The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale Groundwater Supply

Phase II: Demonstration of Pilot-Scale Treatment Technologies

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Executive Summary

The City of Glendale, along with the Cities of Los Angeles, Burbank, and San Fernando, initiated a research program with the goal of developing a full-scale hexavalent chromium (Cr(VI)) treatment system capable of treating contaminated groundwater from the San Fernando Valley Superfund site, located in and adjacent to the City of Los Angeles, to very low Cr(VI) concentrations. Cr(VI) has become a pressing concern for many people due to its presence in drinking water supplies throughout the United States and its potential adverse health effects. There is no proven technology to reliably remove Cr(VI) in drinking water to very low levels.

Chromium is present in water as the harmless Cr(III) species and the potentially carcinogenic Cr(VI) species. Total Cr is regulated by a federal maximum contaminant level (MCL) of 100 μ g/L and a State of California MCL of 50 μ g/L. Currently, no federal or state MCL exists for Cr(VI) in drinking water, although California is required by State law to set a Cr(VI) MCL. The intentions of the State to regulate Cr(VI) coupled with public concern over the presence of Cr(VI) in the drinking water led to studies evaluating treatment options for San Fernando Valley groundwater, which contains significant Cr(VI) concentrations.

The City of Glendale's four-phase program includes: Phase I: A bench-scale study to improve the understanding of fundamental chromium chemistry and to screen promising treatment technologies for their ability to treat and remove Cr(VI) to very low levels, Phase II: A pilotscale study to evaluate treatment technologies for removing Cr(VI) to very low levels in public drinking water supplies, Phase III: A demonstration-scale study to finalize technology evaluation and address costs and residuals issues, and Phase IV: Full-scale implementation of an effective Cr(VI) treatment technology.

The results of Phase II pilot testing are detailed in this report. Phase II consisted of two segments: Phase II-A—vendor proof-of-technology validations, and Phase II-B—evaluation of additional technologies and effective technologies in more depth. Vendors and technologies were selected based upon pre-established criteria including maturity of technology, demonstrated performance as an industrial waste treatment or remediation process or other applications for Cr(VI) treatment, capacity and ability to scale up, technical soundness of the treatment process, and the ability to achieve NSF certification for drinking water application.

Bench-scale testing suggested that technologies capable of removing Cr(VI) to less than 5 μ g/L would include the following classes of technologies: strong-base anion exchange resin (column and reactor applications), adsorptive media, membrane treatment by nanofiltration and reverse osmosis, and coagulation/precipitation of reduced Cr(III). Of these technologies, membrane treatment results in too great of a loss of water and was therefore not carried forward as a viable technology for Glendale. The other three technology classes were included in pilot testing, as well as adsorptive media (zeolite and GAC) and weak-base anion exchange. Sulfur-modified iron adsorptive media, while promising in bench-scale work, was not technologically mature enough for pilot testing. Table ES-1 lists the vendors selected for pilot testing, the technologies tested, and the vendor-independent technology included in the study.

Supplier	Technology	Media Tested
Calgon Carbon Corporation	Strong-Base Anion Exchange (Column)	WT201, WT202, WT203, WT204
	Granular Activated Carbon (GAC)	Filtrasorb 600, Filtrasorb 200 PHA
Filtronics	Reduction/ filtration	Reduction with sulfite and Filtration with Electromedia®
Orica Watercare	Strong-Base Anion Exchange (Reactor)	Proprietary MIEX [®] resin
US Filter in Partnership with Rohm & Haas	Strong-Base Anion Exchange (Column)	Amberlite PWA 410 Cl
	Weak-Base Anion Exchange Resin (Column)	Duolite [®] A7
Water Remediation Technologies (WRT)	Adsorptive Media (Zeolite)	Z-24™
(MEC and CDM)	Reduction/ Coagulation/ Filtration using Ferrous Sulfate	-

Table ES-1. Phase II Pilot Tested Cr(VI) Removal Technologies

Cr(VI) and total Cr were the key parameters measured in both influent and effluent samples to determine the effectiveness of the different technologies. Although the blended Glendale source water contained an average of 10 μ g/L Cr(VI), the City envisions treating two individual wells ranging from 40 to 60 μ g/L Cr(VI). To test the ability of treatment technologies at the higher levels (which may increase), pilot testing was conducted using blended source water with Cr(VI) added to the level of 100 μ g/L. This higher influent concentration also enabled an evaluation of 95% chromium removal by the technologies, well above the method detection limits.

The impact of other water quality parameters on the technologies and the effect of the technologies on the water quality were also tested. Routine measurements included pH, temperature, conductivity, alkalinity, hardness, turbidity, and iron. For anion exchange technologies, anions including sulfate, nitrate, silicate, phosphate, and arsenic were measured to determine competitive removal and any peaking from column technologies.

Pilot testing revealed that most of the technologies tested could remove Cr(VI) to levels below 5 $\mu g/L$, although capacities and reliability widely varied. Table ES-2 provides a comparison of the treatment technologies in terms of the bed volumes of water treated (i.e. volume of water treated divided by the volume of media).

The strong-base anion exchange resin with the greatest Cr(VI) removal capacity in the pilot testing was provided by US Filter/ Rohm & Haas, compared to Calgon's four strong-base resins tested. The strong-base resin exhibited chromatographic peaking of nitrate and phosphate in the first quarter of bed life (i.e. before 5 μ g/L was achieved). Peaking resulted in a 3 to 4 times increase in the effluent concentration compared to the influent, which caused nitrate to exceed

the maximum contaminant level of 10 mg/L as N. Consequently, multiple resin beds may be needed in a strong-base resin system to provide blending of nitrate.

Orica's MIEX® pilot unit was able to remove Cr(VI) to levels below 5 µg/L for slightly more than half of the samples collected. Tests showed that the likely factors limiting Cr(VI) removal were resin dose and high sulfate levels of 90 mg/L. Although chromatographic peaking is not a concern in the continuously-stirred MIEX® system, reliability in Cr(VI) removal to low levels did not meet the capabilities of the fixed-bed strong-base resin technology.

Weak-base anion exchange resin (from US Filter/ Rohm & Haas), which has not been widely used in drinking water applications, showed a remarkable ability to remove and retain Cr(VI). Weak-base resin achieved ten to twenty times more bed volumes of treatment compared to strong-base resins. In the process, the weak-base resin accumulated 3.2% chromium on the resin. However, successful weak-base resin use for Cr(VI) removal depends on pH depression to below 6.0. Pilot findings indicated that the ideal pH range may be between 5.5 and 6.0, to maximize Cr(VI) removal and minimize Cr(III) release. The mechanism of chromium retention by the weak-base anion exchange resin is not fully understood and requires additional testing. Nevertheless, pilot testing showed that this technology would provide an effective single-pass disposable resin option for Cr(VI) removal.

Adsorptive media tested in the pilot study included both WRT zeolite media and Calgon GAC. Both WRT media and Calgon GAC removed Cr(VI) to concentrations below 5 µg/L, although the number of bed volumes to breakthrough was one-third of the most effective strong-base anion exchange resin. In addition, the WRT zeolite media required contact times ten to fifteen times longer than the resins. Pilot results confirm literature findings that GAC is not able to treat many bed volumes before Cr(VI) breakthrough.

Two different reduction/filtration technologies were pilot-tested. The vendor-supplied technology, provided by Filtronics, was not able to both reduce Cr(VI) and remove total Cr from the influent water. Filtronics' pilot unit included reduction of Cr(VI) to Cr(III) with sodium sulfite (or bisulfite), then oxidation of the water with sodium hypochlorite for iron precipitation on the dual-media filter. Very high concentrations of reductant and oxidant were used by Filtronics, and results showed that Cr(III) removal could not be achieved during the testing period.

In comparison, the reduction/coagulation/filtration pilot unit designed and set up by McGuire Environmental Consultants and subcontractor Camp Dresser and McKee was highly effective in both reducing Cr(VI) and removing total Cr. This pilot unit used ferrous sulfate for reduction and precipitation of Fe-Cr particles, aeration columns to coagulate iron particles, and dual-media filtration (sand and anthracite) to remove the Fe-Cr particles. In pilot testing, a number of operational parameters were optimized, including the iron-to-chromium dose ratio, pH of reduction and filtration, filter loading rates, and backwash needs.

Product		Technology	Cr(VI) less than 5µg/L?	Bed Volumes to Break- through	Regen- erable?	Chromato- graphic peaking	Residuals	Other Issues
Calgon	SBA resin WT-201	lon Exchange (Column)	Yes	1,000	Yes	Yes	Brine	
	SBA resin WT-202	lon Exchange (Column)	Yes	1,000	Yes	Yes	Brine	
	SBA resin WT-203	lon Exchange (Column)	Yes	350	Yes	Yes	Brine	
	SBA resin WT-204	lon Exchange (Column)	Yes	1,400	Yes	Yes	Brine	
	Carbon F600	Adsorption	Yes	600	Yes	No	-	
	Carbon F200PHA	Adsorption	Yes	600	Yes	No	-	
Filtronics	Electro- media [®]	Reduction/ Filtration	No	N/A	N/A	No	Backwash	Requires high concentr- ations of reductant & oxidant
Orica	MIEX®	Ion Exchange (Continuous flow reactor)	Yes – Not reliably	N/A	Yes	No	Brine	
US Filter/ Rohm &	SBA (Amberlite ilter/ PWA m & 410Cl)	Ion Exchange	Yes	1,900	Yes	Yes	Brine	Effective regenera- tion
Haas	WBA (Duolite A7)	(Column)	Yes	38,000	No	Yes	Media	Requires pH 5.5-6.0
WRT	Z-24™	Surface reduction/ adsorption	Yes	620	No	No	Media	Requires long contact times
-	RCF	Reduction/ Coagulation/ Filtration	Yes	N/A	N/A	N/A	Backwash	Most effective at ambient pH

Table ES-2. Comparison of the Results for the Pilot Tested Technologies

Pilot testing revealed that the most effective Cr(VI) removal technologies were strong-base anion exchange resin, weak-base anion exchange resin, and reduction/coagulation/filtration for Glendale's source water. Of the three effective pilot-tested Cr(VI) removal technologies, regenerable strong-base anion exchange and reduction/coagulation/filtration are somewhat standardized technologies in other drinking water and industrial wastewater treatment applications, respectively. The third successful pilot-tested technology, weak-base anion exchange, is distinctive in its high capacity for Cr(VI) and represents a new, innovative technology application.

For the pilot-tested technologies, residuals waste streams were tested for hazardous characteristics and investigated for possible minimization of waste stream volume. Testing showed that strong-base anion exchange resin could be regenerated with a strong salt solution, which could be recycled one or more times before disposal. Weak-base anion exchange resin could be used as a disposable media due to its high capacity for Cr(VI), and residuals could be minimized by fully exhausting the resin. Reduction/coagulation/filtration generates backwash water and solids, which were rapidly separated using polymers. All residuals (brine or solids) associated with these three technologies were hazardous by the California waste extraction test (WET). However, solids from weak-base anion exchange and reduction/coagulation/filtration passed the federal toxicity characteristic leaching procedure (TCLP) test.

Additional research is needed to fully explore this new weak-base anion exchange technology and to determine if the City of Glendale should test weak-base resin at demonstration-scale. Further testing of the weak-base resin is needed in initial demonstration-scale testing, including pH control optimization to maximize Cr(VI) removal, determination of resin capacities with tight pH control, identification of operational requirements for a weak-base anion exchange resin system, and residuals management requirements.

Chapter 1

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Pilot-Scale Studies of Hexavalent Chromium Removal from Drinking Water

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ABSTRACT

The goal of this research was to, for the first time, evaluate pilot-scale treatment technologies for Cr(VI) removal to less than 5 µg/L (i.e. 95% removal). A major focus was to evaluate manufacturer-provided pilot systems with media that was effective in bench-scale studies, or technologies that were promising but could not be appropriately tested at the bench scale. Technologies tested included ion exchange systems (i.e. column strong- 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 GAC). In vendor-independent tests, reduction with ferrous sulfate, coagulation, and filtration was also tested. Regeneration efficiency was also determined for the best-performing strong-base anion exchange resin, including the impact of recycling brine to minimize residuals. Technologies able to

consistently treat to levels below 5 μ g/L included column strong-base anion exchange, weakbase anion exchange, and reduction/coagulation/filtration using ferrous sulfate.

INTRODUCTION

Drinking water utilities face the challenge of addressing emerging water quality concerns in order to ensure adequate protection of public health sometimes without final federal or state drinking water regulations. Total chromium, Cr(III) plus Cr(VI), has been part of national drinking water regulations since 1975. The federal regulatory maximum contaminant level (MCL) for total Cr is 100 μ g/L, while the MCL in California is 50 μ g/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 μ g/L, which contributed to a public health goal (PHG) of 2.5 μ g/L for total Cr (OEHHA, 1999). Although this PHG was later rescinded and is currently under review, the potential for a new Cr(VI) MCL and a lower California total Cr MCL provided motivation to identify treatment technologies able to remove Cr to levels far lower than the current limits.

In 2000, public concern over the presence of Cr(VI) in drinking water was stimulated in large part by the movie *Erin Brockovich*, which highlighted a groundwater chromium pollution lawsuit in Hinkley, California. In response to this public concern, the City of Glendale, with the participation of the Cities of Los Angeles, Burbank, and San Fernando, initiated a four-phase program to develop full-scale treatment capable of removing Cr(VI) from San Fernando Valley groundwater, which contains plumes of high concentrations of Cr(VI) as a result of poor historical disposal practices. As recently as February 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 μ g/L of Cr(VI). The well is only 60 feet 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 μ g/L levels.

The Glendale four-phase program includes: (1) A bench-scale study that improved the understanding of fundamental Cr chemistry and screened promising treatment technologies (AWWARF, 2004), (2) A pilot-scale study that evaluated treatment technologies for removing Cr(VI) to low levels 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 paper reports on the results of the pilot-scale tests of a wide variety of Cr(VI) treatment technologies.

Until this comprehensive program, no treatment technology was shown to reliably reduce Cr(VI) in drinking water to levels below 5 µg/L. Industrial and hazardous waste applications of various technologies, including anion exchange (Jakobsen et al, 1977; Yalcin et al, 2001; Rengaraj et al, 2003) and reduction with ferrous iron (Eary et al, 1988; Fendorf et al, 1996; Sedlak et al, 1997; Schlautman et al, 2001), typically treated Cr(VI) to levels 10 to 1000 times greater than that targeted in this testing. Bench-scale drinking water studies have shown that Cr(VI) can be removed by strong-base anion exchange (Clifford, 1990; Bahowick et al, 1996), by reduction of Cr(VI) to Cr(III) (Lee et al, 2003), by adsorptive media, and by reverse osmosis (AWWARF, 2004). Initial tests in Germany and China have also

suggested that weak-base anion 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 to identify an effective treatment option for demonstration-scale testing. Factors considered in the performance evaluation included the ability to remove Cr to low levels, the impact of Glendale groundwater quality on technology performance, system operational requirements, and residuals stream disposal needs. Since Cr(III) is oxidized to Cr(VI) in distribution systems by chlorine and chloramines (AWWARF, 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 Superfund North Operable Unit (NOU) wells in the San Fernando Valley. General water quality is shown in Table 1. As a blend, Glendale groundwater from the four NOU wells averaged 10 μ g/L Cr(VI). To reflect higher concentrations in individual wells and to provide more rigorous testing above method detection limits, the Cr(VI) concentration in the blended source water was spiked to 100 μ g/L Cr(VI) using a flow-paced metering pump with diluted 10% chromic acid (H₂CrO₄)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 fullscale treatment, and NSF certification status. Technologies tested included strong- and weakbase anion exchange columns provided by US Filter Corporation in partnership with Rohm & Haas Company (USF/R&H), strong-base anion exchange and granular activated carbon (GAC) columns by Calgon Carbon Corporation (Calgon), reactor-based strong-base anion exchange by Orica Watercare (MIEX[®]), adsorptive media by Water Remediation Technology (WRT), and reduction with sodium bisulfite or sulfite followed by filtration provided by Filtronics, Inc.

Each pilot unit received spiked influent water at a flow rate of between 0.2 and 2.0 gallons per minute (gpm), (0.8-7.6 L per minute), 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 unit tested.

The USF/R&H system included two separate treatment trains for strong- and weak-base anion exchange. The strong-base anion exchange (SBA) resin tested was a Type 2 Amberlite PWA410 chloride-based resin contained within two vessels in lead-lag configuration. The weak-base anion exchange (WBA) resin evaluated was Duolite[®] A7, which was also tested in a lead-lag configuration of two vessels. The WBA resin required pH depression to less than 6 for Cr(VI) removal, which was accomplished by USF/R&H using a preceding cation exchange column that exchanged influent calcium and magnesium ions for hydrogen ions.

Calgon's pilot unit included four SBA resins (WT201, 202, 203, and 204) and two GAC media (Filtrasorb 600 and Filtrasorb 200PHA).

Orica's Magnetized Ion Exchange (MIEX[®]) process consisted of continuously-stirred mixing tanks for anion exchange. The SBA resin 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.

WRT evaluated a natural zeolite media (Z- 24^{TM}) shown by bench-scale testing to be effective at Cr(VI) removal. Six columns were operated in series (in up-flow mode) to achieve the needed EBCT for Cr(VI) removal. WRT used a pre-treatment de-aeration column to decrease the oxygen content of the groundwater prior to Cr(VI) removal.

Filtronics tested a system consisting of a reductant (sodium bisulfite or sulfite) to reduce Cr(VI) to Cr(III) then an oxidant (hypochlorite) to increase the redox potential of the water to a slightly positive potential before sending it to an Electromedia[®] dual-media filter.

Following the pilot testing of 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, and filtration using ferrous sulfate.

Resin regeneration with brine recycle was tested using 6 or 26% NaCl operated in concurrent flow mode with 5 bed volumes of brine for regeneration. The USF/R&H SBA PWA410 chloride-based resin was used as a representative SBA resin. This test also included the use of an auto sampler to monitor Cr(VI) removal more frequently and to capture any chromatographic peaking of other competing anions.

Reduction with ferrous sulfate, coagulation, and filtration (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 $(6\% \text{ v/v} \text{ diluted})^2$, 36N sulfuric acid³, sodium hydroxide (50% by weight)³, and polymer filter aid addition⁴; a 100 gallon (379 L) reduction tank; four 15 gallon (57 L) aeration columns in series with coarse bubble diffusion plates; two parallel granular dual-media filter columns containing 12" (30 cm) of silica and 24" (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 Fe(II):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/sf (122 to 245 L per minute/ m^2), and filter operational run times ranging from 6 to 48 hours.

Laboratory Methods. Total Cr, Cr(VI), total iron, and arsenic concentrations were measured at the Utah State University Water Research Laboratory (USU). In the field, total Cr and total Fe samples were acidified to a pH of less than 2 with 70% trace metal clean nitric acid³. Cr(VI) samples were preserved with 50% NaOH³ to a pH greater than 10. Total Cr, Fe, and As concentrations were measured by inductively coupled plasma mass spectrometer (ICP-MS)⁵ with an octopole reaction system (USEPA, 1999). Cr(VI) samples were analyzed by ion chromatograph (IC)⁶ with an AD25 post-column UV-visible detector (USEPA, 1996). All samples were 0.45 um filtered before injection into the ICP-MS and IC. Samples with the potential for high iron and/or turbidity (such as all RCF samples) were filtered then split, with half of the split run as-is and half digested using 4% concentrated HCl and 2% hydroxylamine-hydrochloride at 85°C for 24 hours.

Quality assurance/ quality control (QA/QC) samples routinely measured included duplicates (10% of all samples), field blanks (at least one per sample collection day), matrix spikes (at least 5% of all samples or once 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 EPA toxicity characteristic leaching procedure (TCLP, USEPA Publication SW-846) and the California waste extraction test (WET; 22 CCR 66261). The USF/R&H WBA resin was also analyzed for total metals content by x-ray fluorescence (XRF)⁷ at Wellesley College. Brine samples were

measured for total Cr using an inductively coupled optical emission spectrometer $(ICP-OES)^8$ and for sulfate and chloride using an IC⁹ at the University of Colorado at Boulder.

Field Methods. To determine the impacts 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 colorimeter¹⁰ was used to determine trends in various parameters, including sulfate, nitrate, silicate, phosphate, alkalinity, hardness. Other water quality parameters measured were temperature and pH¹¹, conductivity¹², and turbidity¹³. Operational measurements were also recorded, including flow rates, head loss, and other details specific to each technology.

RESULTS AND DISCUSSION

USF/R&H SBA Resin. The USF/R&H Amberlite PWA 410 Cl SBA resin achieved removal of Cr(VI) to less than 5 μ g/L in the pilot test, as was suggested in earlier bench-scale work (AWWARF, 2004). Breakthrough curves for Cr(VI) removal by the resin are shown in Figure 1, illustrating that the first column reached an effluent concentration of greater than 5 μ g/L after 1,900 bed volumes (BV) of water treated. Breakthrough in the lag column occurred at 3,800 BV. Each column had an empty bed contact time of 3 to 4 minutes.

