ESTCP
Cost and Performance Report

(ER-200636)

Field Demonstration of a Novel Biotreatment Process for Perchlorate Reduction in Groundwater

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ACRONYMS AND ABBREVIATIONS

ClO_4^-	perchlorate
DI	deionized water
DO	dissolved oxygen
DPH	Department of Public Health
EBRT	empty bed retention time
ESTCP	Environmental Security Technology Certification Program
$FeCO_3$	siderite
FOB	freight on board
ID	inside diameter
Mo	molybdenum
MPN	most probably number
$NaHCO_3$	sodium bicarbonate
ND	non-detect
NRC	National Research Council
PCE	perchloroethylene (also known as tetrachloroethene)
ppm	parts per million (or mg L^{-1})
ppb	parts per billion (or µg L^{-1})
R&D	research and development
RfD	reference dose
TCE	trichloroethylene (also known as trichloroethene)
UMBBD	University of Minnesota Biocatalysis/Biodegradation Database
USEPA	U.S. Environmental Protection Agency
ZVI	zero valent iron

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ACKNOWLEDGEMENTS

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1.0 EXECUTIVE SUMMARY

A technology demonstration was conducted at the Well #2 in Rialto, CA, to treat perchlorate-contaminated groundwater using a novel biological treatment system.

1.1 TECHNOLOGY DESCRIPTION

The new treatment relies on autotrophic perchlorate reducing bacteria immobilized on zero valent iron (ZVI). As ZVI corrodes in water, hydrogen is released from the reduction of water, which is then used by perchlorate-reducing bacteria as a source of electrons. Extensive research in the laboratory had shown that the process was very promising. Also, hydrogen has significant advantages compared to organic carbon as an electron donor. It minimizes biomass growth and has a low potential for disinfection by-products precursors compared to organic substrates such as acetate. Other potential advantages include the possible reduction (biotic or abiotic) of nitrate, trichloroethylene (TCE), hexavalent chromium, and the possible control by metals by adsorption.

1.2 OBJECTIVES OF THE DEMONSTRATION

The main objective of this project was to test and demonstrate the efficacy of the ZVI-supported biological reduction of perchlorate. Additional objectives were to obtain pertinent data that will guide full-scale design and operation, provide relevant data for treatment cost estimation and comparison, provide the necessary data leading to possible permitting of the process by California Department of Public Health (DPH), and disseminate the results in various forms to promote technology transfer. As will be described below, significant treatment performance issues occurred that motivated further laboratory studies to help identify the causes of the problems observed in the field.

1.3 DEMONSTRATION RESULTS

A trailer mounted pilot demonstration system was designed, built, and mobilized at Well #2 in Rialto. It consisted of a water holding tank, the ZVI packed bed (300 gal) with approximately 4400 lb cast iron aggregate (mesh size 3/5), two parallel sand filters for post-treatment removal of bacteria and iron leaving the ZVI bioreactor, and ancillary monitoring and control equipment. Shortly after the start of the system, a pretreatment unit was installed to remove some of the influent water dissolved oxygen (DO), as the influent water was found to be saturated with oxygen. The treatment system was designed to treat a nominal water flow of 20 gpm, corresponding to an empty bed water residence time of 15 minutes, i.e., similar to many of our units that were operated in the laboratory. The experimental plan called for a number of tests at various flowrates, perchlorate concentrations, and overall operating conditions to fully evaluate the process.

The pilot reactor was operated at the Well #2 site from August 2007 to May 2008, during which time the uptime exceeded 98%. However, treatment performance varied considerably, with essentially 3 months of flawless operation, followed by numerous treatment performance problems that eventually forced the shutdown of the system.

During the initial 3 months, the average effluent concentration of perchlorate was 1.8 ± 0.9 parts per billion (ppb); nitrate was <0.01 mg L^{-1} NO_3-N; iron ranged from 0 to 0.05 mg L^{-1}; and coliforms, fecal coliforms, and E. *coli* in the reactor effluent were all below the detection limits. Extensive characterization of the ZVI bioreactor was achieved. One caveat was that these excellent results were obtained at a flow of 4 gpm, i.e., well below the nominal treatment capacity of 20 gpm. Problems occurred before the treatment performance at high flow could be determined.

After approximately 3 months of operation, perchlorate and nitrate removal began to deteriorate, with less that 40% perchlorate and nitrate removal for the remaining 5 months of testing. This was unexpected as laboratory bioreactors ran over 2 years without a problem. Several hypotheses for the loss in treatment efficacy were tested. These included a severe reduction of the ZVI bed hydraulic conductivity, loss of perchlorate-reducing bacteria or of biological activity, or loss in iron reactivity. Various attempts were made to recover full treatment capacity, but all failed and full treatment capacity was never recovered. The most likely explanation to the reactor upset was a loss of hydraulic conductivity, although it is likely that biological factors and iron reactivity also played a role.

The problems experienced with the pilot demonstration bioreactor severely limited the scope of this study. The original experimental plan could not be followed; a number of project goals could not be reached or even attempted. Significant efforts were then placed on a series of laboratory experiments with scaled-down ZVI columns aimed at determining the causes of the failure of the field unit. These led to the conclusion that probably not a single factor was responsible for the failure of the demonstration unit. Instead, a combination of adverse conditions, with perhaps design and operating choices (nature of pretreatment, low water flow), were probably responsible for the failure of the bioreactor in the field. Thus the water chemistry was instrumental, and it remains unclear whether similar failure would have been observed if the demonstration had been carried out at a different facility with groundwater with a different composition.

1.4 IMPLEMENTATION ISSUES

The main findings can be summarized as follows:

- A short start-up (~10 days) can be achieved with proper inoculation of the ZVI.
- Effective treatment of both perchlorate and nitrate was observed for a period of nearly 3 months, after which treatment performance issues occurred.
- When the reactor was operational, the influent perchlorate concentrations was on average 42 ± 4 ppb while the effluent concentration was 1.8 ± 0.9 ppb, the nitrate influent concentration was 4.5 ± 0.3 mg L^{-1} NO_3-N, and effluent concentration was <0.01 mg L^{-1} NO_3-N; effluent iron ranged from 0 to 0.05 mg L^{-1}, and coliforms, fecal coliforms and E. *coli* in the reactor effluent were all below the detection limit. One caveat was that these results were obtained at a flow fivefold lower than the nominal treatment capacity. Thus, performance summarized in this report is not at nominal capacity, and cost estimate could not be accurately predicted due to the operational challenges experienced during the test period.

- Conversion of perchlorate to harmless chloride was stoichiometrical with one mole of chloride released per mole of perchlorate reduced.

- Both Fe^{2+} and Fe^{3+} were detected in the bioreactor effluent. Fe^{2+} was oxidized to insoluble Fe^{3+} species in the sand filter without the need of dosing hydrogen peroxide.

- Treatment failure after 3 months was attributed to losses in the hydraulic conductivity due to accumulation of iron corrosion products and deposition of mineral precipitates. Some passivation of the ZVI probably also contributed to treatment failure.

- Laboratory experiments illustrated the importance of ZVI mesh size, influent water alkalinity and dissolved oxygen on the evolution of the ZVI bed porosity, hydraulic conductivity, and chemical composition of the deposits at the iron surface. These experiments led to the conclusion that probably not a single factor was responsible for the failure of the demonstration unit. Instead, a combination of adverse conditions, with perhaps design and operating choices, caused failure of the bioreactor in the field.

