BENCH SCALE APPLICATION OF THE HYBRIDIZED ZERO VALENT IRON PROCESS FOR THE REMOVAL OF DISSOLVED SILICA FROM WATER

A Thesis

by

NILESH MOHAN MORAR

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Chair of Committee,	Yongheng Huang
Committee Members,	Bill Batchelor
	Elena Castell-Perez
Head of Department,	Stephen W. Searcy

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ABSTRACT

Dissolved silica in water is notorious for precipitating on industrial equipment. Scale formation can occur within tubes of a boiler, heat exchangers, and cooling towers, turbine blades are susceptible to deposit formation, and reverse osmosis membranes are susceptible to glass like scaling all leading to reduced efficiency. Conventional chemical treatment methods such as hot lime, activated alumina, and MgO require heavy dosage of chemicals and have limited pH ranges for which removal is effective. A more robust and cost-effective dissolved silica removal technique is desirable.

The hybridized zero-valent iron (hZVI) process, now commercially available as Pironox^{TM}, uses zero-valent iron (Fe^0) as its main reactive media developed to remove heavy metals/metalloids, reactive oxyanions, and impurities from water/wastewater. The distinctive feature of this novel chemical treatment platform is the controlled formation of magnetite as the main iron corrosion product in the presence of aqueous Fe^{2+}. The hZVI system was shown to reduce dissolved silica from 70 mg/L to below 5 mg/L in a pilot scale demonstration for treating flue-gas desulfurization wastewater.

In this study bench scale tests were performed using a single stage, continuously stirred tank reactor to optimize the removal efficiency of dissolved silica (100 mg/L as SiO$_2$) using the hZVI process. It was demonstrated the continuous formation of magnetite in an hZVI system played a key role in achieving high system performance with respect to dissolved SiO$_2$ removal. Using ZVI grains with an average diameter of 5 microns optimal reagent dosages were determined to be 27.9 mg/L (0.5 mM) Fe^{2+} and

10 mg/L (0.72 mM) to 15 mg/L (1.07 mM) NO_3-N.   With added Fe^{2+} and nitrate at

these dosages or higher removal efficiency was 88% to 99% over a broad range of pH

6.8 to 9.8 offering a more flexible approach to removing dissolved silica from water

when compared to conventional treatment methods. Using the optimal reagents the

hZVI system sustained dissolved silica removal with >95% efficiency over an extended

period. It was also shown that increasing the reactor temperature from 25°C to 90°C did

not attenuate dissolved SiO_2 removal in an hZVI system.

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NOMENCLATURE

$Al(OH)_3$	Aluminum Hydroxide
$\gamma\text{-}Al_2O_3$	Aluminum Oxide
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcium Carbonate
$Ca(OH)_2$	Calcium Hydroxide (lime)
CTB	Cooling Tower Blowdown
EDS	Energy Dispersive X-ray Spectroscopy
HCl	Hydrochloric Acid
HRT	Hydraulic Retention Time
$H_3SiO_4^-$	Silicate Anion
H_4SiO_4	Mono-Silicic Acid or Ortho-Silicic Acid
$H_6Si_2O_7$	Dimeric Silicic Acid
hZVI	Hybridized Zero-Valent Iron
Fe^0	Elemental Iron
Fe^{2+}	Ferrous
$FeCl_2$	Ferrous Chloride
Fe_2O_3	Hematite
Fe_3O_4	Magnetite
$\alpha\text{-}FeOOH$	Goethite
$\gamma\text{-}FeOOH$	Lepidocrocite

hZVI	Hybridized Zero-Valent Iron
M	Molarity (moles/L)
MgO	Magnesium Oxide
N	Normality (eq/L)
Na_2CO_3	Sodium Carbonate or Soda Ash
NaOH	Caustic Soda
$NaNO_3$	Sodium Nitrate
Na_2SiO_3	Sodium Metasilicate
NH^{4+}	Ammonium
NO_3-N	Nitrate as Nitrogen
P	Pressure
SEM	Scanning Electron Microscope
SiO_2	Silicon Dioxide or Silica
T	Temperature
ZVI	Zero-Valent Iron

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1. INTRODUCTION

Bench scale tests were performed to evaluate the effectiveness and optimal conditions for the removal of dissolved silica from water using a hybridized zero-valent iron (hZVI) process. The hZVI system employs a highly reactive $ZVI/Fe_3O_4/Fe^{2+}$ mixture demonstrated to remove heavy metals in laboratory and pilot scale tests offering a potentially cost competitive alternative to other available water treatment methods. This success has led to the exploration of removing dissolved silica from water using this technology.

Pure silicon is rarely found in its elemental form but rather as silica (SiO_2) and is comprised of two of the most abundant elements in the earth's crust. Accordingly, its ubiquitous presence in water should come as no surprise. Silica is commonly found as quartz, which is the major constituent of sand, but is present in water predominantly as mono-silicic acid. Silicic acid is unregulated and is not on the United States Environmental Protection Agency's primary or secondary contaminant candidate list as there are generally positive benefits on human health and there is no obvious toxicity. For example, silica may help prevent atherosclerosis and maintain bone health (Martin, 2007). Its presence in water, however, is of significant concern in industrial applications.

1.1 Concentration of silica in natural waters

Soluble silica is present in surface water and groundwater concentrations generally ranging from 1 – 20 mg/L and 7 – 45 mg/L, respectively (Davis et al., 2001)

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and may be as high as 100 mg/L (Koo et al., 2001). Seawater has far less dissolved

silica and its concentration generally ranges from 2 - 14 mg/L (Iler, 1979). The

regulation of silica in seawater is due to both biological and inorganic removal.

Interestingly, planktonic diatoms consume silicic acid in order to support their cell wall

structure without which they would not survive. It is estimated there are nearly 100,000

species in existence (Bien et al., 1958; Ning, 2010). Concentrations of silica in river

water range from 5 - 35 mg/L; however, it is reduced to 5 - 15 mg/L as it approaches the

sea (Iler, 1979). Soil water has a range of 10 - 60 mg/L dissolved silica and it is not as

easily reduced due to saturation at soil sorption sites. Geothermal aquifers have

significantly higher concentrations ranging from 300 - 700 mg/L at temperatures

between 200 and 350°C. Volcanic and oil production fields well waters may have

concentrations ranging from 50 - 300 mg/L (Ning, 2003, 2010).

1.2 Problem statement

Dissolved silica in water is notorious for precipitating on industrial equipment

and reverse osmosis membranes leading to reduced efficiency. Dissolved silica may

also compete with removal of other contaminants in treatment systems.   The formation

of silica scale within tubes of a boiler in a steam power plant is a very old and dreaded

issue. Siliceous scale formed within these tubes can inhibit rapid heat transfer creating

local overheating and tube failure (Behrman and Gustafson, 1940).   Likewise, heat

exchanger tubes used in geothermal power plants are susceptible to silica scale

formation reducing both flow pressure of the brine and efficiency of heat transfer

(Sugama and Gawlik, 2002).   Silicic acid is also extremely volatile in steam and may

polymerize and deposit on turbine blades reducing efficiency. Prevention of deposition requires near complete removal of dissolved silica (Iler, 1979). The Electric Power Research Institute reported in 70% of power plants water use may be restricted due to the presence of high concentrations of dissolved silica (Gill, 1998).

High concentrations of silica in geothermal water may be severely problematic in the development of power due to scale formation in cooling towers (Iler, 1979). Cooling towers are commonly used in both power plant and manufacturing facilities to facilitate the evaporative cooling process. Heat transfer surfaces in cooling towers may be susceptible to silica scale formation inhibiting heat transfer. To mitigate this problem, water called cooling water blowdown (CTB) is removed from the system and replaced with fresh water in order to dilute silica. However, CTB is typically discharged into the sewer system and is unable to be recycled (Liao et al., 2009).

Fouling of reverse osmosis membranes is a common problem in desalination plants that reduces the flow rate of the feed water. A gradient of dissolved solids, referred to as concentration polarization, may form at the surface of the membrane. As the silicic acid concentration becomes supersaturated, glass-like scaling develops at the surface of the membrane. Membrane fouling may be irreversible requiring complete replacement of the membranes (Koo et al., 2001; Braun et al., 2010).

The maximum concentration of dissolved silica that can be in water without forming scales is dependent on the application. Al-Rehaili (2003) reported high-pressure boilers required less than 8 mg/L, while the concentration in steam turbines require a much lower concentration of 20 μg/L. Up to 10 mg/L dissolved silica may be

tolerated in feed to reverse osmosis systems without fouling if they are operated with less than 98% recovery rates (Potts et al., 1981).

There are several studies on various chemical treatment methods for removing dissolved silica from water through the 1940's and 1950's. Although there have been refinements to these methods since that time there has been very little in the way of new discoveries. Notable exceptions are reverse osmosis and ion exchange. Both are highly efficient at removing dissolved silica from water; however, these methods have the downside of higher energy and replacement costs.

Popular chemical treatment methods such as hot lime, activated alumina, and MgO require substantial dosage of chemicals for effective treatment. The difficulty of removing dissolved silica using these methods are typified by multi-step processes, a limited range of pH under which removal is effective, and excessive sludge production. Removing dissolved silica from water in a cost effective manner remains challenging.

2. LITERATURE REVIEW

2.1 Chemistry of silica

Silicon is a group IV element on the periodic table and is a metalloid having characteristics of both a metal and non-metal. It is arguably second only to carbon in terms of complexity of chemistry. Both have four valence electrons in their outer shell providing significant flexibility for bonding. Unlike carbon, however, the volume of available literature on silicon is comparably limited and its chemistry is not as fully understood. Iler (1979) compiled perhaps the most comprehensive silica chemistry text summarizing nearly all of the available literature through the publication date.

The compound silica shares properties with water. Both are similar in volume and primarily comprised of oxygen by mass bonded with either silicon or hydrogen atoms. Amorphous SiO_2 has 1.17 g oxygen per cm^3 while water has 0.89 g oxygen per cm^3 assuming water density of 1 g/cm^3. Hence, water is one of the few liquids in which silica is soluble (Iler, 1979).

2.1.1 Speciation in water

In general, silica hydrolyzes in water to form silicic acid. Silica is generally known to be present in natural water as $Si(OH)_4$ and can easily be re-written as H_4SiO_4, a weakly acidic acid. It is generally termed either mono-silicic or ortho-silicic acid and its molecular geometry is tetrahedral in shape. The dissolution of silica in water is shown in equation 1 (Iler, 1979):

$$(SiO_2)_x + 2H_2O \leftrightarrow (SiO_2)_{x-1} + Si(OH)_4 \tag{1}$$
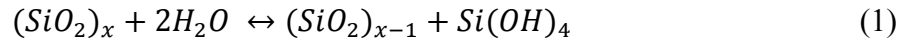
Mono-silicic acid has a pK$_a$ of 9.8 (Benjamin, 2002), the pH where approximately one half of the silicic acid disassociates to form silicate anions represented by equation 2:

$$Si(OH)_4 + H_2O \leftrightarrow H_3O^+ + H_3SiO_4{}^- \tag{2}$$
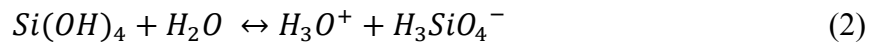
Natural waters generally have a pH ranging from 6.5 to 8.5. Therefore it would be expected most of the mono-silicic acid would not de-protonate in natural waters. Further de-protonation is possible at the second higher pK$_a$ of 11.8 (Ning, 2010).

There does not appear to be a comprehensive study on silica speciation in water particularly for higher order oligomers. While available silica speciation data is limited at near neutral pH (Zotov and Keppler, 2002) there is general agreement within available literature that the monomeric species is predominantly present in water (Ning, 2010). At various temperature and pressure ranges Zotov and Keppler (2002) concluded the dimer silica species ($H_6Si_2O_7$) most likely accounts for most of the polymeric soluble species. At near neutral pH the dimer species may represent up to 6% of the species present. Some research has indicated the dimer species may be present in quantities up to 50%, with increasing pH. Other higher order polymeric species may also exist in natural waters albeit in insignificant quantities (Cary et al., 1982) (Davis et al., 2001).

2.1.2 Solubility

Silica may be present in water as dissolved or colloidal forms. The most soluble colloid, amorphous silica, is generally soluble in the water ranging from 70 mg/L to 150 mg/L at standard conditions. For larger particle sizes of amorphous silica prepared from sodium silicate, the solubility is at the lower end of this range. On the other hand, quartz or sand exhibit much lower solubility approximately equal to 6 mg/L. The relationship for determining solubility of amorphous silica has been demonstrated, within a pH range of 2 to 8, to be a function of both particle size and surface energy. The broad range of particle size may also be attributed to impurities, crystalline structure and/or the level of inner hydration between molecules (Alexander, 1957) (Iler, 1979).

In general as temperature increases the solubility of silica increases. Historical experiments performed with various types of silica, including amorphous silica, have shown a near linear relationship between solubility and temperature (Marshall, 1980b). This relationship best describes why cooling of water may cause scale and deposit formation. The solubility at near ambient temperature ranges from 100 to 150 mg/L. However, at higher temperatures, mono-silicic acid is very volatile and polymerizes with increasing temperature (Iler, 1979). Fournier and Rowe (1977) completed an exhaustive review of solubility as a function of temperature and completed experiments, including the effects of pressure, to refine the results for both amorphous silica and quartz. Solubility was shown to maximize at 1660 mg/kg at 340°C and to be 890 mg/kg at the critical point (Fournier and Rowe, 1977).

As pH increases beyond 8.5, the solubility of silica increases exponentially. There does not appear to be agreement for determining solubility at lower levels of pH. The reference in Okamoto (1957) exhibits a nearly level slope until pH 8.5 (Okamoto et al., 1957). Other studies have shown a slight decrease in solubility until pH 7 to 8 (Alexander et al., 1954) (Tarutani, 1989). The increase in solubility above pH 8.5 is attributable to the formation of the silicate anion while the solubility of $Si(OH)_4$ is unaffected (Alexander et al., 1954).

Marshall et al. have completed an exhaustive study on the effect of certain electrolytes on the solubility of amorphous silica. At temperature ranges between 25 and 300°C, increasing $NaNO_3$ from approximately 0 to 6 molar decreased solubility. At 25°C solubility decreased by approximately 60%. In general, solubility in the presence of electrolytes increased with temperature (Marshall, 1980a). Ten separate sets of salts dissolved in water were tested to determine the their effect on the solubility of silica. NaCl exhibited similar results as $NaNO_3$. Saturated $CaCl_2$ achieved the greatest effect, with a 95.7% decrease in solubility. The effect of electrolytes on the solubility of silica was ultimately dependent on the cation with the order being first the divalent cations Mg^{2+} and Ca^{2+}, followed by Li^+, Na^+, and K^+. Neutral pH 5 to 7.5 was reported. Equilibrium was reached within 18 hours for solutions with more than 1 M salt concentration (Marshall and Warakomski, 1980). Mixed electrolyte solutions were also later considered (Marshall and Chen, 1982).

