Assessing arsenic removal by zero valent iron under various water quality and precoat filtration conditions

Paul T. Pepler

*University of New Hampshire, Durham*

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ASSESSING ARSENIC REMOVAL BY ZERO VALENT IRON UNDER VARIOUS WATER QUALITY AND PRECOAT FILTRATION CONDITIONS

BY

PAUL T. PEPLER
B.S. in Environmental Science: Ecosystems,
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THESIS

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Thesis Director
Dr. M. Robin Collins
Professor of Civil Engineering

Dr. Kevin H. Gardner
Associate Professor of Civil Engineering

Dr. Jenna Jambeck
Assistant Professor of Environmental Engineering

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Date
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ABSTRACT

ASSESSING ARSENIC REMOVAL BY ZERO-VALENT IRON UNDER VARIOUS WATER QUALITY AND PRECOAT FILTRATION CONDITIONS

By

Paul T. Pepler
University of New Hampshire, September, 2009

Arsenic contamination in drinking water is a world wide public health concern. Previous studies with zero valent iron (ZVI) have indicated its effectiveness in the removal of arsenic from contaminated waters. This study examined a range of water quality conditions to determine the optimal conditions for As removal while minimizing iron dissolution. This information was used to assess the modification of precoat filtration with ZVI for arsenic removal.

ORP exerts a significant influence on arsenic removal with the greatest removals (>99%) occurring at high ORPs and the smallest removals occurring at low ORPs. ZVI amended precoat filtration studies displayed the greatest arsenic removals (58%-71%) with a 22 minute contact time in the presence of chlorine (Cl₂). ZVI amended precoat filtration is an effective arsenic removal strategy. Values of pH must be chosen to minimize iron dissolution keeping effluent iron concentrations below the USEPA secondary standard of 0.03mg/L.
CHAPTER 1

INTRODUCTION

1.1 Background

Arsenic is listed as a class A human carcinogen in the United States of America and is regulated in drinking water at 0.010mg/L. This maximum contaminant level (MCL) was revised from an MCL of 0.050mg/L in January 2001 and became effective in February 2002. Public water systems had to be in compliance by January 2006 (USEPA, 2000). All community water systems and non-transient, non community water systems must comply with this regulation regardless of size (USEPA, 2003). There are currently 54,000 community water systems in the USA.

Small systems are subject to greater costs per gallon related to economies of scale—it costs less per gallon to treat large quantities. The expected increase for small systems (serving fewer than 10,000 people) is between $38 and $327 per household per year, as opposed a range of $0.86 to $32 per household per year for larger systems (USEPA, 2001). According to the USEPA, best available technologies for the removal of arsenic include ion exchange, activated alumina, oxidation/filtration, reverse osmosis, electrodialysis reversal, enhanced coagulation/filtration, and enhanced lime softening (USEPA, 2003). The reduction of the MCL prompted interest in alternative treatment technologies because of the cost associated with the removal of arsenic.

In October 2001, EPA announced an initiative for additional research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the new arsenic standard (USEPA, 2006). Of the available
alternatives for the removal of arsenic, adsorption technologies are receiving the most attention because they are effective in removing arsenic, easy to implement, generate low residuals, and have relatively low operation and maintenance costs (Chowdhury, et. al., 2002). In 2004, Emese Hadnagy investigated arsenic removal by several adsorbents at the University of New Hampshire. She concluded that zero valent iron (ZVI) was the most promising adsorbent because it exhibited very high arsenic removals and the highest adsorption densities of all adsorbents investigated.

Some limitations to the use of ZVI include the potential to leach dissolved iron from the system and the influence exerted by pH and oxidation reduction potential (ORP) on the removal process. If these obstacles are overcome, ZVI could be an extremely attractive arsenic removal technique.

Hadnagy (2004) also found diatomaceous earth coated with hematite (DECH), a composite adsorbent material, to be a good adsorbent for arsenic, although she did not study this extensively. Since DECH is manufactured through nanotechnology methods, the potential for a high cost related to a proprietary product could be prohibitive. A solution could include dosing ZVI into the source water, where it will be in contact with the arsenic to be removed. The arsenic will bind to the iron and be removed by the diatomaceous earth filter. This would be a low cost solution as both DE and ZVI are inexpensive.

1.2 Objectives

This research investigated the removal of arsenic from drinking water by adsorption on zero valent iron. The main objectives included:

• Assess arsenic removal by zero valent iron under various water quality
conditions to determine optimum conditions for arsenic adsorption and the minimization of iron dissolution.

- Develop a ZVI amended precoat filtration strategy for the removal of arsenic from drinking water while minimizing iron dissolution.

1.3 Research Overview

Experimentation was conducted to meet the above stated objectives on both bench and pilot scale. A bench study was conducted to assess optimal conditions for arsenic removal and the minimization of iron dissolution by ZVI. A full factorial experimental design, consisting of 24 separate batch studies, was used for the bench scale experimentation to determine the influence of pH, ORP, and $SO_4$ on arsenic removal and iron dissolution. X-ray diffraction was used to examine crystalline solids following each run and compared to Geochemist's Workbench chemical modeling software to determine dominant compounds present.

The results from the bench scale experimentation were used to design a pilot scale precoat filtration strategy to remove arsenic from a source water using ZVI. Again, a factorial experimental design was used. The variables investigated included choice of oxidant and contact time. The oxidants used were oxygen and chlorine. The contact time was 2 minutes and 22 minutes. The effect these variables exerted on arsenic removals was investigated as was the effect exerted on the dissolution of iron and the subsequent leaching from the system.
CHAPTER 2

LITERATURE REVIEW

2.1 Arsenic Occurrence and Chemistry

Arsenic contamination in ground water is a world wide public health concern. Well-known high-As groundwater areas have been found in Argentina, Chile, Mexico, China, Hungary, and more recently in West Bengal (India) Bangladesh and Vietnam (Smedley, 2002b). In the United States of America, as of 2002, USGS estimates that 1 percent of the 54,000 U.S. public water supplies currently exceed 50μg/L; 3 percent exceed 20μg/L; 8 percent exceed 10μg/L; and 14 percent exceed 5μg/L arsenic (O’Connor, 2002). Arsenic is naturally occurring in relatively high concentrations in the Northeastern, Midwestern, Western, and Southwestern United States (USEPA, 2003).

Arsenic contamination in groundwater can be naturally occurring as well as anthropogenically induced. Arsenic is a natural constituent in the earth’s crust and is the 20th most abundant element (Singh, 2006). Most environmental arsenic problems are the result of mobilization under natural conditions (Smedley, 2002b) caused by the weathering and dissolution of arsenic bearing rocks, minerals, and ores (USEPA, 2003). Concentrations of naturally occurring arsenic in ground water vary regionally due to a combination of climate and geology (Welch et al. 2000). In fact, a characteristic feature of high groundwater arsenic areas is the large degree of spatial variability in arsenic concentrations in the ground waters (Smedley, 2002b). Anthropogenic sources of arsenic include mining, industry, and chemical waste disposal (Chakravarty, 2002), arsenical pesticides, crop desiccants, and livestock feed additive (Smedley, 2002b).
Under natural conditions, arsenic primarily exists in two valence states, As\(^{+3}\) (arsenite) and As\(^{+5}\) (arsenate). The main difference between the two valence states is the presence of a double bond oxygen in the molecular structure of As(V) (Bang et al., 2002). High concentrations of arsenic are often associated with sulfide minerals and metal oxides (Singh, 2006). Arsenic release from iron oxide appears to be the most common cause of widespread arsenic concentrations exceeding 100μg/L in groundwater (Welch, 2000). The master variables influencing arsenic speciation are pH and Eh, the negative log of the hydrogen ion concentration and electrochemical potential energy of electrons respectively (Figure 2.1).

Two conditions exist which can trigger large scale release of arsenic into groundwater: the development of high pH (>8.5), or the development of strongly

![Figure 2.1: Arsenic Speciation in Water](image-url)
reducing conditions at near neutral pH (Smedley, 2002b). The release of arsenic at high pH may be related to the development of a net negative surface charge on the oxide particle at pH values above the point of zero charge (PZC), which occurs between 7.8 and 8.5 (Benjamin, 2002). With the development of a net negative surface charge on the oxide surface, arsenic would tend to be less strongly bound as arsenate (AsV) has a negative charge and arsenite (AsIII) has zero surface charge. The release of arsenic related to the development of reducing conditions may be the result of the dissolution of iron, or the reduction of arsenate to arsenite, which is less strongly bound.

2.2 Principles of Adsorption

Adsorption is a mass transfer process in which substances dissolved in the aqueous phase accumulate on the solid phase and are subsequently removed from the liquid (Montgomery Watson Harza, 2005). One major advantage of using adsorption technologies for arsenic removal is the lower operation and maintenance cost compared to other technologies (USEPA, 2002). Solids capable of sorption include metal oxides, activated carbon, and ion exchange resins (Benjamin, 2002). The forces responsible for adsorption include: Vander Waals, dipole-dipole, and other weak physical intermolecular forces; electrostatic attraction to oppositely charged surfaces; and covalent bonding (Hemond, 2000). Dzombak and Morel (1990) note that sorption on oxides takes place at specific coordination sites.

Adsorption on metal oxides is strongly dependant on pH, ionic strength, and the presence of competing ions (Dzombak and Morel, 1990). The influence pH exerts relates to the surface charge of metal oxide. The metal ions at the surface of the oxide can bind
with hydroxide to form FeOH. This group can become protonated or deprotonated as in the following equations (Benjamin, 2002).

\[ \equiv \text{FeOH}_2^+ \leftrightarrow \equiv \text{FeOH} + \text{H}^+ \quad (2.1) \]

\[ \equiv \text{FeOH} \leftrightarrow \equiv \text{FeO}^- + \text{H}^+ \]  (2.2)

According to Le Chatelier's Principle, as the pH decreases, the system will shift to the right to maintain equilibrium, and will favor the positively charged FeOH$_2^+$. As pH increases, the negatively charged FeO$^-$ will dominate. This may help explain the trend of increasing arsenic removals with decreasing pH. The iron oxide surfaces exhibit a net positive charge at lower pH values and adsorption of anionic As(V) is enhanced by Coulombic attractions (Su et al., 2001a). Ionic strength has a tendency to influence the electrical double layer. As ionic strength increases, the double layer decreases and the repulsive forces are overcome and particles aggregate (Mercer et al., 2008). This is the objective of coagulation in water treatment. Adsorption occurs at specific sites on the surface of the oxide. Phosphate, silicate, and molybdate compete strongly with arsenic for sorption sites (Su et al., 2001b).

### 2.3 Removal Mechanisms

#### 2.3.1 Surface Complexation

The mechanism of arsenic removal by ZVI is dependant on water quality conditions, specifically pH and oxidation reduction potential (ORP). Changes in these conditions lead to changes in iron surface chemistry as well as arsenic speciation. Su et al., (2001a) observed that sorption on the ZVI surface and precipitation appear to be the primary removal mechanisms for both arsenite and arsenate. Generally, under relatively
anaerobic conditions, acidic conditions are favorable to arsenate removal and alkaline conditions are favorable to arsenite removal (Sun et al., 2006).

It appears that arsenite is not reduced to As(0) by electrochemical coupling with iron corrosion in the short term (Manning et. al., 2002), but long term reduction of arsenite on Fe⁰ has been observed (Su et al., 2001b). XPS spectra showed that arsenite was reduced to As(0) within 5 days under reducing conditions, where as under oxidizing conditions adsorption on ferric hydroxides was responsible for removals (Bang, 2005b, Sun et al., 2006).

Much has been written about the adsorption mechanism. It is agreed that arsenic removal occurs as a result of adsorption on oxides formed as the result of iron corrosion (Manning et. al., 2002; Lackovic et. al., 2000; Farrell et. al., 2001; Su et. al., 2001b). Arsenic is removed by the formation of covalent, inner-sphere arsenate complexes on the oxides formed through the corrosion of ZVI (Manning et. al., 2002. and references therein). Light scattering confirmed inner-sphere surface complexation of As(III) with NZVI (Kanel et al, 2005). Bang et. al. (2005a) report arsenic removals are directly proportional to the amount of iron oxides formed at different pH values: both removals and oxides generated increased with decreasing pH. Continued corrosion and the subsequent formation of iron oxides is necessary for continued As removal (Yu et. al. 2006). Further, freshly formed oxides have a greater adsorption capacity than aged oxides (Farrell et. al., 2001).

A third mechanism occurs under conditions conducive to sulfate reduction to sulfides—usually attributed to microbial activity. Sulfate was reduced and precipitated in
columns during an eight month study and arsenic removals were related to sulfur precipitation (Nikolaidis et al., 2003).

The highest observed capacity in a column treating ground water was 4.4mg/g (Nikolaidis et al., 2003). A maximum adsorption capacity of 3.5mg As(III)/kg nanoscale zero valent iron (NZVI) was calculated by Freundlich isotherm (Kanel et al, 2005).

Post-treatment dissolution experiments produced very small amounts of dissolved arsenic species (Lackovic et al., 2000). Longer retention times resulted in smaller amount of desorbable arsenic by phosphate extraction (Su et al., 2001a). TCLP analysis of spent media indicated the arsenic concentration in the leachate was two orders of magnitude lower than the regulated 5mg/L for TCPL results (Nikolaidis et al., 2003).

2.3.2 Influence of pH and Eh

The pH dependence of arsenic adsorption to iron oxides can be explained by both rates of iron corrosion and subsequent formation of corrosion products as well as by the protonation of both adsorbent and adsorbate as explained above. Iron corrosion increases with decreasing pH as explained by the common ion effect or La Chatelier’s Principle. As pH decreases, equations 2.3 and 2.4 are driven to the right to maintain equilibrium. In the presence of oxygen, water, and hydrogen ions, Fe⁰ is oxidized to produce ferrous ions (eq.2.3). Under similar conditions, these ions are further oxidized to ferric ions (eq.2.4). These ions then react with water to produce ferric oxides, on the surface of which arsenic sorption occurs. Equation 2.4 has an opposite response to decreasing pH than equation 2.3 and 2.4 suggesting there is a point on the pH scale where adsorption is optimized.

\[
2Fe⁰ + O_2 + 4H^+ = 2Fe^{2+} + 2H_2O 
\] (2.3)
\[ 4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ = 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (2.4) \]

\[ \text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3\text{H}^+ \quad (2.5) \]

Bang et. al. (2005b) saw the corrosive release of iron was much faster at pH 4 than at pH 7. This is supported by work performed by Katsoyiannis et. al. (2008) where arsenite oxidation by O\(_2\) occurred faster than arsenate sorption at pH 3, arsenite oxidation and arsenate sorption occurred in parallel at pH 5 and 7, but more slowly at pH 7, and at pH 9 arsenite oxidation again occurs faster than arsenate sorption. At low pH formation of ferric oxides is limiting and at high pH oxidation of Fe\(^0\) is limiting.

Arsenic species protonate and deprotonate in response to changing pH. The \(pK_a\) values for arsenite (AsIII) are 9.2, 14.22, 19.22, and the \(pK_a\) for arsenate (AsV) are 2.19, 6.94, 11.5 (Bang et al., 2002 and references therein). Adsorption of As (III) by ferric oxides is favored at neutral to alkaline pH, and is maximized at about pH 9 (Yu et. al. 2006, Su et al., 2001a), where as adsorption of arsenate decreases with increasing pH from 3-10 (Su et al., 2001a). Under aerobic conditions, low pH is favorable to the removal of arsenic compounds. Greater than 93% arsenite and 99% arsenate removals were achieved when batch studies were open to the atmosphere as opposed to 4% arsenite and 9% arsenate removal when purged with nitrogen (Bang et al., 2002). Removals of total arsenic occurred fastest at pH 6 with greater than 99% removal in two hours (Bang et al., 2002).