- Overall, the technology, while being novel and potentially offering cost and other benefits for perchlorate and nitrate removal, is susceptible to environmental factors and further study is needed. Thus the technology is not yet demonstrated and it requires further study prior to full-scale implementation.

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2.0 INTRODUCTION

2.1 BACKGROUND

The discovery of perchlorate (ClO_4^-) in a large number of groundwater and surface water supplies, coupled with its disruption of the production of thyroid hormones, resulted in perchlorate being added to the U.S. Environmental Protection Agency's (USEPA) candidate contaminant list (Zhang et al., 2002; USEPA, 2002). Ion exchange has been used successfully for perchlorate treatment, but it requires an additional process to treat the contaminated brine solution, which can be relatively expensive overall. Thus, bioremediation may be the preferred method because microorganisms can completely transform ClO_4^- into harmless chloride, eliminating the contaminant from the environment (Zhang et al., 2002; Coates and Achenbach, 2004). Perchlorate is reduced to harmless chloride by bacteria that use perchlorate as final electron acceptor, as shown in Figure 1.

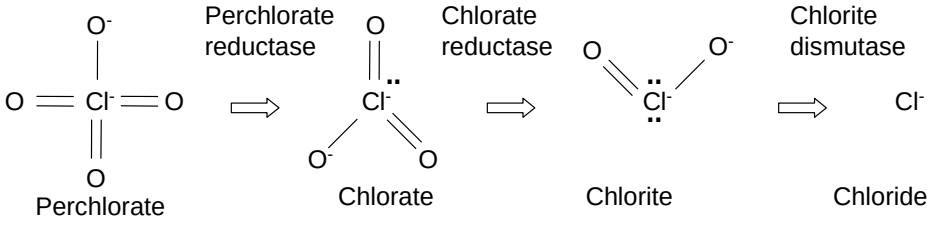

Figure 1. Pathway for the biological reduction of perchlorate.
(redrawn from University of Minnesota Biocatalysis/Biodegradation Database [UMBBD], http://umbbd.msi.umn.edu/pco/pco_map.html)

An important factor in perchlorate biotreatment is the selection of the electron donor needed to support the relevant bacteria and reduction of perchlorate (Giblin et al., 2000a, b). Hydrogen gas has significant advantages compared with organic carbon as an electron donor for perchlorate reduction. It minimizes biomass clogging and can be more cost-effective than acetate, ethanol, or methanol and minimizes the potential for disinfection by-products precursors (Logan, 1998; Ziv-El and Rittmann, 2009).

An in situ method for generating hydrogen gas is corrosion of ZVI. ZVI is nothing but iron and is marketed in a granular form with sizes ranging from nano-sized ZVI to cm-size or even greater chunks. ZVI is nontoxic and has been shown to have great versatility in supporting biological or chemical reductions of compounds such as nitrate, TCE, chromate, and uranyl. As such, ZVI is being used widely as reactive filling material in permeable reactive barriers, chemically reducing and/or adsorbing a variety of contaminants (Powell et al., 1998).

As iron corrodes in water, H_2 is released (Reaction 1) which can then be utilized by perchlorate-reducing bacteria.

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2(g) \qquad \text{(Reaction 1)}$$

We have recently shown that ZVI corrosion can be coupled with perchlorate-reducing microorganisms to reduce perchlorate without the need for external hydrogen gas addition (Yu et al., 2006, Yu et al., 2007). Extensive batch and column experiments were conducted in the laboratory prior to this project to prove the concept and determine the applicability of perchlorate reduction supported by ZVI.

2.2 OBJECTIVES OF THE DEMONSTRATION

The overall objective of this project was to validate in the field novel treatment of perchlorate-contaminated water using the ZVI-autotrophic bioreactor. Additional objectives were to:

- Obtain pertinent data that will guide full-scale design and operation
- Provide relevant data for treatment cost estimation and comparison
- Provide the data leading to possible permitting of the process by California Department of Public Health
- Disseminate the results in various forms to promote technology transfer.

Originally, it was anticipated that demonstration would be conducted at two different sites: 1) Well #2 within the City of Rialto, and 2) a second location with different perchlorate concentrations and/or different water chemistries. As will be described in Section 6.1, significant challenges were experienced in maintaining effective perchlorate treatment over several months. Hence, demonstration of continuous treatment was conducted only at Well #2. Thereafter, research and development (R&D) efforts were directed towards understanding the causes of the upsets observed at Well #2.

2.3 REGULATORY DRIVERS

Currently, there is no federal drinking water standard for perchlorate. Several states impacted by perchlorate contamination have set advisory levels ranging from 1 ppb to roughly 20 ppb. In January 2009, USEPA issued an Interim Drinking Water Health Advisory level (USEPA, 2008) of 15 ppb based on the recommendations of the National Research Council (NRC) of the National Academies, as reported in "Health Implications of Perchlorate Ingestion" (NRC, 2005). The NRC recommended and USEPA adopted a reference dose (RfD) of 0.7 μg kg^{-1} day^{-1}. The health advisory level of 15 ppb is thought to be a high value by many observers, especially in light of much lower advisory levels set by different states.

In any case, the problem of drinking water contamination with perchlorate has been very visible. This has motivated various water districts to adopt a proactive attitude to the problems caused by perchlorate contamination and has stimulated scientists and engineers to develop new methods of treatment.

3.0 TECHNOLOGY

3.1 TECHNOLOGY DESCRIPTION

Treatment of perchlorate relies on the corrosion of ZVI, which releases hydrogen. At the surface of ZVI particles, microorganisms are naturally attached and use hydrogen to reduce perchlorate to chloride (Yu et al., 2006, 2007). For continuous treatment, ZVI is packed in a column through which the contaminated water is passed. The effluent of the bioreactor contains some dissolve iron and bacteria (nonpathogenic). Iron is oxidized chemically and precipitated iron and bacteria are removed by passing the water through a sand filter.

Outstanding results were obtained in the laboratory with bench-scale units (Yu et al., 2006, 2007). A high rate of perchlorate reduction, low endpoint of treatment (concentration <6 ppb), and absence of chlorite and chlorate were achieved. The optimum pH for ZVI-supported perchlorate-reducing bacteria was found to be between 7 and 8. And 100% perchlorate removal (effluent <4 ppb) was obtained treating tap water spiked with as much as 500 µg L^{-1} perchlorate. Nitrate-nitrogen concentration in the tap water ranged between 3.4 and 5.9 mg L^{-1}. Below a nitrate-nitrogen concentration of 5 mg L^{-1} of NO_3-N, perchlorate removal was not affected. Above 5 mg L^{-1} of NO_3-N, the rate of perchlorate degradation decreased but was not inhibited. Complete perchlorate removal has been observed at (empty bed) retention times (EBRTs) less than 40 minutes under most conditions. Effective treatment was observed at retention times as low as 9 minutes, and the maximum perchlorate elimination capacity was greater than 4000 mg per $m^3_{bioreactor}$ per hour. Overall, operation of the lab scale bioreactors for over 24 months proved that stable and sustained treatment could be achieved (Yu et al., 2007). Further, iron corrosion studies showed that the ZVI in the reactor would last for several years. This all stimulated demonstration of the technology in the field.

