LABORATORY STUDIES OF IN-SITU REDOX MANIPULATION FOR REMEDIATION OF PCE, TCE AND CR(VI) CONTAMINATED GROUNDWATER IN ATLANTIC COASTAL PLAIN SEDIMENTS

by

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(Under the Direction of VALENTINE A. NZENGUNG and GARY L. MILLS)

Conventional groundwater treatment methods, such as pump and treat are expensive and generally ineffective, especially for redox sensitive contaminants. An alternative to pump and treat technology is the development of an in-situ permeable, subsurface reactive zone designed to intercept and treat groundwater contaminants.

One recent innovation is the subsurface injection of an aqueous chemical reductant to create a treatment zone with low redox potential. This technology is referred to as in-situ redox manipulation (ISRM) and is capable of removing redox sensitive contaminants such as chlorinated solvents (TCE, PCE) and toxic metals (Cr) from groundwater. These contaminants are present in groundwater at the Department of Energy's Savannah River Site (SRS), located near Aiken, SC. Therefore, SRS subsurface sediments were used as a test matrix in a study evaluating the efficiency of ISRM for treating PCE, TCE and Cr(VI) contaminated groundwater on the SRS. The ISRM method consists of: 1) creation of an Fe(II) reactive zone by the injection of dithionite reagent that reduces Fe(III) naturally present in the aquifer sediment, 2) removal of oxidized groundwater contaminants by reaction within the reduced Fe(II) barrier.

The study results indicate that dithionite treatment does not negatively impacts the hydraulic properties of the aquifer if the pH of the injection solution is properly buffered. The reducing capacity attained within the treated sediments was very effective in treating groundwater containing Cr(VI). Based on the measured Cr(VI) treatment capacity, other redox sensitive toxic metals, such as uranium, and plutonium can be successfully remediated in SRS groundwater using the ISRM technology. The slow kinetics of PCE and TCE transformation in contact with dithionite reduced SRS aquifer sediments indicate that the treatment was only partially effective for remediation of these contaminants. Additional studies are necessary to evaluate the relationship between PCE and TCE reaction kinetics and groundwater velocity in order to optimize the design of the ISRM systems for field deployment.

INDEX WORDS: In situ, Remediation, Dechlorination, Immobilization, Precipitation, Dithionite, PCE, TCE, Chromium, Chlorinated solvents, Toxic metals, Redox, Reduction, Reactive zone, Ground water, Savannah River Site,

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DEDICATION

I dedicate this work to my parents for their moral support throughout my academic endeavors and to my loving wife, Rini, for her patience, understanding and support in all obvious and unobvious ways during my graduate career.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Among the many environmental problems that have received attention in recent decades is subsurface contamination caused by hazardous wastes. For many years, industrial and agricultural practices have proceeded without regard for proper disposal of the generated wastes and consequently, has deteriorated environmental quality and ecosystem integrity. Often, industrial fluids heavily contaminated with heavy metals and organics infiltrated through the vadose zone and tainted groundwater reservoir, leading to expensive contamination of soils and groundwater (Adriano, 2001).

For many years, there was a general lack of concern for the environment and a widespread but unfounded assumption that the subsurface environment would adsorb or degrade almost unlimited amounts of chemical contaminants. Historically, prevailing popular views held that the passage of water through soil exerted a purifying effect and that wastes dumped on the ground somehow were cleansed from the system. The application of highly sensitive analytical techniques to environmental analysis has revealed the extent of contamination in soil and groundwater and thus, provided scientific and public awareness of the potential for detrimental health effects. The occurrence and fate of trace levels of organic and inorganic compounds in the environment and the adoption of new regulations to address these concerns has spawned the need for development and implementation of strategies to cleanup (remediate) the environment by either removing or immobilizing the hazardous contamination to meet the regulatory limits.

Remediation approach. The practice of remediation engineering itself has progressed from the mid 1970s and continues to evolve today. The last decade has seen a significant improvement of remediation technologies from the early containment systems to today's aggressive site closure techniques. Pump and treat systems, the primary remediation technique during the early days, have been found to be ineffective and were replaced by more targeted extractive techniques, namely, soil vapor extraction and air sparging. As the industry matured, a greater emphasis has been placed on *in situ* nonextractive techniques such as funnel and gate systems and, eventually to mass destruction techniques such as *in situ* reactive zones (IRZ) as the preferred remediation technologies. The development of in situ reactive zones as engineered anaerobic or aerobic systems, is essentially an outgrowth of the efforts to enhance the natural processes, that contribute towards degradation of many contaminants. Since 1993, the IRZ technology has been successfully applied to remediate compounds such as chlorinated ethenes and ethanes, phenols, pesticides, and perchlorates at more than 100 sites (Suthersan, 1998). In addition, the IRZ technology has been successfully applied to precipitate the following dissolved metals in contaminated sites: Cr(VI), Ni, Cu, Pb, Cd, Zn and Hg (U.S. EPA, 2002).

In situ Reactive Zone. The concept of in situ reactive zones is based on the creation of a subsurface zone, where migrating contaminants are intercepted and permanently immobilized or degraded into harmless end products. Treated groundwater after exiting the treatment zone follows its natural course where the maximum contamination levels fall below regulatory standards. The application of this technology can be classified into three categories: 1) anaerobic, 2) aerobic, and 3) chemical oxidation systems. The engineered anaerobic systems can be created by manipulation of the reduction-oxidation (redox) potential of an aquifer, which is a viable approach for in situ remediation of redox sensitive groundwater contaminants.

The remediation of redox sensitive groundwater contaminants in engineered anaerobic systems is based on two mechanisms: transformation of organic compounds to innocuous end products and immobilization of metals. The presence of electron donors in anaerobic environment may lead to reductive transformation of chlorinated solvents to less toxic products by electron transfer (reaction 1), whereas, reduction followed by immobilization or precipitation further aid in the removal of redox sensitive toxic metals (reaction 2 and 3) in contaminated ground water to below regulatory limits.

$$\mathrm{Fe(II)} + \mathrm{R\text{-}Cl_n} + \mathrm{H^+} + 2e^- \rightarrow \mathrm{Fe(III)} + \mathrm{RHcl_{n-1}} + \mathrm{Cl^-} \qquad (1)$$

$$\mathrm{Fe(II)} + \mathrm{M^{n+}} + e^- \rightarrow \mathrm{Fe(III)} + \mathrm{M^{(n-1)+}} \qquad (2)$$

$$\mathrm{M^{n+}} + \mathrm{nH_2O} + e^- \rightarrow \mathrm{M^{(n-1)+}(OH)_n} + \mathrm{nH^+} \qquad (3)$$

Creation of a spatially fixed IRZ in an aquifer requires the proper selection of reagents such that they cause few side reactions and that reagents and products be relatively nontoxic. Several methods have been used to develop anaerobic treatment zones, including microorganisms (Ishibashi et al 1990), reduced iron (Rai et al., 1987, 1989; Sass and Rai, 1987; Eary and Rai, 1988, 1989; Blwoes et al., 1997, 2000; Patterson et al., 1997; Peterson et al., 1997; Brigatti et al., 2000; Seaman et al., 1999), organic carbon (Bloomfield and Pruden, 1980), and organic complexes (Wittbrodt and Palmer, 1995).

Abiotic IRZ. Among the abiotic reductants, Fe(II) sources are the most commonly used reactants to manipulate the redox potential of the aquifer (U.S. EPA, 2002). The net remediation of groundwater contaminants by Fe(II) is equivalent to iron corrosion with the contaminants serving as the oxidizing agents. Many reactive salt solution including ferrous salt solution, sodium sulfite, sodium dithionite, sodium bisulfite, sodium metabisulfite and sulfur dioxide are commonly used as reducing agents in industrial remediation processes (Higgins et al., 1997; Eary and Rai, 1988; Schroeder and Lee, 1975; Davis and Olsen 1995; Saleh et al., 1989; Seaman et al., 1999). These reducing agents can be delivered to the subsurface at hazardous waste sites by several methods, including the use of injection wells and infiltration galleries. The injection of Fe(II) salt solutions reduces contaminants by supplying electrons to them and most of these reduction reaction products are less toxic. For the chlorinated contaminants, which are mostly non-ionic, the pH of the groundwater normally does not affect the efficiency of the treatment process. However, the oxidation and hydrolysis of Fe(II) can lower the pH in poorly buffered system, which may affect the solubility of heavy metals. Use of buffered ferrous solution can reduce the efficiency of such systems as more Fe(II) is consumed by dissolved O_2 present within the system (Seaman et al., 1999).

In systems containing reduced sulfur species (i.e., $S_2O_4^{2-}$, $S_2O_3^{2-}$, SO_3^{2-}, HSO_3^-, and S^{2-}), conditions favorable for precipitation of many heavy metals are attained and in addition, Fe(III) can be reduced to Fe(II) which subsequently may degrade chlorinated organics. Except for dithionite, the optimal pH for ISRM using sulfur species occurs at 2 to 2.5 (Higgins et al., 1997). The latter conditions can be realized in natural system by adding acid to groundwater, which could potentially cause unacceptable environmental effects. However, buffer dithionite solution, when added as the reactive solution for in situ remediation, enhances the redox capacity of soil and sediments by reducing the iron bearing soils and sediments (Jhaveri and Sharma, 1968; Stucki et al., 1976, 1984; Rueda et al., 1992; Gates et al., 1996; Amonette et al., 1994; Fruchter et al., 1996, 2000; Larson and Cervini-Silva, 1998; Istok et al., 1999; U.S. EPA, 1995; Szecsody et al., 1998, 2000; Cervini-Siva et al., 2000; Nzengung et al., 2001). This treatment creates reducing conditions within the matrix favorable for the reduction of redox sensitive contaminants while maintaining neutral to alkaline pH in the groundwater necessary for the complete precipitation of heavy metals. Moreover, the dithionite and its reaction products are nontoxic (Stucki et al., 1993). The half-life of dithionite in the subsurface is about 2 to 3 days (U.S. EPA, 1995), adequate for reducing a number of redox sensitive inorganic and organic compounds including Cr(VI) (Amonette et al., 1994; Fruchter et al.,1996, 2000; Istok et al., 1999), uranium (Szecsody et al., 1998), chlorinated alkanes (Amonette et al., 1994; Larson and Cervini-Silva, 1998; Cervini-Silva, 2000), and chlorinated alkenes (Szecsody et al., 2000; Nzengung et al., 2001; Thornton et al., 1998) to less toxic forms, while ensuring that dithionite does not persist as a contaminant in the groundwater. Amonette et al. (1994) observed that roughly 90% of the carbon tetrachloride (0.50 $\mu l\ L^{-1}$) was destroyed by dithionite-reduced sediment within a week. As reported by Cervini-Silva (2000), the reduction of halogenated aliphatics, including carbon tetrachloride (CCL_4), trichloroethene (TCE), and tetrachloroethene (PCE) was facilitated when ferruginous smectite in an aqueous suspension was reduced by dithionite under anoxic conditions. Dithionite-reduced aquifer sediments have been shown to degrade TCE in groundwater at a sufficiently fast rate, $t_{1/2}$ = 12 h to19 h (Szecsody et al., 2000). Dithionite reduced reactive barriers developed at the laboratory and field scale at the Department of Energy (DOE)'s Hanford site showed the ability to reduce Cr(VI) from 1 mg L^{-1} to below the analytical detection limit (8 μg L^{-1}) with a treatment capacity equivalent to 7-12 years (Fruchter et al., 1996).

Sodium dithionite as a reducing agent. Sodium dithionite is used in vat dying, bleaching, and the manufacture of various chemicals as a powerful reducing agent. The reduction potential of dithionite is similar to that of other reduced sulfur species, but it is much more reactive. This enhanced reactivity stems from a weak S-S bond that allows the ion to split into two sulfoxyl ($SO_2\bullet^-$) free radical species (Dunitz, 1956; Lynn, 1964; Nickless, 1968). When aqueous dithionite is added to soils or sediments having clay and iron oxide minerals, this reagent forms an inner sphere complex with surface Fe (III). The active free radical i.e., $SO_2\bullet^-$ (reaction 4) binds to the mineral surface and transfers an electron to structural Fe(III), reducing it to Fe(II) (reaction 5) yielding sulfite (SO_3^{2-}) as a degradation product (Rueda et al.,1992). Alternatively, a dithionite ion undergoes a disproportionation reaction that yields thiosulfate ($S_2O_3^{2-}$), and bisulfite (HSO_3^-), which eventually oxidize to sulfate (SO_4^{2-}). Once the reducing environment is created within the aquifer, migrating contaminated ground water from other parts of the aquifer carrying redox sensitive contaminants, such as chlorinated solvents would be degraded (eq 1) and metals and radionuclides would be immobilized (eq 2 & 3) to less mobile or less toxic forms.

$$2\,S_2O_4^{2-} + H_2O \quad <=> \quad 4\,SO_2\bullet^- + H_2O \tag{4}$$

$$4\,SO_2\bullet^- + Fe^{3+} + H_2O \;=>\; Fe^{2+} + SO_3^{2-} + 4H^+ \tag{5}$$

The dithionite generated in situ redox barrier, as developed at the Gloucester landfill site near Ottawa, Ontario and the Department of Energy (DOE)'s Hanford site consists of the injection, reaction, extraction, and finally remediation phases (Ludwig, 1998; Fruchter et al., 1996, 2000; Williams et al., 1999; Szecsody et al., 1998, 2000; Istok et al., 1999). Briefly, a freshly prepared buffered dithionite solution is injected into the sediment for a suitable period to reduce the solid phase Fe(III). Following injection, the injected reagents are allowed sufficient contact time to react with the aquifer material. Next, the unreacted reagents and dithionite degradation products are withdrawn by a brief period of extraction pumping. Thus, the redox manipulated barrier is formed by a transfer of reductive capacity from aqueous $S_2O_4^{2-}$ ions to solid phase Fe, which functions to remediate redox sensitive contaminants in groundwater that enters the barrier by transferring electrons from the solid phase to oxidized contaminants.

Efficiency of dithionite treatment. The successful design of a redox sensitive IRZ depends on effective interaction of the injected reagents and the subsurface matrix to manipulate the redox status to optimize the required reactions necessary to effect remediation. These interactions may vary between contaminated site and in fact, may vary due to heterogeneity within a given site. The geologic and hydrogeologic setting in which an IRZ system is deployed influences its effectiveness. The longevity of the barrier depends on the accessible Fe sites and redox capacity of the aquifer sediments. The types of mineral surfaces encountered will have a significant effect on the rate of dithionite disproportionation (Fruchter et al., 1996).

Successful application of ISRM technology requires careful selection of the concentration of injected dithionite solution and buffer (Fruchter et al., 1996; Amonette et al., 1994; Nzengung et al, 2001). Because the stability of the aqueous dithionite is enhanced at the higher pH (Rinker et al., 1965), the dithionite solutions need to be buffered to maintain alkaline pH. Successful application also requires a favorable balance between dithionite transport and reaction kinetics. Therefore, the duration of dithionite injection and reaction time can be optimized for site-specific aquifer characteristics. The ultimate design objective of the IRZ system should be to (1) deliver the electron donor rapidly; (2) to create a uniformly mixed reactive zone in the subsurface; and (3) to maintain the optimum geochemical condition for enhanced reduction/degradation of the target contaminations.

Application of ISRM at Savannah River Site. One potential site for application of the ISRM approach is the DOE's Savannah River Site (SRS), located near Aiken, SC. The highly weathered aquifer sediments of the Southeastern Atlantic Coastal Plain underlying the SRS are composed largely of only slightly reactive minerals principally quartz and kaolinite coated with variable-charged Fe-oxides (Storm and Kaback, 1992; Seaman et al, 1996; Bertsch and Seaman, 1999; Vulava and Seaman, 2000). A generalized description of hydrogeology at the SRS includes a sand unit, four major clay units, and a water table which lies about 40 m below the surface (Eddy et al., 1991).

Over many years, the water table aquifer has been contaminated with wastewater containing high level of various metals (Cr, Ni, Co, Cd, Pb, and Hg), radionuclides (Cs, U, Th, Ra, Sr, and tritium), and organic compounds (TCE, PCE, pesticides, PCBs) from various nuclear materials processing facilities on the SRS (Pickett, 1990; Evans et al., 1992; Looney et al., 1988, 1990; Newman et al., 1993; Eddy et al., 1991; Dapkus and Williams, 1997; Sataay et al., 1995; WSRC, 1999). Initial batch and column experiments using dithionite reduced SRS aquifer materials have demonstrated the treatment capability of tetrachloroethene (Nzengung et al., 2001, Heath, 2000; Payne, 2001; Uddin et al., 2001) and hexavalent chromium (Uddin et al., 2001). The goal of this research was to (1) determine optimum experimental conditions for creating a dithionite ISRM system in SRS aquifer materials (chapter one); (2) evaluate using batch and dynamic transport experiments, the effectiveness of dithionite reduced SRS aquifer materials in degrading PCE and TCE (chapter three), Cr(VI) (chapter four) in SRS groundwater. The results of this study will be a necessary prerequisite for evaluating the feasibility of deploying field-scale treatability trails of ISRM technology in southeastern Coastal Plain aquifer sediments.

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CHAPTER 2

OPTIMAL DESIGN OF AN IN SITU CHEMICAL REACTIVE BARRIER USING DITHIONITE TO TREAT REDOX SENSITIVE CONTAMINANTS IN A SOUTHEASTERN COASTAL AQUIFER[1]

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ABSTRACT

Batch and dynamic column experiments were conducted with dithionite reduced Atlantic Coastal Plain aquifer sediments collected from the Savannah River Site (SRS) to develop a permeable treatment zone in the subsurface that provides maximum redox capacity. Optimization experiments included the use of citrate or bicarbonate-carbonate buffered dithionite solution. The use of bicarbonate-carbonate buffered dithionite solution (34.5 mmol) maintained a stable alkaline solution ($pH > 8$) and minimized both colloid mobilization and dithionite disproportionation. Dithionite disproportionation and subsequent oxidation were described by pseudo-first-order reaction kinetics in oxygenated solution without sediment and by pseudo-second-order kinetics in solution containing SRS aquifer sediments. Dithionite injection/withdrawal experiments conducted in columns indicated that dithionite treatment completely reduced the surface bound Fe and 39.6% of structurally bound Fe(III). The reduced sediment was capable of removing ambient dissolved O_2 ($8.2\ mg\ L^{-1}$) from ~173 column pore volumes (PV) of artificial groundwater at a flow rate of ~7.0 $cm\ d^{-1}$ (Darcy velocity). Based on the different forms of Fe extracted from reduced sediment, it was determined that 12 PV of dithionite solution injection and reaction time ≥ 6 hours were needed to achieve maximum reduction of SRS sediments in packed columns.

INDEX WORDS: iron, dithionite, reduction, Savannah River Site, kinetics, redox manipulation, buffer, remediation, in situ, column, batch, barrier

INTRODUCTION

Over the past decade, permeable reactive barriers have been developed and used as an alternative to traditional pump and treat systems for groundwater remediation. This technique, first reported by McMurthy and Elton (1985), involves construction of permanent, semi permanent, or replaceable units across the flow path of a dissolved phase contaminant plume. As the contaminated groundwater moves passively through the permeable reactive zone, contaminants are scavenged or degraded and uncontaminated groundwater emerges from the downgradient side of the reactive zone.

Ideally, the selected reactive materials within the barrier should be: (1) Inherently benign in nature, (2) sufficiently reactive to remain effective for an extended duration, (3) sufficiently insoluble to remain in place for a reasonable length of time, (4) designed to maintain their permeability as secondary precipitates accumulate (5) capable of degrading or immobilizing the target contaminants within the aquifer and (6) less expensive than competitive groundwater remediation strategies. Several reactive media, such as granular activated carbon, organic matter, zero-valent iron (Gillham and O'Hannesin, 1994; Blowes et al, 1997; Powell et al, 1995), ferrous iron containing compounds/minerals (Patterson et al., 1997; White et al., 1996; Brigatti et al., 2000) have been used in the creation of permeable reactive barriers. A potential disadvantage of existing permeable treatment zone technologies is the high cost of trench construction, especially for depths greater than ~ 10 m (Istok et al., 1999; NRC, 1999). Also, at sites where the extent of contamination is extensive, the use of such a barrier is impractical (Seaman et al., 1999). Zero valent iron over time is likely to form an oxide film on the surface, which subsequently reduces the reactivity of the barrier (Wang and Zhang, 1997). Another potential processes leading to decreased reactivity within the treatment zone precipitation of secondary minerals on reactive surfaces, possibly clogging the system and resulting in preferential flow of contaminants through/around the barrier (Blowes et al., 2000).

An alternative approach to eliminate the cost of trench construction and to attain long-term performance of the reactive barrier is the injection of reactive solutions to create permeable treatment zones in the subsurface. Among various reactive solutions explored for subsurface injection are aqueous Fe(II) (Eary and Rai, 1988; Kaplan et al., 1994; Fendorf and Li, 1996; Sedlak and Chan, 1997; Seaman et al., 1999; Amonette, 2000), lime (Kleinmann et al., 1983; Fetter, 1991; RTDF, 1999), Fenton's reagent (Chen et al., 2001), and potassium permanganate (Huang et al., 2001).

The use of sodium dithionite solutions for in situ redox manipulation (ISRM) to treat redox sensitive groundwater contaminants offers a promising alternative to other types of permeable reactive barriers (Amonette et al., 1994; Fruchter et al., 1997). The ISRM method of treating redox sensitive contaminants in groundwater involves injection of dithionite solution, which is a strong reductant in basic solutions. The two sulfoxyl radicals produced from each dithionite ion can reduce naturally occurring transition metals, of which iron is the most abundant and accessible element associated with mineral phases of soil and sediments. Once the fixed reducing zone is created within the aquifer by reducing the solid phase iron present in the mineral oxides and clay minerals, redox sensitive contaminants are degraded (e.g., chlorinated solvents) or immobilized (e.g., metals and radionuclides) as the contaminated groundwater flows through the reactive barrier. The reduction of ferric iron in aquifer material and the accompanying reduction of oxidized contaminants is described by equations 1-3 as follows;

$2S_2O_4{}^{2-}{}_{aq} \Leftrightarrow 4SO_2\bullet^{-}$ (basic solution) (1)

$S_2O_4{}^{2-}{}_{aq} + 2Fe(III)_s + 2H_2O \Rightarrow 2SO_3{}^{-}{}_{aq} + 2Fe(II)_s + 4H^+$ (2)

$2Fe(II)_s + 4H^+ + \text{Contaminant}_{\text{oxidized}} \Rightarrow \text{Contaminant}_{\text{reduced}} + 2Fe(III)_s + 2H_2O$ (3)

Dithionite mediated reduction protocols developed in laboratory studies have been shown to be effective at the field scale (Betts, 1998; Istok et al., 1999). At the Department of Energy (DOE)'s Hanford site and the US Coast Guard facility at Elizabeth City, NC., dithionite created barriers have successfully remediated Cr(VI) contaminated groundwater (Vermeul at al., 1995; Fruchter et al., 1996, 1997; Williams et al., 1999). Other studies have demonstrated the effectiveness of dithionite-reduced soil in treating chlorinated alkanes (Payne, 2001; Amonette et al., 1994; Larson and Cervini-Silva, 1998; Cervini-Silva et al., 2000), chlorinated alkenes (Heath, 2000; Nzengung et al., 2001; Szescody et al., 2000; Thornton et al., 1998), uranium (Szescody et al., 1998), and nitroaromatics (Rodriguez et al., 1999) in contaminated groundwater.

Sodium dithionite is used in vat dying, bleaching, and the manufacture of various chemicals as a powerful reducing agent. This reagent when used for Fe(III) reduction is known to form inner sphere complexes with surface Fe(III) and parallel outer sphere complexes with iron oxides. Subsequently, Fe(III) is reduced to Fe(II) by electron transfer yielding sulfite ($SO_3{}^{2-}$) as degradation product (Rueda et al., 1992). In addition to reduction reactions, dithionite ions undergo a disproportionation reaction that yields thiosulfate ($S_2O_3{}^{2-}$) and bisulfite ($HSO_3{}^{-}$), which may further oxidize to sulfate ($SO_4{}^{2-}$).

The installation of a dithionite redox manipulated barrier at the Hanford site involved multiple steps, which include injection, reaction, extraction and finally remediation phases (Amonette et al., 1994; Fruchter et al., 1997, 2000). Freshly prepared buffered dithionite solution was injected into the sediment for 17.1 hours at a rate of 20 gpm to reduce the solid phase Fe(III). After an additional reaction time of 18.5 hours, the unreacted reagent, buffer and reaction products were withdrawn from the aquifer representing 4.9 injection volumes. Thus, a transfer of reductive capacity from aqueous $S_2O_4^{2-}$ to solid phase Fe created the reactive barrier. This barrier functions to remediate redox sensitive contaminants in groundwater that enters the barrier by transferring electrons from the solid phase to oxidized contaminants.

