Long-term performance monitoring for a permeable reactive barrier at the U.S. Coast Guard Support Center, Elizabeth City, North Carolina

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Abstract

A continuous hanging iron wall was installed in June, 1996, at the U.S. Coast Guard (USCG) Support Center near Elizabeth City, NC, United States, to treat overlapping plumes of chromate and chlorinated solvent compounds. The wall was emplaced using a continuous trenching machine whereby native soil and aquifer sediment was removed and the iron simultaneously emplaced in one continuous excavation and fill operation. To date, there have been seven rounds (November 1996, March 1997, June 1997, September 1997, December 1997, March 1998, and June 1998) of performance monitoring of the wall. At this time, this is the only full-scale continuous 'hanging' wall installed as a permeable reactive barrier to remediate both chlorinated solvent compounds and chromate in groundwater. Performance monitoring entails the following: sampling of 10–5 cm PVC compliance wells and 15 multi-level samplers for the following constituents: TCE, *cis*-dichloroethylene (*c*-DCE), vinyl chloride, ethane, ethene, acetylene, methane, major anions, metals, Cr(VI), Fe(II), total sulfides, dissolved H_2, Eh, pH, dissolved oxygen, specific conductance, alkalinity, and turbidity. Electrical conductivity profiles have been conducted using a Geoprobe™ to verify emplacement of the continuous wall as designed and to locate upgradient and downgradient wall interfaces for coring purposes. Coring has been conducted in November, 1996, in June and September, 1997, and March, 1998, to evaluate the rate of corrosion on the iron surfaces,

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precipitate buildup (particularly at the upgradient interface), and permeability changes due to wall emplacement. In addition to several continuous vertical cores, angled cores through the 0.6-m thick wall have been collected to capture upgradient and downgradient wall interfaces along approximate horizontal flow paths for mineralogic analyses. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Permeable reactive barriers (PRBs) are a promising new technology for the passive, in situ treatment of contaminated groundwater [1–3]. A PRB can be defined as ''an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a preferential flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals at points of compliance'' [4]. Theoretically, almost any contaminant could be treated if the required transformation is known and the requisite geochemical or microbiological conditions can be created through the emplacement of some suitable reactive media. Processes which can reduce the aqueous concentration of a contaminant include: adsorption, precipitation, oxidation, reduction, chemical or microbiological transformations or combinations of these processes.

A permeable in situ subsurface reactive barrier composed of 100% granular zero-valent iron (ZVI) was installed in June, 1996, at the U.S. Coast Guard Support Center near Elizabeth City, NC to treat overlapping plumes of chromate and (Cr(VI)) and chlorinated solvent compounds (trichloroethylene (TCE), *cis*-dichloroethylene (*c*-DCE), and vinyl chloride (VC)). Concentrations in excess of 10 mg/l Cr and 19 mg/l TCE had been detected in the groundwater at the site since 1991. The wall was emplaced using a continuous trenching machine. The continuous trencher excavates native soil and allows the iron to be emplaced in one continuous operation. Excavated aquifer materials were brought to the surface by an excavating belt, and then conveyed to the side of the machine. A 0.6-m wide trench box, called a 'boot', located behind the excavating belt, kept the trench open to allow backfill with iron filings which were poured into the boot using front-end loaders. An estimated 3.2 m^3 of iron-filings were emplaced per linear meter and about 280 ton of iron was installed. The installation was completed during a 6-h period on June 22, 1996.

The PRB is 46 m long, 7.3 m deep and 0.6 m wide and oriented perpendicular to groundwater flow (Fig. 1). The PRB consists of 100% Peerless Iron (Peerless Metal Powders). The iron has an average grain size of 0.4 mm and surface area of 0.8 to 0.9 m^2/g. In prior laboratory studies ZVI was shown to reduce Cr(VI) to an insoluble mixed Cr–Fe hydroxide [5] and reductively dechlorinate TCE [1]. The objectives for this study were to evaluate the effectiveness of a PRB to reduce groundwater concentrations of Cr(VI), TCE, *c*-DCE and VC to below regulatory target limits; determine if this method of PRB emplacement was feasible and that the installed system is effective in intercepting and 'treating' the dissolved contaminants. In addition, the study provides
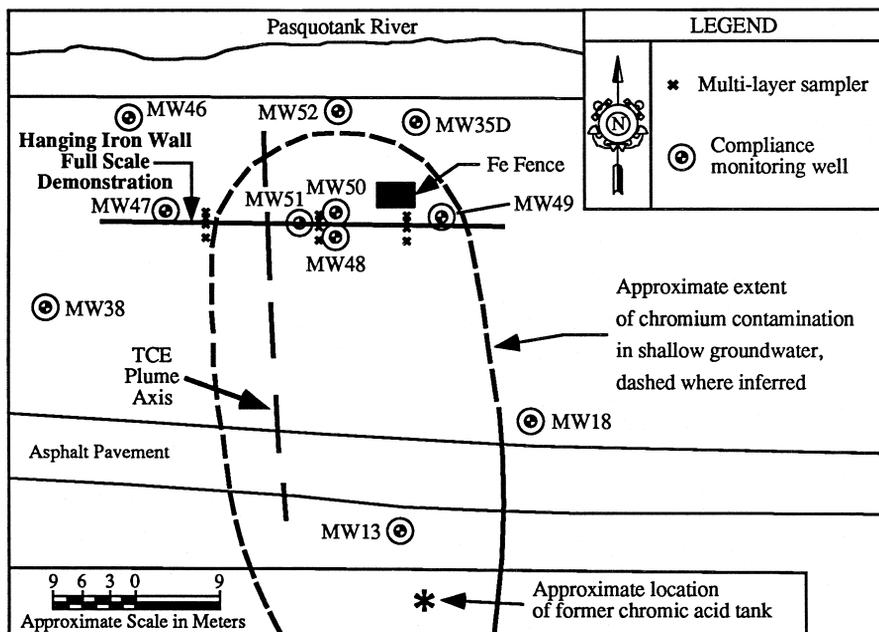
Fig. 1. Map of field site showing hangar 79 (source area), location of chromium and chlorinated solvents plume (plan view), monitoring wells, and iron wall.

valuable data on the long-term effectiveness this technology for groundwater remediation.

