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Performance evaluation of a permeable reactive barrier for remediation of dissolved chlorinated solvents in groundwater

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Abstract

A pilot-scale permeable reactive barrier (PRB) consisting of granular iron was installed in May 1995 at an industrial facility in New York to evaluate the use of this technology for remediation of chlorinated volatile organic compounds (VOCs) in groundwater. The performance of the barrier was monitored over a 2-year period. Groundwater velocity through the barrier was determined using water level measurements, tracer tests, and in situ velocity measurements. While uncertainty in the measured groundwater velocity hampered interpretation of results, the VOC concentration data from wells in the PRB indicated that VOC degradation rates were similar to those anticipated from laboratory results. Groundwater and core analyses indicated that formation of carbonate precipitates occurred in the upgradient section of the iron zone, however, these precipitates did not appear to adversely affect system performance. There was no indication of microbial fouling of the system over the monitoring period. Based on the observed performance of the pilot, a full-scale iron PRB was installed at the site in December 1997. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Permeable reactive barriers (PRBs) containing granular iron have been installed at several commercial sites in the United States to degrade chlorinated volatile organic

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compounds (VOCs) in groundwater [1]. Although the results of laboratory studies conducted to determine reaction mechanisms have been widely disseminated [2,3], much less information has been published on the field-scale application of this technology.

One of the more complete performance records exists for a pilot-scale PRB installed in May 1995 at a former industrial facility in upstate New York. Past release of solvents at the site created a plume of trichloroethene (TCE) and related byproducts in the shallow sand aquifer at the site [4]. The water table at the site is about 1 m below ground level, and the aquifer is bounded by a clay layer at a depth of 4 to 5 m. Following encouraging results from laboratory treatability tests, the decision was made to proceed with a field demonstration.

The pilot-scale system installed at the site consisted of a funnel-and-gate located in an area of the plume containing the highest VOC concentrations. The gate section, 3.7 m long × 1.8 m wide (Fig. 1), was constructed by driving sealable sheet piling into the underlying aquitard at a depth of about 4.5 m. Native material was excavated and replaced with a center 0.9-m thick section of granular iron flanked by 0.5 m thick layer of pea gravel on both upgradient and downgradient sides. The purpose of the pea gravel
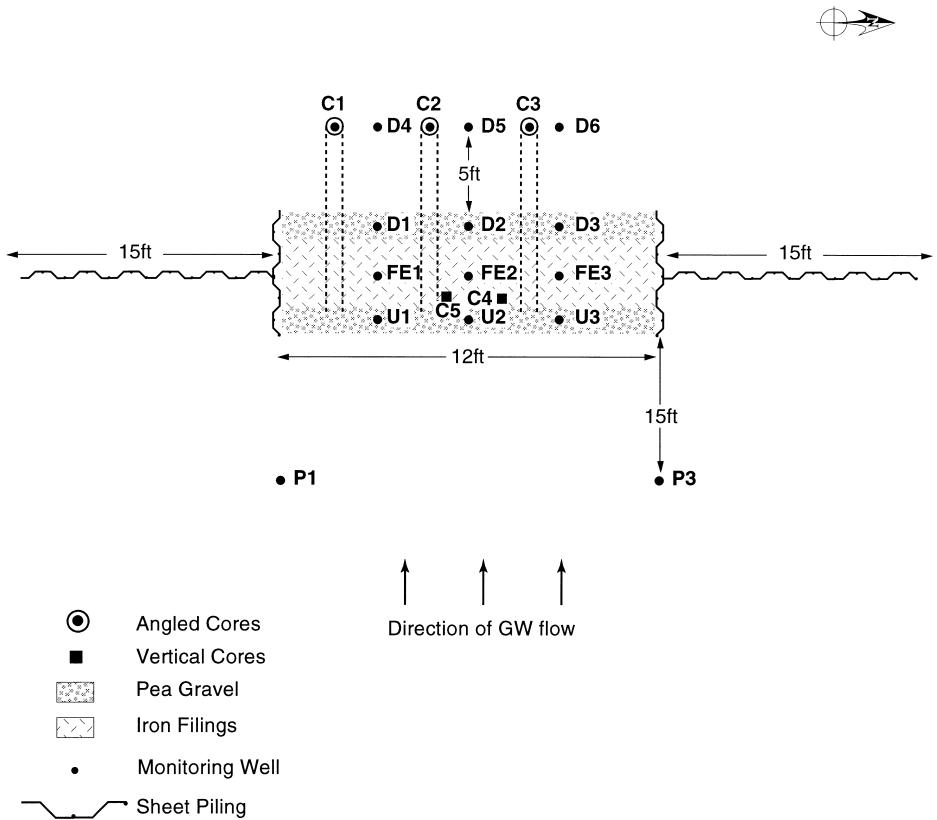

