The goal of this research was the initial evaluation of several pilot-scale treatment technologies for hexavalent chromium removal to <5 µg/L (i.e., 95% removal). A major focus was to assess manufacturer-provided pilot systems with media that were effective in bench-scale studies as well as technologies that were promising but could not be appropriately tested at bench scale. The technologies tested included ion exchange systems (i.e., column strong-base and weak-base anion exchange and reactor-based strong-base anion exchange), a reduction/filtration unit using sodium sulfite, and proprietary adsorptive media systems (zeolite and granular activated carbon). In vendor-independent tests, reduction with ferrous sulfate, coagulation, and filtration was also evaluated. Regeneration efficiency was determined for the best-performing strong-base anion exchange resin, including the effect of recycling brine to minimize residuals. Technologies able to consistently treat to concentrations <5 µg/L included column strong-base anion exchange, weak-base anion exchange, and reduction–coagulation–filtration using ferrous sulfate.

BY MICHAEL J. MCGUIRE,
NICOLE K. BLUTE,
CHAD SEIDEL, GANG QIN,
AND LEIGHTON FONG

Pilot-scale studies
of Hexavalent Chromium Removal
from drinking water

D rinking water utilities face the challenge of addressing emerging water quality concerns to ensure adequate protection of public health, sometimes without final federal or state drinking water regulations. Total chromium, i.e., trivalent chromium [Cr(III)] plus hexavalent chromium [Cr(VI)], has been regulated by national drinking water regulations since 1975. The federal regulatory maximum contaminant level (MCL) for total Cr is 100 µg/L, whereas the MCL in California is 50 µg/L. Although no federal limit has been established for Cr(VI) in drinking water, California's Department of Health Services has a mandate by state law to establish a Cr(VI)-specific MCL. The Cr(VI) carcinogenic de minimis risk level established by the state in 1999 was 0.2 µg/L, which contributed to a public health goal (PHG) of 2.5 µg/L for total Cr (OEHHA, 1999). Although this PHG was later rescinded and is currently under review, the potential for a new MCL for Cr(VI) and a lower California MCL for total Cr provided the impetus to identify treatment technologies able to remove Cr to levels far lower than the current limits.

In 2000, public concern about the presence of Cr(VI) in drinking water was stimulated in large part by the movie *Erin Brockovich*, which highlighted a groundwater Cr pollution lawsuit in Hinkley, Calif. In response to this public concern, the city of Glendale, Calif. with the participation of the California cities of Los Angeles, Burbank, and San Fernando, initiated a four-phase program to

A flow-paced chromium spiking system was used to deliver 100 µg/L hexavalent chromium to the influent groundwater source (left) that was used in the pilot units. Parallel lead/lag pilot-scale trains of strong base (two large canisters) and weak base (small canisters) anion exchange resin were used for the study (second from left). Ion exchange columns tested strong-base anion exchange with brine regeneration and recycle (second from right). An autosampler was used to collect samples from the ion exchange skid to capture chromatographic peaking (right).

develop full-scale treatment capable of removing Cr(VI) from San Fernando Valley groundwater, which contains plumes of high Cr(VI) concentrations resulting from poor historical disposal practices.

As recently as Feb. 23, 2005, the *Los Angeles Times* reported that a well monitoring the movement of a Cr(VI) plume from a Pacific Gas & Electric contamination site (the Topock station) near the Colorado River contained 354 µg/L of Cr(VI) (*Los Angeles Times*, 2005). The well is only 60 ft (18 m) from the river and upstream of the withdrawal points for southern California and Arizona water supplies. Such reports have kept Cr(VI) in the public eye and have resulted in a continued effort to develop cost-effective treatment technologies that can remove Cr(VI) to very low µg/L concentrations.

Glendale's four-phase program includes (1) a bench-scale study that improved the understanding of fundamental Cr chemistry and screened promising treatment technologies (Brandhuber et al, 2004), (2) a pilot-scale

study that evaluated treatment technologies for removing Cr(VI) to low concentrations in Glendale groundwater, (3) a demonstration-scale study that will finalize the technology evaluation and address additional costs and residuals issues, and (4) full-scale implementation of an effective Cr(VI) treatment technology. This article reports on the results of the pilot-scale tests for a variety of Cr(VI) treatment technologies.

Until this comprehensive program, no treatment technology had been shown to reliably reduce Cr(VI) in drinking water to concentrations <5 µg/L. Industrial and hazardous waste applications of various technologies, including anion exchange (Rengaraj et al, 2003; Rengaraj et al, 2001; Yalcin et al, 2001; Jakobsen & Laska, 1977) and reduction with ferrous iron (Schlautman & Han, 2001; Sedlak & Chan, 1997; Fendorf & Li, 1996; Eary & Rai, 1988), typically treated Cr(VI) to levels 10–1,000 times greater than those targeted in this testing. Bench-scale drinking water studies have shown that Cr(VI) can be removed by strong-base anion (SBA) exchange (Bahowick et al, 1996; Clifford, 1990), by reduction of Cr(VI) to Cr(III) (Lee & Hering, 2003), by adsorptive media, and by reverse osmosis (Brandhuber et al, 2004). Initial tests in Germany and China have also suggested that weak-base anion (WBA) exchange resin may be effective at removing Cr(VI) from water (Höll et al, 2002).

