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Treatment of Hexavalent Chromium in Chromite Ore Processing Solid Waste Using a Mixed Reductant Solution of Ferrous Sulfate and Sodium Dithionite

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We investigated a method for delivering ferrous iron into the subsurface to enhance chemical reduction of Cr(VI) in chromite ore processing solid waste (COPSW) derived from the production of ferrochrome alloy. The COPSW is characterized by high pH (8.5−11.5) and high Cr(VI) concentrations in the solid phase (up to 550 mg kg^{-1}) and dissolved phase (3−57 mg L^{-1}). The dominant solid-phase minerals are forsterite (Mg_2SiO_4), brucite ($Mg(OH)_2$), and hydrocalumite [$Ca_4(Al, Fe)_2(OH)_{12}X\cdot 6H_2O$), $X = (OH)_2^{2-}$, SO_4^{2-}, CrO_4^{2-}]. The method utilizes $FeSO_4$ in combination with $Na_2S_2O_4$ to inhibit oxidation and precipitation of the ferrous iron, thereby preventing well and formation clogging. Laboratory batch tests using a 0.05 M $FeSO_4$ + 0.05 M $Na_2S_2O_4$ solution indicated effective treatment of both dissolved and solid-phase Cr(VI). Contrary to treatments with $FeSO_4$ and $FeCl_2$ alone, the combination resulted in both complete removal of Cr(VI) from solution and sustained Fe(II) concentrations in solution after a 24 h period. A field test involving injection of 5700 L of a 0.07 M $FeSO_4$ + 0.07 M $Na_2S_2O_4$ solution into a COPSW saturated zone (pH 11.5) indicated no well and formation clogging during injection. Examination of a core collected 0.46 m from the injection well following injection indicated effective treatment of the solid phase Cr(VI) based on analysis of water, phosphate solution, and high temperature alkaline extracts. The combined reductant solution also imparted a residual treatment capacity to the COPSW allowing for subsequent treatment of dissolved phase Cr(VI); however, dissemination of the iron in the highly alkaline environment appeared to be impeded by the inability to sufficiently lower the pH with distance from the injection well to avoid precipitation of $Fe(OH)_2$ and likely also $FeCO_3$. Injection of a 0.2 M $FeSO_4$ + 0.2 M $Na_2S_2O_4$ solution into another COPSW saturated zone (pH 9) indicated much more effective dissemination of the injected iron.

Introduction

Hexavalent chromium (Cr(VI)) is a known carcinogen, whereas, trivalent chromium (Cr(III)) is an essential micronutrient for many living organisms. The maximum concentration level for total chromium in drinking water has been set at 0.1 mg L^{-1} by the U.S. Environmental Protection Agency (U.S. EPA). In the absence of strong oxidants such as manganese oxides, Cr(III) is stable and virtually immobile in the subsurface due to its propensity to form sparingly soluble phases of chromic or mixed Cr−Fe hydroxide (*1*−*3*).

A variety of chemical reductants can reduce Cr(VI) to Cr(III). One group of reductants is reduced sulfur compounds such as hydrogen sulfide (*4*−*6*), iron sulfide (*7*, *8*), sodium sulfite (Na_2SO_3), sodium metabisulfite ($Na_2S_2O_5$) (*9*−*12*), and sodium diothionite ($Na_2S_2O_4$) (*13*−*17*). A second group includes iron-based reductants such as zerovalent iron (Fe^0) (*18*−*21*), dissolved Fe(II) (*22*−*25*), Fe(II) associated with hematite (α-Fe_2O_3) and biotite [$K(Fe, Mg)_3AlSi_3O_{10}(F,OH)_2$] (*26*), magnetite ($Fe_3O_4$) (*27*), and carbonate green rust [$Fe(II)_4Fe(III)_2(OH)_{12}CO_3\cdot 2H_2O$] (*28*, *29*). A third group includes free organic compounds such as hydroxylamine (*17*), ascorbate (*17*, *30*), oxalate and citrate (*31*), organic acids with TiO_2 as a catalyst (*32*, *33*), and soil organic matter (*34*, *35*).

Some reductants have been used in full-scale field applications to treat Cr(VI). An Fe^0-based permeable reactive barrier (PRB) has been successfully used to intercept and treat a Cr(VI)-containing plume at a site in Elizabeth City, NC (*36*). Sodium dithionite in combination with K_2CO_3 buffer has been used to treat groundwater Cr(VI) at the Hanford site in Richland, WA (*13*−*15*) and in groundwater and vadose zone soils at the Elizabeth City, NC site (*16*, *17*). The mechanism of Cr(VI) treatment in $Na_2S_2O_4$ applications involves the conversion of Fe(III) in soils/sediments to Fe(II) by $Na_2S_2O_4$ and the subsequent reduction of Cr(VI) to Cr(III) by Fe(II) to form the $Cr_xFe_{1-x}(OH)_3$ solid (*13*−*17*). The success of the $Na_2S_2O_4$ technology is thus based on sufficient quantities of dithionite-reducible iron being associated with the soil/sediment.

Groundwater at the Macalloy Corporation Superfund site in North Charleston, SC has been impacted by dissolved Cr(VI) originating from chromite ore processing solid waste (COPSW) disposed of in natural depressions over several decades. The COPSW, derived from the production of ferrochrome alloy between 1941 and 1988 using the submerged arc furnace process, consists primarily of pebbly slag, conditioning tower sludge, and electrostatic precipitator dust. Much of the COPSW currently lies beneath the water table at the site. Impacted groundwater flows to a tidal marsh located immediately adjacent to the 125 acre site (*37*). Unpublished results of our preliminary field investigation showed that groundwater within the COPSW zone is characterized by high pH (8.5−11.5) and high dissolved Cr(VI) concentrations (3−57 mg L^{-1}).

Few options exist for the direct treatment of COPSW at the site. Biotic treatments are not feasible since the high pH conditions are unfavorable for microbial activity. Direct treatment with $Na_2S_2O_4$ is not feasible due to the low dithionite-reducible iron content of the COPSW (as determined by batch study data presented herein). Ferrous sulfate ($FeSO_4$) has been effectively used to treat Cr(VI) in wastewater treatment operations via chemical reduction of Cr(VI) to Cr(III) and subsequent precipitation of a mixed trivalent chromium and ferric hydroxide; however, a recent investigation by Geelhoed et al. (*38*) showed the limitations of using $FeSO_4$ for direct treatment of Cr(VI) in a chromite ore processing residue (COPR) derived from the production of dichromate. They indicated that the addition of $FeSO_4$ to an infiltrating solution in test columns containing the COPR was not only ineffective in treating the solid phase Cr(VI) but that it also greatly increased leaching of Cr(VI) from the COPR.