The longevity of the barrier depends on the presence of dissolved oxygen (DO) and the concentration of contaminants entering the treatment zone (Istok et al., 1999). Other factors that may influence the efficiency of the treatment zone include redox-buffering capacity of the aquifer solids and the accessible Fe sites. Experimental evidence indicates that while the dithionite treatment reduces and dissolves amorphous and some crystalline Fe(III) oxides, structural iron within the phyllosilicate clay minerals remains largely intact in the sediment, forming the Fe(II) barrier. Although dissolved Fe(II) may re-adsorb to surfaces, the absence of discrete crystalline phase may affect the efficiency of the ISRM. Dithionite disproportionation rates are affected by mineral Fe content (Amonette, 2000; Fruchter et al., 1996) and the types of mineral surfaces encountered (Nzengung et al., 2001; Gates et al., 1997, 1998). This means that in addition to the obvious need to assess available Fe(III) content in soils and sediment, a determination of the mineralogy is an essential step in the design of an in situ dithionite injection system. Successful application of ISRM technology requires the use of an optimum concentration of dithionite solution and buffer (Amonette et al., 1994; Szecsody et al., 2000; Nzengung et al, 2001). Decomposition of dithionite in aqueous solution is faster at acidic pH (Rinker et al., 1965). Because the stability of the aqueous dithionite is enhanced at the higher pH, the dithionite solution needs to be buffered. Successful application also requires a favorable balance between dithionite transport and reaction kinetics. Therefore, the duration of dithionite injection and reaction time requires careful study to achieve optimum reducing capacity of the treated aquifer materials.

The feasibility of applying this technology is being considered at Department of Energy's (DOE) Savannah River Site (SRS), located near Aiken, SC. The highly weathered aquifer sediments of this Southeastern Atlantic Coastal Plain are composed largely of quartz and kaolinite, coated with variable charged Fe-oxides (Storm and Kaback, 1992; NRC, 1994; Seaman et al., 1996; SNL, 1996; Bertsch and Seaman, 1999; Vulava and Seaman, 2000). Over many years, the water table aquifer has received wastewater containing various metals, radionuclides and organic compounds from nuclear materials processing facilities on the SRS (Looney et al, 1990; Eddy et al., 1991; Evans et al., 1992; Newman et al., 1993; U.S. EPA, 1997; Riley and Zachara, 1992). Initial batch experiments suggested that dithionite-reduced SRS aquifer materials are capable of degrading tetrachloroethene (Nzengung et al., 2001; Heath, 2000; Payne, 2001). The goal of this research was to determine optimum design conditions for creating ISRM treatment zones in an Atlantic Coastal Plain aquifer at the SRS for the purpose of treating redox sensitive contaminants in groundwater. The specific objectives were (1) to study the reaction kinetics of dithionite in contact with SRS aquifer materials using batch and flow-through column techniques; (2) to determine the optimum dithionite and buffer concentration for efficient reduction of the aquifer solids; and (3) to determine the reaction times kinetics necessary for efficient transformation of chlorinated organic solvents in contact with the reduced barrier materials.

MATERIALS AND METHODS

Aquifer materials. Laboratory batch and column experiments were performed using subsoil collected from 150 cm below ground surface in a forested area on the SRS. This subsurface material is typical of the coarse textured, highly weathered aquifer sediments from the Tobacco Road Formation and displays characteristics similar to sediments underlying the Southeastern Coastal Plain. Tree roots and debris were manually removed and the sediments were air dried, and sieved to obtain the < 2 mm fraction, then stored at 4 ^{o}C. Various physical and chemical characteristics of this material are listed in Table 2.1.

Chemicals and solutions. All chemicals used in the study were of analytical reagent grade. All test solutions were prepared in "artificial groundwater" (AGW) with a chemical composition representative of the groundwater found in this region (mg L^{-1}): 1.00 Ca^{2+}, 0.37 Mg^{2+}, 0.21 K^{+}, 1.40 Na^{+}, and 0.73 SO_4^{2-} (Strom and Kaback, 1992). A concentrated AGW stock was subsequently diluted with Milli-Q (Millipore Corp.) water to the desired concentration before use. All glassware, column materials, and reaction tubes were acid washed with 20% hydrochloric acid and then rinsed with Milli-Q^{TM} water prior to use.

Preparation of dithionite solution. Reduction of structural Fe(III) and other redox sensitive metals using dithionite was performed using the procedure adapted from Stucki et al. (1984) and Amonette et al. (1994). All chemicals and reagents necessary for dithionite solution preparation were prepared and stored under N_2 atmosphere. The dithionite solutions were prepared with deoxygenated artificial ground water (DAGW). The DAGW was prepared by first boiling Milli-Q water, purging with N_2 gas and mixing with a predetermined volume of the AGW stock solution. The DAGW was then transferred immediately to a Coy^{TM} anaerobic chamber under nitrogen atmosphere and stored overnight to further deplete any residual oxygen. The citrate-bicarbonate buffer was prepared by adding 0.58 M sodium bicarbonate and 0.05 M sodium citrate to AGW (Stucki et al., 1984). The carbonate-bicarbonate buffer was prepared with K_2CO_3 (4 times the dithionite concentration) and $KHCO_3$ (0.4 times the dithionite concentration) after Istok et al. (1999). Immediately before each experiment, the dithionite solution was prepared by adding a known or predetermined mass of dithionite to the buffer solution. For laboratory column experiments, tritium (~200 pCi L^{-1}) was added to dithionite stock solution and used to determine the physical transport characteristics of the columns (i.e., PV, flow velocity and hydrodynamic dispersion). The dithionite solution was stored prior to injection in a collapsible Teflon bag (Kevlar^{TM}) with no headspace to prevent reaction with atmospheric O_2 (Creutz and Sutin, 1974).

Batch transformation kinetics. The kinetics of dithionite decomposition in soil solution and the efficiency of SRS aquifer material reduction were measured in batch experiments conducted entirely inside the anaerobic chamber at ambient temperature (25 ± 2 ^{o}C). Prior to the batch experiments, oxygen in aquifer materials was removed by drying the sediments in the anaerobic chamber overnight. Aquifer materials (15 g) were added (in duplicate) to Oak Ridge polyethylene centrifuge tubes, and saturated with DAGW to obtain a solid to solution ratio of 1.0. After rotating the tubes on an end-over-end shaker at the rate 8 rpm for 48 h, buffered dithionite solution was added to the tubes to achieve a final dithionite concentration of ~34.5 mmol. The control consisted of buffered dithionite solution prepared in AGW without soil. The samples and the controls were mixed continuously on an end-over-end rotary shaker and were sacrificed for analysis at pre-determined specific time intervals. The aqueous and solid phases were separated by centrifugation at 10,000 rpm (12,000 rcf) for 30 minutes at 25 ^{o}C, filtered under anaerobic condition (0.22 um pore size polycarbonate membrane) and analyzed for dithionite and its degradation products. Residual reductants were removed from the solid phase by three washes with deoxygenated 0.1 M $NaHCO_3$ (pH ~ 8.32) solution, followed by one wash with DAGW to remove excess carbonate from the solid phases (Amonette et al., 1994). The reduced sediment was air-dried and preserved in the inert atmosphere for subsequent analysis of redox capacity, and distribution of Fe species.

Column studies. A laboratory scale barrier system was developed by using a continuous flow-through column system. A 5.0 cm ID, 10 cm long plexiglass column was used for dithionite treatment experiments and a 1.25 ID, 15 cm long chromatography column was used for treatment method optimization experiments. The plexiglass columns were packed with aquifer materials to a uniform bulk density. Each end of the soil columns were packed with acid washed sand layers (< 1 cm) to help disperse flow throughout the entire cross-section of the column. Columns were stored at 4 ^{o}C prior to conducting the leaching experiment to minimize the biological activity. Dry packed columns were flushed with carbon dioxide gas for ~30 minutes to replace the air pockets inside the columns. Then the columns were oriented vertically and slowly saturated in an upflow direction with AGW at a Darcy's velocity of ~7.0 cm d^{-1} using a peristaltic pump. The soil columns were initially flushed with AGW until equilibrium was reached (~10

PV) based on pH and conductivity of the effluent. The column PV and porosity were determined gravimetrically and confirmed using a conservative tracer (^3H_2O). A typical bulk density of 1.60 g cm^{-3} and porosity of 0.40 were obtained.

Following AGW saturation, the soil columns were treated with freshly prepared buffered dithionite solution at a constant inlet flow rate (Darcy velocity of ~72 cm d^{-1}) to reduce the aquifer materials. The effluent pH, electrical conductivity (EC), DO (mg/L) and redox potential (mV) were continuously monitored throughout the experiments using in-line flow through electrodes at the column outlet. The effluents collected with a generic fraction collector were analyzed for turbidity (NTU), dithionite, total Fe, Fe(II), and trace metal concentrations. Effluents were filtered before analysis for dithionite, tritium, iron, and trace metals. Effluent samples were quickly screened for ^3H_2O to indicate when tracer breakthrough was complete.

Solid phase extraction. Fe minerals are typically finely particulate or poorly crystalline and identification of these minerals is difficult using direct x-ray diffraction methods (Jenne, 1977). Therefore, various chemical extractions (Heron et al., 1994b) for Fe speciation were conducted to determine the distribution of Fe species as summarized in Table 2.2. Basically both mild acid extractions and strong acid extractions were performed to distinguish easily reducible iron forms from a much larger bulk mass of iron inherently present in sediments. For the wet extraction procedure, triplicate samples each of 1.0 g air-dried soil were digested under anaerobic conditions (Table 2.2). Extracts were centrifuged, filtered though 0.1 μm membrane filter, and stored in acid-washed opaque bottles at 4 °C. Samples collected and preserved in this manner can be stored without significant changes to the Fe redox state since microbial substrates have been removed, the pH is low enough to keep metals solubilized, and the iron oxidation rate is negligible (To et al., 1999).

In order to assess the redox capacity of the aquifer materials treated with dithionite, solid phases were extracted using a modified chromate oxidation method (Pedersen et al., 1991) originally developed by Mebuis (1960) for determination of soil organic carbon. In brief, 1.0 g of reduced sample was treated with 9.5 ml of digestion solution in sealed 40 ml EPA headspace vial for 1 h at 140 ^{o}C. The digestion solution was 0.02 N potassium dichromate in 60% (w/w) trace metal grade sulfuric acid. After digestion and cooling, extracts were filtered, and residual dichromate was analyzed. All total redox capacity (TRC) results were given in mmol Cr(VI) per kg soil.

Analytical measurements. Dithionite concentrations were determined immediately after collection by measuring UV absorbance at 315 nm with a UV-Vis spectrophotometer (Cary 500 scan, Varian). DO levels in column effluents were determined using an automatic measurement system consisting of a flow through O_2 electrode (Microelectrodes, Inc., Bedford, NH). Trace metals in the effluents were analyzed using atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectrometry (ICP-MS).

Iron, chromium, and sulfate analysis in aqueous samples were analyzed using a prepared reagents and a Hach DR890 colorimeter (Hach Company, Loveland, CO). For iron determination, iron extraction and analysis was accomplished following a procedure adopted from Komadel and Stucki (1988). For Fe(II) measurements,1,10-phenanthroline indicator was added to the sample to form an orange color proportional to the ferrous iron concentration. For total iron measurements, a prepackage mixture (Hach Company, Loveland, CO) of 1,10-phenanthroline-p-toluenesulfonic acid salt, sodium citrate, sodium hydrosulfite, sodium metasulfite and sodium thiosulfate was added to the samples. Fe(III) was calculated as total Fe minus Fe(II) measured in the same extract. Cr (VI) in the samples was determined by adding a 1,5-diphenylcarbohydrazide reagent combined with an acidic buffer which reacts to give a purple color with an intensity proportional to the amount of Cr(V) present (AWWA, 1998). For ^3H_2O analysis, one milliliter of each effluent fraction was mixed with 10 ml of scintillation cocktail and counted for 20 minutes in a liquid scintillation counter (Minaxi Tri-Carb 4000 Parkard Instrument Co., Downers Grove, IL). For mineral characterization, dithionite treated sediments were examined using high resolution thermo-gravimetric analyzer (TGA 2950, TA Instruments Inc.) and x-ray diffraction (XRD, Scintag, Inc.).

RESULTS AND DISCUSSION

Influence of sediment characteristics on effectiveness of ISRM. SRS aquifer materials are generally coarse in texture. The predominant clay mineral identified by XRD was kaolinite (Table 2.1). The low permanent charge in kaolinite renders the ditrigonal siloxane cavities unreactive and the principal surface reactive sites are therefore located along the edge sites (Davis and Kent, 1990). Also, the aquifer material has negligible organic carbon, low BET surface area, and little Fe present in layer silicates, which suggest that SRS aquifer materials may not be suitable for application of ISRM technology. However, other investigators (Nzengung et al., 2001) have observed that Fe-poor aquifer materials can effectively catalyze the reduction of oxidized organic compounds. Nzengung et al. (2001) showed that Fe-poor montmorillonite, when reduced by dithionite was more reactive than dithionite reduced Fe rich ferruginous smectite. The lower reactivity of ferruginous smectite was attributed to the decrease in clay swelling that results from partial or total collapse of interlayer space due to the increase in layer charge. The collapse in clay layer renders the interlayer Fe inaccessible for surface mediated reactions (Stucki et al., 1984; Lear and Stucki, 1989; Gates et al., 1998). Therefore, the presence of iron in sediment does not necessarily improve the efficiency of surface catalyzed reduction reactions. Rather, the location and accessibility of the Fe in the clay mineral structure is of greater importance than the amount of Fe present. Interestingly, glass beads treated with dithionite under similar conditions catalyzed the degradation of tetrachloroethene, PCE (Heath, 2001; Payne, 2001), which suggests that redox sensitive metals may not be solely responsible for catalyzing these reactions. X-ray diffractograms of SRS sediments indicate that quartz is the most dominant mineral phase in sand and silt sized fractions, with kaolinite as the major mineral phases in the clay sized fraction (Seaman et al, 1996; Vulava and Seaman, 2000; Hudson, 1994; Lott, 1999; Nuessle, 2001). The observed reactivity of dithionite treated quartz sand and quartz sand plus goethite in degrading chlorinated ethenes (Payne, 2001) suggests that dithionite treated sandy sediment at the SRS could be used to create effective ISRM treatment barriers.

The chemical extraction techniques (Table 2.2) used to quantify iron species in the aquifer sediments described in Figure 2.1 showed that the accessible Fe(II) (48-h, 0.5 M HCL extraction) and bulk Fe(II) (21-d, 5 M HCL extraction) content in the sediment are small (Figure 2.1a). Also, a significant fraction of the Fe(II) is likely to be leached during dithionite treatment, while the remaining Fe(II) would be inaccessible for reaction.

The distribution of the Fe(III) in SRS sediment suggests that about 11 % of the ferric iron constitutes soluble Fe(III), amorphous (ferrihydrite) and poorly crystalline mineral phases such as lepidocrocite, and akageneite (Figure 2.1b). These Fe(III) fractions are considered to be very reactive (Kennedy et al., 1998; Davis and Kent, 1990) and more subject to reductive dissolution than goethite (Postma, 1993). For dithionite treated SRS sediments, surface-bound Fe fractions are likely to contribute most of the redox capacity. In spite of the fact that some of the Fe(III) may be lost from the aquifer after dithionite treatment as dissolved Fe(II), a portion of the dissolved iron may readsorb to mineral surfaces, or may precipitate as siderite ($FeCO_3$). Dissolved and reduced Fe sorbed to smectite shows more reactivity with carbon tetrachloride than smectite with no sorbed Fe (Rodriguez et al., 1999). Therefore, Fe(II) sorbed onto the various SRS aquifer materials should present reactive surface sites following dithionite treatment (Table 2.1). Additionally, Fe(II) may be derived from more stable crystalline phase or residual Fe(III) bound in the clay and silicate minerals. If the poorly crystalline Fe(III) is not completely reduced, it may consume some of the electrons produced after dithionite treatment, thereby reoxidizing some of the Fe(II) even before it reacts with the contaminants. Therefore, the complete reduction of reactive redox sensitive metals at accessible surface sites has great potential in the in-situ reduction of oxidized contaminants.

Dithionite solution and buffer. The formation of metal sulfide and siderite on sediment precipitates was noted for highly concentrated buffered dithionite solution and for extended dithionite sediment contact time. The formation of black precipitates on the sediment was occasionally detected when the pH was maintained above 9.0. The precipitation of siderite or FeS may poison reactive surface sites and render them inaccessible for reaction with contaminants. Therefore the optimum concentration of buffered dithionite that effectively reduces the aquifer material while mobilizing a minimal amount of Fe(II) is preferred. In previous studies, laboratory batch experiments to determine the optimum dithionite concentration using different clay minerals and iron oxides showed that the most efficient transformation of PCE, trichloroethene (TCE) and trichloroethane (TCA) was obtained with sediment treated with 34.5-36.6 mmol aqueous dithionite solution (Nzengung et al., 2001; Heath, 2000; Payne, 2001). The results of batch reduction experiments by Szecsody et al. (2000) using Hanford sediment suggested that aqueous dithionite solution lower than 40 mmol would be optimum to minimize dithionite disproportionation reactions. Based on the above findings, 34.5 mmol aqueous dithionite solution was chosen for our ISRM experiments.

The low cation exchange capacity and organic carbon content of the SRS aquifer sediment suggest that it has a limited buffering capacity. The unbuffered 34.5 mmol dithionite solution prepared using AGW had an initial pH ~ 7.0 (Figure 2.2a). When the same concentration of dithionite solution was added to the SRS soil solution, the production of protons from Fe reduction and dithionite disproportionation caused the pH drop to ~ 6.5. Since the stability of aqueous dithionite is low at this pH and the reaction of dithionite with soil Fe causes iron mobility (Figure 2.2b), it is important to add buffer to maintain a basic pH that can provide a minimum of four moles of acid buffering capacity for each mole of dithionite in solution.

Various treatment have been used to control the pH of dithionite solutions, including citrate-bicarbonate (Stucki et al., 1984; Gates et al., 1997, 1998; Nzengung et al., 2001) and carbonate-bicarbonate (Amonette et al., 1994; Fruchter et al., 2000). Since carbonates are the main natural pH buffer in groundwater, citrate-bicarbonate and carbonate-bicarbonate buffer were applied to the aquifer sediments to determine the optimum buffer concentration for dithionite treatment. Citrate is mainly used as a chelating or complexing agent for ferrous and ferric iron during the extraction of free iron oxides (Jackson et al., 1986). The dithionite solution buffered with citrate-bicarbonate prepared following the procedure adopted from Stucki et al. (1984) showed a decrease of initial pH from 8.5 to 8.2 in batch experiments conducted with soil-to-solution ratio of 0.5 and 1% (mass/volume) (Nzengung et al., 2001). When the citrate buffered dithionite solution was used to reduce SRS aquifer sediment in column experiments, mobilized colloids were detected in the effluent, apparently as a result of formation of citrate-Fe complexes (Rueda et al., 1992). The reductive dissolution of Fe minerals by citrate buffered dithionite solution, as suggested by Stucki (1984), stripped away the Fe oxide coatings that act as cementing agents for the kaolinite/quartz based matrix resulting in the dispersion and transport of silicate minerals. Potassium carbonate-bicarbonate buffered dithionite had an initial pH of about 11 and decreased to about 10 without obvious colloid mobilization when mixed with SRS sediment in batch and column experiments. Therefore, the bicarbonate-carbonate solution was selected as the preferred buffer to control pH of dithionite solution used for creating the ISRM treatment barrier.

The optimum buffer concentration to efficiently reduce the SRS sediment was determined by measuring the pH and the amount of Fe(II) mobilized in batch vials with varying amounts of potassium carbonate-bicarbonate (6.0x, 5.0x, 4.0x, 3.0x, 2.0x, 1.0x, 0.5x and 0.0x) relative to the dithionite concentration. At the lower buffer concentrations, reduction and disproportionation reactions produced H^+ protons that exceeded the sediment and solution buffering capacity, so the pH decreased during the experiments. The results indicate that there was little effect on solution pH with varying buffer concentration, except at very low (0.5x, 1.0x) buffer concentrations (Figure 2.2a). The results also indicate that at the 0.5x and 1.0x buffer concentrations, Fe dissolution was significant (Figure 2.2b). At the observed pH of ~7 and low to moderate redox conditions, the solubility of Fe was very high (up to 3%). For buffer concentrations between 0.5 and 2.0x, the addition of dithionite increased the mobility of iron. Using optimum dithionite concentration of 34.5 mmol and a bicarbonate-carbonate buffer concentration of 3x (i.e., 3 times the concentration of dithionite added to the column), a basic pH of > 8 was sustained in the columns with little or no iron mobilization.

Kinetics of dithionite decomposition. The half-life of unbuffered dithionite in oxygenated solution is on the order of a few minutes (Fruchter et al., 1994). Batch experiments were conducted to evaluate the stability of dithionite in synthetic SRS ground water. The decomposition of 34.5 mmol buffered dithionite solution exposed to air (Figure 2.3) was described by pseudo-first-order reaction kinetics ($k_1 = 0.1221\ h^{-1}$, and $t_{1/2} = 5.68$ h, $R^2 = 0.97$). This observation is consistent with previous studies that determined the decomposition of dithionite at concentrations < 0.1 M (Morello et al., 1964; Jhaveri and Sharma, 1968; Singh et al., 1978; Sridhar, 1987; Shaikh and Zaidi, 1993). For higher concentrations of dithionite (> 0.1M), second order reaction kinetics was reported by other investigators (Jhaveri and Sharma, 1968; Fukushima et al, 1978; Shaikh and Zaidi, 1993).

The buffered dithionite in synthetic SRS groundwater under anoxic condition was stable for ~ 100 h and the dithionite decomposition kinetics with SRS sediment contact under anoxic condition was described by pseudo-second-order reaction kinetics ($k_2 = 2.3 \times 10^{-3}\ h^{-1}$, $t_{1/2} = 12.39$ h, $R^2 = 0.97$) (Figure 2.4). In similar studies, Amonette et al., (1994) obtained rate constant of $2.9 \times 10^{-2}\ h^{-1}$ ($t_{1/2} = 24$ h) for heterogeneous decomposition of dithionite in Hanford sediment. An initially fast degradation rate was followed by slower kinetics thereafter. We used a two-site simultaneous reaction model to describe the heterogeneous reaction, where reaction of dithionite with reactive surface sites (amorphous iron oxides) and less accessible reaction sites (crystalline iron oxides, layered clay minerals) are initiated at the same time. The reduction reactions at amorphous iron sites are very rapid while slower reduction kinetics occurs at the relatively less accessible mineral sites. The ferric iron reduction rate by dithionite was observed to be much faster than dithionite disproportionation at the beginning of the experiment. As observed by Amonette et al. (1994) and Szecsody et al. (2000), a larger amount of dithionite was consumed by disproportionation with increasing contact time. For SRS sediments, the disproportionation of dithionite was faster after 100 hours of contact time (data not shown).

Optimum conditions for ISRM of SRS soil columns. A series of batch and column experiments were conducted to obtain information on ISRM design factors such as the dithionite solution injection rate, concentration and reaction time required to manipulate/enhance the redox capacity of the aquifer materials. In batch experiments, SRS aquifer materials were treated with dithionite solution for different durations to determine the highest achievable reductive capacity. To determine an optimum injection rate, four columns packed with SRS aquifer materials as previously described, were reduced with dithionite for 2, 12, 24, and 48 PV. In order to determine the most optimum time for the reaction phase, five different columns packed with the aquifer sediments were injected with buffered dithionite and allowed to react for zero, 6, 12, 24, and 48 hours, respectively. Extraction of reduced iron from the reduced columns and reaction vials showed that higher reduction was achieved in columns with increasing injection time (Figure 2.7). However, no change in the exchangeable Fe(II) fraction was observed with increasing duration of injection, which suggested that no additional formation of dissolved Fe(II) phases occurred by increasing the severity of treatment (Figure 2.7a). Most of the Fe(II) was observed in the 0.5 M HCl extractable phase, which consisted primarily of monosulfide (FeS) and partly of siderite. As mentioned earlier, the accessible Fe(II) phase in untreated SRS aquifer materials was very low. Therefore, the higher Fe(II) in the 0.5 M HCl extractable phase after dithionite treatment is attributed to reduced ferrihydrite, lepidocrocite, and partly of akageneite, goethite and hematite. Fe(II) contributed from the 5 M HCl extractable phase increased very slowly with higher reduction duration, which may be due to reduction of structural Fe(III) mineral phases present in the sediment. The concentration of Fe(II) in the aquifer material subjected to same dithionite injection duration and different reaction times suggest that the reduction of accessible Fe sites was achieved mostly during the injection phase with little additional reduction during the reaction phase (Figure 2.7b). The interpretation of redox capacity of sediment using different Fe extraction methods may be applied qualitatively because there are multiple mineral phases present on natural sediments and these Fe extraction techniques are not capable of separating different Fe fractions with much accuracy. Therefore, an investigation of redox capacity of reduced sediment based on a chromate oxidation method was performed. The result of this study are presented in Figure 2.8.

The data shows that there was no significant increase in the redox capacity after 12 PV of dithionite injection (Figure 2.8a). The amount of chromate reduced was not in agreement with the amount of Fe(II) that should be available to react (Figure 2.7a). This data indicated that reduction of Fe(III) by the injection of greater than 12-PV might not have much effect on the total redox capacity of the sediments. Therefore, 12-PV of injection can be applied as the optimum injection duration. Based on Figure 2.7b and Figure 2.8b, it was determined that reaction time equal to 6 hours or higher was needed to achieve optimum reduction of packed columns of the SRS sediment. The Fe(II) species (Figure 2.7c) for different contact time in batch experiments indicated that amount of accessible Fe(II) in reduced batch sediments was similar to reduced column sediments (Figure 2.7a).This data indicated that an approximately 19 hours or more dithionite contact is needed to achieve optimized reduction in batch experiments; however, the reduction capacity of reduced batch sediments (Figure 2.8c) did not indicate any clear trend of optimum dithionite contact time.