The objective of this pilot study was to evaluate the performance of a number of Cr(VI) treatment technologies and identify an effective treatment option for demonstration-scale testing. Factors considered in the performance evaluation included the ability to remove Cr to low concentrations, the effect of Glendale groundwater quality on technology

TABLE 1   Water quality of Glendale, Calif., source water for pilot testing

Constituent	Average Concentration in Blended Water From NOU Wells
Alkalinity—*mg/L as CaCO$_3$*	215
As—*µg/L*	0.5
Cl—*mg/L*	68
Conductivity—*µmho/cm*	850
Hardness—*mg/L as CaCO$_3$*	332
NO$_3$ as N—*mg/L*	5.3
pH	7.4
PO$_4$—*mg/L*	0.25
SiO$_4$—*mg/L*	27
SO$_4$—*mg/L*	90
Turbidity—*ntu*	0.09

As—arsenic, CaCO$_3$—calcium carbonate, Cl—chloride, N—nitrogen, NO$_3$—nitrate, NOU—north operable unit, PO$_4$—phosphate, SiO$_4$—silicate, SO$_4$—sulfate

TABLE 2 Pilot tests of vendor-supplied treatment technologies

Technology	Volume of Media	Flow Rate	EBCT or Contact Time	Residual
SBA resin (column)*	0.35 cu ft (0.010 m³)	1.5–2.0 gpm (5.7–7.6 L/min)	1–2 min	Brine
GAC adsorption*	0.35 cu ft (0.010 m³)	0.5 gpm (1.9 L/min)	5 min	Media
Reduction/filtration†	NA	0.5 gpm (1.9 L/min)	NA	Backwash
Magnetized ion exchange (continuous reactor)‡	40–60 mL resin/L water	2.5 gpm (9.5 L/min)	30-min contact time	Brine
SBA resin (column)§	1 cu ft (0.028 m³) per column	2.0 gpm (7.6 L/min)	3–4 min per column	Brine
WBA resin (column)§	0.5 cu ft (0.014 m³) per column	1.5–2.0 gpm (5.7–7.6 L/min)	2–3 min per column	Media
Surface reduction/zeolite adsorption**	7 cu ft (0.20 m³) in six serial columns	1.5–2.0 gpm (5.7–7.6 L/min)	30-min total	Media

*Calgon Carbon Corp., Pittsburgh, Pa.
†Filtronics Inc., Anaheim, Calif.
‡Orica Watercare, Denver, Colo.
§US Filter Corp., Warrendale, Pa., and Rohm & Haas Co., Philadelphia, Pa.
**Water Remediation Technology, Arvada, Colo.

EBCT—empty bed contact time, GAC—granular activated carbon, NA—not applicable, SBA—strong-base anion, WBA—weak-base anion

performance, system operational requirements, and residuals stream disposal needs. Because Cr(III) is oxidized to Cr(VI) in distribution systems by chlorine and chloramines (Brandhuber et al, 2004), the successful technology was required to remove both Cr(III) and Cr(VI).
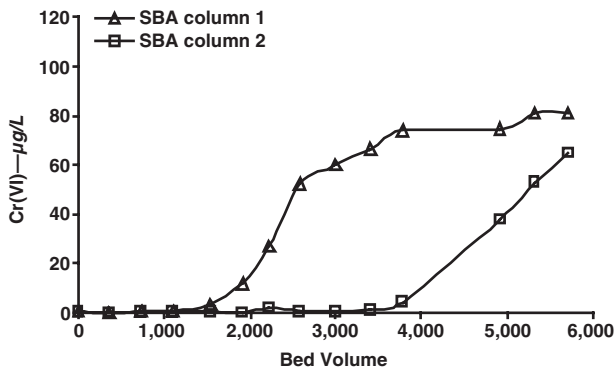
MATERIALS AND METHODS

Groundwater quality. Water for pilot testing was obtained from Glendale's North Operable Unit wells, a US Environmental Protection Agency (USEPA) Superfund site in the San Fernando Valley. General water quality is shown in Table 1. As a blend from the four NOU wells, Glendale groundwater averaged 10 µg/L Cr(VI). To reflect higher concentrations in individual wells and provide more rigorous testing above method detection limits, the Cr(VI) concentration in the blended source water was spiked to 100 µg/L Cr(VI) using a flow-paced metering pump with diluted 10% chromic acid.[1]
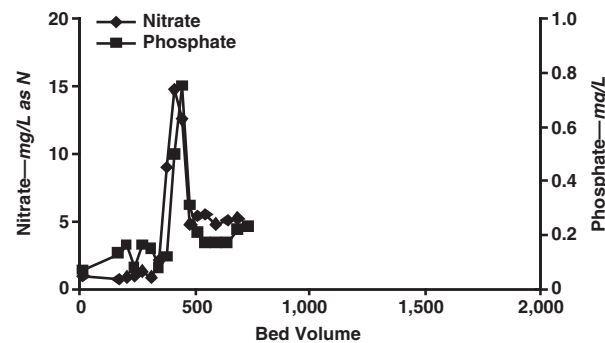
Pilot units. Pilot-tested technologies were selected from manufacturer responses to a request for proposals. Selection criteria included the technological feasibility of the approach for Cr(VI) removal, maturity of the technology, past performance in testing, capability for scaling up to full-scale treatment, and certification status by the National Sanitation Foundation. Technologies tested included (1) SBA and WBA exchange columns (provided by two vendors in partnership), (2) SBA exchange and granular activated carbon (GAC) columns (provided by a different vendor), (3) reactor-based magnetized ion exchange, (4) zeolite adsorptive media, and (5) reduction with sodium bisulfite or sulfite followed by filtration.

FIGURE 1 Cr(VI) breakthrough curves for SBA 1

Cr(VI)—hexavalent chromium, SBA—strong-base anion

FIGURE 2 Chromatographic peaking of nitrate and phosphate for SBA 1

N—nitrogen, SBA—strong-base anion

Each pilot unit received spiked influent water at a flow rate of between 0.2 and 2.0 gpm (0.8 and 7.6 L/min), according to manufacturer specifications. Table 2 lists the type of technology, flow rate, volume of media, empty bed contact time (EBCT), and type of residuals waste for each pilot technology tested.

The first pilot unit included two separate treatment trains for SBA and WBA exchange. The SBA resin tested was a type 2 chloride-based resin[2] (SBA 1) that was contained within two vessels in lead-lag configuration. The WBA exchange resin[3] was also tested in a lead-lag configuration of two vessels. According to the manufacturer, the WBA resin required pH depression to <6 for Cr(VI) removal, which was accomplished by using a preceding cation exchange column that exchanged influent calcium and magnesium ions for hydrogen ions.

The second pilot unit included four SBA resins[4] (SBA 2, 3, 4, and 5) and two GAC media[5] (GAC 1 and 2).

The magnetized ion exchange process consisted of continuously stirred mixing tanks for anion exchange. The resin[6] (SBA 6) contained a magnetic component in its structure to allow rapid agglomeration and settling of the resin from the treated water. Five percent of the resin was continually regenerated with brine in a separate stream and reintroduced into the mixing tanks to provide continuous operation.