2.1.3 Polymerization

In general, $Si(OH)_4$ polymerizes in water to the extent it is supersaturated. Accordingly, polymerization tends to occur at higher concentrations. Without the presence of solid phase amorphous silica, $Si(OH)_4$ will polymerize first to form higher order dissolved oligomers. There is a propensity to form siloxane (Si-O-Si) bonds as $Si(OH)_4$ condenses. Nucleation takes place in the form of ring-like, spherical structures. The rate of polymerization is proportional to the OH^- concentration above pH 2 (Iler, 1979). Polymerization increases with pH and is maximized at pH 9 (Goto, 1956). The reaction rate was also shown to increase with temperature in the range of 26° to 65°C (Greenberg and Sinclair, 1955).

Ostwald ripening occurs as smaller particles dissolve and redeposit onto larger particles. Accordingly, particle size increases while the number of particles decreases. At pH above 7 particle evolution is more rapid until a diameter of 5-10 nm is reached. Particle evolution is characterized by gelling. As pH further increases the silicate ion gradually dominates. Aggregation of particles diminishes due to repelling of negatively charged ions. Silicic acid, therefore, more easily polymerizes than the silicate anion. However, the presence of salt with a concentration greater than 0.2 – 0.3 N may enhance aggregation by lowering the ionic charge on silicate particles at ambient temperature (Iler, 1979).

2.1.4 Molybdate reactive test

The standard assay for determining the concentration of dissolved silica in water is the molybdate reactive test. This colorimetric test involves the formation of

molybdosilicic acid by reaction of silicic acids and molybdate at low pH. The concentration of dissolved silica is proportional to the intensity of color development. Only "reactive" silica may be measured using this test. Mono-silicic acid reacts very quickly while polymeric species require longer development times (Alexander et al., 1954). The monomeric species reacts within 75 seconds while the dimer reacts within 10 minutes (Ning, 2010).

2.2 Historical methods for removing dissolved silica

In any industrial enterprise, the treatment for removal of a contaminant such as silica must be economically viable and practically feasible. Both have been a challenge in the removal of silica from water. The purpose of this discussion is not a complete economic analysis of options. However, with a viable chemical treatment option economics are most likely the main driver for implementation of a particular method for removal.

The removal mechanisms for conventional chemical treatment methods include precipitation, co-precipitation, and adsorption. In most cases, the added reagents greatly exceed the proportion of silica removed. These methods may also have unintended effects such as increased hardness, alkalinity, or excessive sludge production. pH may also be required to be adjusted to achieve the desired outcome.

2.2.1 Lime soda softening

The addition of magnesium in combination with lime soda softening has been moderately successful by adsorption of silica onto magnesium hydroxide precipitate. The lime ($Ca(OH)_2$) and soda (Na_2CO_3) softening process entails the precipitation of

magnesium hydroxide and calcium carbonate to remove hardness from water. At a pH greater than 10.5, the reported data for silica removal in a study of industrial municipal wastewater operating plants showed 68% removal efficiency of dissolved silica at best. The initial silica concentration was reduced from 22 mg/L to 7 mg/L with an initial and final magnesium hardness (as $CaCO_3$) of 330 mg/L and 12 mg/L, respectively. In a similar laboratory demonstration removal efficiency was higher at 78%. Initial silica concentration was reduced from 64 mg/L to 14 mg/L with an initial and final magnesium hardness of 458 mg/L and 15 mg/L, respectively (Behrman and Gustafson, 1940).

Caustic soda (NaOH) was shown to improve silica removal efficiency from cooled deep well groundwater at two reverse osmosis pilot plants with better results as compared to lime soda softening in the same study. With initial silica concentration of 34.6 mg/L, removal efficiency was reported at 80% with 225 mg/L dosage of caustic soda at approximately pH 9 (Al-Rehaili, 2003). In laboratory tests removal efficiency was higher at 90.6% using 200 mg/L caustic soda with an initial concentration of 37.3 mg/L dissolved silica at pH 10.1. The mechanism for removal may either be co-precipitation with insoluble metal hydroxides or precipitation by formation of magnesium silicate or calcium silicate (Sheikholeslami and Bright, 2002).

Added MgO produced better results than lime soda softening, particularly when temperature was increased to to 95°C resulting in significantly reduced stirring time. The evolution of this method began with addition of dolomitic lime, containing 35.5% MgO and a mixture of calcium compounds. The addition of dolomitic lime without soda ash reduced silica concentrations from 20.5 mg/L to 1.8 mg/L. However, the process

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required removal of hardness from the water resulting from the calcium present in the dolomitic lime followed by reducing alkalinity for preparation and use as boiler feeder water. With the same equivalent dosage of MgO of 103 mg/L as in the dolomitic lime, silica concentration was reduced to 0.4 mg/L without the need to remove excess hardness at pH 9.9. The requirement to remove alkalinity was also alleviated. Accordingly, added MgO was the preferential method (Betz et al., 1941). Added MgO may also be used in the same process with lime soda softening for removing hardness from water. For example, at 95°C silica was removed from 20 mg/L to below 1 mg/L with added MgO, $Ca(OH)_2$, and Na_2CO_3 of 150 mg/L, 15 mg/L, 140 mg/L, respectively. Silica removal was maximized at pH 10.1 (Betz et al., 1940, 1941).

2.2.2 Aluminum and iron

$Si(OH)_4$ reacts, under certain conditions, with other acids and a limited number of basic metal cations such as iron, uranium, chromium, and aluminum. Aluminum has been more commonly used for dissolved silica removal than iron. Iler (1979) through personal communications with Goto determined $Si(OH)_4$ reacted with Al^{3+}. $Si(OH)_4$ removal was maximized at pH 9. It is not entirely clear to what extent silicic acid concentrations were reduced, however, over "long periods" colloidal aluminum silicate was formed at 25°C. $Si(OH)_4$ was also shown to adsorb onto crystalline $Al(OH)_3$ in several layers, initially rapid and then at a much slower rate (Iler, 1979). Similar results were obtained using $\gamma-Al_2O_3$ (Huang, 1975).

Adsorption of silica on activated alumina was shown to be an effective method for dissolved silica removal. Adsorption of 4.5 mg dissolved silica on 2.5 g activated

alumina was maximized at pH 8-8.5 with 90% efficiency in laboratory tests (Bouguerra et al., 2007). The alumina may also be regenerated. The downside was regeneration of the alumina required acidification followed by dosage with an alkali requiring further chemical consumption (Behrman and Gustafson, 1940). As with other historical treatment methods, the quantity of activated alumina required far exceeded silica removed. The addition of alum and sodium aluminate improved silica removal when combined with the lime soda softening process in jar tests using wastewater from two pilot plants. However the best results obtained were around 50% efficiency (Al-Rehaili, 2003). Removal by sodium aluminate has been shown to significantly reduce the concentration of dissolved silica; however, required dosages that were inordinately high (Behrman and Gustafson, 1940).

In contrast, removal by iron has historically provided limited success in the removal of dissolved silica. A major drawback was a limited band of pH to permit removal. For example, a pH of 9 was required when ferric sulfate was added to water to precipitate ferric oxide for maximum silica removal (Behrman and Gustafson, 1940). There is limited recent literature on the removal of dissolved silica by iron/iron oxides. In one case, adsorption of silicates onto iron oxides such as goethite, hematite, and magnetite were investigated. The maximum concentration of silicic acid in solution was 19.2 mg/L. At pH 7 approximately 30% was adsorbed onto magnetite within a 24 hour period. The results concluded adsorption of silicic acid was proportional to surface area of the iron oxide present. According to the study, surface area increased in the order of

magnetite, goethite, and hematite. Sorption was also maintained over a wide range of

pH and maximized at pH 8 (Jordan et al., 2007).

Another study analyzing the effects of silica on the removal of 1,1,1 –

trichloroethane by iron noted low silica adsorption at a pH of 7.3. Adsorption of silica

improved with increasing pH while reducing the removability of the contaminant (Kohn

et al., 2003). The study revealed permeable reactive barriers may be "deactivated" by

adsorption of silica by preventing the corrosion of iron to facilitate the removal of the

contaminant (Kohn et al., 2003). While the study was not focused on the removal of

silica, this underscored the need to remove silica from water in order to enhance the

removal other contaminants.

2.2.3 Reverse osmosis

Reverse osmosis is a membrane filtration technology becoming increasingly

popular in water treatment and desalination in a wide variety of industries (Malaeb and

Ayoub, 2011). Reverse osmosis is the most efficient non-chemical treatment method to

remove dissolved silica (Koo et al., 2001). Dissolved silica may be removed with

efficiency greater than 98%. However, fouling of membranes by silica scale formation

on membranes is a major shortcoming in this type of treatment.   Silica scaling can

obstruct membranes increasing the cost and efficiency using this technology.

2.2.4 Ion exchange

Ion exchange involves the use of resins as the mechanism for contaminant

removal. Due to dissolved silica's ionic state at high pH, strong base anion resins are

required for silica removal using this technology. Near complete removal can be

accomplished, for example, for water used in high pressure boilers near supercritical

pressure where silica can be extremely volatile (Iler, 1979).   A significant downside of

this technology is the need to replace resins as they age and competition with other

anions that may be present in the water.

2.3. Emerging technology using zero-valent iron

2.3.1 Brief history of zero-valent iron

As the name implies, zero-valent iron (ZVI or Fe^0) is elemental iron.

Chemically, ZVI is a reducing agent and may provide electrons to react with various

oxidants including many environmental contaminants. Gillham and O'Hannesin (1994)

originally developed the corrosion of ZVI as a method to reduce contaminants such as

halogenated hydrocarbons (Gillham and O'Hannesin, 1994). The use of ZVI grains as

the main reactive media to construct Permeable Reactive Barriers (PRBs) has been a

promising solution developed over the last twenty years for the removal of contaminants

in subsurface environments.

However, there are significant limitations to the traditional ZVI application for

the removal of contaminants. The iron may be subject to passivation principally by the

formation of iron oxides and oxy-hydroxides such as hematite (Fe_2O_3) and goethite (α-

FeOOH) on the surface of the ZVI thereby inhibiting the removal of contaminants by

chemical reaction with the iron. In other words, the potential for using ZVI as a

reducing agent to remove contaminants is diminished once the oxides form. The

presence of nitrate in water has been specifically cited as a contributor to passivation

(Luo et al., 2010).
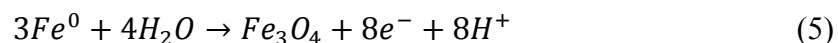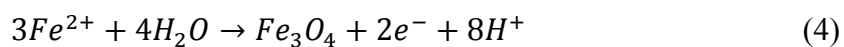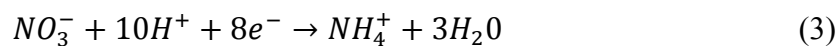
2.3.2 Hybridized zero-valent process

With an improved understanding of iron corrosion and the passivation

mechanism, Huang (2013) and his team at Texas A&M University developed a simple

yet effective method to overcome the ZVI passivation problem, allowing ZVI media to

maintain its reactivity indefinitely for contaminant removal until the media exhausts.

The general approach is to regulate aqueous Fe^{2+} to create a chemical environment in a

ZVI system that facilitates the formation of magnetite as the main iron corrosion

product, which exist either as a surface coating on ZVI grains or as a discrete particulate

matter independent from ZVI grains. A unique fluidized bed reactor system is used to

harvest the ZVI reactivity for continuously and effective removal of various target

contaminants from a wastewater. The process is known as hybridized ZVI in the

literature and is now commercially available as Pironox^{TM} by Evoqua Water

Technologies LLC (Alpharetta, GA).

The effectiveness of the hZVI system for metal/metalloids removal has been

demonstrated in both laboratory tests and field demonstrations. Molybdate (MO_4^{2-}) was

shown to be completely reduced and removed using this system (Huang, Tang et al.

2012). Hexavalent selenium (as selenate, or SeO_4^{2-}) and Hg(II) have been shown to be

decreased from 22 mg/L and 1.14 mg/L to ~10 µg/L and ~10 ng/L, respectively, in a

continuously treated pilot scale demonstration for treating flue-gas desulfurization

wastewater (Huang et al., 2013). As(III), As(V), Cr(VI), Cd(II), Pb(II), and Cu(II) were

also shown to be reduced to sub-ppb levels. Dissolved silica was decreased from 70

mg/L to less than 5 mg/L at near-neutral pH and ambient temperature in the same
demonstration (Huang et al., 2013).

The presence of aqueous Fe^{2+} is the distinctive feature of the hZVI process that
overcomes the passivation problem of the traditional ZVI approach (Huang et al., 2003;
Zhang and Huang, 2006). $Fe^{2+}_{(aq)}$ regulates the iron surface chemistry and allows for
conversion of iron corrosion products, likely to be ferric oxides or oxy-hydroxides that
would otherwise passivate the ZVI, to magnetite. The formation of magnetite as the
predominant iron corrosion product on the surface of the ZVI is a second feature of the
process. Unlike iron oxides such as hematite and goethite, magnetite has a distinctive
stoichiometry in that two oxidation states of iron are present in the compound. In
essence, magnetite possesses excellent electron conductivity comparable to that of many
metals. The unique property, in conjunction with intrinsic structural defects and
flexibility, allows electrons to efficiently migrate outwards from the ZVI core through
the coating to the solid-liquid interface where reactions may be hosted (Huang et al.,
2012).

The half-reactions used to derive the magnetite formation equation are shown in
equations 3 through 5.

