.3. Primary contaminant concentrations over the course of oxic and anoxic batch tests.

Uranium concentrations decreased in PIC batches under both oxic and anoxic test conditions, to below the MDL within 75 hours under anoxic conditions. This removal was sustained for the duration of the batch tests. Additionally, approximately 98% of As and 95% of Re was removed within the 100 hours of the batch tests. Strontium removal was limited compared to As and the other radionuclides (with approximately 30-40% removal).

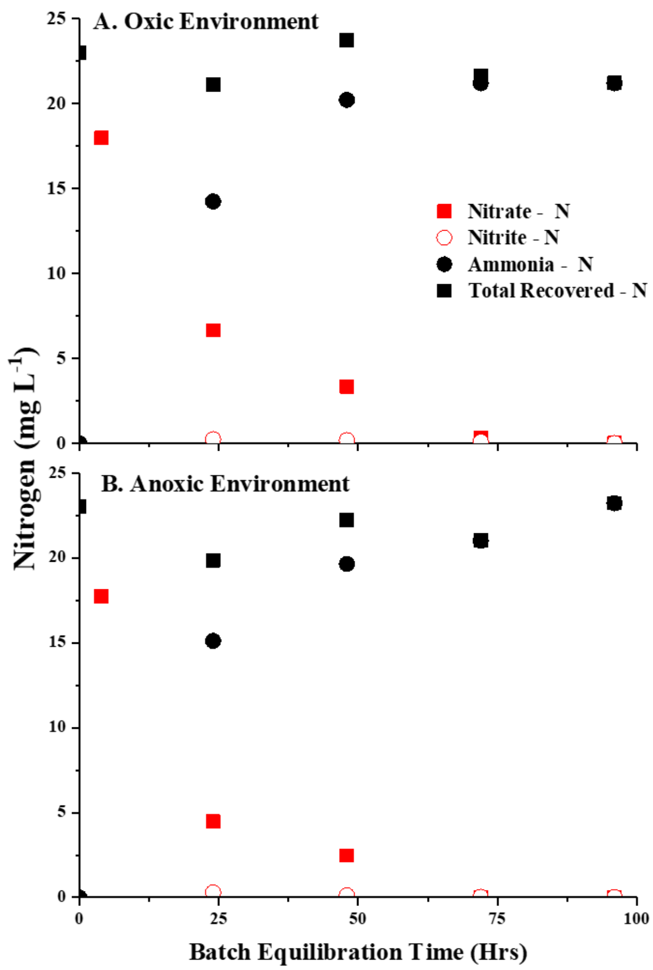


Figure 2.4. Nitrate, nitrite, ammonia, and total recovered N concentrations over the course of oxic and anoxic batch tests.

Nitrate concentrations decreased over the course of the experiments, with values below the minimum detection level of the test (~4 mg L$^{-1}$ as N) recorded after approximately 72 hours. Nitrite was generated, but concentrations never exceeded 1 mg/L at any point in the test duration. There was good recovery of total solution N, and near-total conversion to $NH_3$.

## 2.4 Discussion

In all PIC-containing vessels, the pH increased steadily to a value above 9.0 before stabilizing and remaining high for the duration of the experiment. These results were expected, due to the consumption of $H^+$ and production of $OH^-$ as part of the ZVI-$H_2O$ system (Crane and Scott, 2011; Tosco et al., 2014):

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2\,(g)} + 2OH^-_{(aq)} \quad \text{(Eq. 4)}$$

$$2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow 2Fe^{3+}_{(aq)} + H_{2\,(g)} + 2OH^-_{(aq)} \quad \text{(Eq. 5)}$$

The pH may also be increased due to the consumption of protons:

$$Fe^{2+}_{(s)} + 2H^+_{(aq)} + 1/2O_{2(aq)} \rightarrow 2Fe^{3+}_{(aq)} + H_2O_{(l)} \quad \text{(Eq. 6)}$$

The positive potential of this half-cell ($E^0$ = +0.46 V) indicates that this interaction (Eq. 6) is more likely to occur than that of Eq. 4 ($E^0$ = -1.60 V). In other words, the increase in pH is likely driven by the consumption of protons in the oxidation of $Fe^{2+}$ to $Fe^{3+}$, rather than the creation of hydroxide during the oxidation of $Fe^0$ to $Fe^{2+}$.

Previous studies of ZVI have shown good removal of U under acidic pH conditions, with effectiveness decreasing as pH increases (Yan et al., 2010). Zhang et al. (2017) found that a deficit of $H^+$ at higher pH (1.92, compared to 1.62) lead to a temporary increase in pH, and a concurrent decrease in the denitrification rate. In this experiment, neither an alkaline pH nor an increase in pH inhibited contaminant immobilization by PIC (this experiment was not designed to assess the kinetics of contaminant removal).