The fourth of the pilot units was a natural zeolite media[7] previously evaluated by bench-scale testing and shown to be effective at Cr(VI) removal. Six columns were operated in series (in upflow mode) to achieve the needed EBCT for Cr(VI) removal. The manufacturer used a pretreatment deaeration column to decrease the oxygen content of the groundwater prior to Cr(VI) removal.
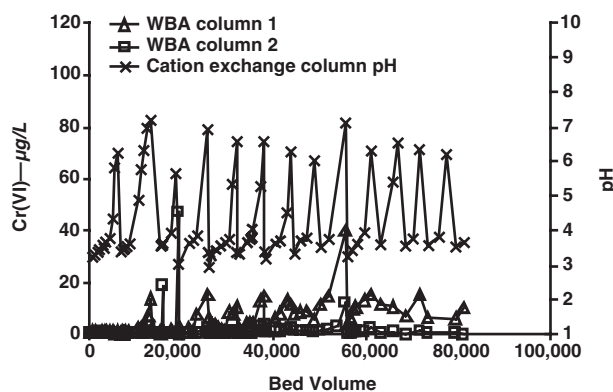
The fifth pilot unit, a reduction/filtration system, consisted of a reductant (sodium bisulfite or sulfite) to reduce Cr(VI) to Cr(III) and an oxidant (hypochlorite) to increase the redox potential of the water to a slightly positive potential before it was sent to a dual-media filter.[8]

Following the pilot testing of the vendor-provided systems, two additional tests were performed to more closely evaluate potential technologies: a brine-recycle experiment using an SBA resin and a test of reduction–coagulation–filtration (RCF) using ferrous sulfate.

Resin regeneration with brine recycle was tested using 6 or 26% sodium chloride operated in concurrent flow mode with five bed volumes (BV) of brine for regeneration. SBA 1 resin was used as a representative SBA resin. This test also included the use of an autosampler to monitor Cr(VI) removal more frequently and capture any chromatographic peaking of other competing anions.
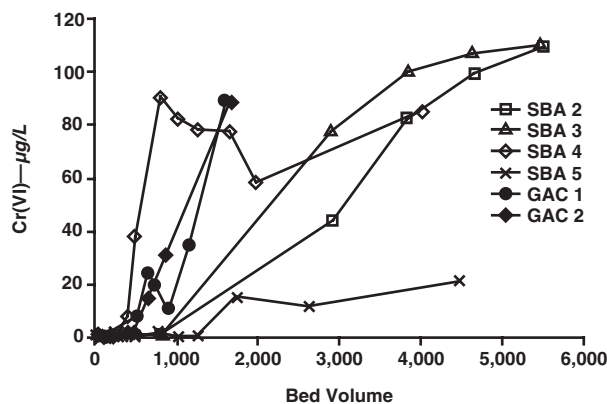
RCF was tested using a manufacturer-independent pilot unit. The RCF pilot system consisted of the following major components: peristaltic chemical feed pumps for ferrous sulfate[9] (6% volume per volume diluted), 36N sulfuric acid,[10] sodium hydroxide (50% by weight),[10] and polymer filter aid addition;[11] a 100-gal (379-L) reduc-

FIGURE 3 Relationship between WBA removal of Cr(VI) and pH variation

Cr(VI)—hexavalent chromium, WBA—weak-base anion

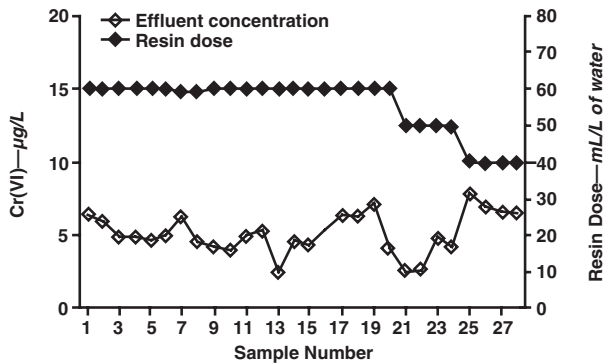**FIGURE 4** Cr(VI) breakthrough curves for SBA 2–5 and GAC 1 and 2

Cr(VI)—hexavalent chromium, GAC—granular activated carbon, SBA—strong-base anion

tion tank functioning in continuously stirred reactor mode; four 15-gal (57-L) aeration columns in series with coarse-bubble-diffusion plates; two parallel granular dual-media filter columns containing 12 in. (30 cm) of silica and 24 in. (61 cm) of anthracite coal; and a backwash module to achieve a 20–30% bed expansion rate. Variables tested with the RCF system included the mass ratio of ferrous iron [Fe(II)] to Cr(VI) ranging from 10:1 to 50:1, pH in the reduction tank and in the aeration columns and filters, filter loading rates ranging from 3 to 6 gpm/sq ft (122 to 245 L/min/m^{2}), and filter operational run times ranging from 6 to 48 h.
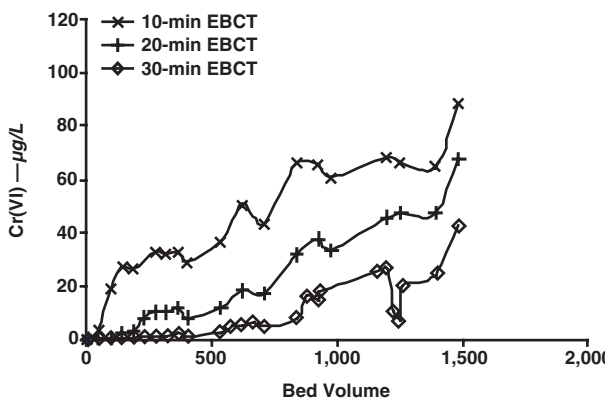
Laboratory methods. Total Cr, Cr(VI), total iron (Fe), and arsenic (As) concentrations were measured at the

FIGURE 5 Magnetized ion exchange treatment efficiency and resin dose as a function of sample number

Cr(VI)—hexavalent chromium

FIGURE 6 Cr(VI) breakthrough curves for zeolite media at 10-, 20-, and 30-min EBCT

