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Different Strategies for Biological Remediation of Perchlorate Contaminated Groundwater

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ABSTRACT OF THE DISSERTATION

Different Strategies for Biological Remediation of Perchlorate Contaminated Groundwater

by

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Dr. Mark R. Matsumoto, Chairperson

Perchlorate (ClO_4^-) has gained attention recently due to its interference with thyroid gland function. In infants and unborn children, inadequate thyroid hormone production can cause mental retardation and thyroid tumors. Since new perchlorate standards will be proposed in 2013, and if a stricter standard is imposed, cost effective technologies will be in high demand. The overall objective of this research was to evaluate two perchlorate bioremediation strategies using indigenous soil bacteria: 1) an autotrophic strategy using zero-valent iron (ZVI) to generate hydrogen as the electron donor and alkalinity in the form of (bi)carbonate as the carbon source for cell growth and maintenance and 2) a heterotrophic strategy using organic substrates as the electron donor and the carbon source for cell growth and maintenance.

The first strategy was evaluated on perchlorate-contaminated groundwater from West Valley Water District Well #2 located in Rialto, CA (*Chapter III*). A mobile treatment system consisting of a water holding tank, a ZVI packed bed and two parallel sand filters was placed at the site. In the first three months, the system experienced excellent performance, as measured by the tested parameters meeting the California drinking water standards. The effluent concentration of perchlorate was non-detectable (below 4 μg/L), nitrate effluent concentration was less than 0.01 mg/L as N, effluent iron ranged from 0 to 0.05 mg/L. Coliforms, fecal coliforms and E. *coli* in the reactor effluent were below the detection limit of 2 MPN/100mL. However, significant loss of perchlorate performance was observed after 3 months operation. The reason was attributed to the reduction of hydraulic conductivity and flow channeling.

A laboratory column experiment was conducted to investigate the hydraulic condition change in the ZVI beds (*Chapter IV*). Effects of flow rate and (bi)carbonate on hydraulic condition were evaluated by performing hydraulic conductivity tests, SEM examination, and tracer tests. The results indicated that the decrease of hydraulic conductivity was more pronounced in the low flow reactors than in the higher flow reactors. This result appeared to contradict the hypothesis that increasing the flow rate will accelerate the hydraulic conductivity reduction. (Bi)carbonate was determined to be the primary cause of the hydraulic conductivity reduction. The decrease in hydraulic conductivity was most severe in the segment receiving the higher concentration of $NaHCO_3$. Hydraulic conductivity decreased from $10^{-2.73}$ cm/s to $10^{-7.33}$ cm/s after

constantly feeding 24 mM of $NaHCO_3$ for 41 days. The reduction of hydraulic conductivity was caused by the formation of mineral precipitates.

Because of the lack of long-term perchlorate reduction in the autotrophic ZVI-based system, an alternative strategy that utilized organics as both the electron donor and carbon growth source was tested for perchlorate bioremediation (*Chapter V*). Laboratory microcosm and column tests were employed to assess the effectiveness of selected organic substrates on reducing perchlorate from two different locations of a real perchlorate-contaminated site. One location (source area) had 70 mg/L of perchlorate in groundwater, and another one (plume edge, referred to "biobarrier") had 500 µg/L of perchlorate. The effect of adding nutrients was also examined. For the high concentration source area treatment, emulsified oil substrate (EOS) and glycerin were determined to be the most effective organics from the microcosm testing. Hence, they were selected for column testing. The results revealed that amending soil with EOS had significant advantages over using glycerin as a soil amendment. After a single injection of EOS, perchlorate can be reduced to less than 4 µg/L for 4 months. Perchlorate reduction was not initiated in glycerin-amended soil. Glycerin had to be constantly added into the influent to treat perchlorate to non-detectable level. For the low concentration biobarrier treatment, compost/mulch, EOS, and EHC (a combination of carbon plant-based carbon source and zero-valent iron) had similar perchlorate removal rates in microcosm tests. EOS appeared to have greater longevity than EHC in the column tests. The addition of nutrients had minor benefit on both sites treatments.

Comparing the two strategies, using organic substrate was more feasible for perchlorate bioremediation in terms of overall performance and longevity.

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CHAPTER I INTRODUCTION

Perchlorate is most commonly used in the manufacture of solid propellant for rockets and missiles. It is also used as a component of air bag inflators, fireworks, additives in lubricating oil, etc. [1, 2]. Perchlorate interferes with the iodide uptake by the thyroid gland, decreasing production of thyroid hormones. Inadequate thyroid hormone production can cause mental retardation in infants and unborn children[3, 4] .

There are currently no regulatory criteria for perchlorate concentration in drinking water issued by the U.S. Environmental Protection Agency (USEPA). However, an interim health advisory level of 15 µg/L was established in 2009 (US Environmental Protection Agency, 2008). Some states have, however, set maximum contaminant levels (MCLs) for perchlorate drinking water. California established a perchlorate MCL of 6 µg/L for drinking water in 2002; Massachusetts has an MCL of 2 µg/L. In January 2011, the California Office of Environmental Health Hazard Assessment (OEHHA) proposed a 1 µg/L public health goal for perchlorate, with a target implementation date of February 2013 [5]. This will be very problematic for southern California, Arizona, and Nevada, which have many perchlorate-contaminated sites and also with high levels of contamination. The Colorado River is the primary source of irrigation water for most food crops grown in Southern California and Southwestern Arizona. It has been found that perchlorate concentration in the Colorado River range from 2 to 9 µg /L and is derived from aerospace- and defense-related fuel industries once located near the Las Vegas Wash [6]. Strict new perchlorate regulations will increase the cost for

contaminated water treatment. Thus, seeking effective and low cost technologies for perchlorate remediation is urgent.

Ion exchange, membrane technologies, activated carbon adsorption have been widely used in perchlorate treatment [7-11]. However, these systems generate concentrated perchlorate and saline waste streams, which need further treatment before disposal. In addition, the high treatment cost cannot be ignored [12, 13]. Biological removal of perchlorate has been studied in the past decades [14-16]. In the biological treatment process, perchlorate acts as electron acceptor and, when in the presence of an electron donor, perchlorate can be degraded to harmless chloride by perchlorate reducing microorganisms (PRMs).

Hydrogen has gained interest as an electron donor because it is cost effective and has low microorganism yield [17, 18]. Perchlorate can be biodegraded to chloride by *Dechloromonas* sp with H_2 as the electron donor and carbon dioxide as the carbon source [19]. However, production and/or handling of hydrogen gas is problematic, and its low water solubility poses challenges for delivery to perchlorate reducing bacteria. Therefore, to address these safety concerns and implementation challenges, ZVI has been shown to generate hydrogen via iron corrosion reactions with water [20-22]. The concept of ZVI-PRMs has been demonstrated by Yu et al. [22]. Perchlorate was reduced to a non-detectable level (4 µg/L) from 500 µg/L of influent concentration at the hydraulic retention time ranging from 63 hr to 42 minutes.

Based on the previous work of Yu et al., the first portion of this research was a field scale demonstration of the laboratory tested concept. The objective of this study

was to test and demonstrate the efficacy of the ZVI supported biological reduction of perchlorate at an actual contaminated site. A trailer mounted pilot demonstration system was designed, built, and mobilized at West Valley Water District Well #2 in Rialto, CA. Perchlorate treatment performance was evaluated at different flow rates. Perchlorate reduction significantly decreased after 3 months of operation. To troubleshoot the problems encountered in the pilot study, possible reasons for the loss of perchlorate reduction were formulated and then investigated. The three hypotheses were: (i) insufficient PRMs attached to the ZVI surface; (ii) insufficient H_2 production; and (iii) hydraulic loss. Conducting laboratory experiments using ZVI taken from the field reactor tested the first two hypotheses. The results indicated that PRMs were present in sufficient number and that the ZVI retained H_2 production capacity. Based on the rates of perchlorate degradation achieved from the removed ZVI, perchlorate should have been completely removed after passing the ZVI bed at the flow rate of 4 gpm. The third hypothesis was examined by performing a tracer test. The result shown there was a 31.7% drop in residence time after a 3-month operation. Hence, it was hypothesized that the poor perchlorate treatment performance may be attributed to the hydraulic loss within the reactor, which led to the second portion of study (Chapter IV).

Carbonate and bicarbonate are the principal species that contribute to alkalinity in water. Bicarbonate was fed into the ZVI reactor at the start-up period to promote the growth of PRMs, however, it can also lead to the formation of iron corrosion products, which clog the system. The objective of the second portion of this research (Chapter IV) was to gain a better understanding of the formation of iron corrosion products and the

reduction of hydraulic conductivity in the ZVI bioreactor. Laboratory column experiments were conducted to determine the hydraulic condition change at different flow rates as well as different bicarbonate concentrations.

Due to significant problems encountered with the ZVI-H_2 system in maintaining effective perchlorate treatment over several months, an alternative perchlorate bioremediation strategy using organic substrates as the electron donor and the carbon source for cell growth and maintenance was evaluated. Several organic substrates were selected to evaluate their efficiency for in situ perchlorate bioremediation at a high concentration source area and for low concentration in groundwater with a biobarrier. Both laboratory microcosm and column experiments were conducted to assess this strategy. The results indicated that emulsified oil substrate (EOS) has a relatively better treatment performance than other substrates at both source area and biobarrier application. However, multiple injections should be made due to the depletion of compounds in the real application.

In summary, the overall objective of this study was to test and evaluate two different strategies for biological remediation of perchlorate contaminated water. Sub-objectives were to:

- Test and demonstrate the efficacy of the ZVI supported biological reduction of perchlorate.
- Evaluate the bicarbonate effect on hydraulic reduction and corrosion products formation in the ZVI reactor.

- Assess an alternative strategy for perchlorate biological reduction. Determine the ability of various organic compounds as electron donors for perchlorate biodegradation and to justify which compound is more suitable for in-situ application.

CHAPTER II BACKGROUND

2.1 PERCHLORATE

Perchlorate (ClO_4^-) has become a common environmental contaminant in groundwater because of its wide use in energetic boosters or solid oxidants in rockets and missiles, fertilizers, fireworks, and air bag inflators, etc. [1, 2]. Pure perchlorate salts can be absorbed through the skin; however, the principal pathway of perchlorate entering human body is by ingestion. Perchlorate in water is a human health concern due to its effect on thyroid hormone formation through iodide uptake inhibition, which will result in thyroid tumors. Inadequate thyroid hormone production can also cause mental retardation in infants and unborn children [3, 4].

Perchlorate contamination has been found throughout the United States (Figure 1.1), especially in the southwestern states of Nevada, Utah, and California, which have many perchlorate-contaminated sites and also with high levels of contamination. Christen reported the worst contamination was in the Las Vegas, Nevada area, where groundwater contamination ranged from 630,000 to 3,700,000 µg/L perchlorate [23]. The entire supply of ammonium perchlorate for the U.S. Department of Defense (DoD) and the National Aeronautics and Space Administration (NASA) was produced in Nevada from approximately 1951 through 1998. Improper disposal of perchlorate or leaks from the facilities to the environment led to widespread soil and groundwater contamination. Logan reported that perchlorate has been found in 30% of the wells sampled in California, and is above the state's action level in 9% of those wells [19]. Wells in California exceeding the action level have been closed, treated via ion exchange,

or the waters are diluted with perchlorate-free water before public use [24]. Over 70% of the U.S. winter lettuce crop was irrigated with perchlorate-laden Colorado River water has led to its detection in milk and lettuce [25, 26]. Although mass production of perchlorate began as early as the 1940s and was first detected in parts per million concentrations in groundwater wells in eastern Sacramento County, California in 1955, it was not categorized as an environmental contaminant until the past decade [4, 27, 28].

There are currently no regulatory criteria for perchlorate concentration in drinking water issued by the U.S. Environmental Protection Agency (USEPA). However, an interim health advisory level of 15 µg/L was established in 2009 (US Environmental Protection Agency, 2008). Some states have much higher standards; California set a maximum contaminant level (MCL) for perchlorate of 6 µg/L in drinking water in 2002, and Massachusetts is at 2 µg/L.

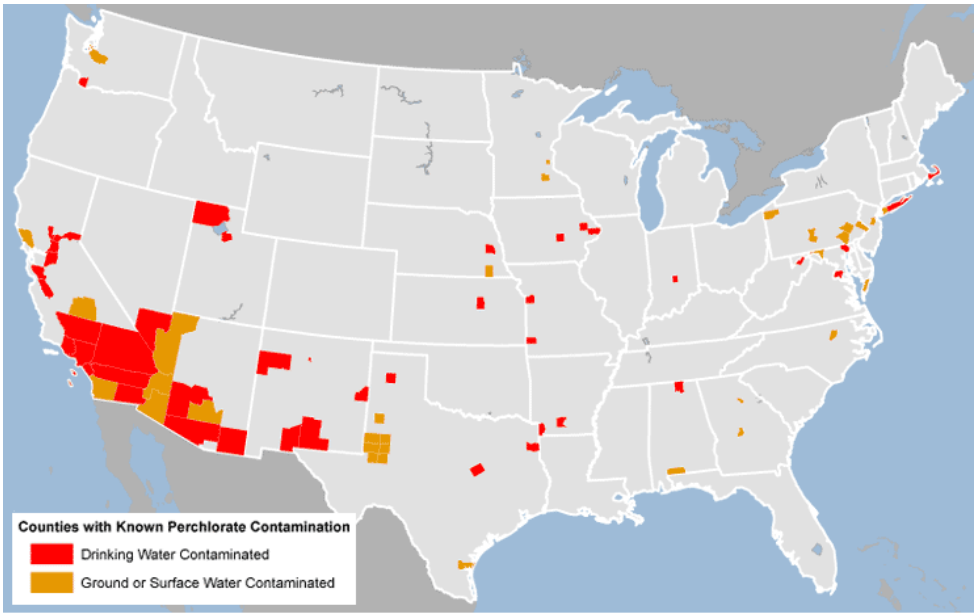


Figure 2.1 Perchlorate contamination throughout U.S.

Perchlorate is very un-reactive in solutions, extremely soluble in water, and difficult to remove by adsorption reactions. Therefore, treatment options are limited [29]. Technologies applicable for treating perchlorate contamination in drinking water and groundwater include ion exchange, membrane technologies (electrodialysis and reverse osmosis), activated carbon adsorption, and bioremediation [7-11]. Among these technologies, ion exchange and membrane technologies are mature technologies for perchlorate treatment. However, these systems generate concentrated perchlorate and saline waste streams which need further treatment before disposal [12, 13]. Bioremediation technology has been successfully demonstrated in the past decades. Bioremediation technology uses microorganisms capable of reducing perchlorate into harmless chloride in the presence of an electron donor and carbon source at near neutral pH. Perchlorate reducing microorganisms (PRMs) can use a wide variety of organic substrates as electron donors including ethanol, methanol, vegetable oil, acetate, and lactate [14-16]. The most acceptable pathway for perchlorate reduction is via the following sequence:

ClO_4^- (perchlorate) → ClO_3^- (chlorate) → ClO_2^- (chlorite) → Cl^- (chloride) + O_2

The final product is harmless chloride and has been proven by showing a good mass balance with perchlorate [30, 31].

2.2 ZERO-VALENT IRON REACTIVE BARRIER

Recently, the feasibility of using hydrogen as the electron donor for perchlorate degradation has been examined in the laboratory [2, 32, 33]. Hydrogen has been shown to be a cost effective and efficient electron donor, which can achieve the same removal

efficiency as other electron donors. Hydrogen also has the advantage that microorganism yield is considerably less than that for organic electron donors. High biomass yield can lead to reactor biofouling [17, 18]. However, the low solubility and storage concern of hydrogen gas makes it difficult to be implemented in the large scale field application. Therefore, as an alternative, zero-valent iron (ZVI) was chosen as a hydrogen supplier by producing hydrogen under anaerobic conditions in the presence of water [20-22]. ZVI has been widely used as a reactive medium in permeable reactive barrier (PRB) for contaminated groundwater treatment. When contaminated groundwater passes through the ZVI PRB, the treated groundwater coming out from another side is expected to meet the target level (Figure 1.2).

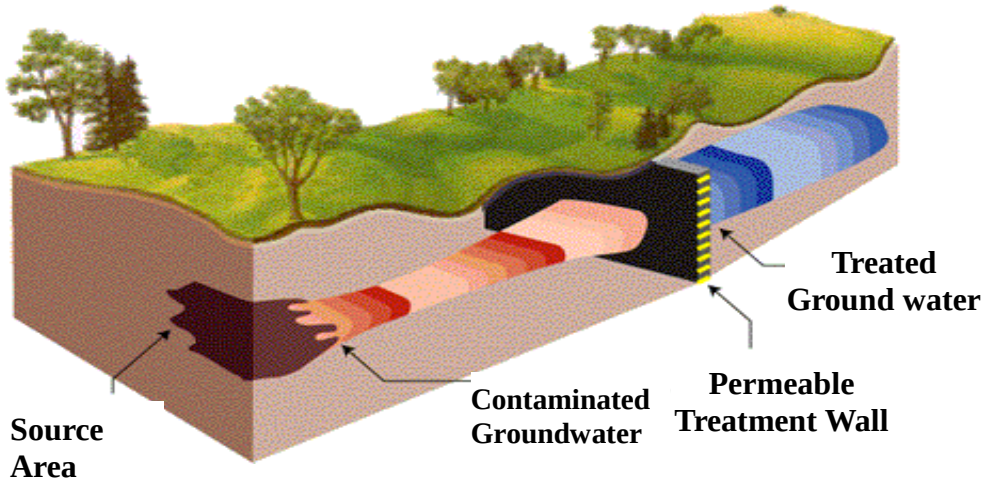


Figure2.2 Schematic of a permeable reactive barrier (PRB)

TCE, hexavalent chromium, arsenic can be abiotically treated to the target level by ZVI [20-22, 34]. Thermodynamically, ZVI can reduce perchlorate by chemical reduction. However, the reduction is very slow due to the large activation energy barrier. Huang et al reported that there was only 30-60% removal efficiency using ZVI only [35].

The chemical reduction process is too slow to be used in situ for perchlorate remediation. In order to increase the removal rate of perchlorate, external energy was introduced to lower the kinetic energy barrier for perchlorate reduction. Gu et al. reported complete perchlorate removal was achieved in 1 hour by increasing the experimental temperature to 195°C [36]. Oh et al. also reported 98% of perchlorate was removed in 1 hr at 200 °C by using microwave heating [37]. Although heating can enhance the removal rate, the high cost means this method cannot be widely used. Until now, the study of perchlorate biodegradation using ZVI was still at the laboratory stage; there is no full-scale application in the ZVI-PRB system reported.

The main characteristics of iron corrosion in water are the release of ferrous iron into solution, iron precipitates, the production of hydrogen, and an increase in pH [38]. Thus, there is a concern about diminished ZVI-PRB reactivity and longevity over time due to the potential clogging of pore volume, coverage of reactive surface, and reduction of permeability caused by iron corrosion products (ICPs) [39-41]. The formation of ICPs and the reduction of porosity had been observed in PRB case studies (Table 2.1).

Table 2.1 Summary of PRB some case studies

Site location	Contaminant(s)	Performance	References
Y-12 Site Oak Ridge, TN	U, Nitrate	Produce 0.15 mm thick precipitates in the first 30 months. Fe reactivity decrease, estimated lifetime as 15 years.	[42]
Denver Federal Center Denver, Colorado	CAHs	Gate porosity drop 0.35% per year.	[43]
U.S. Coast Guard Elizabeth City, NC,	Chromate, TCE	Porosity reduction primarily happened at the entrance, about 3.2% decreasing after 4 years.	[44]
Copenhagen Freight Yard Copenhagen, Denmark	TCE, DCE, VC	Loss of performance after one year due to poor hydraulic condition, hydrogen production equal to 5% pore space per day.	[45]

A ZVI-PRB system can be described as a plug flow reactor in which hydraulic characteristics, perchlorate reducing microorganism density, pH, and hydrogen production varies longitudinally within the reactor. It has been reported that porosity and permeability change affect flow path, leading to preferential flow in some situations [39, 46]. Preferential flow affects residence time, which is directly related to the effective reduction of the contaminants. Perchlorate concentration, pH, cell density, and hydraulic conditions are a function of column length. In the entrance portion of the reactor, the most significant hydraulic changes occur at the interface where groundwater first enters

the ZVI system [42, 47, 48]. Plugging in the entrance zone is mainly due to dissolved oxygen in the groundwater (Reaction 2.1). Dissolved oxygen is consumed in the system entrance, and the released hydroxide will raise the pH leading to the precipitation of ferrous hydroxide (Reaction 2.2). Ferrous hydroxide is thermodynamically unstable and may further oxidize to magnetite (Reaction 2.3).

Beyond the beginning portion of the column, the groundwater is anaerobic, and iron corrosion continues via reactions with water and ions in natural groundwater. Hydrogen will be produced when iron reacts with water (Reaction 2.4 -2.8). The specific ICPs depends on the water chemistry, although other ions like phosphate can cause vivianite ($Fe_3(PO_4)_2$) precipitation. The most common precipitates found in the ZVI PRBs are magnetite (Fe_3O_4), maghemite (Fe_2O_3), goethite (α-FeOOH), lepidocrocite (γ-FeOOH), siderite ($FeCO_3$), mackinawite (FeS), green rusts and calcite ($CaCO_3$) [49-51].

$$2Fe^0 + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \quad (2.1)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2(s) \quad (2.2)$$

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O \quad (2.3)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (2.4)$$

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3(s) + H^+ \quad (2.5)$$

$$4Fe(OH)_2 + Cl^- \rightarrow Fe_3^{II}Fe^{III}(OH)_8Cl + e^- \quad (2.6)$$

$$6Fe(OH)_2 + CO_3^{2-} + 2H_2O \rightarrow Fe_4^{II}Fe_2^{III}(OH)_{12}(CO_3 \cdot 2H_2O) + 2e^- \quad (2.7)$$

$$6Fe(OH)_2 + SO_4^{2-} + 2H_2O \rightarrow Fe_4^{II}Fe_2^{III}(OH)_{12}(SO_4 \cdot 2H_2O) + 2e^- \quad (2.8)$$

2.3 ORGANIC SUBSTRATES FOR TREATMENT OF PERCHLORATE CONTAMINATED GOUNDWATER

Biological treatment includes ex-situ bioremediation and in situ bioremediation. Ex situ bioremediation involves pumping contaminated process wastewater or extracted groundwater into an above ground reactor vessel (i.e. bioreactor). Extensive research had been performed to investigate the effectiveness of perchlorate ex situ treatment using organic substrates [52-56]. A full scale bioreactor built at a Superfund site in Rancho Cordova, CA treated influent perchlorate concentration of 2,500 µg/L to less than 4 µg/L with ethanol as the electron donor and carbon source [56]. Careful control of the environmental conditions (such as pH, temperature, oxygen, nutrient sources, etc.) and the hydraulic flow and residency time of the contaminated water supply are necessary to support the growth of the microorganisms. The high capital and maintenance cost limit the application of ex situ bioremediation.

Unlike ex situ treatment, in situ treatment doesn't require pumping the groundwater for aboveground treatment, which will largely reduce the energy cost. Instead of extracting the groundwater out, the organic substrate is brought into the aquifer. The most common methods for adding the organic substrate is to flush it into the contaminated zone using injection wells. Several groups have completed large scale pilot studies of perchlorate bioremediation utilizing organic substrate injection wells [57-61]. In the above studies, the treatment medium was not restricted to contaminated groundwater, but also contaminated soil. Organic substrate can also be added to the permeable reactive barriers (PRBs) for in situ bioremediation. Perchlorate can be

degraded as groundwater flows through it. Organic reactive materials used in PRBs include soybean oil, mulch, compost, woodchips, and the combination of several materials [62].

Although utilizing organic substrates in the full scale studies have proved its feasibility for in situ bioremediation, there are potential challenges to applying this technology. Water quality might be changed along with the addition of organic substrates. Injection of organic substrates will result in strong reducing conditions in the aquifer. The naturally existing metals such as arsenic, iron and manganese can be mobilized at strong reducing conditions. Also, the substrate can be utilized by sulfate reducers to produce hydrogen sulfide, which is not desired because of the odor. Another limitation is the injection of substrate might be affected by the geology and hydrology condition in the contaminated site. The dispersion of the substrate will be slow and difficult in a low permeability subsurface.

CHAPTER III PERCHLORATE BIODEGRADATION IN ZERO-VALENT IRON SYSTEMS

3.1 ZERO-VALENT IRON PERMEABLE BARRIER

As mentioned before, perchlorate can be reduced to chloride in the presence of an electron donor. Hydrogen gas is released when zero-valent iron (ZVI) comes into contact with water. Using zero-valent iron makes the microorganisms naturally attach to the iron surface, allows the direct contact between the microorganism, hydrogen and perchlorate [22]. The advantage of this technology makes it possible to design ZVI bioreactors or ZVI – PRBs for perchlorate bioremediation. The feasibility of this technology has been demonstrated by Yu et al [22, 63] in laboratory batch and column experiments. In the batch studies, 100% perchlorate removal was achieved when treating tap water spiked with 500 μg/L perchlorate with the absence of chlorite and chlorate. Final perchlorate effluent concentrations were lower than the detection limit (4 μg/L). The optimum pH for ZVI-supported perchlorate reducing bacteria was found to be between 7 and 8, which is within the range of most groundwater systems (pH 6-8). Perchlorate reduction rate decreased, in the presence of nitrate.

In the column experiment, complete removal of perchlorate at an influent concentration of 500 μg/L with an effluent concentration below the detection limit was maintained for over sixteen months with over 4000 pore volumes of lab-synthesized solution being treated through the column. The empty bed retention time ranged from 63 hours to as low as 11 minutes.

Demonstration of field ZVI-supported biological reduction of perchlorate was motivated by these laboratory results. The laboratory experiments formed the basis for the design of a pilot-scale demonstration unit. The laboratory column experiments were operated at controlled pH (near neutral), room temperature (23 ± 2°C), and low DO (below 0.2 mg/L). Additionally, the synthesis water used in the laboratory experiment contained various nutrients (trace metals, nitrogen, phosphorus, carbon and buffers, etc.) that the microorganisms could draw upon for optimum growth. Whether similar treatment performance could be achieved in the relatively complex groundwater environment was unknown.

The main objective of this pilot study was to test and demonstrate the efficacy of the ZVI-supported biological reduction of perchlorate in a field application and to obtain pertinent data to guide full-scale design and operation. To achieve these goals, a trailer-mounted pilot demonstration system was designed, built, and mobilized at West Valley Water District (WVWD) Well #2 in Rialto, CA. The U.S. Environmental Protection Agency (EPA) requires all drinking water systems to monitor for total coliforms (including fetal coliforms and E. coli) in distribution systems. The EPA states that no more than 5.0% of samples can test positive for total coliform in a month [64]. Hence, treatment performance was not only evaluated by monitoring perchlorate concentration, but also included coliforms, fecal coliforms and E. *coli*. Challenges experienced in maintaining effective perchlorate treatment were illustrated and possible solutions to solve the problems were implemented.

3.2 MATERIALS AND METHODS

3.2.1 Materials.

All the chemicals used in this study were reagent grade (Fisher Scientific). Cast Iron Aggregate Type 20/30 (corresponding to 0.60-0.84 cm) and 3/5 mesh (corresponding to 4.0-6.7 cm) ZVI (Peerless, Detroit, MI) were used in the field study. Detailed instrumentation and controls are shown in Figure 3.1, while size and various equipment information are reported in Table 3.1. A high-density polyethylene (XLPE) black tank (48"×77") served as the main ZVI bioreactor. Polyethylene (PE) black tanks were used for the surge tank (52"×60") and sand filter tank (24"×54"). A submersible pump (3/4 hp, 20 gpm@42' H) was used to feed the groundwater to the ZVI reactor. Inoculates and chemicals were fed into the reactor by a centrifugal pump. The Schedule 40 and 80 pipes, adapters, unions, flange and flowline level control were purchased from Harrington Industrial Plastics. The pressure (0-250 psi), pH (0-14), ORP (± 2000 mV) and flow (3-200 gpm) sensors were also provided by Harrington Industrial Plastics. The temperature sensor (0-480^{o}C), thermocouple, compression fittings, flow meter, power supply and inlet/outlet valve were ordered from Dwyer Instruments, Inc. The Membrana/Liqui-Cel vacuum/membrane degassing unit was manufactured by Liqui-Cel Membrane Contractors.

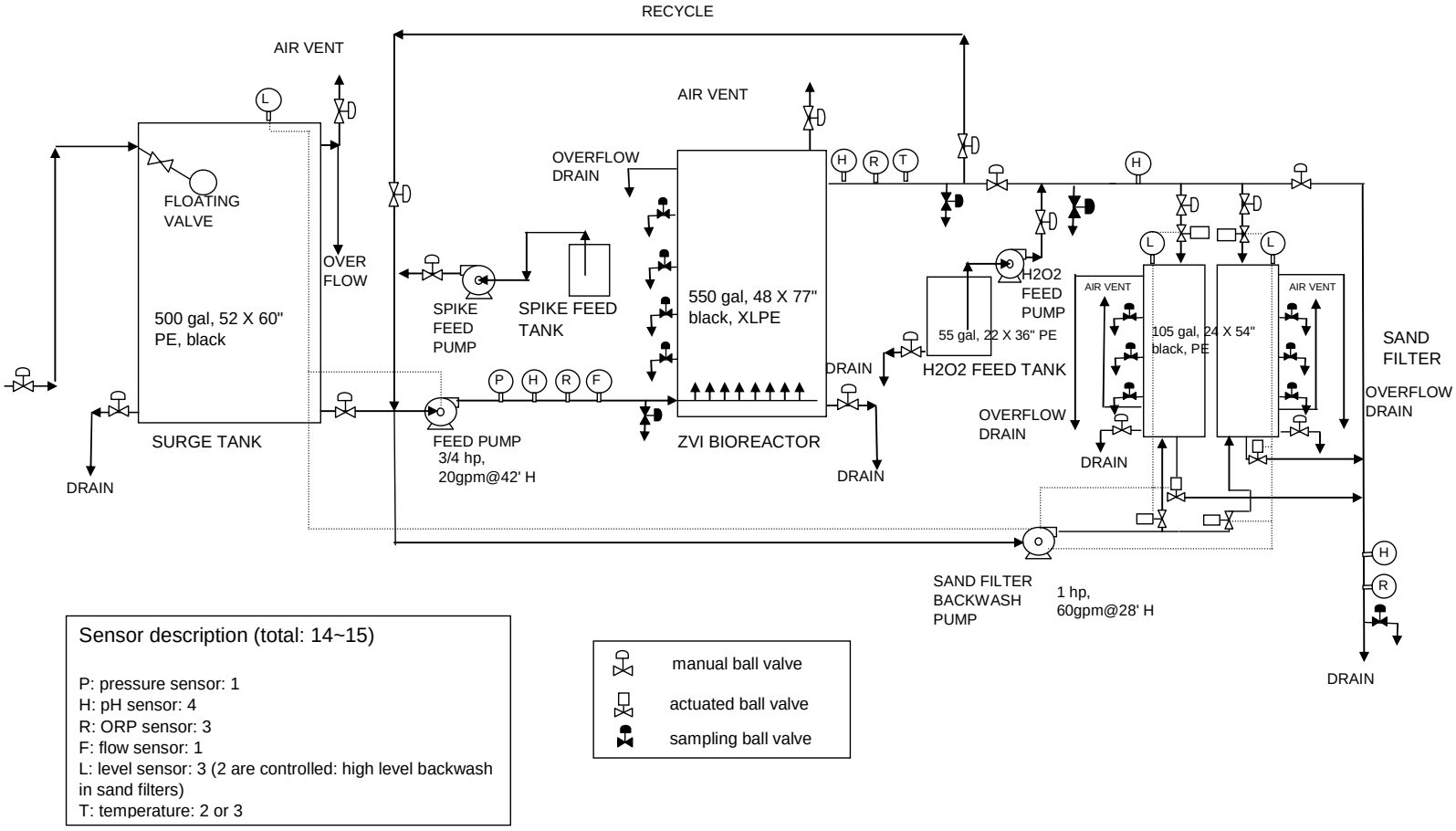


Figure 3.1 Flowsheet and instrumentation of the demonstration system (not to scale).

Table 3.1 ZVI bioreactor construction details

Parameter	Value	Comments
ZVI bed diameter × height	48” ID × 38” height	
ZVI bed volume	300 gallons	
ZVI type and source	Cast Iron Aggregate Type 3/5 ZVI (Peerless)	
ZVI mass	Approx. 4400 lbs. (2000 kg)	The density of (solid) iron is approximately 7000 kg/m^3
ZVI bed porosity (initial)	75%	Iron shavings of irregular form, many thin curly strips resulted in surprisingly high porosity
Sand filters	100 gallons each	Two filters operating in parallel. Gravity feed
Water feed tank volume	500 gallons	
Water flow (nominal)	20 gpm for EBRT of 15 min	Maximum flow tested was 4 gpm
Pre-treatment to remove part of dissolved oxygen	1) Initially, custom built ZVI fluidized bed in water feed tank 2) Membrane degasser rated 20 gpm	

3.2.2 Field Bioreactor Demonstration.

Water quality data for the groundwater obtained from Well No. 2 are shown in Table 3.2. The site groundwater contained 74 μg/L of perchlorate, 26 mg/L of nitrate and 230 mg/L of bicarbonate. The pH was 7.8, which is favorable for perchlorate biodegradation. However, the deep well and the specific hydro-geological conditions resulted in the water being oversaturated with dissolved oxygen. The high DO in the influent was of concern due to 1) the possibility of gas pockets forming within the ZVI bed due to oversaturated conditions, 2) high redox conditions detrimental to biological reduction of perchlorate, and 3) increased iron corrosion rates resulting in decreased hydraulic conductivity.

Table 3.2 Historical average groundwater data

Water Quality Parameters	Mean
Perchlorate (μg/L)	74
Nitrate (mg/L)	26
Chloride (mg/L)	13
Sulfate (mg/L)	12
Carbonate/Bicarbonate (mg/L)	<3/230
pH	7.8
Total Dissolved Solids (mg/L)	260
Specific Conductance (Ms/cm)	445
Volatile Organics (μg/L)	ND

The flow sheet of the pilot reactor is shown in Figure 3.2. Figure 3.3 is a picture of the system installed at the site.

