

# FINAL REPORT

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

ESTCP Project ER-200636

JUNE 2010

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Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE <b>JUN 2010</b>		2. REPORT TYPE <b>N/A</b>		3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Field Demonstration of a Novel Biotreatment Process for Perchlorate Reduction in Groundwater</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Environmental Security Technology Certification Program (ESTCP)</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>ESTCP Project ER-200636, The original document contains color images.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>SAR</b>	18. NUMBER OF PAGES <b>68</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

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## **List of Acronyms and Abbreviations**

DO	Dissolved oxygen
DPH	Department of Public Health
EBRT	Empty Bed Retention Time
EDX	Energy-dispersive X-ray analysis
GW	Groundwater
NRC	National Research Council
ORP	Oxydo-reduction potential
PCE	Perchloroethylene (also known as perchloroethene)
PE	Polyethylene
ppm	Parts per million (or $\text{mg L}^{-1}$ )
ppb	Parts per billion (or $\mu\text{g L}^{-1}$ )
PRB	permeable reactive barriers
PRM	Perchlorate reducing microorganisms
RfD	Reference dose
SEM	Scanning electron microscopy
TCE	Trichloroethylene (also known as trichloroethane)
UCR	University of California, Riverside
USEPA	U.S. Environmental Protection Agency
XLPE	Cross-linked polyethylene
ZVI	Zero valent iron

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## **Acknowledgements**

The principal investigators would like to acknowledge the Environmental Security Technology Certification Program (ESTCP) for funding of the demonstration project under award ER-0636. Todd Webster and Sam Wong of Shaw Environmental (later Basin Water Inc.) provided outstanding support at the Rialto Well #2 site. The principal investigators also acknowledge the hard work of Seongyup Kim, Yue Wang, Jason Hu and many other students or researchers who participated in the study. The contribution of Karel Matous (Department of Aerospace and Mechanical Engineering, University of Notre Dame) with his micro-CT of ZVI is acknowledged.



## Executive Summary

A technology demonstration was conducted at the Well #2 in Rialto, California to treat perchlorate contaminated groundwater using a novel biological treatment system. 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. Prior to this technology demonstration, we conducted extensive research in the laboratory to determine the treatment performance under a range of simulated field conditions and to develop a better understanding of the treatment process. The results of the laboratory studies formed the basis of this ESTCP award, as they showed that the process was very promising with relatively high perchlorate reduction rates. 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, TCE, hexavalent chromium, and the possible control by adsorption of chromium, uranium, and arsenic ions. The concept could also be translated into subsurface treatment, for example in a funnel and gate reactive barrier.

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 1) obtain pertinent data that will guide full-scale design and operation, 2) provide relevant data for treatment cost estimation and comparison, 3) provide the necessary data leading to possible permitting of the process by California DPH, and 4) disseminate the results in various forms to promote technology transfer. As will be described below, significant treatment performance issues occurred with the demonstration unit after three months of operation. This motivated further laboratory studies to help identify the causes of the problems observed in the field.

To achieve the project goals, a trailer mounted pilot demonstration system was design, built, and mobilized at Well #2 in Rialto. The system consisted of a water holding tank, the ZVI packed bed (300 gallons) with approximately 4400 lbs. 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 pre-treatment unit was installed to remove some of the influent water dissolved oxygen (DO), as the 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 and its suitability for full-scale treatment of groundwater contaminated with perchlorate.

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 three months of flawless operation, followed by numerous treatment performance problems that eventually forced the shutdown of the system.

The initial three months of operation were characterized by high perchlorate and nitrate removal rates meeting regulatory limits. The average effluent concentration of perchlorate was  $1.8 \pm 0.9$  ppb, nitrate was  $<0.01 \text{ mg L}^{-1} \text{ NO}_3\text{N}$ , iron ranged from 0 to  $0.05 \text{ mg L}^{-1}$ , and coliforms, fecal coliforms and *E. coli* in the reactor effluent were all below the detection limit. 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. The experimental plan called for an initial phase at low flow prior to increasing the throughput of the unit. Problems occurred before the treatment performance at high flow could be determined.

After approximately three months of operation, perchlorate and nitrate removal by the ZVI reactor system began to deteriorate, with subsequent operation achieving only 40% perchlorate and nitrate removal for the remaining 5 months of testing. The reactor upset was totally unexpected as we ran biotreatment systems in the laboratory for much longer than 3 months without a problem. The loss in treatment performance could not be traced back to any outside event (power failure, visible symptom, or else). Thus, several hypotheses were formulated to explain the loss in treatment efficacy and these were systematically tested. These included the a severe reduction of the ZVI bed hydraulic conductivity<sup>1</sup>, 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 scale-down ZVI columns aimed at determining the causes of the failure of the field unit. One series of experiments determined that water high flows were 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  $\text{NaHCO}_3$  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 ( $\text{FeCO}_3$ )) 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  $20 \text{ mg L}^{-1}$  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 pre-treatment, low water flow), were probably responsible for the failure of the bioreactor in the field. Thus the water chemistry was instrumental, and it remains

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<sup>1</sup> The hydraulic conductivity is the ease with which water can move through a given medium, here the ZVI bed. The hydraulic conductivity is usually represented by the symbol K.

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.

The main findings can be summarized as follows:

1. A short startup (~10 days) can be achieved with proper inoculation of the ZVI.
2. Effective treatment of both perchlorate and nitrate was observed for a period of nearly three months, after which treatment performance issues occurred.
3. When the reactor was operational, the effluent concentration of perchlorate was  $1.8 \pm 0.9$  ppb, nitrate effluent concentration was  $<0.01 \text{ mg L}^{-1} \text{ NO}_3^- \text{N}$ , effluent iron ranged from 0 to  $0.05 \text{ mg L}^{-1}$ , 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 of 4 gpm, which is 5 fold less than the nominal treatment capacity of 20 gpm. Problems with the bioreactor occurred after three months, i.e., before the groundwater could be increased to its nominal capacity.
4. Conversion of perchlorate to harmless chloride was stoichiometrical with one mole of chloride released per mole of perchlorate reduced.
5. Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were detected in the bioreactor effluent.  $\text{Fe}^{2+}$  was effectively and spontaneously oxidized to insoluble  $\text{Fe}^{3+}$  species in the sand filter without the need of dosing hydrogen peroxide.
6. Treatment performance declined after three months of operation. Despite multiple attempts to restore treatment efficacy, removal of perchlorate and nitrate remained low. Failure was attributed to significant losses in the hydraulic conductivity caused by the accumulation of iron corrosion products and deposition of mineral precipitates. Some passivation of the ZVI probably also contributed to the failure of the process.
7. Laboratory experiments with scaled-down system operated in mostly abiotic mode with selected conditions 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 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 pre-treatment, low water flow), was responsible for the failure of the bioreactor in the field.
8. 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 prior to implementation.

On the basis of the findings, the following recommendations were made:

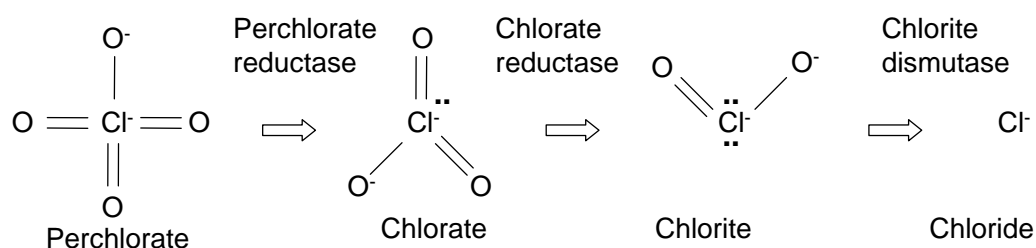
1. Water chemistry, in particular alkalinity, nitrate concentration and DO are particularly important for ZVI bioreaction systems and greater attention should be given to these parameters.

2. 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.
3. 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.
4. 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.
5. 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.
6. The technology is not yet demonstrated and it requires further study prior to full-scale implementation.

## 1. INTRODUCTION

### 1.1 Background

The discovery of perchlorate ( $\text{ClO}_4^-$ ) in a large number of ground and surface water supplies, coupled with its disruption of the production of thyroid hormones, resulted in perchlorate being added to the U.S. EPA's candidate contaminant list (Zhang et al., 2002; US-EPA, 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 preferred method because microorganisms can completely transform  $\text{ClO}_4^-$  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 1.1. Chlorate is rarely seen; for details on the biology of perchlorate reduction, see the excellent review by Coates and Achenbach, 2004.



**Figure 1.1** Pathway for the biological reduction of perchlorate (redrawn from UMBD, [http://umbbd.msi.umn.edu/pco/pco\\_map.html](http://umbbd.msi.umn.edu/pco/pco_map.html) ).

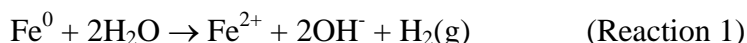
One strategy for perchlorate biological reduction involves the use of an organic carbon and energy source such as acetic acid or corn syrup to promote the reduction of perchlorate by native or added heterotrophic microorganisms. The disadvantage of this approach is that the non-specific substrate stimulates the growth of a broad spectrum of heterotrophic microorganisms and leads to excess biomass and biofouling (Grindstaff, 1998). Therefore, 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., 2000ab).

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 (Logan, 1998; Ziv-El and Rittmann, 2009). *Dechloromonas* sp., which are able to reduce perchlorate to chloride using  $\text{H}_2$  as the electron donor and carbon dioxide as carbon source, have been identified in the laboratory (Zhang et al., 2002; Giblin et al., 2000b). However, production and/or handling of hydrogen gas is problematic, and its low water solubility poses challenges for delivery to perchlorate reducing bacteria.

An in-situ method for generating hydrogen gas is corrosion of zero-valent iron (ZVI). ZVI is nothing else than iron, usually with a purity greater than about 95%. It is marketed in a granular form with a wide range of available sizes ranging from nano-sized ZVI to cm-size or even greater chunks. ZVI is non-toxic and it has been shown to have great versatility in supporting

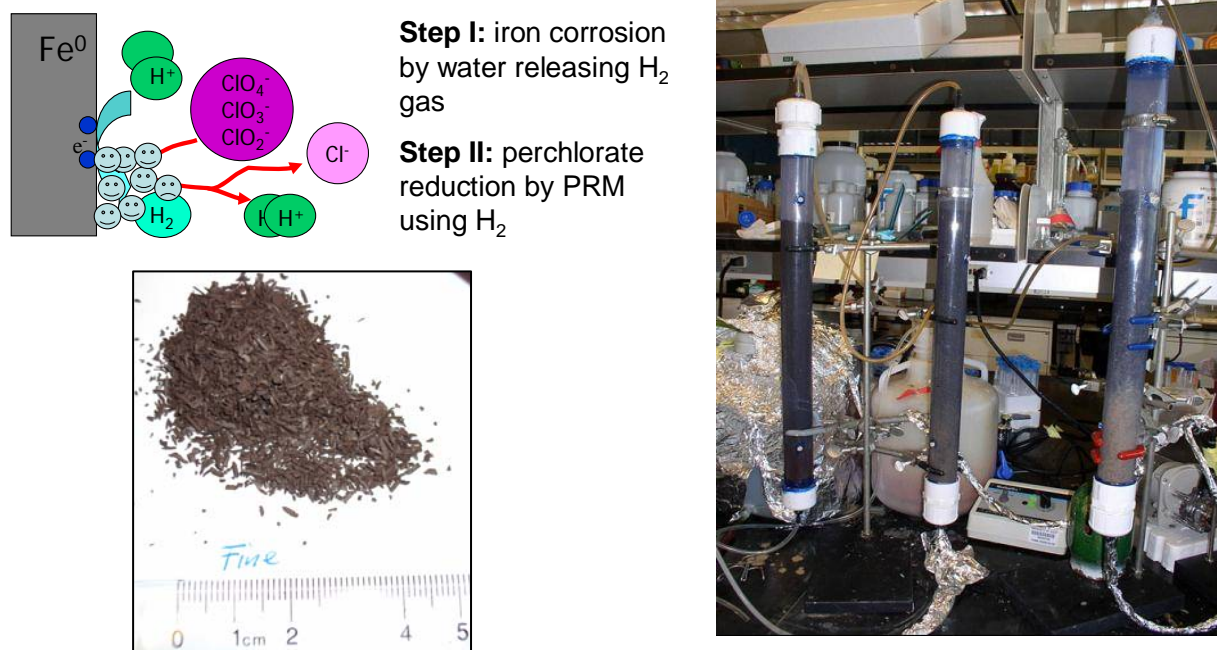
biological or chemical reductions of compounds such as trichloroethylene (TCE), chromate and uranyl. As such, ZVI is being used widely as reactive filling material in permeable reactive barriers chemically reducing and/or adsorbing a variety of contaminants (Powell et al., 1998).

However, due to the large activation energy required, direct chemical reduction of perchlorate using ZVI is too slow to be used for perchlorate remediation. But, as iron corrodes in water,  $H_2$  is released (Reaction 1) which can then be utilized by perchlorate reducing bacteria.



We have recently shown that ZVI can be coupled with perchlorate-reducing microorganisms (PRM) to degrade perchlorate without the need for external hydrogen gas addition or organic carbon source (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. The schematic description of the zero-valent iron/autotrophic perchlorate reducing microorganisms process is shown in Figure 1.2. The advantage of this novel approach lies in that:

1. Production/handling equipment and transport of  $H_2$  is eliminated.
2. Biofouling is reduced as relatively few organisms can grow on the surface of ZVI with  $H_2$  and carbonate alone as substrates.
3. Other contaminants, such as nitrate, TCE, chromium, uranium, and arsenic, can also be treated concurrently with ZVI.



**Figure 1.2** Schematic description of perchlorate biotreatment using ZVI and perchlorate reducing microorganisms (PRM) (top left) and picture of laboratory flow through bioreactor systems (right) consisting of a packed bed of ZVI through which the contaminated water flows upwards. Bottom left picture shows fine (unused) ZVI (bar scale in cm).

## **1.2 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 technology. Additional objectives were to:

1. Obtain pertinent data that will guide full-scale design and operation.
2. Provide relevant data for treatment cost estimation and comparison.
3. Provide the necessary data leading to possible permitting of the process by California DPH.
4. 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 is described in Section 5.1, significant challenges were experienced in maintaining effective perchlorate treatment over several months. Hence, demonstration of continuous treatment was only conducted at Well #2. Thereafter, R&D efforts were directed towards understanding the causes of the upsets observed at Well #2.

## **1.3 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, the U.S. Environmental Protection Agency (US-EPA) issued an Interim Drinking Water Health Advisory level (US-EPA, 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 EPA adopted a Reference Dose (RfD) of  $0.7 \mu\text{g kg}^{-1} \text{day}^{-1}$ . 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 engineering to develop new methods of treatment.

## 2. TECHNOLOGY

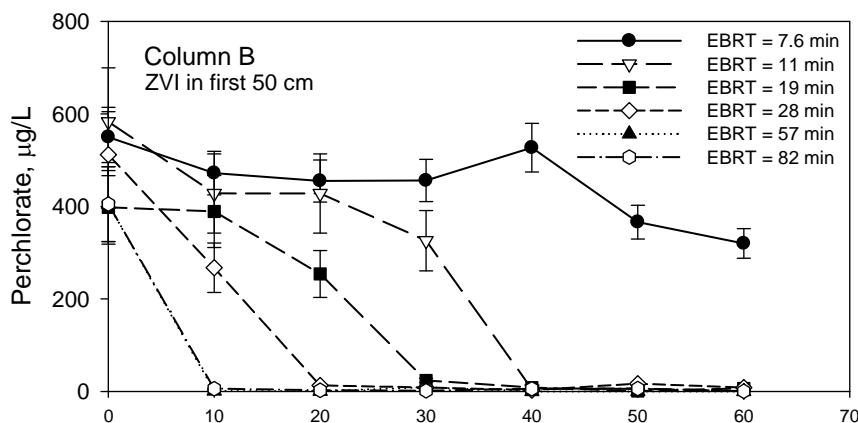
### 2.1 Technology Description

Treatment of perchlorate relies on the corrosion of zero-valent iron 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 and 2007). The schematic description of the zero-valent iron/autotrophic perchlorate reducing microorganisms process was shown in Figure 1.2 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 (non-pathogenic). Iron is oxidized chemically and precipitated iron and bacteria are removed by passing the water through a sand filter.

Demonstration of ZVI-supported biological reduction of perchlorate was motivated by outstanding results obtained in the laboratory with pilot units. Some laboratory results are shown in Figure 2.1. ZVI not only produced  $H_2$  for perchlorate reduction, but also served as a support for bacteria, making it possible to design fixed bed bioreactors packed with ZVI. Effective treatment of perchlorate in flow through ZVI packed bed bioreactors has been demonstrated (Yu et al., 2006 and 2007). A high rate of perchlorate reduction, low end-point of treatment (concentration <6 ppb, see Table 1), 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, which is within the range of most groundwater systems (pH 6-8). 100% perchlorate removal (effluent <4 ppb) was obtained treating tap water spiked with as much as  $500 \mu g L^{-1}$  perchlorate (Figure 2.1). 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. Perchlorate removal still occurred at a slower rate. Complete perchlorate removal was been observed at (empty bed) retention times (EBRTs) less than 40 minutes (Figure 1.2) 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. Microbiological studies successfully defined the best operating practices during bioreactor inoculation and startup (Yu et al., 2007).

Overall, operation of the lab scale ZVI packed bed for over 24 months proved that stable and sustained treatment could be achieved (Yu et al., 2007). Many samples collected from the reactor effluent had non-detect (<2-4 ppb on our ion chromatograph) perchlorate concentrations. Selected samples collected when the bioreactor was operated at liquid empty bed contact time ranging from 1-2 hours, were analyzed for perchlorate using ion chromatography-mass spectrometry. Perchlorate effluent concentrations in these samples were below the detection limit of 70-100 ppt. Further, iron corrosion studies showed that the ZVI in the reactor would last for several years. This is consistent with numerous studies on ZVI in-situ reactive barriers showing that ZVI lasts for several years.





**Figure 2.1** Typical results from the laboratory flow through bioreactors. Here, the effect of flow rate on the axial perchlorate concentration profile is shown. Influent  $\text{ClO}_4^- = 400$  to  $600 \mu\text{g L}^{-1}$ . EBRT is the empty bed retention time. The actual retention time of the groundwater in the system is shorter.

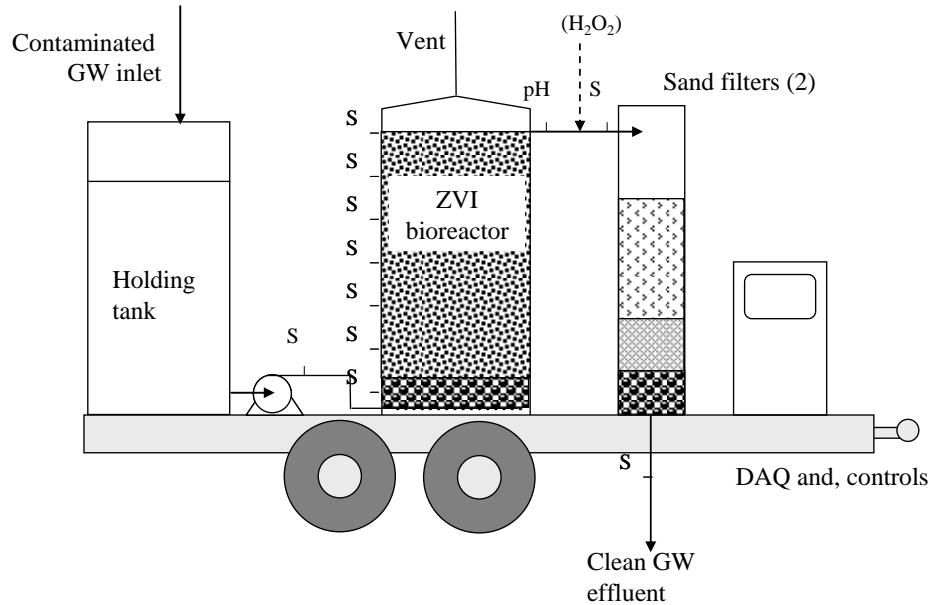
<b>Table 2.1</b> Summary of column experiments (EBRT = 41 min)		
	<b>Influent</b>	<b>Effluent</b>
<b>pH</b>	7.5 - 7.6	7.5 - 7.6
<b>Perchlorate (<math>\mu\text{g L}^{-1}</math>)</b>	500	0.7 - 6
<b><math>\text{Fe}^{2+}</math> (<math>\text{mg L}^{-1}</math>)</b>	N/A	0.2 - 2
<b>Alkalinity (<math>\text{mg L}^{-1} - \text{CaCO}_3</math>)</b>	150	40 - 60
<b>Heterotrophic Bacterial Count (<math>\text{CFU mL}^{-1}</math>)<sup>1</sup></b>	N/A	$(5.7 - 13.2) \times 10^3$

<sup>1</sup>No speciation of bacteria was conducted during the laboratory phase.