Anoxic conditions favor U removal by ZVI, while oxic conditions typically hinder it (Fiedor et al., 1998). However, in this experiment DO levels present in the oxic batch tests showed little effect on U removal. Although Re and U were removed from solution more quickly under anoxic conditions, removal still proceeded under oxic conditions. Crane and Scott (2014) observed U re-release after 48 hours in oxic batch tests, with no corresponding re-release in anoxic batches. No U re-release was recorded during the 100 hours of this research’s batch tests.

The composition of the batch test solution provided several potential impediments to U removal, including the presence of multiple redox-sensitive contaminants at high concentrations and the presence of ions shown to interrupt U reduction by and/or adsorption to ZVI. Despite these impediments, 100 μg $L^{-1}$ U was removed to at or below MDL within 100 hours, with no re-release recorded.

PIC was still able to immobilize U even in the presence of high concentrations of other redox-sensitive contaminants. Furthermore, the majority of the other contaminants were also immobilized during the batch test. The exception was Sr, which showed only limited immobilization. However, Sr was included as a surrogate for $^{90}$Sr, which is only found as a fission product in anthropogenic nuclear activity and thus is not a primary contaminant of concern in the environment. U, Re, and As, all of which *are* environmental contaminants of high concern, were all removed efficiently by PIC.

Furthermore, the presence of $Ca^{2+}$ and $HCO_3^-$ did not impede U, Re, As, or $NO_3^-$ removal. No re-release of contaminants was recorded over the 100-hour batch tests. Crane et al. (2015b) observed that 1 mg $L^{-1}$ U was re-released from ZVI after 48 hours at a ZVI-to-$HCO_3^-$ ratio of 0.005. In this experiment, U was not re-released even up to 100 hours agitation time at a ZVI-to-$HCO_3^-$ ratio of 0.05. This indicates that PIC may be more resistant to the effects of $Ca^{2+}$ and $HCO_3^-$ observed with other ZVI materials.

Nitrate was also effectively removed. Nitrite was transient and its buildup was limited (below the DWS of 1 mg $L^{-1}$ as N). As $NO_2^-$ is the most hazardous species to human health in this N reduction series, its rapid and near-total conversion to $NH_3$ is desirable. The extent of this conversion to $NH_3$ is also consistent with other experiments (Zhang et al., 2017).

# CHAPTER 3

## Porous Iron Composite Material for Remediating Chromium

Chromium (Cr) is a metal used in many industries, but it is also a common groundwater contaminant. As Cr exposure presents a variety of health hazards, its removal is vital to preserve sources of drinking water. Many existing removal technologies are limited by their cost or secondary waste generation, and are significantly less effective at environmentally relevant concentrations which approach the drinking water standard of 100 μg $L^{-1}$ Cr. Zero valent iron effectively immobilizes Cr, but is limited by inefficiencies at circumneutral pH and the influence of environmental redox status. Batch experiments were performed to assess the ability of a novel porous iron composite material (PIC) to remove Cr, using a solution of 100 μg $L^{-1}$ Cr(VI) in both oxic and anoxic environments. The PIC showed at least 80% removal of Cr(VI) and at least 75% removal of total Cr, with more complete removal in the oxic environment. The solution pH measured above 4 throughout the experiment and was not adjusted.

### 3.1 Introduction

#### 3.1.1 Chromium

Chromium (Cr) is a common metallic element with many industrial uses. It is extremely important in metallurgy, and also commonly utilized in leather tanning, pigment production, and electroplating (Kotaś and Stasicka, 2000). The primary sources of Cr are ores such as chromite ($FeCr_2O_4$). Deposits of Cr occur throughout the United States, although the majority of Cr is produced in Asia and Africa (U.S. Geological Survey, 2012). While natural oxidation of Cr from minerals can result in groundwater Cr contamination, anthropogenic activity such as the discharge of high-Cr industrial wastewater (Dhal et al., 2013) and the shallow, unconfined burial of solid waste (Jardine et al., 1999) are the primary sources of Cr contamination.

Chromium has several potential oxidation states ranging from -2 to +6 (Testa et al., 2004). Hexavalent (Cr(VI)) and trivalent (Cr(III)) are the two most commonly found in aquatic environments (Krishnamurthy and Wilkens, 1994), as well as the most biologically relevant. Hexavalent Cr is considered more dangerous than Cr(III) (Ajouyed et al., 2010). Chromium exposure is associated with a variety of negative human health effects: it is a potential carcinogen and a strong oxidizing agent, which means it poses a risk to cell function (Kotaś and Stasicka, 2000). The World Health Organization DWS for Cr is 50 µg $L^{-1}$ (World Health Organization, 1996). The current EPA Drinking Water Standard (DWS) for Cr in drinking water is 0.1 mg $L^{-1}$ (100 µg $L^{-1}$); there is no standard for Cr(VI) specifically. In 2014, the California State Water Resources Control Board established a maximum contaminant level (MCL) of 10 µg $L^{-1}$ Cr(VI), but it was withdrawn in 2017; the current state MCL for total Cr is 50 µg $L^{-1}$.

