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Hexavalent Chromium Removal by Reduction with Ferrous Sulfate, Coagulation, and Filtration: A Pilot-Scale Study

GANG QIN,*,† MICHAEL J. MCGUIRE,† NICOLE K. BLUTE,† CHAD SEIDEL,† AND LEIGHTON FONG‡

Malcolm Pirnie, Inc., Santa Monica, California, and Glendale Water and Power, Glendale, California

A flow-through pilot-scale system was tested for removal of Cr(VI) from contaminated groundwater in Glendale, California. The process consisted of the reduction of Cr(VI) to Cr(III) using ferrous sulfate followed by coagulation and filtration. Results indicated that the technology could reduce influent Cr(VI) concentrations of 100 μg L^{-1} to below detectable levels and also remove total Cr (Cr(VI) plus Cr(III)) to very low concentrations (<5 μg L^{-1}) under optimized conditions. Complete reduction of Cr(VI) to Cr(III) was accomplished with Fe(II) doses of 10–50 times the Cr(VI) concentration even in the presence of significant dissolved oxygen levels. The overall Cr removal efficiency was largely determined by the filterability of Cr(III) and Fe(III) precipitates, of which a relatively high filtration pH (7.5–7.6) and high filter loading rate (6 gpm ft^{-2}) had negative impacts. The pilot system was able to operate for an extended time period (23–46 h depending on the Fe:Cr mass ratio) before turbidity breakthrough or high head loss. Backwash water was effectively settled with low doses (0.2–1.0 mg L^{-1}) of high molecular weight polymer. Backwash solids were found to be nonhazardous by the toxicity characteristic leaching procedure but hazardous by the California waste extraction test.

Introduction

Chromium (Cr) is widely used in diverse products and processes (*1*). Industrial applications of Cr include electroplating, pigment production, leather tanning (*2*), and controlling biofilms in cooling towers (*3*). Inadequate storage and improper disposal practices of Cr have caused incidents of soil and groundwater contamination in many areas (*1*, *4*).

Cr redox species in aquatic systems primarily include trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI) (*5*). Cr(III) occurs primarily as a cation in solution and forms complexes with inorganic and organic ligands (*6*). Cr(III) hydroxide ($Cr(OH)_3$) exhibits a low solubility at a neutral pH range. In contrast, Cr(VI) occurs as an anion in the aqueous phase as $HCrO_4^-$, CrO_4^{2-}, or $Cr_2O_7^{2-}$ depending on pH and Cr(VI) concentration (*1*, *7*). The toxicity of Cr(III) and Cr(VI) differs significantly. Cr(III) is generally considered to be benign and an essential trace nutrient for animals and humans (*8*, *9*). Cr(VI) can be toxic to bacteria, plants, and animals (*10*, *11*).

Cr(VI) removal by reduction to Cr(III) with ferrous iron, Fe(II), and subsequent precipitation, coprecipitation, or coagulation has been investigated (*12*–*16*). This chemical process has also been widely used in industrial Cr treatment for concentrations in the milligram/liter range (*12*). Recent public concern regarding Cr(VI) in drinking water has prompted the investigation of treatment technologies with the potential to remove Cr to levels well below the current USEPA drinking water maximum contaminant level (MCL) of 100 μg L^{-1} and the California MCL of 50 μg L^{-1} for total Cr (i.e., Cr(VI) plus Cr(III)).

Only limited research has examined the possibility of achieving low Cr treatment goals using reduction processes to treat contaminated drinking water. Recent studies investigating the reduction of Cr(VI) with ferrous sulfate in batch bench-scale experiments yielded mixed results (*16*, *17*). The process was effective for the removal of Cr from drinking water in one study (*17*) but not in the other (*16*). Both studies demonstrated that ferrous sulfate effectively reduces Cr(VI) but that subsequent Cr(III) removal by filtration is not effective under all conditions. Since Cr(III) can be reoxidized to Cr(VI) by chlorine and chloramine disinfectants (*16*), removal of both Cr(III) and Cr(VI) (i.e., total Cr) is vital to a successful Cr treatment technology.

A reduction/coagulation/filtration (RCF) pilot system was constructed to evaluate the treatment process in Glendale, California. The purpose of the study was to determine the technological feasibility of the RCF system to treat Cr(VI) contaminated groundwater to less than 5 μg L^{-1} total Cr (i.e., greater than 95% removal efficiency). This work also addressed residuals management issues for the RCF process to understand disposal needs, including the potential for the separation of Cr-containing solids from backwash water and the hazardous characteristics of the residuals.

TABLE 1. Major Quality Parameters of the Glendale Groundwater Used for Pilot Testing

constituent	typical concentration
alkalinity	215 mg L^{-1} as $CaCO_3$
arsenic	0.5 μg L^{-1}
chloride	68 mg L^{-1}
conductivity	840 μS cm^{-1}
hardness	332 mg L^{-1} as $CaCO_3$
nitrate	5.3 mg L^{-1} as N
pH	7.4 pH units
phosphate	0.25 mg L^{-1} as PO_4
silicate	27 mg L^{-1} as SiO_2
sulfate	87 mg L^{-1} as SO_4
turbidity	0.09 NTU

Materials and Methods

Influent Water Preparation. Source water to the pilot system was provided by a blend of Glendale's North Operable Unit production wells at the Glendale Water Treatment Plant (GWTP). Table 1 shows major water quality parameters of the source water. The Cr(VI) concentration in the blended source water averaged 9 μg L^{-1} (*18*), although Cr(VI) levels in three of Glendale's eight wells approach 50–60 μg L^{-1}.

