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ENVIRONMENTAL RESEARCH BRIEF

Innovative Measures for Subsurface Chromium Remediation: Source Zone, Concentrated Plume, and Dilute Plume

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Introduction

Many sites in the United States are contaminated with toxic metals such as lead, cadmium, and chromium. Under normal conditions, subsurface chromium contamination exists in two stable oxidation states: hexavalent, [Cr(VI)] and trivalent [Cr(III)]. Cr(VI) is both toxic and mutagenic; Cr(III) is of less health concern and, because of its lower water solubility, its aqueous concentrations are generally below water quality standards. In the subsurface, Cr(VI) generally exists in the anionic chromate (CrO_4^{2-}) or bichromate ($Cr_2O_7^{2-}$) forms which are relatively soluble and mobile. Thus, the risk associated with ground-water contamination is high and remediation of ground water contaminated with Cr(VI) is of critical importance. The conventional approach for remediating contaminated ground water sites has been water-based pump-and-treat. In recent years it has been recognized that this approach can require protracted periods of time to approach treatment goals (Keely, 1989; Palmer and Wittbrodt, 1991; Palmer and Fish, 1992).

The behavior of chromium in soils depends upon various factors, including: the form of chromium present, soil pH and mineralogical properties, and presence of organic matter. Several authors have studied the behavior of chromium in soils as a function of these factors (Bartlett and Kimble, 1976; Zachara et al., 1989; Ainsworth et al., 1989; Eary and Rai, 1991; Anderson et al., 1994). The presence of organic matter and Fe(II) is responsible for reduction of Cr(VI) to Cr(III) (Eary and Rai, 1991; Anderson et al., 1994). Addition of multivalent anions (e.g., phosphate and sulfate) was found to decrease chromate adsorption due to competition for the same adsorption sites (i.e., ion exchange -- Bartlett and Kimble, 1976; Zachara et al., 1989; Puls et al., 1994a). Tucker et al. (1992) showed the ability of a cationic polyelectrolyte to partially solubilize a solid $BaCrO_4$ phase. Puls et al. (1994a) showed the ability of an anionic surfactant, sodium dodecyl sulfate (SDS), to significantly enhance the elution of chromate in column studies.

Subsurface chromium contamination at the U.S. Coast Guard Support Center, near Elizabeth City, North Carolina, is the focus of this research. A brief description of the site is given here to provide a context for this research. For further details on the site, the interested reader should consult Puls et al. (1994a, b). A chrome plating shop was operated at the Coast Guard facility for more than thirty years. Activities in this shop resulted in the release of chromic acid into the soils below the shop. While some Cr(VI) was reduced to Cr(III) in the vadose zone soils, the reducing capacity of these soils was eventually overwhelmed and ground-water contamination resulted. Although the most concentrated portion of the dissolved plume is down gradient from the source zone, the plume has not yet separated from the source zone. This indicates that the remaining source zone soils continue to leach chromium into the ground water. The

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dilute portion of the plume has migrated down gradient towards an adjacent river.

As such, the contamination at this site can be divided into three regions: (1) the source zone soils, (2) the concentrated portion of the ground-water plume, and (3) the dilute portion of the ground-water plume. Applying conventional pump-and-treat methods to all three regions will be highly inefficient. Pump-and-treat remediation of the concentrated plume without regard for the other regions will also be inefficient, as the dilute portion of the plume will continue to migrate to the river and the source zone materials will continue to leach into the plume. Therefore, using an integrated approach to simultaneously address these three regions will be most effective. The technologies chosen for each of the three regions must be tailored to the unique characteristics of that region.

This environmental research brief reports on innovative measures for addressing each of these three regions. For the source zone, surfactant-enhanced chromium extraction is evaluated for expediting the removal of chromium from the source zone soils, thereby mitigating the continual feeding of the ground-water plume. For the concentrated plume, polyelectrolyte-enhanced ultrafiltration (PEUF) is evaluated as an innovative treatment process with desirable operating characteristics (less sludge production, higher quality final water, etc.). Relative to the dilute plume, the hydrogeological effectiveness of hydraulically passive, chemically reactive barrier systems is evaluated (i.e., *in situ* reduction of Cr(VI) to Cr(III)). It is proposed that the collective use of these three innovative technologies will significantly improve the remediation of subsurface chromium contamination. Research evaluating each of these technologies is the focus of subsequent sections.

Surfactant-Enhanced Chromium Extraction: Source Zone Soils

Background:

This section focuses on an innovative technology for expediting elution of chromium from the source zone soils. If the source zone soils are not addressed, the plume will continually be replenished and the efficacy of the plume treatment methods will be compromised. As mentioned above, introduction of multivalent anions and surfactants has been observed to enhance chromium elution from contaminated soils. This research further evaluates the use of surfactant systems to expedite chromium extraction from the source zone soils.

Surfactants (surface-active-agents) are amphiphilic molecules consisting of lipophilic and hydrophilic groups. This amphiphilic structure results in the surface active nature of surfactants and causes them to concentrate in interfacial regions. Above a specific concentration, surfactant molecules form dynamic aggregates or micelles. The concentration above which micelles form is known as the critical micelle concentration (CMC). Aqueous-phase micelles have a hydrophobic interior and a hydrophilic exterior, causing them to behave like dispersed oil drops. Solubilization is the phenomenon by which non-polar species partition into the organic interior of the micelles. Micelles and polar/ionic species interact mainly through hydrogen bonding and electrostatic forces (Shimamoto and Mima, 1979). Recently, surfactant-enhanced pump-and-treat remediation has been of great interest (Nash, 1987; Abdul and Gibson, 1991; Harwell, 1992; West, 1992; Edwards et al., 1992; Palmer et al., 1992; Fountain, 1992; West and Harwell, 1992; Rouse et al., 1993; Shiau et al., 1994; and Sabatini et al., 1995).

The main factor considered in evaluating surfactant systems for chromium remediation is the efficiency of chromate extraction (ratio of chromate removal by surfactant to chromate removal by water). It is hypothesized that surfactants can displace the adsorbed chromate by either ion exchange, precipitation-dissolution and/or counterion binding mechanisms, and that further enhancement in extraction may be achieved if surfactants with solubilized complexing agents are used. Laboratory batch and column studies were conducted to evaluate these hypotheses using contaminated soil from the U.S. Coast Guard site.

The surfactants used in this research along with some of their relevant properties are summarized in Table I. These surfactants were selected based on their type (anionic, zwitterionic, etc.), their susceptibility to losses (e.g., precipitation and sorption), their ease of regulatory acceptance (having USFDA direct food additive status), and experience with them in prior research (Rouse et al., 1993; Shiau et al., 1994). Chromium contaminated soil samples were obtained from the U.S. Coast Guard Support Center, Elizabeth City, North Carolina, at depths from 1.5 ft to 6.5 ft. The fraction organic carbon content in Elizabeth City soils varied from 0.0006 to 0.0027 (Puls et al., 1994a). Batch and column studies, as well as chemical analyses, were conducted according to standard procedures, as documented elsewhere (Nivas et al., 1996).

Batch Extraction Studies:

Batch studies were conducted using 3.0 g of soil and 15 ml of solution. Figure I compares the Cr(VI) extraction from Elizabeth City soil using deionized (D.I.) water and surfactants. The amount of Cr(VI) removed is observed to increase with anionic surfactant concentration. At concentrations greater than the CMC, Cr(VI) removal was relatively constant (see Figure I and Table II). Upon equilibration D.I. water solubilized 2.64 ppm of Cr(VI). The ratio of maximum Cr(VI) removal by surfactants to that of D.I. water ranged from 2.1 for Dowfax 8390 to 2.8 for Deriphat-160 (see Table II).

Anionic surfactants could enhance Cr(VI) extraction by ion exchange, precipitation-dissolution, and counterion binding. The experimental data are not consistent with counterion binding as the enhancement would begin and increase above the CMC. Surfactant precipitation-Cr(VI) dissolution also does not appear to be the mechanism since surfactants with high precipitation resistance are expected to be much less efficient (e.g., Dowfax 8390). However, the data are consistent with ion exchange as the primary extraction mechanism because the enhancement occurs below the CMC and is independent of the precipitation potential of the surfactant. Additional analysis of the sorption data further corroborates this conclusion (as presented in Nivas et al., 1996).