Fig. 1. Plan view of monitoring well and coring location, New York.

was to minimize the effects of high velocity layers in the aquifer by spreading flow vertically across the reactive zone; and to serve as locations for monitoring well placement. The piling on the long axis of the box was then removed to create a flow through reaction section or gate (Fig. 1). The gate section was flanked by funnels comprised of sealable-joint sheet piling extending 4.6 m laterally on either side, to a depth of 5 m. Modelling completed by Starr and Cherry [5] indicated that this configuration creates a larger upgradient capture zone relative to funnels angled more acutely to the gate. Monitoring wells shown in Fig. 1 were made of 2-in. diameter PVC, and screened across most of the saturated thickness of the iron, pea gravel or aquifer. The installation took about 10 days to complete.

2. Performance evaluation methods

2.1. Groundwater sampling

The monitoring wells were sampled monthly from June to December 1995 under auspices of the US EPA SITE Program [6]. Additional samples were collected in June 1997 immediately prior to coring activities. The number of wells sampled and analyses completed on the samples varied depending on the sampling event. Samples were collected using individual disposable teflon bailers for each sampling event and each well [7]. Analyses included the following [8]:

- VOCs using Method SW-846 8260A;
- Major anions including chloride (Method MCAWW 325.2), sulfate (Method MCAWW 375.4) and bicarbonate alkalinity (MCAWW 310.1);
- Metals (cations) by Method SW-846 3010/6010A;
- pH, redox potential (E_h), dissolved oxygen, specific conductance, and temperature using field electrodes.

2.2. Groundwater velocity

Groundwater velocity is a critical parameter in evaluating PRB performance [9]. It enables calculation of field-scale VOC degradation rates and can also be used to estimate the plume capture zone upgradient of the PRB. Three methods of determining groundwater velocity were used during this evaluation:

- hydraulic head measurements;
- conservative tracer tests;
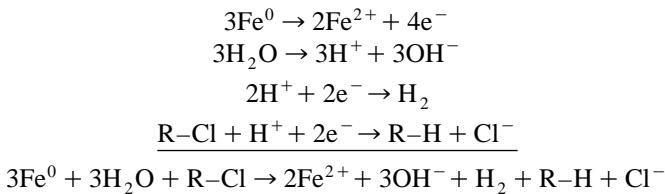- in-well velocity meters.

2.3. Analyses of PRB cores

A drive point/piston sampler was used to obtain angle cores from the PRB in June 1997 [10]. Since laboratory studies had indicated that significant inorganic changes in aqueous chemistry occur near the upgradient interface, efforts were made to collect continuous core samples that passed from the upgradient interface into the iron zone. A

complete continuous angle core (Fig. 1) was obtained from the interface, and subdivided into 5 cm sections for analysis. Mineralogical analyses performed on the core samples included total carbonate using acid digestion, and surface mineralogical studies using electron dispersive X-ray (EDX), Raman spectroscopy, and scanning electron microscopy (SEM). Microbial enumerations and total lipid biomass determinations were also completed. Hydraulic conductivity values were calculated from laboratory permeameter tests on a second angled core.

