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The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test

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Abstract

A small-scale field test was initiated in September 1994 to evaluate the in situ remediation of groundwater contaminated with chromate using a permeable reactive barrier composed of a mixture of zero-valent Fe, sand and aquifer sediment. The site used was an old chrome-plating facility located on a U.S. Coast Guard air base near Elizabeth City, North Carolina. Dissolved chromate concentrations were reduced to less than 0.01 mg/L via reduction from Cr(VI) to Cr(III) as a result of the corrosion of the Fe. As the Fe corrodes, pH increases, oxidation-reduction potential declines, dissolved oxygen is consumed, and Fe(II) is generated. Mineral phases formed as a result of the Fe corrosion include ferrous sulfides and various Fe oxides, hydroxides, and oxyhydroxides. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The extraction and treatment of contaminated ground water at hazardous waste sites continues to be an extremely costly endeavor, the effectiveness of which is often dubious at best (National Research Council, 1994). New, in situ treatment technologies are currently being developed which take advantage of chemical reactions at the surface of zero-valent Fe which are capable of transforming or degrading contaminants into non-toxic or immobilized chemical forms (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Powell et al., 1995; Agrawal and Tratnyek, 1996; Blowes et al., 1997). Instead of trying to remove the contaminated water from the subsurface for above-ground treatment, the emplacement of a permeable reactive geochemical barrier composed of zero-valent Fe which intercepts the contaminated plume and transforms the contaminant to a non-toxic form is attractive for a number of reasons. First, the in situ approach requires no above-ground treatment facilities and the space can be returned to its original use. Second, there is no need for expensive above-ground treatment, storage, transport, or disposal. Third, there is little or no operation and maintenance costs.

When Fe corrodes in aerobic waters, Fe^{2+} and Fe^{3+} ions and OH^- ions are produced, O^2 is consumed and amorphous $Fe(OH)_3$ precipitation is expected. In anaerobic systems, Fe^{2+} and OH^- and H_2 are produced and sulfide formation is possible

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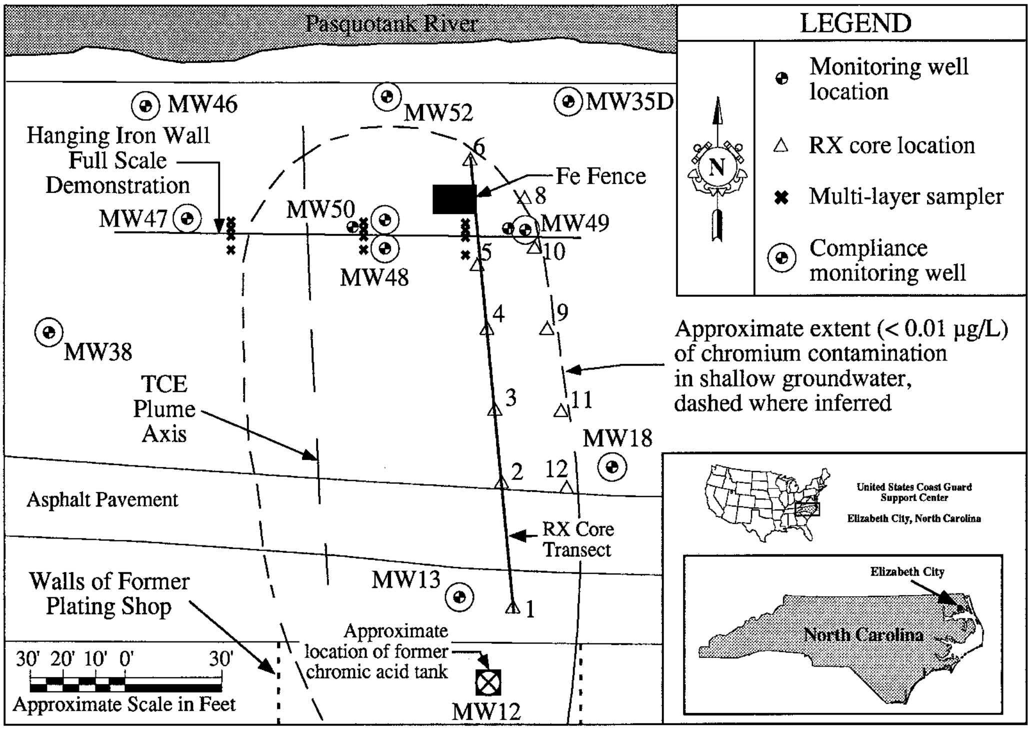

Fig. 1. U.S. Coast Guard site map, showing locations of some monitoring wells, RX coring locations, Fe "fence" location and proposed location of full-scale demonstration for continuous permeable reactive Fe wall.

when sufficient SO_4 is present. Several solid phase Fe species may precipitate as a result of the Fe corrosion process resulting in the potential immobilization of inorganic contaminants as coprecipitates. Significant downgradient geochemical changes are likely to occur with these in situ treatments resulting in steep geochemical gradients depending on initial hydrogeochemical conditions and barrier composition. Field performance monitoring of contaminant fate and geochemical alteration is needed to elucidate these chemical transformations and to understand the potential limitations of this technology. As Fe corrosion proceeds, Fe oxides and other minerals will form which will decrease porosity in the reaction zone and Fe reactivity, but it is unclear how quickly this will affect overall system performance.

