

In Situ Cr(VI) Reduction within Coarse-Textured, Oxide-Coated Soil and Aquifer Systems Using Fe(II) Solutions

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Batch and column techniques were used to evaluate the in situ Cr(VI) reduction and immobilization using Fe(II) solutions within the sediments of the Atlantic Coastal Plain. Remediation treatments included Cr-free groundwater and buffered and unbuffered Fe(II) solutions as either FeCl₂ and FeSO₄. The slow release of Cr(VI) from the Fe-oxide rich subsurface sediment following exposure to Cr-free solutions indicated that simple pump-and-treat procedures would require extended operation time to meet regulatory standards. In situ reduction was confirmed by the loss of Cr(VI) and Fe(II) from solution and a drop in pH compared to control systems. Batch and column-effluent Cr(VI) decreased with increasing Fe(II), generally falling below detection limits as the persistence of Fe(II) occurred. However, Cr_{Dissolved}, presumably Cr(III), exceeded regulatory limits due to the low pH (≈3.0) induced by oxidation and hydrolysis of Fe(II). Acetate-buffered Fe(II) solutions maintained an elevated pH in the presence of Cr(VI) reduction, making the treatment effective at lowering Cr_{Dissolved} in batch evaluations. Acetate increased Cr(VI) mobility in columns ahead of the reactive Fe(II) front, suggesting that in situ reduction using soluble chemical additives may be somewhat ineffective due to the enhanced migration of Cr, either Cr(III) or Cr(VI), induced by the treatment solution.

Introduction

The success of groundwater remediation efforts is often limited by the strong partitioning of contaminants to the immobile solid aquifer matrix. Their slow release makes it inefficient and costly to reclaim an aquifer by simply capturing and treating the groundwater (1). Stollenwerk and Grove (2) observed that leaching 320 pore volumes (PV) of Cr-free groundwater was required to meet the drinking water standard (DWS) for sediments contaminated with Cr(VI). The likelihood of reclaiming such an aquifer using current pump-and-treat technologies is doubtful, since they typically cycle one aquifer PV per year (1). In contrast, soil flushing may be adequate to meet regulatory standards for aquifer and soil materials that display little ability to retain Cr(VI) (3).

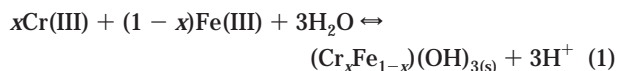
An understanding of the mechanisms controlling Cr mobility in soil is essential to developing effective remediation

strategies. The fate of Cr depends largely on its chemical speciation in response to local geochemical conditions. In nature, Cr occurs primarily in one of two redox states, the relatively benign and immobile trivalent form, Cr(III), and the toxic, more mobile, hexavalent forms, chromate (CrO₄²⁻) or dichromate (Cr₂O₇²⁻). Despite different toxicities, current EPA regulations fail to account for redox state with the DWS for Cr_{Dissolved} set at 0.1 mg L⁻¹ (≈1.9 μM) (4).

Variable charge minerals such as Fe- and Al-oxides act as sorbents of Cr(VI) (5–8) and, therefore, limit migration in soil and aquifer systems (2, 9). However, organic acids and inorganic anions commonly present in groundwater, such as SO₄²⁻, PO₄³⁻, and to a lesser degree NO₃⁻ and Cl⁻, are effective competitors for sorption sites (5–8, 10). In fact, the introduction of benign competitive species may represent a cost-effective method of increasing the efficiency of Cr(VI) extraction (3).

Chemical reduction of Cr(VI) to Cr(III) offers an attractive alternative to extraction for reducing the mobility and toxicity of Cr. However, Cr remains in place and may, due to reoxidation, become a health or regulatory concern at a later date. For example, soils containing significant quantities of Mn-oxides may, under some conditions, readily oxidize Cr(III) to Cr(VI) (10, 11). Reduction of Cr(VI) by naturally occurring Fe(II)-bearing minerals followed by sorption or precipitation has often been invoked to explain migration behavior in the field (12–15). In a similar manner, the use of solid-phase reduced-Fe sources has been proposed as reactive, flow-through barriers to Cr(VI) migration (16, 17). At sites where the use of such barriers is impractical due to the depth and extent of contamination, the in situ manipulation of redox status using reactive solutions offers a promising alternative. Methods for treating Cr(VI)-containing wastewater generally consist of reduction to Cr(III) followed by pH adjustment to neutrality to favor precipitation of Cr(OH)₃ or mixed oxyhydroxide phases (18). Batch experiments have demonstrated the ability of Fe(II) salts to reduce and immobilize Cr(VI) in contaminated soils (19, 20); however, their application has not been adequately evaluated in dynamic transport studies which are more analogous to conditions experienced in the field.