To evaluate potential removal of Cr(VI) from those high level wells, the source water was spiked with chromic acid (H_2CrO_4) (Acros Organics). Ten percent (w/v) chromic acid was spiked into a 100-gallon high-density polyethylene (HDPE) mixing tank using a flow-paced electronic metering

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* Corresponding author phone: (310) 829-1441; fax: (310) 829-2155; email: dqin@pirnie.com.
† Malcolm Pirnie, Inc.
‡ Glendale Water and Power.

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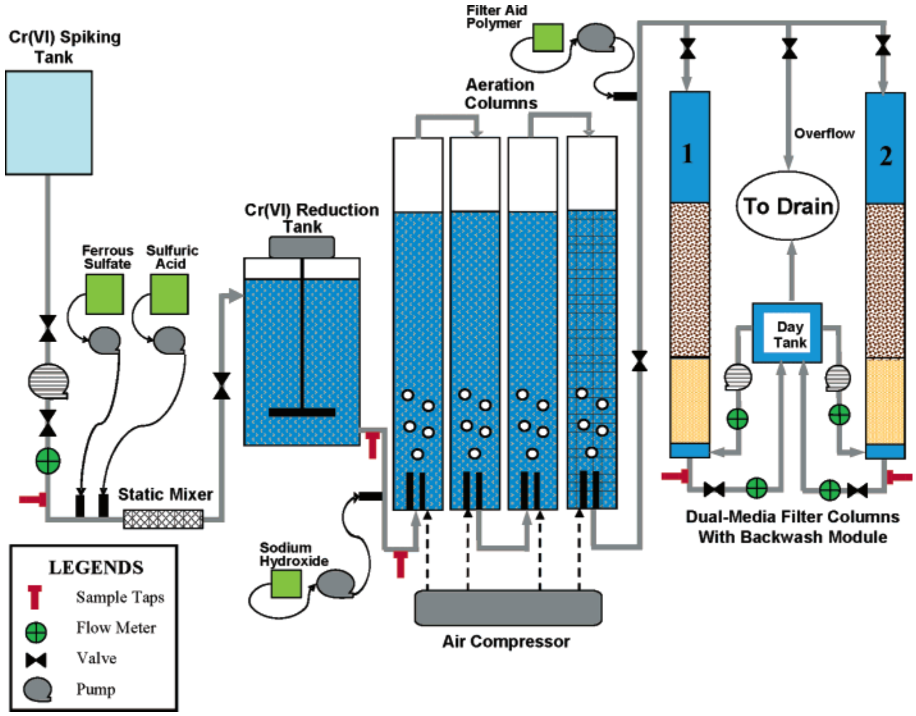

FIGURE 1. Schematic diagram of the RCF pilot system.

pump to achieve a Cr(VI) concentration of approximately 100 μg L^{-1}. The spiked tank water was then used as influent water fed to the RCF pilot system.

RCF Pilot System. The RCF pilot system consisted of the following major components: peristaltic chemical feed pumps for ferrous sulfate, sulfuric acid, sodium hydroxide, and polymer filter aid addition, a reduction tank, four aeration columns in series, two parallel granular dual-media filter columns, and a backwash module. Figure 1 shows a schematic diagram of the pilot system. The system received Cr(VI)-spiked water at a flow rate of approximately 2 gpm. Industrial-grade $FeSO_4$ (6% v/v, diluted from MKM 20% ferrous sulfate) was injected as a reductant in all tests. Analytical-grade H_2SO_4 (36N Fisher Brand) was added to adjust the pH in select tests. Influent water, $FeSO_4$, and H_2SO_4 were mixed in an inline static mixer before flowing into a 100-gallon reduction tank equipped with a variable-speed mechanical stirrer. The reduction tank provided approximately 1 h of detention time with continuous mixing, which was kinetically sufficient to enable the reaction of Cr(VI) with Fe(II) at near-neutral pH (*16*). Oxidation of Fe(II) to Fe(III) also occurred in the reduction tank and aeration columns due to the presence of 3−4 mg L^{-1} dissolved oxygen (DO) in the influent water.

The pilot system included an injection point on the effluent line from the reduction tank, into which analytical grade NaOH (50 wt %, FisherBrand) could be added for pH adjustment to maximize Fe(II) oxidation in the aeration columns. Water from the reduction tank was then pumped into four identical aeration columns operated in series, which were fit with coarse bubble diffusers. These columns were 10 ft. tall and 6 in. diameter, providing a total of approximately 30 min of detention time (with overflow of the columns allowed). An air compressor was used to blow air through coarse bubble diffusers installed at the bottom of the columns. The purpose of the aeration columns was to promote the oxidation of excess Fe(II) to Fe(III) with DO and facilitate the coagulation of Cr(III) with Fe(III). The aerated effluent was then filtered by one of two dual-media filters (filter 1 or 2) using 0.2 mg L^{-1} of filter aid polymer added upstream of the filters (Ciba MagnaFloc E40). The two granular media filters were 4.5 in. diameter filled with 12 in. of silica sand topped with 24 in. of anthracite coal. These columns were operated in parallel to simultaneously test different loading rates.

The backwash module consisted of a 55-gallon HDPE tank to store a portion of the treated effluent for backwash, an air compressor for filter scouring, and transfer pumps. Before each operational run, the columns were backwashed with air scouring and bed fluidization using approximately 10 gallons of water. The bed expansion rate was controlled at 20−30%, and the entire backwash procedure was complete within 10 to 12 min.