2. Field site, materials and methods

2.1. Study site

The field site is located at the U.S. Coast Guard (USCG) Support Center near Elizabeth City, NC, about 100 km south of Norfolk, VA and 60 km inland from the Outer Banks region of North Carolina. The base is located on the southern bank of the Pasquotank River, about 5 km southeast of Elizabeth City. Hangar 79, which is only 60 m south of the river, contains a chrome plating shop which had been in use for more than 30 years and discharged acidic chromium wastes and associated organic solvents through a hole in the concrete floor. These wastes infiltrated the soils and entered the aquifer below the shop's foundation [6]. Sampling results from a monitoring network consisting of more than 40 monitoring wells and about 100 Hydropunch™ and Geoprobe™ monitoring points indicate that the Cr(VI) plume is about 35 m wide, extends to 6.3 m below ground surface and extends laterally about 60 m from the hangar to the Pasquotank river. Multi-level samplers installed near the barrier wall location indicate that the bulk of the contamination resides from 4.5 to 6.5 m below ground surface.

The site geology has been described in detail elsewhere [3,6], but essentially consists of typical Atlantic coastal plain sediments, characterized by complex and variable sequences of surficial sands, silts and clays. In general, the upper 2 m of the aquifer are sandy silty clays which pinch out towards the north, or near the Pasquotank river, where sandy fill predominates. Fine sands, with varying amounts of silt and clay, and silty clay lenses form the rest of the shallow aquifer.

Groundwater flow velocity is extremely variable with depth, with a highly conductive layer at roughly 4.5 to 6.5 m below ground surface. This layer coincides with the highest aqueous concentrations of chromate and chlorinated organic compounds. The groundwater table ranges from 1.5 to 2.0 m below ground surface and the average horizontal hydraulic gradient varies from 0.0011 to 0.0033. Slug tests conducted on monitoring wells with 1.5 m screened intervals between 3 and 6 m below ground surface indicate hydraulic conductivity values of between 0.3 to 8.6 m/day [7].

2.2. Wall emplacement verification

Wall emplacement was verified using a conductivity probe manufactured by Kejr Engineering that was advanced through the soil/iron interface using a Geoprobe™. The tool provides real-time, specific conductance data vs. depth on a portable computer. The radius of influence of the probe is 2–3 cm. The data was used to identify the location of the plume, the outlines of where the iron was emplaced, and the density of packing of the iron filings within the aquifer.

The wall was cored using a 5-cm i.d. Geoprobe™ core barrel equipped with plastic sleeves. Vertical and angled cores (30°) were collected to recover iron filings from different portions of the wall. The vertical cores were collected where the conductivity profiles were obtained to verify the results of the conductivity probe and obtain samples for geochemical and microbiological analyses. Angled cores were also obtained where the conductivity profiles were obtained to evaluate wall thickness, iron packing density and evaluate geochemical and microbiological changes occurring at the upgradient and downgradient interfaces of the wall. Locations for conductivity data and cores were obtained between MW47 and MW49 (Fig. 2). Solids have been analyzed using scanning electron microscopy with energy dispersive X-ray (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) analyses. While the latter enables speciation analysis, only total elemental analysis can be obtained using SEM-EDS.

2.3. Monitoring network

A detailed monitoring network consisting of two rows of multi-level sampling bundles and one row of mini-well clusters was installed in the vicinity of the PRB. The multi-level monitoring points were installed in transects parallel to groundwater flow and perpendicular to the iron wall (Fig. 2). Each transect contains five multi-level samplers. In each transect, there is one sampler located 3 m upgradient, one 1.5 m downgradient and the other three are located approximately equidistant within the wall. Each sampler has between 7 and 11 monitoring points for a total of 147 discrete monitoring points.
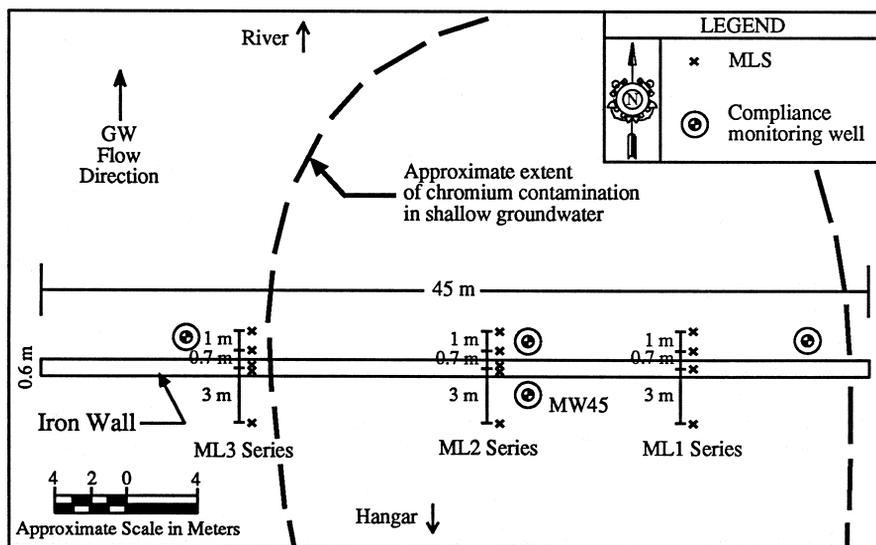
Fig. 2. Map of immediate vicinity where iron wall was installed and location of multi-layer sampling points with respect to the iron wall.