Chromium is an important industrial metal used in the manufacture of alloys, leather, lumber, and a host of diverse chemical products (Nriagu, 1988a, 1988b). Inadvertant releases of Cr to the environment have occurred in many of these industries. Chromium is found primarily in two oxidation states in subsurface environments: Cr(VI) and Cr(III). Whereas Cr(VI) is extremely toxic and carcinogenic (Bianchi et al., 1984; Ono, 1988), Cr(III) is actually essential in human nutrition (Mertz, 1981). Chromium(VI) or hexavalent Cr exists primarily as chromate (CrO_4^{2-}) or bichromate ($HCrO_4^-$) anions and does not sorb strongly to most soils under slightly acidic to alkaline conditions. Above pH 6.5, CrO_4^{2-} will generally dominate, while below pH 6.5, $HCrO_4^-$ will be the predominate species in aqueous solutions. Under most natural environmental conditions, Cr(III) readily precipitates as $Cr(OH)_3$ or as the solid solution $Fe_xCr_{1-x}(OH)_3$ (Rai et al., 1987; Sass and Rai, 1987), which is a very insoluble phase supporting dissolved aqueous Cr concentrations below 10 µg/L.

Concerns about the impact of Cr on human health and the environment require an evaluation of the potential risk of Cr entering the groundwater flow system and being transported to potential receptors. At sites where such potential exits, active remedial measures such as excavation or pump-and-treat are often undertaken. Experience at sites where pump-and-treat remediation of Cr-contaminated groundwater is currently underway, suggests that although it is feasible to remove high levels of Cr from the subsurface, as concentrations decrease it becomes more difficult to remove the remaining Cr using conventional pump-and-treat remedial approaches (Wittbrodt and Palmer, 1992). While several new remedial technologies are being investigated, there is still concern about the cost of such remediation technology, and at many sites there is a debate about the need for expensive remediation in light of risk assessment and cost-benefit analyses.

The field test had multiple objectives:(a) to evaluate whether zero-valent Fe could remediate, in situ, groundwater contaminated with chromate using a permeable reactive barrier system; (b) determine if results of prior laboratory studies (Powell et al., 1995) were consistent with field observations and results; (c) evaluate which geochemical parameters might best indicate effective system performance; and (d) identify "new" mineral phases formed as a result of barrier emplacement which might affect long-term system performance.

Table 1
Physical characteristics of components of reactive mixture used in the permeable barrier wall

	% Vol.	% Wt.	D_b (g/cm$_3$)	Surf. Area[1] (m$_2$/g)
MSB Fe	25	28	2.1	1.1
AI&M Fe	25	31	2.3	8.3
Aquifer sediment[2]	25	23	1.8	5.8
Sand	25	18	1.4	< 1

[1] BET (Brunauer, Emmett, Teller) surface area, using N_2.
[2] Surficial aquifer sediment at Elizabeth City site.

2. Site description

The field site is located at the U.S. Coast Guard (USCG) Support Center near Elizabeth City, North Carolina, about 100 km S 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 SE of Elizabeth City. Hangar 79, which is only 60 m S of the river (Fig. 1), contains a chrome plating shop which had been in use for more than 30 a and discharged acidic Cr wastes and associated organic solvents through a hole in the concrete floor. These wastes infiltrated the soils and the underlying aquifer immediately below the