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The ineffective treatment of solid-phase Cr(VI) was attributed to the almost immediate precipitation of the iron upon entering the high pH columns. The increased leaching of Cr(VI) from the test columns was attributed to the exchange of SO_4^{2-} in the infiltrating solution with CrO_4^{2-} in the layered minerals associated with the COPR. In another study, use of $FeSO_4$ and $FeCl_2$ solutions in both batch and column studies to treat Cr(VI) in coarse-textured, oxide-coated soil and aquifer materials resulted in limited success due to the low pH ($\approx$3) induced by oxidation and hydrolysis of Fe(II) and low pH buffering capacity of the soil (*39*). The low pH conditions induced by oxidation and hydrolysis of the Fe(II) did not prevent the reduction of Cr(VI) to Cr(III) but rather prevented precipitation of Cr(III) that is required to bring total dissolved-phase Cr concentrations below regulatory levels. Iron chelates such as *N*-hydroxyethyl-ethylenediamine-tetraacetic acid (HEDTA) have also been shown to enhance Cr(VI) reduction by Fe(II); however, HEDTA also accelerates Fe(II) oxidation by dissolved O_2 (*40*).

In our study, we did not consider use of $FeSO_4$ or $FeCl_2$ alone as a treatment option because of the known tendency of Fe(II) to oxidize to Fe(III) and precipitate out of solution upon injection into subsurface systems. Tremaine and Keel (*41*) injected a 4.3 mM $FeSO_4$ solution (pH = 2.6, adjusted with H_2SO_4) into a circumneutral pH Cr(VI)-containing aquifer. Even in the presence of added acid, a buildup in back pressure was observed during injection indicating that well and/or aquifer formation clogging was occurring and the injection process subsequently had to be abandoned. Oxidation and precipitation of iron was a particular concern with the high pH and high alkalinity COPSW. To address this concern, we conducted laboratory tests using $FeSO_4$ and $FeCl_2$ in combination with $Na_2S_2O_4$. Sodium dithionite (*42*) and sodium sulfite (*43*) have been used for removing oxygen from oilfield injection waters via eqs 1 and 2.

$$S_2O_4^{2-} + 2O_2 \rightarrow 2SO_4^{2-} \tag{1}$$

$$SO_3^{2-} + 0.5O_2 \rightarrow SO_4^{2-} \tag{2}$$

Sodium dithionite in water undergoes dissociation and disproportionation reactions to form primarily sulfoxyl radicals ($SO_2^{\bullet-}$), sulfites (SO_3^{2-}), and thiosulfates ($S_2O_3^{2-}$) via eqs 3 and 4 (*13*).

$$S_2O_4^{2-} = 2SO_2^{\bullet-} \tag{3}$$

$$4SO_2^{\bullet-} + H_2O = 2SO_3^{2-} + S_2O_3^{2-} + 2H^+ \tag{4}$$

During dissociation reactions, dithionite can reduce structural iron in clays and dissolve and reduce amorphous and some crystalline Fe(III) oxides to produce one or more Fe(II) species (*44*).

$$SO_2^{\bullet-} + Fe^{3+} + H_2O = Fe^{\bullet 2+} + SO_3^{2-} + 2H^+ \tag{5}$$

The oxidation of 1 mol of dithionite by Fe(III) to 2 mol of sulfite ultimately results in the production of 4 mol of acid. Although $Na_2S_2O_4$ itself was observed to be ineffective in treating the Cr(VI) associated with the COPSW in a preliminary batch study conducted, we theorized that $Na_2S_2O_4$ could serve as both an oxidant inhibitor and an acid generator to help stabilize Fe(II) in solution and thereby facilitate Fe(II) delivery into the subsurface. We hypothesized that the greater stability of Fe(II) in the presence of $Na_2S_2O_4$ would prevent well and formation clogging during injection. We also hypothesized that the combination of the two reductants might be able to sufficiently lower the pH of the COPSW during injection to limit precipitation of $Fe(OH)_2$ that might otherwise inhibit effective dissemination of Fe(II) in the subsurface. We conducted laboratory batch tests to compare the treatment potential of the $FeSO_4/Na_2S_2O_4$ combination with other reductants and reductant combinations in treating the COPSW from the Macalloy Corporation site. We subsequently conducted field tests to evaluate the feasibility of using this reductant combination for in situ COPSW treatment at the site.

Materials and Methods

Laboratory Batch Tests. A COPSW sample (LFISB005) obtained from the saturated zone at a depth of 3 m below ground surface (bgs) from the Macalloy Corporation site was used in the laboratory batch tests. The sample was air-dried and gently ground to pass through a 2 mm sieve. A titration of 2.5 g in 25 mL of deionized water using 1.0 M HCl was performed to determine the pH buffering capacity of the COPSW. The pH readings were recorded 10 min after each HCl addition under constant mixing using a magnetic stirrer.

We used deionized water at pH 5.7 and a 5 mM KH_2PO_4/5 mM K_2HPO_4 solution at pH 7.0 to estimate water soluble and exchangeable solid-phase Cr(VI), respectively. For evaluation of chemical reduction effectiveness, we considered 23 reductants/reductant combinations (Table 1) at concentration levels of 0.01, 0.025, and 0.05 M for $Na_2S_2O_4$, $FeCl_2$, and $FeSO_4$ with or without $K_2CO_3/KHCO_3$ buffers (0.05 or 0.1 M), 0.05 M for citric acid [$HOC(COOH)(CH_2COOH)_2$] and hydroxylamine sulfate [$(NH_2OH)_2{\cdot}H_2SO_4$], and 1.0 g of Peerless Fe^0 (40 wt %) (Peerless Metal Powders and Abrasives, Detroit, MI). All chemicals except Peerless Fe^0 and $Na_2S_2O_4$ (Sigma) were ACS reagent or analytical grade. Because solutions containing both $FeCl_2$ or $FeSO_4$ and $Na_2S_2O_4$ were found to produce some elemental sulfur (as detected by X-ray diffraction of the precipitate) when allowed to stand for an extended period of time, fresh solutions were made prior to testing. Additionally, to assess the long-term effectiveness of citric acid as a reductant, extraction with 0.05 M citric acid was performed for 30 and 60 days. For all batch tests, 2.5 g of the COPSW sample were equilibrated with 25 mL of each of the extractants/reductants for 23.5 h on a shaker at 100 rpm at 23 °C. The suspensions were then centrifuged at 3600 rpm for 0.5 h followed by filtration through a 0.22 μm Millipore nitrocellulose membrane.