The multi-level sampling bundles are composed of 10, 0.32 cm i.d. teflon sampling tubes attached to a 1.26 cm schedule 80 PVC center stock. The mini-well clusters are composed of 7, 1.26 cm i.d. schedule 80 PVC wells. Well screens are 15 cm long and spaced 50 cm apart, beginning at approximately 7 m below ground surface and up to 4 m below ground surface for the mini-wells and up to 2 m below ground surface for the bundles. In addition to the multi-level samplers, there are also 10 traditional 5-cm i.d. PVC 'compliance' monitoring wells located upgradient, downgradient, below, in, and immediately adjacent to the wall (Fig. 2).

2.4. Field analyses

Analyses for chromate (Cr(VI)), ferrous iron (Fe(II)), dissolved sulfide (S^{2-}), dissolved oxygen (DO), dissolved hydrogen (H_2), specific conductance, temperature, pH, redox potential (Eh), alkalinity, and turbidity were performed in the field. The species Cr(VI), S^{2-}, and Fe(II) were analyzed colorimetrically with a UV/VIS spectrophotometer (Hach DR2010). Cr(VI) was analyzed directly using 1,5-diphenylcarbazide as a complexing agent, Fe(II) using 1,10-Phenanthroline as a complexing agent, and S^{2-} using the Methylene blue method (Standard Methods, 1992). Dissolved oxygen was measured using a CHEMets® colorimetric test kit which utilizes a rhodazine-D colorimetric technique and in some cases using a ORION model 810 DO meter with ORION 81010 DO electrode. Conductivity and temperature measurements were made using a conductivity probe and meter (ORION Conductivity meter, model 128 and/or model

135). Eh and pH measurements were made using platinum redox and glass bulb pH electrodes (ORION 9678BN combination redox electrode; ORION Ross 815600 combination pH electrode or ORION 9107BN pH electrode) in a sealed flow-through cell. Alkalinity measurements were made by titration with standardized H_2SO_4 acid using a Each® digital titrator and bromocresol green–methyl red indicator. Turbidity was measured with a Hach® turbidimeter (model 2100P). Dissolved H_2 analyses were performed using a GC headspace equilibration technique [8].

2.5. Groundwater sampling and analysis

Groundwater samples were collected with a peristaltic pump. Samples were taken behind the pump head for inorganic analytes and before the pump head for organic analytes to minimize losses of volatiles and gases using low-flow sampling techniques [9]. All samples were collected following equilibration of water quality parameters (DO, pH, Eh, specific conductance). Equilibration of water quality parameters was defined as three successive readings within $\pm 10\%$ for DO and turbidity, $\pm 3\%$ for specific conductance, ± 10 mV for Eh, and ± 0.1 for pH. Samples were collected after turbidity equilibrated during purging and this was typically less than 5 NTUs for this method [9]. Filtered and unfiltered samples were taken for metals and cation analysis and acidified to pH < 2 with ultra-pure concentrated nitric acid. Filtered samples were filtered with 0.45 um filters (Gelman aquaprep and/or Gelman high capacity barrel filters). Total metals were analyzed using a Jarrell-Ash Model 975 Inductively Coupled Plasma (ICP). Anion samples were unfiltered and unacidified and analyses were performed using ion chromatography (Dionex DX-300) or using Waters capillary electrophoresis method (N-601).

A stainless steel sampling manifold was utilized to collect organic compounds and dissolved gases. These manifolds are designed to minimize losses from volatilization and or sorption to pump tubing. Volatile organic compounds (TCE, *c*-DCE and VC) were analyzed using automated purge and trap gas chromatography analysis with a Tekmar LSC 2000 sample concentrator and Hewlett-Packard model 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID). Methane, ethylene and ethane were analyzed using a MTI GC equipped with a thermal conductivity detector. Quantitation levels for these gases are 10 to 1000 ppm.