### 2.3.3 Iron Corrosion Products

Under anaerobic conditions Fe\(^0\) reacts with water according to the following reaction (Su et al., 2001a):

\[ \text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 4\text{H}^- \]
\[
\text{Fe}^0 + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \quad (2.5)
\]

In the presence of dissolved oxygen, \( \text{Fe}^0 \) reacts with water according to the following reaction (Su et al., 2001a):
\[
\text{Fe}^0 + 2\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{Fe}^{2+} + 4\text{OH}^- \quad (2.6)
\]

In the presence of dissolved oxygen ZVI corrodes to produce intermediaries, like \( \text{H}_2\text{O}_2 \), which are mainly responsible for the oxidation of asenite to arsenate (Katsoyiannis et. al, 2008). Arsenate does not participate in the oxidation of \( \text{Fe}^0 \): Water is the primary oxidant (Farrell, 2001). Manning et. al. (2002) presented evidence of arenite oxidation during iron corrosion in the presence of dissolved oxygen.

The corrosion of ZVI produces a heterogeneous mixture of the iron oxides lepidocrocite and either magnetite or maghemite (Manning et. al., 2002). Similarly, Kanal et al. (2005), saw nano ZVI corrode to produce magnetite/maghemite and lepidocrocite over 60 days. The passivated film which forms on the iron surface were composed of \( \text{Fe(OH)}_2 \) and \( \text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3 \) (Gui and Devine, 1994, 1995, as cited by Gu et.al, 1999). Using X-ray adsorption spectroscopy, Melitas et al., (2002b) showed the presence of elemental iron, magnetite, and mixed valent oxide phases in the reacted iron fillings. These were not passivating—iron corrosion was not inhibited. During an eight month study, columns filled with equal masses of sand and iron leached 73% of the iron (Nikolaidis et al., 2003).

Sulfide formation occurred after approximately 2 months in a column study. This was attributed to the development of a microbial population which was stimulated by excess \( \text{H}_2 \) generated by corrosion of ZVI enhanced by sulfate and bicarbonate (Gu et. al., 1999). Gu et. al. (1999) found mackinawite (\( \text{Fe}_8\text{S}_8 \)), lepidocrocite (\( \gamma-\text{FeOOH} \)), akaganeite
($\beta$-FeOOH), and magnetite/maghemite ($Fe_3O_4$) were the most abundant iron oxyhydroxide minerals identified by X-ray diffraction analysis.

When compared to a solution lacking As(V), iron corrosion was up to 5 times slower in the presence of 100$\mu$g/L As(V). Corrosion was not, however, slowed further by the increase in As(V) from 100$\mu$g/L to 20,000$\mu$g/L (Melitas et al., 2002b).

### 2.4 Rate of Arsenic Removal

#### 2.4.1 Kinetics

Arsenate removal rates are dependant on the continuous generation of iron oxide adsorption sites and limited by mass transfer via diffusion through iron corrosion products (Melitas et al., 2002b). Lackovic et al., (2000), report that the removal efficiency is related to surface area or type of iron used and improves with time. Farrell et al., (2001) showed kinetics of arsenic removal by corroding iron can be described by the following equation:

\[
dC/dt = -(k_0C)/(k_0/k_1+C) \quad (2.7)
\]

where C is arsenic concentration, t is time $k_0$ is the zero order rate constant, and $k_1$ is the first order rate constant. Melitas et al., (2002b) found the rate of arsenate removal varied from zero to first order kinetics with respect to As(V) concentration. This rate order was dependant on the availability of adsorption sites and As(V) concentration.

Arsenic removals can also be described by a pseudo first order kinetics model (equation 2.8) with k values of 0.494/hour and 0.266/hour for arsenate and arsenite respectively (Bang et al., 2002).

\[
-d[As]/dt = k_{obs}[As] \quad (2.8)
\]
Using a pseudo 1st order reaction rate, the half life of As V in the presence of ZVI at pH 6 was reported to be 2.14h and 3.96 for As III. The half life of As V increased to 8.72h when pH was increased to 7 (Bang et. al. 2005a). Pseudo first-order reaction kinetics was found to describe removals with correlation coefficients ($r^2$) between 0.82 and 0.96 (Su et al., 2001b,a).

Arsenite adsorption kinetics were about 1000 times faster when nanoscale ZVI was used as opposed to micron sized ZVI (Kanel et al, 2005). Aging the ZVI for two months in a bicarbonate solution significantly improved arsenate removals at pH 9 (Yu et. al. 2006).

2.4.2 Mass Transfer Efficiency

A strong correlation between Reynolds number and increasing arsenite removal suggest mass transfer plays an important role in As removal by ZVI, and it is suspected that diffusion within the oxides is the rate limiting step (Yu et. al. 2006). Using a mathematical model and data from column studies Nikolaidis et al., (2003) found that the mass transfer coefficient was a function of flow rate.

By increasing the dissolved oxygen concentration in the influent water, corrosion of iron and the generation of adsorption sites is accelerated. This however, may produce a thicker oxide layer causing greater mass transfer resistance for arsenic removal (Melitas et al., 2002b). Under Mixing conditions, iron corrosion is accelerated, oxide film formation at the Fe° surface is avoided or delayed, and the corrosion products’ nucleation and precipitation in the bulk solution is accelerated (Noubactep, 2008). Therefore a passivating layer does not form which would limit diffusion of As to the iron surface, iron corrosion, or the formation of iron oxides. This suggests that utilization of Fe° in
drinking water treatment should maximize mixing and avoid designs where iron is stationary, for example in sand columns.

2.4.3 Competition for Sorption Sites

The inner-sphere complex-forming phosphate, silicate, and molybdate compete strongly with arsenic for sorption sites, whereas sulfate and chloride do not (Su et al., 2001b). Under low ORP conditions, results from column studies showed a 25% reduction in removals in the presence of 50 mg/L sulfate. No sulfide was detected. This suggests a competitive effect of sulfate with arsenite (Lackovic et al., 2000). Borate and organic matter decrease the rate of arsenate removal at high concentrations and chloride, carbonate, nitrate, phosphate, manganese and sulfate enhanced removals (Biterna et al., 2007). Humic acid was seen to inhibit arsenic removal attributable to the high adsorption affinity of Fe$^{2+}$ and Fe$^{3+}$ (Liu et al., 2009).

Carbonate exerted a negative influence on arsenite removal only at high carbonate concentrations (Yu et al. 2006). Su et al. (2001b) found that the presence of bicarbonate at 1μm/L and 100μm/L noticeably decreased the pseudo first order rate constants for As(V) and As(III). Liu et al. (2009) saw the reverse trend where the presence of bicarbonate enhanced arsenic (V) removals. Differences in experimental conditions confound the results. Specifically, the pH of solution was not the same for the HCO$_3$ solution and the comparison (NaCl) in the experiments performed by Su et al. Iron corrosion is pH dependant and decreases with increasing pH. The experiments performed by Lui et al used the same initial pH 7. This provides a better comparison.

2.4.4 Design Criteria
Using a designed experiment, Nikolaidis et al., (2003) determined that volumetric loading should be used for designing arsenic removal systems, as opposed to surface loading. Also, the length to diameter ratio should be approximately 5 to avoid plugging (Nikolaidis et al., 2003). Detention time in a water column can be as low as 10 minutes (Nikolaidis et al., 2003). Bang et. al. (2005a) found that an iron column followed by a sand filter can be used to remove arsenic and iron from water at near neutral pH, in the presence of 6mg/L DO and an empty bed contact time of 1 minute (iron column). A column with a hydraulic detention time of two hours can be used to remove >98% of arsenic (Sun et al., 2006). When four different ZVI fillings were compared, surface area was not the primary factor controlling the interaction of ZVI and arsenic, as the product with the least surface area had the greatest removals (Su et al., 2001a).

2.5 Precoat Filtration

Precoat filtration was developed by the United States Army during World War II, to remove a protozoan parasite, *Entamoeba histolytica*, from drinking water in the Pacific war zone (AWWA, 1995). Some advantages of precoat filtration include a smaller footprint requirement than other filtration options, no chemical requirements, a lower volume of treated water is required for cleaning, and the solids are easily dewatered (AWWA, 1995). Some disadvantages include the inability to see the filter in operation and its use is limited to water of good quality with no color because there is no chemical interaction of dissolved substances with the filter (Spencer, 1991).

Precoat filtration removes particles at the surface of a pre-deposited media, usually diatomaceous earth (DE), with straining as the primary removal mechanism (MHW, 2005). Prior to the filtration run, a media is deposited on the septa, designed to
support the media, by recirculating water from a slurry tank through the septa until all media is deposited and the water runs clear. The media should cover the entire surface of the septa with a coating approximately 1/16 – 1/8 in. thick. This usually requires 0.15-0.20 lb/ft$^2$ (AWWA, 1995).

When the precoat application is complete, the influent is changed from the precoat recycle tank to the source water. During the filtration run, a body feed of media is dosed to the influent stream at a rate of 1mg/L for every mg/L of discrete particles and up to 10 mg/L for every mg/L of amorphous solids (AWWA, 1995). The purpose of the body feed is to maintain filter cake porosity and prolong filtration run time. The run is terminated when terminal head loss is reached—usually 29-44 lb/in$^2$ in pressurized systems (MHW, 2005).

When terminal head loss is reached and the run is complete, the media is removed from the septum by draining the filter element and opening a valve which directs high-pressure water at the septum. The media, filtered material, and water exit through a drainage port located at the base of the filtration unit.
CHAPTER 3

METHODS AND MATERIALS

This research took place in two stages: Bench and pilot scale. The bench scale experimentation was conducted to assess the optimal water quality conditions for arsenic removal by zero valent iron (ZVI) while minimizing the dissolution of iron from ZVI. The pilot scale experimentation was conducted to develop a ZVI amended precoat filtration strategy for the removal of arsenic from drinking water while minimizing iron dissolution. The bench scale experimental design and setup is presented first followed by the pilot scale experimental design and set up.

3.1 Bench Studies: Assessing Arsenic Removal by ZVI under Varying Water Conditions

A bench study was conducted to assess the optimal pH and oxidation-reduction potential (ORP) conditions for the removal of arsenic by ZVI, the minimization of iron dissolution from ZVI, and the influence exerted on these by the presence of sulfate. The subsequent sections describe the experimental design and set up used in this phase of the study.

3.1.1 Experimental Design

The experimental design for the bench study was a $4^1 \times 3^1 \times 2^1$ full factorial design without replication (Table 3.1). With the use of a factorial design, influences of main factors and their interactions can be statistically analyzed. Settings for pH ranged from 5 to 8 in one unit increments. Settings for ORP were high, medium, and low (NaOCl as Cl$_2$ addition, O$_2$ bubbled, N$_2$ bubbled). Settings for sulfate were high and low (250mg/L, 0
Table 3.1 Batch Study Experimental Design

<table>
<thead>
<tr>
<th>Trial</th>
<th>pH</th>
<th>mv</th>
<th>SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>O₂</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>O₂</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Cl₂</td>
<td>+</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>Cl₂</td>
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<tr>
<td>7</td>
<td>6</td>
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<tr>
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<td>6</td>
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<tr>
<td>11</td>
<td>6</td>
<td>Cl₂</td>
<td>+</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>Cl₂</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>7</td>
<td>N₂</td>
<td>+</td>
</tr>
<tr>
<td>14</td>
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<td>N₂</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>7</td>
<td>O₂</td>
<td>+</td>
</tr>
<tr>
<td>16</td>
<td>7</td>
<td>O₂</td>
<td>-</td>
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<td>17</td>
<td>7</td>
<td>Cl₂</td>
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<td>O₂</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>8</td>
<td>Cl₂</td>
<td>+</td>
</tr>
<tr>
<td>24</td>
<td>8</td>
<td>Cl₂</td>
<td>-</td>
</tr>
</tbody>
</table>

mg/L). The response variable was arsenic percent removal.

3.1.3 Experimental Set Up

The bench experiments were performed in a climate controlled room with a constant temperature of 20°C (Figure 3.1). Each trial was performed in a one-liter continuously stirred reaction vessel. Oxidation-reduction potential (ORP), pH, and sulfate concentrations were varied, according to the experimental design, in order to determine optimal arsenic removal conditions using ZVI and the minimization of iron dissolution.

During the experiments the pH was maintained at a constant value using a pH controller.
stat—the Consort R305. Hydrochloric acid (0.05N) and sodium hydroxide (0.05N) were used to titrate. During the experiment the redox condition was maintained by bubbling oxygen or nitrogen through a fritted glass coarse diffuser or adding chlorine (sodium hypochlorite). The Consort was used as a data logger for pH and ORP and recorded values every minute for the duration of the experiment.

In order to maintain a consistent ORP value in the batch reactor, a stabilization period is required. A former French exchange student at UNH, Mathilde Le Roux, determined that over night bubbling (15 hrs) with O₂ or N₂ was sufficient to stabilize redox conditions (Le Roux, 2005). In order to reach higher ORP values and expand the range previously investigated, chlorine (Cl₂) was chosen as an appropriate oxidant. Experiments to determine adequate dosing of Cl₂ were performed by varying Cl₂
concentrations while maintaining similar ionic strengths by adjusting the sodium chloride (NaCl) concentration. It was determined that 1.4mL of 5% NaOCL is adequate because ORP conditions stabilized and remained stable for approximately 12 hours (Figure 3.2). This produced an initial concentration of 95.25 mg/L as Cl₂. Two hours will provide adequate stabilization time and will allow time for the experiment’s completion prior to a substantial drop in ORP in conditions.

Each treatment began with a redox stabilization period after the addition of 700mL reverse osmosis (RO) water, 140 mg 40-mesh ZVI, 205 mg NaCl, and 258.9 mg Na₂SO₄ (for sulfate runs) to an one-liter Teflon reaction vessel. Concentrations were chosen to be consistent with past work at UNH.

After stabilization, 1.4mL (1000mg/L) arsenic (V) was added to achieve an initial As concentration of 2 mg/L. Two samples were taken immediately to determine As concentrations one minute after addition. Five hours after As addition, samples were taken and analyzed for dissolved As, As III, dissolved iron, ferrous iron, sulfate and sulfide where appropriate. Kinetics studies performed by Mathilde Le Roux showed that steady state conditions, with respect to arsenic removals, were reached after approximately 1.5 hours for all pH values 5-8. Samples were taken after five hours to be conservative.

Filtered solids were freeze dried immediately following each run. If N₂ was bubbled during the run, the filtration was performed in a glove box purged with N₂. After drying, the solids were analyzed by X-ray diffraction to determine crystalline compounds present and the primary compounds responsible for arsenic removal. These compounds
were compared to output from Geochemist’s Workbench (GWB), an equilibrium modeling software.

3.2 Pilot Studies: Modifying Precoat Filtration with ZVI for Arsenic Removal

Using data from the bench studies, a pilot scale diatomaceous earth (DE) filtration study was designed to assess the removal of arsenic from contaminated source water by ZVI addition. The next two sections discuss the experimental design and set up used for the pilot studies.

3.2.1 Experimental Design

The ZVI amended DE filtration study was designed as a $2^2$ full factorial without replication (Table 3.2). Settings for oxidant were high and low, Cl$_2$ or O$_2$, respectively. The settings for contact time were high and low, 22 minutes and 2 minutes, respectively. Oxidant choice is of interest for two reasons. First, Cl$_2$ is a much stronger oxidant
Table 3.2 Pilot Study Experimental Design

<table>
<thead>
<tr>
<th>Trial</th>
<th>Oxidant</th>
<th>Contact Time, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl₂</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>O₂</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>Cl₂</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>O₂</td>
<td>2</td>
</tr>
</tbody>
</table>

that O₂ and may affect the generation rate of sorption sites related to the faster kinetics of iron corrosion. Second, at lower pH values the kinetics of ferrous iron oxidation decrease exponentially—Cl₂ addition may be necessary to prevent the leaching of dissolved iron from the system. In this case it is desirable to achieve a chlorine residual of 0.5-2mg/L which is a common range for distribution systems in the United States.

Contact time is of interest because sorption reactions do not occur instantaneously. Generally, removals increase as the reaction progresses toward equilibrium. The low setting represents the time required for water to move through the DE filter system from the point of ZVI dosing to the filter. All mixing occurred in the lines and in the filter apparatus. The higher setting was determined using a kinetics study performed by Emese Hadnagy (Figure 3.3a), as part of her Master’s Thesis (Hadnagy, 2004). It was desirable to increase the detention time by an amount not to exceed the exponential part of the curve. This will produce large increases in arsenic removal for small increases in contact time. Twenty minutes additional contact produces this desired result.