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 captured and described. Using an auto sampler, chromatographic peaking was detected and quantified for the USF/R&H SBA resin. Bicarbonate, nitrate, phosphate, and sulfate were initially removed by the resin; subsequently, nitrate peaked at approximately 410 BV with 15 mg/L as N and phosphate peaking occurred at 450 BV with 0.8 mg/L as PO₄ (Figure 2). Influent water concentrations of nitrate and phosphate were 5 mg/L as N and 0.2 mg/L PO₄, which demonstrates that peaking can increase the effluent concentration by three to four times the influent concentration. For implementation of the SBA resin 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 nitrate 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% NaCl solution was not effective in regenerating the resins, as observed by a decrease in BV to breakthrough from 1,900 to less than 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 BV, 1,200 BV, 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 due in part to the increasing sulfate concentration in the brine (up to 18,000 mg/L).

USF/R&H WBA Resin. Cr(VI) removal by the USF/R&H Duolite A7 WBA resin is illustrated by the breakthrough curves (Figure 3), which show that the WBA resin achieved consistent breakthrough (greater than 5 μ g/L) only after reaching 38,000 BV of water treated by the lead column. Peaks observed before constant breakthrough were due 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. approximately 80,000 BV).

Unlike SBA resins, WBA resin removal of Cr(VI) was found to be strongly dependent on pH, with optimal removal in the pH range of 5.5 to 6.0. USF/R&H 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 illustrates that the excursions are due mainly to pH values above 6.

Total Cr was also measured in the effluent from the WBA resin to calculate Cr(III) by difference, since no method exists to directly measure Cr(III). The appearance of Cr(III) in treated effluent was unexpected since 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. Nevertheless, Cr(III) concentrations exceeding 5 μ g/L were observed largely when pH was lower than 5.5. The mechanism for Cr removal by the WBA resin is not fully clear, and additional work is needed to determine both the mechanism and the effectiveness of Cr removal with a constant influent pH. These data show a promising technology for Cr(IV) removal as long as the pH to the WBA resin column is maintained between 5.5 and 6.0.

Calgon SBA Resins and GAC media. Calgon's pilot test of four different SBA resins demonstrated a range of Cr(VI) removal capacities (Figure 4), with up to 1,000 BV until 5 μ g/L breakthrough occurred for WT201, 1,000 BV for WT202, 350 BV for WT203, and 1,400 BV for WT204. These resins showed a lower capacity than the USF/R&H SBA resin. However, the

pilot unit provided by Calgon encountered air entrainment issues that may have contributed to the lesser performance of these SBA resins.

Pilot testing of two Calgon GAC columns showed 25 to 30% of the capacity for Cr(VI) as observed for USF/R&H SBA resin, with breakthrough at approximately 600 BV for Filtrasorb 600 and Filtrasorb 200 PHA (Figure 4).

MIEX[®]. The driving force for Cr(VI) removal by the MIEX[®] pilot unit was 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 resin per liter of water, 20 minutes contact time, and a 5% regeneration rate. For this resin dose range, Cr(VI) removal efficiency in pilot testing ranged from 92 to 97%, with the goal of treatment to less than 5 μ g/L achieved in 16 out of 28 samples (Figure 5). Testing showed that MIEX[®] was impacted by high levels of sulfate (90 mg/L), as shown by removals of 80% of the influent sulfate. On average, 43% of influent nitrate was removed by the MIEX[®] system. Compared to column-based SBA approaches, MIEX[®] does not exhibit chromatographic peaking once the operation is in steady state. Unlike SBA columns, however, the MIEX[®] pilot system required filtration on the effluent to keep turbidities below 1.0 NTU. The MIEX system also showed an increase in effluent conductivity by 12%, most likely resulting from insufficient resin rinsing during regeneration.

WRT Adsorptive Media. WRT Z-24TM media successfully removed Cr(VI) for 620 BV before breakthrough of 5 μ g/L (Figure 6). Compared to other tested technologies, Z-24TM media required a much longer EBCT of 30 minutes that was achieved using 6 treatment columns in series. Figure 6 shows the breakthrough curves for EBCTs of 10, 20 and 30 minutes

(corresponding to effluent from columns 2, 4, and 6, respectively). The high EBCT required by the Z-24[™] media would translate into large columns required for full-scale treatment.

Filtronics Reduction/Filtration. Filtronics tested a reduction/filtration pilot unit using four different 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 Cr(VI) in the influent. 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 to 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).

Reduction/Coagulation/Filtration. Cr(VI) reduction with ferrous sulfate and Cr(III) removal by coagulation and filtration were tested under 17 different conditions, with variables including Fe(II):Cr(VI) mass ratio, 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% occurred for a 10:1 mass ratio (Figure 8).

In bench-scale testing using Glendale groundwater (AWWARF, 2004), better total Cr removal was achieved at a pH of 6.5 compared to 7.5 and 8.0. Pilot testing showed that a reduction in pH did not impact the Cr(VI) reduction or filtration of total Cr at the pilot scale. Previous studies have shown that Fe(II) oxidation rates can be increased at higher pH values of 7.5 compared to 6.5 (Sung et al, 1980; Davison et al, 1983). However, total Cr removal efficiencies lower than 95% were observed only at a pH of 7.5 or 7.6 when filter loading rates were low at 3 or 4 gpm/sf (122 or 163 L per min/m²). Data collected during two of three pilot testing runs indicated that a

higher filter loading rate of 6 gpm/sf (245 L per min/m²) may have reduced total Cr removal. Ambient pH conditions (between 7.1 and 7.3) of the groundwater provided optimal RCF performance of the conditions tested.

Two extended runs (up to 46 hours) were tested to determine if backwash system needs could be reduced. Fe(II):Cr(VI) mass ratios of 15:1 and 25:1 were tested with ambient pH conditions and a filter loading rate of 4 gpm/sf (163 L per min/m²). The Fe(II):Cr(VI) mass ratio significantly affected the run performance. Figure 9 shows that total Cr concentrations remained below 2 μ g/L for up to 46 hours for the dose strategy of 25:1, with turbidity of less than 1 NTU and a head loss across the filter exceeding 100 inches (254 cm) of water. In contrast, Figure 10 illustrates breakthrough of total Cr and turbidity at 23 hours for a dose strategy of 15:1.

Different mechanisms of filtration can be invoked to explain Figures 9 and 10. At a 25:1 mass ratio, the steady increase in head loss and no sharp turbidity breakthrough over 46 hours reflect physical straining at the filter surface as the principal filtration mechanism. The rapid breakthrough at 23 hours for the 15:1 mass ratio suggests that the filtration mechanism for the lower ratio involved penetration of Fe-Cr precipitates into the filter and exceedance of the filter bed storage capacity. The difference in the mechanism of filtration may be due to capacity of the 25:1 dose to form larger particles that 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. The 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.

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

disposable USF/R&H WBA resin, WRT media, and backwash solids from RCF. All residuals passed the federal requirements for disposal as a non-hazardous waste, but all were classified as hazardous for disposal in California based on the more rigorous WET procedure. Additional testing by XRF spectrometry demonstrated that the WBA resin capacity for Cr was at least $3.2 \pm 0.2\%$ (32,000 µg/g as Cr).

Residuals minimization via brine recycle was tested in the USF/R&H SBA resin regeneration experiment, showed promise in effectively regenerating SBA resin a number of times if 26% brine is used.

Solid-liquid separation of backwash water from the RCF process was significantly improved by the addition of high molecular weight polymer, which resulted in the backwash water containing less than 100 μ g/L of total Cr and 10 mg/L of Fe after 20 minutes of settling with 0.2 mg/L of polymer (and less than 0.5 μ g/L total Cr and 4.6 mg/L Fe with 1.0 mg/L of polymer). Preliminary results show that the backwash water may be able to be recycled to the head of the plant with fine-tuning of the settling process.

SUMMARY AND CONCLUSIONS

Several pilot tested technologies were successful in achieving the treatment goal of 5 μ g/L Cr(VI) removal from drinking water. Column strong-base anion exchange resins demonstrated more reliability in reaching the treatment goal than a reactor system. The best-performing SBA resin achieved 1,900 BV to a breakthrough of 5 μ g/L. Adsorptive media, including zeolite media and GAC, had comparatively much lower capacity with approximately 600 BV. Weak-base anion exchange showed higher than anticipated capacity for Cr(VI) removal up 38,000 BV.

Strict pH control is required for WBA resin performance and should be further tested to identify the resin's true capacity under controlled 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 with reduction with ferrous sulfate, coagulation, and dual-media filtration was very effective in both reducing Cr(VI) and removing total Cr for a period of six hours to two days before backwash was needed.

Critical issues to consider in demonstration testing were highlighted and examined in pilot testing, including chromatographic peaking of competitive anions for SBA resins, operational strategies, and process residuals management and minimization.

All of the successful strategies identified in this research have the potential for removing Cr(VI) from drinking water to levels below or even far below the 5 µg/L goal of this research. Because there are no operational facilities demonstrating the reliable attainment of these low Cr(VI) levels, the City of Glendale is proceeding with the design of a demonstration-scale treatment program to further test selected technologies at well head treatment flow rates (500 gpm).

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TABLES

Table 1.	Water	quality	of	Glendale source	water	for	pilot	testing
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Average Concentration in Blended Water from the NOU wells
215
0.5
68
850
332
5.3
7.4
0.25
27
90
0.09

 Table 2. Pilot tests of vendor-supplied treatment technologies

Supplier	Technology	Technology Volume of Media Flow Rate		EBCT or Contact Time	Residual
Calgon	Ion Exchange (Column)	0.35 ft ³ (0.010 m ³)	1.5-2.0 gpm (5.7-7.6 L/min)	1-2 min	Brine
	GAC Adsorption	0.35 ft ³ (0.010 m ³)	0.5 gpm (1.9 L/min)	5 min	Media
Filtronics	Reduction/ filtration	on/ filtration N/A 0.5 gpm (1.9 L/min)		N/A	Backwash
Orica	Ion Exchange (Continuous reactor)40-60 mL resin/ L water2.5 gpm (9.5 L/min)		2.5 gpm (9.5 L/min)	30 min contact time	Brine
US Filter/ Rohm & Haas	SBA Resin (Column)	1 ft ³ per column (0.028 m ³)	2.0 gpm (7.6 L/min)	3-4 min per column	Brine
	WBA Resin (Column)	0.5 ft ³ per column (0.014 m ³)	1.5-2.0 gpm (5.7-7.6 L/min)	2-3 min per column	Media
WRT	Surface reduction/ adsorption	7 ft ³ in 6 serial columns (0.20 m ³)	1.5-2.0 gpm (5.7-7.6 L/min)	30 min total	Media



Figure 1. USF/R&H SBA Cr(VI) breakthrough curves



Figure 2. USF/R&H SBA chromatographic peaking of nitrate and phosphate



Figure 3. USF/R&H WBA Cr(VI) removal and pH variation during testing



Figure 4. Cr(VI) breakthrough curves for Calgon's SBA resins and GACs



Figure 5. MIEX[®] treatment efficiency and resin dose as a function of sample number collected



Figure 6. WRT breakthrough curve for 10, 20, and 30 minute EBCTs



Figure 7. Filtronics Cr(VI) reduction and removal by filtration





loading rates (FLR in gpm/sf) for Filters 1 and 2



Figure 9. RCF 46-hr run at a 25:1 Fe:Cr ratio: total Cr, head loss and turbidity



Figure 10. RCF 24-hr run at a 15:1 Fe:Cr ratio: total Cr, head loss and turbidity



Figure 11. TCLP and California WET results for the pilot tested technologies with disposable

media or solid residuals

FOOTNOTES

- ¹ J.T. Baker, Phillipsburg, NJ.
- ² MKM (Mineral King Minerals), Hanford, CA.
- ³ FisherBrand, Hampton, NH.
- ⁴ Ciba MagnaFloc E40, Ciba Specialty Chemicals, Suffolk, VA
- ⁵ Agilent 7500C, Agilent Technologies, Palo Alto, CA.
- ⁶ Dionex DX-320, Dionex Corporation, Sunnyvale, CA.
- ⁷ Spectro XEPOS pED-XRF, Spectro Analytical Instruments, Inc., Marlborough, MA.
- ⁸ ARL 3410+, Thermo Electron Corporation, Waltham, MA.
- ⁹ Dionex Series 4500i, Dionex Corporation, Sunnyvale, CA.
- ¹⁰ Hach DR-890, Hach Company, Loveland, CO.
- ¹¹ SensION 1 pH Meter, Hach Company, Loveland, CO.
- ¹² Hach CO150 Conductivity Meter Hach Company, Loveland, CO.
- ¹³ Hach 2100P Turbidimeter, Hach Company, Loveland, CO.

Chapter 2

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Pilot Studies of Hexavalent Chromium Removal in Drinking Water by Ion Exchange Technologies

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Short Title: Hexavalent Chromium Removal by Ion Exchange Technologies

ABSTRACT

Public concern regarding hexavalent chromium, Cr(VI), in drinking water, coupled with the State of California's regulatory mandate has encouraged the investigation of treatment technologies to remove Cr(VI) to concentrations well below the USEPA and California total chromium standards. Ion exchange technologies were evaluated for Cr(VI) removal in Glendale,

California. Technologies tested include strong and weak base anion exchange resins, in column and reactor configurations, from US Filter with Rohm & Haas, Calgon Carbon Corporation, and Orica Watercare. Residuals management issues, including resin regeneration, resin disposal options and waste minimization strategies, were assessed.

The best performing strong base resins treated approximately 1,900 bed volumes of water before exceeding the targeted goal of 5 μ g/L Cr(VI). Chromatographic peaking by lesser-preferred anions, including nitrate, was demonstrated for one strong base resin. The weak base resin exhibited much higher Cr(VI) removal capacity— treating more than 38,000 bed volumes of water without regeneration. However, the weak base resins required tight pH control for effective removal of Cr(VI). Finally, the continuously mixed strong base resin system (MIEX[®]) demonstrated the ability to remove Cr(VI) to 5 μ g/L approximately half of the time using high resin doses.

Key words: Chromium, ion exchange, pilot, residuals, treatment

INTRODUCTION

Chromium (Cr) has been widely used in industry, notably for alloys, electroplating, pigment production, leather tanning, and biofilm control in cooling towers (Fishbein 1981; Brandhuber *et al.* 2004; Jacobs & Testa 2005). Inadequate storage and improper disposal practices have caused Cr to be released into groundwater (Calder 1988; Palmer & Wittbrodt 1991). Cr can also enter groundwater supplies, rivers, and freshwater lakes from the weathering of Cr-bearing minerals in bedrock and soils (Robertson 1975; Nriagu & Nieboer 1988; Cox & McLeod 1992; Kaczynski & Kieber 1993).

In aqueous systems, Cr primarily occurs in two oxidation states: trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI). Aqueous Cr(III) is commonly present as cationic species, including $Cr(OH)^{2+}$ and $Cr(OH)_{2}^{+}$, and is an essential trace nutrient (Motzer 2005). In contrast, Cr(VI) occurs as anionic species, including $HCrO_{4}^{-}$, CrO_{4}^{2-} and $Cr_{2}O_{7}^{2-}$ and is toxic to bacteria, plants, and animals (Richard & Bourg 1991; USEPA 1998; Kimbrough *et al.* 1999).

Although Cr(VI) is classified as a human carcinogen by inhalation (USEPA 1998), its toxicity by ingestion is controversial (Flegal *et al.* 2001). USEPA set a drinking water maximum contaminant level (MCL) for total Cr at 100 μ g/L to protect public health. The State of California adopted an even lower 50 μ g/L MCL for total Cr and by California law must adopt a Cr(VI) MCL. In 1999, the California Office of Environmental Health Hazard Assessment (OEHHA) identified *de minimis* cancer risk levels for Cr(VI) and total Cr at 0.2 and 2.5 μ g/L, respectively. However, scientific uncertainties of the health effects of Cr(VI) by ingestion led OEHHA to later rescind the PHG and the State to delay the adoption of the Cr(VI)-specific MCL. Nevertheless, public concern and the intentions of California to set a Cr(VI) MCL have prompted the investigation of treatment technologies with the potential to remove Cr to concentrations well below the current USEPA and California standards.

Anion exchange removal technologies have been successfully used in industrial applications with relatively high concentration treatment goals (Jakobsen & Laska 1977; Rengaraj *et al.* 2001; Yalcin *et al.* 2001; Rengaraj *et al.* 2003). Several bench-scale studies have shown the potential for ion exchange to remove Cr(VI) to lower concentrations (< 50 μ g/L) in drinking water (Bahowick *et al.* 1996; Clifford 1999; Höll *et al.* 2002; Brandhuber *et al.* 2004).

The purpose of this study was to determine the technological feasibility of treating Cr(VI) contaminated drinking water to very low levels (i.e. less than 5 μ g/L with 95% removal

efficiency). Residuals from tested anion exchange treatment processes were also evaluated, including Cr-containing regenerant brine and the resin itself. The potential for regeneration of top-performing ion exchange resins with recycled brine was tested to determine if waste brine volume could be minimized. Tests were performed on disposable spent media to determine if the media would be classified a hazardous waste under federal or California regulations.

METHODS

Pilot Testing Approach. The City of Glendale, in cooperation with the Cities of Los Angeles, Burbank, and San Fernando, is implementing a four-phase program culminating in the installation of a full-scale treatment system for low-level Cr(VI) removal. The four-phase program includes a bench study, pilot study, demonstration study, and full-scale implementation. The bench study improved the understanding of Cr in drinking water chemistry and screened promising Cr(VI) treatment technologies (Brandhuber *et al.* 2004). The pilot study, a portion of which is reported in this paper, evaluated vendor-provided pilot units and several vendorindependent technologies for Cr(VI) removal. The results from the pilot study will be used to select one or two technologies for demonstration testing and full-scale implementation.

Three ion exchange vendor pilot units were tested at the Glendale Water Treatment Plant (GWTP) in Glendale, California between August 2003 and June 2004. Strong base anion (SBA) exchange tests were run for approximately one to three weeks each and the weak base anion (WBA) exchange test lasted eight months. Test duration was based on the time needed for the systems to achieve Cr(VI) complete breakthrough, with each system initially anticipated to be run for a maximum of six weeks. Influent and effluent water from the pilot units were tested to

determine Cr(VI) removal efficiency and the impact of the units on other water quality parameters.

Influent Water Quality. During the first three weeks of pilot testing, the source water was obtained from the blended effluent of the GWTP before chlorination. The addition of a phosphate-based sequestering agent for upstream air stripping presented a challenging water quality for the first two vendors (Orica and an adsorptive media vendor). Moreover, the blended GWTP effluent was not fully representative of the individual wells with Cr(VI) contamination approaching 50 μ g/L. Therefore, the piping system was amended to supply untreated North Operating Unit (NOU) water to the pilot units. Both of the initial two vendors were permitted to begin their tests again using the new supply. Table 1 shows the major parameters of the source water after the piping change. The Cr(VI) concentration in the source water averaged 9-10 μ g/L (Glendale Water & Power 2002).

In order to evaluate potential removal of Cr(VI) from these higher Cr(VI) wells and to quantify 95% Cr(VI) removal at levels higher than the method detection limits, the blended source water was spiked with 10% chromic acid (H₂CrO₄) (J.T. Baker). Chromic acid was spiked into a 100 gallon influent blending tank using a flow-paced electronic metering pump to achieve a Cr(VI) concentration in the influent tank of 100 μ g/L. The spiked tank water was then fed to all pilot systems at rates between 0.2 and 2 gallons per minute (GPM).

Vendor Pilot Systems. The pilot systems tested in this study were provided by Orica WaterCare (Orica's MIEX[®]), US Filter in partnership with Rohm & Hass (USF/R&H), and the Calgon Carbon Corporation (Calgon).

Orica WaterCare MIEX[®] *System.* The MIEX[®] pilot unit was a continuous anion exchange reactor that used a macroporous, SBA resin containing a magnetized component within the resin structure. The small resin bead size (180 μ m) provided a large surface area for anion exchange, and the magnetic component allowed for rapid resin agglomeration and settling.

Figure 1 shows a flow diagram for the MIEX[®] pilot system. Influent water was pumped into the reactor mixing tanks at a flow rate of 2 GPM. The mixing tanks provided between 5 and 30 minutes of contact time for anion exchange before the resin-water suspension flowed by gravity to the resin separation tank. Treated effluent then flowed over the weir of the separation tank. The resin beads settled by magnetized agglomeration to the tank bottom, where the resin was returned to the mixing tank for another loading cycle. Between 5 to 10% of used resin beads were continuously removed for regeneration through a side loop using 100-120 g/L NaCl dosed at 360 g NaCl per L of resin. A constant amount of fresh resin (including a portion of regenerated resin) was pumped into the mixing tank to maintain the desired resin dose.

USF/R&H Pilot System. The USF/R&H pilot system consisted of two separate trains each containing two anion exchange columns in lead-lag configurations. Two anion exchange resins manufactured by Rohm & Haas were tested, including Amberlite[®] PWA410 Cl, an SBA resin, and Duolite[®] A7, a WBA resin. The SBA resin was a Type 2 quaternary amine gel structure resin with a styrene divinylbenzene copolymer bead. The WBA resin was a crosslinked phenol-formaldehyde polycondensate with secondary amine functional groups.