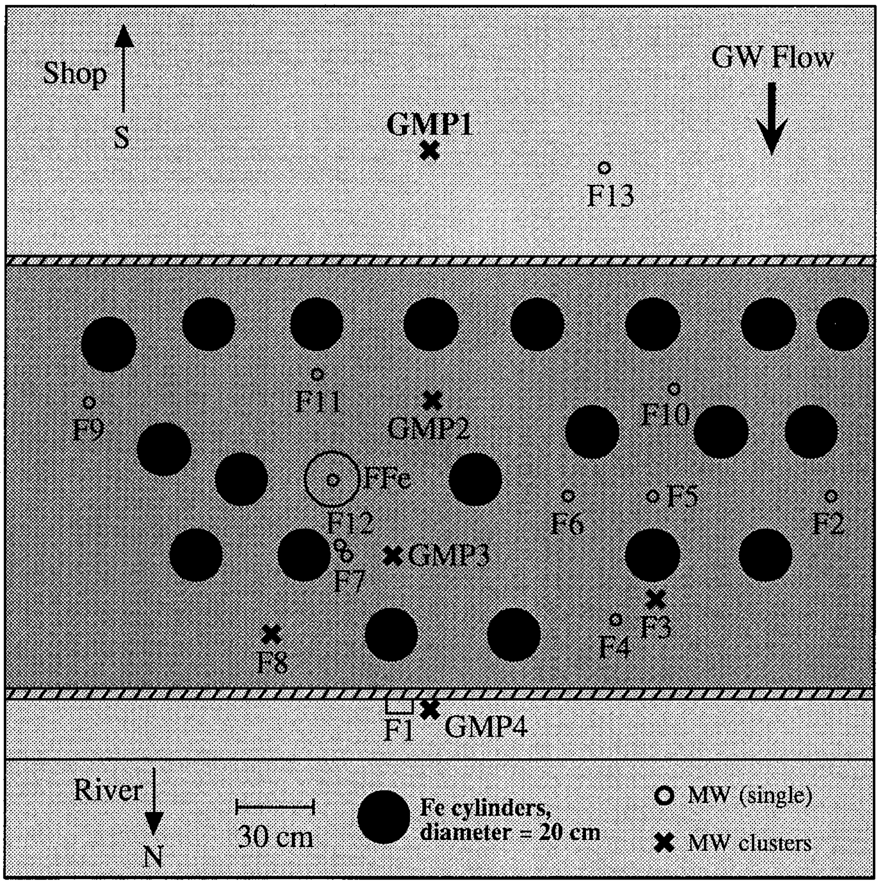

Fig. 2. Iron "fence" area showing locations of reactive Fe cylinders and monitoring points in plan view.

shop's foundation resulting in soil concentrations which exceed 10,000 ppm Cr (Puls et al., 1994a).

The site geology has been described in detail elsewhere (Puls et al., 1994a, 1994b) but essentially consists of typical Atlantic coastal plain sediments, characterized by complex and variable sequences of surficial sands, silts, and clays. Groundwater flow velocity is extremely variable with depth, with a highly conductive layer at roughly 5 to 6 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.

3. Methodology

Two sources of Fe were mixed with native surficial aquifer material and a No.10–No. 50 mesh washed sand for use in the field test. The aquifer sediments were obtained using large diameter (16-cm i.d.) hollow-stem augers and from the same location into which the reactive mixture was emplaced into the subsurface. The sand was obtained locally from a hardware store and composed primarily of silica. Low-grade steel waste stock, obtained from Ada Iron and Metal (AI&M, Ada, OK), was turned on a lathe (without cutting oils using diamond bits) to produce 200 L of turnings. A second Fe material was heated cast Fe in the form of Fe chips obtained from Master Builder's Supply (MBS, Streetsboro, Ohio). The latter material was primarily in the 0.1 to 2 mm size range while the former was primarily in the 1 to 10 mm size range. The MBS Fe exhibited greater total S and C content than the AI&M Fe. Laboratory testing with these two types of Fe indicated that the AI&M Fe was significantly more reactive for chromate than the MBS Fe (Powell et al., 1995), whereas the MBS Fe had been shown to be very effective for reducing chlorinated solvent compound concentrations (Clausen et al., 1995). The sand was added to the mixture for increased permeability and poured into the large diameter hollow-stem augers forming a series of Fe cylinders. A summary of physical characterization data for the components of the reactive mixture is presented in Table 1. The 4 materials were mixed in equal volumes on-site and poured through the hollow-stem augers which had been drilled to the appropriate depth. Drilling began on September 13 and was completed September 16, 1994. The estimated diameter of the emplaced reactive Fe cylinders was 20 cm and they were installed from 3 to 8 m below ground surface. The diameter of the Fe cylinders was greater than the inner diameter of the hollow-stem augers, because as the augers were withdrawn the mixture was added to spill out and occupy space created by the external auger flights. A total of 21 such cylinders were installed in 3 rows like "fence" posts as indicated in Fig. 2. Spacing of the cylinders was such that "gaps" were on the order of 0.03–0.15 m.

Table 2
Screen interveal depth of the monitoring wells in the iron fence area

Well	Screen Interval Depth (m)
F1	4.3–5.5
F2	4.8–5.2
F3	5.1–5.4
F4	5.0–5.4
F5	5.0–5.4
F6	5.1–5.5
F7	4.8–5.2
F8	4.8–5.1
F9	4.7–5.1
F10	5.0–5.3
F11	4.6–4.9
F12	4.7–5.0
F13	5.0–5.3
Ffe	4.7–5.1
GMP1-1*	4.5–4.8
GMP1-2	4.9–5.2
GMP1-3	5.4–5.7

* Other GMP well clusters (GMP2, GMP3, GMP4) are screened at approximately the same depths.

3.1. Monitoring system and field analyses

Twenty-five monitoring wells were installed within the approximately 27.5 m^3 treatment zone. Most are 1.9-cm i.d. polyvinyl chloride (PVC) wells with 30- or 45-cm long screens which are completed between 4.2 and 6.0 m below ground surface (Table 2). The GMP series of wells were installed in June, 1994, prior to the emplacement of the Fe mixture, to acquire pre-installation hydrologic and geochemical data. Additional monitoring wells were installed following emplacement of the Fe mixture, and were driven into place to minimize disturbance to the test area. In addition to the permanent well sampling points, temporary sampling points were also utilized to increase the spatial resolution of the data. This sampling was performed using a Geoprobe® where the drive points were hydraulically driven into place to the required depths with minimal disturbance to the test zone. Locations for the monitoring points are shown in Fig. 2.