Chlorine dose was determined with a chlorine demand study using a contact time equal to the time the chlorine is in contact with the ZVI during the iron filtration run. The response variable was percent arsenic removed. The iron concentration was based on work performed by Hadnagy where she developed an adsorption isotherm for arsenic and
Figure 3.3: Kinetic study (a) % removal, (b) aqueous arsenic concentration, and (c) arsenic adsorption density (ionic strength=0.01M, alkalinity=60mg/L CaCO$_3$/L; pH=6; t=3hrs; T=22-23 C; initial arsenic concentration=0.4-1.0mg/L; GFA and goethite=111mg/L; AA=167mg/L; and ZVI=56mg/L).

Source: Hadnagay, 2004
ZVI. For short contact times, the arsenic adsorption density was approximately 5mg/g (Figure 3.3c). The corresponding concentration of iron required to remove an arsenic concentration of 2mg/L is 200mg/L.

3.2.2 Experimental Set Up

The objective of the pilot scale was to utilize the data obtained from the bench scale study to develop a DE filtration strategy to remove ZVI which had been dosed to the source water to remove arsenic. This was accomplished using a Manville one square foot vertical leaf precoat filter (Figure 3.4). The filter apparatus is a pressurized DE system complete with pumps, tubing, and pressure gauges (Figure 3.5). The pilot scale ZVI amended DE filtration studies were performed in the Water Treatment Technology Assistance Center (WTTAC) high bay located in Gregg Hall.

Figure 3.4: Manville one square foot vertical leaf precoat filter used in pilot study.
Four separate trials were conducted at an optimal pH value of 6, while choice of oxidant and contact time of ZVI with arsenic contaminated source water were varied. Oxidants were chlorine (sodium hypochlorite) and dissolved oxygen (DO). Contact times were two minutes and twenty two minutes. Samples were taken every hour for the duration of the four hour experiment and analyzed for arsenic, iron, free chlorine, and turbidity. Pressure, ORP, pH, DO, and temperature were recorded at each sampling event.

Prior to the introduction of raw water to the filter, a precoat must be established using 0.2lbs DE/ft$^2$ of filter surface area. This is accomplished using a recycle line and a precoat tank. Water is recycled through the precoat tank until the water runs clear and all DE is retained on the vertical leaf. At this point, raw water is introduced to the filter by closing the precoat valve and opening the raw water valve. The raw water was prepared using 300 gallons of RO water, 292.21 mg/L NaCl (0.005M) for background ionic strength, 25mg/L HCO$_3^-$ for buffering capacity, 2 mg/L As, and was mixed with a submersible pump.

When using the low setting for contact time, the raw water was fed directly to the pump. The flow rate of 1 gpm and was regulated with a Dwyre flow meter. This flow was dosed with ZVI from a second tank using a Y joint and a peristaltic pump at a rate of 95mL/min and a concentration of 200 mg/L. A separate body feed pump was used to inject diatomaceous earth at a rate and concentration identical to the iron feed. The purpose of body feed is to prolong filtration runs by maintaining filter cake porosity. The total flow from the iron dosing tank and the body feed never exceeded 5%. The mixture was passed through the filter where the iron and arsenic were intended to be removed.

When the high setting for contact time was used, the raw water and the iron dose
Figure 3.5: Schematic of a Manville one square foot filtration apparatus.
Source: Spencer, 1991
Modification: Addition of iron dosing tank by P. Pepler
were introduced to a continuously stirred tank. A volume of 20 gallons was maintained. At a flow rate of 1 gpm, the average residence time was increased by 20 minutes. All other configurations remained the same.

The settings for oxidant, high and low, were achieved by the addition of 36 mL of 5% NaOCl to 300 gallons of source water for an initial concentration of 1.5 mg Cl₂/L and by bubbling compressed air at a rate of 15 standard cubic feet per hour (scfh) through four diffuser stones in the source water tank.

The zero valent iron was preconditioned for 24 hours prior to each filtration run. During the preconditioning, the iron dosing tank was maintained at pH 6, continuously mixed, and bubbled with compressed air at a rate of 3 liters per minute. The water contained 292.2 mg/L NaCl, 34.42 mg/L NaHCO₃ and 9.6 g/L ZVI.

3.3 Sampling Techniques

Samples were taken for arsenic analysis, iron (ferrous and total) analysis, sulfate and sulfide analysis, as well as a crystalline solids analysis. All aqueous samples were first filtered through Whatman GD/XP syringe filters (<0.45 µm, PTFE). Samples collected for total iron and arsenic were then acidified with two drops concentrated nitric acid and refrigerated at 4°C. Solids were collected for analysis on a Whatman filter (0.7 µm) and freeze dried. If the run was bubbled with N₂, this procedure was performed in a glove box with high purity N₂ flowing to clear 2 volumes per hour.

3.4 Analytical Methods

All analytical methods followed procedures according to Standard Methods for the Examination of Water and Wastewater, EPA standards, or manufacturer’s instructions.
3.4.1 Arsenic Measurements

The total arsenic remaining in solution after adsorption (5hrs) and filtration was measured at Resource Labs using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP) EPA method 200.7/6010. Arsenic III remaining in solution after adsorption (5hrs) and filtration was measured at Resource Labs using ICP after arsenic V was removed by an ion exchange column containing 5mL Purolite A300 Strong Base Anion Gel. Arsenic V was determined by the difference between $\text{As}_T - \text{As(III)}$. The capacity of the resin is 1.4eq/L. The maximum total of all negatively charged ions each experimental run is 0.0154eq/L. With a sample volume of 60mL, 0.66mL of resin is required. To be conservative, 5mL was used.

3.4.2 Iron Measurements

*Total iron.* Total iron remaining in solution after filtration was measured at Resource Labs using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP) EPA method 200.7/6010.

*Ferrous Iron by Hach DR/2000 Direct Reading Spectrophotometer.* The instrument was operated according to the manufactures instructions using Hach 8146—1,10 Phenanthroline Method adapted from Standard Methods for the Examination of Water and Wastewater. The range was 0-3.00mg/L and method detection limit was 0.008 mg/L Fe$^{2+}$.

3.4.3 Sulfur Measurements

*Total Sulfate.* Total sulfate remaining in solution after filtration was measured at Resource Labs using Ion Chromatography USEPA 300.
Sulfide by Hach DR/2000 Direct Reading Spectrophotometer. The instrument was operated according to the manufactures instructions using Hach Method 8131—Methylene Blue Method, equivalent to USEPA method 376.2. The range was 0-0.600mg/L S²⁻. The method detection limit was 0.005mg/L S²⁻.

3.4.4 Solids Measurement

Solids retained on a Watman GF/F 0.7μm filter were analyzed using X-Ray diffraction in the Materials Science Laboratory in Parsons Hall on the campus of the University of New Hampshire. The instrument was operated according to the manufactures instructions. The data were analyzed using Jade 3 software which compares the output from the X-ray diffraction to over 70,000 diffraction patterns.

3.5 Quality Assurance / Quality Control

All procedures in this study were draw from US EPA approved methods, Standard Methods, or instrument manufacturer’s instruction (Details Provided in Standard Operating instructions, Appendix 1). QA/QC procedures are summarized in Table 3.3.

3.5.1 Ferrous Iron Measurements

Hach DR 2000 Direct Reading Spectrophotometer method 8146 was used to measure ferrous iron. To determine accuracy, six dilutions of ferrous ammonium sulfate were measured with the Hach DR/2000 and compared to total iron measurement performed by Resource Labs (RLI) using EPA method 200.7. Initial sample conditions are such that all iron in solution is present in the ferrous form—therefore, total iron should be equal to ferrous iron. The results from both tests were strongly correlated showing an $R^2=0.9956$ (Figure 3.6).
Table 3.3 Summary of Quality Assurance / Quality Control Procedure

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Replicate</th>
<th>Standard</th>
<th>QC measure</th>
<th>Limit of Quantification</th>
</tr>
</thead>
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<tr>
<td>Total Iron</td>
<td>a</td>
<td>Lab (RLI)</td>
<td>Calibration on blank, 7 readings of same sample, find standard error</td>
<td>0.005mg/L</td>
</tr>
<tr>
<td>Ferrous Iron</td>
<td>a</td>
<td>Yes</td>
<td>Calibration on blank, 7 readings of same sample, find standard error</td>
<td>0.008mg/L</td>
</tr>
<tr>
<td>Arsenic (III) &amp; (V)</td>
<td>a</td>
<td>Lab (RLI)</td>
<td></td>
<td>0.01mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>a</td>
<td>Lab (RLI)</td>
<td></td>
<td>0.5mg/L</td>
</tr>
<tr>
<td>Sulfide Hach DR2000</td>
<td>a</td>
<td>Yes</td>
<td>Calibration on blank, 7 readings of same sample, find standard error</td>
<td>0.005mg/L</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>Yes</td>
<td>Calibration on two buffers, 7 readings of same sample, find standard error</td>
<td>na</td>
</tr>
<tr>
<td>Redox</td>
<td></td>
<td>Yes</td>
<td>Calibration on standard, 7 readings of same sample, find standard error</td>
<td>na</td>
</tr>
</tbody>
</table>

a: During every sampling event, at least one sample collected and analyzed in duplicate for sample variability assessment (hidden sample).

Data from the Hach DR 2000 were consistently lower than those produced by RLI. A curve was produced. Six measurements were taken on the same sample and the resulting standard deviation was 0.000347mg/L.

3.5.2 Sulfide Measurements

Hach DR 2000 Direct Reading Spectrophotometer method 8131 was used to measure sulfide concentrations. Three dilutions were made and measured. The expected and measured concentrations were plotted against each other and showed a strong correlation: $R^2=0.9848$ (Figure 3.7).
Figure 3.6: Accuracy check of the Hach DR/2000. Comparison of dissolved iron concentrations as measured using an ICP and Hach DR/2000.

Figure 3.7: Accuracy check of the Hach DR/2000. Measured sulfide concentrations using the Hach Method 8131—Methylene Blue Method compared to three dilutions.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Bench Studies: Assessing Arsenic Removal by ZVI under Varying Water Conditions

The objective of the bench study was to assess the optimal pH and oxidation-reduction potential (ORP) conditions for the removal of arsenic by ZVI, the minimization of iron dissolution from ZVI, and the influence exerted on these by the presence of sulfate. The experiments were conducted under controlled conditions in a one liter continuously stirred batch reactor. A full factorial experimental design was used with four settings for pH, three settings for ORP, and 2 settings for sulfate, for a total of 24 runs.

A stabilization period of 18 hours prior to arsenic addition was used to achieve consistent ORP values. The stabilization consisted of bubbling the ZVI solution with O₂ or N₂ at the specified pH values. When using Cl₂ the stabilization period was 2 hours. This also provided a period of ZVI pretreatment where under oxidizing conditions sorption sites were created by the corrosion of the ZVI surface. Samples were taken five hours after arsenic addition to ensure equilibrium conditions had been achieved.

4.1.1 Steady State / Equilibrium Determination

To ensure that data generated at different experimental conditions is comparable, it is necessary to determine the time at which equilibrium conditions have been achieved. This can be accomplished through the use of kinetic studies. Previously at UNH, Mathilde Le Roux (2005) performed kinetic studies under identical experimental conditions as this study with the exception of the elevated ORP conditions created by the
addition of sodium hypochlorite. Le Roux determined that equilibrium conditions were achieved at all pH values from 5-9 with in 1.5 hours when the reactor was bubbled with oxygen or nitrogen. To be conservative, La Roux chose to take samples five hours after arsenic addition. To be consistent with La Roux's work, the same time interval was used in this study. One additional experiment was necessary to determine when equilibrium was reached under elevated ORP conditions. Arsenic removals reached equilibrium conditions within 2 hours at pH 8 in the presence Cl₂ (Figure 4.1). ORP values ranged from 776-725mV.

4.1.2 Influence of pH, ORP, and Sulfate on Arsenic Removals

Arsenic removals varied from >99.75% to 10 % during the bench study. The greatest removals were achieved at pH 6 with the addition of Cl₂, with and with out SO₄ addition. These settings were the only two where the final arsenic concentration was below the detection limit (0.005mg/L which is 97.75% of the initial concentration of 2mg/L). The

![Graph showing Arsenic Removal Kinetic Study. NaCl=0.005M, ORP Range: 776-726mV.](image)

**Figure 4.1** Arsenic Removal Kinetic Study. NaCl=0.005M, ORP Range: 776-726mV.
subsequent sections will discuss, individually, the influence exerted by each main water quality factor on the removal of arsenic.

**Influence of pH on Arsenic Removals.** Within the range of pH values examined, 5-8, pH did not contribute a large influence on arsenic removals by zero valent iron. When all else was held constant, arsenic removals in the presence of chlorine were above 98% for all pH values from 5 to 9 (Figure 4.2 (a)). When chlorine was replaced with oxygen, removals were generally high (>96%) but dropped from 96.5 at pH 7 to 69.5% at pH 8 (Figure 4.2 (b)). This value, 69.5%, achieved at pH 8 and approximately 300mV, was likely the result of a filtration error as total iron in this sample was 8.4mg/L, and ferrous iron was 0.05mg/L. This may indicate that some material bypassed the filter. When the solution was bubbled with nitrogen, removals were generally low (Figure 4.1(c)). Removals were lowest at pH 6 where only 10% of the arsenic was removed as opposed to 15% for all other pH values.

The lack of an influence exerted by pH is unexpected but not unexplainable. As discussed above, the primary influence of pH is related to the dissolution of ferrous iron from the ZVI and oxidation of ferrous to ferric. Ferric iron precipitates, generating new sorption sites, upon which removal of arsenic is dependant (Melitas et al., 2002b). Dissolution of ferrous iron is greater at lower pH values and the kinetics of ferrous oxidation to ferric oxide is greater at higher pH values. It is expected that the over all generation rate of ferric oxide from ZVI is maximized at a specific pH value. Previous studies have shown that arsenic removals occur fastest at pH 6 (Bang et al., 2002).

Since this study looked at equilibrium conditions rather than kinetics, two conditions masked the influence of pH. These include the 18 hour preparation of the iron
prior to the arsenic spike and the long contact time (5 hours). This allowed time for the generation of sorption sites (under oxidizing conditions) as well as time for the arsenic to migrate to the sorption sites. Any design which uses shorter contact times or preparation times will need to consider the impact pH has on kinetics.

**Influence of Oxidation Reduction Potential (ORP) on Arsenic Removals.**

Oxidation reduction potential seems to have a major influence on the removal of arsenic by zero valent iron. When an oxidant was added by bubbling O2 or adding Cl2, (Figure 4.2 a,b), removals were generally high (90 - >99.75% removals) for all pH values except pH 8 with O2 where a 69.5% removal was achieved. Dilution was responsible for between 1.0% and 8.1% of the reduction under these conditions. As ORP was increased by changing the oxidant (N2→O2→Cl2), removals increased at every pH value. When the reactor was purged with nitrogen, removals were generally low (10-15%) at all pH values (Figure 4.2c). Under these conditions approximately 50% of arsenic was detected as As(III) (Table 4.1). This may have contributed to the reduced removals as As(III) is not as readily removed as As(V) (Bang et al., 2002). Dilution from the pH stat was responsible for between 0.8% and 2.3% of the reduction in concentration under these conditions.

Since the removal of arsenic is dependant on the continuous generation of sorption sites generated by the corrosion of iron, it follows that removals would be greatest under oxidizing conditions. This suggests that choice of oxidant may not be important if contact time and zero valent iron pretreatment times are long enough. If, however, one hopes to minimize contact time, kinetics will be an important factor to address.
Figure 4.2 Arsenic removal and iron dissolution using ZVI under various water quality conditions, w/ out SO₄. NaCl = 0.005M. Numbers represent concentration values.
Figure 4.3 Arsenic removal and iron dissolution using ZVI under various water quality conditions, w/ SO$_4$. NaCl = 0.005M.

Numbers represent concentration values.
Influence of Sulfate on Arsenic Removals. The presence or absence of sulfate did not appear to have a major influence on arsenic removals (Figure 4.4). The same general trends are observed in the absence of SO₄ (Figure 4.2) as were observed in the presence of SO₄ (Figure 4.3). At pH 8, while bubbling oxygen, a 20% reduction in arsenic removal was observed in the absence of sulfate. This reduction was likely the result of experimental error, as the dissolved iron concentration was 8.4mg/L, much higher than expected under these conditions. It is suspected that some material bypassed the filter increasing both the iron and arsenic concentration in the effluent. Any particulate iron which broke through the filter would likely be dissolved upon preservation with concentrated nitric acid.