Each of the identical SBA columns contained 0.028 m³ of Amberlite[®] PWA410 Cl resin. The manufacturer-specified operating pH range for Cr(VI) removal by the SBA resin was 0 to 13, which is a large range due to ionization of the quaternary amine functional groups. In contrast, the WBA resin removed Cr(VI) only in the acidic pH range of less than 6, which is when the

secondary amine functional groups are protonated (Clifford *et al.* 1999). USF/R&H used a 0.1 m^3 strong acid cation exchange column to reduce pH to less than 6 prior to the two lead-lag WBA columns, which each contained 0.014 m³ of Duolite[®] A7 resin.

Figure 2 shows a schematic of the USF/R&H pilot units. The SBA train was operated continuously at a flow rate of 2 GPM with an empty bed contact time (EBCT) of 3.7 minutes for a period of 3 weeks. The WBA train was operated at 2 GPM with an EBCT of 1.9 min for each column for 8 months due to high removal efficiency. During that unexpectedly long period, the exhausted cation exchange column was replaced numerous times and backwashes of the WBA resin columns were necessary on occasion. The total amount of water passing through each train was recorded using flow totalizers.

Calgon Pilot System. The Calgon pilot system was a flow-through anion exchange column skid consisting of 4 identical columns operated in parallel (Figure 3). Each column was 10 cm in diameter, with approximately 1.2 m of media in each column. The flow rate of the system was controlled at approximately 2 GPM, corresponding to the EBCT of 1 to 2 minutes. Four types of strong base anion exchange resins were tested, including WT201, WT202, WT203, and WT204. WT201 was a Type 1 resin, WT202 had tri-alkyl ammonium functional groups in chloride form on copolymer of styrene and divinylbenzene, WT203 was a crosslinked polystyrene resin with quaternary amine functional groups, and WT204 was a secondary amine phenol-formaldehyde copolymer.

Sampling Strategy of Pilot Systems Operations. Samples from each pilot system were collected from sampling ports after the Cr(VI) spiked influent blending tank and from the treated

water effluent line. Additional samples were collected depending on the pilot unit (e.g. between two columns for a unit with a lead-lag configuration).

The sampling frequency was at least daily for the duration of the pilot tests with the exception of the USF/R&H WBA unit, which lasted much longer to breakthrough and was sampled at least twice per week. MIEX® was sampled three times per day since the system quickly achieved steady state. Process measurements, including flow rate and head loss, were recorded daily.

Influent and effluent samples were measured for Cr (total and hexavalent), iron (total), pH, temperature, conductivity, turbidity, alkalinity, nitrate, sulfate, phosphate, silicate, and arsenic (Table 2). Other water quality parameter measurements varied depending on the type of removal technology.

Brine Recycling Experiment. A separate pilot unit was constructed for SBA regeneration testing and brine recycle. This unit consisted of two duplicate parallel columns using Amberlite[®] PWA410 Cl resin, which was used as a representative SBA resin that demonstrated a good removal efficiency. The columns were 7 cm in diameter with 50 cm of resin and one BV was equal to 0.0016 m³. Column flow rates were approximately 0.16 GPM, corresponding to a 2.5 min EBCT.

Regeneration was accomplished by feeding 5 BV of concentrated brine (either 6% or 26% NaCl solution) from the 20 L brine tank in concurrent flow through the resin at 0.026 GPM, followed by slow rinse with 2 BV of Cr(VI) spiked influent water at 0.026 GPM and fast rinse using 24 BV of influent water at 0.16 GPM. The brine was prepared by dissolving non-iodized food-grade NaCl in unspiked well water. The overall regeneration period lasted approximately 3 hours, after which the columns were brought back online.

An automated sampler comprised of a controller and set of 12 solenoid valves with plastic tubing connected to 12 sample bottles was installed on the pilot unit to enable around-the-clock sampling. The controller was programmed to open and close parallel solenoid valves at specified time intervals. A portion of the column effluent was diverted to the automated sampler when a valve was open. Sampling frequency ranged from two to eight hours depending on the cycle.

Cr(VI) concentrations in influent and effluent samples were closely monitored in the field to determine real-time performance with subsequent regeneration cycles. During the first and second normal operation cycle, nitrate, phosphate, silicate, and sulfate concentrations were also measured to capture chromatographic peaking.

Laboratory methods. Total Cr and Cr(VI) concentrations were measured using established methods at the Utah State University (USU) Water Research Laboratory. Before the samples were shipped to USU, total Cr samples were acidified to a pH of less than 2 with 2% HNO₃ and Cr(VI) samples were preserved with NaOH to a pH greater than 10. These samples were analyzed within 30 days of collection. Total Cr concentrations were measured by Agilent 7500C inductively coupled plasma mass spectrometer (ICP-MS) with an octopole reaction system, in accordance with USEPA Method 200.8 (USEPA 1994) and with a detection limit of 1.0 μ g/L. Iron and arsenic concentrations were determined by ICP-MS at the USU laboratory along with total Cr. When high iron and/or turbidity measurements were detected in the effluent, the preserved samples were passed through a 0.45 μ m filter and split. Half of the split was run as-is while the other half was digested using 4% concentrated HCl and 2% hydroxylamine-hydrochloride (10 g NH₂OH-HCl) at 85°C for 24 hours.

Cr(VI) samples were analyzed using a Dionex DX-320 ion chromatograph (IC) with an AD25 post-column UV-visible detector (USEPA 1996). The IC method detection limit was 0.2 μ g/L. The guard and analytical columns were Dionex Ion Pac NG 1 and Dionex Ion Pac AS 7, respectively. The sample loop volume was 500 μ L and the reaction coil volume was 700 μ L. Preserved samples were filtered through a 0.45- μ m filter prior to analysis to protect the column.

For brine samples, Cr was measured using an ARL 3410+ inductively coupled optical emission spectrometer (ICP-OES), and sulfate and chloride were quantified with a Dionex Series 4500i IC at UC Boulder.

Spent WBA resin from the USF/R&H pilot unit was tested for hazardous waste characteristics. The toxicity characteristic leaching procedure (TCLP) was run in accordance with EPA methods (Publication SW-846). The California Waste Extraction Test (WET) was also performed to evaluate hazardous waste characteristics as required by State of California (22 CCR 66261). The CA WET test is usually considered a more rigorous test for some elements like Cr and As because it uses citrate extractant rather than acetate, a longer extraction time (48 hours instead of 18 hours), and anoxic conditions. The spent WBA resin was also analyzed using x-ray fluorescence (XRF) using a Spectro XEPOS pED-XRF at Wellesley College (Wellesley, Massachusetts) to determine the total amount of Cr and other elements retained by the WBA resin.

Field methods. Many water quality parameters were measured on the day of sample collection in the field (Table 2). Cr(VI) was measured with an onsite Hach DR/890 colorimeter using Hach Method 8023. The detection limit of this method for Cr(VI) was approximately 10 μ g/L, which was 50 times higher than the USU laboratory method. Field measurement of Cr(VI)

enabled a quick evaluation of pilot system performance but was not used to quantify the breakthrough curves.

Sulfate, nitrate, silicate and phosphate were measured in the field using Hach methods to investigate the removal of these potentially competitive anions by the tested technologies. In addition, other chemical and physical parameters (such as pH, conductivity, alkalinity, hardness, turbidity, and temperature) were measured to determine the impact of treatment processes on finished water quality and control system operations.

Quality Assurance/Quality Control. QA/QC sampling included duplicates, matrix spikes, matrix spike duplicates, and field blanks. Duplicates were collected for at least 10% of samples. The relative percent differences (RPD) between duplicate analyses were consistently less than the target of 20%. Matrix spikes were performed for at least 5% of all samples analyzed in the laboratory, or at least once per sample run to determine measurement accuracy. For total Cr measurements by ICP-MS, the data acceptance criterion for spike recovery was between 70 and 130%. For Cr(VI) analysis by IC, spike recovery of 79 –122% was deemed acceptable. Data outside of these ranges were rejected and samples were rerun. Field blanks were collected at least once per day to identify any possible contamination caused by field sample handling, transport, storage, preservatives, or deionized water.

RESULTS AND DISCUSSION

MIEX[®] Pilot System

Cr Removal. MIEX[®] was the only ion exchange system tested twice: first (and most extensively) when the initial influent water was blended GWTP treated effluent (i.e. containing a

phosphate-based sequestering agent), and second when the untreated NOU water was used for pilot testing. Three operating parameters, including resin contact time, resin dose, and regeneration rate as a percentage of the applied resin dose, were adjusted to optimize system performance during the initial testing of this unit. Resin dose was found to be critical to the overall Cr(VI) removal performance. Contact time had less of an impact on Cr(VI) removal, while regeneration rate (between 5-20%) showed little impact. Optimal operating conditions were achieved with a resin dose between 40 to 60 mL resin per L of water, 20 min contact time, and 5% regeneration rate.

Reevaluation of the MIEX[®] system using raw NOU water focused on evaluating Cr(VI) removal efficiencies under these pre-determined conditions. Figure 4 shows the Cr(VI) removal efficiency of the MIEX[®] unit with the applied resin dose. The removal efficiency ranged from 92% to 97% at the applied resin dose of 40 to 60 mL/L. The goal of 5 μ g/L Cr(VI) was achieved approximately half of the time (i.e. 16 out of 28 samples). Total Cr and Cr(VI) concentrations confirmed that no Cr oxidation state change occurred during the ion exchange process.

Impacts of Other Anions. Sulfate, nitrate, silicate, and phosphate were analyzed to determine their removal by the MIEX[®] resin and to evaluate competition for ion exchange sites. Although chromate ions have a relatively high affinity for common anion exchange resins, the presence of other anions at much higher concentrations can impair Cr(VI) removal efficiency. Results from the pilot testing showed negligible removal of phosphate and silicate by the MIEX[®] system. In contrast, an average of 43% of nitrate and 80% of sulfate were removed by the system. The high sulfate levels in the influent water (90 mg/L) likely limited the complete removal of Cr(VI).

Finished Water Quality. Other water quality parameters were measured to determine additional impacts of the pilot unit on finished water quality. No significant change was

observed in hardness. pH slightly increased from 7.4 to 7.6, possibly due to bicarbonate removal of 10 to 20%. Effluent turbidity in the second round of MIEX® testing was less than 0.20 NTU due to the addition of a 0.45 μ m filter. In contrast, the first round of testing yielded turbidity spikes of up to 3.5 NTU with no filtration. Conductivity was approximately 12% higher in the effluent (820 μ S/cm) possibly due to insufficient rinsing during the resin regeneration process.

USF/R&H Pilot System: Strong Base Anion Exchange

Cr Removal. Figure 5 shows the breakthrough curves characterizing Cr(VI) removal by the SBA columns. The influent Cr(VI) concentration averaged 85 μ g/L. Fluctuations in the influent Cr were caused by the inaccuracy of the electronic metering pump at the lower end of the effective range. Effluent from the first column reached the 5 μ g/L Cr(VI) breakthrough point by 1,900 BV. The second column achieved breakthrough of 5 μ g/L by 3,800 BV, consistent with loading in the first lead column in the lag column. No Cr oxidation state changes were detected through the pilot units.

Impacts of Other Anions. In using anion exchange technologies for drinking water treatment, the problem of chromatographic peaking has been hypothesized but not detailed. Chromatographic peaking is a phenomenon in anion exchange column processes in which the less preferred but more prevalent competitive anions accumulate on the column and are then displaced by more preferred species, resulting in a temporarily high effluent concentration of the less preferred species. For the SBA train, initial removal of bicarbonate, nitrate, phosphate, and sulfate was observed. However, the peaking phenomena were not effectively captured for the USF/R&H unit by a daily sampling frequency. A more detailed chromatographic peaking evaluation is presented later in the discussion of brine recycling experiment.

Finished Water Quality. The SBA train initially depressed the effluent pH to 5.5 due to bicarbonate removal. The effluent pH returned to the influent pH level within 350 BV of water treated. No impacts of the SBA train on hardness and conductivity were observed. The turbidity of the effluent remained below 0.5 NTU.

USF/R&H Pilot System: Weak Base Anion Exchange

Cr Removal. Figure 6 displays the Cr(VI) breakthrough curves for the WBA train. The influent to the serial anion exchange columns was the effluent from the cation exchange column operated to generate H^+ and reduce pH. The WBA resin did not consistently discharge treated water at greater than 5 µg/L Cr(VI) until approximately 38,000 BV (112,000 gallons) for WBA Column 1. No breakthrough curve was observed for Column 2 up to 80,000 BV. Isolated peaks of Cr(VI) in both column profiles were attributable to pH excursions and backwashing needs.

Impact of pH on System Performance. Effective Cr(VI) removal by WBA resin was found to depend on pH, in contrast to SBA resins. The WBA resin required an acidic pH less than 6 to maintain positively charged exchange sites. A pH adjustment system was necessary in the WBA train because the influent pH was approximately 7.5. In this pilot study, USF/R&H supplied a strong acid cation exchange column for pH adjustment. Calcium and magnesium in the influent water were exchanged for hydrogen ions, which decreased the pH of influent to the WBA train.

A disadvantage of using cation exchange column as a pH control device for pilot testing was the continuous increase of pH due to exchange site exhaustion. When the cation exchange column effluent pH was approaching or found to be higher than pH 6, a new column was installed. On occasion, the system exceeded pH 6 before a new cation exchange column could be put online. Figure 7 presents the effluent pH of the cation exchange column (i.e. influent pH to anion exchange columns) as a function of BV treated. Bed volumes shown in Figure 7 correspond to the BV equivalent of the WBA columns for direct comparison with the breakthrough curve in Figure 6.

A comparison of Figures 6 and 7 shows that peak Cr(VI) excursions coincided with a relatively high pH conditions (pH > 6), demonstrating decreased Cr(VI) removal efficiency at pH values greater than 6. Figure 6 also shows three samples with high Cr(VI) concentrations from Column 2, although no indication of sustained breakthrough was observed. The 12 μ g/L peak (at 55,400 BV) was caused by a pH of 7.1. However, the other two elevated concentrations (19 μ g/L at 15,800 BV and 47 μ g/L at 19,400 BV) were not caused by high pH and the Cr(VI) concentrations from Column 1 were 0.8 μ g/L and 1.1 μ g/L, respectively. These two Cr(VI) surges in Column 2 were believed to be caused by excessive particle loading in the resin bed, which caused channeling of a portion of the influent water directly to the effluent. Column 2 returned to normal operation after backwash. Later, measures were taken to reduce influent particle loading by preventing algae growth in the water lines and influent blending tank, including changing to dark tubing and covering the influent mixing tank.

Cr(VI) Reduction in the WBA Treatment Train. Unlike previous results from the MIEX[®] system and the SBA train, effluent Cr(VI) and total Cr concentrations differed for the WBA treatment train. Figure 8 presents the difference between Cr(VI) and total Cr to show the Cr(III) concentrations in effluents from WBA Columns 1 and 2. Compared to the Cr(VI) breakthrough curves in Figure 6, the Cr(III) concentrations in Columns 1 and 2 were frequently above 5 μ g/L. The negative values for the Cr(III) concentrations are due to the method of calculating Cr(III) by difference (total Cr – Cr(VI)), and these negative values were typically less than 2 μ g/L. The

higher values of -11 μ g/L at 57,900 BV and -12 μ g/L at 63,100 BV were apparently caused by difference in analytical variability of total Cr and Cr(VI).

Since Cr(VI) was the dominant Cr species in the influent water, the presence of Cr(III) in the effluent was an indication of reduction reactions occurring on the resin surface or in the resin matrix. The mechanism of Cr removal by WBA resin is not fully understood. However, the resemblance between Figures 7 and 8 shows that pH impacts the Cr(III) profile. An inverse behavior was observed, with relatively higher pH (between 5.5 and 6) corresponding to lower Cr(III) concentrations (usually less than 5 μ g/L). This suggests that the optimum pH range to minimize total Cr in the effluent is 5.5 – 6. Further research is necessary to determine the Cr removal mechanisms by the WBA resin and capacity of the resin under constant pH conditions.

Finished Water Quality. The major impacts of the WBA train on finished water were caused by the cation exchange column, including the reduction of hardness and alkalinity. These problems should be resolved by replacing the cation column with an acid feed system. Due to the requirement of a low pH for Cr(VI) removal by the WBA resin, caustic addition may be needed in the effluent to raise the pH and stabilize calcium carbonate deposition and dissolution.

Characterization of Spent Resin. Due to extremely long run times (38,000 BV) of WBA resin for Cr(VI) removal compared to SBA resins (1,900 BV), the WBA resin could be used as a disposable media in drinking water treatment applications. TCLP and CA WET tests were performed to determine whether the spent WBA resin would be considered hazardous waste. The Cr(VI) extractable concentration revealed by the TCLP was 0.03 mg/L, which is less than the regulatory level of 5.0 mg/L. The spent resin would be considered non-hazardous waste for Cr under federal requirements. However, the spent resin exceeded the CA WET test limits with a Cr concentration in the extraction liquid of 7.0 mg/L– higher than the 5.0 mg/L soluble

threshold limit concentration. The spent WBA resin would be characterized as hazardous waste if disposed of in a California landfill.

In addition to extraction tests on WBA residuals, total solid phase Cr was determined using xray fluorescence spectrometry. The spent resin contained the astonishingly high Cr concentration of $3.2 \pm 0.2\%$ (32,000 µg/g as Cr), compared to 6 µg/g in the fresh resin. Other elements adsorbed on WBA spent resin were also determined by XRF (Table 3), including inorganic ions at background levels in the water that were concentrated on the resin.

Calgon Pilot System: Strong base anion exchange

Figure 9 shows the Cr(VI) breakthrough curves of four strong base anion exchange resins using Calgon's pilot system. The run lengths to 5 μ g/L breakthrough were approximately 1,000 BV for WT201, 1,000 BV for WT202, 350BV for WT203, and 1,400 BV for WT204. Compared with the Amberlite[®] PWA410 Cl resin in the SBA train of USF/R&H system, the resins tested in the Calgon system were less effective due to either less effective Cr(VI) removal and/or pilot unit design. The Calgon pilot skid experienced difficulties with air entrainment and subsequent loss of resin contact volume. The concentrations of Cr(VI) and total Cr were similar among both influent and effluent samples, indicating that only Cr(VI) was removed by the resins.

Brine Recycling Experiment

USF/R&H SBA Amberlite[®] PWA410 Cl resin was chosen for a regeneration experiment as discussed in the Materials and Methods section. Since the two columns were operated in the same manner using the same resin, one column was served as a duplicate to confirm the results from the other column. Results from these two columns were virtually identical; therefore data

from only one column are shown in the following discussion. The pilot system operated until full breakthrough occurred, at which point the resin was regenerated. A total of seven cycles (Runs 1 to 7) were conducted using the same resin with recycled brine.

Regeneration with 6% NaCl Brine. Runs 1 through 4 were regenerated with 6% NaCl brine (Regenerations 1 through 3). Figure 10 shows the corresponding breakthrough curves. For Run 1, the 5 μ g/L Cr(VI) breakthrough point occurred at 1,900 BV, which was akin to the performance of SBA train in the USF/R&H pilot system. The bed volumes required for 5 μ g/L Cr(VI) breakthrough decreased dramatically from 1,900 BV (Run 1) to less than 500 BV for Run 2, and less than 380 BV for Run 3, indicating the 6% NaCl was not an effective regenerant for Cr(VI) using this type of resin. The initial peak in the Run 4 breakthrough curve was due to the leakage of brine into the sample line and is not representative of the system performance.

Regeneration with 26% NaCl Brine. A saturated brine (26% NaCl) was subsequently tested for Runs 5 through 7 (Regenerations 4 through 7), which was achieved by adding NaCl to the 6% brine that had been reused three times. Figure 11 shows the breakthrough curves for Runs 5 through 7. The run lengths to a breakthrough of 5 μ g/L Cr(VI) were approximately 1,500 BV, 1,200 BV, and 500 BV, respectively. Runs 5 through 7 demonstrated a better Cr(VI) removal performance than those using 6% NaCl regenerant (Runs 2 through 4). However, the run lengths were shorter after regeneration even with 26% NaCl, compared to 1,900 BV obtained for the fresh resin (Run 1).

Brine Accumulation of Cr(VI) and Sulfate. After 7 regenerations, Cr(VI) in the recycled brine increased from 0.15 mg/L to 112 mg/L. Figure 12 illustrates the accumulation of Cr(VI) in the brine. The steady increase of Cr(VI) in the brine demonstrated that the Cr(VI) concentration in the brine was not the likely limit on regenerability. Regeneration efficiencies, computed as the

ratio of recovered Cr(VI) from regeneration to the calculated amount of Cr(VI) accumulated on the resin, are shown in Figure 12 for each recycle. The recovered Cr(VI) from regeneration was calculated by multiplying the increase in the brine Cr(VI) concentration for each cycle by the brine volume. The Cr(VI) retained on the resin was calculated as the difference between the area under influent and effluent Cr(VI) breakthrough curves (Figures 10 and 11). The regeneration efficiency fluctuated between 39% and 132%. Less than 100% regeneration was observed using 6% brine and after the first regeneration with 26% brine, with the best efficiency occurring for the fourth regeneration (Figure 10). The calculated regeneration efficiency of Regeneration 1 (39%) was lower than that of Regeneration 2 (75%) and Regeneration 3 (68%). This result was observed despite the initial use of fresh brine for Regeneration 1, which contained less Cr(VI) and sulfate than in later runs. For Regeneration 4, the brine concentration was increased from 6% to 26%. The higher chloride concentration in the brine helped to remove more Cr(VI) than Run 4, resulting in a 132% regeneration efficiency that included Cr accumulated on the resin during the previous run. Successive regenerations then fell below 100% and demonstrated a decreasing trend in regenerability.