3. Results and discussion

3.1. Location of iron wall

Conductivity data for the upgradient portion of the aquifer near ML1 is shown in Fig. 3a. Also plotted are the chloride + sulfate concentrations for this same location (Fig. 3b). There is a strong correlation between the two sets of data demonstrating the utility of this tool for locating the plume vertically within the aquifer. Fig. 4 shows conductivity data for a vertical core through the wall where conductivity differences are due to differential packing of the iron. This was probably due to differential settling of the
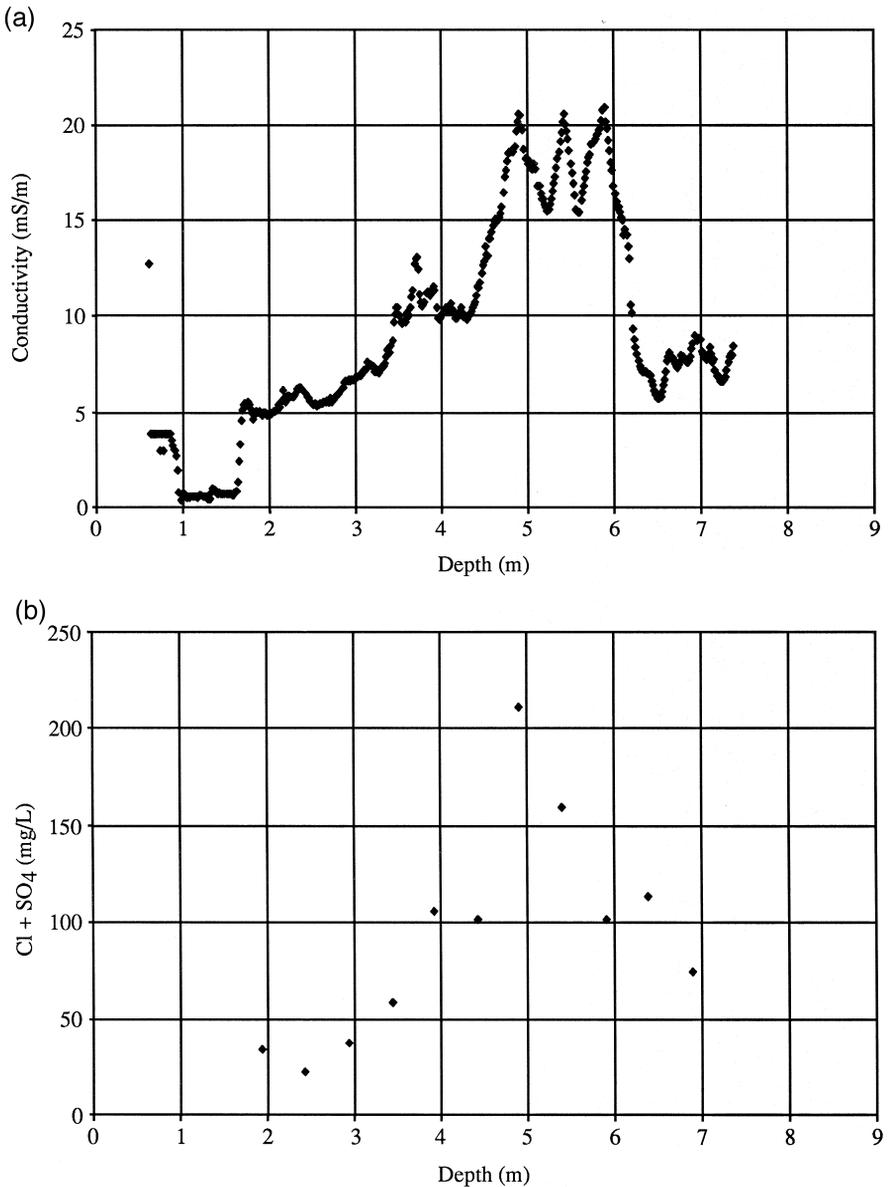
Fig. 3. (a) Plot of conductivity data for aquifer near ML1. (b) Plot of sum of chloride and sulfate concentrations in ML1 showing correlation with the conductivity data.

varying size of the iron filing particles within the saturated zone. Conductivity values greater than 100 mS/m indicate the presence of the granular iron. Differences in conductivity between the aquifer sediments and the iron filings were as much as 2 orders of magnitude, making this a very useful tool in locating the relatively thin wall (0.6 m).

Fig. 4. Plot of conductivity data for vertical section of the iron wall showing variation in conductance due to differential packing density of the iron and differences between conductivity of iron and aquifer sediment.

Fig. 5 shows conductivity data for an angle coring ($\sim 30°$) which passes into the upgradient interface at approximately 5.7 m or about 4.7 m vertically from the surface.
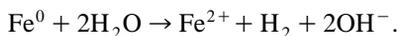

Fig. 5. Plot of conductivity data for angle core (30°) through the wall, indicating a wall thickness of about 45 cm at this location (depth is not vertical, but on a 30° angle).