Cr(VI)—hexavalent chromium, EBCT—empty bed contact time

Utah State University (USU) Water Research Laboratory in Logan. In the field, total Cr and total Fe samples were acidified to a pH of <2 with 70% trace metal clean nitric acid.[10] Cr(VI) samples were preserved with 50% sodium hydroxide[10] to a pH >10. Total Cr, Fe, and As concentrations were measured by an inductively coupled plasma mass spectrometer[12] (ICP–MS) with an octopole reaction system (USEPA, 1999). Cr(VI) samples were analyzed by an ion chromatograph[13] (IC) with a postcolumn ultraviolet-visible detector[14] (USEPA, 1996). All samples were filtered through a 0.45-µm filter before injection into the ICP–MS and IC. Samples with the potential for high Fe and/or turbidity (e.g., all RCF samples) were filtered and then split, with half of the split run as is and half digested using 4% concentrated hydrochloric acid and 2% hydroxylamine-hydrochloride at 85ºC for 24 h.

Routinely measured quality assurance/quality control (QA/QC) samples included duplicates (10% of all samples), field blanks (at least one per sample collection day), matrix spikes (at least 5% of all samples or one per sample run), and matrix spike duplicates. QA/QC data acceptance criteria were established for each method and complied with throughout pilot testing.

The hazardous character of different residuals was evaluated at USU using the USEPA toxicity characteristic leaching procedure (TCLP) (USEPA, 1992) and the California waste extraction test (WET; CCR, 1991). The WBA resin was also analyzed for total metals content by X-ray fluorescence (XRF)[15] at Wellesley College, Wellesley, Mass. Brine samples were measured for total Cr using an inductively coupled optical emission spectrometer[16] and for sulfate and chloride using an IC[17] at the University of Colorado at Boulder.

Field methods. To determine the effects of water quality on and by the different technologies, a range of water quality parameters were routinely measured at the pilot testing site. A portable colorimeter[18] was used to determine trends in various parameters, including sulfate, nitrate, silicate, phosphate, alkalinity, and hardness. Other water quality parameters measured were temperature and pH,[19] conductivity,[20] and turbidity.[21] Operational measurements were also recorded, including flow rates, head loss, and other details specific to each technology.

RESULTS AND DISCUSSION

SBA 1. The SBA 1 resin achieved Cr(VI) removal to <5 µg/L in the pilot test, as had been suggested by earlier bench-scale work (Brandhuber et al, 2004). Figure 1 shows the breakthrough curves for Cr(VI) removal by the resin, which indicate that the first column reached an effluent concentration of >5 µg/L after 1,900 BV of water treated. Breakthrough in the lag column occurred at 3,800 BV. Each column had an EBCT of 3–4 min.

Chromatographic peaking of competitive anions can occur with SBA resins when less-preferred but more highly concentrated anions collect on the resin and then are displaced en masse by more-preferred anions. Short-term concentration increases are expected but in practice have not been well described. An autosampler was used to detect and quantify chromatographic peaking for SBA 1. Bicarbonate, nitrate, phosphate, and sulfate were initially removed by the resin; subsequently, nitrate peaked at approximately 410 BV with 15 mg/L nitrate (NO_3^-) as nitrogen (N) and phosphate peaking occurred at 450 BV with 0.8 mg/L phosphate (PO_4; Figure 2). Influent water concentrations of nitrate and phosphate were 5 mg/L NO_3^- as N and 0.2 mg/L PO_4, which demonstrates that chromatographic peaking can increase the effluent concentration by three to four times the influent concentration. For implementation of SBA 1 in Cr(VI) treatment of this water, blending of treatment column flows would be required to smooth nitrate peaks

and avoid exceeding the MCL of 10 mg/L NO_3^- as N.

SBA resin use for Cr(VI) removal will require frequent regeneration with sodium chloride brine. The potential for minimization of brine volume was explored in this pilot testing by recycling brine and evaluating Cr(VI) removal efficiencies. An initial 6% sodium chloride solution was not effective in regenerating the resin, as evidenced by a decrease in BV to breakthrough from 1,900 to <500 BV after the first recycle, with further deterioration of Cr(VI) removal after the second and third recycles. An increase in the salt content of the recycled brine from 6 to 26% increased the time to breakthrough for three additional runs to 1,500, 1,200, and 500 BV. The higher-salinity brine initially increased the regeneration efficiency by more effectively removing Cr(VI) from the resin. These results demonstrate that brine recycle is possible for regenerating this resin if 26% brine is used. The eventual decrease in efficiency with successive regenerations may be attributable in part to the increasing sulfate concentration in the brine (e.g., up to 18,000 mg/L was observed).

WBA resin. Cr(VI) removal by the WBA resin is shown by the breakthrough curves (Figure 3), which indicate that the WBA resin achieved consistent breakthrough (>5 µg/L) only after reaching 38,000 BV of water treated by the lead column. Peaks observed before constant breakthrough were attributed to pH excursions and the need for backwashing. Breakthrough did not occur for the lag column by the time the pilot test was finished (i.e., ~80,000 BV).

Unlike the SBA resins, the WBA resin removal of Cr(VI) was found to be strongly dependent on pH. The vendor partners used a cation exchange column for pH depression before the WBA resin columns. The cation exchange column was replaced when pH approached 6, signaling column exhaustion, although occasionally the pH exceeded 6 before replacement. Figure 3 shows the Cr(VI) concentration and pH variation during testing, which indicates that the excursions were attributable mainly to pH values >6.
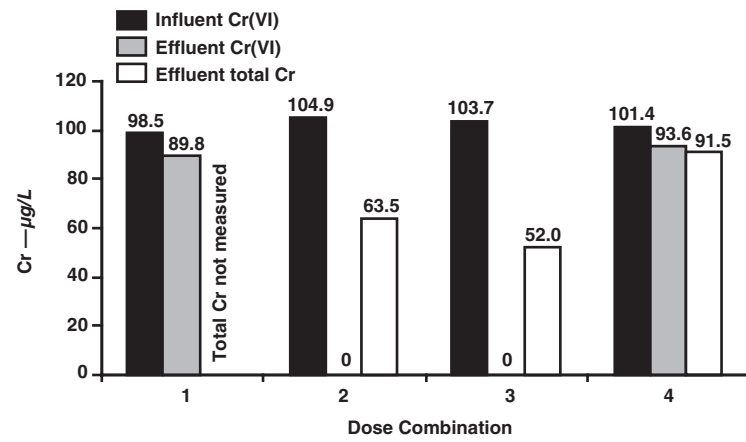
Because no analytical method exists to directly measure Cr(III), total Cr was measured in the effluent from the WBA resin in order to calculate Cr(III) by difference. The appearance of Cr(III) in the treated effluent was unexpected because the source water and spiking solution were composed entirely of Cr(VI), which indicates that reduction occurred on the resin surface or in the resin matrix. Cr(III) concentrations exceeding 5 µg/L in the effluent were observed mainly when pH was <5.5.