Sulfate accumulation in the brine likely impacts the regeneration process using recycled brine. Figure 13 shows the concentration of sulfate following each regeneration. Sulfate levels increased from 160 mg/L in the fresh brine to 18,000 mg/L after 7 regeneration cycles.

Chromatographic Peaking. Chromatographic peaking of anions was observed in USF/R&H SBA pilot unit, but the peaking trend was not clearly resolved due to insufficient sampling frequency. An automated sampler constructed to capture complete chromatographic peaking profiles (refer to Materials and Methods) was used during Runs 1 and 2 to obtain samples every two hours. Similar chromatographic peaking profiles were observed in both Runs 1 and 2,

indicating that the impact of one regeneration was negligible on the peaking behavior. Nitrate peaking occurred at approximately 410 BV, which was a little earlier than the phosphate peaking at 450 BV (Figure 14). The maximum concentration of phosphate was 0.8 mg/L, or 4 times as high as the influent concentration of 0.2 mg/L (Figure 14). The peak concentration of nitrate was 15 mg/L, or 3 times of the influent concentration of 5 mg/L. Importantly, the nitrate peak concentration exceeded the nitrate MCL of 10 mg/L as N. If an SBA resin is used for Cr(VI) removal, the issue of nitrate chromatographic peaking must be considered in the system. SBA treatment columns should be operated to blend down any peak episodes.

CONCLUSIONS

A variety of anion exchange technologies was evaluated for their ability to remove Cr(VI) to low levels in a drinking water supply. Column-based strong base anion exchange was effective in reducing Cr(VI) concentrations to less than 5 μ g/L with more reliability than a mixed reactor system. The best-performing SBA resin produced approximately 1,900 bed volumes of effluent before reaching a breakthrough level of 5 μ g/L. SBA system design must account for chromatographic peaking of nitrate, which was documented during pilot testing. SBA resin regeneration was found to perform better with 26% NaCl brine compared to 6% brine, and the regenerant might be recycled a few times before Cr(VI) removal deteriorates. Sulfate buildup in the recycled brine was the likely causative factor in the Cr(VI) removal deterioration.

A USF/R&H weak base anion exchange resin exhibited a much greater Cr(VI) removal capacity (38,000 BV) before breakthrough, compared to the SBA resin. However, removal of total Cr by WBA resin required tight pH control between pH 5.5 and 6. Due to its high capacity for Cr(VI), the WBA resin may be best suited for operation as a disposable media. The spent

WBA resin from pilot testing passed the TCLP but exceeded the CA WET test Cr requirements for hazardous waste toxicity and would be considered a hazardous waste for disposal in California. Additional testing of promising WBAs resin would be necessary prior to implementation in a full-scale drinking water application.

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Constituent	Influent Concentration
Alkalinity (mg/L as CaCO ₃)	215
As (µg/L)	0.5
Cl (mg/L)	68
Conductivity (µmho/cm)	840
Hardness (mg/L as CaCO ₃)	332
NO ₃ -N (mg/L)	5.3
pH	7.4
$PO_4 (mg/L)$	0.25
$SiO_2(mg/L)$	27
SO ₄ (mg/L)	87
Turbidity (NTU)	0.09

 Table 1. Major Parameters of the Glendale Groundwater

	Analytical	Analysis	QA/QC Methods		
Parameters	Method	Location	Duplicates	Matrix Spikes	Field Blanks
Total Cr	EPA 1636	USU Lab	10% of samples	5% of samples	1/unit/day
Cr(VI)	EPA 200.8	USU Lab	10% of samples	5% of samples	1/unit/day
Total Iron	SM 3120 B	USU Lab	10% of samples	5% of samples	1/unit/day
Arsenic	EPA 200.8	USU Lab	10% of samples	5% of samples	1/unit/day
Cr(VI)	Hach ¹ 8023	Field	10% of samples	None	1/unit/day
Sulfate	Hach 8051	Field	10% of samples	None	1/unit/day
Nitrate	Hach 8039	Field	10% of samples	None	1/unit/day
Silicate	Hach 8185	Field	10% of samples	None	1/unit/week
Phosphate	Hach 8048	Field	10% of samples	None	1/unit/week
pH	$SM^2 4500H^+B$	Field	10% of samples	None	None
Conductivity	SM 2510B	Field	10% of samples	None	None
Alkalinity	Hach 8203	Field	10% of samples	None	None
Hardness	Hach 8030	Field	10% of samples	None	None
Turbidity	SM 2130B	Field	10% of samples	None	None
Temperature	SM 2550	Field	10% of samples	None	None

Table 2. Analytical Methods, Locations, and QA/QC Methods

¹ Hach 2004; ² *Standard Methods* 1995.

Constituents	Concentration on Spent Resin (µg/g)	Concentration on Fresh Resin (µg/g)
Chromium	32,000	< 6
Sulfur	43,000	< 2
Phosphorus	1,400	10 - 90
Chloride	1,300	40 - 50
Vanadium	880	< 3
Uranium	490	< 0.9

Table 3. Major Elements Adsorbed on WBA Spent Resin



Figure 1. Flow diagram of Orica WaterCare MIEX[®] system



Figure 2. Flow diagram of USF/R&H SBA and WBA systems



Figure 3. Flow diagram of the Calgon pilot unit



Figure 4. Cr(VI) removal efficiency and effluent concentration for the MIEX[®] pilot unit.



Figure 5. Breakthrough curves for Cr(VI) of the USF/R&H SBA treatment train as a function of

bed volumes treated.



Figure 6. Breakthrough curves of Cr(VI) for the WBA treatment train as a function of bed volumes treated.



Figure 7. WBA treatment train pH variation observed due to cation column exhaustion



Figure 8. Effluent Cr(III) concentrations from the WBA resin columns as a function of bed

volumes treated.



Figure 9. Breakthrough curves for Cr(VI) of the Calgon pilot columns as a function of bed volumes treated.


Figure 10. Cr(VI) breakthrough curves for Runs 1 through Run 4. Run 1 used fresh resin and was followed by Regeneration 1 using fresh 6% NaCl brine. Successive regenerations used the same recycled brine.



Figure 11. Cr(VI) breakthrough curves for Run 1 (for comparison) and Runs 5 through Run 7. For Runs 5 through 7, the SBA resin was regenerated using recycled 26% NaCl brine.



Figure 12. Accumulation of total Cr in the brine (left axis) and regeneration efficiency (right axis). Run 1 was followed by Regeneration Cycle 1, etc.



Figure 13. Accumulation of sulfate in the recycled brine.



Figure 14. Chromatographic peaking of nitrate and phosphate for Run 2. The average influent nitrate and phosphate concentrations were 5 mg/L and 0.2 mg/L, respectively.

Chapter 3

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

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Abstract

A flow-through pilot-scale system was tested for removal of Cr(VI) from contaminated groundwater in Glendale, California. The process consisted of 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 μ g L⁻¹ to below detectable levels and also remove total Cr (Cr(VI) plus Cr(III)) to very low concentrations (< 5 μ g L⁻¹) under optimized conditions. Complete reduction of Cr(VI) to Cr(III) was accomplished with Fe(II) doses of 10 to 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 sf⁻¹) had negative impacts. The pilot system was able to operate for an extended time period (23 – 46 hr depending on the Fe:Cr mass ratio) before turbidity breakthrough or high head loss. Backwash water was effectively settled with low doses (0.2 to 1.0 mg L⁻¹) of high molecular weight polymer. Backwash solids were found to be non-hazardous by the TCLP test but hazardous by the California WET test.

Introduction

Chromium (Cr) is widely used in diverse products and processes (1). Industrial applications of Cr include electroplating, pigment production, and leather tanning (2), as well as 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, co-precipitation, or coagulation has been investigated (*12-16*). This chemical process has also been widely used in industrial Cr treatment for concentrations in the mg L⁻¹ 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 μ g L⁻¹ and the California MCL of 50 μ g 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 μ g 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.

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 μ g L⁻¹ (*18*), although Cr(VI) levels in two of Glendale's eight wells approach 50-60 μ g L⁻¹.

In order to evaluate potential removal of Cr(VI) from those high level wells, the source water was spiked with chromic acid (H₂CrO₄) (Acros Organics). Ten percent (w/v) chromic acid was spiked into a 100-gallon HDPE mixing tank using a flow-paced electronic metering pump to achieve a Cr(VI) concentration of approximately 100 μ g 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 dualmedia 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 FeSO₄ (6% v/v, diluted from MKM 20% Ferrous Sulfate) was injected as a reductant in all tests. Analytical grade H₂SO₄ (36N FisherBrand) was added to adjust the pH in select tests. Influent water, FeSO₄, and H₂SO₄ were mixed in an in-line static mixer before flowing into 100-gallon reduction tank equipped with a variable-speed mechanical stirrer. The reduction tank provided approximately 1 hr 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 to 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% by weight, 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 to 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:

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

Sampling locations included the feed water 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 hr during normal 6 hr operational runs. For

extended 24 and 48 hr runs, these parameters were measured every 3 hr 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 collected for Fe analysis were 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% HNO₃, FisherBrand). Cr(VI) samples 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 μ m 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 hr 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 ⁴⁰Ar¹²C mass interference with ⁵²Cr. Germanium (⁷⁴Ge) was used as the internal standard. Cr(VI) samples were analyzed using a Dionex DX-320 ion chromatograph (IC) with an AD25 post-column 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 μ L with a reaction coil of 750 μ L.

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 California waste extraction test (WET) (22).

Total suspended solids (TSS) analysis on backwash water was 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 Sens*ION*[®] 1 portable pH meter with a gelfilled 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 using diphenylcarbohydrazide reagent (24). However, field measurements of Cr(VI) were not reported in this paper because the method was not sensitive enough to reliably detect concentrations below 10 μ g 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-KER²). 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 minute 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 non-hazardous 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 hr to evaluate the feasibility of achieving less than 5 μ g L⁻¹ of total Cr in the effluent and to optimize operating conditions. Two extended runs (Runs 16 and 17) were conducted for 24 and 48 hr 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):O₂). 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 μ g L⁻¹), corresponding to the molar ratio ranging from 9:1 to 56:1. Cr(VI) concentrations were

measured on both the unfiltered influent and 0.45 μ m 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 of 50:1 and 25:1, and 98.5% with an R 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.

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.

Based on the 4:1 stoichiometry between Fe(II) and DO, the source groundwater (DO of 3 - 4 mg L⁻¹ or 94 – 125 μ M) would be able to theoretically oxidize up to 500 μ M (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 re-oxidize 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 μ m 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 μ m 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 Run 1 to Run 15 (6 hr 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 sf⁻¹. During the first three runs, filtration rates of 4 and 6 gpm sf⁻¹ were tested in parallel. In Runs 1 and 3, the total Cr removal efficiency of Filter 1 (6 gpm sf⁻¹) was lower than that of Filter 2 (4 gpm sf⁻¹) 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 sf¹), supported the hypothesis that high filtration rate (6 gpm sf⁻¹) had an adverse impact on total Cr removal. The filtration rate of 6 gpm sf⁻¹ 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 CO₂ 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 to 3 were not included in the figure due to the higher filtration rate (6 gpm sf⁻¹). For pH values less than 7.5, total Cr removal efficiency was greater than 98%. For filtration at pH 7.5 to 7.6, the total Cr removal efficiency decreased to less than 50% on occasion. Speciation of the filter effluent samples on all runs (Run 1 to 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 to 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 through 9 and Run 11, which had no pH control. An R of 25:1 or 15:1 was used along with a filtration rate of 4 gpm sf⁻¹ (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 hr). In Run 16, the effluent total Cr concentration was below 2 μ g L⁻¹ for up to 46 hr of operation (Figure 3), corresponding to a Cr removal efficiency of greater than 98%. Run 17 lasted 23 hr, during which the effluent total Cr concentration was below the detection limit of 1.0 μ g 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 hr 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 hr 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 in. to 23 in. of water over the 23 hr 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 non-straining 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 dualmedia 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 Supplementary Information). Figure 5 reveals the total Cr and Fe concentrations in the backwash water after 20 minutes of settling with each polymer and dose. The backwash water contained less than 100 μ g 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 μ g L⁻¹ of total Cr and 4.6 mg L⁻¹ of total Fe. Based on these 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 non-hazardous 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 considered non-hazardous 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

Figure S1 provides the 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.

Constituent	Typical Concentration					
Alkalinity	215 mg L^{-1} as CaCO ₃					
Arsenic	0.5 $\mu g L^{-1}$					
Chloride	68 mg L^{-1}					
Conductivity	840 μ S cm ⁻¹					
Hardness	332 mg L^{-1} as CaCO ₃					
Nitrate	5.3 mg L^{-1} as N					
рН	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					

Table 1. Major quality parameters of the Glendale groundwater used for pilot testing

	E C			P	Loading Rate (gpm sf ⁻¹)		Cr Removal Rate (%)			
Run	Fe:Cr Mass Ratio (R)	Reduction pH Goal	Aeration/ Filtration pH Goal	Measured Reduction pH	Measured Aeration/ Filtration pH	Run Duration (hr)	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	24	4	-	-	-

Table 2. Operating conditions and system performance of the RCF system. Data plotted for Runs 16 and 17 in Figures 3 and 4.



Figure 1. Schematic diagram of RCF system.



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(II): Cr(VI) 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



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.



Figure 4. RCF system performance for extended Run 17 with 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 minutes of settling with three types of high molecular weight polymer at two doses (0.2 mg L^{-1} and 1.0 mg L^{-1}).

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Chapter 4

Conceptual Cost Estimates for Pilot-Tested Hexavalent Chromium Removal Technologies

Nicole Blute, Chad Seidel, and Michael J. McGuire

Abstract

Pilot testing of hexavalent chromium (Cr(VI)) removal technologies revealed that strong base anion exchange (SBA), weak base anion exchange (WBA), and reduction/coagulation/filtration (RCF) could treat contaminated groundwater in Glendale, California to low levels (i.e. less than 5 μ g/L, or 95% removal). Using an approach that included the evaluation of vendor cost proposals and independent cost models, we developed conceptual level cost estimates for these Cr(VI) removal technologies. Capital costs, operating costs, and residuals management costs were estimated to determine the cost drivers for the different technologies. Three different size systems were considered, including 0.7 MGD (500 gpm wellhead treatment), 3 MGD (e.g. treatment of two or three large wells), and 10 MGD (e.g. treatment of the combined flow for the 8 wells feeding the Glendale Water Treatment Plant). Ranges for cost estimates are provided in this evaluation to reflect the different treatment options and treatment uncertainties, which are identified and discussed in this paper.

Background

Hexavalent chromium, Cr(VI), is not specifically regulated in drinking water. However, total chromium, Cr(III) plus Cr(VI), has been part of national drinking water regulations since 1975. The federal regulatory maximum contaminant level (MCL) for total Cr is 100 μ g/L, while the MCL in California is 50 μ g/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 μ g/L, which contributed to a public health goal (PHG) of 2.5 μ g/L for total Cr (OEHHA, 1999). Although this PHG was later rescinded and is currently under review, the potential for a new Cr(VI) MCL and a lower California total Cr MCL motivated the effort to identify treatment technologies able to remove Cr(VI) to levels far lower than the current limits. In addition to identifying such treatment technologies, understanding the treatment costs of these Cr(VI) removal technologies is critically important for regulatory development and drinking water utilities that face chromium treatment in the future.

Significant research efforts spearheaded by the City of Glendale have evaluated treatment technologies for chromium removal at both the bench- and pilot-scale. These efforts were prompted in 2000 by public concern over the presence of Cr(VI) in drinking water. In response to this public concern, the City of Glendale, with the participation of the Cities of Los Angeles, Burbank, and San Fernando, initiated a four-phase program to develop full-scale treatment capable of removing Cr(VI) from San Fernando Valley groundwater, which contains plumes with high concentrations of Cr(VI).

The Glendale four-phase program includes:

• Phase I: A bench-scale study that improved the understanding of fundamental Cr chemistry and screened promising treatment technologies (AwwaRF, 2004),

• Phase II: A pilot-scale study that evaluated treatment technologies for removing Cr(VI) to low levels in Glendale groundwater (McGuire et al., 2005),

• Phase III: A demonstration-scale study that will finalize the technology evaluation and address additional costs and residuals issues, and

• Phase IV: Full-scale implementation of an effective Cr(VI) treatment technology.

Until this comprehensive program, no treatment technology had been shown to reliably remove Cr(VI) in drinking water to levels below 5 μ g/L, and no cost estimates of treatment have been developed. This paper reports on the development of conceptual cost estimates for Cr(VI) removal technologies tested in Phase II pilot testing. Near the end of the Phase II pilot-scale study, cost information was solicited from vendors for technologies shown to remove Cr(VI) in pilot testing. This vendor-supplied cost information was evaluated in light of independent estimates for technology capital and O&M components to develop feasibility-level cost estimates. Cost estimates for the RCF technology not tied to a specific vendor were independently developed.

Cost Development Approach

Technology cost estimates were developed by: (1) soliciting vendor-specific technology cost information directly from vendors and (2) developing independent cost information using existing literature, professional judgment, and industry cost models. Estimates were developed for three system sizes with design flow rates of 0.7 MGD (500 gpm), 3 MGD, and 10 MGD. The conceptual level cost estimates developed in this project are considered to fall within the
range of Class 5 to Class 4 Estimates as defined by the Association for the Advancement of Cost Engineering (AACE) International. These levels of engineering cost estimating are generally conducted on the basis of limited preliminary information and without detailed information such as process and instrumentation diagrams, engineering layouts, and equipment schedules. This level of cost estimating is appropriate for strategic planning purposes, assessment of initial viability, evaluation of alternative plans, project feasibility screening, and long range capital planning. Typical accuracy ranges recognized for Class 5 to Class 4 estimates are -30% to +50%.

Vendor Cost Solicitation. Technology cost information was requested from vendors for those technologies tested in Phase II and shown to remove Cr(VI) in pilot tests (McGuire et al., 2005). This included U.S. Filter Corporation in partnership with Rohm and Haas (US Filter/R&H) weak- and strong-base ion exchange, Orica Watercare MIEX[®] continuous ion exchange, Water Remediation Technologies (WRT) Z-24TM adsorptive media, and Calgon Carbon strong-base ion exchange. The cost information requested of vendors included capital and operation and maintenance (O&M) costs for the treatment technology and any required residuals management components. Technology cost information was provided for US Filter/R&H weak- and strong-base ion exchange and the MIEX[®] continuous ion exchange process. WRT and Calgon did not provide cost information, and cost estimates were not developed since these technologies exhibited a lower volume of water treated compared to SBA resin.

Although MIEX® was only able to achieve the treatment goal of 5 μ g/L approximately half of the time during pilot testing (i.e. removal ranged from 92-96%), this technology was included

in this cost analysis since this removal efficiency might be acceptable to Glendale or other utilities in the future, depending on future regulations.

Independent Cost Development. Vendor-supplied cost information was amended using independently-developed capital-cost multipliers and labor estimates. Standard capital cost multipliers included are described in Table 1. Exceptions to these values are noted in the subsequent technology cost descriptions.

Capital Cost	Cost Multiplier
Piping, valves, and electrical	25% of technology capital cost
Site work	10% of technology capital cost
Bonds, insurance, and contractor	10% of loaded technology capital costs*
Engineering	12% of loaded technology capital costs*
Contingency	15% of total technology costs ⁺

Table 1. Standard Capital Cost Multipliers

*Loaded technology capital costs include the piping, valves, and electrical and site work multipliers.

⁺Total technology cost includes technology cost with all cost multipliers applied.

The independent cost development effort also estimated treatment costs for reduction with ferrous sulfate, coagulation, and filtration (RCF) technology that was demonstrated to successfully remove Cr(VI) at the pilot scale using a manufacturer-independent pilot unit. These costs were developed using EPA estimates (USEPA, 2001), the W/WCost\$ industry cost model (Culp/Wesner/Culp 1998), and direct communication with treatment technology equipment and supply contacts.

General Cost Assumptions. A capital interest rate of 4% with a recovery period of 20 years was used to annualize all technology capital costs. All costs are expressed in January 2005

dollars. Labor costs were estimated for each technology based on full-time equivalents (FTEs) with a loaded annual salary of \$100,000 (typical estimate for Glendale, California).

Technology Cost Development Case Studies

US Filter/R&H Pilot System: Weak Base Anion Exchange

Treatment Process Description. The US Filter/R&H weak base anion exchange system consists of lead/lag resin vessels with upstream acid addition. The Duolite A7 WBA resin is intended be used as a once-through, non-regenerable media. Figure 1 illustrates the WBA ion exchange system unit process diagram.