ISRM proof of principle. Dithionite injection/withdrawal experiments were conducted in laboratory scale columns to study dithionite transport properties under physical conditions that are analogous to field conditions to obtain data needed to optimize the design of a deployed ISRM system. The experiments consisted of injecting two PV of aqueous dithionite over four hours, followed by an 18 hr reaction/equilibration phase and finally a remediation phase. During the remediation phase, oxygenated synthetic SRS ground water was injected through the column to reoxidize the reduced aquifer material. The characteristics of the column effluent solutions are presented in Figure 2.5 and Figure 2.6. The highest effluent concentration of dithionite approached

78% of the initial injectate concentration (C_o) by the end of the four-hour injection phase (Figure 2.5d). At the end of the reaction phase of 18 hours, dithionite concentrations decreased to about 45% of the injectate concentration, which indicated that 33% of the injected dithionite was degraded during the reaction period of 18 hour (Figure 2.6e). The effluent dithionite concentration continued to decrease during the remediation phase and fell below detection limit (~ 17.4 mg L^{-1}) after 3.7 PV of oxygenated groundwater. The influent pH of 11 decreased to 9.6 and 10.35 in the effluent solution after one and two PV of dithionite injections, respectively (Figure 2.5a). As Figure 2.5 indicates, column head pressure, along with turbidity and iron concentration increased after one PV during the injection phase due to the mobilization of colloidal materials; however less than 1% of the total Fe was mobilized from the column sediments. Except for this small discharge of colloids during the first PV injection, no further colloid mobilization or sediment plugging was observed as a result of the altered Eh and pH conditions. The breakthrough curve of tritium, pressure, and electrical conductivity during injection and remediation phases suggested that the colloid mobilization did not change the column hydraulic and chemical properties (Figures 2.5 and 2.6). The injected reagents and reaction products were recovered within the first five-PV of the remediation phase, which gave an estimate of the withdrawal volume needed to recover the residual injected reagents. While some trace metals were mobilized in the withdrawn injectate, the trace metal concentrations were well below the South Carolina purge water criteria (data not shown). This suggests that the dithionite treatment will not impact thr hydraulic properties of the SRS aquifer.

Oxygen removing capacity of dithionite treated sediments. As described above, oxygenated groundwater (O_2 concentration ~ 8.22 mg L^{-1}) simulating contaminant flows (assuming O_2 is the only electron acceptor) was leached through the reduced column to determine the reductive capacity of the treated sediment. Reaction stoichiometry was estimated by determining the number of PV of oxygen-saturated water needed to reoxidize the reduced sediment (Figure 2.6). The reducing conditions were maintained for 173 PV. Integration of the effluent oxygen breakthrough curve indicated that 2.90 mmol of O_2 (i.e., 0.16 mg O_2 per g of reduced sediment) were consumed by Fe(II) and other reductive intermediates in the treated sediment (Appendix A). Based on the total Fe(III) content (5 M HCl extractable, see Table 2.2) of the sediment (0.50 wt %) and that 4 moles of Fe(II) is oxidized for one mole of oxygen, it was calculated that the dithionite treatment reduced as much as 45% of the available Fe(III) originally present in the sediment. It was considered that 0.5 M HCl extractable Fe(III) and a fraction of 5 M HCl extractable Fe (III) of the sediments were reduced by the dithionite treatment. Based on this assumption, the ISRM was found to reduce the most accessible form of Fe (ferrihydrite, lepidocrocite and akageneite) completely and 39.6% of structurally bound crystalline phase Fe (goethite and hematite).

Conclusions. The bench-scale studies evaluating optimized dithionite injection rate and reaction time will improve our ability to better design pilot field demonstration/validation studies for the deployment of ISRM systems for remediation of halogenated organic compounds and redox sensitive metals. This study has determined an appropriate buffer (carbonate/bicarbonate) that minimizes the mobilization of colloids and maintains the hydraulic integrity of the ISRM system when applied to Atlantic Coastal Plain aquifer sediments. However, the parameters derived from these studies are not necessarily optimized for field deployment. The porosity of the packed sediment columns is greater than that measured for these sediments in the aquifer formation. Thus, the mineral surface interactions of ground water solutes is expected to be greater under field conditions providing more favorable reaction efficiency. In addition, the flow rates employed in the column studies are at the upper range of those measured within the aquifer systems in the Atlantic Coastal Plain sediments at the SRS. Higher groundwater velocities will result in lower solute residence times within the treatment zone. Thus, for contaminants (e.g., PCE, TCE; see chapter 3) with slower reduction rates, the higher flow velocities used in the column experiments may not provide sufficient time in the treatment zone to allow effective degradation and will under predict the treatment effectiveness for field conditions. Additional studies are necessary to evaluate the relationship between reaction kinetics and groundwater velocity in order to optimize the design of the ISRM systems for field deployment. Because iron mineral surfaces mediate degradation of redox sensitive pollutants, more sophisticated analytical techniques such as scanning electron microscopy (SEM) may better elucidate the role of different Fe structures (minerals).

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Table 2.1. Physical and chemical properties of SRS aquifer materials (Tobacco Road sand) used in the batch and column studies.

Texture[a]		Loamy sand
Particle-size distribution[b], %	Soil mineralogy[c]	
Sand (>53 μm)	q>>>f	92.65
Silt (53-2 μm)	q>>> k	2.55
Clay (<2 μm)	k>>q>goe, mi, gibb, hem	4.80
[d]Water dispersible clay (wt %)		0.056
[d]pH$_{DI}$		5.10
[d]pH$_{AGW}$		5.00
[d]pH$_{KCl}$		4.21
[d]EC$_{DI}$ (μS/cm)		4.29
[e]Cation exchange capacity (meq/100 g)		2.30
[f]Total organic carbon (g /100 g)		0.09
[g]BET surface area (m^2/g)		2.51
	Redox sensitive transition metals[h], g / 100 g	
Iron		0.48923
Manganese		0.00099
Chromium		0.00018
	Extractable Fe, g Fe / 100 g	
[i]5 M HCl, 21-d		0.51
[j]CDB Fe		0.37
[k]0.5 M HCl		0.05
[l]AO Fe		0.02
[m]0.5 M HCl, 1-h		0.01

[a] general soil classification of US Department of Agriculture

[b] hydrometer analysis

[c] determined by X-ray diffraction, where q = quartz, f = feldspar, k = kaolinite, goe =goethite, mi = mica, gibb = gibbsite, hem = hematite

[d] 1:2 soil: solution in deionized water (DI), AGW, or 1 M KCl for 30 minutes

[e] ammonium acetate method (Rhoades, 1982; Thomas, 1982)

[f] TOC, total organic carbon, dry combustion method (Nelson et al., 1982)

[g] by Micrometrics ASAP-2010

[h] EPA method 3051; Microwave assisted acid digestion

[i] Heron et al., (1994a)

[j] citrate-dithionite-bicarbonate extraction (Jackson et al., 1986)

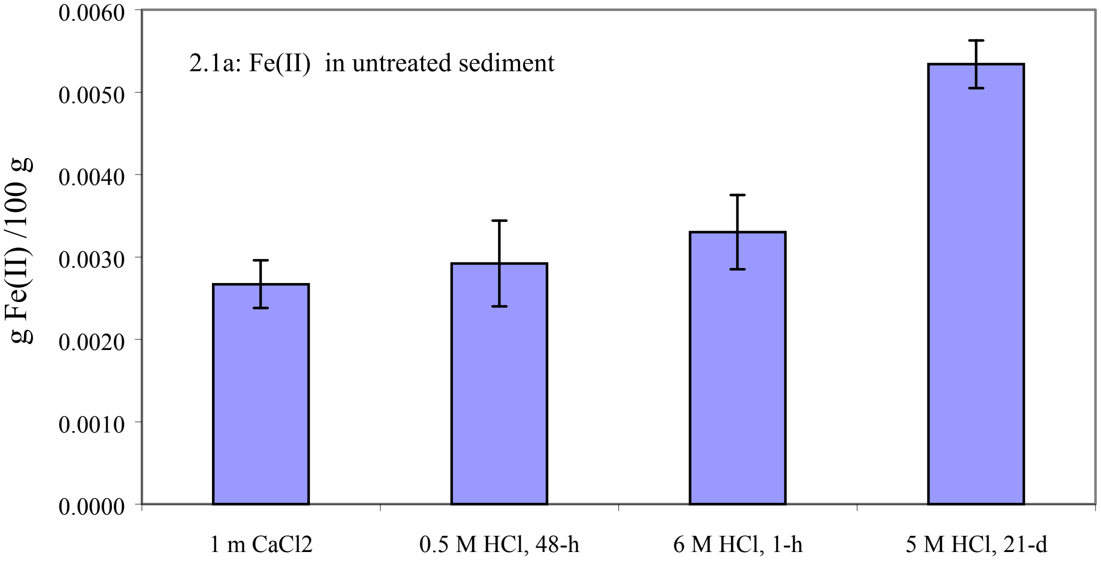
[k] Lovely et al., (1986), modified by Kennedy et al., (1999)

[l] ammonium oxalate extraction (Jackson et al., 1986)

[m] Christensen et al., (2001)

Table 2.2. Chemical extractions used for quantification of iron species in aquifer sediments.

extractants	target compounds	extraction period	amount obtained in SRS aquifer material, g/100 g	References
1 M $CaCl_2$	ion exchangeable Fe(II)	24 h	0.0027	Hodgson et al. (1960) Heron et al. (1994b)
0.5 M HCl	monosulfides, ferrihydrite, lepidocrocite, partly akageneite, partly siderite	48 h	0.047	Lovely et al. (1986) Kennedy et al. (1999)
0.5 M HCl	ferrihydrite	1 h	0.0104	Christensen et al. (1999)
6 M HCl	acid volatile sulfides (AVS) primarily mackinawite, troilite	1 h	0.0033	Heron et al. (1994b)
5 M HCl	magnetite, siderite, akageneite, goethite, hematite, magnetite, fraction of Fe bound to clays and silicates	21 d	0.5072	Heron et al. (1994b)



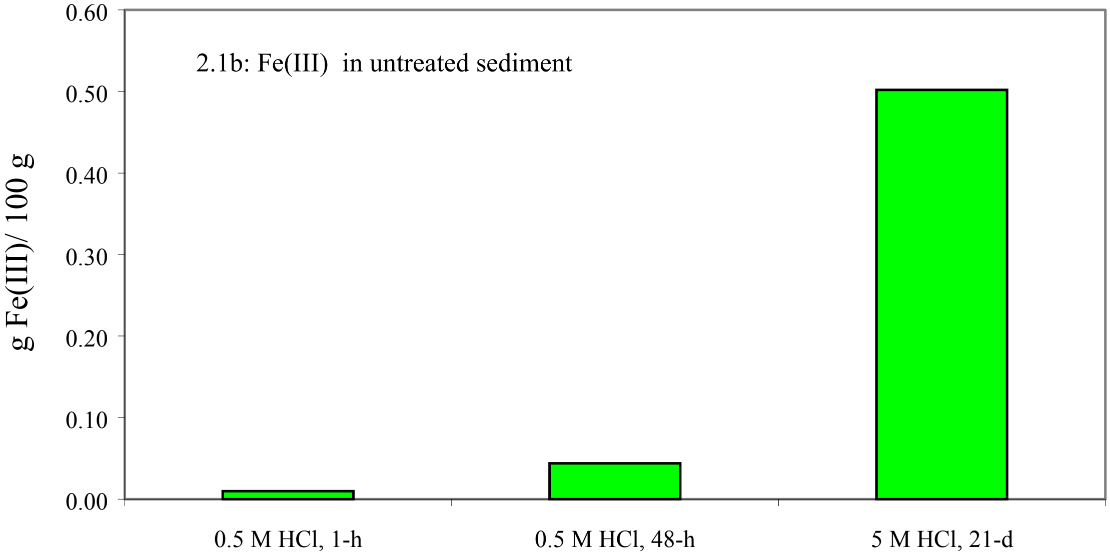


Figure 2.1. Distribution of Fe species in SRS aquifer materials. Different extraction methods described in Table 2.2 were used. Iron monosulfide in the sediment was calculated as Fe(II) soluble in 0.5 M HCl minus Fe(II) soluble in 1 M $CaCl_2$. The fraction of Fe (II) extracted by 5 M HCL but not 0.5 M HCl is referred to as residual Fe(II). Poorly crystalline Fe(III) was calculated as the amount of Fe(II) extracted with 0.5 M HCl minus the amount of Fe(III) extracted for 1h with 0.5 M HCl. Fe(III) extracted with 5 M HCL minus Fe(II) extracted with 0.5 M HCL was attributed to the crystalline and structural mineral phases, respectively.

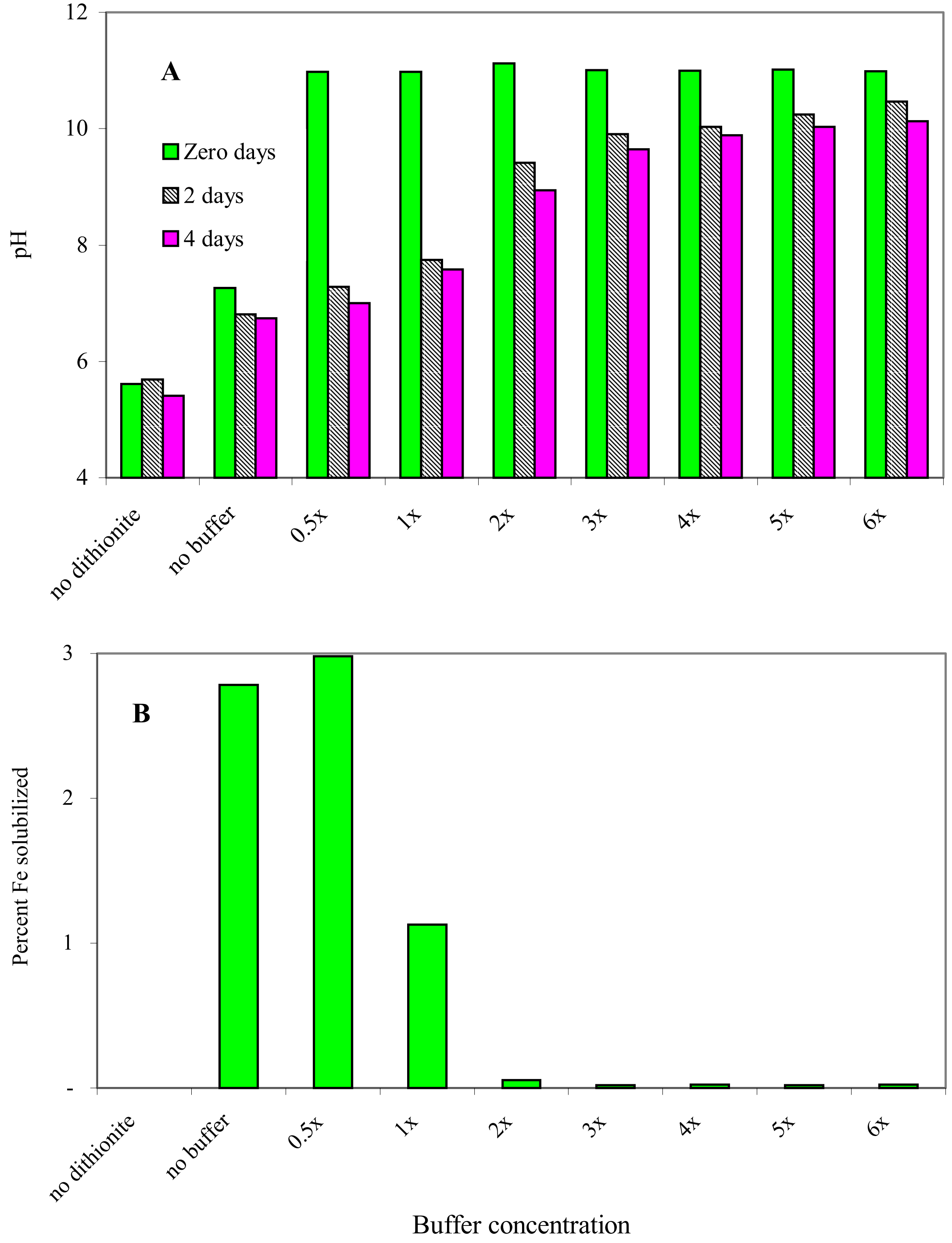


Figure 2.2. (A) The relation between solution pH and buffer concentrations during dithionite treatment of SRS sediments after 0, 2, and 4 days. Concentrations of potassium carbonate-bicarbonate buffer were varied (6x, 5x, 4x, 3x, 2x, 1x, 0.5x, 0x) relative to the dithionite concentration of 0.34 mM. (B) Percent Fe solubilized with varying buffer concentrations.

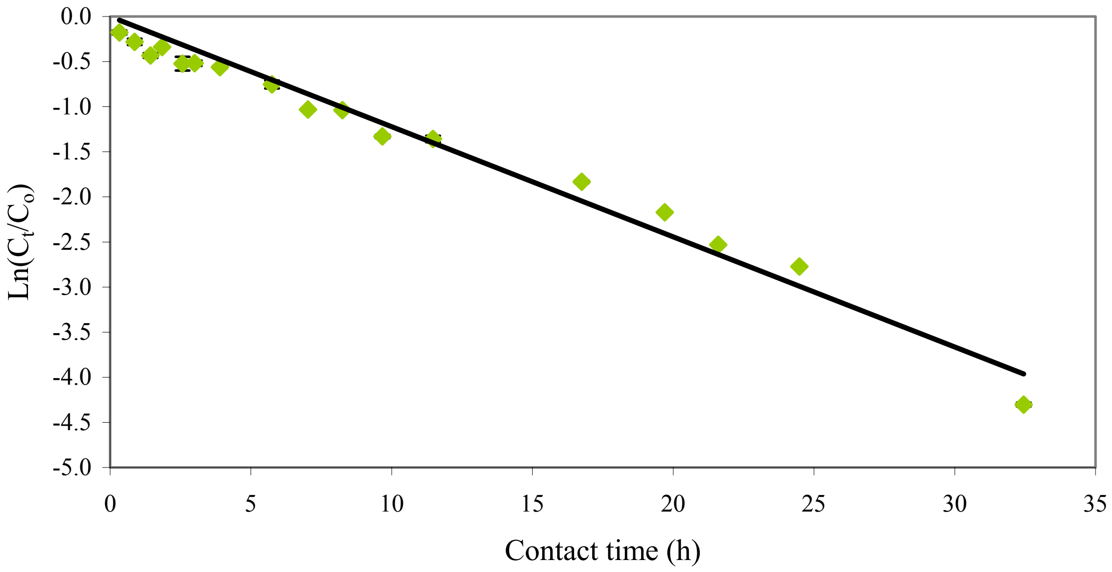


Figure 2.3. Pseudo first order rate plot for decomposition of aqueous dithionite in simulated SRS ground water solutions buffered at pH ~ 11 in contact with air at 25 °C. Initial concentration = 34.5 mM; $k_1 = 0.1221$ ($R^2 = 0.97$); $t_{1/2}$ =5.7 hr.

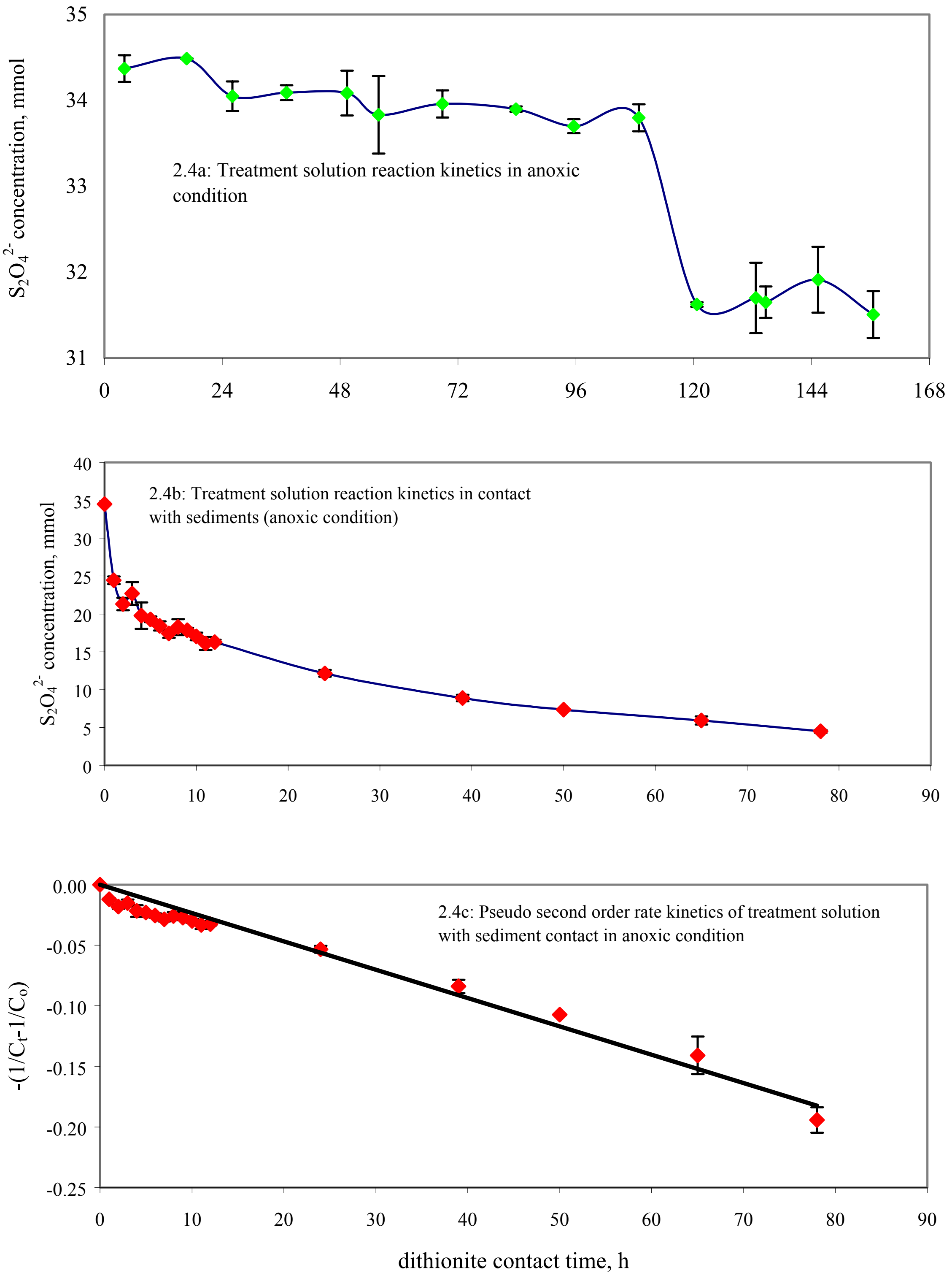


Figure 2.4. Decomposition of aqueous, buffered dithionite solution under anoxic condition with/without contact with SRS aquifer sediments at 25 ^{o}C. Solid: solution ratio = 1.0; initial concentration = 34.5 mM; $t_{1/2}$ = 12.39 hr, and k_2 = - 0.00234 hr

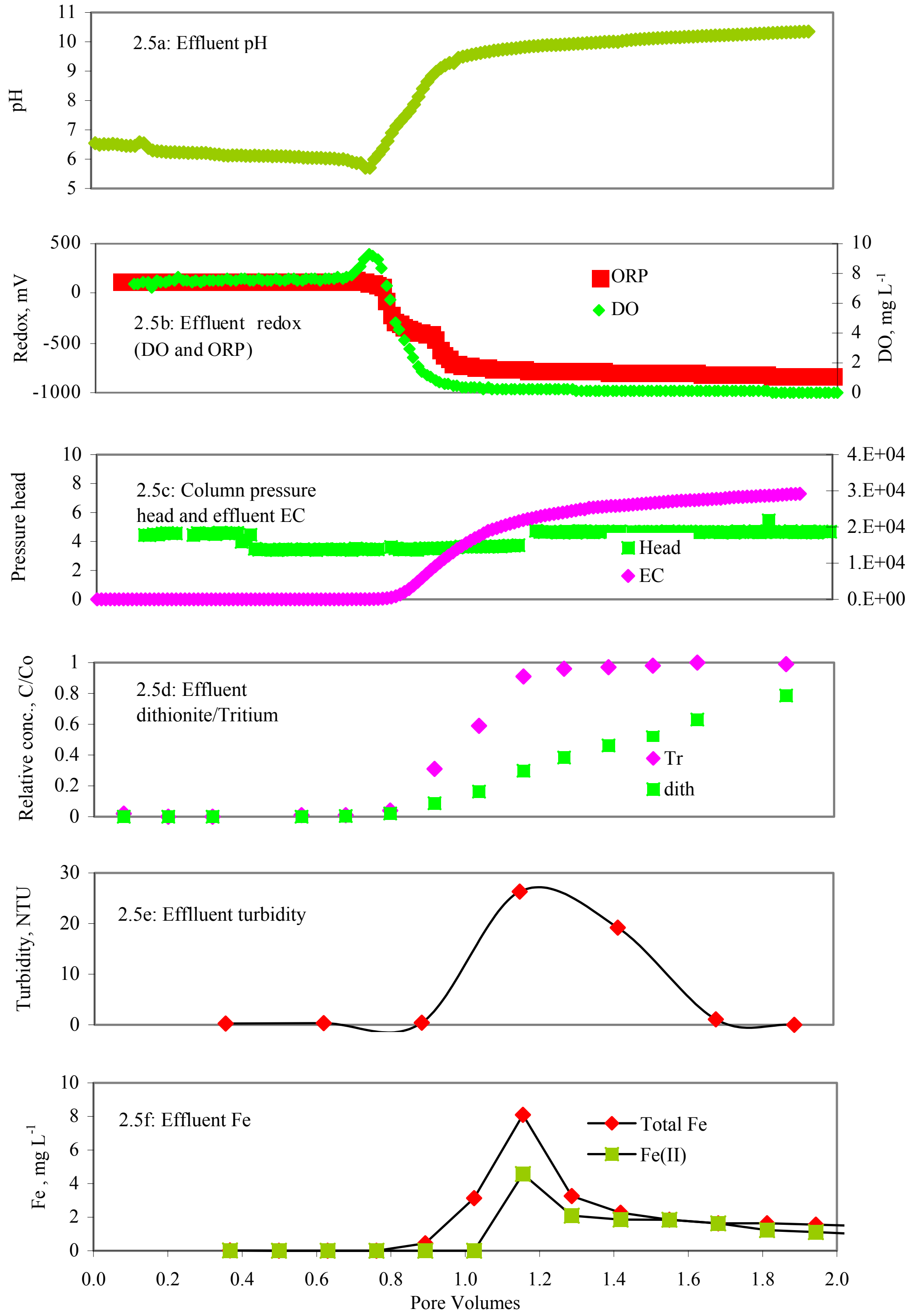


Figure 2.5. Influence of buffered dithionite treatment solution (34.5 mmol $S_2O_4^{2-}$, 0.138 mol K_2CO_3, 0.0138 mol $KHCO_3$, pH~11) on column effluent pH, redox, DO, hydraulic head, electrical conductivity (EC) and dissolution of Fe through the course of dithionite injection phase Two-pore volume of dithionite solution was injected into column at a Darcy velocity ~ 72 cm d^{-1}.