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 2.2, detailed instrumentation and controls are shown in Figure 2.3, while size and various equipment information is reported in Table 2.2. Figure 2.4 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 5.1, pre-treatment of the water to remove dissolved oxygen was added to the system shortly after startup 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  $\text{Fe}^{2+}$  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,

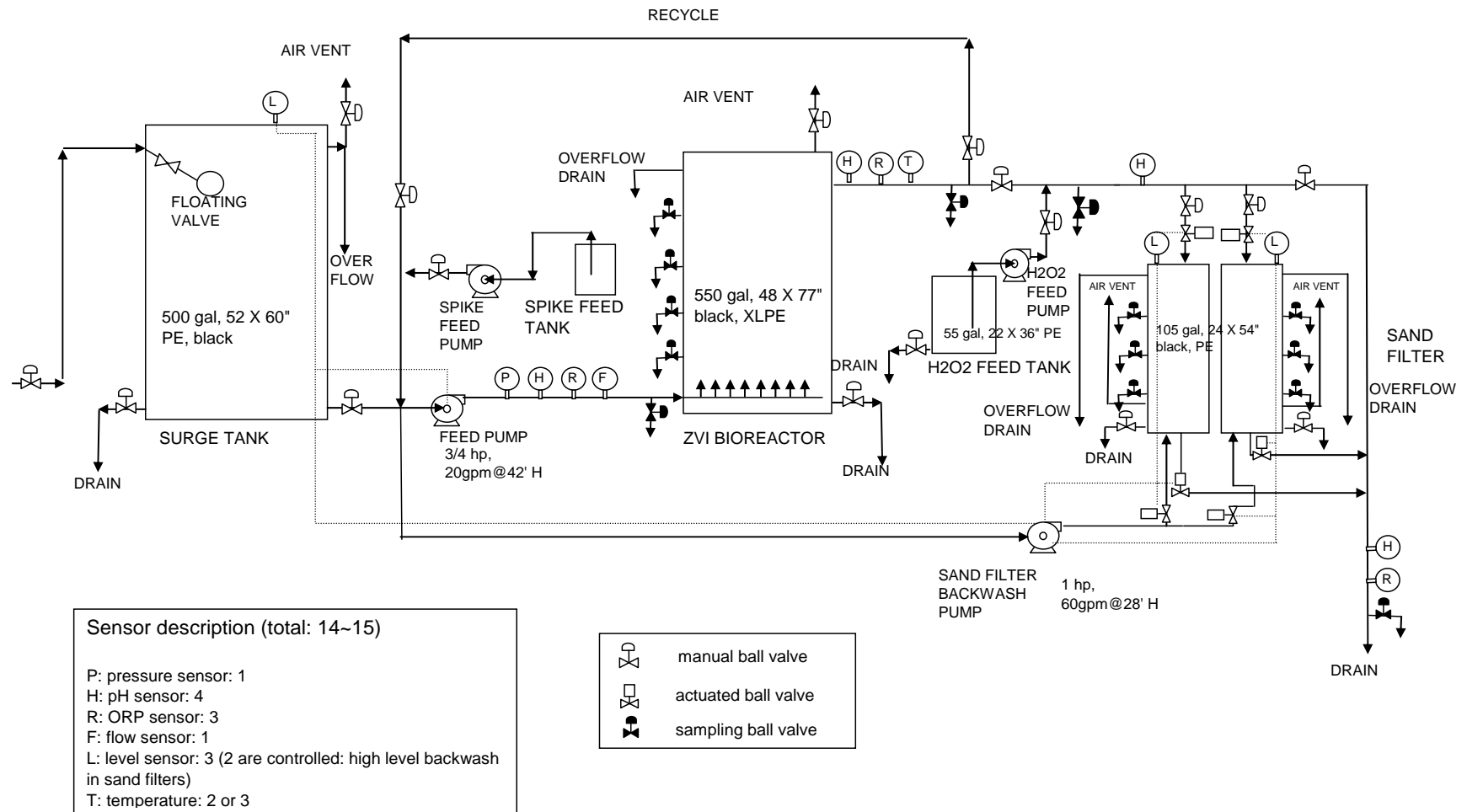
the other treats the water stream exiting the bioreactor. For the backflush, fresh water is pumped upwards through the sand filter. The effluent is directed to the drain going to the catch basin.



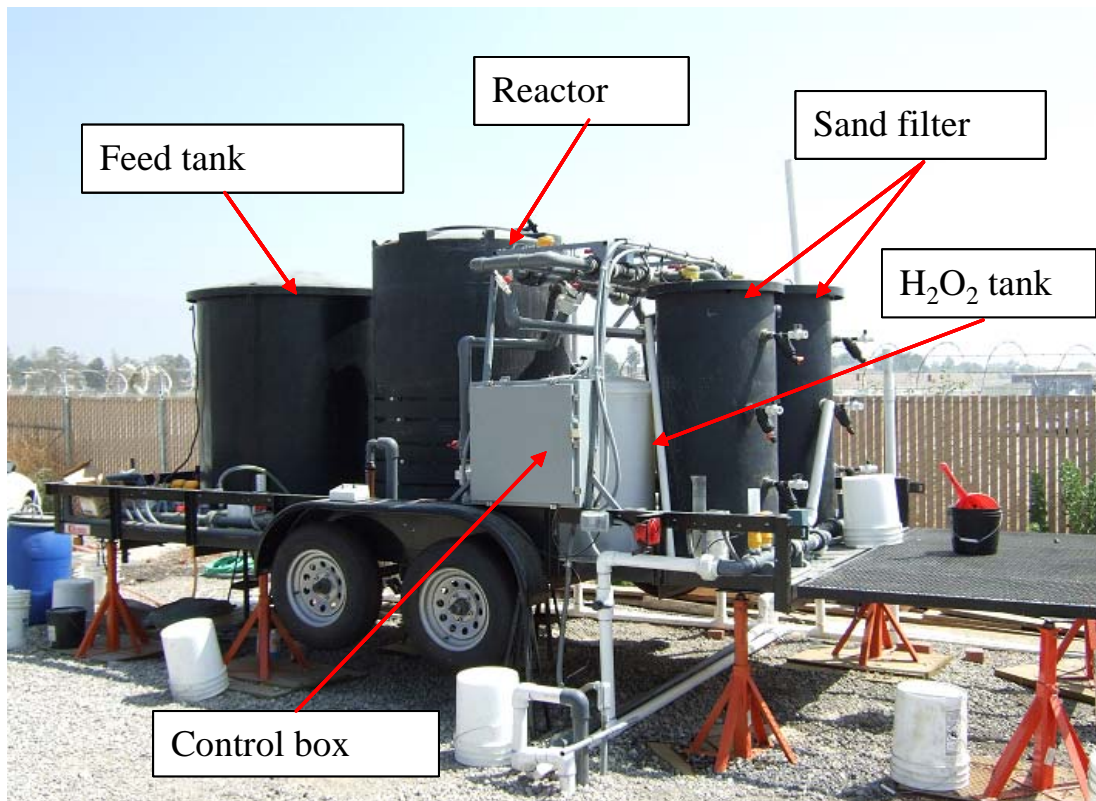
**Figure 2.2** Schematic of the trailer mounted pilot demonstration system (not to scale, controls not shown). S = sampling port. Homogeneous distribution of the water at the bottom of the bioreactor is achieved via a network of perforated pipes. Backflush for the sand filters not shown. As mentioned in the text, pre-treatment of the contaminated water to remove dissolved oxygen was implemented after the startup of the system, but is not shown on the schematic.

**Table 2.2.** 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 <sup>-3</sup>
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	



**Figure 2.3** Flowsheet and instrumentation of the demonstration system (not to scale).



**Figure 2.4** Picture of the demonstration system at the Rialto well #2 site. Membrane degassing pre-treatment not shown.

## 2.2 Key System Design Criteria

The key design criteria for ZVI bioreactor treatment systems include:

1. The size of the ZVI bioreactor tank. Bioreactor size and flow of groundwater to be treated are linked. For effective treatment, water needs a given contact time with the ZVI in the bioreactor. Thus, a long contact time will require larger ZVI bioreactors, and is associated with higher capital costs. Obviously, process optimization seeks to minimize the required contact time, to reduce the bioreactor volume and capital costs.
2. The mesh size and mesh range of the ZVI. The finer the ZVI, the more ZVI surface area for bacteria immobilization and the greater the reactivity of ZVI. However, beds made with finer ZVI will have a lower porosity and thus will have a greater tendency to clog.
3. The nature and design of post-treatment. Post-treatment should be effective in removing both dissolved and suspended iron. It should remove possible bacteria flushed from the system, and potentially restore aerobic conditions in the treated water. The system as designed was equipped with sand filters and optional injection of hydrogen peroxide (or hypochlorite) as needed.
4. The possible requirement to remove some dissolved oxygen as a pre-treatment step to biological reduction of ZVI. Biological reduction of perchlorate requires anaerobic conditions.

## 2.3 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 a ion exchange resin or in a 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 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 (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  $\text{Fe}^{2+}$  and insoluble  $\text{Fe}^{3+}$  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  $5 \text{ mg L}^{-1}$  of  $\text{NO}_3^- \text{N}$  will reduce the rate of perchlorate, thus requiring a larger and more expensive treatment system.

### 3. PERFORMANCE OBJECTIVES AND ASSESSMENT

The performance objectives of the demonstration study are provided in Table 3.1 and attainment of each specific performance objective is commented below. Experimental details supporting the conclusions are provided in Chapter 5.

**Table 3.1.** Performance objectives. See Section 3.1 for details on meeting 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 $> 1 \text{ g m}^{-3} \text{ h}^{-1}$ 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 $< 6 \text{ }\mu\text{g/l ClO}_4$ , $< 0.3 \text{ mg/l Fe}$ ; $< 1 \text{ mg/l NO}_3\text{-N}$ ; other contaminants and bacteria to be defined	Yes, but only at lower water flowrate. Nominal flowrate could not be tested.
Quantitative	Startup time	Startup time shorter than 5 days	No; startup 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/startup time after period of down time (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 h 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 $< \$0.2 / 1000 \text{ gal}$	No or inconclusive because of performance issues

### 3.1 Performance Objectives

As will be discussed in details in Chapter 5, the ZVI bioreactor performed flawlessly for about three months after the initial startup. Thereafter performance dropped and bed plugging issues were observed. Despite intensive troubleshooting efforts, optimum treatment performance was never recovered. For these reasons, the process was not evaluated to the extent anticipated when the project was initiated. As a result of process failure, many performance objectives were either not tested, or were not met. This is detailed in the next Sections.

#### 3.1.1 Ease of Operation and Maintenance (Qualitative)

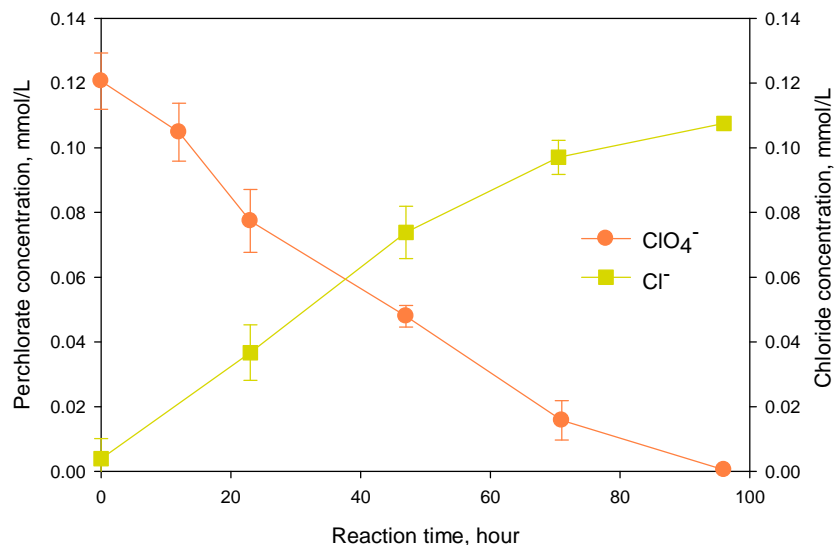
Reaching this objective was inconclusive for the following reasons. When the system was removing perchlorate effectively, it required very little maintenance or attention. The system is indeed easy to operate and requires low maintenance. Besides the feed of a few chemicals ( $\text{NaHCO}_3$ , possibly a molybdenum salt) during the startup of the bioreactor and sporadically later for culture maintenance, there is no chemical feed needed. The bioreactor system was successfully operated without  $\text{H}_2\text{O}_2$  addition (intended for  $\text{Fe}^{2+}$  oxidation) after the bioreactor. Also, there are only a few moving parts, there is no control loop to check or sensors to calibrate on a frequent basis. This eased the operation and maintenance. 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. The problems that were experienced were significant. 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.

#### 3.1.2 Reduction of Perchlorate to Chloride (Quantitative)

This objective was met; stoichiometric conversion of perchlorate to chloride was observed. Because of background chloride concentration in waters usually treated and the low level increase (due to the low concentrations of perchlorate), determination of stoichiometric conversion of perchlorate to chloride requires that the experiment be conducted in chloride free medium. A typical result is shown in Figure 3.1 which demonstrated that there was a 1:1 correspondence of perchlorate reduced and chloride formed.

#### 3.1.3 Specific Volumetric Performance (Quantitative)

The objective was to treat groundwater and meet regulatory objectives at volumetric perchlorate reduction rates  $> 1 \text{ g m}^{-3} \text{ h}^{-1}$  or empty bed retention time shorter than 45 min. This objective was not met. The experimental plan called for increasing the groundwater flowrate (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. Because the perchlorate concentration in the influent was low, the loading was low and the volumetric perchlorate reduction rate was only  $0.03 \text{ g m}^{-3} \text{ h}^{-1}$ . Higher flowrates, which would have possibly resulted in higher volumetric rates were not attempted. After the loss of treatment performance, the bioreactor never recovered full treatment performance and greater flowrates/shorter empty bed retention times were not tested.



**Figure 3.1** Perchlorate reduction (in a shake flask) by perchlorate reducing bacteria and stoichiometric release of chloride.

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

The objective was obtain effluent concentrations below  $6 \mu\text{g L}^{-1}$  for perchlorate, below  $0.3 \text{ mg L}^{-1}$  for iron, less than  $1 \text{ mg L}^{-1} \text{ NO}_3^- \text{N}$ ; 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 3.2.** ZVI bioreactor average performance over the first three months, when operated at an empty bed residence time of 75 min.

	Influent concentration	Effluent concentration
Perchlorate	$42 \pm 4 \text{ ppb}$	$1.8 \pm 0.9 \text{ ppb}$
Nitrate	$19.5 \pm 1.4 \text{ ppm}$ (as nitrate) or $4.5 \pm 0.3 \text{ mg L}^{-1} \text{ NO}_3^- \text{N}$	$<40 \text{ ppb}$ (as nitrate) or $<0.01 \text{ mg L}^{-1} \text{ NO}_3^- \text{N}$
Iron	Variable due to pre-treatment	$0-0.05 \text{ mg L}^{-1}$
Bacteria	ND	Coliforms, fecal coliforms and <i>E. coli</i> in the reactor effluent were below the detection limit of 2 MPN/100mL

When the reactor was functioning well, during the initial startup phase, the effluent concentrations of perchlorate, nitrate, iron and bacteria were all below the target effluent levels. It should be noted however that when these measurements were made, the flow had not yet been increased to its nominal capacity of 20 gpm. Effluent concentrations can be expected to increase with increases in the treated water flow, but problems prevented testing at the nominal flow capacity.



### 3.1.5 Short Startup 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. Although we have started numerous bioreactors in the laboratory, some reaching successful treatment within the 5 day window, startup time in the field bioreactor was slower than anticipated. The reasons for the slow startup are unclear. Even so, it is likely that specific measures such as greater bacteria inoculation or feeding of ancillary nutrients or substrates could reduce the startup time. This was not investigated in the field bioreactor.

### 3.1.6 ZVI life (Quantitative)

The objective was 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. Practically, that also means that ZVI life exceeded the duration of the project, but some quantitative determinations of the ZVI exhaustion rate were expected on the basis of which ZVI life would have been estimated with greater accuracy. As will be discussed in detail in Chapter 5, significant bed porosity problems occurred with the ZVI which prevented sustained treatment of the groundwater. Plugging of the ZVI bed was observed as a result of the accumulation of corrosion products and mineral precipitation. While these phenomena did not exhaust the ZVI per say, some passivation of the iron probably occurred. In any case, operation of the ZVI bioreactor had to be discontinued. Under these circumstances, no firm conclusions could be made on the ZVI life. It is very possible that different operating modes or preventive maintenance could prevent the plugging of ZVI beds, although specific measures are not known yet, and their effects on the ZVI life and the rate at which ZVI needs to be replaced are also not known. For these reasons, the conclusion is that reaching this objective was inconclusive.

### 3.1.7 Ability to Treat both Low and High Concentrations of Perchlorate (Quantitative)

Because of the problems experienced with the ZVI bioreactor system, this objective was not tested. High concentrations (high ppm levels) were successfully treated in our lab-scale ZVI bioreactors.

### 3.1.8 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) ( $<5 \text{ mg L}^{-1}$ ). These were found to pose no special environment health risk or cost liability.

### 3.1.9 Robustness (Quantitative)

The original plan was to systematically demonstrate the ability of the system to treat to regulatory standards a) concentration spikes and b) recovery/startup time after period of down

time (e.g., power outage). The robustness was not tested in a systematical 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 shut down 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 demonstrate some level of process robustness.

#### 3.1.10 Low Downtime and Low Maintenance (Quantitative)

The goal was that the downtime should be less than 0.01% and maintenance less than 2 h 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. Perchlorate effluent concentrations were consistently below regulatory levels. In terms of maintenance, the system required about 1 to 1.5 h of routine maintenance per week, mainly to check the integrity of the system, to download data from the data acquisition system, and occasionally calibrate a sensor probe. Note that possible additional maintenance requirements to prevent bed plugging issues will be on top of these maintenance needs, but are not yet known.

#### 3.1.11 Treatment Costs (Quantitative)

The objective was to keep total capital and operating costs for 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 to firmly establish guidelines for ZVI bioreactor sizing and did not allow to fully evaluate the required operation and maintenance costs.

#### 4. 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 1950's. 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 4.1. Relevant to the project is the fact that the water is pumped from 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 4.1.** Concentrations of relevant species in the water at well #2.