Based on the length of travel on a 30° angle this indicates a wall thickness of 45 cm, or 15 cm less than the designed thickness of 60 cm. This was a worse case example of more than 10 such angle corings to date. Other measurements have ranged from 48 to 55 cm. None have been as wide as 60 cm. Some minor vertical discontinuities have been observed from the conductivity data and confirmed with coring. The few cores collected thus far together with the conductivity probe data indicate the iron was emplaced approximately as expected depth-wise; some locations indicate the iron to be slightly deeper than designed (7.3 m) and some shallower. Core retrieval was difficult due to the 'looseness' of the material. Where cores were angled through the wall and into the sediment (either upgradient or downgradient), the sediment acted as an effective 'plug' to keep the iron in the core barrel.
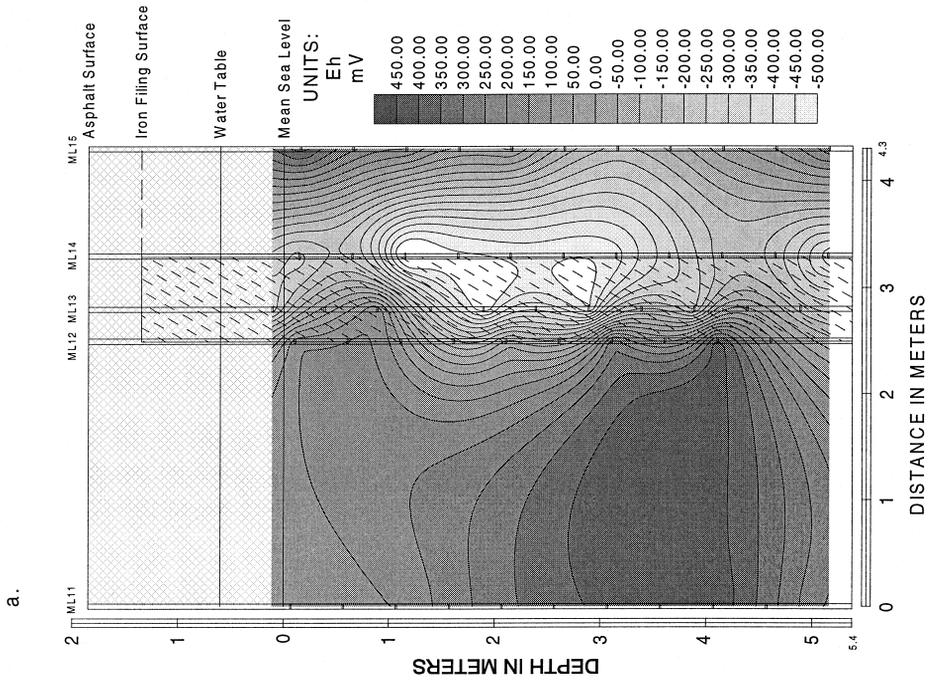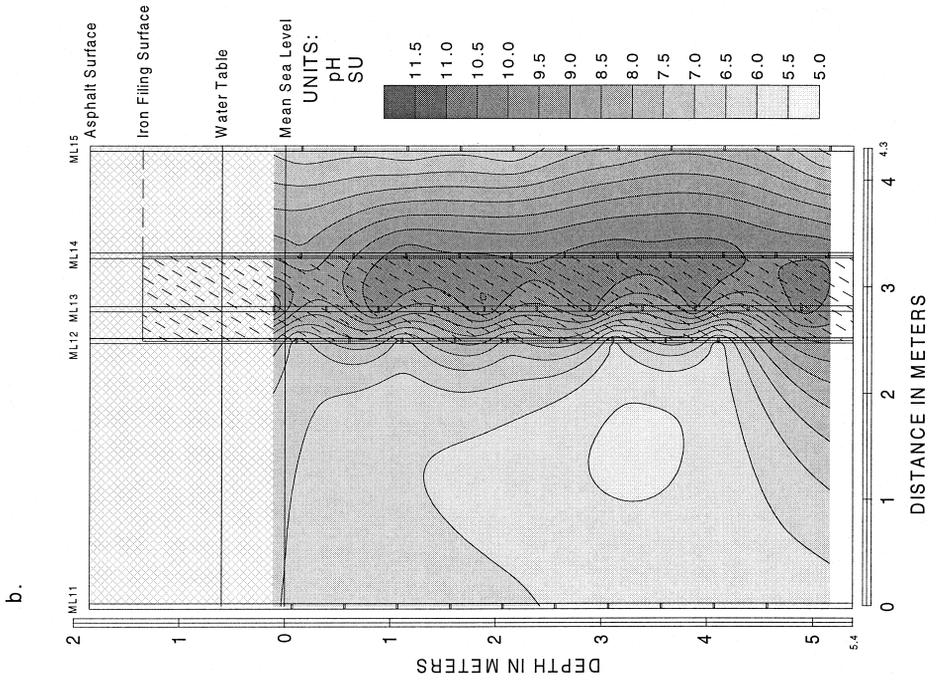
3.2. Iron corrosion

Ferrous iron concentrations within the wall increase from background levels within the aquifer of less than 0.5 mg/l to as much as 14.8 mg/l but are variable with depth, location and time. Total iron concentrations are similar to ferrous iron values indicating most of the soluble iron is in the ferrous form. Within 1.5 m downgradient, ferrous iron concentrations persist as high as 2.2 mg/l. Eh values within the wall are as low as -600 mV but generally range from -250 to -550 mV, whereas upgradient Eh ranges from 250 to 450 mV (Fig. 6a). Upgradient pH ranges from 5.7 to 6.5, whereas within the wall the pH is generally between 9 and 10.7 (Fig. 6b). DO values within the aquifer range from 0.2 to 2.0, whereas within the wall, DO is generally less than 0.2. Dissolved hydrogen increases from background concentrations of less than 10 nM to greater than 1000 nM. These data are consistent with the effects of the iron corrosion reaction. The following equation shows that the oxidation of the iron filings would be expected to generate ferrous iron and dissolved hydrogen, decrease Eh and increase pH:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-.$$

Water is unstable under the extremely reducing conditions observed and suggest that the reduction of water may be occurring. Geochemical conditions within 1.5 m downgradient of the wall show increasing reducing conditions over time, indicating that a 'redox front' may be moving downgradient from the wall (Fig. 7) and the area affected by reducing conditions may increase over time.