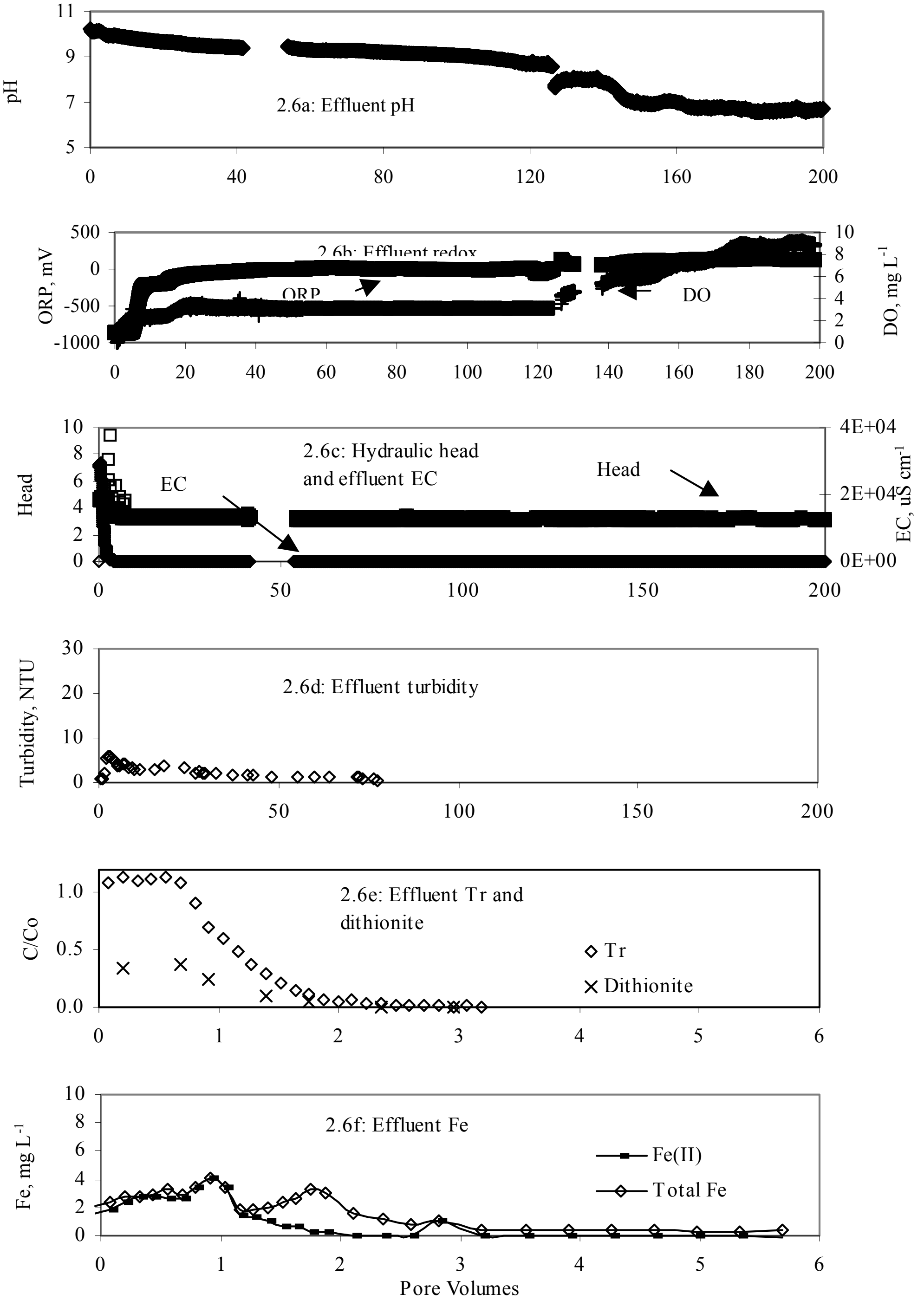


Figure 2.6. Results showing changes in column effluent parameters due to continuous leaching of oxygenated AGW through the reduced SRS sediment column.

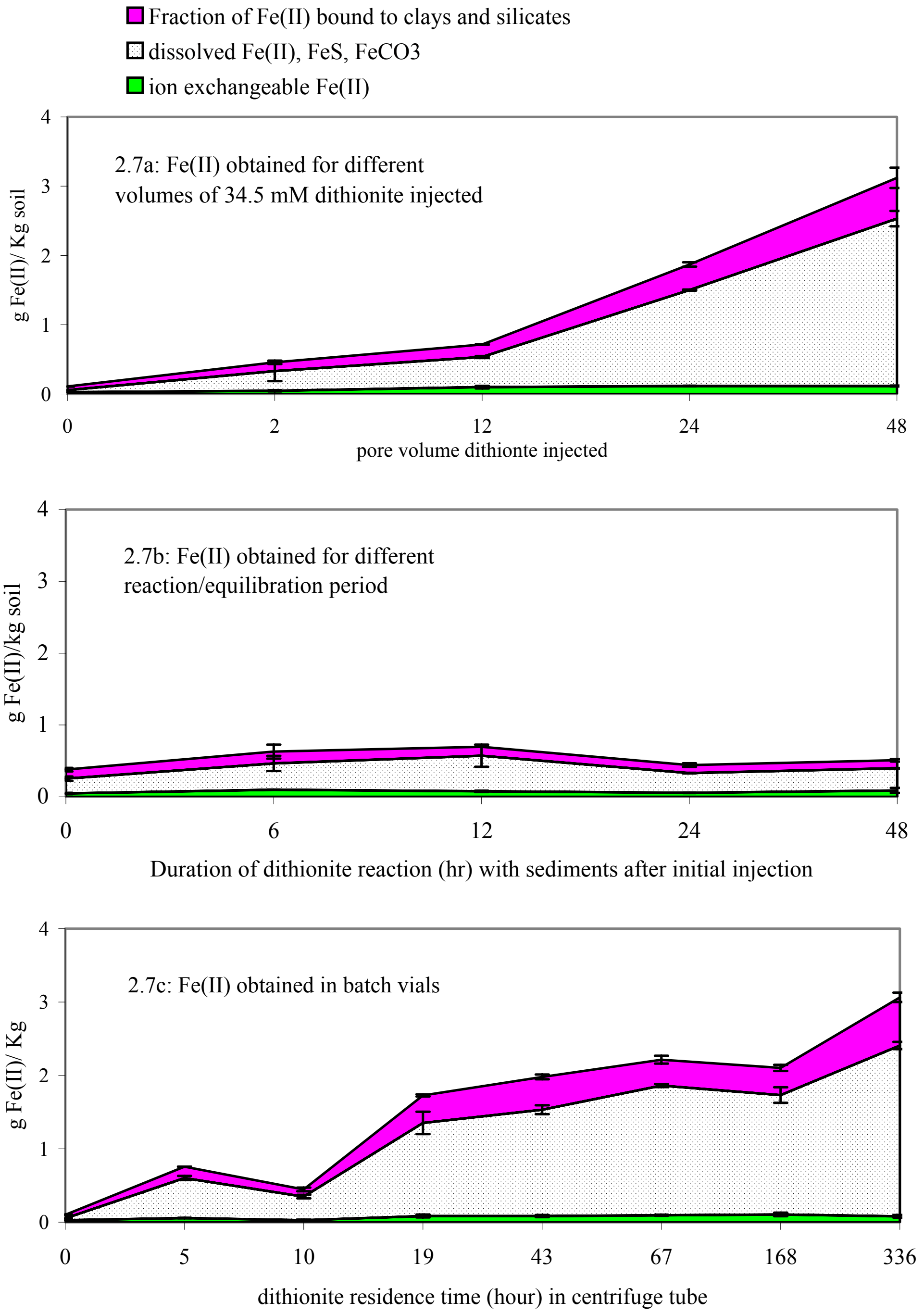


Figure 2.7: Tentative distribution of Fe (II) species in SRS aquifer sediment after different dithionite treatments adopted to determine the optimum treatment approach. The fractions of Fe (II) extracted using the 1 M $CaCl_2$, 0.5 M HCl and 5 M HCl extraction methods were explained in Table 1. Figure 2.7a and 2.7b shows the amount of Fe (II) phase obtained for different injection and reaction time periods in column experiments and Figure 2.7c shows the amount Fe (II) obtained in batch experiments.

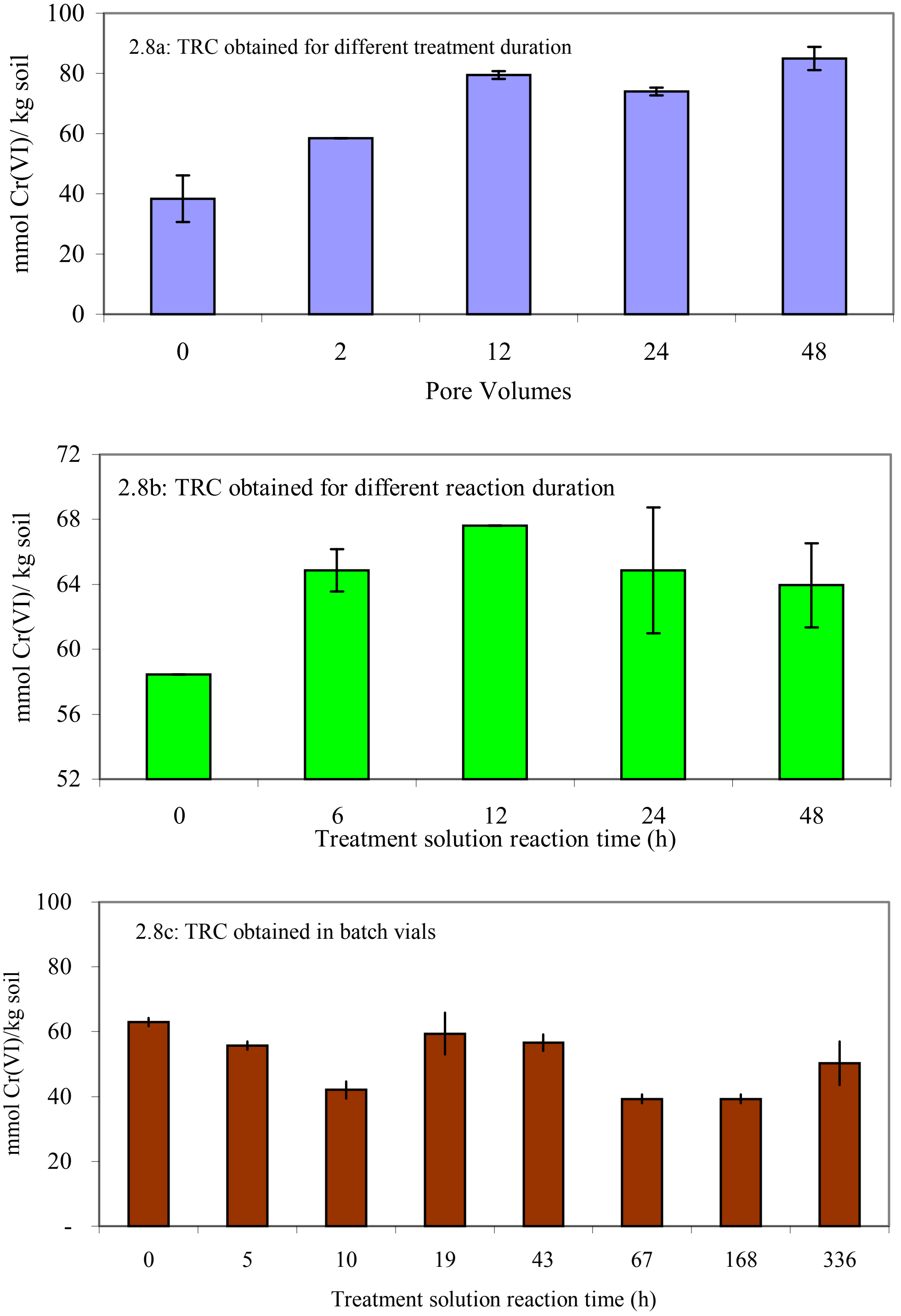


Figure 2.8. Measured total reductive capacity (TRC) of the SRS aquifer sediments after dithionite-induced reduction was completed. For TRC measurements, chromate oxidation method was used. Results shown in Figures 2.8a & 2.8b are for reduced column sediments and the figure 2.8c corresponds to dithionite treatment using batch equilibration

CHAPTER 3

REDUCTIVE DECHLORINATION OF VOLATILE HALOGENATED ALIPHATIC COMPOUNDS BY DITHIONITE TREATED AQUIFER MATERIALS AT THE SAVANNAH RIVER SITE[1]

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ABSTRACT

Dynamic column experiments were used to evaluate the use of in situ redox manipulation (ISRM) of Atlantic Coastal Plain Sediments using dithionite reduction for remediation of groundwater contaminated with PCE and TCE. A treatment scheme previously developed based on the oxygen removal capacity of reduced sediments was employed. This treatment included injection of two pore volumes (PV) of carbonate-bicarbonate buffered dithionite solution, a ≥ 8 h reaction time, and removal of residual dithionite from the reduced column sediments. Previous results indicated that the redox potential and total redox capacity achieved in these sediments following dithionite treatment should be sufficient to reduce PCE and TCE. However, the results from this study found this treatment to be inadequate for significant dechlorination of PCE or TCE contaminants in oxygenated groundwater. A likely explanation for the poor efficiency observed for the chlorinated solvents are kinetic constraints on the reduction reaction. The flow rates employed in the column studies are at the upper range of those measured within the aquifer systems in the Atlantic Coastal Plain sediments at the SRS and may have limited solute interaction within the residence time of contaminants in the column. In addition, ground water dissolved oxygen concentrations at SRS are typically lower by a factor of ten than that was used in the pack sediment columns. Thus, the degradation efficiency may be considerably greater in anaerobic or low-oxygen conditions when the competition of PCE and TCE with oxygen is reduced or eliminated. Further studies are necessary to evaluate the effects of these parameters on treatment efficiency.

INDEX WORDS: dithionite, Atlantic coastal plain sediments, PCE, TCE, reduction, Savannah River Site, in situ treatment, reactive zone, column studies, dechlorination, remediation, groundwater, chemical treatment

INTRODUCTION

Of the 25 most commonly identified contaminants at hazardous waste sites in the United States, 10 are chlorinated organic compounds (National Academy of Sciences, 1994), commonly originating as cleaning and degreasing solvents. In a U.S. Environmental Protection Agency (EPA) sampling survey of 945 groundwater based drinking water supplies (Westrick, et al., 1984), trichloroethene (TCE) and tetrachloroethene (PCE) were the most frequently detected volatile organic compounds (VOCs), other than trihalomethanes. TCE and PCE have been found in 852 and 771, respectively, of the 1,430 National Priorities List (NPL) sites identified by the EPA (ASTDR, 1997). The widespread occurrence of these chlorinated aliphatic hydrocarbons in the environment has driven research to understand their transformation and persistence in natural and engineered systems.

Organic contaminants may undergo biotic and abiotic reactions in the environment. For permanent aquifer restoration, many recent studies have focused on the abiotic transformation or degradation of chlorinated aliphatic hydrocarbons by using an in situ permeable reactive barrier. Laboratory (Gillham and O’Hannesin, 1994; Farrell et al., 2000; Imhoff et al., 1998; Cervini-Silva et al., 2000, 2001; Butler and Hayes, 1999, 2000, 2001; Weseasooriya and Dharmasena, 2001; Arnold and Roberts, 2000; Casey et al., 2000; Sivavec et al., 1995, 1997) and field tests (Focht et al., 1996; Gillham, 1996; O’Hannesin et al., 1998; Morkin et al., 2000) have shown that under highly reducing conditions and in the presence of reactive mineral surface, chlorinated aliphatic hydrocarbons (CAH), such as TCE will degrade to nontoxic compounds such as ethane, ethylene and carbon dioxide with half lives ($t_{1/2}$) on the order of hours. The role of transition metals such as Fe and Mn in catalyzing the reductive transformation of CAHs is more pronounced in redox reactions involving soils and sediments (Stumm et al., 1981; Oscarson et al., 1981). For example, laboratory batch experiments reported by Butler and Hayes (1999) indicated that PCE and TCE are transformed by Fe(II) in homogeneous iron sulfide solutions with reaction $t_{1/2}$ of ~ 19 and 50 days, respectively. Wilson (1995) presented rates for reductive dechlorination of CAHs (TCE $t_{1/2}$ = 7.1 d, PCE $t_{1/2}$ = 13.9 d) in zero valent iron reactive barriers, which demonstrate the importance of transition metals in the remediation of aquifers.

CAHs may serve as electron acceptors during redox reactions (Holliger et al., 1993; Maymo-Gatell, et al., 1999; McCarty, 1997). However, for dechlorination to occur, a suitable electron donor must be present. Naturally occurring iron bearing oxides, sulfides, clay minerals (e.g., smectite) and reduced metal species such as Mn(II) have been shown to serve this function (Voudrias and Reinhard, 1986; Butler and Hayes., 1999, 2000; Hassan, 2000; Weseasooriya and Dharmasena, 2001; Kriegman King and Reinhard, 1992, 1994; Cervini-silva et al., 2001, 2000; Klausen et al., 1995; Weissmahr, et al., 1997; Amonette et al., 1994; Betts, 1998; Roberts et al., 1996; Farrell et al., 2000; Nzengung et al., 2001). In these reactions, hydrogen is formed and serves as the primary electron donor for dehalogenation reactions. Given an appropriate electron donor under anaerobic conditions, PCE is reductively dechlorinated and results in more environmentally-benign materials, such as ethene, ethane and carbon dioxide (Roberts et al., 1996; Butler and Hayes, 1999; Farrell et al., 2000; Nzengung et al., 2001; Li et al., 1999). The results of these studies suggest that the reduced iron species having high specific surface areas serve as electron donors or electron transfer mediators in the reductive dechlorination of CAHs in anaerobic environments.

In situ redox manipulation using dithionite. It has recently been shown that the transformation rates of CAHs can be greatly accelerated when the reducing capacity of soils and sediments are enhanced by reducing the solid phase Fe and Mn with aqueous dithionite solution (Larson and Cervini-Silva, 1998; Cervini-Silva et al., 2000, 2001; Amonette et al., 1994; Szecsody et al., 2000; Nzengung et al., 2001; Rodriguez et al., 1999; Thornton et al., 1998; Betts, 1998). For example, Amonette et al. (1994) have shown that roughly 90% of the carbon tetrachloride (CCl_4) added to dithionite-reduced sediment was dechlorinated within a week. Cervini-Silva (2000, 2001) suggested that the reduction of CCl_4, TCE and PCE was facilitated when ferruginous smectite, in aqueous suspension, was reduced by dithionite under anoxic conditions. Dithionite reduced Ft. Lewis, Washington aquifer sediments have been shown to degrade TCE in groundwater at a rapid rate with an observed $t_{1/2}$ of 12-19 hours (Szecsody et al., 2000).

The effectiveness of sodium dithionite ($Na_2S_2O_4$) as a reducing agent for iron bearing soils and clays has been widely demonstrated (Gan et al., 1992; Komadel et al. 1990; Stucki et al., 1976, 1984, 1993; Amonette et al., 1994; Gates et al., 1996, 1997, 1998; Rueda et al., 1992; Jhaveri and Sharma, 1968). The reduction potential of dithionite is similar to other reduced sulfur species, but the reaction rate is much greater. This enhanced reactivity stems from a weak S-S bond that allows the ion to breakdown into two-sulfoxyl ($SO_2^{-}\bullet$) free radicals via a monomerization reaction (Dunitz 1956;

Lynn et al., 1964; Nickless, 1968). When aqueous dithionite solution is added to soils or sediments having clay and iron oxide minerals, the active free radical e.g., $SO_2\bullet^-$ (eq 1) sorbs to the mineral surface and transfers an electron to structural Fe(III), reducing it to Fe(II) (eq 2). The CAHs contaminated groundwater, upon entering into the reduced zone, accepts the electron liberated from Fe(II) and is convert to less chlorinated CAHs via hydrogenolysis (eq 3) or dihalo-elimination (eq 4).

$2\ S_2O_4^{2-} + H_2O \iff 4\ SO_2\bullet^- + H_2O$ (1)

$4\ SO_2\bullet^- + Fe(III) + H_2O \Rightarrow Fe(II) + SO_3^{2-} + 4H^+$ (2)

$CAH_{\text{oxidized}} + H^+ + e^- \Rightarrow CAH_{\text{reduced}} + Cl^-$ (3) hydrogenolysis

$CAH_{\text{oxidized}} + 2\ e^- \Rightarrow CAH_{\text{reduced}} + 2\ Cl^-$ (4) dihalo-elimination

Amorphous and poorly crystalline iron phases, mostly present as surface coatings readily dissolve after dithionite reduction. The dissolved Fe(II) has been shown to adsorb to other surfaces in the reduced zone, thus adding to the redox capacity of the sediments. Dithionite ion and its reaction products are relatively nontoxic (Stucki et al., 1993), which has limited the use of most other reductants. Also, the unreacted dithionite can be recycled to reduce operational costs. As a result, dithionite is favored as an environmentally suitable reducing agent to artificially control in situ redox conditions.

The creation of a dithionite-generated in situ redox barrier, as deployed at the Gloucester landfill site near Ottawa, Ontario and the Department of Energy (DOE)'s Hanford Site consist of the following steps: injection, reaction, and finally remediation (Amonette et al., 1994, 2001; Fruchter et al., 1997, 2000; Ludwig, 1998; Istok et al., 1999; Szecsody et al., 2000; Chilakapati et al., 2000; Thornton et al., 1998; Betts, 1998). During the injection phase, a buffered dithionite solution is introduced into the aquifer treatment zone. This is followed by a reaction phase during which the injected reagents are allowed to react with sediment. In the remediation phase, the reactive barrier formed during the injection and reaction phases functions to transform CAHs contaminants in groundwater migrating through the barrier to innocuous products. The effectiveness of the dithionite-induced reduction of CAHs relies on the presence of redox sensitive metals or minerals in the sediments (Cervini-Silva et al., 2000, 2001; Amonette et al., 1994; Szecsody et al., 2000). If the amount of reducible iron is insufficient to create an effective reduced zone in the aquifer, the CAHs may not be completely degraded because of the overall limited redox capacity of the reduced zone.

An estimated five to ten percent of the groundwater at the DOE's Savannah River Site (SRS) near Aiken, SC has been contaminated by industrial solvents, metals, or other constituents used or generated by operations at SRS. Similar to other superfund sites in the United States (U.S. EPA, 1993, 1997; Riley and Zachara, 1992; INEEL, 1997), TCE and PCE have been found to be the most widespread dense-non-aqueous-phase liquid (DNAPL) and are of great environmental concern because they pose a serious threat to human health (Eddy et al., 1991; Evans et al., 1992; U.S. EPA, 1997, Saaty et al., 1995; Riley et al., 1992; CERE, 1995). The objective of this study was to evaluate the effectiveness of dithionite reduced SRS aquifer materials in detoxifying PCE and TCE. The results of this study will assist the DOE in selecting appropriate remediation plans in the overall clean-up strategy for the SRS.

