City of Glendale Water and Power
141 N. Glendale Ave • Level 4 • Glendale, CA

The Treatment of Hexavalent Chromium in the City of Glendale Groundwater Supply: Phase III Demonstration-Scale Treatment Technology Evaluation

EPA Science and Technology Grant

June 2008

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1. Executive Summary

The City of Glendale Water and Power (Glendale) is leading a four-phase program to identify and implement drinking water treatment technologies for hexavalent chromium, Cr(VI), in groundwater supplies. Phase I included bench-scale studies to screen a wide array of potential technologies. Based on the results of Phase I, six treatment options were evaluated in Phase II pilot testing. The results of Phase II identified three leading contenders: weak-base anion exchange resin (WBA), reduction/coagulation/filtration (RCF) using ferrous sulfate, and strong-base anion exchange resin (SBA). While appealing from a residuals management perspective, WBA represented a new application in drinking water treatment and required additional study before selection for testing in the Phase III demonstration study or Phase IV full-scale implementation. RCF has been successfully used at full scale in industrial applications treating higher Cr(VI) concentrations; however, cost savings could be realized with further optimization of an RCF drinking water treatment system. SBA is the most mature of the technologies but, by comparison, generates residuals that can be challenging for some utilities.

This report highlights the documents produced with support from the EPA's Science and Technology Grant program (S&T). The first part of this S&T program involved extensive testing of the WBA resin, termed the Bridge Project due to the link between the Phase II pilot testing and the Phase III demonstration testing. Results of the Bridge Project are highlighted in the American Water Works Association Research Foundation (AwwaRF) report executive summary (Chapter 2) and the Inorganic Contaminants Workshop proceedings (Chapter 3). Testing confirmed that two WBA resins exhibited very high Cr(VI) removal capacities resulting in the cost-effective use of the resins as disposable media, thereby minimizing the quantity of residuals generated. WBA resin was also found to require pH depression to approximately pH 6 for optimal Cr(VI) removal.

Following the Bridge Project, Glendale convened an Expert Workshop to obtain a recommendation for selection of the treatment technologies in Phase III demonstration testing. The Expert Workshop panel consisted of drinking water treatment experts from the California Region 9 EPA, the California Department of Public Health, academia (UCLA, Utah State University, University of Colorado at Boulder, and Lehigh University), municipalities (MWDSC, LADWP), and consulting (McGuire Malcolm Pirnie). The public was invited to participate in the workshop, with the proceedings broadcast to the community over public access television. A summary of the Expert Workshop proceedings is provided in Chapter 4.

The Expert Panel unanimously agreed that RCF should be tested in the Phase III demonstration study. Panelists also recommended further study of the WBA treatment technology to increase understanding of the mechanism responsible for the high Cr(VI) removal capacity of the WBA resins. SBA resin was not advised due to questions about the ability to treat and dispose of brine waste in the long term.

Based on the Expert Panel recommendations, Glendale conducted additional testing of the WBA resin at Lehigh University. A Quality Assurance Project Plan (QAPP) for the Lehigh testing is included in Chapter 5. The final Lehigh report is attached as Chapter 6. In-depth geochemical analyses of the resins were also performed at Wellesley College, MIT, and Argonne National Laboratories (described in Water Quality and Technology Conference proceedings, Chapter 7, and Inorganic Contaminants Workshop proceedings, Chapter 8). Results of these studies proved that a traditional ion exchange mechanism was not solely responsible for the high Cr(VI) removal capacities of the WBA resins. Instead, Cr(VI) is reduced to Cr(III) by the resins and retained on the resin beads in a fairly homogeneous distribution. No Cr(III) precipitates were observed on the resins, indicating a low risk of Cr(III) breakthrough as particles.

Results from these studies encouraged Glendale to proceed with testing of WBA resin at the demonstration scale. The availability of unused vessels at one well site (GS-3) containing high Cr(VI) concentrations offered cost savings for WBA treatment over the other potential treatment technologies.

Chapters 9 and 10 present the Experimental Design and QAPP for the demonstration-scale WBA system operation, respectively. The Experimental Design outlines study objectives, protocols, and the plan for operational evaluations. Appendices of the Experimental Design also include the Preliminary Design Report and a pump curve evaluation of the current well pump. Specific demonstration study sampling, testing, and measurement procedures are described in the QAPP, in addition to quality assurance/quality control checks and data assessment methods.

Glendale currently has three wells containing rising concentrations of Cr(VI) that will require treatment in the near future to reach City Cr(VI) goals. GS-3 will be treated with WBA resin due to the lower costs offered by the existing infrastructure. The other two wells, GN-2 and GN-3, would require a new treatment system. Glendale intends to build an RCF demonstration system to treat a portion of one or both of these wells. Phase II pilot testing showed that RCF held promise for Cr(VI) treatment; however, this study did not optimize the design of the facilities and tested a treatment system with 45 minutes of Cr(VI) reduction time and 18 minutes of aeration/coagulation time. Glendale realized the potential cost savings associated with scaled-down capital facilities and conducted additional pilot testing of a modular RCF system. Chapter 11 presents the results of the optimization pilot testing, which indicated that the aeration step could be eliminated if 45 minutes of reduction time was retained.

In summary, the S&T grant enabled significant advances in the understanding by the water utility community of two Cr(VI) treatment technologies for achieving less than 5 parts-per-billion (microgram per liter) treatment goals. The RCF optimization pilot results give some encouragement that a treatment goal of 1 ppb may be achievable. As a result of this program, Glendale now has critical information to build demonstration-scale systems for both WBA and RCF treatment technologies to treat high-chromium groundwater wells.

2. AwwaRF Report

Hexavalent Chromium Removal Using Anion Exchange and Reduction with Coagulation and Filtration

Hexavalent Chromium Removal Using Anion Exchange and Reduction With Coagulation and Filtration

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FIGURES

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EXECUTIVE SUMMARY

Public concern about hexavalent chromium [Cr(VI)] in drinking water supplies and potential adverse health effects, coupled with California's intention to set a Cr(VI) specific drinking water standard, have prompted the investigation of cost-effective treatment technologies for Cr(VI) removal to well below the current federal and California maximum contaminant level (MCL) for total chromium (i.e., the federal MCL of 100 μg/L and the California MCL of 50 μg/L).

Following the discovery of high Cr(VI) concentrations in several groundwater extraction wells and plumes heading toward production wells, the City of Glendale, Calif. (Glendale), in partnership with the Cities of Los Angeles, Burbank, and San Fernando, devoted significant resources to identify effective Cr(VI) removal technologies from drinking water. Glendale initiated a four-phase research program, which includes: (1) the Phase I Bench-Scale Study that improved the understanding of fundamental chromium chemistry and screened promising treatment technologies, (2) the Phase II Pilot-Scale Study that evaluated Cr(VI) treatment technologies under field conditions, (3) the Phase III Bridge Project and Demonstration-Scale Study to further test a promising technology, to construct a demonstration-scale treatment facility, and to finalize the technology and cost evaluation, and (4) the Phase IV Full-Scale Implementation. Phases I and II of the program are complete and the study results were published in reports (Brandhuber et al. 2004, MEC 2005) and peer-reviewed journal articles (Qin et al. 2005, McGuire et al. 2006).

In the Phase II Pilot-Scale Study, weak-base anion (WBA) exchange resin demonstrated an unexpectedly high Cr(VI) removal capacity that might make its use cost-effective as a disposable media. Before the WBA resin was considered for testing in the Phase III Demonstration-Scale Study, however, a study designated as the Phase III Bridge Project was conducted to further investigate the removal of Cr(VI) with WBA resins. This report presents the findings and results of the Phase III Bridge Project, which was intended to "bridge" pilot-scale and demonstration-scale testing. Key objectives of the Phase III Bridge Project included:

- Conducting treatment studies to confirm the efficiencies of WBA resins for Cr(VI) removal from Glendale groundwater
- Characterizing WBA resin residuals to elucidate Cr(VI) removal mechanism(s)
- Investigating residuals handling and disposal options
- Refining cost estimates of effective Cr(VI) treatment technologies (WBA, strong-base anion (SBA) exchange resin, and reduction/coagulation/filtration (RCF)
- Convening an expert panel to recommend treatment technologies for demonstration-scale testing

The Phase III Bridge Project began with a bench-scale isotherm evaluation to screen six promising WBA resins for Cr(VI) removal from spiked Glendale groundwater at two pH values (5.9 and 6.4). Table ES.1 lists the names and characteristics of the six resins tested. SIR-700 and Duolite A7 resins outperformed the other four WBA resins for Cr(VI) removal at both pH conditions and were selected for subsequent flow-through pilot testing. Of note in isotherm testing was that both resins required more than 64 days to reach equilibrium with Cr(VI) in solution. The high Cr(VI) capacities of the SIR-700 and Duolite A7 resins coupled with the slow kinetics to reach

Table ES.1
Weak-base anion exchange resins evaluated in bench-scale isotherm testing

Manufacturer	Resin name	Matrix	Functional group
Rohm & Haas	Duolite A7	Phenol-formaldehyde polycondensate	Secondary amine
ResinTech	SIR-700	Epoxy polyamine	Proprietary amine
Sybron	Lewatit S4528	Styrene-divinylbenzene (macroporous)	Tertiary & quaternary amine
Purolite	A146	Styrene-divinylbenzene (macroporous)	Tertiary amine
Purolite	A830	Polyacrylic-divinylbenzene (macroporous)	Complex amine
Dow	Monosphere 66	Styrene-divinylbenzene (macroporous)	Tertiary amine

equilibrium indicated that a mechanism other than ion exchange might be involved in Cr(VI) removal by the WBA resins.

Bench-scale isotherm testing was followed up by short-term mini-column (0.5-inch* diameter) testing and longer-term pilot-scale column (2.5-inch diameter) testing. The selection of an appropriate pH for pilot-scale testing was determined using mini-columns for ten days. Mini-column testing results for pH values ranging from 5.6 to 7.2 showed different breakthrough characteristics for the two resins tested (SIR-700 and Duolite A7). However, both resins favored low pH for Cr(VI) removal to achieve a treatment goal of less than 5 µg/L. A pH of 6.0 was selected as the reduced pH at which to test Cr(VI) removal capacities in the longer-term pilot tests.

SIR-700 and Duolite A7 resins were tested in pilot-scale columns at a pH of 6.0 and ambient pH of 6.8, the latter of which was examined to evaluate the potential for reduced acid addition but more frequent resin replacement. Figure ES.1 shows the Cr(VI) breakthrough curves of both resins, highlighting the importance of a reduced pH for Cr(VI) removal. At pH 6.0, the Duolite A7 resin treated approximately 45,000 bed volumes (BV) of water before 5 µg/L Cr(VI) (and total Cr) effluent concentrations were observed. The consistent removal performance over an extended period indicated that the Duolite A7 resin could be used as an effective single-pass resin for Cr(VI) removal in Glendale groundwater.

Although the SIR-700 resin treating pH 6.0 water showed an early 5 µg/L breakthrough point at 2,200 BV, the Cr(VI) removal performance improved during the testing period such that effluent total Cr and Cr(VI) concentrations were less than 5 µg/L at the end of the pilot-scale testing (i.e., after treating approximately 113,000 BV of water). Improved Cr(VI) removal through the testing is not typical of ion exchange breakthrough curves, suggesting another removal mechanism may have contributed significantly to Cr(VI) removal or the resin required additional conditioning prior to use.

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* Note: Information regarding SI units and U.S. customary units appear in Appendix A.

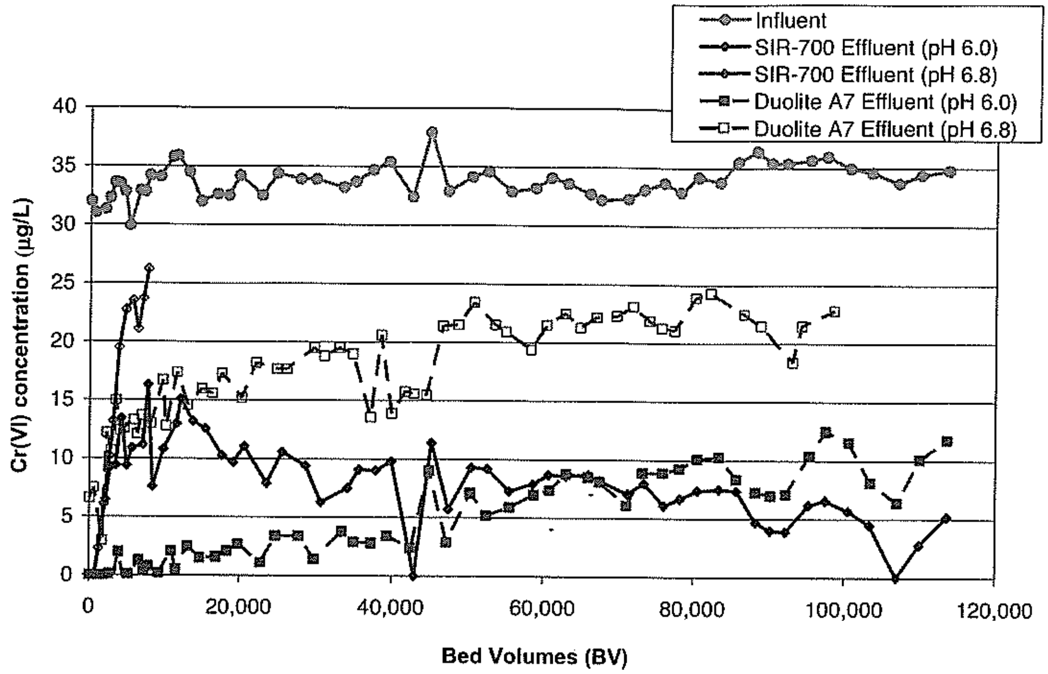

Figure ES.1 Pilot-scale column breakthrough curves of Cr(VI) at pH 6.0 and ambient pH (6.8) for Duolite A7 and SIR-700 resins

Once pilot testing was complete, spent resins were removed and tested for hazardous waste characteristics. The spent SIR-700 and Duolite A7 resins operated at pH 6.0 passed the federal toxicity characteristic leaching procedure (TCLP) but failed the California Waste Extraction Test (WET) and thus would be characterized as probable hazardous wastes for disposal in California. The spent Duolite A7 resins also had total uranium concentrations exceeding 500 µg/g (i.e., the trigger for low-level radioactive waste designation) after treating approximately 113,000 BV of water, indicating that the operating life of the Duolite A7 resin may need to be limited to avoid generating a low-level radioactive waste.

Mechanisms for Cr(VI) removal with WBA resins were also investigated in the Phase III Bridge Project. Chromium speciation on spent resins was assessed using x-ray absorption near-edge structure (XANES) spectroscopy. Figure ES.2 shows the Cr XANES spectra of resin residuals samples and known trivalent chromium [Cr(III)] and Cr(VI) reference compounds. The Cr spectral overlap of the spent resins and the trivalent chromium reference compound [Cr(III) acetate] and the lack of any pre-edge absorption peak indicated that Cr(III) was the dominant species retained on both resins, comprising more than 95% of the total chromium present. The XANES analysis provided direct evidence that the reduction of Cr(VI) to Cr(III) was an important part of the Cr(VI) removal mechanism by the SIR-700 and Duolite A7 WBA resins.

In addition to the technical evaluations, cost estimates of WBA resin application at the demonstration-scale were developed and compared with the other two promising Cr(VI) removal technologies: SBA and RCF. Detailed annualized cost estimates of various technologies are shown in Table ES.2. Although the annualized cost estimates were lowest for the SBA option at

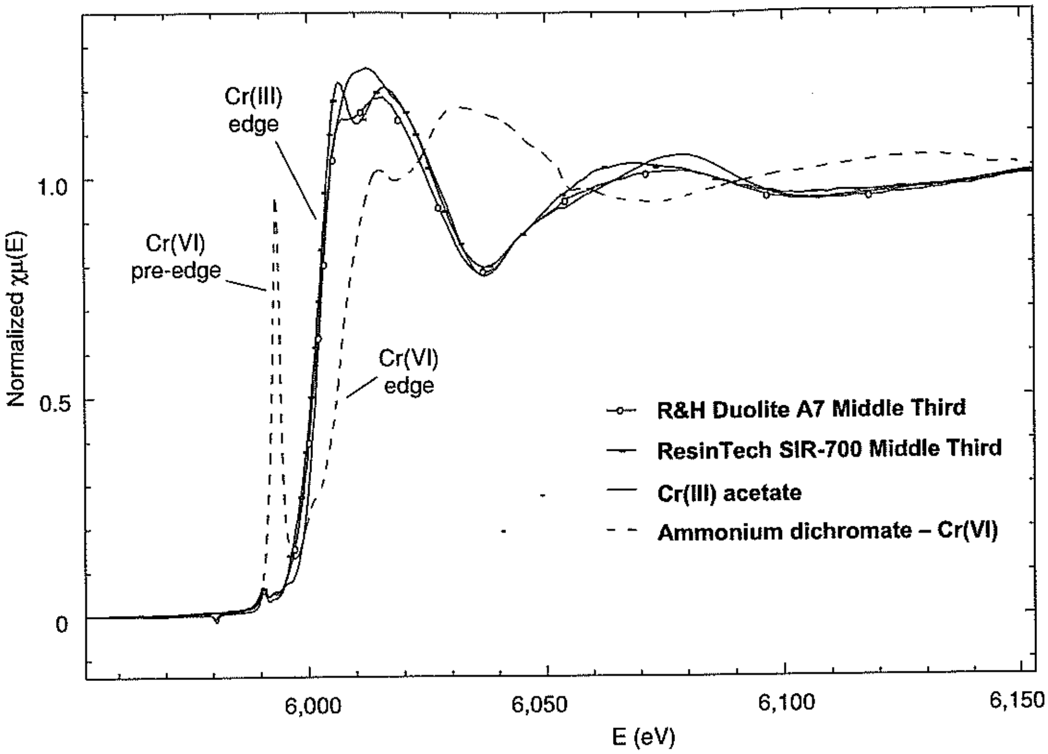

Figure ES.2 Cr XANES spectra of resin samples and selected Cr reference compounds

Table ES.2
Annualized treatment cost estimates for Cr(VI) removal

Technology	Flow (gpm)	Annualized costs ($/AF)		
		Capital	O&M	Total
WBA	500 (Retrofit)	100	340	440
	500	170	350	520
	1,000	120	340	460
SBA	500	190	170	360
	1,000	110	130	240
RCF	500	280	190	470
	1,000	180	120	300

both potential flow rates (500 gpm and 1,000 gpm), the uncertain future of brine disposal could make the SBA process cost-prohibitive. At 500 gpm, a retrofit WBA system (i.e., converting two existing GAC contactors to ion exchange vessels at the Glendale GS-3 well site) was determined to be a cost-effective Cr(VI) treatment technology implementation for Glendale. For a 1,000 gpm system, the RCF process is more cost-effective than WBA resin due largely to lower operations and maintenance (O&M) costs.

After reviewing the technical and cost information from the Phase I, Phase II, and Phase III Bridge Project, an expert panel concluded that the RCF system should be tested in the Phase III Demonstration-Scale Study. Further investigation of the Cr(VI) removal mechanism by the WBA resins was recommended; consequently, additional bench-scale studies will be conducted prior to the demonstration-scale study. Demonstration-scale testing of SBA resin was not advised by the panel.

Based on the results from the Phase III Bridge Project, limited available funding for capital costs, and the goal of achieving the most reduction in the water supply's Cr(VI) levels, the City of Glendale is planning to implement a 500-gpm Phase III Demonstration-Scale WBA system at the Glendale GS-3 well site by retrofitting existing vessels. Although the RCF process was recommended by the expert panel, the relatively high capital costs associated with this technology might only allow the City of Glendale to build a smaller-scale RCF treatment system, which is planned in conjunction with the WBA retrofit. An RCF system would be installed for well treatment at a location adjacent to the Glendale Water Treatment Plant (GWTP).

3. ICW 2006 Proceedings

Hexavalent Chromium Removal from Drinking Water Using Anion Exchange Technologies

Hexavalent Chromium Removal from Drinking Water Using Anion Exchange Technologies

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ENVIRONMENTAL CONSULTANTS

Outline

- Introduction
- SBA Resin Pilot Tests
- WBA Initial Pilot Tests
- WBA Follow-up Bench and Pilot Tests
  - pH Control
  - Resin Type
- Residuals Management
- Conclusions

Outline

- Introduction

Introduction

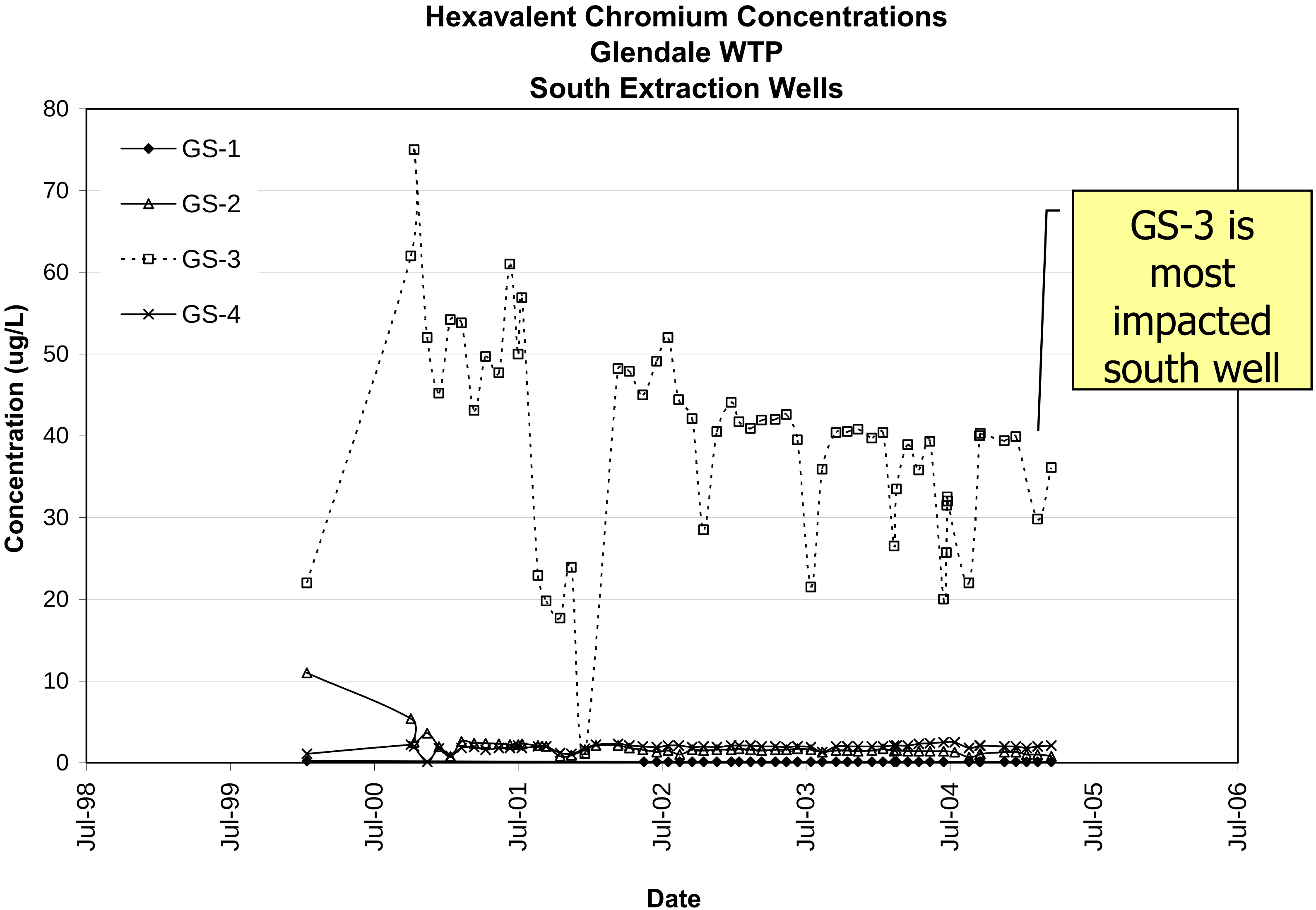
- Cr(VI) Occurrence:
  - Significant monitoring database in California (UCMR)
    - Over 6,700 drinking water sources sampled
    - 67% of sources below 1 µg/L detection limit
    - 3% of sources above 10 µg/L
  - National occurrence data from AwwaRF project concurs with California results
- Chromium Chemistry:
  - Cr(VI): Negative charged anion ($HCrO_4^-$ or CrO_4^{2-}) at typical drinking water pH values
  - Cr(III): Positively charged or neutral molecule in near-neutral pH range
- Health Effects:
  - Cr(VI) confirmed carcinogen by inhalation
  - National Toxicology Program study results were expected in 2005

Introduction

Notes:
1. The address of Glendale Water Treatment Plant is 820 Flower St., Glendale, 91201.
2. The location of groundwater wells is estimated due to the lack of data.
3. The scale bar is not shown here because the projection of the map is unknown.
4. Prepaired by Gang Qin.

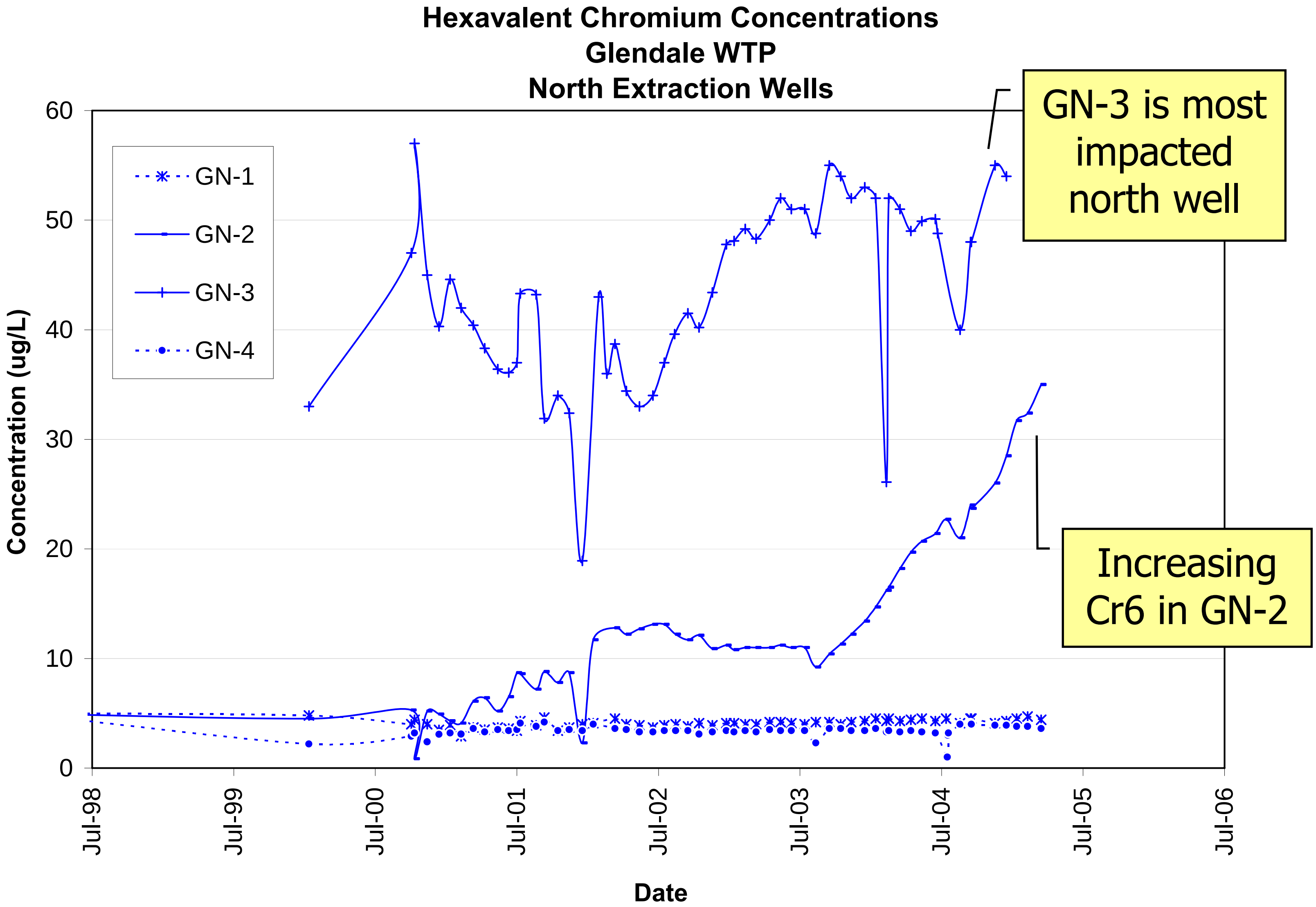
- Glendale treats and serves water from 8 VOC contaminated wells that also contain Cr(VI)
- Flow from the wells is approximately 5,000 gpm
- Three wells with concentrations of 40-60 µg/L – plumes advancing
- Blending of Cr(VI) concentrations
- Glendale treated water meets current regulations for total chromium
  - USEPA MCL of 100 µg/L
  - California MCL of 50 µg/L

Introduction



GS-3 is most impacted south well

Introduction



GN-3 is most impacted north well

Increasing Cr6 in GN-2

Introduction

- General Water Quality Parameters of Glendale Groundwater

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

Introduction: Glendale Cr(VI) Treatment Program Implementation

Implementation Phase	Objective	Participants
Phase I Bench Study	• Chromium redox chemistry • Bench treatment evaluation • Small scale column performance	AwwaRF City of Glendale LADWP City of Burbank City of San Fernando NWRI
Phase II Pilot Study	• “Mature” industrial technologies • “Best” bench study performers • Long term column performance	USEPA City of Glendale
Phase III Demonstration	• “Best” overall performer(s) • Residuals management • Operational requirements • Confirm unit costs	USEPA City of Glendale AwwaRF Funding requests from Federal, State, Local Sources
Phase IV Implementation	• Full scale treatment system	Future Partnerships: USEPA State Local

Glendale Pilot Testing

- Treatment Goal: < 5 µg/L, or 95% Cr(VI) removal
- Performed on raw well water at Glendale Water Treatment Plant with additional Cr(VI) spiked to 100 µg/L Cr(VI)

Outline

- Introduction
- SBA Resin Pilot Tests

SBA Resin Pilot Testing

- US Filter in partnership with Rohm and Haas supplied traditional strong-base anion exchange resin for Cr(VI) removal
- Two columns were operated in lead-lag configuration

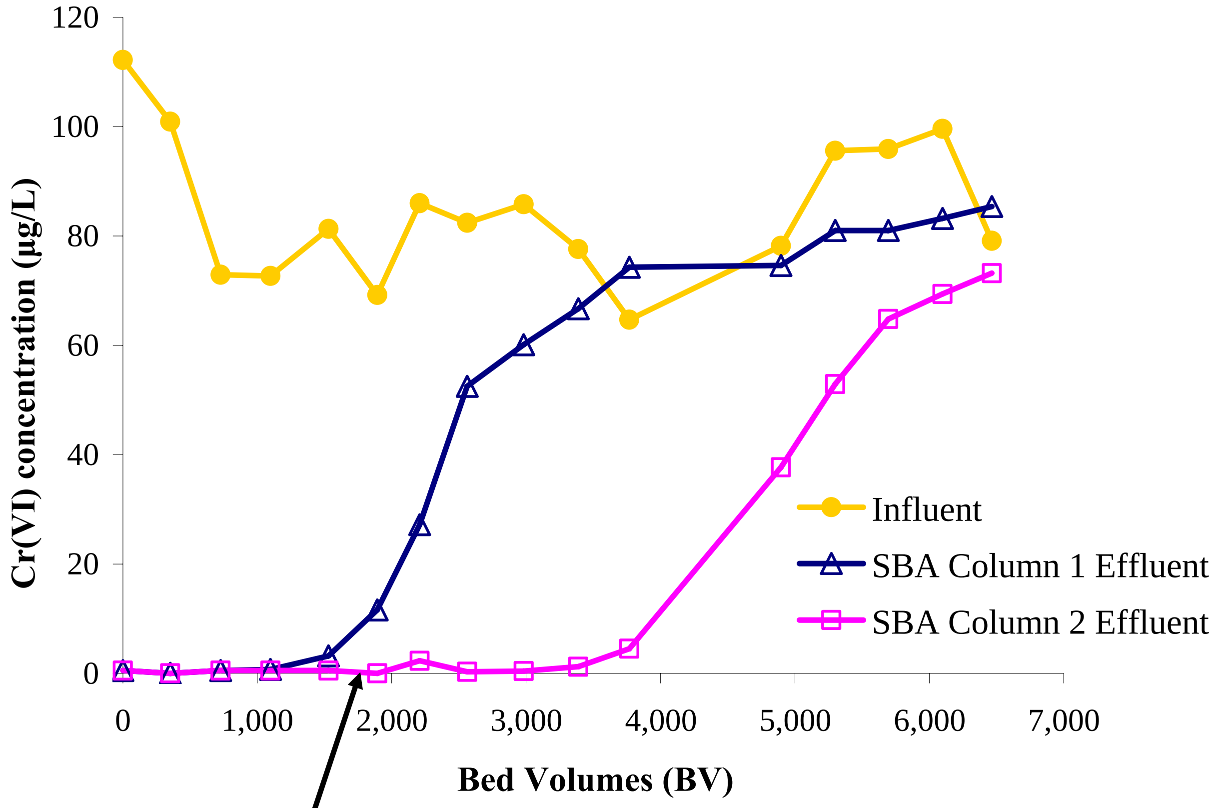
USF/Rohm & Haas SBA Resin:
Amberlite PWA 410 Cl Resin