$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O \tag{3}$$

$$3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + 2e^- + 8H^+ \tag{4}$$

$$3Fe^0 + 4H_2O \rightarrow Fe_3O_4 + 8e^- + 8H^+ \tag{5}$$

Among the assumptions that Huang et al. (2003) made was Fe^{3+} and Fe^{2+} in the magnetite formed product were in the ratio of 2:1. Based on electron and mass balance, the formation reaction of magnetite in the presence of nitrate as the source of oxygen was shown to follow the stoichiometry shown in equation 6:

$$NO_3^- + 2.82 Fe^0 + 0.75 Fe^{2+} + 2.25 H_2O \rightarrow NH_4^+ + 1.19 Fe_3O_4 + 0.50 OH^- \qquad (6)$$
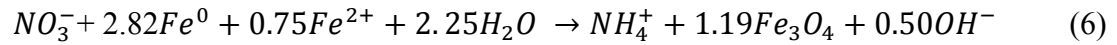
Huang and Zhang (2005) also showed dissolved oxygen as effective at forming magnetite in the presence of adequate $Fe^{2+}_{(aq)}$ without passivation of the system. The corrosion product was predominantly lepidocrocite using both uncoated and magnetite coated ZVI (equations 7 and 8, respectively) followed by the formation of magnetite (equation 9) (Huang and Zhang, 2005):

$$4 Fe^0 + 3 O_2 + 2 H_2O \rightarrow 4\gamma \ FeOOH \qquad (7)$$

$$4 Fe_3O_4 + O_2 + 6 H_2O \rightarrow 12\gamma \ FeOOH \qquad (8)$$

$$8\gamma \ FeOOH + Fe^0 \rightarrow 3 Fe_3O_4 + 4 H_2O \qquad (9)$$
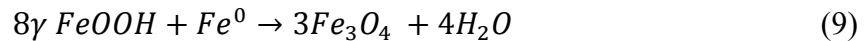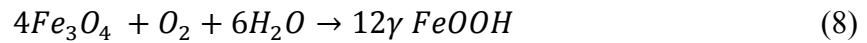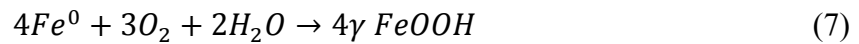
In the case of dissolved oxygen, the role of Fe^{2+} was more likely to act as a catalyst rather than determine the iron corrosion product, noting that reactions 7 to 9 are likely to occur dynamically depending on the layers formed on the ZVI coated surface and the presence or absence of dissolved oxygen. Once oxygen is depleted equation 9 takes

control. Oxygen reduction was shown to have minimal interference with nitrate reduction to form the iron corrosion products (Huang and Zhang, 2005).

3. OBJECTIVE

This study aims to examine selected factors that may affect dissolved silica removal in the hZVI treatment system and to explore various operation conditions for achieving high system performance with respect to dissolved silica removal. The key hypothesis was continuous formation of magnetite from iron corrosion process is essential for the hZVI system to achieve high silica removal. The specific objectives of this study were to:

(1) determine dissolved silica removal efficiency achievable using the hZVI technology with an average ZVI diameter of 5 microns in a single stage, continuously stirred tank reactor with a 4 hour hydraulic retention time and feedwater influent concentration of 100 mg/L as SiO_2;

(2) establish the relationship between the reagent dosages of ferrous (Fe^{2+}) and nitrate (as N) and the system removal efficiency of dissolved silica; and

(3) evaluate the effect of temperature on removal efficiency with the operating temperature varied from 25°C to 90°C.

4. MATERIALS AND METHODS

4.1 Reactor treatment system setup

A single stage, continuously stirred tank reactor was utilized for all tests. The 2-liter stainless steel reactor was divided by a partition separating the reaction zone and settlement zone. A mixer (JB Series electric stirrer) was affixed to a stand and suspended centrally in the reaction zone approximately 4 cm above the bottom of the reactor. Mixing speed was selected to ensure fluidization and even gradient of the ZVI media throughout the reaction zone. An acrylic baffle was positioned between the settlement and reaction zone to minimize loss of hZVI from fluidization in the settlement zone. 2.5-cm thickness foam was placed on the surface of the mixing zone to minimize diffusion of oxygen into the reactor. **Figure 1** and **Figure 2** show a schematic of the treatment system.

Analytical grade reagents were used. A peristaltic pump (7519-10, Masterflex L/S) was employed to introduce the reagents. NO_3-N was prepared using $NaNO_3$ (Alfa Aesar) and Fe^{2+} using $FeCl_2 \bullet 4H_2O$ (J.T. Baker). The reagents were dissolved in a single container using deionized water (E-pure, Barnstead). The pH of the reagent solution was adjusted to ~2.0 with the addition of HCl (J.T. Baker). A separate peristaltic pump was used to introduce the feedwater. The feedwater containing 100 mg/L dissolved silica (as SiO_2), was prepared by dissolving $Na_2SiO_3 \bullet 9H_2O$ (Aqua Solutions) in a purified water produced by a reverse osmosis membrane unit (FP7110T-08, Flotec) with
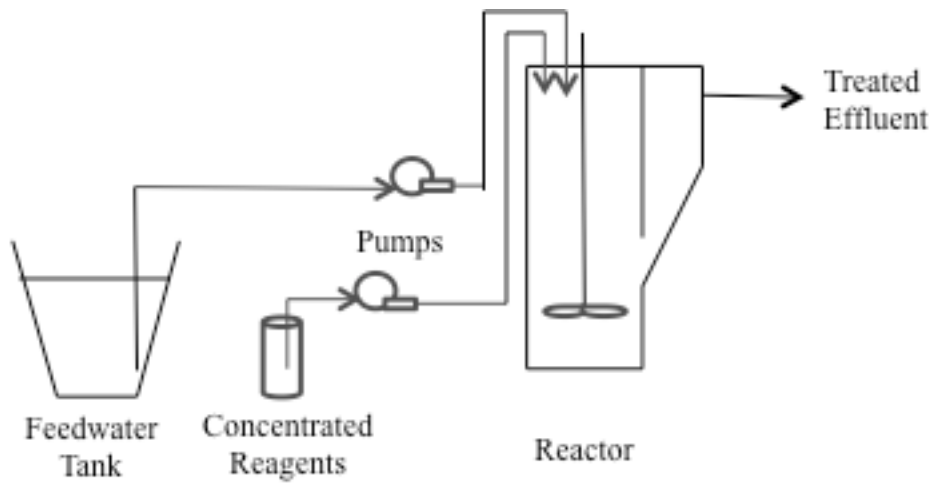
Figure 1. Schematic of hZVI treatment system (adapted from Huang et al., 2013).
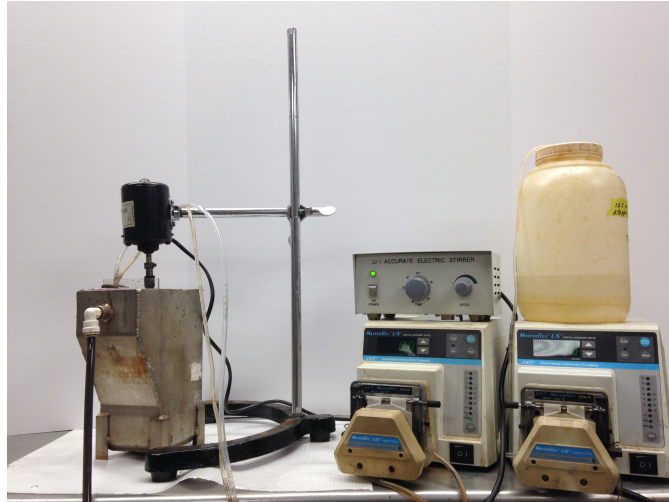
Figure 2. Photograph of the treatment system.

measured total dissolved solids < 16 mg/L.   After allowing the silica to completely

dissolve for 4 hours, the feedwater pH was adjusted to between 7 and 8 using HCl in

order to mimic the pH range of natural waters and provide comparability between

results.

The feedwater influent was introduced directly into the reactor at a rate of 8.33

ml/min, corresponding to an HRT of 4 hours. Fe^{2+} and NO_3-N were prepared at 25

times the intended dosing concentration and were introduced at a rate of 0.33 ml/min (a

dilution ratio of 25 when compared the reagent feeding rate with that of feedwater

pumping rate).   Temperature tests were conducted by immersing the reactor in a water

bath (89032-204, VWR Scientific). Temperature was measured in the reaction zone

using a generic laboratory thermometer.

4.2 Nitrate-Fe^{2+} method to precondition the media

ZVI powder (>94% purity, Sagwell Science and Technology Co., Ltd.) with an

average diameter of 5 microns was employed for all tests.   In this study, apart from two

control tests (Reactors 1 and 2), three reactors (Reactors 3, 4, 5) were preconditioned to

create an hZVI system. In each case, prior to introducing the feedwater influent and the

concentrated reagents, the hZVI system was created by allowing the ZVI media to react

with nitrate in the presence of externally added Fe^{2+}.   The process started with adding 2

L DI water to the reactor and then 150 g virgin ZVI powder (5 μm). Pre-weighed (3.4 g)

$NaNO_3$ was then added into each reactor, corresponding to a dosage of 280 mg/L as N.

$FeCl_2$ was added at a concentration of 17.5 mM (Reactor 3) or 20 mM (Reactors 4 and

5).   No adjustments to pH were made. The mixer was then turned on to allow nitrate

reduction by ZVI following equation 6. After 24 hours, a water sample collected from

the reactor was analyzed. It was found nitrate was reduced to 44.0 mg/L, 6.8 mg/L and

6.1 mg/L in Reactors 3, 4, and 5, respectively. Dissolved Fe^{2+} was not detected in any of

the samples.   Based on equation 6, Reactor 1 consumed 5.3 g of ZVI and produced 9.3 g

of magnetite. Reactors 2 and 3 consumed 6.2 g of ZVI and produced 10.8 g of

magnetite. Upon the nitrate-Fe^{2+} preconditioning, the conventional ZVI system was

converted into a hybrid system and the magnetite produced was present as both

magnetite-coated ZVI powder and discrete magnetite phases suspended in the reactor

mixture. The hZVI system was subsequently used for dissolved silica removal tests.

The variables that were explored in these tests were the feedwater influent concentration

of SiO_2, dosages of Fe^{2+} and nitrate, temperature, and salinity. Tests were conducted

once daily prior to 6 HRT (24 hours) with up to a maximum of 30 minutes of downtime

before the end of each run to replenish the feedwater influent and/or replace Fe^{2+} and

nitrate to the desired dosages for the next test run when required.

4.3 Analytical methods

NO$_3$-N was measured using ion chromatography (Dionex DX-500) equipped

with a CD-20 conductivity detector and an IonPac AS-22 separation column with a

minimum detection limit of 0.1 mg/L, in general, for anions. Both Fe^{2+} and dissolved

silica (as SiO_2) were measured colorimetrically on a UV-VIS spectrometer (T80, PG

Instruments). The 1,10-phenanthroline method was used to measure aqueous Fe^{2+} with a

minimum detection limit of 0.1 mg/L. The molybdate reactive test, method C, was used

to measure the concentration of dissolved silica with a minimum detection limit of 0.1

mg/L (APHA-AWWA-WEF, 1998). All treated effluent samples were acquired from the settlement zone of the reactor and filtered using a 0.45 μm pore size filter.

4.4 Media characterization

A sample of the media was analyzed by scanning electron microscope (SEM) (JSM-7500F, JEOL) accessorized with an energy dispersive x-ray spectroscopy (EDS) system (Oxford). The sample was prepared by withdrawing a 10 mL sample of the media in solution from the reaction zone following 12 days of continuous treatment of preconditioned media with feedwater influent containing 100 mg/L dissolved silica (as SiO_2) and dosages of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N over the same time period. After the media was allowed to settle the supernatant was decanted. The media was placed on 0.45 μm pore size filter paper in order to remove excess moisture, dried in an anaerobic chamber, and removed just prior to being analyzed.

4.5 Test methods

4.5.1 Control tests

Control tests were performed to evaluate whether a conventional ZVI only system or a ZVI/Fe^{2+} only system could effectively remove dissolved silica without the benefit of a hybridized ZVI system. Two separate systems were created without preconditioning the media. Reactor 1 was created solely with 150 g virgin ZVI powder and operated for two days without any added Fe^{2+} or nitrate. Reactor 2 was created with 150 g virgin ZVI powder and dosed with 14.0 mg/L (0.25 mM) Fe^{2+}. Thereafter, the Fe^{2+} dosages were increased to 27.9 mg/L (0.50 mM) and 55.8 mg/L (1.0 mM) for a combined total of 7 days. No nitrate was dosed in Reactor 2. The concentrations were

selected to encompass the range of Fe^{2+} dosages explored in this study. For both Reactor 1 and Reactor 2 the feedwater influent concentration was 100 mg/L SiO_2 on all days. The tests were conducted at room temperature (22°C +/- 2°C).

4.5.2 Performance benchmark tests using an hZVI system

The purpose of this test was to establish a performance benchmark for dissolved silica removal by varying both the feedwater influent concentration and the dosages of Fe^{2+} and nitrate. At the beginning of day 1, feedwater containing 200 mg/L SiO_2 was introduced upon concluding preconditioning of Reactor 3. At the same time, 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N were dosed to the reactor. At the beginning of day 3 the concentration of SiO_2 in the feedwater was reduced to 100 mg/L. The reagent dosing concentrations were not changed. At the beginning of day 4 the reagent dosing concentrations were reduced to 14.0 mg/L (0.25 mM) Fe^{2+} and 5 mg/L (0.37 mM) NO_3-N. The test lasted 4 days after preconditioning at room temperature (22°C +/- 2°C).

4.5.3 Fe^{2+} and nitrate dosing tests

The aim of this test was to observe how system performance changes as a function of varying the Fe^{2+} and nitrate concentrations each day. After preconditioning Reactor 4, the hZVI system was operated to treat the feedwater and remove dissolved silica under varying dosages of Fe^{2+} and nitrate for 24 days (3 days were omitted from the day count when the system was idle). The feedwater influent concentration was 100 mg/L SiO_2 and held constant on all days. The tests were conducted at room temperature (22°C +/- 2°C).

The results from tests performed in Section 4.6.2 established a target dissolved SiO_2 removal efficiency of >95% with feedwater influent concentration of 100 mg/L SiO_2. At this benchmark, reagent dosages were 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N. Based on the benchmark, Reactor 4 tests were designed and divided into three distinct phases. The first phase was designed to explore dissolved silica removal at reagent dosages approximate to 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N to observe whether SiO_2 removal efficiency could be improved as compared to the benchmark efficiency of >95% with changes in Fe^{2+} and nitrate dosages over a much narrower range than Reactor 3. At the beginning of day 1, reagent dosages were introduced at 34.9 mg/L (0.625 mM) Fe^{2+} and 12.5 mg/L (0.86 mM) NO_3-N. Reagent dosages were reduced in lockstep on each successive day first by reducing NO_3-N by 2.5 mg/L (0.18 mM) and then Fe^{2+} by 7 mg/L (0.125 mM) until a final dosage of 20.9 mg/L (0.375 mM) Fe^{2+} and 5 mg/L (0.36 mM) NO_3-N was reached on day 6.