Figure 1. Unit process diagram of US Filter/R&H WBA ion exchange system

This system includes acidification of the influent to protonate the resin for optimal Cr(VI) removal. US Filter specified that the volumetric design flow rate for this media is 2.5 gpm/ft³. Cost estimates are based on removal of Cr(VI) to approximately 80,000 bed volumes. For this resin life, US Filter proposed to replace resin approximately every 166 days resin replacement

using hydraulic sluicing methods. US Filter estimated that a weekly low-volume backwash may be necessary to reclassify the media bed, which would yield non-hazardous wash water.

Pilot testing results. Phase II pilot testing revealed that the US Filter/R&H WBA resin could effectively remove Cr(VI) to less than 5 μ g/L for an extended period of time. Operated in lead/lag configuration, Cr(VI) breakthrough occurred for the first vessel at approximately 40,000 bed volumes, and breakthrough of the second vessel was not seen even past 80,000 bed volumes. Compared to SBA resin, WBA resin could achieve at least 20 times the capacity before achieving breakthrough. As a result, WBA resin was identified as a possible once-through resin for Cr(VI) treatment.

Initial pilot testing raised some critical and yet unanswered questions, such as the optimum pH needed for treatment (thought to be approximately pH 6), the actual media capacity when a continuous pH is maintained, and the possibility that other WBA resins may be effective at Cr(VI) removal. Consequently, a Phase III Bridge Project was proposed to answer these questions and determine the potential for WBA treatment of Cr(VI) in drinking water.

Capital Cost Development. For the 0.7 MGD demonstration system, two 8 ft. diameter vessels would be plumbed in lead/lag configuration similar to the strong-base anion exchange system.

US Filter proposed that the 3 MGD system, which would provide full-scale implementation of treatment for two or three joined well flows, include four 12 ft. diameter HP1220 non-regenerable vessels plumbed in two lead/lag trains. US Filter stated that hydraulic sluicing would be used to fill and empty the vessels on site.

The 10 MGD system US Filter proposed includes the same equipment in the 3MGD scenario with the addition of 6 vessels (total of ten 12 ft. diameter vessels). For each flow rate, US Filter

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included chemical feed system equipment. The initial resin inventory is also included in the capital cost estimate.

One time capital costs developed included the following:

- Resin and contactors
- Chemical feed equipment
- Interconnecting piping, valves, and electrical (25%)
- Site work (10%)
- Bonds, insurance, and contractor O&P (10%)
- Engineering (12%), and
- Contigency (15%).

Operation and Maintenance Cost Development. Operating costs for the WBA system were provided by US Filter and adjusted as necessary. Estimates include the following:

- Media replacement every 166 days, at an estimated \$350 per cubic foot
- Chemicals (including hydrochloric acid for pH depression)
- Non-hazardous liquid waste disposal for backwash, estimated at \$2 per 1,000 gallons
- Resin disposal, and
- Labor costs.

The US Filter/R&H weak base anion exchange system costs are dominated by O&M costs predominantly comprised of resin costs and acid costs for pH depression. The resin replacement costs are driven by two key assumptions: (1) the anticipated resin usage rate is based on 80,000 bed volumes to breakthrough; and (2) the cost of resin estimated at \$350/ft³. The breakthrough estimate of 80,000 BVs was demonstrated during pilot testing under non-ideal pH conditions and the testing was concluded before complete breakthrough could be established. A more certain

breakthrough estimate will be developed during future field testing of WBA resins under controlled pH conditions. The cost of WBA resins varies and may decrease if the marketplace expands for its use in drinking water. These factors will inevitably lower the resin replacement costs estimated in this effort.

Since the weak base anion exchange resin requires pH depression to approximately 6, the acid needs are significant in Glendale's highly buffered water. At a pH of 5.9, approximately 125 mg/L HCl may be needed, which corresponds to about 700 gallons of 31.5% HCl per day for a flow rate of 0.7 MGD. At a cost of about \$0.80/gallon, the acid would cost approximately \$204,000 per year. Alternately, if the resin can effectively remove Cr(VI) at a pH of 6.5, the acid quantity needed could be reduced by half. One of the critical tests in the Phase III Bridge Project will be the identification of the highest pH at which Cr(VI) removal with WBA resin is possible.

Labor costs for the WBA system were estimated at 0.125 FTEs, 0.25 FTEs, and 0.5 FTEs for the 0.7, 3, and 10 MGD system sizes, respectively.

Residuals streams from the WBA system are limited to spent resin and backwash water. US Filter proposed that the spent resin would be sent to their RCRA Part B-permitted, storage, treatment and recovery facility in Roseville, MN at costs ranging from 237 to \$547 per ton. Instead, we used the estimate of \$140 per ton for disposal of hazardous waste in California (Frey et al, 2003).

Estimated Cost Range. Based on vendor-provided cost estimates and an independent analysis of costs, we developed our best estimate of the cost range for WBA resin at the present time. Figures 2 and 3 show the capital cost and O&M cost estimates for the 3 different size

systems. Figure 4 displays the cost estimates for the 3 systems on an annualized basis in dollars per acre foot.



Figure 2. Capital cost estimates of the WBA exchange treatment system



Figure 3. Operating cost estimates of the WBA exchange treatment system for 2 different pH depression targets



Figure 4. Total annualized cost estimates (\$/AF) of the WBA exchange treatment system for 2 different pH depression targets requiring different acid quantities

As noted previously, the O&M costs are the largest cost component of the annualized costs, which are due to both resin replacement frequency and acid needs. The following may have a significant impact on these cost estimates:

- Capital costs: Contactors present at the GS-3 site may be retrofit for ion exchange, thereby saving at least \$172,000 for the 0.7 MGD system.
- Media replacement: May be more or less frequent than the pilot-scale estimate of 80,000 bed volumes. Other WBA resins may also offer more cost-effective alternatives
- Acid for pH depression: May need more or less acid depending on the additional pilot testing. Potential cost differences may be significant.

Consequently, these estimates need to be validated with additional pilot testing in the Phase III Bridge Project to determine resin life and acid quantities in order to establish better cost estimates.

US Filter/R&H: Strong Base Anion Exchange

Treatment Process Description. The US Filter/R&H strong base anion exchange system consists of lead/lag resin canisters along with brine silo/storage, brine distribution equipment, brine collection/recycle equipment and liquid waste storage tanks (Figure 5). The volumetric design flow rate for this system using the Amberlite PWA410Cl resin is 2.5 gpm/ft³. This SBA resin is designed for off-line regeneration and will remove Cr(VI) for an estimated 1,900 bed volumes (as shown in pilot testing). Resin regeneration will occur approximately every 4-5 days with salt brine.



Figure 5. Unit process diagram of US Filter/R&H SBA ion exchange system

Pilot testing results. Phase II pilot testing showed that US Filter/R&H SBA Resin PWA410Cl was effective at removing Cr(VI) to less than 5 μ g/L for approximately 1,900 bed volumes. The SBA resin was effectively regenerated using a saturated brine solution up to 7 times during pilot testing. The need for a lead/lag configuration was confirmed when

chromatographic peaking of nitrate was observed, yielding effluent concentrations exceeding the MCL for nitrate.

Capital Costs. US Filter proposed a 0.7 MGD system including two 8 ft. diameter HP810 regenerable ion exchange vessels plumbed in a lead/lag configuration. Estimates provided by US Filter included brine storage tanks and transfer of brine to an off-site location for disposal. Alternately, a brine treatment system could be installed as shown in Figure 5 (more detail provided in the MIEX[®] case study).

Four 12 ft. diameter HP1220 regenerable vessels were recommended by US Filter for a 3 MGD treatment system in two lead/lag configurations. Capital costs include additional liquid hazardous waste storage tanks required for 3 MGD.

US Filter provided cost estimates for a 10 MGD system that includes six additional 12 ft. diameter vessels for a total of ten vessels plumbed in lead/lag configuration. As for the 3 MGD size, 10 MGD will require additional liquid hazardous waste storage tanks.

One time capital costs developed included the following:

- Resin and contactors
- Regeneration tanks
- Chemical feed systems
- Brine treatment system
- Interconnecting piping, valves, and electrical (25%)
- Site work (10%)
- Bonds, insurance, and contractor O&P (10%)
- Engineering (12%), and
- Contigency (15%).

Orica proposed a brine treatment system to precipitate out Cr(VI) from brine with ferrous sulfate, which would be designed to produce a small volume of hazardous solid waste leaving the bulk volume of the brine non-hazardous for sewer disposal. We considered this brine treatment system to be applicable to the brine produced by the SBA resin to be able to compare costs of the two different SBA technologies. Capital costs for this brine treatment system were estimated to at the levels proposed by Orica.

Operation and Maintenance Costs. Operating costs for the SBA system were provided by US Filter and included resin replacement on a 3-year cycle and resin regenerating costs including salt. Estimates include the following:

- Resin replacement, at an estimated \$110 per cubic foot
- Resin regeneration chemicals (salt)
- Non-hazardous backwash water
- Non-hazardous or hazardous brine disposal
- Hazardous solid precipitated from the brine, and
- Labor costs.

Labor costs for the SBA system were estimated at 0.5 FTEs, 1 FTEs, and 2 FTEs for the 0.7, 3, and 10 MGD system sizes respectively.

To minimize waste from the SBA system, US Filter proposed brine recycle. Pilot testing indicated that brine recycle was possible for effective regeneration of the resin. For these cost estimates, brine recycle for 7 cycles was considered. Regenerated resin may require replacement at approximately 3-year intervals, and this spent resin will be disposed of as a non-hazardous solid. Regenerant and slow rinse liquid waste will be classified and disposed of as a hazardous

liquid. Fast rinse and backwash liquid waste will be classified and disposed of as non-hazardous liquid.

Residuals disposal cost estimates provided by US Filter were driven by estimated disposal costs of \$1.25/gallon for hazardous spent brine. As noted above, brine treatment was also considered in our calculations, which significantly reduced O&M costs for US Filter/R&H SBA exchange treatment.

Estimated Cost Range. Based on vendor-provided cost estimates and an independent analysis of costs, the best estimate of the cost range for SBA resin with US Filter's proposed configuration is presented in this section. Figures 6 and 7 show the capital cost and O&M cost estimates for the 3 different size systems.

Figure 8 displays the cost estimates for the 3 systems on an annualized basis in dollars per acre foot. Costs are at least double for the cases in which brine is considered hazardous waste and disposed of off-site. Brine treatment (using a system similar to that proposed by Orica) substantially reduced the residuals component of the treatment costs. If, however, sewer disposal of the brine is not possible at some time in the future, the costs of treatment with SBA resin would be better reflected by the estimates for hazardous brine disposal.

Limited research has demonstrated the brine treatment approach, and it is uncertain what the capital (e.g. dewatering equipment) and O&M (e.g. increased labor necessary to manage spent brine treatment and sludge disposal, estimated here to be an extra 0.5 FTE) requirements would actually be for such a spent brine treatment system. Consequently, the residuals cost estimates for the brine treatment systems may not reflect all of the anticipated costs associated with this approach. At this time, however, these costs reflect the best estimates available for such a brine treatment system.



Figure 6. Capital cost estimates of the US Filter/R&H SBA treatment system for disposal of brine as hazardous waste or treatment of brine



Figure 7. Operating cost estimates of the US Filter/R&H SBA treatment system for disposal of brine as hazardous waste or treatment of brine



Figure 8. Total annualized cost estimates (\$/AF) of the SBA exchange treatment system for disposal of brine as hazardous waste or treatment of brine

Reduction, Coagulation, Filtration

Treatment Process Description. The removal of hexavalent chromium, Cr(VI), by reduction to trivalent chromium, Cr(III), with ferrous sulfate and subsequent coagulation with ferric iron and filtration was demonstrated to successfully remove Cr(VI) during pilot testing. The RCF pilot unit consisted of a reduction tank, aeration columns, and dual-media granular filters and included chemical feed points for pH control before the reduction tank and aeration columns, ferrous sulfate addition before the reduction tank, and filter aid polymer addition prior to the filters.

Since the RCF process had never been utilized to remove Cr(VI) in a potable drinking water supply, the RCF technology costs had to be estimated using a range of sources including: EPA estimates (USEPA, 2001), the W/WCost\$ model (Culp/Wesner/Culp, 1998), and direct communication with equipment and chemical suppliers. Figure 9 illustrates the RCF system unit process diagram.



Figure 9. Unit process diagram of reduction, coagulation, filtration (RCF) system

Pilot testing results. Pilot testing efforts identified optimal operating conditions. At ambient pH conditions and a Fe(II):Cr(VI) mass ratio of 25:1, the system continuously removed Cr (both Cr(VI) and Cr(III)) to below detectable levels for 48 hours before exceeding filter head loss and turbidity goals. The pilot system was backwashed with air scour and fluidization of the bed. The bed expansion rate was controlled at 20 to 30%, and the entire backwash procedure was complete within 10 to 12 minutes.

Waste minimization and disposal options for the chromium-containing backwash water solids were also investigated during pilot testing. It was determined that the backwash solids could be rapidly settled with low doses (0.2 to 1.0 mg/L) of high molecular weight polymer. The resultant settled backwash water may be suitable for recycle to the head of the system, while the

settled backwash solids would be then dewatered. The liquid residual from the dewatering process would be classified as non-hazardous and sent to sewer. The dewatered solids would be classified and disposed of as hazardous solid waste.

Capital Costs. Capital costs for the RCF process include the ferrous sulfate feed system, reduction and coagulation basin, dual media filters, backwash pumping, and waste handling treatment equipment. Since the pilot testing identified ambient pH conditions as optimal, pH adjustment equipment has not been included in this estimate. Likewise, since aeration towers may not have been critical during pilot testing, aeration equipment was not included in this estimate. However, the reduction and coagulation basin could be adjusted to include aeration. Non-mechanical dewatering has been assumed for the 0.7 and 3 MGD system sizes; mechanical dewatering has been assumed for the 10 MGD system size.

One time capital costs developed included the following:

- Ferrous sulfate feed system
- Mixing chamber/ flocculation basin
- Backwash waste handing and treatment (fill and draw backwash gravity thickener with non-mechanical dewatering rolloff for the 0.7 MGD and 3 MGD systems; fill and draw backwash gravity thickener with filter presses for solids dewatering in the 10 MGD system)
- Interconnecting piping, valves, and electrical (15%)
- Site work (5%), and
- Contigency (15%).

Capital cost multipliers applied to the RCF cost estimates were modified to reflect the inclusion of such costs in the technology estimates developed from various models. Since some piping, valve, and electrical costs are included in the technology cost estimates, a 15% multiplier was used for those costs. The site work multiplier was lowered from 10% to 5% to reflect site work costs included in the technology cost estimates. The capital cost multipliers for bonds, insurance, and contractor and overhead profit, as well as engineering, were not applied because they were included in the technology estimates from the models.

The capital costs estimated for the RCF system are higher than the other technologies evaluated, primarily due to the cost of filters and backwash waste handling and treatment equipment required to dewater the backwash solids.

Operation and Maintenance Costs. Operational costs for the RCF process included ferrous sulfate and labor costs. Estimates include the following:

- Ferrous sulfate costs
- Non-hazardous liquid dewatering waste disposal
- Hazardous sludge disposal, and
- Labor costs.

Ferrous sulfate costs were assumed at \$0.20 per gallon as 5% iron (Kemiron Companies, Inc., 2005). Ferrous sulfate usage was based on a dose ratio of 25:1 Fe:Cr (2.5 mg/L as Fe for 100 μg/L Cr). Residuals disposal costs were estimated based on previous research for disposal in California (Frey, et al. 2003). Non-hazardous, liquid sewer disposal costs are estimated at \$2 per 1,000 gallons. Hazardous, solid disposal cost estimates are \$140 per ton including transport and disposal. Labor costs for the RCF system were estimated at 0.5 FTE, 1 FTEs, and 2 FTEs for the 0.7, 3, and 10 MGD system sizes respectively.

Residuals streams produced by the RCF process include dewatering liquids classified as non-hazardous and sent to sewer, as well as dewatered chromium-containing coagulation solids disposed of as hazardous solid waste. These residuals stream volumes were estimated based on full-scale operational conditions including 24-hour filter run times with a 15-minute backwash duration at 15 gpm/ft². These conditions result in a backwash water volume of 4% of the treated flow. Following settling, the settled sludge volume was assumed to be 5% of the backwash volume. Non-mechanical dewatering was assumed to achieve 60% dewatering and mechanical dewatering was assumed to achieve 80% dewatering. The resultant dewatered sludge density was estimated at 55 lbs/ft³.

The RCF residuals disposal cost estimates rely heavily on the operational assumptions for the process including filter run times, backwash duration and quantity, settled backwash water sludge volume, and dewatering efficiency. These operational assumptions dictate the total volumes of dewatering liquids classified as non-hazardous that are sent to sewer, as well as dewatered chromium-containing coagulation solids disposed of as hazardous solid waste. With no full-scale operational history for the RCF process, these assumptions are limited to field pilot testing experience. These estimates will be refined as further research is conducted.

Estimated Cost Range. Based on models and pilot testing results, the best estimate of the cost range for an RCF system at the present time is presented here. Figures 10 and 11 show the capital cost and operating cost estimates for the 3 different size systems. Figure 12 displays the cost estimates for the 3 systems on an annualized basis in dollars per acre foot.

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As compared to the ion exchange technologies, the costs for the RCF system are characterized by relatively low O&M costs and relatively high capital costs.



Figure 10. Capital cost estimates of the RCF treatment system



Figure 11. Annual operating cost estimates of the RCF treatment system



Figure 12. Total annualized cost estimates (\$/AF) of the RCF treatment system

Orica Watercare MIEX[®]

Treatment Process Description. Orica Watercare's MIEX[®] process consists of continuouslystirred mixing tanks with SBA exchange resin. The SBA resin contains a magnetic component in its structure to allow rapid agglomeration and settling of the resin from the treated water. Figure 13 displays the unit process diagram for the MIEX[®] process. Three operating parameters, including resin contact time, resin dose, and regeneration rate as a percentage of the applied resin dose, control the system performance during operation.



Figure 13. Unit process diagram of Orica Watercare MIEX[®] system

Pilot testing results. Phase II pilot testing demonstrated that MIEX[®] removed Cr(VI) with an efficiency ranging from 92 to 96% at an applied resin dose of 40 to 60 mL/L. Since the treatment goal was 5 μ g/L, the system achieved this goal approximately half of the time. Pilot

testing revealed that high sulfate levels of about 100 mg/L were likely to have impaired the Cr(VI) removal efficiency.

Since MIEX[®] is a process that continually regenerates a portion of resin, some carryover of brine was noted in the conductivity measurements, which were approximately 10% higher than the influent water. On average, MIEX[®] effluent conductivity was 912 μ S/cm (approximately 570 mg/L TDS) compared to 828 μ S/cm for influent water (approximately 516 mg/L TDS). This may have an impact on consumer acceptability of MIEX[®]-treated water when the groundwater levels of TDS are already high.

Capital Costs. Capital costs for the MIEX[®] process include the initial resin inventory; resin contactors, settlers, and tanks; regeneration system skids; brine waste treatment equipment; and all associated system pumps, valves, and instrumentation. The 10 MGD system size includes concrete costs for contactors and settlers.

One time capital costs developed included the following:

- Resin and contactors
- Regeneration tanks
- Brine treatment system
- Interconnecting piping, valves, and electrical (25%)
- Site work (10%)
- Bonds, insurance, and contractor O&P (10%)
- Engineering (12%), and
- Contigency (15%).

The cost information provided by Orica Watercare (2005) was based on a 40 mL/L resin dose and 30 minute contact time for all treatment system sizes. Regeneration rate was assumed at 10% for the 0.7 MGD (500 gpm) system size, while the 3 and 10 MGD system sizes utilized a 5% regeneration rate.

The MIEX[®] process capital costs exhibit significant economies of scale since the technology can accommodate large treatment systems with larger unit processes rather than multiple smaller unit processes.

Operation and Maintenance Costs. Operating costs for the MIEX[®] process were provided by Orica including resin replacement, resin regenerating costs (salt costs), and plant power consumption. Estimates include the following:

- Resin replacement when loss rate is 2 gallons of resin per million gallons of water treated, at an estimated \$11 per liter per cubic foot
- Resin regeneration costs, including salt at \$50/ton
- Plant power consumption for continuous resin pumping
- Non-hazardous or hazardous brine disposal
- Hazardous solid precipitated from the brine, and
- Labor costs.

Salt consumption rates were estimated to be 1,043 lbs/MG for the 0.7 MGD system and 1,169 lbs/MG for the 3 and 10 MGD systems. Labor costs for the MIEX[®] process were externally estimated to be 0.5 FTEs, 2 FTEs, and 3 FTEs for the 0.7, 3, and 10 MGD system sizes respectively.

Orica proposed two potential waste disposal options for the MIEX[®] process:

- 1. Sewer disposal of non-hazardous liquid waste for the 0.7 MGD system, provided the regeneration system is operated (less efficiently) to maintain a non-hazardous brine, and
- Spent brine treatment by coagulation to enable sewer disposal of resultant non-hazardous liquid waste and off-site disposal of resultant hazardous solid waste for the 3 and 10 MGD systems.