Experimental Conditions and Sampling Plan. Due to the number of pilot system components, a matrix of operating parameters was developed to determine the impacts of the different variables on Cr removal efficiency. In this study, the mass ratio (R) of Fe(II) to Cr(VI), pH in the reduction tank and aeration/filtration columns, filter loading rate, and filter operational run time were all evaluated. Table 2 lists the different test conditions of those parameters. Cr removal efficiency of processes within the treatment train or through the whole system was calculated as follows

$$\text{Cr removal efficiency} = (1 - [\text{Cr}_{\text{out}}]/[\text{Cr}_{\text{in}}]) \times 100\% \quad (1)$$

Sampling locations included the feedwater influent, the reduction tank, before and after the aeration columns, and the filtered effluent. Total Cr, Cr(VI), and total Fe concentrations were measured on influent and effluent samples every 2 h during normal 6 h operational runs. For extended 23 and 46 h runs, these parameters were measured every 3 h in effluent samples using an autosampler and at least once daily in influent water. Online turbidimeters and pressure sensors were installed on each filter column to continuously record turbidity and head loss measurements on chart recorders.

Laboratory Methods. All Cr samples were collected in new HDPE bottles in the field. Samples were collected for Fe analysis in certified trace metal clean bottles (IChem). Total Cr, Cr(VI), and total Fe concentrations were measured at the Utah State University Water Research Laboratory (USU). Immediately after collection, total Cr and total Fe samples were acidified to a pH of less than 2 with trace metal clean nitric acid (70% HNO_3, Fisher Brand). Cr(VI) samples

TABLE 2. Operating Conditions and System Performance of the RCF System. Data are Plotted for Runs 16 and 17 in Figures 3 and 4

run	Fe:Cr mass ratio (R)	reduction pH goal	aeration/ filtration pH goal	measured reduction pH	measured aeration/filtration pH	run duration (hr)	loading rate (gpm ft^{-2})		Cr removal rate (%)	
							filter 1	filter 2	filter 1	filter 2
1	50:1	ambient	ambient	7.3	7.3	6	6	4	87.1	99.7
2	50:1	6.5	ambient	6.6	6.7	6	6	4	99.9	99.8
3	50:1	6.5	7.5	6.7	7.5	6	6	4	28.6	47.4
4	50:1	7	7.5	7.1	7.6	6	3	4	80.0	83.1
5	50:1	7	ambient	7.1	7.1	6	3	4	98.7	99.7
6	50:1	ambient	ambient	6.9	7.2	6	3	4	99.1	99.4
7	50:1	ambient	ambient	7.0	7.3	6	3	4	100	100
8	25:1	6.5	7.5	6.6	7.5	6	3	4	97.4	88.2
9	25:1	ambient	ambient	7.3	7.5	6	3	4	100	100
10	25:1	ambient	ambient	7.3	7.5	6	3	4	100	100
11	25:1	ambient	ambient	7.2	7.5	6	3	4	99.9	99.9
12	25:1	6.5	ambient	6.6	6.9	6	3	4	99.9	100
13	10:1	6.5	7.5	6.5	7.5	6	3	4	98.9	99.1
14	10:1	6.5	ambient	6.5	6.9	6	3	4	99.7	99.7
15	10:1	ambient	ambient	7.3	7.5	6	3	4	95.2	96.1
16	25:1	ambient	ambient	7.1	7.4	46	4			
17	15:1	ambient	ambient	7.1	7.4	23	4			

were preserved with NaOH to pH > 10 and analyzed within 30 days. For total Cr and total Fe, an aliquot was removed and filtered with a 0.45-μm filter prior to analysis. Then the remaining sample was digested using 4% HCl with 2% of a 10% (w/v) hydroxylamine−hydrochloride solution at 85 °C for 24 h to dissolve any iron precipitates. Both digested and undigested splits were analyzed, and little difference was observed. Digested sample results are reported in this paper, thereby reflecting the maximum amount of Cr and Fe that passed through the filters.

Total Cr and Fe concentrations were measured using an Agilent 7500C inductively coupled plasma mass spectrometer (ICP-MS) with octopole reaction system, in accordance with EPA Method 200.8 (*19*). The octopole system used helium gas at 6 mL min^{-1} as a collision gas to eliminate the ^{40}Ar^{12}C mass interference with ^{52}Cr. Germanium (^{74}Ge) was used as the internal standard. Cr(VI) samples were analyzed using a Dionex DX-320 ion chromatograph (IC) with an AD25 postcolumn UV−visible detector according to EPA Method 1636 (*20*). The guard column was a Dionex Ion Pac NG 1, and the analytical column was a Dionex Ion Pac AS 7. The sample loop volume was 500 μL with a reaction coil of 750 μL.

Hazardous characteristics of the settled backwash solids were also determined in the USU laboratory. Two tests were performed, including the federal toxicity characteristic leaching procedure (TCLP) (*21*) and the California waste extraction test (WET) (*22*).

Total suspended solids (TSS) in backwash water were measured using EPA Method 160.2 (*23*) by a certified laboratory.

Field Methods. Water quality parameters were also measured in the field immediately after sample collection. pH was determined using a Hach SensION 1 portable pH meter with a gel-filled electrode (*25*). In addition to the online turbidimeter, turbidity grab samples were determined using a Hach 2100P meter (*25*). For real-time screening of Cr(VI) reduction in the RCF process, Cr(VI) was measured with onsite colorimetry using the ChromaVer 3 Hach Method 8023 with diphenylcarbohydrazide reagent (*24*). However, field measurements of Cr(VI) are not reported in this paper because the method was not sensitive enough to reliably detect concentrations below 10 μg L^{-1}.