Hexavalent Cr is highly mobile, and the more thermodynamically stable species in most natural waters of pH 6.5-8.5 (Schroeder and Lee, 1975). Its most common forms are chromate ($CrO_4^{2-}$, $HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$) (Gheju et al., 2008). These ions do not form insoluble precipitates at any pH (Nriagu 1988; Barrera-Díaz et al., 2012). Conversely, Cr(III) readily forms insoluble precipitates such as $Cr(OH)_3$ (Kotaś and Stasicka, 2000; Gheju et al., 2008). Thus, factors affecting Cr oxidation are highly influential for controlling Cr contamination.

Because the reduction of Cr(VI) to Cr(III) decreases its toxicity and environmental mobility, chemical methods of Cr remediation frequently utilize reduction. Conventional methods of Cr removal include reduction via polymers, organic matter, or sulfide compounds; ion exchange; reverse osmosis; electrocoagulation and electrodissolution; photocatalytic reduction; and biological methods like microbial reduction and phytoremediation have all been explored, with varying levels of success (Barrera-Díaz et al., 2012).

Many of these methods come with significant drawbacks. The generation of secondary wastes, including ferric hydroxide, sulfur dioxide gas, and/or toxic sludge, are a primary concern. The adsorption or precipitation of Cr is strongly controlled by pH (Schindler et al., 2018), with the best removal results found under highly acidic conditions. Additionally, while these methods are effective at treating the high Cr concentrations found in wastewater, many are significantly less effective at more dilute and environmentally relevant concentrations (i.e., near the DWS of 0.1 mg $L^{-1}$) (Barrera-Díaz et al., 2012; Dhal et al., 2013).

### 3.1.2 Zero Valent Iron

Zero valent iron (ZVI) has received increasing interest in recent years as a material for the immobilization of redox-sensitive contaminants. Contaminants successfully immobilized include organic contaminants, especially chlorinated solvents (Puls, Paul, and Powell, 1999; O'Carroll et al., 2013; Fu et al., 2014); radionuclides (Naftz et al., 2003; Fu et al., 2014; Tosco et al., 2014), and a wide variety of heavy metals, including arsenic, copper, lead, nickel, cobalt, and cadmium (O'Carroll et al., 2013), as well as Cr (Gould, 1982; Lai and Lo, 2008; Wilkin et al., 2005). Permeable reactive barriers (PRBs) utilizing ZVI have demonstrated successful removal of Cr from groundwater (Blowes et al., 1997; Wilkin et al., 2005).

Contaminant removal occurs via a complex process of reduction, adsorption, and precipitation (Blowes et al., 1997; Kotaś and Stasicka, 2000; Testa et al., 2004; Wilkin et al., 2005). For Cr, reduction and precipitation appear to be the more important processes (Li and Zhang, 2007). The removal of Cr involves the oxidation of $Fe^0$ to $Fe^{2+}$ and $Fe^{3+}$, followed by the co-precipitation of mixed Cr(III)-Fe(III) (oxyhydroxide) phases, as nano-size clusters or as chromite (Yoon et al., 2011). Fu et al. (2014) describes the reduction and precipitation of Cr by $Fe^0$ and subsequent Fe oxides in acidic conditions:

$$Cr_2O_7^{2-} + 2Fe^0 + 14H^+ \rightarrow 2Cr^{3+} + 2Fe^{3+} + 7H_2O \qquad \text{(Eq. 1)}$$

$$Cr^{3+} + Fe^{3+} + 6OH^- \rightarrow Cr(OH)_3 \downarrow \; + Fe(OH)_3 \downarrow \qquad \text{(Eq. 2)}$$

ZVI particles have a thin surface “shell” of Fe oxides that protects the $Fe^0$ core (O’Carroll et al., 2013). The $Fe^0$ atoms readily donate electrons to reduce the Cr under standard conditions, oxidizing the Fe in turn. The particle surface then acts as a substrate for Cr adsorption and/or precipitation of solids (Li and Zhang, 2007). Table 3.1 illustrates the redox processes that favor this electron movement. A positive redox potential ($E^0$) indicates a reaction favorable under standard conditions, with reductions occurring in order of decreasing potential. A negative $E^0$ indicates an unfavorable reaction. However, because half-reactions may be written in either direction, reversing the order also reverses the sign of $E^0$. In other words, an unfavorable reduction becomes a favorable oxidation. In Table 3.1, the *oxidations* of $Fe^0$ to $Fe^{2+}$ and $Fe^0$ to $Fe^{3+}$ thus have positive $E^0$ of 0.44 V and 0.04 V, respectively.