It was hypothesized that the extraction of chromate from the contaminated soil could be enhanced if a chromium complexing agent is solubilized into the surfactant micelles. Solubilization assays were conducted for sodium dodecyl sulfate (SDS) and aerosol OT (AOT) using diphenyl carbazide (DPC) as the solubilizate. In both cases the aqueous solubility of DPC increased with concentration beyond the CMC (maximum surfactant

Table I *Relevant Properties of Surfactants and Complexing Agent Used in this Study*

Surfactant	Type	Chemical Formula	Average Molecular Weight	CMC (mM)	Obtained from
SDS[a]	Anionic[b]	$C_{12}H_{25}OSO_3Na$	288.4	8.20[c]	Fisher Scientific
AOT[d]	Anionic[b]	$(C_9H_{17}O_2)_2CH_2CHSO_3Na$	444.6	1.124[e]	American Cyanamid Co.
Dowfax-8390	Anionic	$C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$	642	3.00[f]	Dow Chemical Co.
Deriphat-160	Zwitter ionic	$R\text{-}NH(CH_2COONa)_2$	373	--	Henkel Corp.
T-Maz 20	Non ionic[b]	$C_{12}H_{24}O_2H_3(CH_2CHO)_{20}O_2CH_2CHO_3$	1228	0.039[b]	PPG/Mazer
DPC[g]	--	$C_6H_5(NH)_2CO(NH)_2C_6H_5$	242	--	Fisher Scientific

[a] SDS - sodium dodecyl sulfate
[b] USFDA Direct Food Additive
[c] Mukerjee and Mysels, 1971
[d] AOT - aerosol OT
[e] Shiau, et al., 1994
[f] Obtained from Dow Chemical Company
[g] Complexing agent -- Diphenyl Carbazide

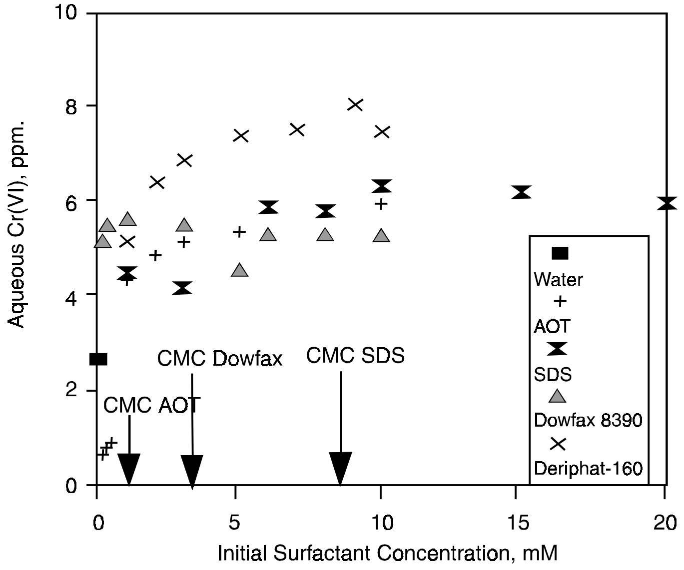

Figure I *Extraction of Cr(VI) by surfactants from Elizabeth City soil in batch systems.*

concentration evaluated was 20 mM). While the aqueous DPC concentration is 1.56 mM, at 20 mM surfactant concentrations SDS and AOT solubilized 8.67 mM and 5.33 mM of DPC, respectively.

Figure II shows the extraction of Cr(VI) using surfactant-solubilized DPC. Use of DPC in the batch studies required shifting to a solids based concentration (mg Cr / Kg soil). The results of these studies are summarized in Table III. Upon equilibration, water solubilized 11.3 mg of Cr/Kg of soil. The chromium removal increased with surfactant concentration, with maximum removal being evidenced above the CMC. The maximum ratio of chromium removal, with and without surfactants, ranges from 9.3 for SDS to 12.0 for Dowfax 8390 (see Table III); thus, the addition of a chromium complexing agent enhanced the extraction of Cr(VI) by an order of magnitude greater than that obtained with D.I. water. The ratio of surfactant concentration at which these removals were achieved to the CMC ranged from 2.5 for SDS to 8.3 for AOT. In all cases the surfactant-solubilized DPC outperformed the surfactant only results (see Table II). This demonstrates that the micellar-DPC extraction can further improve chromium removal relative to surfactant only systems. The results of these studies show an enhancement of 3.7 to 5.7 times over those of surfactants alone.

Table II *Results of Cr(VI) Extraction Studies by Surfactants and Hydrotropes from Elizabeth City Soil*

Extracting Agent	Extracting agent conc. at max. Cr(VI) removal, mM	Ratio to CMC	Max. Cr(VI) Conc., ppm	Ratio of Cr(VI) removal by extracting agent to that by water
D.I. water	--	--	2.6	1
AOT	3	2.7	5.2	2.0
SDS	10	1.2	6.4	2.5
Dowfax 8390	1	0.3	5.6	2.1
Deriphat-160	5	--	7.4	2.8

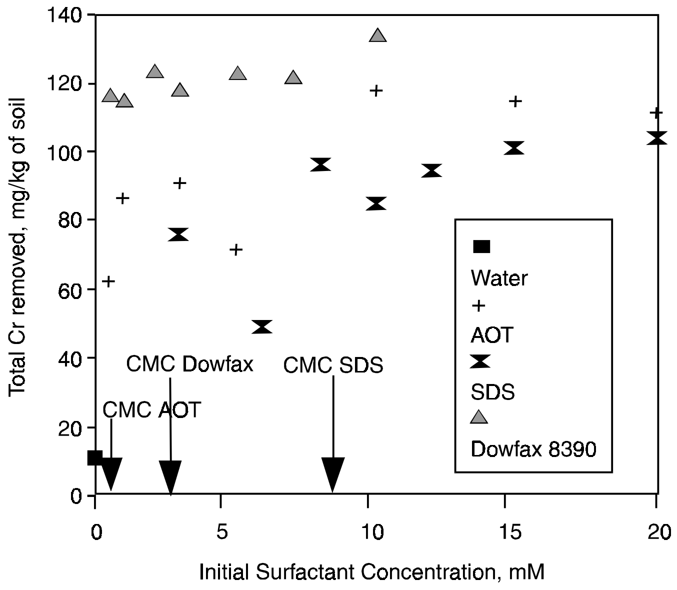

Figure II *Extraction of Cr(VI) by surfactants with DPC from Elizabeth City soil in batch systems.*

Column Extraction Studies:

Column studies were conducted in 2.5 cm diameter by 15 cm long glass chromatography columns; the average porosity and pore water velocities were 0.39 and 9.1 cm/h, respectively. Figure III shows the results of column studies evaluating Cr(VI) removal using water, 10 mM AOT and 10 mM Dowfax 8390. Deriphat-160 was not included in these experiments due to its extensive sorption in the batch studies. The results are presented as the Cr(VI) concentration versus the number of pore volumes of solution injected. Table IV summarizes the results from these column studies (for further details on column studies see Nivas et al., 1996). Dowfax 8390 showed maximum Cr(VI) removal followed by AOT and D.I. water. In all three cases the maximum Cr(VI) effluent concentration was obtained between 1.34 and 1.76 pore volumes.

The trends in the column results are similar to those observed for batch tests. For the column studies, when the Cr(VI) concentrations in the effluent went below 0.5 ppm, injection was stopped. After a week of no flow, the pumping of 10 mM Dowfax 8390 was continued in order to determine if the Cr(VI) removal mechanism was rate limited, as shown in Figure III. The effluent Cr(VI) concentration increased from 0.34 ppm to 3.34 ppm after the flow interruption. This demonstrates that the Cr(VI) removal mechanism may have been rate limited. Injection of 10 mM Dowfax 8390 to the originally water flushed column also increased the effluent Cr(VI) concentrations from 0.2 ppm to 2.38 ppm (see Figure III).

Figures IV and V show Cr(VI) removal using surfactant-solubilized DPC. The results of these studies are also summarized in Table IV. The maximum Cr(VI) removal in the effluent is higher than that observed with surfactants alone (10.3 ppm and 19.7 ppm for AOT-DPC and Dowfax 8390-DPC columns, respectively). This is about 1.7 to 1.9 times greater than that obtained in columns flushed by AOT and Dowfax 8390 alone. In batch systems, addition of DPC enhanced the extraction by 3.7 to 5.7 times over that of surfactants alone. Thus, the removal efficiency enhancement in column studies is less than that observed in the batch systems. The number of pore volumes required to reach maximum Cr(VI) removal concentrations was longer than anticipated as evidenced in Figure V (11.22 and 12.06 pore volumes for AOT and Dowfax 8390 with DPC, respectively, versus 1.54 and 1.76, respectively, for surfactants alone). The slope of the percentage removed relative to water alone curves is very low until about 10 pore volumes. The lack of peaks at 1.54 to 1.76 pore volumes, which were observed in surfactant only - no DPC columns, indicates that monomer/Cr(VI) ion exchange is not occurring.

It is postulated that two competing mechanisms are taking place in the surfactant-DPC systems. First, DPC exits the micelles and forms a Cr(VI)-DPC complex with the solids-associated chromate (this process is apparently rapid enough to prevent monomer-Cr(VI) ion exchange). Second, the extraction of the Cr(VI)-DPC complex into the micellar core occurs, due to complexation with the micellar-phase DPC. It appears that prior to 10 pore volumes the former mechanism dominates; hence, there is no rapid increase in the removal of Cr(VI) in the early stages of injection. During this phase the formation of Cr(VI)-DPC complex was clearly seen by the pink coloration of the medium (the pink color being indicative of the Cr-DPC complex). Once the solids-associated chromium has been complexed, the extraction of chromate anions and solubilization of Cr-DPC complex takes place. This is indicated by the increase in the slope of both curves after 10 pore volumes in Figure V. However, at about 12 pore volumes the removal efficiency of both the systems again starts to decrease, possibly due to the diminishing solubilization potential of micelles already saturated with DPC. At this point injection of pure micellar solutions of surfactants would be expected to enhance the solubilization of the solid associated Cr(VI)-DPC complex.