3. Results and discussion

3.1. Observed VOC degradation

Consistent trends in VOC concentration were observed throughout the monitoring period. The highest VOC concentrations over the first seven months of operation were observed in the center transect in the October sampling event (Table 1). A graph of TCE concentrations for the three transects of monitoring wells in the seventh month of operation is shown in Fig. 2. While upgradient VOC concentrations showed some variability, concentrations at or near the detection limit were reported at the midpoint of the iron. These declines in concentration of TCE and related compounds were interpreted to reflect the degradation of these VOCs by zero-valent iron, according to the following reaction [11], which considers only the presence of water, zero-valent iron and a chlorinated organic compound R–Cl:

$$3Fe^0 \rightarrow 2Fe^{2+} + 4e^-$$
$$3H_2O \rightarrow 3H^+ + 3OH^-$$
$$2H^+ + 2e^- \rightarrow H_2$$
$$\underline{R-Cl + H^+ + 2e^- \rightarrow R-H + Cl^-}$$
$$3Fe^0 + 3H_2O + R-Cl \rightarrow 2Fe^{2+} + 3OH^- + H_2 + R-H + Cl^-$$

Low to non-detectable VOC concentrations were maintained or increased slightly downgradient, likely due to incomplete flushing of the downgradient plume and/or desorption of VOCs from aquifer sediments.

Table 1
Observed VOC concentrations along the center transect

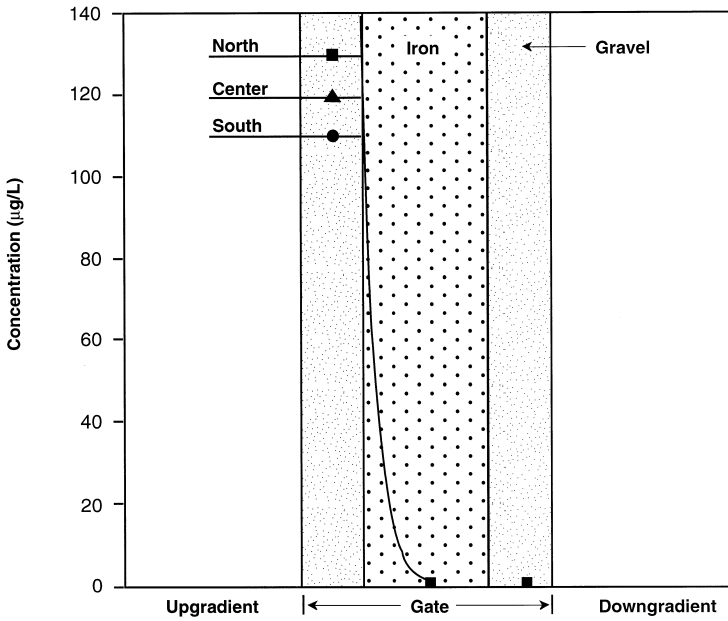| Well location	Concentrations along center transect (mg/l)					
	TCE		cDCE		VC	
	October 1995	June 1997	October 1995	June 1997	October 1995	June 1997
Upgradient pea gravel	160	189	450	298	79	53
Midpoint of iron zone	< 1.0	2.0	2.0	< 7.8	< 1.0	< 0.7
Downgradient pea gravel	1.5	< 1.7	7.5	15	1.2	< 0.7

Fig. 2. TCE concentration in the seventh month of operation.