<b>Contaminant</b>	<b>Concentration Range</b>
<b>Measured (this project)</b>	
Perchlorate	49 to 65 ppb
Nitrate	4 to 7 mg NO <sub>3</sub> <sup>-</sup> N L <sup>-1</sup>
TCE	ND to 3 ppb
Other organics	ND
Dissolved oxygen	>8 mg L <sup>-1</sup>
Alkalinity	148-156 mg CaCO <sub>3</sub> L <sup>-1</sup>
TOC	10-12 ppm
<b>Historical averages<sup>1</sup></b>	<b>Mean / Low / High</b>
Perchlorate	74 / 34 / 88 ppb
Nitrate	26 / 23 / 28 mg L <sup>-1</sup> (as NO <sub>3</sub> <sup>-</sup> )
Chloride	13 / 12 / 13 mg L <sup>-1</sup>
Sulfate	12 / 11 / 12 mg L <sup>-1</sup>
Carbonate / Bicarbonate	<3/210 / <3/210 / <3/210 mg L <sup>-1</sup>
pH	7.8 / 7.7 / 7.9
Total Dissolved Solids	260 / 260 / 260 mg L <sup>-1</sup>
Conductivity	445 / 430 / 460 μS cm <sup>-1</sup>
Volatile organics	ND / ND / ND

<sup>1</sup>Communicated by ESTCP and the City of Rialto

## 5. RESULTS

### 5.1 Field Data of Perchlorate Biotreatment at Well #2

#### 5.1.1 Dealing with the high dissolved oxygen in the water influent

The pilot demonstration was mobilized early July 2007. After mobilization at Well #2, significant concerns were raised about the high dissolved oxygen in the water extracted at the site. Examination of the water holding tank used by Shaw Environmental for their demonstration revealed that the water was probably oversaturated in oxygen, as a result of the deep well and the specific hydro-geological conditions. The high DO in the influent 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 until DO is reduced by ZVI to essentially nil.

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. The water was continuously looped through the fluidized bed; chemical oxidation of ZVI served to remove the dissolved oxygen. The design and sizing was based on tests conducted in the laboratory, which had shown effective and continuous DO removal using this method for over 30 days. Typically 5-6 mg L<sup>-1</sup> DO in the influent could be reduced to 1-1.5 mg L<sup>-1</sup> in the effluent of the fluidized bed at an empty bed contact time of 32 s. Initially, the same coarse ZVI (3/5 mesh) was used in the pretreatment as in the bioreactor, but after 20 days, the ZVI was replaced by a finer one (20/30 mesh) for two reasons:

1. Fine ZVI is more reactive and therefore is able to remove a greater amount of dissolved oxygen
2. Fine ZVI can be fluidized at lower flowrates. Fluidization was desired as it eliminates concerns of bed plugging in the pre-treatment process.

Every 3-4 days, 4-6 lbs of ZVI were removed from the fluidized bed and replaced with fresh ZVI. Determination of corrosion rate (in the laboratory) and closure of the iron balance showed that the corrosion rate was between 1.3 and 1.8 mg<sub>Fe</sub> h<sup>-1</sup> g<sup>-1</sup><sub>Fe</sub>. This is a very high value due small size of the ZVI and possibly the added shear existing in the fluidized bed. An amount of 0.0505 g ZVI is needed to deoxygenate one L of DO saturate water. This translated in 5.5 kg of ZVI per day for the field demonstration reactor if it was operated at its maximum flowrate of 20 gpm.

The system was operated with the ZVI fluidized bed unit removing DO for 150 days. The water in the 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 pre-treatment 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 vacuum/membrane degassing unit was manufactured by Membrana/Liqui-Cel and consisted in two membrane modules, each rated 10 gpm. The vision was that for low water flows, the membrane modules would be connected in series maximizing the removal of DO, while for

flows between 10 and 20 gpm, the two modules would be operated in parallel. The target DO in the influent of the ZVI bioreactor was to be at least below 4 ppm, and preferably below 1 ppm.

#### 5.1.2 System startup and initial treatment performance

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 gallon 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. There were several reasons for selecting the low flow rate: 1) we were initially limited by the discharge rate because of the size of our drain line, 2) the DO removal unit was only installed on day 7, 3) some laboratory experiments suggested that a slow start was better to establish a healthy perchlorate reducing culture.

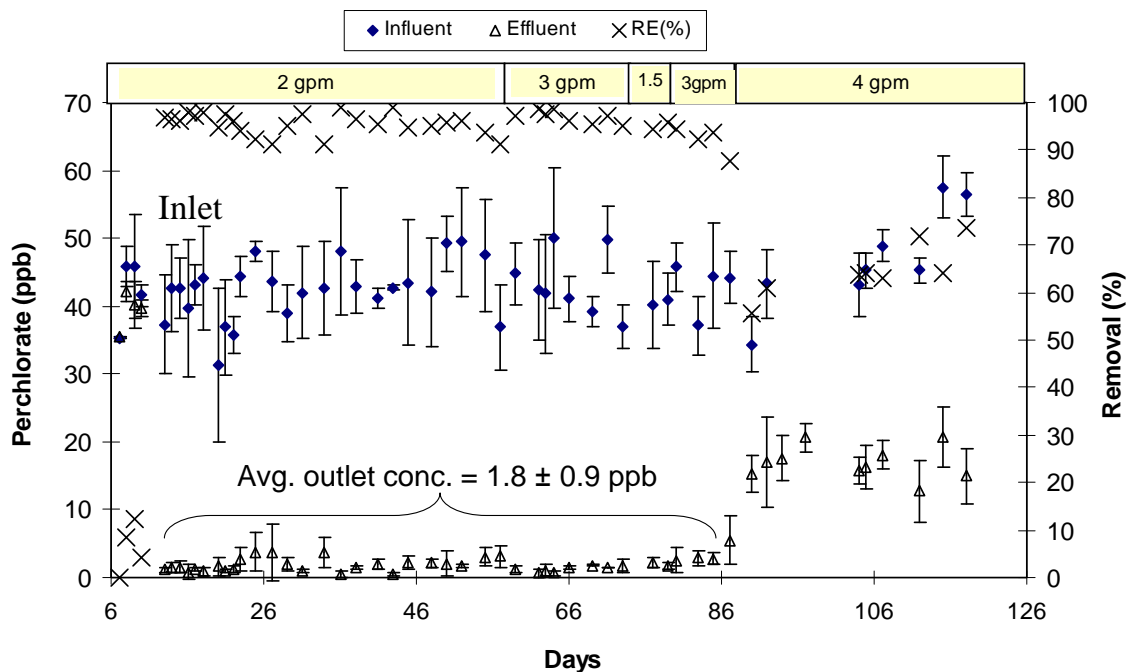
For the first 10 days, there was no noticeable removal of perchlorate. In an attempt to accelerate startup by providing a greater carbon supply to the autotrophic perchlorate reducers, 120 mg L<sup>-1</sup> sodium bicarbonate (NaHCO<sub>3</sub>) and more inoculum were added to the system, after which removal of perchlorate rapidly reached values greater than 95% on day 13. This demonstrated that the proposed biotreatment could be established rapidly. On day 20, the feeding of NaHCO<sub>3</sub> was reduced to 60 mg L<sup>-1</sup> and it was stopped on day 29.

The evolution of the perchlorate removal with time is shown in Figure 5.1. 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:

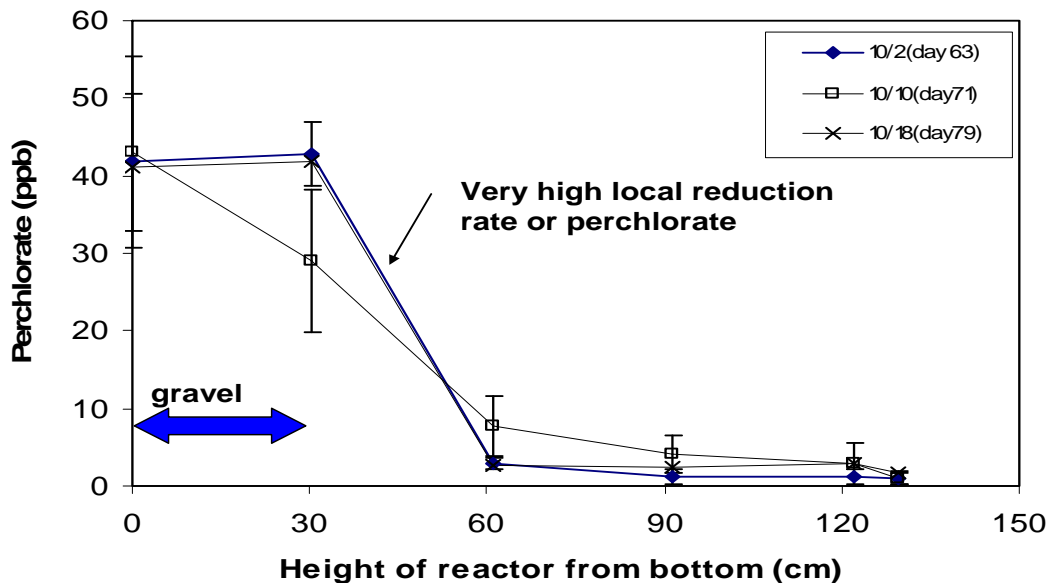
- The influent perchlorate concentration was on average  $42 \pm 4$  ppb
- The effluent perchlorate ranged from essentially non-detect (ND), i.e., below 0.5 ppb to 3 ppb, with an average of  $1.8 \pm 0.9$  ppb. Thus, the removal was on average 95.5%.
- Excellent removal of nitrate was observed with less 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 MPN/100mL
- 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

Selected results are presented and discussed next. Perchlorate and nitrate concentration profiles along the height of the bioreactor are reported in Figure 5.2 and 5.3, respectively. The profiles for perchlorate reflect the fact that, as expected, no removal of perchlorate occurred in the gravel zone which purpose was to provide a homogenous water distribution. However, perchlorate was rapidly removed in the ZVI bed, even while nitrate was being biologically reduced (Figure 5.3). This is an interesting observation as in many cases reported by ourselves and by others [Zhang et al., 2002; Yu et al., 2006 and 2007; Ziv-El and Rittmann, 2009], perchlorate reduction is often inhibited by the presence of nitrate. Here, nitrate concentrations were moderate (~5 mg L<sup>-1</sup> of NO<sub>3</sub>-N), i.e., around the upper limit for when we have observed effective co-treatment of

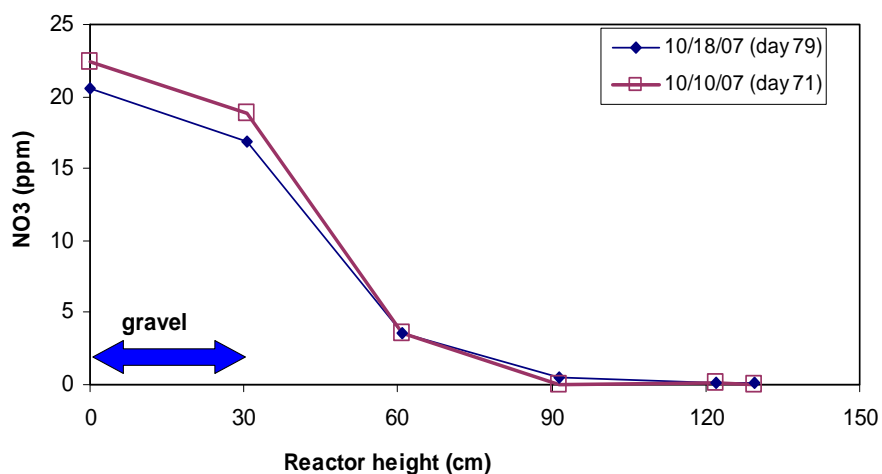
perchlorate and nitrate in the laboratory [Yu et al., 2007]. Overall nitrate removal was high as reported in Figure 5.4 and remained high for well over 100 days. Problems that developed with the reactor and nitrate removal after 130 days will be discussed later in the next section.



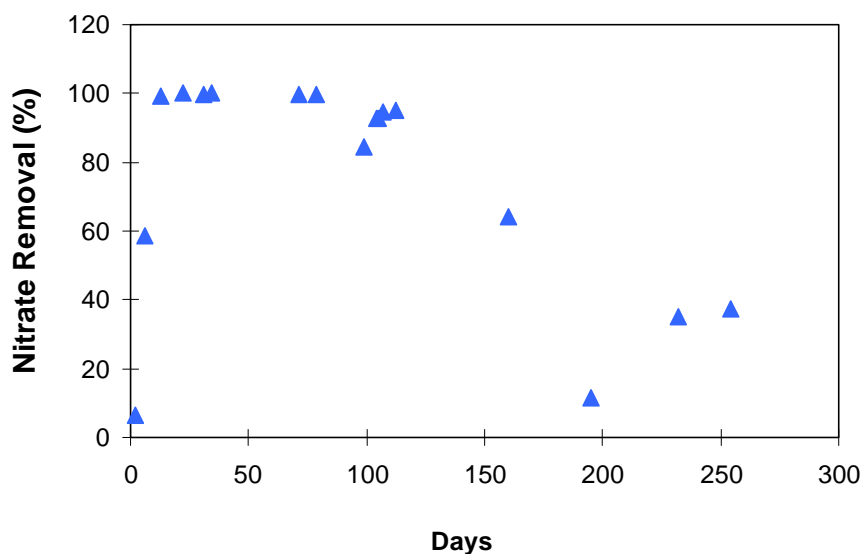
**Figure 5.1** Perchlorate inlet and outlet concentrations over the first 4 months of operation.



**Figure 5.2** Perchlorate concentration profiles in the ZVI bioreactor at selected dates.



**Figure 5.3** Nitrate concentration profiles in the ZVI bioreactor at selected dates.

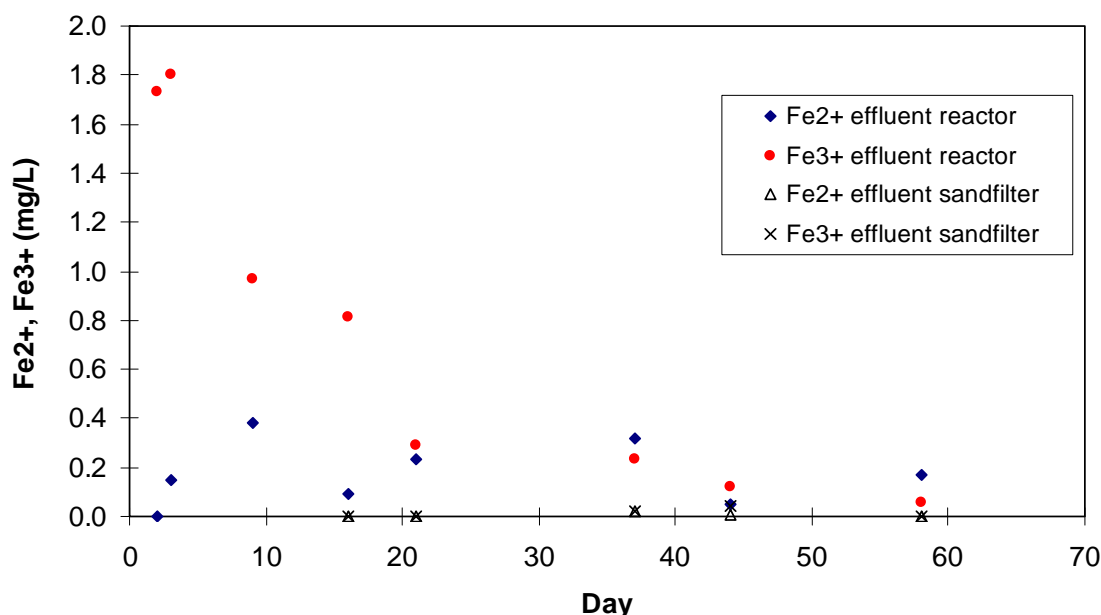


**Figure 5.4** Nitrate removal over the duration of the field demonstration.

Iron species in the bioreactor and sand filter effluents are reported in Figure 5.5.  $\text{Fe}^{3+}$  concentration in the bioreactor effluent gradually decreased over time from high ( $>1 \text{ mg L}^{-1}$ ) initial values to less than  $0.2 \text{ mg L}^{-1}$  while  $\text{Fe}^{2+}$  in the bioreactor effluent remained relatively constant at concentrations around  $0.2 \text{ mg L}^{-1}$ . The fate of iron and some attempt at establishing a mass balance on iron over the system are of particular importance in light of the problems that developed later in the project.

Assuming a high average total effluent concentration of iron  $0.8 \text{ mg L}^{-1}$  and a water flowrate of 2 gpm, this represents an iron release rate of only  $8.7 \text{ g day}^{-1}$ . This can be compared to the value estimated from the expected iron corrosion rate and should match it if all reacted iron is found in the effluent. Depending on the method, different estimates of the iron corrosion rate were obtained. An iron corrosion rate of 50 mg Fe per kg ZVI per day for fresh ZVI was estimated by measuring the DO removal rate in water in a closed vessel fitted with a DO probe and metered amounts of ZVI. At this corrosion rate, the rate of release of iron from the ZVI bioreactor should be in the order of 100 g per day. Separate corrosion rate determinations in shake flasks in our labs (Yu, 2006) yielded rate of 26 to 90 mg iron per kg ZVI per day or an expected rate of iron release of 52 to  $180 \text{ g day}^{-1}$ . While both methods may result in high estimates of iron corrosion rate, the experimental value for the rate of iron release from the bioreactor remains low compared to the anticipated iron corrosion rate. Thus, it is likely that some insoluble iron corrosion products were not flushed out of the reactor. If this occurred, it could over time lead to plugging of the reactor since iron corrosion products have a greater specific volume than metallic iron. The low rate of iron flushing from the system was a surprise. It is unclear if the relatively low water flow (i.e., lower shear and turbulences) during the experiment was a contributing factor in the low flushing of insoluble iron forms.

The concentrations of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  after the sand filters (Figure 5.5) reflect the fact that the sand filters were very efficient at removing iron. The low iron concentrations in the sand filter effluent meant that no hydrogen peroxide was needed to oxidize  $\text{Fe}^{2+}$ . Spontaneous oxidation was sufficient. Turbidity measurements (not shown) ranged from 30 to 50 NTU in the reactor effluent and were always less than 4 NTU in the sand filter effluent.