Each mole of Cr(VI) reduced to Cr(III) requires 3 mol of Fe(II) (21–23). In aerobic systems where Cr(VI) is likely to persist, dissolved oxygen (DO) may interfere with the redox couple by competing for Fe(II). However, significant Cr(VI) reduction due to Fe(II) can occur in even well-aerated systems (10, 18). Above pH 5, Cr(III) readily precipitates as Cr(OH)₃; however, Cr(III) can substitute for Fe within hydrous Fe oxides (24). In the presence of Fe(III), Cr(III) readily precipitates as a mixed phase



for which the solubility of Cr(III) is less than that of the pure Cr(OH)₃ (18, 21). The hydrolysis and precipitation of Fe(III) and Cr(III) generate acidity as indicated by the above reaction. In poorly buffered systems such reactions may lower pH to the point where the precipitation of Cr(OH)₃ or the mixed Fe(III)/Cr(III) hydroxide is suppressed. This is not a concern in the water-treatment industry because the pH can be easily adjusted to ensure precipitation prior to disposal. As an in situ treatment method, however, the addition of base is likely to reduce the efficiency of Cr(VI) reduction by increasing losses of Fe(II) via oxidation by O₂. Therefore, the effectiveness of Fe(II) solutions in reducing and immobilizing Cr(VI) likely

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TABLE 1. Select Properties of the Orangeburg Surface Soil Horizon and Tobacco Rd Subsurface Sediment

	Orangeburg series	Tobacco Rd
pH _{water} ^a	5.52	5.30
	g 100 g ⁻¹	g 100 g ⁻¹
total organic carbon	0.76	0.02
CDB ^b Fe	0.19	0.74
particle size distribution ^c	g 100 g ⁻¹	g 100 g ⁻¹
sand	85.5	87.2
silt	7.8	4.5
clay	6.6	8.3
clay mineralogy ^d	k, HIV, gibb	k, g, m

^a 2:1 solution/soil ratio in deionized water. ^b Citrate-dithionite-bicarbonate extraction. ^c Micro-pipet method. ^d Determined by X-ray diffraction: k = kaolinite, HIV = hydroxy-interlayered vermiculite, gibb = gibbsite, q = quartz, g = goethite, and m = mica.

depends on the ability to control solution pH without consuming reactive Fe(II), while still favoring Cr(III) precipitation. The objective of the present study was to evaluate in batch and dynamic transport systems the effectiveness of using buffered and unbuffered Fe(II) solutions as reducing agents for the in situ stabilization of Cr(VI).

Materials and Methods

A surface soil from the Orangeburg Series (Typic Paleudult, fine-loamy, siliceous, thermic) and an aquifer sediment from the Tobacco Rd Formation displaying characteristics typical of the Atlantic Coastal Plain were collected on the Departments of Energy's Savannah River Site (SRS), near Aiken, SC (Table 1). Samples were stored in a field-moist state at 4 °C prior to batch or column studies. Both materials were coarse in texture and displayed negligible intrinsic capacity to reduce Cr(VI) (25). Kaolinite was found to be the primary clay mineral constituent for both materials, but the Orangeburg sample also contained hydroxy-interlayered vermiculite (HIV) with trace amounts of gibbsite and quartz. The Tobacco Rd sample consisted of kaolinite, goethite, and mica (illite). The total organic carbon (TOC) and free Fe-oxide content for both materials were determined using dry combustion (26) and citrate-dithionite-bicarbonate (CDB) extraction methods (27), respectively.

Batch Sorption and Reduction Studies. Five-gram samples of the soil and aquifer materials were weighed into 50 mL centrifuge tubes with four treatment replicates. Cr(VI) sorption was evaluated in two background solutions: deionized water (DIW) and synthetic groundwater (SGW). The SGW, based on routine groundwater monitoring data from the SRS (28), contained the following (mg L⁻¹): 1.00 Ca²⁺, 0.37 Mg²⁺, 0.21 K⁺, 1.40 Na⁺, and 0.73 SO₄²⁻. As a control, equivalent treatment levels were replicated in soil-free centrifuge tubes to account for sorption to the tubes or possible redox transformations during equilibration. The tubes were then placed on a reciprocating shaker for ≈18 h. Preliminary kinetic experiments indicated that 18 h was sufficient time to achieve equilibrium with respect to Cr(VI) sorption. After equilibration, the tubes were centrifuged for 15 min at 15 000 rpm, and the supernatant was passed through a 0.2 μm pore-size polycarbonate membrane filter prior to Cr(VI) analysis using the diphenylcarbazide method with a detection limit of ≈0.1 μM (29). Solution-phase Cr(VI) concentrations in the tubes containing soil were compared to the control tubes at each treatment level to quantify sorption based on their difference. Subsequent extraction with 10 mM K₂HPO₄/KH₂PO₄ (pH 7.2) confirmed that Cr(VI) loss from solution resulted from reversible sorption rather than reduction to Cr(III) followed by precipitation.

Five-gram samples of the aquifer sediment were placed in four replicate centrifuge tubes and the weight of the tube

+ soil was recorded. Thirty-five milliliters of the SGW containing 1.4 mM Cr(VI) as K₂Cr₂O₇ was added to each tube and equilibrated for 18 h on a reciprocating shaker. After equilibration, the tubes were centrifuged and the supernatant was filtered and acidified as described above for storage prior to analysis. The tubes were then reweighed to estimate the amount of total Cr(VI), sorbed plus the entrained solution, remaining in each tube. Fe(II)-containing solutions used in the batch and column experiments were prepared using N₂ gas-purged DIW. Thirty-five milliliters of buffered (pH ≈ 5.6) or unbuffered FeSO₄ solution at concentrations ranging from 0 to 2.2 mM Fe(II) were then added to replicate tubes and reacted for 6 h on a reciprocating shaker. Samples were then centrifuged and filtered as above, and a fraction of the supernatant was acidified for total Cr_{Dissolved} analysis. A fraction of the unacidified filtrate was immediately passed through a syringe containing sufficient cation-exchange resin (AG 50W-8X Resin, Bio-Rad Laboratories) to remove Fe(II), Fe(III), and Cr(III) prior to analysis for Cr(VI). The pH of the remaining supernatant and the total weight of each tube were then determined. The filtrates were analyzed for Cr(VI) and total Cr_{Dissolved} using the diphenylcarbazide method and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), respectively.