Residuals Management. Waste minimization and disposal options for Cr-containing backwash water and solids were investigated as part of the feasibility evaluation of RCF for drinking water treatment. Approximately 10 gallons of backwash water from one of the filter columns was collected, and a portion of the backwash solid-laden water was split into six 2-L jar testers (Phipps and Bird B-KER^2). Cationic (Ciba LT 22S), nonionic (Ciba LT 20), and anionic (Ciba Magnafloc E40) high molecular weight polymers were tested for their efficiency in settling the backwash solids from water. The three polymers were dosed into separate jars at two different concentrations (0.2 and 1.0 mg L^{-1}), and the suspensions were immediately mixed at 300 rpm for 2 min then allowed to settle. Supernatant samples were collected at 1, 2.5, 5, 10, 15, and 20 min intervals for total Cr and Fe analyses.

Since the nonionic polymer dosed at 1.0 mg L^{-1} demonstrated the most rapid settling in jar testing, the remaining backwash solution was settled using this polymer at a 1.0 mg L^{-1} dose. The settled solids were collected and tested for hazardous or nonhazardous waste classification using the TCLP and WET procedures.

Results and Discussion

A total of 17 operational runs were conducted in this pilot study (Table 2). The first 15 runs were conducted for 6 h to evaluate the feasibility of achieving less than 5 μg L^{-1} of total Cr in the effluent and to optimize operating conditions. Two extended runs (runs 16 and 17) were conducted for 23 and 46 h durations.

Reduction of Cr(VI) to Cr(III). Cr(VI) reduction coupled with Fe(II) oxidation requires a 3:1 molar ratio of Cr(VI) to Fe(II)$_{(aq)}$ at pH > 6.5, yielding a solid with this molar ratio that may contain Cr(III) either sorbed to or coprecipitated with Fe(III) hydroxide (*12*, *17*). In well-oxygenated aqueous systems, DO can also oxidize Fe(II) (*12*, *17*), whereby the stoichiometric oxidation of Fe(II) by DO occurs in a molar ratio of 4:1 (Fe(II):O$_2$). At pH > 7, Cr(VI) reduction may be impacted by the reaction of DO with Fe(II) (*17*).

In the pilot study, the Fe(II) doses selected ranged from 10 to 50 times the Cr(VI) mass (~100 μg L^{-1}), corresponding to a molar ratio ranging from 9:1 to 56:1. Cr(VI) concentrations were measured on both the unfiltered influent and 0.45 μm filtered effluent from the reduction tank to determine Cr(VI) in solution after the reduction tank. An average of 99.7% Cr(VI) reduction efficiency was achieved for runs with an *R* value of 50:1 and 25:1 and 98.5% with a mass ratio (*R*) value of 10:1. Therefore, high concentrations of Fe(II) (*R* = 10:1 to 50:1) resulted in near complete Cr(VI) reduction in the presence of 3 to 4 mg L^{-1} of DO.

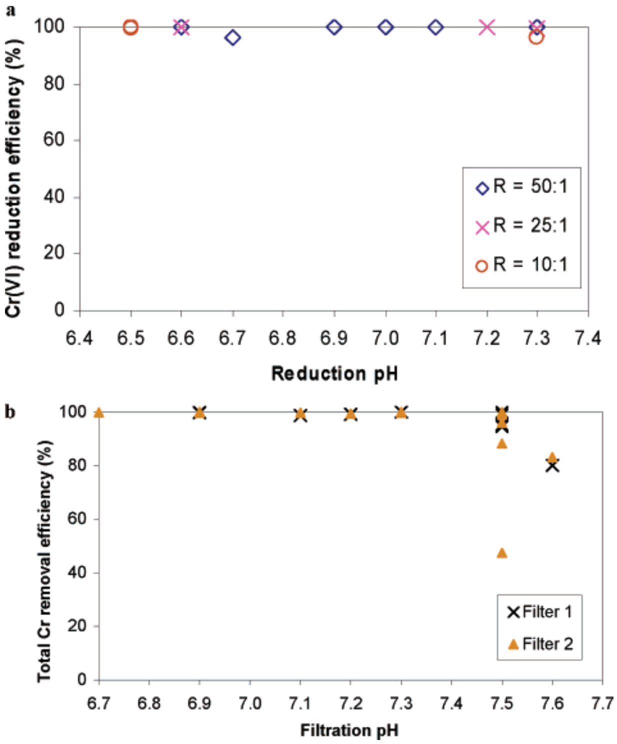

FIGURE 2. The impact of pH on pilot system performance. (a) Impact of pH on Cr(VI) reduction efficiency in the reduction tank for Fe:Cr mass ratios of 50:1, 25:1, and 10:1. (b) Impact of filtration pH on total Cr removal efficiency through the whole RCF process

Three pH conditions were tested in the reduction tank: 6.5, 7.0, and ambient pH (approximately 6.9 to 7.3). The pH targets of 6.5 and 7.0 were maintained within 0.1 pH unit with H_2SO_4 injection into the influent line upstream of the reduction tank. Table 2 shows the actual pH in the reduction tank for each run. The purpose of testing lower pH conditions in the reduction tank was to enhance Cr(VI) reduction relative to Fe(II) oxidation by DO and to limit the reaction of Fe(II) with silicate, which was hypothesized to inhibit Cr(VI) reduction in bench scale work using Glendale groundwater (*16*). Figure 2a shows the Cr(VI) reduction efficiency as a function of pH inside the tank. Little variation observed for Cr(VI) removal between pH 6.5 and 7.3 indicated that pH was not an important parameter in reducing Cr(VI) to Cr(III) for this range when excess Fe(II) was present. Therefore, pH control in the reduction tank was determined to be unnecessary for the RCF system when treating Glendale groundwater.