It is worth noting that even though differences were very small, removals under oxidizing conditions were always slightly greater in the presence of SO₄ (Figure 4.4).

![Arsenic removal using ZVI under various water quality conditions. Ct=5hrs. Arsenic C₀=2mg/L, NaCl=0.005M, ZVI=200mg/L, SO₄=250mg/L](image-url)
This is likely attributable to the increase in ionic strength. Under reducing conditions, when N₂ was bubbled, there was a slight increase in arsenic removals in the absence of sulfate at pH 5 and 8. It is possible that this difference is a result of an ionic strength influence or a result of analytical error.

As discussed in Chapter 2, sulfate does not compete strongly with arsenic for sorption sites (Su et al., 2001b), and only contributes to arsenic removals under reducing conditions where sulfate is reduced to sulfide and precipitates, removing arsenic (Nikolaidis et al., 2003). Sulfide was only detected during one experiment at pH 8 while bubbling N₂ where 15% removals were achieved. The majority of the sulfate added was detected as sulfate and measured between 230 and 260mg/L under all conditions.

4.1.3 Assessing Iron Dissolution from ZVI under Varying Water Quality Conditions

Ferrous Iron. Ferrous iron concentrations (Fe²⁺) were highest at low pH values under all experimental settings (Figure 4.5a). In the absence of an oxidant, Fe²⁺ concentrations increased exponentially from 0.52 to 17.26mg/L with decreasing pH. In the presence of chlorine, Fe²⁺ concentrations were below detection limits under all conditions except one run. During the run at pH 5, all chlorine was consumed prior to the conclusion of the experiment and the Fe²⁺ concentration reached 1.56 mg/L (Table 4.1). Under the same conditions, in the presence of SO₄, the chlorine residual was maintained and Fe²⁺ was undetected.

In the presence of O₂, the Fe²⁺ concentration was low at pH values 7 and 8 (0.08-0.12mg/L) and increased with decreasing pH to a maximum of 2.36mg/L at pH5 in the absence of sulfate (Table 4.1). A concentration of 12.03mg/L was measured at pH 5, in the presence of sulfate and O₂, but the oxygen was not flowing during this run. The rate
Figure 4.5 Influence of pH and ORP on dissolved iron concentrations from a 200mg/L ZVI solution NaCl=0.005M, Ct=5hrs.
Table 4.1 Dissolved iron and arsenic speciation at various pH and ORP conditions in a 200mg/L ZVI solution. NaCl=0.005M, Ct=5hrs.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>SO4, (mg/L)</th>
<th>Fe2+, mg/L</th>
<th>Fe3+, mg/L</th>
<th>Iron, mg/L</th>
<th>Fe2+, mg/L</th>
<th>Fe3+, mg/L</th>
<th>Iron, mg/L</th>
<th>Fe2+, mg/L</th>
<th>Fe3+, mg/L</th>
<th>Iron, mg/L</th>
<th>Fe2+, mg/L</th>
<th>Fe3+, mg/L</th>
<th>Iron, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>250</td>
<td>10.95</td>
<td>7.05</td>
<td>18</td>
<td>1.71</td>
<td>5.49</td>
<td>7.2</td>
<td>3.44</td>
<td>0.26</td>
<td>3.7</td>
<td>0.11</td>
<td>0.39</td>
<td>0.5</td>
</tr>
<tr>
<td>O2</td>
<td>250</td>
<td>12.03</td>
<td>4.97</td>
<td>17</td>
<td>0.46</td>
<td>&lt;0.01</td>
<td>0.46</td>
<td>&lt;0.01</td>
<td>&lt;0.023</td>
<td>0.023</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.65</td>
</tr>
<tr>
<td>Cl2</td>
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<td>&lt;0.01</td>
<td>&lt;0.012</td>
<td>0.012</td>
<td>&lt;0.01</td>
<td>&lt;0.067</td>
<td>0.067</td>
<td>&lt;0.01</td>
<td>&lt;0.018</td>
<td>0.018</td>
<td>&lt;0.01</td>
<td>&lt;0.082</td>
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<td>9.74</td>
<td>27</td>
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<td>7.9</td>
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</tr>
<tr>
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<td>6.34</td>
<td>8.7</td>
<td>0.41</td>
<td>0.18</td>
<td>0.59</td>
<td>0.08</td>
<td>0.11</td>
<td>0.19</td>
<td>0.12</td>
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<td>&lt;0.01</td>
<td>0.08</td>
<td>&lt;0.01</td>
<td>0.082</td>
<td>&lt;0.01</td>
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<tr>
<td>As(III)</td>
<td>As(V)</td>
<td>AsT</td>
<td>As(III)</td>
<td>As(V)</td>
<td>AsT</td>
<td>As(III)</td>
<td>As(V)</td>
<td>AsT</td>
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<td>As(V)</td>
<td>AsT</td>
<td>As(III)</td>
<td>As(V)</td>
</tr>
<tr>
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<td>0.68</td>
<td>1.12</td>
<td>1.8</td>
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<td>1.58</td>
<td>1.8</td>
<td>0.67</td>
<td>1.13</td>
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<td>1.06</td>
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<tr>
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<td>250</td>
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<td>0.024</td>
<td>0.024</td>
<td>0.01</td>
<td>-0.002</td>
<td>0.008</td>
<td>0.04</td>
<td>0.016</td>
<td>0.056</td>
<td>0.054</td>
<td>0.146</td>
<td>0.2</td>
</tr>
<tr>
<td>Cl2</td>
<td>250</td>
<td>&lt;0.005</td>
<td>0.006</td>
<td>0.006</td>
<td>0.011</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.008</td>
<td>-0.003</td>
<td>0.005</td>
<td>&lt;0.005</td>
<td>0.017</td>
<td>0.017</td>
</tr>
<tr>
<td>N2</td>
<td>0</td>
<td>0.36</td>
<td>1.34</td>
<td>1.7</td>
<td>0.57</td>
<td>1.23</td>
<td>1.8</td>
<td>0.68</td>
<td>1.02</td>
<td>1.7</td>
<td>0.58</td>
<td>1.12</td>
<td>1.7</td>
</tr>
<tr>
<td>O2</td>
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<td>0.015</td>
<td>0.042</td>
<td>0.033</td>
<td>-0.005</td>
<td>0.028</td>
<td>0.026</td>
<td>0.041</td>
<td>0.067</td>
<td>0.074</td>
<td>0.536</td>
<td>0.61</td>
</tr>
<tr>
<td>Cl2</td>
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<td>0.032</td>
<td>0.032</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.011</td>
<td>0.011</td>
<td>0.008</td>
<td>0.004</td>
<td>0.012</td>
<td></td>
</tr>
</tbody>
</table>

Fe²⁺ values corrected using calibration curve in Chapter 3.
Fe³⁺ values determined by difference.
of Fe\textsuperscript{2+} oxidation by oxygen increases by 100-fold per pH unit above 5.5 (Montgomery Watson Harza, 2005). At pH values below 6, dissolved oxygen may not be sufficient to keep iron in the oxidized form and prevent the transport of iron from the system (Table 4.1). This is a necessary condition as the USEPA secondary standard for iron in drinking water is 0.3mg/L. At pH values below 6, a residual of Cl\textsubscript{2} may be necessary in order to avoid leaching iron from the ZVI filtration system.

**Total Dissolved Iron.** Total dissolved iron concentrations were generally higher at lower pH values and followed a similar pattern to ferrous iron concentrations (Figure 4.5b). This trend of decreasing iron concentrations with increasing pH is related to the solubility of iron. The dissolution of iron is a function of pH and has a minimum value of approximately $10^{-7.27}$ M at pH10 (Figure 4.6).

In the absence of an oxidant, while bubbling N\textsubscript{2}, dissolved iron concentrations

![Figure 4.6 Solubility of iron as a function of pH. Includes Fe\textsuperscript{2+} and Fe\textsuperscript{3+} complexes of Cl\textsuperscript{-} and OH\textsuperscript{-} in equilibrium with Fe(OH)\textsubscript{2} and Fe(OH)\textsubscript{3}.](image-url)
increased exponentially with decreasing pH values. The highest concentration of 27mg/L was achieved while bubbling N₂, at pH5 in the absence of SO₄ (Table 4.1). Under reducing conditions, dissolved iron was above the secondary standard of 0.30mg/L at all pH values and ranged form 0.5-27mg/L.

While bubbling O₂, dissolved iron concentrations ranged from <0.01-17mg/L. Concentrations generally decreased with increasing pH with one exception: At pH 8 in the absence of SO₄, as discussed above. Concentrations were above the secondary standard at all pH values except pH 7 where dissolved iron ranged from 0.023-0.19mg/L.

In the presence of Cl₂, dissolved iron concentrations were generally low—below the secondary standard of 0.30mg/L and ranged from <0.005-0.082mg/L with one exception (Table 4.1). At pH 5, in the absence of SO₄, dissolved iron concentrations reached 3.1mg/L. During this run, Cl₂ was consumed prior to the conclusion of the run. This likely led to the dissolution of iron.

A preliminary assessment was conducted using the measured concentrations of ferrous and ferric iron and the Nerst equation to evaluate how measured ORP values compared to calculated Eh values. Values were consistently different suggesting that other redox couples need to be considered or the analytical measures need refinement.

4.1.4 Relating Arsenic Removals to Selected Chemical Speciations (As, Fe, S)

The experimental conditions in the batch experimentation covered a wide range of pH and ORP values. These are often master variables in water chemistry and can exert a driving force on chemical systems. The compounds involved speciate according to thermodynamics.
Using equilibrium conditions, graphs can be drawn using lines which represent equal concentrations of products and reactants with respect to pH and Eh (reduction potential). This offers to an ability to visually represent equilibrium conditions under various conditions simultaneously. A computer modeling software, Goechemist’s Workbench, was used to produce Eh-pH diagrams for arsenic, sulfur, and iron under conditions similar to those used in the bench study. Percent removals of arsenic were superimposed on these diagrams at positions which represent the conditions of the experiment in an effort to understand the relationship between chemical speciation and arsenic removals. The subsequent sections present this information.

**Arsenic.** Arsenic exists as several different species in natural waters. These include $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$, and $\text{As(OH)}_3$ (Figure 4.7a). Bang et al. (2002) saw smaller kinetic rate constants for As(III) ($\text{As(OH)}_3$) than for As(V) ($\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$) and observed greater than 93% arsenite and 99% arsenate removals were achieved when batch studies were open to the atmosphere as opposed to 4% arsenite and 9% arsenate removal when purged with nitrogen. This information suggests that arsenic removals may vary depending on which species is present.

Arsenic removals were high in the regions where As(V) is the dominant aqueous arsenic species (Figure 4.7). These removals were generally greater than 96% and there does not seem to be any difference in arsenic removals between the two regions where different As(V) species predominate. In regions where aqueous As(III) species dominate removals were low (10-15%). It appears that under the conditions of this experiment, water quality conditions have to favor the predominance of an As(V) species if arsenic removals are to occur.
Figure 4.7 Dissolved arsenic species predominance with respect to Eh and pH. Percent arsenic removals achieved in the bench study are plotted at the corresponding conditions. (a) No sulfate. (b) Sulfate present

Batch conditions: Contact time=5hrs, NaCl=0.005M, ZVI=200mg/L, As C₀=2mg/L.
Predominant aqueous arsenic species formed in the presence of SO₄ are very similar to species which predominate in the absence of SO₄ with the exception of species formed under extremely reducing conditions (Figure 4.7b). Crystalline arsenic solids only are only formed at elevated ORP values (Figure 4.8) in the absence of SO₄, and these conditions favor the predominance of Scorodite, FeAsO₄·2H₂O. Here removals vary from 69.5% to >99.75%. The same general trends exist in the presence of 250mg/L SO₄ (Figure 4.8a) as in the absence of SO₄ (Figure 4.8b) except under extremely reducing conditions. Under these conditions several aqueous species and several crystalline species are predominant. It should be noted that none of the solids indicated in Figures 4.8 were detected by X-ray diffraction (Table 4.3).

This lack of detection may be attributable to several causes. First, it is possible that the length of the experiment was insufficient to permit the formation of these species. Second, it is possible that it was not detected because although an arsenic species may be the dominant species formed from the aqueous components, the mass of ZVI was two orders of magnitude larger than the mass of arsenic and may have masked its detection.

Sulfur. The majority of the experiments occurred in the region where sulfate is the dominant aqueous form of sulfur (Figure 4.9a). Removals in this region vary from 10% to 99.6%. There does appear to be a slight increase in removal at low ORP values at pH 8 and approximately -250mV where AsS₂ dominates. At elevated ORP values, where FeSO₄⁺ is the dominant aqueous species, removals are generally greater than 99%. When removals are compared to crystalline sulfur speciation, it appears that removals are >90% where Jarosite-Na dominates (Figure 4.9b). There is a region where no crystalline species dominate and SO₄ is the dominant sulfur species. Arsenic removals in
Figure 4.8 Crystalline arsenic species predominance with respect to Eh and pH. Percent arsenic removals achieved in the bench study are plotted at the corresponding conditions. (a) No sulfate. (b) Sulfate present. Batch conditions: Contact time=5hrs, NaCl=0.005M, ZVI=200mg/L, As C\(_0\)=2mg/L.

Species represented by chemical formula only represent areas where no crystalline arsenic species predominate.
this region range from 10% to 99.6%. Again, the crystalline species depicted in the
diagram were not detected by X-ray diffraction. The explanation for this may be similar
to the explanations given above with respect to arsenic. Also, this diagram depicts the
dominant sulfur species, not necessarily the dominant species in the system.

Iron. Figure 4.10 presents results from batch studies run with and without sulfate
addition, superimposed on an Eh-pH diagram for aqueous iron species generated using
conditions similar to the batch studies. While there is a slight difference in the dissolved
iron speciation in the presence of SO₄, this region in the predominance diagram (Low
pH—high Eh) is outside the experimental conditions (Figure 4.10). Removals are
consistently high, >99%, in the region where Fe³⁺ species (Fe(OH)₂⁺ and Fe(OH)⁰) are
the dominant aqueous form of iron with one exception at pH 8, as discussed above
(Figure 4.10a). Removals in the region where Fe²⁺ is the dominant aqueous form,
removals vary from 10% to 99.7%. The higher removals were achieved at higher ORP
values, closer to the line of equal Fe²⁺/Fe³⁺ dominance.

When crystalline iron species were modeled (Figure 4.11), all experiments
occurred in regions where Fe³⁺ species (FeAsO₄·2H₂O, Fe₂O₃) dominate except in the
presence of SO₄ under reducing conditions where pyrite is the dominant iron species. At
higher mV values, where FeAsO₄·2H₂O is dominant, removals vary from 69.5% to
>99.75%. Under conditions which favor Fe₂O₃ dominance, removals vary from 10% to
97.9%. The conditions in one experiment, pH 8 and approximately -300mV, favored a
mixed oxide (Fe³⁺/Fe²⁺) species (Fe₃O₄) and the removal achieved was 15%. Similar
patterns are observed in the presence of 250mg/L SO₄ (Figure 4.11). The one difference
is at lower redox values—FeS₂ becomes the dominant crystalline solid (Figure 4.11b) as
Figure 4.9 Sulfur species predominance with respect to Eh and pH. Percent arsenic removals achieved in the bench study are plotted at the corresponding conditions. (a) Dissolved species. (b) Crystalline species. Batch conditions: Contact time=5hrs, NaCl=0.005M, ZVI=200mg/L, As C₀=2mg/L.

Species represented by chemical formula only represent areas where no crystalline sulfur species predominate.
Figure 4.10 Dissolved iron species predominance with respect to Eh and pH. Percent arsenic removals achieved in the bench study are plotted at the corresponding conditions. (a) No sulfate. (b) Sulfate present. Batch conditions: Contact time=5hrs, NaCl=0.005M, ZVI=200mg/L, As C₀=2mg/L.
Figure 4.11 Crystalline iron species predominance with respect to Eh and pH. Percent arsenic removals achieved in the bench study are plotted at the corresponding conditions. (a) No sulfate. (b) Sulfate present. Batch conditions: Contact time=5hrs, NaCl=0.005M, ZVI=200mg/L, As C0=2mg/L.
Species represented by chemical formula only represent areas where no crystalline species predominate.
opposed to Fe₃O₄ and FeO.