Column Studies: Cr(III), Cr(VI), and Fe(II) Analysis. Ten cm long columns (5 cm ID) were packed to a uniform bulk density of ≈1.60 Mg m⁻³ with the field-moist materials, oriented vertically and slowly saturated (<0.14 L d⁻¹) from the outlet with SGW. The volumetric water content (θ ≈ 0.40) or pore volume (PV) was assumed to be equivalent to the column porosity because of the coarse texture of the matrix. After saturation, columns were oriented horizontally and leached with 1.0 mM Cr(VI) as K₂Cr₂O₇ for 16 PV at a constant inlet flow rate of 1.44 L d⁻¹ (Darcy Vel. ≈ 0.7 m d⁻¹) to simulate a contamination event. Preliminary studies indicated that the outlet Cr(VI) concentration began to approach the inlet value following 16 PV of leaching. After the Cr(VI) solution, columns were leached with one of several treatment solutions, including SGW, and acetate-buffered and unbuffered FeSO₄ and FeCl₂ solutions (0.5–5.0 mM) to evaluate the efficacy of various Fe(II) salts at stabilizing Cr(VI) within the column matrix. Each treatment was replicated at least twice using fresh sediment materials. Retardation and oxidation of Fe(II) in the absence of Cr(VI) were evaluated by leaching non-contaminated columns with the Fe(II) treatment solution for 34 PV. The pH of the column effluent was monitored continuously using a flow-through cell. Changes in hydraulic conductivity resulting from column plugging as a function of treatment chemistry were evaluated using a pressure transducer (0–1 PSI, Omega Inc.) located at the column inlet.

Unbuffered Fe(II)-containing inlet solutions were replenished every 6–8 h to ensure a relatively constant inlet flux of Fe(II). Oxidation prior to injection was typically ≤5% and the formation of an Fe(III) precipitate in the inlet reservoir prior to injection was not observed for any treatment solutions. The buffered Fe(II) treatments consisted of pH adjusted (pH 5.6), 50 mM Na-acetate solutions which were continuously purged with N₂ to avoid oxidation and subsequent precipitation of Fe.

Chemical speciation of effluent constituents in dynamic transport studies can be logistically difficult, especially when discrete, chemically reactive samples are constantly being generated for a period of several days. A sampling scheme was developed in which discrete effluent fractions were analyzed for a specific chemical component of interest, for example Fe(II). The Fe(II) concentration in the column effluents was monitored using a modified ferrozine method (30) in which the spectrophotometric reactants were added to the fraction tube prior to sample collection to inhibit oxidation by Cr(VI) or O₂ prior to analysis. A magnetic

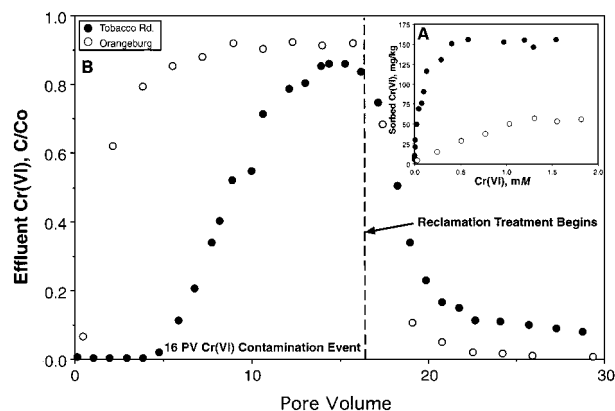


FIGURE 1. Batch (A) and column (B) data comparing the Cr(VI) sorption capacity of the Orangeburg soil and Tobacco Rd sediment.

stirring bar included in each ferrozine-containing tube was agitated during sample collection by continuously spinning a second magnetic stirring bar mounted just beside the fraction collector to ensure sufficient mixing of the column effluent and ferrozine solution.

Fraction tubes collecting samples for Cr(VI) analysis were equipped with a funnel apparatus packed with the exchange resin used in batch reduction studies to remove Fe(II), Fe(III), and Cr(III) from the effluent as it passed into the fraction tube. Periodically, a funnel apparatus was included in a ferrozine-containing tube to confirm its effectiveness in removing Fe(II). In addition to spectrophotometric analysis of Fe(II) and Cr(VI), select effluent fractions were immediately filtered after collection and acidified for analysis of soluble metals using ICP-MS. The effectiveness of the sampling protocol in stabilizing Cr(VI) and Fe(II) was confirmed in preliminary studies in which separate solutions containing either the Fe(II) or Cr(VI) reagents were added simultaneously and quantified using known standards. Turbid column effluents ($\text{NTU} > 1$) were digested using a microwave-assisted HNO_3/HF -based method (EPA Method 3052) followed by ICP-MS analysis to estimate Cr_{Total} . In addition, select effluent suspensions were concentrated for thermal gravimetric analysis (TGA) as an indicator of kaolinite and goethite contents (31).

Residual Chromium Extraction. After completion of a given leaching experiment, the column was drained and the soil was removed, air-dried to evaluate the potential oxidation of reduced Cr, and homogenized for subsequent extraction studies. Residual Cr(VI) was extracted with 0.01 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ buffered at pH 7.2 (25). Total residual Cr was determined using HNO_3/HF -based digestion followed by ICP-MS analysis.