Laboratory experiments formed the basis for the design of our pilot scale demonstration unit. The flow sheet of the pilot reactor is shown in Figure 2. Detailed instrumentation and controls are shown in Figure 3, while size and various equipment information is reported in Table 1. Figure 4 is a picture of the system installed at Well #2.

In short, groundwater is pumped directly from Well #2 into the water holding tank. As will be discussed in Section 6.1, pretreatment of the water to remove dissolved oxygen was added to the system shortly after start-up at Well #2 after it was identified that the groundwater was saturated with oxygen, which is detrimental to ZVI and biotreatment. Indeed, the redox potential needs to be reduced for biological reduction of perchlorate to occur. From the holding tank, contaminated groundwater is pumped upwards through the ZVI bed, after which it flows by gravity to the two sand filters. Hydrogen peroxide can be added as needed to the reactor effluent and prior to sand filtration to oxidize any Fe^{2+} dissolved (in practice, hydrogen peroxide feed was never turned on as it was not needed). The treated water is then trickled through the sand filters, either operated in parallel or sequentially, as desired. The sand filter effluent is directed to the drain, which goes to the catch basin. Periodically, the sand filters are backflushed. While one filter is backflushed, the other treats the water stream exiting the bioreactor. For the backflush, fresh water is pumped upwards through the sand filter. The effluent is directed to the drain going to the catch basin.

Table 1. ZVI bioreactor construction details.

Parameter	Value	Comments
ZVI bed diameter × height	48 in ID* × 38 in height	
ZVI bed volume	300 gal	
ZVI type and source	Cast iron aggregate type 3/5 ZVI (Peerless)	
ZVI mass	Approx. 4400 lb (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 gal each	Two filters operating in parallel. Gravity feed
Water feed tank volume	500 gal	
Water flow (nominal)	20 gpm for EBRT of 15 min	Maximum flow tested was 4 gpm
Pretreatment to remove part of dissolved oxygen	1) Initially, custom built ZVI fluidized bed in water feed tank 2) Membrane degasser rated 20 gpm	

*ID = inside diameter

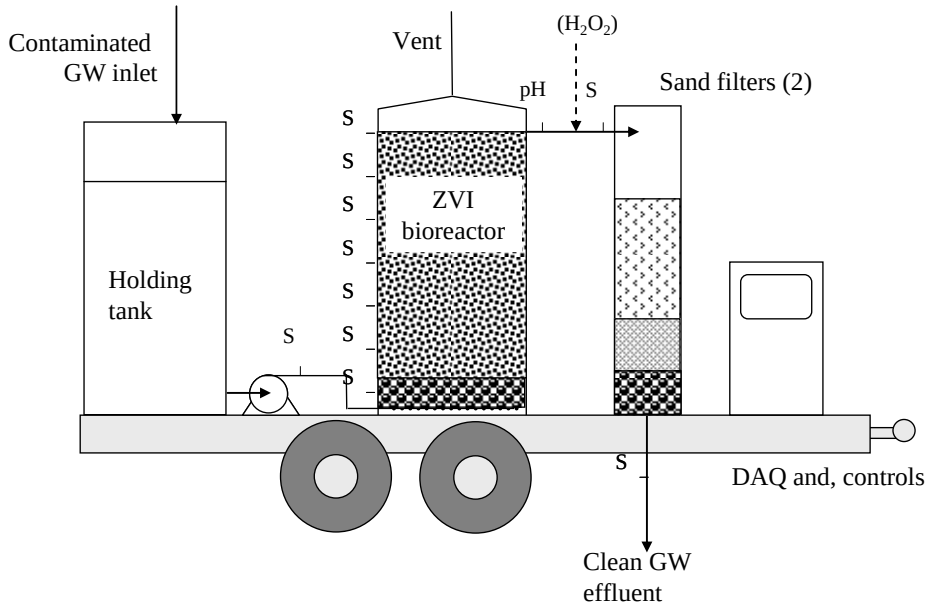

Figure 2. Schematic of the trailer mounted pilot demonstration system.
(not to scale, controls not shown) S = sampling port
Homogeneous distribution of the water at the bottom of the bioreactor is achieved via a network of perforated pipes. Backflush for the sand filters not shown. As mentioned in the text, pretreatment of the contaminated water to remove dissolved oxygen was implemented after the start-up of the system but is not shown on the schematic.

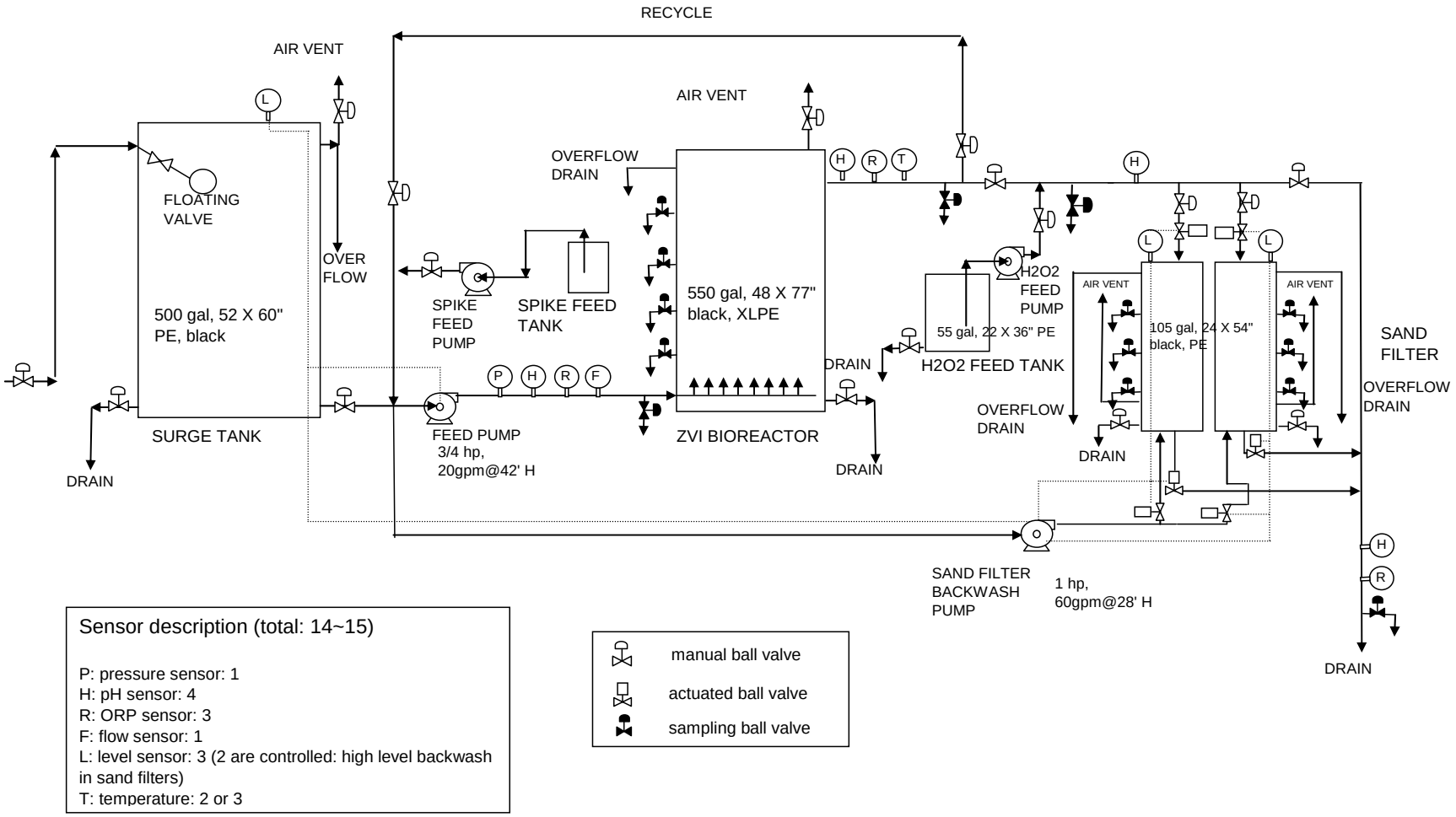

Figure 3. Flowsheet and instrumentation of the demonstration system.
(not to scale)

