Emplacement verification and long-term performance monitoring of a permeable reactive barrier at the USCG Support Center, Elizabeth City, North Carolina

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Abstract A continuous hanging iron wall was installed in June 1996, at the US Coast Guard (USCG) Support Center near Elizabeth City, North Carolina, 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 six quarterly rounds of performance monitoring of the wall which are summarized in this paper. 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.

INTRODUCTION

Permeable reactive barriers (PRBs) are a promising new technology for the passive, in situ treatment of contaminated groundwater (Gillham & O’Hannesin, 1994; Blowes et al., 1995; Puls et al., 1995). 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” (US EPA, 1997). 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 other processes.

A permeable in situ subsurface reactive barrier composed of 100% granular iron was installed in June, 1996, at the US Coast Guard Support Center near Elizabeth City, North Carolina to treat overlapping plumes of chromate (Cr(VI)) and chlorinated solvent compounds (trichloroethylene (TCE), cis-dichloroethylene (c-DCE), and vinyl chloride (VC). Concentrations in excess of 10 mg l\(^{-1}\) Cr and 19 mg l\(^{-1}\) TCE had been detected in the groundwater at the site since 1991. 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. An estimated 3.2 m$^3$ of iron-filings were emplaced per linear metre and a total of approximately 280 t of iron was installed. The installation was completed in 6 h on 22 June 1996.

The PRB is approximately 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, Inc.). The iron has an average grain size of 0.4 mm and surface area of 0.8 to 0.9 m$^2$ g$^{-1}$. In prior laboratory studies zero-valent iron was shown to reduce Cr(VI) to an insoluble mixed Cr-Fe hydroxide (Powell et al., 1995) and reductively dechlorinate TCE (Gillham & O'Hannesin, 1994).

The objectives of this study were to evaluate the effectiveness of a permeable reactive barrier in reducing groundwater concentrations of Cr(VI), TCE, c-DCE and VC to below regulatory target limits; to determine if this method of PRB emplacement was feasible and effective in intercepting and “treating” the dissolved contaminants; and to begin to evaluate the long-term effectiveness this technology for groundwater remediation.

STUDY SITE

The field site is located at the US Coast Guard (USCG) Support Center near Elizabeth City, North Carolina, about 100 km south of Norfolk, Virginia 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 (Fig. 1), 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 the underlying aquifer immediately below the shop’s foundation (Puls et al., 1994). Sampling results from a monitoring network consisting of more than 40 monitoring wells and about 100 Hydropunch™ and Geoprobe™ monitoring points indicated 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. Multilevel 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 geology of the site has been described in detail elsewhere (Puls et al., 1994; Puls et al., 1995). Groundwater flow velocity is extremely variable with depth, with a highly conductive layer at roughly 4.5 to 6.5 m below the 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 the ground surface indicate hydraulic conductivity values of between 0.3 to 8.6 m day$^{-1}$ (Sabatini et al., 1997).

**METHODS**

**Wall emplacement verification**

A conductivity probe manufactured by Kejr Engineering, Inc. was advanced using a Geoprobe™ to verify the exact placement of the iron in the aquifer. This tool provides conductivity data which reflects both the aqueous chemistry and the lithology. Its radius of influence around the probe is 2–5 cm. The tool provides real-time specific conductance data versus depth which can be displayed on a portable computer. Coring of the wall was also performed using a Geoprobe™ with 5 cm i.d. core barrels equipped with plastic sleeves to corroborate the conductivity profiles and recover iron for further testing and evaluation.

**Monitoring well network**

A detailed monitoring network consisting of two rows of multilevel sampling bundles and one row of mini-well clusters was installed in the vicinity of the PRB. The multilevel monitoring points were installed in transects parallel to the groundwater flow and perpendicular to the iron wall (Fig. 2). Each transect contains five multilevel 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 seven and 11 monitoring points for a total of 147 discrete monitoring points.
Field analyses

Analyses for chromate (Cr(VI)), ferrous iron (Fe(II)), dissolved sulphide (S²⁻), dissolved oxygen (DO), specific conductance, temperature, pH, redox potential (Eh), alkalinity, and turbidity were performed in the field. The species Cr(VI), S²⁻, and Fe(II) were analysed colourimetrically with a UV/VIS spectrophotometer (Hach DR2010). Dissolved oxygen was measured using a CHEMets® colourimetric test kit which utilizes a rhodazine-D colourimetric 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 in a sealed flow-through cell. Alkalinity measurements were made by titration with standardized H₂SO₄ acid using a Hach® digital titrator. Turbidity was measured with a Hach® turbidimeter.

Groundwater sampling, storage 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. 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 ±10% for DO and turbidity, ±3% for specific conductance, ±10 mV for Eh, and ±0.1 for pH. Filtered and unfiltered samples were taken for metals and cation analysis and acidified to pH < 2 with ultra-pure concentrated nitric acid. Total metals were analysed 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 (Waters Method N-601).