VOC degradation rates, the slope of concentration vs. time curves (k_1 and k_2 shown in Fig. 3) are commonly expressed in half-lives; the time required to reduce the concentration by 50%. Concentration vs. distance profiles from the monitoring wells were converted to concentration vs. time profiles using an estimate of groundwater velocity of 0.2 m/day (see Section 3.2) and compared to half-lives predicted from the
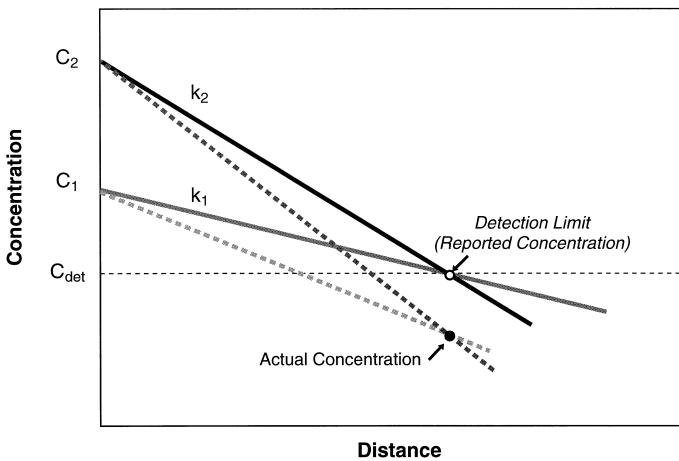

Fig. 3. Uncertainty in calculated degradation rates.

laboratory study (Table 2). Note that if a higher velocity is used in the calculation, the half-lives would be shorter.

It should be noted that the half-lives determined from the field data are conservative estimates of the actual half-lives since VOC concentrations of 1 μg/l (the detection limit) were used for monitoring well concentrations in the middle of the iron zone. There is no way of knowing the distance at which the detection limit was actually reached (Fig. 3). As shown in Fig. 3, half-lives can also vary according to variations in the influent concentration. This effect is particularly apparent in the calculation of TCE half-lives, which are generally below 3 h at other field installations. In spite of the uncertainty, cDCE and vinyl chloride half-lives compare well with values predicted from laboratory studies.

3.2. System hydraulics

The three methods of determining groundwater velocity at the site produced estimated groundwater flow velocities in the treatment gate from 0.2 to 0.7 m/day (Table 3). These field measurements compared reasonably well with a velocity of 0.34 m/day and a capture zone of about 7.5 m predicted by a two-dimensional plan view particle tracking model of the system developed during system design. The model was based on groundwater velocities in the aquifer of about 0.2 m/day. The bromide tracer was injected into fully screened wells located in the upgradient pea gravel. To minimize hydraulic disturbance, only 9.5 l of tracer solution was added to each of the three wells, resulting in small pencil-like plumes emanating from each well. The tracer was detected in each of the wells in the iron zone, but only in one sample. This single detection indicated a groundwater velocity through the gate of about 0.36 to 0.49 m/day. Dilution of the bromide solution upon injection could have reduced the possibility of detection. Furthermore, because of the small dimensions of the tracer plumes, small deviations in groundwater flow direction away from the downgradient monitoring wells would result in intercepting only a small portion of the tracer or possibly missing it all together. Evidence of this has been observed in similar tracer tests [9,12].

Calculations using water table elevations are limited by the accuracy of measurement (small differences in water level elevations over short distances) and the uncertainty in hydraulic parameters (porosity and hydraulic conductivity of the iron). The in-well velocity meter gave velocity magnitudes that were in the range anticipated. Although the

Table 2
Observed chlorinated volatile organic compound half-lives

VOC	Predicted half-life (h)[a] from laboratory studies	Half-life (h) from monitoring well data
TCE	0.4 to 1.1	< 4.0
cDCE	1.5 to 4.0	3.0 to 5.0
VC	2.0 to 6.0	5.0 to 10.0

[a]Rates at two velocities adjusted for temperature.

Table 3
Groundwater flow velocity estimates in the treatment gate

Method of measurement	Groundwater flow velocity estimate
Groundwater flow model prediction; $\bar{v}_{Aquifer} = 0.2$ m/day	0.3 m/day
Hydraulic head measurements (June to December 1995)	< 0.2 to 0.4 m/day
Bromide tracer test (August 1996)	0.4 to 0.5 m/day
Velocity meter (September 1996)	0.2 m/day
Velocity meter; $\bar{v}_{Aquifer} = 0.1$ to 0.2 m/day (June 1997)	0.3 to 0.7 m/day

direction of velocity vectors obtained with the meter were somewhat variable, most showed flow in a westerly direction (through the system).
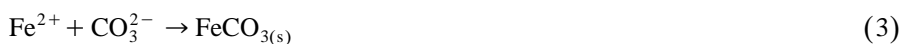
Laboratory permeameter tests performed on undisturbed angle core samples gave hydraulic conductivity values ranging from 6×10^{-2} to 10^{-1} cm/s. These compare favourably with hydraulic conductivity values of 5×10^{-2} to 10^{-1} cm/s for 'fresh' iron. Though this result is encouraging, the core materials were disturbed and therefore the results may not accurately reflect the in situ effect of precipitation on hydraulic conductivity.