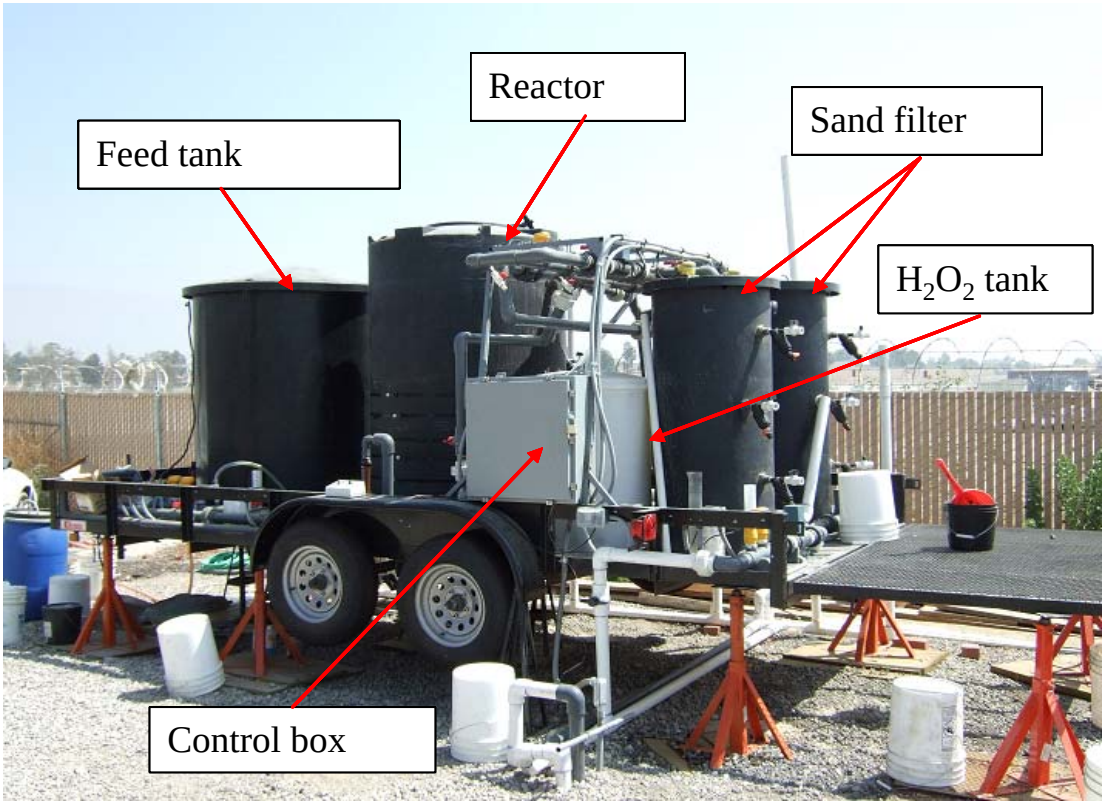

Figure 4. Picture of the demonstration system at the Rialto Well #2 site.
Membrane degassing pretreatment not shown.

3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

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

- Potentially lower costs compared to other perchlorate treatment methods.
- Reduction of the perchlorate to chloride rather than concentration of perchlorate on a matrix such as an ion exchange resin or in concentrated brine.
- Lower potential for disinfection by-products 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 feed of an organic substrate.
- Possibility of treating both perchlorate and possible co-contaminants such as nitrate, chlorinated solvents such as TCE, and perchloroethylene (PCE) by biological reduction and/or reaction with ZVI, and arsenic hexavalent chromium and/or uranium by adsorption on corrosion products.
- Simple rugged process, potentially requiring low maintenance.

- The concept can be translated into subsurface treatment, e.g., funnel and gate reactive barriers.
- Applicability to high concentrations of perchlorate. Laboratory experiments have shown that the process can handle very high concentrations of perchlorate (parts per million [ppm] levels), making it potentially applicable to treat ion exchange brines.

Technical risks and limitations inherent to the system are:

- Currently, limited demonstration of the technology has been conducted in the field.
- Post-treatment is required to remove soluble Fe^{2+} and insoluble Fe^{3+} and possibly suspended bacteria from the effluent.
- The distribution and fate of iron corrosion products is largely unknown. These may cause ZVI bed plugging or ZVI passivation, leading to a decrease of treatment performance. Prior reports on ZVI reactors (both biological and abiotic reactors) identified that plugging of ZVI beds and conditions leading to plugging are not well understood (Henderson and Demond, 2007)
- The process 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 presence of nitrate at concentrations above 5 mg L^{-1} of NO_3-N will reduce the rate of perchlorate removal, thus requiring a larger and more expensive treatment system.

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4.0 PERFORMANCE OBJECTIVES

The performance objectives of the demonstration study are provided in Table 2; further information on attaining each objective is provided in Section 7.

Table 2. Performance objectives.

Type of Performance Objective	Performance Criteria	Performance Metrics	Actual Performance: Objective Met
Qualitative	Ease of operation and maintenance	Evaluation by site operator	Inconclusive
Quantitative	Reduction of perchlorate to chloride	Stoichiometrical conversion of perchlorate to chloride	Yes
Quantitative	Specific volumetric performance	Treatment meeting regulatory objectives at reduction rates > 1 g m^{-3} h^{-1} or empty bed retention time shorter than 45 min	No, highest flowrate tested before performance problems started corresponded to a 75 min empty bed retention time
Quantitative	Exceed regulatory standards for removal of perchlorate, iron, bacteria and possible other contaminants (e.g., nitrate)	Effluent concentrations <6 µg/L ClO_4^-, <0.3 mg/L Fe; <1 mg/L NO_3-N; other contaminants and bacteria to be defined	Yes, but only at lower water flowrate. Nominal flowrate could not be tested.
Quantitative	Start-up time	Start-up time shorter than 5 days	No; start-up time was about 10-11 days
Quantitative	ZVI life	ZVI replacement frequency should not prevent cost effectiveness of the process	Inconclusive
Quantitative	Ability to treat both low and high concentrations of perchlorate	Meet regulatory standards for influent in the low ppb range up to 1000 ppb perchlorate	Not tested at Well #2
Quantitative	Production of waste	Waste should not prevent cost effectiveness of the process or negatively affect environmental impact of process	Yes
Quantitative	Robustness	Ability to treat to regulatory standards a) concentration spikes and b) recovery/start-up time after period of downtime (e.g., power outage)	Yes, though robustness was not tested in a systematical manner
Quantitative	Low downtime and low maintenance	Downtime <0.01% and maintenance lower than 2 hr per week	Yes, when system was operating. Downtime was less than 0.01%.
Quantitative	Treatment costs	Total capital and operating for projected large-scale system <$0.2/1000 gal	No or inconclusive because of performance issues

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5.0 SITE DESCRIPTION

This project was conducted at Rialto Well #2, which is located close to California State Route 210 highway. The groundwater in this region has been impacted by perchlorate contamination from various sources, some dating back to the 1950s. Details of the source of the contamination and of the site hydrology were outside the scope of this project.