At about 14 pore volumes the AOT-DPC column was switched to flushing with 20 mM AOT only (no DPC). This initially increased the Cr(VI) removal concentration in the effluent from

Table III *Results of Cr(VI) Batch Extraction Studies by Surfactants with Solubilized DPC from Elizabeth City Soil*

Extracting Agent	*Extracting agent conc. at max. Cr removal, mM*	*Ratio to CMC*	*Max. Aqueous Cr Conc., mg/Kg of soil*	*Ratio of Cr removal by extracting agent to that by water*
D.I. water	*--*		*11.3*	*1*
SDS	*20*	*2.5*	*106*	*9.3*
AOT	*10*	*8.3*	*119*	*10.4*
Dowfax 8390	*10*	*3.3*	*135*	*12.0*

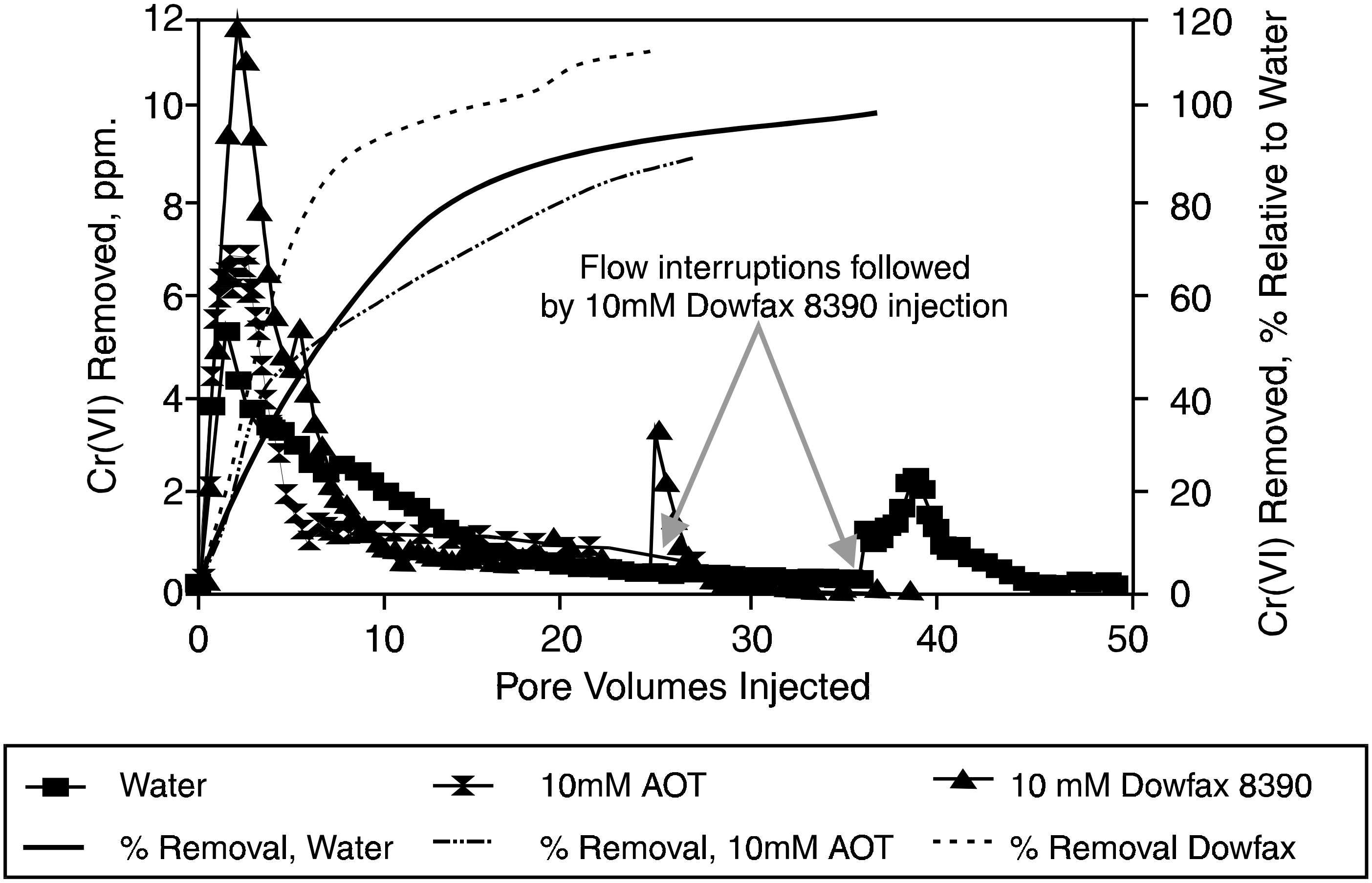

Figure III *Removal of Cr(VI) by D.I. water and surfactants in columns.*

0.86 ppm to 4.22 ppm (see Figure IV); however, the enhancement was only temporary. Subsequent introduction of Dowfax 8390 alone, at a concentration of 10 mM, again increased the Cr(VI) concentrations in the effluent (from 1.83 ppm to 7.11 ppm, as shown in Figure IV). The injection of 10 mM Dowfax 8390 was continued until 25 pore volumes, by which time around 175% of Cr(VI) was removed relative to D.I. water.

Similarly, the column flushed with solubilized DPC in 10 mM Dowfax 8390 was switched to surfactant only at about 16 pore volumes. This switch increased the Cr(VI) concentration in the effluent from 10.11 ppm to 15 ppm. The injection of 10 mM Dowfax 8390 was continued until Cr(VI) removal in the effluent was negligible. The total Cr(VI) removed was 213% relative to D.I. water in less than 20 pore volumes, as opposed to the surfactant only case which achieved only 125% after 25 pore volumes. An interesting point to note is that in this column run, the tailing of the concentration with time was not observed (see Figure IV). The lack of an elution tail is obviously advantageous for chemically-enhanced pump-and-treat processes.

It is suggested that the removal of Cr(VI) from the soil can be further enhanced by optimizing the time of switching from injection of surfactant with DPC to surfactant alone and/or by increasing the surfactant concentration. The time of switching should be immediately after the complete formation of Cr-DPC complex of the solids-associated chromate. For example, at about 10 pore volumes the formation of Cr-DPC complex appeared to be

Table IV *Cr(VI) Extraction from Columns by Water, Surfactants Alone, and Surfactant- Solubilized DPC*

Extracting Agent	*Max. Cr(VI) removed in effluent, ppm*	*Ratio of Cr(VI) removed by extracting agent to that by D.I. water*	*Total Pore volumes flushed*
D.I. Water	*5.3*	*1*	*35.9*
AOT	*7.0*	*1.3*	*26.5*
Dowfax 8390	*11.8*	*2.2*	*24.4*
AOT with DPC	*10.3*	*1.9*	*24.3*
Dowfax with DPC	*19.7*	*3.7*	*18.9*

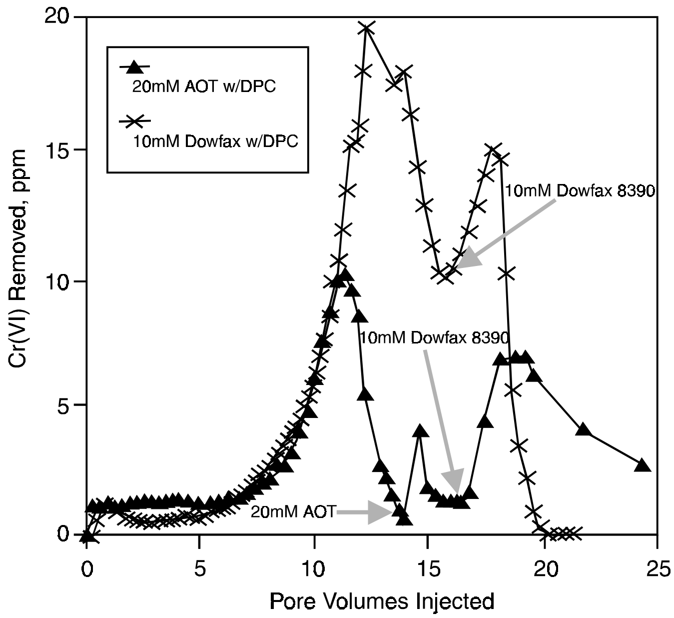

Figure IV *Removal of Cr(VI) by surfactants with DPC in columns.*

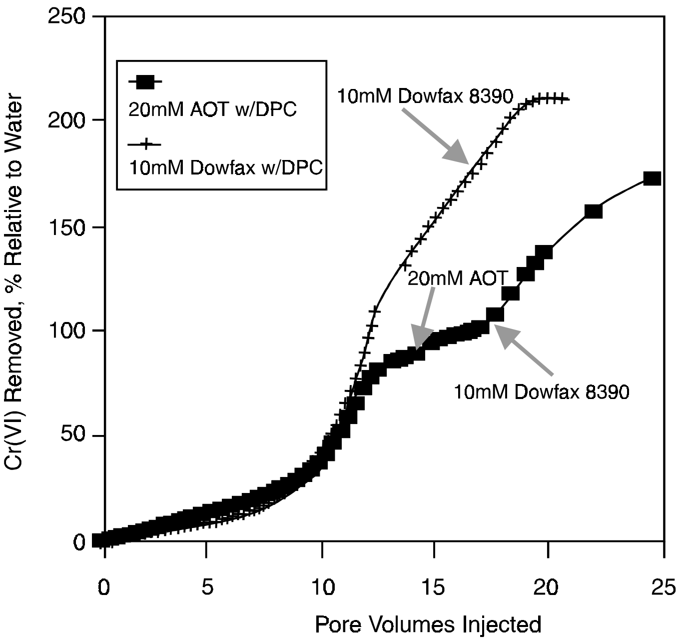

Figure V *Percentage removal of Cr(VI) by surfactants with DPC in columns.*

complete. Switching at this time to pure micellar solutions would have resulted in extraction of Cr(VI) in fewer pore volumes. By increasing the concentration of the surfactant-DPC mixture, the surface capacity for DPC could be satisfied in fewer pore volumes; higher surfactant concentrations for complex extraction would likewise expedite this process. It should be noted that the concentrations for the column runs were selected based on results from batch studies which indicated that extraction efficiency was leveling off at surfactant concentrations of 10-20 mM; this illustrates the importance of conducting column studies and not relying solely on batch results.