Table 3.1. Standard redox potentials ($E^0$) for Cr (as chromate and dichromate) and Fe in aqueous solution at 25 °C. Values from Bard et al. (1985).

| Solution | Half reaction | $E^0$ (V) |
|---|---|---|
| Chromium | $CrO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$ | 1.51 |
| Chromium | $Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$ | 1.36 |
| Iron | $Fe^{3+} + 3e^- \leftrightarrow Fe_{(s)}$ | -0.04 |
| Iron | $Fe^{2+} + 2e^- \leftrightarrow Fe^0$ | -0.44 |

Chromium sorption to ZVI and Fe oxides is strongly controlled by pH (Ajouyed et al., 2010; Yoon et al., 2011). At acidic pH, Cr(VI) (in the form of chromate) is thermodynamically very likely to be reduced (Table 3.1). The corrosion of the $Fe^0$ surface creates Fe oxides that may aid in contaminant reduction and initially exposes more $Fe^0$ at the particle surface (Nurmi et al., 2005). Removal capacity has generally observed to be higher with decreasing pH (Gheju et al., 2008; Yoon et al., 2011). However, the ultimate effect of corrosion may be to increase initial reactivity while decreasing longevity (O’Carroll et al., 2013).

The impact of the presence of dissolved oxygen (DO) on Cr immobilization by ZVI is not yet fully understood. With many contaminants, ZVI is typically less effective in the presence of oxygen, due to DO's status as an alternate electron acceptor (O'Carroll et al., 2013; Fu et al., 2014). However, results have been more mixed for Cr removal, with some experiments finding minimal or even positive impact of DO (Schlautman and Han, 2001; Yoon et al., 2011). This might be due to the contribution of oxygen to the corrosion of the Fe surface (Tosco et al., 2014):

$$Fe^0_{(s)} + 2H^+_{(aq)} + 1/2O_{2\,(g)} \rightarrow 2Fe^{2+}_{(aq)} + H_2O_{(l)} \qquad \text{(Eq. 3)}$$

$$2Fe^{2+}_{(aq)} + 2H^+_{(aq)} + 1/2O_{2\,(g)} \rightarrow 2Fe^{3+}_{(aq)} + H_2O_{(l)} \qquad \text{(Eq. 4)}$$

One concern of ZVI use to treat contaminants is long-term loss of efficiency due to surface passivation (O'Carroll et al., 2013; Fu et al., 2014). Effective contaminant immobilization by ZVI relies upon electron transfer from a particle's $Fe^0$ core to its surface (Nurmi et al., 2005; Li and Zhang, 2007). The precipitation of Cr(III) solids on the surface of the particle contributes to passivation by inhibiting electron transfer from the particle's core (Hu et al., 2010).

Available surface area is typically a limiting factor in contaminant removal by ZVI. One way that the surface area of ZVI, and thus its contaminant removal, may be enhanced is by reducing particle size, often to nano-scale particles (nZVI) (Rivero-Huguet and Marshall, 2009). However, this avenue is not without its downsides. The aggregation of particles is a consistent concern with nZVI. Aggregation reduces available surface area (Nurmi et al., 2005) and may decrease the conductivity of a PRB (Sun et al., 2006).

The objective of this study was to evaluate the ability of a novel porous iron composite material to immobilize environmentally relevant concentrations of Cr. This objective was achieved through a series of laboratory batch reaction experiments.

### 3.2 Materials and Methods

#### 3.2.1 Solutions

A stock solution of 5 mg/L Cr(VI) was created by dissolving potassium dichromate ($K_2Cr_2O_7$) in Milli-Q $H_2O$. This solution was diluted to create a Cr(VI) concentration of 0.1 mg/L.

#### 3.2.2 Iron Material

These experiments used a novel porous iron composite (PIC) material developed by Höganäs North America LLC (Hu 2011) to investigate the removal of aqueous Cr. The PIC material consists primarily of Fe(0), with a smaller percentage of Fe oxides. It has a specific surface area of 10 $m^2$ $g^{-1}$ (Hu 2011; Seaman et al., 2018). The material's irregular surface and high specific surface area for its particle size is intended to facilitate contaminant removal without the challenges of aggregation observed in ZVI of smaller particle size (i.e., nZVI). Preliminary experiments suggest the PIC is also effective under typically challenging removal conditions (i.e., oxic environments and circumneutral pH) (Seaman 2015).

#### 3.2.3 Batch Tests

A series of batch tests to evaluate the ability of PIC to remove Cr was conducted. Two-hundred mL of a 0.1 mg $L^{-1}$ Cr(VI) solution was added to 5 g PIC in 250-mL plastic bottles. The test setup was repeated in either an oxic environment (laboratory bench) or an anoxic environment (glove bag maintained at 2% $H_2$ via addition of 95% $N_2$/5% $H_2$ gas mixture; Coy Vinyl Anaerobic Chambers, Grass Lake, MI). Batch vessels were agitated on an orbital shaker (~100 rpm) for the duration of each test to facilitate equilibration and particle dispersal.