Column 1
Lead SBA

Column 2
Lag SBA

SBA Resin Pilot Testing

Lead-Lag Columns with
3.7 min EBCT



14,000 gallons
1,900 bed volumes

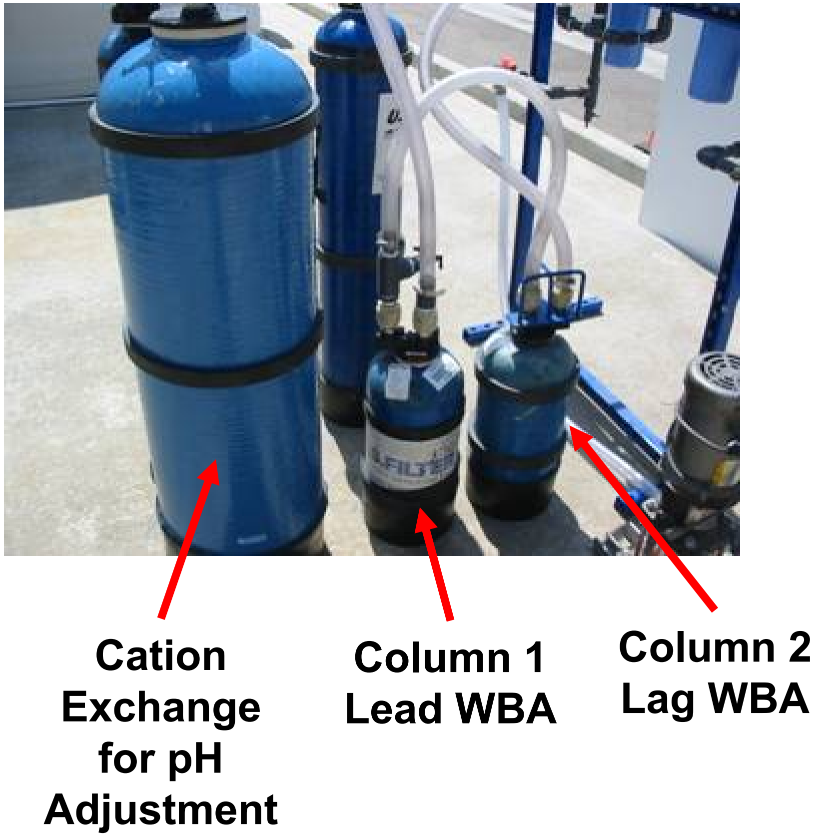
Outline

- Introduction
- SBA Resin Pilot Tests
- WBA Initial Pilot Tests

WBA Resin Initial Pilot Testing

- US Filter in partnership with Rohm and Haas supplied a new weak-base anion exchange resin
- Cation exchange was used to reduce pH to less than 6

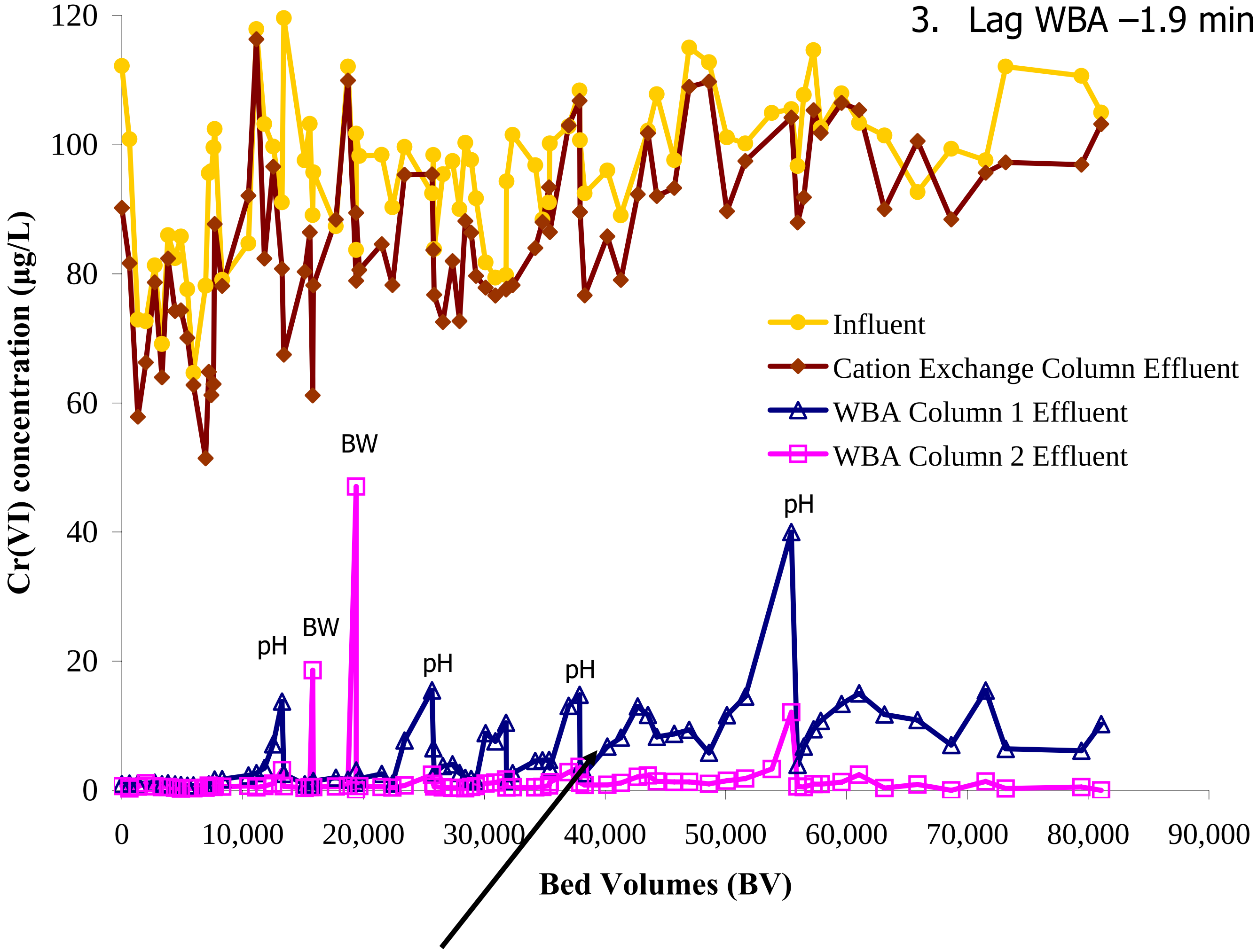
Weak base anion exchange
Duolite A7



WBA Resin Initial Pilot Testing

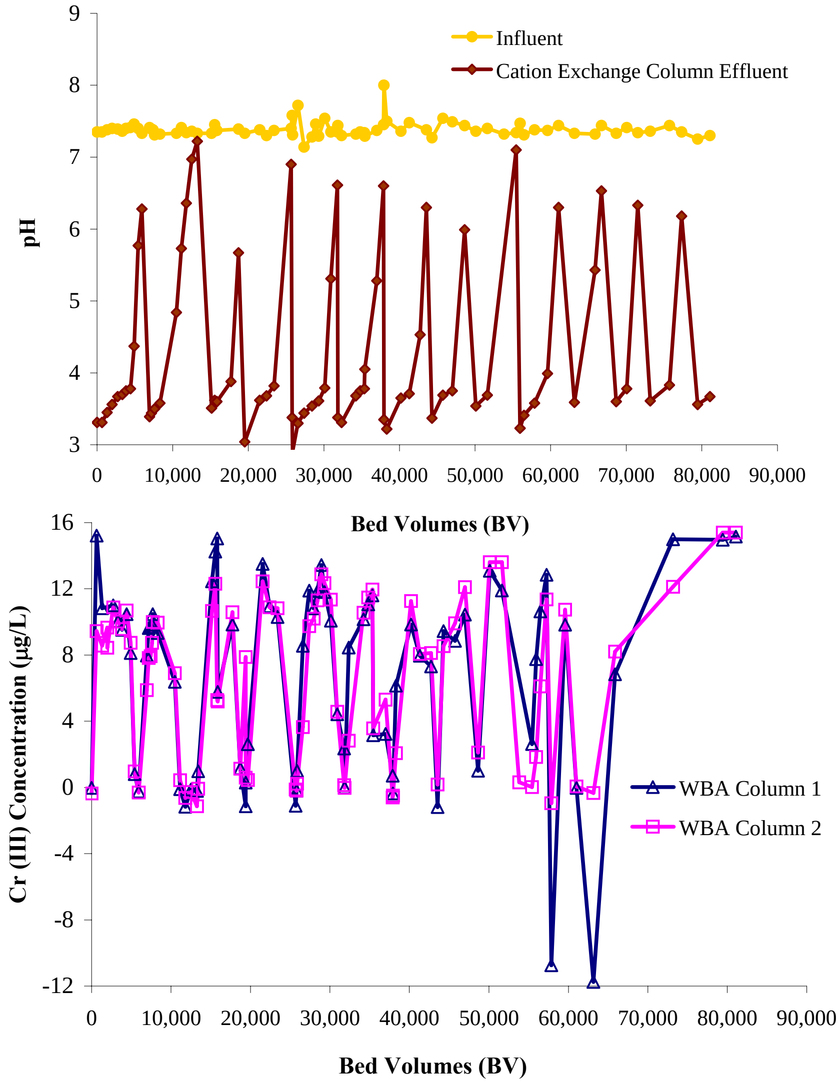
Three Columns

1. Cation exchange for pH depression
2. Lead WBA – 1.9 min EBCT
3. Lag WBA –1.9 min EBCT

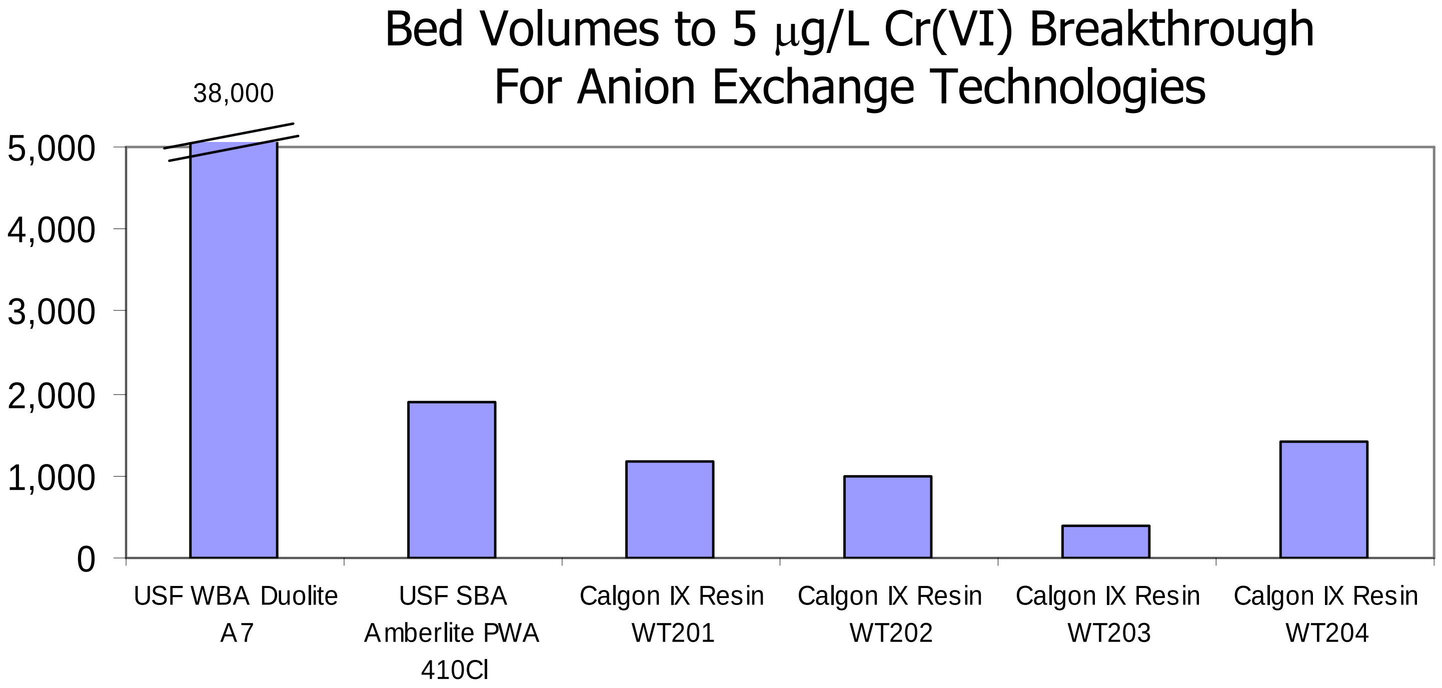


40,000 bed volumes

WBA Resin Initial Pilot Testing



WBA & SBA Resin Comparison

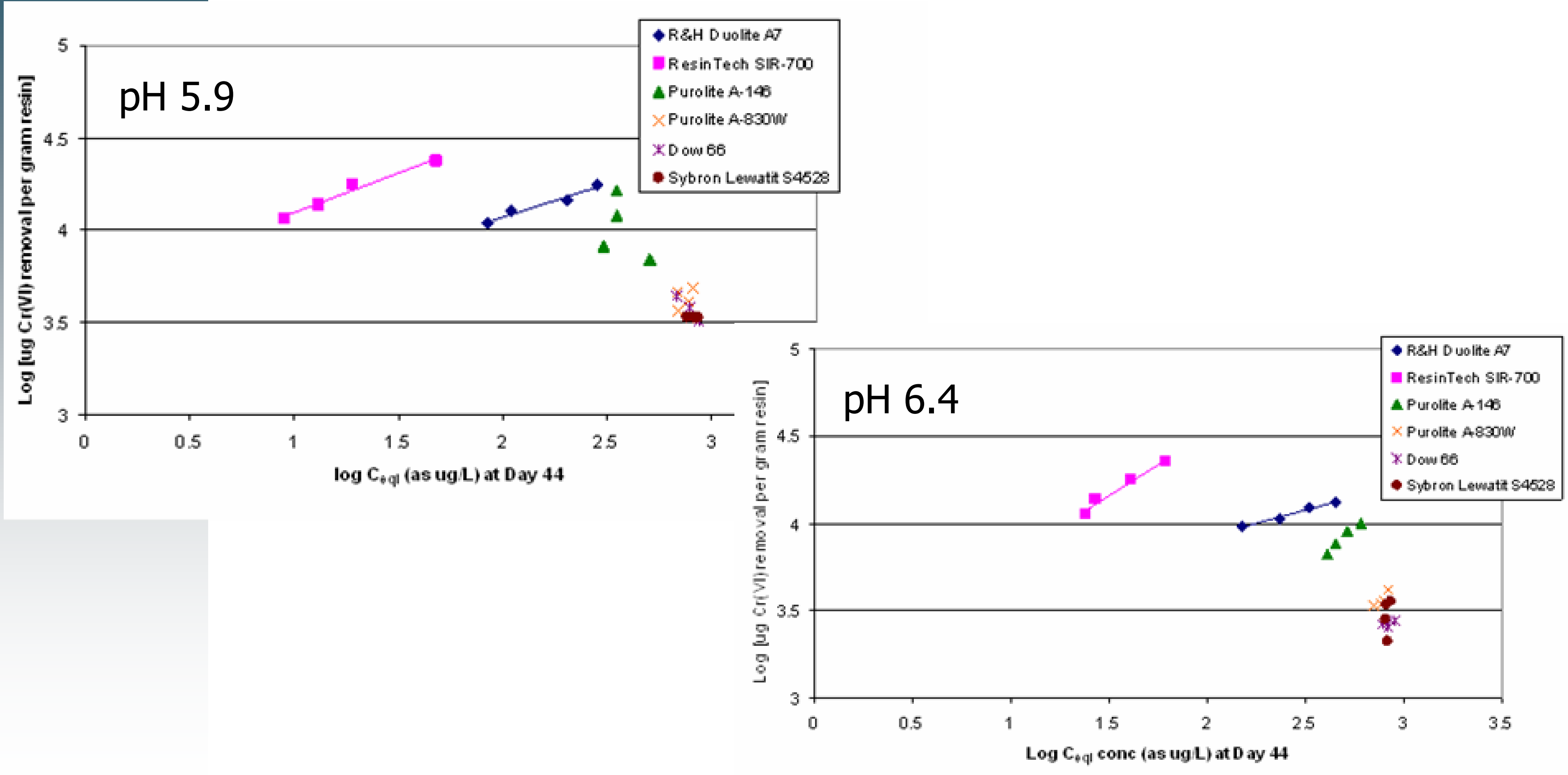


Outline

- Introduction
- SBA Resin Pilot Tests
- WBA Initial Pilot Tests
- WBA Follow-up Bench and Pilot Tests
  - pH Control
  - Resin Type

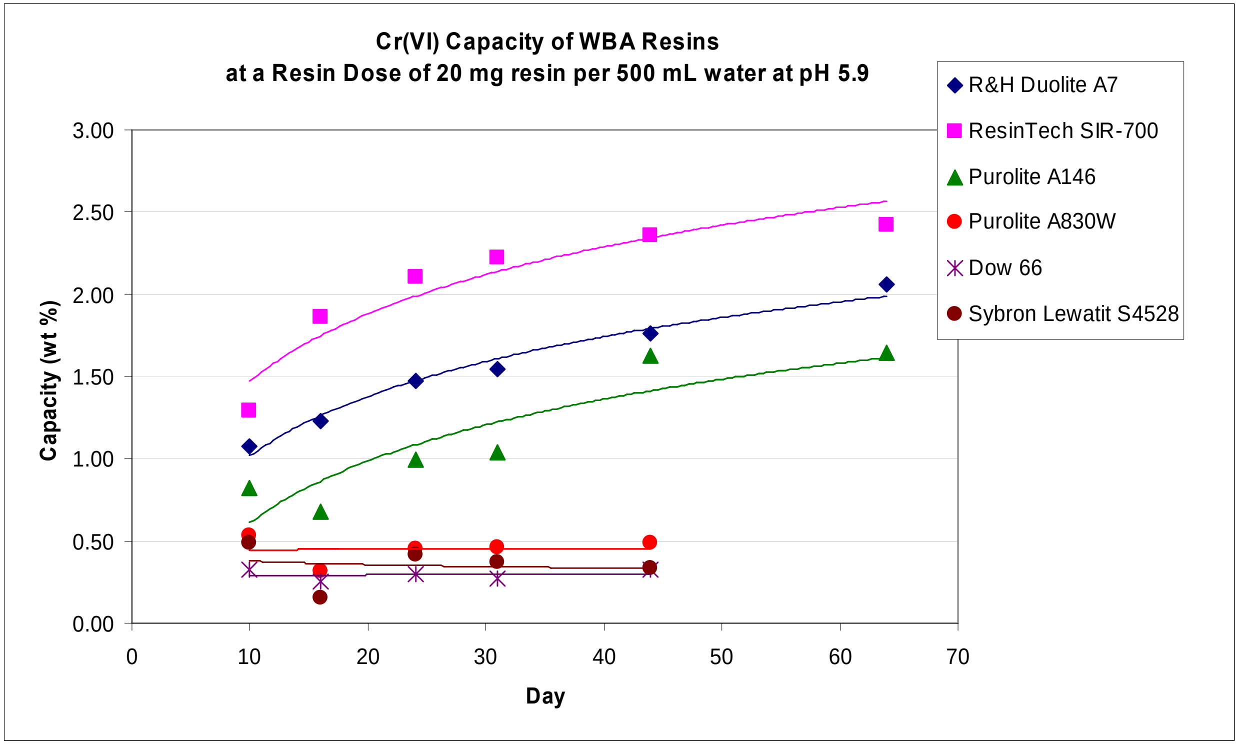
WBA Follow-up Bench Tests

- Results of Bench Tests with 6 Resins



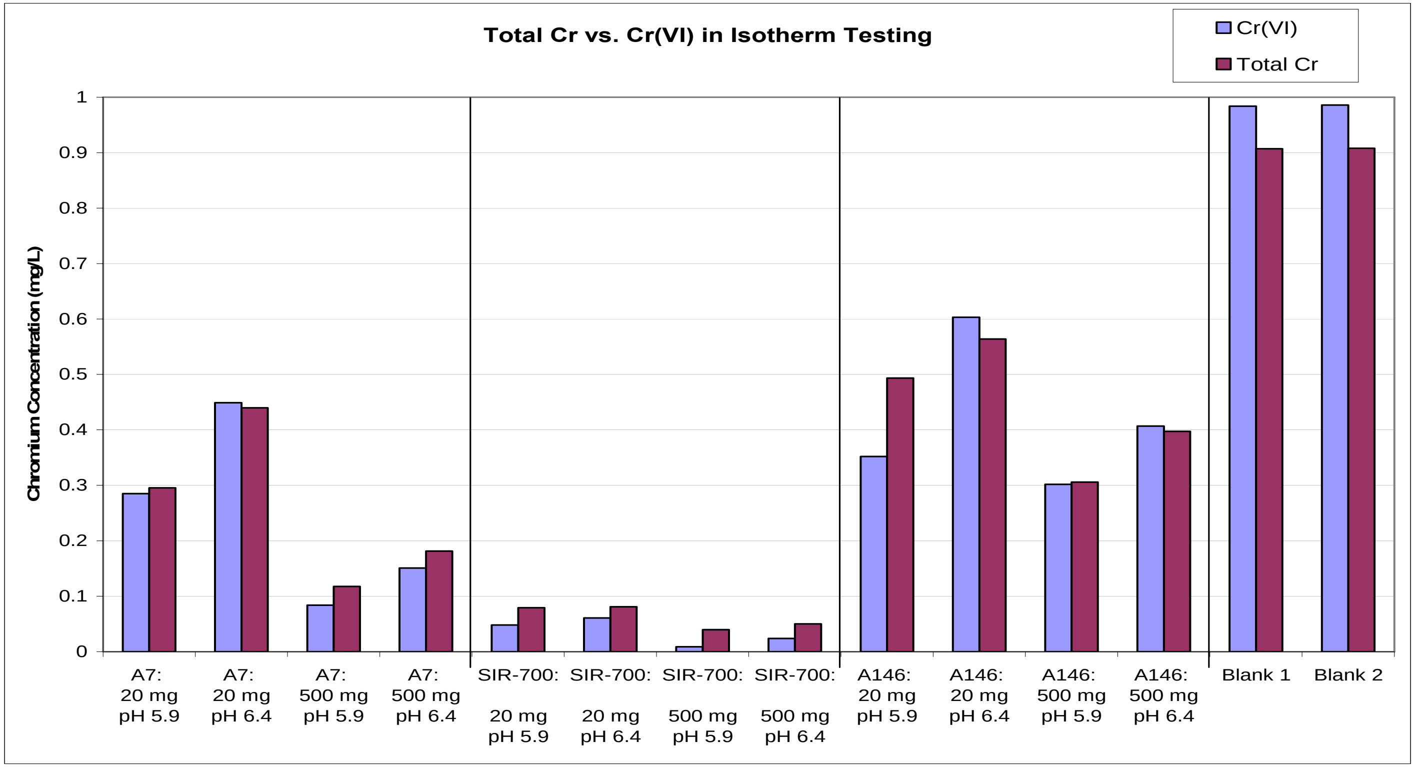
WBA Follow-up Bench Tests

- Results of Bench Tests with 6 Resins
  - Cr(VI) dose: 1 mg/L
  - Resin dose: 10 mg resin/L
  - pH 5.9 and 6.4 tested



WBA Follow-up Bench Tests

- Results of Bench Tests with 6 Resins
  - Analysis of total Cr and Cr(VI) in solution was done to see if Cr(VI) reduction to Cr(III) was occurring
  - Results indicate that most of the Cr in solution after 44 days was Cr(VI) except for SIR-700 at low resin doses

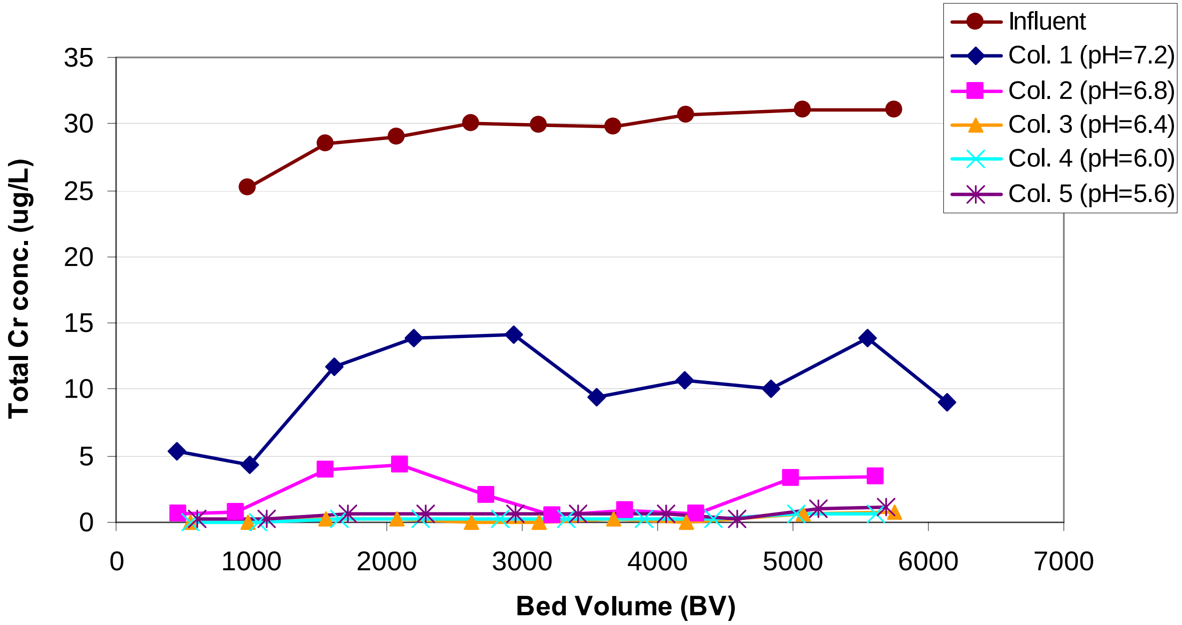


WBA Follow-up Pilot Tests

- Mini-columns: variable pH test
- Pilot-columns: constant pH for capacity test

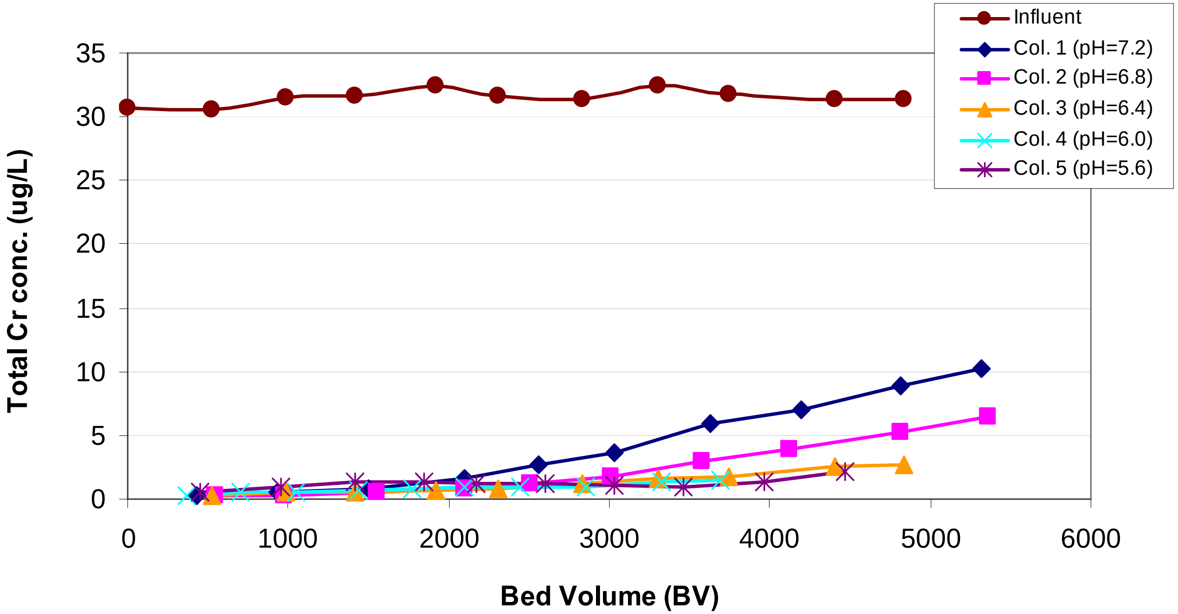
WBA Follow-up Pilot Tests

- Mini-Column Testing – Rohm & Haas Duolite A7
  - Investigation of 5 different pH values to determine if the resins were not effective at higher pHs
  - Results below showed that a pH of 6.4, and potentially a pH up to 6.8, have the potential to be effective
  - Capacity is not indicated by the mini-column tests but will be tested in pilot-columns



WBA Follow-up Pilot Tests

- Mini-Column Testing – ResinTech SIR-700
  - Similar investigation of 5 different pH values to determine if the resins were not effective at higher pHs
  - The beginnings of breakthrough may have occurred in the mini-column tests for this resin at pH values of 6.8 and 7.2
  - Capacity will be tested in pilot-columns



WBA Follow-up Pilot Tests

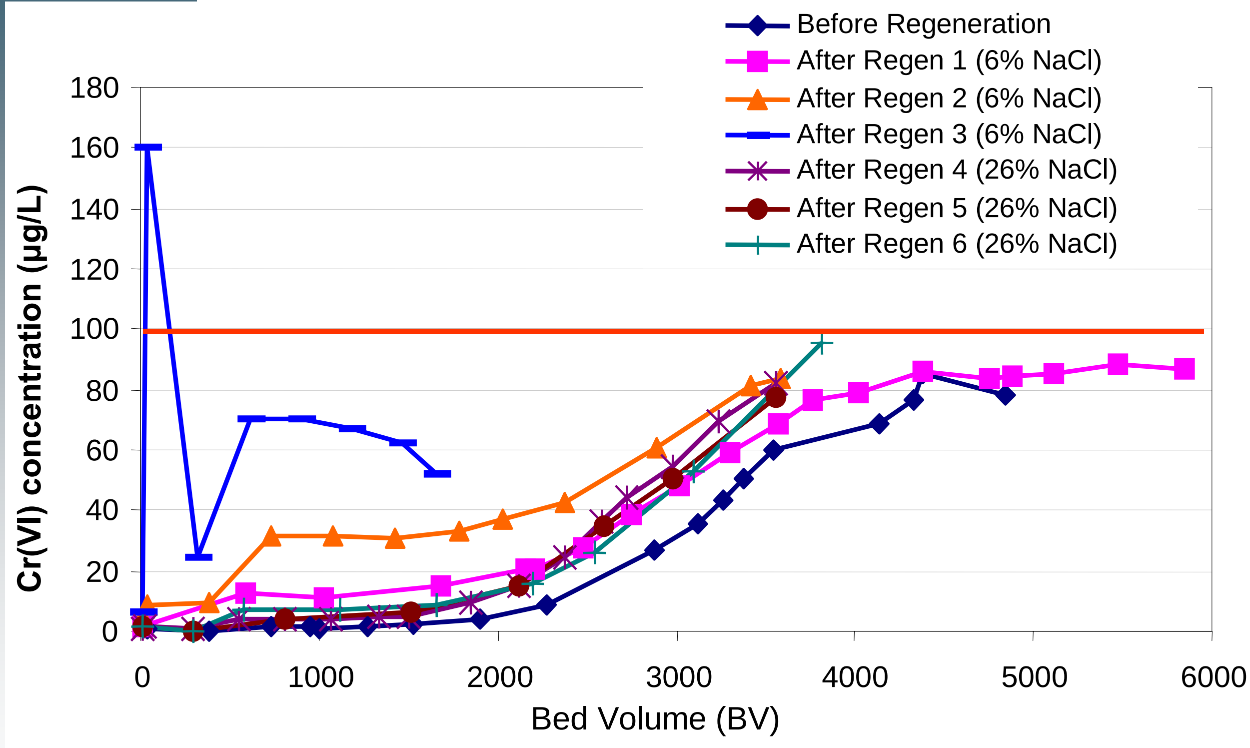
- Pilot-Column Testing
  - Based on mini-column findings showing that a pH in the range of 5.5 to 6.0 may not be necessary for Cr(VI) removal, the pilot-columns are being run under the following conditions:
    - pH 6.0 to evaluate capacity at a constant pH
    - pH 6.8 to test removal capacity at ambient pH of the groundwater well
  - Two resins are being tested, including ResinTech SIR-700 and Rohm & Haas Duolite A7

Outline

- Introduction
- SBA Resin Pilot Tests
- WBA Initial Pilot Tests
- WBA Follow-up Bench and Pilot Tests
  - pH Control
  - Resin Type
- Residuals Management

Residuals Management: SBA Resin

- Regeneration using 26% NaCl was more effective than 6% NaCl



Residuals Management: WBA Resin

- Accumulation of chromium and other elements on weak base resin (from Phase II testing of Duolite A7)
- Additional residuals analysis will be performed on the spent weak-base resins tested at the pilot scale

Element	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

Outline

- Introduction
- SBA Resin Pilot Tests
- WBA Initial Pilot Tests
- WBA Follow-up Bench and Pilot Tests
  - pH Control
  - Resin Type
- Residuals Management
- Conclusions

Conclusions

- Fixed-bed strong-base and weak-base anion exchange technologies are leading candidates for drinking water treatment of Cr(VI)
- SBA resins could be regenerated using 26% brine, with potential for effective brine recycle
- WBA resin has a high capacity for Cr(VI); pH depression needs are being explored
- WBA resin has the potential for use as a single-pass disposable resin to minimize hazardous waste volumes

Acknowledgments

- USEPA: Bruce Macler
- City of Glendale: Don Froelich, Leighton Fong
- Utah State University: Laurie McNeill
- University of Colorado: Gary Amy
- Wellesley College: Daniel Brabander
- LADWP: Pankaj Parekh
- MWDSC: Sun Liang
- CDHS: Rick Sakaji
- CDM: Erik Jorgensen, Charles Cron
- MEC: Phil Brandhuber, Michelle Frey, Jim Leserman, Ken Reich

4. Expert Panel Summary

Summary of Expert Panel Workshop on “Chromium 6 Removal Demonstration Facilities”

McGuire
MALCOLM PIRNIE
ENVIRONMENTAL CONSULTANTS

MEMORANDUM

TO: Peter Kavounas, City of Glendale Department of Water and Power

FROM: Michael J. McGuire, Nicole Blute, and Danny Qin (McGuire Malcolm Pirnie, Inc.)