In summary, batch results demonstrate that surfactant systems have the potential to enhance chromium elution by a factor of 2 to 3 (surfactants alone) to an order of magnitude (surfactant-complexing agent systems versus water alone). While column studies corroborated results of batch tests, they also illuminated operational considerations that require additional research. Thus, while this technology shows great promise for enhancing chromium extraction from soils, further laboratory and field scale studies are necessary prior to full scale implementation.

Polyelectrolyte-Enhanced Ultrafiltration: Concentrated Plume

Background:

The research presented in this section focuses on an innovative treatment process for ground water extracted from the concentrated portion of a contaminant plume. This treatment process has improved operational characteristics relative to existing technologies and will thus further optimize the pump-and-treat methodology for the concentrated plume. The next section will discuss a passive approach for dealing with the dilute portion of the plume (where pump-and-treat would become less efficient).

For several years, a particular area of research at the University of Oklahoma has involved the combination of colloids (e.g., surfactant micelles and polyelectrolytes) with ultrafiltration membranes to remove contaminant materials from aqueous streams (Christian et al., 1988; Sasaki et al., 1989; Christian et al., 1990; Christian et al., 1992; Tucker et al., 1992; Krehbiel et al., 1992). These colloid-enhanced ultrafiltration (UF) techniques have the potential to be used in low-energy, efficient, and selective processes for removal of target ions or molecules. One focal point has been the development of an efficient process for removal of toxic metals and metalloids in anionic form (e.g., chromate, arsenate and selenate) from aqueous streams or ground water. In addition to removal of these ions to potable water levels, the ultrafiltration method does not, unlike many current techniques, further degrade the overall water quality in the process of removing one or more toxic components. A specific goal has been to selectively remove the toxic ion in the form of a compact solid waste and produce effluent water with essentially the same ionic strength as that which enters the process.

In contrast with reverse osmosis, ultrafiltration is not generally a direct method for removal of ions from aqueous streams. The pore size of UF membranes is characterized by a molecular weight cutoff (MWCO) value which is a rough estimate of the size of molecules which are retained by the membrane. For instance, a MWCO of 5000 Daltons indicates that a molecule with a molecular weight larger than 5000 will be largely retained by the membrane. In a hypothetical example, inorganic ions such as chloride, sodium, and chromate in aqueous solution are much smaller than this and will freely pass through the UF membrane. However, if a soluble polymer of molecular weight greater than the MWCO is added to the stream to be filtered and, if the polymer binds chromate, then both the polymer and the chromate will be retained by the membrane. Figures VI and VII present qualitatively a polyelectrolyte/chromate mixture and subsequent binding of

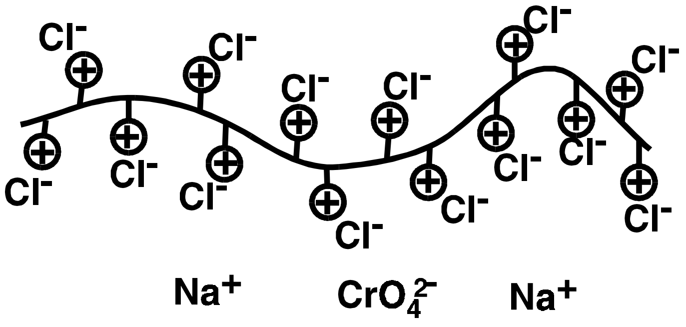

Figure VI *Homogeneous aqueous mixture of polyelectolyte and chromate.*

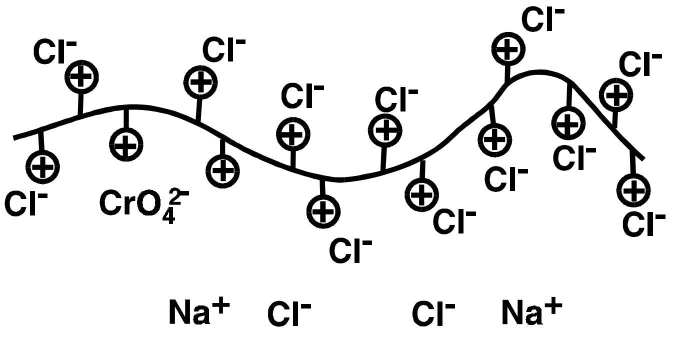

Figure VII *Chromate ion replaces chloride ion on the cationic polymer.*

the chromate ion to the polymer. The solution passing through the membrane (permeate) will be depleted in chromate while the solution retained by the membrane (retentate) will be enriched in chromate (and polymer). The concentration of chloride and sodium ions will be essentially the same on both sides of the membrane since these ions are not bound to the polymer.

Conventional removal of chromate is commonly done through lowering aqueous pH by addition of acid, adding a reducing agent such as sodium sulfite, and finally, adding lime or other base to raise the solution pH and precipitate the reduced chromium as the Cr(III) hydroxide. The chromate reduction process uses a substantial quantity of acid, base and reducing agent with the result that the effluent water from this conventional process has increased ionic strength due to salt loading (Kosarek, 1981). For example, the product water from one recently implemented chromate reduction process has a sulfate ion concentration of 1700 ppm. This may be compared with an input level of only 34 ppm sulfate in the feed ground water (Buehler, 1993). Further use or disposition of the product water containing such high sulfate ion concentrations might be restricted. Additionally, a large sludge volume is produced from the reduction process because other metal hydroxide compounds precipitate along with the chromium hydroxide. Chromium is a minor component in this precipitate due to both indiscriminate hydroxide precipitation and the fact that the hydrous oxides thus produced have a very low solids content, typically on the order of 10%-20%.

The polyelectrolyte-enhanced ultrafiltration (PEUF) process for chromate (CrO_4^{2-}) removal involves addition of a cationic polyelectrolyte [poly(dimethyldiallylammonium chloride)] to a feed stream containing Cr(VI); the solution is then filtered with a UF membrane cartridge, so that the chromate-polymer mixture will be retained in a small volume (the retentate), while a large fraction of the feed solution is produced as highly purified water. Either chromate or bichromate {$HCrO_4^-$} will bind to the polyelectrolyte. Model calculations show that at pH 6.5 there is essentially a 50:50 mixture of the chromate and bichromate anions in aqueous solution (with a trace amount of dichromate anion). At pH 7.0, ca. 76% of the total chromium exists as the chromate anion. As long as the solution pH is above 6.0, a significant fraction of the Cr(VI) in solution will exist as a divalent anion and will replace monovalent chloride counterions on the polymer. Other anions in ground water such as sulfate and phosphate will also bind to the polymer but sulfate is expected to be the main competing ion in the pH range 6-8 due to mineral solubility considerations.

The binding of chromate with polymer creates membrane selectivity since the polymer-chromate complex is too large to pass through pores in the membrane. Ions which are not bound to the polymer pass freely through the membrane. Due to the membrane transparency for unbound ions there is no salt or brine retention by the membrane and the process can be carried out at low applied pressures (10-100 psi). Figure VIII depicts the membrane separation.

Permeate water from the membrane is of lower ionic strength than the feed water and is substantially reduced in chromate concentration. In laboratory experiments PEUF has been used to remove 99.9% of chromate from feed water containing as much as 5 ppm Cr(VI). The retentate solution from the membrane is a concentrated solution of polymer and chromate (and sulfate, if present). This mixture is treated to separate the polyelectrolyte for reuse in the process. Although several mechanisms might be used for polymer-chromate separation in the retentate liquid, one method is the addition of barium chloride at less than stoichiometric ratios to precipitate sulfate and chromate as a compact solid waste.

Field Test:

A small scale field test of the PEUF process for the removal of chromate from ground water at the U. S. Coast Guard Support Base in Elizabeth City, North Carolina, was conducted in March 1993. Figure IX gives a schematic of the overall process which was employed. The field test consisted of a complete process implementation to remove Cr(VI). The ground water from three different monitoring wells contained Cr(VI) levels of 2.1 to 3.8 ppm, as well as several hundred ppm of dissolved solids including ca.