Each batch vessel was sampled at regular intervals: at 10 minutes, 30 minutes, and 1, 2, 4, 24, 48, 72, and 96 hours. Frequent samples were taken at first to attempt to observe the expected rapid initial removal, with less frequent sampling to monitor Cr re-release as the test went on. Three mL were removed and separated into two aliquots. One aliquot was immediately analyzed for Cr(VI). The other was preserved for analysis of total Cr by acidification to 2%

$HNO_3$. The amount removed from the solution was small in order to minimize the effects of destructive sampling. The pH of the sample or of the remaining suspension were also measured at the time of sampling; pH measurements extended past the initial 72 hours of reaction time, until 144 hours.

### 3.2.4 Analysis

The concentration of Cr(VI) in solution was determined by the 1,5-diphenylcabazide method as described in EPA Method 7196A. The concentration of total Cr in solution was determined by inductively coupled plasma-mass spectrometry (ICP-MS) on a NexIon 300 (Perkin Elmer, Inc.), in accordance with the quality assurance (QA) and quality control (QC) protocols of EPA method 6020A (USEPA, 2007).

## 3.3 Results

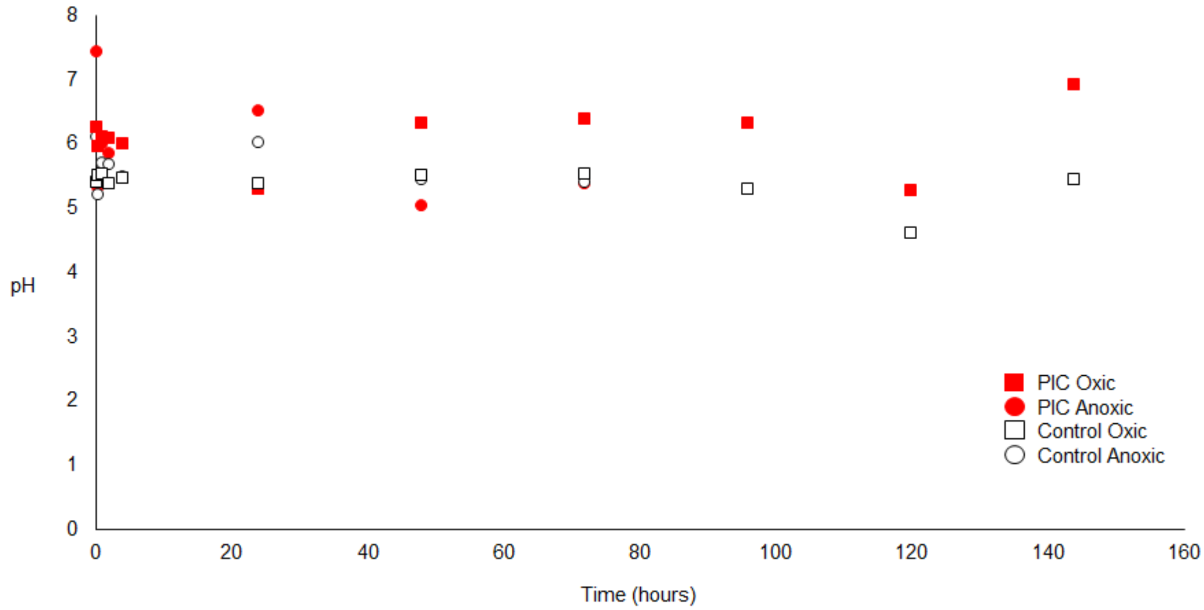


Figure 3.1. Mean measurements of pH over the course of the batch tests. Anoxic measurements cover only the first 72 hours of reaction time.

There was no clear effect on pH from the presence of PIC (Figure 3.1). While oxic PIC vessels tended to have higher pH than oxic control vessels, the opposite was true for anoxic vessels. There was some variability in pH, but no clear upwards or downwards trend, and the increases or decreases were observed concurrently in both PIC and control vessels.