MATERIALS AND METHODS

Experimental design. Repacked columns containing aquifer sediments were used in dynamic flow experiments to investigate the transformation kinetics of TCE and PCE in dithionite treated SRS aquifer material. Control experiments using untreated columns were conducted to check for losses of PCE and TCE attributable to mechanisms other than reduction (mainly due to sorption to sediments). Acidic conditions significantly increase the dithionite decomposition rate in aqueous solution (Rinker et al., 1965; Cervini-Silva et al., 2001; Nzengung et al., 2001; Erbs et al., 1999) and consequently, reduce the efficacy of dithionite to generate electrons for CAH reduction. Buffers such as carbonate-bicarbonate and citrate-bicarbonate have been shown to stabilize basic dithionite solutions and facilitate CAH transformation. Both citrate-carbonate and potassium carbonate-bicarbonate buffers were evaluated separately to determine which is more efficient for CAH transformation while minimizing adverse changes in the physical properties, mainly a reduction in the hydraulic conductivity of the aquifer matrix. All experiments were conduced at ambient temperature (23 ± 2 ^{o}C).

Aquifer materials. Experiments were performed using uncontaminated, highly weathered, coarse textured materials collected from a subsurface exposure on the SRS. This subsurface material is typical of sediments from the water table aquifer (Tobacco Road Formation) and the underlying first confined aquifer (Barnwell Formation) and has characteristics similar to highly weathered sediments throughout the Southeastern Coastal Plain. The general characteristics are given in Table 3.1. These sediments will be referred as the SRS aquifer materials throughout the text. They were air dried and stored at 4 ^{o}C in plastic bags prior to use in dynamic column experiments.

Chemicals and Solutions. All chemicals were reagent or ACS grade and were used as received. All chemicals and reagents necessary for dithionite solution preparation were stored in a Coy^{TM} anaerobic chamber under nitrogen atmosphere. Deionized water (DI) obtained from a Milli-Q plus water system (Millipore Corp., Bedford, MA) was used to prepare all aqueous solutions. Column experiments were conducted using "artificial groundwater" (AGW), the chemical composition of which is representative of the groundwater found at the SRS and vicinity (Strom and Kaback, 1992). Oxygen-free water was prepared by first boiling the DI water in a Pyrex flask, then purging with N_2 gas while the water cooled. The groundwater solution was then immediately transferred to the anaerobic chamber and stored overnight to remove the residual oxygen. The necessary salts were added to this oxygen-free water to match the composition of AGW. This solution will be referred to as deoxygenated AGW (DAGW) in the remaining text.

Citrate-bicarbonate buffer was prepared by adding 0.889 M sodium bicarbonate and 0.033 M sodium citrate to AGW (Stucki et al., 1984). Carbonate-bicarbonate buffer was prepared with K_2CO_3 (4 times the dithionite concentration) and $KHCO_3$ (0.4 times the dithionite concentration) as described in Chapter Two. Stock solutions of simulated contaminated AGW containing PCE or TCE were prepared using certified standards (ULTRA Scientific, RI, AccuStandard Inc., CT), and stored in a collapsible Teflon bag (Kevlar) with no headspace. Glassware and column materials were acid washed with 20% hydrochloric acid, followed by repeated rinses in DI. In addition, all the glassware (except volumetric, which was rinsed three times with methanol and ethanol) was muffled at 400 ^{o}C for 4-h before use.

Preparation of dithionite solution. Immediately before the experiment, the dithionite solution was prepared inside the oxygen-free chamber by first mixing the buffer with DAGW and adding sodium dithionite. The buffered dithionite solution was transferred to a Teflon bag to prevent dithionite reaction with atmospheric O_2, which is extremely fast (Creutz and Sutin, 1974).

Column studies. Dynamic flow experiments were used to investigate the reducing capacity of dithionite-reduced sediments under simulated SRS aquifer conditions. Prior to experimental measurements, a protocol was developed for packing, degassing and conditioning sediment columns to ensure column reproducibility and eliminate experimental artifacts. Glass columns (15 cm x 2.5 cm i.d.; Kontes, NJ) were packed with aquifer materials in small increments (Benker et al., 1998) to establish uniform bulk density and to attain homogeneous distribution of soil particles. The ends of the column were packed uniformly with small quantity of acid washed, well-graded 20-30 mesh Ottawa sand to facilitate solutes distribution throughout the column. After packing, the columns were tightly capped with Teflon fittings.

Dry packed columns were flushed with carbon dioxide gas for ~30 minutes to replace the air pockets inside the columns (Imhoff et al., 1998; Benker et al., 1998); thus facilitating column saturation. The columns were then oriented vertically and slowly saturated in an upflow direction with AGW stored in a gas impermeable Teflon sample bag (Kevlar). Columns were initially saturated with AGW very slowly (Darcy velocity ~12.0 cm d^{-1}) to inhibit the development of any preferential flow path throughout the columns. After initial saturation, approximately 10-PV of AGW was flushed through the column to achieve complete water saturation without entrapping air bubbles. A constant flow rate (Darcy velocity ~72 cm d^{-1}) was maintained using a piston type pump (SciLog). Stainless steel tubing (1/16 in. i.d.) and valves (Swagelok) were used to plumb the entire experimental setup because of the low adsorptive capacity for organic solvents (Reynolds et al, 1990; Bercelona et al., 1984). A bypass valve was added upstream of the column so that the influent solutions could be sampled. Column effluents were collected at regular intervals using an automated fraction collector (Gilson Liquid Handler 215, Gilson Inc.) that injects samples directly into presealed GC headspace vials equipped with crimp-sealed PTFE faced butyl rubber septa (Agilent Technology).

The sample volume was quantified by weighing the sample vials before and after sample collection. The bulk density and porosity of the packed columns were determined gravimetrically. Typical bulk density and porosity values were 1.60 g cm^{-3} and 0.40, respectively. The PV was determined using a short pulse (~ 2 PV) of tracer solution containing ^3H_2O. The cumulative effluent volume at which the tracer concentration (C) equaled 0.5 the initial concentration (C_o) is the calculated column PV.

Once the packed column was saturated with AGW, a freshly prepared buffered dithionite solution (concentration ~ 34.5 mmol) mixed with ^3H_2O (~200 pCi mL^{-1}) was introduced into the column for 2-PV (Darcy's flow ~ 72 cm d^{-1}), after which the column sediments were allowed to react with the dithionite for 18-h. Following reduction, two PV of oxygen free AGW was introduced into the column to remove residual dithionite and its degradation products. At this stage, the reduced column sediments are designed to simulate a reactive barrier with the potential to remediate groundwater contaminated with PCE and/or TCE.

Aqueous solution containing PCE or TCE (concentration ~1.0 mg L^{-1}) was then injected into the column to simulate migration of contaminated groundwater through the reduced sediment. The effluents were collected to quantify aqueous CAHs and ^3H_2O concentrations. In separate experiments, the sorption of PCE and TCE to unreduced sediments was also determined.

Analytical measurements. One mL of column effluent was collected in headspace vials and preserved at 4 ^oC. CAH concentrations were determined using an automated headspace analyzer coupled with a gas chromatograph. Following CAH analysis, the remaining water was analyzed for ^3H_2O. CAHs calibration curves were constructed by sampling headspace vials containing known amounts of standard mixtures containing PCE, TCE, DCE (all isomers) and vinyl chloride (VC). Mixed standards of CAHs were prepared by diluting concentrated standards (ULTRA Scientific, RI; AccuStandard Inc., CT) in 9:1 AGW-methanol. Non-CAH gases were determined separately by sampling the headspace with a gas-tight syringe and direct injection into a gas-chromatograph. Gas standard mixtures (Altech, IL) were used for calibration that contains ethyne, ethane, methane, and carbon dioxide (as 1% concentration) in nitrogen.

A HP 5890 GC equipped with an electron capture detector (ECD) was used for the analysis of PCE, TCE, DCE, and vinyl chloride. A DB-VRX 60 m x 0.25 mm x 1.4 μm-capillary column was used for separation of CAHs. The oven temperature was held at 45 ^oC for 10 minutes, then ramped to 177 ^oC at 12 ^oC min^{-1} and held for 0.5 min. Helium was used as the carrier gas with a flow rate of 1.8 mL min^{-1}. The injector and detector temperatures were 200 and 300 ^oC, respectively. Samples were introduced into the GC with an HP 7694 automated headspace sampler programmed to equilibrate samples at 50 ^oC for 10 min.

Methane, ethane, ethene, and ethyne were determined using a HP 6890 GC equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). One mL aliquot of equilibrated vial headspace was manually sampled using a gastight syringe and injected directly onto the GC inlet. A HP-PLOT Mole Sieve 5A (HP 19095P-MS5) column (15 m x 0.53 mm ID x 50 µm film) was used to separate the gases. Helium was used as carrier gas with a flow rate of 3.8 mL min^{-1}. The initial oven temperature was set at 40 °C for one minute, followed by a temperature increase of 25 °C min^{-1} to 100 °C, and a subsequent temperature increase of 30 °C min^{-1} to 200 °C and held there for 25 minutes (31.73 min total run time). Injector and detector (both FID and TCD) temperatures were maintained 150 and 250 ^oC, respectively.

^3H_2O was determined in 1 ml aliquots of column effluent fractions mixed with 10 mL of scintillation cocktail in 25 mL plastic scintillation vials and counted for 20 minutes in a liquid scintillation beta counter (Minaxi Tri-Carb 4000 Packard Instrument Co., IL). The mobile clay size colloids were collected on 0.1 µM pore size membranes using vacuum filtration and analyzed using a Thermo Gravimetric Analyser (TA Instruments) to determine the clay mineralogy. These results were confirmed by X-ray diffraction (XRD, Scintag, Inc.).

RESULTS AND DISCUSSION

Effect of dithionite treatment buffered with carbonate-bicarbonate. Column experiments conducted for the carbonate-bicarbonate-dithionite (CBD) treatment provided information on dithionite transport properties and helped to obtain information on design factors. The experiments consisted of the injection of two-PV of CBD solution (pH ~ 10.5), an 18-h reaction phase and removal of residual dithionite. This treatment was followed by a remediation phase in which oxygenated AGW was pumped through the column. The characteristics of the column effluent parameters are shown in Figures 3.1 and 3.2

During the initial dithionite injection, the pH of the column effluent was ~ 4.8, which increased to the influent pH of 10.5 (Figure 3.1). The effluent pH and low iron mobility (less than 1%) during dithionite injection indicated the high buffering capacity of the influent solution and was sufficient to neutralize the H^+ produced by iron reduction and dithionite disproportionation. During the remediation phase when the column was flushed with oxygenated AGW as a surrogate for redox sensitive contaminants, the effluent pH decreased slowly due to H^+ generated by the oxidation of Fe(II) (Figure 3.2a). After ~125 PV of column oxidation, the pH decreased more rapidly. This pH drop is attributed to limited acid buffering capacity of the sediments. After 173 PV, the pH dropped to 6.5 and the dissolved O_2 of the column effluent approached the level of the influent solution (Figure 3.2b). During the remediation phase, no enhanced mobility of colloids was observed. While some trace metals were mobilized during the dithionite treatment and groundwater remediation phase, the trace metal concentrations were well below the drinking water limit (Buonicore, 1996).

Oxygen removing capacity (ORC) of dithionite treated sediment. When the CBD reduced zone was leached with O_2 saturated water (assuming O_2 is the only electron acceptor), each mole of O_2 consumed four moles of electrons (eq 5-6). The oxygen removing capacity (ORC) is a convenient method to express treatment capacity in terms of the number of PV of contaminated groundwater that must pass through a unit volume of reduced aquifer sediments before contaminant breakthrough occurs.

$O_2 + 2\ H^+ + 2\ e^- \Leftrightarrow H_2O_2$ (5)

$H_2O_2 + 2\ H^+ + 2\ e- \Leftrightarrow H_2O$ (6)

$4\ Fe(II) + O_2 + 4\ H^+ \Leftrightarrow 4\ Fe(III) + 2H_2O$ (7)

Oxygen breakthrough curves through the CBD treated sediment were convex in shape, indicating substantial oxygen reduction to H_2O in the column, where reducing conditions were maintained until 173 PV of oxygen saturated water had passed through the column. Integration of the effluent oxygen breakthrough curve indicated 2.90 mmol of O_2 consumption from oxygenated water by Fe(II) in the treated sediment (Appendix A). Based on the initial available Fe(III) content of the sediment (0.37 wt %) and assuming 4 moles of Fe(II) were oxidized to consume one mole O_2 (eq 7), it was calculated that the dithionite treatment reduced 61% of the available Fe(II) originally present in the sediment.

Another way to quantify treatment capacity (Fruchter et al., 1996) is to estimate the barrier longevity (L_b) in time units using $L_b = T_c * W_b / V_w$ (where, T_c is the treatment capacity in PV, W_b is the barrier width in length units, and V_w is the expected pore water velocity at the emplacement location). Based on the CBD treatment applied to SRS sediment in the present study ($T_c = 173$, $W_b = 5$ cm and $V_w = 169$ cm d^{-1}), the barrier lifetime calculated was 5 days, which may indicate a limited performance of the reactive wall. However, regenerating the reactivity of the aquifer materials through reinjection application of treatment solution can extend the limited treatment capacity of the aquifer material.

PCE and TCE transformation in CBD treated sediment. The abiotic degradation of PCE contaminated groundwater was investigated in the CBD treated aquifer material, where the mass of PCE removed by the treated column was compared to contaminant mass loss due to sorption in unreduced sediments.

For the unreduced column, no PCE degradation products were observed in the effluents and the total mass recovery of 95% PCE was calculated based on the integrated PCE concentration in the effluents. The results of PCE transport experiments through the CBD treated column accounted for 50% of the initial PCE. Traces of TCE and t-1, 2 DCE were observed as PCE degradation products; however, the poor mass balances of PCE and degradation products indicate that all the products or intermediates formed were not completely identified. Batch equilibration studies by Heath (2000) and Payne (2001) indicated the production of ethyne and CO_2.

The PCE breakthrough curves (Figure 3.3a) of the untreated sediment were symmetrical and consistent with those observed for the conservative tracer. No degradation products were observed in unreduced sediments. However, PCE curves in the treated column were skewed and breakthrough was observed only after nearly 8 PV, indicating significant reduction of PCE by the CBD treated sediments. Of the degradation products observed in the effluents of the dithionite treated column, TCE was the dominant product, with small amount of t-1,2 DCE and 1,1-DCE. No VC was detected. This is likely due to the high detection limit for VC by the ECD. Headspace gas analysis showed the presence of ethyne, methane, and ethene in some samples. The presence of ethyne suggested a secondary degradation pathway (Thornton et al., 1998) by hydrogenolysis. A hydrocarbon intermediate peak was observed in all samples, which may be attributed to coupling of radical intermediates formed in the PCE transformation (Butler and Hayes, 1999). The PCE removing capacity, as determined by integrating the PCE breakthrough curves, was 0.003 mmol PCE kg^{-1} of treated sediment (Appendix B). It is important to note that the PCE treatment capacity values were determined using PCE solution prepared using AGW that contained ~ 8.22 mg L^{-1} dissolved O_2. As the presence of oxygen also contributed to the oxidation of Fe(II), it was assumed that use of AGW resulted in smaller PCE reductive capacity values than would have been obtained if DAGW had been used in the column experiments. Additional experiments investigating the degradation of TCE in CBD reduced sediments in similar fashion as described in PCE transformation experiments indicate little or no degradation of TCE (Figure 3.3b).

Reactions between dissolved Fe (II) and decomposition products of dithionite (thiosulfate, sulfite, and bisulfite) have been shown to lead to the formation of secondary iron minerals such as FeS, FeS_2 and $FeCO_3$ within the sediment-water matrix (Rickard, 1975; Nzengung et al., 2001; Drever, 1988). These minerals react very slowly with chlorinated organics, and thus, reduce the efficiency of the dithionite treatment (Butler and Hayes, 1999). If the dithionite concentration is high, some of the dithionite may likely be consumed by mineral formation and unavailable for PCE degradation. The poisoning of reactive minerals surface sites due to the precipitation of secondary minerals may reduce accessibility of structural Fe(II) and Mn(II) sites for reaction with CAHs at the mineral edges and planer surfaces where the reaction are thought to occur (Nzengung et al., 2001). Therefore, successful dithionite treatment requires careful selection of dithionite and buffer concentrations and a favorable balance between dithionite transport and reaction kinetics (Istok et al., 1999; Amonette et al., 1994; Nzengung et al, 2001). Optimization studies for dithionite treatment for SRS aquifer material were conducted using batch reaction experiments by Nzengung et al. (2001) and column studies (chapter two). Using these optimized treatment parameters, the sediments were reduced with the CBD (34.5 mmols of dithionite concentration) for 12 PV, followed by 6 hour of reaction time. However, the results (data not shown) of the PCE/TCE transformation through these efficiently redox manipulated aquifer materials did not show any additional PCE transformation.

Role of solid phase reactive sites on CAHs transformation. Although the CBD treated SRS aquifer sediments showed only limited capacity to reduce PCE or TCE, the same treatment was observed to be effective in reducing a substantial amounts of both Cr(VI) and O_2 in AGW. If redox equilibrium completely defined the reaction (i.e., no effect from activation energy), the order in which one substrate selectively reacts would depend on its formal standard reduction potential (Szecsody et al., 2000). For the reductive transformation of simple organic compounds, the order of preference can be determined by summing the oxidation states of the elements in the molecules with more oxidized compounds having the greater potential for reductive transformation (Schwarzenbach et al., 1988; Amonette et al., 2001). The standard reduction potential for the Fe(III)/Fe(II) couple in the aqueous, adsorbed, and mineral phase ranged from

+ 0.77 V to – 0.63 V at pH = 7 (Amonette et al., 2001) and thus, a number of redox sensitive contaminants are amenable for reduction by Fe(II) under typical conditions. For example, groundwater containing a number of inorganic and organic contaminants when flowing through a permeable redox barrier containing adsorbed and structural Fe(II) would be reduced in the following order of preference: uranium (VI) > DO > chromate > CCl_4 > PCE > TCE.

Typically, most of the reductive capacity of aquifer sediments is associated with Fe(II) within the lattice structure and on the surfaces of clay minerals. The aquifer materials used in the present study (Table 3.1) has < 5% clay. Thus, Fe oxyhydroxide minerals account for most of the reactive surface sites (Vulava and Seaman, 2000; Bertsch and Seaman, 1999; Seaman et al., 1996, 1997). Other factors that affect the overall redox reactivity are the location and accessibility of the iron in the clay mineral structure. Recently, it was suggested that in the presence of any mineral surface, even in the absence of redox sensitive metals, dithionite may reductively transform PCE, TCE, and TCA (Heath 2000; Payne, 2001).

A possible explanation for the poor efficiency observed in the column experiments treating PCE and TCE may be kinetic constraints on the reduction reaction. As previously noted (Chapter 2), the porosity of the packed sediment columns is greater than that measured for these sediments in the aquifer formation and this may limit solute interaction within the residence time of contaminants in the column. Thus, the mineral surface interactions of ground water solutes are expected to be greater under field conditions providing more favorable reaction efficiency. In addition, the flow rates employed in the column studies are at the upper range of those measured within the aquifer systems in the Atlantic Coastal Plain sediments at the SRS. Higher groundwater velocities will result in lower solute residence times within the treatment zone. Thus, for contaminants (e.g., PCE, TCE) with slower reduction rates, the higher flow velocities used in the column experiments may not provide sufficient time in the treatment zone to allow effective degradation and will under predict the treatment effectiveness for field conditions. Additional studies are necessary to evaluate the relationship between PCE and TCE reaction kinetics and groundwater velocity in order to optimize the design of the ISRM systems for field deployment.

ENVIRONMENTAL SIGNIFICANCE

The CBD reduced SRS sediments were partially effective in remediation of the oxygenated PCE contaminated SRS groundwater, the treatment may be useful for remediation of more oxidized halogenated hydrocarbon such as CCl_4 and redox sensitive inorganic contaminants such as Cr(VI), U(VI), Pu(III, IV), and Tc(V, VI) (NRC, 1999). Addition of Fe(II) solution has been effective in reducing halogenated aliphatic and other redox sensitive contaminants when the proton activity of the solution is buffered (Hassan, 2000; Sivavec et al., 1995, 1997; Butler and Hayes, 1999, 2000, 20001; Weerasooriya and Dharmasena, 2001; Seaman et al., 1999; Davis and Olsen, 1995; Amonette, 2000; Klausen et al., 1995). In this study the efficiency of PCE and TCE treatment was determined using aerobic AGW that was saturated with oxygen (8.2 mg/L). Ground water dissolved oxygen concentrations at SRS are typically lowers by a factor of ten. Thus, the degradation efficiency may be considerably greater in anaerobic or low-oxygen conditions when the competition of PCE and TCE with oxygen is reduced or eliminated.

In addition the efficiency may be further improved with lower flow groundwater velocity, which will increase the residence time of contaminants in the treatment zone. Further studies are necessary to evaluate the effects of these parameters on treatment efficiency.

The oxidation of dithionite treated sediment appears to be more complex than can be described with a single oxidation reaction and is likely controlled by both chemical and physical processes. It is likely that the major controlling factor that determines the efficiency of the treatment is the amount of reducible Fe in the sediment. Although Fe-oxides are the most significant phases that react with dithionite, other mineral phases present may also be reduced and utilize some of the dithionite. The second important factor is the oxidation of the reduced sediment by advection of DO in groundwater. Most of the groundwater contaminants at the SRS were reported in water table aquifers where the DO content is moderately high in comparison to the deeper aquifer. Moreover, there is a chance that a large percentage of the reduced zone created would be oxidized just by oxygen diffusion in the vadose zone in sediments near the water table. The long term behavior and performance of the reduced zone can be affected due to clay transport out of the sediment. In addition, the mobility of metals and nonmetals contaminants such as arsenic may increase due to the reducing condition created, as reduced species of these elements are more mobile under low Eh condition. These factors need to be considered and, if necessary, evaluated prior to the deployment of IRSM in contaminated aquifers at the SRS.

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Table 3.1. Physical and chemical properties of SRS aquifer materials (Tobacco Road sand) used in the batch and column studies.

Texture[a]		Loamy sand
Particle-size distribution[b], %	Soil mineralogy[c]	
Sand (>53 μm)	q>>>f	92.65
Silt (53-2 μm)	q>>> k	2.55
Clay (<2 μm)	k>>q>goe, mi, gibb, hem	4.80
[d]Water dispersible clay (wt %)		0.056
[d]pH_{DI}		5.10
[d]pH_{AGW}		5.00
[d]pH_{KCl}		4.21
[d]EC_{DI} (μS/cm)		4.29
[e]Cation exchange capacity (meq/100 g)		2.30
[f]Total organic carbon (g /100 g)		0.09
[g]BET surface area (m^2/g)		2.51
	Redox sensitive transition metals[h], g / 100 g	
Iron		0.48923
Manganese		0.00099
Chromium		0.00018
	Extractable Fe, g Fe / 100 g	
[i]5 M HCl, 21-d		0.51
[j]CDB Fe		0.37
[k]0.5 M HCl		0.05
[l]AO Fe		0.02
[m]0.5 M HCl, 1-h		0.01

[a] general soil classification of US Department of Agriculture

[b] hydrometer analysis

[c] determined by X-ray diffraction, where q = quartz, f = feldspar, k = kaolinite, goe =goethite, mi = mica, gibb = gibbsite, hem = hematite

[d] 1:2 soil: solution in deionized water (DI), AGW, or 1 M KCl for 30 minutes

[e] ammonium acetate method (Rhoades, 1982; Thomas, 1982)

[f] TOC, total organic carbon, dry combustion method (Nelson et al., 1982)

[g] by Micrometrics ASAP-2010

[h] EPA method 3051; Microwave assisted acid digestion

[i] Heron et al., (1994a)

[j] citrate-dithionite-bicarbonate extraction (Jackson et al., 1986)

[k] Lovely et al., (1986), modified by Kennedy et al.., (1999)

[l] ammonium oxalate extraction (Jackson et al.., 1986)

[m] Christensen et al., (2001)

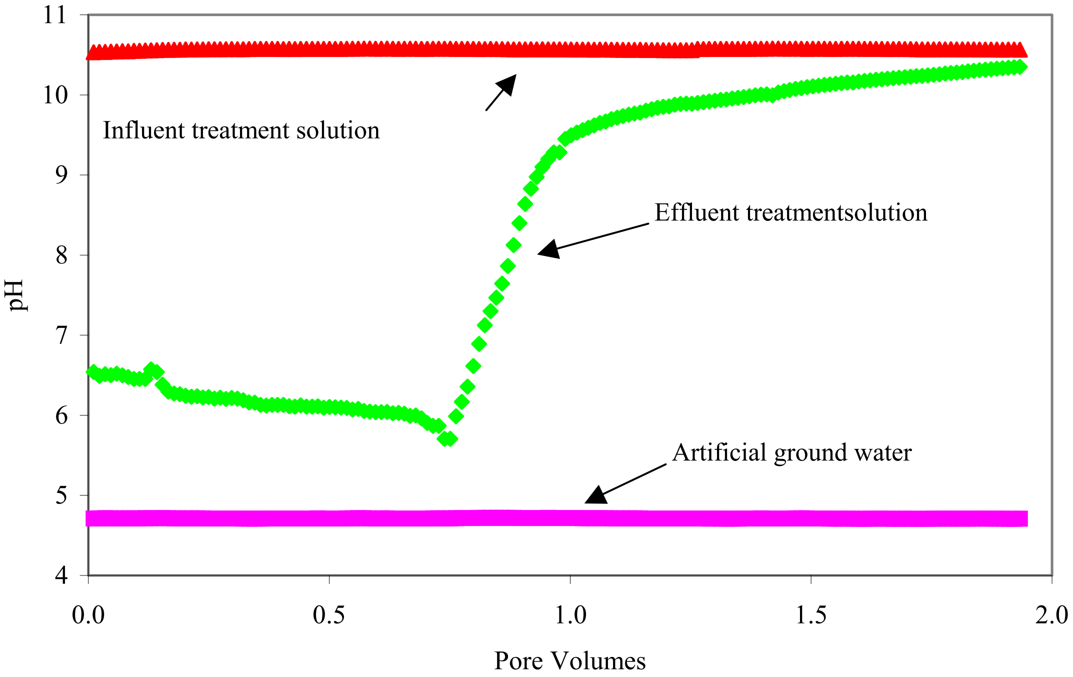

Figure 3.1. Treatment of column sediments with carbonate-bicarbonate-dithionite (CBD) solution to manipulate the redox capacity of the SRS aquifer sediments. During the injection of treatment solution, the pH of the column effluent increased from background pH of 4.7 to ~ 10.5.