The Well #2 site hosted several demonstration projects funded by ESTCP. The water was continuously extracted from a single well, from where it was distributed to the different demonstration projects. The water average contaminant level is reported in Table 3. Relevant to the project is the fact that the water is pumped from a relatively deep and oxic zone in the aquifer. At the time of the demonstration, contamination with organics or chlorinated solvent was not detected, except for traces of TCE. As a result of these conditions, the water is saturated or oversaturated with oxygen. This posed some challenges for effective treatment, as biological reduction of perchlorate requires anaerobic conditions and low redox conditions.

Table 3. Concentrations of relevant species in the water at Well #2.

Contaminant	Concentration Range
Measured (this project)	
Perchlorate	49 to 65 ppb
Nitrate	4 to 7 mg NO_3-N L^{-1}
TCE	ND to 3 ppb
Other organics	ND
Dissolved oxygen	>8 mg L^{-1}
Alkalinity	148-156 mg $CaCO_3$ L^{-1}
TOC	ND (<0.5 ppm)
Historical averages[1]	**Mean / Low / High**
Perchlorate	74 / 34 / 88 ppb
Nitrate	26 / 23 / 28 mg L^{-1} (as NO_3^-)
Chloride	13 / 12 / 13 mg L^{-1}
Sulfate	12 / 11 / 12 mg L^{-1}
Carbonate / bicarbonate	<3/210 / <3/210 / <3/210 mg L^{-1}
pH	7.8 / 7.7 / 7.9
Total dissolved solids	260 / 260 / 260 mg L^{-1}
Conductivity	445 / 430 / 460 µS cm^{-1}
Volatile organics	ND / ND / ND

[1]Provided by ESTCP and the City of Rialto

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6.0 TEST DESIGN AND RESULTS

6.1 FIELD DATA OF PERCHLORATE BIOTREATMENT AT WELL #2

After mobilization of the pilot in July 2007, significant concerns were raised about the high DO in the water of Well #2. The water was oversaturated in oxygen, which could cause a number of problems, including trapped gas in the ZVI bed (causing channeling), high redox conditions detrimental to biological reduction of perchlorate, and undesirable iron corrosion. To remove DO from the influent, initially, a small size ZVI fluidized bed and a submersible pump for the water recycle were installed in the water feed tank. Typically, DO in the influent could be reduced to 1-4 mg L^{-1}. The system was operated with the ZVI fluidized bed unit removing DO for 150 days. The water in our holding tank had the typical color of iron rust as a result of fine particles of Fe(III) in suspension. Later, with concerns that insoluble Fe(III) from the pretreatment carried to the bioreactor would plug the main ZVI bed and the realization that the ZVI pretreatment would not suffice for the removal of DO at the nominal water flow of 20 gpm, a membrane degasser was installed upstream of the water holding tanks and the ZVI fluidized bed was removed. The target DO in the influent of the ZVI bioreactor was to be at least below 4 ppm, and preferably below 1 ppm.

Actual treatment of perchlorate started August 1, 2007. The reactor was inoculated with soil from a rapid infiltration plant where nitrate is biologically removed. Soil was mixed with water in 55 gal drums and allowed to settle. The supernatant was then fed to the ZVI bioreactor. The reactor was started at a relatively low influent flow rate (~2 gpm) corresponding to an (empty bed) residence time of about 150 min. For the first 10 days, there was no noticeable removal of perchlorate. In an attempt to accelerate start-up by providing a greater carbon supply to the autotrophic perchlorate reducers, 120 mg L^{-1} sodium bicarbonate ($NaHCO_3$) and more inoculum were added to the system, after which removal of perchlorate rapidly reached values greater than 95% on Day 13. This demonstrated that the proposed biotreatment could be established rapidly.

The evolution of the perchlorate and nitrate removal with time are shown in Figures 5 and 6, respectively. Until about Day 86, treatment efficacy was high and very low perchlorate effluent concentrations were achieved. During this period, the average performance of the ZVI bioreactor was as follows:

- The influent perchlorate concentration was on average 42 ± 4 ppb.
- The effluent perchlorate ranged from essentially non-detect (ND), i.e., below 0.5 ppb to 3 ppb, with an average of 1.8 ± 0.9 ppb. Thus, the removal was on average 95.5%.
- Excellent removal of nitrate was observed with less than 40 ppb nitrate in the effluent for an average inlet nitrate of about 20 ppm. This amounts to over 99.8% removal.
- 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 most probable number (MPN)/100 mL.
- During the first 90 days, there was no build up of back pressure in the bioreactor.

- The pH of the effluent was between 7.2 and 7.7, i.e., about 0.2 to 0.3 units above the pH of the influent water.

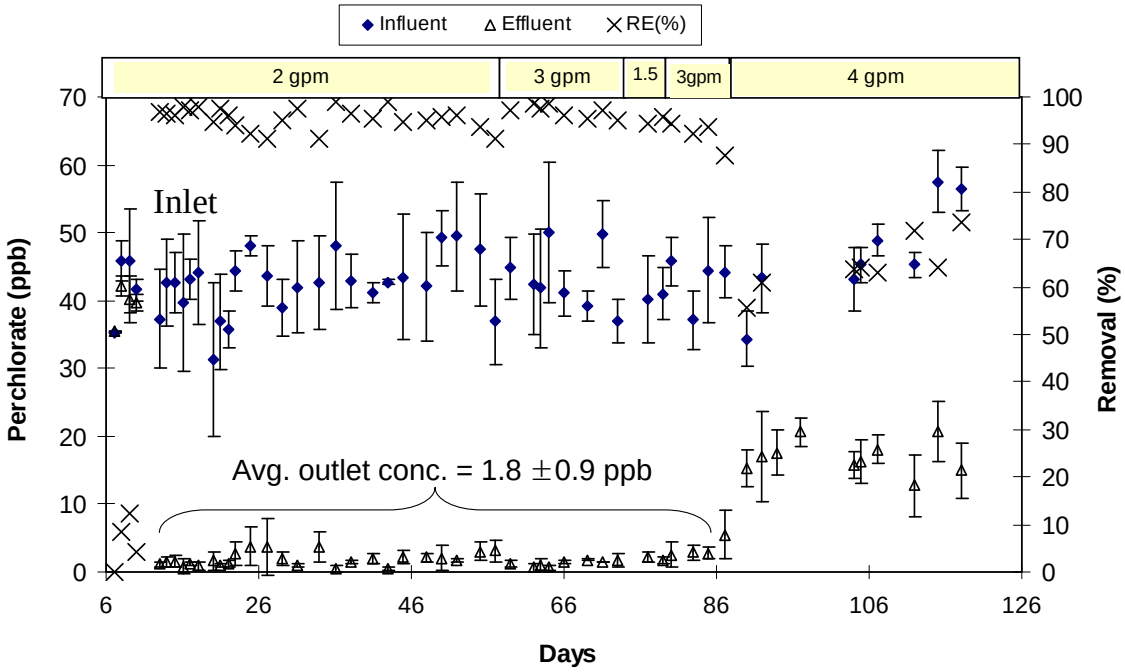

Figure 5. Perchlorate inlet and outlet concentrations over the first 4 months of operation.