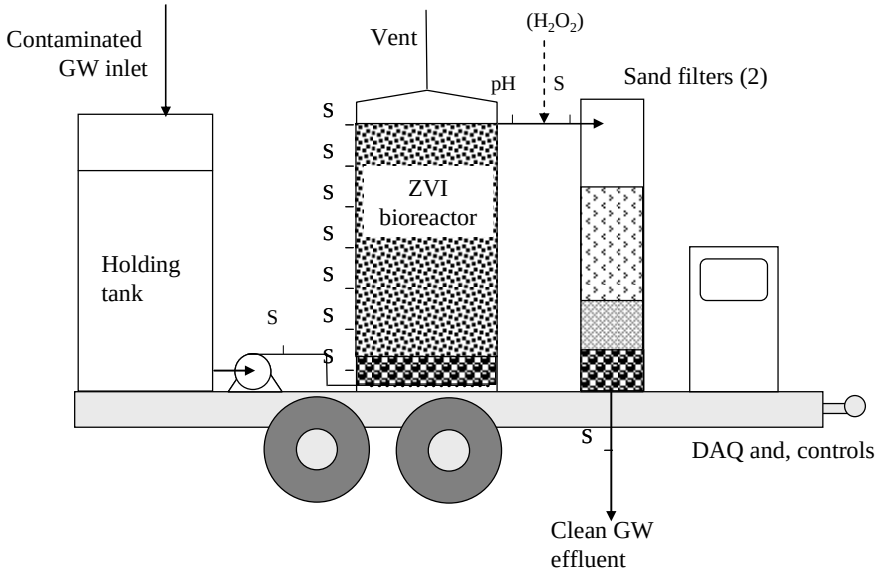


Figure 3.2 Schematic of the trailer mounted pilot demonstration system (not to scale, controls not shown). S = sampling port. Homogeneous distribution of the water at the bottom of the bioreactor is achieved via a network of perforated pipes. Backflush for the sand filters not shown. As mentioned in the text, the holding tank was switched to the pre-treatment of the contaminated water to remove dissolved oxygen.

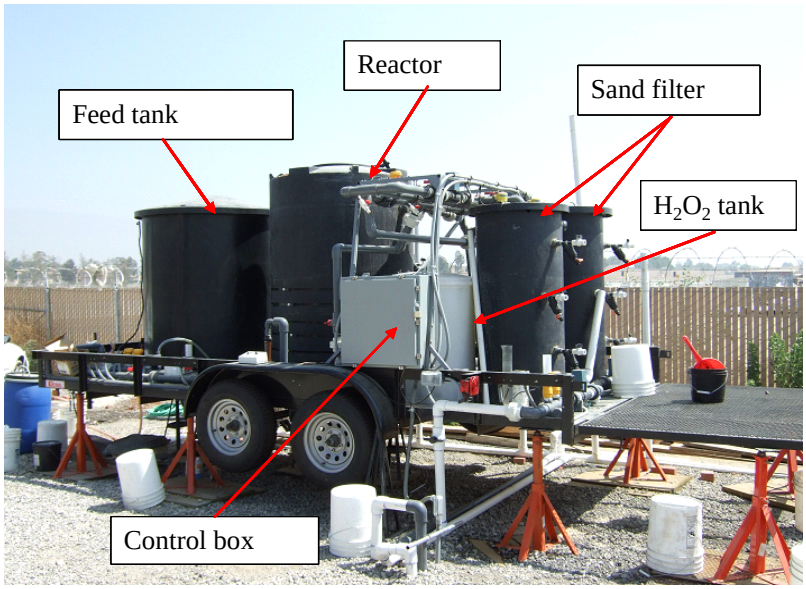


Figure 3.3 Picture of the demonstration system at the Rialto well #2 site. Membrane degassing pre-treatment not shown.

Three processes were involved in the pilot system: deoxygenating (to address the high DO conditions), perchlorate bioreduction, and particulate/solid removal.

Deoxygenation. Dissolved oxygen will compete for the electron donor with perchlorate and accelerate the corrosion of iron. The purpose of deoxygenation was to minimize the above effects by removing dissolved oxygen before it entered the ZVI bioreactor. Oxygen reduction was promoted by using ZVI to remove the dissolved oxygen from the influent. Initially, coarse ZVI (3/5 mesh) was used and the holding tank served as a fluidized bed reactor for dissolved oxygen removal. By this treatment, dissolved oxygen in the influent ranging from 6–13 mg/L was reduced to less than 2 mg/L in the effluent which was then fed into the ZVI-packed bed bioreactor After 20 days of operation, the coarse ZVI (3/5 mesh) was replaced with one of smaller size (20/30 mesh). Since the smaller ZVI has larger surface area than the coarse ZVI has,

compared with the coarse ZVI, the smaller size ZVI was able to remove more dissolved oxygen in the same time frame, and also, it can be fluidized at lower flow rates rather than settle down at the bottom of the tank.

To calculate the amount of fresh ZVI (20/30 mesh) needed to maintain the dissolved oxygen level below 2 mg/L, the following values were applied: 6 mg/L of initial dissolved oxygen concentration, 2 mg/L of target DO concentration after deoxygenation pretreatment, 1.5 mg Fe/kg Fe/hr of iron corrosion rate. To calculate the iron corrosion rate, an experiment was conducted by measuring the DO removal rate in water in a closed vessel fitted with a DO probe and 120 g type 20/30 ZVI. The test lasted for 8 hours and an iron corrosion rate of 1.5 mg Fe/kg Fe/hr was determined. Therefore, if the reactor operated at the flow rate of 20 gpm, 5.5 kg of ZVI was added per day. The frequency of fresh ZVI addition was determined by the dissolved oxygen level in the holding tank effluent. About 6 kg of ZVI were taken out from the fluidized bed reactor every 3-4 days and replaced by the fresh 20/30 mesh ones. Unfortunately, the effluent of the holding tank clogged the bioreactor due to the formation of fine iron oxide particles. In addition, the ZVI pretreatment could not sufficiently remove the dissolved oxygen at a high flow rate. Therefore, after 150 days of operation with ZVI as a pretreatment for dissolved oxygen removal, a Membrana/Liqui-Cel vacuum/membrane degassing unit, which consisted of two membrane modules, was installed to replace the fluidized bed tank. The maximum flow rate was 10 gpm for each module. The degassing unit has variable flow possibilities by connecting the two membrane modules in series (low flow rate) or in parallel (high flow rate). Also, the degassing unit was

easy to operate and maintain. The pretreatment reactor then served as a feed tank to store the groundwater influent.

Perchlorate reduction. The 500 gallon tank (48" ID × 77" height) was first packed with 12 inch height gravel from the bottom and followed by about 2 tons of ZVI (3/5 mesh, Peerless). The purpose of the gravel was to prevent clogging in the entrance port and to distribute the flow as well. The total bed height was 50 inches, and the bed volume was 300 gallons. Four side sampling ports were installed every 12-inches around the reactor bed. The system equipped with an on-line monitor system to record ORP, pH and temperature.

To initially seed the reactor with perchlorate-degrading organisms, soil obtained from a rapid infiltration tertiary wastewater treatment plant (Colton CA) was mixed with water in a 55-gallon drum and allowed to settle down. The supernatant was then fed to the ZVI bioreactor. The presence of perchlorate degrading bacteria in this site soil had been tested in the laboratory column experiment prior the field study, and the column was successfully seeded as the same manner as conducted in the field. To establish the amount of perchlorate biodegrades and also to let them easy to adapt to the environment, the reactor was started at a relatively low influent flow rate of 2 gpm, which corresponding to an empty bed retention time of 150 min. The contaminated groundwater from the holding tank was pumped through the ZVI bed in an upward direction, after which it flowed by gravity to the sand filters. In the first week, since perchlorate degradation was not initiated, extra (bi)carbonate was fed to the system to enhance removal efficiency at the start-up period. Influent and effluent samples were

taken on a periodically basis for dissolved oxygen, pH, ferrous/ferric iron, nitrate, and perchlorate analysis. Effluent coliforms, fecal coliforms and E. *coli* were measured periodically in effluent samples. To determine the trends of perchlorate and nitrate along with the depth of the reactor, perchlorate and nitrate concentrations were measured for the samples taken from the side sampling ports at selected times.

Hydrogen peroxide can be added as needed to the reactor effluent and prior to sand filtration to oxidize any dissolved Fe^{2+} (in practice, hydrogen peroxide feed was never turned on as it was not needed).

Particulate/Solid removal. The purpose of the sand filter was to remove the particulates formed during the perchlorate treatment process. The treated water from the ZVI bioreactor entered the sand filter to remove the solids and then drained to the catch basin by gravity.

3.3 ANALYSIS

Perchlorate concentration was analyzed using a Dionex 1000 Ion Chromatograph (Dionex Corp.; Sunnyvale, CA, USA) with an IonPac® AS 16 analytical column (4×250 mm) and AG 16 guard column (4×50 mm). Nitrate was determined by an IonPac® AS 14 analytical column (4×250 mm) and AG 14 guard column (4×50 mm). The detection limits for perchlorate and nitrate were 4 µg/L and 100 µg/L (as N), respectively. Soluble ferrous iron and total iron were determined by 1, 10-Phenanthroline colorimetric method at 510 nm wavelength. The detection limits for Ferrous and total iron were 0.05 mg/L. Soluble ferric iron concentration was calculated by subtracting

ferrous iron concentration from total iron. Coliforms, fecal coliforms and *E. coli* were tested by E.S. Babcock & Sons (ESB) California Environmental Testing Laboratory.

3.4 RESULTS AND DISCUSSION

3.4.1 Overall Performance of ZVI Field Bioreactor.

The performance of the bioreactor for degrading perchlorate is shown in Figure 3.4. Initial flow rate at the start of the experiment was equal to 2 gpm, which corresponded to 3.5×10^{-4} ft/s velocity and 150 min empty bed residence time (EBRT). During the first week, there was no noticeable removal of perchlorate. Therefore, 120 mg/L of sodium bicarbonate ($NaHCO_3$) and perchlorate degraders were reseeded into the reactor to promote removal. After that 95% perchlorate removal was achieved rapidly on day 13, and the perchlorate effluent concentrations were below the detection limit of 4 µg/L. $NaHCO_3$ was reduced to 60 mg/L at day 20 after perchlorate removal was stabilized at 90 % for a week, and then no more $NaHCO_3$ was added after day 29. After the reactor performed at a steady state for 31 days, the flow rate was increased to 3 gpm (EBRT = 100 min) on day 51. Complete perchlorate removal was maintained for 35 days and then on day 86 the flow rate was increased to 4 gpm (EBRT = 75 min). When the flow rate was increased to 4 gpm, an increase in the perchlorate effluent concentration was observed and removal efficiency kept declining. Perchlorate concentration in the effluent stayed between 6 µg/L and 24 µg/L until day 150, corresponding to a removal of 60-70%. After day 150, the perchlorate effluent concentration gradually increased until reaching close to the influent level, where only 10% removal efficiency can be achieved. A similar degradation trend was also seen for nitrate (Figure 3.5). Despite a three-order

magnitude higher concentration, nitrate was degraded completely until day 112, which was one month longer than 100% perchlorate removal. The bioreactor still achieved about 35% nitrate removal at the end of the study (Day 254). Nitrate competed with perchlorate for the electron donor and its degradation occurred earlier than perchlorate. Hence, when nitrate concentration in the effluent reached breakthrough, poor removal would be expected for perchlorate.

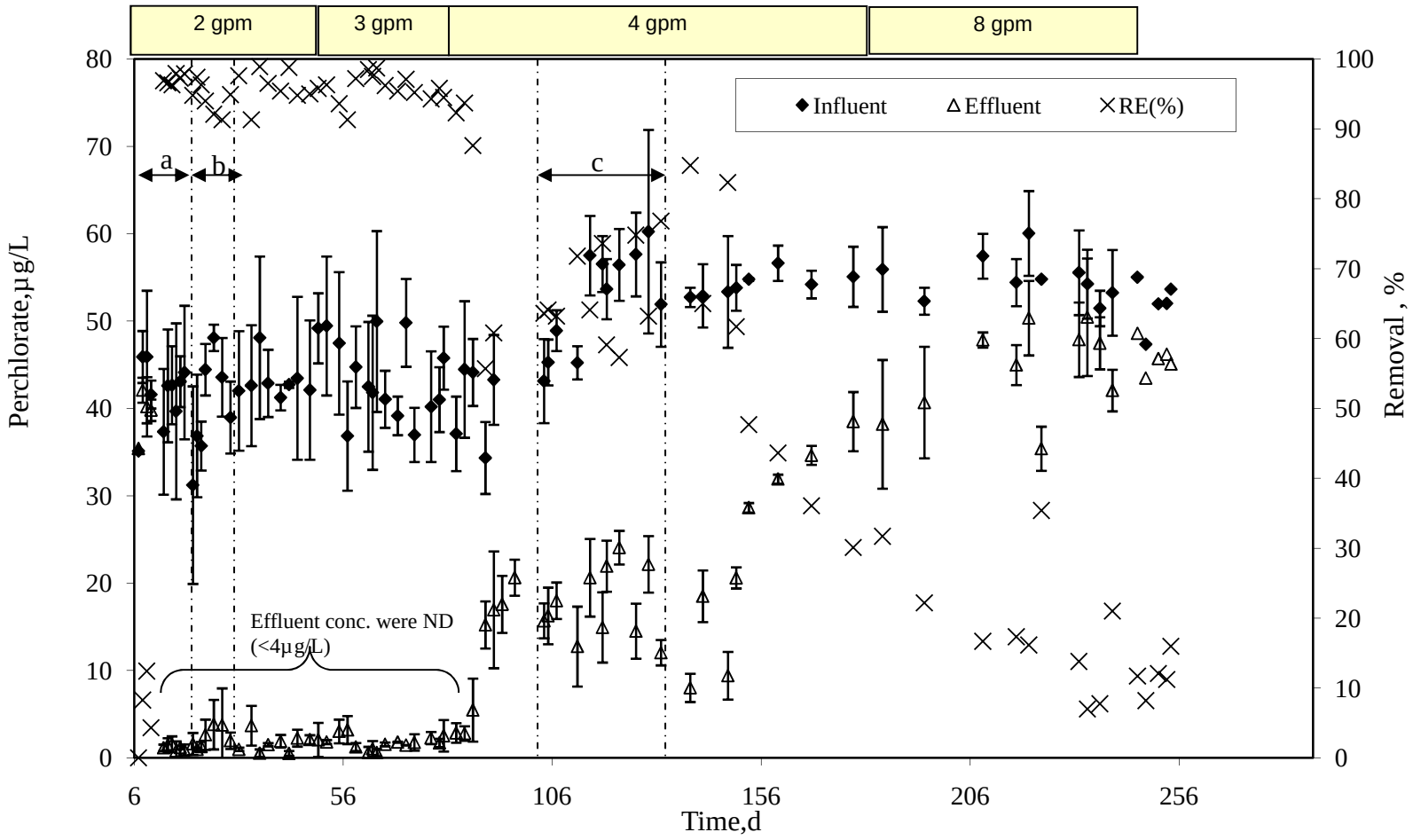


Figure 3.4 Perchlorate inlet and outlet concentrations over entire study.
Addition of $NaHCO_3$: (a) Day 6 – Day 20: 120 mg/L; (b) Day 20 – Day 29: 60 mg/L; (c) Day 101 – Day 132: 60 mg/L

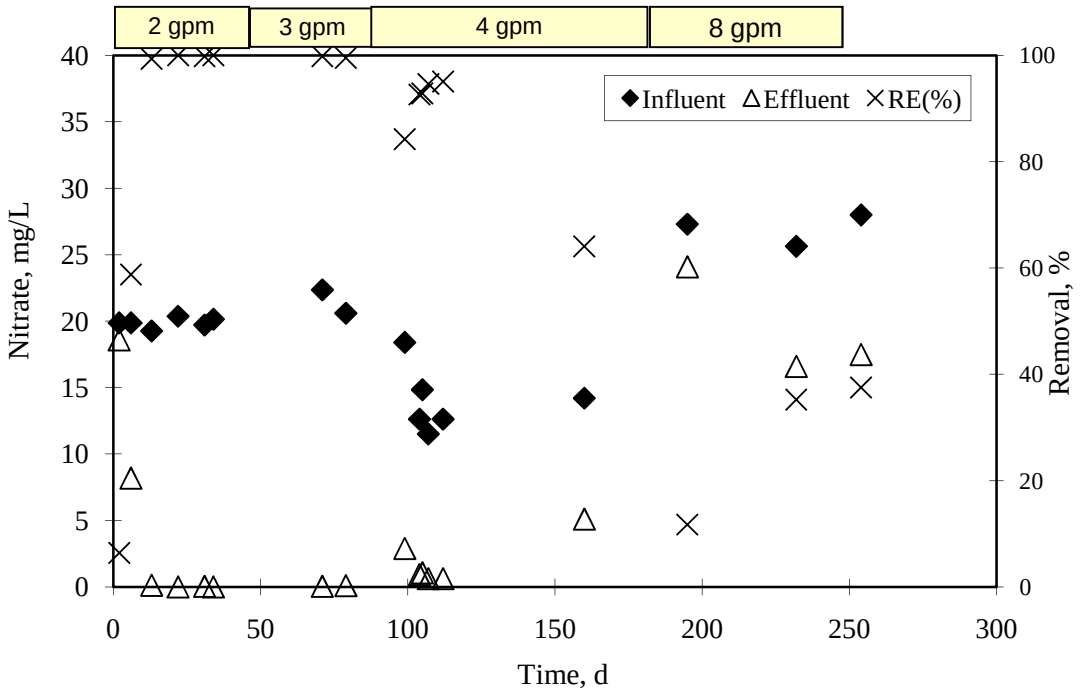


Figure 3.5 Nitrate removal over the duration of the field demonstration.

To determine where degradation happened, measurements of perchlorate and nitrate concentration profiles along the reactor height were conducted on selected days, and the results are shown in Figure 3.6 and 3.7, respectively.

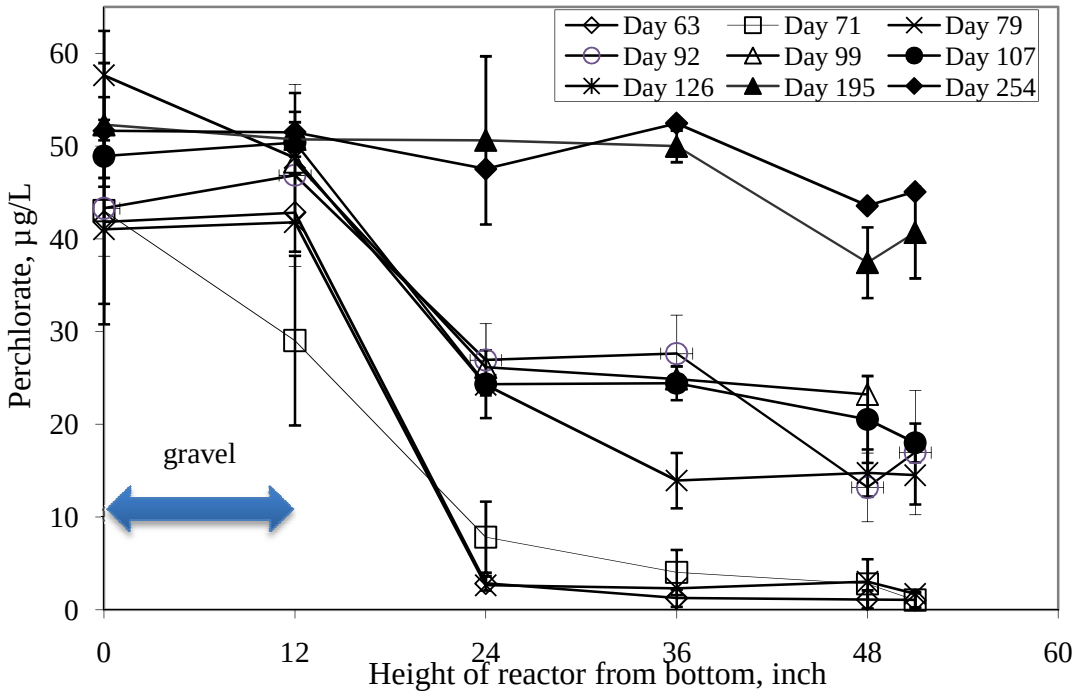


Figure 3.6 Perchlorate concentration profiles in the ZVI bioreactor at selected dates.(Flow rates: 2 gpm from Day 0 to Day 50; 3 gpm from Day 51 to Day 84; 4 gpm from Day 86 to Day194; 8 gpm from Day 195 to Day 256)

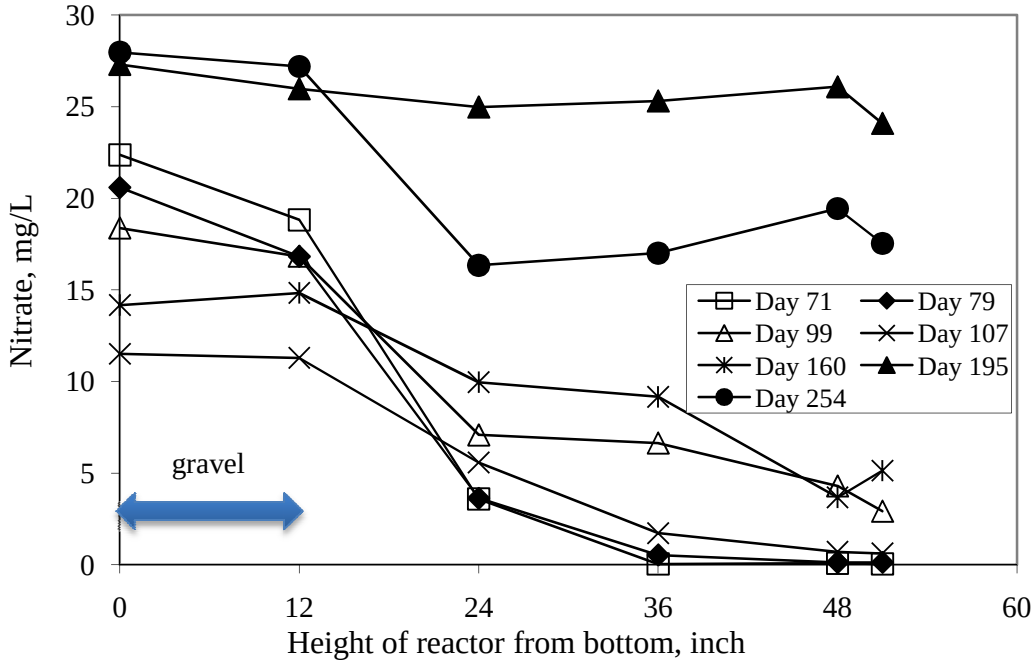


Figure 3.7 Nitrate concentration profiles in the ZVI bioreactor at selected dates.

Reduction of perchlorate and nitrate followed the same trend over time and also along the flow direction (reactor height). It is not a surprise that perchlorate or nitrate were not reduced in the first 12 inch of the reactor from the bottom since this layer contained gravel for the purpose of providing homogenous water distribution. After the bottom gravel section, both perchlorate and nitrate was removed at a very high local degradation rates. The concentration profiles were a reflection of the reactor treatment performance. Perchlorate and nitrate concentrations at each of the side sampling ports increased with operation time. Although some researchers reported that nitrate will inhibit perchlorate degradation [65, 66], it is not shown in this study. The effects of nitrate on perchlorate reduction should be related to the type of the bacteria, nitrate and perchlorate concentration, biomass and electron donor amounts, etc.

System performance was expressed as perchlorate elimination capacity (EC) as in Equation 3.1, where C_{in} and C_{out} are the influent and effluent perchlorate concentrations, respectively, Q is the influent flow rate and V the volume of the ZVI bed volume. EC represents the amount of pollutant degraded per unit of reactor bed volume per unit time; it is often reported as a function of the pollutant loading L (Equation 3.2) [63].

$$EC = \frac{(C_{in} - C_{out})Q}{V} \qquad \text{(Equation 3.1)}$$

$$L = \frac{C_{in}Q}{V} \qquad \text{(Equation 3.2)}$$

The maximum perchlorate elimination capacity (EC) was found to be 0.034 $g/m^3/h$ (Figure 3.8). This number is two orders of magnitude lower than the published reports on perchlorate removal rates in flow through systems using H_2 gas as the electron donor [67-69]. However, in those studies, the experiment was conducted in a well-controlled laboratory environment with several advantages. The reactor was seeded multiple times to ensure high biomass content. Nutrients containing trace metals, carbons, nitrogen and phosphorus, etc. were provided to support the bacteria growth. The reactor was backwashed occasionally to prevent biofouling. It is reasonable to achieve a relatively higher EC under optimum conditions.

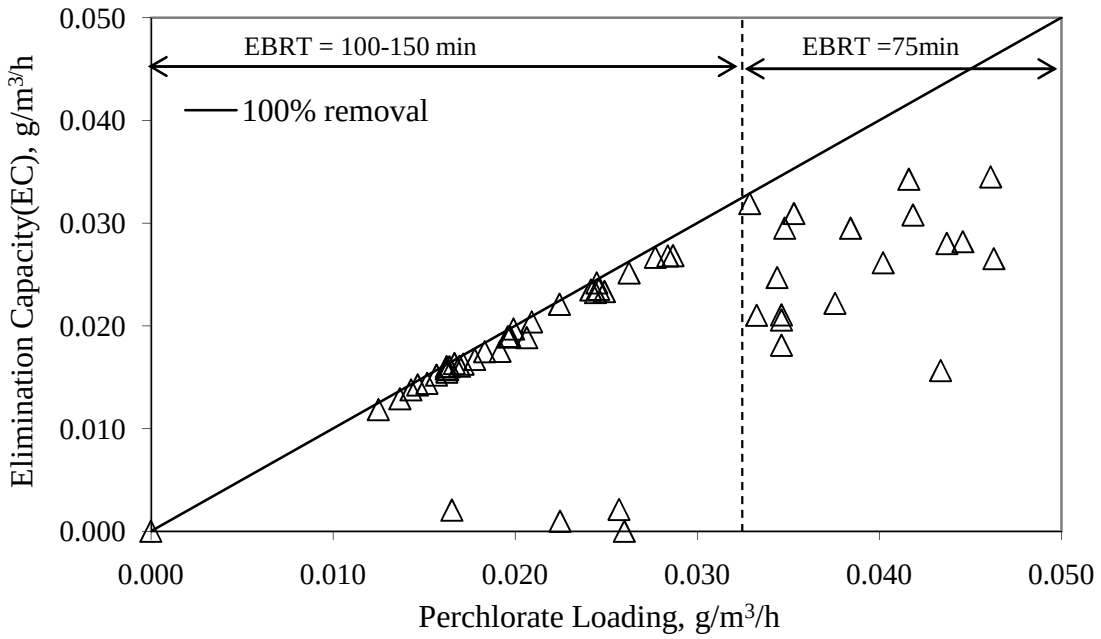


Figure 3.8 Perchlorate elimination capacity as a function of perchlorate loading. Flow rate = 2 – 4 gpm, influent ClO_4^- = 40 to 60 µg/L.

Iron species in the effluents of the reactor and sand filter are shown in Figure 3.9. The soluble Fe^{3+} concentration in the reactor effluent declined from 1.8 mg/L to less than

0.1 mg/L over 60 days. At the same time, the soluble Fe^{2+} concentration in the reactor effluent remained constant at 0.2 mg/L. Fe^{2+} and Fe^{3+} were not detected in the sand filter effluents, which indicated the sand filter was very efficient at removing iron. The iron data can be used to determine the fate of iron (soluble or insoluble) by establishing a mass balance between total corroded iron and total iron output.

Assuming the average total effluent concentration of iron is 1.0 mg/L, water flow rate of 2 gpm, the estimated effluent total iron mass flow is 10.9 g/d. If all the corroded iron is in soluble form, then the total iron in the effluent should match the value of iron corroded. To calculate the iron corrosion rate, an experiment was conducted as the same procedure as described in Section 3.2.2, except using type 3/5 ZVI. The test lasted for 4 hours and an iron corrosion rate of 233.3 mg Fe/kg Fe/d (4.2 mmol Fe/kg Fe/d) was determined. This calculation was made under the assumption that the effective corrosion weight of the ZVI is the total ZVI amount in the vessel, which is not accurate. The passivation of ZVI prevents further oxidation if the iron surface is covered by the iron corrosion products. At this corrosion rate and with the total ZVI weight of 2000 kg in the reactor, about 466.6 g iron should be released from the reactor every day. Unfortunately, only 2.3% was found in the effluent. Therefore, the majority of iron in the system was in insoluble forms and was not flushed out with the effluent. Because the insoluble iron stayed in the systems, the iron corrosion products occupied the pore space and plugged the reactor, even more, hydrogen production would be limited.

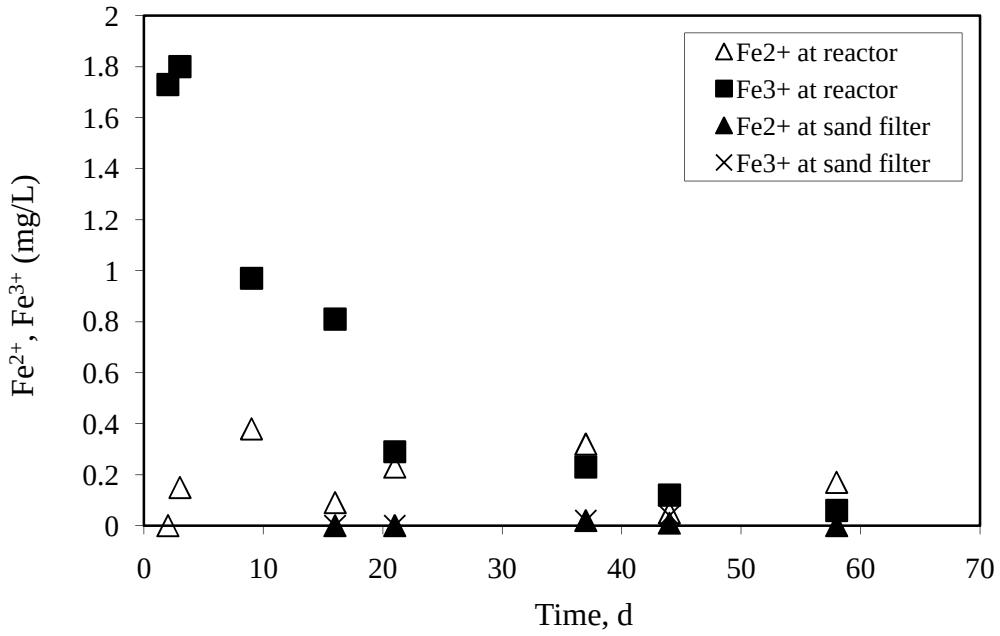


Figure 3.9 Iron species in the effluents of the reactor and sand filters.

Evolution of the alkalinity consumed over time in the ZVI bioreactor on selected dates is reported in Figure 3.10. The carbonate in the system served as a carbon source for the autotrophic bacteria's cell growth. However, an unavoidable situation was the reaction of carbonate with iron to form precipitates. There were no alkalinity measurements taken during the first 28 days. $NaHCO_3$ was fed into the ZVI bioreactor daily from Day 6 to Day 29, which resulted in the high consumption of alkalinity at the first measurement. After day 30, consumption of alkalinity followed a decreasing trend over time, which is reasonable because after a high amount of carbonate being consumed in the system, the iron surface must be occupied by lots of iron corrosion products. Alkalinity consumption was reduced with the diminishing of active iron surface. The alkalinity concentration profiles in the ZVI bioreactor at day 71 and day 162 are shown in Figure 3.11. There was very little or no alkalinity consumption in the first 12 inch, which

was packed with gravel. Alkalinity decreased along the direction of flow. Note that the alkalinity profile of day 162 was obtained well after significant performance problems were observed with the bioreactor, but that the profile was essentially identical to the trend observed while the bioreactor was performing well. This indicates that the main process for alkalinity uptake is probably abiotic. The details of the carbonate effect on the formation of iron precipitates and the hydraulic condition of ZVI bioreactor will be further discussed in Chapter IV.

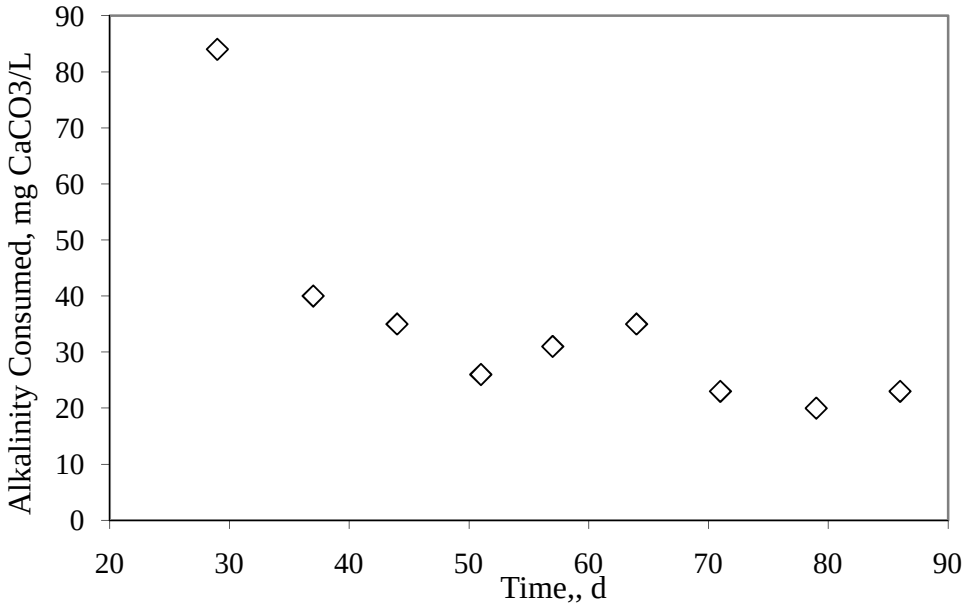


Figure 3.10 Evolution of the alkalinity consumed over time in the ZVI bioreactor at selected dates.