3.3. Mineralogic analyses

Limited mineralogic analyses of cores have been completed. Due to increased pH within the wall, there is a shift in equilibrium form a bicarbonate to a carbonate dominated system. Analysis of total inorganic carbon to evaluate precipitation of likely carbonate phases (e.g. siderite [$FeCO_3$], calcite [$CaCO_3$]), shows increases in inorganic carbon within the iron compared to the upgradient aquifer sediments. This is true for both the upgradient and downgradient interfaces, but differences are greater for the
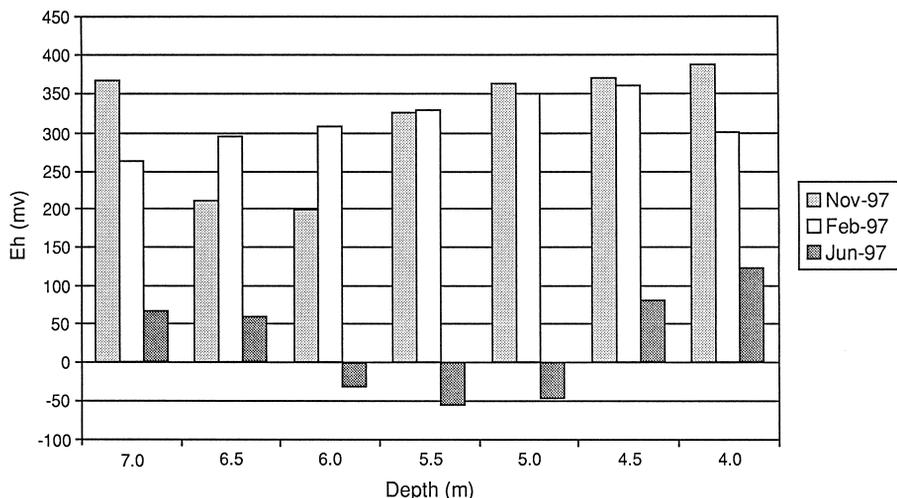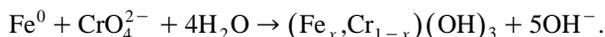
Fig. 7. Eh changes over time in multi-level sampler ML25 showing evolution of increased reducing conditions at this location, 1.5 m downgradient of the iron wall.

upgradient cores (Fig. 8). The most ubiquitous mineral phases observed thus far are amorphous iron (oxy)hydroxides and possibly green rust (general stoichiometry of $[Fe_4^{2+}Fe_2^{3+}(OH^-)_{12}]^{2+}\cdot[SO_4^{2-}\cdot H_2O]^{2-}$). These observations have been made with SEM-EDS and additional studies are underway.

3.4. Chromate treatment

The center of the Cr(VI) plume resides between 4.5 and 5.5 m below ground surface while the extent of the plume ranges from 4 to 7 m below ground surface. Cr(VI) concentrations decline from upgradient values as high as 5.1 mg/l to less than detection limits (< 0.01 mg/l) within the first few centimeters of the wall. No chromate is detected downgradient of the wall. Chromium concentrations for the east and west multi-level sampling transects are shown in Fig. 9a and b. Under the highly reducing conditions which prevail within the wall, the reduction of Cr(VI) to Cr(III) is predicted and the subsequent formation of an insoluble precipitate is formed as shown below:

$$Fe^0 + CrO_4^{2-} + 4H_2O \rightarrow (Fe_x, Cr_{1-x})(OH)_3 + 5OH^-.$$

Geochemical modeling calculations indicate that this precipitate should form and support Cr(III) aqueous concentrations less than 0.01 mg/l. Cr(III) has been detected on the surface of the iron in a few cores using XPS analysis. Cr has also been detected in