Statistical Analysis. The theoretical residual Fe(II) concentration for the batch experiments was determined by subtracting the amount of Fe(II) required (3Fe(II) to 1Cr(VI)) to reduce the residual Cr(VI) within each sample tube (i.e. sorbed plus entrained Cr(VI)) and then dividing by the range of Fe(II) treatment levels. Deviation from expected residual Fe(II) concentrations was evaluated for the buffered and unbuffered treatments with T tests against mean = 0. The PV at which Cr(VI) fell below the DWS for the Fe(II) treatments was compared with a two-way ANOVA, with FeSO_4 vs FeCl_2 as one main effect and treatment concentration as the other.

Results and Discussion

Cr(VI) Sorption in Batch and Columns. Despite similar textures, pH, and clay mineralogy, the two sediments displayed considerably different affinities for Cr(VI) in batch and column experiments (Figure 1). The subsurface sample containing more Fe oxides and less organic matter retained

at least twice as much Cr(VI) as the surface soil at a given solution concentration (Figure 1A). The Tobacco Rd sediment displays a high affinity for Cr(VI) at low solution concentrations that levels off in a Langmuir-type fashion. Therefore, Cr(VI) would likely be transported through the surface soil and retained to a greater degree within the Fe-oxide rich subsurface materials. The SGW minimally reduced Cr(VI) sorption compared to DIW, yielding sorption curves that were virtually identical, presumably due to the low ionic strength of the SGW.

Chromium breakthroughs are plotted in dimensionless concentration (C/C_0) where C_0 represents the inlet Cr(VI) concentration, 1 mM (52 mg L^{-1}). For comparison, the retardation factor (R) for Cr(VI) was defined as the PV at which the effluent concentration, C/C_0 , equaled 0.5. Cr(VI) was moderately retarded in the surface soil ($R \approx 2.5$), and complete breakthrough ($C \approx C_0$) did not occur during the course of leaching (Figure 1B). After switching to Cr-free SGW, the outlet Cr(VI) concentration decreased rapidly. In addition to dispersion, the tailing observed in the surface soil may be indicative of the nonlinear sorption behavior displayed in the batch sorption isotherms or possibly kinetically limited desorption. Despite the limited sorption capacity of the surface soil, effluent Cr(VI) remained above the DWS throughout the course of leaching with SGW. As expected, Cr(VI) was retarded (i.e. sorbed) to greater extent in the Tobacco Rd columns ($R \approx 8.4$). The high affinity for Cr(VI) at low surface coverages (i.e. nonlinearity) was manifested in the extensive tailing which may also reflect the slow desorption kinetics from goethite (32), the dominant sorptive phase within these materials. Similar to previous column studies (2), a rapid decrease in effluent Cr(VI) concentration occurred when the inlet solution was replaced with Cr-free water (Figure 1B). However, the effluent Cr(VI) remained elevated well above the DWS even after leaching with 84 PV of SGW (data not shown), indicating that simple pump-and-treat procedures using Cr-free water may require extended operation time to meet regulatory requirements. Because of the higher potential to retain Cr(VI), batch- and column-reduction studies focused mainly on the Fe-oxide rich subsurface material.

Batch Reduction. In batch, Cr(VI) in solution decreased with increasing Fe(II) addition for both the buffered and unbuffered treatment solutions (Figure 2A); however, the total $\text{Cr}_{\text{Dissolved}}$ in unbuffered, filtered samples leveled off at ≈ 0.05 mM (2–3 mg L^{-1}) despite the presence of residual unreacted Fe(II) (Figure 2B). The high levels of $\text{Cr}_{\text{Dissolved}}$, well above the DWS (0.1 mg L^{-1}), likely resulted from the lower pH, ≈ 3.3 , induced by Fe(III) and Cr(III) hydrolysis, which may have kinetically hindered further Fe(II) oxidation by O_2 (Figure 2C). Similar results have been reported for studies evaluating the intrinsic reduction potential of subsurface soils under acidic conditions (10). $\text{Cr}_{\text{Dissolved}}$ in the present study is less than the reported solubility of $\text{Cr}(\text{OH})_3$ or a mixed Fe/Cr hydroxide (10, 33), $\text{Fe}_{0.75}\text{Cr}_{0.25}(\text{OH})_{3(\text{am})}$, which exceeds the DWS at a pH of ≈ 4.7 (Figure 2D). In addition to inhibiting precipitation, the resulting pH is below the adsorption threshold for Cr(III) on Fe(III) hydrous oxides (34), the likely sorptive phase in the subsurface material. In the buffered system (pH ≈ 5.6), total $\text{Cr}_{\text{Dissolved}}$ was below the DWS once the 3:1 equivalence point for the redox couple was reached. However, significant Fe(II) oxidation in excess of that required for Cr(VI) reduction occurred in the buffered system ($T = -6.63$, $p = 0.003$, $n = 8$) presumably due to the faster oxidation kinetics in the presence of DO compared to the low-pH, unbuffered system.