Removal of Total Cr and Fe by Aeration and Filtration. Since greater than 98% of Cr(VI) was reduced within the reduction tank, the overall Cr removal efficiency using the RCF system depended on the removal of Cr(III) by subsequent aeration and filtration.

On the basis of the 4:1 stoichiometry between Fe(II) and DO, the source groundwater (DO of 3−4 mg L^{-1} or 94−125 μM) would be able to theoretically oxidize up to 500 μM (28 mg L^{-1}) of Fe(II), which is far greater than the Fe(II) dosage used in the pilot study (up to 5 mg L^{-1} of Fe(II) at R = 50:1). An additional aeration step was included in the RCF system to promote the oxidation and precipitation of excess Fe(II). The aeration columns provided longer time (which may have been necessary at lower pH), additional DO, and a turbulent flow scheme to promote complete Fe(II) oxidation and coagulation. As a side note, bench-scale studies had previously demonstrated that oxygen is not likely to reoxidize Cr(III) to Cr(VI) (*16*).

The aeration step may not be needed if further research confirms that most of the Fe(II) to Fe(III) oxidation by ambient DO occurs in the reduction tank. This study did not assess Fe oxidation directly but rather focused on Cr(VI) reduction and removal. Data collected, however, showed that 0.45 μm filtered total Fe concentrations measured between the effluent from the reduction tank and effluent from the aeration columns exhibited a clear reduction in soluble or colloidal Fe during transport through the aeration columns, which may reflect coagulation and formation of precipitates large enough to be trapped on a 0.45 μm filter.

Two critical operating conditions identified for total Cr and Fe removal were filter loading rate and filtration pH. Table 2 lists the total Cr removal efficiency from runs 1 to 15 (6 h runs). The system was largely capable of achieving the 95% removal goal, with the exception of several anomalous runs.

Filter Loading Rate. The filters were operated at 3, 4, and 6 gpm ft^{-2}. During the first three runs, filtration rates of 4 and 6 gpm ft^{-2} were tested in parallel. In runs 1 and 3, the total Cr removal efficiency of filter 1 (6 gpm ft^{-2}) was lower than that of filter 2 (4 gpm ft^{-2}) by 13 and 19%, respectively. In run 2, however, there was no difference in the total Cr removal efficiency between filters 1 and 2. Although it is difficult to draw any conclusions from these limited data, the better performance from runs 6 and 7, which were operated under the same conditions as run 1 except at reduced filtration rates (3 and 4 gpm ft^{-2}), supported the hypothesis that high filtration rate (6 gpm ft^{-2}) had an adverse impact on total Cr removal. The filtration rate of 6 gpm ft^{-2} was suspended from testing in the subsequent runs due to these initial findings.

Filtration pH. Higher pH values (e.g., 7.5 compared to 6.5) have been found to increase the Fe(II) oxidation rate by DO (*26*, *27*). For several runs, NaOH was added prior to the aeration columns to raise the pH to promote complete Fe(II) oxidation. Two pH conditions were evaluated: 7.5 and ambient (on average 7.2−7.3, but ranging up to 7.5). Under ambient conditions, the aeration/filtration pH was higher than the reduction pH by an average of 0.2 pH units (Table 2), which may be due to losses of CO_2 in the aeration columns.

Figure 2b shows that pH in the aeration and filtration processes might be crucial to achieving greater than 95% total Cr removal. Note that results from filter 1 of runs 1−3 were not included in the figure due to the higher filtration rate (6 gpm ft^{-2}). For pH values less than 7.5, total Cr removal efficiency was greater than 98%. For filtration at pH 7.5−7.6, the total Cr removal efficiency decreased to less than 50% on occasion. Speciation of the filter effluent samples on all runs (runs 1−17) showed negligible Cr(VI), demonstrating that the major Cr species in the effluent, when measurable, was Cr(III). The lesser degree of total Cr removal at higher pH (7.5−7.6) might be due to differences in particle filterability at the higher pH. More research would be necessary to identify the differences in Fe(III) and Cr(III) precipitate formation under various pH conditions.

Extended Runs. Runs 16 and 17 were operated for an extended period of time to demonstrate the system capability for longer filter runs, which would reduce backwash needs. The operating conditions for these extended runs were determined based on the system performance from the previous 15 runs. Ambient pH conditions in both reduction tank and aeration/filtration processes were chosen due to the excellent total Cr removal efficiencies (>99%) observed in runs 6−9 and 11, which had no pH control. An *R* value of 25:1 or 15:1 was used along with a filtration rate of 4 gpm ft^{-2} (Table 2). Runs 16 and 17 were terminated when filter breakthrough occurred or head loss across the filter exceeded 100 in. of water.

The pilot system was able to achieve the goal of 95% Cr removal for an extended time (23 to 46 h). In Run 16, the effluent total Cr concentration was below 2 μg L^{-1} for up to