DATE: October 31, 2006

SUBJECT: Summary of Expert Panel Workshop on "Chromium 6 Removal Demonstration Facilities"

INTRODUCTION

An expert panel workshop for the Tailored Collaboration project "City of Glendale, California Chromium 6 Removal Treatment Demonstration Facility – Phase III Bridge" (Bridge Project) was held on October 12, 2006 at the City of Glendale Council Chambers. The expert panel meeting was co-hosted by the USEPA, Glendale Water and Power, and the AWWA Research Foundation (AwwaRF).

The expert panel members at the workshop included Pankaj Parekh from LADWP, Sun Liang from MWDSC, Bruce Macler from USEPA, Richard Sakaji from California DHS, Mel Suffet from UCLA, Laurie McNeill from Utah State University, Arup SenGupta from Lehigh University, and Gary Amy from UNESCO (attending via teleconference). The panel discussion was moderated by Traci Case from AwwaRF.

The expert panel meeting was open to the public. More than 30 people interested in chromium 6 issues attended the event. The City of Glendale also broadcast the meeting live on Glendale public television and over the internet via streaming media.

CHARGE TO THE EXPERT PANEL

Glendale's charge to the Expert Panel was to identify cost-effective Chromium 6 treatment technologies that are appropriate for further testing at the demonstration scale (approximately 500 gpm or 1,000 gpm treatment capacity) based on the technical information presented at the meeting.

The criteria the panel was charged to consider in the evaluation process included the following:

- Technology maturity
- Probable success in Glendale and elsewhere
- Cost of the treatment facilities
- Ease of operations and maintenance, including future reliability of the treatment processes
- Required permitting and approval processes

CHROMIUM 6 TREATMENT TECHNOLOGIES CONSIDERED

In response to the public concern about the presence of Chromium 6 in drinking water, the City of Glendale, along with Cities of Los Angeles, Burbank, and San Fernando, initiated a comprehensive four-phase program to develop a technology (or technologies) for Chromium 6 removal from drinking water supplies. The four-phase program includes: Phase I - A bench-scale study to improve the understanding of fundamental chromium chemistry and to screen promising treatment technologies; Phase II - A pilot-scale study to further evaluate the promising technologies under flow-through conditions; Phase III - A demonstration-scale study to finalize the technology evaluation and address other related issues (e.g. cost and residuals disposal); and Phase IV - Full-scale implementation of a treatment technology. So far, Phases I and II are complete. The expert panel meeting was part of the Phase III study, in which one or more technologies was recommended for demonstration-scale testing.

Based on Phases I, II and III research efforts, three technologies emerged as leading candidates for consideration in demonstration testing:

- Reduction/Coagulation/Filtration (RCF) using ferrous sulfate,
- Fixed Bed Weak Base Anion Exchange Resin (WBA) with constant pH control, and
- Fixed Bed Strong Base Anion Exchange Resin (SBA) with brine treatment.

SUMMARY OF THE EXPERT PANEL DISCUSSIONS

Expert panel discussions about the three technologies are summarized below according to the technology.

RCF System

Brief Description

During the RCF process, Chromium 6 is first reduced to Chromium 3 with the addition of excess ferrous iron (Fe^{2+}), which is oxidized to ferric iron (Fe^{3+}). Chromium 3 then either precipitates or forms a co-precipitate with the ferric iron. The ferric iron/chromium 3 forms larger floc particles during the coagulation (aeration) stage. Particles are then removed by a dual-media filter (or other filter, such as a microfiltration membrane) in the final step.

Advantages

The expert panel generally favored this technology for the following reasons:

- The mechanism of RCF treatment is fully understood
- RCF is a proven technology for the application of Chromium 6 removal, as evidenced by the successful operation of a similar system at Topock, California
- RCF can be optimized during the demonstration-scale study to accommodate potential rising Chromium 6 concentrations in the influent water
- California DHS permitting will likely be easier for the RCF system compared to the other two technologies

Disadvantages

The panel expressed the following disadvantages of the RCF system:

- The capital cost of construction the RCF system is very high (a preliminary cost estimate indicated that the construction of a 500 gpm RCF system could cost $2.8 million, and a 1000 gpm system could cost $3.5 million)
- RCF may require frequent operator oversight and continuous monitoring to optimize the removal of Chromium 6
- A related treatment process is an accepted best available technology (BAT) for arsenic removal, but DHS does not permit its use in small systems due to operational complexities

WBA System

Brief Description

The mechanism of Chromium 6 removal by WBA resins was originally believed to be similar to that of strong base anion exchange (SBA) resins, except that the WBA resins are only useful in the acidic pH range where the functional groups are protonated and thus act as positively charged exchange site to attract Chromium 6 (as chromate ion). However, the WBA resin (Duolite A7 resin provided by Rohm & Haas) tested in the Phase II pilot study showed a much greater Chromium 6 removal capacity compared with all of the other SBA resins tested (approx. 20 times). Other observations, such as leakage of Chromium 3 during periods of low pH, indicated that an ion exchange mechanism alone could not explain the high capacity of the WBA resin.

As part of the Phase III study, a range of WBA resins were tested for capacity and the impact of pH on capacity. Duolite A7 resin again showed a high Chromium 6 capacity along with another WBA resin (ResinTech SIR-700, which did not perform quite as well as the Duolite A7 initially but improved over time). It has been confirmed that more than 95% Chromium 6 retained on both resins was converted to Chromium 3, as evidenced directly by x-ray absorption spectroscopy. So far, the true mechanism of Chromium 6 removal and retention by the WBA resins has not been fully understood but is known to involve a reduction process.

Advantages

The expert panel discussed the advantages of the WBA system, including the following:

- WBA resins have demonstrated a high Chromium 6 removal capacity (approximately 20 times higher than the conventional SBA resins tested)
- The operation of WBA system is comparatively easy, especially for a small system
- The WBA resins will be used in a single-pass, disposable mode, eliminating the need for resin regeneration with brine
- The WBA system can absorb the fluctuations in influent Chromium 6 concentrations, although resin replacement will be more frequent at higher influent concentrations

Disadvantages or Uncertainties

The WBA resin was the most thoroughly discussed technology during the expert panel meeting, primarily because the mechanism for Chromium 6 removal is not fully understood. Pilot studies have indicated that besides ion exchange, reduction/oxidation and/or complexation could also play a role in Chromium 6 removal by the WBA resins. One panel member then raised the question: “Do we want to select a technology where mechanism is not understood?”

The expert panel also expressed other concerns regarding the WBA system besides an incomplete understanding of the mechanism, including:

- Nitrosamine (including NDMA) leaching from the WBA resins
- Potential for formation/release of organic resin byproducts (e.g. formaldehyde or phenol, which are resin constituents)
- Taste and odor issues related to the use of the resins if formaldehyde or phenol are released
- Cost of the WBA system (the highest annualized treatment cost among the three technologies)
- The need to pre-condition the resins, which may explain the improved removals over time for the SIR-700 resin
- California DHS permitting may be difficult since the removal mechanism is not well understood
- The need for strict pH control of the influent water

SBA System

Brief Description

SBA resin is a commonly used technology in drinking water treatment for anion removal. Chromium 6 is retained on the SBA resin (as chromate ion) by exchanging with chloride previously bound to the resin. The SBA resins can be reused by regenerating the resins with concentrated brine (salt) solutions. Pilot testing demonstrated up to seven regeneration cycles.

BasinWater provided a proposal for a regenerable SBA system for Chromium 6 treatment. By contrast, US Filter did not provide a follow-up proposal since they no longer offers regenerable SBA for Cr(VI) removal. During recent testing in Colby, Kansas, US Filter encountered difficulty in regenerating the resin to full capacity after approximately 12 to 15 regeneration cycles. Consequently, US Filter now markets only the WBA system and a single-pass SBA system.

Advantages

The advantages of the SBA system discussed by the expert panel included:

- SBA is an established technology for other contaminants and the mechanism is well understood
- The overall Chromium 6 treatment cost using the SBA system (including capital and O&M cost) is the least among the three technologies
- The SBA system can absorb fluctuations in influent Chromium 6 concentrations

Disadvantages

Disadvantages and uncertainties associated with the SBA system at this time were discussed by the expert panel, including:

- Brine disposal: The high concentration of total dissolved solids (TDS) and chloride in the brine may ultimately limit its discharge into the sanitary sewer systems. At the Northern well site (in Glendale), the Glendale Wastewater Treatment Plant will not accept high chloride brine. It is uncertain as to whether Hyperion would accept brine discharge at the Southern well site (which is located in Los Angeles). To avoid these problems, BasinWater proposes to truck the treated brine to a sewer connection leading to the Hyperion Wastewater Treatment Plant. It was deemed uncertain that this connection would be available into the future and could be depended upon.
- Quantity of brine BasinWater claims to generate is orders of magnitude lower than other SBA ion exchange technologies in the area for other contaminants, which either reflects efficiency in the BasinWater system or a lower-than-actual estimate or brine production
- Uncertainty in the ability to repeatedly regenerate SBA resin

EXPERT PANEL RECOMMENDATIONS

At the end of the meeting, the expert panel provided the following overall recommendations:

- All panel members recommended that the RCF system be tested in the demonstration scale study
- All panel members recommended that the mechanism of the WBA resins be thoroughly investigated in additional bench-scale studies. The understanding of the WBA mechanism will not only help Glendale in the demonstration-scale study but also provide a new solution to other water utilities needing chromium treatment
- If funding is available, the demonstration-scale study should include both RCF and WBA systems
- The SBA system should not be further tested at demonstration-scale

Cc: Traci Case
Don Froelich
Leighton Fong
Expert Panel Members

5. Lehigh University WBA Testing QAPP

Additional Bench-Scale Testing on the Mechanisms of Weak Base Anion Exchange Resins

The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale Ground Water Supply:

Phase II and III
Demonstration of Pilot Scale Treatment Technologies

Additional Bench-Scale Testing on the Mechanisms of Weak Base Anion Exchange Resins

QUALITY ASSURANCE PROJECT PLAN

Addendum
May 17, 2007

Revised
June 22, 2007

City of
Glendale
Water & Power
GWP

Reliable • Competitive • Trusted

Table of Contents

0. Approval by Project Participants

__________________________________ __________________
Bruce Macler, Ph.D, USEPA Date

__________________________________ __________________
Peter Kavounas, P.E., City of Glendale Date

__________________________________ __________________
Michael J. McGuire, Ph.D., P.E. McGuire Malcolm Pirnie Date

__________________________________ __________________
Arup SenGupta, Ph.D., Lehigh University Date

<u>Distribution List of Principal Project Participants</u>
Each organization included in this project is to receive and retain a copy of this QAPP.

Names of Individuals	Contact Information
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Michael J. McGuire, Ph.D., P.E. McGuire Malcolm Pirnie	**McGuire Malcolm Pirnie** 1821 Wilshire Blvd., Suite 302, Santa Monica, CA 90403 Phone: (310) 829-1441; Email: mmcguire@pirnie.com
Arup SenGupta, Ph.D. Lehigh University	**Lehigh University** 13 E. Packer Ave, Bethlehem, PA Phone: (610) 758-3534 ; Email: aks0@lehigh.edu

1. Project Description and Objectives

Please refer to the Phase II QAPP for a detailed project description of the Phase II Demonstration of Pilot Scale Treatment Technologies project.

1.1 Purpose of Additional Study on Weak Base Anion Exchange Mechanism-

The Phase II Demonstration of Pilot Scale Treatment Technologies project demonstrated the performance of several potential removal technologies for hexavalent chromium. The Phase III – Bridge Project continued the Phase II work by conducting further testing of weak base anion exchange resins using constant pH conditions. Since the protocols were identical in the Phase II and Phase III testing, the QAPP dated July 31, 2003 covered both phases. The results of Phases II and III were presented to the Project Advisory Committee in an expert workshop held on October 12, 2006 for the purpose of identifying one more treatment technologies for testing at demonstration scale (i.e., 500 gpm).

Based on high capacities observed in Phases II and III, the PAC recommended additional testing of the weak base anion exchange resin to identify the mechanism for hexavalent chromium removal. As one of the expert panelists, Dr. Arup SenGupta of Lehigh University agreed to formulate and conduct the required additional experiments. This QAPP covers the supplementary bench-scale work undertaken with the purpose of further assessing the removal mechanism of weak base anion exchange resin.

1.2 Bench Testing Facility

Laboratory facilities were provided at Lehigh University under the guidance of Dr. Arup SenGupta. Refer to Section 5 for additional details on the methods.

1.3 Project Objectives

In the Phase II and/or Phase III testing of weak base anion (WBA) exchange resins, testing confirmed that:

- Two WBA resins tested, Duolite A7 and SIR-700, had a high chromium (VI) capacity;
- A pH of 6.0 enabled hexavalent chromium removal to low levels (< 5 ppb) and maximized capacity;
- Hexavalent chromium was reduced to trivalent chromium on the weak base resins and removed but the underlying mechanism was still uncertain; and
- Copper was removed by WBA resins along with hexavalent chromium, which together with a previously reported study (Zhao et al., 1998) possibly indicates that the presence of covalently bonded copper ion exchange may promote ligand exchange with chromate ions, thereby enhancing hexavalent chromium removal for some resins.

The primary goals for the additional work at Lehigh University include the following:

- Gain more information on the mechanism of chromium removal by WBA resins using leaching tests with exhausted WBA resins. For example, extraction of chromium with NaCl, NaOH, and H_2SO_4 will provide information on how the chromium is bound and in what oxidation state.
- Determine whether a high hexavalent chromium capacity (>2,000 bed volumes) is observed for strong-base anion (SBA) exchange resins run at low pH. This will provide information about whether the hexavalent chromium removal is largely a function of speciation at low pH (i.e., enabling enhanced ion exchange) or a function of the resin characteristics (i.e., enabling redox reactions).
- Assess whether copper plays a role in chromium removal by the resins. This will be tested by separate column runs with copper loaded resins.

The plan for evaluation of these goals is defined in Table 2.

2. Project Organization

2.1 Key Points of Contact

Please refer to the above Distribution List of Principal Project Participants for the key points of contact at each organization.

2.2 QA Managers

With respect to data quality assurance, Lehigh University is charged with the tasks of experimental design, analytical measurements, data management, data reduction and data validation. The Phase II and Phase III project manager, Dr. Michael J. McGuire, is independent of the work at Lehigh University and will provide additional data quality assurance.

Lehigh University will be conducting the laboratory experiments and chromium analyses. Dr. Arup SenGupta will supervise laboratory analysts to perform measurements and conduct the data reduction and interpretation.

2.3 Responsibilities of Project Participants

Each project participant responsible for accomplishing tasks in this addendum is listed in the table below. Also listed are the team members' affiliations and overall and specific project involvement. Project involvement roles specified here include: Planning, Coordination, Sample Collection, Analytical Measurements, Data Reduction, Data Validation, and Report Preparation.

Table 1. Project Participant Roles

Team Member	Title & Organization	Overall Project Involvement	Specific Involvement
Peter Kavounas	Water Services Administrator, City of Glendale	Glendale Project Management	Coordination
Donald Froelich	Project Manager, City of Glendale	Glendale Project Management	Coordination
Michael McGuire	Vice-President, MMP	Project Manager	Coordination
Nicole Blute	Project Engineer, MMP	Deputy Project Manager	Coordination Planning
Arup SenGupta	Professor, Lehigh University	Experimental Design and Analytical Support	Planning Analytical Measurements Data Validation Report Preparation
Sudipta Sarkar	Postdoctoral Fellow, Lehigh University	Analytical Support	Sample Collection Analytical Measurements Data Reduction Report Preparation
Prasun Chatterjee	Graduate Student, Lehigh University	Analytical Support	Sample Collection Analytical Measurements Data Reduction

3. Experimental Approach

3.1 General Approach and Test Conditions

The evaluation of the hexavalent chromium removal mechanism by weak base anion exchange resins will include a number of tests to achieve the project objectives. In general, mechanistic testing will include bench-scale testing.

3.2 Sampling Strategy

The sampling strategy for this testing will focus on influent and effluent samples from column runs collected at various time points along the breakthrough or extraction runs. Refer to Table 2 for the evaluation strategy of each objective.

3.3 Sampling/Monitoring Locations

Refer to Section 3.2.

3.4 Sampling/Monitoring Frequency

Sampling frequency will be conducted at a rate determined to be sufficient during individual tests; the frequency is expected to vary based on individual test objectives (Section 3.6) and is subject to change during bench tests. Analyses conducted on the same day as sample collection will enable the rapid increase or decrease in sampling frequency, as necessary, to assess the stated objectives.

3.5 Identification of Measurements

The critical parameter during bench-scale runs is primarily total chromium, and in some tests, hexavalent chromium and copper. Refer to Section 3.6 Evaluation of Project Objectives for details on specific tests.

3.6 Evaluation of Project Objectives

Primary project objectives will be assessed as shown in Table 2.

Table 2. Project Objectives and Evaluation Strategy

Objective	Evaluation Strategy
Gain more information on the mechanism of hexavalent chromium removal by WBA resins using leaching tests on spent resins from Phase III	• Extraction of hexavalent chromium from spent resins using 6% NaCl and 2% NaOH to provide information about whether Cr is electrostatically exchanged onto the resin (as chromate) • Extraction of chromium by dissolution from spent resins using 2% H_2SO_4 to assess mass balance • Various iterations of NaCl + NaOH followed by H_2SO_4, and the reverse order of extractants, will be conducted to investigate the speciation. Samples will be analyzed for both hexavalent and total chromium • Extraction of hexavalent chromium with NH_3 to provide information on whether Cr is bound by a mechanism of ligand exchange by any copper that is covalently bonded with the resin functional groups. • Interruption of column operation for a day and increase of the flow rate to observe if more chromium is removed with a longer contact time

	with the resin (i.e., to assess whether intraparticle diffusion or reduction is the rate limiting step)
Determine whether a high hexavalent chromium capacity (>2,000 bed volumes) is observed for a strong-base anion exchange resin run at low pH	• Run an SBA resin at low pH (~5) to determine the point of breakthrough in Glendale water
Assess whether copper plays a role in chromium removal by WBA resin	• Pre-load copper onto virgin resin to perform a comparison of chromium breakthrough profile with and without copper (i.e., assessing whether copper is needed for to achieve the high hexavalent chromium capacities observed) • Extraction of hexavalent chromium from these resins using NH_3 to provide information on whether chromate is bound by a mechanism of ligand exchange with copper. • Pre-load copper onto virgin resin to observe if ligand exchange occurred for arsenate (i.e., a molecule that is not expected to be reduced by the resin)

4. Sampling Procedures

4.0 Method to Establish Steady-State Conditions

Not applicable to this addendum. Rather than focusing on long-term performance, this testing uses a series of short-term tests to evaluate the mechanism of chromium removal by weak base resins.

4.1 Known Site-Specific Factors Affecting Sampling and Monitoring Procedures

None.

4.2 Site Preparation Prior to Sampling

Not applicable to this addendum. All testing will be performed in the Lehigh University laboratory.

4.3 Sampling/ Monitoring Methods

Chemical and physical analytes that will be measured in bench-scale testing include hexavalent chromium, total chromium, copper, and pH. The analytical methods are shown in Table 3 with the planned schedule of quality assurance sampling activities. Quality assurance sampling includes instrument calibration curves at the beginning and end of each run, accuracy checks with verified standards after every 5 samples, replicate analyses on each sample, and distilled water blanks.

Table 3. Analytical Methods & Quality Assurance/Quality Control Samples

			QA/QC Samples			
Sample Analysis	**Analytical Method**	**Analysis Location**	**Calibration Curve**	**Accuracy Checks**	**Replicates**	**Blanks**
Total Chromium	SM 3113B (GFAAS)	Lab	Beginning and end of sample runs	20% of samples	100% of samples	5% of samples
Hexavalent Chromium	SM 3500-Cr D (Colorimetric)	Lab	Beginning and end of sample runs	20% of samples	10% of samples	5% of samples
pH	SM 4500H+ B (Electrometric)	Lab	Weekly	None	100% of samples	None
Copper	SM 3113B (GFAAS)	Lab	Beginning and end of sample runs	20% of samples	100% of samples	5% of samples

4.4 Split Sampling

Not applicable to this addendum. Refer to Section 6.1 for information on replicate analyses.

4.5 Calibration of sampling/monitoring equipment

Calibration curves will be used for each of the analytical methods.

4.6 Avoidance of Cross-Contamination

Sample contamination will be avoided by practicing clean sampling techniques. Samples will be collected directly into acid-cleaned sample bottles without contacting the interior surfaces of the bottles. All glassware will be pre-cleaned with 10% HCl followed by distilled water rinses.

4.7 Selection of Representative Samples

Samples will be collected at a sufficient frequency to enable evaluation of the objectives. Sampling ports at the influent and effluent of the columns will be used. For leaching tests, approximately 2 L of extractant liquids will be run through the beds and captured; samples will be collected from the composite effluent. For initial breakthrough runs (e.g., SBA at reduced pH), samples will be collected at a sufficient frequency to enable development of the breakthrough curves. Availability of the analytical method at the site of bench-scale testing, coupled with analyses conducted each day of testing, enables the analyst to assess whether the sampling frequency should be increased or decreased.

4.8 Sample Amounts Required for Analyses

For applicable samples, the following amounts will be collected for laboratory analysis:

- 20 mL for total chromium,
- 100 mL for hexavalent chromium,
- 20 mL for Cu, and
- 100 mL for pH.

Total Cr and copper measurements require a minimum sample volume for each analysis of approximately 0.02 mL. To ensure that adequate volume is available for quality control purposes, the total sample volume collected will be 20 mL.

For hexavalent chromium measurements, the minimum sample volume required for each analysis is less than 5 mL. To ensure that adequate volume is available for quality control purposes, the total sample volume collected for hexavalent chromium analysis will be 100 mL.

4.9 Sample Containers

All samples will be collected using glassware cleaned in 10% HCl and rinsed in distilled water.

4.10 Sample Identification

Samples will be collected and analyzed by the same person, thus avoiding the need for chains of custody and extensive sample identification procedures typically needed for samples shipped to commercial laboratories. Samples will be identified numerically in the laboratory.

4.11 Sample Preservation Methods

Samples will not be filtered nor will they typically be preserved. Samples will be analyzed on the same day as collected. If samples cannot be analyzed on the same day for total chromium, samples will be acidified with 5% nitric acid as recommended in the GFAAS method.

4.12 Sample Holding Time Requirements

Samples for total, chromium, hexavalent chromium, copper, and pH will be analyzed on the same day of collection. Although not anticipated, total chromium and copper samples could be acidified with 5% nitric acid and analyzed within one month of holding time.

4.13 Sample Shipment

Water samples from GS-3 will be shipped from the site of collection (the GS-3 well) to Lehigh University using a reputable shipping company. Analytical samples will be measured at Lehigh and will not require additional shipping.

4.14 Sample Chain-of-Custody

Samples will be considered “in custody” when they are in someone’s physical possession or view, locked up, or stored in a secure area accessible only by authorized personnel. A minimal number of persons participating in sample handling and custody is desirable.

4.15 Sample Archives

Samples will be stored until after personnel at Lehigh review sample data and associated quality control analyses. Unless directed otherwise, samples will then be disposed of in accordance with Environmental Health and Safety Regulations for Hazardous Chemical Waste.

5. Testing and Measurement Protocols

5.1 Measurement Methods

Laboratory measurements will conform to EPA guidelines and recommended test methods, including those in *Standard Methods for the Examination of Water and Wastewater* (1995), as listed in Table 3.

Samples for total chromium and copper will be analyzed using Perkin Elmer Simultaneous Multi-element graphite furnace atomic absorption spectrometer (GFAAS), following Standard Method 3113B (1995). For chromium, a magnesium nitrate matrix modifier solution will be dispensed into each sample (0.015 mg $MgNO_3$ per sample). For copper, a palladium/magnesium nitrate matrix modifier will be used. Elemental analysis will be conducted using hollow cathode lamps specified for each element.

Samples for hexavalent chromium will be analyzed using a Perkin Elmer Lambda 2 UV/vis spectrophotometer according to Standard Method 3500-Cr, the 1,5-diphenylcarbohydrazide colorimetric method (1995). Note that hexavalent chromium analyses will only be conducted on high-chromium concentration extractants; hence, the relatively high detection limit of 50 ppb for this method is acceptable.

pH will be measured using an Accumet AR15 bench-top pH meter.

5.2 Verification of Unproven Methods

Not applicable.

5.3 Calibration Procedures

Cr total measurements will be performed as described in Section 5.1 using a GFAAS. An initial four-point calibration curve is run each analysis day, followed by quality control samples run every 6th sample to ensure method accuracy. Perkin Elmer certified standards will be cross-checked with standards prepared in-house using potassium dichromate salts. DI water will be run as a blank after every 15 samples. The blank should be less than 2.2 times the method detection limit (MDL), and standards should be within 90 – 110% of the calibrated values. If these criteria are not met, the samples analyzed on just prior to the anomalous blank/standard will be rerun.

For hexavalent chromium analysis, the UV/vis spectrometer will be calibrated each day with a blank and at least three standards. The blank should be less than the MDL, and accuracy check standards analyzed every 6th sample should be within 90 – 110% of the calibrated value. If these criteria are not met, the analysis run is stopped and the instrument will be recalibrated.

The Accumet AR15 pH meter will be calibrated at least once per week, and then tested with the buffer solutions each day.

6. QA/QC Checks

6.1 Quantitative Acceptance Criteria for Data

Sensitivity for both total chromium and hexavalent chromium analyses in the Lehigh University laboratory have been determined by Dr. Arup SenGupta. The method detection limits for the total chromium method is 5 μg/L and for the hexavalent chromium method is 50 μg/L. Samples found to be less than these values will be reported as "below detection limit, or <MDL." Samples that are measured as higher than the highest calibration standard will be diluted and re-run. The

% Relative Standard Deviation (RSD) on replicate samples should generally be less than 10% (except for blanks).

Accuracy (a combination of random and systematic error) in total chromium and hexavalent chromium analyses will be evaluated by measuring several concentrations of standards (both certified and laboratory-prepared from salts) interspersed throughout the analytical runs. For both the GFAAS and UV/vis spectrophotometric methods, standards should be between 90 – 110% of the known value.

Precision (random error) will be investigated by performing repeat analyses of the same sample on the same analytical instruments. One hundred percent of total chromium and copper samples will be analyzed in replicate with the GFAAS as part of the instrument’s autosampler program. The RPD between the duplicate analyses should be less than 20%.

6.2 Additional Project-Specific Quality Assurance Objectives

Not applicable.

6.3 Procedures to Assess QA Objectives

Quality assurance objectives will be assessed as detailed in this QAPP. Laboratory analyses will be subjected to numerous procedures to assess quality assurance objectives. Sample accuracy will be tested by comparing sample concentrations to certified standards and standards prepared from salts. All total chromium and copper samples will be measured in replicate.

7. Data Reporting, Data Reduction, & Data Validation

7.1 Data Reporting Requirements

Total chromium concentrations will be reported as the average concentration of two replicates, in units of μg/L. Hexavalent chromium concentrations will be reported in μg/L.

7.2 Laboratory Data Deliverables

Laboratory data will be reported in a final technical memorandum as well as in spreadsheet form. Data will include total chromium, hexavalent chromium, and copper concentrations as applicable to achieve the stated objectives. Lehigh University will gather all data and prepare summary tables and graphics to characterize the findings of the bench tests. Quality assurance procedures (refer to Section 7.4) will be used to validate and confirm the data.

7.3 Data Reduction Procedures

In the laboratory, analytical measurements will be converted to concentrations by running appropriate calibration curves (on the same instrument) and interpolating the sample values. Data from the GFAAS are output to a printer and to a spreadsheet in electronic form. Data from the UV/Vis spectrometer are output to a printer and entered manually into a computer spreadsheet.

All data will be input into Microsoft Excel worksheets, from which project objectives can be evaluated using graphical and statistical procedures.

7.4 Data Validation Procedures

Depending on the testing protocol, the types of QA/QC samples may include the following:

- Certified standards and laboratory-prepared standards that are used to assess the accuracy of laboratory procedures (representing 20% of the total number of analyses).
- Laboratory blank samples that are used to detect potential problems in the sample collection methods.
- Laboratory duplicate samples that are subjected to replicate analyses to determine laboratory precision.

At Lehigh University, a person other than the analyst will compare ten percent of all spreadsheet data to original hard-copy printouts. The analyst will ensure that all QC criteria are met, and the analysis manager will review all QC data monthly.

Calculations performed in a spreadsheet will be carefully examined to ensure the accuracy of the formulas, data input, and results. After data has been validated and reduced, the McGuire Malcolm Pirnie Project Manager will review the files to ensure that the data are not suspect. Any quality control data that do not meet the acceptance criteria, in the laboratory, will be flagged and either reported with an explanatory note or excluded from the data reduction with an explanatory note.

7.5 Data Storage Requirements

At Lehigh University, one hard copy and one electronic copy of all data will be maintained. Project data will be entered into a laboratory notebook and kept onsite.

7.6 Final Project Documentation

The product document from this project will be a final technical memorandum from Lehigh University.

8. Assessments

8.1 Audit Schedule

Internal audits are not scheduled for this project. However, the project manager at Lehigh University (Dr. SenGupta) will review the QC data to ensure that QC objectives are being met.

8.2 Corrective Action Procedures

Corrective action procedures that will be in place for this project include the following:

Identification and definition of the problem
Corrective action will be required if analytical data is determined to be out-of-control. An analytical batch will be considered to be out-of-control when replicate samples, accuracy check samples, calibration blanks, the standard curve, or other external reference samples fail to meet the QC criteria.

Investigation and determination of the cause of the problem
When an analysis is determined to be out-of-control, steps will be taken to determine the cause. First, it must be determined whether a calculation error has occurred. Then the instrument used in the analysis will be checked against performance specifications. The indicators of being out-of-control will be a clue to the problem. For example, wrong readings of sample checks may indicate the instrument is not properly set-up or standards are bad; if duplicates are not within precision limits, there may be a problem with contamination; or if blanks are too high, contamination has probably occurred.

Determination of a corrective action to eliminate the problem
Dr. SenGupta will meet with the analyst(s) to determine why the project has deviated from the goals outlined in the QA/QC plan and immediate steps will be taken to correct discrepancies.

- Instrument Calibration
  If results of the daily calibration sample check are out of control, as indicated by flagged values, causes may include instrument malfunction or improper set-up, bad standards, or operator error. The first step will be to check instrument performance. The instrument will be set-up again under direct supervision. If this does not bring the system back into control, then standards will be re-made and analyzed. If the problem is operator error, the analyst will be re-trained and put through a rigorous QC check before he/she can continue with the sample analyses.

- Accuracy
  When a result is out-of-control as indicated by flagged values for accuracy check samples, steps will be taken to determine the cause. First, calculations will be checked. Then the instrument will be checked for proper set-up. The sample(s) will be reanalyzed. If these steps do not bring the analysis under control, then the accuracy check sample will

be prepared again and analyzed. It may be necessary at this time to prepare fresh standards. If all of the above procedures do not bring the analysis into control, analysis will be performed by standard addition. All samples analyzed in the batch containing the out-of-control sample will be re-analyzed by the procedure used to bring the analysis back into control.

- Precision

  When a result for duplicate analysis falls out of the acceptable range, as indicated by flagged values, steps will be taken to determine the cause. First, calculations will be checked. Then the instrument performance will be evaluated. The samples will be reanalyzed. If these procedures do not bring the samples back into an acceptable range, then all samples in the analytical batch will be prepared again and analyzed.