Fe(II) Solutions-Chloride vs Sulfate Salts: Column Results. Until initiation of the various extraction/stabilization treatments, Cr(VI) mass recoveries for all columns were quite similar. In all instances, the effluent Cr(VI) concentrations

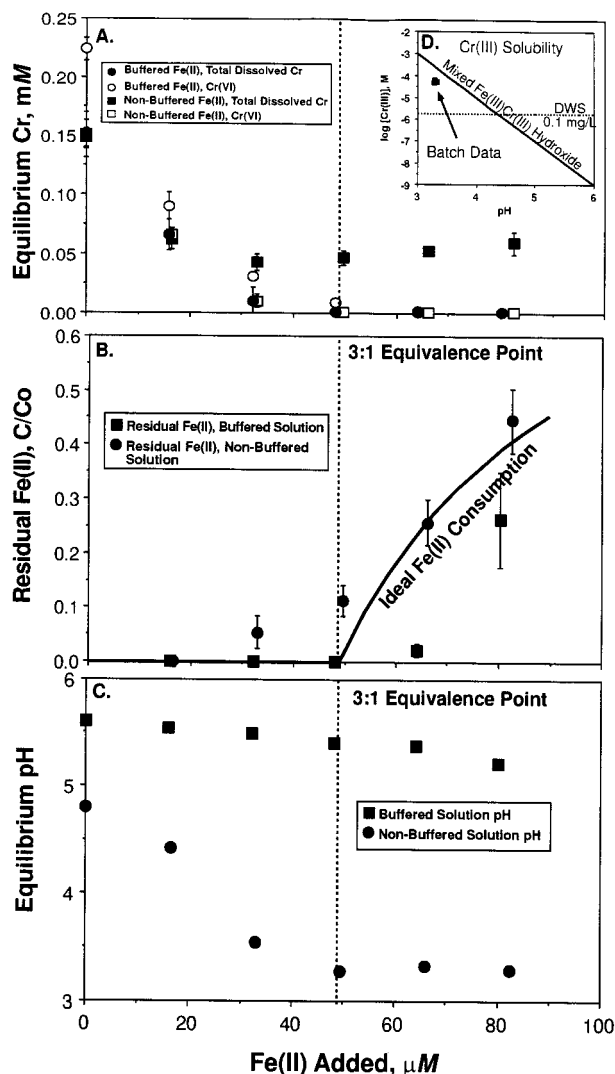


FIGURE 2. Batch reduction of Cr(VI) in Tobacco Rd sediment for buffered (pH 5.6) and nonbuffered FeSO_4 solutions: (A) $\text{Cr}_{\text{Dissolved}}$ and $\text{Cr(VI)}_{\text{Dissolved}}$, (B) residual Fe(II) compared to ideal estimates required for complete Cr reduction, and batch pH (C). Bars indicate standard deviation. Inset (D): predicted Cr(III) solubility for Fe(III)/Cr(III) hydroxide, $\text{Fe}_{0.75}\text{Cr}_{0.25}(\text{OH})_{3(\text{am})}$, as a function of solution pH. $\text{Cr}_{\text{Dissolved}}$ for unbuffered Fe(II) treatments and the DWS (0.1 mg L^{-1} ; $\log [\text{Cr}] \approx -5.7$) included for comparison.

for the Fe(II) treatments fell below the DWS much sooner than for the conventional Cr-free SGW treatment and generally correlated with the observed breakthrough and persistence of Fe(II) (Figure 3).

The duration of leaching required to meet the DWS for "Cr(VI)" decreased significantly with increasing Fe(II) inlet concentration (Table 2). A conservative estimate of that slope (using 50 PV as the value for 0.5 mM FeSO_4) is -8.3 (95% confidence interval = -4.7 to -11.8 , $T = -4.6$, $p = 0.001$, after correcting from main effect of Cl^- versus SO_4^{2-}). At a given Fe(II) concentration, FeCl_2 was significantly more effective than FeSO_4 at lowering effluent Cr(VI) (difference = 10.9 PV , 95% confidence interval = 4.0 to 17.7 , $T = 3.1$, $p = 0.012$, correcting for $\log(\text{Fe})$ and using 50 PV for 0.5 mM FeSO_4), presumably due to the faster oxidation/reduction kinetics in the presence of Cl^- compared to SO_4^{2-} (35, 36), and possibly the greater Cr(VI) migration observed for SO_4^{2-} -containing solutions (Figure 3A). Competition with SO_4^{2-} for sorption sites actually enhanced Cr(VI) migration ahead of the reactive Fe(II) front, resulting in a secondary peak in effluent Cr(VI) that was not observed for the SGW or FeCl_2