3.3. Inorganic geochemistry

As groundwater moves through granular iron, the pH of the groundwater increases and the E_h decreases as a consequence of iron corrosion. As the pH increases, bicarbonate (HCO_3^-) in solution converts to carbonate (CO_3^{2-}) to buffer the pH increase:

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \tag{1}$$
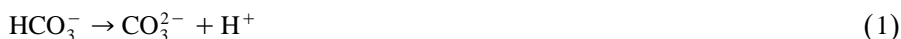
The carbonate then combines with cations $(Ca^{2+}, Fe^{2+}, Mg^{2+},$ etc.) in solution to form mineral precipitates:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)} \tag{2}$$

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_{3(s)} \tag{3}$$

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_{3(s)} \tag{4}$$

These reactions were reflected in the aqueous geochemical results throughout the monitoring period (Table 4). Results are shown from wells along the centre transect (Fig. 1). Results were very consistent both laterally across the wall and over time through the monitoring period. Upgradient groundwater was near neutral in pH and slightly aerobic, while at the midpoint of the iron the pH was generally between 9 and 10 and E_h of less than -300 mV were common. Downgradient of the gate pH increased to background levels while the E_h of the groundwater remained slightly lower than in the aquifer upgradient of the gate. Declines in aqueous calcium, alkalinity and sulphate were observed throughout the test. Iron concentrations did not increase substantially over background, indicating rapid precipitation of the ferrous iron introduced into solution from corrosion of the iron material.

Results of the carbonate mineral determinations on the core samples are shown in Fig. 4 The maximum carbonate content of about 6% $CaCO_3$ (6 g/100 g solid), obtained

Table 4
Changes in inorganic chemistry along centre transect

| Chemical parameter (unit) | Monitoring well location | | | |
	U2	FE2	D2	D5
Ca (mg/l)	90.6	9.6	15.4	33.6
Fe (mg/l)	< 0.1	0.158	< 0.1	0.159
Mg (mg/l)	12.7	7.33	4.23	5.95
Mn (mg/l)	0.388	0.0574	0.195	0.174
K (mg/l)	1.93	1.86	1.02	< 1.0
Na (mg/l)	29.4	29.6	23.4	15.5
HCO_3 (mg/l)	291	47.8	56.5	Na
Cl (mg/l)	47.4	49.2	42.8	Na
SO_4 (mg/l)	17.2	< 5.0	< 5.0	Na
pH	7.39	9.46	8.56	7.06
E_h (mV)	261	− 459	− 156	−16.5

from the sample nearest the upgradient interface, rapidly declines with distance with values of less than 1% beyond a distance of 15 cm.

The carbonate content present in the core samples and the changes in bicarbonate alkalinity observed in monitoring well samples were used to develop independent estimates of the mass of carbonate deposited in the iron zone over a 2-year period. The latter estimate is dependent on the assumed flow rate of groundwater passing through the treatment zone. At a flow velocity of 0.2 m/day, and a porosity of about 0.5 for the iron, about 76 m^3 (76,000 l) of groundwater passed through a 1 m^2 cross-sectional area of the gate prior to coring. The average decline in calcium concentration between wells in the upgradient iron zone and wells at the midpoint of the iron zone was about 80 mg/l. Using these data, about 15 kg of calcium carbonate would have been deposited in this 1 m$^2 \times 0.46$ m long section of iron. The mass of carbonate estimated from core samples, obtained by approximating the area under the curve shown in Fig. 4, is about 15 kg. The agreement between these two values is remarkable, given the uncertainties involved in calculating each estimate.