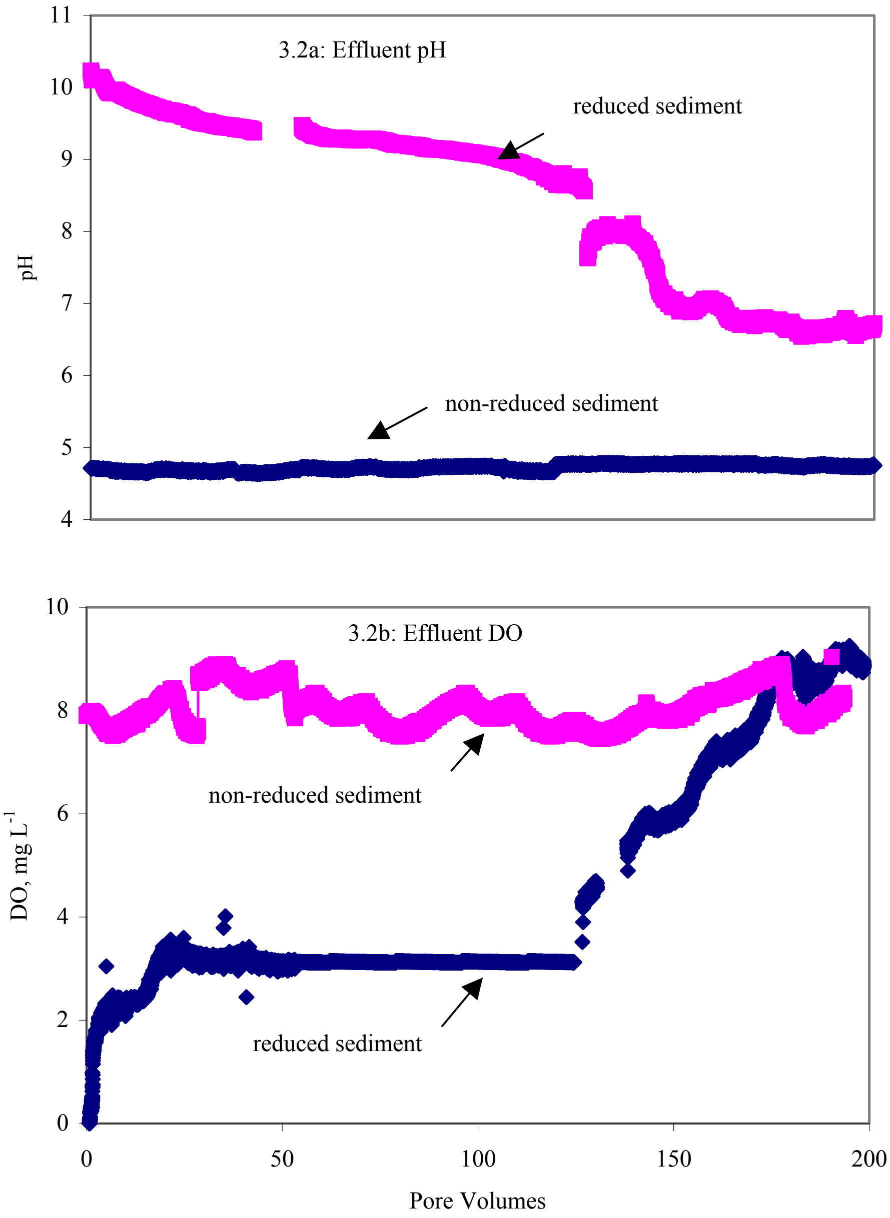

Figure 3.2. Results showing reduced column effluents parameters. Oxygenated AGW was leached through the reduced column as a surrogate for redox sensitive contaminants.

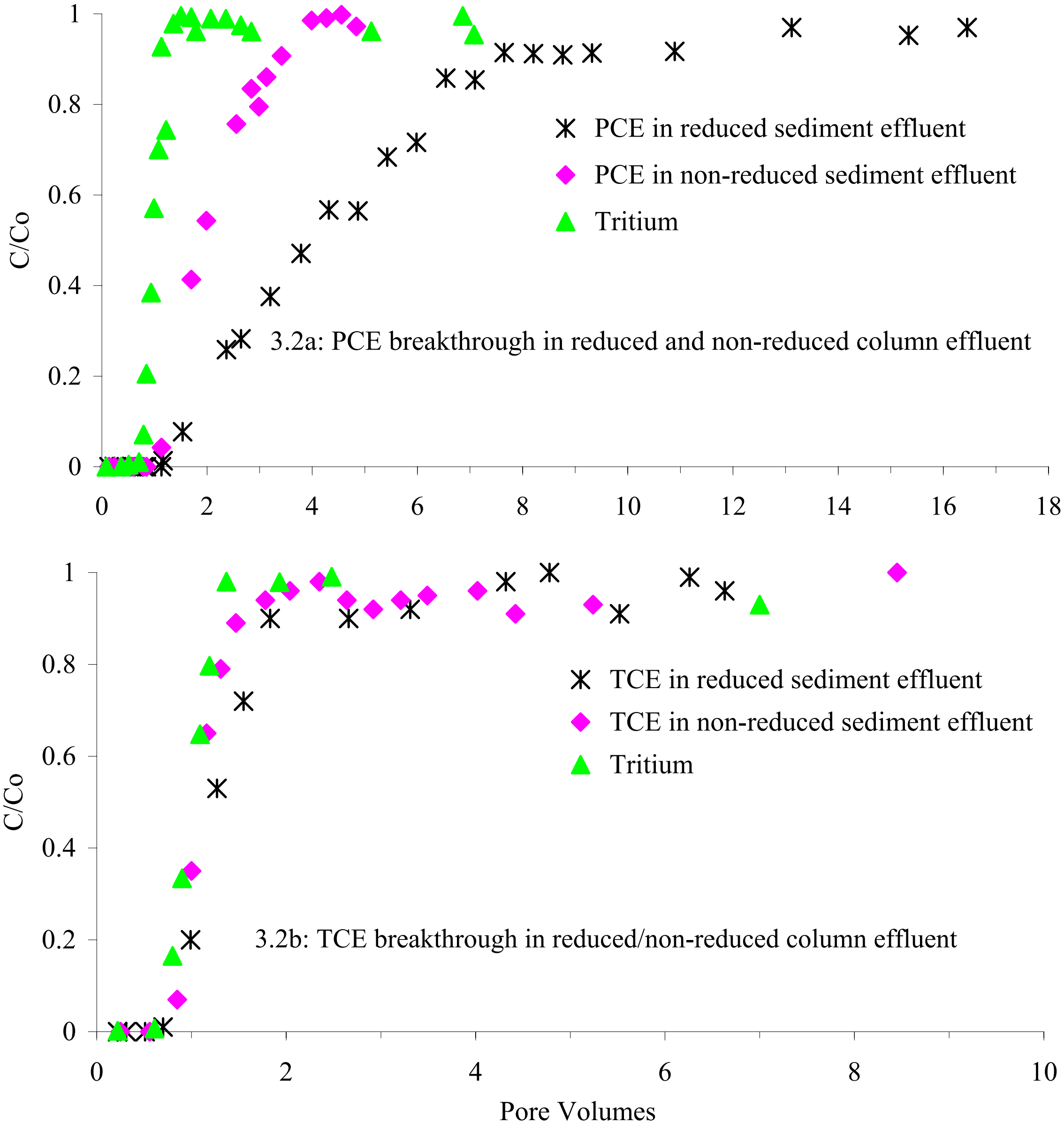

Figure 3.3: Transformation of CAHs through reduced/non-reduced SRS subsurface sediments. The influent concentration of PCE and TCE was ~ 1 mg L^{-1}.

CHAPTER 4

IN SITU Cr(VI) REDUCTION USING DITHIONITE TREATMENT WITHIN COARSE TEXTURED, OXIDE RICH SOUTHEASTERN ATLANTIC COASTAL PLAIN AQUIFER SEDIMENTS[1]

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ABSTRACT

Batch and column techniques were used to evaluate the in situ reduction and immobilization of Cr(VI) using buffered (pH~11) dithionite solutions (conc.~ 34.5 mmol) to create a redox barrier within the sediments of the Atlantic Coastal Plain. In batch experiments conducted in an O_2 free environment, the sediments were treated with dithionite and then the reaction products were removed prior to Cr(VI) addition. In control systems, the aquifer material displayed significant capacity to sorb Cr(VI) (sorbed/mass) in the absence of the reductant due to the presence of Fe oxides. However, dithionite treated sediments displayed a higher capacity (sorbed/mass) to retain Cr(VI), presumably through reduction to Cr(III) followed by hydrolysis and precipitation. In column systems, the sediments were leached (Darcy velocity ~ 72 cm d^{-1}) with dithionite solution and then allowed to equilibrate prior to the introduction of Cr(VI) (inlet conc.~ 1 mmol). Dissolved oxygen was also monitored in the column effluent as an indication of the reductive capacity of the treated sediments. In control columns without dithionite, full Cr(VI) breakthrough (C = Co) occurred at approximately 3 PV, consistent with limited adsorption observed in batch. Much greater Cr(VI) retention was observed in the dithionite treated columns (C = Co at ~ 73 PV; mass sorbed/soil) even though a portion of the reductive capacity was consumed by dissolve O_2, the dominant oxidative species likely present in a Cr(VI) plume.

Key words: dithionite, chromate, upper coastal plain, reduction, reductive capacity, groundwater remediation, in situ remediation

INTRODUCTION

Numerous industrial, construction, and military practices generate solid and aqueous waste products that are enriched with various heavy metals including chromium (Cr). The uncontrolled disposal of these wastes has resulted in chromium contamination of surface and subsurface waters at numerous sites (Barnhart, 1997; Calder, 1988; Palmer and Wittbrodt, 1991). Chromium concentrations as high as 50,000 mg L^{-1} have been detected in groundwater at superfund sites (Banerjee et al., 1988; Guzman et al., 1990).

Once chromium enters the environment, its most stable oxidation states are Cr(III) and Cr(VI). Cr(III) is thermodynamically more stable as a sorbed surface complex or in a solid phase (such as oxyhydroxides precipitates) than as an aqueous complex (Anderson, 1994; Gan et al., 1996). In the environment, Cr(III) is relatively immobile and is considered an essential nutrient for humans (Anderson, 1989; Fendorf, 1995; Higgins et al., 1997). Almost all known sources of Cr(VI) are derived from human activities (World Health Organization, 1988). Cr(VI) is acutely toxic, mutagenic (Blanchi et al., 1984), teratogenic (Abbasi and Soni, 1984) and carcinogenic, even when present in very low concentrations in water (NAS, 1974). Based on toxicity to aquatic life and on possible harmful effects on man, the concentration of Cr in surface and ground water in the United States is regulated under the Safe Drinking Water Act (maximum concentration limit = 0.1 mg L^{-1}) and the Clean Water Act (ambient water quality criteria = 0.011 mg L^{-1}). Cr(VI) moves readily through the soil and aquatic environment and is thermodynamically stable as an anionic solution species (CrO_4^{2-}or $Cr_2O_7^{2-}$) over the same pH range where Cr(III) tends to precipitate. Therefore, the reduction of Cr(VI) to Cr(III) and the subsequent formation of insoluble Cr(III) precipitates can be used as a means of remediating chromium-contaminated sites (U.S. EPA, 1980).

In situ remediation of chromium by reduction: Conventional groundwater treatment methods such as pump and treat are expensive and generally not very effective in removing low levels of Cr from the subsurface (Wittbrodt and Palmer, 1992). Electrokinetic remediation has been shown to be effective for Cr remediation (Banerjee, el al., 1988), but removal efficiency is strongly affected by the soil types and pH (Reddy et al., 2001). An alternative to extraction is the creation of a geochemically reactive zone in the path of flowing contaminated groundwater. Such engineered barriers are developed by adding reducing agents in solution from the surface or by the physical emplacement of reactive solids, such as zero-valent iron in a trench (Astrop et al., 2000). As the plume migrates through the barrier, Cr(VI) is reduced to Cr(III) and an immobile Cr(III) precipitate forms.

Commonly used reducing agents include organic carbon (Bloomfield and Pruden, 1980), organic complexes (Wittbrodt and Palmer, 1995), soil microorganisms (Ishibashi et al., 1990), H_2S (Thornton et al., 1999; Pettine et al., 1998; Saleh et al., 1989; Mattison 1992) and reduced iron (Rai, et al., 1987, 1989; Sass and Rai, 1987; Eary and Rai, 1988, 1989; Blowes et al., 1997, 2000; Patterson et al., 1977; Peterson et al., 1997; Brigatti et al., 2000). Among these reductants, solids and solutions containing Fe(II) sources are the most commonly used. Once Cr(VI) is reduced to Cr(III), its solubility is largely dictated by the groundwater pH (Eary and Rai, 1988). Below pH 3.5, Cr(III) exists predominantly as the free ion (eq 1)(Buerge and Hug, 1997), which is relatively mobile:

$$HCrO_4^- + 3Fe(II) + 7H^+ = Cr(III) + 3Fe(III) + 4H_2O \quad (1)$$

With increasing pH, Cr(III) forms different Cr hydroxide precipitates (eq 2)(Blowes et al., 1997; Rai et al., 1987, 1989):

$$\mathrm{Cr(III)} + 3\mathrm{OH}^- = \mathrm{Cr(OH)_3(s)} \qquad (2)$$

co-precipitates with Fe(III) as oxide (eq 3) (Sass and Rai, 1987; Eary and Rai, 1988) or as oxyhydroxide solid (eq 4) (Schwertmann et al., 1989):

$$x\mathrm{Cr(III)} + (1-x)\mathrm{Fe(III)} + 3\mathrm{H_2O} = (\mathrm{Cr}_x\mathrm{Fe}_{1-x})(\mathrm{OH})_3(\mathrm{s}) + 3\mathrm{H}^+ \qquad (3)$$

$$x\mathrm{Cr(III)} + (1-x)\mathrm{Fe(III)} + 2\mathrm{H_2O} = \mathrm{Cr}_x\mathrm{Fe}_{1-x}\mathrm{OOH(s)} + 3\mathrm{H}^+ \qquad (4)$$

or complexes with dissolved organic matter, or adsorbs onto clays and oxides.

The presence of oxidants other than Cr(VI) in the groundwater may affect the reduction efficiency. Although dissolved oxygen (DO) is the dominant oxidant, trichloroethylene (TCE), nitrate, uranium (U) or other reducible species may be present as contaminants in the groundwater. Competition for the reductant between Cr(VI) and other oxidants, especially DO may substantially affect the reductive capacity of the reactive solute or in situ barrier (Seaman et al., 1999).

A range of solid phases containing reduced iron have been observed to promote the reduction and precipitation of Cr(VI) in natural systems, including elemental iron (Blowes et al., 2001), iron sulfides (Patterson et al., 1997), iron carbonates (Blowes et al., 1997), iron bearing oxyhydroxides (Eary and Rai, 1989; Peterson et al., 1997) and iron bearing aluminosilicate minerals (Eary and Rai, 1989; Peterson et al., 1997; Brigatti et al., 2000). A major drawback to the use of solid phase reactive walls is the necessity to remove and/or replace the reactive material once the reductive capacity has been depleted. The use of solid phase reductants is also limited to relatively shallow sites where such materials can be practically installed.

Many reactive solutions including ferrous salts, sodium sulfite, sodium dithionite, sodium bisulfite, sodium metabisulfite and sulfur dioxide are commonly used as reducing agents in industrial Cr(VI) reduction processes (Higgins et al., 1997; Eary and Rai, 1988; Davis and Olsen, 1995; Saleh et al., 1989; Seaman et al., 1999). Soluble reducing agents can be delivered to the subsurface at hazardous waste sites by subsurface injection or infiltration galleries. Ferrous solutions can be used to reduce Cr(VI), but the oxidation of Fe(II) to Fe(III) and subsequent hydrolysis can reduces the pH and inhibit Cr(III) precipitation (Seaman et al., 1999). Buffered Fe(II) solutions have been shown to reduce Cr(VI) and subsequently precipitate Cr(III) in a mixed iron(III)-chromium(III) hydroxide solid, $(Cr_xFe_{1-x})(OH)_{3(s).}$ However, abovementioned Fe(II) is more readily consumed by other redox sensitive species, such as dissolved $O_{2,}$ at the higher pH (Seaman et al., 1999).

Among the sulfur species, hydrogen sulfide is one of the strongest reductants capable of reducing Cr(VI) under sulfate reducing conditions. However, the abovementioned sulfur solution when added to the subsurface may not directly reduce Cr(VI); rather it reduces Fe(III) present in aquifer system to Fe(II) that supplies electron for Cr reduction. Optimal reduction for sulfur species, excluding dithionite, occurs under acidic conditions, pH ~ 2-2.5 (Higgins et al., 1997). In contrast, However, buffered dithionite solutions (pH ~ 7.5 -11) enhance the redox capacity of soils and sediments by reducing the iron bearing phases (Stucki et al., 1976, 1984; Rueda et al., 1992; Amonette et al., 1994; Fruchter et al., 1997; Istok et al., 1999; Cervini-Silva et al., 2000; Nzengung et al., 2001), providing low redox conditions favorable for the reduction of Cr(VI) (Amonette et al., 1994; Fruchter et al., 1996, 2000; Istok et al., 1999) and maintaining a suitable groundwater pH for Cr(III) precipitation. Dithionite is effective in reducing a number of inorganic and organic compounds, including Cr(VI) (Amonette et al., 1994; Fruchter et al., 1996, 2000; Istok et al., 1999), U(VI) (Szecsody et al., 1998), alkanes (Amonette et al., 1994; Cervini-Silva et al., 2000) and alkenes (Nzengung et al., 2001; Szecsody et al., 2000; Thornton et al., 1998; Betts, 1998). Dithionite's short aqueous half-life of 2-3 days (Palmer and Puls, 1994) ensures that it doesn't persist as a groundwater contaminant. Dithionite reduced reactive barriers developed at the laboratory and field scale at DOE's Hanford site showed the ability to reduce Cr(VI) from 1 mg L^{-1} to < 8 µg L^{-1} with a treatment capacity for the contaminant plume equivalent to 7-12 years (Fruchter et al., 1996, 1998).

In situ Redox Manipulation (ISRM) using dithionite. The reduction potential of dithionite is similar to that of other sulfur species, but it is much more reactive. This enhanced reactivity stems from a weak S-S bond that allows the ion to breakdown into two-sulfoxyl ($SO_2{}^{o}$) free radicals (Lynn, 1964). When aqueous dithionite is added to soils or sediments, the active free radical (e.g., $SO_2\bullet^{-}$) approaches the mineral surface and transfers an electron to structural Fe(III), reducing it to Fe(II) (eq 5-6). The Cr(VI) contaminated groundwater, upon entering into the reduced zone accepts the electron liberated from Fe(II) and is reduced to Cr(III), which forms an insoluble precipitate of $Cr(OH)_3$ or $(Cr_xFe_{1-x})(OH)_{3(s)}$ as long as the pH of groundwater plume is between 5 to 12 (eq 2-4).

$$2\ S_2O_4^{2-} + H_2O \quad <=> \quad 4\ SO_2\bullet^{-} + H_2O \qquad (5)$$

$$4\ SO_2\bullet^{-} + Fe(III) + H_2O \quad => \quad Fe(II) + SO_3^{2-} + 4H^{+} \qquad (6)$$

The use of dithionite to form a redox barrier consists of three steps: subsurface injection, reaction with the aquifer matrix, and finally remediation of the contaminated groundwater (Amonette et al., 1994; Fruchter et al., 1996, 2000; Istok et al., 1999; U.S. EPA, 1995; Szecsody et al., 1998, 2000; Cervini-Silva et al., 2000; Nzengung et al., 2001; Thornton et al., 1998; Chilakapati et al., 2000; Betts, 1998). First, a buffered dithionite solution is injected within the aquifer zone of interest downgradient from the plume. During the reaction phase, the dithionite is given sufficient time to react with the sediment to form the barrier before the residual solution is removed from the aquifer by pumping.

A potential site for application of this treatment approach is the Department of Energy's Savannah River Site (SRS), located near Aiken, SC. The water-table aquifer at the SRS has been contaminated as a result of various industrial activities associated with nuclear material processing (NRC, 1997; U.S. EPA, 1997; Riley and Zachara, 1992). To date, the ISRM approach has not been widely tested on highly-weathered geological materials like the Upper Coastal Plain sediments present on the SRS, with the exception of the batch studies of Nzengung et al. (2001). The fact that dithionite is commonly used in the extraction of Fe oxides suggests that such a treatment may be deleterious to the physical integrity of the sediments, an aspect that has not been adequately addressed in previous studies. Therefore, the objective of this study is to use batch equilibration and column techniques to evaluate the effectiveness of dithionite reduced SRS aquifer materials in reducing and immobilizing Cr(VI).

MATERIALS AND METHODS

The effectiveness of dithionite in creating a reactive barrier for Cr(VI) migration was evaluated in a series of batch and dynamic flow experiments conducted at ambient temperature (25 ± 2 ^{o}C).

Local subsoil collected from a depth of 150 cm in a forested area on the SRS was used in the present study. This subsurface material from the Tobacco Rd. formation is typical of the coarse textured, highly weathered sediments found within the water table aquifer and the underlying first confined aquifer on the SRS. This material is similar to the sediments underlying the southeastern coastal plain of the U.S. (Eddy et al., 1991; Seaman et al., 1996, 1997; Bertsch and Seaman, 1999). The subsurface material, referred to as the SRS aquifer material, was air dried, sieved (< 2 mm), and stored at 4 ^{o}C prior to the batch and column studies.

Chemicals and Solutions. All chemicals and reagents necessary for the dithionite solution were stored in the Coy Anaerobic Chamber under an N_2 atmosphere. Milli-Q plus deionized water (DIW) was used to prepare all solutions. All test solutions were prepared in “artificial groundwater” (AGW), the chemical composition of which is representative of the groundwater composition found at the SRS and vicinity (Strom and Kaback, 1992). Oxygen free water was prepared by boiling the DIW, followed by purging with N_2 gas while cooling the water, which was then transferred immediately to the anaerobic chamber. A concentrated spike of cation-anions was added to this oxygen free water to yield the composition (Ca^{2+} 1.00 mg L^{-1}, Mg^{2+} 0.37 mg L^{-1}, K^{+} 0.21 mg L^{-1}, Na^{+} 1.40 mg L^{-1}, SO_4^{2-} 0.73 mg L^{-1}) of AGW. Carbonate-bicarbonate buffer was prepared with K_2CO_3 (4 times the dithionite concentration) and $KHCO_3$ (0.4 times the dithionite concentration) (Istok et al., 1999). Immediately before each experiment, the dithionite solution was prepared inside the coy chamber by mixing the buffer with oxygen free AGW, prior to the addition of sodium dithionite. Tritium (^3H_2O; ~200 pCi mL^{-1}) was used in the column experiments as a conservative tracer to assess the influence of dithionite treatment on the physical characteristics of the aquifer materials. Stock solutions of Cr(VI) were prepared using potassium dichromate powder ($K_2Cr_2O_7$) previously heated at 105 ^{o}C for two hours.

Batch transformation kinetics. The batch experiments were conducted inside the Coy^{TM} anaerobic chamber. Prior to the batch experiments, residual oxygen in the aquifer materials was removed by drying the sediments inside the Coy chamber overnight. Twenty-five g of aquifer materials were added in duplicate to Oak Ridge centrifuge tubes, followed by equilibration in twenty-five mL of oxygen free AGW for 48 hours using an end-over-end rotary shaker at the rate of 8 rpm.

For the dithionite treatment, concentrated dithionite solution was spiked to the water saturated aquifer materials within the tubes to achieve a final dithionite concentration of ~ 34.5 mmol. After two weeks of equilibration, the residual dithionite products were removed from the tubes by repeated washing and centrifugation. The first three washes were conducted with deoxygenated 0.1 M $NaHCO_3$ (pH ~ 8.3) to quench the reaction, and the fourth wash was with oxygen free AGW to remove excess carbonate from the solid phase (Amonette et al., 1994).