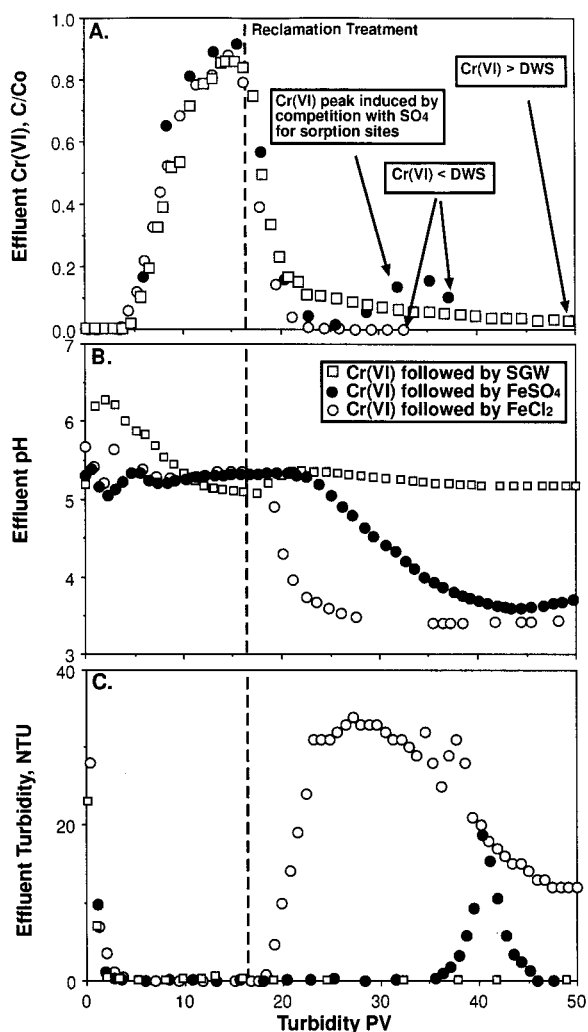


FIGURE 3. Cr(VI) breakthrough (A), effluent pH (B), and effluent turbidity (C) for Tobacco Rd sediment columns contaminated with Cr(VI) followed by SGW or 5.0 mM Fe(II) as FeCl_2 or FeSO_4 .

treatments. The depressed effluent pH measured in-line confirmed that significant Cr(VI) reduction occurs within the matrix (Figure 3B). A consistently earlier Fe(II) breakthrough and a higher effluent pH were observed when the treatment solutions were leached through control columns that were not contaminated with Cr(VI), again confirming Cr(VI) reduction within the column matrix. These data were compared to the contaminated columns to account for Fe(II) losses in reactions other than Cr(VI) reduction.

Effluent turbidities for the FeCl_2 treatments, measured immediately after sample collection, were generally much higher than FeSO_4 or even FeCl_2 treatments leached through noncontaminated control columns (Figure 3C). This suggests that Fe(III) precipitates resulting from oxidation and hydrolysis, generally greater for FeCl_2 compared to FeSO_4 , were suspended and transported from the aquifer matrix or the sampling tubing directly adjacent to the column outlet. However, several lines of evidence indicate that the suspensions may, in part, result from colloid dispersion and transport resulting from the acidifying hydrolysis reactions. In previous column studies using similar sediments, Seaman et al. (31, 37) observed that native Fe oxides may be dispersed and transported as positively charged colloids under mildly acidic conditions ($\text{pH} < 4.5$). The FeSO_4 treatment also decreased the effluent solution pH with a concomitant increase in effluent turbidity. However, the effluent turbidity decreased with continued leaching which may reflect the flocculating

TABLE 2. Cr Mass Recoveries (C/C_0) as a Function of Remediation Treatment: Effluent-Recovered Cr ($Cr_{Dissolved}$), PV at Which Cr(VI) Fell Below the DWS, Final Effluent Cr Concentration ($[Cr]_{50PV}$), PO_4^{3-} -Extractable Cr(VI) (Exchangeable), Residual Cr (Digestion), and Total Mass Recovered^h

remediation treatment		recovered	Cr(VI) <	$[Cr]_{50PV}^c$	PO_4^{3-} exch	residual	total Cr
units		$Cr_{Dissolved} C/C_0^a$	DWS PV ^b	(mg L ⁻¹)	Cr(VI) C/C_0^d	Cr C/C_0^e	recovery C/C_0^f
Unbuffered Treatments							
FeSO ₄	SGW	0.68	> 50	1.35	0.31	0.34	1.03
	0.5 mM	0.59	> 50	1.83	0.05	0.54	1.04
	2.5 mM	0.64	23.7	0.61	^g BDL	0.33	0.97
	5.0 mM	0.70	21.0	0.55	BDL	0.25	0.96
FeCl ₂	0.5 mM	0.56	24.9	1.01	BDL	0.45	1.00
	2.5 mM	0.67	20.1	0.75	BDL	0.31	0.98
	5.0 mM	0.61	17.2	0.41	BDL	0.31	0.92
pH 5.6 Buffered Treatments (50 mM Acetate)							
5.0 mM FeSO ₄		0.70	19.1	0.02	BDL	0.24	0.93
no Fe(II)		0.87	> 50	2.10	0.12	0.08	0.95

^a Sum of recovered Cr based on ICP-MS analysis of filtered effluent samples. ^b PV at which Cr(VI) fell below the DWS. ^c Final effluent Cr concentration in filtered samples. ^d Phosphate extractable Cr(VI). ^e Residual Cr = (total Cr) - (native Cr). ^f Total mass recovered Cr = (Σ effluent $Cr_{Dissolved}$) + (residual Cr) - (native Cr). ^g BDL = below detection limits (<0.168 mg kg⁻¹). ^h Each data set reflects the average of two or more replicate columns.

ability of SO_4^{2-} , as predicted by the Schulze-Hardy Rule of colloid stability for a positively charged phase (37). HF-digested effluent suspensions were elevated in Fe, Al, and to a lesser degree Si, K, and other trace elements that generally correlated with sample turbidity but cannot be explained based on precipitation reactions involving the treatment solutions. In fact, the levels of colloidal Fe in the effluent suspensions were greater than the Fe(II) treatment concentration. This suggests that native Fe oxides and clay minerals present within the sediments were mobilized as a result of the acidic pH. TGA results indicated the suspensions consisted primarily of goethite, with lesser amounts of noncrystalline Fe oxides and kaolinite. The rapid formation of crystalline Fe oxides by oxidizing Fe(II) solutions (38), however, makes it difficult to exclude precipitation resulting from the Fe(II) treatments as a possible source for some fraction of the goethite.