Volatile organic compounds (TCE, c-DCE and VC) were analysed using automated purge and trap GC analysis with a Tekmar LSC 2000 sample concentrator and Hewlett-Packard model 5890 gas chromatograph. Methane, ethylene and ethane were analysed using a Hewlett-Packard model 5890 gas chromatograph equipped with flame ionization and electron capture detectors.

RESULTS AND DISCUSSION

Location of the iron wall

Conductivity data for the upgradient portion of the aquifer near ML11 is shown in Fig. 3. Also plotted are the [chloride + sulphate] concentrations for this same location. 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. Figure 4 shows conductivity data for a vertical core through the wall where differences in conductivity are due to differential packing of the granular iron. Conductivity values greater than 100 mS m\(^{-1}\) indicate the presence of iron. Differences in conductivity between the aquifer sediments and the iron filings were more than two orders of magnitude in some locations, making this a very useful tool in locating the relatively thin wall (0.6 m). Based on limited preliminary electrical conductivity profiles, the wall is approximately 45–58 cm thick compared with the 60 cm design. Some minor

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**Fig. 3** Plot of conductivity data versus sum of chloride and sulphate concentrations in groundwater showing correlation between the two data sets.
vertical discontinuities were observed in the conductivity data and have been confirmed with coring. These small “gaps” are probably due to “bridging” within the trencher hopper during iron emplacement.

Iron corrosion

Ferrous iron concentrations within the wall increase from background levels within the aquifer of less than 0.5 mg l\(^{-1}\) to as much as 14.8 mg l\(^{-1}\) 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 as high as 2.2 mg l\(^{-1}\) persist. Eh values within the wall are as low as -600 mV but generally range from -250 to -550 mV, whereas upgradient Eh ranges from 300 to 600 mV. Upgradient pH ranges from 5.7 to 6.5, whereas within the wall the pH is generally between 9 and 10.7. DO values within the aquifer range from 0.2 to 2.0, whereas within the wall DO is generally less than 0.2. These data confirm that the iron is corroding. Geochemical conditions 1.5 m downgradient of the wall show increasing reducing conditions over time, indicating a “redox front” may be moving downgradient from the wall.

Chromate treatment

The centre of the Cr(VI) plume resides between 4.5 and 5.5 m below the ground surface while the extent of the plume ranges from 4 to 7 m below the ground surface. Cr(VI) concentrations decline from upgradient multi-layer sampling point values as high as 5.1 mg l\(^{-1}\) to less than detection limits (<0.01 mg l\(^{-1}\)) and less than the regulatory limit or maximum contaminant level (MCL) of 0.1 mg l\(^{-1}\) within the first few centimetres of the wall. No chromate is detected downgradient of the wall. Under the highly reducing conditions which prevail within the wall, the reduction of
Cr(VI) to Cr(III) is predicted and the formation of an insoluble precipitate is expected to form as shown below:

$$\text{Fe}^0 + \text{CrO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow (\text{Fe}_{x} \text{Cr}_{y} \text{OH})_3 + 5\text{OH}^-$$

Geochemical calculations confirm that this precipitate should form and support Cr(III) aqueous concentrations less than 0.01 mg l$^{-1}$.

**Chlorinated organic compounds treatment**

The vast majority of the multi-layer sampling ports show reduction of the chlorinated compounds. 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 organic solvent compound concentrations are highest. An adjoining 2 in compliance well showed TCE concentrations above regulatory limits in November (50 µg l$^{-1}$) and June 1997 (156 µg l$^{-1}$) but was below target levels in March 1997 (3.4 µg l$^{-1}$). Maximum influent concentrations in this central portion of the plume have been as high as 5652 µg l$^{-1}$. These concentrations generally decrease to less than 5 µg l$^{-1}$ within the wall but exceed 50 µg l$^{-1}$ at the lowest depth. There are some indications that the TCE plume may have dipped lower in this part of 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 vinyl chloride (greater than 2 µg l$^{-1}$ but less than 5 µg l$^{-1}$) in a few sampling ports, but this is not reflected in the adjoining compliance wells. Downgradient vinyl chloride concentrations in the multilayer samplers have declined with time and the highest concentration observed in the September 1997 sampling round was 2.8 µg l$^{-1}$.

Results thus far indicate that the barrier is successfully reducing TCE, c-DCE and vinyl chloride concentrations to less than MCL values for the vast majority of the monitored portions of the wall. Where MCL goals are not met, it is possible that reaction rates within the barrier are lower than densities measured in the laboratory, due to less dense packing of the iron within the trench compared to those measured in laboratory columns. Likewise, there are pockets within the wall where there is little or no iron and other small areas where the wall thickness is less than the design thickness of 60 cm, so the residence time may be slightly less than expected.

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REFERENCES