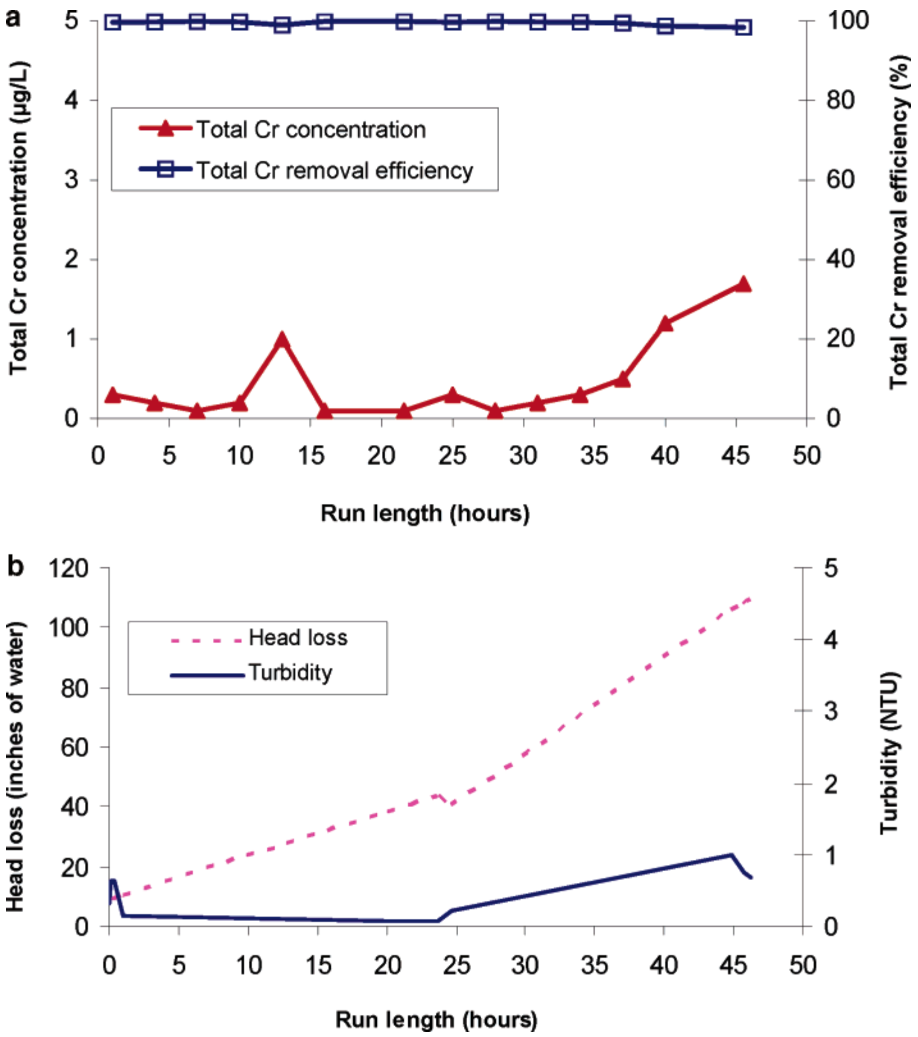

FIGURE 3. RCF system performance of extended Run 16 with a 25:1 Fe:Cr mass ratio and no pH adjustments. (a) Total Cr removal performance for run 16, including total Cr effluent concentrations and total Cr removal efficiency. (b) Head loss and effluent turbidity profiles for run 16.

46 h of operation (Figure 3), corresponding to a Cr removal efficiency of greater than 98%. Run 17 lasted 23 h, during which the effluent total Cr concentration was below the detection limit of 1.0 μg L^{-1} (Figure 4).

Although runs 16 and 17 were operated under identical conditions with the exception of the Fe:Cr mass ratio, the patterns of turbidity and head loss profiles significantly differed. In run 16 (Figure 3), the effluent turbidity was less than 1 NTU, demonstrating that no filter breakthrough occurred after 46 h of operation. The system operation was terminated at that time due to the head loss across the filter column that exceeded 100 in. of water, which is a typical terminal head loss value for modern treatment plants to avoid turbidity breakthrough and air binding (*28*). In run 17 (Figure 4), filter breakthrough occurred after 23 h of operation when the effluent turbidity increased from less than 0.1 NTU to 46 NTU within 5 min and remained above 10 NTU. The head loss of run 17 gradually increased from 10 to 23 in. of water over the 23-h period.

The difference in turbidity and head loss profiles for runs 16 and 17 likely reflects different mechanisms of filtration. In run 16, physical straining at the filter surface was the principal filtration mechanism, as evidenced by the steady increase in head loss without a turbidity breakthrough (*29*). A nonstraining mechanism prevailed in run 17, in which Cr(III) and Fe(III) precipitates penetrated into the filter media causing a slow increase in head loss followed by a rapid turbidity breakthrough as the precipitate storage capacity of the filter was exceeded.

Particle size is a major factor in determining the mechanism of filtration in a granular dual-media filter. The difference in total Cr removal profiles in runs 16 and 17 may be explained by the higher Fe:Cr ratio (25:1), which could form bigger particles that were effectively removed by physical straining. The lower Fe:Cr ratio (15:1) may have formed smaller particles that penetrated the filter bed and were removed not by straining but by retention in the filter media bed. These findings suggest that a higher Fe:Cr mass ratio is more effective at trapping Fe(III) and Cr(III) particles for longer filter runs. If straining at the filter surface is chosen as the removal mechanism, sufficient hydraulic head must be applied to overcome the rapid buildup in the head loss.