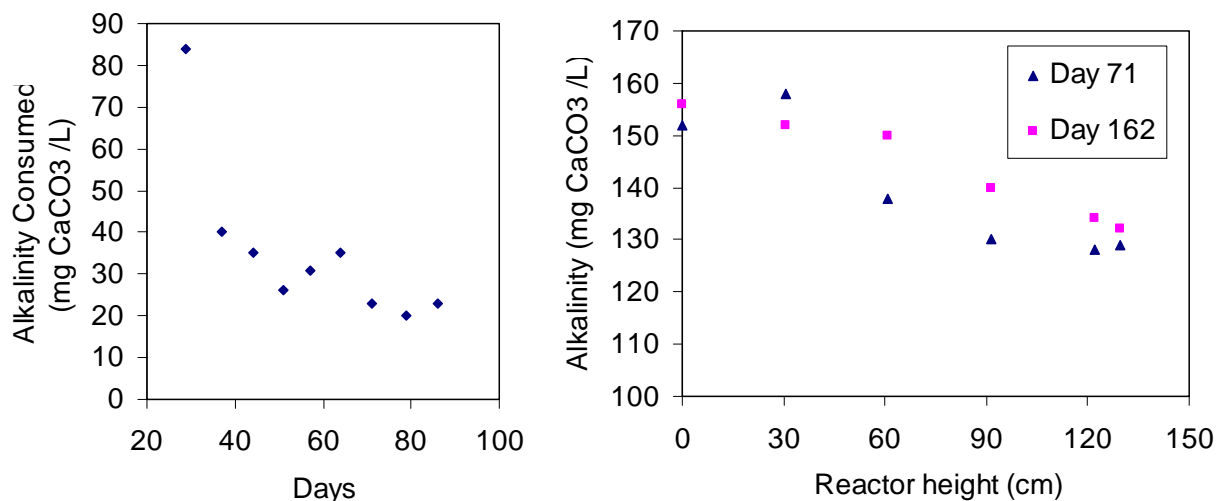


**Figure 5.5** Iron species in the effluents of the reactor and sand filters.

Alkalinity data are reported in Figure 5.6. No measurements were made during the first 28 days. Consumption of alkalinity is primarily by precipitation of carbonates with iron, as will be

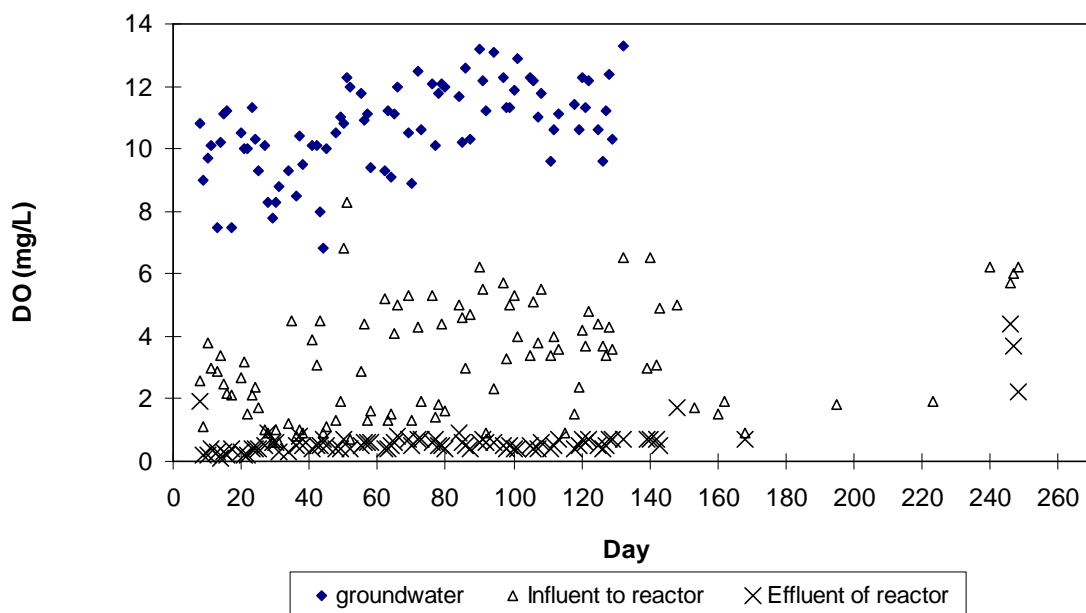


discussed later in Section 5.2.2, although some alkalinity is expected to be taken up by autotrophic bacteria, for cell growth. Figure 5.6 shows that during the initial bicarbonate feeding period, a high rate of alkalinity consumption was observed. Profiles along the height show that alkalinity decreased quasi linearly with penetration along the reactor. 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 this observed while the bioreactor was performing well. This indicates that the main process for alkalinity uptake is most probably abiotic.



**Figure 5.6** Evolution of the alkalinity consumed over time (left) and alkalinity concentration profiles (right) in the ZVI bioreactor at selected dates. Note that the first 30 cm are packed with gravel for proper liquid distribution.

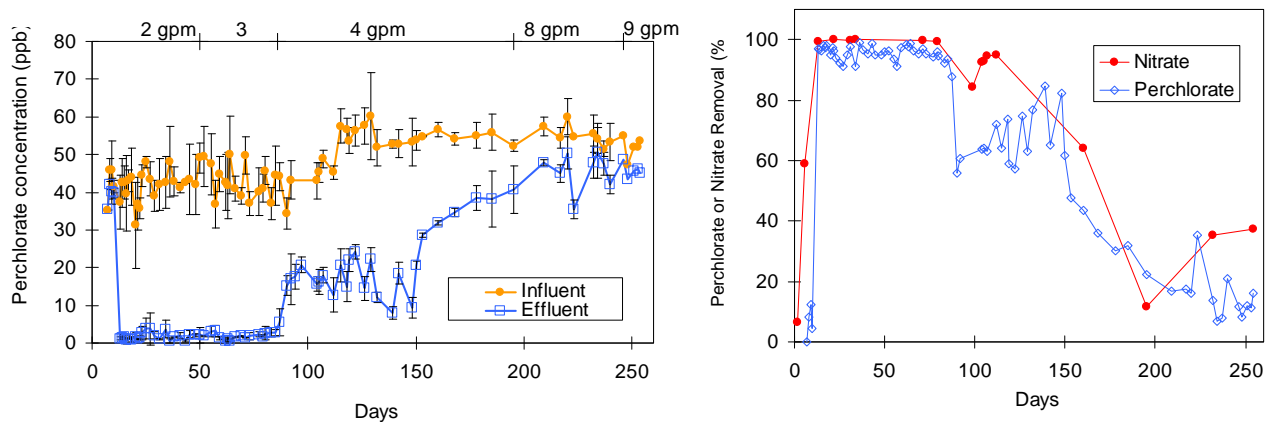
Dissolved oxygen concentrations are reported in Figure 5.7. The data illustrate the fact that the well water was oversaturated with oxygen and that the ZVI pre-treatment system was effective at removing some of the influent DO, but that it could not consistently maintain an effluent DO below 2 ppm. The high variability of the DO fed to the ZVI bioreactor is due to the batch loading of fresh ZVI and removal of used ZVI in the pre-treatment system. Note that the bioreactor effluent DO was always below 1 ppm. On Day 150, the ZVI pre-treatment was replaced by the membrane degasser and low influent DO were consistently obtained. We did note that the membrane degasser required periodical rinsing with a mild acid solution, probably to remove precipitated carbonates.



**Figure 5.7** Evolution of the dissolved oxygen. On day 150, the degassing membrane module was installed on the influent feed.

### 5.1.3 Treatment performance problems and troubleshooting measures

After about 80 days of operation, an increase in the perchlorate effluent concentration was observed and treatment performance deteriorated. Within about a week, the outlet perchlorate concentration increased to 12-18 ppb (see e.g., Figure 5.1), corresponding to a removal of 60-70% only (Figure 5.8). Careful examination of Figure 5.8 reveals that the upset was very sudden and that perchlorate removal reached a temporary steady value of 60-70% until day 150, after which it gradually decreased further to removals around 10%. Despite less frequent analysis for nitrate, a slightly different trend was detected for the removal of nitrate. Possibly, nitrate removal was not greatly affected until after about day 100, after which removal gradually decreased until about day 200.



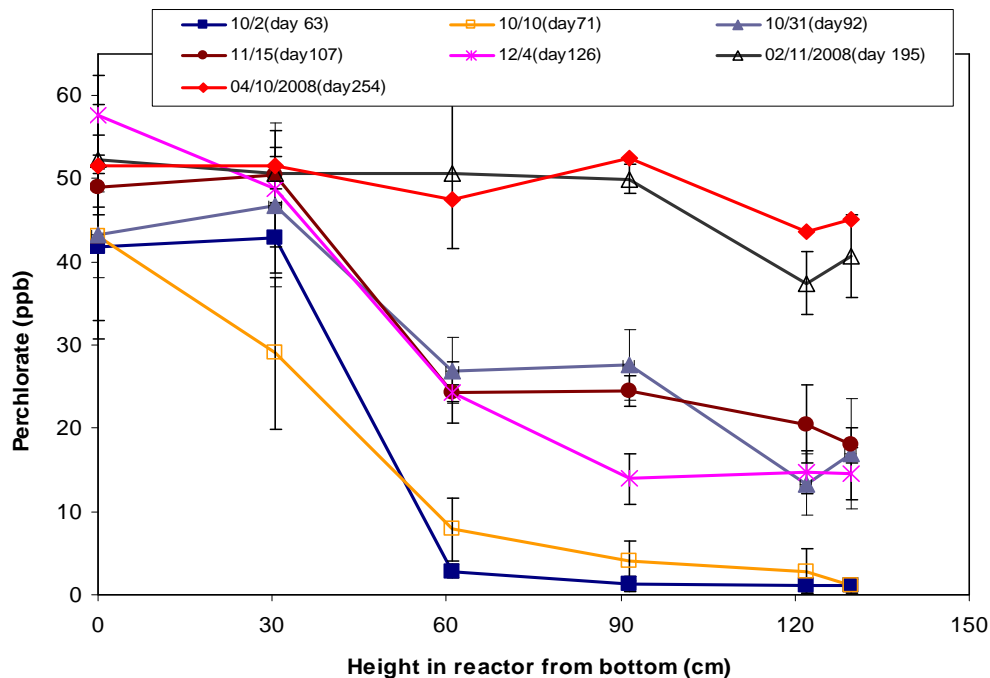
**Figure 5.8** Perchlorate inlet and outlet concentrations (left) and comparison of nitrate and perchlorate removal over time (right).

The reactor upset was totally unexpected as we ran biotreatment systems in the laboratory for much longer than 3 months without a problem. The loss in treatment performance could not be traced back to any outside event (power failure, visible symptom, or else). Thus, several hypotheses were formulated in an attempt to explain the loss in treatment efficacy and these were systematically tested. Various attempts were made to recover full treatment capacity, but as will be discussed, all failed and full treatment capacity was never recovered.

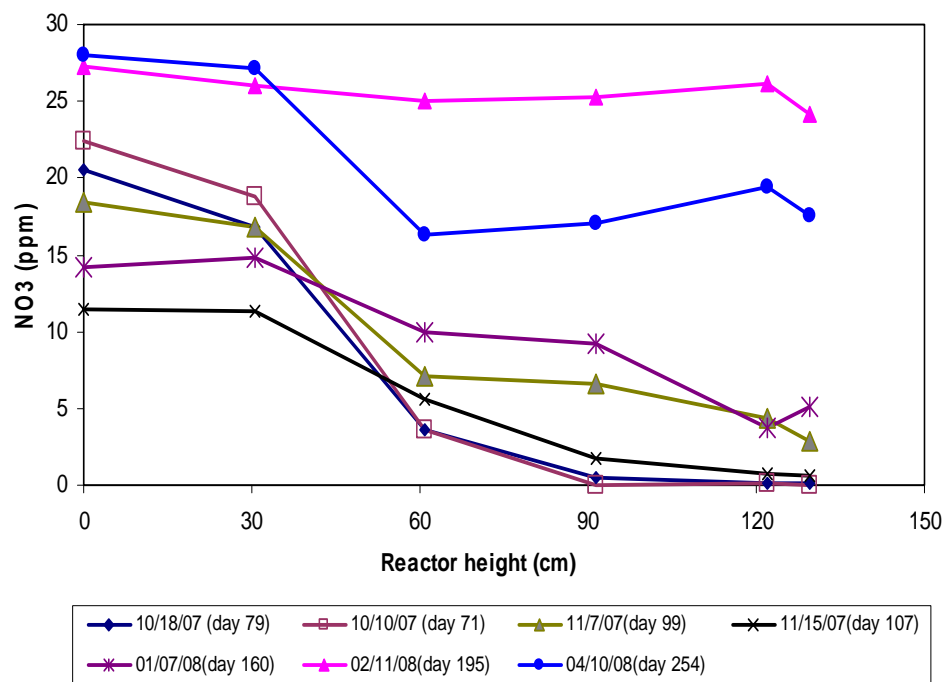
The measures taken and tests performed were as follows:

- Day 63-254: regular determination of nitrate and perchlorate concentration profiles along the height (Figures 5.9 and 5.10) were conducted. These determinations served to evaluate where bacterial reduction occurred. The concentration profiles showed that before problems occurred, perchlorate removal was very fast and was mostly localized in the first 30 cm of ZVI. As performance deteriorated, perchlorate breakthrough occurred and increased penetration of perchlorate in the bioreactor was observed. Nitrate concentration profiles were somewhat slower to be affected by the reactor deteriorating conditions (Figure 5.10).
- The loss of performance occurred at a time when outside temperatures decreased, however, the groundwater and bioreactor temperatures remained relatively constant and the decrease in temperature was less than 2 °C. Thus temperature is not expected to be a determining factor.
- The reactor was re-inoculated on Day 110, but this did not have any effect.
- Day 101-132: start feeding 60 ppm  $\text{NaHCO}_3$ . The hypothesis was that the density of bacteria perchlorate reducing was too low and that bacteria was carbon limited. As will be presented in Section 5.2, we now know that bicarbonate addition promotes deposition of carbonates green rust which affects the hydraulic conductivity of the bed. Thus, this action was probably more harmful than beneficial.
- Day 105-111: start adding 1 ppm ammonium phosphate to the reactor. The hypothesis was that the perchlorate reducing bacteria density was too low and that bacteria may have been phosphate limited.
- Day 121-127: start adding 2.5 ppm lactate. Parallel experiments from our laboratory indicated that perchlorate degradation by our mixed cultures of autotrophic hydrogen utilizing bacteria may be enhanced by short periods of feeding with either lactate or acetate, as a source of organic carbon and energy (note that later, these results could not be confirmed). Thus, lactate (2.5 ppm) was fed to the influent of the reactor for 6 days. During that time, total organic carbon (TOC) measurements were conducted to determine the extent of axial penetration of the lactate through the ZVI bed. Lactate was not detected beyond the first sampling port indicating that it was consumed (as expected) by the bacterial culture in the reactor. In retrospect, it might have been better to have injected lactate in the first sampling port instead of in the inlet feed in order to stimulate activity deeper in the bed. The lactate feeding did not lead to any noticeable improvement of performance after lactate feeding was stopped. Possibly, bacteria growing heterotrophically on the added lactate were not the autotrophic perchlorate reducing bacteria.

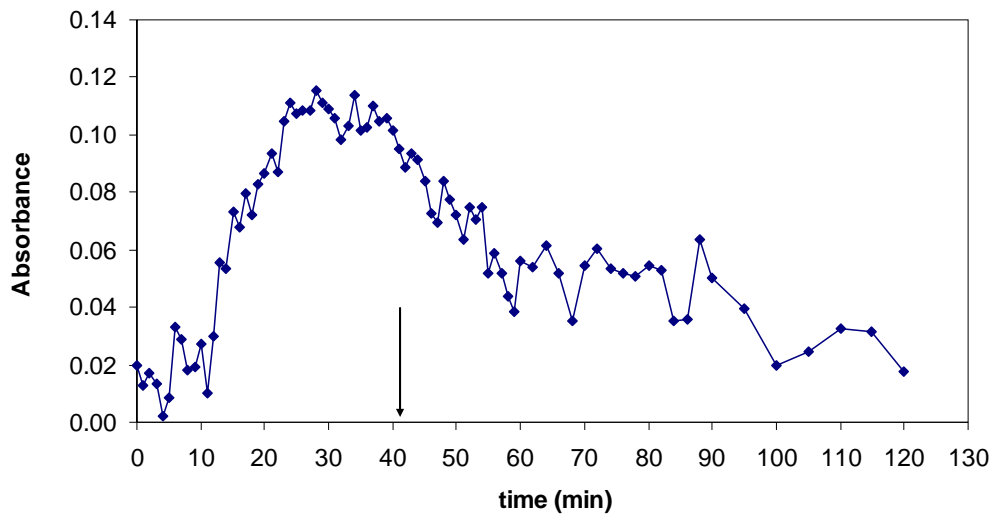
- Day 135 through 160: Several tracer tests were conducted by injecting pulses food coloring in the influent water and monitoring the absorbance of the water in the ZVI reactor effluent. These tests were conducted to determine whether short-circuiting of the water in the bioreactor occurred. The tests revealed that there were some short circuits (Figure 5.11), but still, the average residence time of the water in the ZVI bioreactor system was much greater than experienced before in the laboratory, hence it was concluded that short-circuiting was probably not the main cause of the lower performance. Note that we did not conduct tracer tests when the reactor was removing perchlorate to below the detection limit, hence assessment of short circuiting was made difficult.
- Pressure drop through the ZVI bed was monitored. Until day 77, pressure drop was not measurable; it then increased to about 1.5-2 psi up to day 125, after which it rapidly increased to 5-6 psi. This indicated some build up of deposits and decrease of hydraulic permeability in the ZVI bed.
- The pH was monitored throughout the entire experiment. As is expected for a ZVI system, there was a modest increase (about 0.2 to 0.4 pH units) between the influent and effluent water, but the effluent pH was always between 7.2 and 7.9, which is within the range of adequate pH values.
- Day 143: 3.2 kg (7 Lbs) of  $\text{NaHCO}_3$  (as a source of carbon for bacteria) was added in the water feed tank at once. This did not lead to any performance improvements and as mentioned earlier probably resulted in further deposits of detrimental precipitates.
- Day 150: the membrane degassing unit was started. This reduced the inlet DO significantly.
- Day 140-180: Testing the corrosion rate of ZVI. ZVI samples from the bioreactor were brought back to the lab to determine their corrosion rate, which was found to be in the range normally expected, indicating that hydrogen production was adequate.
- Day 140-180: Testing for the presence of perchlorate reducing bacteria in the reactor. ZVI samples from the bioreactor were analyzed for the presence of perchlorate degrading bacteria. The results showed presence of perchlorate reducing bacteria, however, the density of perchlorate reducing bacteria was not determined, and therefore it is not possible to totally rule out a biological limitation.



**Figure 5.9** Perchlorate concentration profiles in the ZVI bioreactor at selected dates. Note that the first 30 cm are packed with gravel for proper liquid distribution.



**Figure 5.10** Nitrate concentration profiles in the ZVI bioreactor at selected dates. Note that the first 30 cm are packed with gravel for proper liquid distribution.



**Figure 5.11** Tracer residence time distribution in the ZVI bioreactor on day 145. The arrow shows the mean residence time of 41 min, while the theoretical bed residence time was 60 min (80 min EBRT and original porosity of 75%). Thus there was some reduction of the bed porosity or some short-circuiting occurring in the system.

In light of this information, the most plausible reason for the low performance of the ZVI bioreactor was a hydraulic problem within the bed with significant short circuiting of the water and poor contact between the water undergoing treatment and the ZVI-supported bacteria. Still, it is possible that combination of effects, e.g., short-circuiting combined with localized passivation of the iron played a role. It should be noted that hydraulic problems have been reported to be more frequent in ex-situ ZVI reactors than in-situ ZVI barriers (Henderson and Demond, 2007). This is believed to be because of the higher throughput to which ex-situ reactors are exposed but is not well understood.

On July 14, 2008, the operation of the pilot bioreactor at Well #2 in Rialto was discontinued because of the low treatment performance and the failure to recover treatment despite multiple attempts. Also, unrelated to treatment issues, safety concerns at the site increased after the other demonstration projects decommissioned and personnel presence at the site decreased. The compound was frequently broken into, and both equipment and the wheels of our trailer were stolen.

When the bioreactor was decommissioned, visual observation of the bed was conducted. The ZVI bed, which was at startup a highly porous packed bed, had been converted to a solid and compact mass of iron and iron corrosion products. The removal of the ZVI from the reactor bed required cutting the top of the reactor tank and working bit by bit through the ZVI bed with pick axes and shovels. Large blocks of ZVI glued together by corrosion products could be removed (Figure 5.12). The ZVI masses had a low porosity and certainly a low permeability (Figure 5.13). This contrasted sharply with the ZVI that had been installed a year before. The loss of porosity and permeability 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.



The failure to demonstrate long-term treatment and the observation made with the field reactor triggered a series of laboratory experiments that were conducted after with the objective 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 results are presented and discussed in the next two sections.



**Figure 5.12** Pictures of large blocks of ZVI taken out of the reactor when it was dismantled showing the solid structure of the ZVI bed.



**Figure 5.13** 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.

## 5.2 Laboratory Evaluation of Porosity Decrease and Corrosion Products

### 5.2.1 Effects of Carbonate on Permeability and Residence Time Distribution

A review of all field results as well as a survey of the literature lead to the suspicion that carbonate may have played a role in the problems that were experienced in the field bioreactor. On the one hand, carbonate is needed as it serves as a source of carbon for the autotrophic perchlorate reducing bacteria, on the other hand, carbonates can potentially react with ferrous or ferric irons to form iron corrosion precipitates. Depending on the extent of precipitation and on the chemistry of precipitation, this can 1) affect the ZVI corrosion rate and thereby the perchlorate reduction rate, and 2) result in excessive deposits and plug the ZVI bed resulting in high back pressures, non-homogeneous flow paths and process instability.