Table 3 summarizes the WBA column average effluent data for Cr(III) and Cr(VI) sorted by influent pH values. The data show that for an influent pH of <5.5, Cr(III) average effluent values were >8 µg/L. Above pH 5.5, Cr(III) concentrations were ~1 µg/L. For Cr(VI), Table 3 indicates that the average effluent value was significantly higher when the pH was >6. These findings support the strong pH influence on WBA resin CR(VI) removal reported by other researchers (Höll et al, 2002).

The mechanism for Cr removal by the WBA resin is not clear, and additional work is needed to determine both the mechanism and the effectiveness of Cr removal with a constant influent pH. As part of the introductory investigations for the Glendale demonstration-scale testing program, controlled experiments testing the effect of pH on WBA resin removals of Cr are underway. This study

TABLE 3 Mean effluent concentrations of Cr(III) and Cr(VI) from WBA resin lead column (<40,000 BV) as a function of influent pH

pH Range	Cr(VI)—µg/L	Cr(III)—µg/L
<5.5	4.9	8.6
5.5–6	4.1	1.7
>6	14.8	0.5

BV—bed volume, Cr—chromium, Cr(III)—trivalent chromium, Cr(VI)-hexavalent chromium, WBA—weak-base anion

FIGURE 7 Cr(VI) reduction and removal by filtration

Cr—chromium, Cr(VI)—hexavalent chromium, EBCT—empty bed contact time, HOCl—hypochlorite, NaHSO₃—sodium bisulfite, Na₂SO₃—sodium sulfite
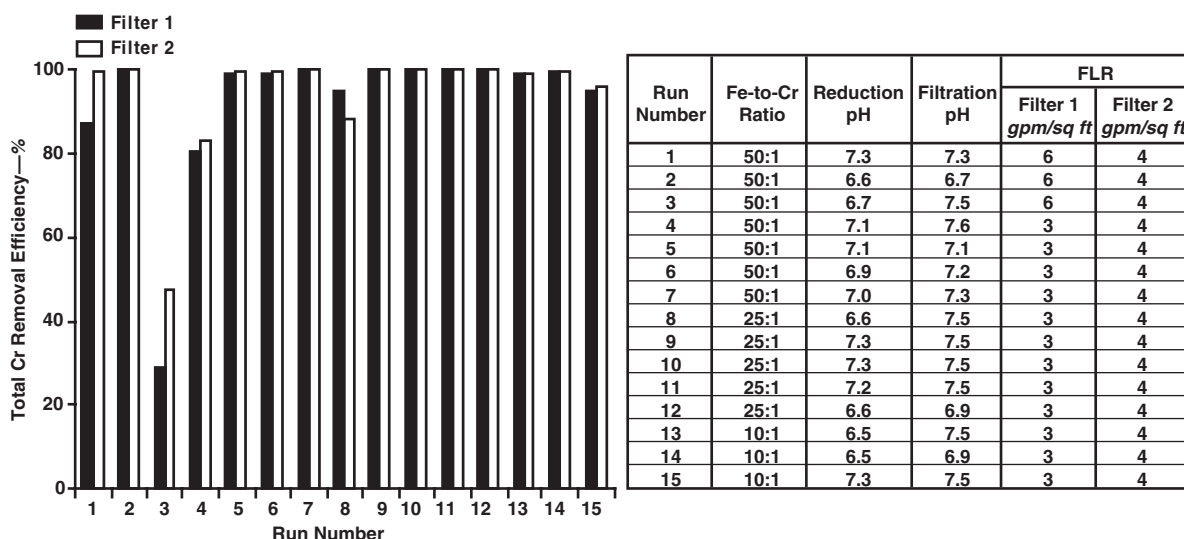
1—23,600 mg/L NaHSO₃, 1,500 mg/L HOCl, 2—36,200 mg/L NaHSO₃, 767 mg/L HOCl, 3—36,200 mg/L NaHSO₃, 767 mg/L HOCl, 4—4,500 mg/L Na₂SO₃, 767 mg/L HOCl

FIGURE 8 RCF average Cr removal efficiencies for a 6-h run as a function of different variables

Run Number	Fe-to-Cr Ratio	Reduction pH	Filtration pH	FLR	
				Filter 1 *gpm/sq ft*	Filter 2 *gpm/sq ft*
1	50:1	7.3	7.3	6	4
2	50:1	6.6	6.7	6	4
3	50:1	6.7	7.5	6	4
4	50:1	7.1	7.6	3	4
5	50:1	7.1	7.1	3	4
6	50:1	6.9	7.2	3	4
7	50:1	7.0	7.3	3	4
8	25:1	6.6	7.5	3	4
9	25:1	7.3	7.5	3	4
10	25:1	7.3	7.5	3	4
11	25:1	7.2	7.5	3	4
12	25:1	6.6	6.9	3	4
13	10:1	6.5	7.5	3	4
14	10:1	6.5	6.9	3	4
15	10:1	7.3	7.5	3	4

Cr—chromium, Fe—iron, FLR—filter-loading rate, RCF—reduction–coagulation–filtration

Variables include Fe-to-Cr mass ratio, reduction pH, coagulation and filtration pH, and FLR for filters 1 and 2.

indicates that WBA may be a promising technology for Cr(VI) removal if the pH of the feed to the WBA resin column is between 5.5 and 6.0. Determination of the precise upper pH limit for Cr(VI) removal requires more testing with a controlled pH.