Monitoring before and after "fence" installation was conducted for the following: pH, Eh, dissolved O_2, alkalinity, total Cr, chromate, total Fe, Fe(II), total dissolved sulfide, and major cations and anions. The species Cr(VI), S^{2-}, and Fe(II) were analyzed colorimetrically with a UV/VIS spectrophotometer (Hach

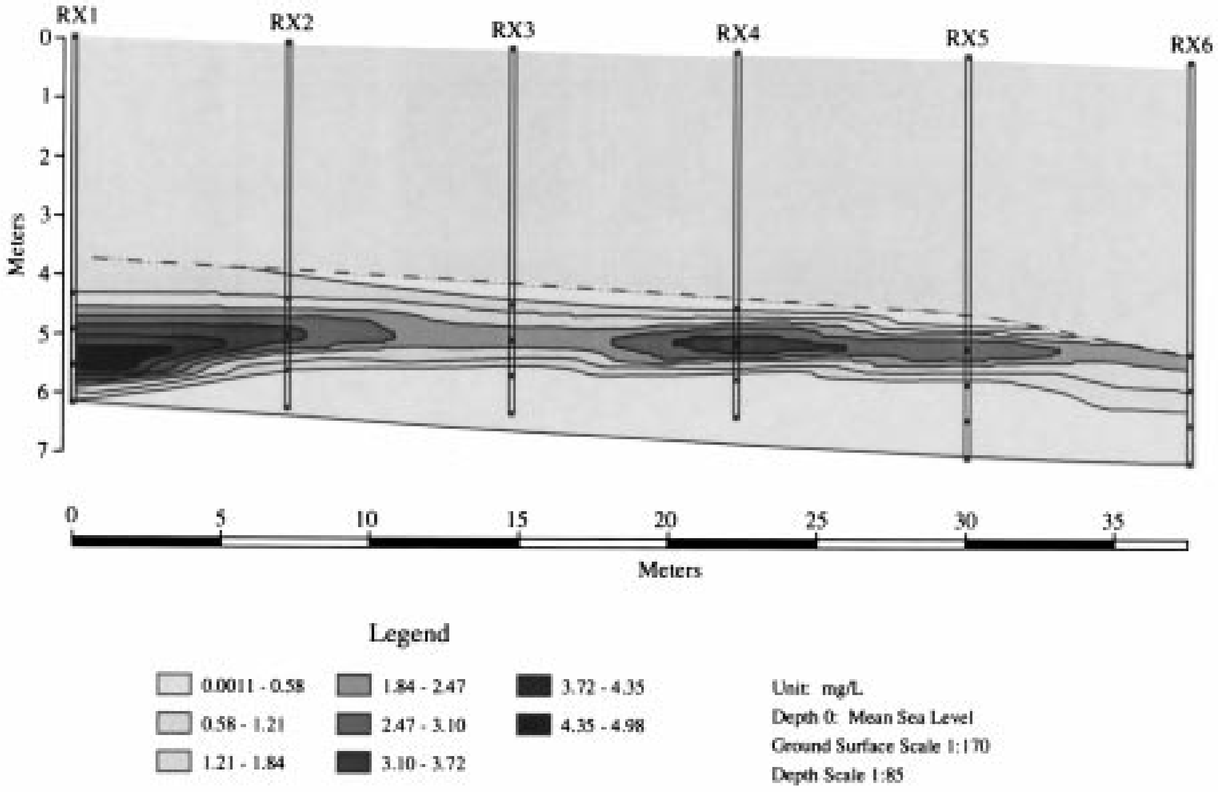

Fig. 3. North–south trending cross-section (RX1 through RX6, Fig. 1) showing vertical distribution of chromate within the aquifer.

DR2010). Chromium(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 for the Examination of Water, 1992). Dissolved O_2 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 Pt 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 Hach® 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 (Chapelle et al., 1996).

3.2. Ground water sampling and laboratory analysis

Ground water 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. All samples were collected following equilibration of water quality parameters (DO, pH, Eh, specific conductance). Equilibration of water quality parameters was defined as 3 successive readings within ±10% for DO and turbidity, ±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. Filtered and unfiltered samples were taken for metals and cation analysis and acidified to pH <2 with ultra-pure concentrated HNO_3. Filtered samples were filtered with 0.45 μm 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).