An additional brine disposal option not provided by Orica but considered in this discussion is:

3. Hazardous waste disposal of the spent, untreated brine.

For the 0.7 MGD system, Orica provided specifications for a system in which the brine waste generated would be suitable for sewer discharge (i.e. meet the total chromium discharge limit of 10 mg/L established in the Phase II pilot testing discharge permit). While this option may meet the current permit requirements, it may not be operationally or politically feasible. If this strategy is not possible, costs of hazardous liquid waste disposal are presented. If all brine was treated as hazardous rather than non-hazardous for this 0.7 MGD case, residuals disposal costs would increase by a factor of one hundred.

The 3 and 10 MGD regeneration systems were designed by Orica to minimize the volume of waste produced. Orica proposed that the waste brine could be treated to precipitate hazardous solid chromium-containing waste, with non-hazardous liquid brine discharge to sewer. To minimize the hazardous waste volume, the brine treatment proposed included the addition of 460 to 1,150 mg/L ferrous sulfate to reach a pH of 3 to 4 and enable chromium precipitation, followed by a pH increase to 8. Orica stated that the solids would be separated using a filter press and the non-hazardous liquid would be discharged to the sewer.

Estimated Cost Range. Based on vendor-provided cost estimates and an independent analysis of these costs, the best estimate of the cost range for MIEX[®] treatment is presented in

this section. Figures 14 and 15 display the capital cost and operating cost estimates for the 3 different size systems. Figure 16 illustrates the cost estimates for the 3 systems on an annualized basis in dollars per acre foot.

For the 0.7 MGD case, three different cost estimates were prepared to provide a range in treatment costs that hinge on brine disposal.

- If the MIEX[®] system was operated to minimize brine volume and brine was disposed of as hazardous waste (at \$1.25/gallon), the costs would be extremely high due to the volume of brine used ("Hazardous Brine" in Figure 16).
- The application of brine treatment, such as proposed by Orica for the 3 and 10 MGD systems, would substantially reduce treatment costs ("Treated Brine in Figure 16). However, non-hazardous brine disposal is dependent on permit conditions.
- 3. If Orica was able to keep brine Cr(VI) concentrations below 10 mg/L (by operating less efficiently with respect to maximum brine recycles) and discharge the brine to the sewer, costs would be even lower ("Sewered non-hazardous brine" in Figure 16). This third option is contingent on permit conditions.

The feasibility of the brine treatment approach is not known, and it is uncertain what the actual capital (i.e. dewatering equipment) and O&M (i.e. increased labor necessary to manage spent brine treatment and sludge disposal) requirements would be for such a spent brine treatment system. Consequently, the residuals cost estimates for the brine treatment systems may not reflect all of the anticipated costs associated with this approach. At this time, however, these costs reflect the best estimates available.



Figure 14. Capital cost estimates of the MIEX® treatment system for disposal of brine as hazardous waste or treatment of brine



Figure 15. Operating cost estimates of the MIEX® treatment system for disposal of brine as hazardous waste or treatment of brine



Figure 16. Total annualized cost estimates (\$/AF) of the MIEX® treatment system for disposal of brine as hazardous waste or treatment of brine

Conclusions

Cost estimates were developed for chromium treatment technologies tested in Glendale's Phase II Pilot Testing using vendor-based estimates and independent cost models. Technologies for which cost estimates were prepared include weak base anion exchange, strong base anion exchange (fixed bed and reactor-based), and reduction/coagulation/filtration using ferrous sulfate. For each technology, the following cost drivers were identified:

- US Filter/ Rohm & Haas Weak Base Anion Exchange (Duolite A7 resin): More than 85% of the annual costs were operating costs, including resin replacement and acid for pH depression. This technology is particularly advantageous as a once-through treatment system with only solid residuals (i.e. no brine).
- US Filter/ Rohm & Haas Strong Base Anion Exchange (PWA410Cl resin): Costs varied significantly depending on the disposal of brine whether brine was treated to yield a non-hazardous brine and hazardous solid precipitate, or if brine was disposed of as hazardous liquid waste. Demonstration testing of a brine treatment system would be critical to make this technology cost-competitive with the other technologies.
- Orica Watercare MIEX® Continuous Strong Base Anion Exchange: Although MIEX® was not able to consistently achieve Glendale's goal of treatment to less than 5 µg/L Cr(VI), cost estimates were developed for comparison. Costs were largely driven by brine disposal and overall annualized costs were higher than for the USF SBA system.
- Reduction/Coagulation/Filtration: Annual costs were split between capital costs, operating costs, and residuals costs. Residuals disposal contributed the largest annual cost, followed by capital due to the need for filters and backwash handling and treatment.

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Overall, cost estimates developed in this project revealed that costs were lowest for SBA with brine treatment (assuming non-hazardous brine could be disposed to the sewer over the long term), followed by RCF, WBA with an optimized higher pH of 6.5, SBA without brine treatment, and WBA with a pH of 5.9.

Additional testing of WBA resin in the Phase III Bridge Project will better define the costs associated with this new technology (e.g. higher pH or lower resin replacement frequency) since it is the most operationally simple technology due to the minimal residuals volumes generated. Subsequent Phase III Demonstration Testing will then enable optimization of the technology or technologies selected for wellhead treatment.

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Supplementary Information

Technology Cost Estimates:

- USF Weak Base Anion Exchange with pH 5.9
- USF Weak Base Anion Exchange with pH 6.5
- USF Strong Base Anion Exchange with Brine Disposal as Hazardous Waste
- USF Strong Base Anion Exchange with Brine Treated (Liquid Non-Hazardous Waste and Solid Hazardous Waste)
- Reduction/Coagulation/Filtration
- Orica MIEX® Continuous Strong Base Anion Exchange with Brine Disposal as Hazardous Waste
- Orica MIEX® Continuous Strong Base Anion Exchange with Brine Treated (Liquid Non-Hazardous Waste and Solid Hazardous Waste)
- Orica MIEX® Continuous Strong Base Anion Exchange with Brine Sewered as Non-Hazardous Waste (i.e. less efficient brine use)

Technology Cost Estimate: USF WBA pH 5.9

Manufacturer	US Filter/Rohm & Haas			De	esign Capacity				
			0.7 MGD						
Technology	WBA Duolite A7		(500 gpm) 3 MGD				10 MGD	Assumptions	
Capital Costs (O	ne-time \$)								
	Resin/Media	\$	185,040	\$	784,668	\$	2,615,560	Vendor quote for initial purchase	
	Contactor/tanks	\$	171,714	\$	326,667	\$	816,667	Vendor quote for 3 and 10 MGD systems; Assumed	
								contactor/tank for 0.7 MGD same capital costs as the SBA	
		_	10.000	•	40.000	•	04.500		
	Chemical feed equipment	Э Ф	272 414	ې و	1 127 005	\$	24,500	vendor quote	
	Subiolal	φ	575,414	φ	1,121,995	φ	3,430,727		
	Piping, Valves, Electrical (25%)	\$	93,354	\$	281,999	\$	864,182	Includes interconnecting piping between equipment	
								components, including all isolation valves, check valves, etc.;	
								components and to existing power distribution: estimate does	
								not include piping to/from the treatment system	
	Site Work (10%)	\$	37,341	\$	112,800	\$	345,673		
	Subtotal	\$	504,109	\$	1,522,793	\$	4,666,581		
	Bonds Insurance Contractor O&P (10%)	¢	50 /11	¢	152 279	¢	466 658	O&P for design and construction of system (specific	
	Donus, insurance, contractor Our (10%)	Ψ	50,411	Ψ	152,215	Ψ	400,000	equipment and capital items described above include O&P	
								from US Filter)	
	Engineering (12%)	\$	60,493	\$	182,735	\$	559,990	Site layout, hydraulic profile, process flow, design	
								considerations, etc.	
	Subtotal	\$	615,013	\$	1,857,808	\$	5,693,229		
	Contingency (15%)	\$	92,252	\$	278.671	\$	853.984		
	Subtotal Capital Costs	\$	707,265	\$	2,136,479	\$	6,547,214		
Operating Costs	(Annual \$)								
	Media replacement	\$	203,161	\$	862,387	\$	2,872,575	Non-regenerable resin/media; replacement assumed at	
								80,000 bed volumes (approximately every 166 days)	
	Chemicals	\$	204,400	<u> </u>	876,000	<u></u>	2,920,000	pH 5.9; HCl at \$0.80/gallon	
	Liquid waste disposal / Non-hazardous	<u>\$</u>	312	<u> </u>	1,3/3	<u></u>	3,432	Backwash. Assume disposal in sanitary sewer, \$2/kgal	
	Resin/media disposal	¢ ¢	1,162	<u>~</u>	25,012	<u>\$</u>	16,688	Assume 0.25 ETE for 500 apm: 0.25 ETE for 2 MGD: 0.5 ETE	
	Labor	φ	23,000	φ	23,000	φ	50,000	for 10 MGD (assume loaded salary = $$100,000$)	
	Subtotal Operating Costs (annual)	\$	434,035	\$	1,769,772	\$	5,862,695		
	MGD		0.7		3		10		
	Annual Capital		\$52,042		\$157,206		\$481,755		
	Annual O&M (no resid disp)	\$	432,561	\$	1,763,387	\$	5,842,575		
	Annual Residuals Management	\$	1,474 \$486.077	\$	\$1 926 979	\$	\$6 344 450	-	
	Total Annual (\$/year)		400,077 1 90		φ1,9∠0,976 \$1.76		\$0,344,450 \$1.74		
	· ciai / a.i.iddi (ψ/kgal)		\$		\$0		\$1	_	
	Annual Capital (\$/AF)		\$66.37		\$46.78		\$43.01		
	Annual O&M (no resid disp) (\$/AF)		\$551.67		\$524.75		\$521.59		
	Annual Residuals Disposal (\$/AF)		\$1.88		\$1.90		\$1.80	4	
	I otal Annual (\$/AF)		\$619.92		\$573.43		\$566.40		

Residuals Production Estimate

	Units			De	esign Capacity			
Residuals		0.7 MGD			3 MGD		10 MGD	Assumptions
		(500 gpm)						
Liquid, Non Hazardous	gallons/year	156,000			686,400		1,716,000	
Liquid, Hazardous	gallons/year	0			0		0	
Solid, Non Hazardous	tons/year	0			0		0	
Solid, Hazardous	tons/year	8.3			35.8		119.2	
Liquid, Non Hazardous	\$/year	\$	312	\$	1,373	\$	3,432	
Liquid, Hazardous	\$/year	\$	-	\$	-	\$	-	
Solid, Non Hazardous	\$/year	\$	-	\$	-	\$	-	
Solid, Hazardous	\$/year	\$	1,162	\$	5,012	\$	16,688	Cost of \$547, 254, 237 per ton given by USF; \$140 used instead
Total Residuals Disposal	\$/year	\$	1,474	\$	6,385	\$	20,120	
Technology Cost Estimate: USF WBA with pH 6.5

Manufacturer	US Filter/Rohm & Haas			De	sign Capacity			
			0.7 MGD					
Technology	WBA Duolite A7		(500 gpm)		3 MGD		10 MGD	Assumptions
Capital Costs (Or	ne-time \$)	•	105.010	•	704.000	•	0.015 500	
	Resin/Media	\$	185,040	\$	784,668	\$	2,615,560	Vendor quote for initial purchase
	Contactor/tanks	Ф	171,714	ф	320,007	Ф	816,667	vendor quote for 3 and 10 MGD systems; Assumed
								estimate (same vendor)
	Chemical feed equipment	\$	16 660	\$	16 660	\$	24 500	Vendor quote
	Subtotal	\$	373.414	ŝ	1.127.995	\$	3.456.727	
		·	,	-	.,,	-	-,,	
	Piping, Valves, Electrical (25%)	\$	93,354	\$	281,999	\$	864,182	Includes interconnecting piping between equipment
								components, including all isolation valves, check valves, etc.;
								also includes instrumentation, electrical work between
								components and to existing power distribution; estimate does
	Site Work (10%)	\$	37 341	\$	112 800	\$	345 673	not include piping tom
	Subtotal	\$	504.109	\$	1.522.793	\$	4.666.581	
		·	,	-	.,,	-	.,,	
	Bonds, Insurance, Contractor O&P (10%)	\$	50,411	\$	152,279	\$	466,658	O&P for design and construction of system (specific
								equipment and capital items described above include O&P
								from US Filter)
	Engineering (12%)	\$	60,493	\$	182,735	\$	559,990	Site layout, hydraulic profile, process flow, design
								considerations, etc.
	Subtotal	\$	615,013	\$	1,857,808	\$	5,693,229	
	Quette and (450()	¢	00.050	¢	070 074	¢	050.004	
	Contingency (15%)	¢	92,252	¢	278,671	¢	6 5 47 01 4	
Operating Costs	(Annual ¢)	φ	101,205	φ	2,130,479	φ	0,547,214	
Operating Costs	(Annual \$) Media replacement	\$	203 161	\$	862 387	\$	2 872 575	Non-regenerable resin/media: replacement assumed at
	Media replacement	Ψ	200,101	Ψ	002,007	Ψ	2,012,010	80.000 bed volumes (approximately every 166 days)
	Chemicals	\$	102.200	\$	438.000	\$	1.460.000	pH 6.5: HCl at \$0.80/gallon
	Liquid waste disposal / Non-hazardous	\$	312	\$	1,373	\$	3,432	Backwash. Assume disposal in sanitary sewer, \$2/kgal
	Resin/media disposal	\$	1,162	\$	5,012	\$	16,688	Resin replacement
	Labor	\$	25,000	\$	25,000	\$	50,000	Assume 0.25 FTE for 500 gpm; 0.25 FTE for 3 MGD; 0.5 FTE
								for 10 MGD (assume loaded salary = \$100,000)
	Subtotal Operating Costs (annual)	\$	331,835	\$	1,331,772	\$	4,402,695	
	MGD		0.7		3		10	
	Annual Capital	•	\$52,042	•	\$157,206	•	\$481,755	
	Annual O&M (no resid disp)	\$	330,361	\$	1,325,387	\$	4,382,575	
	Annual Residuals Management	\$	1,4/4 \$202.077	\$	6,385	\$	20,120	-
	Total Annual (\$/year)		من م		⊉1,400,9/8 \$1.26		φ4,004,450 \$1.24	
	i otar Amidai (\$/Kgai)		ψ1.50		ψ1.30		ψ1.34	
1	Annual Capital (\$/AF)		\$66.37		\$46.78		\$43.01	T
	Annual O&M (no resid disp) (\$/AF)		\$421.33		\$394.41		\$391.25	
	Annual Residuals Disposal (\$/AF)		\$1.88		\$1.90		\$1.80	
	Total Annual (\$/AF)		\$489.58		\$443.09		\$436.06	

			Design Capacity			
Residuals	Units	0.7 MGD	3 MGD	10 MGD	Assumptions	
		(500 gpm)				
Liquid, Non Hazardous	gallons/year	156,000	686,400	1,716,000		
Liquid, Hazardous	gallons/year	0	0	0		
Solid, Non Hazardous	tons/year	0	0	0		
Solid, Hazardous	tons/year	8.3	35.8	119.2		
Liquid, Non Hazardous	\$/year	\$ 312	\$ 1,373	\$ 3,432		
Liquid, Hazardous	\$/year	\$-	\$-	\$-		
Solid, Non Hazardous	\$/year	\$-	\$-	\$-		
Solid, Hazardous	\$/year	\$ 1,162	\$ 5,012	\$ 16,688	Cost of \$547, 254, 237 per ton given by USF; \$140 used instead	
Total Residuals Disposal	\$/year	\$ 1,474	\$ 6,385	\$ 20,120		

Technology Cost Estimate:	USF	SBA with	Hazardous	Brine	Off-Site Dis	posal
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Manufacturer	US Filter/Rohm & Haas			De	esign Capacity			
			0.7 MGD					
Technology	SBA PWA410CI		(500 gpm)		3 MGD		10 MGD	Assumptions
Capital Costs (C	One-time \$)		00.000	^	000 700	•	700.001	March and the Control of the Control
	Resin/Media	\$	60,000	\$	230,769	\$	769,231	Vendor quote for initial purchase
	Contactor/tanks	ф С	25.000	¢ ¢	420,000	ф Ф	1,050,000	Vendor quote: Includes Bring storage, Haz Waste Collection
	Regeneration tanks	φ	23,000	φ	55,000	φ	200,000	Pumping
	Chemicals/chemical feed	s	30,000	\$	40 000	\$	50,000	Vendor quote
	Subtotal	\$	286,714	\$	745,769	\$	2,069,231	
	Piping, Valves, Electrical (25%)	\$	71,679	\$	186,442	\$	517,308	Includes interconnecting piping between equipment components, including all isolation valves, check valves, etc.; also includes instrumentation, electrical work between components and to existing power distribution; estimate does not include piping to/from the treatment system
	Site Work (10%)	\$	28.671	\$	74.577	\$	206.923	
	Subtotal	\$	387,064	\$	1,006,788	\$	2,793,462	1
	Bonds, Insurance, Contractor O&P (10%)	\$	38,706	\$	100,679	\$	279,346	O&P for design and construction of system (specific
								from US Eiltor)
	Engineering (12%)	\$	46,448	\$	120,815	\$	335,215	Site layout, hydraulic profile, process flow, design considerations, etc.
	Subtotal	\$	472,218	\$	1,228,282	\$	3,408,023	
	Contingency (15%)	\$	70,833	\$	184,242	\$	511,204	
	Subtotal Capital Costs	\$	543,051	\$	1,412,524	\$	3,919,227	
Operating Costs	s (Annual \$)							
	Media replacement	\$	13,000	\$	50,000	\$	166,667	Assumes a 3 year resin life
	Chemicals	\$	28,695	<u>\$</u>	122,979	<u></u>	409,929	
	Liquid waste disposal / Non-hazardous	\$	2,238	<u> </u>	9,832	<u></u>	25,045	Backwash. Assume disposal in sanitary sewer, \$2/kgal
	Liquid waste disposal / hazardous	\$	291,735	<u> </u>	1,250,293	<u>.</u>	4,167,644	Brine disposal as liquid nazardous waste
	Resin/media disposal	ð.	1,112	<u></u>	2,497	<u>~</u>	8,322	Assumes a 3 year resin life
	Labor	φ	30,000	φ	60,000	φ	120,000	10 MGD (assume loaded salary = \$60 000)
	Subtotal Operating Costs (annual)	\$	366.780	\$	1.495.601	\$	4.897.607	
L	MGD		0.7		3		10	
	Annual Capital		\$39,959		\$103,936		\$288,384	
	Annual O&M (no resid disp)	\$	71,695	\$	232,979	\$	696,596	
	Annual Residuals Management	\$	295,085	\$	1,262,622	\$	4,201,011	Includes resin/media disposal
	Total Annual (\$/year)		\$406,739		\$1,599,537		\$5,185,991	
	Total Annual (\$/kgal)		\$1.59		\$1.46		\$1.42	
	Annual Capital (\$/AF)		\$51		\$31		\$26	1
	Annual O&M (no resid disp) (\$/AF)		\$91		\$69		\$62	
	Annual Residuals Disposal (\$/AF)		\$376		\$376		\$375	
	Total Annual (\$/AF)		\$519		\$476		\$463]

				Design Capacity			
	Units	0.7 MGD		3 MGD		10 MGD	Assumptions
Residuals		(500 gpm)					
Liquid, Non Hazardous	gallons/year	1,119,0	800	4,916,207		12,522,651	
Liquid, Hazardous	gallons/year	233,3	888	1,000,235		3,334,115	
Solid, Non Hazardous	tons/year		3.3	14.3		47.6	
Solid, Hazardous	tons/year		0	0	1	0	
Liquid, Non Hazardous	\$/year	\$ 2,2	238 \$	9,832	\$	25,045	
Liquid, Hazardous	\$/year	\$ 291,7	'35 \$	1,250,293	\$	4,167,644	
Solid, Non Hazardous	\$/year	\$ 1,1	12 \$	2,497	\$	8,322	
Solid, Hazardous	\$/year	\$. 9	-	\$	-	
Total Residuals Disposal	\$/year	\$ 295,0	85 \$	1,262,622	\$	4,201,011	