- Blank contamination

  If the reagent blank shows contamination (i.e. concentrations greater than the MDL) during analysis, materials and reagents used to make that blank will be replaced before additional samples are prepared. Also glassware and sample preparation will be re-evaluated to ensure that contamination is not occurring during these processes. Standards prepared with contaminated reagents will be discarded, and samples will be reprocessed.

- External reference sample analysis

  The inability of the laboratory to analyze an external reference sample is indicative of analytical problems related to sample preparation procedures, instrument operation, or calibration. If the calibration check sample within the same analytical batch analysis is also out-of-control, a problem with the instrument or operator performance is indicated. Corrective action will be taken as described earlier. If the calibration check sample is within the control limits, the problem may be with the sample preparation procedure. At this point the calibration standards will be prepared again and analyzed. If this fails to bring the measurement back into control, the procedure will be reevaluated to determine if there are points within the procedure likely to be the source of contamination or loss of the analyte. All samples analyzed in the batch with the out-of-control sample will be re-analyzed by the procedure used to bring the sampled back into control.

8.3 Implementation of Corrective Action

The analyst at Lehigh University has the authority to implement corrective action (described in Section 8.2 Investigation and Determination of the Cause of the Problem) during an analysis run if quality control samples are determined to be out-of-control.

The project manager at Lehigh University, Dr. SenGupta, will review QC logs and will consult with the analyst if further corrective action is identified as necessary. Following any corrective action, the primary investigators will ensure that the analysis is truly back in control, as indicated by consistently met quality control criteria.

9. References

Standard Methods for the Examination of Water and Wastewater. 19th ed. 1995.

6. Lehigh University Report on WBA Testing

Trace Cr(VI) Removal by Weak Base Duolite A7 and SIR-700 from Groundwater in Glendale, CA: Underlying Mechanism

Trace Cr(VI) Removal by Weak Base Duolite A-7 and SIR-700 from Groundwater in Glendale, CA : Underlying Mechanism

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13 E. Packer Avenue
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Executive Summary

During the last six months, we carried out a series of laboratory experimental studies using two weak-base anion exchange resins: Duolite A-7 from Rohm and Haas Co., and SIR-700 from ResinTech Co. Chromium-contaminated Glendale water, spiked Glendale water and synthetic water were used in the study. For comparison and appropriate understanding of underlying Cr(VI) removal mechanism, a strong-base anion-exchange resin was also included in the investigation. Major conclusions resulting from the study can be summarized as follows:

1. Cr(VI) removal by Duolite A-7 and SIR-700 takes place by selective anion exchange followed by Cr(VI) reduction to Cr(III) which is insoluble and retained within the resin phase.
2. At neutral or above-neutral pH, Cr(VI) removal by Duolite A-7 and SIR-700 diminishes drastically due to the lack of protonated anion exchange sites. At acidic pH, conventional strong-base anion exchange resins exhibit relatively poor removal of Cr(VI) because of their inability to reduce Cr(VI) to Cr(III). Thus, both anion exchange sites and reductive potential are simultaneously needed for an ion exchange resin to achieve efficient Cr(VI) removal. Duolite A-7 as well as SIR-700 satisfy these requirements at slightly acidic pH following adequate protonation of weak-base exchange sites. Also, the process is operationally simple; any fluctuation in the influent Cr(VI) concentration has no noticeable effect on the treated water quality.
3. During lengthy column runs, chromium appearing at the exit of the column is only Cr(VI) i.e., $HCrO_4^-$ and/or CrO_4^{2-}. Cr(III) is essentially absent in the treated water. Inside the exhausted Duolite A-7 and SIR-700, however, only Cr(III) is present.

4. Removal of copper from Glendale water has no favorable impact on Cr(VI) removal. Thus, even in the absence of copper, Cr(VI) removal by Duolite A-7 and SIR-700 is very efficient. However, both Duolite A-7 and SIR-700 have the ability to remove copper(II) and other transition metal cations due to the presence of nitrogen-containing functional groups.
5. All other conditions remaining identical, Cr(VI) removal is enhanced by lower influent pH and longer empty bed contact time (EBCT).
6. During the field trial of SIR-700 by Malcolm Pirnie, it was observed that Cr(VI) removal for the first few thousand bed volumes was relatively poor. Inadequate protonation of SIR-700 was the underlying reason for inefficient Cr(VI) removal. Both Duolite A-7 and SIR-700 should be equilibrated at slightly acidic pH (3-4) prior to starting the column run for Cr(VI) removal.
7. It is hypothesized that repeating organic groups (Phenol formaldehyde in Duolite A-7 and epoxy in SIR-700) are responsible for reducing Cr(VI) and the resulting organic substances are retained within the ion exchange resins following oxidation. More widely used anion exchange resins with polystyrene matrices are unable to reduce Cr(VI).
8. Results of our laboratory experiments and the earlier findings from the field trials performed by Malcolm Pirnie provide suggestive evidence that intraparticle diffusion within the ion exchangers is the rate limiting step for Cr(VI) removal.

Experimental Results and Major Findings

Selected experimental results and their discussion are presented here for elucidation of underlying Cr(VI) removal mechanism by two weak-base anion exchange resins: Duolite A-7 and SIR 700.

EXPERIMENT I.

Two fixed-bed column run experiments were carried out in the laboratory with Glendale, CA GS-3 water at slightly acidic pH where $HCrO_4^-$ is the predominant chromate species. A strong-base anion exchange resin (Purolite A-600) and Duolite A-7 were the two sorbents under identical experimental conditions. Figure 1 provides the chromate effluent histories for the two runs; empty bed contact time (EBCT) and superficial liquid velocity (SLV) are included in Figure 1. Note that chromate removal is well over an order of magnitude lower for the strong-base anion exchange resin compared to Duolite A-7. Previous research studies established that ion exchange is the primary chromate removal mechanism for strong-base anion exchange resins.

Finding: Ion exchange alone cannot be the sole chromate removal mechanism for Duolite A-7. The same conclusion is applicable for SIR 700.

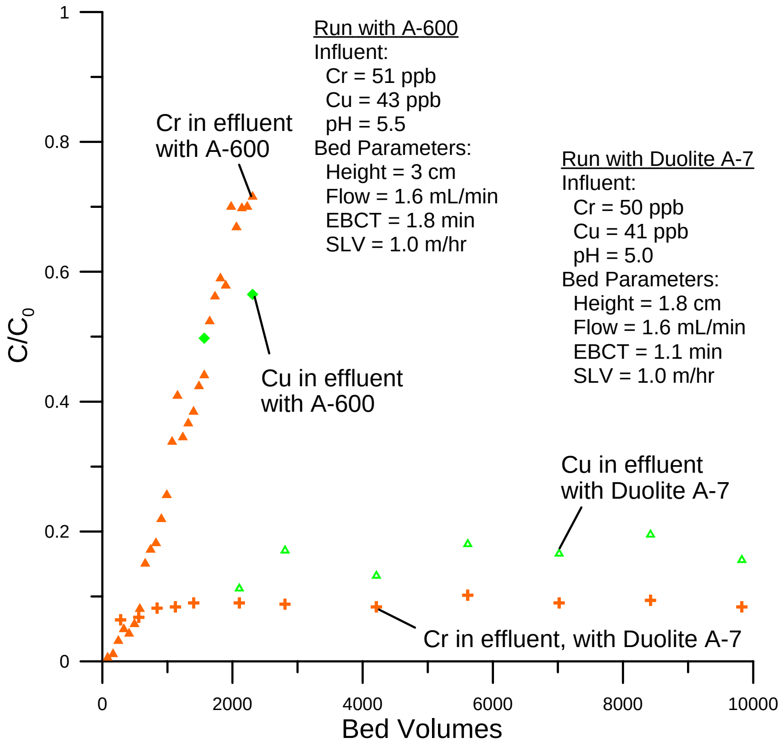

Figure 1. Effluent breakthrough profiles for Glendale well water for strong-base anion exchange (SBA) resin (Purolite, A-600) and weak-base anion exchange(WBA) resin (Duolite, A-7) .

EXPERIMENT II.

It was earlier observed by Malcolm Pirnie that there was a difference between the chromium removal characteristics of SIR-700 and Duolite A-7. Duolite A-7 showed high chromate removal for Glendale water from the very beginning of the run. On the contrary, SIR-700, did not show good removal of chromium for the first 2200 bed volumes but chromate removal improved markedly beyond that point. In our laboratory, SIR 700 was first pre-conditioned with a brine solution with a pH of 3.5 and then fixed-bed column run was carried out with Glendale water. Figure 2 represents chromium breakthrough profile of SIR-700. It may be noted that adequate protonation of WBA resin improves the initial performance of the resin. Also, pre-conditioning of the resin at acidic pH did not cause any significant drop in pH at the exit of the column.

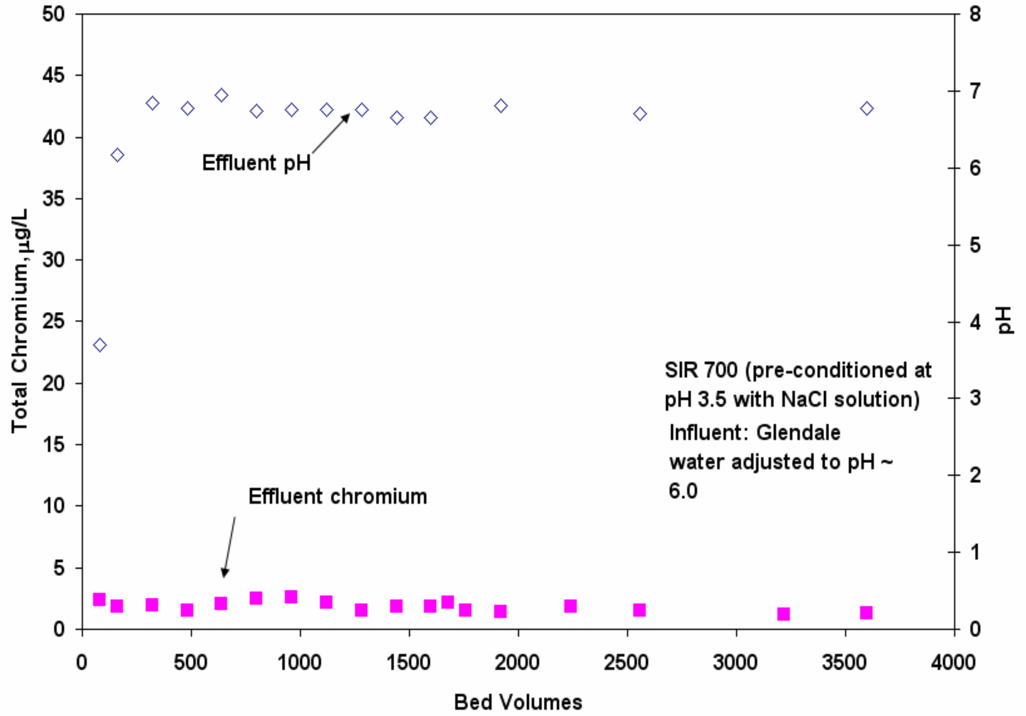

Figure 2. Chromate breakthrough history for WBA resin SIR-700 pre-conditioned with slightly acidic NaCl solution.

EXPERIMENT III

Figures 3 and 4 present effluent chromate breakthrough profiles for two separate column runs: one with parent SIR-700 and the other with copper-preloaded SIR-700 resins. In both cases synthetic water containing about 100-120 ppb chromium (VI) with other background electrolytes was used as the feed. Note that the chromate breakthrough profiles for both the parent and copper loaded resins are very similar. Thus, the presence of copper in the resin phase does not have any noticeable impact towards chromium removal i.e, ligand exchange is not the underlying reason for very high chromate removal capacity of SIR-700. It was observed that copper was simultaneously removed from the Glendale well water by both SIR-700 and Duolite A-7.

Nitrogen-containing chelating functional groups of Duolite A-7 and SIR-700 are responsible for their high sorption affinity toward copper (or other transition metal cations).

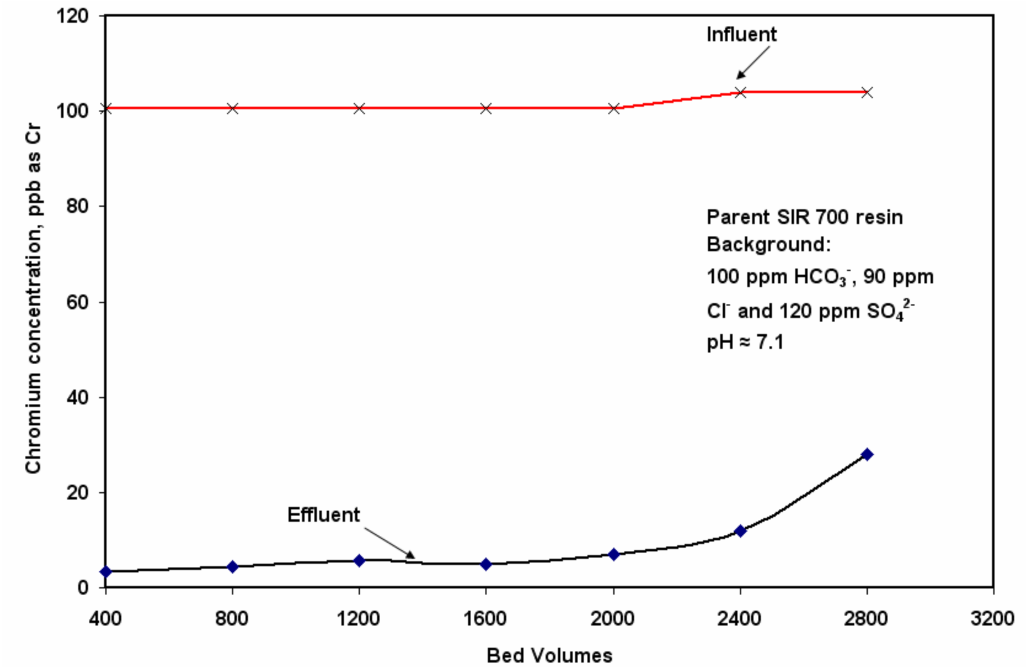

Figure 3. Breakthrough chromate profile for column run with parent SIR-700 resin

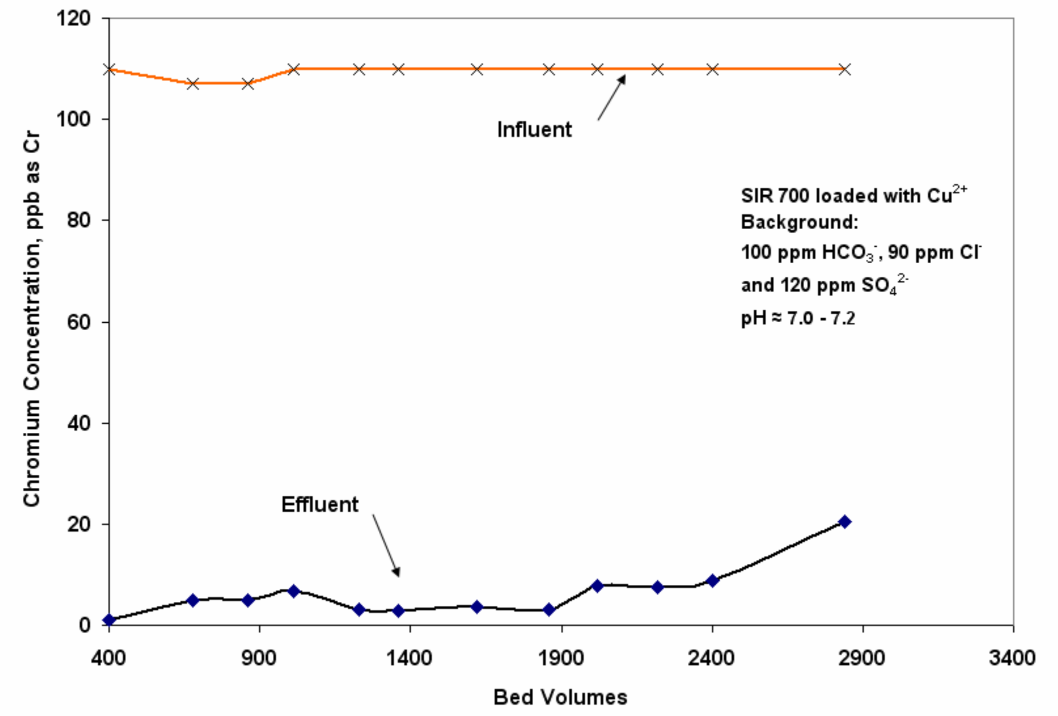

Figure 4. Breakthrough chromate profile with copper-preloaded SIR-700.

EXPERIMENT IV

Figure 5 represents chromate breakthrough profile for Duolite A-7 column run using Glendale well water. Note that the column run continued for more than 25,000 bed volumes. Analysis of the effluent obtained during the run confirmed the presence of only chromium(VI) in the effluent; no chromium(III) was observed in the effluent.

Chromium concentration in the influent was spiked to 200 ppb at 26,000 bed volume. As a result, there was an immediate increase in the concentration of chromate breakthrough. A one-day stop in the column run caused an immediate drop in the effluent chromium concentration (as observed in the curve in the inset of Figure 5). A sharper breakthrough profile was observed after the column run is resumed. This behavior is characteristic of a process rate-limited by intra-particle diffusion. The influent pH during the run was maintained at 5.5. The effluent pH was observed to be around 6.7 during the column run. For nearly every column run, the effluent pH was equal or greater than the influent pH.

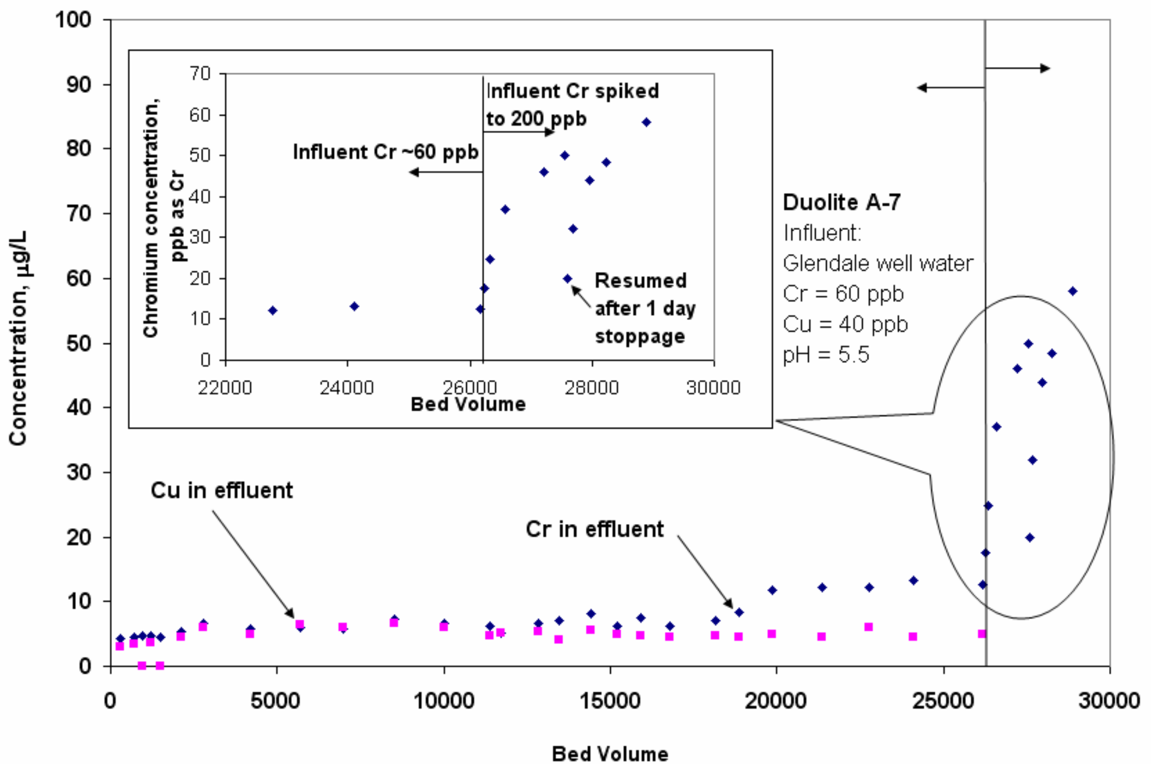

Figure 5. Effluent history of Duolite A7 column run for Glendale well water.

EXPERIMENT V

Table 1 shows results of desorption/elution experiments for exhausted Duolite A-7 and SIR-700 obtained after the field studies at Glendale. Note that Cr(VI) is absent in the eluted solution; Cr(III) is the only chromium present within Duolite A-7 and SIR-700 regradless of the chemical composition of the regenrant.

Table 1

Elution with 6% NaCl & 2% NaOH followed by 2% H_2SO_4

Resin	6% NaCl & 2% NaOH			2% H_2SO_4		
	Total Cr	Cr(VI)	Total Cu	Total Cr	Cr(VI)	Total Cu
	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g
Duolite A-7	0.605	0.006	0.664	2.9	0.00	21.8
SIR-700	0.607	0.012	0.21	0.931	0.00	7.13

EXPERIMENT VI

Figure 6 represents chromate breakthrough profile for SIR-700 with synthetic feed water for which the influent pH was deliberately changed during the column run. For the initial period of the column run, pH of the influent was kept around 7.0. An early breakthrough of 60 ppb was observed after 3800 bed volumes. At that point, the influent pH was reduced to 5.0. Chromate at the exit of the column dropped to 20 ppb.

Figure 7 represents the effect of empty bed contact time or surface loading rate for the removal process inside the column. It is noted that when the surface loading rate is doubled by doubling the flow rate, there was a decrease in the chromium removal performance i.e., chromate at the exit of the column increased. The breakthrough profile, however, returned close to its earlier value when the original flow rate was restored.

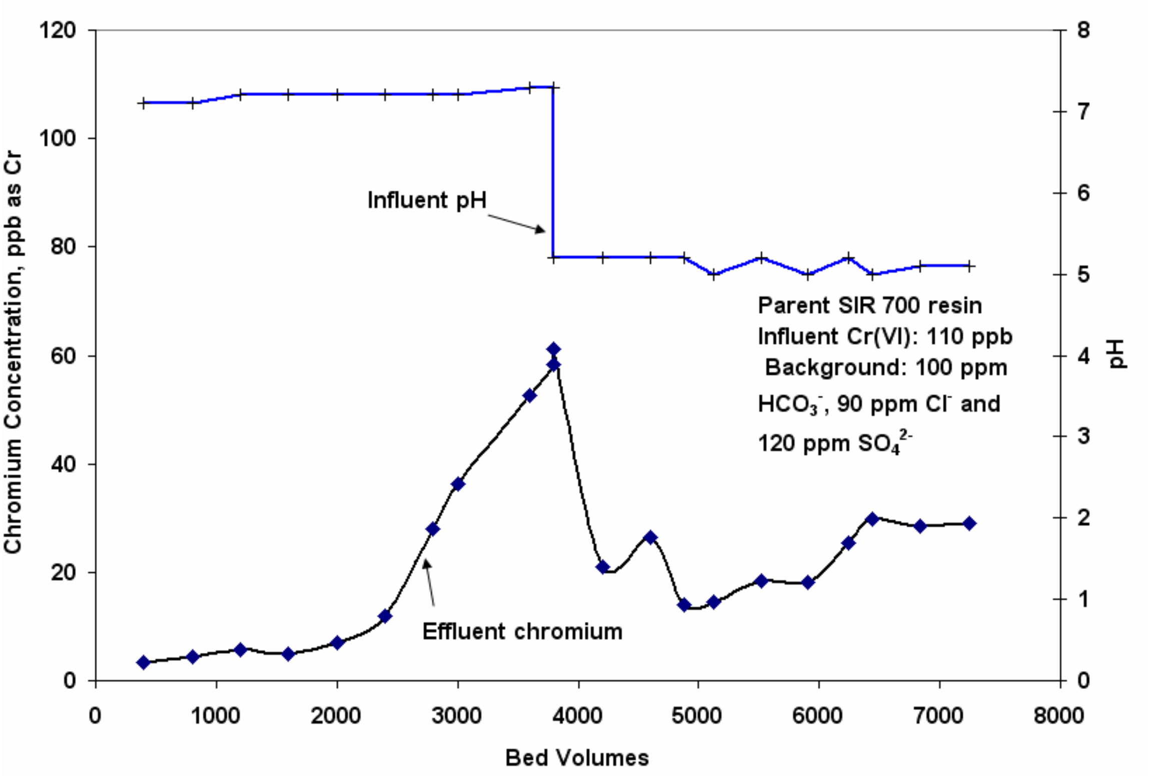

Figure 6. Effect of step change in influent pH on Chromium(VI) removal by SIR-700 during a column run

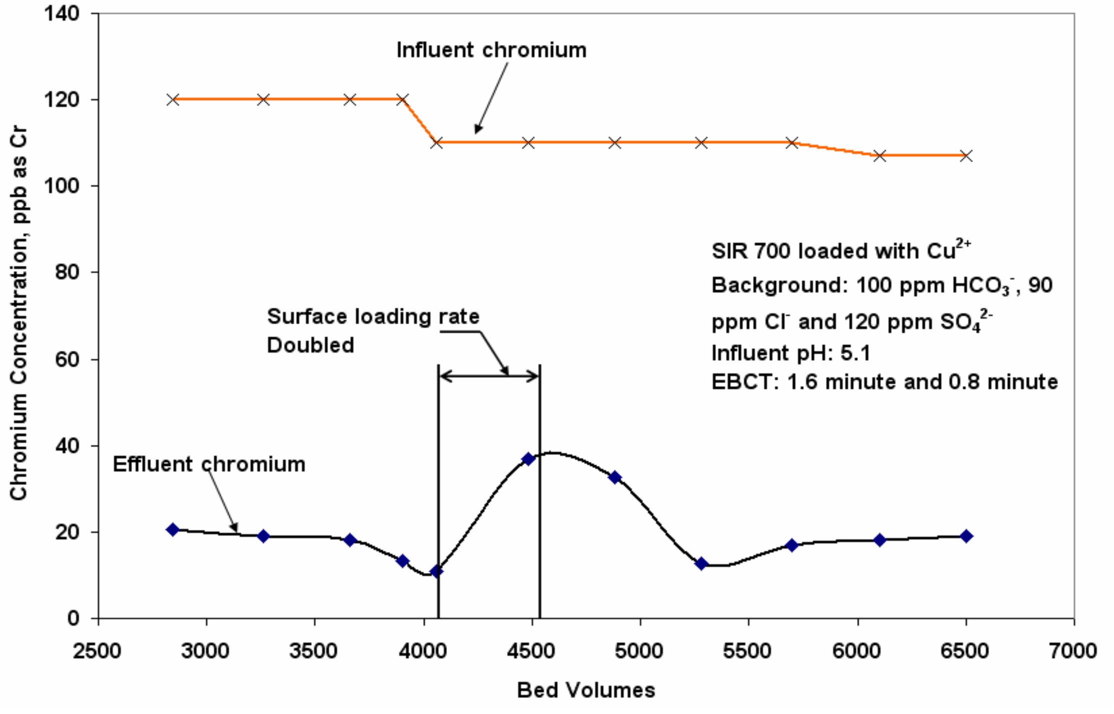

Figure 7. Effect of surface loading rate or EBCT on chromium breakthrough concentration. EBCT was decreased from 1.6 minute to 0.8 minute during the period marked in the figure.

7. WQTC 2007 Proceedings

State-of-the-Art Geochemical Techniques in Evaluating Drinking Water Treatment Contaminant Removal Processes

Presented at the AWWA Water Quality Technology Conference, Charlotte, North Carolina
November 4-8, 2007

State-of-the-Art Geochemical Techniques in Evaluating Drinking Water Treatment Contaminant Removal Processes

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Daniel J. Brabander, Associate Professor, Wellesley College

Matthew Newville, Argonne National Laboratory, Advanced Photon Source, Argonne, IL

Peter Kavounas, Water Service Administrator, City of Glendale Water and Power, Glendale, CA

INTRODUCTION

The City of Glendale, California has been leading a research program to identify effective hexavalent chromium treatment technologies for impacted groundwater wells. The research effort to date has involved a range of funding agencies and organizations, university partners, and local cities. This work has been supported by the EPA, State of California, AwwaRF, and the Cities of San Fernando, Burbank, and Los Angeles. University partners have included Utah State University, UCLA, University of Colorado at Boulder, Wellesley College, and Lehigh University. This extensive university and multi-organizational support has enabled the investigation of the mechanism of hexavalent chromium removal by a new treatment technology application– weak-base anion exchange.

In early pilot studies, weak-base anion exchange resin demonstrated a high capacity for hexavalent chromium. Initial technology testing, however, revealed a few hints that the reduction of hexavalent chromium to trivalent chromium occurred on at least one weak-base resin, but not on strong-base resins. Another research group also observed the high capacity of a weak-base resin for chromium and hypothesized that chromium reduction occurred (Höll et al. 2002), although no evidence of this mechanism was provided. The appearance of this possible chromium reduction process coupled with the high chromium capacity of the weak-base resin led the project team to investigate the mechanism of chromium retention by the resins.

METHODS

Pilot testing revealed that two of six weak-base anion exchange resins tested exhibited a high chromium capacity exceeding 1% by weight. To evaluate the mechanism for chromium accumulation by weak-base resins, we applied a suite of high-tech geochemical techniques traditionally available at research laboratories. Two weak-base resins, including PWA7 (formerly called Duolite A7) and SIR-700, were run to more than 113,000 bed volumes during pilot testing then subjected to the techniques described below. The resins were divided into thirds (top, middle, bottom) and each section was analyzed separately.

The question of whether hexavalent chromium, Cr(VI) was reduced to trivalent chromium, Cr(III) was explored using a technique new to drinking water treatment studies: x-ray absorption fine-structure spectroscopy (XAFS). The project team applied for and was granted “beam time” on beam line 13-BM-D at Argonne National Laboratory (Argonne, Illinois), a U.S. Department of Energy facility using a synchrotron to generate high-energy x-rays. Previous studies investigating chromium speciation in soil and mineral samples (O’Day et al. 2000, Bond and Fendorf 2003, Berry and O’Neill 2004, Wilkin et al. 2005) showed that this technique could be effective at analyzing solid samples. For this analysis, resin was mounted in the x-ray beam on a sample holder and adsorption spectra were collected in fluorescence mode. Potential oxidation state changes in the beam were ruled out with initial testing. Cr(III), Cr(VI), and Cr(0) reference compounds were analyzed to enable comparison of the resin samples with known oxidation state chromium standards.

Through a partnership with the Wellesley College geology department, three techniques were applied, including x-ray fluorescence spectroscopy (XRF), x-ray diffraction (XRD), and scanning electron microscopy (SEM). A Spectro XEPOS XRF spectrometer was used to assess total concentrations of chromium and other elements accumulated on the resin. XRF samples were prepared by grinding and packing the resin in a sample cup. The presence of crystalline precipitate in or on the resin was investigated using a Rigaku 300 diffractometer with a rotating copper anode for XRD analysis. Finally, SEM analyses were performed using a LEOVP438 with an iXRF energy dispersive analytical system to determine the spatial distribution of chromium on the resin beads.

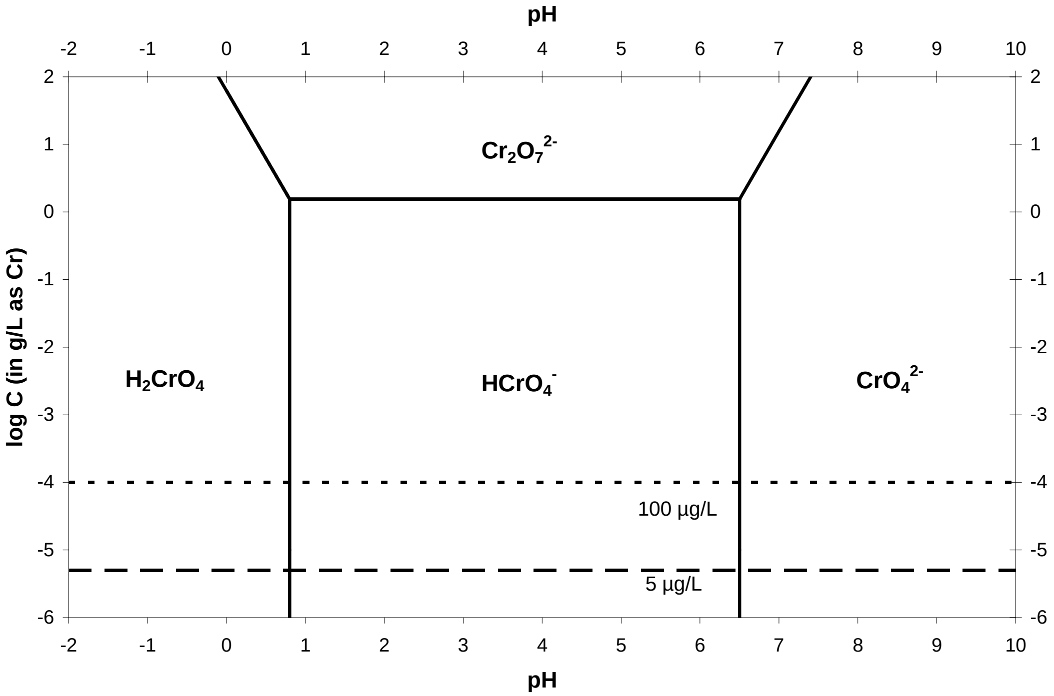
Finally, additional testing of the resins was performed to determine the residuals disposal options for Glendale. The federal toxicity characteristic leaching procedure (TCLP; USEPA 1998) and the California Waste Extraction Test (CWET; DTSC 1991) were conducted to classify the resins as hazardous or non-hazardous waste. Further, the potential accumulation of uranium was investigated using kinetic phosphorescence analysis (KPA; ASTM 5174-91), since earlier pilot testing indicated that uranium may be removed by the resin.