When iron speciation was modeled in the absence of arsenic or sulfate (Figure 4.12), all removals occurred in the region where hematite, Fe₂O₃, was the dominant crystalline form with one exception at pH 8 and -300mV, where magnetite is dominant. While hematite would dominate under equilibrium conditions, kinetic constraints will limit its formation at the time scale of this experiment.

X-ray diffraction was used to analyze the filtered solids generated during the batch study. Magnetite (Fe₃O₄) was detected most frequently—17 out of 24 experiments, followed by elemental iron—14 of 24, followed by Maghemite (Fe₂O₃), Hematite

![Figure 4.12: Crystalline iron species* predominance with respect to Eh and pH. Percent arsenic removals achieved in the bench study are plotted at the corresponding conditions. Batch conditions: Contact time=5hrs, NaCl=0.005M, ZVI=200mg/L. *Modeled with out SO₄ or As. Species represented by chemical formula only represent areas where no crystalline species predominate. Arsenic removed from model.](image-url)
(Fe$_2$O$_3$), AsFe$_2$, Lepidocrocite (FeO(OH)), FeO and As$_2$O$_5$ (Table 4.2).

Elemental iron was detected most frequently under reducing conditions, when N$_2$ was the oxidant of choice (Table 4.2). It was detected in all but two runs for which there are no data (Table 4.3). Magnetite was also detected frequently under reducing conditions, which is expected at higher pH values (Figure 4.11). Hematite was detected only once under reducing conditions—at pH 8, where magnetite is expected to dominate.

Under relatively oxidizing conditions, when O$_2$ was used as an oxidant, magnetite was detected most frequently (Table 4.2). Under these conditions, thermodynamics favor the dominance of hematite, which was detected in three of the eight runs under these conditions. Maghemite was also detected frequently, but is not expected to dominate under any conditions (Figure 4.12).

Under very oxidizing conditions, when Cl$_2$ was used as an oxidant, Magnetite was detected most frequently followed by elemental iron (Table 4.2). Hematite was only detected in three of eight runs under these conditions—conditions in which hematite is expected to dominate (Figure 4.12).

Several possible explanations exist to describe the discrepancies between the

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<th>Crystaline Solid</th>
<th>Oxidant</th>
<th></th>
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<tr>
<td></td>
<td>Nitrogen</td>
<td>Oxygen</td>
<td>Chlorine</td>
<td></td>
</tr>
<tr>
<td>Fe (0)</td>
<td>6</td>
<td>3</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>4</td>
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<td>6</td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
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<td>3</td>
<td></td>
</tr>
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<td>Maghemite</td>
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<td>7</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Lepidocrocite</td>
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<td>1</td>
<td>0</td>
<td></td>
</tr>
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<td>AsFe$_2$</td>
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<tr>
<td>FeO</td>
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<td>0</td>
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Table 4.2 X-Ray diffraction results. Detection frequency of iron species under given water quality conditions in a 200mg/L ZVI solution. Eight samples analyzed per oxidant. NaCl=0.005M, t=5hrs. Temp=20°C.
Table 4.3 Crystalline iron species detected under various water quality conditions. Ct=5hrs, ZVI=200mg/L, Temp=20°C.

<table>
<thead>
<tr>
<th>Trial</th>
<th>pH</th>
<th>Oxidant</th>
<th>SO4</th>
<th>% As Removal</th>
<th>mV</th>
<th>Species detected by XRD</th>
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<td>1</td>
<td>5</td>
<td>N₂</td>
<td>+</td>
<td>10</td>
<td>117</td>
<td>Fe⁰</td>
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<tr>
<td>2</td>
<td>6</td>
<td>N₂</td>
<td>-</td>
<td>15</td>
<td>139</td>
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<td>6</td>
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<td>+</td>
<td>98.8</td>
<td>350</td>
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<tr>
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<td>985</td>
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<tr>
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<td>N₂</td>
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<td>10</td>
<td>20</td>
<td>Magnetite, Fe⁰</td>
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<td>6</td>
<td>N₂</td>
<td>-</td>
<td>10</td>
<td>-50</td>
<td>Magnetite, Fe⁰, Maghemite</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>O₂</td>
<td>+</td>
<td>99.6</td>
<td>286</td>
<td>AsFe₂, Magnetite, maghemite, As₂O₅</td>
</tr>
<tr>
<td>9</td>
<td>7</td>
<td>O₂</td>
<td>-</td>
<td>98.6</td>
<td>320</td>
<td>maghemite</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>Cl₂</td>
<td>+</td>
<td>&gt;99.75</td>
<td>911</td>
<td>Hematite, magnetite, maghemite</td>
</tr>
<tr>
<td>11</td>
<td>7</td>
<td>Cl₂</td>
<td>-</td>
<td>&gt;99.75</td>
<td>908</td>
<td>Maghemite</td>
</tr>
<tr>
<td>12</td>
<td>7</td>
<td>N₂</td>
<td>+</td>
<td>10</td>
<td>-190</td>
<td>Fe⁰</td>
</tr>
<tr>
<td>13</td>
<td>7</td>
<td>N₂</td>
<td>-</td>
<td>15</td>
<td>-167</td>
<td>Fe⁰, Hematite, magnetite</td>
</tr>
<tr>
<td>14</td>
<td>8</td>
<td>O₂</td>
<td>+</td>
<td>97.2</td>
<td>130</td>
<td>Fe⁰, Hematite, magnetite</td>
</tr>
<tr>
<td>15</td>
<td>8</td>
<td>O₂</td>
<td>-</td>
<td>96.65</td>
<td>200</td>
<td>maghemite, hematite</td>
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<tr>
<td>16</td>
<td>8</td>
<td>Cl₂</td>
<td>+</td>
<td>99.75</td>
<td>860</td>
<td>Fe⁰, magnetite</td>
</tr>
<tr>
<td>17</td>
<td>8</td>
<td>Cl₂</td>
<td>-</td>
<td>99.45</td>
<td>228</td>
<td>Fe⁰, Maghemite (Fe₂O₃)</td>
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<td>15</td>
<td>-251</td>
<td>Fe⁰</td>
</tr>
<tr>
<td>19</td>
<td>8</td>
<td>N₂</td>
<td>-</td>
<td>15</td>
<td>-320</td>
<td>Hematite, Fe⁰, Magnetite</td>
</tr>
<tr>
<td>20</td>
<td>8</td>
<td>O₂</td>
<td>+</td>
<td>90</td>
<td>222</td>
<td>Maghemite, magnetite, Fe⁰</td>
</tr>
<tr>
<td>21</td>
<td>8</td>
<td>O₂</td>
<td>-</td>
<td>69.5</td>
<td>222</td>
<td>Hematite, magnetite, maghemite</td>
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<tr>
<td>22</td>
<td>8</td>
<td>Cl₂</td>
<td>+</td>
<td>99.15</td>
<td>715</td>
<td>Maghemite, magnetite, Fe⁰</td>
</tr>
<tr>
<td>23</td>
<td>8</td>
<td>Cl₂</td>
<td>-</td>
<td>99.4</td>
<td>726</td>
<td>Fe⁰, Hematite, magnetite</td>
</tr>
</tbody>
</table>
observations and the predictions of the chemical modeling software. The figures generated by the modeling software reflect equilibrium conditions and not kinetics of formation. It is very likely that the formation of hematite takes longer than the time available during the experiments and other species were detected at a greater frequency. The ZVI was not acid washed to remove any corrosion. The ZVI surface was not likely free from oxides at the beginning of the experiment and this may have influenced the species present at the conclusion of the experiment.

4.1.5 Statistical (ANOVA) Assessment of Selected Water Quality Conditions on Arsenic Removals—pH, ORP, SO$_4$\(^4\)

Analysis of variance (ANOVA) is a statistical method used to separate the variation in the response into two groups: variation due to the treatments and variation due to experimental error. A full factorial design is advantageous because an ANOVA can be performed on the data and a percent contribution can be assigned to each factor's influence on the response.

An assumption used for this analysis is that all things being equal, ORP decreases with increasing pH but the relative oxidizing power is equal if an oxidant is used in an identical manner. So, the factors used in the statistical analysis were oxidant (rather than ORP), pH, and presence or absence of SO$_4$.

The vast majority of variation among treatments, 97.99%, was attributed to the oxidant used (Table 4.4). Within the range of pH values examined, 5-8, pH did not have a significant influence on arsenic removals. Removals were generally high if O$_2$ or Cl$_2$ were used and low if N$_2$ was used (Table 4.3). The interaction of pH and oxidant was significant (p =0.014) but the percent contribution was only 0.59%. While Figure 4.4 shows a general trend of greater removals at lower pH values, the difference is not
statistically significant (Table 4.4). The presence or absence of sulfate did not appear to have a significant effect on arsenic removals (Table 4.4).

Three different tests were used to compare means between oxidant used: Student’s t, Tukey-Kramer, and Hsu’s Multiple Comparison with Best (Figure 4.13). There is not a significant difference between average removals generated in the presence of O₂ or Cl₂. They are both, however, significantly different than the mean removals achieved in the presence of N₂. This suggests that choice of oxidant, Cl₂ or O₂, is not important if contact time and zero valent iron pretreatment times are long enough. If, however, one hopes to minimize contact time, kinetics will be an important factor and choice of oxidant will need to be assessed.

Table 4.4 Analysis of variance and percent contribution for batch study. T=5hours, NaCl=0.005M, ZVI=200mg/L, C₀=2mg As/L, SO₄=0.0025M (if present).

<table>
<thead>
<tr>
<th>Main Factors and Interactions</th>
<th>F Ratio</th>
<th>p</th>
<th>% contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.4</td>
<td>0.088</td>
<td>0.14</td>
</tr>
<tr>
<td>Oxidant</td>
<td>866.9</td>
<td>&lt;.0001</td>
<td>97.88</td>
</tr>
<tr>
<td>pH*Oxidant</td>
<td>6.2</td>
<td>0.014</td>
<td>0.59</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.3</td>
<td>0.543</td>
<td>-0.03</td>
</tr>
<tr>
<td>pH*SO₄</td>
<td>1.5</td>
<td>0.234</td>
<td>0.03</td>
</tr>
<tr>
<td>Oxidant*SO₄</td>
<td>1.6</td>
<td>0.240</td>
<td>0.07</td>
</tr>
<tr>
<td>pH<em>Oxidant</em>SO₄</td>
<td>1.2</td>
<td>0.324</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Figure 4.13 Analysis of Variance by oxidant. T=5hours, NaCl=0.005M, ZVI=200mg/L.
4.2 Pilot Experiments: Assessing the Modification of Precoat Filtration with ZVI for Arsenic Removal

Pilot studies were conducted to reproduce bench scale arsenic removals on a larger scale using a filtration technology rather than batch reactors. Filtration was used largely as a mechanism to capture the zero valent iron (ZVI). The variables investigated applied to the ZVI rather than to filter optimization. This technique is of interest because if successful, ZVI may be a suitable media which can be dosed to contaminated water for the removal of arsenic in a large-scale continuous flow system. A main concern was the dissolution of iron from the ZVI and conditions were chosen to investigate the optimization of arsenic removal while minimizing iron dissolution.

As discussed above, the removal of arsenic by ZVI is dependant on the generation of sorption sites formed as the result of iron oxidation. For this reason, pretreatment of the ZVI was necessary to oxidize the ZVI surface. The pretreatment occurred for a duration of 24 hours immediately preceding each experiment and consisted of bubbling compressed air through the ZVI solution, continuous mixing, and the maintenance of a constant pH value of 6. The pH and ORP were monitored during each pretreatment session and subsequent discussions regarding these conditions will refer to the ZVI prep tank. The pretreated ZVI solution was dosed from this same tank.

The experiment was conducted by dosing pretreated ZVI at a rate of 200mg/L into the source water with an arsenic concentration of 2 mg/L. The source water and iron dosing tank were both at pH6. The ZVI with the arsenic adsorbed was removed using a diatomaceous earth precoat filtration strategy. Two contact times, 2 & 22 minutes, were investigated as well as two oxidants in the source water, O₂ and Cl₂. A mixing tank with a
volume of twenty gallons was added to the system to increase the average contact time by
twenty minutes and will be referred to as the reactor. The filtration rate was 1 gpm/ft².
Arsenic removals increased with increased filtration time under all experimental
conditions. After approximately three hours, removals seem to have reached a steady
state and remain consistent with increased time (Figure 4.14). For this reason, all
comparisons were made at the four hour mark for the pilot studies.

4.2.1 Influence of ORP on Arsenic Removals by ZVI Amended Precoat Filtration

Oxidized ZVI addition enhanced arsenic removals and the presence of Cl₂ resulted
in higher removals than O₂ (Figure 4.15). When the oxidant was Cl₂ and contact time was
2 minutes, ORP was 693mV and arsenic removals achieved were 53%. When Cl₂ was
used as the oxidant and the contact time was 22 minutes, the effluent ORP was
671mV and removals increased by 5% to 58%. When this run “Cl₂, 22min (1)” was
Repeated (Cl₂, 22min (2)), redox values and removals were slightly higher—718mV and
61.5% respectively. When this run was repeated a third time (Cl₂, 22min (3)), with
enhanced pretreatment (higher air flow rate in the ZVI prep tank), removals were 13.69%
greater (71.5%) and ORP was slightly greater (708mV).

The increase in removals from Cl₂, 22min (1) to Cl₂, 22min (3) may be
attributable to the increase in air flow rate in the ZVI prep tank. The increase air flow
could have caused greater turbulence exposing more ZVI surface area susceptible to
dissolution. Under oxidizing conditions this would lead to the formation of more
amorphous solids, more sorption sites, and greater removals of arsenic.

When O₂ was used as the oxidant and the contact time was 2 minutes, the effluent
ORP was 110mV and 42% arsenic removals were achieved (Figure 4.15). When the
Figure 4.14: Pilot arsenic removals achieved as a function of filtration time. *Run “CI2, 22min” was repeated twice; (2) used conditions identical to (1), (3) used identical conditions except ZVI pretreatment air flow rate was increased from 3 to 8 L/min.*

Figure 4.15: Pilot arsenic removals by ZVI as a function of ORP. *Values are from last data point in Figure 4.14*
contact time was 22 minutes and O₂ was used as the oxidant, ORP was 202mV and arsenic removals of 48% were achieved (Figure 4.15).

4.2.2 Influence of ZVI (200mg/L) Contact Time on Arsenic Removals—pH6

Arsenic removals generally increased with increased contact time (Figure 4.14). After 4 hours of run time, 240 gallons/ft² of water had been filtered, 180g/ft² of ZVI had accumulated on the filter, and removals appeared to have reached a steady state. At this point, with a ZVI-arsenic contact time of 2 minutes in the presence on dissolved oxygen, 41.7% arsenic removals were being achieved. When contact time was increased to 22 minutes removals increased by 6% to 47.7%.

In the presence of chlorine with a contact time of 2 minutes and after the system had reached steady state, arsenic removals were 50.5% (Figure 4.14). When the contact time was increased to 22 minutes removals increased by 7.1% to 57.6%. Chlorine residuals were maintained between 1-1.5mg Cl₂/L.

Arsenic removals achieved during the pilot study were not as great as the removals achieved during the bench studies. This is most likely attributable to the large difference in contact time. The bench studies were conducted to assess equilibrium conditions and therefore lasted until this was established. The pilot studies were not intended to reach equilibrium, and therefore removals were not as great.

4.2.3 Influence of ZVI (200mg/L) Contact Time, ORP and ZVI pretreatment on Iron Dissolution by ZVI Amended Precoat Filtration—pH6

While using ZVI to remove arsenic, a main concern was the dissolution of iron from the ZVI. Conditions were chosen to investigate the optimization of arsenic removal while minimizing iron dissolution.
Contact Time. Effluent iron concentrations were generally lower when ZVI-arsenic contact times were 2 minutes as opposed to 22 minutes (Figure 4.16). With O\textsubscript{2} as the oxidant and a 2 minute contact time, the ferrous iron concentration was 0.06mg/L at the four hour mark (Figure 4.16a). With an increase in contact time to 22 minutes, the ferrous iron concentration increased to 0.13mg/L. Total Dissolved iron species, as measured by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), showed a similar trend (Figure 4.16b). At the four hour mark the iron concentration was 0.02mg/L and increased to 0.12mg/L with an increase in contact time to 22 minutes.