SBA 2–5 and GAC media. The vendor's pilot test of four different SBA resins demonstrated a range of Cr(VI) removal capacities. Figure 4 shows up to 1,000

with breakthrough at ~600 BV for GAC 1 and GAC 2 (Figure 4).

Magnetized ion exchange. The driving force for Cr(VI) removal by the magnetized ion exchange pilot unit was a resin dose, above other operating parameters including resin contact time and regeneration rate. Optimal Cr(VI) removal occurred with a resin dose of between 50 to 60 mL of SBA 6 per litre of water, 30-min contact time, and

Reports have kept hexavalent chromium in the public eye and have resulted in a continued effort to develop cost-effective treatment technologies that can remove hexavalent chromium to very low micrograms per litre concentrations.

BV until a 5-μg/L breakthrough occurred for SBA 2, 1,000 BV for SBA 3, 350 BV for SBA 4, and 1,400 BV for SBA 5. These resins demonstrated a lower capacity than that of SBA 1. However, the pilot unit provided by the vendor encountered air entrainment issues that may have contributed to the poorer performance of these SBA resins.

In pilot testing, the two GAC columns demonstrated 25–30% of the Cr(VI) capacity observed for SBA 1,

a 5% regeneration rate. For this resin dose range, Cr(VI) removal efficiency in pilot testing ranged from 92 to 97%, with the treatment goal of <5 μg/L achieved in 16 out of 28 samples (Figure 5). Testing showed that the process was affected by high levels of sulfate (90 mg/L), as indicated by 80% removals of the influent sulfate. On average, 43% of influent nitrate was removed by the system. In contrast to the column-based SBA approaches, the system did not show chromatographic peaking once

the system operated in a near steady-state condition. Unlike SBA columns, however, the system required filtration of the effluent to keep turbidities <1.0 ntu. The system also showed an increase in effluent conductivity of 12%, most likely resulting from insufficient resin rinsing during regeneration.

Zeolite adsorptive media. The zeolite media successfully removed Cr(VI) for 620 BV before breakthrough of 5 µg/L (Figure 6). Compared with the other technologies tested, the zeolite media required a much longer EBCT of 30 min, which was achieved using six treatment columns in series. Figure 6 shows the breakthrough curves for EBCTs of 10, 20, and 30 min (corresponding to effluent from columns 2, 4, and 6, respectively). The high EBCT required by the media would translate into multiple large vessels required for full-scale treatment.
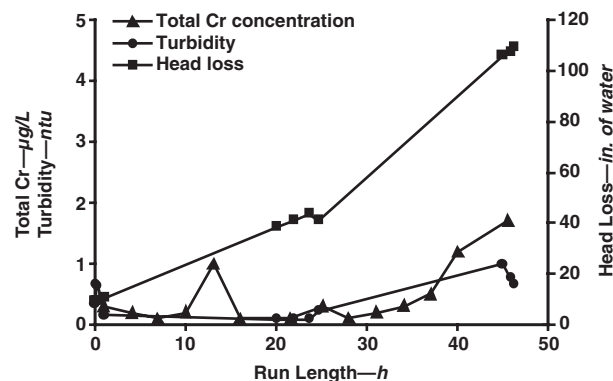
Reduction/filtration. The reduction/filtration pilot unit was tested using four dose combinations of reductant (sodium bisulfite or sodium sulfite) and oxidant (sodium hypochlorite) prior to filtration (Figure 7). The first test resulted in a Cr(VI) effluent concentration similar to the Cr(VI) influent concentration. A higher dose of sodium bisulfite and lower dose of hypochlorite in the second and third tests showed effective reduction of Cr(VI) but only 39–50% removal of total Cr. In the last test, sodium sulfite was used at a lower dose with the same concentration of hypochlorite, which showed ineffective reduction and removal of Cr(VI).

RCF. Cr(VI) reduction with ferrous sulfate and Cr(III) removal by coagulation and filtration were tested under 17 different conditions, with variables including mass ratio of Fe(II) to Cr(VI), pH of reduction, pH of coagulation and filtration, and filter loading rates. An average of 99.7% Cr(VI) reduction efficiency was observed for mass ratios of 25:1 and 50:1, and a slightly lower reduction efficiency of 98.5% was observed for a 10:1 mass ratio. Generally, the RCF system is able to achieve a 95% total Cr removal (Figure 8).

In bench-scale testing of reduction and filtration using Glendale groundwater (Brandhuber et al, 2004), better total Cr removal was achieved at a pH of 6.5 than at 7.5 and 8.0. Pilot testing showed that a reduction in pH did not affect the Cr(VI) reduction or the total Cr filtration. Previous studies have shown that Fe(II) oxidation rates can be increased at higher pH values of 7.5, compared with 6.5 (Davison & Seed, 1983; Sung & Morgan, 1980). However, when filter loading rates were low—3 or 4 gpm/sq ft (122 or 163 L/min/m²)—total Cr removal efficiencies of <95% were observed only at a pH of 7.5 or 7.6. Data collected during two of three pilot testing runs indicated that a higher filter loading rate of 6 gpm/sq ft (245 L/min/m²) also reduced total Cr removal. The groundwater's ambient pH (between 7.1 and 7.3) provided good conditions for RCF operation.
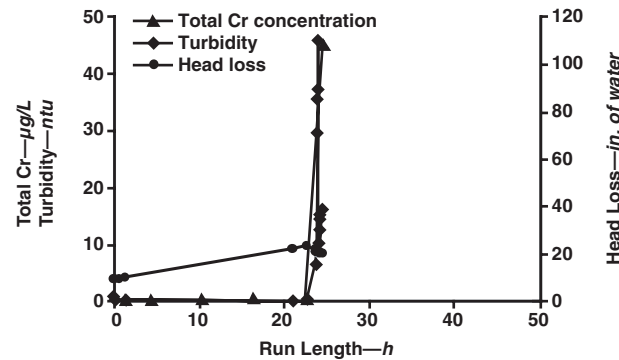
Two extended runs (up to 46 h) were tested to determine if backwash system needs could be reduced. Fe(II)-

FIGURE 9 Total Cr, head loss, and turbidity for RCF 46-h run at an Fe-to-Cr ratio of 25:1