There is no consensus on how carbonate or bicarbonate affects ZVI corrosion rate. Reardon concluded that ZVI corrosion rate was increased when 0.02 M  $\text{NaHCO}_3$  was added (Reardon 1995). Klausen et al. (2003) also concluded that the presence of bicarbonate enhances iron corrosion when present at high concentration (0.02 M), but they observed that iron corrosion was inhibited at low bicarbonate concentration (0.002 M). Agrawal and Tratnyek (1996) evaluated the abiotic reduction of nitro aromatic compounds by ZVI and observed that the reduction rate increased in the presence of moderate concentrations of carbonate, but it decreased at high carbonate concentrations (0.06 M).

There is no magic value for the bicarbonate concentration required for autotrophic cell growth. Typically concentrations in the range of 0.002 to 0.02 M  $\text{NaHCO}_3$  have been used for autotrophic bacteria, although without much justification. Often, the concentration has been chosen to ensure that bicarbonate is provided in excess, so that the carbon source does not become limiting. The question therefore is the potential impact of bicarbonate and of its reaction products with iron on the ZVI bed and its hydraulic conductivity. This was determined in a series of laboratory experiments conducted as follows.

Laboratory columns were setup (Figure 5.14). Each column consisted of five small PVC segments (3.81 cm ID by 10 cm 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. Each section was packed with 30 g sand first to distribute the water evenly flow, followed by 300 g of ZVI (20/30 mesh) filled to the top.

During the first phase of the experiment, Riverside CA tap water which contains 174 mg  $\text{CaCO}_3$   $\text{L}^{-1}$  alkalinity was used as it was deemed representative of local groundwater. Tap water was fed using peristaltic pumps at the following flowrates:

- Column A: 0.13  $\text{cm min}^{-1}$  (typical of a barrier application)
- Column B: 0.26  $\text{cm min}^{-1}$
- Column C: 0.52  $\text{cm min}^{-1}$
- Column D: 1.04  $\text{cm min}^{-1}$  (approaching field reactor conditions)





**Figure 5.14** Picture of the column setup used for the determination of the effect of carbonate on the hydraulic properties of the ZVI bed.

After 192 days of operation, columns A, B and D were stopped, while experiments with column C continued. 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  $\text{NaHCO}_3$ , respectively. These concentrations of  $\text{NaHCO}_3$  correspond to 300 mg  $\text{CaCO}_3 \text{ L}^{-1}$ , 600 mg  $\text{CaCO}_3 \text{ L}^{-1}$  and 1200 mg  $\text{CaCO}_3 \text{ L}^{-1}$  alkalinity. During the entire experiment, the hydrodynamics, initially in the entire column, and later in each section were monitored periodically by running monthly tracer tests using NaCl and standard head loss tests to determine hydraulic conductivity. The hydraulic conductivity describes the ease in which water can go through the pore spaces of a given material. The nature of the iron corrosion products in the ZVI of the C columns were examined using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDX) at the end of the experiment after dismantling the individual ZVI column segments.

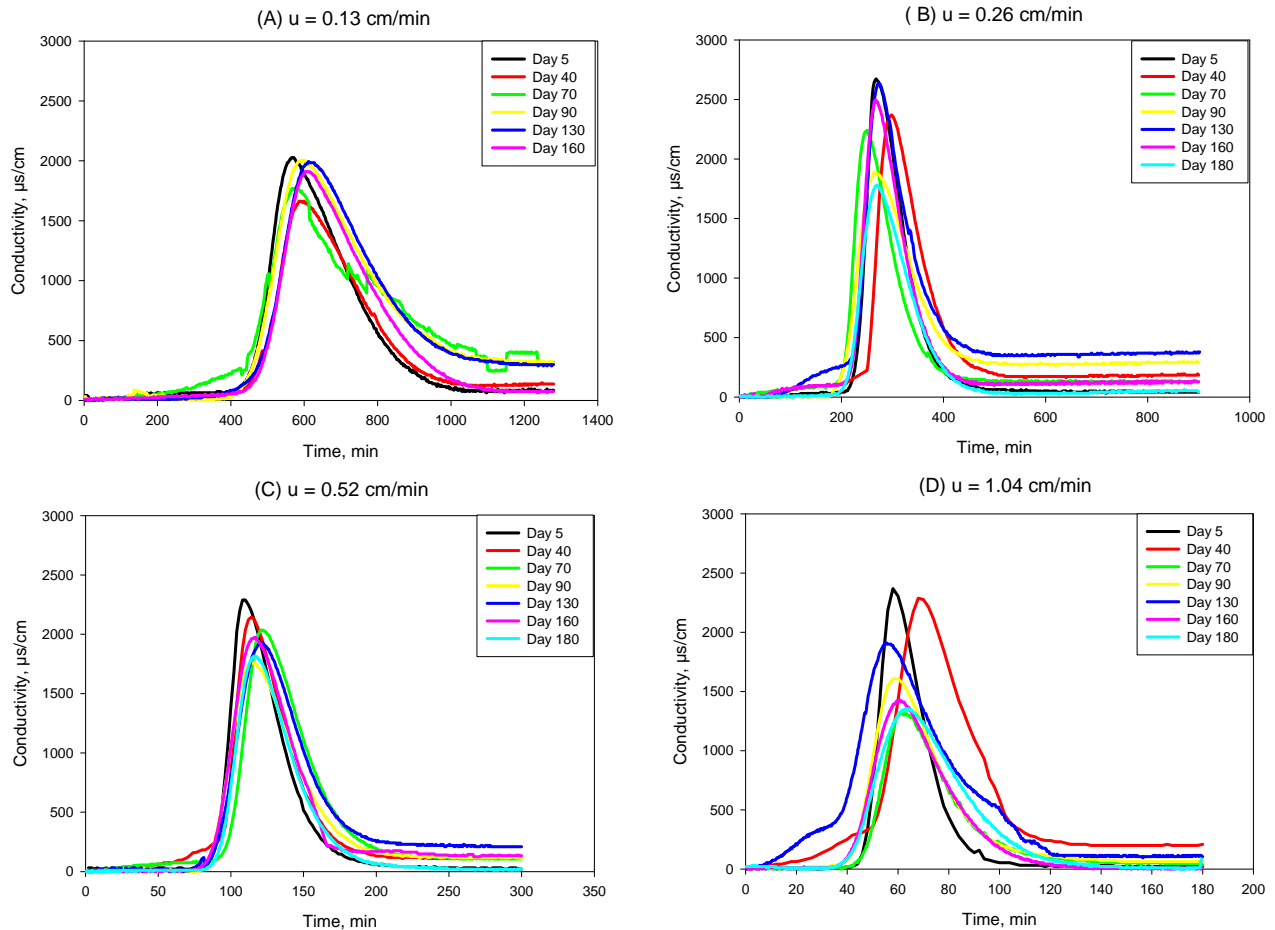
Tracer tests were conducted by injecting 2 mL of a  $200,000 \mu\text{S cm}^{-1}$  NaCl solution in the inlet port of the columns and monitoring the effluent conductivity with a conductivity probe connected to a data logger. For the determination of the hydraulic conductivity, the falling head method was used. Each column segment was connected to a standpipe providing a given water head over the segment undergoing testing. The test consisted in 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:

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

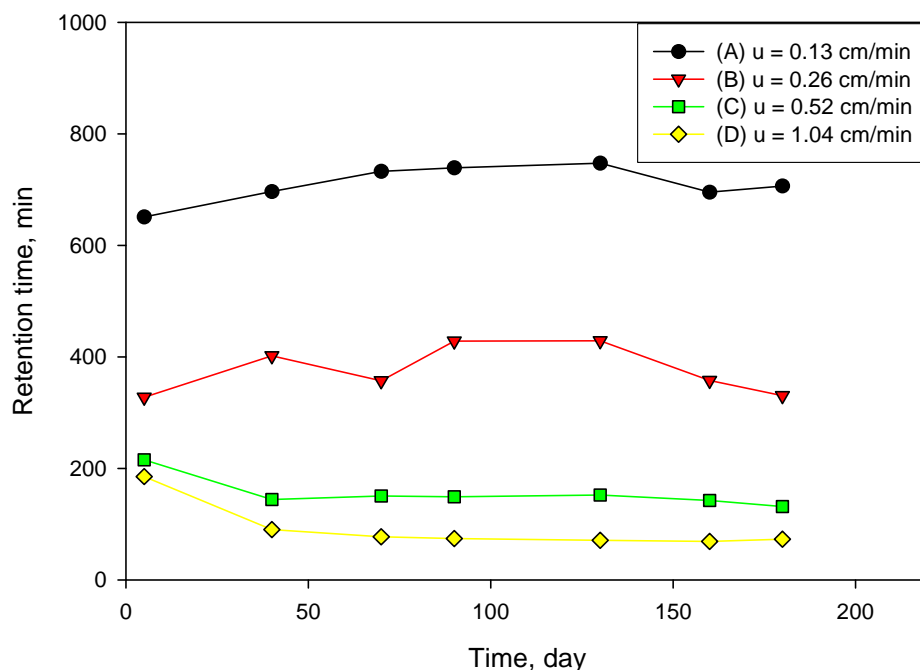
where  $K$  is the hydraulic conductivity ( $\text{cm s}^{-1}$ ),  $h_0$  is the initial water level in the standpipe (cm),  $h_t$  is the water level at time  $t$  (cm),  $A_s$  is the cross section area of the column ( $\text{cm}^2$ ),  $A_c$  is the cross section area of the standing pipe ( $\text{cm}^2$ ), and  $L$  is the length of the packing material (cm).

### Tracer test results

The shape of the effluent tracer signals were symmetrical and fairly consistent over time over the first 190 days for all 4 columns (Figure 5.15). This indicates homogenous flow and constant residence time distribution occurred over time under these conditions. This is further illustrated in Figure 5.16 in which the experimentally determined residence times are reported. Figure 5.15 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 5.16. Detailed Examination of Figure 5.15 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 column operated at lower water velocities.



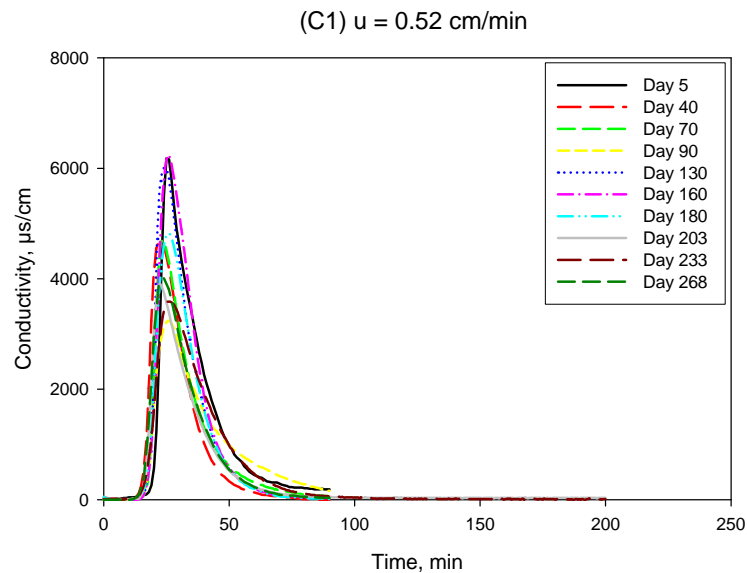
**Figure 5.15** Tracer responses obtained over time in columns A-D operating at different flows.



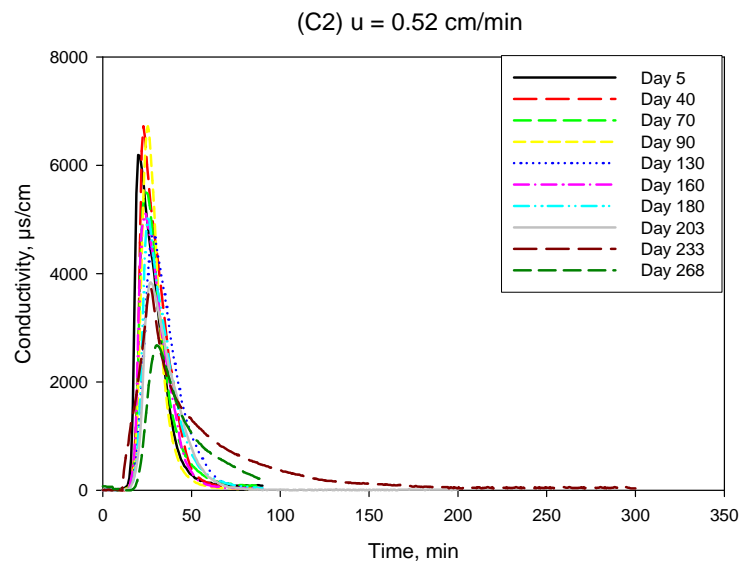
**Figure 5.16** Experimentally determined mean residence time of in the different columns.

Detailed results with the five segments of column C are presented and discussed next. Figures 5.17-5.21 report the results for the entire experiment, i.e., including about 70 days of feeding with elevated bicarbonate concentrations. The tracer responses were symmetrical and relatively constant over the entire duration of the experiment for segments C1 and C2 (i.e. tap water systems). The same consistency was observed for the other columns only for the initial 192 days for the other sections, i.e., for the duration of tap water feeding. Column C3 started to show a long tail for the tracer in the effluent after feeding with 6 mM  $\text{NaHCO}_3$  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  $\text{NaHCO}_3$  compared to column C3. The long tail indicate that there were dead zones inside the reactor and non-homogenous residence time distribution that developed after  $\text{NaHCO}_3$  was supplemented to the water fed to these columns. As will be discussed later, due to severe clogging in columns C4 and C5 over time, water flow was increasingly restricted and no tracer could be recovered during the later stages of the experiment. Columns C4 and C5 had to be stopped after 268 days and 233 days operation, respectively.

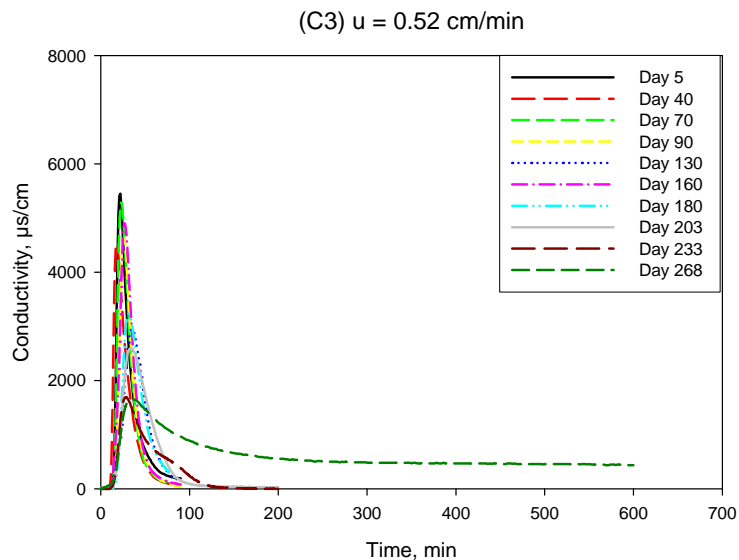
The tracer test results are consistent with hydraulic conductivity results discussed in the next section.



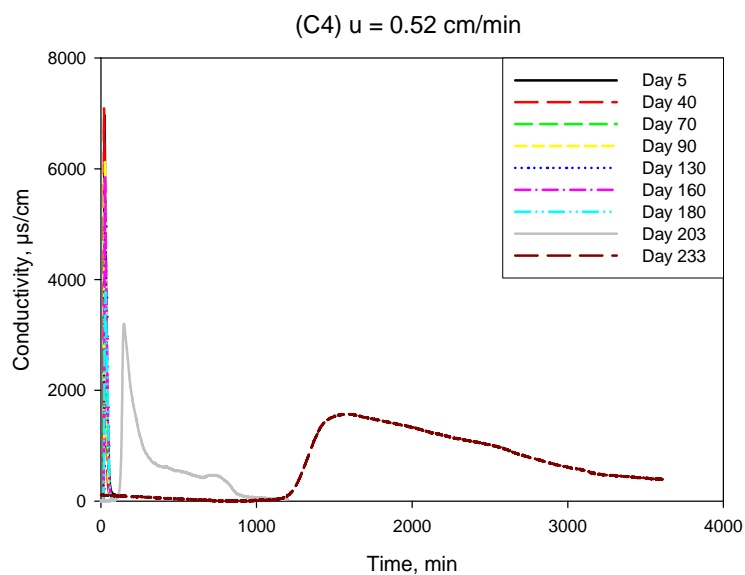
**Figure 5.17** Tracer effluent concentration after column C1 during the entire experiment.



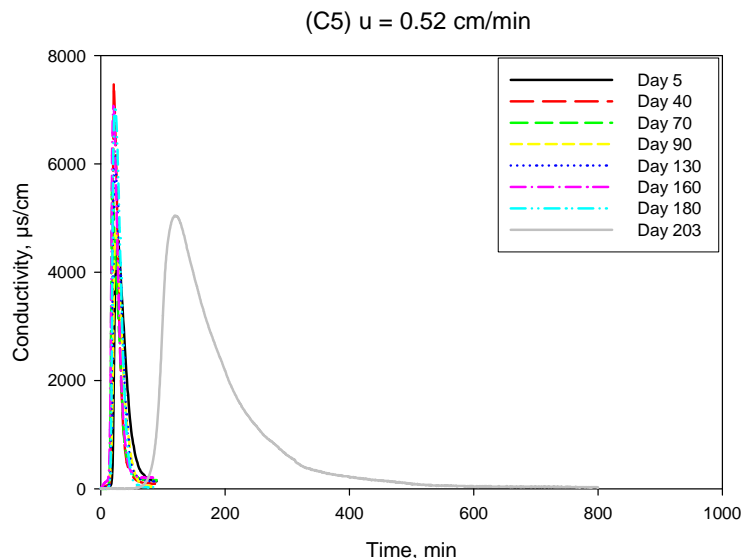
**Figure 5.18** Tracer effluent concentration after column C2 during the entire experiment.



**Figure 5.19** Tracer effluent concentration after column C3 during the entire experiment. 6 mM  $\text{NaHCO}_3$  were fed after day 192.



**Figure 5.20** Tracer effluent concentration after column C4 during the entire experiment. 12 mM  $\text{NaHCO}_3$  were fed after day 192. Delayed tracer output after day 200 reflects lower flow and lower permeability in that column.



**Figure 5.21** Tracer effluent concentration after column C5 during the entire experiment. 24 mM  $\text{NaHCO}_3$  were fed after day 192. Delayed tracer output after day 200 reflects lower flow and lower permeability in that column.

### Hydraulic conductivity results

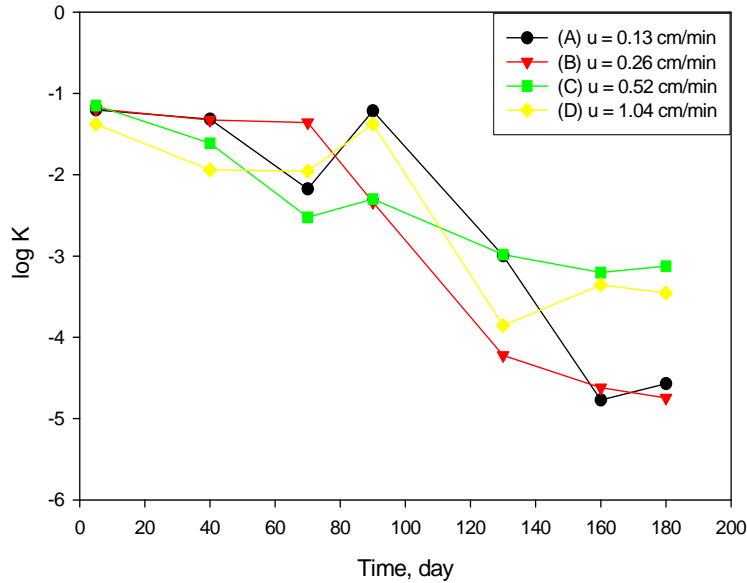
Initially, all columns had roughly the same hydraulic conductivity. Over the first 180 days, a general decreasing trend was observed (Figure 5.22). The decrease of the hydraulic conductivity is due to clogging of the ZVI bed caused by the formation of iron corrosion products. Surprisingly, the decrease was more pronounced in the low flow reactors (A and B) than in the higher flow reactors (C and D). The reasons for this observation are not clear.