Raman spectroscopy, SEM, and to a lesser extent EDX, confirmed the results of carbonate analyses. Examination of samples near the upgradient interface showed significant amounts of calcite and aragonite. Samples from sections of cores further downgradient showed less carbonate precipitates. Several randomly distributed iron oxides and oxyhydroxides were also detected. Calcite and aragonite were the predominant carbonate species observed, with only minor amounts of siderite ($FeCO_3$). Green rusts, complex iron hydroxides containing both chloride, sulphate, and carbonate were observed on a few samples. No sulphide precipitates were observed in the core samples.

The precipitates did not appear to significantly affect system performance. Hydraulic conductivity measurements of core samples approached that of 'fresh' iron, and velocity measurements showed no trend upwards or downwards. Removal of VOCs was also consistent over the monitoring period, indicating no significant effects of precipitation on iron reactivity.

Ground Surface
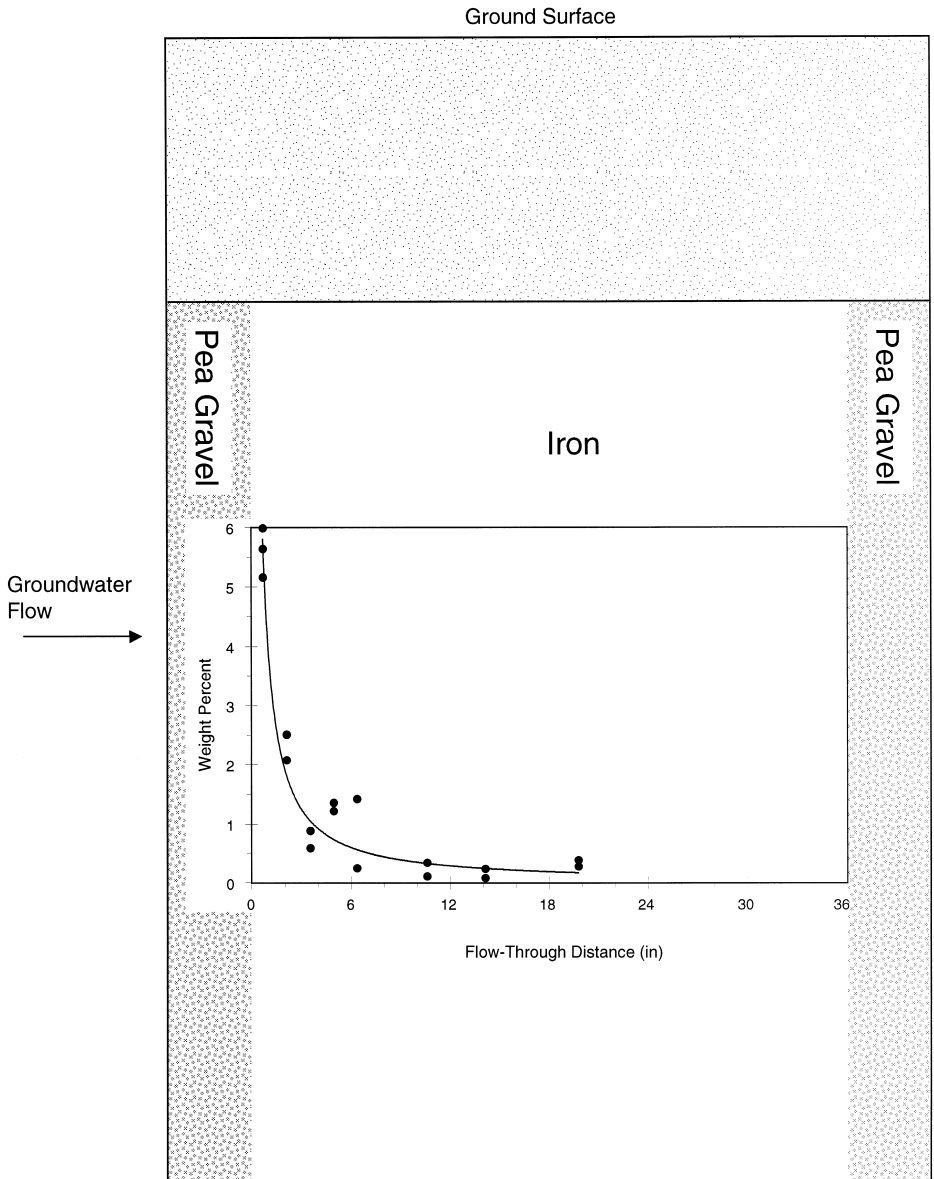
Pea Gravel

Pea Gravel

Iron

Groundwater
Flow →

Fig. 4. Calcium carbonate equivalent, New York.

3.4. Microbial activity

Data on microbial biomass and composition was obtained from groundwater samples collected in the iron zone, in upgradient and downgradient pea gravel zones, and in upgradient and downgradient aquifer monitoring wells for a 6-month period following

construction. The microbial populations in the groundwater samples from upgradient, iron and background zones appeared to be of similar size (10^3 to 10^4 cells/g dry weight) and composition. The microbial biomass in the downgradient gravel and aquifer zones were of similar size but different composition explained by the changes in aqueous geochemistry on the downgradient side of the iron zone, including the production of hydrogen gas from the iron that supports the activity of many obligate anaerobic bacteria. The disappearance of sulphate in groundwater samples from the iron zone may indicate the establishment of a sulphate-reducing bacteria in this zone.

Each 5-cm section of the angle core was subjected to microbial analysis. Lipid biomass results from the iron zone core samples were in the order of 10^6 cells/g dry weight. Microbial enumerations in both the aerobic and anaerobic cultures developed from the iron zone cores ranged from less than the detection limit to 10^4 colony forming units (CFUs)/g wet weight after 28 days of growth [13]. No microbial films were noted on the samples during microscopic examination. The core data supported the lack of microbial growth observed in the groundwater samples from the iron zone.