Dissolved Cr(VI) in the supernatant was determined using a Hach DR 2010 spectrophotometer and Hach method 8023. This method uses 1,5-diphenylcarbohydrazide, which reacts with Cr(VI) to form a magenta complex that is measured at a wavelength of 540 nm. It was discovered that the Hach test kit gave false negatives for Cr(VI) determination in the presence of $Na_2S_2O_4$, even at concentrations as low as 0.0025 M. This appears to be caused by the chemical reduction of Cr(VI) in the sample to Cr(III) by the dithionite or its dissociation products when the acidic diphenylcarbohydrazide reagent is added to the initially alkaline samples to yield a final pH of less than 2. For dithionite-treated samples, total dissolved Cr was thus used as a measure of the presence of Cr(VI). Total dissolved Cr and Fe were determined using inductively coupled plasma−optical emission spectrophotometry (ICP−OES). Dissolved Fe(II) for selected samples was determined using Hach method 8146. This method uses 1,10-phenanthroline, which reacts with Fe(II) to form an orange complex that is measured at a wavelength of 510 nm. Both pH and E_h were measured in the supernatant using pH and redox electrodes. Redox potentials were reported as values relative to the standard hydrogen electrode.

Field Pilot Tests. Two field pilot tests were conducted at the site. The first pilot test was conducted in a saturated COPSW zone (pH $\approx$11.5 and Cr(VI) concentration $\approx$52.0 mg L^{-1}). The second pilot test was conducted in a nearby saturated COPSW zone (pH $\approx$9.0 and Cr(VI) concentration

TABLE 1. Batch Test Results (Mean ± Standard Deviation) of Two Extractants and 23 Reductants for Chromite Ore Processing Solid Waste (COPSW) Material (LEISB005) Reacted for 24 h at 100 rpm at 23 °C ($n = 2$)

Reagent	Initial pH	Equilibrium pH	Equilibrium E_h (mV)	total Cr[a] (mg L^{-1})	total Fe (mg L^{-1})
deionized water	5.70	9.68 ± 0.00	170 ± 2	7.4 ± 0.0	<0.035
5 mM KH_2PO_4/5 mM K_2HPO_4	7.02	9.91 ± 0.00	331 ± 10	8.0 ± 0.0	<0.035
0.025 M $Na_2S_2O_4$	3.71	9.65 ± 0.01	164 ± 4	10.3 ± 0.1	<0.035
0.05 M $Na_2S_2O_4$	3.80	9.72 ± 0.00	132 ± 10	11.8 ± 0.1	<0.035
0.025 M $FeCl_2$	3.42	9.16 ± 0.01	113 ± 26	<0.003	<0.035
0.025 M $FeSO_4$	4.08	9.40 ± 0.00	123 ± 3	<0.003	<0.035
0.05 M $FeCl_2$	3.39	9.12 ± 0.04	−112 ± 22	<0.003	<0.035
0.05 M $FeSO_4$	3.95	9.00 ± 0.02	−203 ± 21	<0.003	<0.035
0.05 M citric acid	2.77	9.10 ± 0.01	363 ± 3	26.2 ± 0.2	0.194 ± 0.057
0.05 M hydroxylamine sulfate	3.81	9.26 ± 0.02	−150 ± 1	0.11 ± 0.01	<0.035
1.0 g Peerless iron		9.82 ± 0.00	254 ± 2	2.90 ± 0.00	<0.035
0.025 M $Na_2S_2O_4$ + 0.05 M $KHCO_3$	7.53	9.86 ± 0.01	203 ± 5	12.2 ± 0.1	<0.035
0.025 M $Na_2S_2O_4$ + 0.05 M K_2CO_3	10.10	10.08 ± 0.00	28 ± 2	12.1 ± 0.1	<0.035
0.05 M $Na_2S_2O_4$ + 0.10 M $KHCO_3$	7.08	9.83 ± 0.01	189 ± 3	14.5 ± 0.1	<0.035
0.05 M $Na_2S_2O_4$ + 0.10 M K_2CO_3	10.10	10.18 ± 0.01	6 ± 5	12.6 ± 0.1	<0.035
0.025 M $FeCl_2$ + 0.025 M $Na_2S_2O_4$	2.98	9.09 ± 0.01	−376 ± 4	<0.003	<0.035
0.05 M $FeCl_2$ + 0.05 M $Na_2S_2O_4$	3.63	9.17 ± 0.00	−213 ± 8	<0.003	<0.035
0.01 M $FeSO_4$ + 0.01 M $Na_2S_2O_4$	3.51	9.53 ± 0.00	191 ± 3	0.41 ± 0.17	<0.035
0.025 M $FeSO_4$ + 0.025 M $Na_2S_2O_4$	3.50	9.39 ± 0.01	−144 ± 7	<0.003	<0.035
0.01 M $FeSO_4$ + 0.05 M $Na_2S_2O_4$	3.43	9.50 ± 0.01	147 ± 7	0.01 ± 0.00	<0.035
0.05 M $FeSO_4$ + 0.05 M $Na_2S_2O_4$	3.32	8.62 ± 0.01	−523 ± 1	<0.003	25.1 ± 8.0
0.05 M citric acid + 0.05 M $FeCl_2$	2.32	8.05 ± 0.01	−106 ± 2	22.5 ± 0.9	622 ± 41
0.05 M citric acid + 0.05 M $FeSO_4$	2.52	8.09 ± 0.00	−115 ± 4	15.6 ± 1.7	692 ± 73
0.05 M citric acid + 0.05 M $FeCl_2$ + 0.05 M $Na_2S_2O_4$	2.50	8.11 ± 0.01	−152 ± 4	26.3 ± 0.1	804 ± 9
0.05 M citric acid + 0.05 M $FeSO_4$ + 0.05 M $Na_2S_2O_4$	2.79	8.08 ± 0.01	−151 ± 1	25.1 ± 0.3	899 ± 31

[a] Total Cr concentrations determined by ICP−OES are provided because the Hach test kit gives false negatives for Cr(VI) determination in the presence of dithionite.

≈5.0 mg L^{-1}). Other baseline determinations of groundwater parameters in monitoring wells before injection included E_h, electrical conductivity, temperature, dissolved O_2, Fe(II), S(−II), major cation and anion concentrations, alkalinity, and total and dissolved organic and inorganic carbon. The groundwater table at the site was generally 1.5 m bgs, and the groundwater flow velocity was approximately 5 cm day^{-1}.