The second phase explored the effect of reducing the NO_3-N dosages daily from 20 mg/L to 5 mg/L in 2.5 mg/L decrements holding the Fe^{2+} dosage constant at 27.9 mg/L (0.5 mM) in order to investigate the influence of nitrate over dissolved SiO_2 removal efficiency (days 8, 11-16). Also studied was the effect of increasing Fe^{2+} to 55.8 mg/L (1.0 mM) holding NO_3-N constant at 10 mg/L (0.72 mM) to investigate the influence of Fe^{2+} on dissolved silica removal (day 9 and 10). Day 9 was repeated on day 10 due to a temporary malfunction of the pH meter. Alternative Fe^{2+} dosages holding NO_3-N constant at 10 mg/L (0.72 mM) were already considered in the first phase.

The final phase explored the impact of substantially overdosing NO_3-N to 40 mg/L (2.86 mM) with Fe^{2+} dosages ranging from 27.9 mg/L (0.5 mM) to 0 mg/L (0 mM) in 7 mg/L (0.125 mM) decrements in order to further enhance understanding of the role Fe^{2+} played in dissolved silica removal when nitrate removal was maximized (days 20-24). As an additional control test, an hZVI only system without added Fe^{2+} or nitrate was conducted (day 17). The benchmark dosages of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N were also periodically evaluated in order to observe system performance over time (days 7,14,18 and 19).

4.5.4 Temperature tests

The aim of this test was to explore dissolved SiO_2 removal as a function of temperature ranging from 25°C to 90°C. After preconditioning Reactor 5, the feedwater influent was introduced containing 100 mg/L SiO_2. Reagents were introduced at concentrations of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N, the minimum reagent dosages to reach a targeted performance of >95% established from tests conducted utilizing Reactor 4. Both the feedwater influent (100 mg/L SiO_2) and Fe^{2+} and nitrate concentrations were held constant over 13 days. On days 1 to 3 the reaction zone temperature was 25°C. At the beginning of day 4 the temperature of the reaction zone was increased to 45°C by immersing the reactor in a waterbath. Thereafter, temperature was increased by 15°C at the beginning of each successive day until a final temperature of 90°C was reached on day 7. The process was repeated in reverse order until 25°C was reached on days 12 and 13.

4.5.5 Salinity tests

The objective of this test was to explore dissolved silica removal efficiency as a function of salt concentration in the feedwater influent. At the beginning of day 14, utilizing Reactor 5, the NO_3-N dosage was increased from 10 mg/L (0.72 mM) to 15 mg/L (1.07 mM) and Fe^{2+} was dosed at 27.9 mg/L (0.5 mM). Both reagent dosages were held constant until the end of day 16. The feedwater influent concentration was 100 mg/L SiO_2 over all days. The nitrate concentration was increased to induce a higher pH by equation 6 under the assumption the silicate anion might be more easily removed in the presence of salt. As a control, at the beginning of day 14 no salt was added to the feedwater influent. At the beginning of day 15 and 16, household sea salt without added anti-caking agents (Morton) as NaCl was added to the feedwater influent in concentrations equal to 0.25 M and 0.4 M (14,600 and 23,400 mg/L), respectively.

5. RESULTS AND DISCUSSION

5.1 Silica removal in a ZVI and ZVI/Fe^{2+} only system

In a ZVI only system dissolved SiO$_2$ removal was not effective. Reactor 1 dissolved silica removal efficiency was 7% and 10% with feedwater influent concentration of 100 mg/L SiO$_2$ on days 1 and 2 corresponding to effluent concentrations of 93 mg/L and 90 mg/L SiO$_2$, respectively. A slight discoloration of the virgin ZVI powder was observed by day 2. SiO$_2$ removal in a ZVI only system might be attributed to the formation of iron oxides such as hematite (Fe$_2$O$_3$) formed by reaction at the ZVI surface with oxygen from the influent feedwater. The mechanism by which the small of amount of SiO$_2$ was removed in a ZVI only system was not clear. The feedwater influent pH was ~7.3 on both days. The reactor pH was 8.1 and 7.8 on days 1 and 2, respectively. Fe^{2+} was not detected in the effluent on either day.

A ZVI/Fe^{2+} system (Reactor 2) showed improved efficiency of dissolved SiO$_2$ removal as compared to the ZVI only test (Reactor 1) with feedwater influent concentration of 100 mg/L SiO$_2$. Augmenting the system with 14.0 mg/L (0.25 mM) Fe^{2+} resulted in SiO$_2$ removal efficiency of 17% and 21% on days 1 and 2, respectively. Augmenting the system with 27.9 mg/L (0.50 mM) resulted in a nominal rise in removal efficiency on day 3 to 23% followed by a decline to 15% and 14% on days 4 and 5. Further augmenting the system to 55.8 mg/L (1.0 mM) Fe^{2+} showed improved performance to 21% and 23% on days 6 and 7 compared to days 4 and 5. However, no apparent trends in SiO$_2$ removal efficiency from increasing the dosage of Fe^{2+} from 14.0

mg/L (0.25 mM) to 27.9 mg/L (0.5mM) over the 7 day period were observed. The performance of Reactor 2 is shown in **Figure 3(a)** (all results in this study for a given day were reported after operating the reactor(s) for ~6 HRT (24 hours) under the test conditions presented.)

As shown in **Figure 3(b)**, pH of the reaction zone ranged from 5.9 to 6.5 over 7 days. pH of the reaction zone was nearly constant through day 4 ranging from 6.2 to 6.4. By day 5, SiO_2 removal performance reached the lowest point (13.5%) at pH 5.9 after dosing the reactor for three days with 27.9 mg/L (0.5 mM) Fe^{2+}. The pH of the reaction zone increased to 6.3 and 6.5 on days 6 and 7, respectively, when the reactor was augmented with 55.8 mg/L (1.0 mM) Fe^{2+}. Concomitantly SiO_2 removal performance increased reaching 22.9% by day 7.

Figure 3(a) shows the Fe^{2+} effluent concentrations were greater than the dosages by 7 mg/L to 15 mg/L, signifying the ZVI was not passivated over the 7 day time course. The source of additional Fe^{2+} in the effluent was likely from the oxidation of the ZVI powder. Over time a gradual browning on the surface of the ZVI powder was observed suggesting the formation of lepidocrocite (γ-FeOOH) by reaction with dissolved oxygen in the influent feedwater (equation 7). To the extent oxygen may have been depleted in the reactor it is possible a small amount of magnetite was formed (equation 9), however, this was not visually observed.
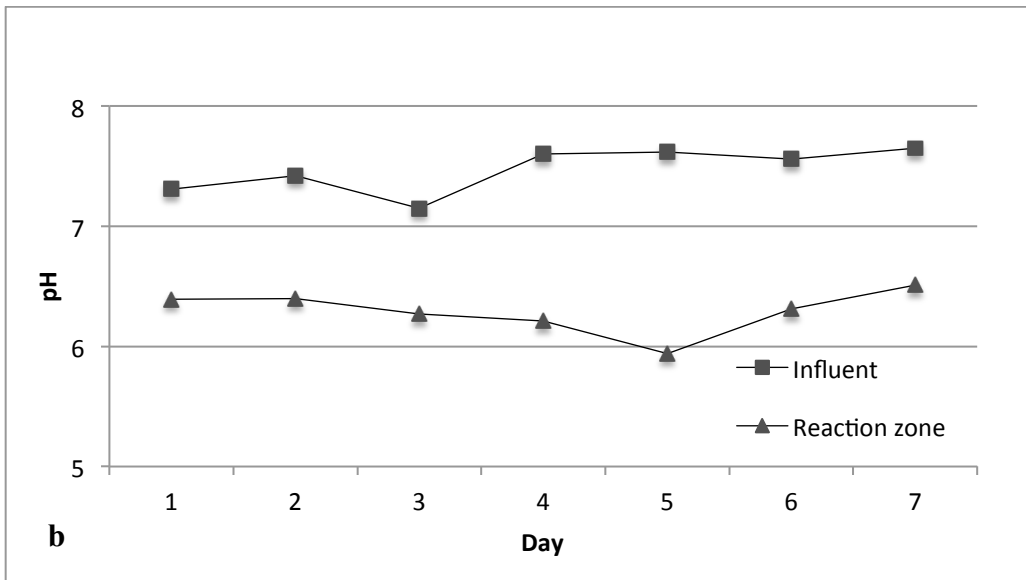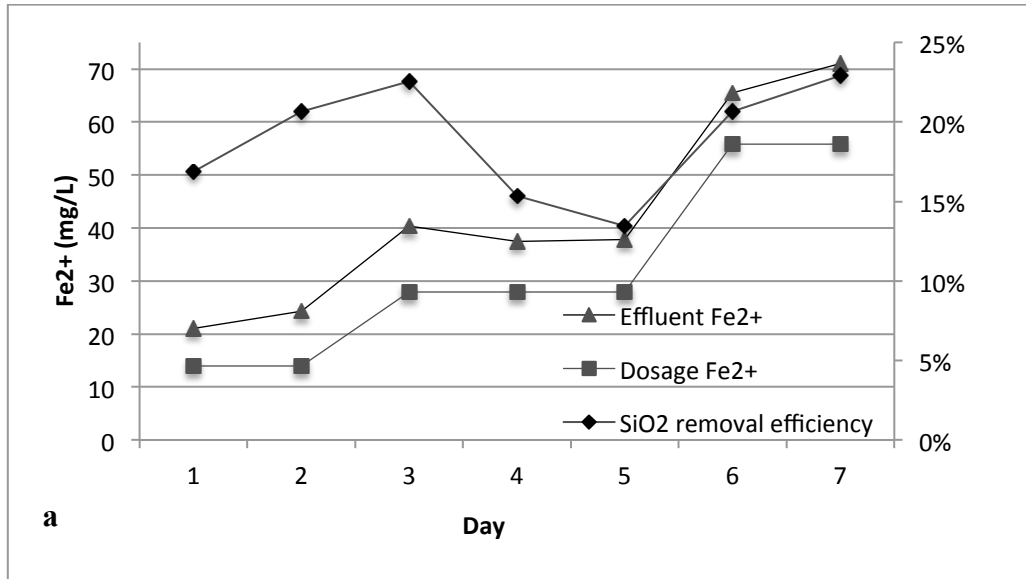
Figure 3. Performance of Reactor 2 in a ZVI/Fe^{2+} only system.
(a) Removal efficiency shown with 100 mg/L SiO$_2$ feedwater influent concentration and Fe^{2+} dosage and effluent concentrations and (b) influent and reaction zone pH.

5.2 Performance benchmark for silica removal in a hZVI system

Compared to a ZVI only system (Reactor 1) and a ZVI/Fe^{2+} only system (Reactor 2) augmenting the system with both Fe^{2+} and nitrate substantially improved the performance of the system (Reactor 3) using preconditioned media for dissolved SiO$_2$ removal as shown in **Figure 4**. Magnetite coated ZVI and discreet magnetite phases in solution were visually observed (both black in color) in the reactor after preconditioning and throughout the 4 day test. After preconditioning Reactor 3, feedwater influent concentration of 200 mg/L SiO$_2$ was introduced to the reactor. The system was augmented with 27.9 mg/L (0.5mM) Fe^{2+} and 10 mg/L (0.72 mM) NO$_3$-N and allowed to operate for 2 days. On day 2, dissolved SiO$_2$ removal efficiency was 78% (day 1 was tested after 2 HRT (12 hours) with dissolved SiO$_2$ removal efficiency of 76% and was not included in this analysis). On day 2, pH 7.7 was measured in the reaction zone, 8.4 mg/L (0.60 mM) NO$_3$-N was consumed, and 5.0 mg/L (0.09 mM) Fe^{2+} was detected in the effluent. Note it was difficult to quantify how much Fe^{2+} was consumed since the amount of Fe^{2+} released from the ZVI cannot be accurately determined.

At the beginning of day 3, the feedwater influent concentration of SiO$_2$ was reduced from 200 mg/L to 100 mg/L. With the same Fe^{2+} and nitrate dosages as day 2, dissolved SiO$_2$ removal efficiency was 96%. It should be noted although efficiency improved on day 3, at 78% removal of 200 mg/L SiO$_2$ on day 2 the net removal of dissolved silica was higher than the run with 96% removal of 100 mg/L SiO$_2$ (156 mg/L
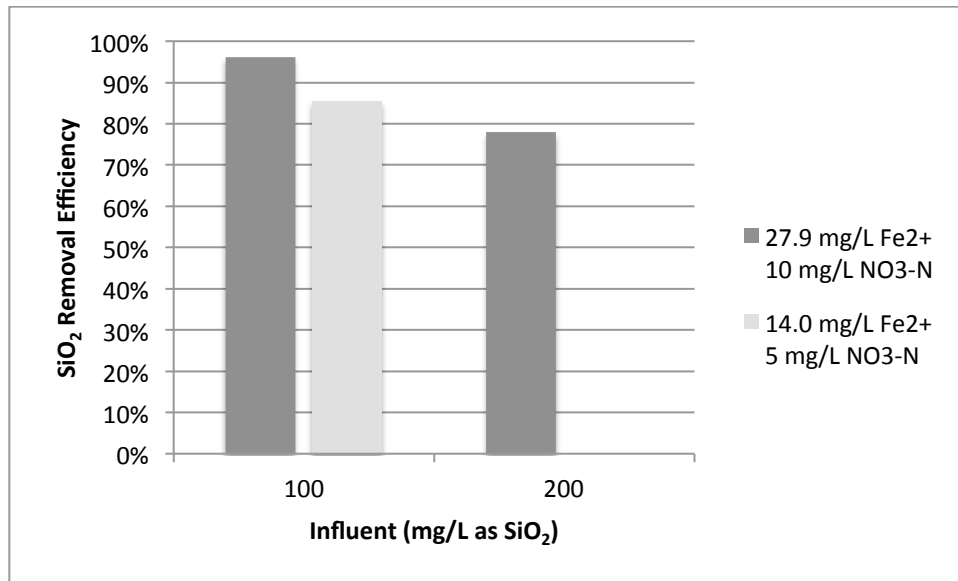
Figure 4. Silica removal efficiency with varied influent and varied reagent concentrations.
(Reactor 3)

vs. 96 mg/L). pH 8.5 was measured in the reaction zone, 9.4 mg/L (0.67 mM) NO_3-N

was consumed, and 8.5 mg/L (0.15 mM) Fe^{2+} was detected in the effluent.   pH was

higher when compared to the run with feedwater influent 200 mg/L SiO_2 (8.5 vs. 7.7).

Similarly, nitrate consumed was higher when compared to the run with feedwater

influent 200 mg/L SiO_2 (9.4 mg/L (0.67 mM) versus 8.4 mg/L (0.60 mM) NO_3-N).

While it appeared dissolved silica and nitrate might compete for removal in an hZVI

system when dissolved SiO_2 concentrations in the feedwater influent were higher it was

difficult to draw meaningful conclusions between the data collected for feedwater

influent concentrations at 200 mg/L versus 100 mg/L SiO_2 given the limited number of

runs. The remainder of this study explores performance with 100 mg/L SiO_2 influent feedwater concentration.