3.5. Implications of pilot-scale performance to full-scale design

Based on the record of pilot-scale performance, the decision was made to proceed with a PRB for full-scale plume remediation at the site. Field-scale half-lives of 4.8, 5.1 and 9.4 h for TCE, cDCE and VC were used in a first order kinetic model to determine the required residence time in the full-scale PRB, together with assumed influent concentrations from recent sampling events and relevant New York state regulatory criteria. The amount of carbonate precipitate (6%) in the upgradient section was calculated to represent a porosity loss of about 10% over 2 years (i.e. a decrease in porosity from about 0.5 to 0.45). Based on this estimate there did not appear to be any need to include design features to remove carbonate precipitates. Periodic (every few years) scarification of the upgradient interface using augering equipment was considered to be a more practical alternative (if required).

The continuous wall configuration was chosen over a funnel-and-gate configuration because of lower construction costs. A continuous wall also minimized the potential for bypass around or beneath the system compared to a funnel-and-gate. The lower velocity through a unit cross-section of a continuous permeable zone, relative to the higher velocity created by funnelling water through a treatment gate, means that the rate of precipitation at the interface should be less in the continuous zone, leading potentially to a longer service life.

Following design, a 0.3-m thick continuous PRB was installed across the entire plume at the facility in December 1997. The pilot-scale PRB was destroyed during full-scale construction.

4. Conclusions

The 2-year evaluation of this pilot-scale system provides encouraging data with respect to the long term performance of iron PRBs for VOC remediation, particularly in view of the multi-year records from other sites which have produced similar results

[11,14]. Consistent VOC degradation was observed over the 2-year period. Microbial populations did not increase in the iron zone relative to the aquifer, and while mineral precipitates formed in the iron zone, they did not appear to represent an insurmountable limitation to the technology. One difficulty identified during the evaluation was that of accurately measuring groundwater velocity through a PRB; in-well meters may provide a reasonable means of measurement for minimal cost.

Acknowledgements

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