RESULTS

Aqueous Chemistry and pH Depression for Weak-Base Treatment

The water quality of the GS-3 well used for pilot scale testing of the weak-base resins is shown in Table 1. In general, chromium was present primarily in the +6 oxidation state. Other parameters are shown in Table 1 to allow later interpretation of the XRF results.

Pilot testing showed that chromium removal by weak-base anion exchange resins requires pH depression to 6.0. Several reasons underlie this need for acid addition. In this pH range and for low ppb concentrations, Cr(VI) is present as $HCrO_4^-$ (Figure 1). At lower pH, Cr(VI) occupies half the number of exchange sites since $HCrO_4^-$ is present rather than CrO_4^{2-}, which is favorable above a pH of 6.5. The weak-base anion exchange sites are also more protonated at lower pH and can more effectively attract the negatively charged $HCrO_4^-$ species. Finally, pH depression reduces the impact of hydroxyl ion competition with Cr(VI) for weak-base resin exchange sites.



Note: The range of interest for the Glendale study was 5 to 100 µg/L Cr(VI).

Figure 1. Aqueous Speciation of Chromium (VI) as a Function of pH

Table 1. Water Quality of the Glendale GS-3 Well Water Used in Pilot Testing

Constituents	Typical Concentration
Alkalinity	200 mg/L as $CaCO_3$
Arsenic (total)	< 2 µg/L
Chromium (total)	35-40 µg/L
Chromium (hexavalent)	35-40 µg/L
Conductivity	850 µS/cm
Copper	20 µg/L
Hardness	350 mg/L as $CaCO_3$
Iron (total)	< 6 µg/L
Manganese	< 20 µg/L
Nitrate	7 mg/L as NO_3
pH	6.8
Phosphate	0.3 mg/L as PO_4
Silicate	33 mg/L as SiO_2
Sulfate	100 mg/L as SO_4
Uranium*	1.4 pCi/L
Vanadium	7 µg/L

*Uranium concentrations were only measured twice: in 2000 (1.48 pCi/L) and 2001 (1.39 pCi/L). Other constituents are typically measured monthly.

Chromium Speciation in the Resin: Cr(VI) vs. Cr(III)

XAFS spectra for chromium reference compounds show that adsorption edge energies increase with oxidation state, such that Cr(III) has its k-edge at a lower energy than Cr(VI). For chromium, however, Cr(VI) exhibits a strong pre-edge feature in spectra due to d-p orbital hybridization; this intensity of the pre-edge is not found in Cr(III) spectra. Figure 2 shows XAFS spectra for two chromium reference compounds – Cr(III) acetate and ammonium dichromate [a Cr(VI) compound] as well as the PWA7 and SIR-700 resins. Data was collected near the k-edges at 0.25 eV increments; consequently, the edge energy difference of 2.75 eV for Cr(VI) vs. Cr(III) standards is significant and could be used to assess chromium speciation in the resins.

Figure 2 indicates that more than 95% of the chromium present on spent resin was in the trivalent, Cr(III), oxidation state. In addition, no crystalline precipitates were identified by XAFS. No pre-edge feature was observed in either of the two resin samples, and the k-edge lines up with the Cr(III) compound rather than the Cr(VI) compound. Consequently, this analysis provided proof that Cr(VI) is reduced to Cr(III) by these two weak-base resins.

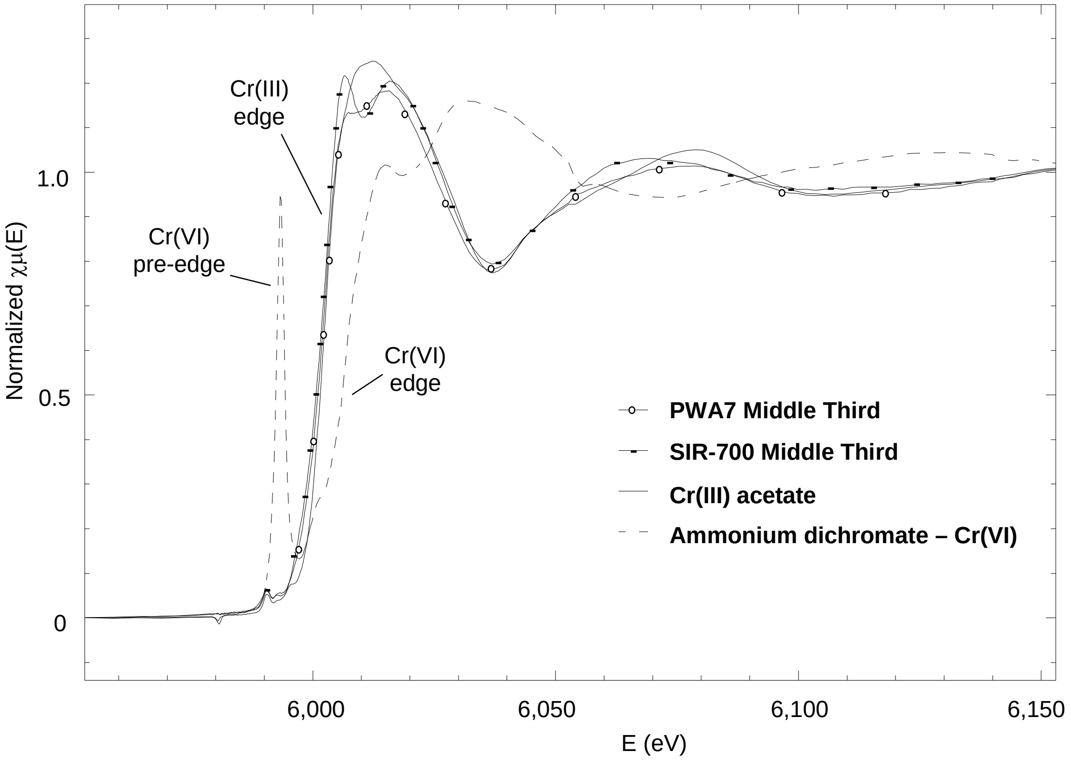


Figure 2. Chromium XAFS Spectra for Spent WBA Resins and Reference Compounds

Accumulation of Chromium and Other Elements on the WBA Resins

XRF analyses provided estimates of elemental concentrations in the spent resins ranging from sodium through uranium on the periodic table. Table 2 shows the XRF results for virgin and spent PWA7 and SIR-700 resins. Chromium concentrations ranged from 7,583 to 14,600 μg/g (ppm) in the PWA7 (corresponding to 0.76 to 1.46% by weight) and 2,701 to 7,560 μg/g in the SIR-700.

Other elements substantially accumulated by the resins included vanadium, copper, uranium, and chlorine. Sulfur amassed on the PWA7 resin but appeared to be leached from the SIR-700 resin. Phosphate was accumulated on both resins but not to a high degree. Copper was highly correlated with chromium for the two resins, although increasing copper concentrations were observed as chromium concentrations increased from bottom to top of the PWA7 resin column. By comparison, SIR-700 resin showed a similar accumulation of copper at all depths. The mechanism for copper removal by the weak-base resins is not known at this time but may offer insight into the resin binding mechanisms.

Table 2. XRF Characterization of Two Weak-Base Resins (in ppm dry resin)

	PWA7				**SIR-700**			
Element	Virgin Resin	Top Third	Middle Third	Bottom Third	Virgin Resin	Top Third	Middle Third	Bottom Third
Silicon	618	567	217	914	<40	241	214	97
Phosphorus	24	219	131	113	333	646	593	489
Sulfur	<2	6,348	6,176	7,214	64,370	37,970	40,240	41,450
Chlorine	31	3,916	3,705	4,044	3,656	4,644	4,779	4,780
Potassium	<9	589	283	148	<9	187	62	<10
Calcium	62	194	129	170	20	87	104	97
Vanadium	<4	1,330	1,915	2,440	<6	3,009	1,580	309
Chromium	8	14,600	10,450	7,583	<7	7,560	4,426	2,701
Iron	35	249	<8	31	39	85	95	<6
Copper	7	28,850	14,020	6,413	3.5	5,112	4,775	4,642
Zinc	3.3	<4	<3	15	1	<2	<2	2
Arsenic	<1	<1	<1	<1	<1	2	2	2
Bromine	0.3	136	105	92	3	99	98	89
Uranium	<1	1,885	860	410	0.7	781	209	35

Distribution of Chromium in the Resin Beads: Precipitates vs. Homogeneous Distribution

The high concentrations of chromium in the weak-base resins together with the reduction of Cr(VI) to Cr(II) and the relatively low solubility of Cr(III) compounds raised the question of whether chromium was retained as a precipitate or was homogeneously distributed through the resin. To investigate this question, XRD and SEM techniques were used.

XRD patterns for both resins indicated that the Cr(III) compound was amorphous in nature rather than crystalline (Figures 3 and 4). Had the Cr(III) been present in the form of typical Cr(III) compounds, such as $Cr(OH)_3{\cdot}3H_2O$ or Cr_2O_3, at concentrations of approximately 1% or more, sharp peaks would have been observed due to x-ray diffraction from repeated crystal lattice structures in the minerals.

SEM imaging in backscatter mode indicated that chromium was homogeneously distributed over the resin beads, as opposed to chromium precipitates present as “hot spots” (Figures 5 and 6). In addition, the spent resin was characterized by a higher brightness than the virgin resin, likely due to the chromium, copper, and maybe uranium concentrations.

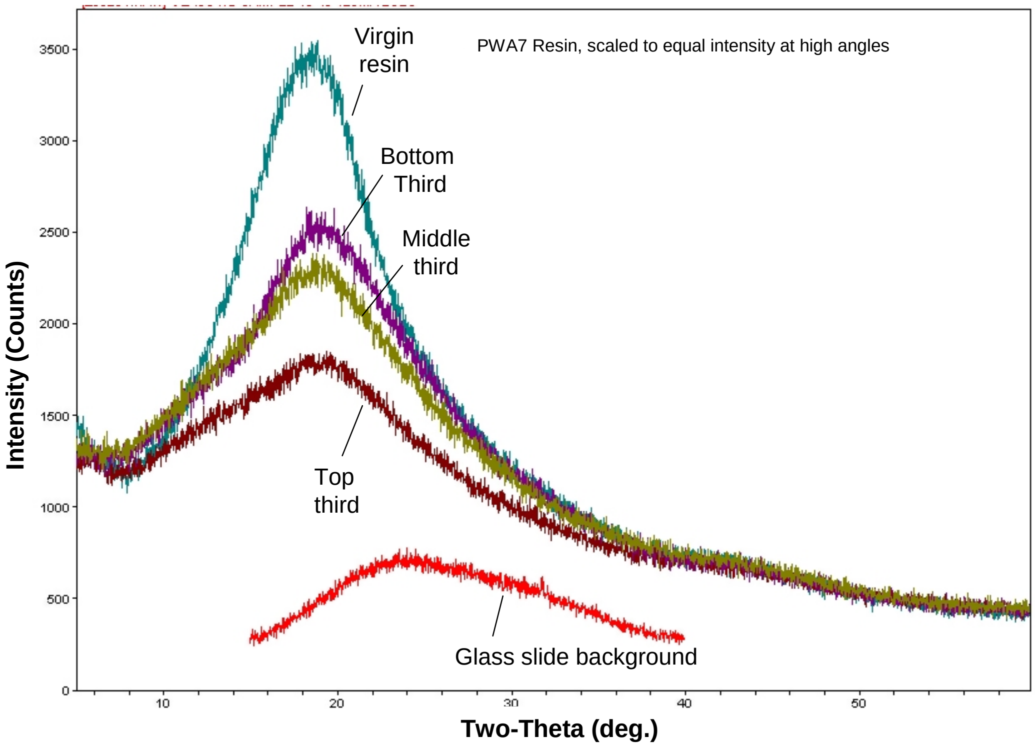


Figure 3. XRD Patterns for PWA7 Resin

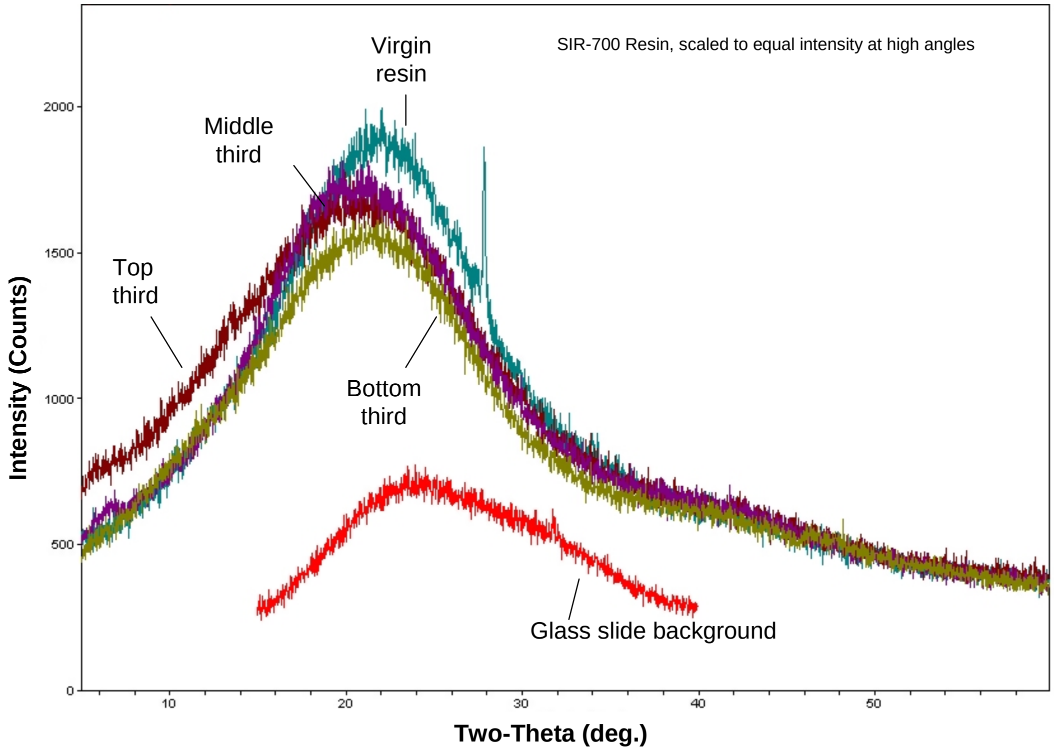


Figure 4. XRD Patterns for SIR-700 Resin

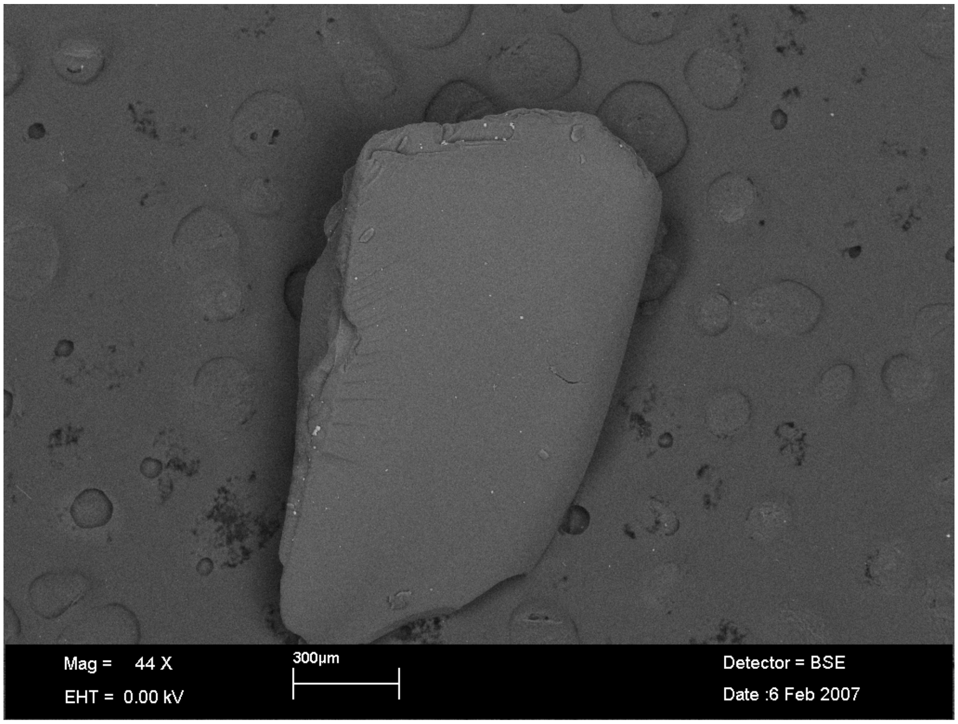


Figure 5. SEM image of virgin PWA7 resin – 44x magnification

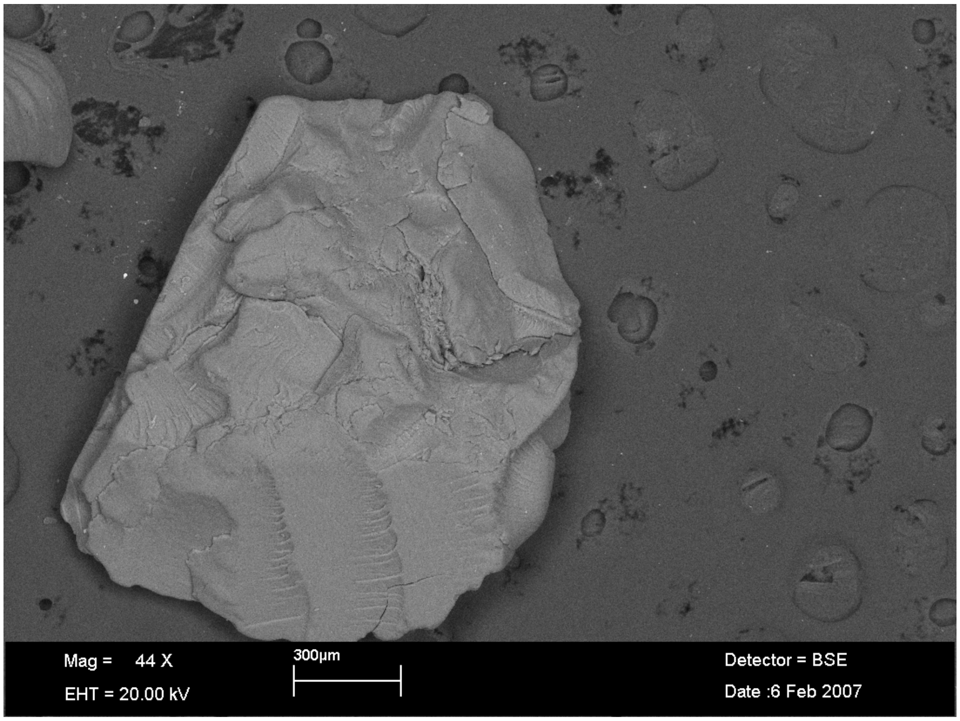


Figure 6. SEM image of spent PWA7 resin (top third) – 44x magnification

Waste Classification

TCLP testing of the spent resins showed that the resins would be non-hazardous according to federal standards. However, the resins would be classified as hazardous waste for disposal in the State of California as a result of CWET results. In the CWET test, the soluble threshold limit concentration (STLC) was exceeded for chromium leached from both resins (i.e., 11,200 ppb for PWA7 and 10,400 ppb for SIR-700). By comparison, the regulatory limit for chromium STLC is 5,000 ppb. Other metals were below the STLC, although copper leached from the PWA7 resin (22,400 ppb) was approaching the 25,000 ppb limit.

The resins also accumulated uranium during hexavalent chromium treatment. PWA7 removed more than double the uranium compared with the SIR-700, and the PWA7 exceeded the low-level radioactive waste trigger level of 500 ppm (Figure 7). As a result, the resin may require a shorter bed life than 113,000 bed volumes (e.g., approximately 100,000 bed volumes) to avoid generation of a radioactive waste.

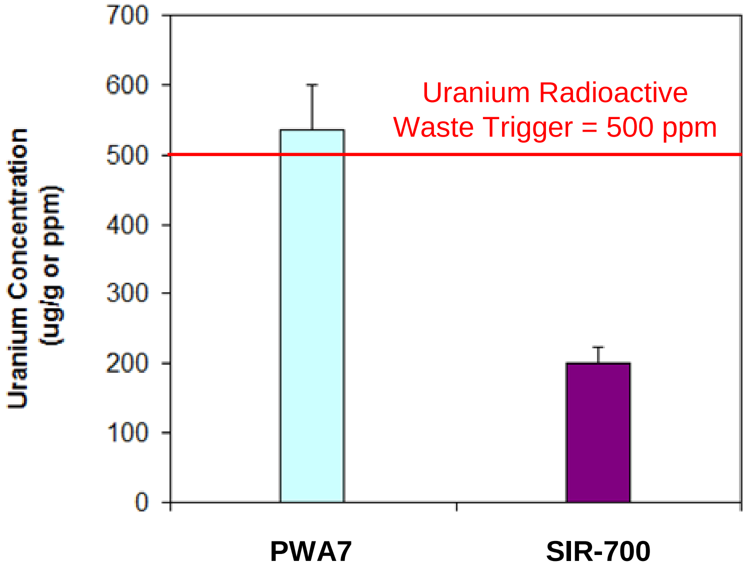


Figure 7. Uranium Concentrations in the Spent Weak-Base Resins

SUMMARY AND CONCLUSIONS

Using the state-of-the-art geochemical techniques applied in this project, the mechanism underlying the effectiveness of weak-base anion exchange resins was found to involve a reduction process. The Cr(III) retained by the resins, however, did not include the formation of a crystalline trivalent chromium compound. Instead, Cr(III) was homogeneously distributed in the resin beads and likely incorporated in the resin matrix. This finding indicates that Cr(III) is strongly bound to the resin and is not present in the form of precipitates that could break through the resin bed.

Regarding treatment residuals, both resins would be classified as a hazardous waste for disposal in California, but neither would be a federal hazardous waste according to TCLP. The treatment life of the PWA7 may be slightly limited by the accumulation of uranium to avoid generation of a low level radioactive waste.

Ultimately, this study has improved the general understanding of the weak-base resin technology and available operational strategies for Cr(VI) removal. Having gained information on weak-base anion exchange Cr(VI) removal mechanisms, Glendale is proceeding with implementation of a demonstration-scale facility to remove Cr(VI) from a 425 gpm well.

ACKNOWLEDGMENTS

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REFERENCES

Berry, A.J.; O'Neill, H.S.C. 2004. A XANES Determination of the Oxidation State of Chromium in Silicate Glasses. *American Mineralogist*. 89(5-6):790-798.

Bond, D.L.; Fendorf S. 2003. Kinetics and Structural Constraints of Chromate Reduction by Green Rusts. *Environ. Sci. Technol.*, 37(12):2750-2757.

Department of Toxic Substances Control (DTSC). 1991. Title 22, *California Code of Regulations* 66261.126, Division 4.5, Chapter 11, Appendix II. Sacramento, California.

Höll, W.H.; Bartosch, C.; Zhao, X.; He, S. 2002. Elimination of Trace Heavy Metals from Drinking Water Using Weakly Basic Anion Exchangers. *Geo- und Wassertechnologie*, 1(2002), 3:5-20.

O'Day, P.A.; Carroll, S.A.; Randall, S.; Martinelli, R.E.; Anderson, S.L.; Jelinski, J.; Knezovich, J.P. 2000. Metal Speciation and Bioavailability in Contaminated Estuary Sediments, Alameda Naval Air Station, California. *Environ. Sci. Technol.* 34(17):3665-3673.

USEPA. 1998. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Publication SW-846.

Wilkin, R.T.; Su, C.; Ford, R.G.; Paul C.J. 2005. Chromium-removal Processes During Groundwater Remediation by a Zerovalent Iron Permeable Reactive Barrier. *Environ. Sci. Technol.* 39(12):4599-4605.

8. ICW 2008 Proceedings

Chromium Treatment for Glendale, California’s Groundwater: Mechanistic Studies of Weak-Base Anion Exchange

Chromium Treatment for Glendale, California's Groundwater: Mechanistic Studies of Weak-Base Anion Exchange

Presentation at the Inorganic Contaminants Workshop

Nicole K. Blute, PhD

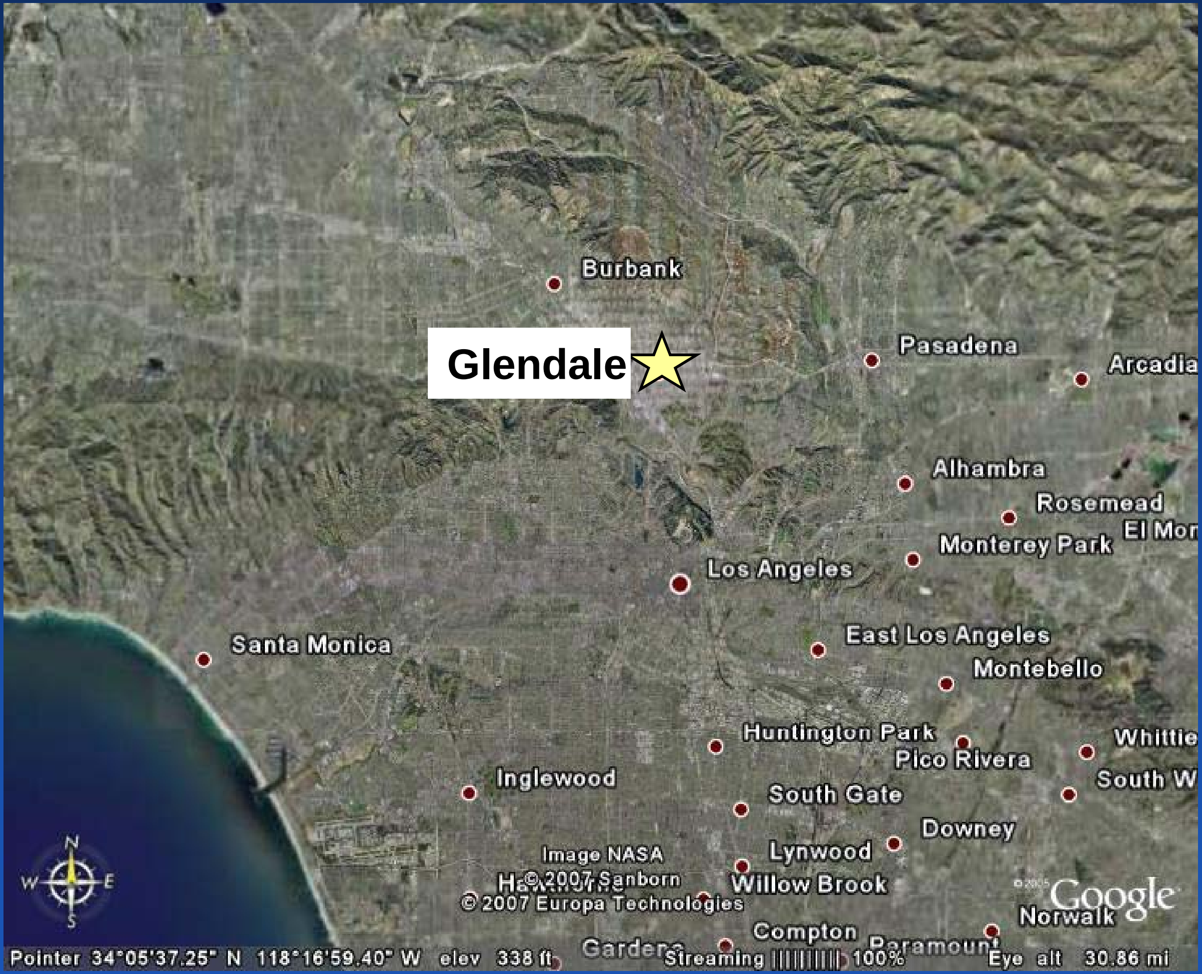
Co-authors: Michael J. McGuire, Peter Kavounas, Daniel J. Brabander, Matthew Newville, Sudipta Sarkar, and Arup SenGupta

January 29, 2008

Outline

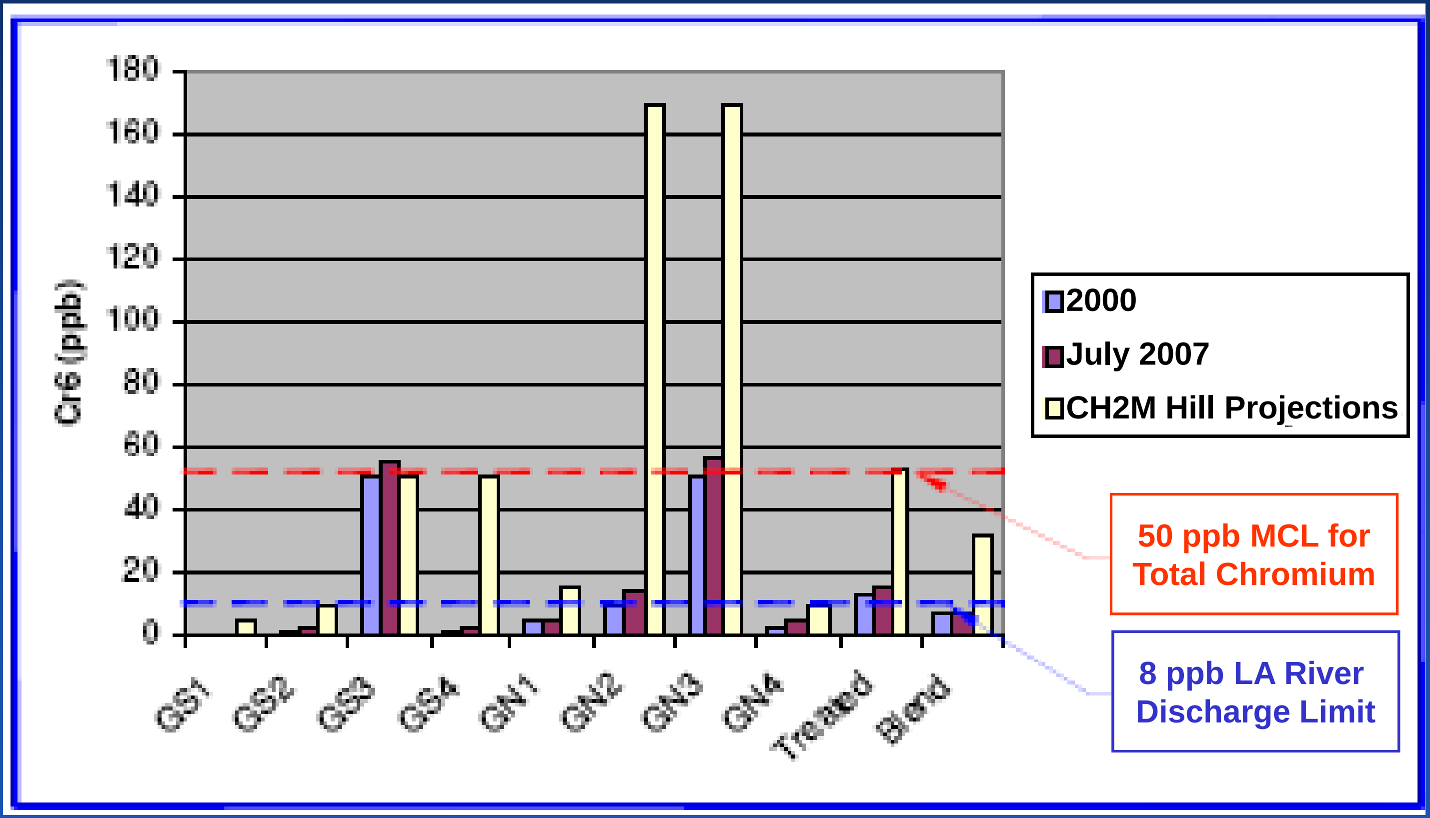
- Introduction to Cr(VI) at Glendale
- Methods for Analyzing Contaminant Removal Processes
    - XRF, XRD, SEM, Chemical tests, XAFS, Leaching procedures
- Treatment Implications from Analytical Results
- Disposal Options for Treatment Residuals
- Summary and Conclusions

Introduction – Case Study of Cr(VI) in Glendale



- GWTP- Facility to treat VOCs (est. 2000)
- Groundwater also contained Cr(VI)
- The movie “*Erin Brockovich*” generated significant media attention in 2000
- The Glendale City Council set a goal more aggressive than the California MCL
- NTP study