On day 4, the reagent dosages were reduced by one-half to 14.0 mg/L (0.25 mM) Fe^{2+} and 5 mg/L (0.36 mM) NO_3-N and reduced performance by 10% to 86% compared to day 3 with the same influent feedwater concentration of 100 mg/L SiO_2. pH 7.9 was measured in the reaction zone, 4.8 mg/L (0.34 mM) NO_3-N was consumed, and 5.0 mg/L (0.09 mM) Fe^{2+} was detected in the effluent. The lower pH on day 4 as compared to day 2 likely resulted in fewer hydroxide ions released (equation 6) from comparatively lower amount of nitrate consumed. A more thorough analysis of the effects of nitrate, Fe^{2+}, and pH on dissolved silica removal will be discussed in **Section 5.3**. Nevertheless, these tests established a target performance benchmark of >95% SiO_2 removal efficiency with reagent dosages of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N based on day 3 results.

5.3 The influence of Fe^{2+} and nitrate on silica removal in a hZVI system

5.3.1 Overall tests results

The main objective of this test was to evaluate how dissolved silica removal efficiency would change as a function of nitrate and Fe^{2+} dosages. Over the test period of 24 days, silica removal efficiency ranged from 64% to 97% with an influent feedwater concentration of 100 mg/L SiO_2 (Reactor 4) using preconditioned media (**Figure 5(a)**). Reactor and feedwater pH ranged from 6.8 to 9.8 and 7.1 to 7.7, respectively, over the same period (**Figure 5(b)**). **Figure 5(c)** and **5(d)** show the dosage and effluent concentrations of Fe^{2+} and nitrate by day.
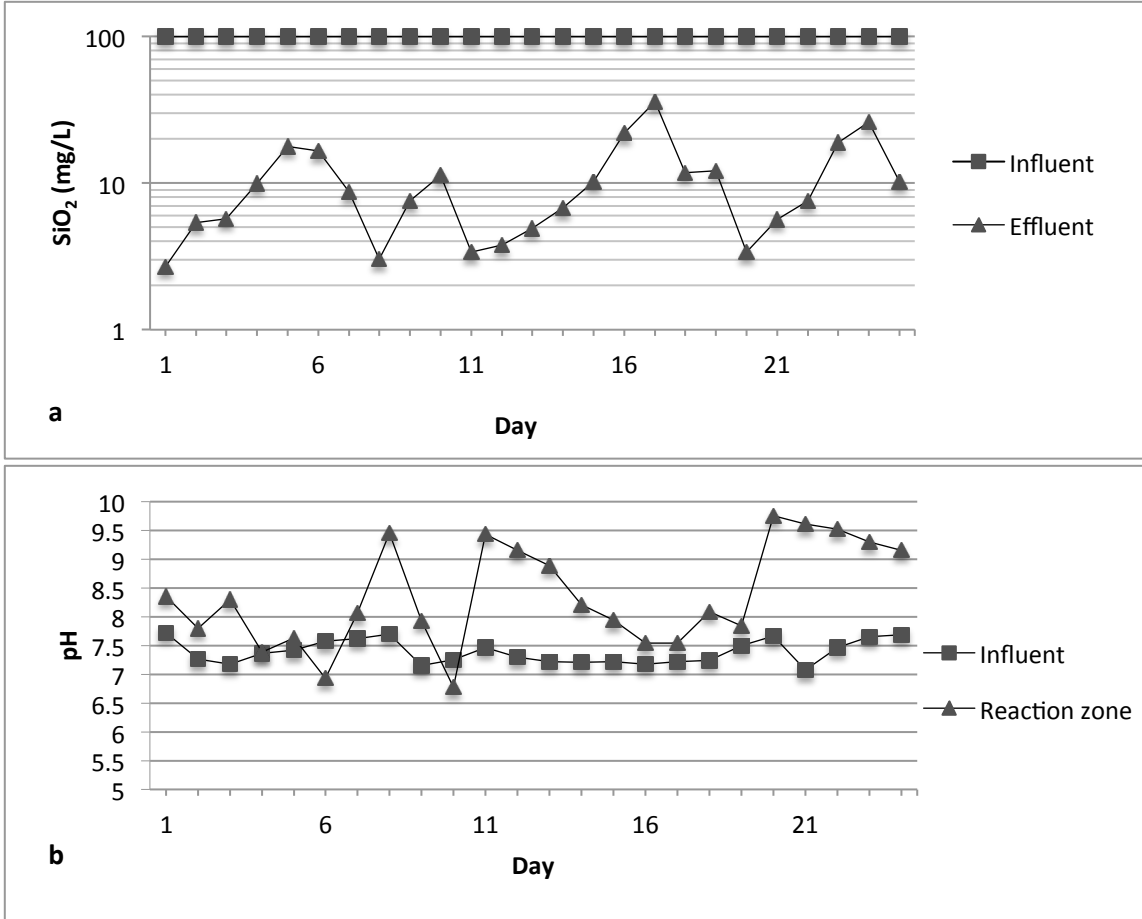
**Figure 5. Summary of test data with varied reagents over 24 days.
(a) Influent and effluent concentrations of dissolved silica (Reactor 3), (b) pH of the
feedwater influent and reaction zone**
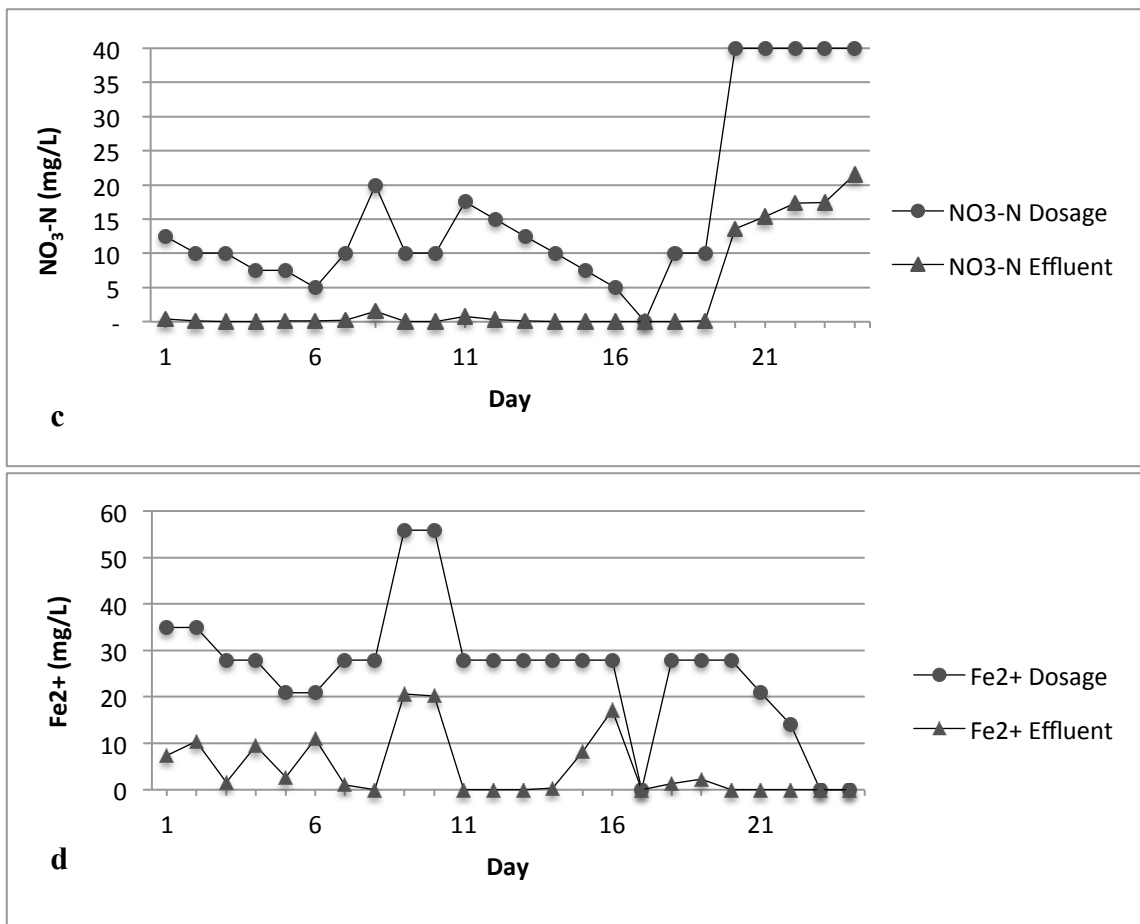
Figure 5 (continued). (c) NO$_3$-N dosage and effluent concentration, and (d) Fe^{2+} dosage and effluent concentration.

The benchmark performance standard of >95% SiO$_2$ removal efficiency was tested on days 3,7,14,18 and 19 with equivalent Fe^{2+} and nitrate to achieve the benchmark (Reactor 3). At dosages of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO$_3$-N SiO$_2$ removal efficiency did not meet the benchmark standard and, in general, declined from 94% (day 3) to 89% (day 19). Fe^{2+} and nitrate were not detected (or near the detection limit) in the effluent in each instance. The exact effects on the

system from varying reagents from day to day and aging of the ZVI grains are not known. Because of the nature of a continuous test, the results of a later stage will inevitably be affected by the antecedent test conditions and media status. While Reactor 4 tests appeared to be beneficial to observe trends by varying the Fe^{2+} and nitrate dosages from day to day, caution should be taken when interpreting the results. Reactor 5 was dosed with constant dosages of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N over 13 days and is discussed later in this chapter.

5.3.2 Impact of varying nitrate and Fe^{2+} dosages on dissolved SiO_2 removal

Figure 6(a) summarizes SiO_2 removal efficiency with step-decreased dosages (days 1 to 6).   Nitrate in the effluent was not detected (or near the detection limit) in all cases, thus all nitrate introduced into the system was consumed during days 1 to 6. NO_3-N dosages of 12.5 mg/L (0.89 mM) and Fe^{2+} dosages of 34.9 mg/L (0.625 mM) (day1) when viewed with NO_3-N dosages of 10.0 mg/L (0.72 mM) and Fe^{2+} dosages of 34.9 mg/L (0.625 mM) (day 2) and 27.9 mg/L (day 3) converged to the performance benchmark of >95% SiO_2 removal efficiency.   Dosages less than 10 mg/L (0.72 mM) NO_3-N and 27.9 mM (0.5 mM) Fe^{2+} (days 4, 5 and 6) were not adequate to meet the performance standard of >95% removal efficiency as shown in **Figure 6(a)**.   In the presence of Fe^{2+}, the benefit on system performance from increasing the NO_3-N dosage was not as great from 10 mg/L to 12.5 mg/L (~2.5 % comparing days 2 and 3 to day 1) as contrasted to dosages from 5 mg/L and 7.5 mg/L to 10 mg/L (~5% to 12% comparing days 4,5, and 6 to days 2 and 3). This provided support for minimum dosages of 27.9
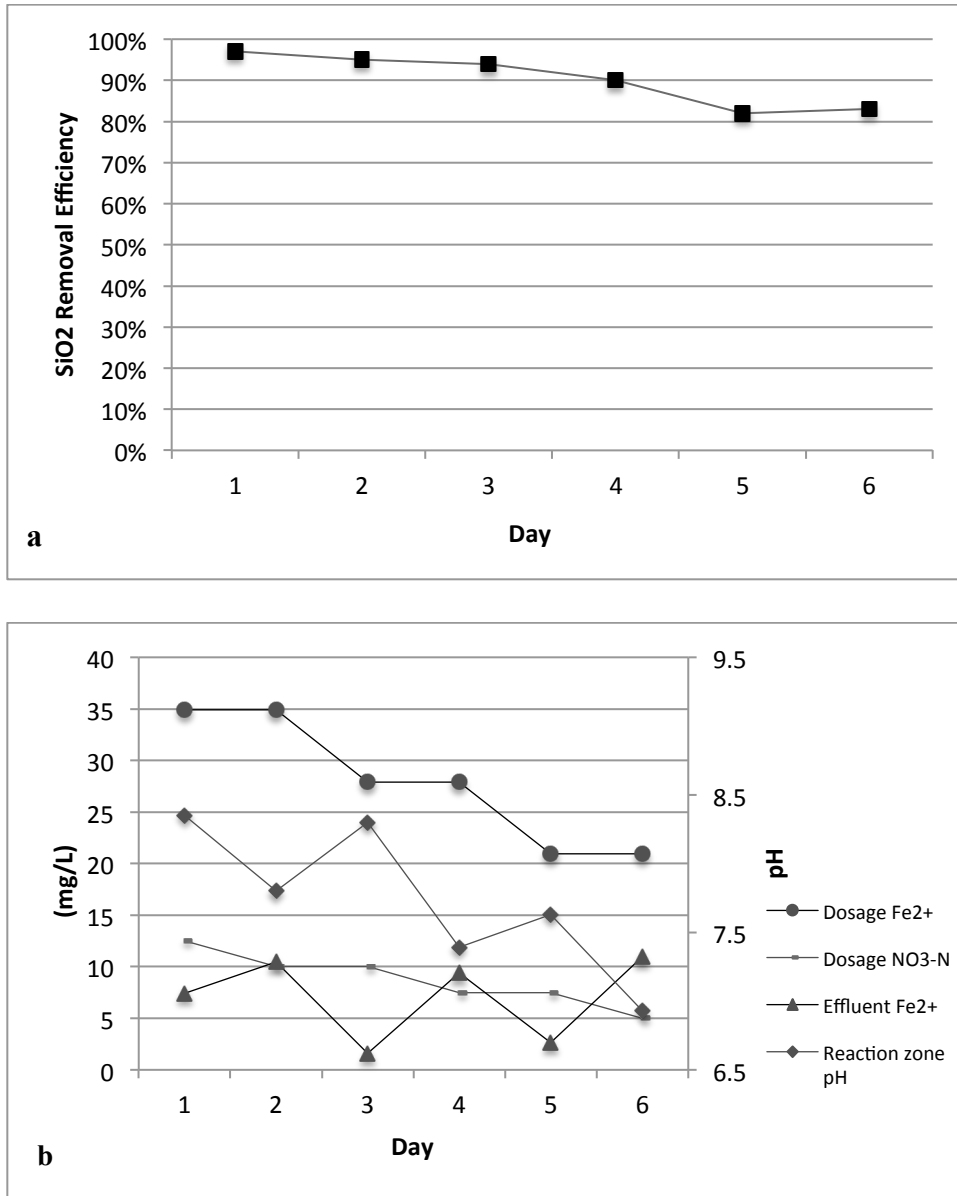
Figure 6. Results of stepped dosages of reagents.
(a) SiO_2 removal efficiency with step decrease in Fe^{2+} and nitrate dosages (days 1 to 6, Reactor 4) and (b) Fe^{2+} and nitrate dosages, pH detected in reaction zone and Fe^{2+} detected in the effluent over the same period (nitrate was not detected (or near the detection limit) in the effluent).

mg/L (0.5 mM) Fe^{2+} and 10 mg/l (0.72 mM) NO_3-N to meet a target performance of >95% removal efficiency.