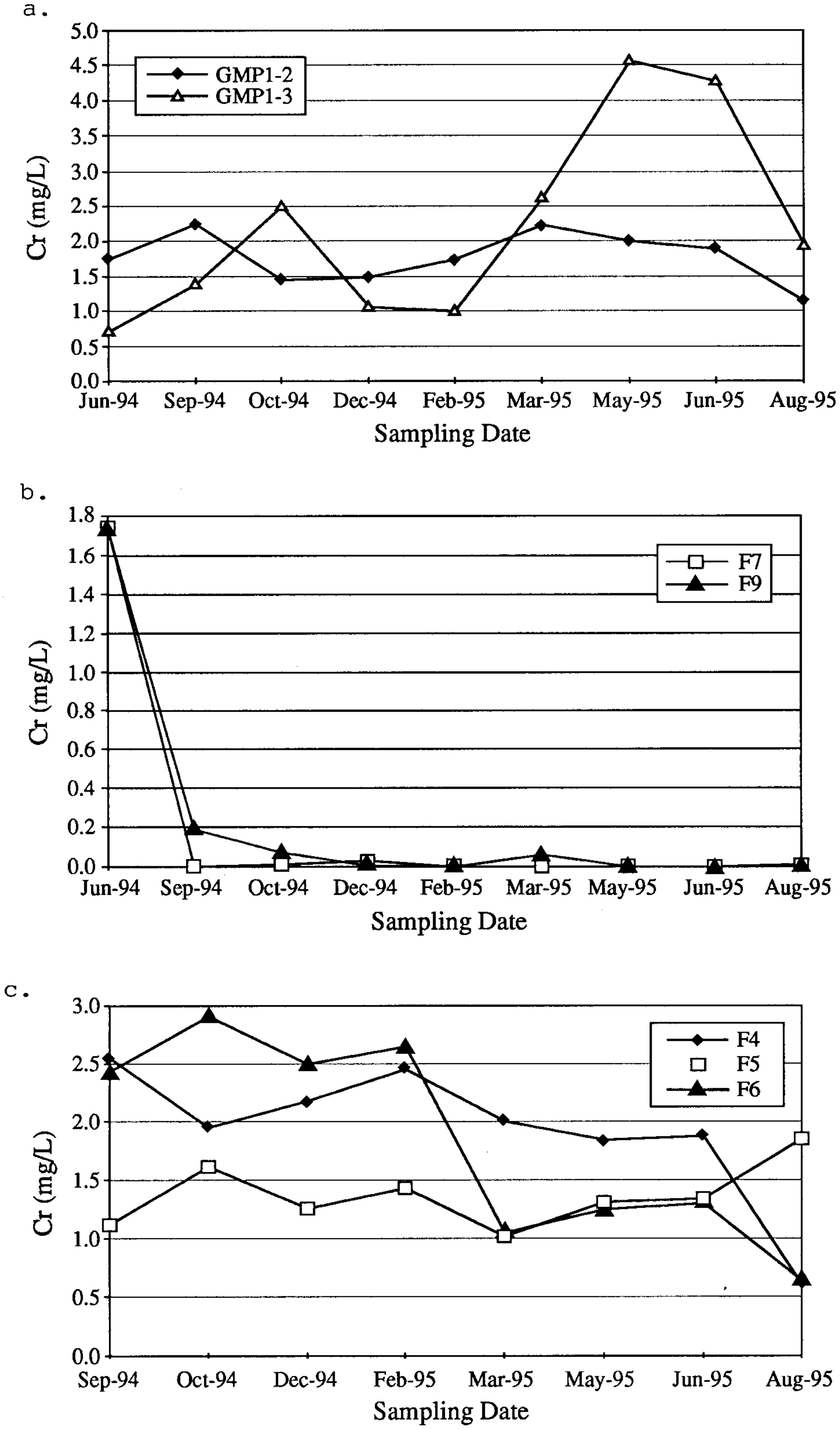

Fig. 4. (a) Chromium concentration over time in two of the upgradient wells (GMP 1-2,!-3) immediately in front of the Fe "fence" area. (b) Chromium concentration over time in two of the wells (F7, F9) immediately downgradient of Fe cylinders within the Fe "fence" area. (c) Chromium concentration over time in two of the wells (F4, F6) located in "gaps" within the Fe "fence" area.

3.3. Contaminant distribution in aquifer

The extent of Cr contamination at the site is shown in plan view in Fig. 1. Fig. 3 shows a cross-sectional distribution for dissolved chromate in the groundwater along a transect running from south (near the plating shop) to north (the river). The RX core transect locations 1 thru 6 are identified in Fig. 1. The chromate plume is narrowly distributed between 4.7 to 6.2 m below ground surface. The cross-section was constructed with over 30 discrete data points collected using a Geoprobe® to collect both aqueous samples and core samples. Site-wide mapping of contaminant distributions in 3 dimensions was accomplished with cone penetrometer, Geoprobe®, Hydropunch®, and traditional monitoring wells resulting in more than 300 discrete sampling points. These data were collected over a period of more than 3 a. While some variation in chromate concentrations in groundwater were observed over this time, very little change was observed in the position of the plume within the aquifer.

Hydraulic conductivity data was estimated "in situ" using pore dissipation techniques with a Hydrocone water sampler and the cone penetrometer at these same RX core locations. This device is able to track the filling rate of the water sampler which is hydraulically pushed to the desired depth to estimate the sediment's horizontal permeability at that location. These measurements were made over 30 cm vertical intervals and results were comparable to those obtained in earlier site characterization testing using constant head permeameter tests and slug tests (Sabatini et al., 1997). These tests confirm the existence of a layer of high permeability which persists from about 4.7 to 6.2 m below ground surface which coincides with the occurrence of chromate in the groundwater. Ground-water flow velocities were approximately 0.1 m/day in this zone.

3.4. Soil coring and surface analytical techniques

The test area was cored using 2.5- and 5-cm i.d. core barrels, 5, 8 and 20 months following installation, to examine the Fe and aquifer sediment surfaces. Cores were obtained with a Geoprobe® where the core barrels were pushed to the desired vertical location to minimize disturbance to the test area. Sediment grain samples were also isolated from water pumped from selected monitoring wells downgradient of Fe cylinders. Electron microprobe (JEOL 733) and scanning electron microscopy with energy dispersive X-ray (Hitachi S-570) were used for surface analyses of sediment samples.