Cr—chromium, Fe—iron, RCF—reduction–coagulation–filtration

FIGURE 10 Total Cr, head loss, and turbidity for RCF 46-h run at a Fe-to-Cr ratio of 15:1
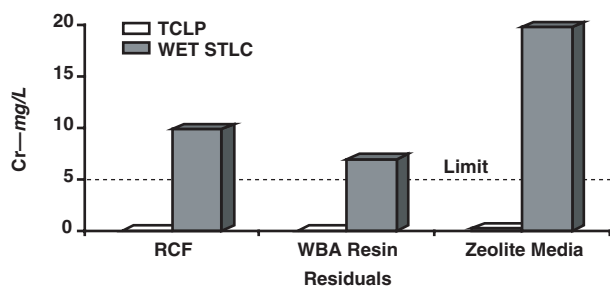
Cr—chromium, Fe—iron, RCF—reduction–coagulation–filtration

to-Cr(VI) mass ratios of 15:1 and 25:1 were tested with ambient pH conditions and a filter loading rate of 4 gpm/sq ft (163 L/min/m²). The Fe(II)-to-Cr(VI) mass ratio significantly affected run performance. Figure 9 shows that total Cr concentrations remained at <2 µg/L for up to 46 h for a dose strategy of 25:1, with turbidity of <1 ntu and a head loss across the filter exceeding 100 in. (254 cm) of water. In contrast, Figure 10 shows breakthrough of total Cr and turbidity at 23 h for a dose strategy of 15:1.

Different mechanisms of filtration may explain Figures 9 and 10. At a 25:1 mass ratio, the steady increase in head loss and no sharp turbidity breakthrough over 46 h may reflect physical straining at the filter surface as the principal filtration mechanism. The rapid breakthrough at 23 h for the 15:1 mass ratio suggests that

FIGURE 11 TCLP and California WET results for the pilot-tested technologies with disposable media or solid residuals

Cr—chromium, RCF—reduction–coagulation–filtration, STLC-soluble threshold limit concentration, TCLP—toxicity characteristic leaching procedure, WBA—weak-based anion, WET—waste extraction test

the filtration mechanism for the lower ratio involved penetration of Fe-Cr precipitates into the filter and exceedance of filter bed storage capacity. The difference in the mechanism of filtration may be attributable to the formation of larger particles with the 25:1 dose; these larger particles are more effectively removed by straining, whereas the lower 15:1 dose may promote the formation of smaller particles that can penetrate the filter bed. Results indicate that a higher dose to achieve the straining mechanism of filtration is likely to be more effective to sustain longer filter run times. Further optimization of Fe(II) dose and filter operations is recommended during demonstration-scale testing if this technology is selected.

Process residuals. Options for residuals waste stream management were considered for each of the pilot-tested technologies. TCLP and California WET results are shown in Figure 11 for the disposable WBA resin, zeolite media, and backwash solids from RCF. All residuals passed federal requirements for disposal as a nonhazardous waste, but all were classified as hazardous for disposal in California on the basis of the more rigorous WET procedure. Additional testing by XRF spectrometry demonstrated that the WBA resin capacity for Cr was at least 3.2 ± 0.2% (32,000 µg Cr per gram resin).

Brine recycle for residuals minimization was tested in the SBA 1 resin regeneration experiment and showed promise in effectively regenerating SBA resin a number of times if 26% brine was used.

Solid–liquid separation of backwash water from the RCF process was significantly improved by the addition of a high-molecular-weight polymer, which resulted in the backwash water containing <100 µg/L of total Cr and 10 mg/L of Fe after 20 min of settling with 0.2 mg/L of polymer; with 1.0 mg/L of polymer, the results were <5 µg/L total Cr and 0.5 mg/L Fe. Preliminary results

indicated that the backwash water may be able to be recycled to the head of the plant with optimization of the settling process.

SUMMARY AND CONCLUSIONS

Several pilot-tested technologies were successful in achieving the treatment goal of <5-µg/L Cr(VI) removal from drinking water. Column SBA exchange resins demonstrated more reliability in reaching the treatment goal than a reactor system. The best-performing SBA resin achieved 1,900 BV to breakthrough of 5 µg/L. Adsorptive media, including zeolite media and GAC, had a significantly lower capacity at ~600 BV. The WBA exchange resin showed higher-than-anticipated capacity for Cr(VI) removal up to 38,000 BV. Strict pH control may be required for WBA resin performance and should be tested further to identify the resin's true capacity under optimized pH conditions.

A pilot unit using reduction (with sulfite) and filtration did not demonstrate the ability to remove both Cr(VI) and total Cr from the source water. In contrast, pilot testing using ferrous sulfate reduction, coagulation, and dual-media filtration was effective in both reducing Cr(VI) and removing total Cr for a period of six hours to two days before backwash was needed.

The pilot testing highlighted and examined several essential issues to consider in demonstration testing. These included chromatographic peaking of competitive anions for SBA resins, operational strategies of the various technologies, and process residuals management and minimization.

All of the successful strategies identified in this study have the potential for removing Cr(VI) from drinking water to concentrations below or even far below the 5 µg/L goal of this research. Because there are few, if any, operational facilities demonstrating the reliable attainment of very low Cr(VI) concentrations, the city of Glendale is proceeding with a demonstration-scale treatment program to further test selected technologies at wellhead treatment flow rates (500 gpm [31.5 L/s]).

ACKNOWLEDGMENT

Sakaji of the California Department of Health Services, and Bruce Macler of the US Environmental Protection Agency (USEPA). This work was funded by a grant from USEPA.

ABOUT THE AUTHORS

Michael J. McGuire (to whom correspondence should be addressed) is vice president of McGuire Malcolm Pirnie, 1919 Santa Monica Blvd., Ste. 200, Santa Monica, CA 90404; e-mail mmcguire@pirnie.com. In 1992, he founded McGuire Environmental Consultants Inc., which he headed until 2005. He was formerly assistant general manager of Metropolitan Water District of Southern California in La Verne, where he had previously directed the utility's water quality division. McGuire has a BS in civil engineering from the University of Pennsylvania and MS and PhD degrees from Drexel University, both in Philadelphia, Pa. Nicole K. Blute is a project engineer with McGuire Malcolm Pirnie in Santa Monica. Chad Seidel is a project engineer with McGuire Malcolm Pirnie in Denver, Colo. Gang Qin is an engineer in the Santa Monica office of McGuire Malcolm Pirnie. Leighton Fong is an engineer with the City of Glendale, Calif.