The reductant solutions used in the pilot tests were a blend of 0.07 M $FeSO_4$ + 0.07 M $Na_2S_2O_4$ for pilot test 1 and a blend of 0.2 M $FeSO_4$ + 0.2 M $Na_2S_2O_4$ for pilot test 2, prepared and delivered to the site by Olin Chemical, Charleston, TN. The pH of both blends was adjusted to 3.5 by the addition of H_2SO_4. Each reductant solution was pressure-injected into the aquifer from a tanker truck through a 5.1 cm diameter PVC well using a 0.5 horsepower centrifugal pump. The injection wells (GP2I-2 for pilot test 1 and RI-1 for pilot test 2) were installed using a Geoprobe Model 6600 unit. GP2I-2 was screened from 3.0 to 4.6 m bgs, and RI-1 was screened from 2.3 to 4.6 m bgs. Approximately 5700 L of the 0.07 M reductant were injected in pilot test 1 at an injection rate of 51 L min^{-1} and a pressure of approximately 7000 kg m^{-2}, and approximately 18 000 L of the 0.2 M reductant were injected (60 L min^{-1}) in pilot test 2 at the same pressure. On the basis of the volumes of reductant injected, the pore volume displacement radii were estimated at 1.75 m for pilot test 1 and 2.5 m for pilot test 2.

Treatment Permanency Test. Ideal treatment of Cr(VI) involves permanent reduction of Cr(VI) to Cr(III). A pre-treatment COPSW core (GPI-1) to a depth of 4.2 m bgs was obtained before reductant injection using the Geoprobe Model 6600 unit at a location 1.0 m from the injection well (GP2I-2) in pilot test 1. A post-treatment COPSW core was also obtained at a distance of 0.46 m from this injection well to a depth of 4.8 m bgs 1 day after injection. The COPSW cores were frozen immediately after collection, shipped to the laboratory on dry ice, and kept frozen until analysis. Cores were thawed and sectioned into 0.3 m sections. Each section was homogenized and transferred into a polyethylene bottle. A subsample was taken from each bottle to determine the moisture content by drying the sample at 105 °C for 24 h and measuring the weight loss. Duplicate moist samples equivalent to 2.5 g of dry mass were weighed into 50 mL polypropylene centrifuge tubes. Appropriate amounts of deionized water or a 5 mM H_2KPO_4/5 mM HK_2PO_4 (pH 7.0) solution were added to the centrifuge tubes to yield a total solution volume of 25 mL. The tubes were shaken at 100 rpm for 23.5 h, 30 days, and 60 days and then centrifuged at 3600 rpm for 30 min. Fifteen milliliters of the supernatant were subsequently removed and passed through a 0.22 μm Millipore nitrocellulose membrane before total dissolved Cr determination using ICP−OES. Selected air-dried and ground core subsamples were subjected to alkaline digestion at 90 °C to determine extractable Cr(VI) using EPA SW-846 Method 3060A, described by James et al. (*45*). Selected core subsamples were also microwave digested in a 10% HNO_3 solution at 175 °C in a sealed pressurized vessel (a modification to EPA SW-846 Method 3051, which uses concentrated HNO_3) and analyzed by ICP−OES.

Residual Treatment Capacity Test. It was theorized that if aquifer sediments are sufficiently dosed with reductant, the treated sediments could acquire a residual treatment capacity for treating dissolved Cr(VI) advectively transported into the treated zone from up-gradient sources. This would presumably be due to the precipitation and/or adsorption of Fe(II) onto the aquifer solid surfaces. To evaluate the residual treatment capacity, the COPSW core sample collected 1 day following injection was tested for its ability to treat aqueous phase Cr(VI). Testing consisted of immersing a homogenized subsample at a 10:1 water-to-solid ratio (v/w) in a 50 mg L^{-1} solution of Cr(VI) and shaking the mixture for 23.5 h. The suspension was centrifuged and filtered, and total Cr concentrations in solution were determined by ICP−OES. Total Cr(VI) in the solid phase was determined with alkaline digestion at 90 °C using EPA SW-846 Method 3060A. Dissolved Cr(VI) concentrations were determined using the Hach Method 8023.

X-ray Diffraction. The untreated COPSW sample was ground with an agate mortar and pestle to pass through a 0.05 mm sieve. The solids were mounted on a zero-background quartz slide for X-ray diffraction (XRD) examination. Treated COPSW solids were collected, filtered, rinsed with water, and dried in an anaerobic (3−5% H_2 in N_2) glovebox before being mounted on a slide inside the anaerobic glovebox. To limit oxidation by air, approximately 20 mg of the reductant-treated solids were mixed with a drop of glycerol to form a smooth paste on the slide. The slide was examined with a Rigaku Miniflex X-ray diffractometer at a scan rate of 0.5° 2θ min^{-1} (FeKα radiation; operated at 30 keV and 15 mA). A third sample collected from the initial purge water of the injection well in pilot test 1 126 days after injection was filtered, rinsed, dried, and mounted in the glovebox before XRD examination.

Results and Discussion

Screening of Reductants. Table 1 provides batch screening test results. Extraction with deionized water (final pH 9.68) yielded a final solution Cr(VI) concentration of 7.4 mg L^{-1} (1:10, w/v), corresponding to an extractable Cr(VI) fraction of 74 mg kg^{-1}. Extraction with a 5 mM KH_2PO_4/5 mM K_2HPO_4 solution resulted in a slightly higher 24 h equilibrium Cr(VI) concentration of 8.0 mg L^{-1} and a solution pH of 9.91. The batch test results indicated that $Na_2S_2O_4$ without an added ferrous iron salt was ineffective in treating the COPSW and actually appeared to promote the release of Cr(VI) from the solid phase. This may be attributed to the absence of any significant dithionite-reducible iron in the COPSW (despite the nitric acid digestible iron content of the COPSW having been measured at close to 1%). In contrast, $FeSO_4$ and $FeCl_2$ were highly effective in treating the COPSW with equilibrium Cr concentrations of less than 0.003 mg L^{-1}. The batch test results also indicated that both of these salts in combination with 0.05 M $Na_2S_2O_4$ achieved treatment of less than 0.003 mg of Cr L^{-1} in solution but that the 0.05 M $FeSO_4$ + 0.05 M $Na_2S_2O_4$ combination achieved a significantly lower 24 h equilibrium pH and E_h than did the combination of 0.05 M $FeCl_2$ + 0.05 M $Na_2S_2O_4$. Because SO_4^{2-} is an ultimate degradation product of $S_2O_4^{2-}$, the presence of $FeSO_4$ may delay the decomposition of $Na_2S_2O_4$ relative to the presence of $FeCl_2$. In contrast to other treatments investigated, this combination was the only successful treatment that resulted in dissolved iron still remaining in solution (25 mg L^{-1}) (Table 1). The reaction between the sediments and 0.05 M $FeSO_4$ + 0.05 M $Na_2S_2O_4$ was rapid with complete removal of Cr(VI) within 0.5 h (data not shown).