4. Results and discussion

Chromium entering the "fence" area was slightly variable over time, particularly with respect to the vertical location of highest concentrations. This is illustrated in Fig. 4a for the GMP1-2 and 1-3 wells. Initially the highest Cr concentration was in the middle well (GMP1-2), but then in October, the lower well (GMP1-3) had the highest concentration. This reversed again in December and February. From March, 1995, the lower well has consistently had the highest Cr concentration. Sampling of the GMP1 wells together with other upgradient wells and temporary sampling points indicated that the influent Cr concentration into the "fence" area from 4.8 to 5.7 m below ground surface during the pilot test ranged from 1.5 to 3.0 mg/L.

4.1. "Fence" performance

Fig. 4b shows the changes in Cr concentrations for wells F7 and F9, located immediately behind Fe cylinders. The data for these wells is contrasted with the influent Cr concentration range shown in Fig. 4a. For wells F7 and F9, Cr concentrations decreased to less than 0.01 mg/L by May 1995.

Fig. 4c shows the results for wells located in "gaps" where water did not contact the Fe cylinders. Wells F4 and F6 shows no evidence of treatment. Well F6 is located in a "gap" similar to F4. Its response was similar to F4. Results for the other wells were similar. Wells F3, F11, F12, and FFe (monitoring well installed within an Fe cylinder) are similar to results for F7 and F9. Wells F8 and F10 showed no reduction in influent chromate concentration similar to F4, F5 and F6. Wells F1, F2, and GMP4 showed some level of treatment effectiveness or reduction in chromate concentration over time. For well F2, Cr concentration decreased initially to less than 0.05 mg/L and subsequently to less than 0.01 mg/L, but then increased to 0.4 mg/L in May 1995. Well F2 is located on the edge of the treated area and the cylinder in front of F2 was created differently than the others. This cylinder had only 10% by volume Fe as opposed to 50% for all the other installed cylinders. This lower amount of Fe was apparently insufficient to maintain remedial effectiveness. Also, being on the edge of the test area, there is more likelihood of untreated water mixing near this well due to variations in groundwater flow direction caused by wind tides on the Pasquotank River. Shifts in flow directions of a few degrees to the NW and NE have been observed depending on wind direction and speed (Sabatini et al., 1997).