Residuals Management. For RCF backwash solids, cationic and nonionic polymer exhibited a faster settling rate compared to anionic polymer, and TSS analysis on the backwash water showed that the backwashing protocol used was sufficient (specific details contained in Supporting Information). Figure 5 reveals the total Cr and Fe concentrations in the backwash water after 20 min of settling with each polymer and dose. The backwash water contained less than 100 μg L^{-1} of total Cr and 10 mg L^{-1} of iron for each case. Under higher dose conditions (i.e., 1.0 mg L^{-1} cationic polymer), the backwash water contained only 0.5 μg L^{-1} of total Cr and 4.6 mg L^{-1} of total Fe. On the basis of these

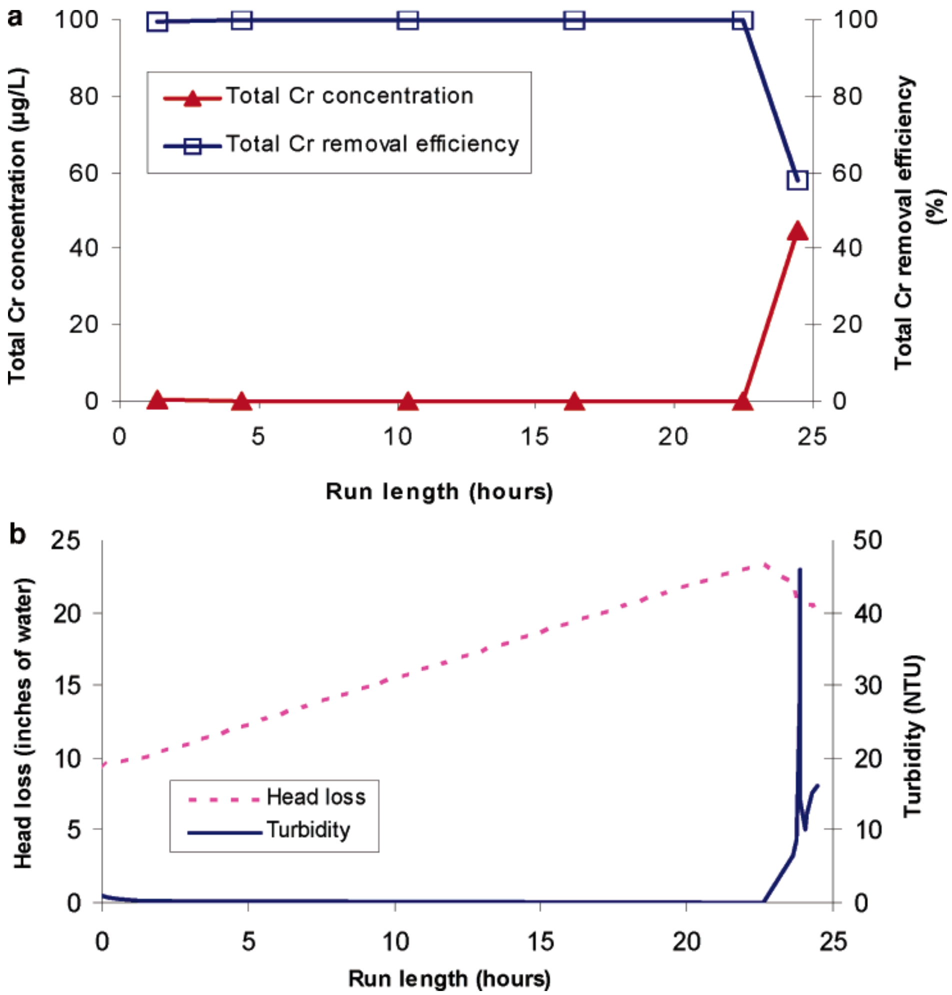

FIGURE 4. RCF system performance for extended run 17 with a 15:1 Fe:Cr mass ratio and no pH adjustments. (a) Total Cr removal performance for run 17, including total Cr effluent concentrations and total Cr removal efficiency. (b) Head loss and effluent turbidity profiles for run 17.

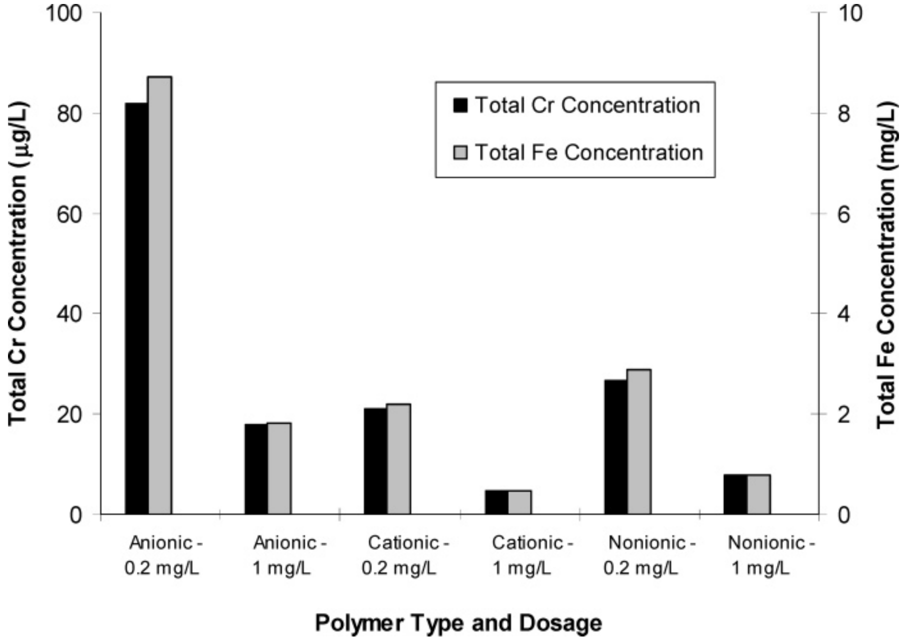

FIGURE 5. Total Cr and total Fe concentrations in RCF backwash water after 20 min of settling with three types of high molecular weight polymer at two doses (0.2 mg L^{-1} and 1.0 mg L^{-1}).

results, the backwash water supernatant may be recyclable to the system influent.