Results based solely on effluent Cr(VI) suggest that in situ reduction may be effective in remediating Cr-contaminated sediments; however, the level of filtered $Cr_{Dissolved}$ remained well above the DWS regardless of oxidation state (Figure 4A). Until Fe(II) breakthrough, the effluent Cr(VI) and $Cr_{Dissolved}$ concentrations were extremely consistent. The disappearance of Cr(VI) in the column effluent generally followed Fe(II) breakthrough leading to significant differences between Cr(VI) and $Cr_{Dissolved}$ with continued leaching. This suggests that the depressed pH associated with Fe(III) and Cr(III) hydrolysis, not observed in Cr-free columns leached with the same Fe(II) solutions, inhibits Cr(III) precipitation (Figure 4C).

Digested Cr_{Total} and $Cr_{Dissolved}$ for turbid effluents typically differed by less than 10%, indicating that, at least initially when the samples were filtered, Cr was predominately in the dissolved phase and not associated with colloids. Consistent with the batch results, the effluent pH was low enough to inhibit Cr(III) precipitation despite the fact that effluent concentrations were less than the reported solubility of $Fe_{0.75}Cr_{0.25}(OH)_3(am)$ (Figure 2D). Fe(II) breakthrough in sediments that had not been contaminated with Cr(VI) was compared with contaminated columns to estimate losses due to reactions other than Cr(VI) reduction. When such losses were accounted for, mass balance estimates indicated that 2.93 ± 0.22 mol of Fe(II) were consumed for each mole of Cr(VI) reduced, consistent with the 3-1 stoichiometry (Figure 4B).

Cr and Fe(II) Breakthrough: Buffered (pH 5.6) Fe(II) Treatment Solutions. Batch and column experiments demonstrated that in situ reduction and precipitation of Cr was

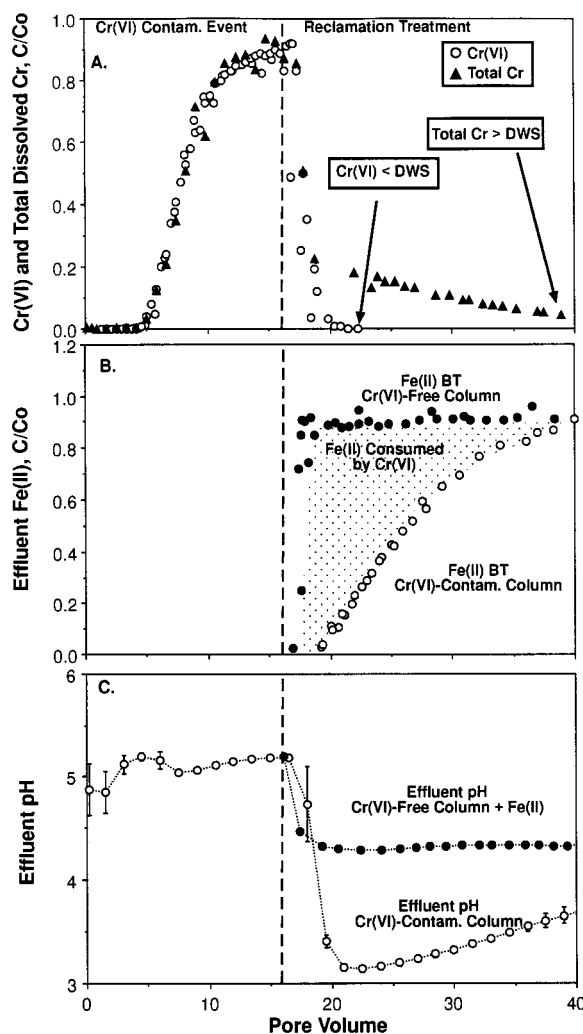


FIGURE 4. Effluent $Cr_{Dissolved}$ and Cr(VI) (A), Fe(II) (B), and pH (C) for Tobacco Rd sediment columns contaminated with Cr(VI) followed by 2.5 mM FeCl₂. Fe(II) breakthrough (B) and effluent pH (C) for Cr(VI)-free columns are included starting at 16 PV for comparison.

difficult, not because of the inability to reduce Cr(VI) using Fe(II) solutions, but because the resulting acidity inhibits Cr(III) precipitation. Thus, Fe(II) treatment solutions were buffered to favor the formation of a mixed Fe(III)/Cr(III)

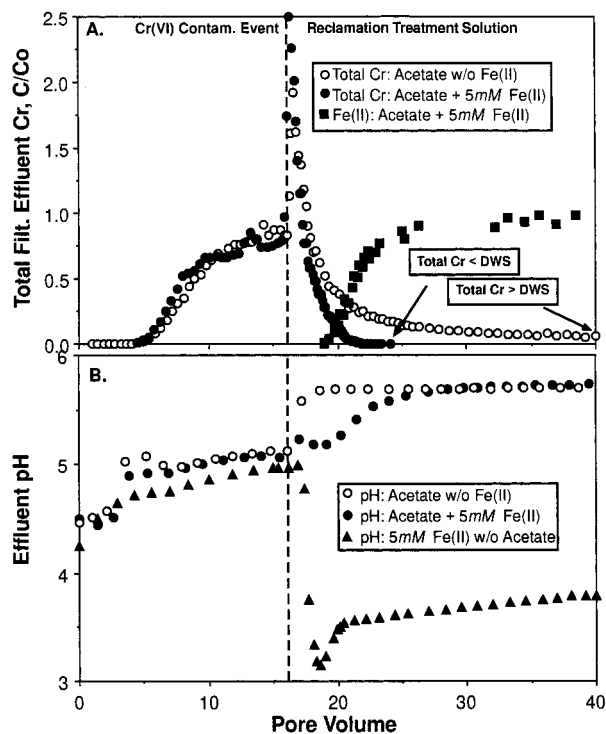


FIGURE 5. Effluent $\text{Cr}_{\text{Dissolved}}$, Fe(II) (A), and pH (B) for Tobacco Rd sediment treated with 0.05 M Na-acetate without Fe(II) or acetate-buffered (pH \approx 5.6) 5.0 mM FeSO_4 . The effluent pH for an unbuffered FeSO_4 treatment is given for comparison.