4.2. Geochemical indicator parameters

Changes in geochemistry over this same time period

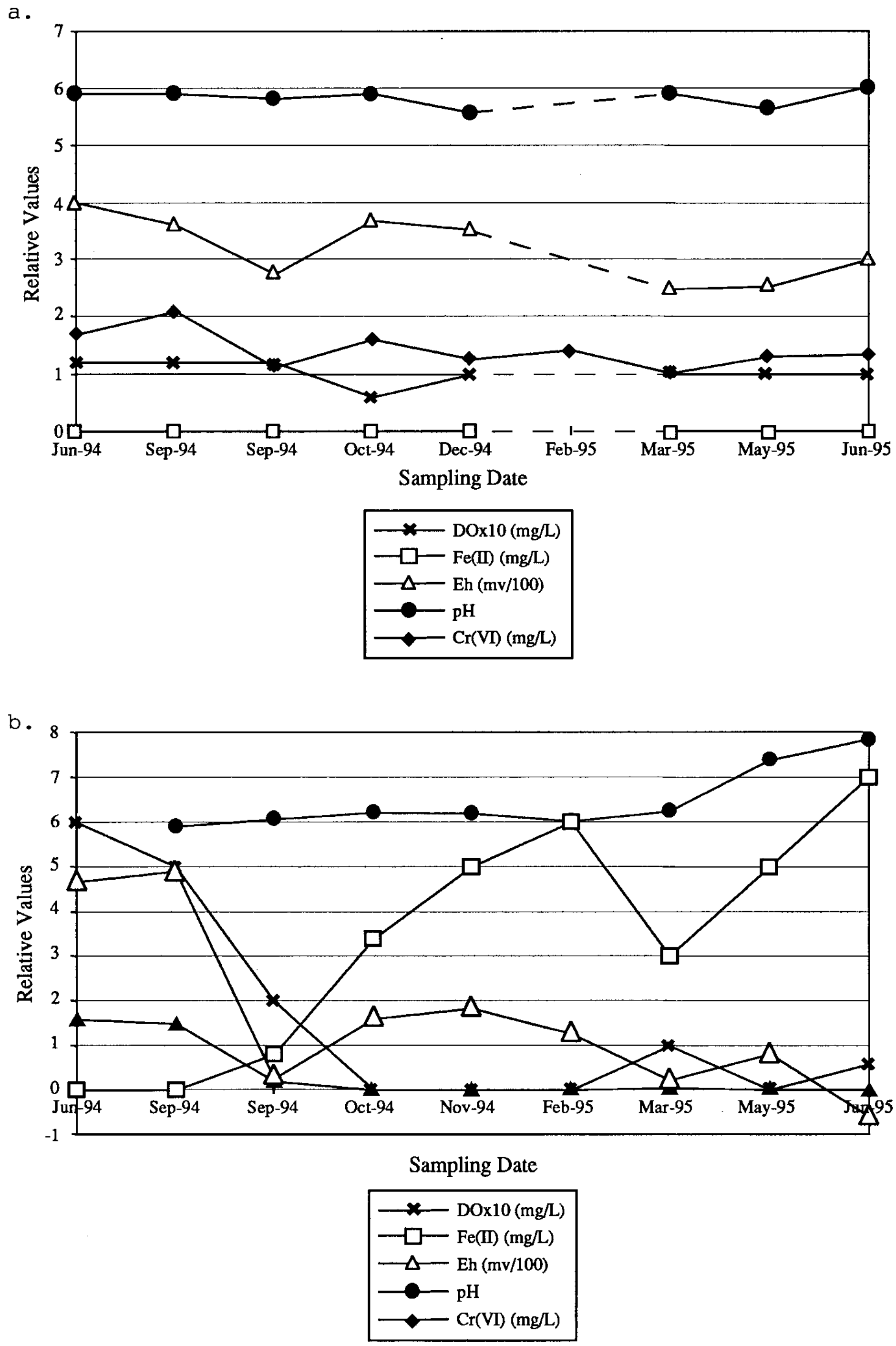

Fig. 5. (a) Variation in geochemical parameters over time in well F5 located in a "gap" within the Fe "fence" area. (b) Variation in geochemical parameters over time in well F9 located immediately downgradient of an Fe cylinder within the Fe "fence" area.

were also periodically monitored. With the disappearance of chromate there is a concomitant appearance of Fe(II), a decrease in Eh, a decrease in dissolved O_2, and increase in pH. These geochemical changes are identical to prior laboratory observations by Powell et al., (1995) and are consistent with the following

Table 3
Geochemical monitoring results for iron "fence" area

	Untreated zones	Treated zones
	GMP1, F4, F5, F6, F8, F10	F3, F7, F9, F11, F12, FFe
Cr(VI)	1–3 mg/L	< 0.01 mg/L
Fe(II)	0	2–20 mg/L
Eh	+200–400 mV	−100 to +200 mV
pH	5.6–6.1	7.5–9.9
DO	0.6–2.0 mg/L	0–0.1 mg/L
Sulfides	0	0–1.4 mg/L
SO_4	40–110 mg/L	7–65 mg/L
Alkalinity	35–80 mg/L*	45–120 mg/L

* As $CaCO_3$.

reactions:

1. $Fe^o + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$
2. $Fe^{2+} + CrO_4^{2-} + 4H_2O\ (Fe_x,Cr_{1-x})(OH)_3 + 5OH^-$

Little difference in geochemical parameters was observed between the upgradient reference wells and the "gap" wells (F4,F5,F6). This is illustrated in Fig. 5a for well F5 where very little variation in geochemical parameters were observed over a period of one year.

A significant difference in redox environment is reflected in the data for the various wells within the test zone (Fig. 2; Table 3). Variation in effectiveness of contaminant removal from the aqueous phase appears to be directly correlated with changes in geochemistry and position of monitoring points relative to the Fe cylinders. Wells located within or immediately downgradient of the Fe cylinders (e.g. FFe, F7, F9) show reduction of chromate to below detection limits as indicated in Fig. 5b for well F9. In these treated zones, Fe(II) is present in excess of 2 mg/L, Eh is reduced to below 200 mv, pH increased to more than 7.5, dissolved O_2 is consumed, dissolved H_2 was greater than 0.01% and total sulfides in water ranged from 0 to 1.4 mg/L. Alkalinity was variable within the fence area, however slight increases were noted where sulfides were detected. In most anaerobic subsurface systems, dissolved sulfide is produced by bacterial reduction of SO_4. The general reaction involves the oxidation of organic matter (as CH_2O):

1. $2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$

The most sensitive geochemical indicators for corrosion-promoted reduction of chromate observed were dissolved O_2 (decreased to <0.1 mg/L) and Fe(II) production (to >2 mg/L). Eh measurements also reflected the existence of treated (complete Cr removal from the aqueous phase), non-treated (no Cr removal) and partial treatment zones. System pH changes lagged considerably due to the aquifer sediment buffering capacity. This was observed in earlier laboratory experiments where pH was monitored in the presence and absence of aquifer sediment with Fe (Powell et al., 1995; Powell and Puls, 1997).

4.3. Mineral formation/identification

Potential likely mineral phases formed under site conditions include siderite; ferrous sulfides; and various Fe oxides, hydroxides, and oxyhydroxides (Blowes et al., 1997; Pratt et al., 1997; Powell et al., 1998). Siderite was not detected anywhere within the test plot. Ferrous sulfides have been detected primarily as coatings on mineral surfaces in wells F3, F7 and F9 and on recovered cores from these same locations. In these same wells increases in alkalinity have been observed suggesting microbial-mediated reduction of S. That these bacteria might thrive in these Fe-rich environments is not surprising. Chromium has been detected on AI&M surfaces using SEM-EDS analysis. Peak heights correspond roughly with the estimated mass of chromate which has moved through the reaction zones over the period of testing (20 months). No Cr has been detected on the MBS surfaces using these same techniques. These observations are consistent with laboratory reactivity tests for Cr using these two sources of Fe filings (Powell et al., 1995) that showed significantly less reactivity by the MBS Fe. While some Cr is likely on the MBS Fe surface, it is not detectable with EDS and significantly less accumulation on the surface has occurred over the 20-month period the Fe was in the subsurface. Fig. 6 shows an AI&M surface illustrating not only the Cr accumulation but also the buildup of a significant oxide layer on the metal surface. The formation of an Fe oxide or hydroxide cement on the Fe metal is evident in all cores recovered after 20 months following Fe emplacement. The formation of these cementatious coatings raises concerns about system longevity with regards to the main-