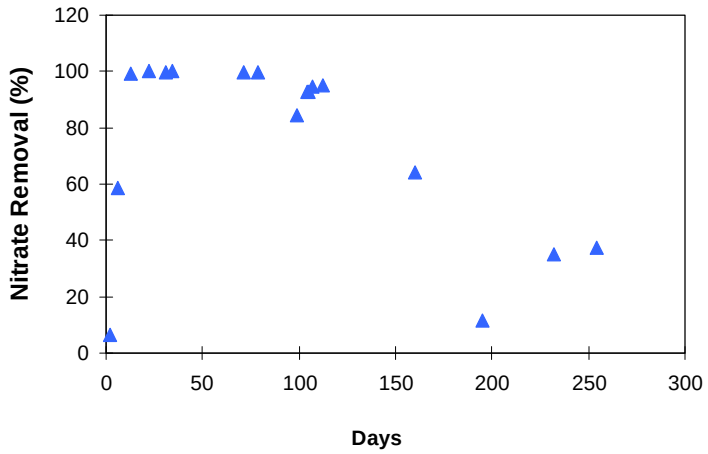

Figure 6. Nitrate removal over the duration of the field demonstration.

After about 80 days of operation, before the water flow rate could be increased to test treatment performance at its nominal capacity, perchlorate removal performance deteriorated. Within about a week, the outlet perchlorate concentration increased to 12-18 ppb (see Figure 5), corresponding to a removal of 60-70% only, and nitrate removal steadily decreased. The reactor upset was unexpected as we ran biotreatment systems in the laboratory for over 2 years without a problem. The loss in treatment performance could not be traced back to any outside event (power failure, visible symptom, etc.). Thus, several hypotheses were formulated in an attempt to explain the

loss in treatment efficacy, and they were systematically tested. Various attempts were made to recover full treatment capacity, but all failed.

The most plausible reason for the bioreactor upset was a hydraulic problem within the bed, causing significant short circuiting of the water and poor contact between the water and the ZVI-supported bacteria. It is also possible that combination of effects, e.g., short-circuiting combined with localized passivation of the iron played a role in the upset.

When the bioreactor was decommissioned, visual observation of the bed was conducted. Initially, the ZVI bed was a highly porous packed bed; over time, it was converted to a solid and compact mass of iron and iron corrosion products. Large blocks of ZVI with low porosity and permeability were glued together by corrosion products (Figure 7). This is likely to have led to preferential paths, consistent with the hypothesis that the performance problems were the result of hydraulic problems within the bed.

Figure 7. Pictures of large blocks (left) **of ZVI taken out of the reactor when it was dismantled showing the solid structure of the ZVI bed, and close view** (right) **of ZVI showing the deposits of iron corrosion products and quasi total loss of porosity.**

The failure to demonstrate long-term treatment with the field reactor triggered a series of laboratory experiments to determine the effect of ZVI corrosion and accumulation of iron corrosion by-products, and of the effects of water chemistry on the water hydrodynamics in the ZVI beds. The main findings are briefly presented next.

6.2 LABORATORY EVALUATION OF POROSITY DECREASE AND CORROSION PRODUCTS

Two parallel laboratory experiments were conducted to determine:

- The effects of carbonate on ZVI bed permeability, chemical deposits, and on the residence time distribution of an inert tracer.

- The effects of ZVI mesh size, the presence or absence of dissolved oxygen or nitrate in the treated water, the presence or absence of bacteria on the ZVI, and the nature of the water (tap water versus deionized [DI] water) on bed porosity and residence time distribution of a tracer.

Figure 8. Pictures of the laboratory column setups.

One series of experiments determined that water high flow through the ZVI reactor was probably not a factor in the failure. However, a two to four order of magnitude loss hydraulic conductivity was observed shortly after water amended with $NaHCO_3$ was fed to ZVI packed beds. The loss of hydraulic conductivity was most severe in units that received water with higher alkalinity. Visual observation, electronic microscopy and energy-dispersive X-ray analysis of ZVI and ZVI surfaces used in these reactors revealed that a variety of iron corrosion products (carbonate green rusts, iron [hydr]oxide, siderite [$FeCO_3$]) and precipitates (mainly calcium carbonate) had formed in significant amounts that could explain the loss in hydraulic conductivity and possibly iron passivation. Separate experiments considered the role of DO, ZVI mesh size and various ions in the water undergoing treatment on porosity losses. Columns packed with fine ZVI and operated with high DO and 20 mg L^{-1} nitrate experienced rapid hydraulic problems leading to plugging. This was not the case with a column packed with fine ZVI and fed low DO deionized water. Some changes in porosity and hydraulic properties were observed in columns packed with coarse ZVI, but despite operation for close to 100 days, no condition led to bed plugging. These led to the conclusion that probably not a single factor was responsible for the failure of the demonstration unit. Instead, a combination of adverse conditions, with perhaps design and operating choices (nature of pretreatment, low water flow), were probably responsible for the failure of the bioreactor in the field.

Overall, the results of the laboratory investigations shed some light on what factors may have contributed to the failure of the ZVI demonstration bioreactor. Water from Well #2 had a medium alkalinity (210 mg L^{-1}), which in itself should not have posed major issues based on the review of earlier studies. However, other contributing factors existed. The water had a high DO and a relatively high nitrate concentration (20 mg L^{-1}). In addition, $NaHCO_3$ was supplemented to the bioreactor initially to promote growth of the autotrophic perchlorate reducing organisms and later during troubleshooting. Finally, pretreatment using fine ZVI in the water feed tank resulted in fine particles of corroded iron. These were carried into the bioreactor and probably remained in the bed rather than passing through, resulting in a loss of porosity and perhaps some reactions with ZVI or reactive corrosion products. Thus, overall, the conditions were likely to result in significant deposits of iron corrosion products into the ZVI bed with possible passivation of the iron surface. This led to hydraulic problems in the ZVI packed bed, which together with low ZVI corrosion rate resulted in the failure of the process.

At the time the performance problems occurred, it was felt that biological kinetic factors were limiting. Thus, several mineral or organic substances were introduced in the ZVI reactor, with the intent to stimulate perchlorate-reducing bacteria. In retrospect, it is likely that such feeding was detrimental to the proper functioning of the ZVI bioreactor and simply resulted in more adverse reactions and mineral deposits in the ZVI bed. One unlikely but possible biological limitation that was overlooked at the time of the field demonstration is molybdenum (Mo) limitation. Mo has been shown to be a required cofactor for perchlorate reduction (Coates and Achenbach, 2004), and it could be that the culture was limited by Mo.