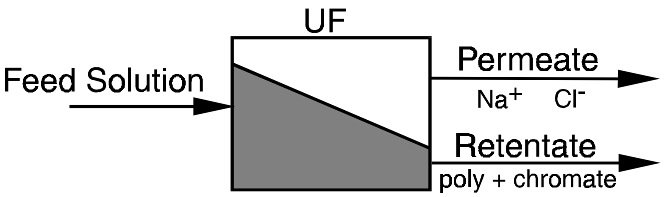

Figure VIII *Ultrafiltration of the aqueous mixture.*

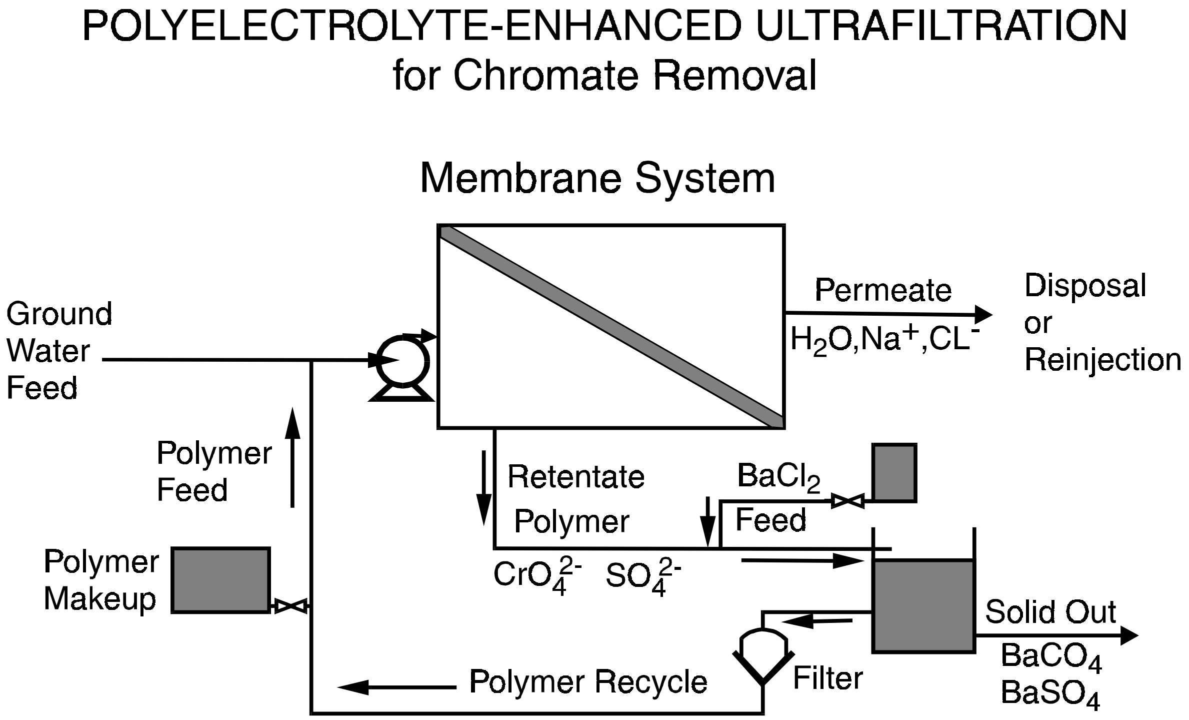

Figure IX *Qualitative schematic of Elizabeth City UF test apparatus.*

90 ppm sulfate, as shown below. The feed water pH was above 6.0 and no pH modification was used in this test. The Cr(VI) and sulfate concentrations detected in several wells were as follows: Well #2, 3.1 ppm, 85 ppm; Well #12, 1.5 ppm, 82 ppm; Well #13, 3.8 ppm, 86 ppm.

The single stage pilot UF apparatus was capable of producing 150 gal/day of purified water. The pilot test was conducted over a five day period. The maximum operating time per day was 12 hours and the longest continuous period of operation was 8 hours. An initial charge of 7 gal. of polymer concentrate was used and this was not augmented during the test period. The UF system was operated at an applied pressure of 50 psig with a feed water recovery (as permeate) fraction of 0.75 to 0.80. Ground water was pumped from a monitoring well at a nominal rate of 450 mL/min, mixed with polyelectrolyte solution (150 mL/min), and then ultrafiltered to produce a permeate (purified water) and a retentate solution containing polymer, chromate, and sulfate ions.

The retentate solution was treated by addition of a small quantity (less than stoichiometric) of barium chloride to precipitate barium sulfate and barium chromate and to partially regenerate the polymer. The renewed polymer was then filtered and recycled to mix with fresh ground water. A very limited quantity of solid precipitate was produced in this test. It was not possible to accurately measure the total barium chromate and barium sulfate solids because these collected in both the polymer retentate tank and on the cartridge filters used in the test. An estimate of the maximum quantity of precipitate which could be produced can easily be made. If it is assumed that the well water contains sulfate at 90 ppm and chromate at 3 ppm (as hexavalent chromium) then complete removal of both these ions as the barium salt would produce 0.83 grams of $BaSO_4$ and 0.055 grams of $BaCrO_4$ for each gallon of ground water treated.

The polyelectrolyte-enhanced ultrafiltration process performed flawlessly during the several day test period. Some permeate analyses for Cr(VI) were done on site by ion chromatography with UV detection of the diphenylcarbazide complex. Ion chromatography analyses were also conducted for sulfate. Chromate levels in the permeate over a several day period were at virtually the detection limit of the ion chromatography apparatus [<50 ppb as Cr(VI)]. Sulfate levels were in the range of 1 to 5 ppm in the permeate. Additional on-site colorimetric analysis with diphenylcarbazide, and analysis of permeate samples brought back to the laboratory, indicated a possible range of Cr(VI) concentration of 30 to 70 ppb, as measured in various UF permeate samples over the course of the test.

The PEUF process has several advantages in ground-water treatment for chromate removal. The purified water produced by the PEUF process has an ionic strength similar to or less than the original ground water. In the Elizabeth City test a few ppm of Cr(VI) and ca. 80 ppm of sulfate were removed from the ground water and replaced with chloride ion. The product water was substantially reduced in ionic strength relative to the feed ground water. This may be contrasted with the great increase in ionic strength of product water (relative to feed water) from the conventional reduction-precipitation treatment for Cr(VI) removal.

Thus, the PEUF product water is suitable for reuse, or reinjection to aid in the remediation process, or direct disposal. The chromate waste is concentrated into a small volume which makes possible either further treatment or easy recovery of Cr(VI). The PEUF process is continuous and does not use large volumes of acid or base for pH modification in contrast with conventional reduction treatment. The polyelectrolyte can be reused many times in the process. Additional direct applications of the PEUF process are found in the removal of arsenic and selenium from aqueous streams. Toxic anion removal from aqueous streams by the PEUF process is the subject of a patent issued to the University of Oklahoma (U.S. #5,302,290).

Hydraulically-Passive Redox Barriers: Dilute Plume

Background:

A variety of field, laboratory and modeling studies were conducted to evaluate the viability of using hydraulically-passive, chemically-reactive barriers for remediation of the dilute subsurface chromium contaminant plume at Elizabeth City. Ideally, these barrier systems would operate by installing the reactive barrier in the path of migration of the contaminant plume. The plume would move through the reactive barrier due to the existing regional gradient; hence, the barrier would be hydraulically passive. Material in the reactive barrier would cause an *in situ* reaction that results in immobilization of the dissolved chromium.

Various *in situ* reactions or contaminant removal mechanisms have been proposed for reactive barriers. Starr and Cherry (1994) discuss five groups of *in situ* reactors based on contaminant removal mechanisms (e.g., sorption, precipitation), chemical delivery (e.g., dissolution of reactants, nutrients), or physical process (e.g., air sparging) proposed for the reactive material or reactive portion of the barrier. The focus of their study was on the hydraulic efficiency of a dual barrier (funnel-and-gate) system that uses low permeability sections (funnels) to direct contaminated water through higher permeability materials (gates) in which reactions would effect contaminant removal.

A *redox* barrier has been proposed for the dilute chromium plume at Elizabeth City, North Carolina (Powell et al., 1995; Puls et al., 1995). The reactive material in the redox barrier would be native aquifer material amended with iron filings. The proposed redox reaction would involve reduction of Cr(VI) to Cr(III) and oxidation of ferrous (Fe^{+2}) iron to ferric (Fe^{+3}) iron. The reacted species would then precipitate as insoluble hydroxides (Powell et al., 1995). This research focuses on the hydrogeological considerations of implementing such barriers.

Field Studies:

A series of site characterization activities were completed at the Elizabeth City site. These activities focused on quantifying hydraulic characteristics of the shallow ground-water formation. Hydraulic conductivity values for the various monitoring wells were developed from slug tests (Bouwer, 1978). Variations in the regional gradient were assessed from synoptic water level observations of the monitoring well network. Finally, the potential impacts on the regional gradient of the river (e.g., wind waves, tidal fluctuations) immediately adjacent to the field site were assessed through continuous water level recorders installed in selected monitoring wells. Ongoing drilling operations provided aquifer material for subsequent laboratory studies. Analyses from periodic sampling episodes were used to generate estimates of total mass and migration of the center of mass of the dilute chromium plume.

In general, the monitoring wells at the Elizabeth City site (Figure X) are completed at two different depths (15 ft or 20 ft) within the shallow aquifer. The shallow wells are screened over the bottom 5 feet; the deeper wells are screened over the bottom 10 feet. Hydraulic conductivity values derived from the slug tests (Table V) show the aquifer to be a fairly uniform, highly conductive, sandy material. However, there does appear to be a slightly lower permeability lens running east-west (parallel to the river) about 60 to 80 feet out from the source zone. The regional gradient (Figure XI) is slightly southeast to northwest and does not deviate seasonally more than a few degrees.