Introduction – Anticipated Cr(VI) Concentrations

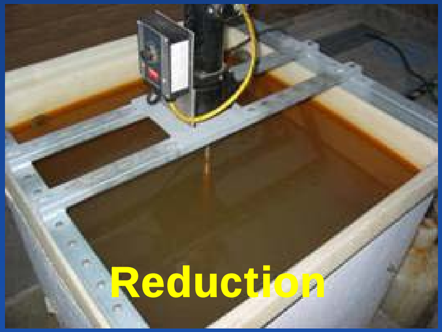


50 ppb MCL for Total Chromium

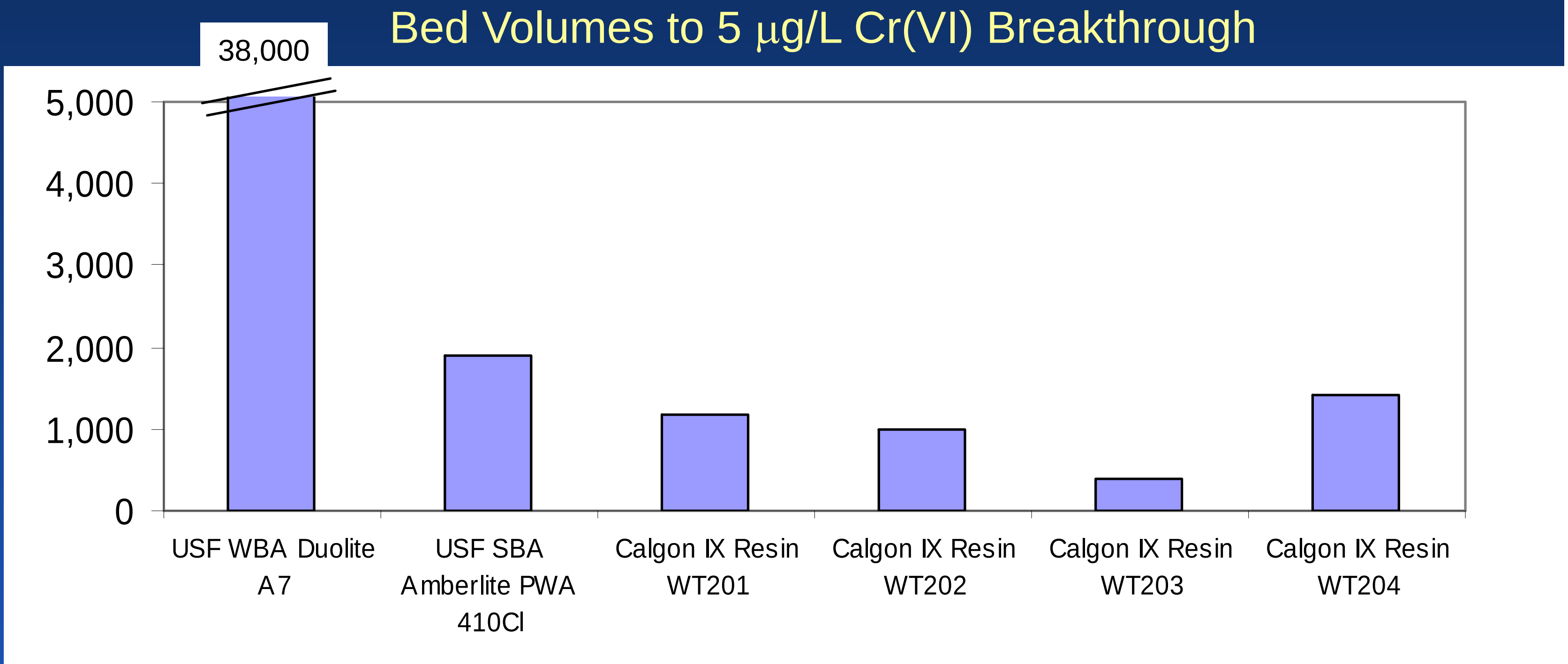
8 ppb LA River Discharge Limit

Introduction – Cr(VI) Treatment Technologies

- Weak base anion exchange (disposable)
- Strong base anion exchange (regenerated)
- Reduction-coagulation-filtration



Introduction – Effectiveness of WBA Resins for Cr(VI) removal



- 10-20x greater capacity of WBA resins
- Follow-up tests indicated up to about 100,000 BV may be expected if vessels operated in lead-lag configuration

Introduction – Glendale Water Quality

Constituents	**Typical Concentration**
Alkalinity	200 mg/L as $CaCO_3$
Arsenic (total)	< 2 µg/L
Chromium (total)	35-40 µg/L
Chromium (hexavalent)	35-40 µg/L
Conductivity	850 µS/cm
Copper	20 µg/L
Hardness	350 mg/L as $CaCO_3$
Iron (total)	< 6 µg/L
Manganese	< 20 µg/L
Nitrate	7 mg/L as NO_3
pH	6.8
Phosphate	0.3 mg/L as PO_4
Silicate	33 mg/L as SiO_2
Sulfate	100 mg/L as SO_4
Uranium	1.4 pCi/L (approx. 1.8 µg/L)
Vanadium	7 µg/L

Introduction – WBA Residuals

- Hints of speciation change:
  - Conversion from amber color to greenish-black
  - Leakage of Cr(III) at low pH

Methods for Analyzing Contaminant Removal Processes

Leachability:
TCLP, WET

Speciation:
XAFS

Elemental Composition:
XRF

Crystallinity:
XRD

Distribution:
SEM

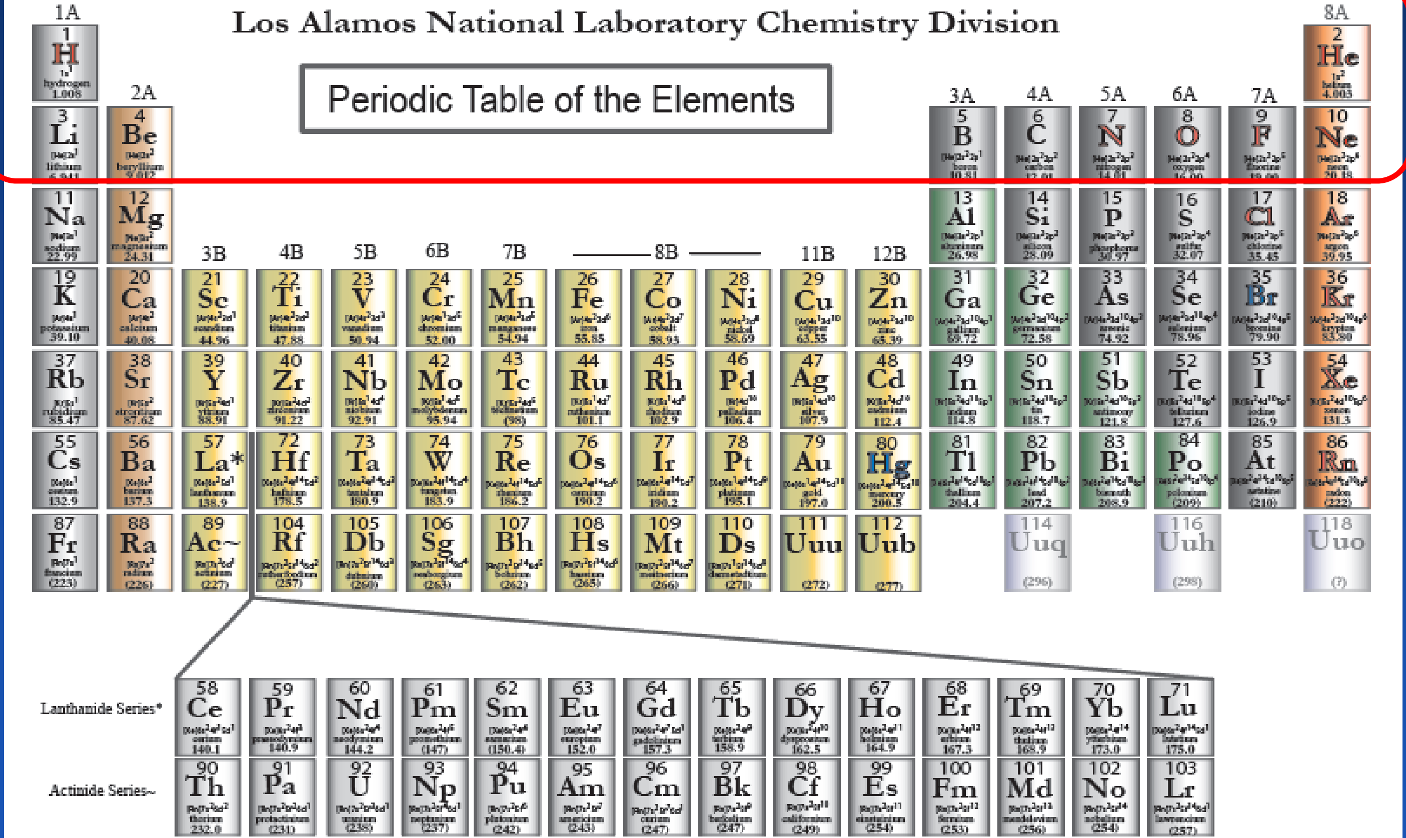
Mechanism:
Chemical Tests

Methods for Analyzing Contaminant Removal Processes - XRF

- Used to determine composition of solid materials
- Elemental composition is quantified from sodium through uranium with detection limits of µg/g levels
- X-rays hit the sample, fluorescent intensities are measured, and internal calibration curves determine the concentration of a range of elements simultaneously

Spectro XEPOS XRF Spectrometer

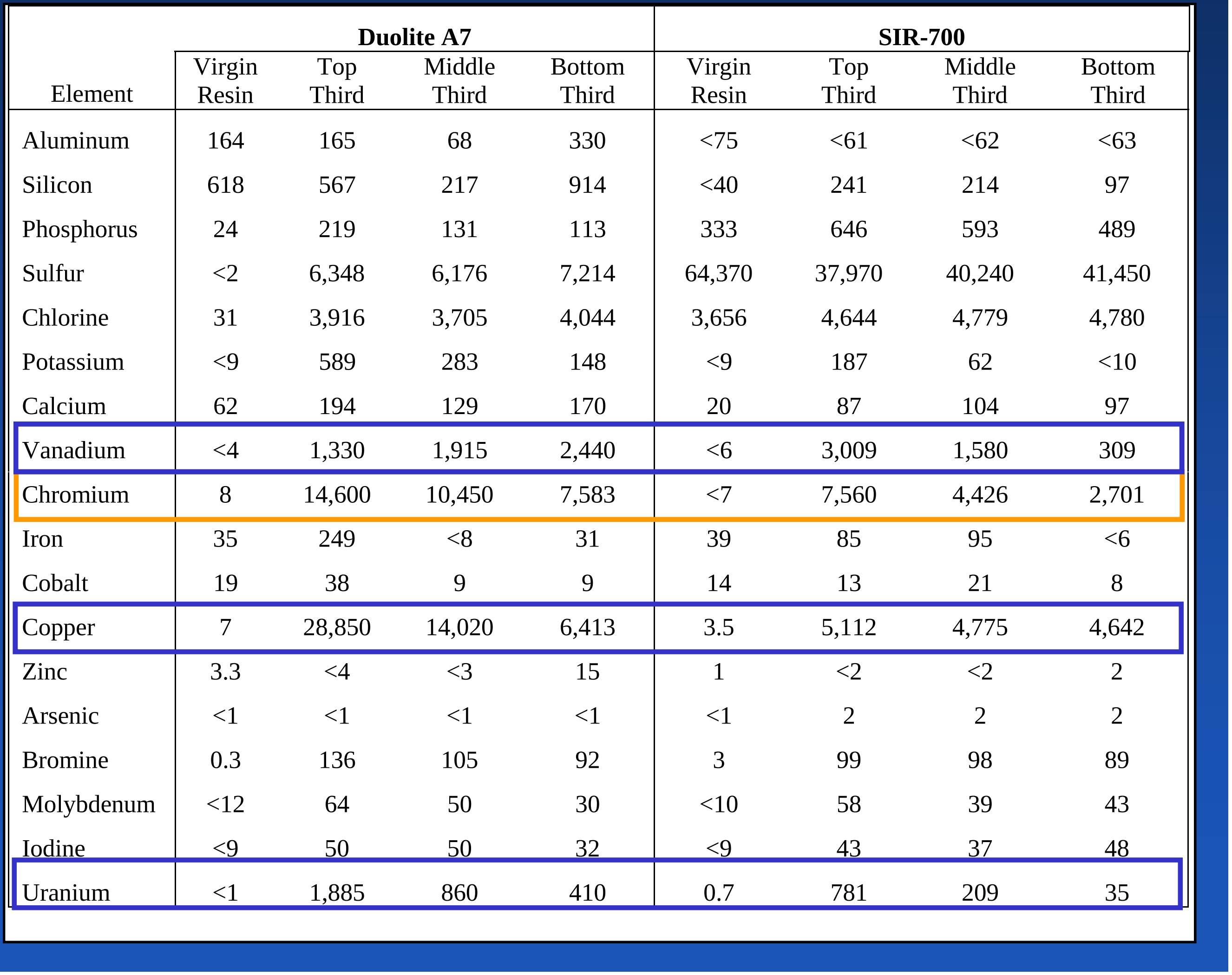
Methods for Analyzing Contaminant Removal Processes - XRF



No elements lighter than Na are detected

Methods for Analyzing Contaminant Removal Processes - XRF

- High concentrations of Cr – up to 1.4%
- Also removal of Cu, U, and V

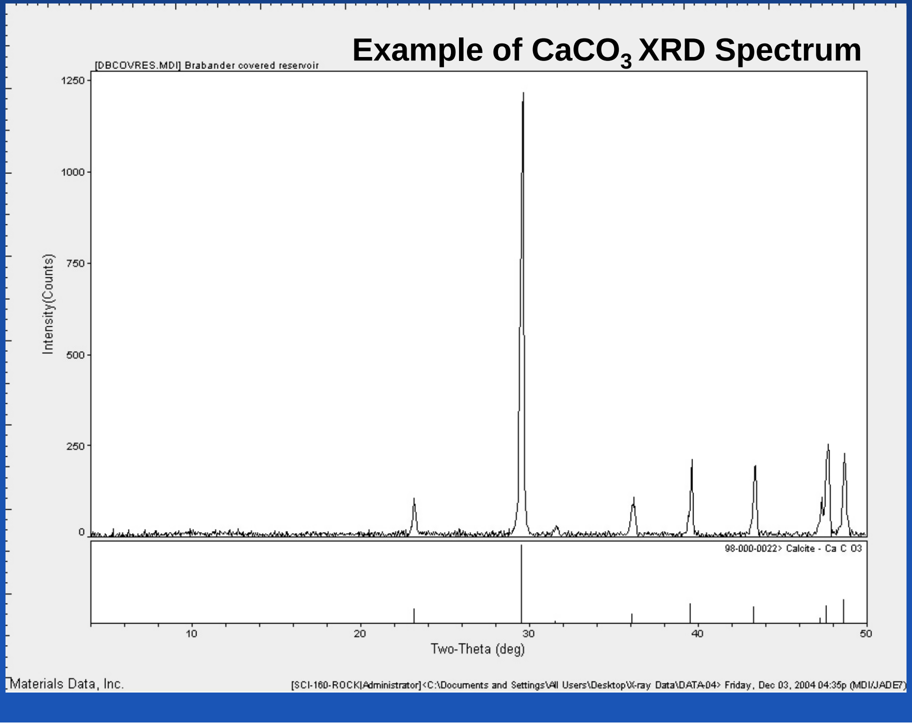


Element	Duolite A7				SIR-700			
	Virgin Resin	Top Third	Middle Third	Bottom Third	Virgin Resin	Top Third	Middle Third	Bottom Third
Aluminum	164	165	68	330	<75	<61	<62	<63
Silicon	618	567	217	914	<40	241	214	97
Phosphorus	24	219	131	113	333	646	593	489
Sulfur	<2	6,348	6,176	7,214	64,370	37,970	40,240	41,450
Chlorine	31	3,916	3,705	4,044	3,656	4,644	4,779	4,780
Potassium	<9	589	283	148	<9	187	62	<10
Calcium	62	194	129	170	20	87	104	97
Vanadium	<4	1,330	1,915	2,440	<6	3,009	1,580	309
Chromium	8	14,600	10,450	7,583	<7	7,560	4,426	2,701
Iron	35	249	<8	31	39	85	95	<6
Cobalt	19	38	9	9	14	13	21	8
Copper	7	28,850	14,020	6,413	3.5	5,112	4,775	4,642
Zinc	3.3	<4	<3	15	1	<2	<2	2
Arsenic	<1	<1	<1	<1	<1	2	2	2
Bromine	0.3	136	105	92	3	99	98	89
Molybdenum	<12	64	50	30	<10	58	39	43
Iodine	<9	50	50	32	<9	43	37	48
Uranium	<1	1,885	860	410	0.7	781	209	35

Methods for Analyzing Contaminant Removal Processes - XRD

- Crystal structure is probed with XRD
- Intensities are measured as a function of the angle at which x-rays are diffracted
- Unique fingerprint is matched to a database of known compounds

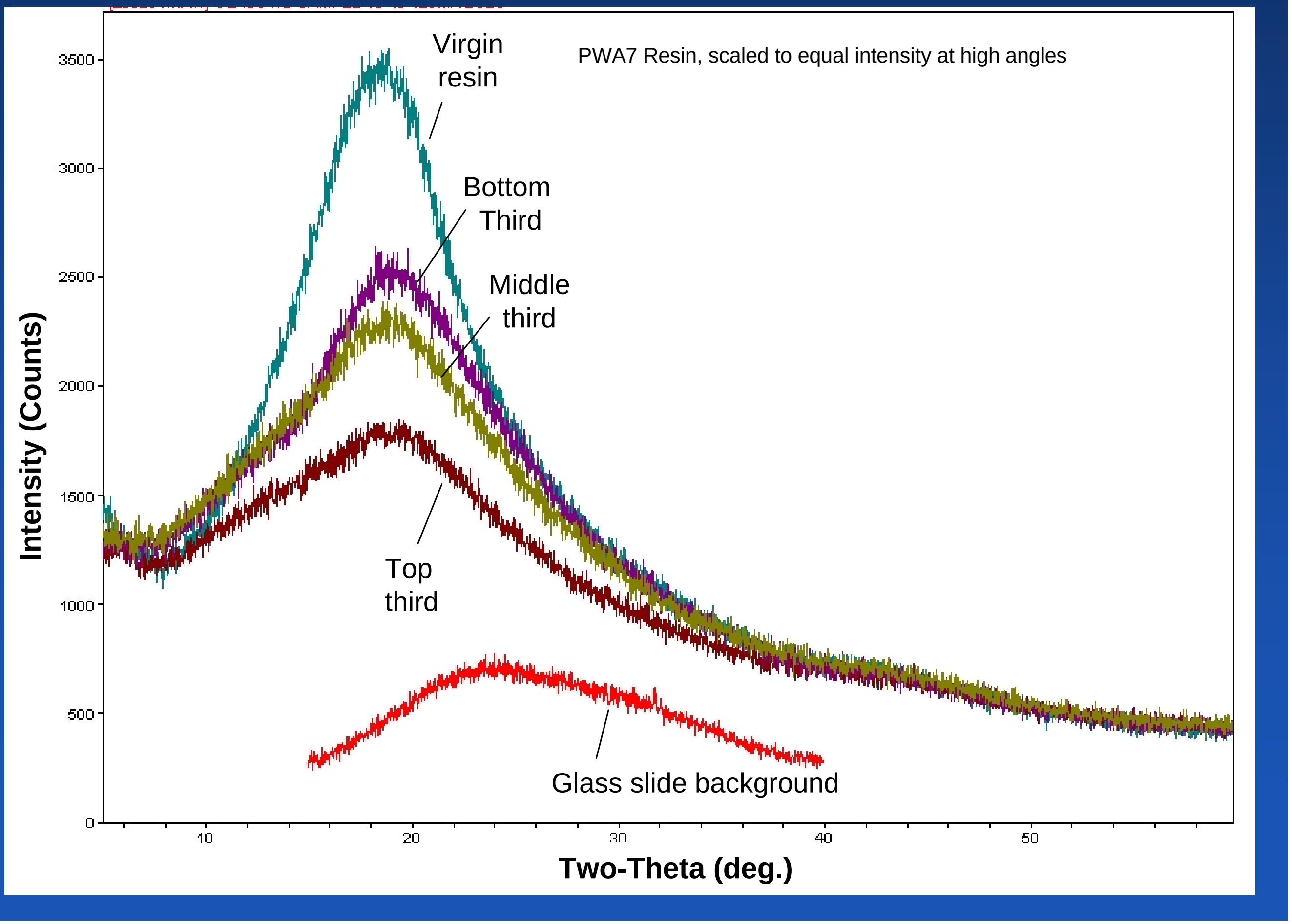
Rigaku 300 diffractometer with rotating copper anode



Example of $CaCO_3$ XRD Spectrum

Methods for Analyzing Contaminant Removal Processes - XRD

- No crystalline precipitates observed comprising >1% of material

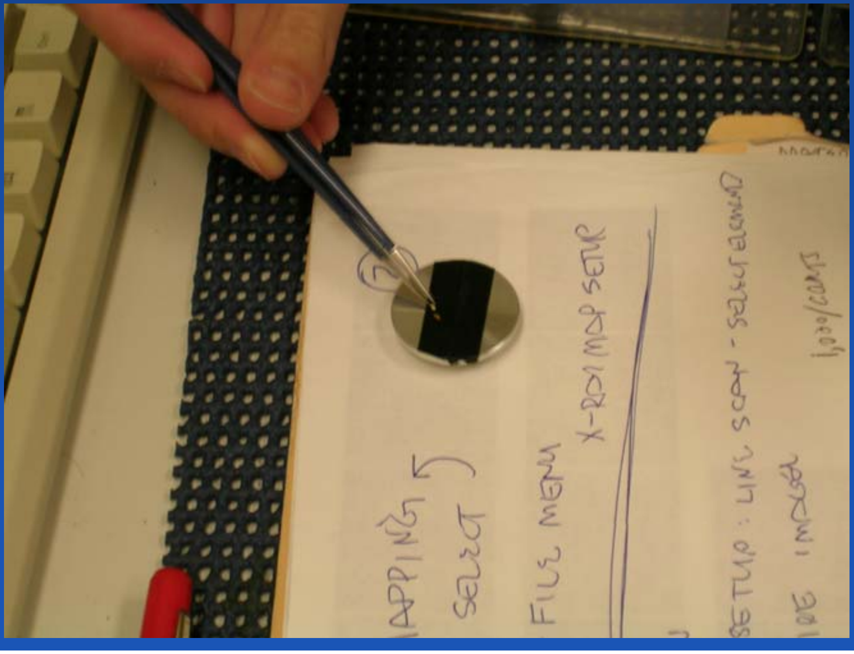


PWA7 Resin, scaled to equal intensity at high angles

Methods for Analyzing Contaminant Removal Processes – SEM

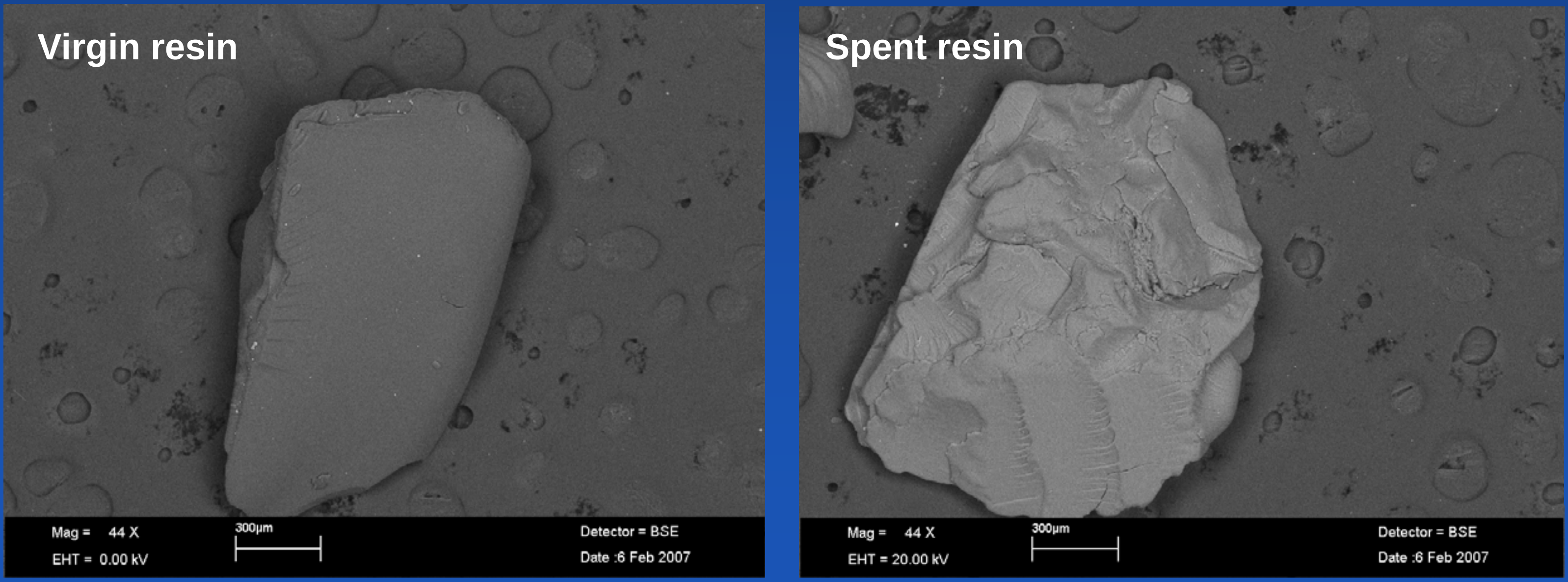
- High magnification of solid samples
- Distribution analysis of Cr – hot spots or homogeneous?

LEOVP438 with iXRF energy dispersive analytical system



Methods for Analyzing Contaminant Removal Processes – SEM-EDX

- Higher brightness on spent resin
- Homogeneous distribution of brightness (i.e., no “hot spots”)
- Contributors to brightness included Cr, Cu, V, U



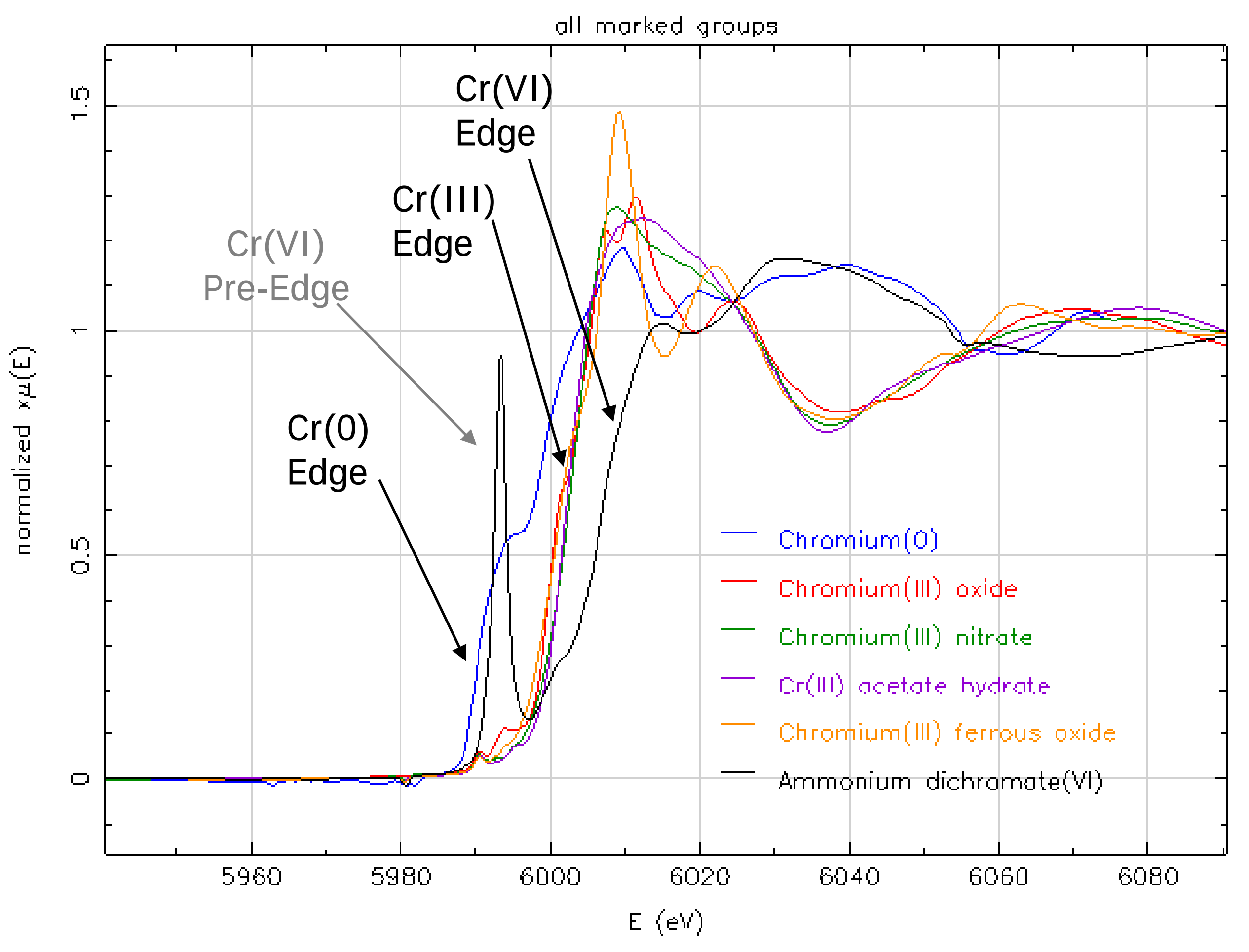
44x magnification

Methods for Analyzing Contaminant Removal Processes - XAFS

- X-ray absorption fine structure (XAFS) analysis was performed at the Advanced Photon Source (APS) facility (Beamline 13-BM) in Argonne National Lab (Chicago, IL)
- XAFS was used to directly determine the Cr oxidation state on the spent resins

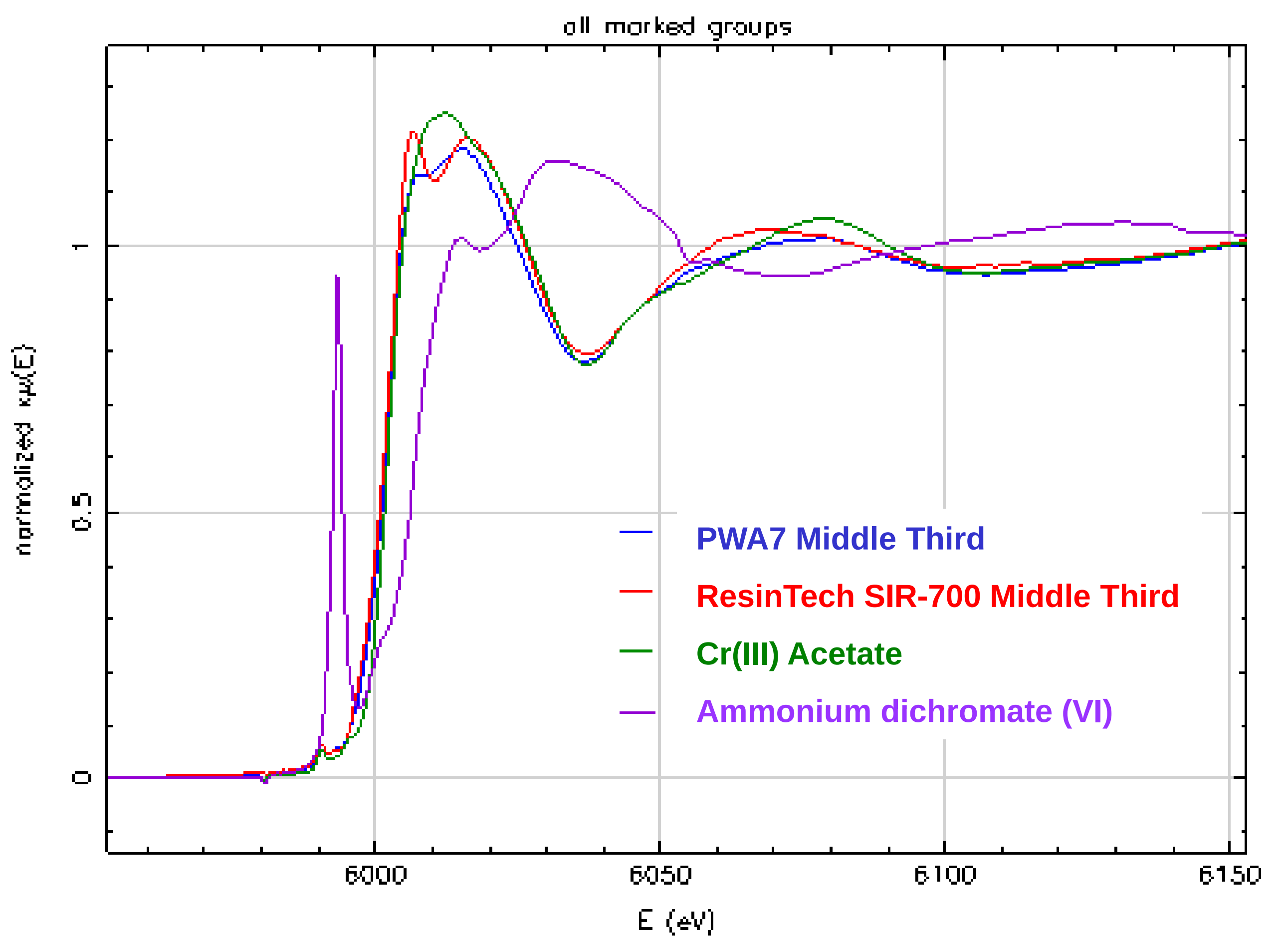


Standard Compound XAFS (Cr edge)