To assess the reductive capacity of the treated sediments, an oxygen free Cr(VI) solution (~ 28 mmol) was added to the tubes. The treated samples and the experimental controls were mixed continuously on an end-over-end rotary shaker for 89 hours. Duplicate sample and corresponding control tubes were sacrificed for analysis at specific time intervals. The liquid was separated from solid phase by centrifugation at 10,000 rpm (12,000 rcf) for 30 minutes at 25 ^{o}C, and the supernatant was filtered (0.22 µm pore size polycarbonate). The pH of the filtrate was determined and a fraction was then acidified for Cr(VI) analysis employing the diphenylcarbazide method (AWWA, 1998). Analysis of dissolved Cr(VI) concentrations were verified using a Hach DR890 colorimeter (Hach Company, Loveland, CO). For comparison, a Cr(VI) batch sorption isotherm was generated using a similar procedure to that described above, except the sediments were not exposed to dithionite prior to Cr(VI) addition.

Column studies. Ten cm long (5.0 cm ID) plexiglas columns were packed in small increments with aquifer material to a uniform bulk density ~ 1.75 g cm^{-3}. Each end of the soil column was packed with acid washed sand layers to help disperse flow throughout the entire cross-section of the column. Packed columns were flushed with CO_2 gas for ~ 30 minutes prior to saturation (flow rate ~ 0.7 cm d^{-1}) with AGW in an upflow direction. After saturation, the column was leached with AGW until the effluent composition stabilized as indicated by pH and electric conductivity (EC). The column PV and porosity were determined gravimetrically. The average PV for the repacked columns was calculated to be ~ 76.0 cm^{3}. A typical bulk density of 1.74 g cm^{-3} and porosity of ~ 0.39 was obtained. The least square inversion method (CXTFIT) of Toride et al. (1995) was used to estimate the transport parameters for the column experiments. The average linear velocity (V) and dispersion coefficient (D) were estimated based on tritium breakthrough. The retardation factor (R) for Cr(VI) in the column due to sorption was calculated using these estimated parameters (Table 4.2).

Following saturation, approximately two PV of freshly prepared buffered dithionite solution were leached through the aquifer materials at a constant inlet flow rate of 0.98 ml min^{-1} (Darcy velocity ~ 72 cm d^{-1}). The pH, EC, DO, and redox potential (mV) were continuously monitored throughout the experiments using flow through electrodes at the column outlet. Changes in the hydraulic conductivity (K) of the column, an indication of formation damage due to dithionite treatment, were monitored using a pressure transducer located at the column inlet. Effluents were filtered (0.22 μm pore size polycarbonate membrane) and analyzed for tritium by liquid scintillation. Turbidity of the column effluents was determined prior to filtration.

After dithionite treatment, the flow was stopped and the injected reagents were allowed to react with the aquifer material for approximately 18 hours. Then AGW containing Cr(VI) (1 mmol ~ 52 mg L^{-1}) in equilibrium with ambient O_2 was leached through the treated sediment and the effluent as collected and analyzed for Cr(VI). Other effluent parameters were monitored as described above. Cr(VI) leaching experiments were also conducted using non-reduced sediments to account for the inherent sorption properties of the aquifer materials. Only one breakthrough experiment was conducted in the treated sediment before the matrix was replaced with fresh aquifer material.

Analytical measurements. Cr(VI) was measured using the diphenylcarbazide method (AWWA, 1998) with absorption measured at 415 nm. Analysis of Cr(VI) concentration was verified using a Hach DR890 colorimeter method 8023 (Hach Company, 2000). Fe(II) and Fe_{total} were measured using Hach method 8146 and 8006, respectively (Hach Company, 2000), which employ phenanthroline method of Komadel and Stucki (1988). The DO level in the column effluent was determined using a flow through O_2 electrode (Microelectrodes, Inc., Bedford, NH). For ^3H_2O analysis, effluent fractions were mixed with scintillation cocktail and counted for 20 minutes in a liquid scintillation counter (Minaxi Tri-Carb 4000 Packard Instrument Co., Downers Grove, IL).

RESULTS AND DISCUSSION

Cr(VI) sorption. Subsurface sediments from the Upper Coastal Plain typically consist of highly weathered, coarse-grained materials with varying quantities of Fe-oxides, a predominance of exchangeable Al^{3+}, acidic pH, low organic matter and pore water ionic strength (Bertsch et al., 1999). The variable charge component of the sediments (Table 4.1) originates from kaolinite, goethite, and gibbsite that dominate the clay fraction (Seaman et al., 1996; Bertsch and Seaman, 1999) and act as the primary reactive mineral phases for surface reactions (Davis and Kent, 1990; Vulava and Seaman, 2000), resulting in a low cation exchange capacity and significant anion exchange capacity. Significant retardation of anionic solutes including Cr(VI) has been observed in studies conducted with similar materials under moderately acidic conditions, pH ~ 4-5 (Seaman et al., 1996; Toner et al., 1989; Boggs et al., 1992; Bolan et al., 1993; Chan et al., 1980; Bertsch and Seaman, 1999).

In batch experiments, a decrease in the equilibrium solution Cr(VI) concentration was attributed to both direct adsorption of Cr(VI) to soil particles and reduction to Cr(III), followed by adsorption and/or precipitation. In order to evaluate the effectiveness of in situ reduction, one should account for Cr(VI) sorption to the sediments in the absence of the chemical reductant. Previous batch equilibrium experiments using SRS sediments showed a Cr(VI) sorption capacity of 3.6 mmol kg^{-1}, with little native ability to reduce Cr(VI) (Seaman et al., 1999). Therefore, Cr(VI) loss in the absence of dithionite or any other added reductant was attributed to adsorption. The Cr(VI) adsorption capacity of the sediments obtained in the batch phase of this study (Figure 4.1a) is similar to the value (~ 2.9 mmol kg^{-1}) reported by Seaman et al. (1999), but somewhat higher than reported in other studies (Adriano et al., 2002). Comparing such values with Cr precipitation following reduction is complicated by the fact that dithionite is effective in reducing and dissolving Fe(III) present in goethite, a major sorptive phase for Cr(VI). Dithionite treatment in batch reaction vials showed an initial drop of pH from 10.5 to 9.5 (Figure 4.1b) and then remained fairly constant for 89 hours of dithionite treatment duration. In fact, most of the Cr(VI) reduction occurred before the first sampling event. In previous studies, Cr(VI) reduction (Eary and Rai, 1988; Ross et al., 1981) is quite rapid, even in the presence of DO. Cr(VI) sorption in the batch experiment was minimal (3.6 mmol kg^{-1}) because of basic pH of the treated soil solution.

The Cr(VI) sorption capacity of the untreated aquifer materials was also calculated from the column experiments (Figure 4.2). Cr(VI) breakthrough for the untreated saturated column displayed little hydrodynamic dispersion. Cr(VI) was moderately retarded (R = 2.6) in the column sediments, with the V = 172.8 cm d^{-1}, and D = 18.50 cm^2 d^{-1}, based on ^{3}H breakthrough. Numerical integration (Appendix C) of the area above the breakthrough curve ($\int_0^1(1\text{-}C/Co)$) for Cr(VI) indicated a sorption capacity of 0.59 mmol Kg^{-1} of soil (Figure 4.2)(Appendix C), much less than adsorbed in the batch kinetic experiments (Figure 4.1a). This is likely due to the much higher initial Cr(VI) concentration (~ 24 mmol L^{-1}) compared to the column experiments (1.0 mmol L^{-1}) and the longer equilibration times inherent in the batch studies.

Effect of dithionite treatment on aquifer materials. The dithionite concentration of the column effluent approached the influent concentration after leaching with two PV of the reductant solution (Figure 4.3a). Dithionite breakthrough coincided with an increase in effluent pH (Figure 4.3b), and deceased in both the DO (Figure 4.3c) and ORP level (Figure 4.3d). A significant increase in the effluent pH from ~ 5 to nearly 11 (Figure 4.3d) can be attributed to the strong buffering capacity of the dithionite treatment solution. Lower redox (-1000 mV) and the depletion of DO in the effluent (Figure 4.3d) indicate that two PV of the treatment solution was sufficient to develop a reducing environment throughout the length of the column.

Dithionite leaching did result in a temporary increase in effluent turbidity (Figure 4.3e), possibly due to the dissolution of Fe oxide coatings that served to structurally aggregate the sediment matrix. However, during the remediation phase, when the Cr(VI) solution was leached through the reduced column, little effluent turbidity was observed. Thus, the dithionite treatment did not have negative impact on the hydraulic properties of the repacked columns. Despite the generation and transport of colloidal material from the column, the hydraulic head at the inlet remained fairly constant throughout the experiment. Formation damage due to aquifer plugging is a common limitation observed in pump and treat remediation systems, and a possible consequence of injecting a reactive solute into an aquifer. Only a small amount of total iron (0.03 mg Fe g^{-1} treated soil ~ < 1% of total iron in the sediment) was released from the column sediments during dithionite treatment (Figure 4.3) and remediation phases. Residual dithionite and reaction products were only detected in the first five effluent pore volumes during the remediation phase. Some trace metals such as Ba, and Sr were mobilized during the dithionite treatment and the subsequent first few PV of the remediation phase, but their concentration was well below the drinking water limit (Buonicore, 1996)

The reduction capacity of the dithionite treated sediment was assessed by measuring the breakthrough of dissolved O_2 (8.22 mg L^{-1}) in the AGW. Each mole of O_2 consumed four moles of electrons when reduced to H_2O. As expected, DO breakthrough was retarded (Figure 4.4a) and the redox potential of treated sediment effluent (Figure 4.4b) was convex in shape, indicating substantial oxygen reduction in the column. In the electron transfer processes within the reactive zone, Fe(II) generated by dithionite treatments liberated the electrons during leaching of AGW with $O_{2.}$ And this oxygen, upon accepting the electron and reacting with protons was converted to H_2O. Since the oxidation of Fe(II) and subsequent hydrolysis generates acidity, the pH of the effluent decreased with continued leaching of AGW (Figure 4.4c). Significant oxygen consumption by the treated sediments continued for 173 PV, with approximately 2.90 mmol of O_2 consumed during the remediation phase (Appendix A). Based on 2-PV of buffered dithionite solution used to reduce the sediment, 3.91 mmol of O_2 g^{-1} dithionite was removed from groundwater.

Cr(VI) reduction by dithionite treated aquifer materials. The reactive barrier developed by treating aquifer material with a buffered dithionite solution was tested for the remediation of Cr(VI). The reduction of Cr(VI) is a proton consuming process and as a result, the pH normally increases with the Cr(VI) reduction. The Cr(VI) reduction that occurred in the reactive barrier was caused by the Fe (II) oxidation that generate protons whereas Cr(VI) reduction accepts protons, thereby canceling each other. The pH (~ 10) of the reduced sediment in batch equilibrations was found to be more or less stable during Cr(VI) reduction in an anoxic environment (Figure 4.1b).

In order to quantify the Cr(VI) reduction by the treated sediment, one must also account for other adsorption processes. The amounts of Cr(VI) reduced (Figure 4.1a) as calculated from subtracting Cr adsorption from total effect of adsorption and reduction was 17.26 mmol of Cr(VI) for per kg of treated soil and a 23.28 mmol of Cr(VI) was precipitated for each g dithionite addition to the sediments. These values indicate that the dithionite treatments caused almost 6 fold increases in the rate of immobilization of Cr(VI), a much higher Cr(VI) treatment capacity than previously (up to 0.2 mg $HCrO_4^-$ g^{-1} sediment) observed at the Hanford site (Istok et al., 1999).

Since Cr(VI) is likely to persist under aerobic conditions, no attempt was made to remove DO from the Cr leaching solution. The resulting Cr(VI) breakthrough curves (Figure 4.4d) obtained from analyzing the column effluent were asymmetrical. The retardation factor for Cr(VI) defined as the PV at which the effluent concentration, C/Co, equaled 0.5 was ~ 55, with complete Cr(VI) breakthrough (i.e., C = 1.0) at ~ 73 PV. Mass balance calculations indicate that approximately 9.16 mmols of Cr(VI) were reduced per kg of treated soil (Appendix C). Since the standard redox potential of DO (0.81 at pH = 7) is higher than that of Cr(VI) (0.72 at pH 7) and the inlet Cr(VI) solution had DO in it, it was expected that at least 73 PV of DO (6.98 mmols of O_2 reduced per kg of treated soil) were consumed by the matrix in addition to Cr(VI) reduction. The reduction capacity of the treated sediments in the batch experiments was almost twice that of the column system, which can be attributed to DO present the leaching solution.

Dissolution and oxidation of Cr(III). In addition to the reduction of Cr(VI), the success of this remediation strategy depends on the efficient precipitation of Cr(III). Since the hydrolysis and precipitation of Fe (III) and Cr(III) generate acidity, the pH of the groundwater has to be maintained above 5, where the solubility of Cr(III) is below the regulatory limit, 0.1 mg L^{-1} (Seaman, et al., 1999).

While evaluating the remediation of Cr in ground water, the potential reoxidation of the Cr(III) to the toxic Cr(VI) form must be considered. DO and manganese are the primary oxidants of Cr(III) in the soil environment (Eary and Rai, 1987). Only limited oxidation of Cr(III) by DO has been reported over a wider pH range (Schroeder and Lee, 1975; Palmer and Puls, 1994; Eary and Rai, 1987). Although there is a correlation between the amount of Cr(III) oxidized and the amount of manganese in soil (Palmer and Puls; 1994, Bartlett and James, 1979; Schroeder and Lee, 1975; Fendorf and Zasoski, 1992), oxidation of Cr due to manganese content would be very negligible for the SRS ground water as was evident from the very low manganese content in the matrix (Table 4.1).

ENVIRONMENTAL SIGNIFICANCE

Our investigations showed that the in situ reactive barrier formed by dithionite treatment of aquifer materials was effective at reducing and immobilizing Cr(VI), even in the presence of DO. This also shows promise for the treatment of other redox sensitive metals such as U, Pu and Tc that are generally less mobile/toxic in a more reduced form.

One key factor concerning the longevity of such barrier is the concentration of Cr in contaminated water. However, the reductive capacity of the reactive zone can be regenerated with additional dithionite treatments. Additional factors that influence the efficiency of in situ reduction include pH dependence of these reactions, the amount and forms of Fe in the matrix, and the presence of oxidants other than the target contaminant. Such complexity necessitates the collection of site-specific data prior to the wide spread deployment of such a remediation strategy.

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Table 4.1. Physical and chemical properties of SRS aquifer materials (Tobacco Road sand) used in the batch and column studies.

Texture[a]		Loamy sand
Particle-size distribution[b], %	Soil mineralogy[c]	
Sand (>53 μm)	q>>>f	92.65
Silt (53-2 μm)	q>>> k	2.55
Clay (<2 μm)	k>>q>goe, mi, gibb, hem	4.80
[d]Water dispersible clay (wt %)		0.056
[d]pH $_{DI}$		5.10
[d]pH $_{AGW}$		5.00
[d]pH $_{KCl}$		4.21
[d]EC $_{DI}$ (μS/cm)		4.29
[e]Cation exchange capacity (meq/100 g)		2.30
[f]Total organic carbon (g /100 g)		0.09
[g]BET surface area (m^2/g)		2.51
	Redox sensitive transition metals[h], g / 100 g	
Iron		0.48923
Manganese		0.00099
Chromium		0.00018
	Extractable Fe, g Fe / 100 g	
[i]5 M HCl, 21-d		0.51
[j]CDB Fe		0.37
[k]0.5 M HCl		0.05
[l]AO Fe		0.02
[m]0.5 M HCl, 1-h		0.01

[a] general soil classification of US Department of Agriculture

[b] hydrometer analysis

[c] determined by X-ray diffraction, where q = quartz, f = feldspar, k = kaolinite, goe =goethite, mi = mica, gibb = gibbsite, hem = hematite

[d] 1:2 soil: solution in deionized water (DI), AGW, or 1 M KCl for 30 minutes

[e] ammonium acetate method (Rhoades, 1982; Thomas, 1982)

[f] TOC, total organic carbon, dry combustion method (Nelson et al., 1982)

[g] by Micrometrics ASAP-2010

[h] EPA method 3051; Microwave assisted acid digestion

[i] Heron et al., (1994a)

[j] citrate-dithionite-bicarbonate extraction (Jackson et al., 1986)

[k] Lovely et al., (1986), modified by Kennedy et al.., (1999)

[l] ammonium oxalate extraction (Jackson et al.., 1986)

[m] Christensen et al., (2001)

Table 4.2. Physical parameters of packed columns, tracer and sorption experiments

Properties of packed column				
L,cm[a]	ρ_b[b]	PV[c], ml	ϕ[d]	Q[e], ml min^{-1}
10	1.74	76.54	0.39	0.95
Results of fitting parameters determined from tritium BTCs				
V[f], cm min^{-1}	D[g], cm^2 min^{-1}	P[h]	α[i], cm	
0.12	0.013	92.3	0.10	
Sorption parameter estimated from BTCs fitted to the analytical solution of convection dispersion solute transport model, CXTFIT				
R[j] = 2.61				

[a] L, column length
[b] ρ_b, bulk density
[c] PV, pore volume
[d] ϕ, porosity
[e] Q, flow rate
[f] V, average linear velocity
[g] D, dispersion coefficient
[h] P, peclet number
[i] α, dispersivity
[j] R, retardation factor

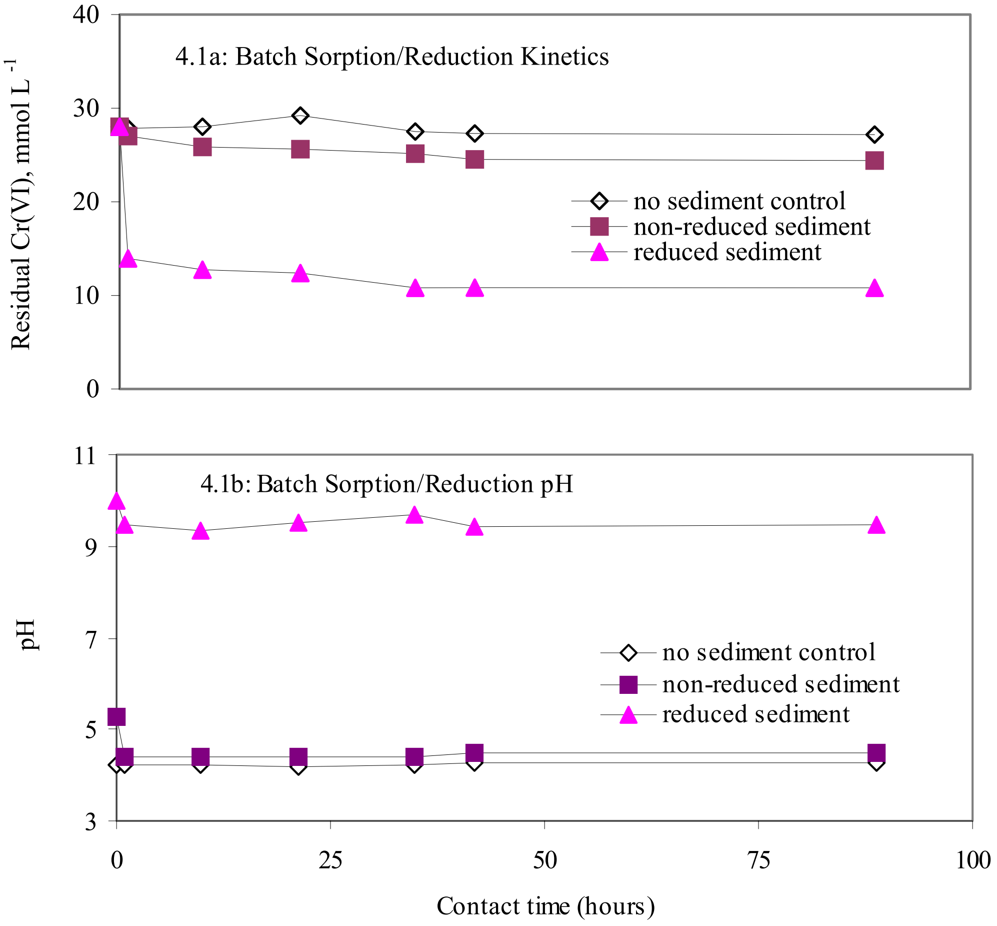

Figure 4.1. Results of batch experiments showing Cr(VI) sorption/reduction kinetics (4.1a) and pH change (4.1b) in equilibrated solution of non-reduced and reduced SRS sediment.

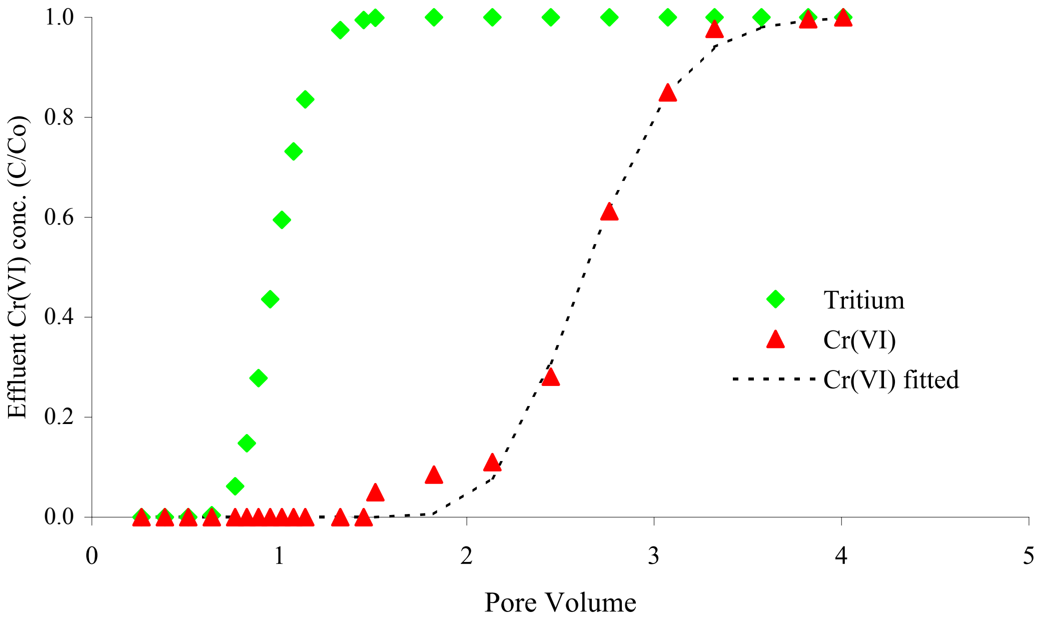

Figure 4.2. Cr(VI) and tritium breakthrough in non-reduced SRS subsurface sediments. The influent concentration of Cr(VI) was ~ 1 mmol.

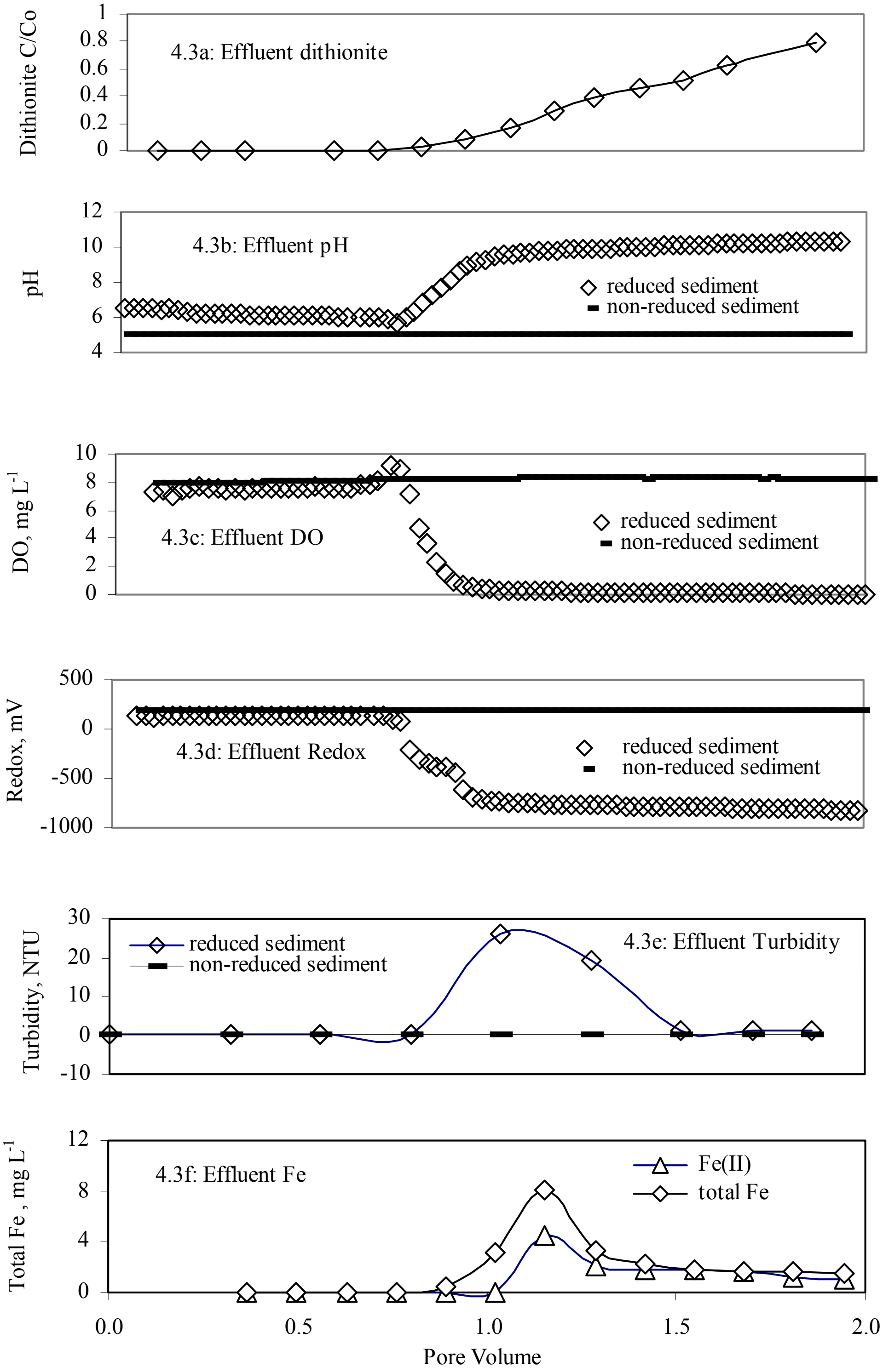

Figure 4.3. Dithionite treatment of SRS subsurface sediments. A two-pore volume of aqueous dithionite was injected into column and the changes in effluent parameters were recorded as above. Effluent turbidity and Fe concentration for the non-reduced column sediment was ~ 0.10-0.20 NTU and below detection limit (0.03 mg L^{-1}), respectively.