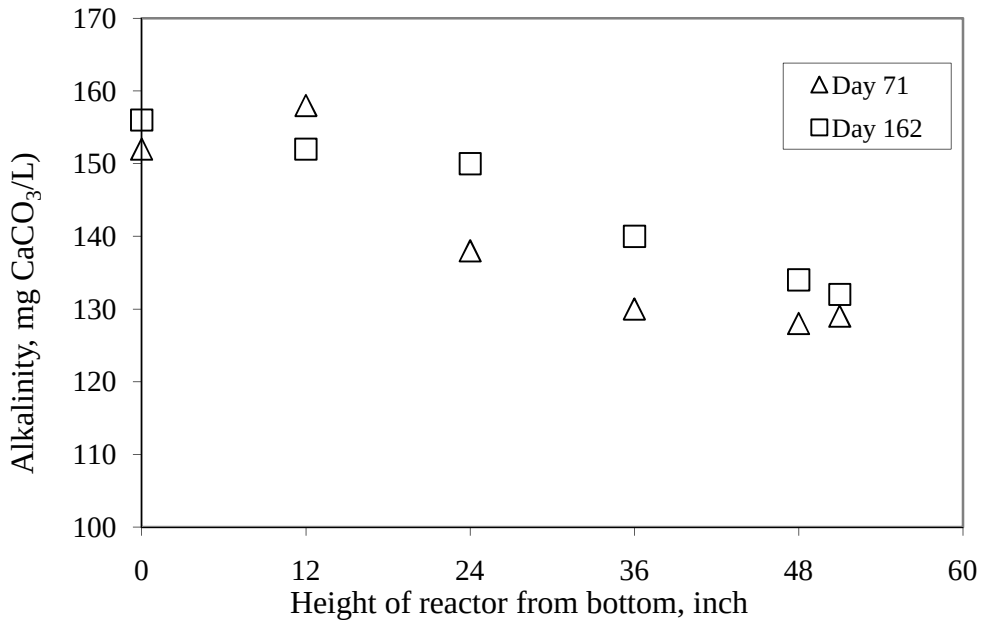


Figure 3.11 Alkalinity concentration profiles in the ZVI bioreactor at selected days. Note that the first 30 cm are packed with gravel for proper liquid distribution.

Sampling of coliforms, fecal coliforms and E. coli from the bioreactor effluent and the effluent of the sand filters indicated that the bacterial counts were below the detection limit of 2 MPN/100mL.

Dissolved oxygen data are reported in Figure 3.12. Although DO concentration in groundwater was not monitored during the entire operation period, the 150-day data illustrated the average DO in the groundwater was 10.8 ± 1.5 mg/L. The groundwater was clearly oversaturated with oxygen. The influent DO was reduced to as low as 1 mg/L with ZVI pre-treatment, but most of the time it stayed above 2 mg/L. The high variability of the DO in the influent was due to the frequency of adding fresh ZVI and removing used ZVI in the pre-treatment system. Even with the high influent DO, the DO in the effluent was always below 1 mg/L. After installing the membrane degasser on Day

150, the low influent DO (lower than 2 mg/L) was consistently maintained for the rest of the experiment. The unexpected high DO noticed in both influent and effluent in the last few days of experiment was caused by membrane fouling. The membrane condition could be resumed by acid washing (usually nitric acid).

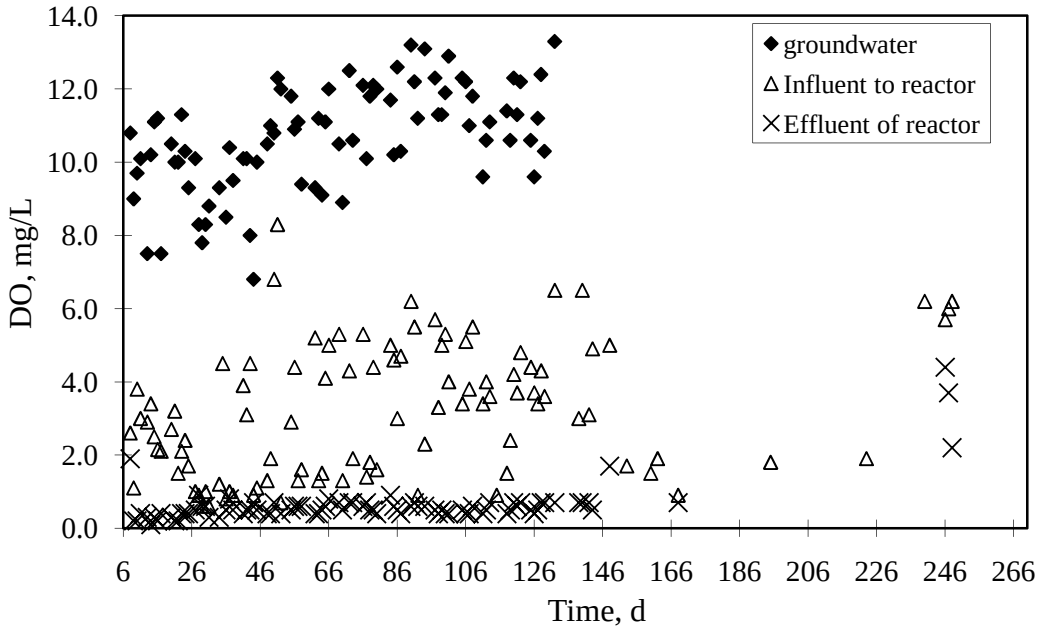


Figure 3.12 Evolution of the dissolved oxygen. On day 150, the degassing membrane module was installed on the influent feed.

As can be seen in Figure 3.13, the pH of the effluent was between 6.9 and 7.9, which was about 0.2 to 0.3 units higher than the pH of the influent. This is what was expected because OH^- was produced during the iron corrosion process. Although most of the hydroxide was precipitated with ferrous or ferric iron, some portion was released to the water and lead to an increased pH in the effluent [38].

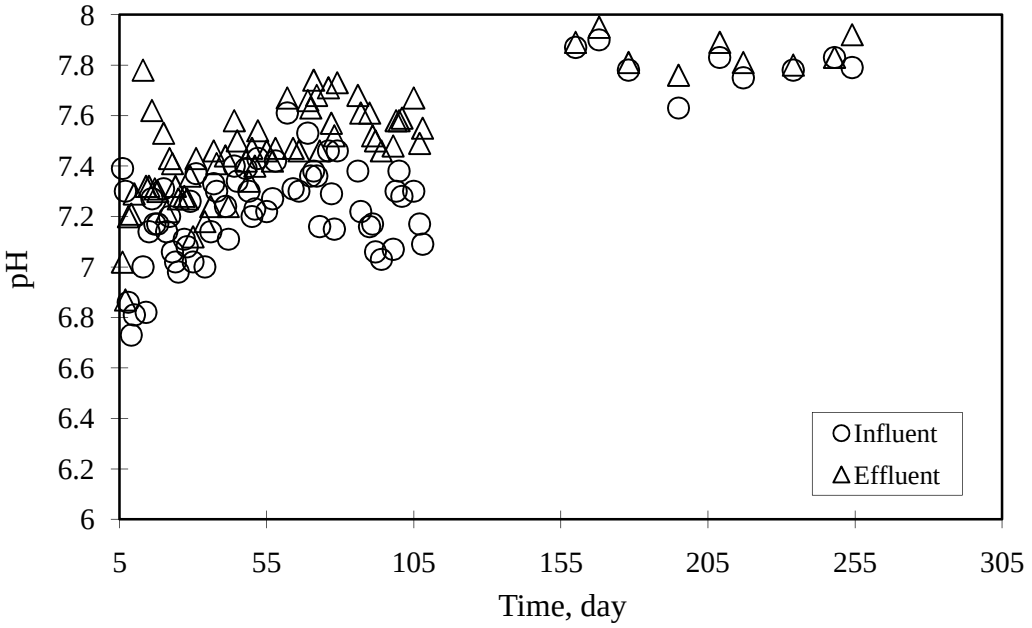


Figure 3.13 pH change in both the influent and effluent over time.

3.4.2 Attempts to Troubleshoot the Reactor Problems.

The poor performance of perchlorate reduction was totally unexpected as a laboratory scale treatment system ran for more than 3 months without a problem, even with a retention time as low as 11 minutes. Thus, three hypotheses were formulated in an attempt to explore the reason of losing treatment performance. Various attempts were made to recover the system, but all failed and full treatment capacity was never recovered. The hypotheses tested were:

Hypothesis 1: The microorganisms in the reactor were insufficient.

The reactor was re-inoculated on Day 110, but this had no effect on perchlorate removal. Then during Day 101-132, in case the growth of bacteria was carbon and phosphate limited, 60 mg/L of sodium bicarbonate, 1 mg/L of ammonium phosphate, and 2.5 mg/L lactate were added into the reactor on Day 101-132, Day 105-111, and Day

121-127, respectively. The addition of sodium bicarbonate was expected to promote bacteria growth, but as will be discussed in Chapter IV, bicarbonate will promote the formation of green rusts and cause severe clogging problems. Hence the addition of bicarbonate may be more harmful than beneficial.

Acetate and lactate have been proven to be very effective as an organic carbon source and electron donor for perchlorate removal. In the parallel experiment conducted in the laboratory, 100% removal can be observed within two days with an initial perchlorate concentration of 500 µg/L. Thus, 2.5 mg/L lactate was fed into the reactor for 6 days. Unfortunately, there was no improvement in treatment performance during or after lactate feeding was stopped. The same result was found after adding ammonium phosphate. Perchlorate removal performance never recovered.

Hypothesis 2: ZVI reactivity was severely reduced resulting in little or no hydrogen was produced.

To address this assumption, ZVI samples were taken from the several inches below the top of reactor to the laboratory to determine the availability of microorganisms and hydrogen. A batch experiment was conducted for this test. First 20 g used ZVI from the field reactor was put in the flask, and filled with 200 mL of 500 µg/L perchlorate solution. The headspace was flushed with nitrogen to maintain an anaerobic condition, and a sample was taken every 2 hours for perchlorate analysis. The results are shown in Figure 3.14.

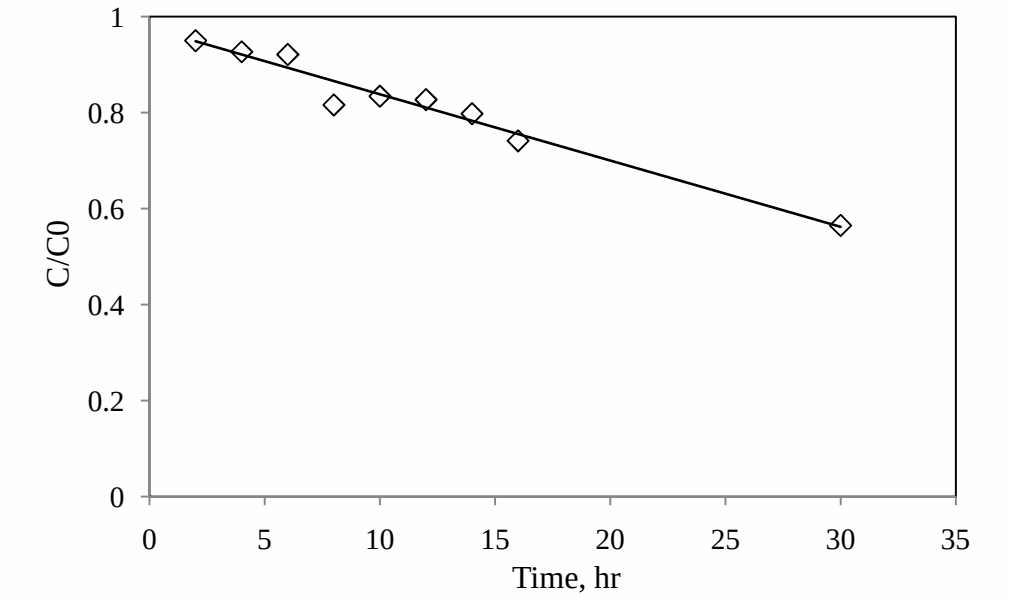


Figure 3.14 Batch experiment result of perchlorate degradation using ZVI from field bioreactor.

A removal elimination capacity of 1.5 µg/kg ZVI/min for the used ZVI was determined by Equation 3.3. At a flow rate of 4 gpm and perchlorate influent concentration of 55 µg/L, the perchlorate loading was 49.96 mg per hour. Theoretically the total amount of perchlorate that can be degraded is 198 mg/h with the calculated EC value (Table 3.3).

$$Elimination\ Capacity\ \left(\frac{\mu g}{kg\ ZVI \cdot \min}\right) = \frac{C_0 \times (1 - |slope|) \times volume}{Mass\ of\ ZVI}$$

(Equation 3.3)

Table 3.3 Theoretical calculation of the possibility of degrading perchlorate

Flow Rate (gpm)	Perchlorate Loading (mg/h)	ZVI Elimination Capacity (µg/kg/min) (Equation 3.3)	Perchlorate can be degraded (mg/h)
4	49.96	**1.5**	198

*All the calculations are based on ZVI mass = 2200 kg, perchlorate influent conc. = 55µg/L.

Taking into consideration that the field reactor was maintained as an open system, if the hydrogen was produced at a much higher rate than it could be consumed, the excess hydrogen would not stay in the reactor like the batch study, which allows a much longer contact time between the bacteria and hydrogen. The batch test also proved the presence of perchlorate degrading bacteria, but since the density of perchlorate reducing bacteria was not determined, the biological limitation cannot be eliminated.

Hypothesis 3: Hydraulic loss.

Another possible reason for performance declination was the permeability and porosity loss in the reactor. Pressure change in the ZVI bioreactor is reported in Figure 3.15. There was no pressure drop until Day 77 and then it increased to 2 psi until Day 125. After that it rapidly increased to 5-6 psi. This indicated a decrease in the permeability of the ZVI bioreactor. The result of pressure change is in good agreement with the perchlorate treatment performance. The perchlorate removal efficiency started to decrease gradually after the pressure increased. A tracer test using green food color was performed and the absorbance of the effluent was monitored on Day 145 when the reactor operated at a flow rate of 4 gpm. The result is shown in Figure 3.16. By integrating the results, a 41 min (arrow in Figure 3.17) average residence time was determined. As compared to the 60 min theoretical value, the 31.7% drop in residence time can be attributed to the permeability and porosity loss.

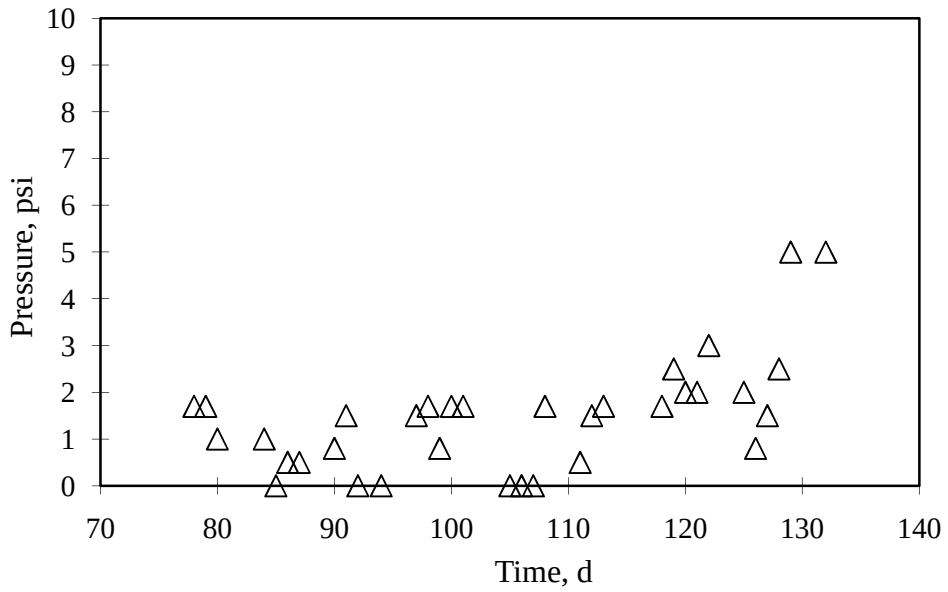


Figure 3.15 Pressure change in the ZVI bioreactor over time.

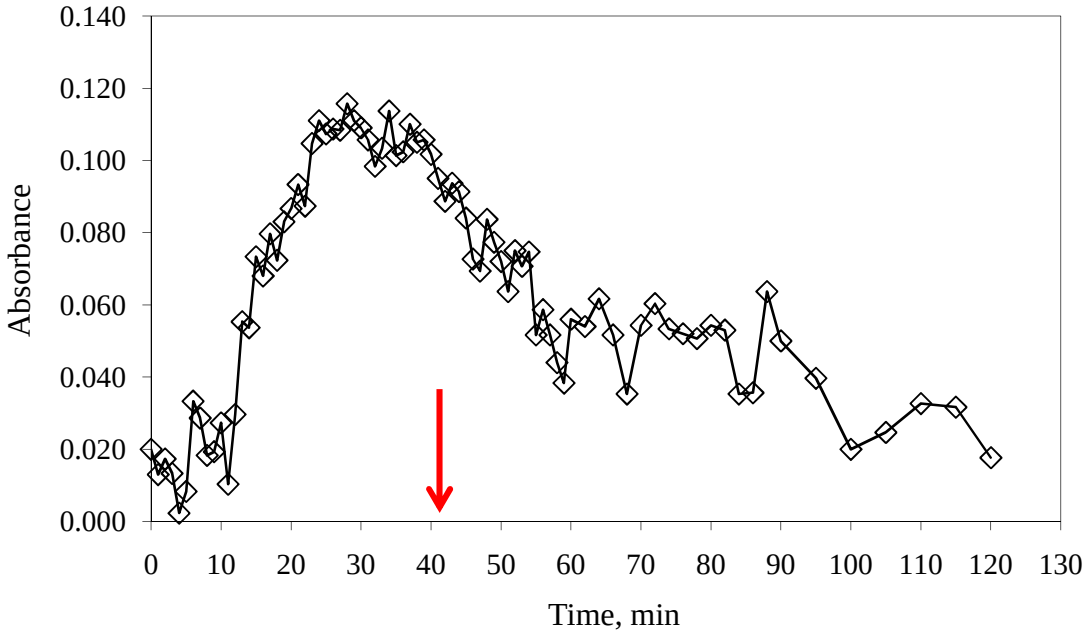


Figure 3.16 Tracer residence time distribution in the ZVI bioreactor on day 145.

After stopping the reactor, the used ZVI was taken out from the core of the reactor for visual observation. The work required using shovels because the ZVI was fused together like a rock. Comparing with the fresh ZVI (Figure 3.17 left) which has a brown color and loose particles, after a 6-month operation the ZVI was converted to concrete solid with orange color and a compact mass of iron and iron corrosion products (Figure 3.17 right). Apparently the used ZVI has a low permeability to let water pass through (Figure 3.18), which led to preferential flow.

Figure 3.17 Pictures of fresh ZVI (left) and large blocks of ZVI (right) taken out of the reactor when it was dismantled showing the solid structure of the ZVI bed.

Figure 3.18 Close views of ZVI taken out of the reactor when it was dismantled showing the heavy deposits of iron corrosion products and quasi total loss of porosity.

3.5 SUMMARY OF THE FINDINGS

In this chapter, a field demonstration of perchlorate treatment using a zero-valent iron packing bed bioreactor was described. The following results can be concluded from this study:

- Excellent reduction of perchlorate was observed for three months with the empty bed retention time of 100 to 150 minutes.
- During the first three months, nitrate, perchlorate and coliforms, fecal coliforms and E. *coli* in the reactor effluent were all below the detection limit.
- After three months of operation, reduction of perchlorate was completely lost, while nitrate was partially degraded.

- Both ferrous and ferric iron were detected in the effluent, but compared to the amount of zero-valent iron reacted, the mass in the effluent is minimal. It is more likely the majority of iron was oxidized to insoluble form.
- Treatment performance was never recovered even with multiple attempts to restore the system. The failure was attributed to the significant loss of hydraulic conductivity.

CHAPTER IV LABORATORY EVALUATION OF POROSITY DECREASE AND CORROSION PRODUCTS FORMATION IN THE ZERO-VALENT IRON REACTOR

4.1 INTRODUCTION

Permeable reactive barrier (PRB) technology has been accepted as an effective strategy for remediating chlorinated organics, heavy metals and radionuclides from groundwater [70-74]. Recently, zero-valent iron (ZVI) has been selected as a reactive medium for PRBs due to its non-toxic, cost saving and readily available characteristics. Several pathways are involved in the contaminant degradation using ZVI. For example, trichloroethylene and chromium are degraded by electron transfer, and perchlorate is reduced by a biological process that is catalyzed by hydrogen. Although the pathways are different, both of them are related to the surface condition of ZVI.

The formation of mineral precipitates will affect the treatment performance by inhibiting the electron transfer or minimizing hydrogen production. H_2 is formed by H^+ ions in the water accepting electrons from the iron surface. This is the same process as for other contaminants like Cr (VI) and TCE. The removal of these contaminants also requires them to accept the electrons released from iron surface. When the iron surface is covered by iron corrosion products (ICPs), the removal rate is limited by how fast the contaminants enter into the iron core, and also limited by how fast the electrons generated from the iron core take to reach to the surface after escaping the resistance of ICPs. The rate of electron transportation is restricted by the porosity and the electron conductivity of the ICPs [75]. Under anaerobic conditions, iron is reduced by water to form Fe_2O_3,

FeOOH, and Fe_3O_4. Fe_3O_4 has high electron conductivity, quite comparable to that of metal [76]. Fe_2O_3 is defined as a semiconductor or even insulator [51]. Thus, the efficiency of electron transfer highly depends on the type of ICPs formed on the iron surface

It has been found that water chemistry plays an important role on the types of precipitation. Carbonate and bicarbonate are the principal species that contribute to alkalinity in water. They are also important to support the growth of autotrophic microorganisms during the biological treatment process. Typical alkalinity level in California groundwater is 44-347 mg/L as $CaCO_3$ [77]. However, very hard waters (alkalinity is greater than 1,000 mg/L as $CaCO_3$) were also measured in parts of southern California [78]. (Bi)carbonate will react with ferrous or ferric iron to form green rusts, furthermore affecting the removal efficiency of the target contaminants and plugging the ZVI systems, which will shorten the life time. Lo et al has reported there was a 33% decrease in the Cr (VI) removal capacity of iron when both carbonate and hardness ions were present [79]. Morrison et al [80] reported on a ZVI system that showed sooner than expected breakthrough of molybdenum and uranium. Therefore, the amount of (bi) carbonate that needs to be added should be carefully decided. Although some similar researches have focused on the potential effect of carbonate in ZVI packed reactors, there is no agreement on how the (bi) carbonate affects iron corrosion rate. Reardon concluded that corrosion rate was increased when 0.02 M $NaHCO_3$ was added [81]. Klausen et al got the same conclusion that the appearance of bicarbonate will enhance iron corrosion at high concentration (0.02M), but they also found iron corrosion was inhibited at low

concentration (0.002M) [82]. Agrawal et al assessed bicarbonate effect by evaluating removal of nitro aromatic compounds by ZVI. It was observed that the rate constant was increased in the presence of moderate concentrations of carbonate. However, the rate constant was decreased at high carbonate concentrations (0.06 M) [83]. There is no accepted value for the bicarbonate concentration required for autotrophic cell growth. Typically concentrations in the range of 0.002 to 0.02 M $NaHCO_3$ have been used for autotrophic bacteria, although without much justification [84]. Additionally, since elevated pH (~10) in the effluent after water passing the ZVI bed has been observed [85], and perchlorate degraders are inactive at elevated pH [86, 87], the addition of $NaHCO_3$ can also act as a buffer to neutralize pH. The question therefore is the potential impact of bicarbonate and of its reaction products with iron on the ZVI bed and its hydraulic condition.

Another consideration of the ZVI field study, which failed to achieve cleanup levels as expected from bench scale tests, is the flow rate effect. Several previous laboratory experiments using a fast flow reactor running for a short term have intended to estimate the ZVI PRBs longevity [88-90]. Unfortunately, insufficient data are available to justify this method. Kamolpornwijit and coworkers estimated the lifetime of the normal groundwater flow PRB was 2 years by running a fast flow column reactor. However, this result overestimated the longevity compared with the 1-year lifetime obtained from a slow flow reactor, which was operated at a normal groundwater flow in the same study. The discrepancy reflects that the estimation and prediction of ZVI PRBs

longevity are significantly dependent on the operation flow rate, which may affect the precipitation kinetics [39].

The hydraulic condition change in the ZVI PRBs has been studied for several years. Most of them focus on the estimation of the porosity change by calculating how much precipitates and gas were formed [41, 91, 92]. Few studies evaluated how the formation of the precipitates will affect the permeability quantitatively. In light of the perchlorate bioremediation results coming out from the ZVI pilot study, it had been concluded that porosity loss and hydraulic conductivity reduction were the main reasons responsible for the poor performance. The hypotheses made were (1) increasing the flow rate will accelerate the hydraulic loss; and (2) the presence of elevated (bi)carbonate will affect the hydrodynamics. Therefore, the objective of this study was to evaluate the effects of flow rate and bicarbonate on the hydraulic condition in the ZVI packed bed reactors. Laboratory ZVI columns were conducted under the various flow rate and bicarbonate concentrations.

4.2 MATERIALS AND METHODS

4.2.1 Materials

All the column reactors were built using 1.5 inch (ID) clear PVC pipe. Chemicals used in this study were reagent grade (Fisher Scientific). 200,000 µS/cm NaCl was prepared by mixing appropriate amounts of NaCl stock solution (2,000 mS/cm) with DI water. During the first phase of the experiment, which investigated the effect of flow rate on hydraulic change, Riverside, CA tap water which contains 6 mg/L DO and 174 mg/L

(as $CaCO_3$) alkalinity was used (Detail water chemistry listed in Table 4.1 [93]). Tap water amended with an appropriate amount of $NaHCO_3$ was used in the biocarbonate effect study. The experiment was performed at room temperature.

Table 4.1 Tap water data in Riverside, CA

Water Quality Parameters	**Mean**
Perchlorate (μg/L)	ND[a]
Nitrate (mg/L)	25
Chloride (mg/L)	31-36
Sulfate (mg/L)	64-78
Carbonate/Bicarbonate (mg/L)	<3/230
Hardness ($CaCO_3$)	223-232
Alkalinity ($CaCO_3$)	165-180
pH	7.3-8.4
Total Dissolved Solids (mg/L)	314-458
Sodium (mg/L)	40-43
Calcium (mg/L)	71-73
Potassium (mg/L)	3-4
Magnesium (mg/L)	11-12

[a]Not detected above the detection limit for reporting

4.2.2 Experimental Methods

4.2.2.1 Effects of flow rate

The effect of flow rate on hydraulic change was examined in four sets of columns (The schematic column set up is shown in Figure 4.1).

Figure 4.1 Picture of the column setup used for the determination of the effect of carbonate on the hydraulic properties of the ZVI bed.

Each column consisted of five small column segments (1.5 inches ID by 4 inches length) connected in series vertically. The purpose of using separate column segments was to enable monitoring of hydraulic changes in the different parts of the column. The five sections were labeled 1 through 5 along the flow direction, and A through D depending on the water flow rate. The column was packed with 30 g sand first to distribute flow, followed by 300 g of 20/30 mesh (0.60 -0.84 cm) ZVI filled to the top. To minimize the effect of air bubbles trapped in the column during the packing process, deionized water (DI) was added first, and then ZVI was laid down inch by inch. Tap water was fed upward into the column via peristaltic pump to prevent air trapping. The designed flow rates for column A, B, C and D were 0.13 cm/min, 0.26 cm/min, 0.52 cm/min and 1.04 cm/min, respectively. The highest flow rate 1.04 cm/min was

approaching field reactor conditions. During the entire operation period, the hydraulic changes in the whole reactor, as well as in each section of the reactor, were monitored periodically by running a head loss test and tracer test.

4.2.2.2 Effects of Alkalinity

After 192 days of operation, columns A, B and D were stopped due to severe clogging, while experiments with column C continued. The effect of adding $NaHCO_3$ on hydraulic condition change was determined by comparing the hydraulic conductivities in each individual segment before and after $NaHCO_3$ addition. $NaHCO_3$ concentration effect was evaluated between all five segments. The different segments of column C were separated and different water compositions were individually fed to each segment. C1, C2 were still fed with tap water, C3, C4 and C5 were changed to tap water amended with 6 mM, 12 mM and 24 mM of $NaHCO_3$, respectively. These concentrations of $NaHCO_3$ corresponded to the alkalinity of 300 mg/L as $CaCO_3$, 600 mg L as $CaCO_3$ and 1200 mg L as $CaCO_3$. Tracer and head loss tests were performed monthly to examine the hydrodynamics in section C1- C5. At the end of the experiment, iron samples were taken at the depth of 0, 3, 5, 7, 9, 11 and 13 cm away from the inlet port after dismantling the individual ZVI column segments for scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDX) analysis. To minimize the oxidation effect causing by exposing to the atmosphere, the iron sample was immediately dried by pure nitrogen gas, and then kept in the anaerobic chamber until analyzed.

4.3 ANALYTICAL METHODS

Inorganic carbon concentration change in the effluent was monitored by Shimadzu 5000 total organic carbon instrument. The nature of the precipitates in the columns were examined using scanning electron microscopy (FEI–Philips XL 30-FEG) equipped with energy-dispersive X-ray analysis (EDAX® EDX) at 20 kv accelerating voltage. Tracer tests were conducted by injecting 2 mL of a 200,000 µS/cm NaCl solution in the inlet port of the columns and monitoring the effluent conductivity with a conductivity probe connected to a data logger. Falling head method was used to determine the hydraulic conductivity [94]. Each column segment was connected to a standpipe with a given water head over the segment undergoing testing. The test consisted of measuring the time required for the water level in the standpipe to drop a given height. The hydraulic conductivity was determined by the following equation:

$$Ln\left(\frac{h_0}{h_t}\right)=\left(\frac{K}{L}\cdot\frac{A_s}{A_c}\right)\cdot t$$

where K is the hydraulic conductivity (cm/s), h_0 is the initial water level in the standpipe (cm), h_t is the water level at time t (cm), A_s is the cross section area of the column (cm^2), A_c is the cross section area of the standing pipe (cm^2), and L is the length of the packing material (cm).

4.4 RESULTS AND DISCUSSION

4.4.1 Effects of Flow Rate

4.4.1.1 Tracer Tests Results

The shapes of the effluent tracer signals were symmetrical and fairly consistent over the first 190 days for all 4 columns (Figure 4.2). This indicates that homogenous flow and constant residence time distribution occurred over time under these conditions. This is further illustrated in Figure 4.3 in which the experimentally determined residence times are reported. Figure 4.3 shows Column D had some variability in the residence time distribution as ZVI aged, but this was not reflected in the actual value of the residence time as is shown in Figure 4.3. Detailed examination of Figure 4.2 shows that the tracer response peak was broadened over time, which is due to the development of heterogeneities over time in the ZVI bed. This finding suggests that ZVI beds operated at high velocities are more susceptible to experience hydraulic changes than the ones operated at lower water velocities.

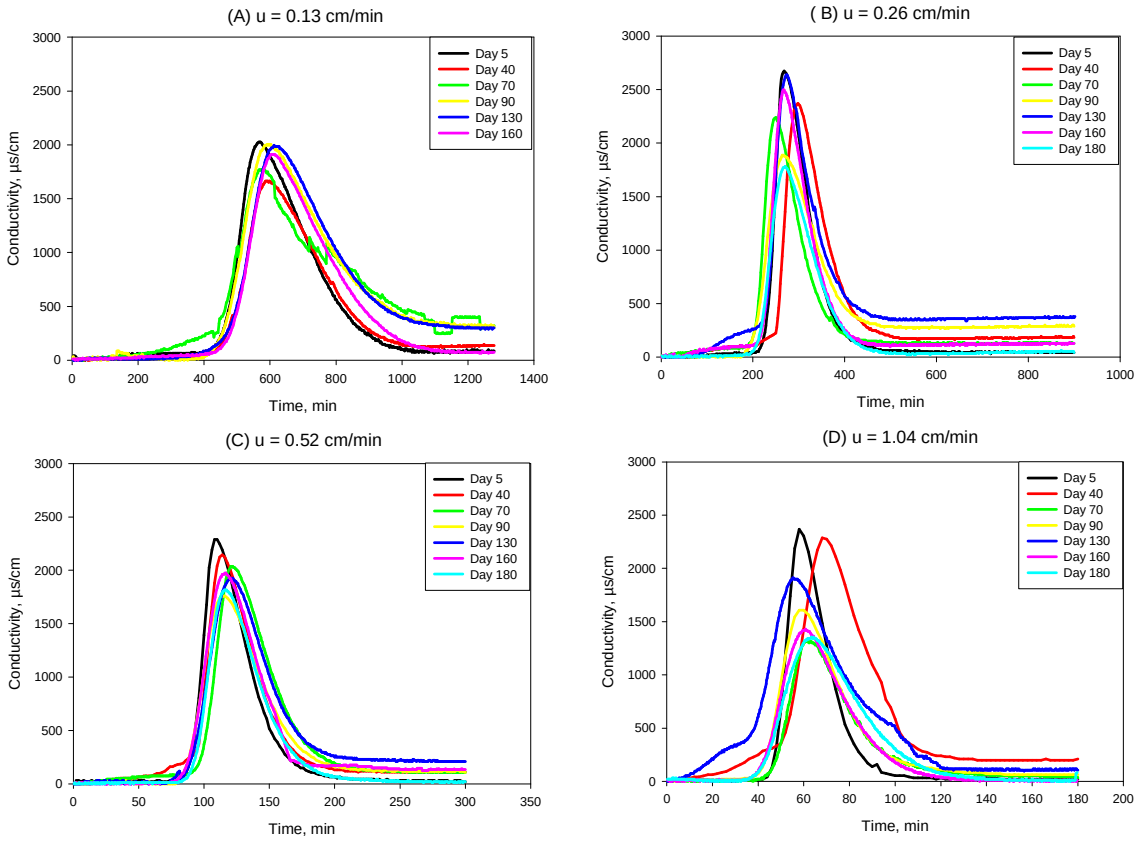


Figure 4.2 Tracer responses obtained over time in columns A-D operating at different flows.