- Edge energies – same for compounds with the same oxidation state
- The Cr(VI) spectrum also has a sharp pre-edge feature – this is absent in Cr(III) spectra
- Pre-edge feature due to d-p orbital hybridization

Spent WBA Resins (Cr edge)



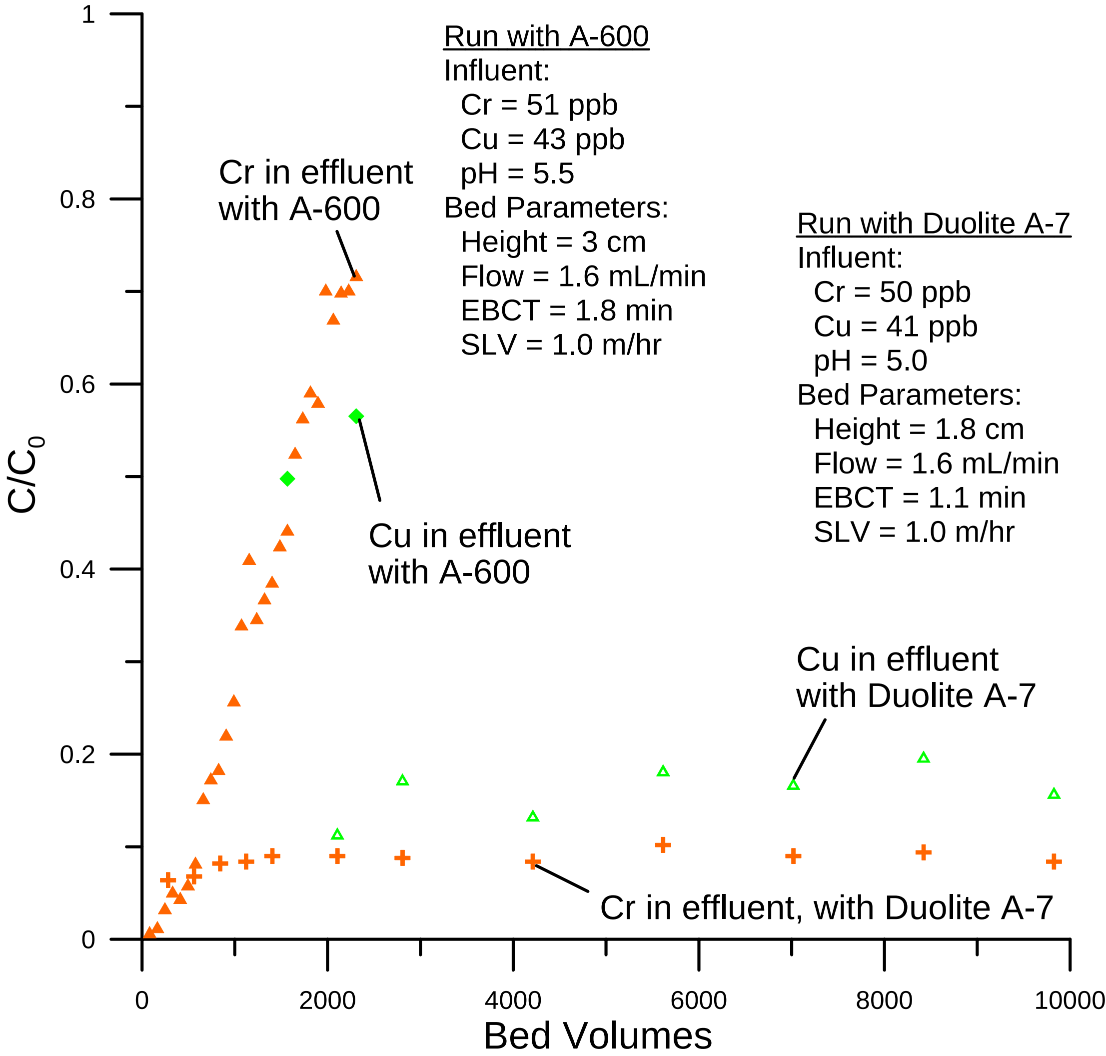
- No pre-edge feature
- Resin spectra overlapped with Cr(III) compounds
- Strong evidence that more than 95% of the Cr in the resins is Cr(III)

Methods for Analyzing Contaminant Removal Processes – Chemical Tests

- Lehigh University lab

Question	Test
Would SBA resin operated at a lower pH also show a similar Cr(VI) capacity due to Cr speciation?	WBA and SBA column tests with pH 5-5.5 water; observe Cr breakthrough curves
Does copper bind to the nitrogen groups and complex Cr(VI), as observed with some SBA resins?	WBA resin column tests using virgin resin and resin pre-loaded with copper; observe Cr breakthrough curves

SBA Resin vs. WBA resin at low pH

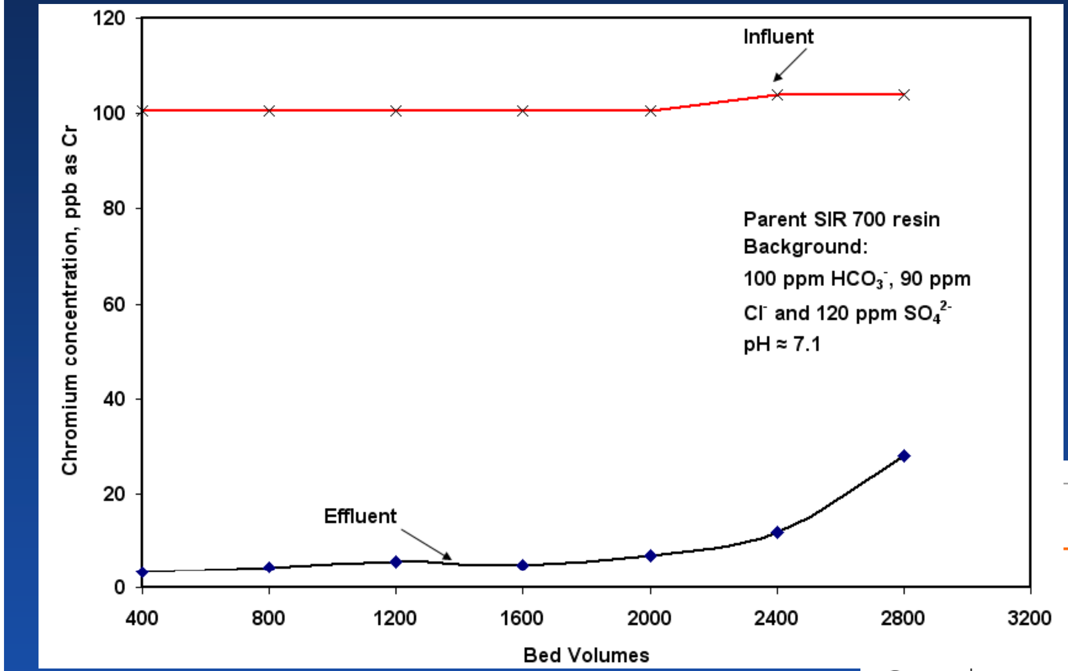


Run with A-600
Influent:
Cr = 51 ppb
Cu = 43 ppb
pH = 5.5
Bed Parameters:
Height = 3 cm
Flow = 1.6 mL/min
EBCT = 1.8 min
SLV = 1.0 m/hr

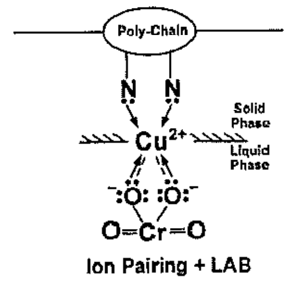
Run with Duolite A-7
Influent:
Cr = 50 ppb
Cu = 41 ppb
pH = 5.0
Bed Parameters:
Height = 1.8 cm
Flow = 1.6 mL/min
EBCT = 1.1 min
SLV = 1.0 m/hr

- Ion exchange not the only mechanism

Cu Involvement in WBA Mechanism

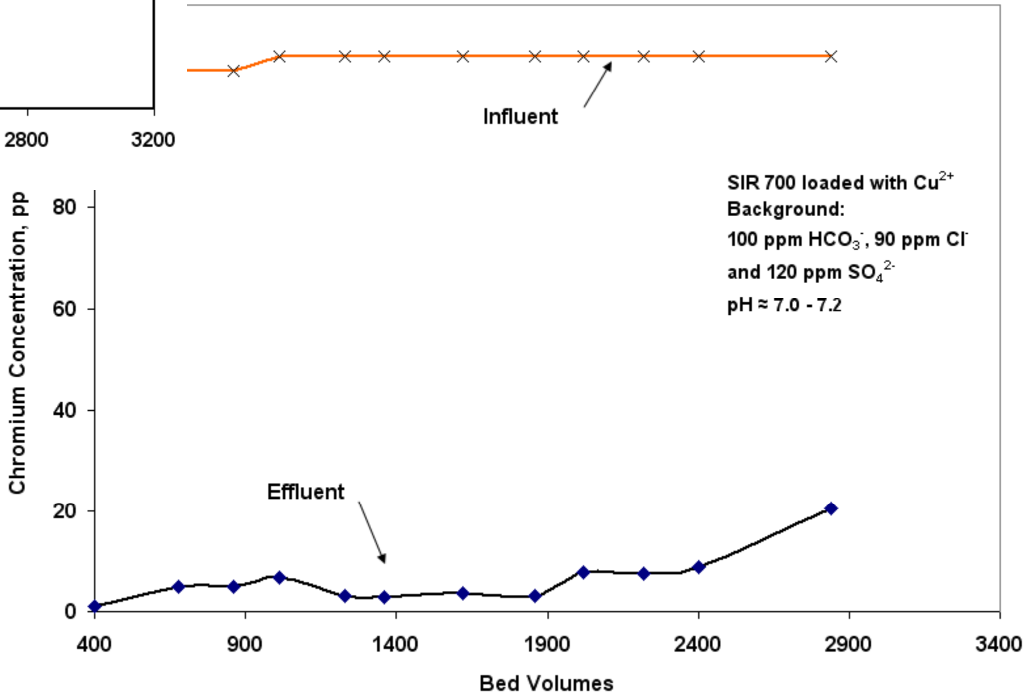


- Tested mechanism:



Zhao et al. 1998

- However, no difference observed between virgin SIR-700 resin and resin pre-loaded with Cu



Treatment Implications from Analytical Results

- Low pH is necessary for maximizing Cr(VI) capacity on WBA resins (but not SBA resins) – protonation of amine group, less OH- competition, $HCrO_4^-$ speciation
- Cr(VI) is reduced to Cr(III) by the two WBA resins, perhaps after being adsorbed
- Cr is not retained on the resins in the form of small precipitates – added stability
- Lack of crystalline solids suggests another electron donor perhaps part of the ion exchange functional groups or the backbone of the resin material
- Other elements are simultaneously removed by the WBA resins, such as U, V, and Cu – may limit operational life

Disposal Options for Treatment Residuals

- Federal RCRA Hazardous Waste Determination
    - Toxicity Characteristic Leaching Procedure (TCLP)
- State-specific requirements
    - e.g., California Waste Extraction Test (CWET)
- Additional tests
    - e.g., Uranium content

Disposal Options for Treatment Residuals – TCLP Results

- PWA7 and SIR-700 resins **passed** the TCLP test for metals analysis

TCLP Metals Analysis Results on Spent WBA Resins*

	Rohm & Haas PWA7	**ResinTech SIR-700**	**Regulatory Limit**
Chromium	260	45	**5,000**
Lead	24	15	**5,000**
Copper	187	607	***/***
Zinc	52	45	***/***

* Concentrations in the table are expressed in µg/L (only detected elements are listed)

Disposal Options for Treatment Residuals – CWET Results

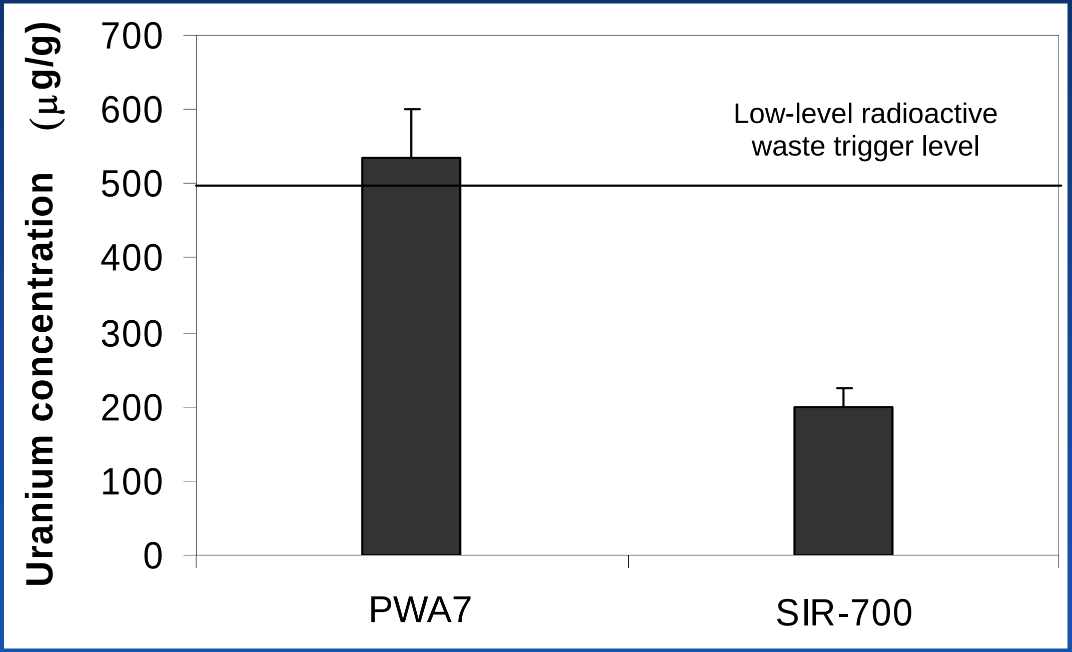
- Both resins **failed** the CWET test
- The copper concentration on the PWA7 resin was also close to the regulatory limit

California WET Metals Analysis (STLC) Results*

	Rohm & Haas PWA7	**ResinTech SIR-700**	**Regulatory Limit**
Barium	29	ND	**100,000**
Beryllium	3	ND	**750**
Chromium	**11,200**	**10,400**	**5,000**
Copper	22,400	13,300	**25,000**
Nickel	52	ND	**20,000**
Vanadium	3,270	3,690	**24,000**
Zinc	443	81	**250,000**
Molybdenum	116	116	**350,000**

* Concentrations in the table are expressed in µg/L (only detected elements are listed). ND = non-detect.

Disposal Options for Treatment Residuals - Total Uranium Results



- PWA7 exceeded 500 ppm after approximately 113,000 BV water treated
- A low level mixed radioactive waste could be avoided by operating to approximately 100,000 BV
- Possibility of ore recovery

Summary and Conclusions

- Mechanism of WBA resin treatment involves reduction of Cr(VI) to Cr(III)
- No evidence of crystalline Cr(III) precipitates on the resins
- WBA resins likely to be classified non-haz waste by federal standards and haz waste by CA standards
- Uranium accumulation may limit useful operational life of one resin rather than capacity

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- UCLA: Mel Suffet
- LADWP: Pankaj Parekh
- MWDSC: Sun Liang
- EBMUD (formerly with CDPH): Rick Sakaji
- CDPH: Heather Collins
- CDM: Charles Cron

Questions?

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9. WBA Demonstration-Scale Experimental Design

Experimental Design and Operations Plan for Hexavalent Chromium Removal Using Weak-Base Anion Exchange Resin: A Demonstration-Scale Study

Glendale Water and Power

141 North Glendale Ave, 4th Floor • Glendale, CA 91206

Experimental Design and Operations Plan for Hexavalent Chromium Removal using Weak-Base Anion Exchange Resin:

A Demonstration-Scale Study

October 2007

(**Note**: The original Experimental Design includes HCl addition; Documents comprising Appendices A and B were subsequently updated with CO_2 pH depression and were substituted for the originals)

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A. Preliminary Design Report
B. Quality Assurance Project Plan
C. Pump Curve Evaluation
D. Corrosivity Evaluation of the Treated WBA Water

1. Introduction

1.1. Project Background

The City of Glendale's groundwater supplies in the San Fernando Valley have been contaminated with a wide variety of chemicals, including hexavalent chromium [Cr(VI)], trichloroethylene (TCE), perchloroethylene (PCE), 1,2,3-trichloropropane (TCP), and others, mainly as a result of the improper disposal of industrial waste products. Volatile organic compounds (VOCs) are treated with air stripping and granular activated carbon (GAC), and the treated water is served to customers. Although Cr(VI) was also found in the groundwater supplies when VOC treatment was installed, Cr(VI) levels were below the maximum contaminant level (MCL) and Cr(VI) treatment was not included with the VOC treatment facilities.

Until June 2007, the health effects of Cr(VI) in drinking water were uncertain; Cr(VI) was a proven carcinogen by inhalation but little evidence existed to demonstrate the impact of Cr(VI) by ingestion. However, a recent study conducted by the National Toxicology Program (NTP) showed that Cr(VI) is a carcinogen by ingestion in animal studies (NTP 2007). Even prior to this study, the governor of California mandated that the California Department of Public Health (DPH) establish a Cr(VI) MCL. First, the Office of Environmental Health Hazard Assessment (OEHHA) must set a public health goal (PHG), which will likely be based on the new NTP findings. In Glendale, public concern about Cr(VI) in the groundwater supply caused the city to embark on a multi-phase study to identify and install Cr(VI) treatment in anticipation of a Cr(VI) MCL lower than the current total Cr [i.e., Cr(VI) plus Cr(III)] MCL in California.

In the year 2000, the City of Glendale, along with the Cities of Los Angeles, Burbank, and San Fernando, initiated a testing program to develop a full-scale Cr(VI) treatment system capable of removing Cr(VI) to low parts-per-billion levels. The **Phase I Bench-scale study** was conducted to improve our understanding of fundamental chromium chemistry and to screen promising technologies for their ability to treat and remove Cr(VI) to very low levels. The Phase I study is complete and the final report was published by AwwaRF (Brandhuber et al. 2004). The **Phase II Pilot-scale study** was initiated in the summer of 2003 to further test the promising Cr(VI) removal technologies at the pilot scale (i.e., several gallons-per-minute flows) using Glendale groundwater. A final report on the Phase II pilot-scale study was completed in 2005 (MEC 2005). Selected results were also published in peer-reviewed scientific journals (Qin et al. 2005, McGuire et al. 2006).

The **Phase III Demonstration-scale study** will finalize the treatment evaluation, residuals assessment, and cost estimate development by implementing one or more Cr(VI) removal technologies at flows of 500 to 1,000 gpm. The initial part of the Phase III effort was designated as the Phase III Bridge project, which included additional studies to finalize testing of weak-base anion exchange resins for Cr(VI) treatment, refinement of treatment technology cost estimates based on Phase III Bridge project results, and assembly of an expert panel to recommend the one or more treatment processes for demonstration-scale testing. The Phase III Bridge project was completed in early 2007. The second part of the Phase III study, the Demonstration-scale study, is the focus of this document and will be discussed in the following sections. **Phase IV** is the construction of a full capacity system to treat all of Glendale's impacted groundwater supplies.

1.2. Project Description

The Phase III Demonstration-scale study will test Cr(VI) removal using weak-base anion exchange resin (WBA) to treat a 425 gpm well. Depending on additional funding availability, the City of Glendale may also construct a reduction/coagulation/filtration (RCF) treatment system on one or more other wells. Treated product water will have reduced Cr(VI) concentrations and will be used for human consumption after blending.

This document is intended to provide the experimental design for the WBA system, which includes the WBA process description (Chapter 2), study objectives (Chapter 3), data collection and sampling protocol (Chapter 4), and operations evaluation (Chapter 5).

The experimental plan of the RCF system is not included in this document. A separate RCF experimental plan will be developed as an additional document at a later time.

2. WBA Process Description

2.1. General

Cr(VI) removal by WBA resin is a novel application of ion exchange for drinking water treatment. Originally, WBA resin was believed to behave similarly to strong-base anion exchange (SBA) resins in terms of removal mechanism, except that the WBA resins are only useful in the acidic pH range where the functional groups are protonated and thus have positively charged exchange sites to attract Cr(VI) as chromate or bichromate anions. However, the WBA resin tested in the Phase II Pilot-scale study (Duolite A7, now called PWA7, resin provided by Rohm & Haas) showed a 20 times higher Cr(VI) removal capacity compared with five SBA resins tested (McGuire et al. 2006). Other observations, such as leakage of trivalent chromium [Cr(III)] during periods in which pH values were lower than 5.5, indicated that an ion exchange mechanism alone was not likely responsible for all of the Cr(VI) removal by WBA resin.

As part of the Phase III Bridge project, five WBA resins were tested to evaluate Cr(VI) capacity. In addition, the impact of pH on the capacity of the top performers was assessed to minimize acid addition requirements. Duolite A7 resin again showed a high Cr(VI) capacity along with another WBA resin (ResinTech SIR-700, which did not perform quite as well as the Duolite A7 initially but improved over time). Testing confirmed that more than 95% of the Cr(VI) retained on both resins was in the form of Cr(III), as observed directly by x-ray absorption spectroscopy. The true mechanism of Cr(VI) removal and retention by the WBA resins is understood to involve ion exchange followed by reduction.

To date, WBA resin has only been tested in bench- and pilot-scale studies for drinking water applications. The proposed demonstration-scale WBA system will be the first installation of this technology in drinking water treatment.

Addition design details not shown in this Experimental Plan are contained within the “Preliminary Design Report: Well GS-3 WBA Chromium 6 Removal Facility” (Malcolm Pirnie, 2007a; Appendix A) or the Detailed Design Drawings.

2.2. Location of the WBA System

The WBA system is proposed to be located at the Glendale South Operable Unit well site GS-3 adjacent to Goodwin Street in the City of Los Angeles. The well site area is a paved truck parking area that is part of a large Ralph’s Grocery Distribution Center. The City of Glendale has an easement within the Ralph’s property. The area is paved with asphalt concrete and is relatively flat. Well GS-3 has a capacity of 425 gpm and is one of the high Cr(VI) concentration wells, with a current Cr(VI) concentration of approximately 35 μg/L. The zoning in the area is manufacturing/commercial. Figure 2-1 shows an aerial photo of the GS-3 well site. Figure 2-2 shows the proposed WBA facility site layout with the property easement boundaries.

The GS-3 site was selected for the WBA system demonstration-scale study for the following reasons: (1) the GS-3 well is one of the high Cr(VI) wells, with a current Cr(VI) concentration of approximately 35 µg/L; (2) a pair of unused GAC vessels at the GS-3 well site can be retrofitted for WBA resin, thus minimizing the capital costs for ion exchange vessels.

Figure 2-1: Aerial photo of the GS-3 well site

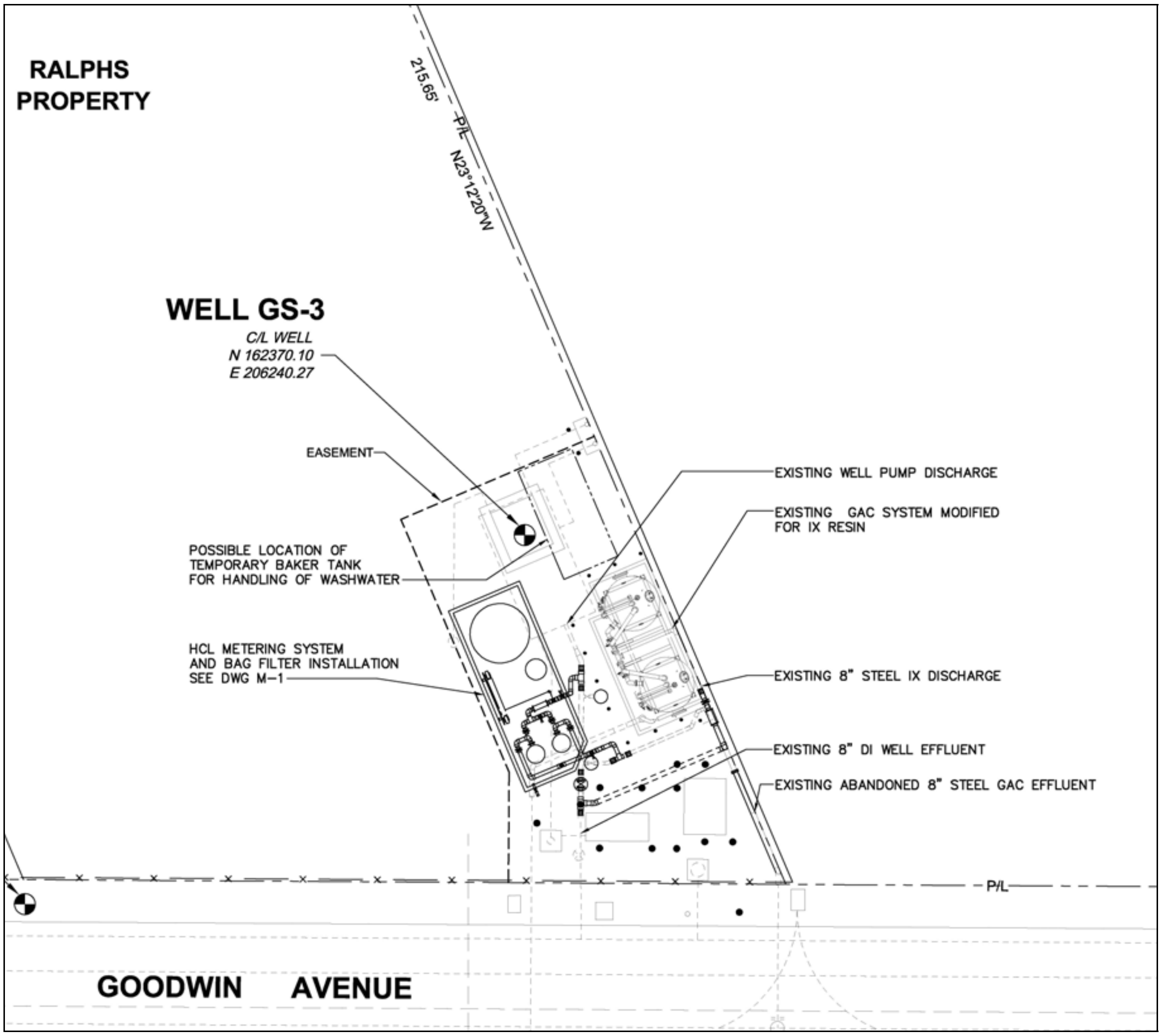

Figure 2-2: WBA facility site layout with property easement boundaries

2.3. WBA Process Components

Figure 2-3 provides a process flow schematic for the WBA system. The system will consist of a pair of lead/lag vessels with upstream acid addition. Due to its high capacity and difficulty in regeneration, WBA resin will be used as a once-through, non-regenerable media.

The major components of the WBA system are briefly described in the following sections. Note that the WBA system design parameters presented below are conceptual only. The construction of the WBA system should follow the detailed design report prepared by the selected contractor.

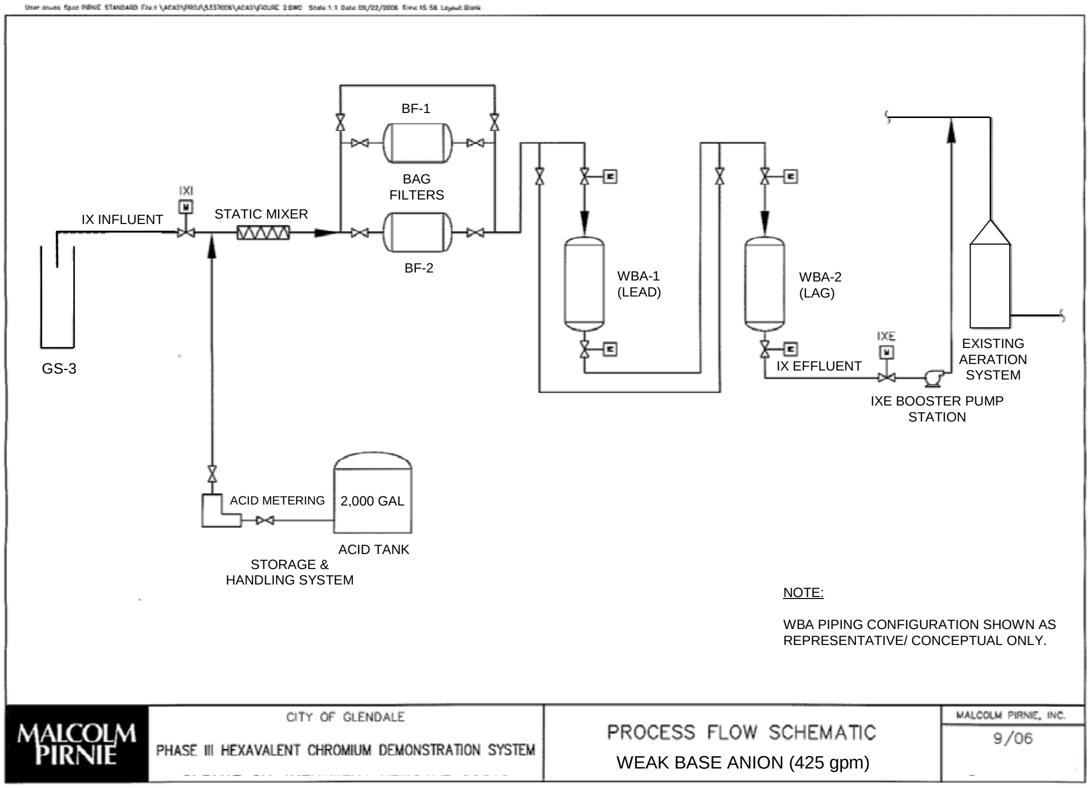

Figure 2-3: Process flow schematic of the WBA system

2.3.1. Ion Exchange (IX) Vessels

The City of Glendale installed two steel vessels adjacent to the Well GS-3 site several years ago for granular activated carbon (GAC) treatment of VOCs. This system was never used for several reasons, including a short-term program to reduce pumping from Well GS-3 and other high Cr(VI) wells and increase pumping from the low Cr(VI) wells. This operational strategy, however, was allowed only temporarily under an agreement with the EPA.

For the demonstration-scale study, the two 8-ft. diameter vessels will be retrofitted to support resin material for Cr(VI) removal. The retrofitted IX vessels will have sample ports to accommodate sampling at the 50% bed depths and on effluent piping of each vessel.

Siemens (formerly US Filter) and Rohm & Haas recommend a volumetric design flow rate for the WBA resin of approximately 2.5 gpm per cubic feet and bed volumes of 185 cubic feet for the 8-ft diameter vessel.

2.3.2. Acid Feed and Control System

The acid feed and control system will be used to inject hydrochloric acid (HCl) into the GS-3 well water to obtain a pH of 6.0. The operating pH of 6.0 was determined to be effective for Cr(VI) removal during the Phase III Bridge project. Major components of the acid feed and control system include an acid storage tank, chemical feed pump(s), an online pH probe, and programmable logic controller (PLC).

Acid requirements for pH depression to 6.0 are approximately 69 mg/L of 36% HCl per gallon of water treated. The daily acid usage for the 425 gpm design flow rate is therefore approximately 100 gallons per day (gpd).

The acid storage tank will have a capacity of 2,000 gallons, with secondary containment and a scrubber system for acid vapor. This volume will provide at least a two week supply of acid.

Two variable speed metering pumps (one operating and one standby) will be located adjacent to the acid storage tank to pump HCl into the raw well water. The chemical pump speed will be flow paced.

2.3.3. WBA Backwash System

The WBA vessels will have the capability for backwashing the resin. Backwash supply water will be provided from the common GS wells' transmission line. Once the headloss across the media bed exceeds a pre-defined value (TBD), backwashing will be initiated. Waste backwash water from the WBA vessels will flow to a temporary roll-off containment tank and then slowly into the sewer.

3. Study Objectives

The objectives of the Phase III Demonstration-scale WBA study include the following:

- Evaluate Cr(VI) removal capacity of WBA resin at the demonstration-scale (approximately 425 gpm) and the ability to scale-up bench and pilot results;
- Quantify demonstration treatment performance with respect to Cr(VI) removal over extended periods of time (i.e., at least one year);
- Assess the impact of WBA resin treatment on finished water quality, including any leaching of nitrosamines, and develop mitigation strategies;
- Optimize day-to-day operations of the WBA treatment system and develop a comprehensive operations and maintenance manual;
- Assess the reliability of the demonstration-scale WBA technology during a year of operations and identify necessary backwashing or fluffing frequency;
- Confirm residuals optimization and disposal strategies identified in the Phase III Bridge project;
- Verify unit cost information developed in the pilot study with actual treatment costs; and
- Publicly disseminate project plans and findings to a wide audience, including water agencies also concerned with Cr(VI) in water supplies, California DPH, the USEPA, and consumers.