Fig. 6. (a) Cross-section of ML1 multi-layer samplers showing Eh distributions upgradient, downgradient and through the iron wall. (b) Cross-section of ML1 multi-layer samplers showing pH distributions upgradient, downgradient and through the iron wall.
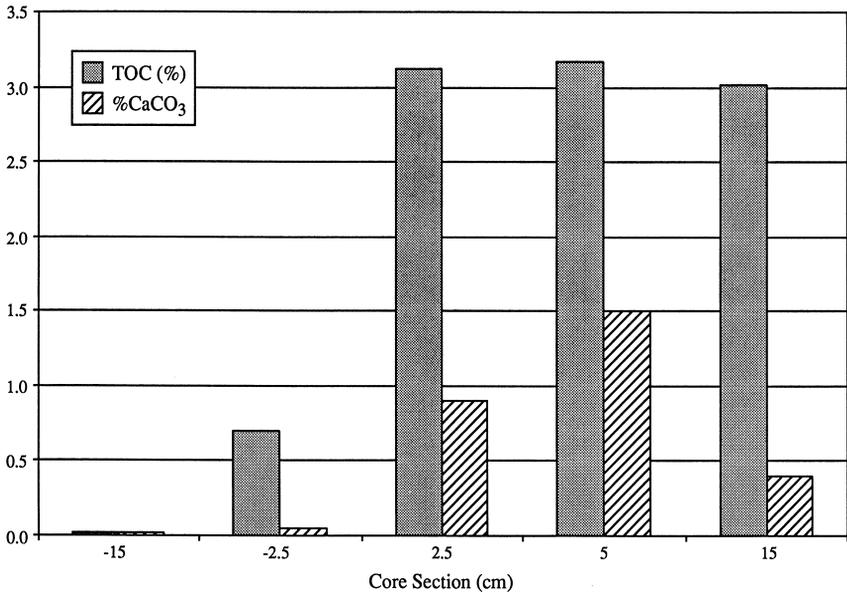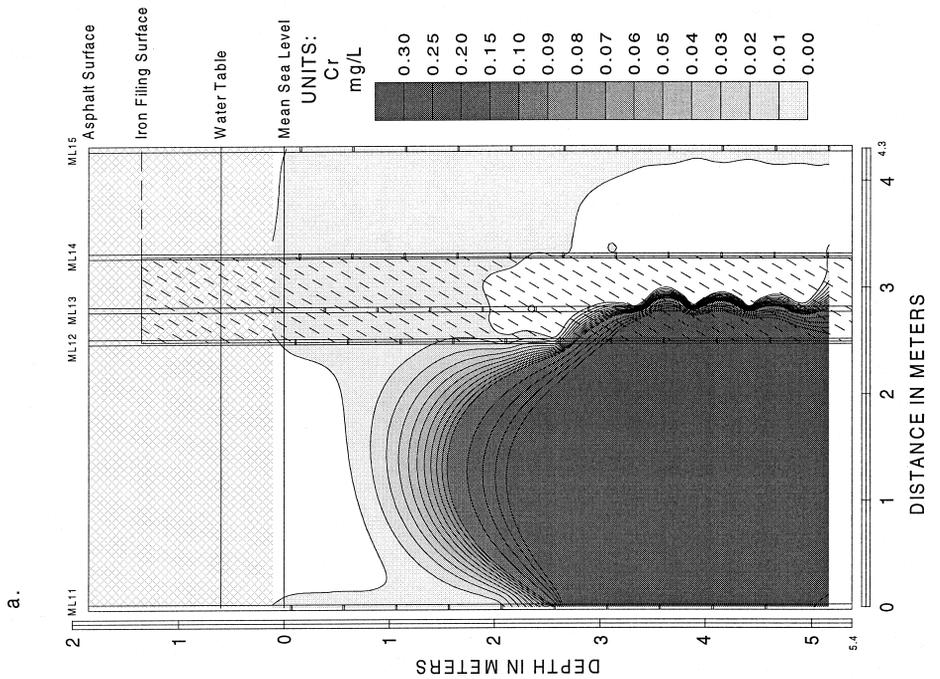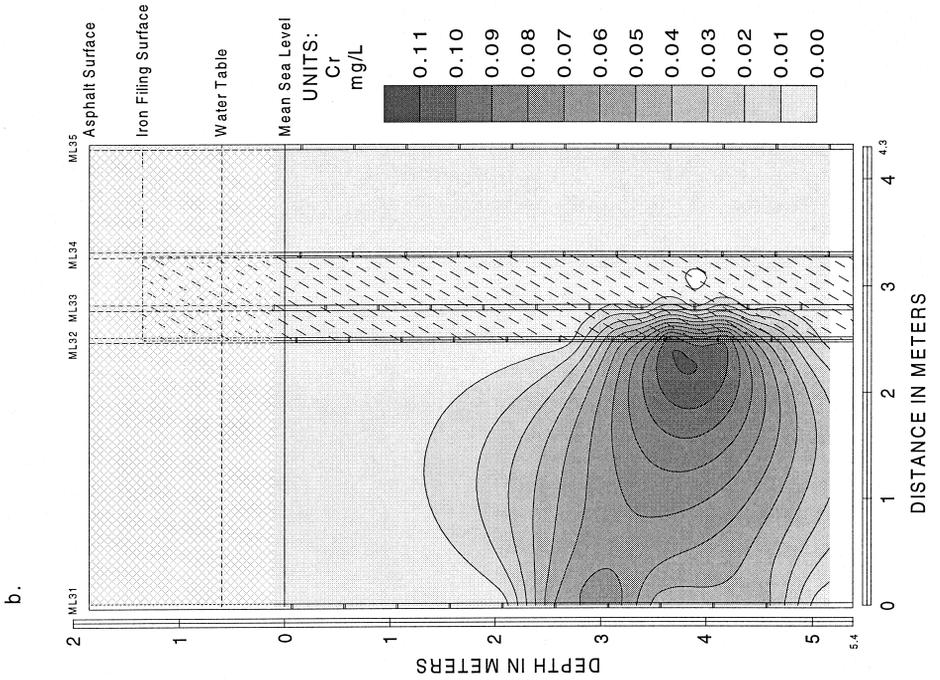
Fig. 8. Inorganic carbon and organic carbon data for upgradient interface core of iron wall (positive distance represents iron, negative distance represents upgradient sediment).
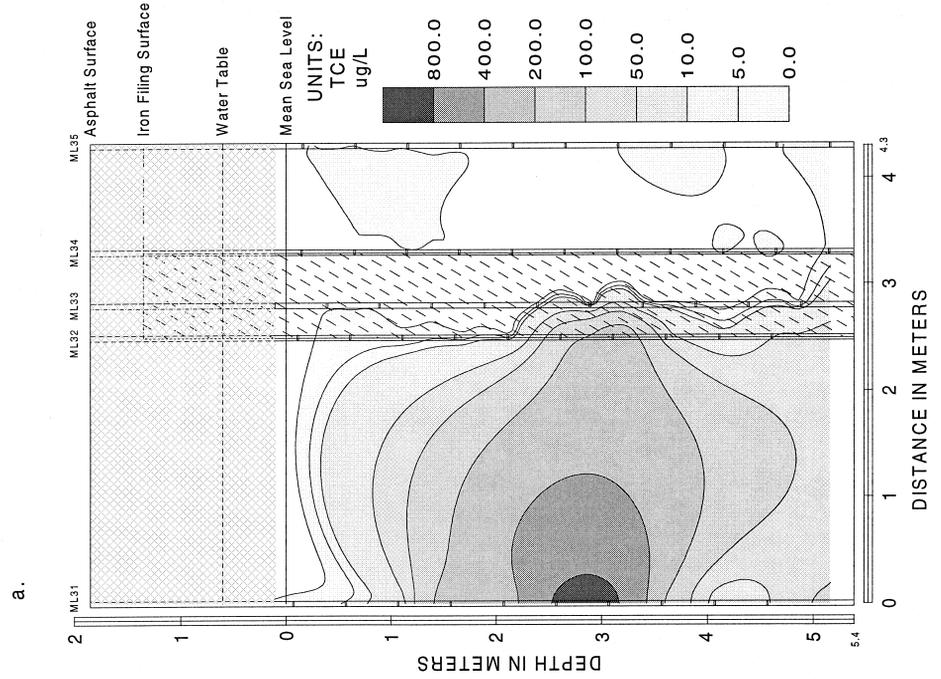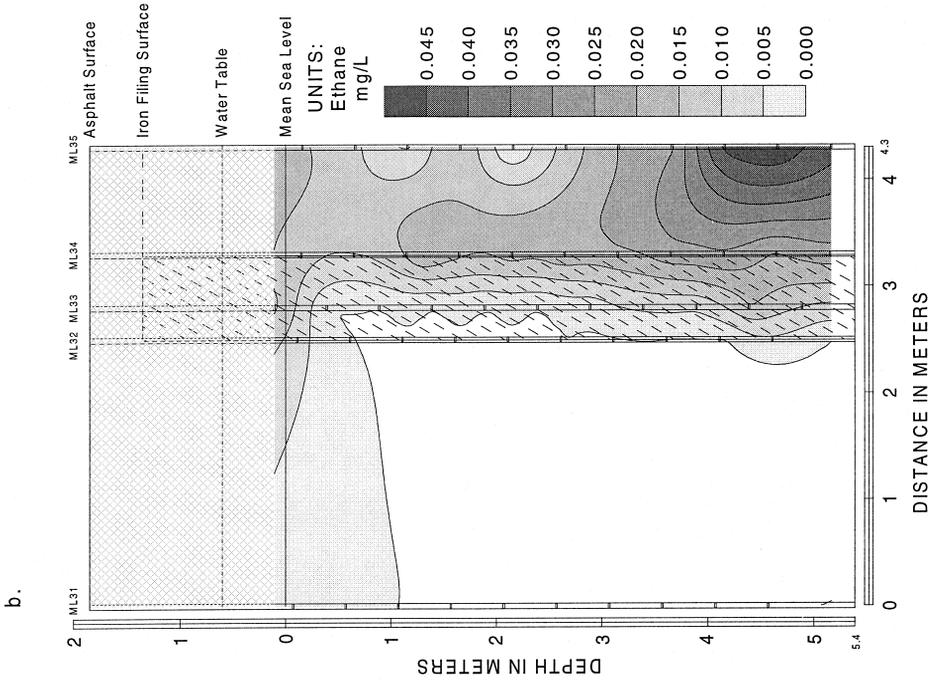
these same samples using SEM-EDS and appears in association with iron as surface coatings on the iron filings.