Figure 6(b) shows pH declined as the nitrate dosage was step decreased with constant Fe^{2+} dosages (days 1 to 2, days 3 to 4, and days 5 to 6). This was explained by correspondingly less nitrate reduction resulting in fewer hydroxide ions being released (equation 6). Higher nitrate dosages appeared to be advantageous to SiO_2 removal. The effects from nitrate dosages on SiO_2 removal are discussed later in more detail.

The results showed a rise in pH from day 2 to 3, and day 4 to 5 (for each pair of days the nitrate dosage was identical while the Fe^{2+} dosage was higher on days 2 and 4 compared to days 3 and 5, respectively) and was explained by comparatively elevated effluent concentrations of Fe^{2+} at 10.4 mg/L (0.19 mM) and 9.4 mg/L (0.17 mM) on days 2 and 4, respectively, to lower effluent concentrations of Fe^{2+} at 1.6 mg/L (0.03 mM) and 2.6 mg/L (0.5 mM) on days 3 and 5, respectively as shown in the **Figure 6(b)**. Accordingly, excess Fe^{2+} in the system appeared to lower pH of the system. This observation was confirmed on day 10 when Reactor 4 was dosed with substantially higher Fe^{2+} at 55.8 mg/L (1.0 mM) Fe^{2+} while holding NO_3-N at identical dosages as days 2 and 3 at 10 mg/L (0.72 mM). Nitrate was not detected in the effluent, similar to days 2 and 3. At these dosages SiO_2 removal efficiency declined to 88% on day 10, respectively, compared to days 2 and 3 at 95% and 94%, respectively. Lower pH 6.8 was noted on day 10 with an Fe^{2+} effluent concentration of 20.1 mg/L (0.36 mM) (compare to pH 7.8 and 8.3 and Fe^{2+} effluent concentrations of 10.4 mg/L (0.19 mM) and 1.6 mg/L (0.03 mM) on days 2 and 3, respectively). Accordingly, for a given level

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of nitrate dosage, overdosing Fe^{2+} in an hZVI system was not advantageous for SiO_2 removal. Based on this observation, dosages with only Fe^{2+} and zero nitrate were not tested as it was concluded the target removal efficiency of >95% with copious amounts of Fe^{2+} could not be met.

It might be inferred from **Figure 6** Fe^{2+} functioned in a more important role than nitrate on dissolved silica removal efficiency at lower nitrate dosages of 7.5 mg/L and 5.0 mg/L on days 4, 5, and 6**.** However, when zero Fe^{2+} and zero nitrate were dosed on day 17, treatment of dissolved silica with only magnetite coated ZVI powder resulted in 64% dissolved silica removal efficiency. Day 17 performance was approximately 17% lower when compared to 82% and 83% removal efficiency with dosage of 20.9 (0.5 mM) mg/L Fe^{2+} and 5 mg/L and 7.5 mg/L NO_3-N on days 5 and 6 respectively, implying both Fe^{2+} and nitrate dosages were required to improve silica removal performance. Comparatively, in a ZVI/Fe^{2+} only system (Reactor 2) the best results were 22% efficiency, 42% less than the magnetite coated ZVI only run (day 17) suggesting the continuous magnetite formation in an hZVI system played a key role in dissolved silica removal. However, the magnetite coated ZVI only run was an isolated test. It may only be inferred Fe^{2+} did not play a significant role in dissolved silica removal without dosing nitrate in an hZVI system, noting, in a ZVI/Fe^{2+} system without preconditioning (Reactor 2) dissolved silica removal efficiency was 22% compared to 10% in a ZVI only system (Reactor 1) at best, a difference of only 12% accounting for Fe^{2+} the only variable.

5.3.3 Impact of varying nitrate with a constant dosage of Fe^{2+}

With a constant dosage of Fe^{2+} at 27.9 mg/L (0.5 mM), various dosages of NO_3-N were explored to determine the impact on SiO_2 removal efficiency as shown in **Figure 7**. Overall, increasing the dosage of nitrate showed convergence to the target SiO_2 removal efficiency of >95%. Increasing NO_3-N from 10 to 15 mg/L (0.72 to 1.07 mM) exhibited an improvement in performance by 3% (days 12, 13, and 14). Increasing the NO_3-N dosage to greater than 15 mg/L (1.07 mM) improved SiO_2 efficiency only nominally as shown on the graph (days 8 and 11). As the dosage of NO_3-N increased from 10 mg/L (0.72 mM) to 20 mg/L (2.86 mM), pH increased from 8.2 to 9.5, notably higher than the cases where excess Fe^{2+} was present in the effluent discussed in Section 5.3.2. No Fe^{2+} was detected in the system over the range of nitrate dosages except in the case of 10 mg/L (0.72 mM) NO_3-N dosage where a nominal amount of 0.6 mg/L (.01 mM) Fe^{2+} was present in the effluent. The data suggests augmenting the system with nitrate in the range of 10 mg/L (0.72 mM) to 15 mg/L (1.07 mM) in an hZVI system with a dosage of 27.9 mg/L (0.5 mM) Fe^{2+} was moderately advantageous with the added effect of eliminating excess Fe^{2+} in the effluent as the nitrate dosage was increased.
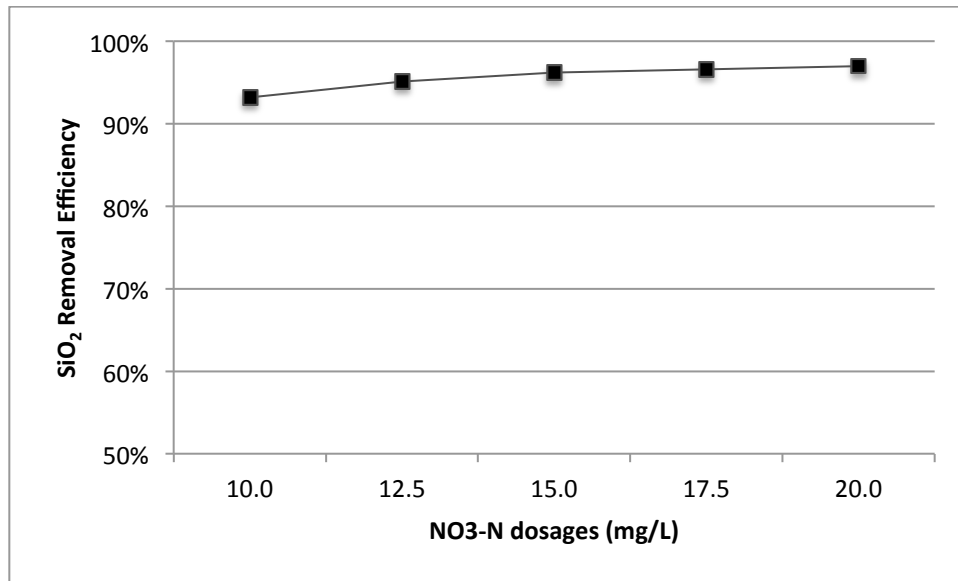
**Figure 7. Constant Fe^{2+}dosage with varying nitrate dosages
(days 8 and 11 to 14, Reactor 4).**

5.3.4 The role of Fe^{2+} on dissolved SiO$_2$ removal

The role of Fe^{2+} should not be disregarded. With a constant dosage of NO$_3$-N at

40 mg/L (2.86 mM), various dosages of Fe^{2+} were explored to determine the impact on

SiO$_2$ removal efficiency. The removal efficiency of dissolved silica with magnetite

coated ZVI without the addition of Fe^{2+} or nitrate was 64% on day 17.   On days 23 and

24, the system was augmented with 40 mg/L (2.86mM) NO$_3$-N nitrate without Fe^{2+}

resulting in 81% and 74% SiO$_2$ removal efficiency, respectively, improving efficiency

by 17% to 10%, respectively, as compared to day 17 (in the absence of dosing Fe^{2+}

maghemite (**γ-**Fe$_2$O$_3$) and/or lepidocrocite (γ-FeOOH) were likely formed on the surface

of the magnetite coated ZVI (Huang and Zhang, 2005)).   With a 40 mg/L (2.86 mM)

NO$_3$-N dosage, dissolved silica removal was 92% with a
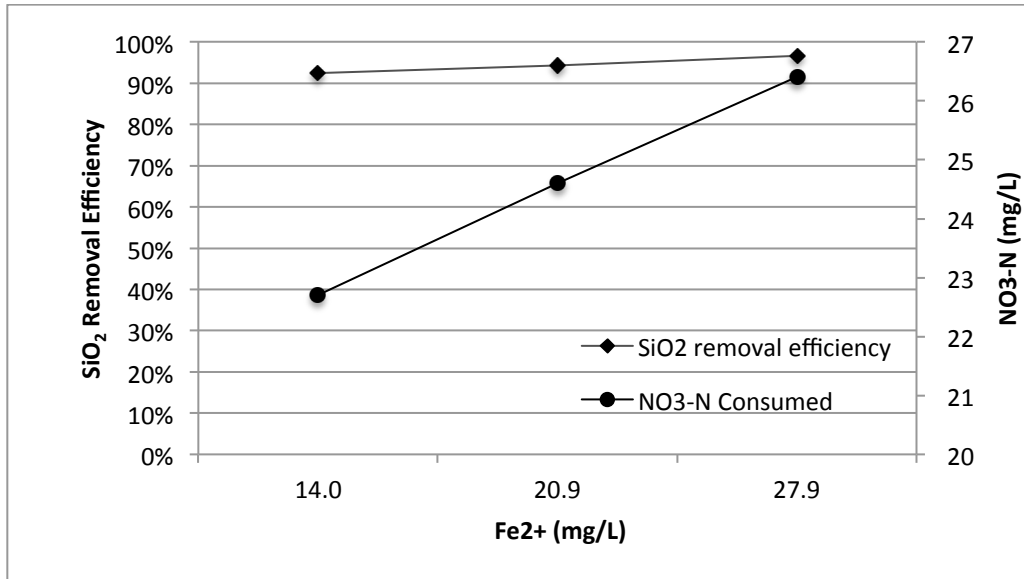
Figure 8. Nitrate overdose at various concentrations of Fe^{2+}.
Removal efficiency in a hZVI system with an overdose of 40 mg/L NO3-N at various Fe2+ dosages and NO3-N consumed (days 20 to 22, Reactor 4).

small dosage of 14.0 mg/L (0.25 mM) Fe^{2+} (day 22) and improved by 11% and 18% compared to days 23 and 24, respectively (**Figure 8**). SiO$_2$ removal efficiency peaked as the Fe^{2+} dosage was further augmented (days 20 and 21) at 97% at a dosage of 27.9 mg/L (0.50 mM) Fe^{2+} (day 20). No aqueous Fe^{2+} was present in the effluent for all tests. The dosage of Fe^{2+} was a limiting factor in nitrate consumption in these tests. NO$_3$-N consumed ranged from 22.7 to 26.4 mg/L as the Fe^{2+} dosage was increased from 14.0 (0.25 mM) to 27.9 mg/L (0.5mM). The pH ranged from 9.5 to 9.7 as the Fe^{2+} concentration increased from 14.0 (0.25 mM) to 27.9 mg/L (0.5 mM) and converged to a target SiO$_2$ removal efficiency of >95%. Thus, the continuous formation of magnetite in

the presence of sufficient Fe^{2+} and reduction of nitrate (equation 6) was shown to be a critical factor to achieve the target performance of >95%.

5.3.5 The role of pH on dissolved SiO_2 removal

On test runs where a minimum of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N (days 1 to 3, 7 to 14, and 18 to 20) SiO_2 removal efficiency ranged from 88% to 97% corresponding to pH 6.9 to 9.8. Similarly, on test runs with a constant dosage of 27.9 mg/L (0.5 mM) Fe^{2+} and a range of 10 mg/L (0.72 mM) to 15 mg/L (1.07 mM) NO_3-N (the maximum effective nitrate dosage based on previous discussion) (days 3, 7, 12 to 14, 18 and 19) SiO_2 removal efficiency ranged from 88% to 96% corresponding to pH 7.8 to 9.2.   Further narrowing the scope, at exact dosages of 27.9 mg/L (0.5 mM) and 10 mg/L (0.72 mM) NO_3-N, SiO_2 removal efficiency ranged from 88% to 94% corresponding to pH 7.8 to 8.3.   On all days within the three ranges, aside from day 1 and day 10, Fe^{2+} and nitrate were not detected (or near the detection limit) in the effluent. The negative impact from lower pH on SiO_2 removal efficiency ranged from 6% to 9% under the tacit assumption no other factors impacted pH other than the relevant dosages of Fe^{2+} and nitrate. This range (6% to 9%) is markedly narrower when compared to the 24% decline in SiO_2 efficiency, from 88% (the lower end of the three ranges) to 64% (day 17 at pH 7.5) when zero nitrate and zero Fe^{2+} were dosed. Moreover, when nitrate dosages were increased to greater than 10 mg/L (0.72 mM), holding Fe^{2+} at 27.9 mg/L (0.5 mM), pH was at the higher end of the range from 8.9 to 9.8 (days 8, 11 to 13, and 20). The rise in pH was attributed to reducing additional nitrate (equation 6) as the nitrate dosage was increased beyond 10 mg/L (0.72 mM).

Accordingly, it appeared pH did not play a significant role in SiO_2 removal in an hZVI system over the test pH range.

The continuous formation of magnetite for high silica removal performance appeared to be a more dominant factor as compared to pH. Accordingly, the hZVI system affords a much wider range of pH over which silica removal is effective, a significant advantage over conventional treatment methods such as lime soda softening with added magnesium that required a much higher pH to be effective. The hZVI system was self-sustaining in that no adjustments to pH were required for the reaction to proceed with the added benefit of effluent pH generally within the range of natural waters.