Technology Cost Estimate: USF SBA with Brine Treatment

Manufacturer	US Filter/Rohm & Haas			De	esign Capacity			
			0.7 MGD					
Technology	SBA PWA410CI		(500 gpm)		3 MGD		10 MGD	Assumptions
Capital Costs (O	ne-time \$)							
	Resin/Media	\$	60,000	\$	230,769	\$	769,231	Vendor quote
	Contactor/tanks	\$	171,714	\$	420,000	\$	1,050,000	Vendor quote
	Regeneration tanks	\$	25,000	\$	55,000	\$	200,000	Vendor quote; includes Brine storage, Haz Waste Collection,
	Chemicals/chemical feed	¢	30,000	¢	40.000	¢	50.000	Puttiping Vendor quote
	Waste treatment	\$	100.000	\$	140,000	\$	220.000	Vendor quote Vendor guote from Orica
	Subtotal	\$	386,714	\$	885,769	\$	2,289,231	
			,		,		, , .	
	Piping, Valves, Electrical (25%)	\$	96,679	\$	221,442	\$	572,308	Includes interconnecting piping between equipment components, including all isolation valves, check valves, etc.; also includes instrumentation, electrical work between components and to existing power distribution; estimate does not include piping toffrom
	Site Work (10%)	\$	38.671	\$	88.577	\$	228,923	not include piping to/nom
	Subtotal	\$	522,064	\$	1,195,788	\$	3,090,462	
	Bonds, Insurance, Contractor O&P (10%)	\$	52,206	\$	119,579	\$	309,046	O&P for design and construction of system (specific equipment and capital items described above include O&P from US Filter)
	Engineering (12%)	\$	62,648	\$	143,495	\$	370,855	Site layout, hydraulic profile, process flow, design considerations, etc.
	Subtotal	\$	636,918	\$	1,458,862	\$	3,770,363	
	Contingency (15%)	\$	95,538	\$	218,829	\$	565,555	
	Subtotal Capital Costs	\$	732,456	\$	1,677,691	\$	4,335,918	
Operating Costs	(Annual \$)							
	Media replacement	\$	13,000	\$	50,000	\$	166,667	Assumes a 3 year resin life
	Chemicals	\$	28,695	\$	122,979	\$	409,929	
	Liquid waste disposal / Non-hazardous	\$	2,705	\$	11,833	\$	31,714	Backwash + treated brine. Assume disposal in sanitary sewer, \$2/kgal
	Waste Brine Treatment and Disposal Cost	\$	3,683	\$	15,965	\$	47,419	Haz solids at \$140/ton and chemicals for brine treatment at \$0.0015/gallon for ferrous sulfate and NaOH
	Resin/media disposal	\$	1,112	\$	2,497	\$	8,322	Assumes a 3 year resin life
	Labor	\$	100,000	\$	150,000	\$	250,000	Assume 1 FTE for 500 gpm; 1.5 FTE for 3 MGD; 2.5 FTE for 10 MGD (assume loaded salary = \$100,000) Extra 0.5 FTE for brine treatment system included
	Subtotal Operating Costs (annual)	\$	149,195	\$	353,274	\$	914,051	
	MGD		0.7		3		10	
	Annual Capital		\$53,895		\$123,447		\$319,044	
	Annual O&M (no resid disp)	\$	141,695	\$	322,979	\$	826,596	The Landau Station of Parameters and
	Annual Residuals Management	\$	7,500	\$	\$476,701	\$	\$7,455	Includes resin/media disposal
	Total Annual (\$/year)		\$203,090 \$0.79		\$476,721 \$0.44		\$1,233,095 \$0.34	
	Annual Capital (\$/AF)		\$69		\$37		\$28	1
	Annual O&M (no resid disp) (\$/AF)		\$181		\$96		\$74	
	Annual Residuals Disposal (\$/AF)		\$10		\$9		\$8]
	Total Annual (\$/AF)		\$259		\$142		\$110	1

				De	esign Capacity			
	Units	0	.7 MGD		3 MGD		10 MGD	Assumptions
Residuals	duals							
Liquid, Non Hazardous	gallons/year	1	,352,396		5,916,441		15,856,766	
Liquid, Hazardous	gallons/year		0		0		0	
Solid, Non Hazardous	tons/year		0		0		0	
Solid, Hazardous	tons/year		11.8	50.6		168.8		
Disposal Cost								
Liquid, Non Hazardous	\$/year	\$	2,705	\$	11,833	\$	31,714	
Liquid, Hazardous	\$/year	\$	-	\$	-	\$	-	
Solid, Non Hazardous	\$/year	\$	-	\$	-	\$	-	
Solid, Hazardous	\$/year	\$	1,654	\$	7,090	\$	23,634	Waste brine treatment solids and resin carryover
Total Residuals Disposal	\$/year	\$	4,359	\$	18,923	\$	55,348	

Technology Cost Estimate: RCF

Manufacturer	N/A	Design Capacity						
			0.7 MGD					
Technology	RCF		(500 gpm)		3 MGD		10 MGD	Assumptions
Capital Costs (C	Dne-time \$)							
	Ferrous sulfate feed system Mixing Chamber	\$	26,253 129,625	\$	39,560 345,288	\$ \$	55,208 576,947	Coagulant feed system from the W/W model 30 minute contact time, G=50, horizontal paddle for 0.7 MGE chamber; costed as a flocculation basin from EPA estimates for 3 and 10 MGD (also compared to W/W model)
	Filters	\$	409,000	\$	1,444,571	\$	3,600,000	Pressure filters for 500 gpm system (Quote provided by Kinetico); gravity filters for 3 and 10 MGD systems; 3 and 10 MGD system costs based on EPA cost information and W/W model
	Backwash pumping	\$	29,411	-		-		Capable of 18 gpm/sq ft for 500 gpm system; 3 and 10 MGD backwash pumping costs are included in filter costs
	Backwash waste handling and treatment	\$	220,000	\$	800,000	\$	2,500,000	Costs for solids handling from EPA estimates, W/W model, and other MEC resources; 0.7 MGD includes fill and draw backwash gravity thickener with non-mechanical dewatering rolloff (3 MGD includes 2 of each those in parallel); 10 MGD includes fill and draw backwash gravity thickeners and filter presses for solids dewatering
	Subtotal	\$	814,289	\$	2,629,419	\$	6,732,155	Estimate does not include piping to the treatment system; costs above do include engineering, contractor O&P, etc.
	Piping, Valves, Electrical (15%)	\$	122,143	\$	394,413	\$	1,009,823	Some piping, valve, and electrical costs are included in the estimates above - so this % is lower than the other technologies.
	Site Work (5%)	\$	40,714	\$	131,471	\$	336,608	Assume some site work included in estimates above
	Subtotal	\$	977,147	\$	3,155,302	\$	8,078,586	
	Contingency (15%)	\$	146,572	\$	473,295	\$	1,211,788	
	Subtotal Capital Costs	\$	1,123,719	\$	3,628,598	\$	9,290,374	
Operating Cost	s (Annual \$) Forrous Sulfate Cost (\$/year)		¢2.555		\$10.040		\$26.407	Formus Sulfate Cast - \$0.20/gallon of 5% Fo solution
	Ferrous Sullate Cost (\$/year)		\$2,555		\$10,949		\$30,497	Ferrous Sulfate Cost = \$958.63/ton as Fe
Liquid dewater	ring waste disposal / Non-hazardous (\$/year)		\$613		\$2,628		\$11,680	Clarified backwash recycled to head of plant, sludge
	Sludge waste disposal / Hazardous (\$/year)	\$	105,206	\$	450,882	\$	751,471	\$140/ton including transport and disposal, ACWA Residuals Report 2004
	Labor	\$	50,000	\$	100,000	\$	200,000	Assume 0.5 FTE for 500 gpm; 1 FTE for 3 MGD; 2 FTE for 10 MGD (assume loaded salary = \$100,000)
	Subtotal Operating Costs (annual)		\$158,374		\$564,459		\$999,648	
	MGD		0.7		3		10	
	Annual Capital		\$82,685		\$266,999		\$683,602	
	Annual O&M (no resid disp)	\$	52,555	\$	110,949	\$	236,497	
	Annual Residuals Management	\$	105,819	\$	453,510	\$	1 63,151 \$1 683 240	
	Total Annual (\$/kgal)		\$0.94		\$0.76		\$0.46	
	Annual Capital (\$/AF)		\$105		\$79		\$61	
	Annual O&M (no resid disp) (\$/AF)		\$67		\$33		\$21	
	Total Annual (\$/AF)		\$307		\$247		φ08 \$150	

			Design Capacity				
Residuals	Units	0.7 MGD	3 MGD	10 MGD	Assumptions		
		(500 gpm)					
Liquid, Non Hazardous	gallons/year	306,600	1,314,000	5,840,000			
Liquid, Hazardous	gallons/year	0	0	0			
Solid, Non Hazardous	tons/year	0	0	0			
Solid, Hazardous	tons/year	751	3221	5368			

nology Cost Estimate: MIEX® with Hazardous Brine Off-Site Disposal
--

Manufacturer	Orica Watercare			De	sign Capacity			
	@		0.7 MGD					
Technology	MIEX®		(500 gpm)		3 MGD		10 MGD	Assumptions
Capital Costs (One-	time \$)							
	Resin/Media	\$	70,200	\$	175,500	\$	585,000	Vendor quote
	Contactor/tanks	\$	125,000	\$	370,000	\$	825,000	Vendor quote; 10MGD system includes costs for concrete
								contactor and settler tanks (\$325K) rather than \$500K
	Descention tech	¢	270.000	¢	540.000	¢	000.000	estimated by Orica
	Regeneration tanks	Э	370,000	Э	510,000	Ф	880,000	and 5% regeneration system for 3 and 10MGD system
								and 5% regeneration system for 5 and 10000 systems.
	Waste Treatment	\$		\$		\$		No Brine Treatment
	Subtotal	\$	565.200	\$	1.055.500	\$	2.290.000	No Bino Hodanon
		ſ	,		,,	,	, ,	
	Piping, Valves, Electrical (25%)	\$	141,300	\$	263,875	\$	572,500	
	Site Work (10%)	\$	56,520	\$	105,550	\$	229,000	
	Subtotal	\$	763,020	\$	1,424,925	\$	3,091,500	
_								
В	onds, Insurance, Contractor O&P (10%)	\$	76,302	\$	142,493	\$	309,150	
	Engineering (12%)	\$	91,562	\$	170,991	\$	370,980	
	Subtotal	\$	930,884	Þ	1,738,409	\$	3,771,630	
	Contingency (15%)	\$	139 633	\$	260 761	\$	565 745	
	Subtotal Capital Costs	\$	1.070.517	\$	1,999,170	\$	4.337.375	
Operating Costs (Ar	nual \$)	Ť	.,,	- T	.,,	- T	.,	
`	Resin Replacement		\$34,675		\$96,360		\$302,950	Vendor guote; Resin loss rate of 2 gal / MG water treated.
	Resin Regeneration Costs (Salt)		\$10,670		\$45,727		\$152,424	Salt Costs of \$72/ton (higher than Orica estimate of \$50).
								Salt consumption same for all 3 systems at 1169 lb/MG.
Plant Powe	er Consumption Cost (for resin pumping)	_	\$1,892		\$6,570		\$21,900	Power Cost: Usage 25 – 35 kWhr/MG (with respect to
								regeneration rate) at 0.12 \$/kWhr.
	Waste Brine Sewer Cost		\$0		\$0		\$0	No sewer disposal
Wa	ste Brine Treatment and Disposal Cost*		\$616,500		\$2,568,750		\$8,563,750	Hazardous off-site disposal at \$1.25/gal. *Waste brine
								disposal costs will be reduced with lower influent chromium
D			#1 0 17		<u> </u>		\$ 15.000	levels (calculated for 100 ug/L).
Resin ca	rryover, Hazardous Solid Disposal Cost	<u> </u>	\$1,047	<i>•</i>	\$4,500		\$15,000	\$140 per ton
	Labor	φ	50,000	φ	200,000	φ	300,000	10 MGD: assume loaded salary = \$100.000
	Subtotal Operating Costs (annual)		\$714 784		\$2 921 907		\$9 356 024	To WOD, assume loaded salary = \$100,000
	MGD		0.7		φ <u>2</u> ,0 <u>2</u> 1,001		φ0,000,024 10	
	Annual Capital		\$78,771		\$147,102		\$319,152	
	Annual O&M (no resid disp)		\$97,237		\$348,657		\$777,274	
	Annual Residuals Management		\$617,547		\$2,573,250		\$8,578,750	
	Total Annual (\$/year)		\$793,554		\$3,069,010		\$9,675,176	
	Total Annual (\$/kgal)		\$3.11		\$2.80		\$2.65	
			.		-			
	Annual Capital		\$100		\$44		\$28	
	Annual O&M		\$124		\$104		\$69	
	Annual Residuals Disposal		\$788		\$766		\$766	
	i otal Annual (\$/AF)		\$1,012		\$913		\$804	

				De	sign Capacity			
	Units	0	.7 MGD		3 MGD	10 MGD	Assumptions	
Residuals		(5	00 gpm)					
Liquid, Non Hazardous	gallons/year		0		0	 0		
Liquid, Hazardous	gallons/year	4	493200		2,055,000	 6,851,000		
Solid, Non Hazardous	tons/year		0		0	 0		
Solid, Hazardous	tons/year		7.5		32.1	 107.1		
Disposal Cost								
Liquid, Non Hazardous	\$/year	\$	-	\$	-	\$ -		
Liquid, Hazardous	\$/year	\$	616,500.00	\$	2,568,750.00	\$ 8,563,750.00		
Solid, Non Hazardous	\$/year							
Solid, Hazardous	\$/year	\$	1,047	\$	4,500	\$ 15,000	Waste brine treatment solids and resin carryover	
Total Residuals Disposal	\$/year	\$	617,547	\$	2,573,250	\$ 8,578,750		

Technology Cost Estimate: MIEX® with Brine Treatment

Manufacturer Orica Watercare		Design Capacity					
		0.7 MGD					
Technology MIEX [®]		(500 gpm)		3 MGD		10 MGD	Assumptions
Capital Costs (One-time \$)					_		
Resin/Medi	a\$	70,200	\$	175,500	\$	585,000	Vendor quote
Contactor/tank	sэ	125,000	Ф	370,000	Þ	825,000	contactor and sottler tanks (\$225K)
Regeneration tank	s \$	370 000	\$	510 000	\$	880.000	Vendor quote: 10% regeneration system for 500gpm system
	Ť	0,0,000	Ŷ	010,000	Ŷ	000,000	and 5% regeneration system for 3 and 10MGD systems.
Waste Treatmer	t \$	100,000	\$	140,000	\$	220,000	Estimate for 0.7 MGD; 3 and 10 MGD vendor quote
Subtota	1\$	665,200	\$	1,195,500	\$	2,510,000	1
Diping Valves Electrical (25%) ¢	166 200	¢	209 975	¢	627 500	
Site Work (10%	φ () φ	66 520	¢ Q	290,075	¢ ¢	251,000	
Subtota	1 \$	898 020	\$	1 613 925	\$	3 388 500	
Custon	'I °	000,020	Ŷ	1,010,020	Ψ	0,000,000	
Bonds, Insurance, Contractor O&P (10%)\$	89,802	\$	161,393	\$	338,850	
Engineering (12%)\$	107,762	\$	193,671	\$	406,620	
Subtota	1\$	1,095,584	\$	1,968,989	\$	4,133,970	
0		404.000	•	005.040	•		
Contingency (15%) \$	164,338	\$	295,348	\$	620,096	
Operating Costs (Annual \$)	s ə	1,259,922	æ	2,204,337	æ	4,754,000	
Resin Replacement	+	\$34,675		\$96,360		\$302.950	Vendor quote: Resin loss rate of 2 gal / MG water treated
Resin Regeneration Costs (Salt		\$10,670		\$45,500		\$152,330	Salt Costs of \$72/ton (higher than Orica estimate of \$50)
rtesin rtegeneration obsis (dan	.,	φ10,070		ψ 1 0,727		ψ102,424	Salt consumption same for all 3 systems at 1169 lb/MG.
Plant Power Consumption Cost (for resin pumping)	\$1,892		\$6,570		\$21,900	Power Cost: Usage 25 – 35 kWhr/MG (with respect to
							regeneration rate) at 0.12 \$/kWhr.
Waste Brine Sewer Cos	st	\$986		\$4,110		\$13,702	Sewer disposal of untreated waste brine (500 gpm system)
							or treated brine (3 and 10 MGD systems), \$2/kgal
Waste Brine Treatment and Disposal Cost	*	\$740		\$3,083		\$10,277	Operating costs of \$0.0015/gallon for waste brine system
							(includes ferrous sulfate and NaOH)
Resin carryover, Hazardous Solid Disposal Cos	t	\$3,500		\$14,560		\$48,580	\$140 per ton
Labo	r \$	100,000	\$	250,000	\$	350,000	Assume 1 FTE for 500 gpm; 2.5 FTE for 3 MGD; 3.5 FTE for
							for bring treatment system
Subtotal Operating Costs (annual)	\$152.463		\$420 410		\$899 833	
MGI	2	0.7		φ+20,+10 3		φ000,000 10	
Annual Capita	al	\$92.707		\$166.614		\$349.812	
Annual O&M (no resid disp)	\$147,237		\$398,657		\$827,274	
Annual Residuals Managemer	í	\$5,226		\$21,753		\$72,559	
Total Annual (\$/year	.)	\$245,170		\$587,024		\$1,249,645	-
Total Annual (\$/kga)	\$0.96		\$0.54		\$0.34	
Annual Conits	N.	¢140		\$F0		¢04	1
Annual Capita	а Л	\$118 \$100		\$50 \$110		\$31 ¢74	
Annual Residuals Disposa	n al	\$7		811¢ A2		47¢ A2	
Total Annual (\$/AF)	\$313		\$175		\$112	1

			Design Capacity		
	Units	0.7 MGD	3 MGD	10 MGD	Assumptions
Residuals		(500 gpm)			
	gallons/year	493,200	2,055,000	6,851,000	All brine treated; 0.7 MGD case proportional to 3 & 10 MGD
Liquid, Non Hazardous					optimized brine production
Liquid, Hazardous	gallons/year	0	0	0	
Solid, Non Hazardous	tons/year	0	0	0	
Solid, Hazardous	tons/year	25.0	104.0	347.0	
Disposal Cost					
Liquid, Non Hazardous	\$/year	\$ 986	\$ 4,110	\$ 13,702	
Liquid, Hazardous	\$/year	\$-	\$-	\$-	
Solid, Non Hazardous	\$/year	\$-	\$-	\$-	
Solid, Hazardous	\$/year	\$ 3,500	\$ 14,560	\$ 48,580	Waste brine treatment solids and resin carryover
Total Residuals Disposal	\$/year	\$ 4,486	\$ 18,670	\$ 62,282	

Technology Cost Estimate: MIEX® with Sewered Non-Hazardous Brine

Manufacturer	Orica Watercare	D	esign Capacity	
			0.7 MGD	
Technology	MIEX®		(500 gpm)	Assumptions
Capital Costs (One-time	\$)			
	Resin/Media	\$	70,200	Vendor quote
	Contactor/tanks	\$	125,000	Vendor quote
	Regeneration tanks	\$	370,000	Vendor quote; 10% regeneration system for 500gpm system
	Weste Treatment			No bring tractment
	Subtotal	\$	565 200	No bille treathent
	Cubicital	Ť	000,200	
	Piping, Valves, Electrical (25%)	\$	141,300	
	Site Work (10%)	\$	56,520	
	Subtotal	\$	763,020	
Bonds	, Insurance, Contractor O&P (10%)	\$	76,302	
	Engineering (12%)	\$	91,562	
	Subtotal	\$	930,884	
	0	¢	400.000	
	Contingency (15%)	\$	139,633	
Operating Costs (Appus	Subtotal Capital Costs	\$	1,070,517	
Operating Costs (Annua	Desis Deslassment	_	\$04 C7E	Vender guete: Desin less rate of 2 col / MC water treated
	Resin Replacement		\$34,073 \$0,940	Self Costs of \$72/top (higher than Origo actimate of \$50)
	Resili Regeneration Costs (Sait)		49,040	Salt consumption less for 0.7 MGD when operated less
				efficiently (1043b/MG)
Plant Power Consumption Cost (for resin numping)			\$1 892	Power Cost: Usage 25 – 35 kWhr/MG (with respect to
	incampuon ocor (ior room pamping)		\$1,00L	regeneration rate) at 0.12 \$/kWhr.
	Waste Brine Sewer Cost		\$5.256	Sewer disposal of untreated waste brine (500 gpm system)
				or treated brine (3 and 10 MGD systems), \$2/kgal
W/acto F	Pring Transmont and Dianogal Cast*		0.9	No Brino trootmont
Resin carryov	er Hazardous Solid Disposal Cost		پ و \$1 047	Vendor quote
rteanteanyou	Labor	\$	50,000	Assume 0.5 FTF for 500 gpm: 2 FTF for 3 MGD: 3 FTF for
	Eabor	Ŷ	00,000	10 MGD: assume loaded salary = \$100.000
S	ubtotal Operating Costs (annual)		\$102,710	
	MGD		0.7	•
	Annual Capital		\$78,771	
	Annual O&M (no resid disp)		\$96,407	
	Annual Residuals Management		\$6,303	
	Total Annual (\$/year)		\$181,480	
	Total Annual (\$/kgal)		\$0.71	
	Appuel Casital		\$100	
			\$100 \$100	
	Annual Residuals Disposal		φ123 ¢0	
	Total Annual (\$/AF)		۵۵ \$231	
	rotar/timodi (ψ/Ar)		ψ201	

		Design Capacity	
	Units	0.7 MGD	Assumptions
Residuals		(500 gpm)	
Liquid, Non Hazardous	gallons/year	2,628,000	
Liquid, Hazardous	gallons/year	0	
Solid, Non Hazardous	tons/year	0	
Solid, Hazardous	tons/year	7.5	
Disposal Cost	tons/year		
Liquid, Non Hazardous	\$/year	\$ 5,256	
Liquid, Hazardous	\$/year	\$-	
Solid, Non Hazardous	\$/year	\$-	
Solid, Hazardous	\$/year	\$ 1,047	Waste brine treatment solids and resin carryover
Total Residuals Disposal	\$/year	\$ 6,303	

APPENDIX A Results for the WRT Adsorptive Media Pilot Unit

Summary

Test Objectives

- 1) Develop breakthrough curve at 5, 10, 15, 20, 25, 30 min EBCT
- 2) Characterize effluent water quality for chromium and selected parameters
- 3) Calculate media capacity for Cr(VI)
- 4) Determine pressure loss across column
- 5) Perform TCLP and WET on exhausted media

Test Condition

WRT Z- 24^{TM} zeolite media Flow = 2 GPM Total EBCT = 30 min

Sampling Parameters

Cr(VI) Total Cr Arsenic Iron Nitrate Phosphate Sulfate Silicate pH Conductivity Alkalinity Hardness Turbidity

Results

See Figures A1 – A32



WRT Adsorptive Media System (6 columns in series preceded by a deaeration column shown to the right)

Note: The WRT system was tested twice. Significant breakthrough of Cr(VI) was observed earlier than expected during the first trial (Trial 1), possibly due to the interference of the phosphate–based sequestering agent. As a result, the source water was changed from plant effluent to raw North Operable Unit well water, followed by a second trial (Trial 2) of the WRT system.