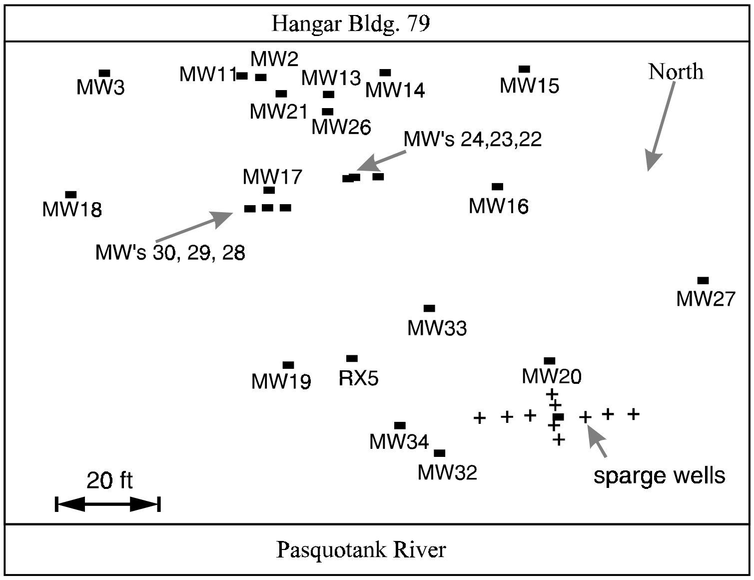

Figure X *Monitoring well locations at Elizabeth City.*

Table V *Hydraulic Conductivity Values from Slug Tests on Selected Monitoring Wells (Calculated Based on Both Partially and Fully Penetrating Assumptions)*

Well	*Casing Diameter (in)*	*Total Depth (ft)*	*Elevation Top of Casing (ft)*	*Screened Interval below T.O.C. (ft)*	*Hydraulic Conductivity (ft/day)*	
					partially penetrating	*fully penetrating*
MW3	*2*	*15*	*107.16*	*92.16 ® 97.16*	*5.1*	*4.9*
MW11	*4*	*25*	*107.15*	*82.15 ® 87.15*	*15.9*	*15.2*
MW16	*2*	*15*	*106.74*	*91.74 ® 96.74*	*2.4*	*2.3*
MW16a					*2.6*	*2.5*
MW17	*2*	*15*	*106.74*	*91.74 ® 96.74*	*2.9*	*2.8*
MW18	*2*	*15*	*106.7*	*91.7 ® 96.7*	*1.3*	*1.2*
MW19	*2*	*15*	*105.86*	*90.86 ® 95.86*	*2.6*	*2.5*
MW20	*2*	*15*	*105.88*	*90.88 ® 95.88*	*8.2*	*8*
MW20b					*5.3*	*5.2*
MW22	*2*	*50*	*106.8*	*56.8 ® 66.8*	*4.7*	*4.3*
MW27	*2*	*20*	*106.29*	*86.29 ® 96.29*	*0.9*	*0.8*
MW27b					*0.3*	*0.3*
MW28	*2*	*20*	*106.45*	*86.45 ® 96.45*	*8.9*	*8.6*
MW28b					*8.8*	*8.6*
MW29	*2*	*20*	*106.73*	*86.73 ® 96.73*	*5.3*	*5.1*
MW29b					*5.4*	*5.3*
MW32	*2*	*15*	*106.4*	*91.4 ® 96.4*	*6.1*	*5.9*
MW32b					*2.5*	*2.4*

The observed movement of the contaminant plume is slower than would be predicted based on the measured hydraulic gradient and conductivity values and projected adsorption effects. It was hypothesized that weather-related or tidal effects in the adjacent river could have reversed the gradient of the shallow ground-water formation for extended periods in the past. The supposed gradient reversal was proposed as one factor contributing to the slow migration of the contaminant plume. A three-month period of continuous water level observations showed infrequent disturbances in the regional gradient. In addition, the magnitudes of these disturbances were small and readily attenuated by the highly conductive aquifer.

Laboratory Studies:

Laboratory studies were conducted to assess the hydraulic characteristics of aquifer materials amended with iron filings. Aquifer materials from four different depth ranges in the unsaturated zone were retrieved from RX5 (Table VI). Constant head column tests, using three different flow rates, were completed on the materials from each depth range. Hydraulic conductivity values reported are the geometric mean of the three measured values. The same tests were conducted on samples of aquifer materials amended with iron filings. The results of the hydraulic conductivity determinations showed no definite trend with respect to the addition of iron filings. Although more decreases than increases in hydraulic conductivity were observed for the iron amended samples, the magnitude of the changes between the different depth ranges far exceeds the variations due to the addition of iron filings.

Changes in hydraulic conductivity associated with redox barriers will result in conflicting effects. The hydraulic conductivity of the reactive barrier must be higher than the surrounding aquifer in order to induce flow of the contaminant plume through the reactive materials. However, increased hydraulic conductivity values will result in decreased residence times within the reactive

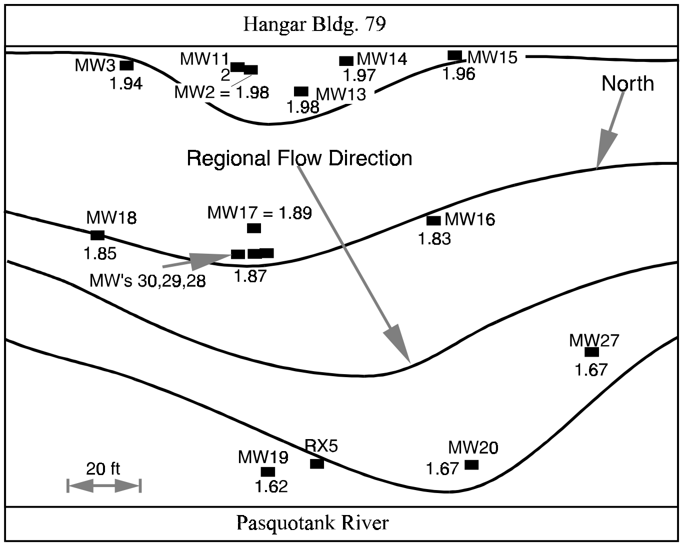

Figure XI *Regional gradient at Elizabeth City.*

Table VI *Laboratory Hydraulic Conductivity Values and Ratios of Aquifer Materials With and Without Iron Filings*

Source (depth)	*%Fe*	*K (ft/day)*	*K Ratio*
RX5 (10'-11')	*0*	*0.56*	*1.00*
	5	*0.15*	*0.27*
	20	*0.28*	*0.49*
RX5 (13'-14')	*0*	*0.71*	*1.00*
	20	*0.19*	*0.27*
RX5 (15'-16')	*0*	*73.6*	*1.00*
	5	*34.8*	*0.47*
RX5 (17'-18')	*0*	*6.36*	*1.00*
	20	*7.41*	*1.16*

barrier, which could reduce the effectiveness of the redox reaction. Moreover, to achieve the higher hydraulic conductivity values, a medium with large grain sizes would have to be added to the native materials. The larger grain sizes will have reduced specific surface areas which could also reduce the effectiveness of the redox reaction. However, Starr and Cherry (1994) note that changes in hydraulic conductivity of more than 1 order of magnitude above the native material result in relatively little increase in the amount of flow through a reactive barrier.

Breakthrough curves for chloride were developed for the aquifer materials with and without iron filings (Figure XII) at the 13 to 14 foot depth range. The iron amended materials appear to show less dispersion than the native materials.

Modeling Studies:

Estimates of total chromium mass in the subsurface and location of the center of mass were developed for four sampling episodes. The mass estimates (Table VII) and center of mass locations were developed using spatial moments and triangular elements (Freyberg, 1986; Knox, 1993). Refinements in the monitoring well network over time resulted in an increased number of wells. However, not all chromium sampling episodes included all available wells. If the spatial network includes the monitoring wells with low (background) levels of chromium that are located outside the actual dissolved chromium plume, the areal extent of the chromium plume appears to increase. Hence, total mass estimates of dissolved chromium are artificially inflated. The latter sampling episodes focused only on those monitoring wells that had previously shown elevated concentrations of dissolved chromium.

Spatial moment calculations show that the center of mass of the chromium plume has migrated out approximately 80 feet from the source area toward the river (Figure XIII). However, samples from monitoring wells near the river taken during the most recent sampling episode indicate that the chromium plume could be discharging into the river. Total mass of dissolved chromium in the plume is probably less than 15 kg (Table VII).

Numerical simulations of alternate barrier configurations were completed using the USGS Method of Characteristics (MOC) model and input data derived from the field and laboratory studies. All simulations utilized the configuration of the plume from the most recent sampling episode as initial conditions. Initial simulations showed that the permeable barrier had to be specified as having a transmissivity value 1000 times higher than the surrounding native materials in order to cause discernable changes in the flowlines of the formation. For each configuration, the solid contour lines indicate the impact of the barrier on the flow path and shape of the plume after eight years of transport. The solid contour lines indicate what portions of the plume would actually pass through the barrier. Those portions of the plume passing through the barrier are assumed to be totally reduced (other research evaluates Cr(VI) removal; Powell et al., 1995). Observation wells were placed on the periphery of the barriers to assess how much of the plume was captured.

Four basic barrier configurations (Figure XIV) were considered; the transverse barrier, the longitudinal barrier, the Y-shaped barrier, and the funnel-and-gate system. The funnel-and-gate system was similar to the Y-shaped barrier, but utilized impermeable funnels to direct flow through the permeable gate similar to the systems analyzed by Starr and Cherry (1994). Each barrier configuration occupied the same number of cells in the transport grid.

Figure XV depicts simulated chromium concentrations in peripheral observation wells over time for each of the four barrier configurations; hence, the figure depicts how much chromium is not removed by each configuration. In general, the transverse barrier performed best in terms of capturing the plume. Starr and Cherry (1994) also found that barriers were most effective when they were oriented predominantly orthogonal to the regional gradient. The Y-shaped barrier performed slightly better than the funnel-and-gate system. Given the increased complexity of construction of the funnel-and-gate systems, questions arise as to the viability of these systems. However, these simulations also showed that the hydraulic conductivity of the barrier must be much higher (two orders of magnitude) than the surrounding media in order to significantly alter the ground-water flow, regardless of the configuration. For the highly conductive formation at Elizabeth City, these results indicate the most viable alternative to be a transverse redox barrier wider than the contaminant plume be placed down gradient of the plume.