3.5. Chlorinated volatile organic compounds treatment

The vast majority of the multi-layer sampling ports show reduction of the chlorinated volatile organic compound (CVOC) concentrations to less than North Carolina (Department Environmental Quality) regulatory target levels (5 μg/l, TCE; 70 μg/l, c-DCE; 2 μg/l VC). With the disappearance of the TCE, c-DCE and VC, there has been a steady increase in detectable ethane, ethene, and acetylene (Fig. 10a,b). These data indicate that the organic compounds are degrading via both reductive dechlorination and β-elimination pathways [10]. Only one port (ML25-1) continues to show levels significantly above target concentrations. This is the deepest port in the middle of the wall where the dissolved CVOC concentrations are highest. An adjoining 5 cm PVC compliance well showed TCE concentrations above regulatory limits in November (50 μg/l) and June 1997 (156 μg/l) but was below target levels in March 1997 (3.4 μg/l). Maximum

Fig. 9. (a) Cross-section of ML2 multi-layer samplers showing chromium concentration distributions upgradient, downgradient and through the iron wall. (b) Cross-section of ML1 multi-layer samplers showing chromium concentration distributions upgradient, downgradient and through the iron wall.

TCE influent concentrations in this central portion of the plume are as high as 5652 μg/l. These concentrations generally decrease to less than 5 μg/l within the wall but exceed 50 μg/l at the lowest depth. There are some indications that the TCE plume may have dipped lower in the aquifer following wall installation which might explain these observations and this is being further investigated. Nowhere do *c*-DCE concentrations exceed regulatory limits. There is some slight elevation beyond target levels for VC (greater than 2 μg/l but less than 5 μg/l) in a few multilayer sampling (MLS) ports, but this is not reflected in the adjoining 2 in PVC compliance wells. Downgradient VC concentrations in the MLS ports have declined with time and the highest concentration observed in the September 1997 sampling round was 2.8 μg/l. These results indicate that the barrier is successfully reducing TCE, *c*-DCE and VC concentrations to less than MCL values for the vast majority of the monitored portions of the wall. Of 29 downgradient MLS ports, MCLs for TCE, *c*-DCE and VC are exceeded in 1, 0 and 3 ports, respectively. Where MCL goals are not met, it is possible that reaction rates within the barrier are lower than those measured in the laboratory. These rates are surface area dependant and thus proportional to the density of the iron filings within the wall. The estimated emplaced iron filings bulk density was 1.64 g/cm^3 (weight of iron emplaced divided by the estimated volume of the trench) or 60% of the laboratory measured value of 2.7 g/cm^3 which was for a tightly packed soil column. Likewise, there are pockets within the wall where there is little or no iron and other areas where the wall thickness is significantly less than the designed thickness of 60 cm.

4. Conclusions

Chromium is removed from the groundwater to less than detection limits (< 0.01 mg/l) and considerably less than regulatory target levels (0.1 mg/l). This is accomplished via redox reactions accompanied by precipitation processes due to the corrosion of the iron. Likewise there is reduction in CVOC concentrations to less than regulatory limits where these compounds are entering and being treated by the iron wall.

Acknowledgements

Fig. 10. (a) Cross-section of ML3 multi-layer samplers showing trichloroethylene concentration distributions upgradient, downgradient and through the iron wall. (b) Cross-section of ML3 multi-layer samplers showing ethane concentration distributions upgradient, downgradient and through the iron wall.

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