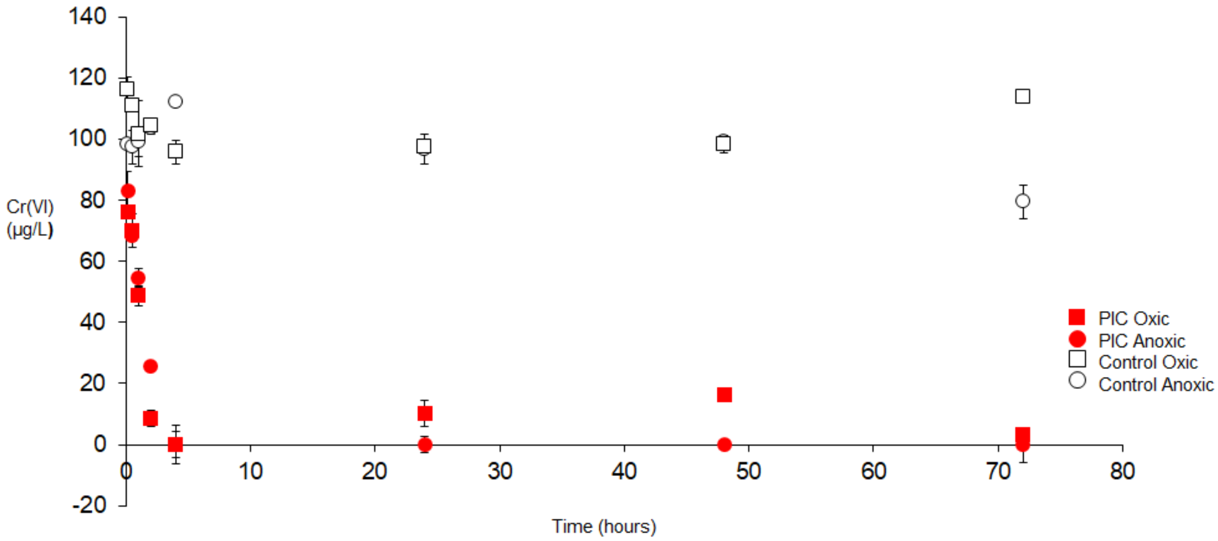


Figure 3.2. Mean measurements of Cr(VI). Error bars indicate standard error. $C_0$ = 100 μg/L.

Concentrations of Cr(VI) in batch solution decreased within the first four hours of reaction in the presence of PIC (Figure 3.2). In both oxic and anoxic batches, this decrease continued until below the minimum detection level of the instrument and was sustained for at least 72 hours. Control batches showed more variability in measurement, but interpreted concentrations remained above 80 μg $L^{-1}$, with no steady decrease as observed in PIC batch tests. There was little observable difference in the rate of Cr(VI) concentration decrease between test environments.

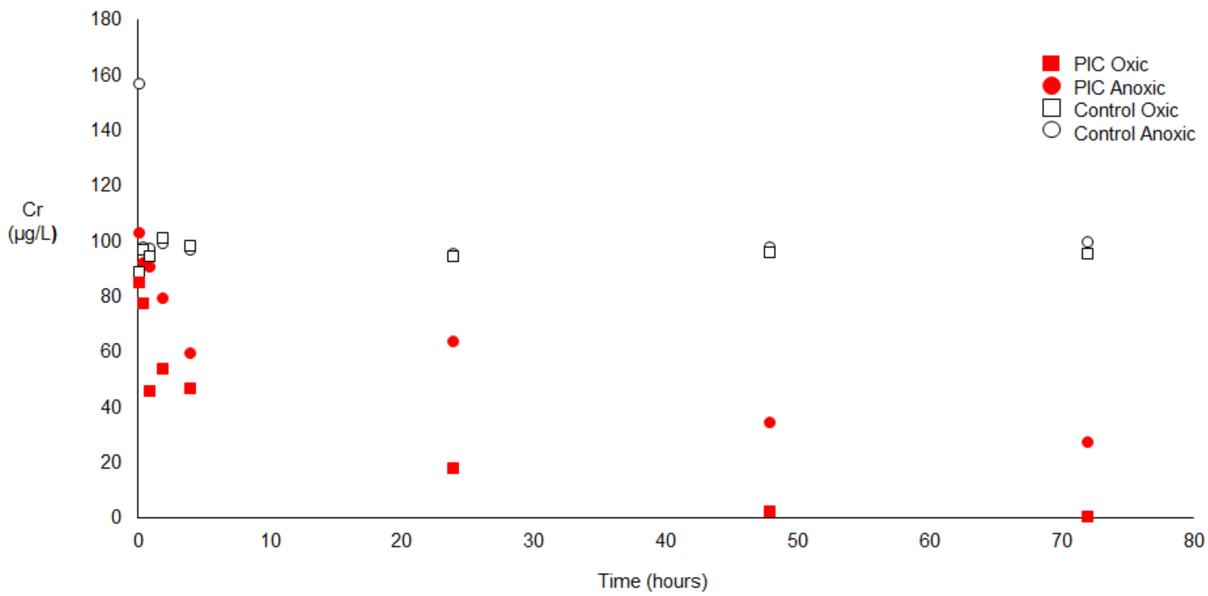


Figure 3.3. Measurements of total Cr concentration in solution. $C_0$ = 100 µg/L.

ICP-MS measurements of total Cr indicate a sustained decrease in Cr solution concentration in the presence of PIC over 72 hours (Figure 3.3). There is an observable difference in the amount of Cr measured in oxic and anoxic batches at sample times. At 24 hours, Cr concentration measured <18 mg $L^{-1}$ in oxic batch, while it was <64 mg $L^{-1}$ in anoxic batch. The oxic PIC batch reached below instrument minimum detection level (MDL) by 72 hours; the anoxic PIC batch only recorded its minimum of < 26 mg $L^{-1}$ in the same time period.

### 3.4 Discussion

PIC showed rapid initial removal of Cr in both oxic and anoxic environments (Figures 3.2 and 3.3). This removal proceeded at a similar rate in both oxic and anoxic batches. Yoon et al. (2011) found that removal was more rapid in oxic batches, but in this experiment, initial removal was comparably rapid in both test environments. (These experiments were not conducted with the goal of determining the reaction kinetics, limiting their applicability to determining specific rate coefficients.) Furthermore, no re-release of Cr was recorded over the 72-hour duration of the batch test. Continuing the batch experiments to record re-release of Cr over a longer period of time would further bolster this data set.