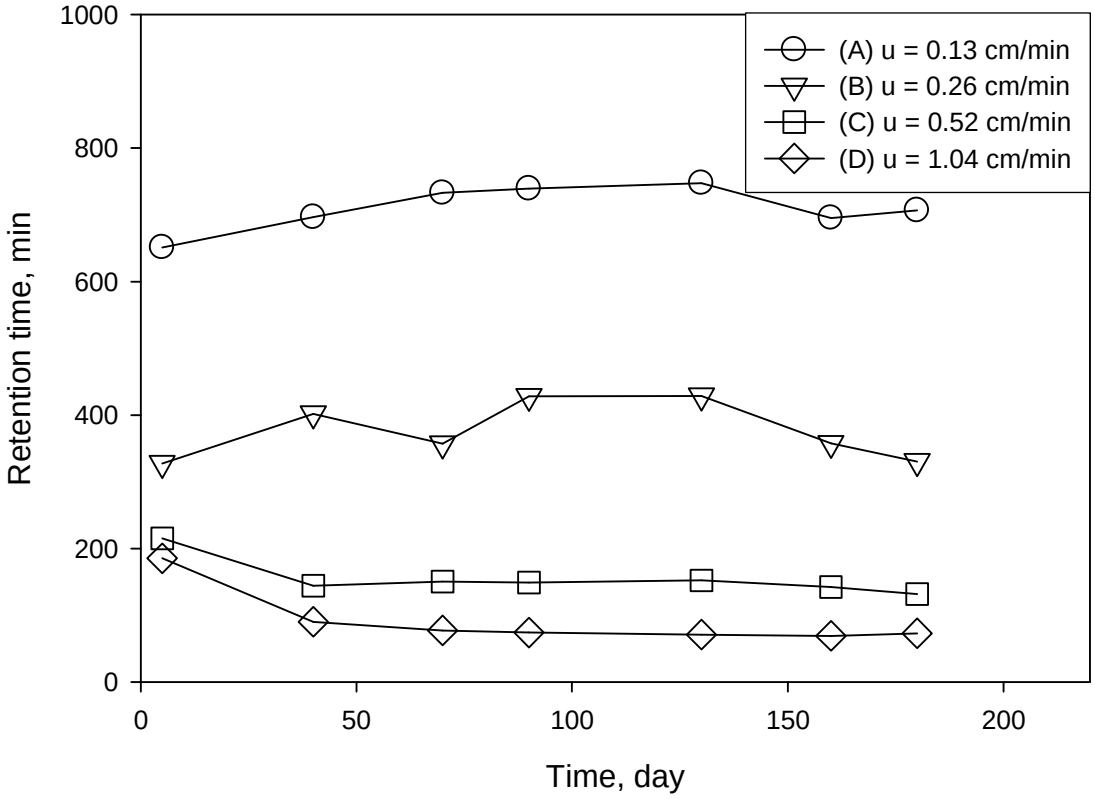


Figure 4.3 Experimentally determined mean residence time in the different columns.

4.4.1.2 Hydraulic Conductivity Results

Initially, all columns had roughly the same hydraulic conductivity at $10^{-1.1} \pm 10^{0.01}$ cm/s. Over the 180 days, a general decreasing trend was observed (Figure 4.4). The final hydraulic conductivity was $10^{-4.6}$, $10^{-4.7}$, $10^{-3.1}$, and$10^{-3.5}$ cm/s in the column A, B, C and D. Surprisingly, the decrease was more pronounced in the low flow reactors (A and B) than in the higher flow reactors (C and D). This result appeared to contradict the hypothesis made earlier. The reasons for this observation are not clear. The decrease in hydraulic conductivity was due to clogging of the ZVI bed caused by the formation of ICPs.

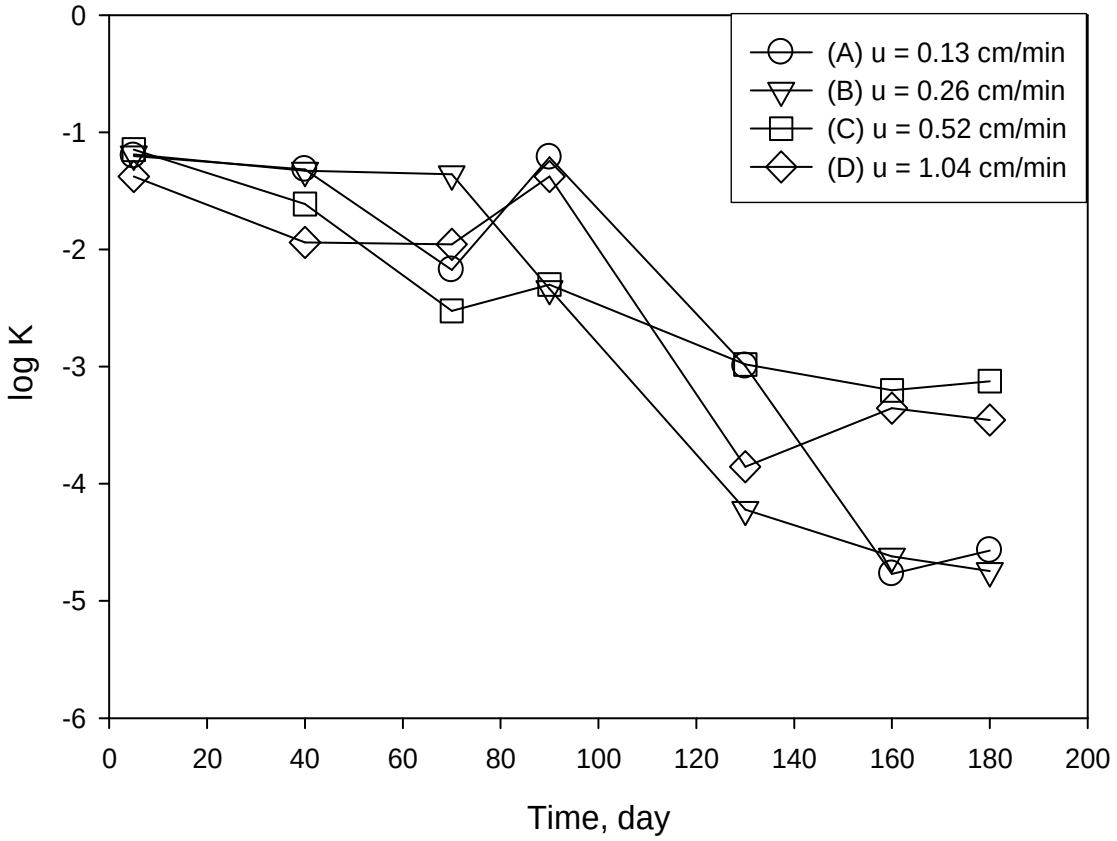


Figure 4.4 Hydraulic conductivity K (in cm/s) of the different ZVI columns operated with tap water at different velocities.

4.4.2 Effects of Alkalinity

4.4.2.1 Formation and Distribution of Mineral Precipitates

SEM images of the ZVI surface as a function of depth as well as EDX spectra of selected spots on the ZVI were shown in Figures 4.5-4.11. Because similar mineral precipitates distribution was found in the C3, C4 and C5, only the SEM and EDX images of C5 were presented here. Visual observation during sampling indicated stratification of the corrosion phenomena. In all the columns, iron samples taken at the first 3 cm of the

reactor bottom were strongly aggregated together. It took some effort to remove the iron samples out of the column because of the formation of a concrete-like structure of the mineral precipitates. Above the first 3 cm of the ZVI layer at the bottom of reactor, the packing became more porous, and the top 3 cm ZVI layer was more like fresh packing. This finding indicated the permeability and porosity losses were not uniform in the system. Additionally, the non-uniform distribution of iron samples can also been confirmed by the naked eye. The iron samples at different depth showed different colors. Samples taken from the first 3 cm of the reactor have an orange color. Samples taken from a depth of 5 cm showed a grayish color, while the iron samples above 5 cm were all black with no visible difference with depth.

The EDX results indicated that the precipitates formed in the reactor were calcium carbonate ($CaCO_3$), siderite ($FeCO_3$), carbonate green rusts ($GR(CO_3^{2}-)$, and other iron oxides (Figures 4.5-4.11). Iron type precipitates dominated throughout the entire column with a weight fraction ranging between 2.65% and 77.2% (Figure 4.12). The distribution of calcium varied with the depth in the column. The fraction of calcium (which came from tap water) decreased with increasing depth except at depth 13 cm. Most of the calcium was captured by the alkalinity at the entrance for the reactor, resulting in the accumulation of calcium carbonate (long rod shape). The calcium carbonate precipitates formed a thick deposit layer, even possibly "gluing" ZVI particles together and is suspected to be a major contributor to the loss of porosity and hydraulic conductivity.

The detection of a large amount of calcium carbonate at the top (L=13 cm) of the column was a surprise as calcium was thought to have been depleted in the first few cm.

A possible reason for the calcium presence at that height may be calcium carried by preferential flow after significant heterogeneities developed in the ZVI bed. As clogging progressed, the fluid prefers to flow through the more permeable area. Vikesland's group found the formation of mineral precipitates and hydrogen gas resulted in the large amount of immobile water present in the iron columns. The heterogeneity was increased with the increasing of immobile water [95, 96].

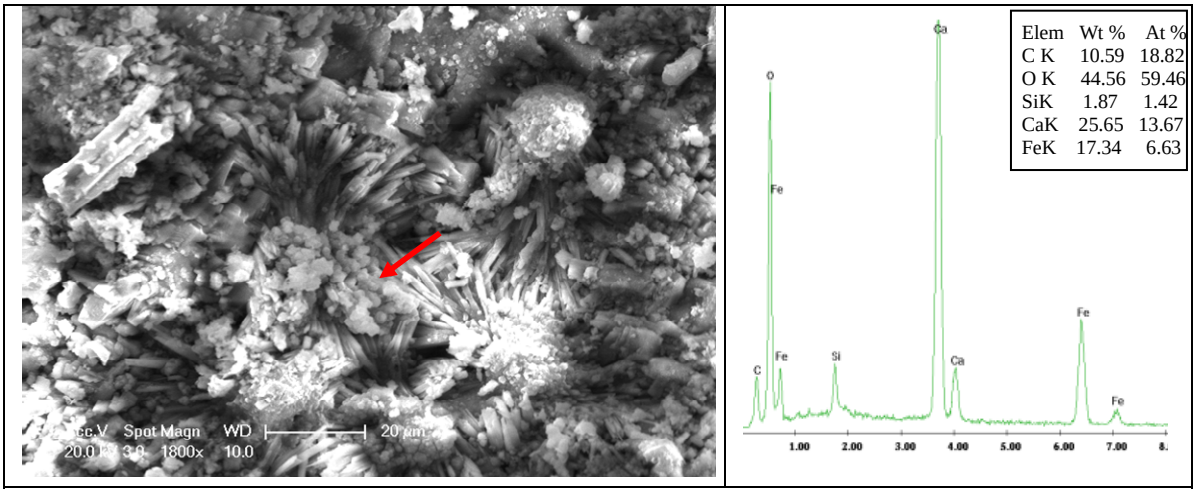


Figure 4.5 SEM image (left) of ZVI in C5 at a height of 0 cm. The right shows the EDX spectrum (x axis in keV) of the spot indicated by the red arrow on the SEM image. Note that the x axis was truncated to improve readability but no peaks were observed above 8 keV.

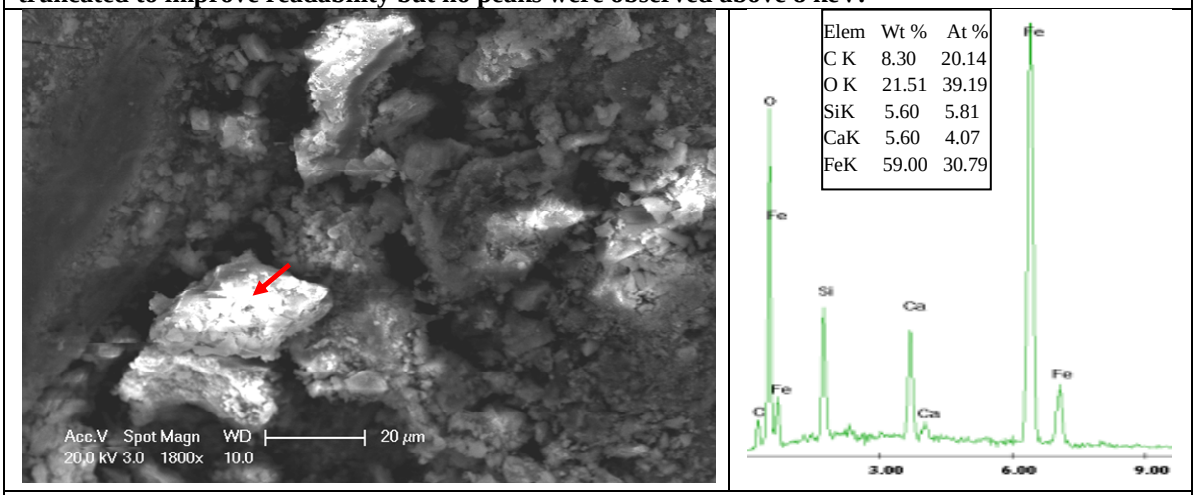
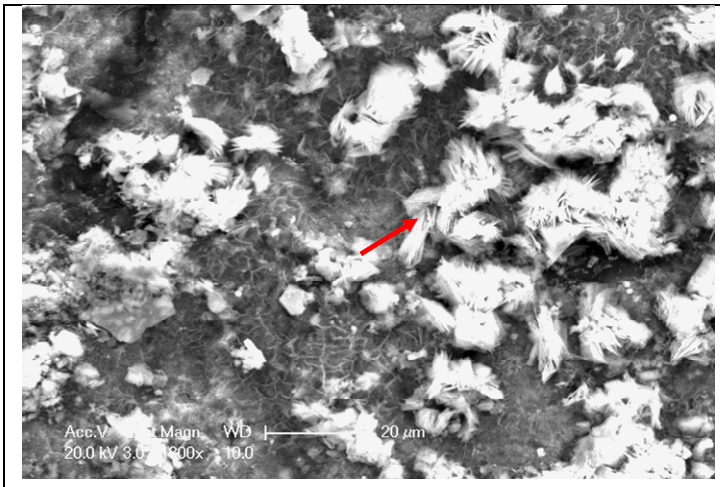


Figure 4.6 SEM image (left) and EDX spectrum (right, x axis in keV) of ZVI in C5 at a height of 3 cm.



Elem	Wt %	At %
C K	4.88	14.77
O K	12.03	27.34
SiK	5.87	7.61
FeK	77.22	50.28

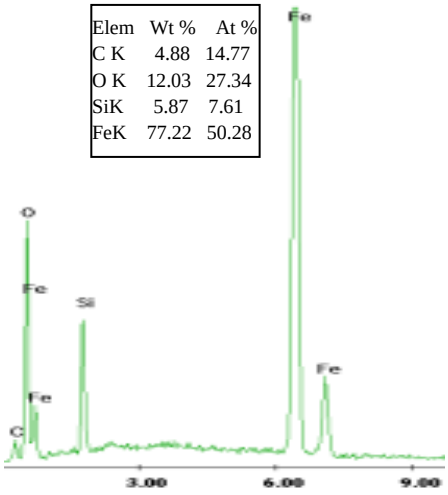
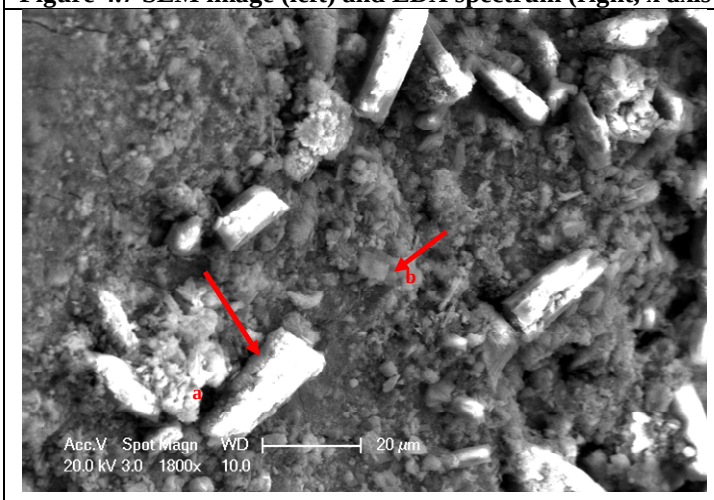


Figure 4.7 SEM image (left) and EDX spectrum (right, x axis in keV) of ZVI in C5 at a height of 5 cm.



a

Elem	Wt %	At %
C K	22.54	33.65
O K	48.10	53.91
SiK	1.04	0.67
CaK	21.21	9.49
FeK	7.10	2.28

b

Elem	Wt %	At %
C K	12.13	22.48
O K	38.11	53.00
NaK	0.96	0.93
SiK	10.52	8.34
FeK	38.28	15.25

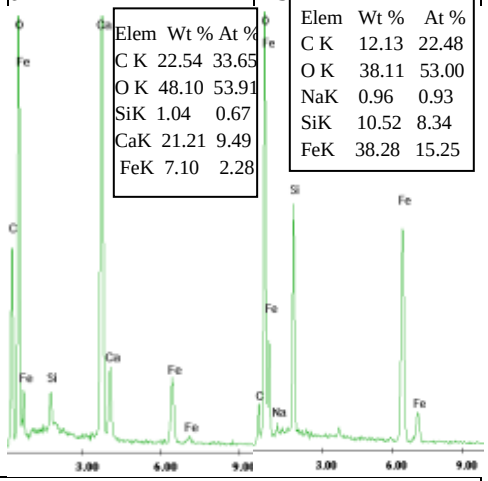
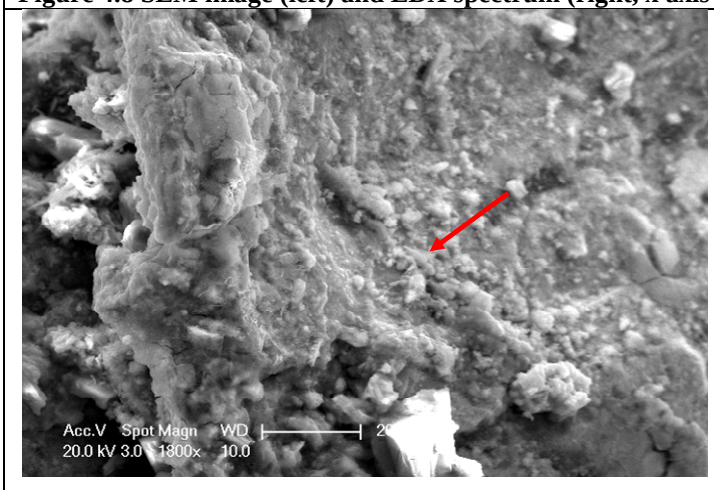


Figure 4.8 SEM image (left) and EDX spectrum (right, x axis in keV) of ZVI in C5 at a height of 7 cm.



Elem	Wt %	At %
C K	12.20	26.26
O K	26.02	42.06
SiK	6.71	6.18
FeK	55.07	25.50

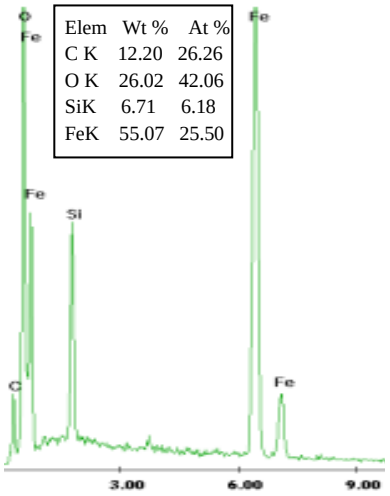
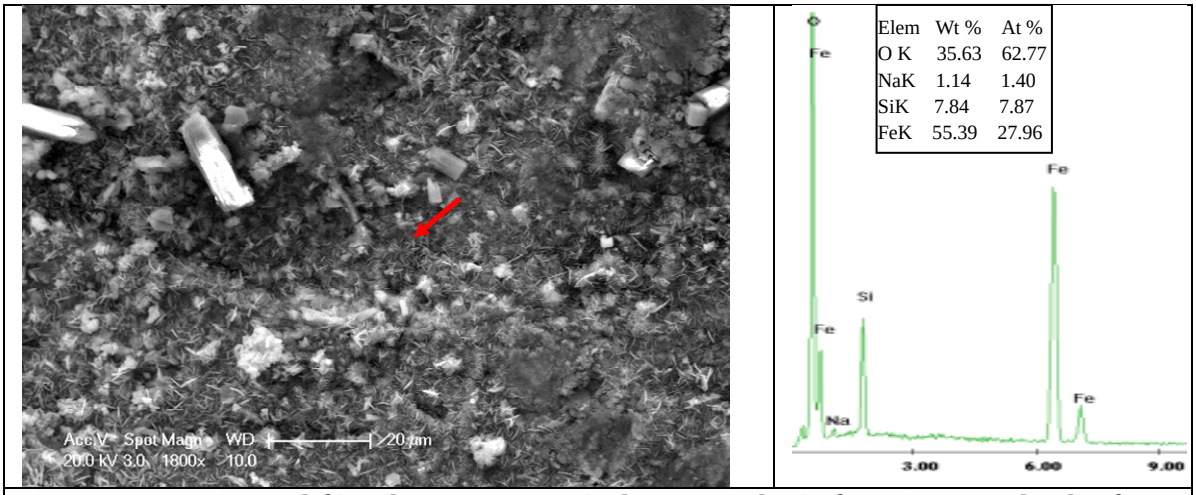
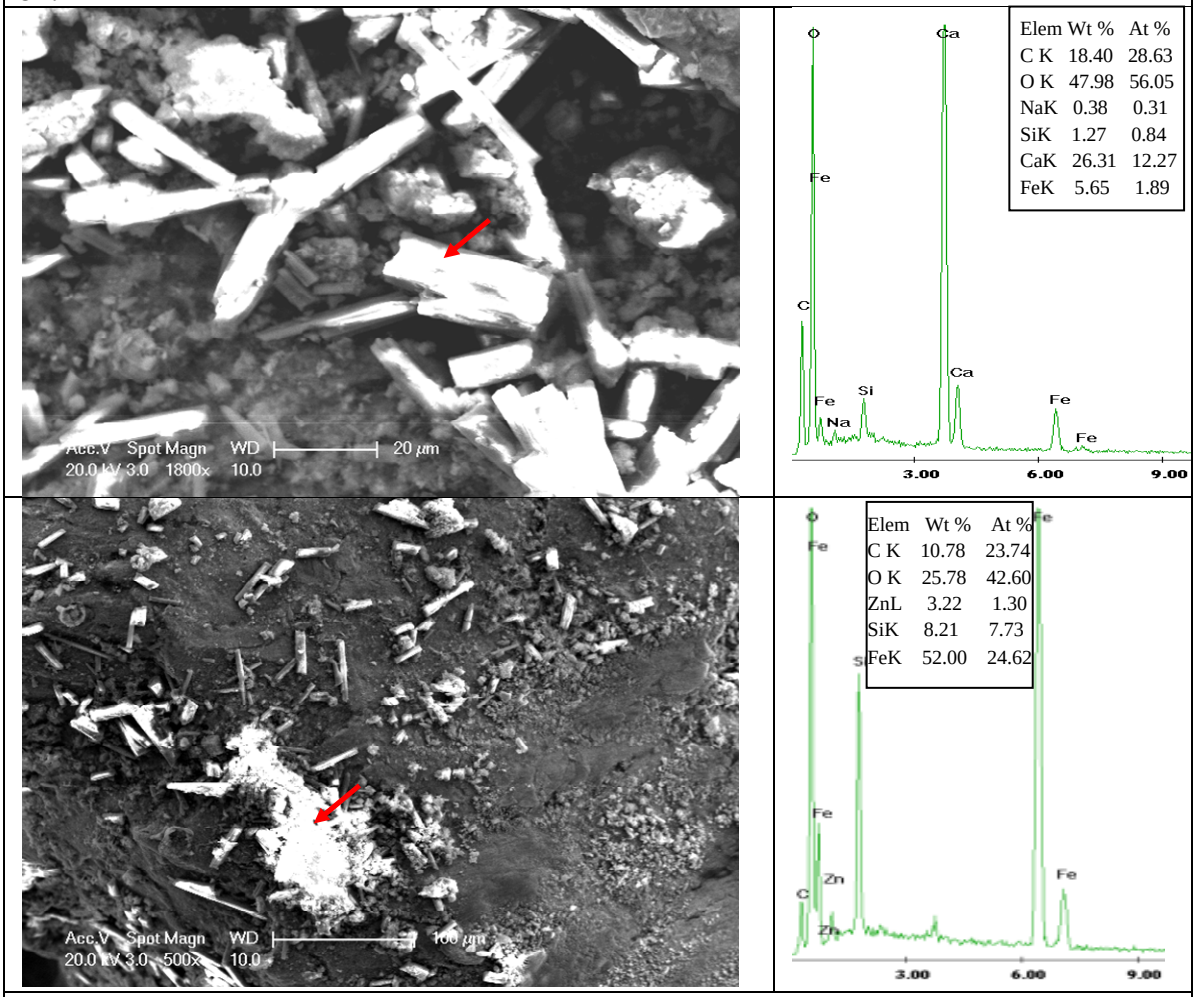


Figure 4.9 SEM image (left) and EDX spectrum (right, x axis in keV) of ZVI in C5 at a height of 9 cm.



Elem	Wt %	At %
O K	35.63	62.77
NaK	1.14	1.40
SiK	7.84	7.87
FeK	55.39	27.96

Figure 4.10 SEM image (left) and EDX spectrum (right, x axis in keV) of ZVI in C5 at a height of 11 cm.



Elem	Wt %	At %
C K	18.40	28.63
O K	47.98	56.05
NaK	0.38	0.31
SiK	1.27	0.84
CaK	26.31	12.27
FeK	5.65	1.89

Elem	Wt %	At %
C K	10.78	23.74
O K	25.78	42.60
ZnL	3.22	1.30
SiK	8.21	7.73
FeK	52.00	24.62

Figure 4.11 SEM images (left) and corresponding EDX spectra (right) of ZVI surface in C5 at a height of 13 cm. Note the lower magnification for the bottom image and the large difference in iron and calcium peaks.

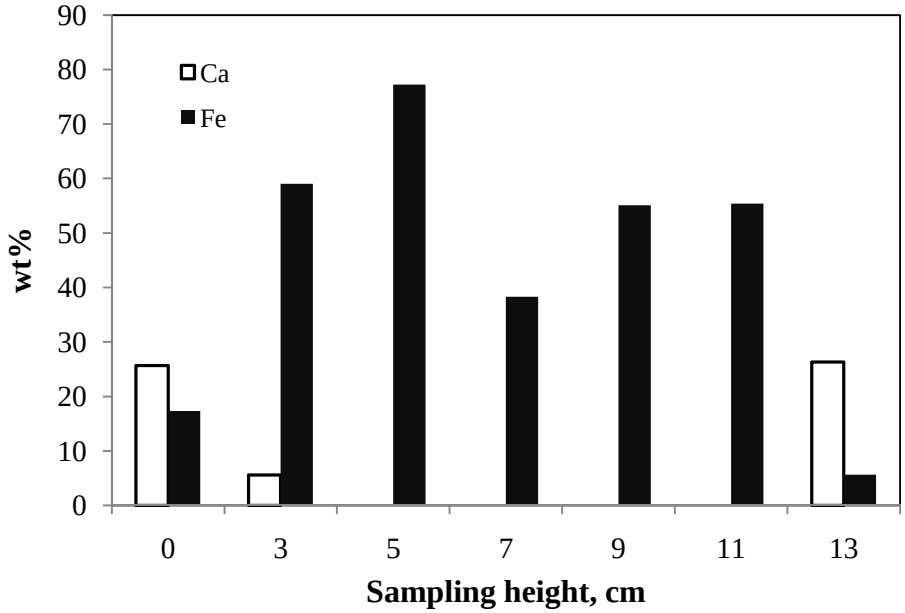


Figure 4.12 Distribution of element Ca and Fe in segment C5.

4.4.2.2 Hydraulic Conductivity

The hydraulic conductivity change in all segments before and after adding $NaHCO_3$ is summarized in Figure 4.13. At the beginning, all the segments started at the similar hydraulic conductivity at $10^{-1.4}\pm10^{0.12}$ cm/s. Even fed with the same type of water, the hydraulic conductivity change in all the columns was not consistent. Although hydraulic conductivity fluctuated, the range of 1 to 2 orders of magnitude during 192 days was observed in all the five segments (Figure 4.13). As expected before, the fast decrease in hydraulic conductivity happened in the entrance segment, which was C1. Because the columns C1 and C2 were fed with tap water during the whole experiment period, the total hydraulic conductivity loss was not as much as the ones that were fed with $NaHCO_3$. There were about 2 orders of magnitude loss in both C1 and C2 until the end of the experiment. Even though alkalinity was not added in C1 and C2, the flow was

restricted due to the loss of permeability and the flow rate was decreased from 0.52 cm/min to 0.16 cm/min after being operated for 268 days.

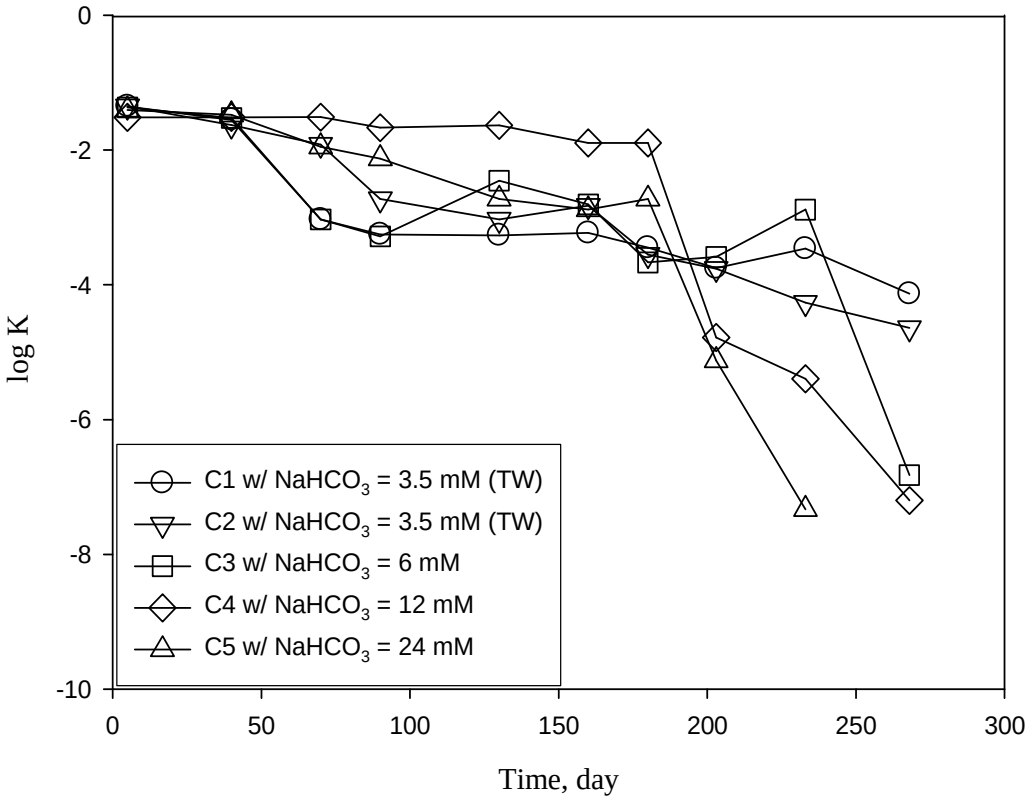


Figure 4.13 Hydraulic conductivity K (in cm s^{-1}) of the different ZVI bed segments over the entire experiment. The first 192 days, tap water (TW) was fed sequentially to C1-C5. After 192 days, the individual segments were fed tap water supplemented with NaHCO3 (see total concentration in legend) while C1 and C2 served as controls.

The hydraulic conditions dramatically changed after adding different concentrations of $NaHCO_3$ in segments C3, C4 and C5. Especially in C5, the hydraulic conductivity decreased from $10^{-2.73}$ cm/s to $10^{-7.33}$ cm/s within 41 days. Although column C4 ($K = 10^{-1.90}$ cm/s) was more permeable than C3 ($K = 10^{-3.67}$ cm/s) right before feeding $NaHCO_3$, the hydraulic conductivity in C4 decreased more than C3 which was

$10^{-7.19}$ cm/s after feeding with 12 mM $NaHCO_3$ for 76 days. Clearly, there is a direct relationship between the $NaHCO_3$ loading and the time to plugging the ZVI column. Within the range of this test, the higher the concentration of $NaHCO_3$ loaded, the faster the reactor got blocked. Due to the complete blockage of the column, C5 was shut down after feeding with $NaHCO_3$ for 41 days, followed by C4 for 76 days and C3 for 108 days. The data presented here indicated that the hydraulic conductivity in the iron based PRBs will be reduced over time in the natural groundwater, and situation will be even worse with elevated $NaHCO_3$ concentrations. For the in situ PRB application, there is a concern that treatment won't be achieved if the fluid bypasses the ZVI through more permeable soil. For the ex situ application, more energy will be needed to pump the water through the system.

Regarding the hydraulic change in each segment, three trends are observed from the data in Figure 4.13. First, the hydraulic conductivity decreased over time in all the segments during the entire experiment. Second, the hydraulic change was not uniform in the column, which highly depends on the initial packing of the reactor Third, high alkalinity water acted as a "killer" for the iron based reactors, resulting in the total blockage of the column in a short time.

4.4.2.3 Inorganic Carbon

The change in inorganic carbon concentration in the effluent is shown in Figure 4.14. Most of the inorganic carbon was consumed within the first week. The carbonate removal rate slowed down in columns C3 and C5 after one week. Inorganic carbon was

removed by Fe^{2+} and $Fe(OH)_2$ (Reaction 2.5 and 2.7). After the fresh iron core was covered by ICPs, the production rate of Fe^{2+} was limited, furthermore, less $Fe(OH)_2$ was formed (Reaction 2.2). Thus, the consumption of inorganic carbon was restricted by the availability of Fe^{2+} and $Fe(OH)_2$. Due to the higher hydraulic conductivity in C4 before adding $NaHCO_3$, it seems like column C4 was more reactive than the other two columns.

The loss of high levels of bicarbonate resulted in the accumulation of carbonate precipitates on the iron surfaces. Moreover, the carbonate precipitates just represented part of the precipitates formed in the system. In addition, iron oxides, which occupied the whole surface of the iron fillings, were another factor responsible for the porosity and permeability reduction of the ZVI system. The density of $CaCO_3$ and $FeCO_3$ are 2.8 g/cm^3 and 3.5 g/cm^3, respectively. The minimum porosity loss can be estimated by assuming all the carbonate precipitate is $FeCO_3$. In column C5, which was amended with the highest concentration of $NaHCO_3$, the average inorganic C retained in the column was 15.83 mg C/g Fe after feeding $NaHCO_3$ for 24 days. This resulted in an 8.02% porosity loss in the whole column. However, this value is calculated based on the assumption that the precipitates were formed uniformly in the systems, which is not the case. As mentioned before, the most severe corrosion happened in the first 3 cm from the inlet. If 50% of C was in the form of $FeCO_3$ in the first 3 cm, the porosity reduction would be increased to 17.38% within 24 days. Unlike column C5, although the hydraulic conductivity of column C3 right before feeding with $NaHCO_3$ was 0.9 magnitude lower than C5, the average porosity loss in the whole column was only 2.56% after introducing $NaCO_3$ for 24 days. It should be noted that the actual porosity loss in the system should

be even higher than the above estimation when taking into account other precipitates such as iron oxides.