Treatment with 0.05 M citric acid for 24 h resulted in a total dissolved Cr concentration of 26.2 mg L^{-1}, greater than that extracted with water or phosphate solution. Treatment with citric acid in combination with Fe(II) and with Fe(II) plus dithionite were not effective (Table 1), despite significant amounts of total dissolved iron remaining in the solution after a 24 h reaction. Longer treatment times with citric acid alone for 30 and 60 days produced slightly lower total Cr concentrations (20.3 and 18.9 mg L^{-1}, respectively), but the results were still far from satisfactory. Since Cr(VI) reduction by organic acids is a function of pH with greater reduction at low pH, the high pH of the waste material presumably prevented effective Cr(VI) reduction. Furthermore, citrate may enter the interlayer of the Cr(VI) containing hydrocalumite, replacing and then releasing Cr(VI) into the solution.

Mechanisms of Cr(VI) Removal in COPSW. Titration data indicated a high pH buffering capacity of COPSW; calculations show that to decrease the pH of the material from pH 10 to 7, the amount of HCl needed was 6.3 mol of H^+ kg^{-1}. This is due to the presence of alkaline metal silicates and metal hydroxide phases in the sample. The COPSW consists largely of forsterite (Mg_2SiO_4) and brucite [$Mg(OH)_2$] with minor amounts of unprocessed ore as chromite ($FeCr_2O_4$) and magnesiochromite ($MgCr_2O_4$), hydrocalumite [$Ca_4(Al, Fe)_2(OH)_{12}X{\cdot}6H_2O$), X = $(OH)_2^{2-}$, SO_4^{2-}, CrO_4^{2-}], and calcite ($CaCO_3$) as supported by the XRD patterns (Figure 1). Trivalent chromium occurs in chromite and magnesiochromite, whereas hexavalent chromium likely occurs in hydrocalumite in the COPSW. Hydrocalumite is an anionic clay mineral composed of portlandite-like principal layers, in which one-third of the Ca^{2+} sites are occupied by Al^{3+} (*46*). The net positive charge generated in the octahedral layers from this substitution is balanced by anions in the interlayers (*47*). Hydrocalumite is known to exhibit a large capacity to incorporate chromate, sulfate, borate, molybdate, and selenate into its structure through anion exchange with hydroxyl ions (*48*−*51*). Other anions may substitute for chromate in the interlayer. A synthesized end member of chromate hydrocalumite shows the uptake capacity of Cr(VI) at 74 700 mg kg^{-1} (*52*). Hydrocalumite is likely a primary source of leachable Cr(VI) in the saturated zone. Hydrocalumite is unstable at low pH, requiring pH values greater than 11.6 to stabilize it (*53*).

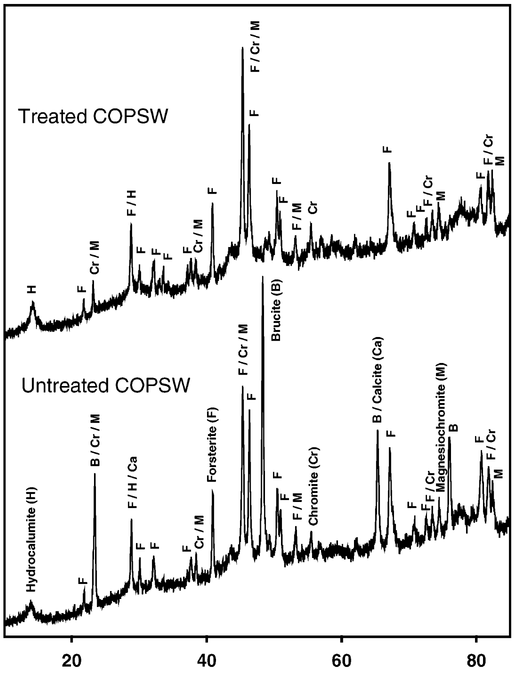

FIGURE 1. X-ray diffraction patterns of the untreated COPSW material (LEISB005) and treated COPSW material collected in the initial purge water (pH = 8.87) from the injection well (GP2I-2) 126 days after injection of a 0.07 M $FeSO_4$ + 0.07 M $Na_2S_2O_4$ solution.

Aqueous Fe(II) reacts with Cr(VI) in both solid and aqueous phases. The reduction of Cr(VI) by Fe(II) can be written as

$$CrO_4^{2-} + 3Fe^{2+} + 8H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \quad (6)$$

Eq 6 is very fast and goes to completion in less than 5 min, even in the presence of dissolved oxygen (*22*). Reaction 6 is pH- and ligand-dependent; at pH >10 or at phosphate concentrations >0.1 M, the rate of oxidation of Fe^{2+} by dissolved O_2 exceeds the rate of oxidation by Cr(VI) (*26*). At pH >4, Cr(III) precipitates with Fe(III) to form a solid solution with the general composition $Cr_xFe_{1-x}(OH)_3$. This reaction limits the total dissolved Cr concentrations as Cr(III) to values that are less than the U.S. EPA drinking water standard of 10^{-6} M between pH 5.0 and 11.0 (*2, 54*)

$$xCrO_4^{2-} + (1 - x)Fe^{2+} + (3 - 8x)OH^- + 4xH_2O \rightarrow Cr_xFe_{1-x}(OH)_3 \quad (7)$$

If the reduction of Cr(VI) by Fe(II) is the only source of Cr(III) and Fe(III), a solid solution with the composition $(Cr_{0.25}Fe_{0.75})(OH)_3$ forms via eq 8 (*22*)

$$\mathrm{CrO_4^{2-} + 3Fe^{2+} + 4OH^- + 4H_2O \rightarrow 4(Cr_{0.25}Fe_{0.75})(OH)_3} \qquad (8)$$

Sodium dithionite is known to be able to reduce structural Fe(III) in aluminosilicates (*55, 56*). The reduced Fe(II) species in the subsurface can exist in many forms: dissolved phase, surface adsorbed species, aluminosilicates, iron oxides, siderite ($FeCO_3$), and iron sulfides. Since the dithionite ion itself in the near neutral to alkaline pH range does not significantly reduce Cr(VI), the Fe(II) ion is the reductant that is oxidized by Cr(VI) to form Cr(III), which readily precipitates to form a mixed Cr−Fe hydroxide phase over a wide pH range.