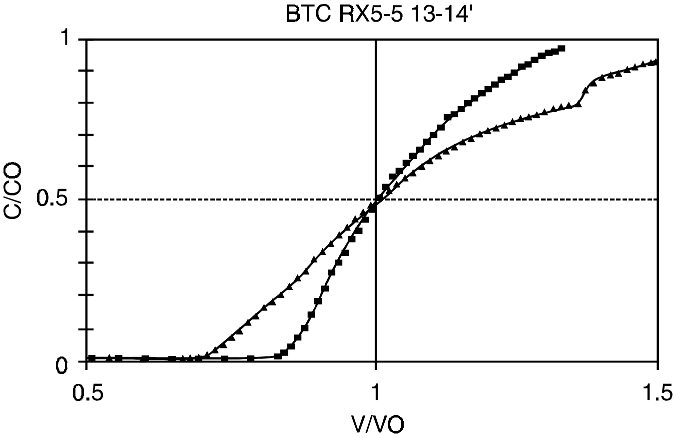

Figure XII *Breakthrough curves for aquifer materials with and without iron filings.*

Table VII *Mass Estimates of Dissolved Chromium*

Sampling Episode	*Total Mass (kg)*	*Monitoring Well Samples in Grid*
June 1991	*9.4*	*12*
April 1992	*8.0*	*10*
July 1992	*4.12*	*12*
March 1993	*4.63*	*7*
June 1993	*5.04*	*11*
September 1993	*14.3*	*8*

Summary / Recommendations

Advanced remediation efforts should consider innovative processes for each of three regions: (1) the source zone soils, (2) the concentrated portion of the contaminant plume, and (3) the dilute portion of the plume. This environmental research brief reports on innovative measures for addressing each of these three regions. For the source zone, surfactant-enhanced chromium extraction was evaluated for expediting the removal of chromium from the source zone soils, thereby mitigating the continual feeding of the ground-water plume. For the concentrated plume, polyelectrolyte-enhanced ultrafiltration (PEUF) was evaluated as an innovative treatment process with desirable operating characteristics (less sludge production, higher quality final water, etc.). Relative to the dilute plume, the hydrogeological effectiveness of hydraulically-passive, chemically-reactive barrier systems were evaluated (*in situ* reduction of Cr(VI) to Cr(III)).

Batch studies demonstrated that surfactant systems can enhance chromium elution by a factor of 2 to 3 (surfactants alone) to an order of magnitude (surfactant-complexing agent systems) versus water alone. While column studies corroborated results of batch tests, they also illuminated operational considerations that require additional research. Thus, while this technology shows great promise for enhancing chromium extraction from soils, further laboratory and field-scale studies are necessary prior to full-scale implementation.

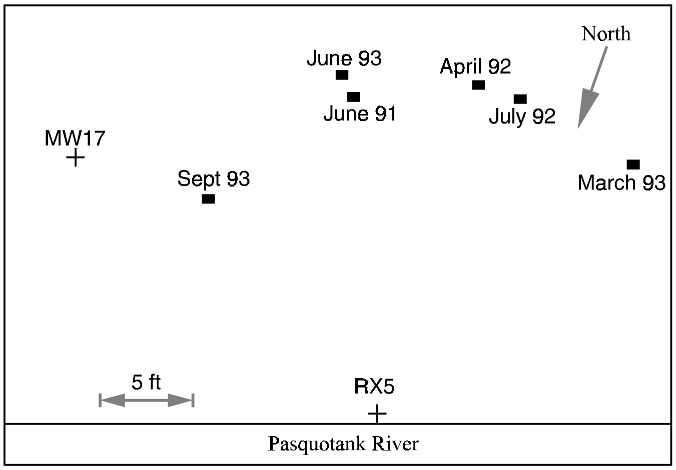

Figure XIII *Center of mass locations based on spatial moment calculations.*

The polyelectrolyte-enhanced ultrafiltration (PEUF) system performed very well during the pilot-scale field demonstration, reducing permeate chromium concentrations to near or below the detection limit (<50 ppb as Cr(VI)). Permeate sulfate levels were reduced to the 1 to 5 ppm range as well. These results were achieved without significant increases in the ionic strength of the treated water, as experienced using conventional reduction-precipitation processes. This along with the reduced chemical demands of the PEUF process, make it a very attractive process. The successful field demonstration reported herein will help to expedite its utilization in full scale systems.

The hydraulic characterization activities demonstrated that the aquifer is relatively homogeneous with respect to hydraulic conductivity and that the natural gradient, which is from the source area toward the Posquotank River, did not deviate significantly with time. Numerical modeling studies focused on identifying optimal orientation and configuration for the hydraulically-passive, chemically-reactive barrier. The difference in hydraulic conductivity between the barrier and the aquifer necessary to alter the flow lines of the contaminant plume was found to be three orders of magnitude. These differences are not practical given the fairly high conductivity of the natural aquifer. The optimal orientation for the barrier was found to be orthogonal to the flow path of the plume. Hence, a simple linear, down gradient barrier, wider than the plume and orthogonal to the flow path, is recommended. As constructed, the barrier is a continuous, hanging (i.e., not keyed into an underlying impermeable formation) wall 150 feet long. The barrier is only slightly more permeable than the natural aquifer, but is longer than the plume is wide; hence, the entire contaminant plume should eventually traverse the barrier. Headloss across the barrier will be monitored to determine residence times of the flowing fluids.

While each of these processes is at different stages of development, it is proposed that the collective use of these three innovative technologies will significantly improve the remediation of subsurface chromium contamination. Future research should continue to evaluate the synergism of these and other innovative technologies as we strive to optimize remediation of subsurface contamination.

Disclaimer

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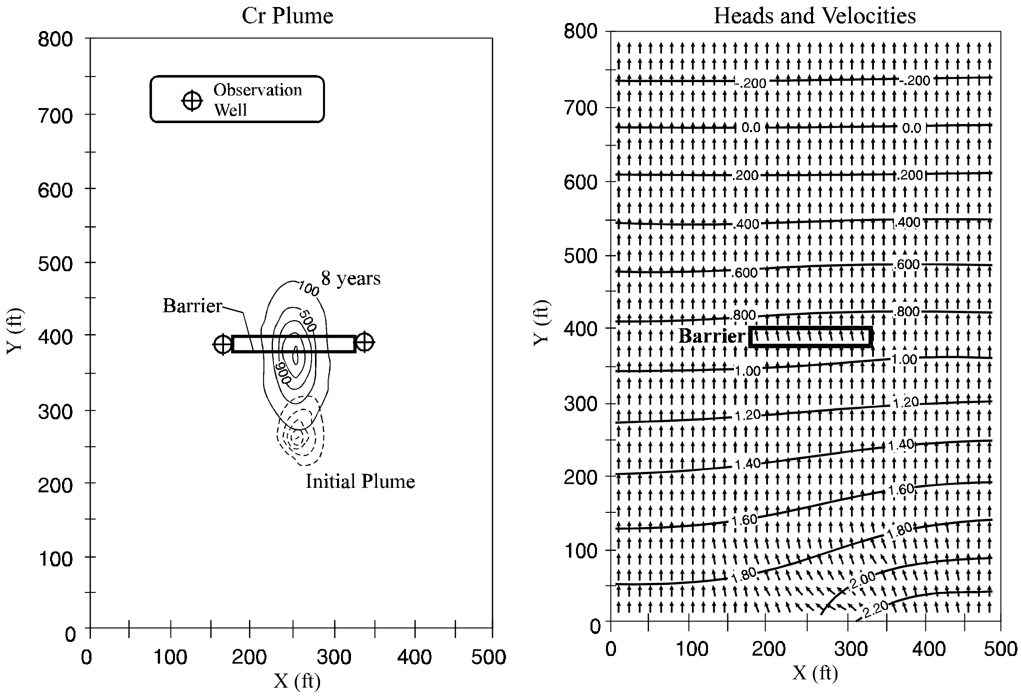
Quality Assurance Statement

All research projects making conclusions or recommendations based on environmentally related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project was conducted under an approved Quality Assurance Program Plan. The procedures specified in the plan were used without exception. Information on the plan and documentation of the quality assurance activities and results are available from the Principal Investigator.