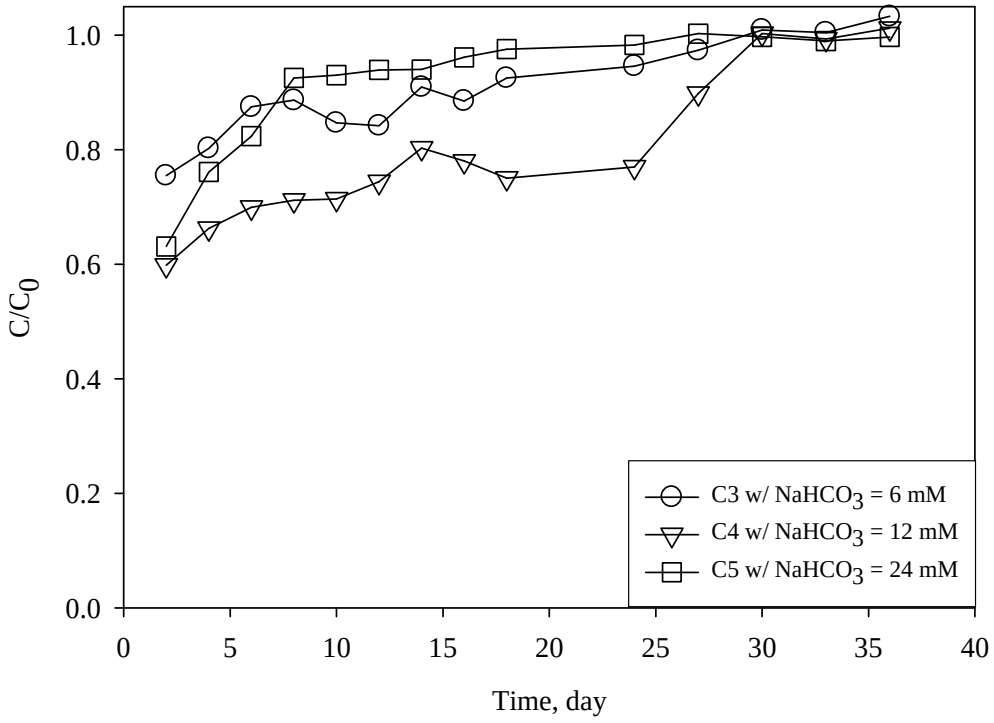
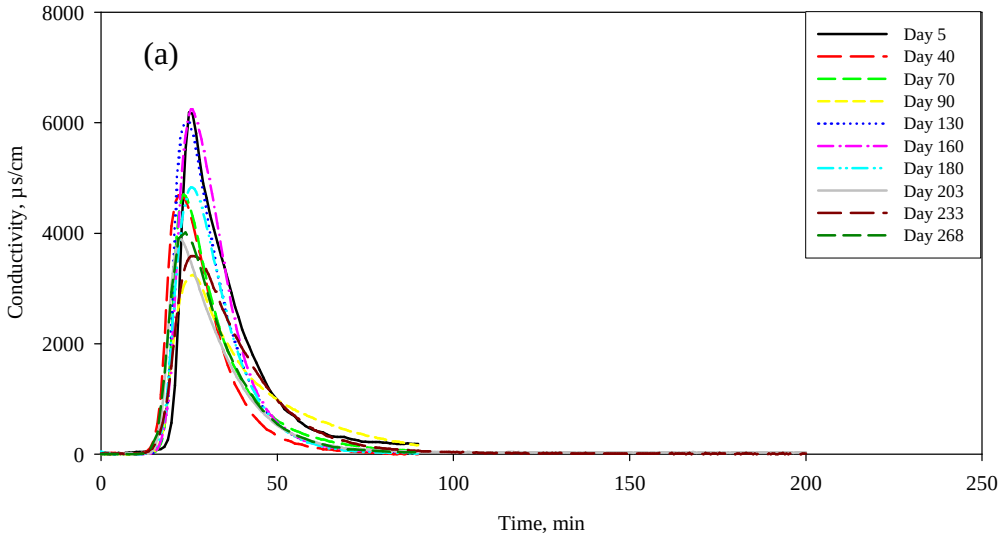


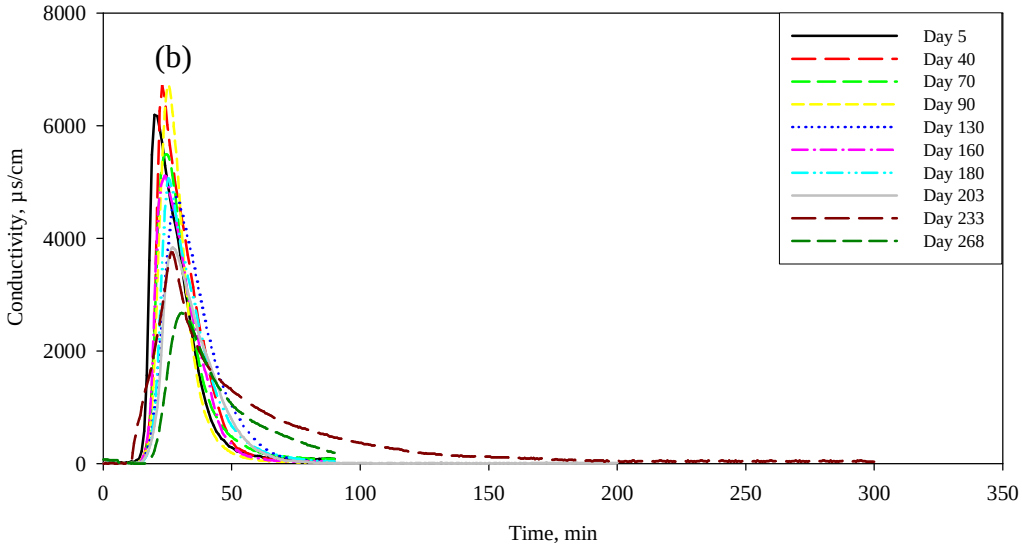
Figure 4.14 Inorganic carbon breakthrough curves in the $NaHCO_3$ amended columns C3, C4 and C5.

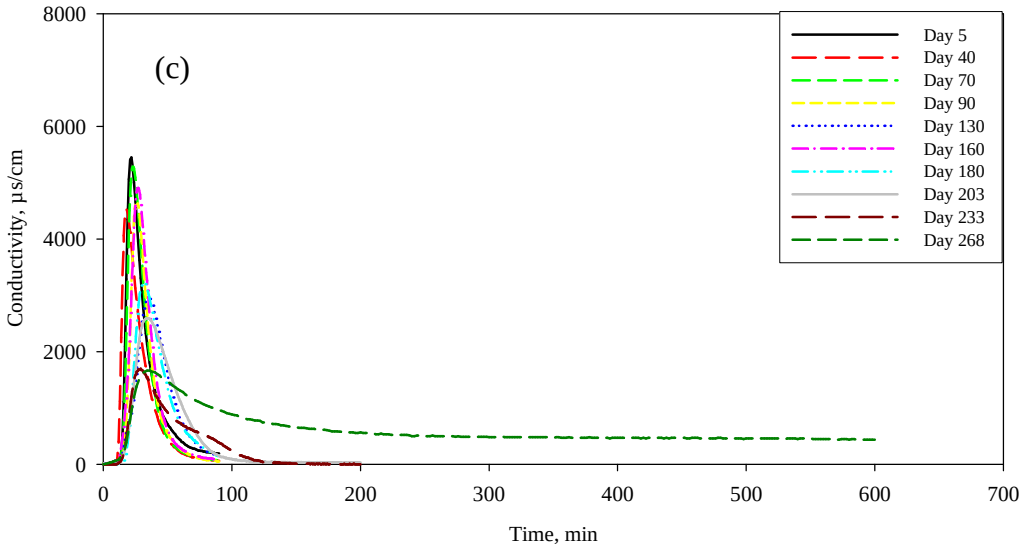
4.4.2.4 Tracer Test

The tracer test technique has been used for many iron PRB studies to determine the flow features and estimate the porosity change [48, 97]. In this study, tracer tests were conducted to determine the characteristics of the fluid transport in the ZVI bed. Detailed results with the five segments are presented and discussed in Figure 4.15. The results included two stages: one is five segments fed with tap water as a whole column for the first 192 days, and another is the period following feeding with elevated $NaHCO_3$

to C3, C4 and C5 separately. The tracer responses were symmetrical and relatively constant during the entire experiment for the segments C1 and C2, which fed with tap water. The same consistency was observed for column C3, C4 and C5 for the initial 192 days. Column C3 started to show a long tail for the tracer in the effluent after feeding with 6 mM $NaHCO_3$ for 41 days (Day 233). This phenomenon became worse on day 268. The same observations were made for columns C4 and C5, which fed with 2 and 4 times more $NaHCO_3$ compared to column C3. The long tail indicated that there were dead zones inside the reactor and non-homogenous residence time distribution that developed after $NaHCO_3$ was supplemented to the water fed to these columns. Due to the severe clogging in C3, C4 and C5, no tracer could be detected after injecting NaCl for 1.5 days, and then C3, C4 and C5 had to be stopped after being amended with $NaHCO_3$ for 108 days, 76 days and 41 days operation, respectively. This result is consistent with the hydraulic conductivity test results.




(b)
Conductivity, µs/cm
Time, min
Day 5
Day 40
Day 70
Day 90
Day 130
Day 160
Day 180
Day 203
Day 233
Day 268
0
2000
4000
6000
8000
0
50
100
150
200
250
300
350


(c)
Conductivity, µs/cm
Time, min
Day 5
Day 40
Day 70
Day 90
Day 130
Day 160
Day 180
Day 203
Day 233
Day 268
0
2000
4000
6000
8000
0
100
200
300
400
500
600
700

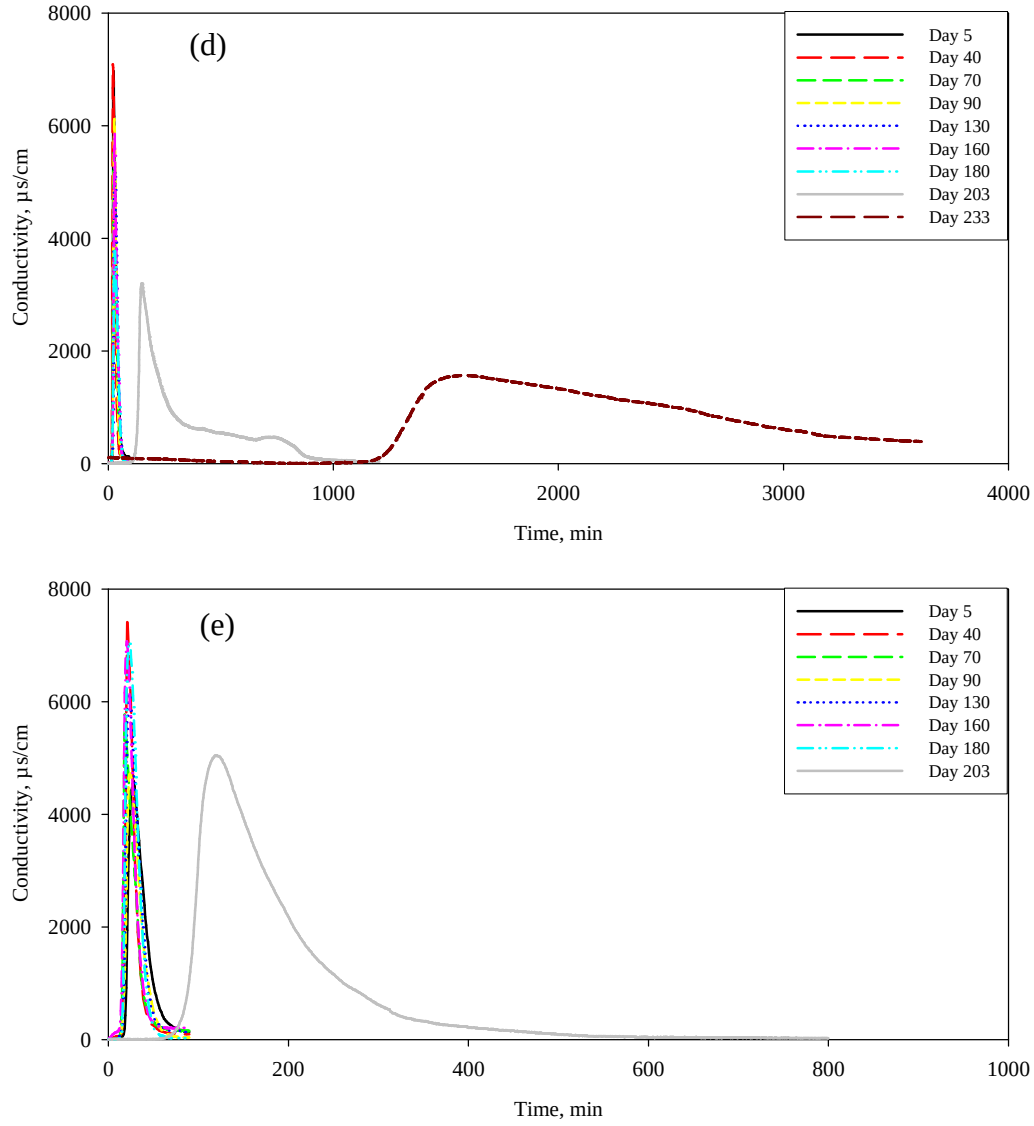


Figure 4.15 Tracer effluent concentration after column C1 – C5. (a) Column C1 which fed with TW during the entire experiment; (b) Column C2 which fed with TW during the entire experiment; (c) Column C3 which fed with 6 mM NaHCO3 after day 192; (d) Column C4 which fed with 12 mM NaHCO3 after day 192; (e) Column which fed with 24 mM NaHCO3 after day 192.

4.5 SUMMARY OF THE FINDINGS

The effect of flow rate and carbonate on the hydraulic change in the ZVI packing bed reactor was evaluated in this chapter. Specific observations of the flow rate effect are as follows:

- A decreasing trend was observed in all the columns that were fed with tap water. The average initial hydraulic conductivity was $10^{-1.1} \pm 10^{0.01}$ cm/s, whereas the final hydraulic conductivity ranged from $10^{-4.7}$ cm/s to $10^{-3.1}$ cm/s after operated for 180 days.
- The decrease of hydraulic conductivity was more pronounced in the low flow reactors (A and B) than in the higher flow reactors (C and D). This result appeared to contradict the hypothesis made earlier.

Specific observations of the (bi)carbonate effect are as follows:

- Dominate precipitates in the reactor: calcium carbonate ($CaCO_3$), siderite ($FeCO_3$), carbonate green rusts ($GR(CO_3^{2-}$). The distribution of precipitates was changing with the depth.
- Hydraulic conductivity was decreasing over time. The changing change was not uniform in the column, which resulting the development of heterogeneity and preferential flow.
- The decreasing of hydraulic conductivity was most severe in the segment which feeding with the higher concentration of $NaHCO_3$. Hydraulic conductivity decreased from $10^{-2.73}$ cm/s to $10^{-7.33}$ cm/s after constantly feeding 24 mM of $NaHCO_3$ for 41 days.

- After amended with $NaHCO_3$, the flow rate was significantly restricted by the reduction of permeability.

CHAPTER V LABORATORY MICROCOSM AND COLUMN STUDIES TO INVESTIGATE IN SITU TREATMENT OF PERCHLORATE-IMPACTED SOURCE AREA AND BIOBARRIER GROUNDWATER

5.1 INTRODUCTION

As described in Chapter III and Chapter IV, significant problems with clogging and hydraulic conductivity reduction were encountered with the ZVI-H2 systems over several months. Performing deoxygenation might minimize the clogging somehow, but addition of sodium bicarbonate resulted in further deposits of detrimental precipitates. Hence, an alternative strategy for in-situ perchlorate remediation was evaluated in this chapter. Unlike the first autotrophic strategy using ZVI to generate hydrogen as the electron donor and bicarbonate associated with alkalinity as the carbon source, the alternative heterotrophic strategy was using organic substrates as the electron donor and the carbon source for cell growth and maintenance.

For in-situ remediation, biological treatment zones can be formed by injecting organic substrates either into the source area or permeable reactive barriers (PRBs). However, continuously injecting organic substrates into the source area is very expensive due to not only the excess substrate waste, but also the equipment and maintenance cost. In comparison, mixing the substrates with the reactive barriers is more economical. These organic substrates serve as both carbon and energy sources for microorganism growth and perchlorate degradation during the anaerobic process. Compared to other physical or chemical processes, biological remediation has the advantages of readily

available perchlorate-reducing microorganisms [30], as well as low operation and maintenance costs. Perchlorate reducing microorganisms have been found to be ubiquitous in the environment; many denitrifiers are capable of degrading perchlorate [30]. The common electron donors used in the in-situ or ex-situ bioremediation are vegetable oil, acetate, acetic acid, etc [14-16].

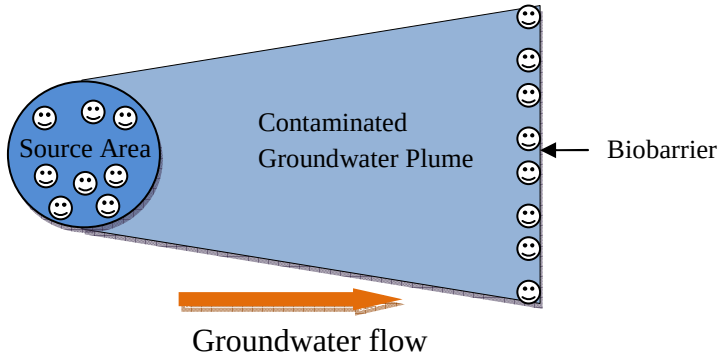


Figure 5.1 Schematic of source area and biobarrier injection configurations (☺represents "injection point")

In this part of study, contaminated soil and water samples were collected from a perchlorate-contaminated site located at Lockheed Martin Corporation's Beaumont Site 2 (Beaumont, CA). Samples were taken from two different locations on the site. Simulation of the location was shown in Figure 5.1. The first location was where the perchlorate groundwater concentration was highest and assumed to be where the primary contamination occurred. This site was referred to as the "source area". Groundwater and aquifer soil samples were taken from the source area to assess whether in situ perchlorate degradation could be promoted by introducing an organic electron donor into the saturated zone.

The second location was near the edge of the perchlorate contaminant plume. Groundwater and aquifer soil samples were taken from this location to assess whether

introducing an organic electron donor into the saturated zone in advance of the perchlorate plume could create a biobarrier. This site was referred to as the "biobarrier" location.

The objectives of this study were to (1) determine the ability of various organic compounds as electron donors for perchlorate biodegradation and to justify which compound is more suitable for in-situ application; (2) compare the longevity of effective perchlorate degradation to the ZVI-based system. To achieve the objectives, treatment of two real groundwater samples with different levels of perchlorate were tested. The purpose of using high concentration perchlorate was to remove perchlorate mass and reduce perchlorate flux in the source area, as well as minimize the effort and cost in treating the downstream plume. Emulsified oil substrate (EOS®598), glycerin, high fructose corn syrup (HFCS 42), acetic acid (HAc) and sodium acetate (NaAc) were selected as the potential amendments for high concentration source area treatment. EOS, EHC and compost/mulch were chosen for removing perchlorate in the low concentration biobarrier. Microcosm tests were used to screen selected amendments in terms of effectiveness in perchlorate biological remediation. Based on the results of the microcosm tests, column tests were conducted to simulate the in-situ permeable barrier treatment.

5.2 MATERIALS AND METHODS

5.2.1 Materials

EOS was obtained from EOS Remediation, Inc. (Raleigh, NC), which contained 59.8% (by weight) soybean oil. Glycerin used in this study was manufactured by U.S.

Glycerin (Kalamazoo, MI). High fructose corn syrup was supplied by Sweetener Products Co (Vernon, CA). Acetic acid and sodium acetate were purchased from Fisher Scientific. EHC (Adventus Americas Inc., Bloomingdale, IL) is a substrate that combines a plant-based carbon/energy source to stimulate microbial activity with a zero-valent iron component to rapidly generate and sustain reducing conditions. Compost and mulch were obtained from a local supplier. The water and soil used throughout the studies were obtained from a perchlorate-contaminated site. Soil from the contaminated site can be a source of perchlorate degrading microorganisms. Additionally, using the water and soil from the site for the laboratory tests provided the closest operating conditions to the real application.

5.2.2 Microcosm Tests

The goal of the microcosm test was to assess the effectiveness of various amendments in stimulating biological perchlorate reduction.

5.2.2.1 High Concentration Source Area Treatment

Source area microcosm test conditions are summarized in Table 5.1. Contaminated groundwater and soil were collected from Lockheed Martin Corporation's Beaumont Site 2 (Beaumont, CA). Source area groundwater was placed into 250 mL flasks together with the aquifer soil as a ratio of 4:1 (w/w). Microcosm control was prepared by soil only without substrate addition to quantify potential perchlorate degradation/loss from natural attenuation. EOS, glycerin, HFCS, HAc, and NaAc were added at the two different dosages as listed in Table 5.1. As recommended by the

manufacturer, EOS, glycerin and HFCS were added at 0.1 and 0.5% (w/w). HAc was at 280 and 1,440 mg/L. NaAc was at 1,000 and 5,000 mg/L. Considering the likely deficiency of nitrogen and phosphorus in the site soil and groundwater (soil and water chemistry data were reported in Section 5.4, Table 5.4), 1 g/L of $(NH_4)_2HPO_4$ was added to the solution for nutrient-amended microcosms. The flasks were sealed with a septum cap and the headspace was purged with nitrogen gas to maintain an anaerobic condition. The microcosms were mixed manually three times per day to promote mixing the solid substrate with the groundwater. All amended and control microcosms were run in triplicate and at room temperature. Water samples were withdrawn through the septum cap and filtered with 0.22 μm filter for later analysis.

Table 5.1 Summary of source area microcosm test conditions

Groundwater(GW) source	**Soil mass + groundwater volume**	**Soil only control**	**EOS**
Aquifer underlying source area High ClO_4- conc.	50 g soil in 200 mL of groundwater	Aquifer soil under-lying source area	EOS added to GW at 0.1 & 0.5% (w/w). For nutrient amended microcosms 1 g/L of $(NH_4)_2HPO_4$ was added to the solution.
Glycerin	**High fructose corn syrup**	**Acetic acid**	**Sodium acetate**
Glycerin added to GW at 0.1 & 0.5% (w/w). For nutrient amended microcosms, 1 g/L of $(NH_4)_2HPO_4$ was added to the solution.	High fructose corn syrup added to GW at 0.1 & 0.5% (w/w). For nutrient amended microcosms 1 g/L of $(NH_4)_2HPO_4$ was added to the solution.	Acetic acid added to GW at 280 and 1,440 mg/L. For nutrient amended microcosms, 1 g/L of $(NH_4)_2HPO_4$ was added to the solution.	Sodium acetate added to GW at 1000 and 5000 mg/L. For nutrient amended microcosms, 1 g/L of $(NH_4)_2HPO_4$ was added to the solution.

5.2.2.2 Low Concentration Biobarrier Treatment

Biobarrier microcosm test conditions are summarized in Table 5.2. Contaminated biobarrier groundwater and soil were collected downgradient from the Lockheed Martin Corporation's Beaumont Site 2 (Beaumont, CA). All experiments were conducted in the 250 mL glass serum bottles. Soil and groundwater were added into each bottle at the ratio of 1:4 (w/w) with the exception of the set with compost as the amendment, where soil was replaced by the same amount of compost. EOS and EHC were fed at the dosage of 0.3% (w/w) and 0.1% (w/w), respectively. Perchlorate reduction experiments were performed both with and without nutrients added. For nutrient amendments, 1 g/L of diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) was added. Controls were prepared without any amendment addition to quantify the natural perchlorate degradation or loss. All of the bottles were sealed with a septum cap, and the headspace was purged with

nitrogen gas before starting the experiment to remove oxygen. The microcosms were mixed manually three times a day to promote mixing. All amended and control microcosms were run in triplicate and at room temperature. Water samples were withdrawn through the septum cap and filtered with 0.22 μm filter for later analysis.

Table 5.2 Summary of biobarrier area microcosm test conditions

Groundwater Source	Soil Mass + Groundwater Volume	Substrate			
		Non-Amended Control (Soil Only)	EOS	Compost	EHC
Plume area near property boundary Low ClO_4^- concentration	50 g soil or compost in 200 mL of groundwater	Subsurface soil near property boundary	Soil mixed with EOS solution to create 0.3% (w/w) EOS/soil mix. For nutrient amended microcosms, 1 g/L of $(NH_4)_2HPO_4$ was added to the groundwater.	Compost only. For nutrient amended microcosms, 1 g/L of $(NH_4)_2HPO_4$ was added to the groundwater.	Soil mixed with EHC to create 0.1% (w/w) EHC/soil mix. For nutrient amended microcosms, 1 g/L of $(NH_4)_2HPO_4$was added to the groundwater.

5.2.3 Column Tests

5.2.3.1 High Concentration Source Area Treatment

After evaluating the effectiveness of selected amendments on perchlorate treatment performance by conducting microcosm tests, column tests were prepared to determine the likely performance of several amendments and biobarrier types to reduce perchlorate. Based on the results of microcosm testing, EOS, glycerin and NaAc were able to remove perchlorate at higher removal rates than HAc and HFCS. However, EOS and glycerin are preferable to sodium acetate when considering the cost and salt addition

to the aquifer. Thus, out of the five substrates tested in the microcosm experiments, EOS and glycerin were chosen for column tests. Three sets of PVC columns (2 inch ID) with the lengths of 6-inch, 12-inch, 18-inch and 24-inch were constructed to access the performance of packing with (1) site soil only (control); (2) EOS (0.3% w/w)-amended soil; and (3) glycerin (0.3% w/w)-amended soil. EOS and glycerin were mixed with the soil before it was packed into the column. Columns were operated in an up-flow mode to prevent air trapping in the pore spaces. During the start-up period, all the columns were operated at a flow rate of 0.5 ft/d. Since the addition of nutrients had limited effect on perchlorate reduction using EOS or glycerin in the microcosm test, no nutrients were added in the column tests. Samples were collected at selected times for perchlorate, nitrate, pH, and TOC analysis. Random samples were taken for metal analysis.

5.2.3.2 Low Concentration Biobarrier Treatment

A summary of the column testing is shown in Table 5.3. Different lengths of packed bed reactors were developed to demonstrate the perchlorate reduction under various conditions. The column test was classified as Phase 1 and Phase 2 based on the type of the amendments. Phase 1 tests included three parallel columns (6-inch ID×24-inch length) which were packed with amendment mixtures. Phase 2 tests consisted of three sets of columns (2 inch ID), and each set included four individual columns. The four individual columns had the same single type amendment, but with different lengths (6-inch, 12-inch, 18-inch and 24-inch). Similar to the microcosm experiments, no

additional bacteria were added to ensure the only source of perchlorate degraders was from the site soil.

Table 5.3. Summary of column operation conditions

	Influent Perc. (µg/L)	Run time(day)	Velocity(ft/d)
Phase 1[a]	500 ±50	0-127	0.5
• Site soil (control)	500 ±50	0-122	0.5
• EHC[c]-amended soil/compost/mulch	500 ±50	0-127	0.5
• EOS[d]-amended soil/compost/mulch			
Phase 2[b]	500 ±50	0-45	0.5
• Site soil (control)	500 ±50	46[e]-56	1.0
• EHC[c]-amended soil	500 ±50	57-71	2.0
• EOS[d]-amended soil	500 ±50	72-94	0.5

[a]Phase 1 column size is 6 inch (ID)×24 inch (L)
[b]Sizes of the four parallel columns in phase 2 column are 2 inch(ID) with the lengths of 6 inch, 12 inch, 18 inch and 24 inch at each packing condition
[c]0.1% (w/w) EHC was mixed with biobarrier soil
[d]0.3% (w/w) EOS was mixed with biobarrier soil
[e]Flow rate in EOS-amended soil column was increased to 1 ft/d at Day 27

In the Phase 1 column test, three parallel columns were packed with the following materials: (1) Control column with site soil only; (2) EHC (0.1% w/w)-amended soil/compost/mulch; (3) EOS (0.3% w/w)-amended soil/compost/mulch. Each reactor consisted of a polyvinyl chloride (PVC) pipe (6-inch ID; 24 in length) with sampling ports every 6-inch on the side. Before packing the medium into the columns, compost and mulch were hand-mixed with site soil. Next, the appropriate amount of EOS and EHC were weighed from the original packs based on the total mass of

soil/compost/mulch. To ensure EOS was thoroughly and evenly mixed with the soil/compost/mulch, the weighed EOS was first mixed with 100 mL of DI water, and then poured as evenly as possible onto the surface of the soil/compost/mulch mixture. Finally the entire EOS- amended soil/compost/mulch medium was hand-mixed to achieve uniformity. Since EHC is a solid compound, it was mixed with soil/compost/mulch directly without adding DI water, and then followed the same manner as EOS- amended soil/compost/mulch. Reactors were packed with a layer of gravel and sand at the bottom, followed by the packing material. A layer of sand was added every 6 inch to assist with sampling. The reactor was operated in an up-flow mode to allow air in the pore space to vent out, and contaminated groundwater was fed into the reactor at a velocity of 0.5 ft/d. Samples were taken from the side ports and effluent periodically for perchlorate, pH, and TOC analysis. Nitrate, nitrite, arsenic, manganese and iron analyses were completed for selected samples.

In the Phase 2 column test, to investigate the perchlorate reduction as a function of travel length and retention time, three sets of PVC columns (2 inch ID) with the lengths of 6-inch (0.15 m), 12-inch (0.30 m), 18-inch (0.45 m) and 24-inch (0.60 m) were developed by using the following packing materials: (1) control with site soil only; (2) EOS (0.3% w/w)-amended soil; and (3) EHC (0.1% w/w)-amended soil. At the start-up period, all the columns were operated in an up-flow mode at a flow rate of 0.5 ft/d. The flow rate was increased to 1.0 ft/d, and later 2.0 ft/d depending on the treatment performance. Effluent samples were taken periodically for perchlorate, pH, nitrate and TOC analysis.

5.3 ANALYSIS

Perchlorate concentration was analyzed using a Dionex 1000 Ion chromatograph (Dionex Corp.,Sunnyvale,CA,USA) with an IonPac® AS 16 analytical column (4×250 mm) and AG 16 guard column (4×50 mm). Nitrate was determined by an IonPac® AS 14 analytical column (4×250 mm) and AG 14 guard column (4×50 mm). The detection limits for perchlorate and nitrate were 4 µg/L and 100 µg/L (as N), respectively. In addition, all the other analyses for the parameters listed in Table 5.4 were conducted according to the EPA standard methods.

5.4 RESULTS AND DISCUSSION

The composition of the source area and biobarrier perchlorate contaminated water and soil is summarized in Table 5.4.

Table 5.4 Composition of the source area and biobarrier perchlorate contaminated water and soil

	Water sample (mg/L)		Soil sample (mg/kg)	
	Source	**Biobarrier**	**Source**	**Biobarrier**
Perchlorate	64.1	0.505	18	0.026
pH (unitless)	7.76	7.71	8.8	9.00
Total Organic Carbon	2.62	1.01	28.1	<10.7
Hardness (as $CaCO_3$)	240	242	-	-
Total Dissolved Solids	839	990	-	-
Total Kjeldahl Nitrogen	0.462	0.35	8.37	48.6
Nitrate (as N)	8.6	8.2	-	-
Total Phosphorus	0.107	0.0245	0.869	0.278
Total Sulfur	20.1	58.5	-	-
Chloride	305	186	-	-
Sulfate	55.6	176	18.7	40.6
Calcium	73.5	81.0	-	-
Magnesium	13.7	9.64	-	-
Potassium	3.47	0.733	-	-
Sodium	187	240	-	-
Arsenic	<0.0400	<0.0400	<4.63	< 4.29
Iron	<0.0666	<0.0400	22,300	13,900
Manganese	0.0325	<0.0300	417	231

5.4.1 Microcosm Tests Results

5.4.1.1 High Concentration Source Area Treatment

5.4.1.1.1 Source Area Groundwater Chemistry

As shown in Table 5.4, perchlorate in both source area groundwater and soil samples were 2 to 3 orders of magnitude higher than biobarrier samples. The source area groundwater contained approximately 64,000 μg/L perchlorate. The pH of the groundwater and soil were 7.8 and 8.8. Nitrogen was present mostly in the form of nitrate, which was 8.6 mg/L as N in groundwater sample. The total organic carbon concentrations were 2.62 mg/L in the groundwater sample and 28.1 mg/kg in the soil sample. Compared with the high levels of perchlorate in the groundwater, the organic carbon concentration was not high enough to meet the electron donor demand for perchlorate biological degradation. In addition, dissolved oxygen and nitrate will compete with perchlorate for the electron donor, so more carbon will be required in the biological treatment process.

Addition of substrate could lead to mobilization of certain naturally occurring constituents such as arsenic, iron, and manganese. This may have a negative effect on water quality after implementing the biological treatment. To evaluate the water quality change after substrate addition, arsenic, iron and manganese were also measured. Arsenic, iron and manganese were present the groundwater at trace levels. Iron and manganese, typical of most soils, were present in the soil samples. The presence of sulfate in groundwater and soil samples (approximately 56 mg/L and 19 mg/kg,

respectively) may be beneficial, as reduced sulfur species (sulfides) resulting from biotreatment can enhance precipitation of some soluble metals.

With respect to nutrients, Total Kjeldahl Nitrogen (TKN), which is the sum of free-ammonia and organic nitrogen compounds, was measured in groundwater and soil samples. The TKN level was 8.4 mg/kg and 0.46 mg/L in soil and groundwater, respectively. Total phosphorus was detected at trace levels in both soil and groundwater samples. These results indicate the macronutrients were present at relatively low levels and additional nutrients might be needed to support the growth of perchlorate degraders.