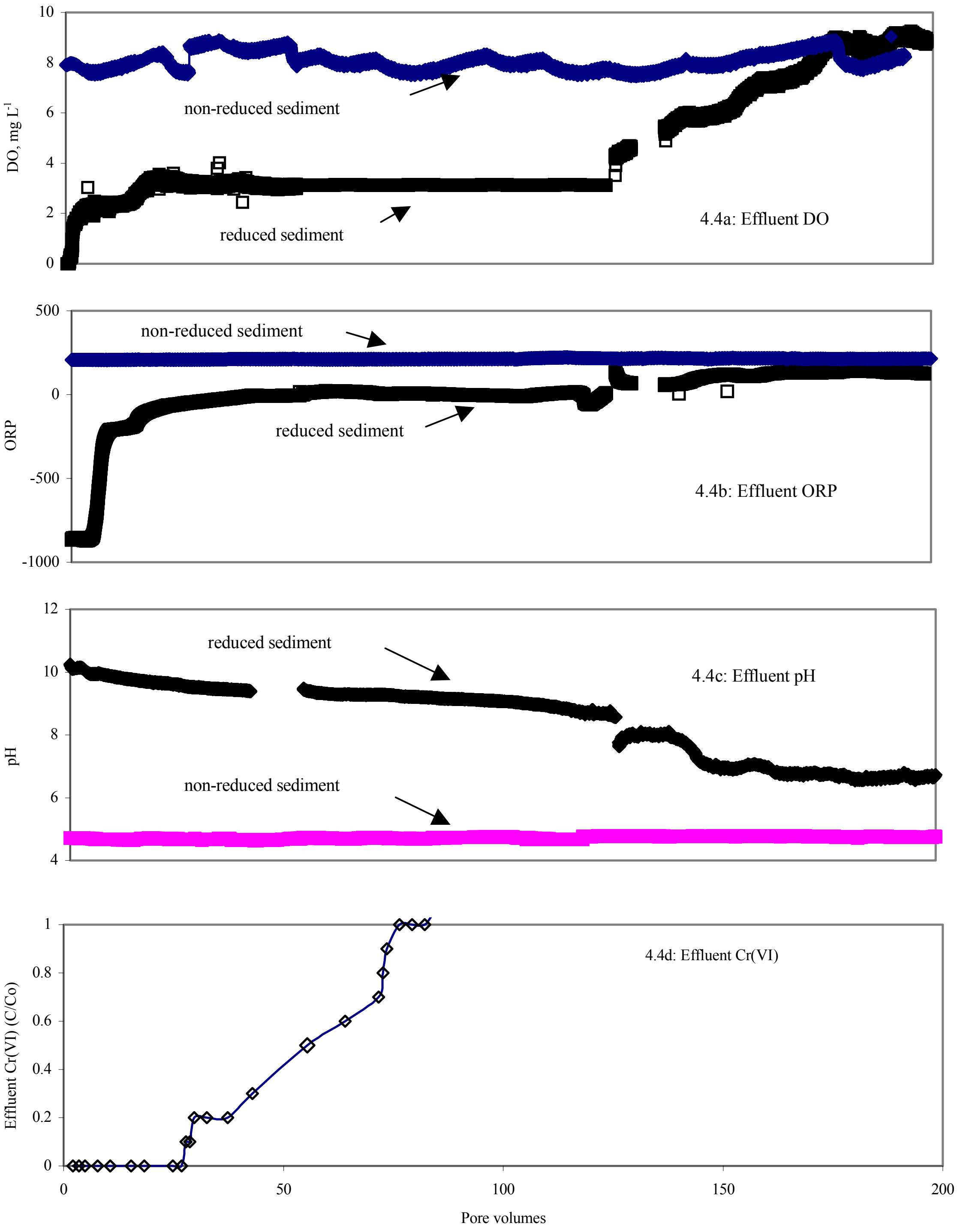

Figure 4.4. Results showing reduced column effluent parameters. Changes in effluent parameters (Fig 4.4a, .4.4b, 4.4c) are due to continuous leaching of oxygenated AGW leached through the reduced column. Fig. 4.4d shows the Cr(VI) remaining in the effluents when oxygenated AGW containing Cr(VI) (~1 mmol) was leached through the reduced column.

CHAPTER 5

CONCLUSIONS

The development of a subsurface reactive zone within aquifer sediments of the Atlantic Coastal Plain by aqueous dithionite injection as demonstrated in laboratory batch and column experiments enhanced the natural redox capacity for degradation of groundwater contaminants such as Cr(VI) and TCE. Although this technology, termed in situ redox manipulation (ISRM), has been successfully demonstrated in basaltic aquifer systems of the Pacific Northwest, its application in the variable-charge, Fe oxide rich, sediments of the Atlantic Coastal Plain has not been evaluated. The results of this research demonstrate that with modification the ISRM technology may be suitable for remediation of certain redox sensitive contaminants in Atlantic Coastal Plain sediments. An important finding of this research is that that the buffer system used for the dithionite treatment must be properly selected in order to prevent destabilization of the sediment matrix with consequent colloid mobilization and reduction in hydraulic properties of the aquifer. Treatment optimization studies showed a bicarbonate-carbonate buffer maintained an alkaline pH, which minimized colloid mobilization while providing effective redox capacity for reducing ground water contaminants.

The dithionite treatment conditions identified in the optimization studies were used to evaluate the efficacy of the ISRM technology for remediation of chromate-contaminated groundwater in Atlantic Coastal Plain aquifer sediments. The permeable reactive barrier established by dithionite injection were observed to be efficient in precipitating/immobilizing 9.2 mmols of Cr(VI) per kg of treated sediments in oxygen saturated groundwater. The results observed for the Cr(VI) treatment capacity of the dithionite reduced sediments indicate that other redox sensitive transition metals and radionuclides, whose redox potentials are close to that of Cr(VI), such as U(VI), Pu(III,IV), and Tc(V,VI) can be successfully removed from contaminated groundwater to regulatory target concentrations.

However, in subsequent studies, the same treatment conditions were observed to be inadequate for significant dechlorination of PCE or TCE contaminated groundwater. A likely explanation for the poor efficiency observed for the chlorinated solvents are kinetic constraints on the reduction reaction since the previous experiments had established both the redox potential and capacity were adequate for complete degradation. The flow rates employed in the column studies are at the upper range of those measured within the aquifer systems in the Atlantic Coastal Plain sediments at the SRS and may have limited solute interaction within the residence time of contaminants in the column. The slower reduction rates compared with Cr(VI) would reduce the efficacy for PCE and TCE degradation. In addition, ground water dissolved oxygen concentrations at SRS are typically lower by a factor of ten than that was used in the pack sediment columns. Thus, the degradation efficiency may be considerably greater in anaerobic or low-oxygen conditions when the competition of PCE and TCE with oxygen is reduced or eliminated. Further studies are necessary to evaluate the effects of these parameters on treatment efficiency.

The application of ISRM using dithionite injection for remediation of redox sensitive groundwater contaminants in non-shallow aquifers is attractive because of the potential efficiency and cost-effectiveness. However, before this technology can be fully deployed additional laboratory, as well as field scale treatability studies (Appendix D), need to be conducted.

APPENDICES

APPENDIX A

ORP Experiment Results

Column parameters

Total soil in column	344.28	g
TRS in column	287.33	g
Porosity	0.35	

Fe species in SRS soil

Total Fe (5 M HCL extractable)	0.51	%
Total Fe(III)	0.5018	%
0.5 HCL extractable Fe(III)	0.0441	%

Dithionite concentrations

Influent dithionite conc.(C/Co)	1	
Effluent dithionite conc during injection	0.78	
Dithionite conc after reaction	0.45	
Dithionite decomposition during reaction	0.33	

Fe solubilization

Fe released-injection phase	2.3375	mg
Fe released-withdrawal phase	5.101	mg
Total Fe solubilized	7.4768	mg
Total Fe lost from system	0.51	%

O_2 reduction capacity of reduced sediment

Total oxygenated water leached though reduced sediment	11.63	liter
DO in water	8.22	mg/L
DO leached throuh sediment	95.62	mg
DO consumed in reduced sediment	46.39	mg
Percent reduced	48.5	%
Soil mass in column	287.33	g
O2 reduction capacity of reduced sediment	161.45	mg/kg sediment

Fe reduced by the dithionite treatment

For oxygen reduction		
4 mole of Fe(II) is required for one mole of oxygen		
Therefore, Fe(II) oxidized during remediation phase	11.598	mmol
	647.736	mg
Fe(III) in column sediment	1441.822	mg
Fe(II) in column sediment	23.56106	mg
Therfore, Fe(III) reduced by dithionite	44.926	%
If 44.92 % of Fe(III) reduced in column, then reduced	0.2254	g Fe(III)/100 g sediment
If assumed that		
0.5 M HCL extractable Fe(III) were completely reduced		
Then,		
Structural Fe(III) reduced during dithionite treatment	0.1813	g/ 100 g sediment
Only structural Fe(III) reduced =	0.4577	g/100 g sediment
	39.618	%

APPENDIX B

PCE Dechlorination Experiment Results

PCE Reduction-Column Experiment

Soil mass	139.06		
Pore volume (PV)	26.7	ml	
PCE MW	165.8	g	
Influent PCE conc.	1	mg/L	
PCE leached	Effluent PCE	Cumulative Mass	
PV	mg/L	mg	
0.24	0.00	0.24	
0.61	0.00	0.37	
0.79	0.00	0.19	
1.16	0.01	0.37	
1.53	0.08	0.35	
2.37	0.26	0.69	
2.65	0.28	0.20	
3.20	0.38	0.37	
3.79	0.47	0.34	
4.31	0.57	0.25	
4.87	0.56	0.24	
5.43	0.68	0.21	
5.98	0.72	0.17	
6.54	0.86	0.12	
7.09	0.85	0.08	
7.65	0.91	0.06	
8.21	0.91	0.05	
8.76	0.91	0.05	
9.32	0.91	0.05	
10.89	0.92	0.13	
13.12	0.97	0.13	
15.34	0.95	0.09	
16.45	0.97	0.04	
Total PCE sorbed+reduced=		4.7937	mg/L
		0.0009	mg/g
PCE reduced = 0.0009-0.0004=		0.0005	mg/g
		0.5237	mg/kg
		0.0032	mmol/kg

PCE sorption-Column Experiment

Soil mass	136.99		
Pore volume	27.65	ml	
Influent PCE conc.	1	mg/L	
PCE leached	Effluent PCE	Cumulative Mass	
PV	mg/L	mg	
0.14	0.00	0.14	
0.37	0.00	0.23	
0.56	0.00	0.20	
0.85	0.00	0.28	
1.13	0.04	0.28	
1.70	0.41	0.44	
1.99	0.54	0.15	
2.56	0.76	0.20	
2.84	0.83	0.06	
2.99	0.80	0.03	
3.13	0.86	0.02	
3.42	0.91	0.03	
3.99	0.99	0.03	
4.27	0.99	0.00	
4.55	1.00	0.00	
4.84	0.97	0.00	
5.12	1.01	0.00	
5.55	1.03	0.00	
5.70	1.04	0.00	
5.99	1.03	0.00	
6.27	1.05	0.00	
6.56	1.06	0.00	
6.86	1.05	0.00	
7.15	1.05	0.00	
Total PCE sorbed=		1.9632	mg/L
		0.0004	mg/g

Oxygen consumed by reduced sediments

Pore volume DO reduced	7.0	ml
O2 concentration water	8.22	mg/L
Total water leached	186.9	ml
Total oxygen consumed	1.536	mg
	0.096	mmol
	0.69	mmol/kg

APPNDIX C
Cr(VI) Immobilization/Precipitation Experiment Results

Cr(VI) Reduction Column Experiment

Sediment mass	351.22	g
Sand	58.89	g
Pore volume (PV)	63.7	ml

PV Cr(VI) leached	Effluent Cr(VI) mmol	Cumulative mass mmol
2.10	0.00	2.10
3.50	0.00	1.40
4.90	0.00	1.40
7.80	0.00	2.90
10.60	0.00	2.80
15.40	0.00	4.80
18.30	0.00	2.90
24.90	0.00	6.60
26.80	0.00	1.90
27.80	0.10	0.95
28.70	0.10	0.81
29.70	0.20	0.85
32.60	0.20	2.32
37.30	0.20	3.76
43.00	0.30	4.28
47.80	0.50	2.88
55.40	0.50	3.80
59.20	0.40	2.09
64.00	0.60	2.40
71.60	0.70	2.66
72.60	1.00	0.15
73.50	1.00	0.00
76.40	1.00	0.00
79.30	1.00	0.00
82.20	1.00	0.00
85.10	1.00	0.00
88.00	1.00	0.00

Total Cr(VI) sorbed+ reduced =		53.75 mmol/L
		2794.74 mg/L
		0.507 mg/g
		506.876 mg/kg
		9.748 mmol/kg
Cr(VI) reduced	=9.748-0.586	=9.161 mmol/kg

Cr(VI) Sorption Column Experiment

Sediment mass	342.22	g
Sand	44.67	g
Pore volume	67.11	ml

PV	Effluent Cr(VI) mmol	Cumulative mass
1.51	0.05	1.472
1.83	0.09	0.298
2.14	0.11	0.280
2.57	0.28	0.346
3.2	0.61	0.349
3.82	0.85	0.167
4.2	0.82	0.064
4.32	0.98	0.012
4.82	1.01	0.003
5.32	1.00	-0.002
5.69	1.00	0.001
15.4	1.00	0.000
18.3	1.00	0.000
27.8	1.00	0.000
37.3	1.00	0.000
59.2	1.00	0.000

Total Cr(VI) sorbed =	2.989 mmol/L
	155.452 mg/L
	0.03 mg/g
	30.484 mg/kg
	0.586 mmol/kg

Oxygen consumed by reduced column sediments

Pore volume DO reduced	73	
O_2 concentration in water	8.22	mg/L
Total water leached	4650.1	ml
Total oxygen consumed	38.224	mg
	2.389	mmol
	6.981	mmol/kg sediment

APPENDIX D

Conceptual design for field test

This appendix discusses the field deployment of the in situ redox manipulation system (ISRM). Establishing the reactive zone ahead of the path of the migrating plume, the primary objective of installation, has not been discussed in previous chapters. Care must be taken to ensure that deployment does not alter groundwater flow such that the plume is diverted around the reactive zone. Therefore, prior to deployment, a detailed hydrogeological characterization of the site is warranted, including determination of the lateral and vertical extent of the contaminant plume.

The reactive barrier can be deployed using one of several techniques involving a single injection/recovery well or multiple wells. Perhaps the simplest, most controlled approach involves using two wells installed across the eventual path of the migrating plume so that the reactive zone can be formed perpendicular to natural groundwater flow (Figure 5.1). One well is used to inject the reactants into the aquifer at the same time the recovery well is being pumped so as to avoid creating a significant hydraulic gradient that could possibly divert the plume away from the barrier. It may be necessary to temporarily halt injection and recovery pumping so that the chemical reductants have time to react with the aquifer materials. After such an equilibration period, injection, at this point with clean water, and pumping may resume to ensure recovery of the residual chemicals. The role of the two wells, i.e., injection vs. capture, may be switched as necessary to generate the most effective reactive barrier; however, simultaneous injection and pumping is likely the best method to control barrier placement and avoid significant mounding that could alter plume migration. Choice of the proper-screened zone within the injection/capture well system may help in directing the reductant solution into the aquifer zone of interest. Additional injection/recovery well pairs can be used to create a more directed funnel to plume migration, and pumping wells can be placed in positions to draw the plume through the reactive zone.

In a single well system, the reactants are injected into the formation ahead of the plume and given the proper time to react with the aquifer matrix before the residual chemicals are withdrawn by pumping the same well (Figure 5.2), similar to the system employed by Pacific Northwest National Laboratory, Richland, Washington (Williams et al., 1994). After the reactants have been removed, the well can then be pumped as necessary to draw the plume into the reactive zone. Depending on the reaction kinetics, the single well system may be a fairly passive means of removing/degrading the contaminant as groundwater is collected for some alternate use.

Reference

Williams, M.D., S.B. Yabusaki, C.R. Cole, and V.R. Vermeul. 1994. In-situ redox manipulation field experiment: Design analysis. p. 1131-1153. *In* G.W. Gee, N.R Wing (ed.) In situ remediation: scientific basis for current and future technologies, Battelle Press, Columbus, OH. Thirty–third Hanford Symposiums on Health and the environment, 7-11 November 1994. Pasco, WA.

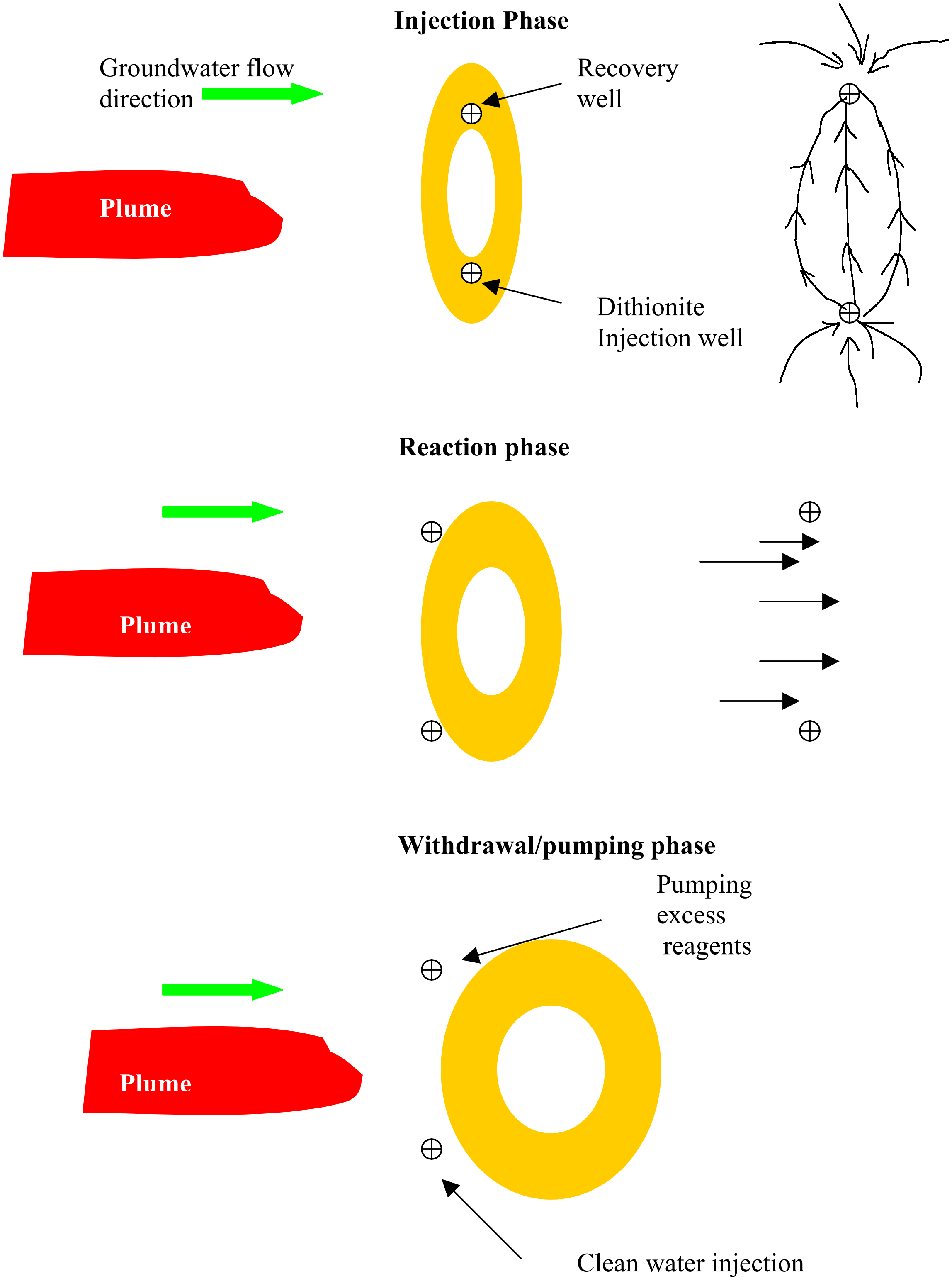

Figure 5.1. In-situ redox manipulation using two or multiple injection/recovery wells

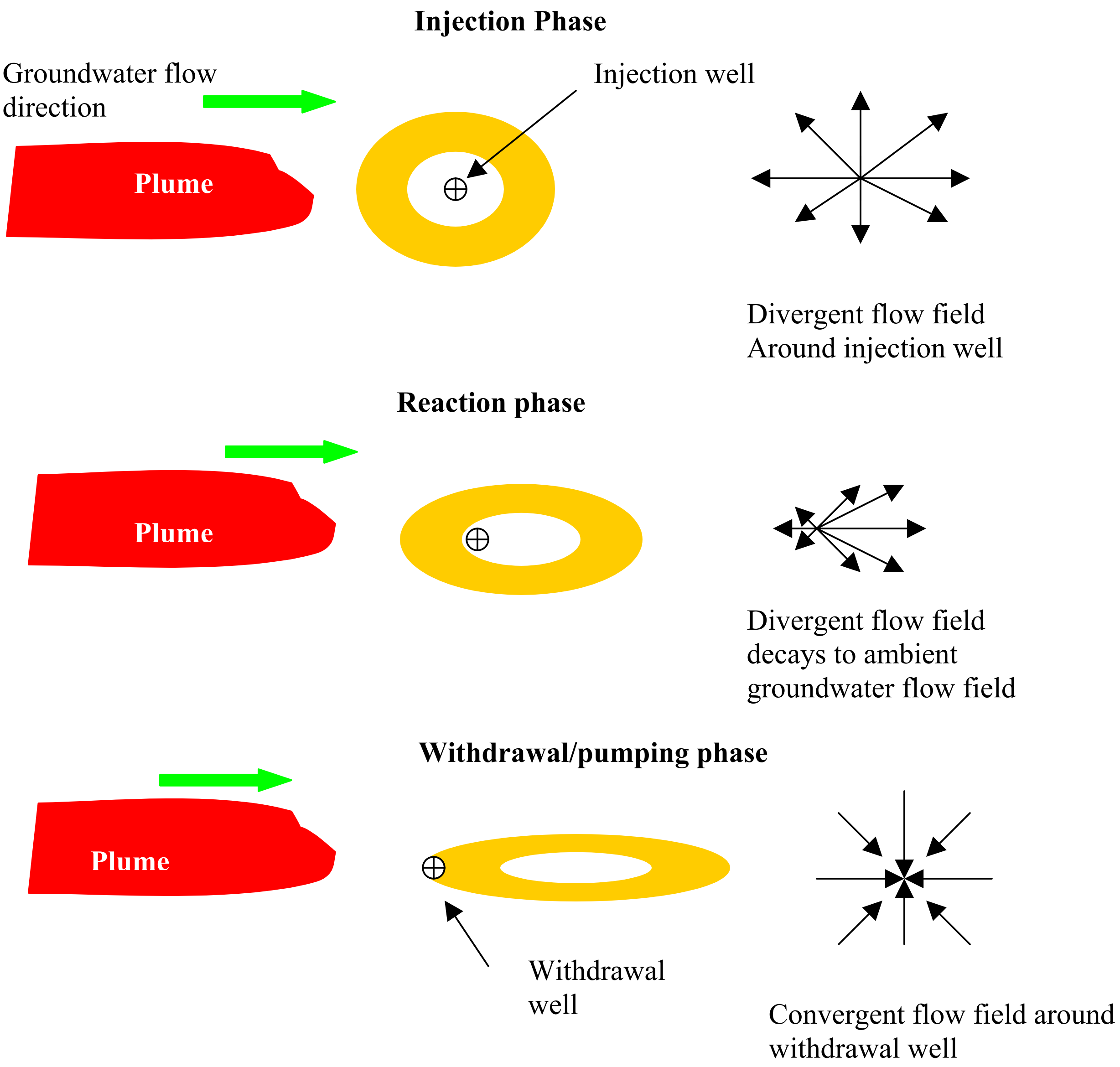

Figure 5.2. In-situ redox manipulation using single well injection/withdrawal test