Within column C, all segments had roughly the same hydraulic conductivity over the first 192 days. Similar to full columns, a general decreasing trend was observed, with the hydraulic conductivity decreasing by about 1.5 to 2 orders of magnitude during that time (Figure 5.23). Not unexpectedly, C1 had the fastest decrease in hydraulic conductivity as it was the first of the five segments. C4 had the lowest decrease of all, while all other segments seemed to reach some kind of steady state around 150 days.

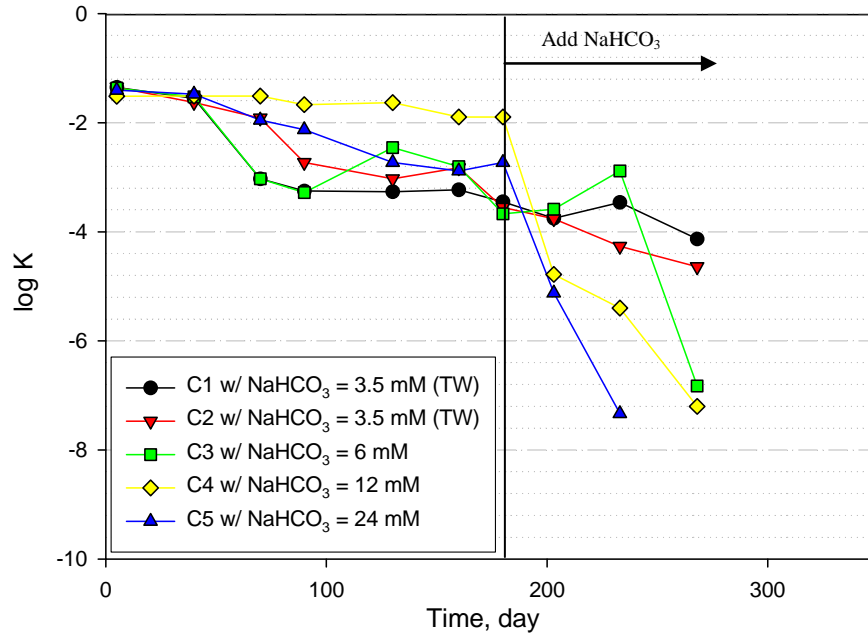
After amending the water with different amounts  $\text{NaHCO}_3$  in C3, C4 and C5, there were important decreases in the hydraulic conductivity in these segments, in particular in C5, for which the hydraulic conductivity decreased 5 magnitudes within 41 days (Figure 5.23). This is an extreme decrease in bed permeability, which as mentioned earlier, led to the complete blockage of the bed and forced shut down of that column. Note that a temporary increase of hydraulic conductivity was observed in C3 from day 203 to 233. This was probably caused by the mechanical failure of the bottom cap of that column, which broke just before taking the hydraulic measurement. It is likely that the ZVI bed was disturbed while changing the cap. Still, the hydraulic conductivity of C3 sharply decreased after that event.

The results of the hydraulic conductivity determinations are also in-line with the tracer tests which showed no significant changes in the residence time distribution during tap water feeding, and important deviations of that behavior after feeding of  $\text{NaHCO}_3$ .

In all cases, the trend in the presence of additional  $\text{NaHCO}_3$  is clear with very important decreases (2 to 4 orders of magnitude) in the hydraulic conductivity compared to the controls. C5 which was fed the highest concentration of  $\text{NaHCO}_3$  was plugged first, followed by C4 and then by C3. Thus, it appears that there may be a direct relationship between the  $\text{NaHCO}_3$  loading and the time to plugging. Interestingly, despite a gradual decrease in their hydraulic conductivity, C1 and C2 did not experience plugging during the experiment.



**Figure 5.22** Hydraulic conductivity  $K$  (in  $\text{cm s}^{-1}$ ) of the different ZVI columns operated with tap water at different velocities.



**Figure 5.23** Hydraulic conductivity  $K$  (in  $\text{cm s}^{-1}$ ) 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  $\text{NaHCO}_3$  (see total concentration in legend) while C1 and C2 served as controls.

### **Formation and distribution of mineral precipitates**

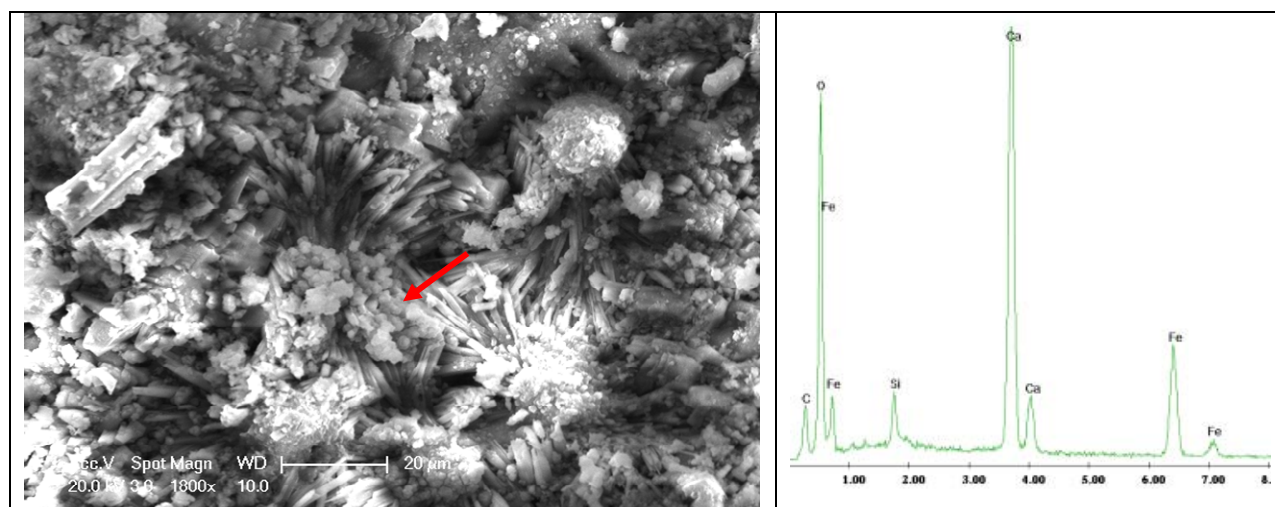
After stopping water flow through C5, iron samples were taken from different depths in that reactor for SEM/EDX analysis. Sample sequence followed the flow direction. To minimize the oxidation effect that would be caused by exposing the ZVI to the atmosphere, the iron samples were immediately dried using nitrogen gas, and then kept in an anaerobic chamber until analyzed.

Visual observation during sampling indicated stratification of the corrosion phenomena. Iron from the first 3 cm were clumped together as a dense solid, resulting in a mechanically strong aggregate. Removing the iron from the PVC column required some effort because of the solid structure the ZVI had formed. After the first 3 cm, the packing became loose while the last 3 cm resembled fresh packing. The non-uniform distribution of iron precipitates was clearly visible by the naked eye: the iron samples at different depth had different colors. Samples taken from the first 3 cm had an orange color, which maybe siderite or carbonate green rusts. Sample taken at 5 cm had a grayish color, while ZVI beyond 5 cm was black with no visible difference with depth, and very similar to the original ZVI despite over 200 days of operation.

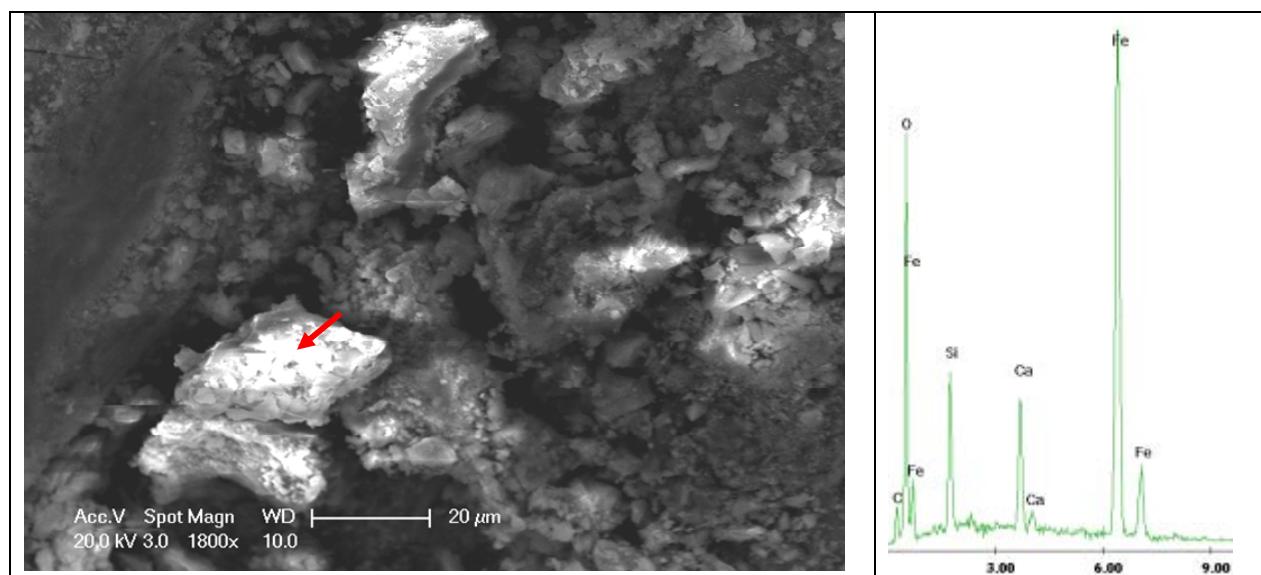
SEM images of the ZVI surface as a function of depth as well as EDX spectra of selected spots on the ZVI are shown in Figures 5.24-5.30. The EDX results indicate that the dominant precipitates in the reactor are calcium carbonate ( $\text{CaCO}_3$ ), siderite ( $\text{FeCO}_3$ ), carbonate green rusts ( $\text{GR}(\text{CO}_3^{2-})$ ), and other iron oxides.

The distribution of the precipitates was clearly changing with the depth in the column. At increasing penetration depth, calcium decreased while the intensity of iron increased, probably as a result of both the availability of calcium and of the redox conditions. Most of the calcium carbonate (long rod shape) accumulated at the entrance of the reactor resulting a thick deposit layer, even possibly “gluing” ZVI particles together and is suspected to be a major contributor to the loss of hydraulic conductivity. Green rusts (GRs) are layered Fe(II)-Fe(III) hydroxi-salts that are often detected in environmental systems with alternating redox conditions and is often the products of both aerobic and anaerobic corrosion (Legrand et al., 2004). Green rusts have also been reported to be the result of the biological reduction of ferric oxihydroxides by dissimilatory iron-reducing bacteria (DIRB) (Fredrickson et al., 1998; Ona-Nguema et al., 2002). Oxidizing species such as dissolved oxygen and nitrate are known to play an important role in the formation and subsequent reaction of such corrosion products. It is not clear whether these were indeed the formation mechanisms involved in the tested system. The detection of 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.

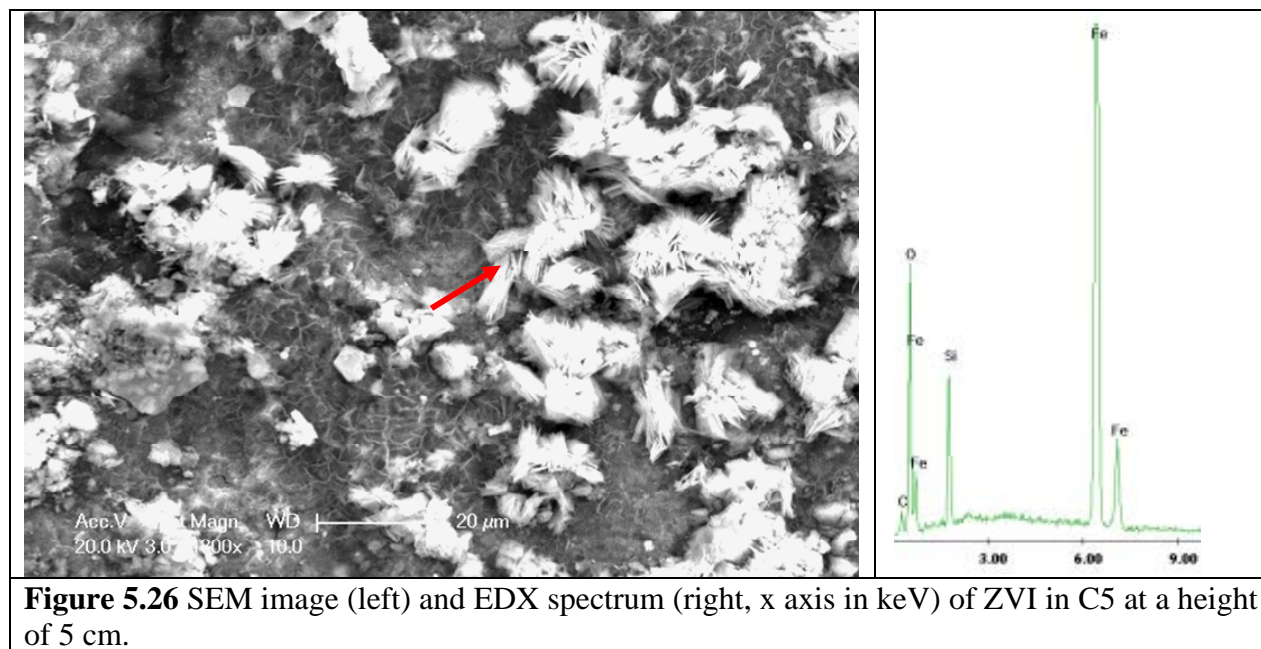


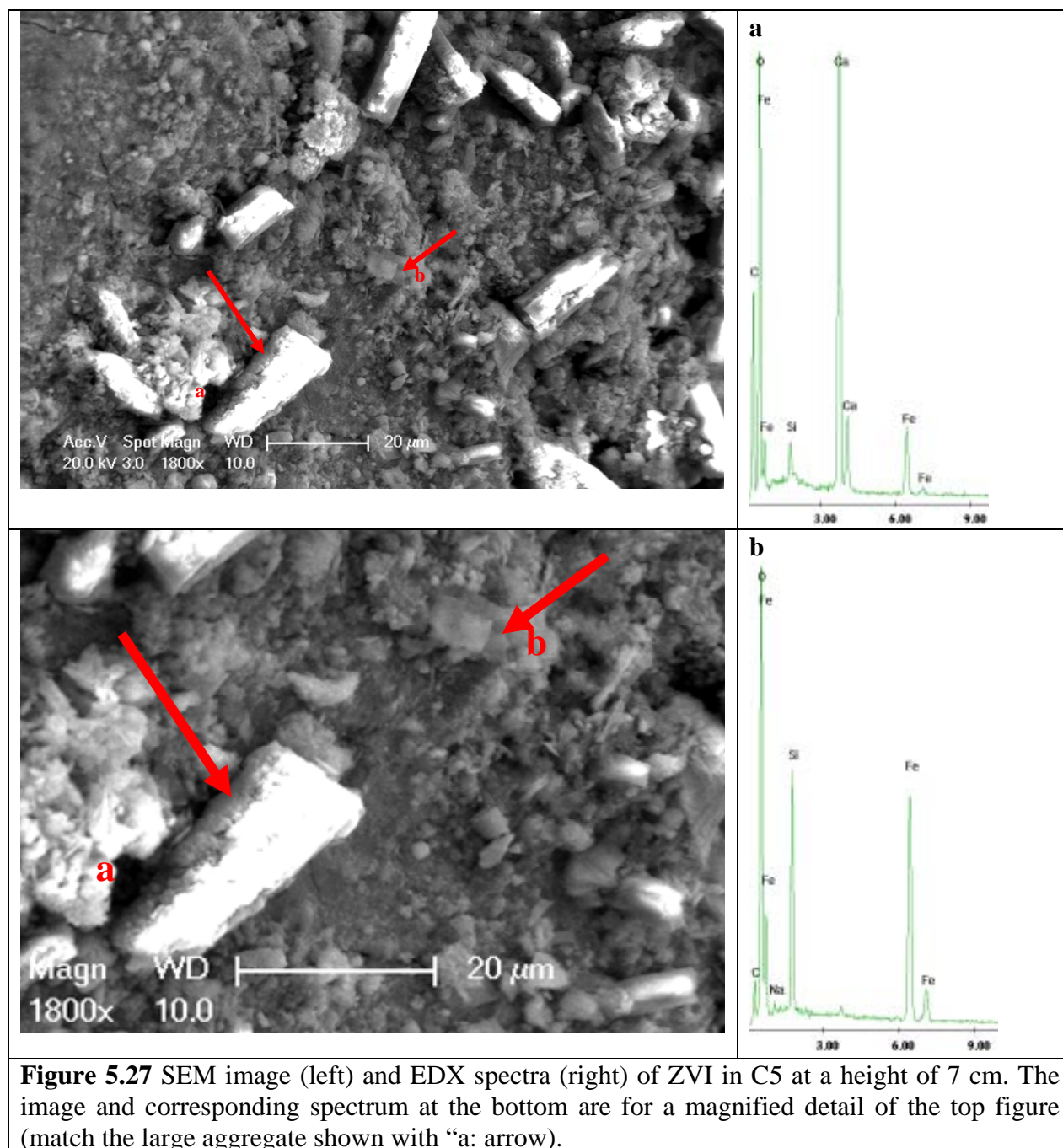


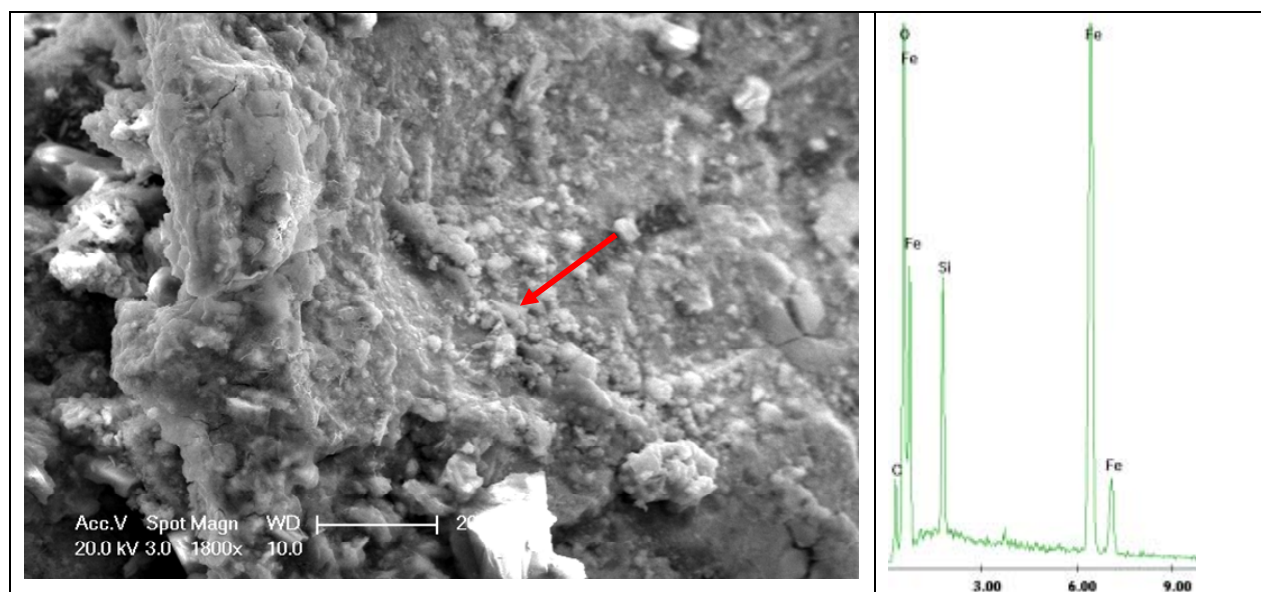
**Figure 5.24** SEM image (left) of ZVI in C5 at a height of 0 cm. The right shows the and EDX spectrum (x axis in keV) of the spot indicated by the red arrow on the SEM image. Note that the x axis was truncated to improve readability but no peaks were observed above 8 keV.