In addition to the factors listed above, it is possible that the relatively tall ZVI bed combined with the relatively low water velocity through the bed limited the shear of ZVI particles and reduced the carry out reacted iron, which instead was captured in the bed and caused hydraulic problems. Intriguing results were obtained with respect to the iron balance, with far less iron flushed out of the ZVI bed than expected based on a calculation of the iron corrosion rate. That indicates that over time, accumulation of reacted iron in the ZVI bed occurred. Corrosion products are known to passivate iron surfaces. Also, nitrate has been shown to inhibit corrosion, while chloride promotes corrosion. Carbonates have been shown to temporarily increase the corrosion of ZVI, though in the long run, carbonate solids are known to passivate iron surfaces. All these point to the fact that the situation is extremely complex and that one should be cautious not to generalize the results. It is possible that very different results would have been obtained if the demonstration project had been conducted at a different location, with different water chemistry and maybe different operating conditions.

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7.0 PERFORMANCE ASSESSMENT

As was discussed in Section 5, the ZVI bioreactor performed flawlessly for about 3 months after the initial start-up. Thereafter performance dropped and bed plugging issues were observed, and despite intensive troubleshooting efforts, optimum treatment performance was never recovered. For these reasons, performance was not assessed to the extent anticipated when the project was initiated, and many objectives were either not tested or not met. This is detailed in the next sections.

Ease of Operation and Maintenance (Qualitative)

Reaching this objective was inconclusive for the following reasons. When the system was removing perchlorate effectively, it required very little maintenance or attention. The system is indeed easy to operate and requires low maintenance. Besides the feed of a few chemicals during the start-up phase and sporadically later for culture maintenance, there is no chemical feed needed. The bioreactor system was successfully operated without H_2O_2 addition (intended for Fe^{2+} oxidation) after the bioreactor. Also, there are only a few moving parts, and there is no control loop to check or sensors to calibrate on a frequent basis. However, when the system started to fail, intensive troubleshooting was conducted, which required high maintenance. It should be clear that failure is an abnormal mode of operation. It remains unclear whether preventive maintenance could have prevented failure. Under these circumstances, evaluation of the ease of operation and maintenance requirements remains speculative; hence the assessment that this objective was inconclusive.

Reduction of Perchlorate to Chloride (Quantitative)

This objective was met; stoichiometric 1:1 conversion of perchlorate to chloride was observed.

Specific Volumetric Performance (Quantitative)

The objective was to treat groundwater and meet regulatory objectives at volumetric perchlorate reduction rates >1 g m^{-3} h^{-1} or empty bed retention time shorter than 45 min. This objective was not met. The experimental plan called for increasing the groundwater flow rate (i.e., decrease the empty bed retention time) incrementally to determine performance at various operating conditions. When performance problems started, the influent water flow had only been increased up to 4 gpm, which corresponds to a 75 min empty bed retention time. After the loss of treatment performance, the bioreactor never recovered full treatment performance and greater flow rates/shorter empty bed retention times were not tested.

Exceed Regulatory Standards for Removal of Perchlorate, Iron, Bacteria, and Possible Other Contaminants (e.g., Nitrate) (Quantitative)

The objective was to obtain effluent concentrations below 6 µg L^{-1} for perchlorate, below 0.3 mg L^{-1} for iron, and less than 1 mg L^{-1} NO_3-N, with other contaminants and bacteria to be defined. When the ZVI bioreactor was operating (at a liquid residence time of 75 min), the following average inlet and outlet concentrations were obtained.

Table 4. ZVI bioreactor average performance over the first 3 months when operated at an empty bed residence time of 75 min.

	Influent Concentration	Effluent Concentration
Perchlorate	42 ± 4 ppb	1.8 ± 0.9 ppb
Nitrate	19.5 ± 1.4 ppm (as nitrate) or 4.5 ± 0.3 mg L^{-1} NO_3-N	<40 ppb (as nitrate) or <0.01 mg L^{-1} NO_3-N
Iron	Variable due to pretreatment	0-0.05 mg L^{-1}
Bacteria	ND	Coliforms, fecal coliforms, and E. *coli* in the reactor effluent were below the detection limit of 2 MPN/100 mL

During the initial start-up phase, the effluent concentrations of perchlorate, nitrate, iron, and bacteria were all below the target effluent levels. However, these measurements were made when the flow had not yet been increased to its nominal capacity of 20 gpm. Effluent concentrations may increase with increases in the treated water flow after reaching the maximum treatment rate, but problems prevented testing at the nominal flow capacity.

Short Start-up Time (Quantitative)
The goal was to obtain effective treatment within 5 days of initial start of the reactor, but this objective was not met. Effective treatment required 10-11 days.

ZVI life (Quantitative)
The objective was that the ZVI replacement frequency should not be a major negative contributor in the cost effectiveness of the process. Based on theoretical ZVI corrosion rate calculations, the life of the ZVI was expected to be several years. Namely, a corrosion rate of 25 to 100 mg iron per kg ZVI per day (as was measured in the laboratory) means that it would take 5.5 to 22 years to corrode 20% of the iron. Because of the problems that were experienced, no firm conclusions could be made on the ZVI life, and this assessment remains inconclusive.

Ability to Treat both Low and High Concentrations of Perchlorate (Quantitative)
Because of the problems experienced in the field, this objective was not tested. High concentrations (high ppm levels) were successfully treated in our lab-scale ZVI bioreactors.

Production of Waste (Quantitative)
The objective was that wastes produced from the ZVI bioreactor system should not prevent cost effectiveness of the process or negatively affect environmental impact of process. This objective was reached. The only waste generated from the system was the sand filter backwash. Originally, it was anticipated that the sand filters would require backwash 2 to 7 times per week, triggered by the accumulation of Fe(III) and bacteria in the filters. In reality, the backwash frequency was less than once every 14 days. Backwash effluent volume was less than 1% of the total water treated and contained moderate concentrations of Fe(III) (<5 mg L^{-1}). These were found to pose no special environmental health risk or cost liability.

Robustness (Quantitative)

The original plan was to systematically demonstrate the ability of the system to treat to regulatory standards concentration spikes and recovery/start-up time after a period of downtime (e.g., power outage). The robustness was not tested in a systematic manner due to the shorter than expected field operation. However, during periods of optimum operation, there were several power failures at the Rialto site, resulting in temporary shutdown of the system. In all cases, the system automatically restarted when power was resumed. Also, no significant effect of the period of non-use could be detected, and effective treatment was maintained. This demonstrates some level of process robustness.

Low Downtime and Low Maintenance (Quantitative)

The goal was that the downtime should be less than 0.01% and maintenance less than 2 hr per week. This objective was reached. When the system was operating, downtime was less than 0.01%, and no treatment performance loss was ever observed. Note that possible additional maintenance requirements to prevent bed plugging issues will be on top of these maintenance needs, but they are not yet known.

Treatment Costs (Quantitative)

The objective was to keep total capital and operating costs for the projected large-scale system below $0.2/1000 gal (or $65 per acre feet). The assessment is that this objective was not reached or is at best inconclusive because the treatment performance problems that were observed prevented firmly establishing guidelines for ZVI bioreactor sizing and did not allow full evaluation of the required operation and maintenance costs.