5.3.6 ZVI consumption for dissolved SiO_2 removal

Over 24 days, based on the daily consumption of nitrate and dissolved oxygen from the feedwater an estimated 40.6 g (equation 6) and 6.2 g (equations 8 and 9) of ZVI, respectively, was consumed. Dissolved oxygen in the feedwater was estimated using Henry's law (P=1 atm, T=25°C). Since dissolved oxygen (DO) in the reactor was non-detected based on previous laboratory experience using an hZVI system (below <0.1 mg/L), it can be concluded all DO was consumed by the activated iron media. This estimate did not include the effects of dissolved oxygen that may have diffused through exposed surfaces on top of the reactor. A total of 28,800 mg (28.8 g SiO_2) was introduced to the reactor by the feedwater influent and 25,700 mg (25.7 g) SiO_2 removed over the same 24 day period. The ratio of Fe^0 consumed to silica removed was 1.82 g/g. Compare to 2.5 g of activated alumina required to remove 4.5 mg SiO_2 reported by

Bouguerra (2007), a ratio of 500 g/g. While the activated alumina may be regenerated with appropriate treatment, ZVI powder is an inexpensive option and commercially available. Huang et al. (2013) also reported the spent media from the treatment of flue-gas desulfurization wastewater was generally below the regulatory standards set by the USEPA by conducting TCLP (toxicity characteristic leachate procedures) tests. It is likely the spent media may be disposed of in a landfill without any required special handling.

5.4 Silica removal as a function of operating temperature

Reactor 5 was dosed with 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) with feedwater influent containing 100 mg/L SiO_2 for 13 consecutive days. The results are shown in **Figure 9**. It was observed temperature (measured in the reaction zone) reached equilibrium each day after approximately 4 hours (8 hours on day 4 when temperature was increased from 25°C to 45°C) after the waterbath temperature was increased. For this reason, the tests were repeated in reverse sequence in 15°C decrements until day 11, after repeating the peak temperature of 90°C on day 8, until 25°C was reached on days 12 and 13.

SiO_2 removal efficiency exceeded 96% on each of the 13 days (**Figure 9(a)**). The performance of Reactor 5 also confirmed the minimum dosages (27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM)) established from evaluating the tests results from Reactor 4 were effective. Fe^{2+} was not detected (or near the detection limit) in the effluent over the 13 day period, while nitrate was nearly completely consumed through

day 6. From days 7 to 13, < 2mg/L nitrate (as N) was detected in the effluent resulting

in less nitrate consumed compared to days 1 to 6 (**Figure 9(b)**). Under these conditions,

a

b
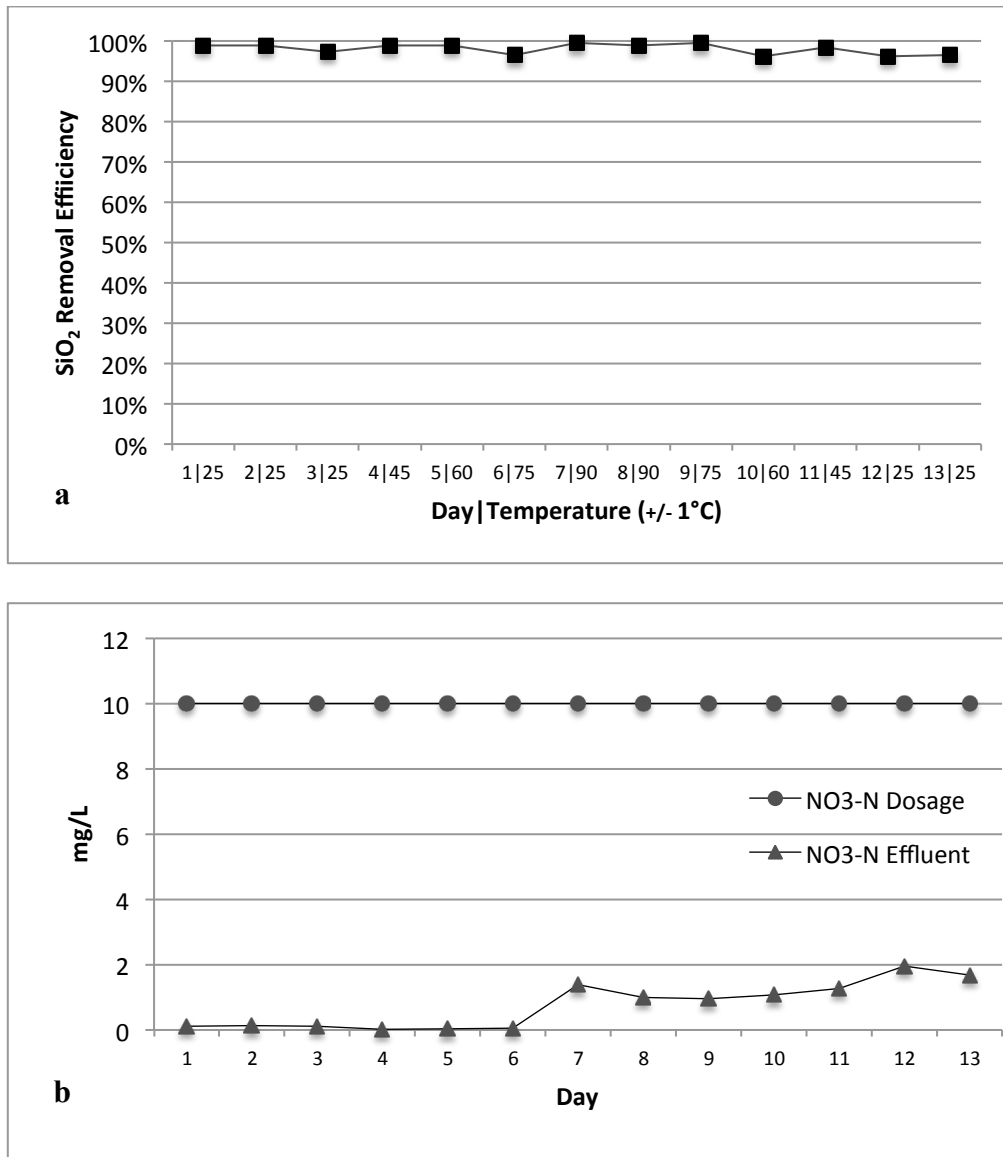
Figure 9. Dissolved silica removal efficiency at a temperature range from 25°C to 90°C.
(a) removal efficiency with 100 mg/L SiO₂ feedwater (Reactor 5), (b) NO3-N dosage and effluent concentration
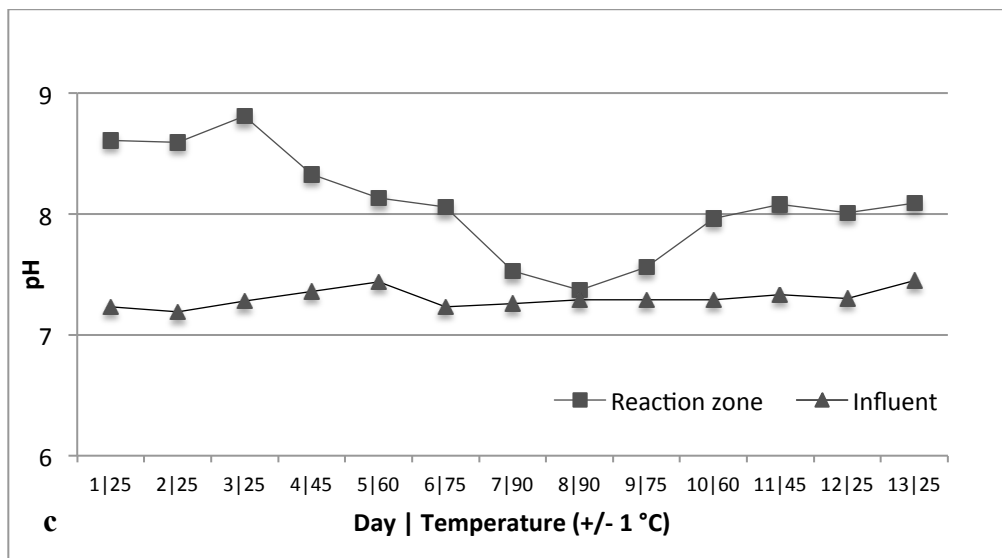
Figure 9 (continued). and (c) pH of the feedwater and reaction zone over the same time period.

Reactor 5 was able to achieve the benchmark performance efficiency >95% dissolved SiO_2 removal.

Removal efficiency peaked at temperatures of 75°C and 90°C at 99% (days 7 and 9). It cannot be concluded increasing temperature enhanced performance of the system since the difference in removal efficiency between the 13 days was 2.6% at most. However, compared to the room temperature tests at 25°C (days 1 to 3, 12, and 13), increasing reactor temperature to within a range of 45°C to 90°C did not attenuate the performance of the system for dissolved SiO_2 removal (**Figure 9(a)**). Unlike conventional methods such as added MgO that required heating to enhance dissolved SiO_2 removal performance, Reactor 5 results strongly suggested temperature does not require adjustment in order to achieve high system performance for dissolved SiO_2

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removal leading to reduced treatment costs. At elevated water temperatures the hZVI system may be effective at removing dissolved silica, for example, in a steam power plant that uses geothermal water to generate electricity. Recycled water may also have high dissolved silica content, for instance, the process of natural gas hydraulic fracturing or bitumen recovery from oil sands that use steam injection in mining and exploration activities.

Figure 9(c) shows the reaction zone pH ranged from 7.4 to 8.8 over the 13 day period. As shown in the figure, from day 6 to 8 pH declined from 8.0 to 7.3 as temperature increased from 60°C to 90°C. Conversely, pH increased 7.3 to 8.0 from day 8 to 11 as temperature declined from 90°C to 45°C. This was not unexpected. While at ambient temperature (25°C) neutral pH is 7, increasing temperature lowers the neutral pH value but not the acidity.

Over 16 days, including 3 days exploring the effects of salinity (Section 5.6), based on the daily consumption of nitrate and dissolved oxygen from the feedwater an estimated 20.0 g (equation 6) and 4.1 g (equations 8 and 9) of ZVI, respectively, was consumed under the same assumptions used in Section 5.3.6. A total of 19,200 mg (19.2 g) SiO_2 was introduced to the reactor by the feedwater influent and an estimated 18,800 mg (18.8 g) SiO_2 was removed over the same 16 day period. The ratio of Fe^0 consumed to SiO_2 removed was 1.28 g/g.

Figure 10 shows a sample of the magnetite coated ZVI grains used for dissolved silica removal with constant reagent dosages of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N after 12 days of treatment. The mechanism by which dissolved silica

is removed in an hZVI system and the role magnetite formation plays is not known.

EDS analysis showed the presence of silicon on the surface of the magnetite coated ZVI

after 12 days of treatment (**Figure 11**).   Whether the mono-silicic acid or the silicate

anion is removed more easily in an hZVI system is uncertain. A precipitate, possibly

silica gel, was also observed on the surface of settlement zone of the reactor. Further

analysis and testing must be performed to understand the surface compounds and/or
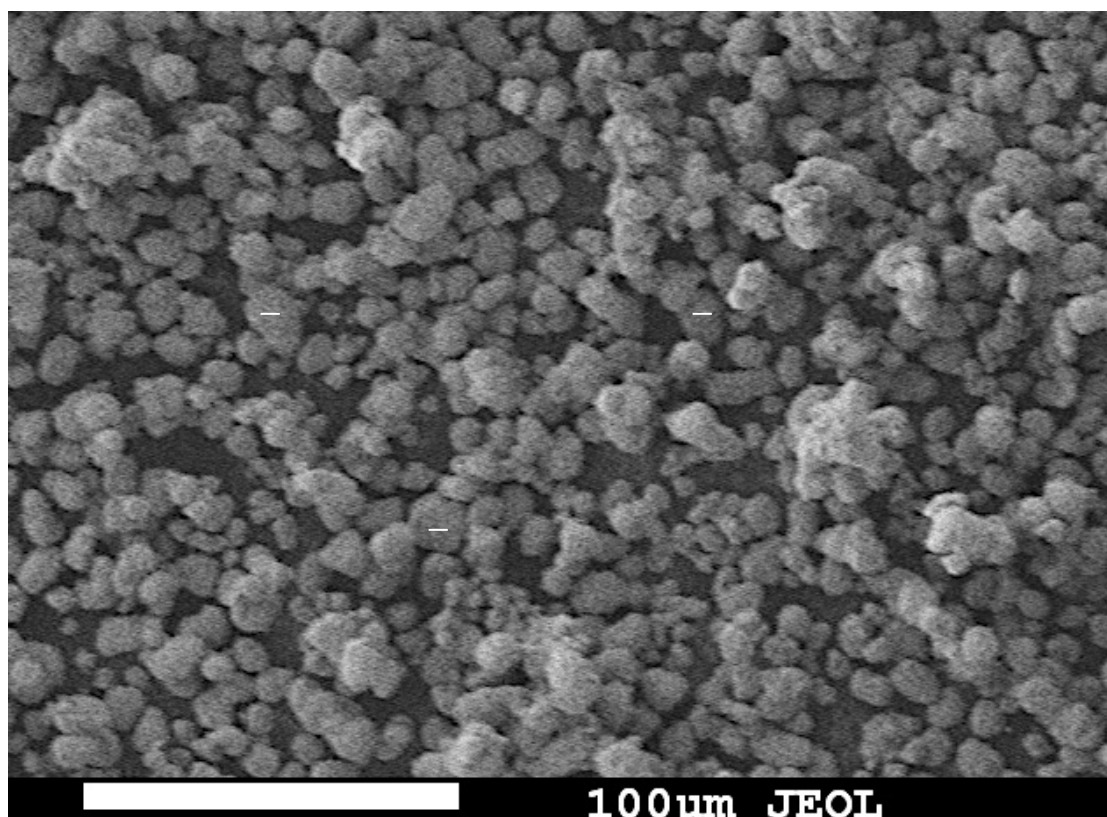
Figure 10. SEM image of magnetite coated ZVI grains.
The image shows enlargement of magnetite pre-coated ZVI after 12 days of
treatment with constant reagent dosages. The white lines on the magnetite coated
ZVI grains indicate a 5 µm length.

precipitates formed in order to further elucidate the exact mechanism and the chemical function of magnetite.
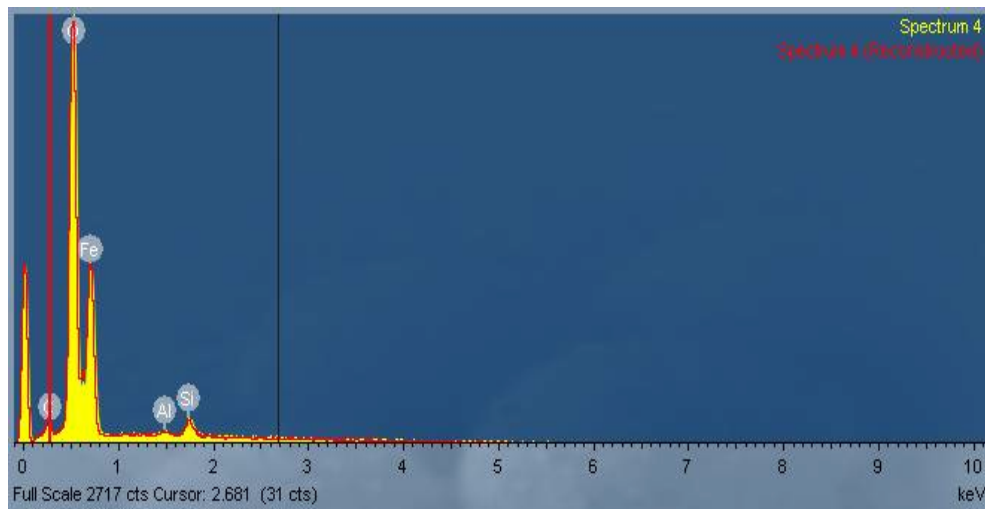
Figure 11. EDS analysis of a single magnetite coated ZVI grain.
The spectrum shows the presence of silicon on the surface after 12 days of treatment.