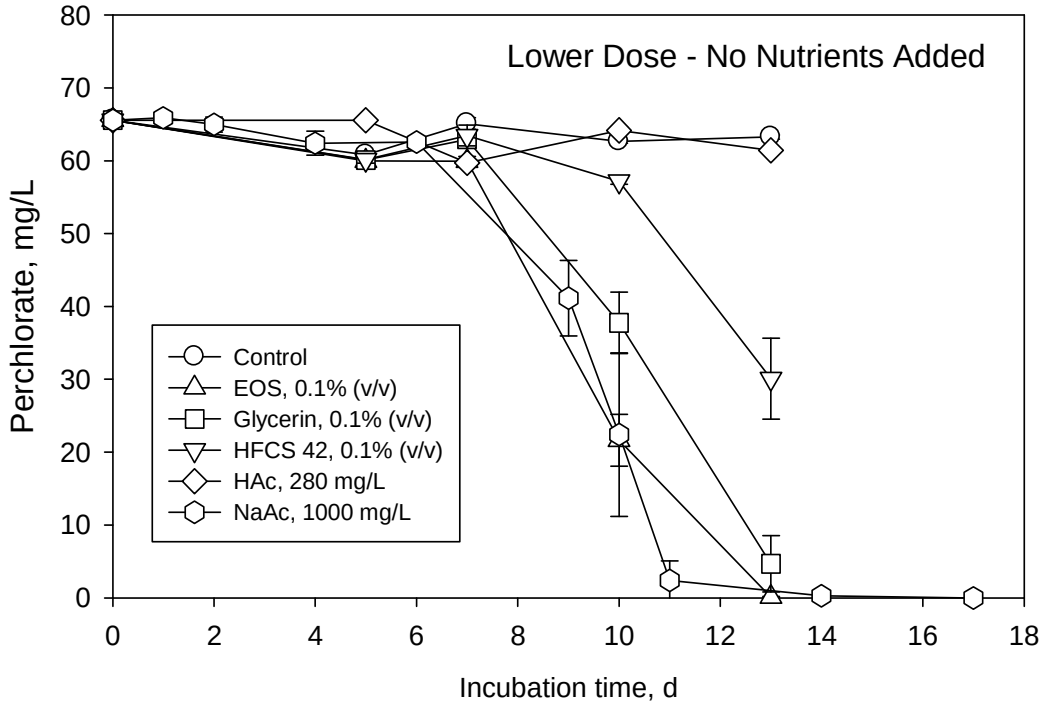
5.4.1.1.2 Impacts of Amendment Dosages and Nutrient Addition on Source Area Groundwater Bioremediation

Source area microcosm results are reported in Figure 5.2 through 5.5. In general, perchlorate degradation will experience a lag time due to the competing electron acceptors dissolved oxygen and nitrate. Reduction of perchlorate will start after the oxidation reduction potential (ORP) decreases to -150 mV [98], which requires the depletion of dissolved oxygen and nitrate. As can be seen from Figure 5.2, without any nutrient addition, complete perchlorate reduction was observed within 17 days in the microcosms receiving EOS, glycerin and NaAc at both the lower and higher dosages. For EOS, complete perchlorate removal was achieved 3 days earlier at the higher dosage compared to the lower dosage. There was no difference in perchlorate degradation in terms of initiation time or removal rate (see the slope of the curve) for glycerin microcosms at lower and higher dosages. For NaAc, the initiation of perchlorate

degradation at the lower dosage occurred earlier than the higher dosage, and complete perchlorate removal was reached three days earlier for the lower dosage. Surprisingly, the higher dosage was harmful rather than beneficial for HFCS treatment. While the lower dosage showed 50 ± 9.2% removal, the higher dosage had 6.8 ± 1.1 % removal instead. The reason for performance drop after increasing HFCS dosage can be contributed to the pH. At the lower dosage, the final pH at Day 13 was 7.0 ± 0.01, which was similar to the starting pH of 7.1 ± 0.04. But at the higher dosage of HFCS, the final pH dropped to 5.7 ± 0.06, which is not favorable for perchlorate bioremediation [99]. Similar explanation can be applied to HAc treatment. The addition of HAc resulted in pH decreasing from 7.6 ± 0.20 to 4.7 ± 0.04 in the solution at the beginning of the tests.

After adding 1 g/L $(NH_4)_2HPO_4$ as an extra nutrient source, the reduction of perchlorate initiated one day earlier compared with no nutrient addition in the lower dosage EOS, glycerin and NaAc microcosms, and near 100% removal was observed in those tests within 10 days. However, in the higher dosages, only EOS treatment neared complete removal of perchlorate. For glycerin, reduction of perchlorate was stabilized at 90.6% until the end of the test. For NaAc, there was a longer delay at higher dosage. No removal was noticed in the HAc microcosm at either lower or higher dosages for the same pH problem as when no nutrients were added. Limited perchlorate reduction was also observed using high fructose corn syrup (HFCS 42) at either dose, with slightly more removal at the higher dose. In any of these cases, the differences, however, are not important in terms of the desired perchlorate treatment objective.

To determine whether nutrients should be added, isolated microcosm results for EOS and glycerin are summarized in Figure 5.4 and Figure 5.5, respectively. At both lower and higher dosages, the addition of nutrient has limited effect on perchlorate reduction using EOS or glycerin. The benefits of nutrient addition were only reflected in decreasing the lag time by 1 to 2 days. Complete removal occurred with or without nutrient addition within a timeframe ranging from 7 to 13 days. Hence, no nutrients were added in the column tests.



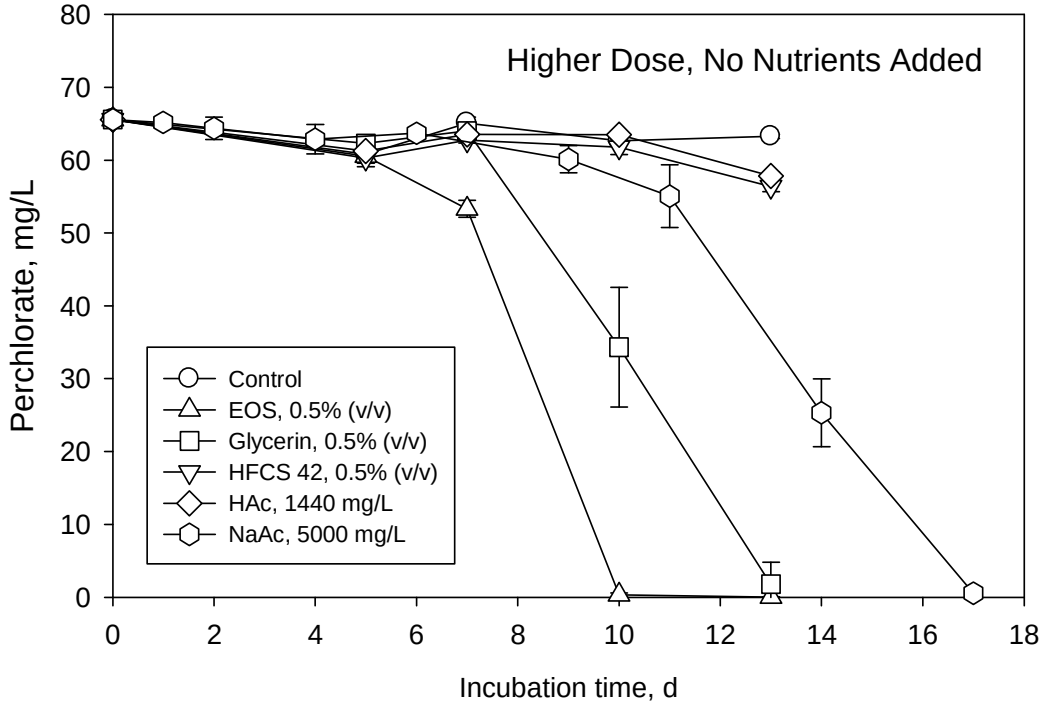


Figure 5.2 Source area groundwater microcosms, no nutrients added (Top: Low dose; Bottom: High Dose)

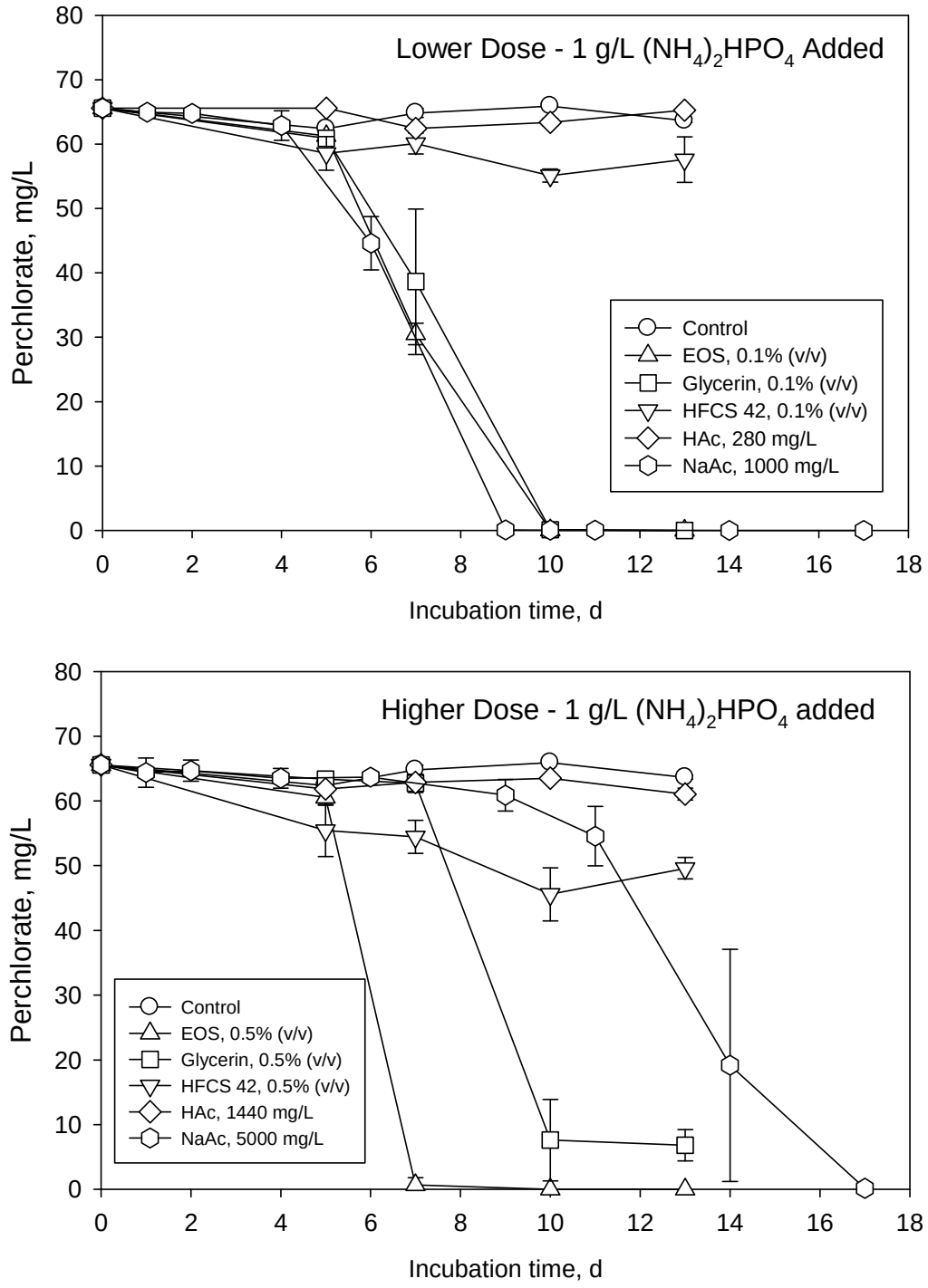
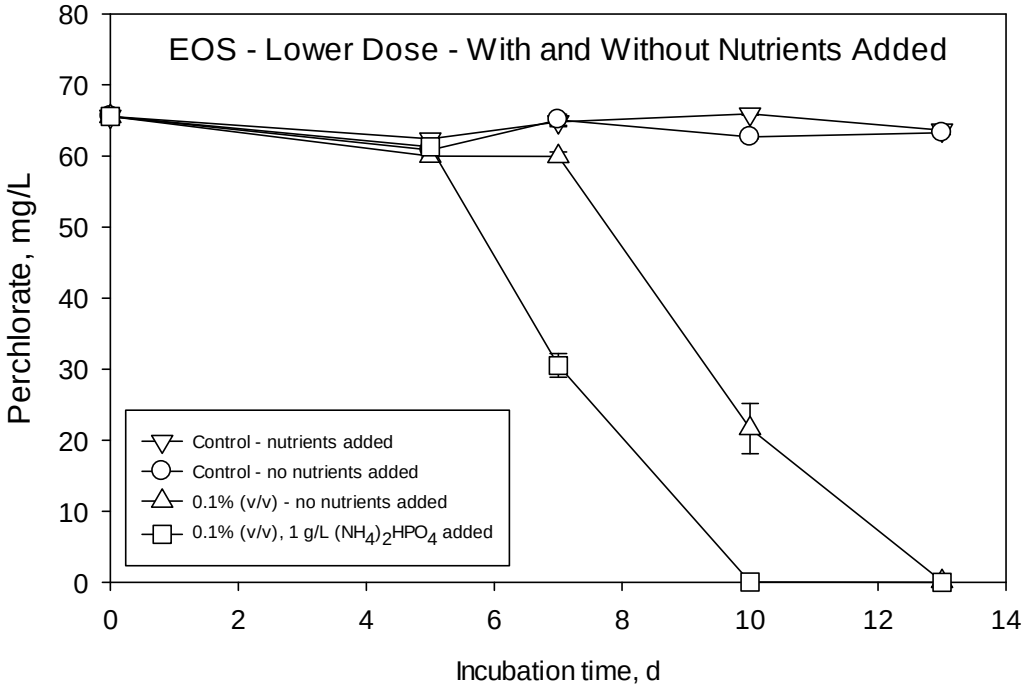


Figure 5.3 Source area groundwater microcosms, diammonium phosphate added (Top: Low dose; Bottom: High Dose)



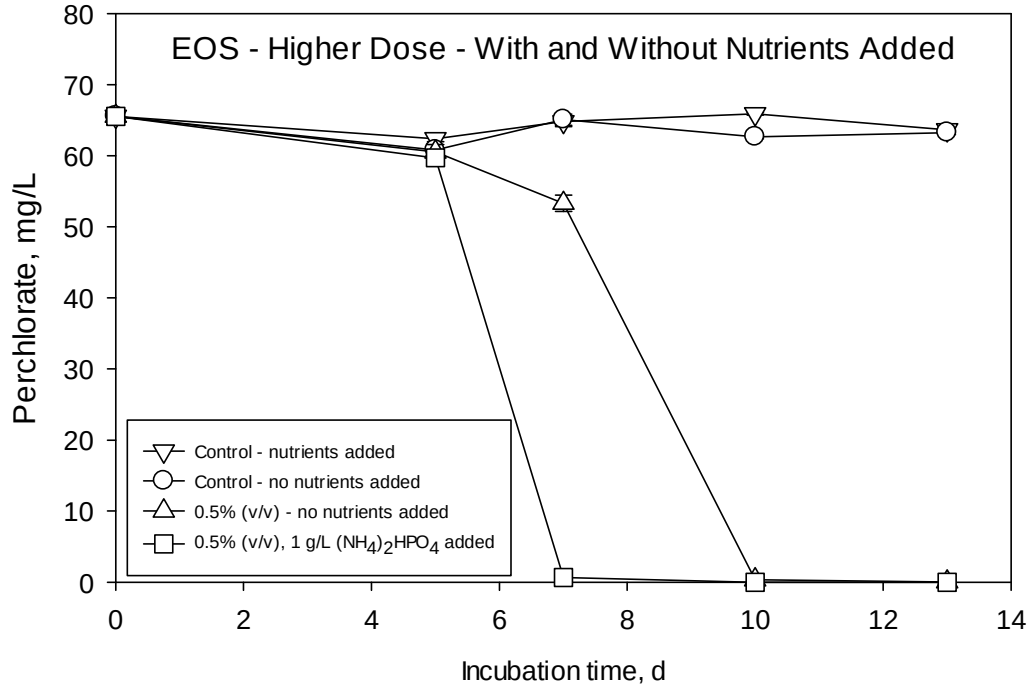
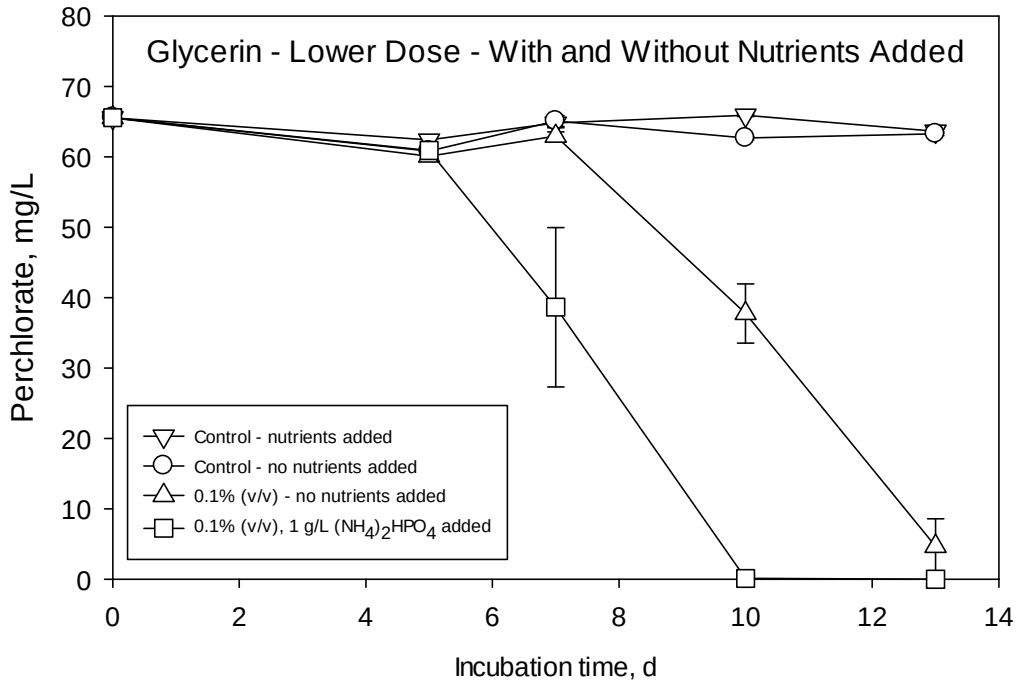


Figure 5.4 Perchlorate reduction in EOS-amended source area microcosms (Top: Low dose; Bottom: High Dose)



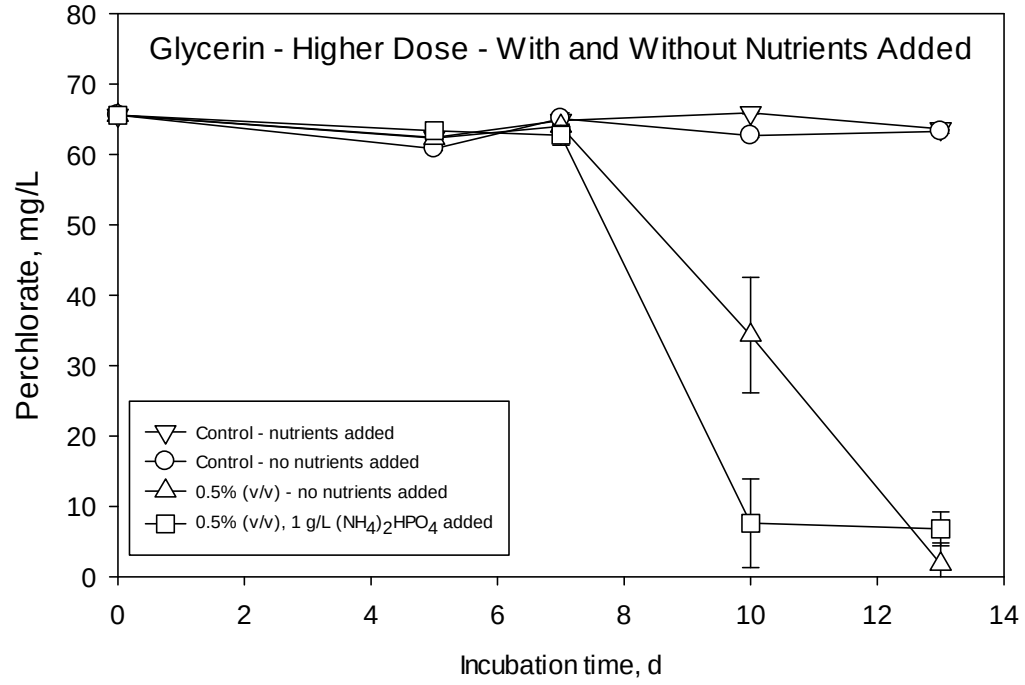
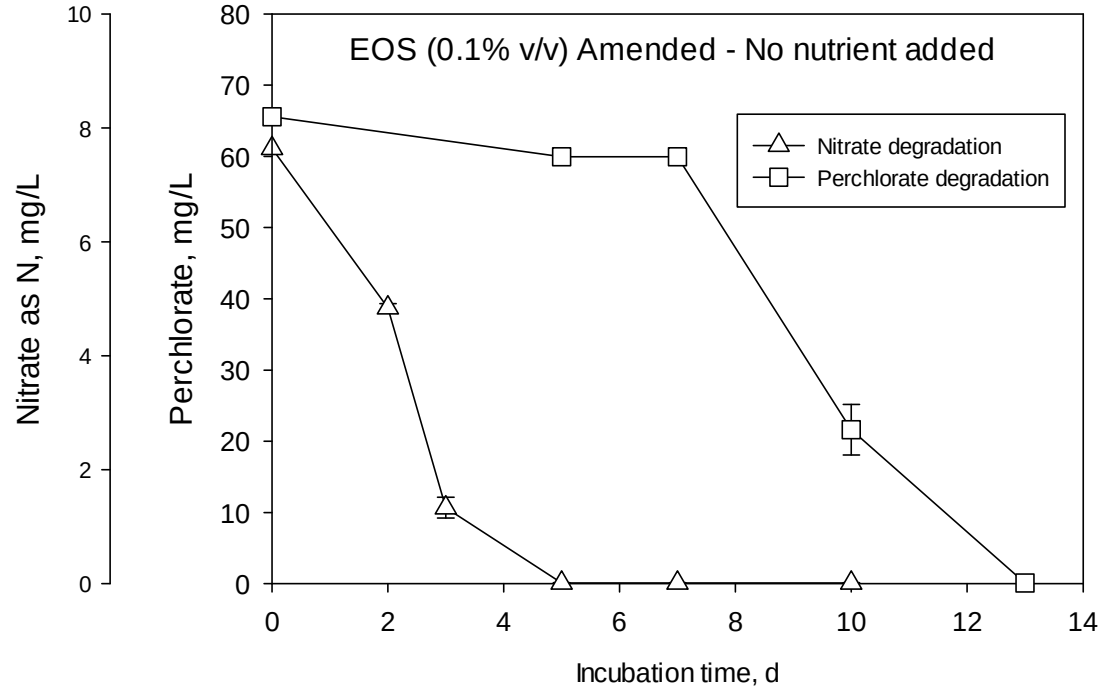


Figure 5.5 Perchlorate reduction in glycerin amended source area microcosms (Top: Low dose; Bottom: High Dose)

5.4.1.1.3 Reduction of Nitrate

Results of nitrate reduction in EOS and glycerin receiving microcosms are reported in Figure 5.6 and Figure 5.7. In the absence of added nutrients, complete removal of nitrate occurred within 5 days and 7 days at both lower and higher dosages in EOS and glycerin treatments, respectively. There was no obvious difference on treatment performance between lower and higher substrate dosage. As expected, nitrate reduction precedes perchlorate reduction.



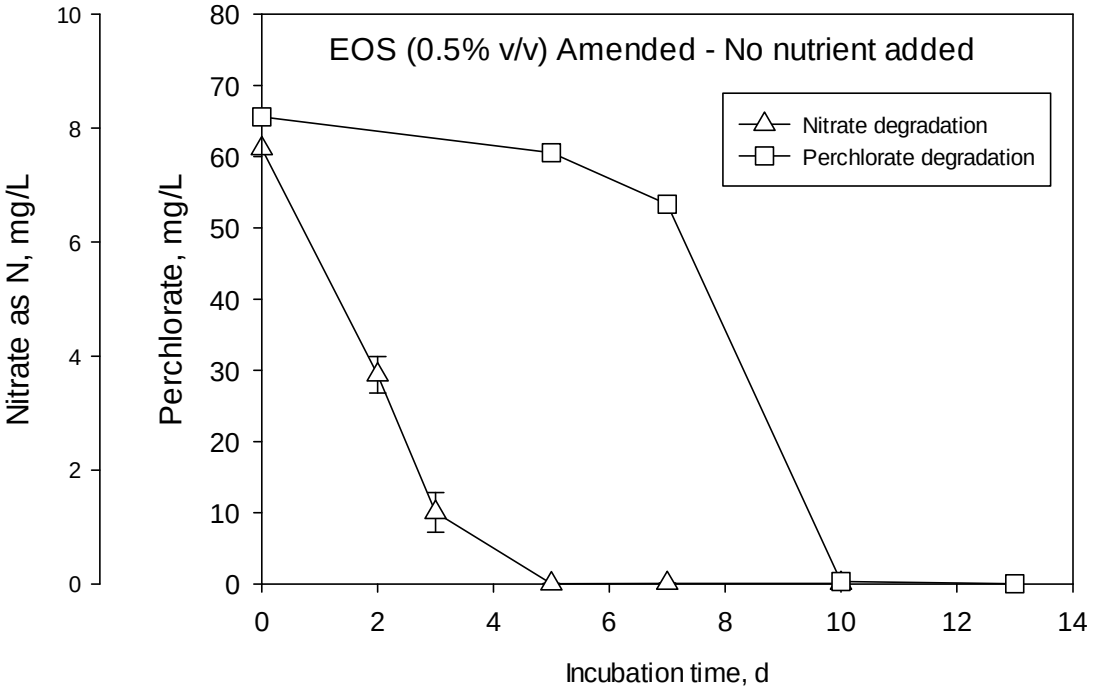


Figure 5.6 Nitrate and perchlorate reduction in EOS-amended source area microcosms

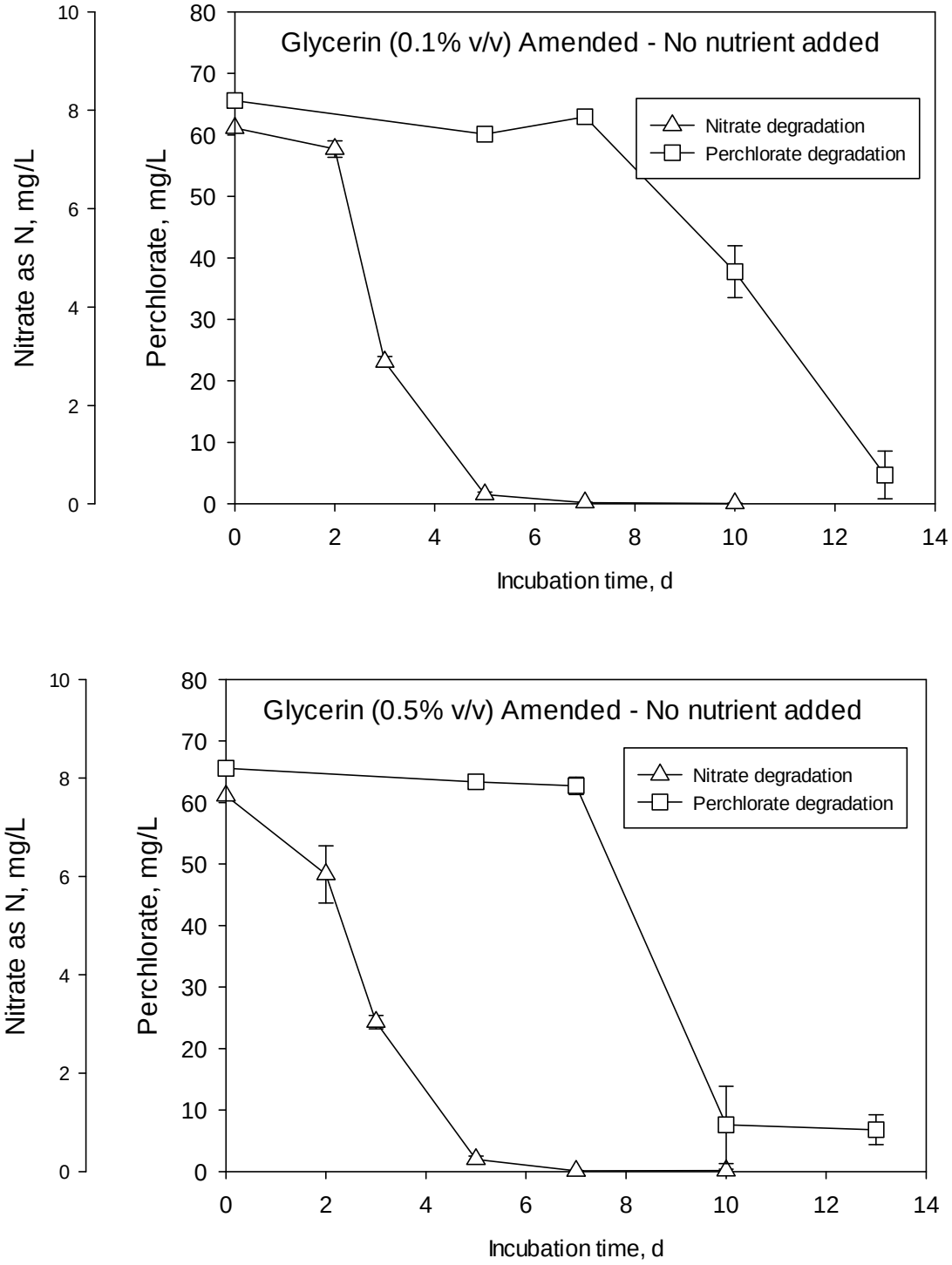


Figure 5.7 Nitrate and perchlorate reduction in glycerin-amended source area microcosms

Figure 5.8 illustrates the sequence of utilization of electron acceptors [98]. In addition to perchlorate, oxygen, nitrate and sulfate are also electron acceptors typically found in the natural environment. As can be seen from the figure, dissolved oxygen reduction and denitrification occur earlier than perchlorate reduction. The favorable ORP for perchlorate reduction is between 0 and -150 mV. Reduction of perchlorate initiated after reaching complete nitrate removal (Figure 5.6 and Figure 5.7)

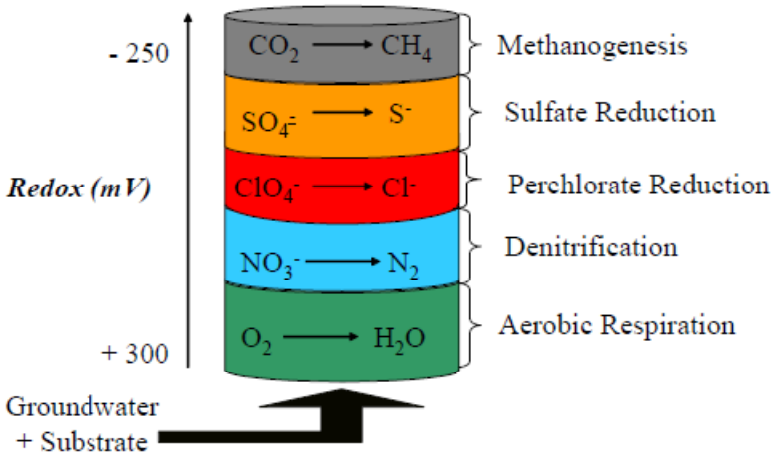


Figure 5.8 Utilization of electron acceptors

5.4.1.1.4 Water Quality Changes

Apart from the primary contaminant (perchlorate) being treated, the secondary water quality, which resulted from the substrate addition, should be carefully considered before implementing anaerobic bioremediation treatment. Because biodegradation of perchlorate can only happen under reducing conditions, the metals such as arsenic, iron and manganese existing either from the natural environment or the addition of substrate will become more soluble, and thus the mobility of these metals will be increased. In addition, nitrite, which is regulated by EPA due to its adverse health effects, may be

formed as an intermediate product of nitrate reduction. Initial and final water quality analyses for these constituents are provided in Tables 5.5, Table 5.6 and Table 5.7.

As expected, no nitrite was formed during reduction of nitrate treated with EOS and glycerin. But it was found in the control microcosms at the end of the test. Arsenic, iron and manganese were all below the detection limit in the control and glycerin microcosm, but minor solubilzation of manganese appeared to occur at the reducing conditions in the EOS microcosms (Table 5.6).

Table 5.5 Initial-final water analyses for control microcosms

Parameter	MDL, mg/L	Without Nutrient		With Nutrient	
		Initial, mg/L	Final, mg/L	Initial, mg/L	Final, mg/L
Nitrite as N	0.090	ND	1.2	ND	1.8
Arsenic	0.070	ND	ND	ND	ND
Iron	0.15	ND	ND	ND	ND
Manganese	0.070	ND	ND	ND	ND

Table 5.6 Initial-final water analyses for EOS-amended microcosms

Parameter	MDL, mg/L	Without Nutrient		With Nutrient	
		Initial, mg/L	Final, mg/L	Initial, mg/L	Final, mg/L
Nitrite as N	0.090	1.7	ND	4.7	ND
Arsenic	0.070	ND	ND	ND	ND
Iron	0.15	ND	ND	ND	ND
Manganese	0.070	0.083	0.39	ND	0.22

Table 5.7 Initial-final water analyses for glycerin-amended microcosms

Parameter	MDL, mg/L	Without Nutrient		With Nutrient	
		Initial, mg/L	Final, mg/L	Initial, mg/L	Final, mg/L
Nitrite as N	0.090	0.57	ND	1.1	ND
Arsenic	0.070	ND	ND	ND	ND
Iron	0.15	ND	ND	ND	ND
Manganese	0.070	ND	ND	ND	ND

5.4.1.2 Low Concentration Biobarrier Treatment

5.4.1.2.1 Biobarrier Groundwater Chemistry

As can be seen in Table 5.4, the initial perchlorate concentration was 505 µg/L and 26 µg/kg in the groundwater and soil, respectively. The pH was 7.7, which is favorable for biological treatment. The total organic carbon level was low, which may require extra addition of organics. Nitrate is present (8.2 mg/L as N) and will compete for the electron donor and organic carbon with perchlorate. Low levels of TKN and phosphorus in the water sample may not be enough to support microorganism growth. Nutrient-amendment was considered when conducting the microcosm experiments.