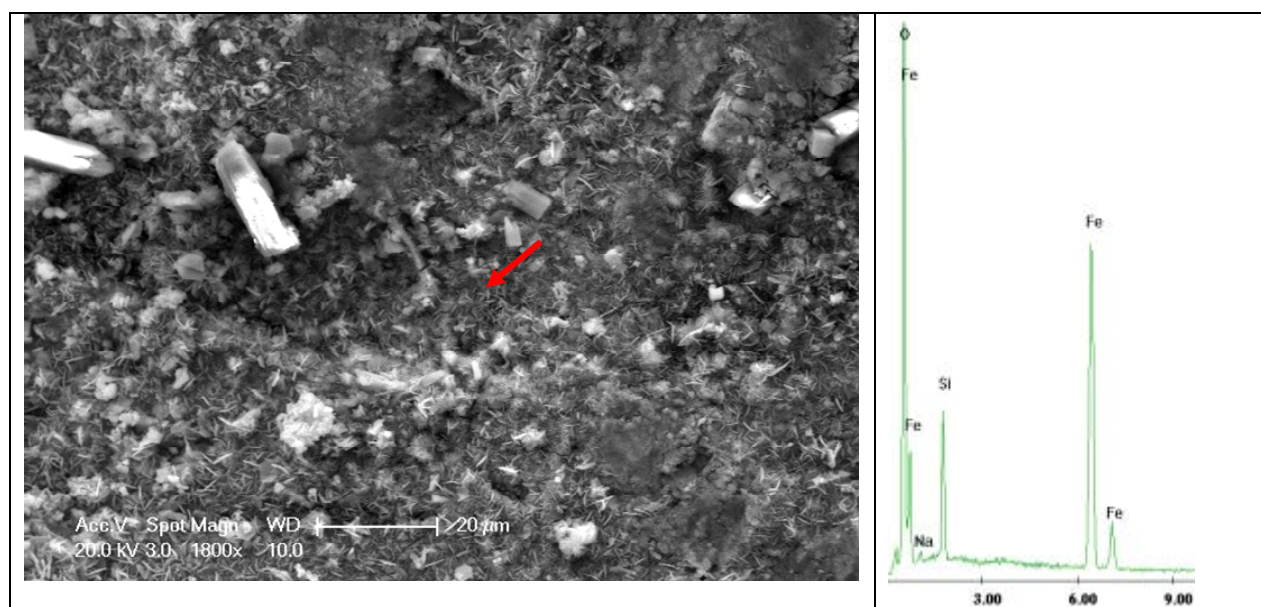
**Figure 5.25** SEM image (left) and EDX spectrum (right, x axis in keV) of ZVI in C5 at a height of 3 cm.





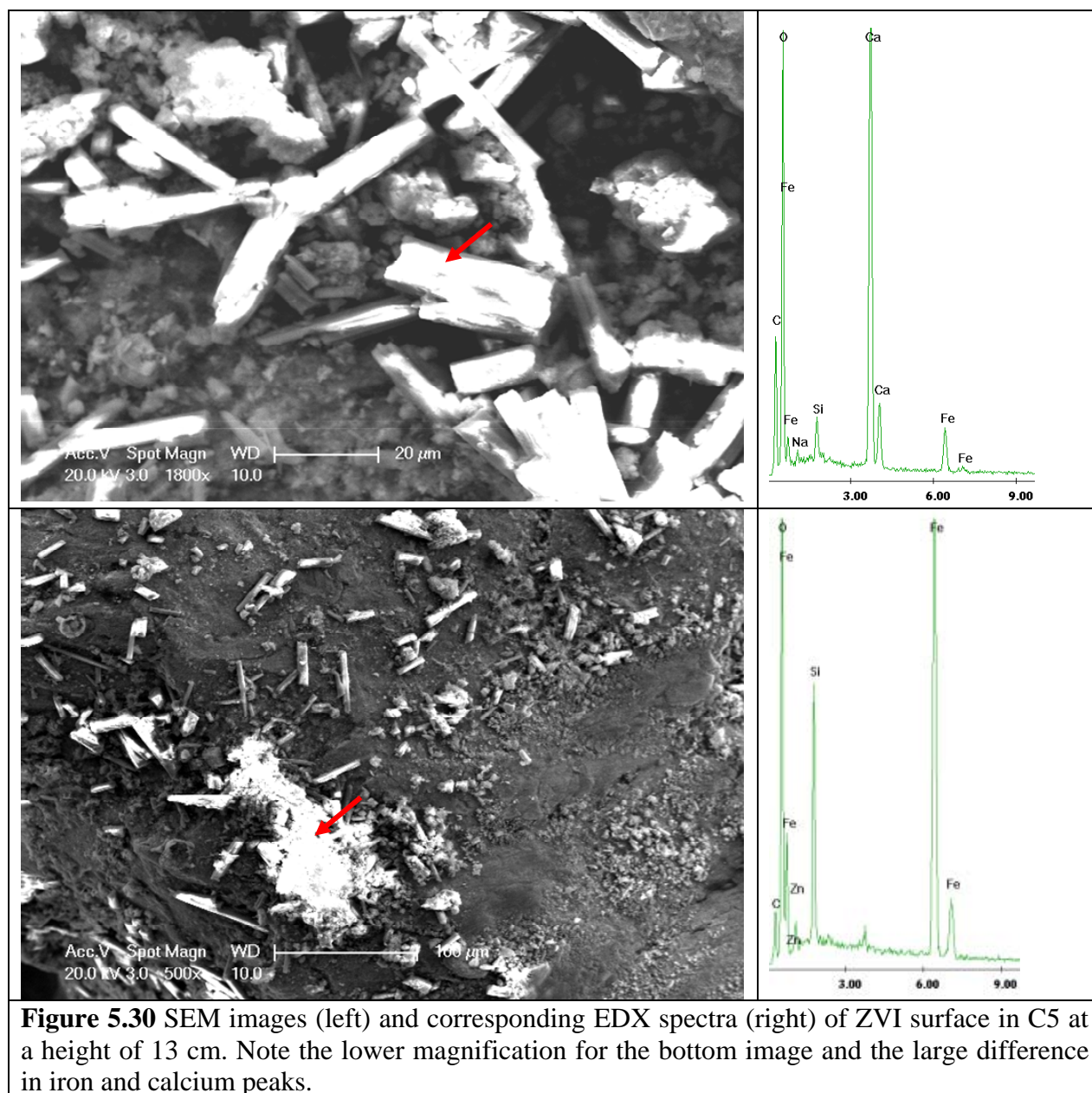


**Figure 5.28** SEM image (left) and EDX spectrum (right, x axis in keV) of ZVI in C5 at a height of 9 cm. Possible dominant species are green rusts, and iron oxides



**Figure 5.29** SEM image (left) and EDX spectrum (right, x axis in keV) of ZVI in C5 at a height of 11 cm.





### 5.2.2 Effects of Selected Parameters on Bed Porosity and Residence Time Distribution

In parallel to the experiments reported in Section 5.2.1, another experiment was setup in an attempt to identify parameters that may be important in the clogging of ZVI beds. The parameters that were investigated included:

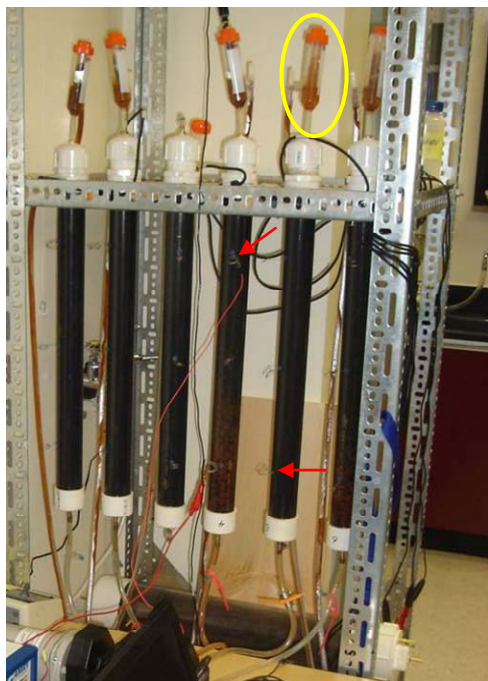
- ZVI mesh size (coarse or fine)
- The presence or absence of dissolved oxygen
- Feeding of tap water vs. deionized (DI) water
- The presence or absence of nitrate in the treated water
- The presence or absence of bacteria on the ZVI

Because of the difficulties associated with the setup and the analysis of multiple parallel ZVI bed systems, only six ZVI columns were installed (numbered R1 through R6). A picture of the experimental setup is shown in Figure 5.31. The conditions for each columns were as follows:

- R1: Fine ZVI, DI water, low DO ( $\sim 1 \text{ mg L}^{-1}$ )
- R2: Coarse ZVI, DI water, low DO ( $\sim 1 \text{ mg L}^{-1}$ )
- R3: Fine ZVI, tap water,  $20 \text{ mg L}^{-1}$  nitrate, high DO ( $\sim 8 \text{ mg L}^{-1}$ )
- R4: Coarse ZVI, tap water,  $20 \text{ mg L}^{-1}$  nitrate, high DO ( $\sim 8 \text{ mg L}^{-1}$ )
- R5: Fine ZVI, tap water,  $20 \text{ mg L}^{-1}$  nitrate, high DO ( $\sim 8 \text{ mg L}^{-1}$ ), bacteria added initially
- R6: Coarse ZVI, tap water,  $20 \text{ mg L}^{-1}$  nitrate, high DO ( $\sim 8 \text{ mg L}^{-1}$ ), bacteria added initially

Each column had an inner diameter of 3.8 cm (1.5") and a ZVI packed height of 65 cm (25.6") for a bed volume of 0.74 L. The coarse ZVI was the same as used in the field experiments (3/5 mesh, from Peerless, Detroit, MI) while the fine ZVI had a mesh of 20/30 (also from Peerless). The initial bed porosity of the coarse ZVI beds was 74 to 86% and the porosity of fine ZVI beds ranged from 61 to 64%.

The water was fed in an upflow mode through each columns using peristaltic pumps at a rate corresponding to an empty bed contact time of 54 min. The flowrate was selected as a compromise between the size of the holding tanks, and the desire to operate the reactors at a shorter empty bed contact time in order to mimic the nominal capacity of the field ZVI bioreactor. Tap water in Durham, NC has an average alkalinity average around  $27 \text{ mg L}^{-1}$  whereas the nitrate average is  $0.6 \text{ mg L}^{-1}$  (as N). In order to obtain a high DO, compressed air was continuously sparged through the water in the respective holding tanks. A low DO was obtained by continuously sparging nitrogen gas through the water and strip dissolved oxygen. The water tank also had a floating lid to minimize direct contact between the water and the surrounding atmosphere. The systems that had bacteria were initially inoculated using sludge and various mixed cultures available in our lab. In total, 100 mL of the mixed culture inoculum (with an optical density of 1.1 at 600 nm) were injected into each ZVI packed bed in separate injections of 10 mL.



**Figure 5.31** Picture of the experimental setup with six ZVI columns operated in parallel with different conditions. The red arrows show the location of the platinized wires for electrical conductivity measurement, while the yellow circle shows the effluent port allowing insertion of a conductivity probe for monitoring tracer response and residence time distribution.

Several analyzes were performed. Similar to experiments reported in Section 5.2.1, tracer tests were conducted on a regular basis by injecting NaCl pulses (1 mL of 1 M or about  $83,000 \mu\text{S cm}^{-1}$ ) in the inlet port and monitoring the conductivity of the effluent at the outlet port of the reactor using a conductivity probe connected to a data logger. Other monitoring included regular nitrate measurements using a Hach kit, ORP of the effluent water using a standard redox electrode. The electrical resistivity of the ZVI bed was measured in an attempt to monitor the buildup of iron corrosion products at the iron surface. The hypothesis was that a fresh ZVI bed would have a high conductivity because of good iron grain to iron grain contact. Over time, with the buildup of less conductive iron corrosion products, the contact resistance would increase. Possibly, the corrosion process could be monitored using a simple Ohmmeter and electrodes permanently installed in the ZVI bed. For this, short platinized wires were permanently inserted in the bed through sampling septa. For the results reported inhere, the spacing between the wires was 36 cm. Micro-CT of miniaturized (coarse) ZVI bed was attempted with the hope to demonstrate and quantify plugging of the ZVI bed and monitor the progression of iron corrosion product deposition. Micro-CT a non-invasive method that can provide a detailed characterization of three dimensional objects. Different materials (e.g., water, oxides, iron) can be differentiated on the basis of their different X-ray absorption. The micro-CT measurements were conducted by Prof. Karel Matous of the Department of Aerospace and Mechanical Engineering, at the University of Notre Dame. Micro-CT were conducted on a Xradia micro-CT machine with capability of resolution down to  $3 \mu\text{m}$  per voxel.

## Results

The initial bed porosity of the three coarse ZVI beds ranged from 74 to 86% while the porosity of the three fine ZVI beds ranged from 61 to 64% (Figure 5.32). This difference was expected. The coarse ZVI has a lot of medium size curly ZVI shavings with large voids, whereas the fine ZVI is much more homogenous in shape. For the first 10 days, tracer responses were very symmetrical and consistent in time (results not shown). As ZVI aged, long tails similar to those reported in Section 5.2.1 were observed, indicative of non-ideal plug flow behavior and indicative of the development of heterogeneities in the ZVI bed. After 10 days of operation, columns R3 and R5, i.e., those packed with fine ZVI operated at high DO, experienced porosity decrease. The back pressure increased as the porosity decreased to around 50%. These columns had to be stopped on day 20 as the back pressure exceeded the capacity of the pump and excessive pressure caused failure of the tubing. No difference was observed between R3 and R5, which only differed by the presence of bacteria (Figure 5.32 top). This may be because of the short duration of the experiment and the slow growth of autotrophic bacteria.

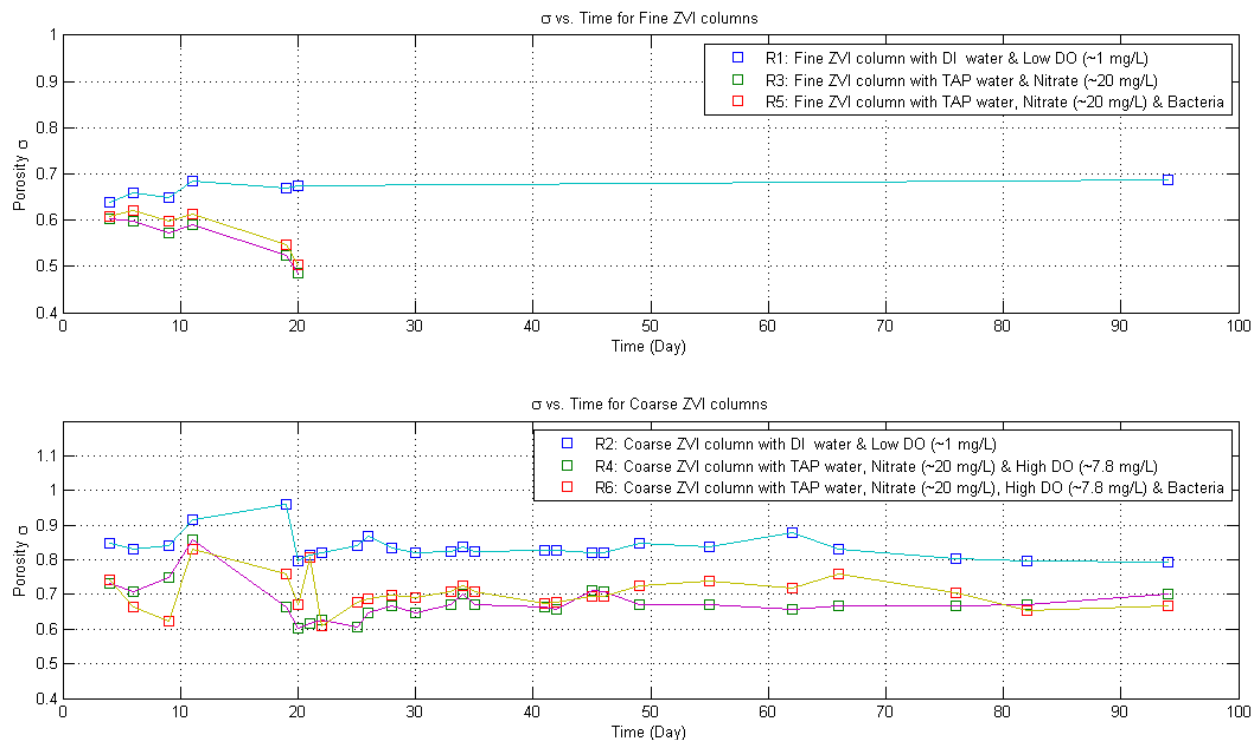
Interestingly, ZVI bed blockage occurred at a porosity of 50%, which is by no means a low value. Also, the column packed with fine ZVI but operated with DI water and low DO did not follow the same trend and was stable for over 90 days of operation. It is unfortunate that the experimental design did not include a fine ZVI column operated with DI and high DO or one with tap water and low DO. This would have allowed to determine if the plugging observed in R3 and R5 was due to high DO, or the mineral salts contained in the tap water (alkalinity and nitrate), or a combination of both. Here, one can speculate that since the alkalinity and nitrate concentration of the tap water was quite low compared to the tests reported in Section 5.2.1, the likely cause of plugging is the presence of high DO, although it would need to be confirmed in a separate experiment.

All three columns packed with coarse ZVI were stable over time (Figure 5.32 bottom). A very minimal (less than 5%) decrease in the bed porosity was observed between the first twenty days and the steady value that was reached after 30 days, although the difference is so small and may not be significant. No difference could be observed between R2, R4 and R6 indicating that the parameters that were varied (water, DO and bacteria) had no effect on the porosity. This is in sharp contrast with the results obtained with the fine ZVI.