FOOTNOTES

[1] J.T. Baker, Phillipsburg, N.J.
[2] Amberlite® PWA 410, US Filter Corp., Warrendale, Pa., and Rohm & Haas Co., Philadelphia, Pa.
[3] Duolite® A7, US Filter Corp., Warrendale, Pa., and Rohm & Haas Co., Philadelphia, Pa.
[4] WT 201, 202, 203, and 204, Calgon Carbon Corp., Pittsburgh, Pa.
[5] Filtrasorb® 600 and Filtrasorb® 200 PHA, Calgon Carbon Corp., Pittsburgh, Pa.
[6] MIEX®, Orica Watercare, Denver, Colo.
[7] Z-24™, Water Remediation Technology, Arvada, Colo.
[8] Electromedia®, Filtronics Inc., Anaheim, Calif.
[9] MKM (Mineral King Minerals), Hanford, Calif.
[10] FisherBrand, Hampton, N.H.
[11] Ciba® MagnaFloc® E40, Ciba Specialty Chemicals, Suffolk, Va.
[12] Agilent 7500C, Agilent Technologies, Palo Alto, Calif.
[13] DX-320, Dionex Corp., Sunnyvale, Calif.
[14] AD25 Absorbance Detector, Dionex Corp., Sunnyvale, Calif.
[15] Spectro XEPOS pED-XRF, Spectro Analytical Instruments Inc., Marlborough, Mass.
[16] ARL 3410+, Thermo Electron Corp., Waltham, Mass.
[17] Dionex Series 4500i, Dionex Corp., Sunnyvale, Calif.
[18] Hach DR-890, Hach Co., Loveland, Colo.
[19] SensION 1 pH Meter, Hach Co., Loveland, Colo.
[20] Hach CO150 Conductivity Meter, Hach Co., Loveland, Colo.
[21] Hach 2100P Turbidimeter, Hach Co., Loveland, Colo.

If you have a comment about this article, please contact us at journal@awwa.org.

REFERENCES

Bahowick, S.; Dobie, D.; & Kumamoto, G., 1996. Ion Exchange Resin for Removing Hexavalent Chromium From Groundwater at Treatment Facilities. UCRL-JC-122285 Abs., Lawrence Livermore Natl. Lab., Lawrence, Calif.

Brandhuber, P. et al, 2004. *Low-Level Hexavalent Chromium Treatment Options: Bench-Scale Evaluation.* AWWA and AwwaRF, Denver.

CCR (California Code of Regulations), 1991. 22 CCR 66261.126, Appendix II, Sacramento, Calif.

Clifford, D. 1990. Ion Exchange and Inorganic Adsorption. *Water Quality and Treatment: A Handbook of Community Water Supplies.* McGraw-Hill, New York.

Davison, W. & Seed, G., 1983. Kinetics of the Oxidation of Ferrous Iron in Synthetic and Natural Waters. *Geochim. et Cosmochim. Acta,* 47:67.

Eary, L.E. & Rai, D., 1988. Chromate Removal From Aqueous Wastes by Reduction With Ferrous Iron. *Envir. Sci. & Technol.,* 22:972.

Fendorf, S.E. & Li, G., 1996. Kinetics of Chromate Reduction by Ferrous Iron. *Envir. Sci. & Technol.,* 30:1614.

Höll, W.H. et al, 2002. Elimination of Trace Heavy Metals From Drinking Water Using Weakly Basic Anion Exchangers. *Goe-und Wassertechnologie,* 1:3:5.

Jakobsen, K. & Laska, R., 1977. Advanced Treatment Methods for Electroplating Wastes. *Pollution Engrg.,* 8:42.

Lee, G. & Hering, J.G., 2003. Removal of Chromium (VI) From Drinking Water by Redox-Assisted Coagulation With Iron (II). *Jour. Water Supply, Res. & Technol.—Aqua,* 52:319.

Los Angeles Times, 2005. PG&E Pressed on Pollution Cleanup. Feb. 23, 2005.

OEHHA (Office of Environmental Health Hazard Assessment), 1999. Public Health Goal for Chromium in Drinking Water. California Environmental Protection Agency, Sacramento.

Rengaraj, S. et al, 2003. Kinetics of Removal of Chromium From Water and Electronic Process Wastewater by Ion Exchange Resins: 1200H, 1500H, and IRN97H, *Jour. Hazard Materials,* 102:2:257.

Rengaraj, S.; Yeon, K.-H.; & Moon, S.-H., 2001. Removal of Chromium From Water and Wastewater by Ion Exchange Resins. *Jour. Hazard Materials,* B87:273.

Schlautman, M.A. & Han, I., 2001. Effects of pH and Dissolved Oxygen on Reduction of Hexavalent Chromium by Dissolved Ferrous Iron in Poorly Buffered Aqueous Systems. *Water Res.,* 35:1534.

Sedlak, D.L. & Chan, P.G., 1997. Reduction of Hexavalent Chromium by Ferrous Iron. *Geochim. et Cosmochim. Acta,* 61:2185.

Sung, W. & Morgan, J.J., 1980. Kinetics and Product of Ferrous Iron Oxygenation in Aqueous Systems. *Envir. Sci. & Technol.,* 14:561.

USEPA (US Environmental Protection Agency), 1999. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma–Mass Spectrometry. EPA-821/R-99/017, Washington.

USEPA, 1996. Method 1636: Determination of Hexavalent Chromium by Ion Chromatography. EPA-821/R-96/003, Washington.

USEPA, 1992. Test Methods for Evaluating Solid Waste. Physical/Chemical Methods. SW-846, USEPA Ofce. of Solid Waste, Washington.

Yalcin, S. et al, 2001. Recovery of Copper (II) and Chromium (III, VI) From Electroplating-Industry Wastewater by Ion Exchange. *Separ. Sci. Technol.,* 36:10:2181.