5.4.1.2.2 Impacts of Amendment and Nutrient Addition on Biobarrier Groundwater Bioremediation

The results of perchlorate reduction using different electron donors are shown in Figure 5.9 and Figure 5.10. In the biotic controls, without the addition of an electron donor, there was no removal of perchlorate either in the absence or presence of nutrients. For both the treatments with and without nutrient addition, the best performance among all the electron donors chosen in this study was EHC (0.001g/g soil) treatment, which achieved 100% removal efficiency after 5 days. Complete removal was achieved in 7 days with EOS (0.003g/g soil) and 64.8% removal efficiency was achieved after 8 days with compost/mulch amended soil.

$(NH_4)_2HPO_4$, which will supply additional nutrients to promote microorganism growth in barren conditions, was chosen here because it is commonly used as fertilizer and yeast nutrient. As can be seen in Table 5.8, although the addition of nutrients did not enhance the removal rate of EHC treatment, it significantly increased the removal rate for

EOS and compost treatment. For example, the compost/mulch removal rate was increased from 39.76 to 90.05 mg/L/d (Table 5.8).

Table 5.8 Perchlorate removal rate with the presence and absence of nutrients using different electron donors

Electron donor	Reduction rate (µg/L/d)	
	w/o Nutrients	w/ Nutrients
EOS	142.0	187.0
EHC	314.2	262.9
Compost/Mulch	39.76	90.05

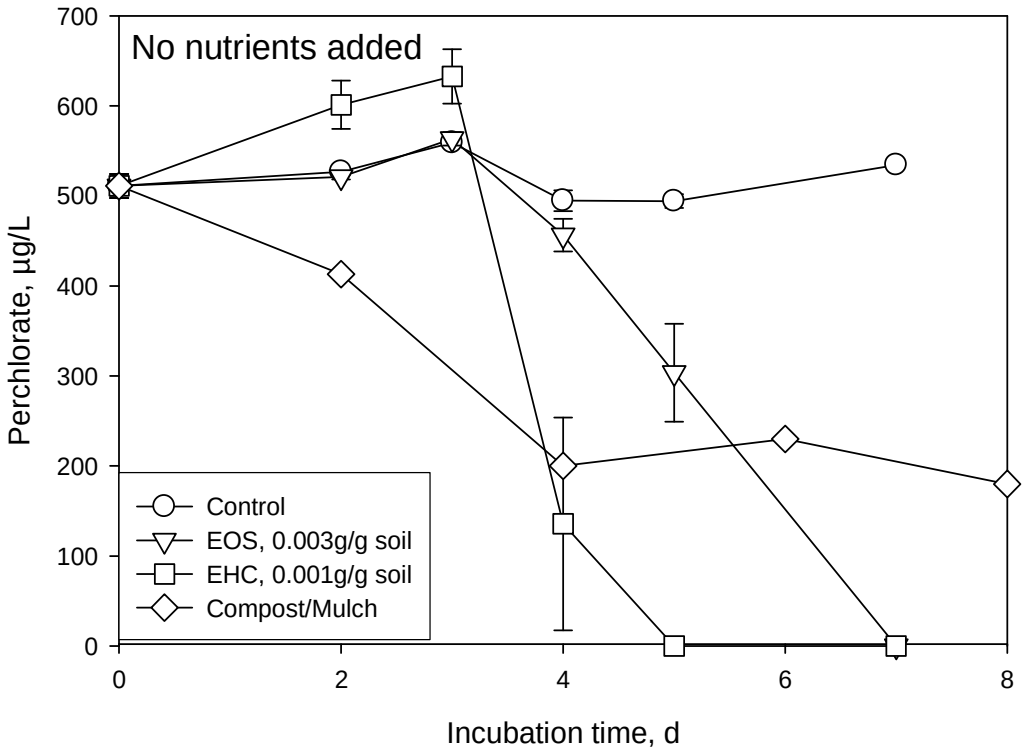


Figure 5.9 Perchlorate reduction in biobarrier microcosms with no nutrients added

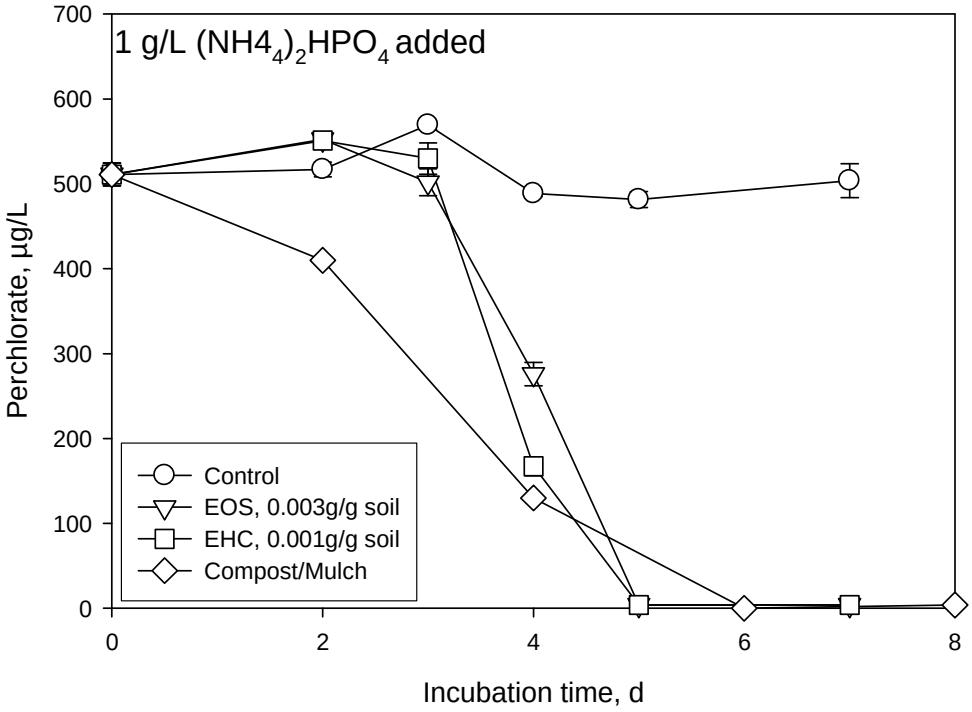


Figure 5.10 Perchlorate reduction in biobarrier microcosms with 1 g/L $(NH_4)_2HPO_4$ added

5.4.1.2.3 Impacts of Nitrate Presence

Besides perchlorate, nitrate is another potential electron acceptor. As shown in Figure 5.11 and 5.12, unlike perchlorate, nitrate removal in both controls with nutrient absence and presence was observed. There is a possibility that the naturally existing organic matter in the soil can be utilized by the denitrifiers to remove nitrate. In all the other three amended treatments, 100% removal of nitrate was achieved within four days or less. The results were similar to the findings of other researchers [22, 100, 101], specifically that nitrate competed for the electron donor with perchlorate, and perchlorate removal was not initiated until most of the nitrate was degraded. The addition of 1 g/L $(NH_4)_2HPO_4$ did not strongly impact EHC and compost/mulch treatments, except for

increasing the nitrate removal efficiency from 20.2% to 84.5% on EOS treatments at Day 2.

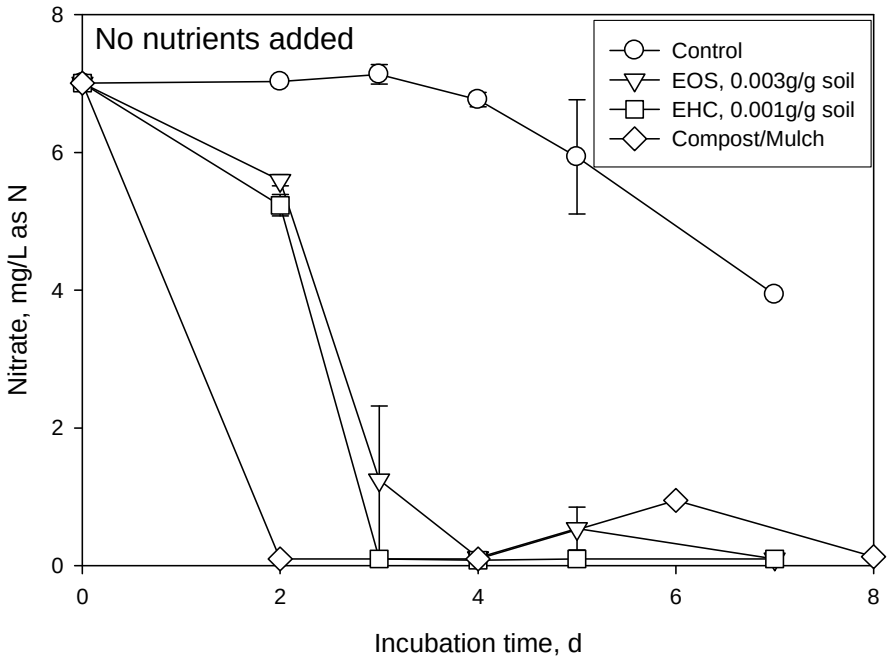


Figure 5.11 Nitrate reduction in biobarrier microcosms with no nutrients added

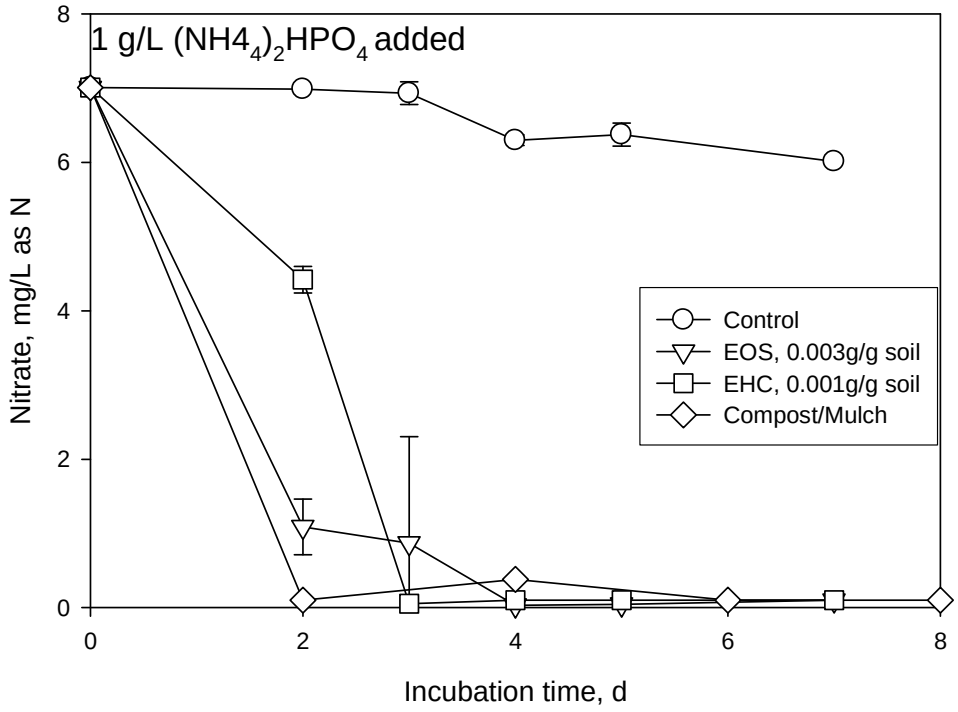


Figure 5.12 Nitrate reduction in biobarrier microcosms with 1 g/L $(NH_4)_2HPO_4$ added

5.4.2 Column Tests Results

5.4.2.1 High Concentration Source Area Groundwater Column Tests

Source area ground water column tests results are summarized in Figure 5.13 through Figure 5.17. Perchlorate concentrations in the influent and effluent after 6-inches, 12-inches, 18-inches and 24-inches of column length are shown. As expected, there was no concentration change in all lengths of control columns during the entire operation time (Figure 5.13), which indicated no natural attenuation occurred. In general, the natural groundwater has a positive ORP. Depletion of dissolved oxygen causes a reduction in ORP and then nitrate or perchlorate degradation can take place.

In the EOS-amended soil columns (Figure 5.14), perchlorate effluent concentration in the 6-inch column slowly decreased in the first two weeks. The reduction of perchlorate reached to a maximum of 45% on Day 16, then maintained about 31% removal efficiency for another 6 weeks. After Day 66, little or no reduction was observed in 6-inch column. The 12-inch, 18-inch and 24-inch columns shared a similar trend in the first 20 days. Perchlorate degradation began slowly over the first two weeks and then proceeded rapidly. After Day 20, perchlorate removal was nearly complete in the 12-inch column, and complete in the 18-inch and 24-inch columns. After about 50 days of operation, perchlorate reduction in the 12-inch column gradually decreased, and stayed at 27% for the rest of the experiment. After about 90 days of operation, a gradual decrease in perchlorate reduction was observed in the 18-inch column, and a final removal of 69% was calculated at the end of experiment. The performance of 24-inch column was relatively stable compared with the other three columns. Perchlorate effluent concentration remained well below 1 mg/L after Day 20 until the end of the experiment. It is more likely the depletion of EOS resulted in the different perchlorate removal performances in these four columns.

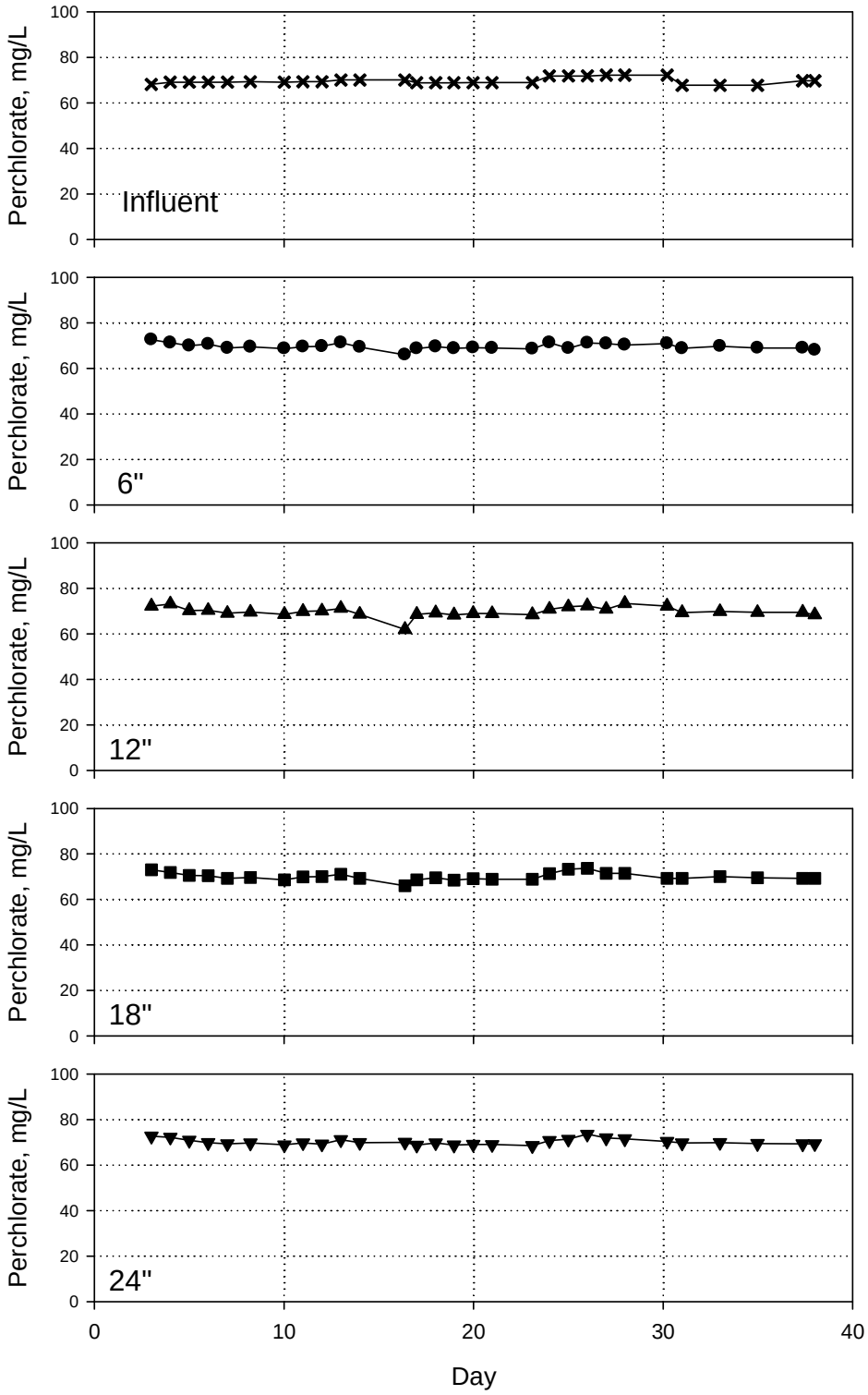


Figure 5.13 Perchlorate reduction in source area control columns

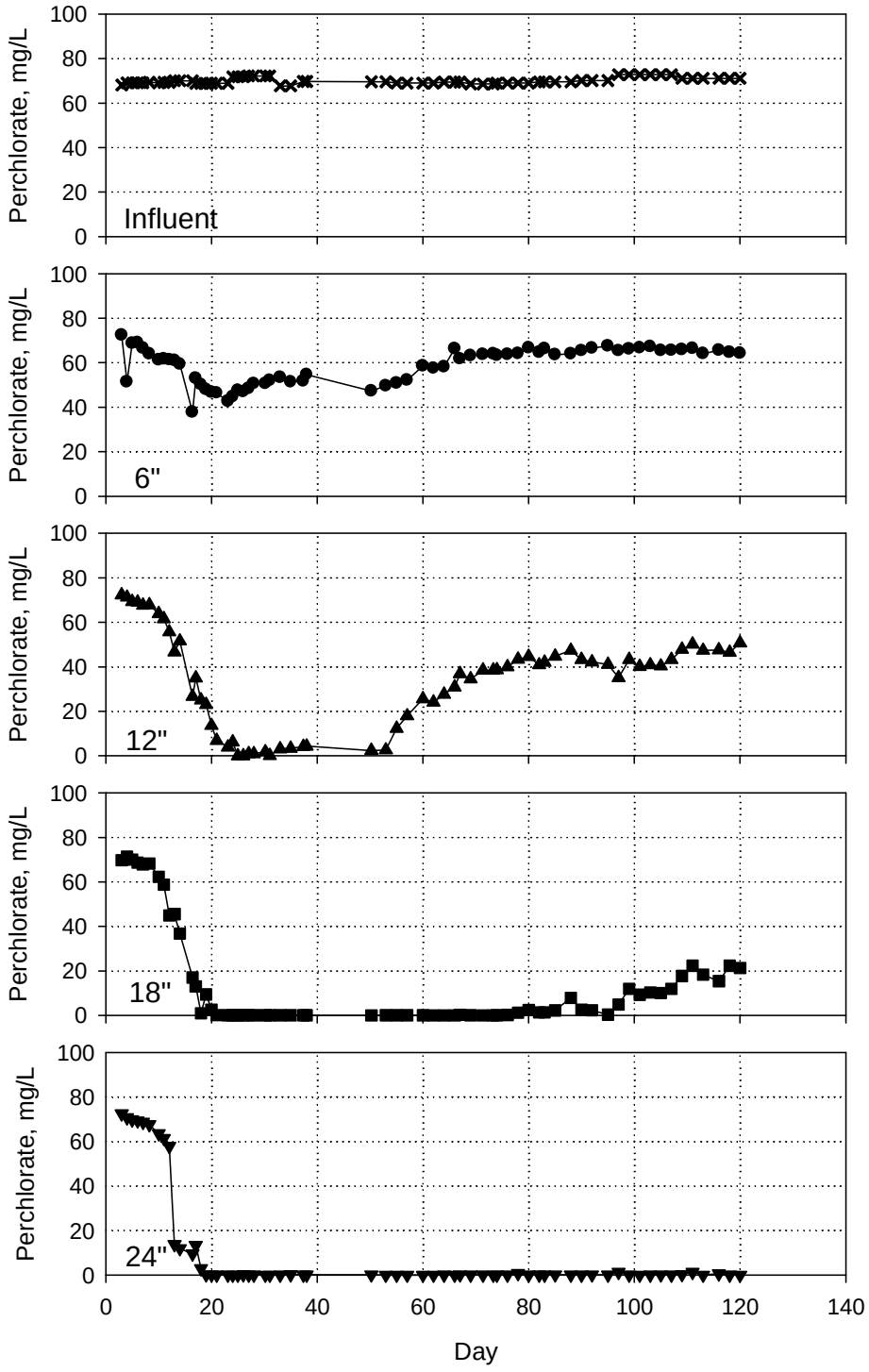


Figure 5.14 Perchlorate reduction in source area EOS-amended columns

Perchlorate concentration profiles at selected sampling times during the column tests are shown in Figure 5.15. Perchlorate reduction remained constant in the 24-inch column after Day 20 whereas perchlorate concentration increased slowly in the 6-inch, 12-inch and 18-inch columns over time. By taking look at the slopes of perchlorate reduction in each length of columns, a decrease in the degradation rate over the 120-day test period can be found (Figure 5.15).

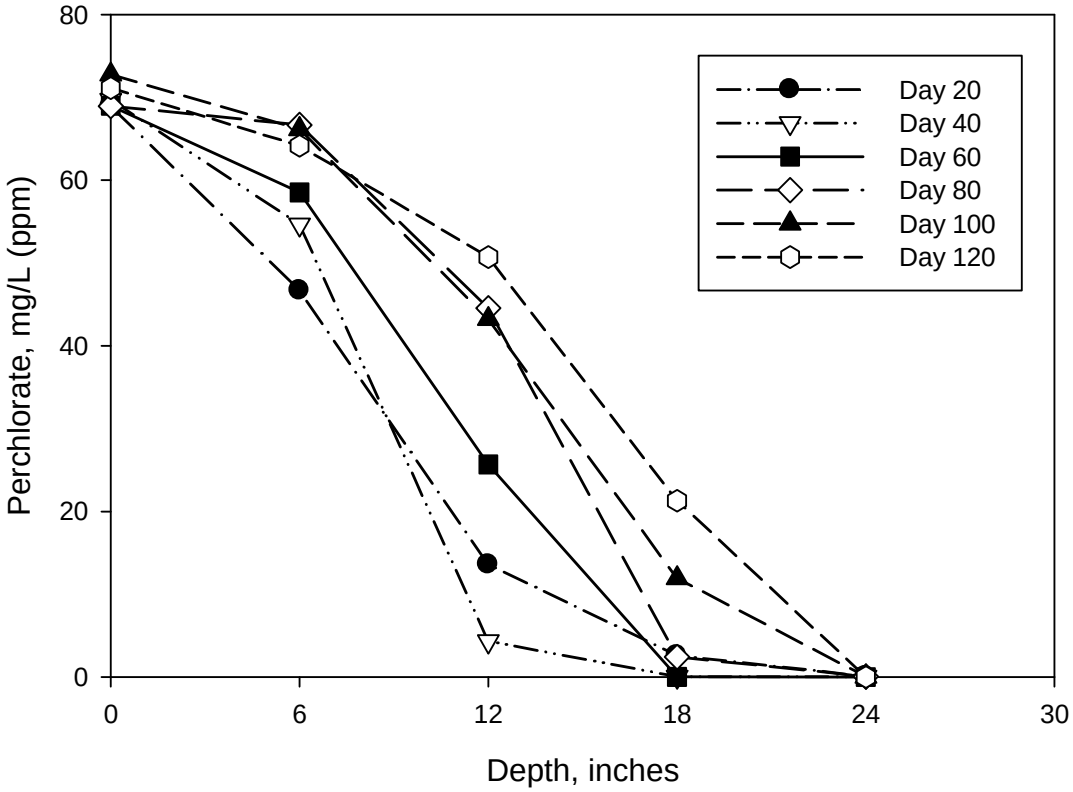


Figure 5.15 Perchlorate reduction profiles in EOS-amended source area columns

Results of perchlorate reduction in glycerin-amended soil are reported in Figure 5.16. Glycerin was mixed with the soil at a concentration of 0.3 % (w/w) prior to being

packed into the column. However, unlike the EOS-amended soil columns, where perchlorate reduction was either initiated or completed within 20 days, the glycerin-amended column had no perchlorate removal during the first 24 days. Thus, instead of injecting substrate to the soil zone, glycerin was added directly into the influent. The concentration of glycerin in the influent varied depending on the treatment performance. There was no concentration change in the influent samples taken from the feed tank during this testing period. Detailed operation conditions are as follows:

- At Day 25, 300 mg/L of glycerin was added into the source area groundwater influent. The concentration of glycerin is equivalent to five times of the stoichiometric amount needed for perchlorate and nitrate degradation. After adding glycerin in the influent, a rapid decrease in perchlorate concentration in the effluent was observed in 12-inch, 18-inch and 24-inch columns, and complete removal of perchlorate was reached at Day 51, Day 32, and Day 32, respectively. Although the perchlorate degradation in the 6-inch column was relatively slow compared with others, a maximum of 86% removal was reached.
- At Day 53, glycerin addition was temporarily stopped. Reduction of perchlorate was completely lost in all the columns.
- At Day 68, 120 mg/L of glycerin was added into the source area groundwater influent. Reduction of perchlorate was resumed in all the columns, and was maintained at above 71% removal in both the 18-inch and 24-inch columns.
- At Day 96, 60 mg/L of glycerin was added into the source area groundwater influent, which is about the stoichiometric amount needed for perchlorate and

nitrate biodegradation. Perchlorate reduction gradually decreased in all the columns until the end of the testing.

Complete reduction of nitrate was observed in the EOS- amended columns during the entire experiment (Figure 5.17). Nitrate reduction in the glycerin-amended columns is shown in Figure 5.18. Prior to Day 14, a decreasing trend of nitrate concentration, or an increasing of nitrate reduction, was observed in all the columns. After that time, nitrate reduction began to decrease, which is in good agreement with perchlorate reduction. As mentioned before, reduction of perchlorate would not be initiated until achieving complete nitrate removal. The trend of nitrate removal revealed that compared with EOS, glycerin is more easily to be biodegraded or leach out from the soil.

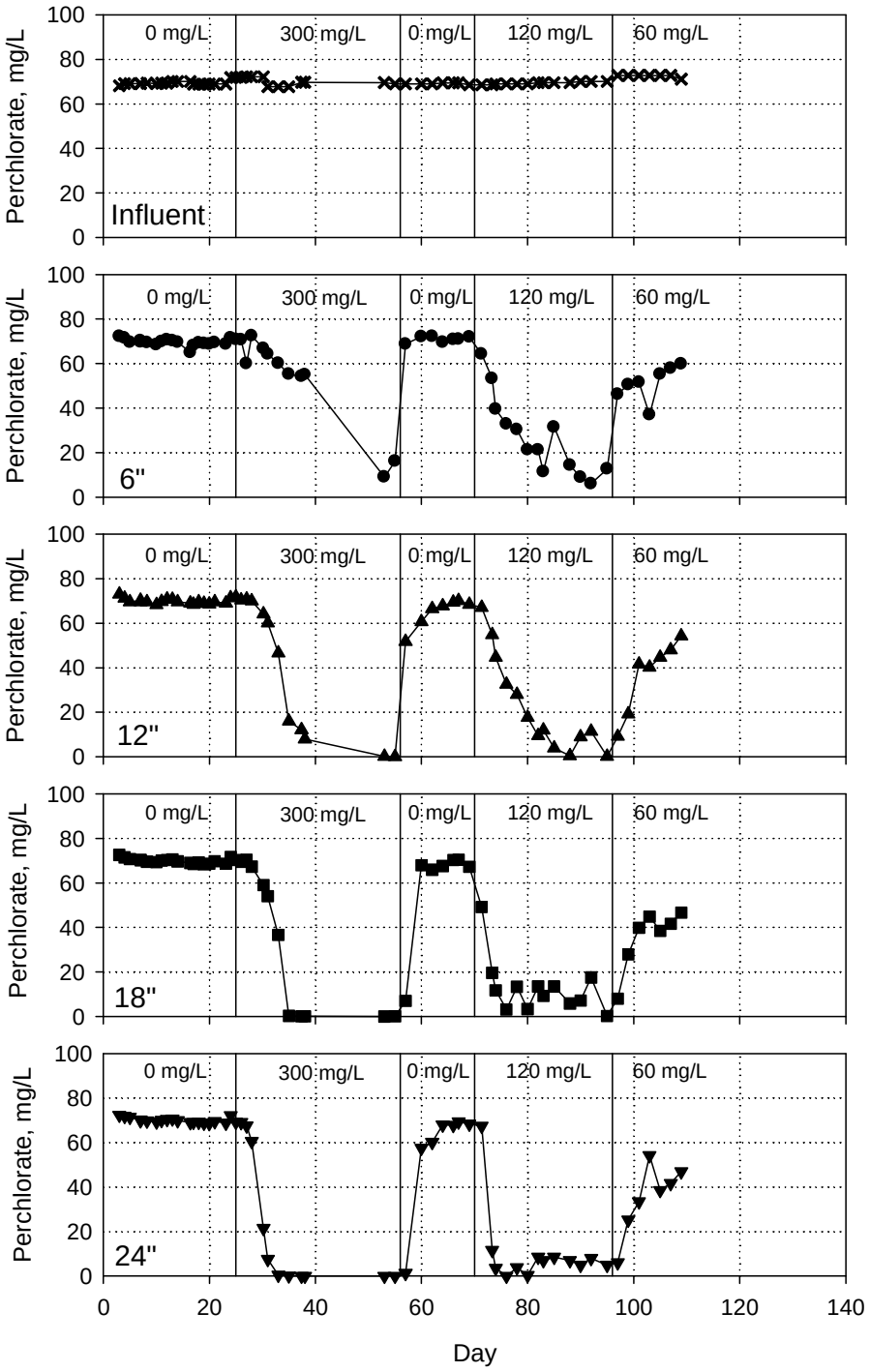


Figure 5.16 Perchlorate reduction in source area glycerin-amended columns. Values across the top of each graph indicate the concentration of glycerin in the influent

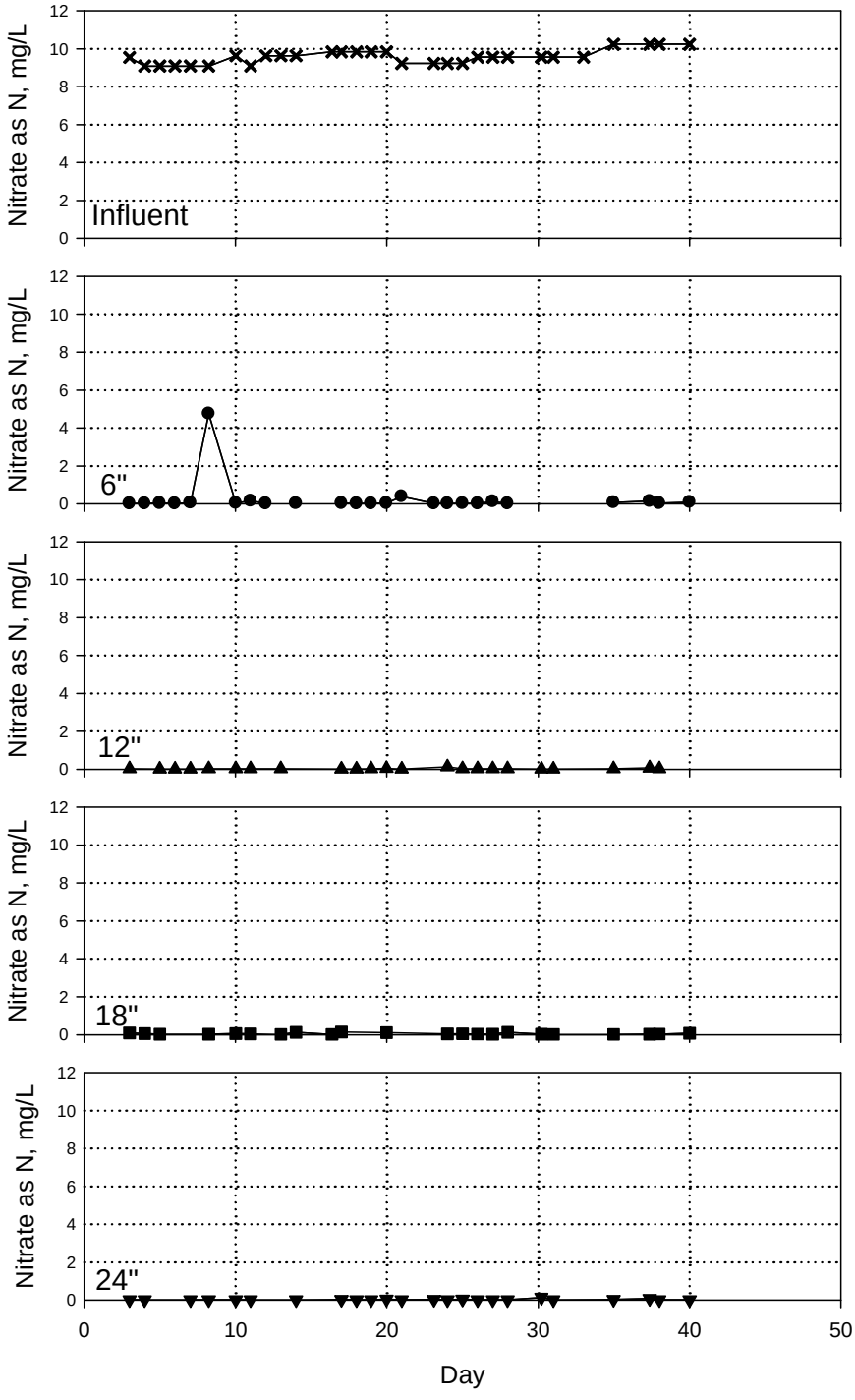


Figure 5.17 Nitrate reduction in source area EOS-amended columns

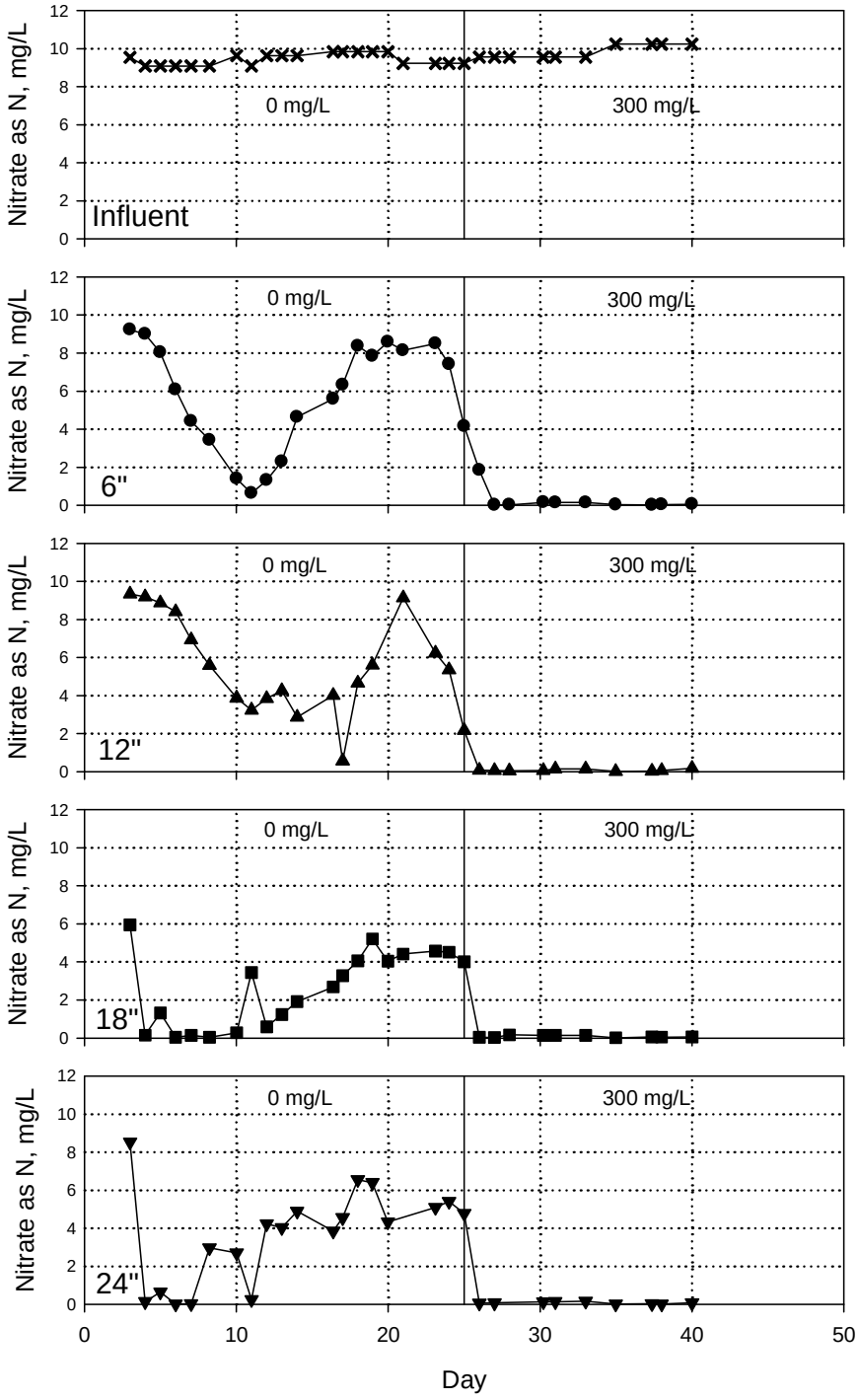


Figure 5.18 Nitrate reduction in source area glycerin-amended columns. Values across the top of each graph indicate the concentration of glycerin in the influent

5.4.2.2 Low Concentration Biobarrier Groundwater Column Tests

5.4.2.2.1 Phase 1 Column Test.

The performance of the EOS-amended soil/compost/mulch and EHC-amended soil/compost/mulch columns is shown in Figure 5.19. With an inlet perchlorate concentration of 500 ±50 µg/L and retention time of 2 days (assuming the porosity was 50%), perchlorate concentration in the effluent in both treatments was below detection limit after 20 days, and the performance was stable during the remaining experiments. Other than monitoring the perchlorate concentration in the effluent, samples were also taken from the side sampling ports on random days to evaluate perchlorate penetration along the flow direction.