The pH of the batch vessels was not controlled during the experiment. No specific effect of pH was able to be assessed, except that a circumneutral pH did not appear to inhibit Cr removal by PIC under these experimental conditions. Yoon et al. (2011) found that the kinetics of Cr removal reached highest efficiency at pH 5, with less efficient removal at pH 4 or 6. Gheju et al. (2008) observed that ZVI reduction capacity was highest at pH 2.5, but a lower pH (i.e., 2) caused excess corrosion, decreasing removal efficiency. These findings suggest that PIC might remove Cr even more effectively under lower pH conditions.

Contaminated system often show an increase in solution pH over time due to the consumption of protons and production of hydroxide observed in the oxidation of ZVI (Riba et al., 2008; O'Carroll et al., 2013; Fu et al., 2014). Previous experiments indicated that PIC immobilization of contaminants also caused an increase in solution pH (Seaman 2015; see also Chapter 2). Although the pH of the oxic batch tended to be slightly more basic than the anoxic batch, the similar pattern of pH variation across batches suggests that PIC immobilization of Cr was not responsible for the variation.

While there is a possibility that sorption, rather than reduction, may have been a more important removal mechanism in these experiments, Cr(VI) is primarily removed via reduction to Cr(III), followed by precipitation/adsorption on the surface of ZVI particles. As $Cr_T$ concentrations were comparable to Cr(VI) concentrations at each data point, it seems as though little or no Cr(III) was present in solution. This indicates that Cr(III) was completely precipitated on the surface of the PIC particle. A more plausible explanation is that the concentration of Cr was simply so low that the consumption of protons in its reduction did not significantly affect solution pH.

The full precipitation of Cr phases makes use of the created Fe oxides (Wilkin et al., 2005):

$$Cr^{6+}_{(aq)} + \; 3Fe^{2+}_{(aq)} \rightarrow Cr^{3+}_{(aq)} + 3Fe^{3+}_{(aq)} \qquad \text{(Eq. 5)}$$

$$xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \leftrightarrow (Cr_xFe_{1-x})(OH)_{3(s)} + 3H^+ \qquad \text{(Eq. 6)}$$

$$xCr^{3+} + (1-x)Fe^{3+} + 2H_2O \leftrightarrow Cr_xFe_{1-x}OOH_{(s)} + 3H^+ \qquad \text{(Eq. 7)}$$

The (oxy)hydroxide precipitates noted in equations 6 and 7 would be expected on the surface of the PIC particles. Yoon et al. (2010) found that primarily chromite precipitated under oxic conditions, while nanoscale Cr(III)/Fe(III) clusters formed under anoxic conditions. Although the amount of Fe in solution was measured, no surface analysis of the particles was conducted in this study. An analysis of the particle surface by X-ray diffraction would be helpful for confirming the nature of the precipitates, the removal mechanism, and the likelihood of Cr re-release under the experimental conditions.

Measurements of oxidation-reduction potential were not taken throughout the batch testing period, due to previous experiments confirming the difference in test environments (see Chapter 2). In this experiment, an oxic environment appeared to facilitate increased Cr removal capacity compared to an anoxic environment. The oxic batch reaching minimum detection levels of Cr by 72 hours, while the anoxic batch solution still contained >20 mg $L^{-1}$ Cr. Previous experiments have indicated PIC's effectiveness removing other contaminants is neither significantly inhibited nor significantly enhanced by an oxic environment (Seaman 2015; see also Chapter 2). Schlautman and Han (2001) found that DO had a minimal impact on Cr(VI) reduction by Fe. A positive effect of $O_2$ was observed by Yoon et al. (2011), who found initial Cr(VI) removal by ZVI proceeded more quickly under oxic conditions than under anoxic conditions. Increased removal may be due to the DO-mediated formation of Fe oxides that further reduce Cr(VI) (as noted in equations 3 and 4), and/or the encouraged formation of Fe(III)-Cr(III) precipitates on the PIC surface (Gheju et al., 2008; Yoon et al., 2011). Again, an assessment of the PIC surface would likely prove illuminating to these uncertainties.

# CHAPTER 4

## Summary and Conclusions

### 4.1 Summary of Findings

Groundwater is a global source of drinking water, but this source is threatened by the contamination of several elements common both in nature and in industry. Contaminants like uranium (U), arsenic (As), nitrate ($NO_3^-$), and chromium (Cr) pose serious human health risks, especially due to the chronic exposure threat posed by their presence in drinking water (Taylor and Taylor, 1997; Kotaś and Stasicka, 2000; Kay et al., 2004; Kapaj et al., 2006). These contaminants are redox-sensitive, meaning that changing their oxidation state changes their mobility and toxicity. Uranium and Cr become relatively immobile and non-toxic once reduced (Ajouyed et al., 2010; Crane and Scott, 2014).