The backwash solids settled with 1.0 mg L^{-1} nonionic polymer were tested using TCLP and California WET tests to determine whether the solids should be classified as hazardous or nonhazardous waste (*21*, 22). The total Cr concentration in the TCLP extraction fluid was 0.003 mg L^{-1} —much lower than the regulatory level of 5.0 mg L^{-1}, indicating the settled backwash solids were nonhazardous for total Cr under federal regulations. However, the total Cr concentration determined by the WET test was 9.8 mg L^{-1}—exceeding the 5.0 mg L^{-1} for soluble threshold limit concentration. Therefore, the backwash solids would be characterized as hazardous waste for disposal in California, which could increase the overall treatment cost of the RCF system by requiring disposal at a hazardous waste facility.

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Supporting Information Available

Figure S1 provides Supporting Information on the effectiveness of different coagulant aids on settling of backwash solids. Figure S2 shows TSS analysis results as a function of time for backwash solid settling. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Nriagu, J. O.; Nieboer, E. *Chromium in the Natural and Human Environments*; John Wiley and Sons: New York, 1988.
(2) Fishbein, L. Sources, transport and alterations of metal compounds: an overview. I. Arsenic, beryllium, cadmium, chromium, and nickel. *Environ. Health Persp.* **1981**, *40*, 43−64.
(3) Lund, H. F. *Industrial Pollution Control Handbook*; McGraw-Hill: New York, 1971.
(4) Palmer, C. D.; Wittbrodt, P. R. Processes Affecting the Remediation of Chromium-Contaminated Sites. *Environ. Health Perspect.* **1991**, *92*, 25−40.
(5) Bartlett, R. J. Chromium cycling in soils and water: links, gaps, and methods. *Environ. Health Perspect.* **1991**, *92*, 17−24.
(6) Hartford, W. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley and Sons: New York, 1979; Vol. 6.
(7) USEPA. Toxicological review of hexavalent chromium. CAS No. 18540-29-9. U.S. Environmental Protection Agency: Washington, D.C, 1998.
(8) Anderson, R. A. Recent advances in the clinical and biochemical effects of chromium deficiency. *Prog. Clin. Biol. Res.* **1993**, *380*, 221−234.
(9) Anderson, R. A. Chromium and parental nutrition. *Nutrition* **1995**, *11*, 83−86.
(10) Richard, F. C.; Bourg, A. C. M. Aqueous geochemistry of chromium: a review. *Water Res.* **1991**, *25*, 807−816.
(11) Kimbrough, D. E.; Cohen, Y.; Winer, A. M.; Creelman, L.; Mabuni, C. A critical assessment of chromium in the environment. *Crit. Rev. Environ. Sci. Technol.* **1999**, *29*, 1−46.
(12) Eary, L. E.; Rai, D. Chromate removal from aqueous wastes by reduction with ferrous ion. *Environ. Sci. Technol.* **1988**, *22*, 972−977.
(13) Fendorf, S. E.; Li, G. Kinetics of chromate reduction by ferrous iron. *Environ. Sci. Technol.* **1996**, *30*, 1614−1617.
(14) Sedlak, D. L.; Chan, P. G. Reduction of hexavalent chromium by ferrous iron. *Geochim. Cosmochim. Acta* **1997**, *61*, 2185−2192.
(15) Schlautman, M. A.; Han, I. Effects of pH and dissolved oxygen on the reduction of hexavalent chromium by dissolved ferrous iron in poorly buffered aqueous systems. *Water Res.* **2001**, *35*, 1534−1546.
(16) Brandhuber, P.; Frey, M.; McGuire, M. J.; Chao, P.; Seidel, C.; Amy, G.; Yoon, J.; McNeill, L.; Banerjee, K. Treatment options for low-level hexavalent chromium removal tested at bench scale. Awwa Research Foundation, 2004.
(17) Lee, G.; Hering, J. G. Removal of chromium(VI) from drinking water by redox-assisted coagulation with iron(II). *J. Water Supply: Res., Technol. Aqua* **2003**, *52*, 319−332.
(18) Glendale Water & Power. Water quality report. 2002, Glendale, CA.
(19) USEPA. Method 200.8: Determination of trace elements in waters and wastes by inductively coupled plasma mass spectrometry. EPA-600/R-94/111, 1994.
(20) USEPA. Method 1636: Determination of hexavalent chromium by ion chromatography. EPA-821/R-96/003, 1996.
(21) USEPA. Test methods for evaluating solid waste, physical/chemical methods. Publication SW-846, 1998.
(22) Department of Toxic Substances Control. Title 22, California Code of Regulations, Division 4.5, Chapter 11, Appendix II.
(23) USEPA. Method 160.2: Residue, Non-Filterable, Gravimetric, Dried at 103−105 °C (TSS). In Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, 1983.
(24) Hach Company. Hach DR/890 colorimeter procedures manual. 2004, Loveland, Colorado.
(25) APHA, AWWA, and WEF. Standard methods for the examination of water and wastewater, 19th ed. American Public Health Association, Washington, DC, 1995.
(26) Sung, W.; Morgan, J. J. Kinetics and product of ferrous iron oxygenation in aqueous systems. *Environ. Sci. Technol.* **1980**, *14*, 561−568.
(27) Davison, W.; Seed, G. The kinetics of the oxidation of ferrous iron in synthetic and natural waters. *Geochim. Cosmochim. Acta* **1983**, *47*, 67−79.
(28) AWWA and ASCE. *Water Treatment Plant Design*, 4th ed.; McGraw-Hill: New York, 2004.
(29) Montgomery, J. M. Consulting Engineers, Inc. *Water Treatment Principles and Design*; John Wiley and Sons: New York, 1985.

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