The term sulfite can be defined in terms of concentration in a more general sense as

$$[\mathrm{S(IV)}] = [\mathrm{SO_2{\cdot}H_2O(aq)}] + [\mathrm{HSO_3^-}] + [\mathrm{SO_3^{2-}}] \qquad (9)$$

Reduction of Cr(VI) by S(IV) is second-order with respect to the [S(IV)] (*9, 10, 12*), and the second-order dependence of the reaction remains valid for the pH range of 1.0 to 5.5. Sulfite is an effective reductant for Cr(VI) under conditions of acidity (pH 2.0−5.0) and $[\mathrm{S(IV)}] = 5[\mathrm{Cr(VI)}_{\mathrm{initial}}]$ (*11*). Comparison of half-lives of Cr(VI) reduction calculated from the results reported by Beukes et al. (*11*) for S(VI) with those of Buerge and Hug (*24*) for Fe(II) indicates that S(IV) reduces Cr(VI) faster than Fe(II) at pH 2−5, whereas Fe(II) is faster at pH >5.

The complete reaction mechanism of reduced sulfur with Cr(VI) can involve several sulfur intermediates and is complicated and unresolved. For the high pH conditions in effect within the COPSW source zone at the site, Cr(VI) reduction is likely to be dominated by Fe(II) with a minor contribution from sulfur-based compounds including sulfites.

Several chemical reactions occur when the $FeSO_4/Na_2S_2O_4$ solution is added to COPSW. An acid−base reaction occurs when the acidic reductant solution (Table 1) dissolves both brucite and calcite. This is evidenced by the absence of these two minerals in the XRD patterns of solids recovered from the pilot test 1 injection well (GP2I-2) 126 days after injection (Figure 1). Hydrocalumite is still present probably due to its slower dissolution kinetics. In the batch test, when 2.5 g of the COPSW were reacted with 25 mL of a 0.05 M $FeSO_4$ + 0.05 M $Na_2S_2O_4$ solution for 24 h, the brucite and calcite were still detected by XRD (data not shown), indicating the high pH buffering capacity of the COPSW. Although detailed mechanisms are unknown, it is probable that the added sulfate displaces the interlayer chromate in the hydrocalumite structure into solution (*38*), the added Fe(II) reduces the Cr(VI) to Cr(III), and an X-ray amorphous $Cr_xFe_{1-x}(OH)_3$ phase likely forms (*22, 23*). Our current understanding of COPSW behavior is incomplete, and further studies are needed to derive specific mechanisms of Cr(VI) reduction and solid phase formation in the COPSW after the addition of Fe(II) and dithionite.

Treatment Permanency Test. Figure 2 shows both 24 h water- and phosphate-extractable Cr profiles in the pre-treatment core (GPI-1) and a post-treatment core for pilot test 1. The extraction data from the post-treatment core over the 3.0−4.5 m depth increment corresponding to the screened interval of the injection well indicate no detectable Cr in the 24 h and 30 days water and phosphate solution extracts (<0.003 mg L^{-1}) (Figures 2b and 3a), respectively. The 60 day aqueous solution extracts indicate some detectable Cr in both water and phosphate extracts for the 4.0−4.3 m depth interval (Figure 3b). At 0.46 m from the injection well over the depth of 3.0−4.5 m, the water extractable Cr decreased from an average of 42.6 mg kg^{-1} to less than 0.03 mg kg^{-1}; phosphate extractable Cr decreased from an average of 78.4 mg kg^{-1} to less than 0.03 mg kg^{-1}; and EPA Method 3060A extractable Cr(VI) decreased from an average of 252 mg kg^{-1} to 31.4 mg kg^{-1}, corresponding to an 87% decrease.

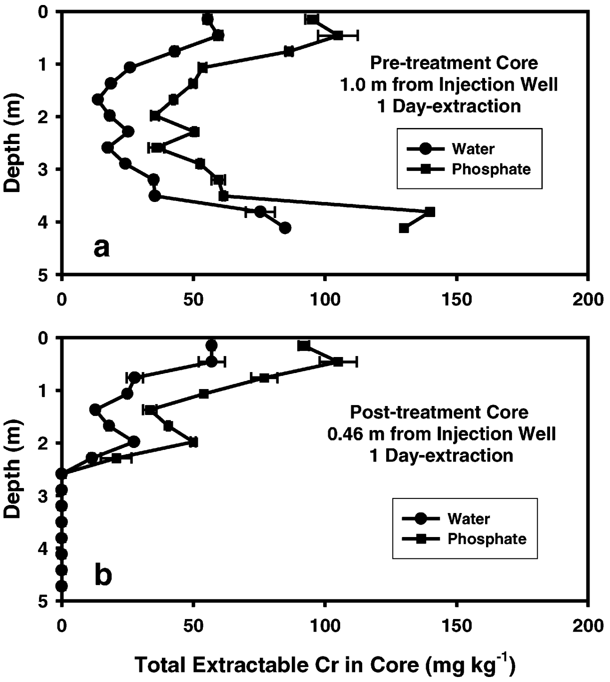

FIGURE 2. One-day water and phosphate extractable Cr in (a) pre-treatment core collected 1.0 m from injection well and (b) reductant-treated core collected 0.46 m from injection well 1 day following reductant injection in pilot test 1.

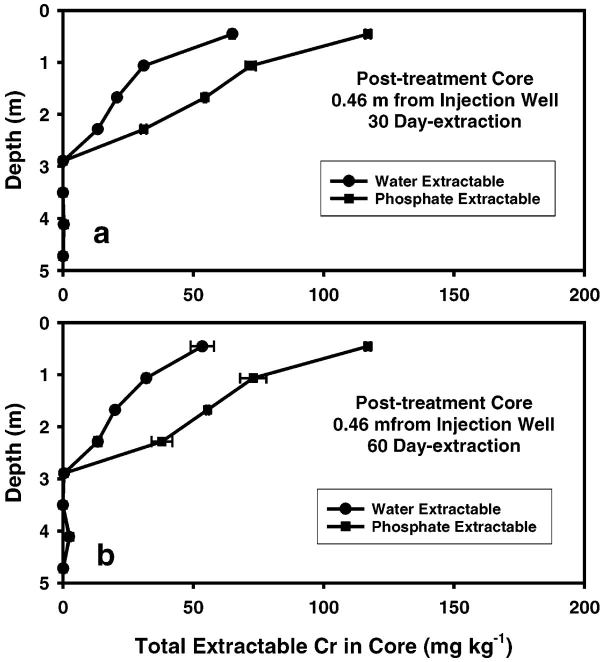

FIGURE 3. Thirty day (a) and 60 day (b) water and phosphate extractable Cr in reductant-treated core collected 0.46 m from injection well 1 day following reductant injection in pilot test 1.