With Cl\textsubscript{2} as an oxidant, the ferrous iron concentration was <0.01mg/L for both 2 and 22 minute contact times. Total dissolved iron showed a different trend however (Figure 4.16b). With a 2 minute contact time dissolved iron concentrations were <0.01 mg/L. With a 22 minute contact time, iron concentrations were 0.36mg/L after four hours but varied between 0.79mg/L and 0.30mg/L during the run.

Since the measured ferrous concentration was <0.01mg/L it was suspected that particulate iron had broken through and dissolved upon preservation with concentrated nitric acid. An effort was made to eliminate the variation attributable to particulate iron breakthrough by incorporating an additional filtration process: The 22 minute Cl\textsubscript{2} run was repeated under identical conditions with one exception—the samples were filtered through a 0.45μm PTFE filter prior to preservation. This, however, did not eliminate the iron in the effluent (Figure 4.16b). In fact, the final concentration was 0.78mg/L. The range was similar (0.57-0.78mg/L).

Dissolved iron in the effluent was unexpected with a residual of chlorine in the system. It was expected that any iron which had dissolved in the ZVI pretreatment tank
Figure 4.16: Dissolved iron concentrations in the pilot study effluent measured hourly for the duration of the filtration run. (a) Ferrous iron concentrations—as measured by the Hach DR2000. (b) Dissolved iron concentrations as measured by ICP-MS.
would be oxidized in the reactor, precipitated, and removed by the filter. It seems possible that dissolved iron concentrations were much higher than expected in the ZVI pretreatment tank and when the ZVI was dosed to the source water, dissolved iron was too great to be removed in the prescribed time.

Oxidation of ferrous iron is strongly influenced by pH and the rate increases 100 fold for each unit increase in pH (Figure 4.17). Tighter control will be needed for the pretreatment of ZVI for this use to ensure dissolved iron does not leave the system. Specifically, increasing the pH of the pretreatment tank will reduce solubility of iron and increase the rate of ferrous oxidation to non-soluble ferric iron.

**ORP.** Dissolved ferrous iron concentrations in the effluent, as measured by the Hach DR-2000, were generally low—below the USEPA secondary standard of 0.3mg/L (Figure 4.16a). When Cl₂ was used as an oxidant, ORP values ranged between 671-

![Figure 4.17: Oxidation rate of ferrous iron proportional to Fe(II) and strongly influenced by pH. 20.5°C, Pₒ=constant. *After Stumm and Lee, 1961.*](image)

**Figure 4.17:** Oxidation rate of ferrous iron proportional to Fe(II) and strongly influenced by pH. 20.5°C, Pₒ=constant. *After Stumm and Lee, 1961.*
693 mV and Fe\(^{2+}\) concentrations were consistently lower than when O\(_2\) was used and just above the detection limit of 0.01 mg/L (Figure 4.16a). When O\(_2\) was used as an oxidant, ORP values ranged between 110-202 mV, Fe\(^{2+}\) concentrations generally increased with time from 0.04 mg/L to 0.13 mg/L and were higher than when runs contained chlorine.

When iron samples were analyzed using ICP-MS, which measures total dissolved iron species, a slightly different trend appeared (Figure 4.16b). Dissolved iron concentrations were generally low, below 0.3 mg/L, in the effluent during all runs with one exception: the 22 minute run containing Cl\(_2\). When contact time was two minutes, iron concentrations were lower when Cl\(_2\) was present (<0.01-0.01 mg/L), than when O\(_2\) was the oxidant (0.02-0.05 mg/L). With a contact time of 22 min and O\(_2\) as the oxidant, concentrations varied from <0.01 mg/L to 0.12 mg/L. With Cl\(_2\) as the oxidant and a contact time of 22 minutes, ORP was 671 mV. Iron appeared in the effluent after one hour of filtration at a concentration of 0.79 mg/L and varied throughout the run. This run was repeated, under identical conditions, except that it was filtered through a 0.45 μg PTFE filter prior to sample preservation with concentrated nitric acid. The resulting iron concentrations were similarly high, ranging from 0.57-0.78 mg/L (figure 4.16b), as discussed above.

**ZVI Pretreatment.** After ruling out particulate breakthrough as the source of the iron in the “Cl\(_2\)-22 minute” effluent, the next potential source to investigate was dissolved iron in the ZVI dosing tank. It is possible that the available oxygen in the iron tank was not sufficient to oxidize the iron which dissolved from the ZVI. This was investigated using the redox files generated during the ZVI pretreatment (Figure 4.18a,b,c; 4.19a,b,c).
Continuous measurements of pH and ORP were recorded during the 24 hour ZVI pretreatment period in the same manor as the bench studies.

Three runs, the O₂ runs at both contact times and the Cl₂ run at 2 minute contact time, produced iron concentrations in the effluent well below the secondary standard of 0.03mg/L (Figure 4.16b). ORP and pH Data were logged during the 24 hour ZVI pretreatment (Figure 4.18). This information was considered to help explain why dissolved iron was low during these runs but high in others. During the 24 hour pretreatment period for these three runs, the redox condition showed positive values indicative of an oxidizing environment (Figure 4.18a,b,c). If any dissolved iron was actually present in the pretreatment tank, it was oxidized or diluted and its concentration reduced to levels below the standard prior to reaching the filter.

Two runs, both the Cl₂ run at the 22 minute contact time and a repeat of this run, produced iron concentrations in the effluent well above the secondary standard of 0.3mg/L. During the pretreatment period for these two runs, the redox condition was negative indicative of a reducing environment (Figure 4.19a,b). Reducing conditions are conducive to the dissolution of iron and may have produced concentrations of dissolved iron in the pretreatment tank which, upon dosing, exceeded the capacity of the chlorine to oxidize and precipitate it in the prescribed contact time. The dissolved iron in the pretreatment tank may have begun to form iron floc when dosed to the source water and exposed to the chlorine. It is very likely that much of the iron was in the colloidal form, and therefore not detected as dissolved iron or removed by filtration.

To further investigate the cause of high iron concentrations in the effluent, Visual Minteq (http://www.lwr.kth.se/english/oursoftware/vminteq/), an equilibrium modeling
Figure 4.18: Water quality conditions during ZVI pretreatment period used for experiments “O₂, 2 min”, “Cl₂, 2 min”, & “O₂, 22 min” ZVI=9.6mg/L, NaCl=0.005M, air flow rate=3L/min. a: O₂, 2 min; b: Cl₂, 2 min; c: O₂, 22 min.
Figure 4.19: Water quality conditions during ZVI pretreatment period used for experiments “Cl₂, 22min (1)”, “Cl₂, 22min (2)”, “Cl₂, 22min (3)”. ZVI=9.6mg/L, NaCl=0.005M. a: Cl₂, 22 min (1), air flow=3L/M. b: Cl₂, 22min, (2), air flow=3L/min c: Cl₂, 22min (3), air flow=8L/min.
software, was used to investigate conditions in the pretreatment tank and the source water as they relate to iron dissolution. According to Visual Minteq, the water quality condition in the ZVI prep tank (Eh=-50mV, pH=6) was favorable to high dissolved iron concentrations (Table 4.5). Under these conditions, 93% of the iron present in the system is in the dissolved form. When this ZVI solution was dosed to the source water stream with an Eh=700 and pH=6, some of the iron would precipitate. It is not likely that all the iron would precipitate because the limits of kinetics of ferrous to ferric oxidation, iron solubility, and time (CT=22 minutes). In fact, equilibrium conditions under the elevated Eh conditions still favor dissolved iron with 17% in the dissolved form.

Elevating the pH reduces ferrous concentrations by two orders of magnitude for each pH unit. To achieve equilibrium iron concentrations below 0.3mg/L, it is necessary to elevate the pH to 10. It is possible that lower pH values can be used if a strong oxidant, longer CT, or some combination is used. This should be investigated in subsequent ZVI research.

Table 4.5: Equilibrium distribution of iron species.

<table>
<thead>
<tr>
<th>pH6 Eh-50</th>
<th>(PREPTANK CONDITIONS)</th>
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</thead>
<tbody>
<tr>
<td>Component</td>
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<tr>
<td>Cl-1</td>
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</tr>
<tr>
<td>E-1</td>
<td>0</td>
</tr>
<tr>
<td>Fe+2</td>
<td>46.508</td>
</tr>
<tr>
<td>Fe+3</td>
<td>1E-16</td>
</tr>
<tr>
<td>H+1</td>
<td>-0.014082</td>
</tr>
<tr>
<td>Na+1</td>
<td>0.005</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Eh700</th>
<th>(EFFLUENT CONDITIONS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>Total dissolved</td>
</tr>
<tr>
<td>Cl-1</td>
<td>0.005</td>
</tr>
<tr>
<td>E-1</td>
<td>0</td>
</tr>
<tr>
<td>Fe+2</td>
<td>8.6267</td>
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<tr>
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</tr>
<tr>
<td>H+1</td>
<td>-0.003278</td>
</tr>
<tr>
<td>Na+1</td>
<td>0.005</td>
</tr>
</tbody>
</table>
To investigate the relationship between the redox condition in the ZVI pretreatment tank and dissolved iron in the effluent, the Cl₂ 22min run was conducted a third time, using identical conditions to the second—with one exception. The air flow in the pretreatment tank was increased from 3 L/min to 8 L/min to insure a positive ORP. The air flow was continued after pretreatment while the solution was being dosed to the source water, which had not been done in the previous experiments. This produced redox conditions of approximately 200mV (Figure 4.19c), well above levels previously achieved (20-70mV). If the elevated ORP in the ZVI pretreatment tank reduced the dissolved iron concentrations, the effluent concentration should be lower than the previous experiment. The results showed that dissolved iron concentrations in the effluent remained high, (0.40-0.53 mg/L) (Figure 4.16b).

It is possible that the increased air flow rate used in Cl₂ 22 (3) increased the turbulence exposing a greater ZVI surface area susceptible to dissolution. This may have led to the greater dissolved iron concentrations and when subsequently exposed to Cl₂, the formation of colloidal iron as an intermediary to the formation of iron floc. Since colloidal iron would not have been removed by the additional 0.45µm filter, it would be detected as dissolved iron in a preserved sample.

According to Figure 4.20, at pH 6, a redox value of 200 mV is still a relatively reducing environment. These conditions favor the dissolved Fe²⁺ species. Conditions in the source water (ORP~700mV) favor the Fe³⁺ amorphous solid species. When the pretreated ZVI (ORP~200mV) was dosed to the source water (ORP~700mV), some of the dissolved iron would be oxidized and precipitate if adequate time was allowed. It is likely that the Cl₂ contact time with the Fe²⁺ was not sufficient to precipitate and
intermediary colloids were formed.

Conditions during ZVI preparation are critical and monitoring ORP conditions alone may not be sufficient to ensure low iron levels in the effluent. It may be necessary to add a stronger oxidant to the pretreatment tank, increase the pH of the pretreatment tank, increase the pH of the source water, or some combination thereof.

4.2.4 Assessing the influence of ZVI addition on Precoat Filtration Operating Parameters

The pH values generally increased with time for all runs but were relatively consistent varying between 5.97 and 6.49 (Figure 4.21). Values were monitored and adjusted as necessary.
Turbidity generally decreased with increasing run time (Figure 4.22). Values decreased from approximately 0.3 NTU to approximately 0.1 NTU by the end of most runs. Three runs did not conform to this pattern: Cl2 22min(1), Cl2 22min(2), and Cl2 22min(3). These are the three runs in which dissolved iron showed up in the effluent. There is no correlation between turbidity and iron concentrations (Figure 4.23).

Pressure generally increased exponentially throughout the duration of the run (Figure 4.24). Initial pressure was between 1.0 and 1.5psi and final pressure varied between 4 and 5.5psi, with two exceptions. When ZVI was not dosed to the source water, the pressure reached 2.5psi within one hour and remained constant for the duration of the run. During the run Cl2 22min (3), pressure increased from an initial value of 1.5psi to a final value of 12.5psi. As discussed above, where high concentrations of dissolved iron are exposed to oxidizing conditions an iron floc is formed. This would contribute to head

![Graph showing pH values under differing water quality conditions](image)

**Figure 4.21:** pH values under differing water quality conditions measured hourly during the pilot precoat filtration studies.
Figure 4.22: Turbidity values under differing water quality conditions measured hourly during the precoat filtration studies.

Figure 4.23: Turbidity as a function of dissolved iron in the effluent during pilot study.
Figure 4.24: Pressure values under differing water quality conditions recorded hourly during the pilot precoat filtration studies.

loss development as witnessed in this run.

Depending on the conditions in the ZVI preparation tank, more or less amorphous solids and iron floc may be generated. This will have to be monitored and the body feed rate adjusted accordingly. Body feed is dosed at a rate of 1mg/L for every mg/L of discrete particles and up to 10 mg/L for every mg/L of amorphous solids in order to maintain filter cake porosity and to minimize head loss development (AWWA, 1995).

Under normal precoat filtration operating conditions, terminal head loss is reached at 35 psi and the run is terminated. Extrapolating from Figure 4.22, head loss would be reached after 8.5-9.75 hours for all runs except Cl₂ 22min (3). This run likely had a greater amount of iron floc, which clog filters faster than discreet particles, generated as a result of the increased air flow rate. Under these conditions, terminal head loss would be reached with in 6.5 hours.
4.2.5 Arsenic Leaching Characteristics from Zero Valent Iron

As discussed in Chapter 2, post-treatment dissolution experiments produced very small amounts of dissolved arsenic species (Lackovic et. al., 2000) and TCLP (Toxicity Characteristic Leaching Procedure) analysis of spent media indicated the arsenic concentration in the leachate was two orders of magnitude lower than the regulated 5mg/L for TCPL results (Nikolaidis et al., 2003). In an attempt to verify this, a leaching study was performed on the spent ZVI media. This was done using a ratio of 10:1 deionized water to dry solids. The container was sealed and turned end over end for 48 hours. The resulting arsenic concentration was 0.040mg/L, 25 times less than the regulated TCPL limit of 1mg/L.

Some studies indicate that the TCLP may not accurately predict the leaching behavior of drinking water treatment residuals containing arsenic (Amlan, et al., 2004; Hooper et al, 1998). When spent media were exposed to conditions more like those in municipal solid waste (MSW) landfills, leached arsenic reached greater concentrations than those achieved using the TCPL. The leaching characteristics of arsenic from ZVI will need to be investigated, in order to dispose of the residuals in a way which will not contaminate ground water.
CHAPTER 5

SUMMARY AND CONCLUSIONS

Conclusions reached as a result of this research are as follows:

• The presence of an oxidant exerts a strong influence on arsenic removals by ZVI, with high removals occurring at elevated ORP values.

• The influence exerted by pH on arsenic removals by ZVI is drastically reduced at pH values 5-8 if sufficient pretreatment time is allowed for the creation of sorption sites.

• ZVI amended precoat filtration is an effective treatment for the removal of arsenic but close attention needs to be paid to conditions as they relate to iron dissolution.

• The pH of the ZVI pretreatment is important because of the possibility of iron dissolution and the kinetics of iron oxidation.

• When using pretreated ZVI to amend precoat filtration for the removal of arsenic, body feed rate may need to be adjusted to minimize head loss development.

• SO$_4$ does not exert a strong influence on arsenic removals by ZVI when pretreatment is used to create sorption sites.

The objective of this research was to investigate the removal of arsenic from drinking water using zero valent iron (ZVI). Specifically, water quality conditions were investigated to determine the optimal pH and redox conditions for the removal of arsenic and to investigate what solids and selected species dominated under these conditions. The influence of sulfate on arsenic removal was also investigated. Simultaneously, the influence exerted by these conditions on the dissolution of iron from the ZVI was investigated. This information was used to fulfill a final objective—to design, build, and
run a pilot scale experiment using a precoat filtration strategy to remove ZVI which had been dosed to the source water to remove arsenic.