Figure A1. Cr(VI) breakthrough curve of each column for Trial 1, where 5 min EBCT indicates the first column, and 10 min EBCT indicates the second column, and etc¹.



Figure A2. Cr(VI) removal performance of the WRT system (Trial 1)



Figure A3. Total Cr removal performance of the WRT system (Trial 1)

¹ 1 Bed Volume equals 52 gallons in the WRT pilot system



Figure A4. Arsenic removal performance of the WRT system (Trial 1)



Figure A5. Iron removal performance of the WRT system (Trial 1)



Figure A6. Nitrate removal performance of the WRT system (Trial 1)



Figure A7. Phosphate removal performance of the WRT system (Trial 1)



Figure A8. Sulfate removal performance of the WRT system (Trial 1)



Figure A9. Silicate removal performance of the WRT system (Trial 1)



Figure A10. pH profile during the WRT pilot testing (Trial 1)



Figure A11. Conductivity profile during the WRT pilot testing (Trial 1)



Figure A12. Alkalinity profile during the WRT pilot testing (Trial 1)



Figure A13. Hardness profile during the WRT pilot testing (Trial 1)



Figure A14. Turbidity profile during the WRT pilot testing (Trial 1)



Figure A15. Total pressure loss of the WRT system (Trial 1)







Figure A17. Cr(VI) breakthrough curve of each column for Trial 2



Figure A18. Cr(VI) removal performance of the WRT system (Trial 2)



Figure A19. Total Cr removal performance of the WRT system (Trial 2)



Figure A20. Arsenic removal performance of the WRT system (Trial 2)



Figure A21. Iron removal performance of the WRT system (Trial 2)



Figure A22. Nitrate removal performance of the WRT system (Trial 2)



Figure A23. Phosphate removal performance of the WRT system (Trial 2)



Figure A24. Sulfate removal performance of the WRT system (Trial 2)



Figure A25. Silicate removal performance of the WRT system (Trial 2)



Figure A26. pH profile during the WRT pilot testing (Trial 2)



Figure A27. Conductivity profile during the WRT pilot testing (Trial 2)



Figure A28. Alkalinity profile during the WRT pilot testing (Trial 2)



Figure A29. Hardness profile during the WRT pilot testing (Trial 2)



Figure A30. Turbidity profile during the WRT pilot testing (Trial 2)



Figure A31. Total pressure loss of the WRT system (Trial 2)



Figure A32. Pressure loss across each column in the WRT system (Trial 2)

APPENDIX B Results for the Filtronics Reduction/Filtration Pilot Unit

Summary

Test Objectives

- 6) Determine operating conditions that obtain 95% removal of Cr(VI) and Total Cr
- 7) Characterize effluent water quality for chromium and selected parameters

Test Condition

Filtration by Electromedia[®] Flow Rate: 0.5 gpm A total of four tests were conducted and each test condition was shown in Figure B1.

Sampling Parameters

Cr(VI) Total Cr

Results

See Figure B1



Filtronics Reduction/Filtration System (reduction column on right, filter on left; chemical addition from cylinders on table)



Figure B1. Cr(VI) and Cr total removal performance of the Filtronics[®] system

APPENDIX C Results for the Calgon GAC Pilot Unit

Summary

Test Objectives

- 8) Develop breakthrough curve
- 9) Characterize effluent water quality for chromium and selected parameters
- 10) Calculate media capacity for Cr(VI)

Test Condition

GAC tested: Filtrasorb 600, Filtrasorb 200 PHA Flow = 0.5 GPM EBCT = 5.2 min

Sampling Parameters

Cr(VI) Total Cr Arsenic Iron Nitrate Phosphate Sulfate Silicate pH Conductivity Alkalinity Hardness Turbidity

Results

See Figures C1 – C13

NOTE: The Calgon system was tested twice (Trial 1 and Trial 2) due to air bubble issues and short-circuiting, which was observed in both tests.



Calgon Pilot Unit (Trial 2 shown; GAC in righthand column



Figure C1. Cr(VI) removal performance of the Calgon GAC columns²



Figure C2. Total Cr removal performance of the Calgon GAC columns



Figure C3. Arsenic removal by the Calgon GAC columns

² 1 Bed Volume equals 2.6 gallons in the Calgon GAC system.



Figure C4. Iron removal performance of the Calgon GAC columns



Figure C5. Nitrate removal performance of the Calgon GAC columns



Figure C6. Phosphate removal performance of the Calgon GAC columns



Figure C7. Sulfate removal performance of the Calgon GAC columns



Figure C8. Silicate removal performance of the Calgon GAC columns



Figure C9. pH profiles for the Calgon GAC columns



Figure C10. Conductivity profiles for the Calgon GAC columns





Figure C12. Hardness profiles for the Calgon GAC columns



Figure C13. Turbidity profiles for the Calgon GAC columns

APPENDIX D Results for the Calgon Strong-Base Anion Exchange Pilot Unit

Summary

Test Objectives

- 11) Develop breakthrough curve
- 12) Characterize effluent water quality for chromium and selected parameters
- 13) Calculate media capacity for Cr(VI)

Test Condition

SBA Resins Tested: WT201, 202, 203, 204 Flow = 2 GPM EBCT = 1.3 min

Sampling Parameters

Cr(VI) Total Cr Arsenic Iron Nitrate Phosphate Sulfate Silicate pH Conductivity Alkalinity Hardness Turbidity

Calgon Pilot Unit (Trial 2 shown; SBA resin in middle two columns

Results

See Figures D1 – D13

NOTE: The Calgon system was tested twice (Trial 1 and Trial 2) due to air bubble issues and short-circuiting, which was observed in both tests.







Figure D2. Total Cr removal performance of the Calgon anion exchange system



Figure D3. Arsenic removal performance of the Calgon anion exchange system

³ 1 Bed Volume equals 2.6 gallons in the Calgon anion exchange system.



Figure D4. Iron removal performance of the Calgon anion exchange system



Figure D5. Nitrate removal performance of the Calgon anion exchange system



Figure D6. Phosphate removal performance of the Calgon anion exchange system



Figure D7. Sulfate removal performance of the Calgon anion exchange system



Figure D8. Silicate removal performance of the Calgon anion exchange system



Figure D9. pH profile of the Calgon anion exchange system



Figure D10. Conductivity profile of the Calgon anion exchange system



Figure D11. Alkalinity profile of the Calgon anion exchange system



Figure D12. Hardness profile of the Calgon anion exchange system



Figure D13. Turbidity profile of the Calgon anion exchange system

APPENDIX E Results for the Orica MIEX[®] Pilot Unit

Summary

Test Objectives

- 14) Determine operating conditions that obtain less than 5 μ g/L Cr(VI) in effluent
- 15) Determine steady state effluent water quality
- 16) Determine regeneration effectiveness

Test Condition

Flow = 2 GPM

Contact time ranges from 10 to 30 min. Resin dose ranges from 20 to 60 ml/L. Brine recycle rate ranges from 90% to 95%.

Sampling Parameters

Cr(VI) Total Cr Arsenic Iron Nitrate Phosphate Sulfate Silicate pH Conductivity Alkalinity Hardness Turbidity

Results

See Figures E1 – E24



MIEX Phase A testing – System components shown include reactor and settler.



MIEX Phase B testing – Computer-controlled system

NOTE: The MIEX® system was tested twice – once with treated GWTP effluent and again with NOU well water. A combination of phosphate-based sequestering agent and higher sulfate levels in the GWTP effluent may have contributed to worse performance in the first test (Phase A) compared to the second test (Phase B).







Figure E2. Total Cr removal performance of the MIEX system (Phase A)



Figure E3. Arsenic removal performance of the MIEX system (Phase A)

⁴ Normal sampling schedule during Phase A included three samples per 8-hour day.



Figure E4. Iron removal performance of the MIEX system (Phase A)



Figure E5. Nitrate removal performance of the MIEX system (Phase A)



Figure E6. Phosphate removal performance of the MIEX system (Phase A)


Figure E7. Sulfate removal performance of the MIEX system (Phase A)



Figure E8. Silicate removal performance of the MIEX system (Phase A)



Figure E9. pH profile of the MIEX system (Phase A)



Figure E10. Conductivity profile of the MIEX system (Phase A)



Figure E11. Alkalinity profile of the MIEX system (Phase A)



Figure E12. Hardness profile of the MIEX system (Phase A)



Figure E13. Turbidity profile (unfiltered) of the MIEX system (Phase A)⁵



Figure E14. Cr(VI) removal performance of the MIEX system (Phase B)⁶



Figure E15. Total Cr removal performance of the MIEX system (Phase B)

⁵ Effluent was unfiltered.

⁶ Normal sampling schedule during Phase B included two samples per day.



Figure E16. Nitrate removal performance of the MIEX system (Phase B)



Figure E17. Phosphate removal performance of the MIEX system (Phase B)



Figure E18. Sulfate removal performance of the MIEX system (Phase B)



Figure E19. Silicate removal performance of the MIEX system (Phase B)



Figure E20. pH profile of the MIEX system (Phase B)



Figure E21. Conductivity profile of the MIEX system (Phase B)





Figure E23. Hardness profile of the MIEX system (Phase B)



Figure E24. Turbidity profile of the MIEX system (Phase B)⁷

 $^{^{7}}$ Effluent was 0.45 μ m filtered.

APPENDIX F Results for the USF/R&H Strong-Base Anion Exchange Pilot Unit

Summary

Test Objectives

- 17) Develop breakthrough curve
- 18) Characterize effluent water quality for chromium and selected parameters
- 19) Calculate media capacity for Cr(VI)

Test Condition

Flow = 2 GPM EBCT = 3.7 min

Sampling Parameters

Cr(VI) Total Cr Arsenic Iron Nitrate Phosphate Sulfate Silicate pH Conductivity Alkalinity Hardness Turbidity

Results

See Figures F1 – F13



USF/R&H SBA Pilot Unit (lead-lag canisters in the foreground)



Figure F1. Cr(VI) removal performance of the USF/R&H SBA system⁸



Figure F2. Total Cr removal performance of the USF/R&H SBA system



 $^{^{8}}$ 1 Bed Volume equals 7.5 gallons in the USF/R&H SBA system.







Figure F5. Nitrate removal by the USF/R&H SBA system



Figure F6. Phosphate removal by the USF/R&H SBA system







Figure F8. Silicate removal by the USF/R&H SBA system



Figure F9. pH profile of the USF/R&H SBA system



Figure F10. Conductivity profile of the USF/R&H SBA system



Figure F11. Alkalinity profile of the USF/R&H SBA system



Figure F12. Hardness profile of the USF/R&H SBA system



Figure F13. Turbidity profile of the USF/R&H SBA system

APPENDIX G Results for the USF/R&H Weak-Base Anion Exchange Pilot Unit

Summary

Test Objectives

- 20) Develop breakthrough curve
- 21) Characterize effluent water quality for chromium and selected parameters
- 22) Calculate media capacity for Cr(VI)
- 23) Perform TCLP and WET on exhausted media

Test Condition

Duolite[®] A7 weak-base anion exchange media Flow = 2 GPM EBCT = 1.9 min

Sampling Parameters

Cr(VI) Total Cr Arsenic Iron Nitrate Phosphate Sulfate Silicate pH Conductivity Alkalinity Hardness Turbidity



USF/R&H WBA System (cation exchange column for pH control on left, followed by two small lead-lag WBA resin canisters in the foreground)

Results

See Figures G1 – G13, Table G1

NOTE: USF/R&H used a cation exchange column before the lead-lag WBA columns to reduce pH to less than 6.



Figure G1. Cr(VI) removal performance of the USF/R&H WBA system⁹



Figure G2. Total Cr removal performance of the USF/R&H WBA system



Figure G3. Arsenic removal by the USF/R&H WBA system

⁹ 1 Bed Volume equals 3.8 gallons in the USF/R&H WBA pilot unit.







Figure G5. Nitrate removal by the USF/R&H WBA system



Figure G6. Phosphate removal by the USF/R&H WBA system







Figure G8. Silicate removal by the USF/R&H WBA system



Figure G9. pH profile of the USF/R&H WBA system







Figure G11. Alkalinity profile of the USF/R&H WBA system



Figure G12. Hardness profile of the USF/R&H WBA system



Figure G13. Turbidity profile of the USF/R&H WBA system

Element*	Concentration (mg/kg)	Virgin Resin Concentration (mg/kg)		
Chromium	32,210**	0.0056		
Sulfur	42,645	< 2		
Molybdenum	1,446	< 17		
Phosphorus	1,384	89.3		
Chloride	1,280	45		
Vanadium	884	< 3		
Calcium	863	120		
Uranium	492	< 0.9		
lodine	489	< 18		
Iron	191	86.8		
Bromine	81	0.5		
Strontium	17	< 5		

Table G1. Concentrations of various elements in spent WBA column 1 resin as measured by x-ray fluorescence spectrometry

* Elements measurable by XRF include those between Na and U on the periodic table. ** The solid phase concentration of 32,2100 mg/kg is equivalent to 3.221 % Cr by weight.

APPENDIX H Results for the Reduction/Coagulation/Filtration Pilot Unit

Summary

Test Objectives

- 24) Determine operating conditions that obtain 95% removal of total Cr
- 25) Characterize effluent water quality for chromium and selected parameters
- 26) Characterize backwash water quality for selected parameters
- 27) Perform TCLP and WET on backwash solids

Test Condition

Reduction with ferrous sulfate, coagulation in aeration columns, filtration by dualmedia (anthracite/sand) filter

See Table H1

Sampling Parameters

Cr(VI) Total Cr Iron pH Turbidity Settleable solids

Results

See Figures H1 – H32







Components of the RCF System (far leftreduction tank, upper left- aeration columns, upper right- filters, bottom right- backwash module)

	E G M		Aeration/ Run		Loading Rate (gpm/sf)	
Date	Fe:Cr Mass Ratio	pH Goal	Filtration pH Goal	(hrs)	Filter 1	Filter 2
June 15, 2004	50:1	Ambient	Ambient	6	6	4
June 16, 2004	50:1	6.5	Ambient	6	6	4
June 17, 2004	50:1	6.5	7.5	6	6	4
June 18, 2004	50:1	7	7.5	6	3	4
June 21, 2004	50:1	7	Ambient	6	3	4
June 22, 2004	50:1	Ambient	Ambient	6	3	4
June 23, 2004	25:1	6.5	7.5	6	3	4
June 24, 2004	25:1	Ambient	Ambient	6	3	4
June 25, 2004	25:1	Ambient	Ambient	6	3	4
July 1, 2004	10:1	6.5	7.5	6	3	4
July 2, 2004	10:1	6.5	Ambient	6	3	4
July 6, 2004	10:1	Ambient	Ambient	6	3	4
July 7, 2004	25:1	Ambient	Ambient	6	3	4
July 8, 2004	25:1	6.5	Ambient	6	3	4
July 9, 2004	50:1	Ambient	Ambient	6	3	4
July 12, 2004	25:1	Ambient	Ambient	46	4	-
July 14, 2004	15:1	Ambient	Ambient	24	4	-

 Table H1. Operating conditions tested in the RCF system



Figure H1. RCF operation on June 15, 2004 with 50:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 6 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H2. RCF operation on June 15, 2004 with 50:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performances

B. Head loss and turbidity profiles



Figure H3. RCF operation on June 16, 2004 with 50:1 Fe:Cr mass ratio, reduction pH at 6.5, no filtration pH adjustment, and filter loading rate at 6 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H4. RCF operation on June 16, 2004 with 50:1 Fe:Cr mass ratio, reduction pH at 6.5, no filtration pH adjustment, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H5. RCF operation on June 17, 2004 with 50:1 Fe:Cr mass ratio, reduction pH at 6.5, filtration pH at 7.5, and filter loading rate at 6 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H6. RCF operation on June 17, 2004 with 50:1 Fe:Cr mass ratio, reduction pH at 6.5, filtration pH at 7.5, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H7. RCF operation on June 18, 2004 with 50:1 Fe:Cr mass ratio, reduction pH at 7.0, filtration pH at 7.5, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H8. RCF operation on June 18, 2004 with 50:1 Fe:Cr mass ratio, reduction pH at 7.0, filtration pH at 7.5, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H9. RCF operation on June 21, 2004 with 50:1 Fe:Cr mass ratio, reduction pH at 7.0, no filtration pH adjustment, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H10. RCF operation on June 21, 2004 with 50:1 Fe:Cr mass ratio, reduction pH at 7.0, no filtration pH adjustment, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H11. RCF operation on June 22, 2004 with 50:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles







Figure H13. RCF operation on June 23, 2004 with 25:1 Fe:Cr mass ratio, reduction pH at 6.5, filtration pH at 7.5, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles





Figure H14. RCF operation on June 23, 2004 with 25:1 Fe:Cr mass ratio, reduction pH at 6.5, filtration pH at 7.5, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H15. RCF operation on June 24, 2004 with 25:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 3 gpm/sf
A. Cr(VI), total Cr and Fe removal performances¹⁰
B. Head loss and turbidity profiles

¹⁰ Only one water sample was collected due to the power outage of the Cr(VI) spike pump in the morning.


Figure H16. RCF operation on June 24, 2004 with 25:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 4 gpm/sf
A. Cr(VI), total Cr and Fe removal performances¹¹
B. Head loss and turbidity profiles

¹¹ Only one water sample was collected due to the power outage of the Cr(VI) spike pump in the morning.



Figure H17. RCF operation on June 25, 2004 with 25:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles





Figure H18. RCF operation on June 25, 2004 with 25:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H19. RCF operation on July 1, 2004 with 10:1 Fe:Cr mass ratio, reduction pH at 6.5, filtration pH at 7.5, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H20. RCF operation on July 1, 2004 with 10:1 Fe:Cr mass ratio, reduction pH at 6.5, filtration pH at 7.5, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H21. RCF operation on July 2, 2004 with 10:1 Fe:Cr mass ratio, reduction pH at 6.5, no filtration pH adjustment, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H22. RCF operation on July 2, 2004 with 10:1 Fe:Cr mass ratio, reduction pH at 6.5, no filtration pH adjustment, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H23. RCF operation on July 6, 2004 with 10:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H24. RCF operation on July 6, 2004 with 10:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H25. RCF operation on July 7, 2004 with 25:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H26. RCF operation on July 7, 2004 with 25:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles





Figure H27. RCF operation on July 8, 2004 with 25:1 Fe:Cr mass ratio, reduction pH at 6.5, no filtration pH adjustment, and filter loading rate at 3 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H28. RCF operation on July 8, 2004 with 25:1 Fe:Cr mass ratio, reduction pH at 6.5, no filtration pH adjustment, and filter loading rate at 4 gpm/sfA. Cr(VI), total Cr and Fe removal performancesB. Head loss and turbidity profiles



Figure H29. RCF operation on July 9, 2004 with 50:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 3 gpm/sf

A. Cr(VI), total Cr and Fe removal performances

B. Head loss and turbidity profiles





B. Head loss and turbidity profiles



Figure H31. RCF operation on July 12, 2004 with 25:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 4 gpm/sf

- A. Cr(VI), total Cr and Fe removal performances
 - B. Head loss and turbidity profiles



Figure H32. RCF operation on July 14, 2004 with 15:1 Fe:Cr mass ratio, no pH adjustment, and filter loading rate at 4 gpm/sf

A. Cr(VI), total Cr and Fe removal performances

B. Head loss and turbidity profiles

APPENDIX I Quality Assurance/Quality Control Data



Table I1. Comparison of Cr(VI) concentrations in duplicate samples taken throughout pilot testing



Table I2. Cr(VI) concentrations in the field and travel blank samples¹²



Table I3. Total Cr concentrations in the field and travel blank samples¹³

 $^{^{12}}$ Blank samples were preserved with NaOH to pH>10 in the field and measured in the USU lab by ion chromatograph in accordance with USEPA Method 1636 (PQL of 0.2 μ g/L). 13 Blank samples were preserved with 2% HNO₃ to pH<2 in the filed and measured in the USU lab by inductively

¹³ Blank samples were preserved with 2% HNO₃ to pH<2 in the filed and measured in the USU lab by inductively coupled plasma – mass spectrometer in accordance with USEPA Method 200.8 (PQL of 1.0 μ g/L).