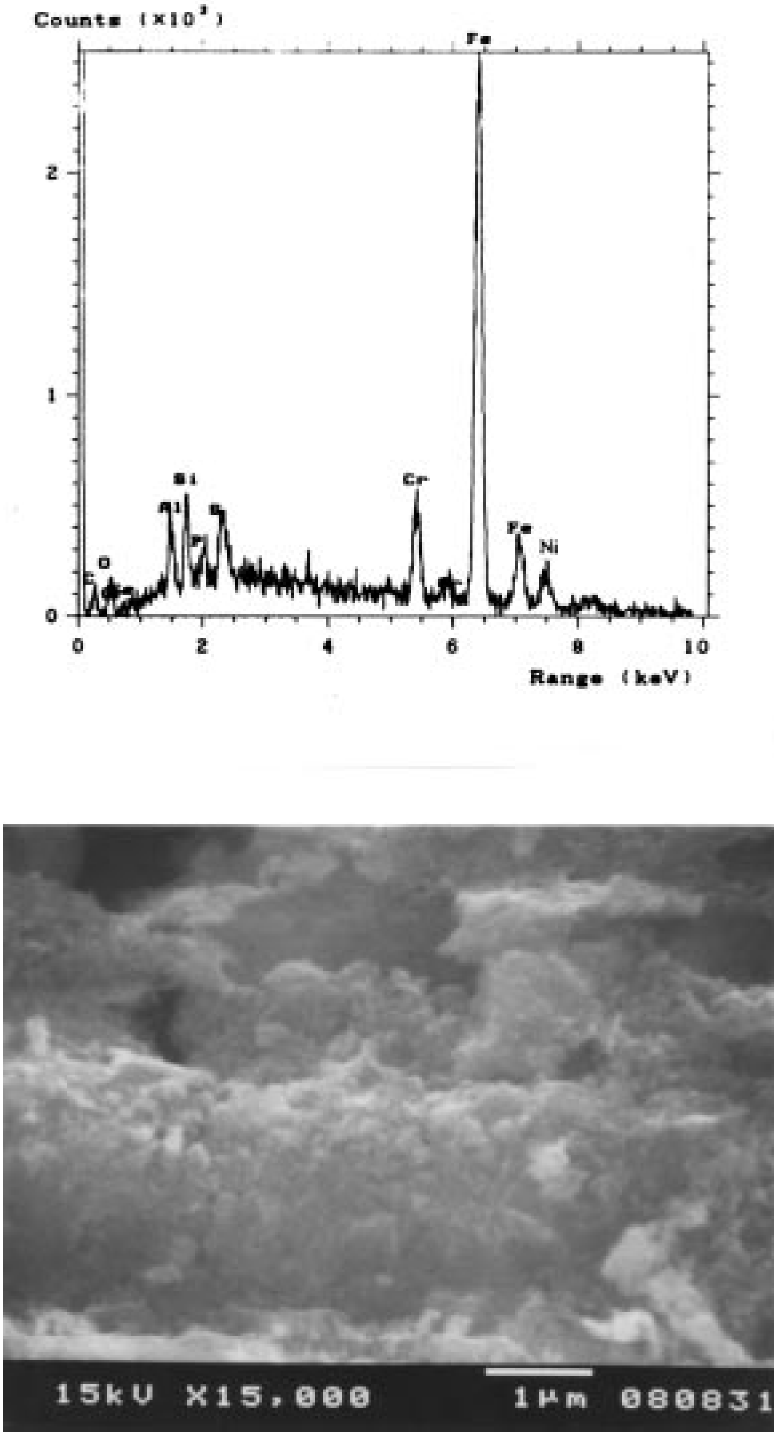

Fig. 6. AI&M Iron surface analyzed by SEM–EDS following subsurface emplacement and exposure to chromate plume for 20 months. Significant Cr has accumulated on the surface.

tenance of sufficient permeability within the Fe reaction zone.

5. Summary

Results indicate that complete treatment of Cr in the ground water at this site is possible using this technology. Chromium concentrations have been reduced to less than 0.01 mg/L, much less than drinking water limits. Significant reductions in TCE were also achieved, although the test was not designed to remediate the chlorinated organic compounds present at the site. The chromate is reduced to the nontoxic and insoluble chromic ion (Cr^{3+}) which presumably forms an insoluble mixed Cr–Fe hydroxide phase via corrosion of the elemental Fe. Untreated "gap" locations in the aquifer suggest that the reaction occurs at or near (surface hydroxide layer) the metal Fe surface which is consistent with laboratory results. Although significant amounts of Fe(II) are produced, the concentrations drop off quickly (<2 m) downgradient of the emplaced Fe. Likely solid phases formed as a result of the Fe corrosion would include metal sulfides, siderite and various Fe oxides, hydroxides and oxyhydroxides. Siderite formation has not been detected, however Fe sulfides have been observed in treated zones. Most Fe oxyhydroxides appear as coatings on mineral grains. Chromium is present in detectable quantities on the AI&M surfaces, but not the MBS Fe surfaces.

5.1. Disclaimer

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement may be inferred.

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