Prior to this work, the use of ZVI as a discrete particle dosed to source water for arsenic removal to be later removed by filtration, has not been investigated. The majority of research conducted has used either columns or batch reactors. The advantage of ZVI dosing is that both rate limiting steps, the creation of sorption sites and mass transfer processes, can be optimized. The ZVI can be prepped in a day tank under specific conditions to optimize the creation of sorption sites. The use of mixing can accelerate the rate of arsenic transport to the sorption site. The iron and arsenic are removed, if conditions are maintained, by the filter with minimal iron dissolution or influence on operating parameters like head loss development or filter run length.

During the bench studies the presence of an oxidant exerted the largest influence on arsenic removals. In the absence of an oxidant, a condition established by bubbling high purity N\textsubscript{2} through diffuser stones in to the solution, removals were very low and varied from 10-15%. Under oxidizing conditions, established by bubbling O\textsubscript{2} or dosing sodium hypochlorite, removals were very high and varied from 90-\rightarrow 99.75% with one exception. At pH 8, in the absence on sulfate, while bubbling O\textsubscript{2}, 69.5% removals were achieved. It is expected that this was an error attributable to a filter error because the iron concentration in the effluent was very high (8.4mg/L) and under the same conditions except in the absence if SO\textsubscript{4}, 90% removals were achieved and the dissolved iron concentration was 0.65mg/L.

During the bench studies, which had a 5 hour contact time, pH did not significantly influence arsenic removals over the range of pH values of 5-8. Removals
were generally high at all pH values when an oxidant (O₂ or Cl₂) was present in the system. As previously stated, the removal of arsenic by ZVI is dependant on the generation of sorption sites generated by the corrosion of iron. The rate of iron dissolution and corrosion is dependant on pH and has been shown to influence arsenic removals.

In column studies the rate of sorption site generation is paramount because the continued input of arsenic can exceed the available sites from a static ZVI dosing. During batch studies with no ZVI pretreatment, removals are closely related to new site generation (Yu et. al. 2006). This study shows that if ZVI is pretreated for a sufficient time (18 hours in this study), creating an abundance of sorption sites, removals are not so dependant on pH. This is especially true if pretreated ZVI will be dosed to the source water at a constant rate. Under these conditions removals will likely be more dependant on mass transfer processes of the arsenic making its way to the sorption site to be removed.

Iron dissolution generally increased with decreasing pH during the bench studies. While bubbling N₂, dissolved iron concentrations were greater than the USEPA secondary standard of 0.30mg/L at all pH values 5-8. In the presence of residual chlorine dissolved iron concentrations below the secondary standard at all pH values except 5.

Dissolved iron concentrations were minimized at pH 7 while bubbling O₂. Concentrations were above the secondary standard at all pH values except 7. At pH 8 dissolved iron concentrations were higher than at pH 7 and higher than concentrations at pH 8 under reducing conditions. This is an unexpected result as the pH of minimum iron solubility is near 11. At pH 6 dissolved iron concentrations were twice as great as the
standard. If a ZVI solution at pH 6 is dosed to source water at a flow less than 5% of the total flow, dilution alone may reduce dissolved iron concentrations to levels well below the standard. Since sorption site generation is maximized at pH 6 (Bang et al., 2002) and dissolved iron concentrations can be reduced through dilution upon dosing, pH 6 may be a reasonable value for the pretreatment of ZVI. If however, dissolved iron appears in the effluent, pH will need to be elevated.

During the pilot scale—ZVI amended precoat filtration—arsenic removals generally increased with increased contact time and increased oxidant strength ranging from 41.7-71.5% removals. A maximum of 71.5% removal was achieved with a 22 minute contact time, a Cl₂ residual of 1.5mg/L, and an elevated pretreatment air flow rate. Dissolved iron was below the secondary standard in all except three filtration runs which used Cl₂ as an oxidant and a 22 minute contact time. Dissolved iron concentrations varied from 0.3-0.78mg/L during these runs but were below 0.12mg/L during all others. The Cl₂ 22min run was repeated twice in an attempt to resolve the issue, to no avail. Additional filtration was incorporated to the first replication in an attempt to eliminate any particulate iron which may have broken through. When this did not eliminate the iron in the effluent, the redox files for the pretreatment periods were examined. This revealed reducing conditions during the pretreatment periods for the runs with the elevated iron concentrations in the effluent and oxidizing conditions during the pretreatment periods for the runs with the low iron concentrations in the effluent. The air flow rate in the ZVI pretreatment tank was increased during the second repeat in an effort to elevate the ORP to a positive value and oxidize the dissolved iron to reduce the levels in the effluent. The ORP during the third pretreatment period was approximately 200mV, and the air flow
continued for the duration of the filtration run. This was well above the values achieved during all runs associated with low effluent iron concentrations. This did not eliminate the iron. Other techniques which may be necessary to eliminate iron in the effluent include the following: increase the pH of the pretreatment tank to at least pH7, increase the pH of the source water to at least pH7, add a stronger oxidant to the pretreatment tank, or some combination of these.

Under normal precoat filtration operating conditions, terminal head loss is reached at 35 psi and the run is terminated. Pressure generally increased exponentially through out the duration of the runs. Final pressure varied between 4 and 5.5psi in all but two experiments. Extrapolating, terminal head loss would be reached after 8.5-9.75 hours of filtration. When ZVI was not dosed to the source water, the pressure reached 2.5psi within one hour and remained constant for the duration of the run. During the run Cl2 22min (3), pressure increased from an initial value of 1.5psi to a final value of 12.5psi. This run likely had a greater amount of amorphous solids and iron floc generated as a result of the increased air flow rate. Under these conditions, terminal head loss would be reached with in 6.5 hours. This suggests that the method of ZVI pretreatment will influence operating parameters and attention should be paid to creating conditions conducive to sorption site creation while minimizing the production of amorphous solids.
CHAPTER 6

RECOMMENDATIONS FOR FUTURE RESEARCH

This research was a preliminary assessment and illustrates that ZVI is an effective adsorbent for arsenic removal which can be added to contaminated source water and later removed by filtration. Several areas need further research to determine the optimal pretreatment conditions to maximize the removal of arsenic while minimizing the dissolution of iron. The following is a list of recommended research topics to achieve this goal.

• Investigate the influence of different ZVI pretreatment pH and ORP values on the removal of arsenic and dissolution of iron.

• Investigate the influence to ZVI pretreatment time on the removal of arsenic and dissolution of iron.

• Investigate the influence of different ZVI pretreatment oxidants on the removal of arsenic and dissolution of iron.

• Investigate the influence of different source water pH values on the removal of arsenic and dissolution of iron.

• Investigate precoating the filter with ZVI to minimize start up times.

Specifically investigate pretreating ZVI for less than two hours at pH 7 using Cl$_2$.

• Investigated the leaching characteristics of arsenic from ZVI under conditions which more closely mimic the conditions in MSW landfills to evaluate if the residuals pose an environmental risk.
REFERENCES


USEPA. 2000. Arsenic Removal from Drinking Water by Coagulation/Filtration and Lime Softening Plants. EPA/600/R-00/063.


APPENDIX A

STANDARD OPERATING PROCEDURES

1. Ph
2. Redox Measurements Potential

3. Laboratory Glassware Cleaning

4. X-Ray Diffraction

5. Ferrous Iron

6. Sulfide
Standard Operating Procedures

1. pH

Principle
pH indicates the hydrogen ion (positively charged hydrogen atom) concentration of a solution, a measure of the solution's acidity. The pH of a solution can be determined directly by measuring the electric potential arising at special electrodes immersed in the solution.

Apparatus
ACCUMET CAT # 13-620-229 sensor
CONSORT R305 meter

Reagents and materials
pH standards (4, 7, 10)
Acid washed Erlenmeyer flask

Method
1. Hold the sensor by the module
2. Align the module with the meter body
3. Push the module firmly into the meter
4. Perform a 2 point calibration
   a. Press CAL
   b. Clean the sensor with distilled water and blot dry with a lint-free tissue
      Place the sensor in the pH 7 standard ensuring the solution is above the cell chamber slot. Hold the sensor in the standard and press CAL. The lower right region of the display will show CAL in progress.
   c. Wait till the automatic endpoint appears
   d. Clean the sensor with distilled water, blot dry with a lint-free tissue and repeat steps b, and c for the next standard.
   e. Meter will indicate calibration successful.
   f. Place the sensor in the sample ensuring the sample is above the cell chamber slot
   g. Record the reading
5. Clean the sensor with distilled water and blot dry with a lint-free tissue

Quality Control
Calibrate instrument prior to its use
Do duplicates of all readings.

References
CORNING, CHECKMATE II, Instruction manual
Standard Operating Procedures

2. REDOX MEASUREMENTS

Principle
Redox potential measurements are used to determine the oxidizing or reducing capacity of a solution and are commonly made in polluted streams, chlorinated waters, industrial waste waters, and other water samples.

Apparatus
a. ORION Redox probe
b. CONSORT R305 meter (with mV reading ability)

Reagents and materials
Clean 250 mL erlenmyer flask
ORION 900001 reference filling solution
ORION 967901 ORP standard

Method
1. Connect the electrode to the meter
2. Choose appropriate filling solution to best match ionic strength of solution.
3. Rinse meter with DI and blot dry with lint free paper
4. Place the electrode in the ORP standard.
5. Filling solution should always be at least one inch above the level of the solution being measured.
6. When the reading stabilizes, press CAL.
7. Adjust mV reading to match standard.
8. Press CAL.
9. Rinse meter with DI and blot dry with lint free paper.
10. Place sensor in sample and record reading once the reading stabilizes.

Calculations
Read mV in meter

Quality Control
Do duplicates of all readings.

References
Orion instruction manual
Standard Operating Procedure

3. LABORATORY GLASSWARE CLEANING

1. Nitric acid washing
   a. Always work under the nitric acid hood, wearing safety glasses, face shield, lab coat, apron and acid resistant gloves.
   b. Use acid neutralizer to clean up spills, dispose acid in appropriately labeled waste container, kept under the hood.
   c. Do not wash metals with acid.
   d. Do not let acid soak in plastic sample containers and caps; only rinse plastic containers.

2. Volumetric flasks, pipettes, beakers, Erlenmeyer flasks, and other glassware (nitric wash)
   a. Empty contents from glassware to hazardous waste collection bottle if the solution contained arsenic or into the drain if it did not and remove all labels.
   b. Rinse 6x with RO water to prevent expending acid.
   c. Carefully pour some nitric acid in glassware and slowly pour it out while rotating glassware so that the acid touches the whole inner surface. Repeat this process 3x.
   d. 5 mL AAS sample vials are soaked in 1:1 nitric acid for 24 hrs instead of step c.
   e. Rinse 6x with RO water.
   f. Wrap openings with foil to protect from dust and dry in 60° C drying oven overnight. Then store under bench.

3. Glass sample vials (40, 50 ml)
   a. Remove labels, remove caps and septa, empty contents (to hazardous waste collection bottle if the solution contained arsenic or into the drain if it did not).
   b. Rinse 6x with RO water.
   c. Soak vials that contained solution with arsenic in 1:1 nitric acid for 24 hrs. For the rest proceed to step e.
   d. Rinse 6x with RO water.
   e. Let soak overnight in soapy water (phosphate free).
   f. Rinse 6x with RO water.
   g. Wrap tightly in foil to protect from dust.
   h. Dry in 103° C oven, overnight.
   i. Bake at 550° C for 2 hours in muffle furnace.

4. Plastic caps, silicone septa
   a. Rinse at least 3x with RO water and then soak overnight in soapy (phosphate free) water.
   b. Rinse 6x with RO water.
   c. Place in glass beaker and cover with foil to protect from dust.
   d. Dry in 60° C oven.
5. **Chromic acid washing**
   a. Always work under the chromic acid hood, wearing safety glasses, face shield, lab coat, apron and acid resistant gloves.
   b. Use acid neutralizer to clean up spills, dispose acid in appropriately labeled waste container, kept under the hood. If the chromic acid has turned blue, it is spent. Do not mix spent acid with good acid.
   c. Do not wash metals with acid.
   d. Do not let acid soak in plastic sample containers and caps; only rinse plastic containers.

References
Standard Operating Procedures

4. X-RAY DIFFRACTION

Principle
In X-ray diffraction (XRD), a monochromatic x-ray beam is directed toward a crystalline sample and the intensities of the x-rays leaving the crystal is measured as a function of the geometric relationship between the sample surface, incident beam direction, and exit beam angle.

Apparatus
X-ray Diffraction Instrument

Reagents and materials
None

Method
Start-up Procedure
6. Check the following before starting:
   --The main power switch on the wall is in the on position.
   --Shutter #1 is in the external position.
   --The (kV) and (mA) are at the lowest setting.
7. Turn on the power switch on the main console (the buzzer will sound).
8. Turn on the water chiller (the buzzer should stop).
9. Check to see that the X-ray ready light is on. If not check the Plexiglas doors.
10. Turn on computer.
11. Turn on the power switch on the small control console and toggle the reset button.
12. Place the sample in the holder and replace cover.
13. Turn on X-rays, slowly turn kV to 40, slowly turn mA to 30.

Running the first sample
At the computer, double click the data scan program icon. Select scan menu. Enter File ID, scan ID, and note if desired. Click setup. Enter desired range. Hit Go. To evaluate your scan, use Jade program.

Running subsequent samples
1. Turn mA to minimum. Turn kV to minimum.
2. Turn x-rays off.
3. Place sample in holder.
4. Turn x-ray on and adjust kV then mA.

Shut down procedure
1. Turn down mA to minimum. Turn down kV to minimum.
2. Turn off x-rays.
3. Wait ten minutes for tube to cool down.
4. Turn off main power.
5. Turn off power on controller console.
6. Turn off water chiller.
7. Shut down computer.

Quality Control

References
UNH ME561 X-ray Laboratory
Instrument instruction manual
Standard Operating Procedures

5. FERROUS IRON

Principle
The 1,10-phenanthroline indicator in Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the iron concentration. Ferric iron does not react. The ferric iron concentration can be determined by subtracting the ferrous iron concentration from the total test.

Apparatus
Hach DR/2000 Direct reading spectrophotometer

Reagents and materials
Ferrous Iron Reagent Powder Pillows
Sample Cell, 25mL, matched pair

Method
1. Enter the stored number for ferrous iron, (Fe$^{2+}$) powder pillows. Press 255 ENTER. Display will show Dial nm to 510.
2. Rotate the wavelength dial until the small display shows: 510nm. Press ENTER.
3. Fill sample cell with 25mL of sample.
4. Add the contents of one ferrous Iron Reagent Powder Pillow to the sample cell. Swirl to mix.
5. Press SHIFT TIMER. A three minute reaction time will begin.
6. When timer beeps, the display will show: mg/L Fe$^{2+}$. Fill a second sample cell with 25mL of sample (the blank).
7. Place the blank into the cell holder. Close the light shield.
8. Press: ZERO. The display will show: Zeroing... then: 0.00mg/L Fe$^{2+}$
9. Place the prepared sample into the into the cell holder. Close the light shield.
10. Press: READ. The display will show: Reading... then the result in mg/L Fe$^{2+}$ will be displayed.

Quality Control
Check accuracy using dilutions of a stock ferrous ammonium sulfate, hexahydrate.
Do duplicates of all readings.

References
Hach Water Analysis Handbook
Standard Operating Procedures

5. SULFIDE

Principle
Hydrogen sulfide and acid-soluble metal sulfides react with N, N-dimethly-p-phenylenediamine oxalate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration.

Apparatus
Hach DR/2000 Direct reading spectrophotometer

Reagents and materials
Sulfide Reagent Set
Sample Cell, 25mL, matched pair

Method
1. Enter the stored number for sulfide (S\textsuperscript{2-}). Press 690 ENTER. Display will show Dial nm to 665.
2. Rotate the wavelength dial until the small display shows: 665nm. Press ENTER.
3. Pipet 25mL of sample into a clean sample cell.
4. Fill a second sample cell with 25mL of deionized water (the blank).
5. Add 1.0mL Sulfide 1 Reagent to each sample cell. Swirl to mix.
6. Add 1.0mL Sulfide 2 Reagent to each sample cell. Immediately swirl to mix.
7. Press SHIFT TIMER. A five minute reaction time will begin. When timer beeps, the display will show: mg/L \text{ S}^{2-}.
8. Place the blank into the cell holder. Close the light shield.
9. Press: ZERO. The display will show: Zeroing... then: 0.000mg/L \text{ S}^{2-}
10. Immediately place the prepared sample into the into the cell holder. Close the light shield.
10. Press: READ. The display will show: Reading... then the result in mg/L \text{ S}^{2-} will be displayed.