precipitate (i.e. pH > 4.7) without greatly increasing Fe(II) losses due to DO. Acetate was the chosen buffer because it (a) has an appropriate pK_a , 4.75, (b) is compatible with the ferrozine method (30), and (c) does not form strong complexes with Fe(II) , Fe(III) , or Cr(III) which could impact reaction kinetics or promote photochemical redox reactions which can occur in the presence of certain ligands (23, 39). For comparison, a Cr(VI) -contaminated column was leached with the buffer solution (50 mM Na-acetate) in the absence of Fe(II) . For treatments containing the buffer, a significant peak in effluent Cr(VI) , much greater than the inlet solution concentration, preceded Fe(II) breakthrough (Figure 5A), resulting in high effluent mass recoveries. As observed for SO_4^{2-} , competition with acetate for anion sorption sites enhanced Cr(VI) migration ahead of the Fe(II) reactant front, leaving less Cr(VI) available for reduction. Such results demonstrating the effect of spatially discrete, reactive plumes would be difficult, if not impossible, to mimic in batch-type experiments, illustrating the importance of dynamic studies for evaluating such coupled reaction/transport processes. Despite the high initial recoveries, effluent Cr(VI) for the acetate-buffered treatment without Fe(II) remained above DWS over the course of leaching.

As observed in batch, acetate was effective at buffering the effluent pH in the presence of Fe(II) oxidation and hydrolysis (Figure 5B). However, greater Fe(II) losses occurred for buffered compared to unbuffered Fe(II) treatments presumably due to the faster kinetics of Fe(II) oxidation by DO at the elevated pH. This indicates that higher Fe(II) application rates are necessary in the buffered system. When the greater loss of Fe(II) in buffered solution due to oxidation by DO was accounted for in control columns, Fe(II) and Cr(VI) effluent recoveries were still consistent with the 3–1 stoichiometry. Acetate-buffered effluents were generally free of turbidity, but rapid precipitation of Fe(III) resulted within hours of sample collection and exposure to O_2 .

Mass Recoveries and Residual Cr. Mass recoveries for effluent and extractable Cr as a function of remediation

treatment are summarized in Table 2. High mass recoveries, the sum of effluent and digestion extractable Cr minus native Cr, were observed for all of the column treatments, with typical recoveries >0.92. The PV at which effluent Cr(VI) fell below the DWS decreased significantly with increasing Fe(II) concentration (see statistical threshold reported above). However, at the lower pH induced by Fe(III) hydrolysis, Cr(III) was readily transported from the columns resulting in a similar effluent mass recovery regardless of the degree of Cr(VI) reduction. For example, effluent mass recoveries ($\text{Cr}_{\text{Dissolved}}$) were similar for all of the unbuffered Fe(II) treatments, ranging from 0.59 to 0.70. Only the acetate-buffered FeSO_4 solution successfully reduced the effluent $\text{Cr}_{\text{Dissolved}}$ levels to below the DWS. However, the enhanced Cr(VI) mobility in the presence of acetate actually increased Cr(VI) recovery compared to unbuffered Fe(II) treatments. Fe(II) solutions were effective at reducing or eliminating PO_4^{3-} -extractable Cr(VI) , with extractable Cr(VI) detected only at the lowest concentration of the unbuffered FeSO_4 treatment, 0.5 mM. The current results clearly illustrate the difficulties encountered in reclaiming a contaminated aquifer. Sorption reactions and diffusive transfer make it extremely inefficient to remediate an aquifer by simply capturing and treating the migrating plume. However, the adverse impact of alternative in situ treatment technologies may not be readily apparent, especially when evaluated in batch experiments. In addition to enhancing Cr(VI) mobility through competition for sorption sites, in situ reduction using Fe(II) solutions may result in well-screen or formation damage that limits the ability to continue long-term Fe(II) application, even though the present study observed no significant column plugging. Finally, the acidity generated by Fe(III) hydrolysis may enhance the mobility of Cr and other sorbed metal contaminants in poorly buffered systems. In shallow systems, Fe(II) can be readily incorporated within the contaminated zone of interest, thus making it more analogous to experimental batch equilibration systems. In such instances, Cr(VI) sorption and transport as affected by competitive anions has little influence on reduction. However, in systems where advective transport occurs, sorption behavior becomes critical since a reactive solution cannot be injected or applied without creating a hydraulic gradient away from the reactive application zone. Incomplete mixing in advective systems can severely limit the effectiveness of reactive chemical additives targeted for a contaminant which can be mobilized under changing geochemical conditions that may actually be induced by the treatment. In addition, depletion of the active agents in reactions other than those of interest, such as loss of Fe(II) through oxidation by DO, can limit the ability to deliver the reactive agent to the zone of interest. Care must be taken to ensure that in situ treatments do not actually increase rather than reduce the migration potential of the target contaminant.

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