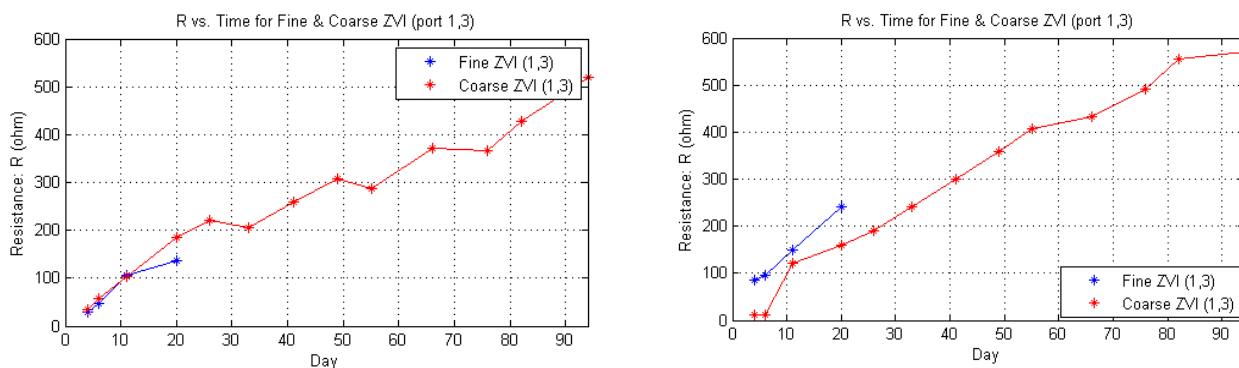
Electrical resistance determinations (Figure 5.33) showed that the resistance increased over time, as was hypothesized as a result of the increase in the contact resistance between the ZVI particles. The actual values of the resistances were relatively similar between the fine and the coarse ZVI beds, starting for most at less than 50 Ohms, and reaching upwards of 500 Ohms for the coarse ZVI columns, after 90 days. The fine ZVI beds which were stopped after 20 days did not have significantly different time courses despite being plugged. No real insight could be derived from these measurements. Direct in-situ determination of the ZVI corrosion rate was attempted using a Gamry potentiostat (model Reference 600, Gamry, Warminster, PA). ZVI in the columns was used as the working electrode, a  $1 \times 1$  cm piece of reticulated vitreous carbon was used as counter electrode and a Ag/AgCl electrode was used as reference electrode. The latter two electrodes were placed in the liquid head above the ZVI bed. Determinations of the ZVI corrosion rate were unsuccessful. Data were noisy and the actual values of corrosion rates did not make physical sense. It is likely that problem was in the way the three electrode



configuration was setup and the contact was made with the ZVI were flawed. While the approach could potentially be useful, it requires further research.



**Figure 5.32** Porosity determined by tracer injection over time for the six ZVI reactors.

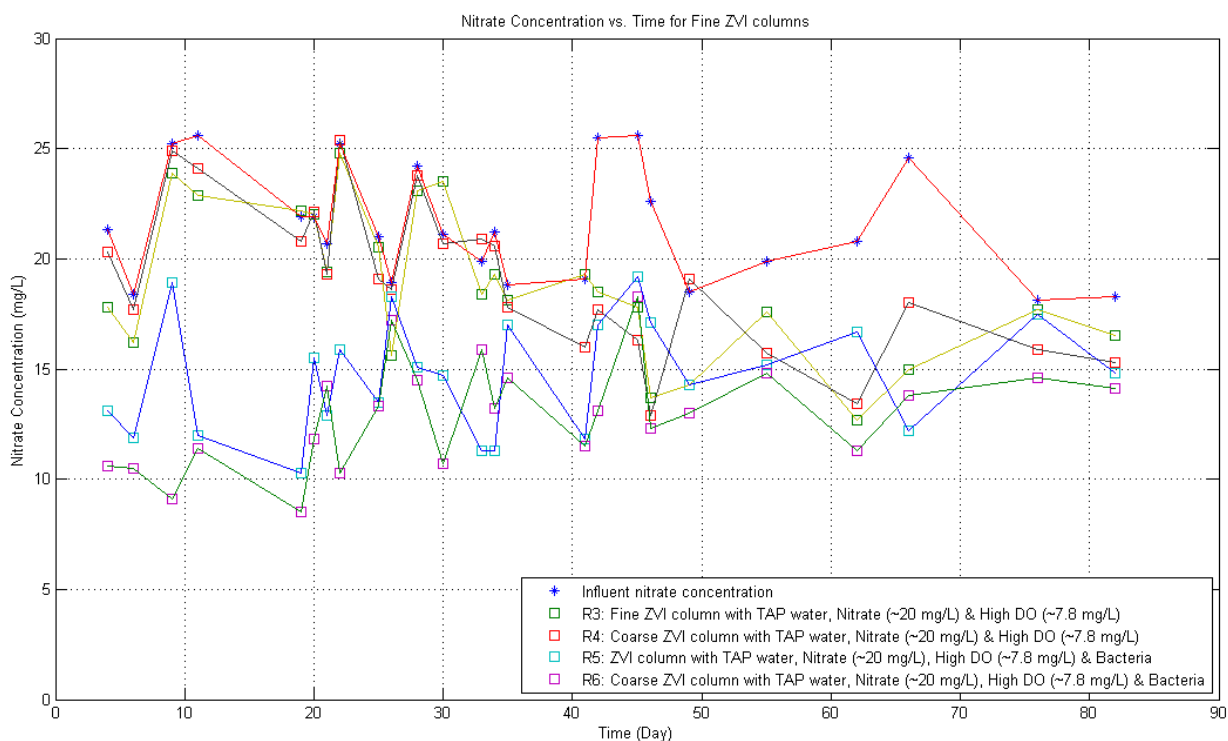


**Figure 5.33** Electrical resistance of selected ZVI reactors: left R3 (labeled fine) and R4 (coarse), and right R5 (fine) and R6 (coarse). R1 and R2 not shown.

Nitrate influent and effluent concentrations are reported in Figure 5.34. For the first 40 days, the two reactors (R3, R4) that were not inoculated with bacteria had outlet concentrations that closely matched the inlet, consistent with the absence of any biological activity. In contrast, the two reactors inoculated with bacteria (R5 and R6) had significantly lower outlet nitrate

concentrations, roughly  $10 \text{ mg L}^{-1}$  lower than the inlet, but increasing with time. Removal of nitrate is the result of autotrophic denitrification supported by hydrogen produced by corroding ZVI, similar to ZVI supported biological perchlorate reduction. Denitrification occurred despite the fact that the influent water was saturated with DO. This is because low ORP conditions were obtained in the ZVI column as is reported in Figure 5.35.

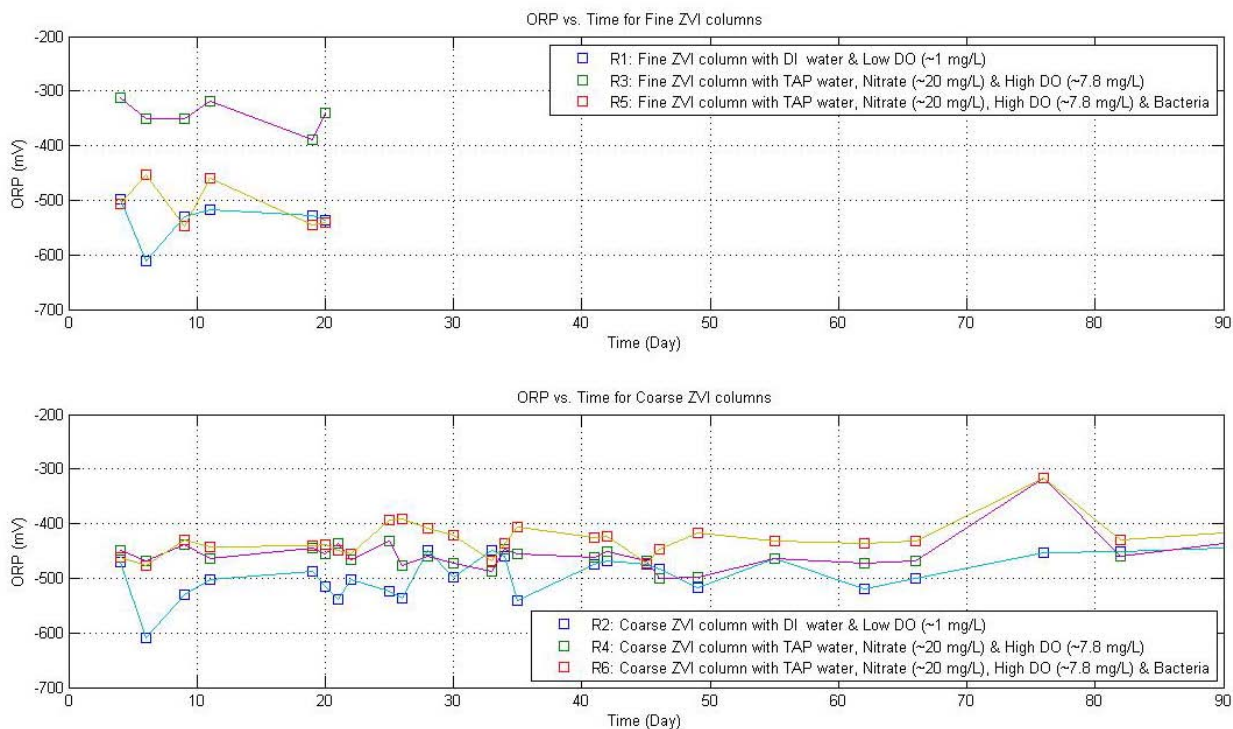
Over time, nitrate reduction was observed in R3 and R4. The most likely explanation for this is that some bacterial contamination occurred in these reactors, resulting in denitrification. Also, removal of nitrate in R5 and R6 decreased after 40 days and stabilized to about  $5 \text{ mg L}^{-1}$  removed. There was no difference between R5 and R6, packed with fine and coarse ZVI respectively. This would suggest that denitrification was not limited by the surface available for bacterial attachment or ZVI surface area for corrosion and hydrogen production. This conclusion is in contradiction with the fact that denitrification rate decreased over time in both reactors. An alternative explanation could be that short circuits and heterogeneous conditions established in the ZVI bed, although this was not observed in residence time distribution determinations discussed for Figure 5.32.



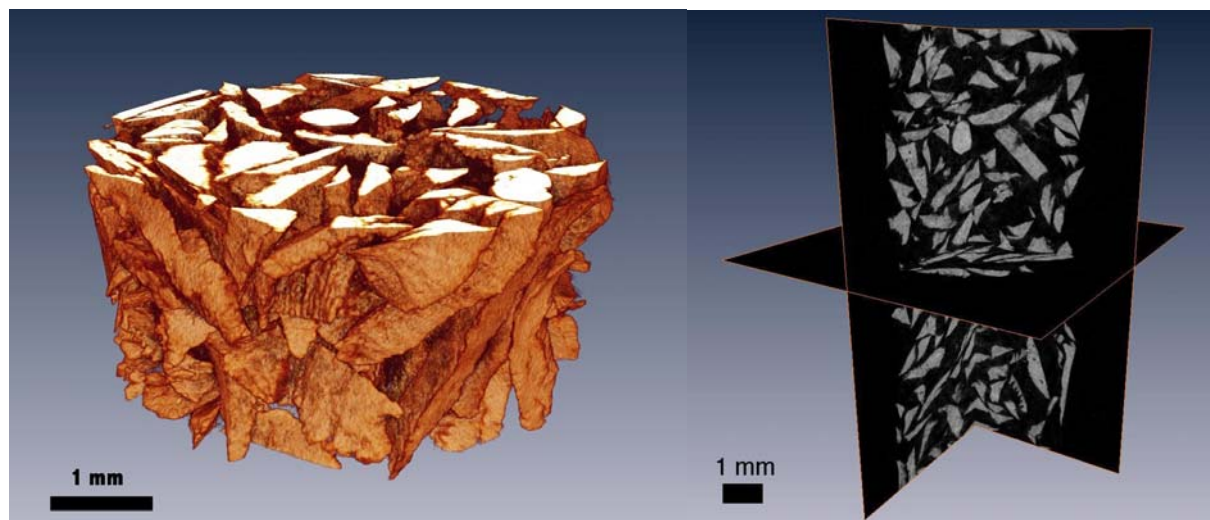
**Figure 5.34** Nitrate concentrations in the influent and effluent of the ZVI reactor. R1 and R2 which had no spiked nitrate are not shown.

The results of the micro-CT are shown in Figure 5.36. The scans were difficult to acquire as iron has strong absorbance of X-rays making it difficult and very slow to obtain good sections with adequate resolution. Hence only coarse, unused ZVI was scanned and results of limited usefulness were obtained. Originally, the intent was to scan fresh and plugged ZVI and be able to

quantitatively determine the amount of ZVI corrosion products that were formed, to locate them on the ZVI and to quantify the porosity reduction resulting from the corrosion process. Only fresh ZVI was scanned and at a relatively low resolution. Still, the image shows the complex inner structure of the ZVI bed. Owing to the difficulties in CT scanning of that sample, no attempts were made to scan plugged ZVI, which would have possibly shown the extent of pore bed blockage.



**Figure 5.35** ORP in the effluent of the ZVI reactors.



**Figure 5.36** Micro-CT of a section of a coarse ZVI bed showing (left) the complex 3D path the water must take through the bed. Right: orthogonal sections of that bed.

### 5.3 Discussion of Field Observations and Laboratory Results

The field demonstration of perchlorate reduction by bacteria on ZVI led to disappointing findings. Initially, excellent perchlorate and nitrate treatment performance was obtained for about three months (though not at the nominal water flowrate). However, before the throughput of water could be increased, significant treatment performance issues occurred and despite intensive troubleshooting, good treatment could never be re-established. Thus, the full potential of the process could not be determined. The field observations and failure to re-establish effective treatment triggered a series of laboratory experiments to determine the effect of ZVI aging and accumulation of corrosion by-products, and the effects of water chemistry on the water hydrodynamics in ZVI beds.

The problems experienced in the field came as a surprise, as prior research in our laboratories had shown that perchlorate reduction could be sustained well over one year. In retrospect, it is likely that two differences between the laboratory and the field played an important role. First, experiments in the laboratory are rarely static and the sporadic dismantling of ZVI bioreactors for examination probably prevented or delayed bed plugging phenomena observed in the field. Second, as will be discussed below, several risk factors for ZVI bed plugging existed in the Rialto well #2 water and but not in the laboratory.

The results of the laboratory investigations conducted after the failure of the field bioreactor and examination of the published literature on ZVI permeable reactive barriers (PRBs) 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 ( $210 \text{ mg L}^{-1}$ ), which in itself should not have posed major issues based on the review of earlier studies (Henderson and Demon, 2007). However, other contributing factors existed. The water had a high DO and a relatively high nitrate concentration ( $20 \text{ mg L}^{-1}$ ). In addition,  $\text{NaHCO}_3$  was supplemented to the bioreactor initially to promote growth of the autotrophic perchlorate reducing organisms and later during troubleshooting. Finally, pre-treatment 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. Molybdenum 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. Perchlorate reducing bacteria are relatively frugal and only need very few nutrients, and we have never observed Mo limitation in our laboratory systems.

A broad body of work exists to support the hypothesis that significant deposits of iron corrosion products occurred in the ZVI bed together with possible passivation of the iron surface. Henderson and Demond (2007) conducted a meta analysis of ZVI reactive barriers in an attempt to define “at risk” conditions for failure. In establishing risk factors, Henderson and Demond did not define whether the resulting failure is caused by reduced reactivity of ZVI or by reduction of permeability, but instead tabulated conditions of successful and failed PRBs. While they stress that “there is disagreement about what factors control PRB longevity” a comparison of key conditions, in particular of flowrate, alkalinity, nitrate concentration and to a lesser extent dissolved oxygen, show that our bioreactor was operated under conditions that would qualify it to be “at risk”. While this does not mean that our ZVI bioreactor was meant to fail, it indicates that conditions were relatively stringent.

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. Rigorous mass balances of iron were not conducted prior to the demonstration, and few investigators have conducted quantitative studies, none of them in ZVI bioreactors. Abiotic studies (mostly in PRBs or laboratory columns) have identified a myriad of corrosion products including iron (hydr)oxides, iron and calcium carbonates, green rusts, magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), wustite ( $\text{FeO}$ ), ferrihydrite ( $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ ), goethite ( $\alpha\text{-FeOOH}$ ), lepidocrocite ( $\gamma\text{-FeOOH}$ ), and  $\text{Fe}^{2+}$  adsorbed onto iron corrosion products (see e.g., Kohn et al., 2005; Henderson and Demond, 2007). Some of these match the corrosion product we measured in the lab and many can 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. Several studies stress that some of these corrosion products are metastable (e.g., green rusts). 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 locations, with different water chemistry and maybe different operating conditions.

## 6. COST ASSESSMENT

One of the objectives of the project was to use the data obtained with the prototype bioreactor to conduct a detailed projection of the cost of the proposed technology if it was to be deployed for typical full scale scenarios. The detailed cost model would have included capital and operating costs for selected 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 costs assessment could not be conducted. The most important cost drivers are briefly mentioned below:

1. Water flow. Bioreactor sizing is based on the water residence time in the ZVI bed. The reactor size (hence capital costs) is expected to increase roughly linearly with the water flow.
2. 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.
3. Concentration of dissolved oxygen in the influent. The requirement for pretreatment aimed at removing dissolved oxygen and the associated expenses depend 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<sup>-1</sup>). Above that threshold, the pretreatment costs will increase roughly linearly with water flow and dissolved oxygen concentration.
4. 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.
5. 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 are unknown.
6. 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 (FOB). The 2009 and 2010 cost of ZVI has varied between \$800 to \$900/per net ton. Thus, some cost variability is expected.
7. Extent and need for post-treatment. Post-treatment should be effective in removing both dissolved and suspended iron. Post-treatment should also remove possible bacteria flushed from the system, restore aerobic conditions in the treated water and possibly disinfect the water prior to distribution. These are well known technologies available from a variety of vendors. Their costs however can only be determined once the influent water, i.e., effluent from the ZVI bioreactor, has been characterized, which could not be achieved in this project. 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. Successful implementation of the demonstration plan would have provided extensive data on the basis of which a paper scale up of the process would have been accomplished. However, the performance problems that were observed prevented to firmly establish guidelines for ZVI bioreactor sizing and did not allow to fully evaluate the required operation and maintenance costs. The unresolved problem of ZVI bed plugging, and the uncertainty on the costs associated with resolving this problems make any cost estimates a mere guess. This realization led to the unfortunate conclusion that the treatment cost objective was not reached, or was at best inconclusive.

## 7. CONCLUSIONS AND RECOMMENDATIONS

A field demonstration of perchlorate biotreatment using bacteria immobilized on ZVI was conducted. Effective treatment of perchlorate was obtained for three months, after which problems occurred. Consequently, project objectives could not be met. Even so, the study lead to the following conclusions:

1. A relatively short startup (~10 days) was observed, after which very effective treatment of both perchlorate and nitrate was observed for a period of nearly three months.
2. When the reactor was operational, the effluent concentration of perchlorate was  $1.8 \pm 0.9$  ppb, nitrate effluent concentration was  $<0.01 \text{ mg L}^{-1} \text{ NO}_3^- \text{N}$ , effluent iron ranged from 0 to  $0.05 \text{ mg L}^{-1}$ , 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 of 4 gpm, which is 5 fold less than the nominal treatment capacity of 20 gpm. Problems with the bioreactor occurred after three months, i.e., before the groundwater could be increased to its nominal capacity.
3. Conversion of perchlorate to harmless chloride was stoichiometrical with one mole of chloride released per mole of perchlorate reduced.
4. Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were detected in the bioreactor effluent.  $\text{Fe}^{2+}$  was effectively and spontaneously oxidized to insoluble  $\text{Fe}^{3+}$  species in the sand filter without the need of dosing hydrogen peroxide.
5. Treatment performance declined after three months of operation. Despite multiple attempts to restore treatment efficacy, removal of perchlorate and nitrate remained low. Failure was attributed to significant losses in the hydraulic conductivity caused by the accumulation of iron corrosion products and deposition of mineral precipitates. Some passivation of the ZVI probably also contributed to the failure of the process.
6. Laboratory experiments with scaled-down system operated in mostly abiotic mode with selected conditions 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 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 pre-treatment, low water flow), was responsible for the failure of the bioreactor in the field.

7. 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 prior to implementation.

In light of these, the following recommendations can be made:

1. Water chemistry, in particular alkalinity, nitrate concentration and DO are particularly important for ZVI bioreaction systems and greater attention should be given to these parameters.
2. 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.
3. 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.
4. 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.
5. 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.
6. The technology is not yet demonstrated and it requires further study prior to full-scale implementation.



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## Appendix: Selected Pictures



Well #2 and splitting of the feed line to the different demonstration projects.



Discharge of the effluent of the different demonstration project to a common line leading to the catch basin.





The ZVI bioreactor on its trailer ready for mobilization. ZVI was loaded into the system at the site.