Quality Control
Performed duplicates of all readings.

References
Hach Water Analysis Handbook
APPENDIX B

ZERO VALENT IRON DIGESTION RESULTS
<table>
<thead>
<tr>
<th></th>
<th>ZVI1 mg/kg</th>
<th>ZVI2 (mg/kg)</th>
<th>AVERAGE mg/kg</th>
<th>STANDARD DEVIATION mg/kg</th>
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<td>As 193.696</td>
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<td>45.54</td>
<td>43.11</td>
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<tr>
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<tr>
<td>Se 196.026</td>
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<td>BDL</td>
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<tr>
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<td>BDL</td>
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<td>Total Mass</td>
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<tr>
<td>Percentage</td>
<td>0.93</td>
<td>1.27</td>
<td>109.57</td>
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</tbody>
</table>
APPENDIX C

PARTICLE SIZE DISTRIBUTION FOR ZERO VALENT IRON
Explanation of Data Reported by Microtrac Instruments

(Terminology, abbreviations and calculations shown on reports)

*Philip E. Plantz, PhD*

Applications Note

SL-AN-16 Rev B

Provided By:
Microtrac, Inc.
Particle Size Measuring Instrumentation
Microtrac data include many values that are essential to developing particle size distribution specifications and evaluating data. Each of these items is explained as well as changes to be expected. The display provides a quick look at values while actual printed reports and exported data are developed in the “Reports” section. For more detailed information, please refer to the “User’s Manual” in the HELP section of Microtrac FLEX software or contact the Microtrac, Inc at 727 – 507 – 9770 in Largo, FL.

PARTICLE SIZE DATA and INFORMATION

Sizes – The default unit for size is micrometers (microns). The sizes in this table are not customizable and are determined by the optical of the instrument. Customized sizes are selectable in the SETUP portion of the software and are displayed in Size Percent Data.

Percentiles – Software selectable Percentile Points in microns, show the percentage of the volume (or weight if the density for all the particles is the same) that is smaller than the size indicated. Percentiles can be shown as percent larger and indicates the volume percent larger than the size shown. The “50 percent point” is the “median diameter” of D50 and represents one type of average particle size.
**Summary Data**

**MV** – Mean diameter in microns of the "volume distribution" represents the center of gravity of the distribution. Mie or modified Mie calculations are used to calculate the distribution. Implementation of the equation used to calculate MV will show it to be weighted (strongly influenced) by a change in the volume amount of large particles in the distribution. It is one type of average particle size or central tendency.

**MI** – (Nanotrac only) Mean diameter of the intensity distribution. Intensity distribution is not calculated using Mie theory or Modified Mie theory.

**Molecular Weight (MW)** – A calculation to provide molecular weight (grams/mole). See equation below for details.

**MN** – Mean diameter, in microns, of the "number distribution" is calculated using the volume distribution data and is weighted to the smaller particles in the distribution. This type of average is related to population or counting of particles.

**MA** – Mean diameter, in microns, of the "area distribution" is calculated from the volume distribution. This area mean is a type average that is less weighted (also less sensitive) than the MV to changes in the amount of coarse particles in the distribution. It represents information on the distribution of surface area of the particles of the distribution.

**CS** - Calculated surface – Provided in units of M²/cc, the value provides an indication of the specific surface area. The CS computation assumes smooth, solid, spherical particles. It may be converted to classical units for SSA of M²/g by dividing thru value by the density of the particles. It should not be interchanged with BET or other adsorption methods of surface area measurement since CS does not take into effect porosity of particles, adsorption specificity or topographical characteristics of particles.

**SD** – Standard Deviation in microns, also known as the Graphic Standard Deviation (SDg), is one measure of the width of the distribution. It is not an indication of variability for multiple measurements. Equation to calculate is: \((84\% - 16\%)/2\).

**SDg or Ai** – Often known as \(\sigma_i\) - Inclusive Graphic Standard Deviation. Includes more than 90% of the distribution and includes tails of distributions. The SD includes only 67% of the distribution.

<table>
<thead>
<tr>
<th>SDg Value</th>
<th>Terminology</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>Very well sorted (Very narrow)</td>
</tr>
<tr>
<td>0.35 - 0.5</td>
<td>Well sorted</td>
</tr>
<tr>
<td>0.50 - 0.710</td>
<td>Moderately well sorted</td>
</tr>
<tr>
<td>0.71 - 1.0</td>
<td>Moderately sorted</td>
</tr>
<tr>
<td>1.0 - 2.0</td>
<td>Poorly sorted</td>
</tr>
<tr>
<td>2.0 - 4.0</td>
<td>Poorly sorted</td>
</tr>
<tr>
<td>&gt; 4.0</td>
<td>Extremely poorly sorted (very broad)</td>
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</tbody>
</table>

**KG** - Often known as SKg - Kurtosis (peakedness) of a distribution is taken from sedimentology and uses phi values for calculation. It measures the departure from normality of a curve. Peakedness refers to "how sharp" a peak is. Terms exist to describe the magnitude of kurtosis or how sharp the peak is. Platykurtic (from the Greek meaning "fat") describes a distribution having low kurtosis while leptokurtic (Greek meaning "slim") describes a distribution having high kurtosis. The following describes values for KG.

<table>
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<tr>
<th>KG Value</th>
<th>Terminology</th>
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<tr>
<td>&lt; 0.67</td>
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<tr>
<td>0.67 - 0.90</td>
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<tr>
<td>0.90 - 1.11</td>
<td>Mesokurtic</td>
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<tr>
<td>1.11 - 1.50</td>
<td>Leptokurtic</td>
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<tr>
<td>1.50 - 3.00</td>
<td>Very leptokurtic</td>
</tr>
<tr>
<td>&gt; 3.00</td>
<td>Extremely leptokurtic</td>
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</table>
Ski - Inclusive Graphic Skewness - Skewness is a measure of how asymmetrical a curve is and how it varies from a normal, bell-shaped curve. Ski includes 90% of the distribution and includes the "tails" of the distribution. A symmetrical curve has a Ski value of 0.00. Values of 1.00 to 0.30 show fines influencing the skew. Values of -0.30 to -1.00 show coarse particles as influencing the skew.

Mz - Graphic Mean provides a less coarse-particle weighted mean particle size than MV. While it includes the median value, it can provide a different and possibly better control value since both small particles and large particles are included in the calculation.

Peaks Summary - Microtrac software automatically provides information on multi-modal distributions. The "Dia", "vol%" and "width" identify individual modes.

Dia - The 50% (D50) of each mode is calculated after determining the minimum and maximum sizes contributing to the specific peak under consideration. For two modes, each will have a separate 50%. When only one mode is present, the Dia will equal the 50% of the particle distribution.

Width - Indicates the width of the peak under consideration. For two modes, each will have a calculated width given in microns. When only one mode is present in the distribution, the width = 2 (SD) = 84% - 16%.

Vol - The calculated contribution in percent of each peak to the total volume of the distribution.

RMS Residual - (Root mean square) Microtrac performs calculations to provide particle size distributions. The calculation is completed when software-decided least error is attained. The RMS is presented as percent.

UDEF Name and UDEF Data - Microtrac software allows the user to perform special calculations to suit a customized need. Each calculation is given a name (UDEF Name) by the user. The result is presented as the data (UDF Data).

Percent Passing, Percent Retained and Percent Channel Data

Percentiles - Values are selectable over the range 1% to 99% in 1% increments. They are calculated and then located in the table. Use SETUP command to access selections.

Tabular Data - The measuring range of the instrument is divided into fixed "channel" or particle sizes. Particles sizes are identified on the left column in units of microns or sieve sizes as selected by the operator. Cumulative data values are on the same line as the particle size and are read as "percent smaller (passing) than". The data may also be displayed as "percent larger (retained) than". For data presented as "percent smaller than", volume percent-in-channel (%-CHAN) values are read as volume percent between the particle size on the same line and the line below. For data presented as "percent larger than" or "%-RETN", the volume percent between sizes is read as the amount between the size on the same line and the size above.

Example: In the data display shown (percent smaller than), 24.06% of the volume is smaller than 44 microns. The percent between adjacent sizes for percent passing format is shown beside the larger size, e.g., 5.19% lies between 44.00 microns and 40.35 microns. When data are presented in the PERCENT RETAINED format, as indicated at the top of the data column, the percent between sizes would be located beside 40.35 microns.

Size Percent Data - Operator may enter up to 100 desired particle sizes. Microtrac will calculate the associated volume percentile.

Cumulative Graph - A cumulative graph, with "%PASSING (pass)" or "%RETAIRED (Ret)" tabular data are presented as a line graph or in 3-D as selected by the 3D button part of the GRAPH TOOLBAR. Graph may be modified by using scrolling arrows and icons located in the graph area. The values used to produce the graph are those in the tabular data identified as "%Smaller" or "% Larger". The percent point for a specific size may be found by determining the point of intersection of the desired
size and the cumulative curve for any size interest and then determining the volume percent from the vertical axis on the left. See above for information on percentile calculation and display.

Microtrac only presents data within the particle size range of a given model or instrument set-up. Particles larger than or smaller than the instrument measuring range are not included as part of the distribution or other data. For this reason, "percent smaller or larger than data begin with 100% at the largest or smallest size measured in a sample, even though some particles may exist outside the measuring range.

Relative Graph (%CH) - When bar graphs are printed or displayed, midpoints of channel sizes are used. Line graphs are automatically developed by connecting the midpoints. Graphical data provide an opportunity to view the distribution at a glance. In the example data display, 5% (using the right axis) of the volume is indicated at approximately 90 microns. Best quantitative data are obtained from the numerical data in the tables. Volume percent in channel data are used to produce the graph.

\[
\begin{align*}
MV &= \frac{\Sigma V_i d_i}{\Sigma V_i} \\
MN &= \frac{\Sigma (V_i d_i^3)}{\Sigma (V_i d_i^3)} \\
MA &= \frac{\Sigma V_i}{\Sigma (V_i/d_i)} \\
MI &= \frac{\Sigma I_i d_i}{\Sigma I_i} \\
MW &= \rho N \frac{(\pi/6)d^3}{5} \\
SD &= \frac{(84\%-16\%)/2}{6.6} \\
\end{align*}
\]

Where:  
\[V = \text{Volume percent between sizes.}\]  
\[d = \text{Size represented by the center between any 2 sizes.}\]  
\[I = \text{Intensity percent between sizes}\]  
\[\rho = \text{Density of the particles}\]  
\[M_z = \frac{(16\% + 50\% + 84\%)}{3}\]  
\[SD_g = [(84\% - 16\%)/4] + [(95\% - 5\%)/6.6]\]  
\[K_g = (95\% - 5\%)/[2.44(75\% - 25\%)]\]  
\[Sk_l = \left\{ \left\{ [16\% + 84\% - 2(50\%)] / (84\% - 16\%) \right\} + \left\{ [5\% + 95\% - 2(50\%)] / (95\% - 5\%) \right\} \right\} / 2\]
APPENDIX D

BENCH RESULTS
| Trial | pH | mv | SO4 | Initial As mg/L | Final As (total) | final As II | Final As III | % As Removal | FeT (mg/L) | Fe+2 mg/L | Fe+3 mg/L | S-2 mg/L | SO4 mg/L | mV |
|-------|----|----|-----|-----------------|-----------------|-------------|---------------|--------------|-------------|-----------|-----------|-----------|----------|----------|----|
| 1     | 5  | N2 | +   | 2               | 1.8             | 0.68        | 1.12          | 10           | 18          | 10        | 8         | <0.001    | 230      | 117      |
| 2     | 5  | N2 | -   | 2               | 1.7             | 0.36        | 1.34          | 15           | 27          | 11.8      | 11.2      | <0.001    | 139      |
| 3     | 5  | O2 | +   | 2               | 0.024           | <0.005      | 0.024         | 98.8         | 17          | 11        | 6         | 0.006     | 330      | 350      |
| 4     | 5  | O2 | -   | 2               | 0.042           | 0.027       | 0.015         | 97.9         | 8.7         | 2.11      | 6.59      | <0.001    | 209      |
| 5     | 5  | Cl2| +   | 2               | 0.006           | <0.005      | 0.006         | 99.7         | 0.012       | <0.01     | 0.012     | <0.001    | 220      | 985      |
| 6     | 5  | Cl2| -   | 2               | 0.032           | <0.005      | 0.032         | 98.4         | 3.1         | 1.37      | 1.73      | <0.001    | 503      |
| 7     | 6  | N2 | +   | 2               | 1.8             | 0.22        | 1.58          | 10           | 7.2         | 1.51      | 5.69      | <0.001    | 240      | 20       |
| 8     | 6  | N2 | -   | 2               | 1.8             | 0.57        | 1.23          | 10           | 7.9         | 3         | 4.9       | <0.001    | -50      |
| 9     | 6  | O2 | +   | 2               | 0.008           | 0.01        | -0.002        | 99.6         | 0.46        | 0.36      | 0.1       | <0.001    | 250      | 286      |
| 10    | 6  | O2 | -   | 2               | 0.028           | 0.033       | -0.005        | 98.6         | 0.59        | 0.32      | 0.27      | <0.001    | 320      |
| 11    | 6  | Cl2| +   | 2               | <0.005          | 0.011       | <0.005        | >99.75       | 0.067       | <0.01     | 0.067     | <0.001    | 230      | 911      |
| 12    | 6  | Cl2| -   | 2               | <0.005          | <0.005      | <0.005        | >99.75       | <0.005      | <0.01     | <0.005    | <0.001    | 908      |
| 13    | 7  | N2 | +   | 2               | 1.8             | 0.67        | 1.13          | 10           | 3.7         | 3.1       | 0.6       | <0.001    | 260      | -190     |
| 14    | 7  | N2 | -   | 2               | 1.7             | 0.68        | 1.02          | 15           | 1.6         | 1.31      | 0.29      | <0.001    | -167     |
| 15    | 7  | O2 | +   | 2               | 0.056           | 0.04        | 0.016         | 97.2         | 0.023       | <0.01     | 0.023     | <0.001    | 240      | 130      |
| 16    | 7  | O2 | -   | 2               | 0.067           | 0.026       | 0.041         | 96.65        | 0.19        | 0.01      | 0.18      | <0.001    | 200      |
| 17    | 7  | Cl2| +   | 2               | 0.005           | 0.008       | -0.003        | 99.75        | 0.018       | <0.01     | 0.018     | <0.001    | 230      | 860      |
| 18    | 7  | Cl2| -   | 2               | 0.011           | <0.005      | 0.011         | 99.45        | 0.082       | 0.01      | 0.072     | <0.001    | 228      |
| 19    | 8  | N2 | +   | 2               | 1.7             | 0.64        | 1.06          | 15           | 0.5         | 0.04      | 0.46      | 0.02      | 230      | -251     |
| 20    | 8  | N2 | -   | 2               | 1.7             | 0.58        | 1.12          | 15           | 0.68        | 0.42      | 0.26      | <0.001    | -320     |
| 21    | 8  | O2 | +   | 2               | 0.2             | 0.054       | 0.146         | 90           | 0.65        | <0.01     | 0.65      | <0.001    | 240      | 230      |
| 22    | 8  | O2 | -   | 2               | 0.61            | 0.074       | 0.536         | 69.5         | 8.4         | 0.05      | 8.35      | <0.001    | 222      |
| 23    | 8  | Cl2| +   | 2               | 0.017           | <0.005      | 0.017         | 99.15        | 0.082       | <0.01     | 0.082     | <0.001    | 230      | 713      |
| 24    | 8  | Cl2| -   | 2               | 0.012           | 0.008       | 0.004         | 99.4         | 0.028       | <0.01     | 0.028     | <0.001    | 726      |
APPENDIX E

PILOT RESULTS
<table>
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<th>Oxidant</th>
<th>CT, min</th>
<th>Time (min)</th>
<th>Time (hours)</th>
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<th>C/Co *100</th>
<th>Iron mg/L</th>
<th>Fe+2 mg/L</th>
<th>psi</th>
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<th>Cl2 mg/L</th>
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