Nitric Acid Digestion. Total Cr, Fe, and S concentrations derived from nitric acid microwave digestion are shown in Figure 4 for the pre-treatment core (GPI-1) at each 0.30 m depth from 0 to 4.2 m and for the post-treatment core collected 0.46 m from injection well at each 0.30 m depth

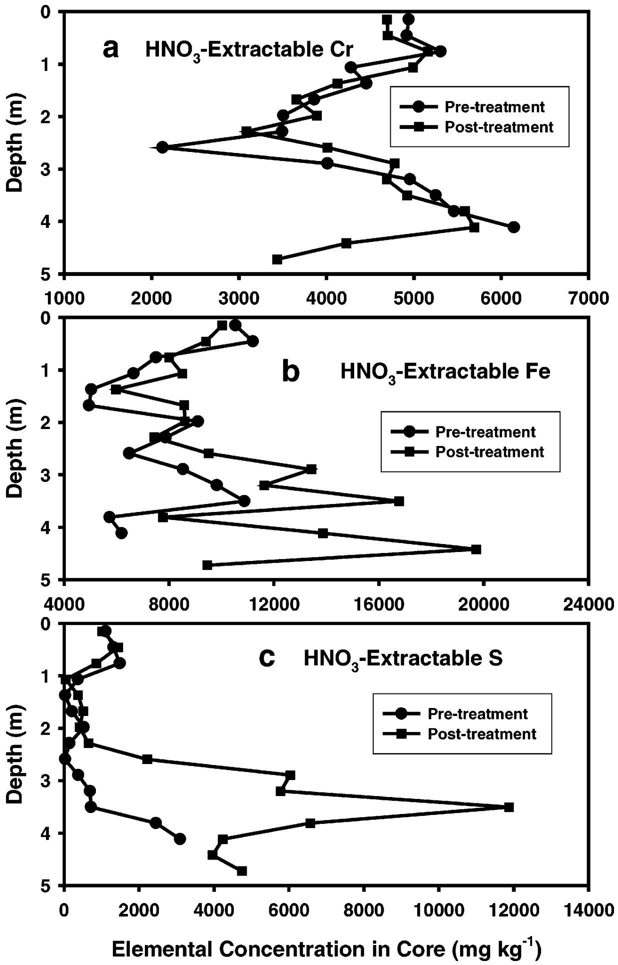

FIGURE 4. Nitric acid-extractable Cr, Fe, and S for pre-treatment and post-treatment cores.

from 0 to 4.8 m. As expected, iron and sulfur showed increased concentrations in the solids following reductant injection. The average total Cr concentrations in the two cores before and after reductant injection (4436 and 4478 mg kg^{-1}, respectively) showed no significant changes. This is consistent with the reduction of dissolved and solid-phase Cr(VI) by Fe(II) to Cr(III) that is then coprecipitated with iron in the solid matrix (*22*, *23*).

Residual Treatment Capacity Test. Test results for a core sample from a depth of 4.5–4.8 m from the post-treatment core indicated that when the treated core sample was immersed in a 50 mg L^{-1} solution of Cr(VI) at a 10:1 water-to-solid ratio (v/w), all Cr(VI) was removed from solution (and presumably converted to Cr(III)). This observation appears to provide evidence of a residual treatment capacity imparted to the aquifer solids. Residual treatment capacity imparted to the COPSW sediments could be due to adsorbed Fe(II), Fe(OH)$_2$, and FeCO$_3$ solid phases. The COPSW (LEISB005) contains 0.68 ± 0.10% ($n = 2$) inorganic carbon, perhaps largely associated with calcite. It is expected that the residual treatment capacity imparted to the sediments following treatment will likely vary as a function of the strength of the reductant added and the ability to uniformly distribute the reductant in the subsurface.

The ability to impart a residual treatment capacity to sediments/solids could have important implications for full-scale treatment of Cr(VI)-impacted subsurface systems. It suggests that full access to and treatment of all source zone sediments during injection may not necessarily be a requirement for successful overall treatment at the site. The more effectively accessed and treated zones could compensate for the less effectively accessed and treated zones by chemically reducing any dissolved Cr(VI) that might potentially be released from the less effectively treated zones.

TABLE 2. Water Chemistry in the Injection Well (GP2I-2) in Pilot Test 1

	time after injection (days)				
	pre-injection	2	40	126	194
Cr(VI) (mg L^{-1})	52.0				
total Cr (mg L^{-1})	48.7	0.003	<0.003	0.752	2.008
sulfate (mg L^{-1})	4570	9780	5220	ND	6840
Fe(II) (mg L^{-1})	<0.01	6.90	<0.01	ND	<0.01
pH	11.53	7.91	9.63	9.82	9.54
E_h (mV)	283	−190	51	51	16

Groundwater Monitoring. During injection of the reductant solution, a decrease in injection pressure was noted over time, contrary to what would have been expected if well or aquifer clogging was occurring. This could be partly caused by dissolution of COPSW by the acidic reductant solution. Groundwater data from the injection well (GP2I-2) in pilot test 1 were collected 2, 40, 126, and 194 days following injection (Table 2). The results indicate that at 2 and 40 days following injection, the total Cr was not detectable (<3 μg L^{-1}) in the injection well. A sample collected from the injection well after 2 days indicated an Fe(II) concentration of 6.90 mg L^{-1}. After 126 days, a total Cr concentration of 752 μg L^{-1} was detected in the well indicating that Cr(VI) concentrations had begun to rebound presumably due to the advective influx of dissolved phase Cr(VI) from up gradient sources; however, this concentration was still orders of magnitude less than the pre-injection measured Cr(VI) concentration of 52 000 μg L^{-1}, suggesting that the COPSW material had acquired a residual treatment capacity capable of treating incoming dissolved phase Cr(VI). Groundwater flow rates through the treatment zone, based on field slug tests conducted and hydraulic gradients in effect at the site, were estimated at approximately 5 cm day^{-1}. Thus, 126 days following injection, approximately 6 m of linear groundwater flow through the treatment zone was estimated to have occurred. After 194 days, corresponding to an estimated 10 m of linear groundwater flow through the treatment area following injection, a total Cr concentration of 2008 μg L^{-1} was measured in the injection well.