Transverse Barrier



Longitudinal Barrier

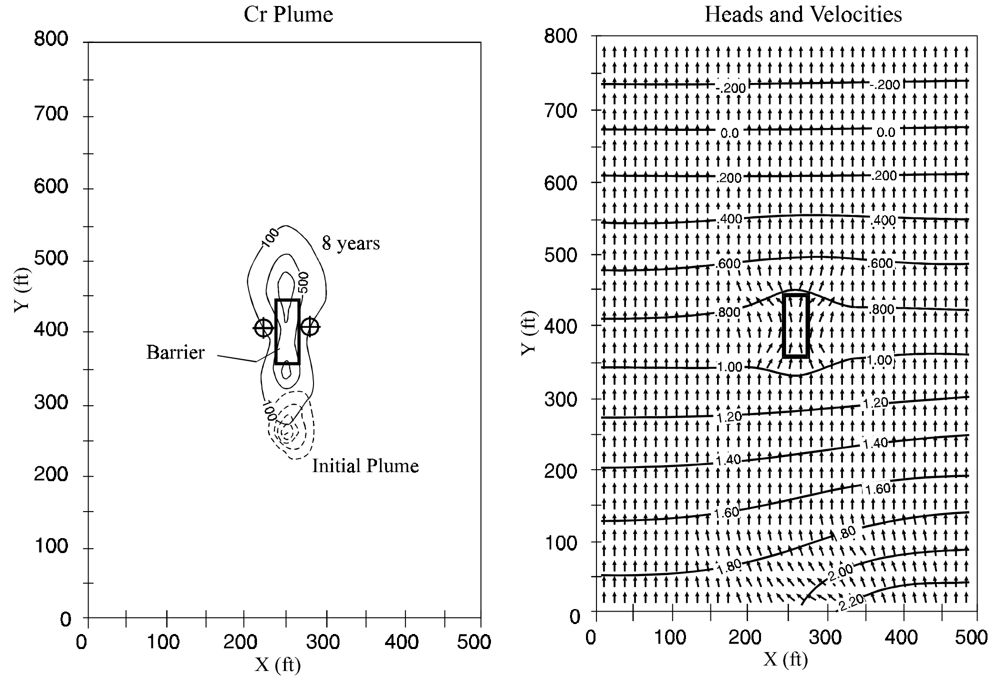
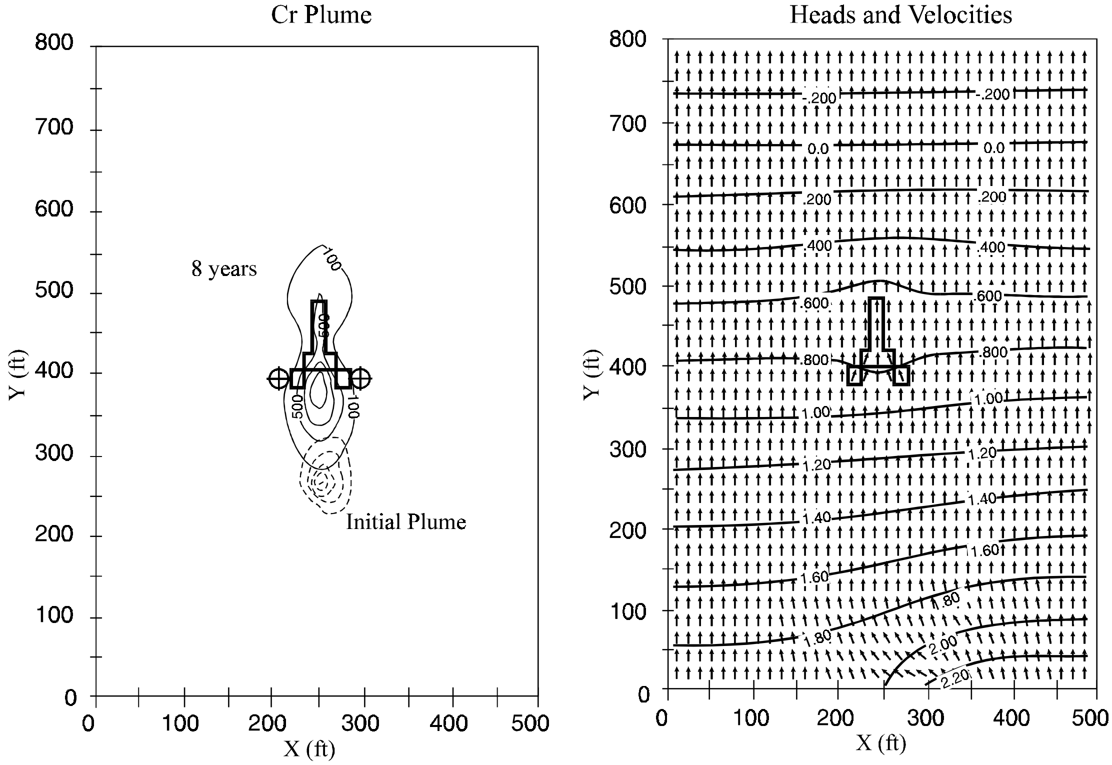


Figure XIV *Redox barrier configurations used in numerical simulations (a) transverse barrier; (b) longitudinal barrier; (c) Y-shaped barrier; (d) funnel and gate.*

Y-Shaped Barrier



Funnel and Gate

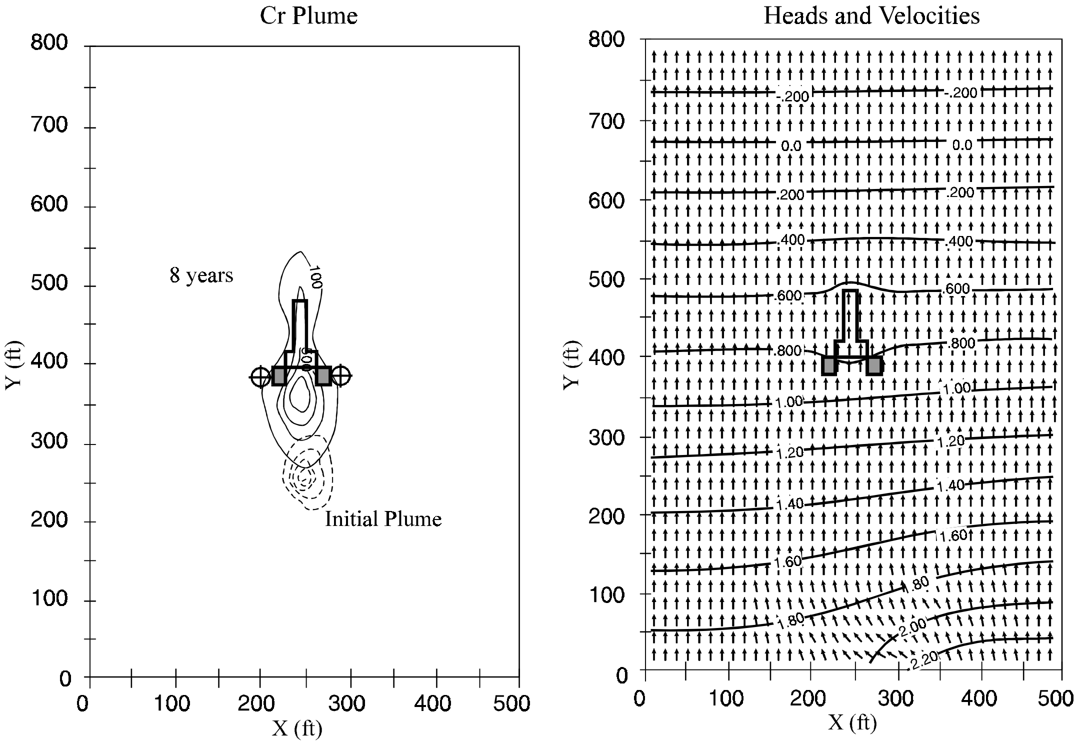


Figure XIV *Redox barrier configurations used in numerical simulations (a) transverse barrier; (b) longitudinal barrier; (c) Y-shaped barrier; (d) funnel and gate.*

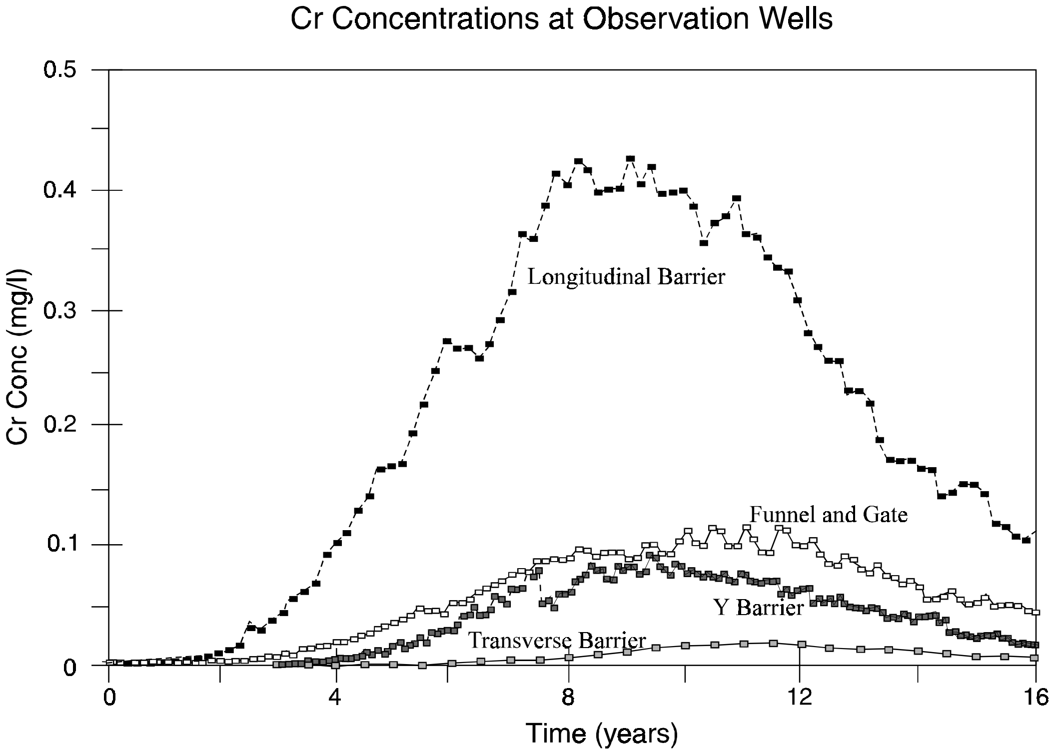


Figure XV *Chromium concentrations for monitoring wells peripheral to redox barriers.*

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