While there exist many effective groundwater remediation technologies, the conventional reliance on “pumping and treat” is generally expensive, inefficient, and require extensive, ongoing maintenance (Mackay and Cherry, 1989; Cantrell, Kaplan, and Wietsma, 1995; Blowes et al., 2000). More recently, *in situ* remediation methods such as the permeable reactive barrier (PRB) provide more cost-effective and versatile groundwater treatment options (Puls, Paul, and Powell, 1999; Blowes et al., 2000; Hashim et al., 2011). A PRB filled with a reactive media and installed in the path of groundwater flow immobilizes contaminants via reduction, adsorption, precipitation, or some combination of mechanisms, depending on the choice of media (Zolla et al., 2007; Obiri-Nyarko, Grajales-Mesa, and Malina, 2014).

Zero valent iron (ZVI) is one media that has received extensive attention over the last two decades for its ability to remove a wide variety of contaminants from groundwater (Cantrell et al., 1995; Mak, Rao, and Lo, 2009; Yan et al., 2010; Yoon et al., 2011; Lenell and Arai, 2016;

Zhang et al., 2017). Its effectiveness is primarily attributable to its ability to readily donate electrons to the contaminant and reduce them, thus decreasing their mobility and toxicity. However, several limitations of ZVI technology have been observed. Contaminant removal is highly dependent upon pH, the presence of dissolved oxygen (DO), and the presence of other ions in solution, such as carbonate ($CO_3^{2-}$) and bicarbonate ($HCO_3^-$). Typically, contaminant removal is much greater and more efficient at acidic pH (Gheju et al., 2008; Jurgens et al., 2010; Yoon et al., 2011; Guo et al., 2015) and in anoxic environments (Crane and Scott, 2014; Li et al., 2015). The presence of complexing ligands also impairs contaminant removal (Langmuir 1978; Ragnarsdottir and Charlet, 2000; Stewart et al., 2010; Yan et al., 2010; Crane et al., 2015b; Banning et al., 2017). Because aquifer conditions often include one or more of these challenging conditions, enhancements to ZVI effectiveness are desirable.

This study assessed the capability of a novel porous iron composite material (PIC) developed by Höganäs North America LLC (Hu 2011) to remove a number of groundwater contaminants, with primary focus on U, As, $NO_3^-$, and Cr. To achieve this objective, several laboratory batch tests were carried out. The batch tests were carried out at a circumneutral pH, and were repeated in oxic and anoxic environments to assess the impact of DO.

The batch experiments using a complex surrogate groundwater solution (Chapter 2) showed near-complete removal of U, As, $NO_3^-$, and rhenium. All contaminants were present at concentrations well above their Drinking Water Standards (DWS), but PIC proved very effective despite this heavy contaminant load. The presence of 200 mg $L^{-1}$ alkalinity (as $CaCO_3$), known to impede U sorption in particular, did not appear to impede removal. Removal was also not impeded by the presence of DO, with similar removal observed in both test environments. This suggests that the PIC may be effective at removing environmentally relevant concentrations of these contaminants as well, even in conditions that typically hinder the effectiveness of typical ZVI materials.

The batch experiments focused on Cr removal (Chapter 3) showed effective removal of both hexavalent Cr and total Cr from solution. Typically, the removal of Cr is dependent upon the reduction of hexavalent Cr to trivalent Cr, and an increase in solution in pH is expected due to the consumption of protons as a factor in this reduction (Riba et al., 2008). However, no such increase was observed in this study. Many conventional Cr removal technologies perform worse at environmentally relevant concentrations of Cr (Barrera-Díaz et al., 2012; Dhal et al., 2013), but the PIC effectively removed Cr at a concentration equal to that of the Drinking Water Standard. This removal occurred in both oxic and anoxic environments, with only slightly better performance in an oxic environment, as has been previously observed in Cr ZVI studies (Schlautman and Han, 2001; Yoon et al., 2011).

## 4.2 Recommendations for Future Research

This study demonstrated the ability of PIC to remove multiple contaminants in conditions considered unfavorable for typical ZVI application. However, several questions remain about the specific chemistry of its removal and its suitability as a PRB media. While some preliminary flow-through column experiments have been conducted for U and using the complex surrogate groundwater solution (Seaman 2015), the same needs to be done to evaluate the removal of Cr. This will assess its practical use in a PRB. The relative importance of reduction, sorption, and/or precipitation for PIC is also uncertain at this point. Primary removal mechanisms differ between contaminants and ZVI materials (Li and Zhang, 2007; O'Carroll et al., 2013; Zhang et al., 2017). Analysis of the spent PIC by X-ray diffraction is needed to characterize the particle surface and precipitates. This will aid in understanding the precise mechanisms of removal, and may also illuminate questions of longevity and contaminant re-release in long-term scenarios.

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