Data from monitoring wells located at a distance of 1 and 1.5 m from the injection well indicated less effective treatment of Cr(VI). At a distance of 1 m, total Cr concentrations were measured at 0.012 μg L^{-1} after 2 days, 3804 μg L^{-1} after 40 days, and 3631 μg L^{-1} after 194 days from an initial concentration in the well of 56 200 μg L^{-1}. Ferrous iron concentrations in groundwater at this location 21 min and 24 h following injection were measured at 34 and 5.5 mg L^{-1}, respectively, indicating that some Fe(II) did travel the 1 m distance. The pH in the groundwater at the 1 m distance 24 h following injection was measured at 8.49 down from a pre-injection value of 11.52, and E_h was measured at −242 mV down from a pre-injection value of 257 mV. The significant pH and E_h decreases observed at this location provide strong supporting evidence of the delivery of significant amounts of the reductant out to this distance. At a distance of 1.5 m from the injection well, the total Cr concentrations were measured at 21 430, 28 440, and 23 320 μg L^{-1} 24 h, 40 days, and 194 days following injection, respectively, from a pre-injection concentration of 44 060 μg L^{-1}. The pH at this distance 24 h following injection decreased to only 11.09 from a pre-injection pH of 11.49, while the E_h decreased from a pre-injection value of 353 mV to 81 mV following injection. A sample collected 80 min following injection from this distance indicated a low Fe(II) concen-

TABLE 3. pH, E_h (mV), Dissolved Fe(II), and Total Cr (mg L^{-1}) in Monitoring Wells as a Function of Distance from Injection Well (RI-1) and Time after Injection in Pilot Test 2

	distance from injecton well (m)															
	0.76				1.5				2.3				3.0			
time (days)	pH	E_h	Fe(II)	Cr	pH	E_h	Fe(II)	Cr	pH	E_h	Fe(II)	Cr	pH	E_h	Fe(II)	Cr
0	9.80	336	<0.01	6.12	9.07	371	<0.01	5.01	9.09	483	<0.01	4.92	8.92	432	<0.01	3.47
2	7.49	−378	92.0	0.029	7.85	−315	29.7	0.011	8.77	−162	1.8	0.135	8.91	29	0.11	2.24
6	7.85	−167	43.5	<0.003	8.03	−263	18.5	0.008	8.71	−147	1.6	0.136	8.97	11	0.06	2.70

tration of only 0.10 mg L^{-1}. The 1.5 m distance corresponds to the approximate limits of treatment anticipated based on displacement of one pore volume by the injected reductant. The limited treatment observed at 1.5 m suggests that most of the Fe(II) likely precipitated and/or sorbed out of solution before reaching the 1.5 m distance. The pH data in particular suggest that the pH of the COPSW saturated zone with increasing distance from the injection well could not be sufficiently lowered to <8.0 during injection to prevent significant precipitation of $Fe(OH)_2$ and likely also $Fe(CO)_3$.

As would be expected, sulfate concentrations were observed to increase following injection from initial concentrations of approximately 5000 mg L^{-1} up to 9800 mg L^{-1} in the injection well (based on 48 h post-injection data). No evidence of any increased mobilization of Cr(VI) in response to increased sulfate levels at these locations following injection was evident based on the data collected.

Data from pilot test 2 conducted in a pH 9 COPSW setting and involving injection of approximately 18 000 L of a 0.2 M $FeSO_4$ + 0.2 M $Na_2S_2O_4$ reductant solution indicated better dissemination of Fe(II) in the subsurface (Table 3). Fe(II) was detected at concentrations of 0.11 and 0.06 mg L^{-1}, respectively, 2 and 6 days following injection at a distance of 3.0 m from the injection well. At 2.3 m from the injection well corresponding to the approximate anticipated limits of treatment (based on displacement of one pore volume by the injected reductant), slightly higher Fe(II) concentrations of 1.8 and 1.6 mg L^{-1} were observed 2 and 6 days, respectively, following injection. The enhanced dissemination of Fe(II) in pilot test 2 and the presence of still measurable amounts of Fe(II) in solution after 6 days at a distance of 2.3 and 3.0 m from the injection well is attributed to the lower initial pH of the COPSW zone as well as the greater volume and higher strength of the reductant injected.

There are several observations that indicate that sustained decreases in the Cr(VI) concentration after treatment are not attributable to dilution. The batch studies indicate that the solid-phase COPSW material yields a 24 h equilibrium Cr(VI) solution concentration of about 7.0 mg L^{-1} when immersed in aqueous solution. Thus, even if no Cr(VI) containing groundwater was to have entered the treatment area from up gradient locations following treatment, one would still expect to see a rebound in Cr(VI) concentrations in the pore water (from leaching and/or dissolution of solid phase Cr(VI)) within 24 h if dilution were the only means by which dissolved Cr(VI) decreases occurred. This was clearly not the case. In the injection well in pilot test 1, the Cr(VI) concentration was still less than 0.003 mg L^{-1} 40 days following treatment. After 126 days, the total Cr concentration was measured at only 0.752 mg L^{-1}. Hydraulic testing conducted in the injection well following treatment indicated a groundwater flow velocity across the site of approximately 5 cm day^{-1}. If a pore volume displacement radius of 1.75 m (3.5 m diameter) for pilot test 1 is assumed (based on the amount of reductant injected), then over a 126 day period, about 1.8 pore volumes would have moved through the treatment area, and after 194 days, about 2.8 pore volumes would have moved through. The up gradient groundwater is highly contaminated with Cr(VI) (>40 mg L^{-1}); thus, a rebound to pre-treatment concentrations as a result of advective flow of contaminated groundwater into the treatment zone should have occurred after 126 days and certainly after 194 days if dilution were the only means by which the observed dissolved phase Cr(VI) decreases occurred. The fact that total Cr concentrations in the injection well remained below 1 mg L^{-1} after 126 days and at 2.0 mg L^{-1} after 194 days from initial pre-treatment concentrations of greater than 48 mg L^{-1} indicates that decreases in dissolved phase Cr(VI) concentrations cannot be attributed to dilution. In addition, as previously discussed, batch tests conducted with core material collected after treatment indicated that the treated COPSW removed all dissolved phase Cr(VI) when the treated material was immersed in a 50 mg L^{-1} Cr(VI) solution. This provides strong evidence of a residual treatment capacity having being imparted to the treated solids such that dissolved phase Cr(VI) entering the treatment zone from up gradient locations are treated.

In conclusion, this study has shown that the combination of $FeSO_4$ and $Na_2S_2O_4$ prevents well and formation clogging associated with ferrous iron injection into a high pH subsurface environment; however, success in effectively disseminating ferrous iron in a high pH subsurface environment in the presence of $Na_2S_2O_4$ is still contingent on limiting the precipitation of $Fe(OH)_2$ that can significantly impede delivery of the iron. Unless a pH of less than 8 can be achieved during injection within the targeted zone, ferrous iron dissemination will likely be compromised.

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