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8.0 COST ASSESSMENT

One of the objectives of the project was to use the data obtained with the prototype bioreactor to conduct a detailed cost analysis of the proposed technology. The detailed cost model would have included capital and operating costs for selected typical scenarios. Unfortunately, because of the problems experienced with the actual demonstration of the process, the pertinent data could not be obtained and therefore a detailed cost assessment could not be conducted. Instead, the most important cost drivers are briefly mentioned below:

- *Water flow.* Bioreactor sizing is based on the water residence time in the ZVI bed. The reactor size (or capital cost) is expected to increase roughly linearly with the water flow.
- *Perchlorate concentration.* Bioreactor sizing depends on the influent perchlorate concentration. Similar to flow, the reactor size and capital costs are expected to increase roughly linearly with the influent perchlorate concentration.
- *Concentration of dissolved oxygen in the influent.* The requirement for pretreatment to remove dissolved oxygen depends on the influent dissolved concentration. It is likely that there is a threshold in dissolved oxygen below which no pretreatment is required (perhaps 2-3 mg dissolved oxygen L^{-1}). Above that threshold, the pretreatment costs will increase roughly linearly with water flow and dissolved oxygen concentration.
- *Concentration of nitrate in the influent.* If present at high concentrations, nitrate will inhibit perchlorate reduction. The mechanisms are complex and involve both some enzyme competition and possible limitation of hydrogen as the electron donor. Exact quantification of how bioreactor sizing is affected by nitrate could not be determined.
- *Presence of carbonate.* As described in the results section, carbonate precipitates at the surface of the ZVI and can cause significant problems. At this time, these problems have not been resolved and the specific impact of carbonate on treatment costs is unknown.
- *Iron costs.* The cost of iron is expected to be a significant part of the overall treatment costs, and in the past decade, the cost of iron has been relatively volatile, with a 3-4 fold increase over a few years. At the time the reactor was constructed (summer 2007), the ZVI cost was $730 per net ton freight on board (FOB). The 2009 and 2010 cost of ZVI has varied between $800 to $900/per net ton. Thus, some cost variability is expected.
- *Extent and need for post-treatment.* Post-treatment should remove both dissolved and suspended iron and possible bacteria flushed from the system; it should restore aerobic conditions in the treated water and possibly disinfect the water prior to distribution. For this, many off-the-shelf technologies are available. Their costs could not be determined since the effluent from the ZVI bioreactor was not defined. As a first approximation, the post-treatment costs should be similar (or

perhaps lower due to the lower bacteria discharge) to those incurred by other perchlorate biotreatment methods.

One objective of the demonstration project was to prove that total capital and operating costs for a projected large scale system could be below $0.2 per 1000 gal (or $65 per acre feet) of water treated. The performance problems that were observed prevented firmly establishing guidelines for ZVI bioreactor sizing and did not allow full evaluation of the treatment costs. The unresolved problem of ZVI bed plugging, and the uncertainty on the costs associated with resolving this problem make any cost estimates a mere guess.

9.0 IMPLEMENTATION ISSUES

Perchlorate biotreatment using bacteria immobilized on ZVI technology is novel and can potentially offer cost and other benefits for perchlorate and nitrate removal. However, it is susceptible to environmental factors. The technology is not yet demonstrated, and it requires further study prior to full-scale implementation. In particular, the following unresolved issues should be considered prior to implementation of the technology:

- Water chemistry, in particular alkalinity, nitrate concentration and DO are particularly important for ZVI biosystems; greater attention should be given to these parameters.
- While there is a large body of literature on abiotic ZVI reactive systems, the effects of bacteria on the ZVI corrosion and on the longevity and stability of ZVI bioreactors remain poorly understood, and further studies are warranted.
- Mineral supplementation used for biological stimulation can have undesirable consequences and result in mineral deposits that can either reduce the bed porosity and/or passivate iron surfaces, and thus should be exerted with care.
- A greater attention should be placed on the iron balance in ZVI packed beds, and the effects of iron mesh size, bed geometry, and bed height/water velocity relationships. Experiments in the lab showed that beds with fine ZVI rapidly plugged when beds of coarse ZVI did not.
- Bed porosity, hydraulic issues, and ZVI passivation are the greatest challenges to long-term sustained treatment performance in ZVI biotreatment systems. Reactor designs other than packed beds should be considered, with designs that can effectively deal with the adverse effects named above. Possible designs include fluidized beds, circulating or moving beds, and other designs that may not yet have been developed.

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10.0 REFERENCES

Coates, J.D., and L.A. Achenbach. 2004. Microbial perchlorate reduction: Rocket-fuelled metabolism. Nature Rev. Microbiol. 2, 569-580.

Giblin, T.L., D.C. Herman, and W.T. Frankenberger, Jr. 2000a. Removal of perchlorate from ground water by hydrogen-utilizing bacteria. J. Environ. Qual. 29, 1057-1062.

Giblin, T.L., D.C. Herman, M.A. Deshusses, and W.T. Frankenberger, Jr. 2000b. Removal of perchlorate in water with a flow-through bioreactor. J. Environ. Qual. 29, 578-583.

Henderson, A.D., and A.H. Demond. 2007. Long-term performance of zero-valent iron permeable reactive barriers: A critical review. Environ. Eng. Sci. 24, 401-423.

Logan, B.E. 1998. A review of chlorate- and perchlorate-respiring microorganisms. Bioremediation J., 2, 69-79.

NRC. 2005. Health Implications of Perchlorate Ingestion. National Research Council of the National Academies. National Academies Press, Washington, D.C.

Powell, R.M., D.W. Blowes, R.W. Gillham, D. Schultz, T. Sivavec, R.W. Puls, J.L. Vogan, P.D. Powell, and R. Landis. 1998. Permeable reactive barrier technologies for contaminant remediation. EPA 600-R-98-125.

UMBBD. 2010. University of Minnesota Biocatalysis/Biodegradation Database, http://umbbd.msi.umn.edu/pco/pco_map.html, accessed April 2010.

USEPA, Office of Research and Development. 2002. Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization. External Review Draft. NCEA-1-0503.

USEPA. 2008. Interim Drinking Water Health Advisory for Perchlorate, http://www.epa.gov/safewater/contaminants/unregulated/pdfs/healthadvisory_perchlorate_interim.pdf, accessed May 2010.

Yu, X., C. Amrhein, M.A. Deshusses, and M.R. Matsumoto. 2006. Perchlorate reduction by autotrophic bacteria supported on zero-valent iron. Environ. Sci. Technol. 40, 1328-1334.

Yu, X., C. Amrhein, M.A. Deshusses, and M.R. Matsumoto. 2007. Perchlorate Reduction by Autotrophic Bacteria Attached to Zero-Valent Iron in a Flow-Through Reactor. Environ. Sci. Technol. 41, 990-997.

Zhang, H., M.A. Bruns, and B.E. Logan. 2002. Perchlorate reduction by a novel chemolithoautotrophic hydrogen-oxidizing bacterium. Environ. Microbiol. 4, 570-576.

Ziv-El, M.C., and B.E. Rittmann. 2009. Systematic evaluation of nitrate and perchlorate bioreduction kinetics in groundwater using a hydrogen-based membrane biofilm reactor. Wat. Res. 43, 173-181.

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APPENDIX A

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