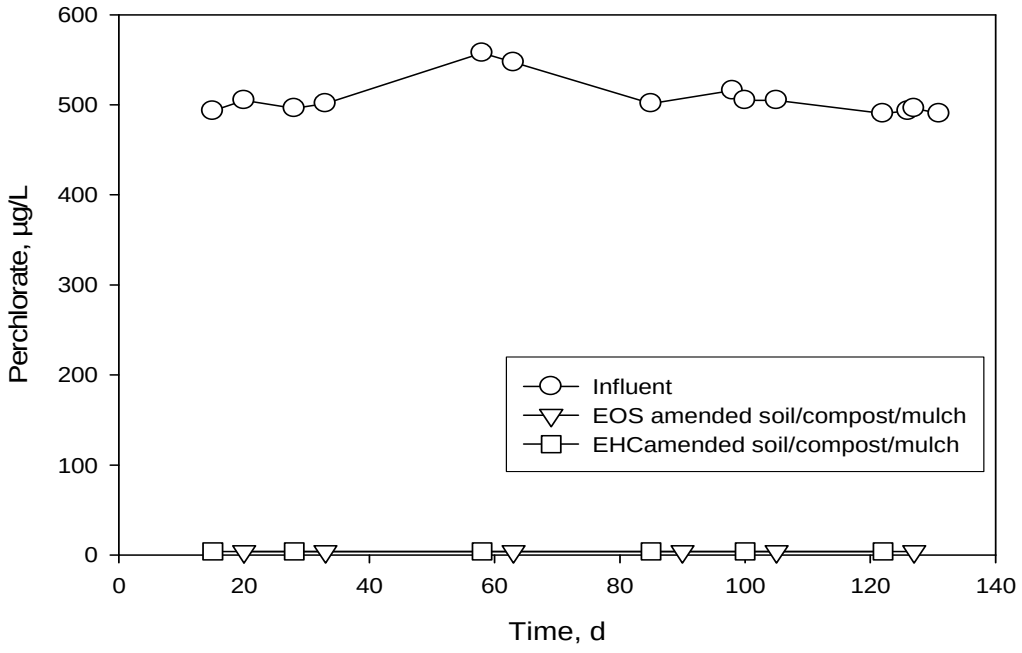


Figure 5.19 Perchlorate reduction in phase 1 Compost/Mulch/Gravel biobarrier columns

The concentration profiles showed within the entire operation period, 67% - 90% removal happened in the first 15 cm of the EOS-amended column (Figure 5.20), and complete removal was achieved when perchlorate migrated to 30 cm. Perchlorate removal in the EHC-amended column was relatively fast. The perchlorate concentration was below the detection limit at the depth of 15 cm or maybe even less (Figure 5.21). It was thought that the dark brown color and high concentration organic matter content in the effluent would be an issue at the start-up period, but the leachate became much lighter at the end of the test, and the TOC concentration decreased from ~1 g/L to 50 mg/L.

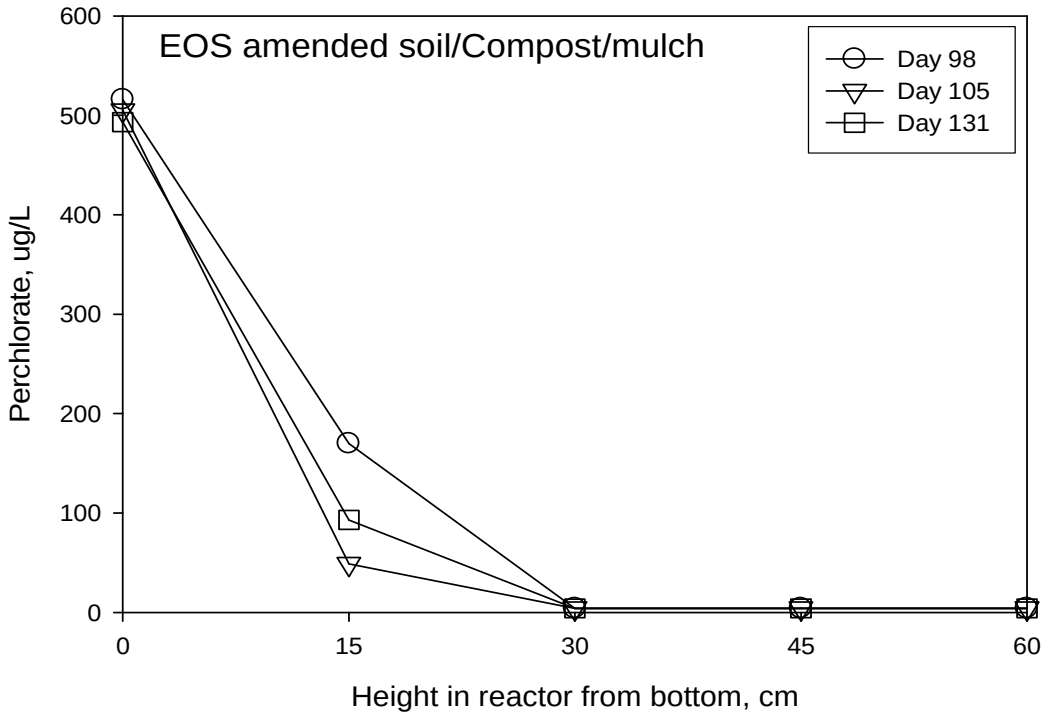


Figure 5.20 Axial concentration profile of perchlorate at selected sampling times in EOS-amended soil/Compost/Mulch treatment.

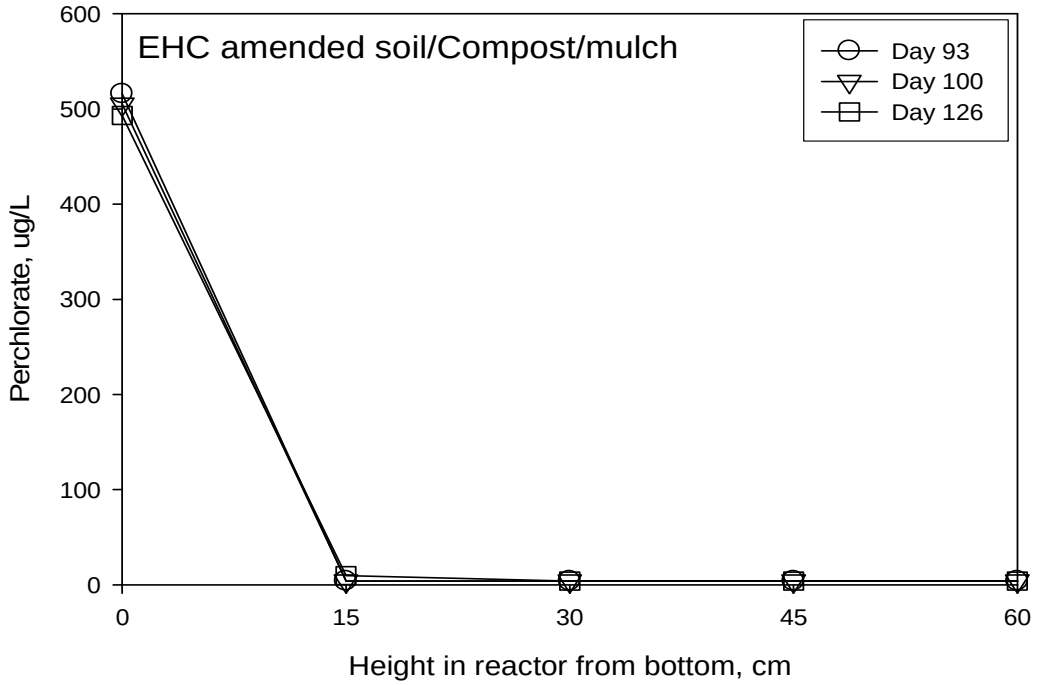


Figure 5.21 Axial concentration profile of perchlorate at selected sampling times in EHC-amended soil/Compost/Mulch treatment.

5.4.2.2.2 Phase 2 Column Test. The performance of the Phase 2 column test is shown in Figure 5.22 and Figure 5.23. A spike in the perchlorate concentrations occurred around Day 38 due to an accidental feeding with an elevated concentration of perchlorate (sample from another site) that was a couple of orders higher than the influent. Despite that error, complete removal was restored within the following two days. The Phase 2 test was 94 days in length. Perchlorate was reduced from 500 ± 50 µg/L to different levels depending on the operation flow rates, or in other words, the retention time.

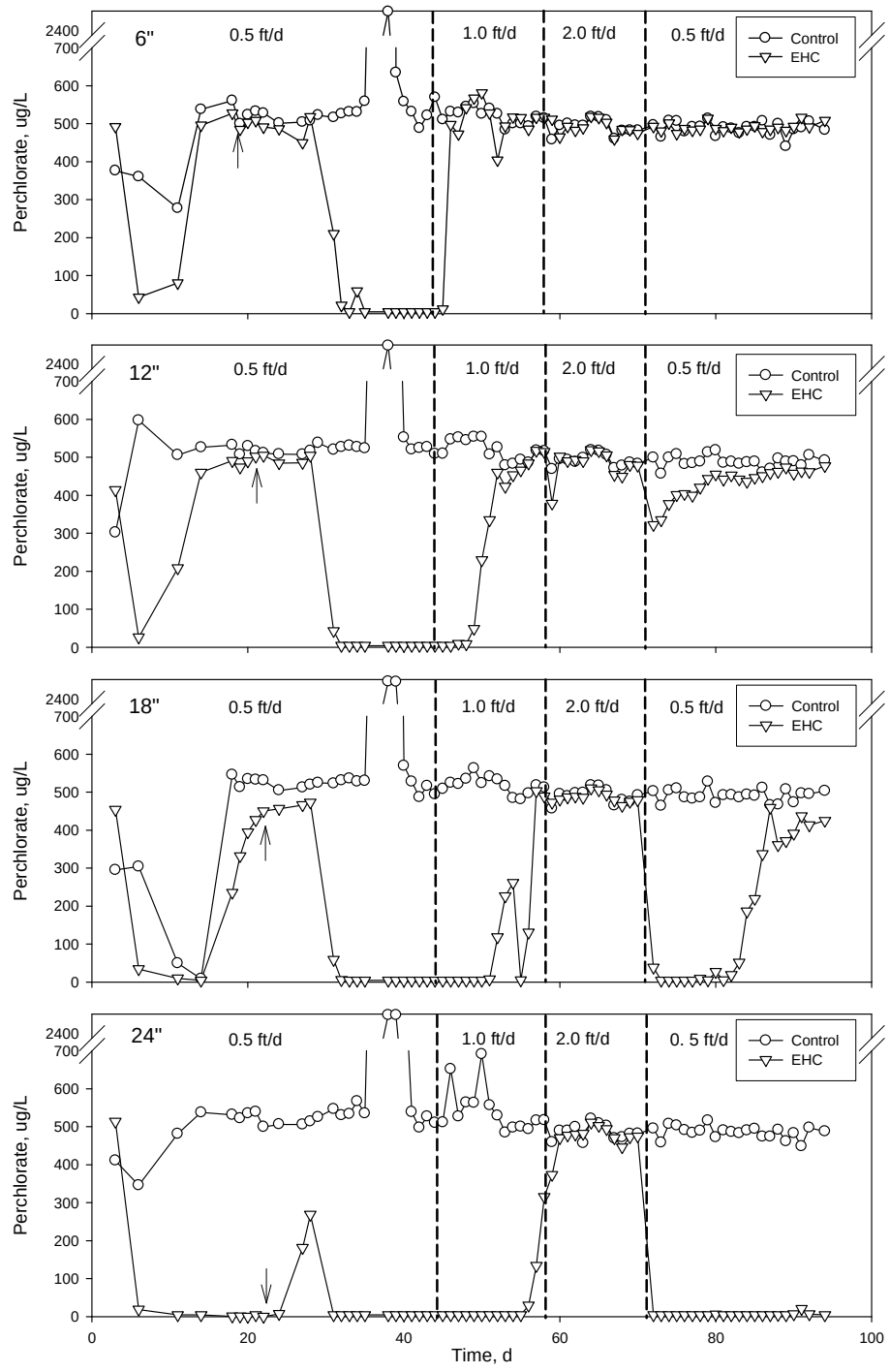


Figure 5.22 Perchlorate reduction in biotic control and EHC-amended soil columns. Arrow symbol indicated the day new columns were initiated.

During the first 45 days of operation, the flow rate was maintained at 0.5 ft/d in all the columns. Apparently there were different fractions of degradation in the control columns even though no organic electron donor was added prior to Day 20. The reason can be contributed to the naturally existing organic matters in the soil, which can serve as the energy and carbon sources for perchlorate biodegradation. After the depletion of the natural soil organic matter, the perchlorate concentration went back to the same level as the inlet for the rest of the experiment.

In the EHC-amended soil columns, although perchlorate removal was observed in the first two weeks for the 12-inch, 18-inch and 24-inch columns, perchlorate concentration in the effluent kept increasing thereafter. The longevity of the EHC-amended column was much shorter than expected. A possible reason was that the column had been prepared about one month before this experiment started. So those columns were replaced by a set of newly prepared columns on Day 22. After several days of fluctuation, complete removal of perchlorate was achieved in all columns, and perchlorate concentration of the effluent was below the detection limit of 4 μg/L. The flow rate was doubled to 1.0 ft/d on Day 46. Perchlorate breakthrough was observed in all the EHC columns at different times, which was related to the length of the column. The longer the reactor, the longer the residence time, and the later the breakthrough appeared. After increasing the flow rate to 2.0 ft/d, there was no reduction in perchlorate. Therefore, the flow rate was reduced to 0.5 ft/d to investigate whether the system would return to the initial performance. No removal was observed in the 6-inch column, but partial or complete removal was observed in the 12-inch, 18-inch and 24-inch columns in

the first few days after the adjustment. Then perchlorate in the 12-inch and 18-inch columns gradually increased to the influent level, but perchlorate remained non-detectable in the 24-inch column until the end of the test. Other than the retention time, depletion of EHC amendment might be another reason causing the different performances between the four columns.

In the EOS-amended columns, complete removal of perchlorate was achieved within two weeks when operated at the flow rate of 0.5 ft m/d. When the flow rate was doubled, perchlorate breakthrough was noticed in the 6-inch length column first, followed by the 12-inch and 18-inch columns. Measurable perchlorate was only found much later for the 24-inch column when it was running at a 1.0 ft/d flow rate. After increasing the flow rate to 2.0 ft/d, the effluent perchlorate matched the feed level in all the columns. Unlike EHC-amended soil columns, no perchlorate was detected in the columns except the shortest one (6-inch) after returning the flow to 0.5 ft/d, which indicated insufficient retention time for that column. The significant differences in the performance between EHC and EOS can be explained by the properties of the substrates. Compared to EHC, EOS adsorbs more strongly to the soil and leaches out at a slower rate than EHC.

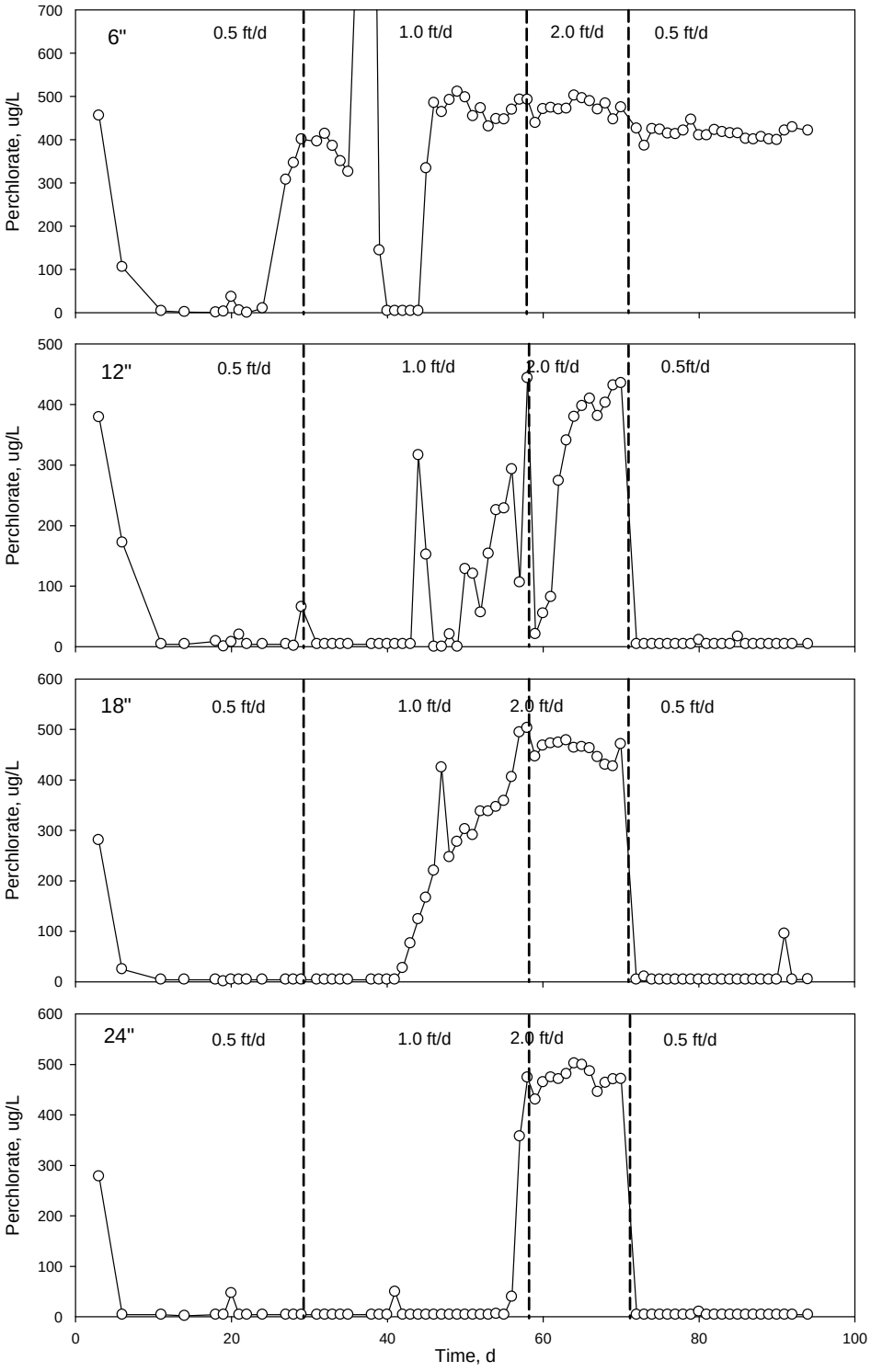


Figure 5.23 Perchlorate reduction in EOS-amended soil columns.

5.4.2.2.3 Water Quality Evaluations

The effluent water quality analyses for nitrite, arsenic, iron and manganese are summarized in Table 5.9.

Table 5.9 Secondary water chemistry analyses for amended barrier columns

Parameter	MDL[a], mg/L	EOS/Compost/ Mulch/Gravel, mg/L	EHC/Compost/ Mulch/Gravel, mg/L	EOS amended soil, mg/L	EHC amended soil, mg/L
Nitrite as N	0.09	ND	ND	ND	ND
Arsenic	0.07	ND	ND	ND	ND
Iron	0.15	2.6	70	~0.5	4.0
Manganese	0.07	0.45	0.77	0.14	0.77

[a]MDL-Method Detection Limit.
[b]ND - Non Detectable.

No nitrite and arsenic were observed in all the column experiments. However, increased concentrations of iron and manganese were noticed relative to the background levels (Table 5.4) in all the effluents. The elevated iron concentration was reasonable for EHC-amended columns. EHC is a mixture of nutrients and zero-valent iron so the addition of EHC will be a potential source of iron. Another possible source was the compost/mulch, as seen by the higher levels of iron and manganese in the compost/mulch amended column compared to the EOS-amended soil column. Although these results indicated a potential for metals to leach from the biobarrier, they can be immobilized by either adsorption to the aquifer matrix or by precipitation with other ions after migrating downstream where the redox condition increases [102].

5.5 ADVANTAGES AND LIMITATIONS OF THE TWO STRATEGIES

In this part of the study, an alternative perchlorate remediation strategy using organic substrates as the electron donor and the carbon source for cell growth was tested and evaluated. To compare this technology with the one using zero-valent iron, the merits and drawbacks of the two strategies are summarized and listed in this section.

The main advantages of the ZVI bioreactor for perchlorate reduction are as follows:

- Lower potential for disinfection by-product precursors compared to heterotrophic biological reduction (e.g., supported by acetate or other organic electron donor) due to the lower growth yield of autotrophic perchlorate reducing bacteria and the absence of an organic substrate feed.
- Although not being tested in this study, there is a potential of treating perchlorate and possible co-contaminants such as nitrate, TCE and PCE arsenic hexavalent chromium and/or uranium.
- A simple rugged process, potentially requiring low maintenance.

Technical risks and limitations inherent to the ZVI system are:

- Currently, no demonstration of the technology has been conducted in the field. There are little available data for comparison.
- The distribution and fate of iron corrosion products is largely unknown. These may cause ZVI bed plugging or ZVI passivation leading to a decrease in treatment performance.

- The process increases the pH, reduces the dissolved oxygen and the redox conditions in the treated water. These parameters may need to be adjusted after treatment.
- The effect of low temperatures on the process is unknown.

The main advantages of using an organic electron donor for perchlorate reduction are as follows:

- Laboratory experiments, the column tests in particular, indicate this technology appears to be a feasible technology to implement in the field. Addition of organic electron donor has the potential to reduce perchlorate to below detection limit (4 µg/L).
- Laboratory experiments showed that the process can handle very high concentrations of perchlorate (ppm levels), making it potentially applicable to treat ion exchange brines.
- Possibility of treating nitrate contamination in farm areas.
- Potential long-lasting in situ treatment technology.

Drawbacks for using an organic electron donor for perchlorate reduction:

- Performance might be affected by the dispersion of amendment within the contaminated site.
- Geology of the aquifer needs to be investigated prior to technology implementation. The cost-effective use of using organics substrates may be limited by the potential impacts on groundwater geochemistry.

- There is a potential of releasing high concentrations of organic substrates, and the compounds formed due to substrate addition, such as methane, sulfide. Post-treatment will be required and the treatment cost will be increased.
- Temperature effects are unknown.

In this research, the ZVI system, unfortunately, failed for long-term treatment. It left many problems and unknowns that need to be further studied, such as the water chemistry effects, the hydraulic issues and ZVI passivation. Great attention should be given to overcoming these challenges. Organic substrates, EOS and glycerin, showed great potential to be applied in the field. The perchlorate concentration in the treated water was below the detection limit 4 µg/L for four months operation. Even though EOS and glycerin may be used to achieve the desired perchlorate degradation, how these amendments would be applied in the field would most likely differ. Glycerin would require constant injection into the groundwater flow. EOS could be injected periodically depending on the EOS showed a greater longevity over glycerin. However, the way EOS distributes thoroughly in the barrier, particularly in low permeable soil, needs to be considered together with the barrier geology when deciding on the organic substrate to use.

Although the treatment cost was not calculated in this study, using organic substrates seems to be more cost effective. ZVI has a higher capital and installation cost compared to organic substrates. Natural organic substrates such as compost and mulch are relatively inexpensive. Overall, in terms of the perchlorate treatment performance

and the longevity, the second strategy, using organic substrates, is more competitive than the one using ZVI.

5.6 SUMMARY OF THE FINDINGS

Major conclusions of the high concentration source area groundwater tests are as follows:

- Among the five selected substrates (EOS, glycerin, high fructose corn syrup, acetic acid and sodium acetate), EOS, glycerin and sodium acetate were shown in microcosm tests to be effective in stimulating biological reduction of perchlorate.
- The rates of reduction were relatively similar for EOS, glycerin and sodium acetate, with complete reduction observed in the microcosms between 7 and 18 days. To reduce the cost and minimize salt addition, EOS and glycerin were chosen for column testing.
- There was no significant difference in the performance of perchlorate reduction after nutrient addition other than to decrease the lag time by about 2 days.
- In the column tests, the treatment with EOS amendment had significant advantages over using glycerin amendment. EOS-amended soil can achieve a nearly complete perchlorate reduction over 120-day operation with one time addition into the soil. In contrast, glycerin should be added on a continual

basis at a five times stoichiometric amount into the influent to achieve a similar treatment performance as using EOS amendment.

- There was no solubilization of metals in the glycerin treatment, but very minimal solubilization of manganese in EOS amendment at reducing conditions.

Major conclusions of the low concentration biobarrier groundwater tests are as follows:

- Complete perchlorate removal was observed within one week in EOS- and EHC-amended microcosms.
- The addition of 1 g/L $(NH_4)_2HPO_4$ nutrient increased the degradation rate of perchlorate in compost/mulch microcosms, but had no effect in the EOS and EHC microcosms.
- In the EOS-amended compost/gravel/mulch and EHC-amended compost/gravel/mulch column tests, no perchlorate was detected from both EOS- and EHC-amended compost/gravel/mulch columns after 15 days.
- In the EOS-amended soil and EHC-amended soil column tests, performance decreased with increasing velocity. Perchlorate removal was lost in all the columns when the velocity was increased to 2.0 ft/d.
- No significant treatment difference was observed between the EOS- and EHC-amended soil columns, although EHC showed a relatively shorter longevity.

- Increased solubilization of iron and manganese was noticed in all the amended column effluents, which are more likely coming from the amendments themselves.

CHAPTER VI SUMMARY

In this research, bioremediation of perchlorate using zero-valent iron and organic electron donors was studied.

Pilot scale ZVI for perchlorate bio-treatment was operated for six months. During the first three months, excellent perchlorate and nitrate removal was obtained. However, the treatment performance gradually declined with the increasing flow rate. The average removal efficiency at the last period was about 10%. The performance cannot be recovered even with intensive troubleshooting attempts. By testing the presence of perchlorate degraders, availability of electron donor (H_2) and hydraulic condition, hydraulic loss was suspected to be the main reason causing the loss of treatment ability. The formation of the ICPs can result in passivation of iron surface, loss of porosity, and internal channeling etc. A future study should focus on how to overcome the hydraulic issues.

As part of the extension study for troubleshooting the problem encountered in the field ZVI demonstration, the laboratory column studies indicated that the presence of elevated (bi)carbonate has a significant adverse impact on the hydraulic conductivity and porosity in the ZVI PRBs. There was a two to five orders of magnitude loss in hydraulic conductivity shortly after influent was amended with $NaHCO_3$. The loss of hydraulic conductivity and porosity were not uniform in the system, the inlet of the flow was where the most severe hydraulic loss happened. SEM and EDX examination revealed the iron surface was covered by the ICPs and calcium carbonate. The formation of those

precipitates finally led to the loss of hydraulic conductivity and porosity. Bed porosity, hydraulic issues and ZVI passivation are the greatest challenges to long-term sustained treatment performance in ZVI treatment systems. This consideration is consistent with other researcher's findings. Westerhoff et al reported the low recovery of ammonium by nitrate reduction due to the loss of permeability [103]. In this case, the life of the ZVI PRB is likely to be ended before the entire mass of ZVI is used up. To overcome these challenges, better reactor design for the in situ and ex situ application should be considered. Possible reactor designs such as fluidized beds, circulating or moving beds can be used. Johnson suggested setting up a pre-treatment reactor to remove the dissolved oxygen [104]. It also can be used to removal certain dissolved chemicals such as alkalinity and calcium before they enter into the ZVI contaminant treatment zone. The hydraulic conductivity can also be increased by mixture packing, which means instead of packing with pure iron, mixing with other inert material. For the in situ applications, a pretreatment zone and adding inert additives can also be considered. Additionally, when hydraulic loss is noticed, rather than replacing the entire barrier, just replacing the front section may be a better way to save the energy and cost.

Besides perchlorate reduction using an immobilized zero-valent iron bioreactor, injection of organic substrates was also evaluated. Two perchlorate-contaminated groundwater, with concentrations of 500 µg/L and 70 mg/L, were sampled from a real contaminated site for testing this strategy. For the high concentration test, Emulsified oil substrate (EOS®598), glycerin, high fructose corn syrup (HFCS 42), acetic acid (HAc) and sodium acetate (NaAc) were selected as the potential amendments. EOS, EHC and

compost/mulch were chosen for low concentration treatment. Both microcosm and column tests were conducted to evaluate the feasibility and efficiency of the selected organic substrates.

In the high concentration source area groundwater treatment, the microcosm tests revealed that EOS, glycerin and NaAc were more effective in perchlorate degradation than HAc and HFCS. Complete perchlorate reduction was observed in the microcosms receiving EOS, glycerin and NaAc at both the lower and higher dosages within 14 days. Nutrient addition had limited effect on perchlorate reduction with EOS or glycerin. The benefits of nutrient addition were only reflected in decreasing the lag time by 1 to 2 days. To minimize the salt addition to the groundwater, EOS and glycerin were considered to be preferable over NaAc as amendments for column tests. In the column tests, the treatment with EOS amendment had significant advantages over the glycerin amendment. EOS-amended soil can achieve a nearly complete perchlorate reduction over 120-day operation with one time addition into the soil. In contrast, glycerin should be added on a continual basis at a five times stoichiometric amount into the influent to achieve a similar treatment performance as using EOS amendment.

In the low concentration biobarrier groundwater treatment, it has been shown that complete nitrate and perchlorate reduction can be achieved in the microcosm tests within the timeframe of 5 to 12 days by adding EOS, EHC or compost/mulch. The benefit of adding nutrient was minimal for EOS- and EHC-amended soil, but nutrient addition enhanced the removal rate by two times for the compost/mulch treatment. Although EHC showed a fastest removal of perchlorate among all the substrates in the microcosm

tests, the longevity of EHC was shorter than that of EOS at the concentrations studied in the column tests. Groundwater flow rate varies upon the local geology condition. Changing the flow rate in the column tests affected perchlorate breakthrough in different ways. At the flow rate of 0.5 ft/d and 1.0 ft/d, a 24-inch length barrier blended with sufficient EOS or EHC should be able to treat perchlorate to the target level. Compost is another good option which can be utilized together with EOS. Compost can serve as both an electron donor and nutrient source. However, the amount of compost should be further investigated due to the elevated TOC content appearing in the effluent (data not shown here). Even though there is a concern about metals leaching (mostly iron and manganese) from the substrate, the metal levels are expected to return to the background level by precipitating with other components in the groundwater after migrating to a higher redox condition.

Perchlorate bioremediation using organic substrates as electron donor and carbon source is more feasible than using ZVI-H_2 as an electron donor and (bi)carbonate as a carbon source. Using organic substrates has the advantages of reliable treatment performance (meets California drinking water standards 6 µg/L), greater longevity, and the potential for being more cost effective.

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