5.5 Silica removal as a function of salinity

An additional 3 days of testing was conducted after the temperature tests (Reactor 5) to explore the effects of salinity on silica removal as an additional consideration, for example, for a reverse osmosis desalination plant where the source of the feedwater may be seawater or brackish waters. Over the 3 days dosages of 27.9 mg/L

(0.5 mM) Fe^{2+} and 15 mg/L (1.07 mM) NO_3-N were kept constant. Fe^{2+} was not

detected in the effluent on all 3 days. The results are shown in **Figure 12**. Dissolved

SiO_2 removal efficiency was 97% on day 14 with no added salt as a control test. As

compared to day 13, the final day of the temperature test, pH increased from 8.1 to 8.9

on day 14. This achieved the objective to increase pH and correspondingly increase the

proportion of silicate anions (equation 2) in the reactor. This was supported by increased

nitrate consumption from 9.3 mg/L (0.66 mM) on day 13 to 11.9 mg/L (0.85 mM) on

day 14 resulting in more hydroxide ions released (equation 6). As the salt concentration

was increased to 14.6 g/L (0.25 M) removal efficiency was unchanged at 97% (day 15)

at pH 8.7 as compared to day 14, however, nitrate consumption (as N) declined to 9

mg/L (0.64 mM). On day 16, the salt concentration was increased further to 23.3 g/L

(0.4 M). Dissolved SiO_2 removal efficiency decline to 95% at pH 8.3. Nitrate

consumption (as N) declined to 7 mg/L (0.64 mM) on day 16. The results are shown in

Figure 12(c). Despite this fact, dissolved SiO_2 removal was greater than >95% on all

three days. The data suggests increasing salinity may have inhibited nitrate reduction.

Accordingly, it cannot be concluded increasing salinity, by itself, was detrimental to

dissolved SiO_2 removal efficiency.   Further research on the effects of salinity in an hZVI

system must be undertaken.
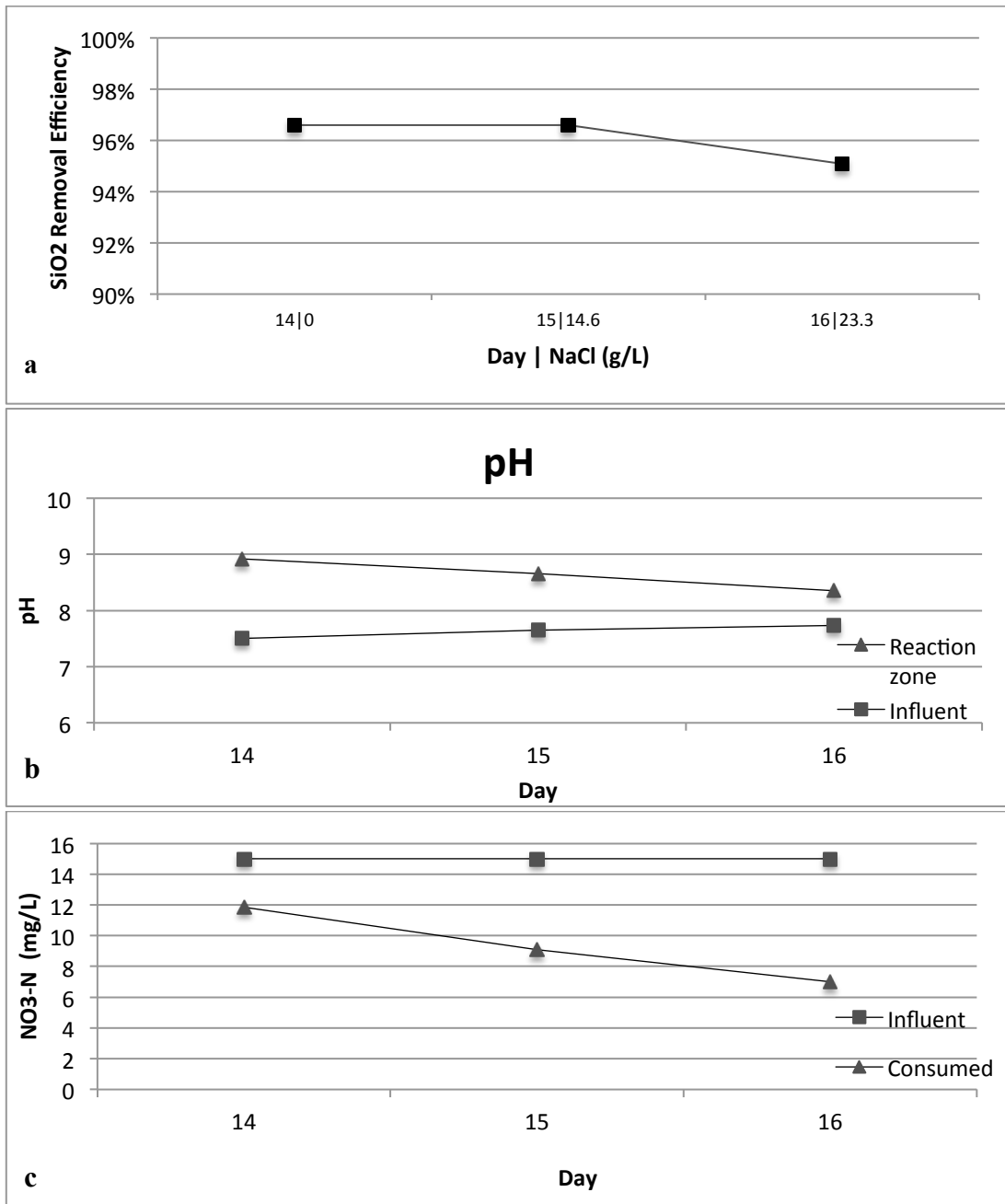
Figure 12 . Summary of data from the effects of salinity.
(a) Removal efficiency at various dosages of sea salt (days 14 to 16), (b) influent and reaction zone pH, and (c) influent concentration and NO_3-N consumed over the same time period.

6. CONCLUSIONS

The hZVI system offers a potentially cost competitive chemical treatment platform to remove dissolved silica from water when compared to conventional treatment methods. Using an average diameter ZVI of 5 microns, dosages at minimum equal to 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N, silica removal efficiency ranged from 88% to 99% across all reactors. pH did not appear to play a dominant role for the removal of dissolved silica over a range of 6.8 to 9.8. Increasing the nitrate dosage from 10 mg/L (0.72 mM) up to 15 mg/L (1.07 mM) appeared to eliminate the effect of lower pH from the presence of excess Fe^{2+} in the effluent and enhanced dissolved silica removal efficiency. Increasing reactor temperature from a range of 25°C to 90°C did not attenuate dissolved silica removal efficiency in the hZVI system. When the system was augmented with constant dosages of 27.9 mg/L (0.5 mM) Fe^{2+} and 10 mg/L (0.72 mM) NO_3-N silica removal efficiency >95% was sustained over an extended period. Magnetite played a key role in dissolved silica removal in the hZVI system. The continuous formation of magnetite on preconditioned ZVI grains was essential for the removal of dissolved silica. Further testing and research is required to further elucidate the exact mechanism for dissolved silica removal in a hZVI system and to explore the effects of salinity.

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APPENDIX

TEST DATA COLLECTED

Date	Day	pH		Fe2+ (mg/L)		NO3-N (mg/L)		SiO2 (mg/L)		
		Influent	Reactor	Dosage	Effluent	Dosage	Effluent	Influent	Effluent	Efficiency
Reactor 3										
12/17/13	1	7.1	8.1	27.9	12.3	10	nt	200	nt	na
12/18/13	2	7.4	7.7	27.9	5.0	10	1.6	200	44.0	78.0%
12/19/13	3	7.6	8.5	27.9	8.4	10	0.6	100	3.8	96.2%
12/20/13	4	7.8	7.9	14.0	5.0	5	0.2	100	14.5	85.5%
Reactor 4										
1/5/14	1	7.7	8.4	34.9	7.4	12.5	0.4	100	2.7	97.3%
1/6/14	2	7.3	7.8	34.9	10.4	10	0.2	100	5.4	94.6%
1/7/14	3	7.2	8.3	27.9	1.6	10	nd	100	5.7	94.3%
1/8/14	4	7.4	7.4	27.9	9.4	7.5	nd	100	9.9	90.1%
1/9/14		Idle								
1/10/14	5	7.4	7.6	20.9	2.6	7.5	0.1	100	17.8	82.2%
1/11/14	6	7.6	6.9	20.9	10.9	5	0.1	100	16.6	83.4%
1/12/14	7	7.6	8.1	27.9	1.0	10	0.2	100	8.7	91.3%
1/13/14	8	7.7	9.5	27.9	nd	20	1.5	100	3.0	97.0%
1/14/14	9	7.2	7.9	55.8	20.5	10	nd	100	7.6	92.4%
1/15/14	10	7.3	6.8	55.8	20.1	10	nd	100	11.3	88.7%
1/16/14	11	7.5	9.4	27.9	nd	17.5	0.8	100	3.4	96.6%
1/17/14	12	7.3	9.2	27.9	nd	15	0.3	100	3.8	96.2%
1/18/14	13	7.2	8.9	27.9	nd	12.5	0.1	100	4.9	95.1%
1/19/14	14	7.2	8.2	27.9	0.4	10	0.1	100	6.8	93.2%
1/20/14	15	7.2	7.9	27.9	8.2	7.5	nd	100	10.2	89.8%
1/21/14	16	7.2	7.5	27.9	17.1	5	nd	100	21.9	78.1%
1/22/14	17	7.2	7.5	0.0	nd	0	nd	100	35.9	64.1%
1/23/14	18	7.2	8.1	27.9	1.3	10	0.1	100	11.7	88.3%
1/24/14	19	7.5	7.8	27.9	2.3	10	0.1	100	12.1	87.9%
1/25/14		Idle								
1/26/14		Idle								
1/27/14	20	7.7	9.8	27.9	nd	40	13.6	100	3.4	96.6%

nd = not-detected, nt=not tested, na=not applicable

TEST DATA COLLECTED (Continued)

Date	Day	pH Influent	pH Reactor	Fe2+ (mg/L) Dosage	Fe2+ (mg/L) Effluent	NO3-N (mg/L) Dosage	NO3-N (mg/L) Effluent	SiO2 (mg/L) Influent	SiO2 (mg/L) Effluent	SiO2 (mg/L) Efficiency
		Influent	Reactor	Dosage	Effluent	Dosage	Effluent	Influent	Effluent	Efficiency
Reactor 4 (continued)										
1/28/14	21	7.1	9.6	20.9	nd	40	15.4	100	5.7	94.3%
1/29/14	22	7.5	9.5	14.0	nd	40	17.3	100	7.6	92.4%
1/30/14	23	7.7	9.3	0.0	nd	40	17.4	100	18.9	81.1%
1/31/14	24	7.7	9.2	0.0	nd	40	21.5	100	26.1	73.9%
Reactor 5										
7/30/14	1	7.2	8.6	27.9	5.1	10	0.1	100	1.1	98.9%
7/31/14	2	7.2	8.6	27.9	2.1	10	0.1	100	1.1	98.9%
8/1/14	3	7.3	8.8	27.9	nd	10	0.1	100	2.6	97.4%
8/2/14	4	7.4	8.3	27.9	nd	10	nd	100	1.1	98.9%
8/3/14	5	7.4	8.1	27.9	nd	10	nd	100	1.1	98.9%
8/4/14	6	7.2	8.1	27.9	0.5	10	0.1	100	3.4	96.6%
8/5/14	7	7.3	7.5	27.9	3.1	10	1.4	100	0.4	99.6%
8/6/14	8	7.3	7.4	27.9	1.8	10	1.0	100	1.1	98.9%
8/7/14	9	7.3	7.6	27.9	1.8	10	1.0	100	0.4	99.6%
8/8/14	10	7.3	8.0	27.9	1.6	10	1.1	100	3.8	96.2%
8/9/14	11	7.3	8.1	27.9	2.3	10	1.3	100	1.5	98.5%
8/10/14	12	7.3	8.0	27.9	1.9	10	2.0	100	3.8	96.2%
8/11/14	13	7.5	8.1	27.9	1.1	10	1.7	100	3.4	96.6%
8/12/14	14	7.5	8.9	27.9	nd	15	3.2	100	3.4	96.6%
8/13/14	15	7.7	8.7	27.9	nd	15	5.9	100	3.4	96.6%
8/14/14	16	7.7	8.4	27.9	nd	15	8.0	100	4.9	95.1%
Reactor 1										
8/24/14	1	7.4	8.1	na	nd	na	na	100	92.6	7.4%
8/25/14	2	7.3	7.8	na	nd	na	na	100	90.3	9.7%

nd = not-detected, nt=not tested, na=not applicable

TEST DATA COLLECTED (Continued)

Date	Day	pH		Fe2+ (mg/L)		NO3-N (mg/L)		SiO2 (mg/L)		
		Influent	Reactor	Dosage	Effluent	Dosage	Effluent	Influent	Effluent	Efficiency
Reactor 2										
8/26/14	1	7.4	6.4	14.0	21.0	na	na	100	83.1	16.9%
8/27/14	2	7.2	6.4	14.0	24.4	na	na	100	79.4	20.6%
8/28/14	3	7.6	6.3	27.9	40.4	na	na	100	77.5	22.5%
8/29/14	4	7.6	6.2	27.9	37.5	na	na	100	84.6	15.4%
8/30/14	5	7.6	5.9	27.9	37.8	na	na	100	86.5	13.5%
8/31/14	6	7.7	6.3	55.8	65.5	na	na	100	79.4	20.6%
9/1/14	7	7.6	6.5	55.8	71.0	na	na	100	77.1	22.9%

nd = not-detected, nt=not tested, na=not applicable