4. Data Collection and Study Protocol

Evaluation of WBA exchange resin for Cr(VI) removal at the demonstration scale will focus on the measurement of key chemical and process parameters to fully test the utility of the treatment process. Of critical importance, Cr(VI) and total Cr concentrations in influent, 50% bed depth, lead vessel effluent, and lag vessel effluent water samples will be monitored. In addition, other process-related parameters and water quality constituents described below will be measured to assess operational effectiveness of the WBA technology and its impact on water quality.

The sections below provide an overview of the data collection and study protocol for the WBA system, which includes monitoring parameters, locations, frequency, and analytical approach. The comprehensive data collection and management plan is contained within the document entitled "The Treatment of Hexavalent Chromium in the City of Glendale Ground Water Supply: Phase III Demonstration-Scale WBA Resin Treatment Technology Evaluation – Quality Assurance Project Plan" (QAPP, Malcolm Pirnie 2007b). The QAPP is provided as Appendix B in this Experimental Design document.

4.1. Monitoring Parameters

4.1.1. Water Quality Parameters

Critical water quality parameters for the demonstration-scale WBA system include Cr(VI), total Cr, and pH. Pilot testing highlighted the importance of pH depression and constant pH control for the effective operation of WBA resin.

Other chemical and physical parameters, including temperature, conductivity, turbidity, and alkalinity, will be routinely measured. Anions that may impact ion exchange, such as sulfate, nitrate, and silicate, will be monitored. Nitrosamines, which have been found to leach from ion exchange resins, will be monitored during WBA facility startup to determine the amount of time necessary to flush the resins.

Table 4-1 summarizes the proposed sampling parameters for the Phase III WBA Demonstration-scale study.

4.1.2. Process Parameters

In addition to chemical and physical water quality analyses, process-related parameters will be recorded to evaluate the operations of the WBA system. The process-related parameters include flow rate, system pressure, headloss through the bag filters and resin vessels (both lead and lag vessels), backwash frequency, empty bed contact time (EBCT), numbers of bed volumes to breakthrough (> 5µg/L), numbers of bed volumes to 50% saturation of the lead vessel, and HCl feed rate and volume use rate.

4.1.3. Treatment Residuals

Treatment residuals, including exhausted ion exchange resin and backwash water, will also be assessed to confirm disposal options using the Toxicity Characteristic Leaching Procedure (TCLP, EPA Method 1311 as mandated by 40 CFR 261) and the California Waste Extraction Test (CWET). Pilot-scale testing indicated that the spent WBA resins would likely be classified a hazardous waste in the State of California based on total chromium concentrations leached during the California WET test. Uranium accumulated on the spent WBA resin will also be determined throughout the testing; PWA7 resin may need to be replaced prior to 50% resin breakthrough to avoid uranium concentrations exceeding 500 mg/kg (i.e., the threshold above which the waste could be classified a low-level radioactive waste). Table 4-1 also lists the required measurements for the treatment residuals

Table 4-1.
Analytical measurements for the WBA demonstration-scale study, identified as Critical (C) and non-critical (N/C) measurements

Sampling Types and Locations	Cr(VI)	Total Cr	pH	Temp.	SO_4^{2-}	NO_3^-	PO_4^{3-}	SiO_2	Alkalinity	Conductivity	Turbidity	Nitrosamines	TCLP, WET tests	Uranium
Raw water (before pH adjustment)			N/C											
Influent (after pH adjustment)	C	C	C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	C		
Lead Vessel 50% bed depth	N/C	N/C												
Lead Vessel Effluent	C	C	C	N/C										
Lag Vessel 50% bed depth	N/C	N/C												
Lag Vessel Effluent	C	C	C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	C		
Residuals (spent resin)													C	C
Residuals (backwash water)		C												

4.2. Monitoring Locations

All the samples collected for analysis will be obtained from the demonstration-scale study site at GS-3. Figure 4-1 shows a schematic of the WBA system with sampling ports for water quality parameters highlighted. Table 4-1 also lists the sampling locations.

Sampling locations for the WBA treatment system include raw water (before acid addition, designated as Sample Port 1, or SP-1), WBA influent (after acid addition, SP-2), lead vessel 50% bed depth (SP-3), lead vessel effluent (SP-4), lag vessel 50% bed depth (SP-5), and lag vessel effluent (SP-6).

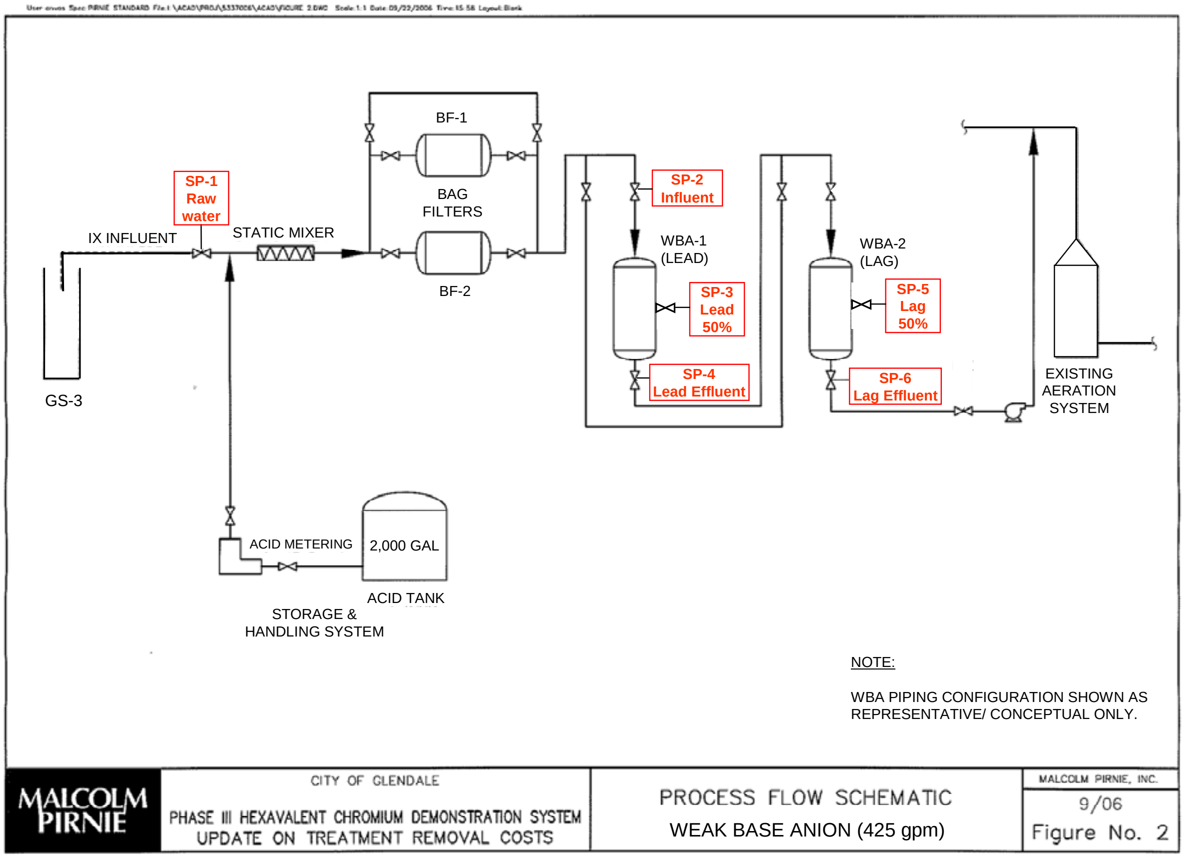

Figure 4-1: Sampling locations for water quality parameters (highlighted in red)

4.3. Monitoring Frequency

4.3.1. Water Quality Parameters

The planned sampling frequency for chemical and physical parameters, shown in Table 4-2, is based on treatment process design and the expected duration of testing (approximately one year for the demonstration-scale study). Samples will be collected at a sufficient frequency to provide enough information to achieve the project's stated objectives. For a predicted bed life of 207 days (based on maximum uranium accumulation), the chromium sampling frequency will capture a 29-point breakthrough curve.

The weekly Cr(VI) and total Cr sampling frequency will be established for the following key sampling points:

- WBA influent
- Lead vessel 50% bed depth
- Lead vessel effluent
- Lag vessel effluent

Once breakthrough occurs such that the lead bed effluent Cr concentration exceeds 5 μg/L, the lag vessel 50% depth location will be added to the list of sampling points monitored weekly and the lead vessel 50% depth curtailed (until the next bed is installed and the lead and lag vessel order is changed).

pH, which is a critical parameter due to its impact on WBA resin treatment, will be measured continuously at a point near the influent sampling point. Note that sufficient mixing is necessary to enable capture of stable pH values representative of the influent to the WBA resin; thus, acid will be added upstream of the bag filters and samples collected after the bag filters and before the lead vessel inlet. pH of lead and lag vessel effluent will be monitored on a weekly basis to evaluate the corrosion potential of the treated effluent on the transmission pipes.

Nitrosamines will be measured during the first week of startup according to California DPH permit requirements.
Non-critical parameters, including temperature, sulfate, nitrate, phosphate, silicate, alkalinity, conductivity, and turbidity, will be measured monthly at the following sampling points:

- Influent
- Lag vessel effluent

The proposed sampling frequencies for the water quality parameters are summarized in Table 4-2.

4.3.2. Process Parameters

Process-related parameters of the WBA system, such as flow rate and head loss, will be measured on a daily basis to determine the initiation of backwash and replacement of bag filters.

4.3.3. Treatment Residuals

The analyses of resin residuals will be performed each time resin changeout is required. Backwash water will be analyzed periodically as specified in the discharge permit.

**Table 4-2.
Monitoring locations and frequencies for water quality parameters**

Analytical Measurements	**Monitoring Locations and Frequency**					
	SP-1: Raw water (before acid addition**)**	**SP-2:** WBA Influent (after acid addition**)**	**SP-3:** Lead vessel 50% bed depth	**SP-4:** Lead vessel effluent	**SP-5:** Lag vessel 50% bed depth	**SP-6:** Lag vessel effluent
Cr(VI)	Monthly	Weekly	Weekly	Weekly	Weekly*	Weekly
Total Cr	Monthly	Weekly	Weekly	Weekly	Weekly*	Weekly
pH	/	Continuously	/	Weekly	/	Weekly
Temperature	/	Continuously	/	Weekly	/	Weekly
SO_4^{2-}	/	Monthly	/	/	/	Monthly
NO_3^-	/	Monthly	/	/	/	Monthly
PO_4^{3-}	/	Monthly	/	/	/	Monthly
SiO_2	/	Monthly	/	/	/	Monthly
Alkalinity	/	Monthly	/	/	/	Monthly
Conductivity	/	Monthly	/	/	/	Monthly
Turbidity	/	Monthly	/	/	/	Monthly
Nitrosamines	/	Start of test[a]	/	Start of test	/	Start of test

[a] Nitrosamines will be analyzed at a frequency required by the DPH permit

* Samples collected only when the lead vessel effluent exceeds 5 μg/L.

4.4. Analytical Approach

The analytical methods for the water quality parameters and treatment residuals will conform to EPA guidelines and recommended test methods, including those in *Standard Methods for the Examination of Water and Wastewater* (APHA 1999). This section briefly describes the analytical approach used in the demonstration-scale study. More detailed information can be found in the QAPP mentioned above.

Chemical and physical analytes will be measured in this demonstration-scale study either in the field or in a laboratory. Laboratory analytical measurements will be sent to one of three labs:

- Truesdail Laboratories, Inc. – for Cr(VI), total Cr, and nitrate
- Montgomery Watson Harza Laboratories – for nitrosamines

- Severn Trent – for TCLP, CWET, and uranium in residuals

The laboratory analyses of total chromium (a California DPH regulated constituent) will be performed by ICP-MS (EPA Method 200.8). Cr(VI) will be analyzed using EPA Method 218.6, which is an ion chromatography method. Nitrate will be analyzed using Method 300.0. Nitrosamines will likely be measured with EPA Method 521 (depending on method availability). Treatment residuals from the WBA treatment process will be analyzed for TCLP (metals), CWET (metals), and uranium analyses prior to disposal. All other parameters will be analyzed using the methods shown in Table 4-3.

Table 4-3.
Analytical methods and locations of analyses for the demonstration-scale study

Sample Analysis	Analytical Method	Analysis Location
Cr(VI)	EPA 218.6 (IC)	ELAP-certified Lab
Total Cr (contract lab for compliance)	EPA 200.8 (ICP-MS)	ELAP-certified Lab
SO_4^{2-}	Hach 8051 (Colorimetric)	Field
NO_3^-	EPA 300.0 (IC)	ELAP-certified Lab
PO_4^{3-}	Hach 8048 (Colorimetric)	Field
SiO_2	Hach 8185 (Colorimetric)	Field
Alkalinity	Hach 8203 (Titration)	Field
Conductivity	SM 2510B (Conductance)	Field
pH	SM 4500H+ B (Electrometric)	Field
Temperature	SM 2550 (Thermometric)	Field
Turbidity	SM 2130 B	Field
Nitrosamines	EPA 521	ELAP-certified Lab
Residuals – TCLP	EPA 1311	ELAP-certified Lab
Residuals – CWET	CWET Test (Title 22)	ELAP-certified Lab
Residuals: Uranium	ASTM5174-91 (KPA method)	ELAP-certified Lab

5. Operations Evaluation

In addition to the water quality issues, ongoing operations and maintenance (O&M) of the demonstration-scale WBA system will be constantly evaluated to optimize the system performance, minimize the negative impact on the distribution system, and reduce the O&M cost of the WBA system.

5.1. O&M Manual

As part of the demonstration study, a draft O&M manual will be prepared along with the experimental plan. The O&M manual will serve as a resource in the operation and maintenance of the demonstration-scale WBA system for the facility operators. In order to achieve optimized system performance, the manual will be updated regularly during the demonstration study to reflect the changes in operational conditions and maintenance schedules. A final O&M manual will be prepared after the demonstration study based on lessons learned.

Components of the O&M manual for the WBA system include, but are not limited to, the following:

- Background on the goals and objectives of the demonstration study
- Description of the WBA technology, including all process components
- Process and instrumentation diagrams (P&IDs)
- Maintenance schedule for all process components
- Replacement schedule or triggers for replacing all process components with a limited life
- Training documents for operations staff, including duties, responsibilities, chain-of-command, and health and safety plan
- Standard Operating Procedures (SOPs), including site inspection sheets, calculations for determining dose rates of acid, procedures for chemical deliveries, procedures for waste handling and disposal, spill control actions, safety information on chemicals, and staffing and emergency call-out procedures
- Notification procedures in case of a chemical feed problem, and
- Reference to QAPP, which contains field and laboratory analytical and sampling procedures and record keeping requirements

5.2. Facility Operation Evaluation

5.2.1. Pump Evaluation

One operational issue associated with the installation of a demonstration-scale WBA system at the GS-3 site will be the pump hydraulics (i.e., projected pumping capacity). As part of the preliminary design of the GS-3 WBA treatment system, we evaluated the hydraulics of the current pump in GS-3 and the system losses expected from the new facilities to determine the projected pumping capacity.

Figure 5-1 shows the current GS-3 pump curve from a test performed in June 2007 by CDM (dark blue line). To bracket the range, two roughness coefficients (C=130 and 100) and two main pressures (45 and 55 psi) were used in the pump curve evaluation. According to the figure, the GS-3 pump has an estimated operating range of between 550 to 600 gpm at 100% pump speed.

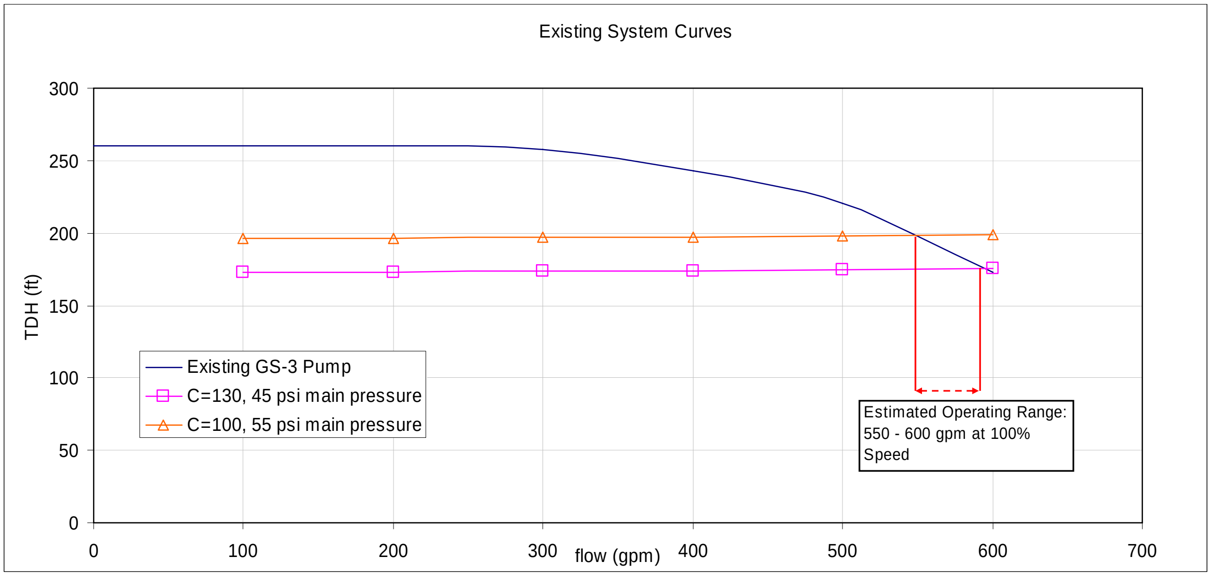

Figure 5-1: Existing system curves for the GS-3 pump without the WBA facility

The addition of a WBA treatment system between the well and the main will introduce pressure losses, due to the bag filters, ion exchange resin beds, and additional piping. For example, the bag filters are estimated to have a 2 psi drop across the filter housing when the filters are clean, and up to a 10 psi drop for dirty filters (i.e., the point at which filter change-out is recommended by the vendor). Figure 5-2 shows the intersection of the actual GS-3 pump curve (dark blue line) and manufacturer provided pump curve (light blue line) with the upper and lower range for the system curves. The upper range is based on clean bag filters (2 psi differential) and the estimated best-case main pressure (45 psi) and C factor (130). The lower range is based on dirty bag filters (10 psi differential) and the estimated worst case main pressure (55 psi) and C factor (100). The estimated operating range for the pump is between 250 and 480 gpm at 100% pump speed.

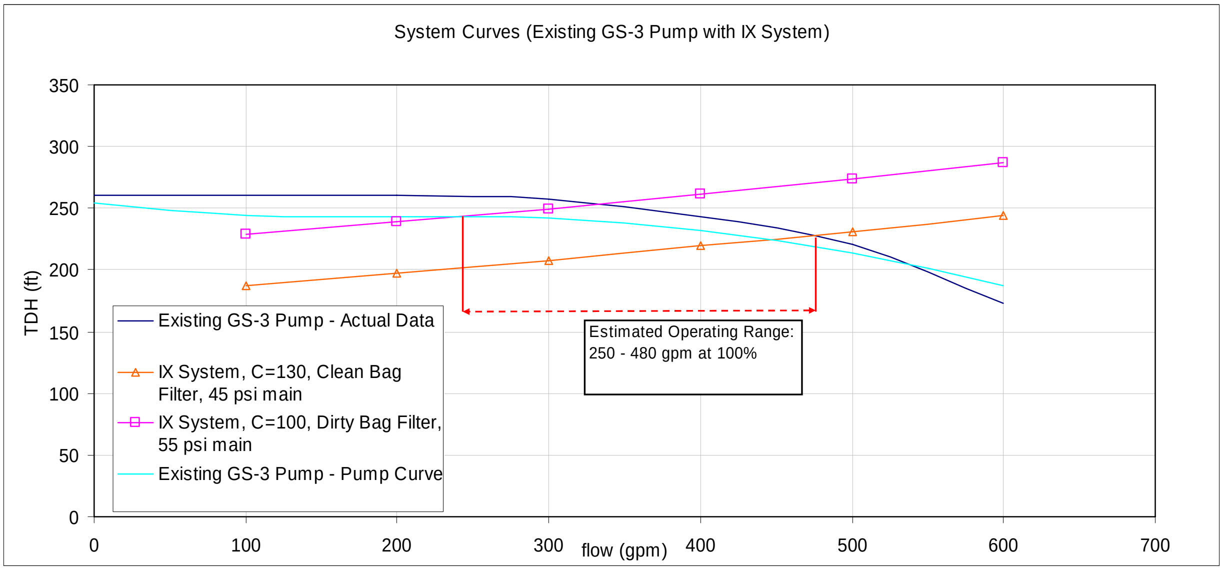

Figure 5-2: Predicted system curves for the GS-3 pump with the WBA facility

Although the pressure losses in the WBA facility will limit the flow compared with the current possible flow capacity of the existing GS-3 pump, Glendale decided to proceed with the preliminary design of the WBA system using the existing GS-3 pump of the existing GS-3 pump. It was noted that pressure losses in the WBA facility will limit the flow compared with the current possible flow capacity of the existing GS-3 pump. However, flow limitations might be overcome during the demonstration-scale study by replacing bag filters on a more frequent basis. The reasons behind that recommendation can be found in a technical memorandum entitled “Pump Curve Evaluation and Decision” submitted to Glendale (Malcolm Pirnie 2007c, Appendix C).

To evaluate the pump hydraulics in the demonstration study, pressure drops and flow rate readings will be recorded on a daily basis.

5.2.2. Backwash and Bag Filter Change Frequency

The frequencies of resin bed backwash and bag filter change are related to the pump hydraulics as described above. For example, flow limitations might be overcome during the demonstration-scale study by replacing bag filters on a more frequent basis (i.e., replacing the dirty filters once 5 psi pressure drop is observed instead of 10 psi). More frequent backwash of the resin bed is also expected to improve the system production capacity. One task of the operational evaluation will then focus on finding the necessary bag filter replacement frequency to maximize treated water flow. The frequencies bag filter changes and any necessary backwashing will be recorded as a part of the operations evaluation.

5.2.3. Corrosivity of the WBA Treated Effluent

The WBA resin was found to require pH reduction for effective use; a pH of 6.0 was shown to both remove Cr(VI) to levels below the treatment goal of 5 µg/L and to maximize Cr(VI) capacity of the resin. In the demonstration study, hydrochloric acid will be injected into the GS-3 well water (originally at a pH of approximately 6.8) upstream of the IX vessels to maintain a constant pH of 6.0. As shown in pilot testing, the pH does not change significantly as the water passes through the IX beds; consequently, the WBA treated water will have a pH of approximately 6.0. The potential for increased corrosivity (due to reduced pH) of this water was another operational concern of the demonstration-scale system.

Based on a technical memorandum prepared by Malcolm Pirnie (2007d, Appendix D), the raw GS-3 well water was already corrosive with respect to calcium carbonate under ambient groundwater conditions [Langelier Saturation Index (LSI) of -0.43 and Calcium Carbonate Precipitation Potential (CCPP) of -34 mg/L]. The addition of WBA treatment, including pH adjustment, will increase the magnitude of the negative LSI and CCPP values to -1.51 and -162 mg/L, respectively (and -1.05 LSI and -101 mg/L CCPP for GS-3 water blended with GS-4 water). However, the impact of this change on the corrosivity of the water toward the cement-mortar lined transmission line is uncertain. This analysis indicated that even raising the pH of the WBA-treated water back to the ambient groundwater pH level of 6.8 would result in original conditions that were corrosive to the mortar lining of the pipes.

Visual inspection of the pipeline condition before and after the demonstration-scale study is strongly recommended to evaluate the impact of WBA treated effluent on the pipeline and the necessity of pH adjustment after treatment.

5.3. Facility Cost Evaluation

The proposed demonstration study breaks new ground by testing the first treatment technology for Cr(VI) removal to low levels in drinking water. Actual cost information from the demonstration-scale study will be valuable to other water utilities requiring Cr(VI) treatment and to the California DPH, who will be charged with setting an MCL for Cr(VI).

During the demonstration study year of operations, the following cost components will be tracked carefully and compiled at the end of the study to provide detailed cost information associated with the demonstration-scale WBA system.

5.3.1. Capital Costs

The capital costs for the demonstration-scale WBA system will be tracked using various tools. Copies of all contracts and invoices (e.g., invoice for WBA resin) will be stored in a single place and managed by dedicated personnel.

5.3.2. O&M Costs

5.3.2.1. Staffing Requirements

Glendale operations staff (mostly sub-contracted to CDM) will record the time spent on routine O&M of the WBA system on a daily basis. In case of an emergency related to the WBA system (e.g., acid feed problem), the operators will also record the time spent to resume the system operation.

5.3.2.2. Acid Dosage

Acid dosage required for the WBA system operation will be tracked along with the volumes used. The volume of acid transferred to the acid storage tank will be recorded each time the acid is delivered to the GS-3 site. In addition, the Glendale operating staff will record the level in the acid storage tank on a daily basis.

5.3.2.3. Resin Changeout Frequency

Based on the pilot testing results, the WBA resin will be changed out approximately every 207 days. In the demonstration study, Glendale staff will record the date and time of each resin changeout event and confirm the amount of resin loaded to the ion exchange vessels.

5.3.2.4. Backwash Water Quantity

Resin backwash may be necessary to reduce any pressure buildup in the vessels. In order to quantify the costs associated with the backwash process, the following information will be recorded for each backwash event: backwash date and time, duration, flow rate, and total volume of water used.

6. References

APHA, AWWA, and WEF. 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. American Public Health Association, Washington, DC, 1995.

Brandhuber, P.; Frey, M.; McGuire, M.J.; Chao, P.; Seidel, C.; Amy, G.; Yoon, J.; McNeill, L.; Banerjee, K. 2004. Treatment Options for Low-Level Hexavalent Chromium Removal Tested at Bench Scale. Denver, Colo.: AwwaRF.

EPA. 1993. Method 300: Determination of Inorganic Anions in Drinking Water by Ion Chromatography. EPA-600/R-93-100.

EPA. 1994. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry. EPA-600/R-94/111.

EPA. 1994. Method 218.6: Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography.

Malcolm Pirnie, Inc. 2007a. Preliminary Design Report: Well GS-3 WBA Chromium 6 Removal Facility. Technical memorandum submitted to the City of Glendale on October 2, 2007.

Malcolm Pirnie, Inc. 2007b. Quality Assurance Project Plan: Phase III Demonstration-Scale WBA Resin Treatment Technology Evaluation. Submitted to the EPA on September 18, 2007.

Malcolm Pirnie, Inc. 2007c. Pump Curve Evaluation and Decision. Technical memorandum submitted to the City of Glendale on July 2, 2007.

Malcolm Pirnie, Inc. 2007d. Corrosivity of the Proposed WBA Resin Treated Effluent due to Acid Addition. Technical memorandum submitted to the City of Glendale on September 24, 2007.

McGuire, M.J.; Blute, N.K.; Seidel, C.; Qin, G.; Fong, L. 2006. Pilot-Scale Studies of Hexavalent Chromium Removal from Drinking Water. *Jour. AWWA.* 98(2):134-143.

McGuire, M.J., Blute, N.K., Qin, G., Kavounas, P., Froelich, D., Fong, L. 2007. Hexavalent Chromium Removal from Drinking Water Using Weak- and Strong-Base Ion Exchange and Reduction/Coagulation/Filtration. Denver, Colo.: AwwaRF.

McGuire Environmental Consultants, Inc. (MEC) 2005. The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale Groundwater Supply: Phase II Demonstration of Pilot-Scale Treatment Technologies. Final report submitted to the City of Glendale. Glendale, CA.

National Toxicology Program (NTP), 2007. Technical Report on the Toxicology and Carcinogenesis Studies of Sodium Dichromate Dihydrate in F344/N Rats and B6C3F1 Mice. Draft.

Qin, G.; McGuire, M.J.; Blute, N.K.; Seidel, C.J.; Fong, L. 2005. Hexavalent Chromium Removal by Reduction with Ferrous Sulfate, Coagulation, and Filtration: A Pilot-Scale Study. *Environ. Sci. Technol.* 39(16):6321-6327.

Appendix A – Preliminary Design Report

Note that the original Preliminary Design Report included as Appendix A was subsequently updated on May 28, 2008. The updated version is contained in this Appendix.

City of Glendale Water and Power
141 N. Glendale Ave. • Level 4 • Glendale, CA 91206

Preliminary Design Report: Well GS-3 WBA Chromium 6 Removal Facility

Revised Final
May 27, 2008

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4. Rohm & Haas PWA7 Product Data Sheet

1. Introduction

The City of Glendale's groundwater supply in the San Fernando Valley has been contaminated with a wide variety of chemicals, including hexavalent chromium [Cr(VI)], trichloroethylene (TCE), perchloroethylene (PCE), 1,2,3-trichloropropane (TCP), and others, mainly as a result of the improper disposal of industrial waste products.

A recent study conducted by the National Toxicology Program (NTP)[1] showed that Cr(VI) is a carcinogen by ingestion in animal studies, and recent legislation in California has mandated that the California Department of Public Health establish a Cr(VI) Maximum Contaminant Level (MCL). In Glendale and other cities such as Los Angeles and Burbank in the San Fernando Valley, public concern about Cr(VI) in the groundwater supply led the city to embark on a multi-phase study to identify and install Cr(VI) treatment in anticipation of a Cr(VI) MCL lower than the current total Cr MCL in California.

In the year 2000, the City of Glendale, along with the Cities of Los Angeles, Burbank, and San Fernando, initiated a testing program to develop a full-scale Cr(VI) treatment system capable of removing Cr(VI) to low part-per-billion levels. The **Phase I Bench-scale study** was conducted to improve the understanding of fundamental chromium chemistry and to screen promising technologies for their ability to treat and remove Cr(VI) to very low levels. The Phase I study is complete and the final report was published by AwwaRF.[2] The **Phase II Pilot-scale study** was initiated in the summer of 2003 to further test the promising Cr(VI) removal technologies at the pilot scale (i.e., several gallons-per-minute flows) using Glendale groundwater. A final report on the Phase II pilot-scale study was completed in 2005.[3] Selected results were also published in peer-reviewed scientific journals.[4,5]

The **Phase III Demonstration-scale study** will finalize the treatment evaluation, residuals assessment, and cost estimate development by implementing one or more Cr(VI) removal technologies at flows of approximately 100 to 1,000 gpm. The initial part of the Phase III effort was designated the Phase III Bridge Project, which included additional studies to finalize testing of weak-base anion exchange resins for Cr(VI) treatment, refinement of treatment technology cost estimates based on Phase III Bridge Project results, and assembly of an Expert Panel that recommended to Glendale construct a demonstration-scale reduction-coagulation-filtration (RCF) treatment system and further evaluate weak-base anion exchange. The Phase III Bridge Project was completed in early 2007.

For the demonstration facilities, the City selected the construction of the test weak-base anion (WBA) exchange system at Well Site GS-3 using an existing 400-500 gpm well and the RCF system adjacent to the existing Glendale Water Treatment Plant. The purpose of this report is to identify the design criteria that will be used for the facility that will demonstrate the effectiveness of WBA resin in removing Cr(VI) to low parts-per-billion levels. The WBA product water will be put to beneficial use by serving the treated water to Glendale's customers. Treatment cost information developed in the Phase II Pilot-scale and Phase III Bridge studies will be updated as a result of this effort, and this information intended to be of use to other utilities requiring Cr(VI) treatment and to the state of California in setting a Cr(VI) MCL.

To date, WBA has only been tested in bench- and pilot-scale studies. The proposed demonstration-scale WBA system will be the first installation of this technology in a drinking water treatment application.

The WBA system that will be constructed and tested in the Phase III Demonstration-scale study will consist of the following major components:

- Modification of existing Vessels for ion exchange treatment (two 8-ft. diameter vessels each containing WBA resin)
- Bag filters (two parallel filter housings containing 20-micron filters),
- Carbon Dioxide Storage Tank, and
- Carbonic Acid feed and control system

The system will consist of a pair of lead/lag vessels installed in series with upstream acid addition. Based on pilot studies, the pH of the raw water must be lowered to approximately a pH of 6.0. The Pilot Scale testing was conducted using Hydrochloric Acid. The demonstration-scale facility will utilize Carbonic Acid instead of Hydrochloric Acid based on requests from the Glendale Respondents Group (GRG) to minimize the use of aggressive chemicals on site. Due to its high capacity and difficulty in regeneration, WBA resin will be used as a once-through, non-regenerable media.

The WBA system will be located at the GS-3 well site adjacent to Goodwin Street in the City of Los Angeles. The GS-3 well was selected for testing the WBA demonstration-scale system for two primary reasons: (1) GS-3 is one of the high Cr(VI) wells,; and (2) a pair of unused GAC vessels exist at the GS-3 well site and can be retrofitted for WBA resin, thus minimizing capital costs for ion exchange (IX) vessels. Over the past two years, Cr(VI) levels in GS3 water have been highly variable due to intermittent operation of the well. In general for the past two years, the Cr(VI) levels have ranged between 40 and 60 ppb with one spike to a maximum of 69 ppb. Given the movement of the plume influencing the GS-3 well, the steady-state Cr(VI) concentration of Cr(VI) is not certain once continuous well operation is re-established.

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[1] National Toxicology Program (NTP), 2007. Technical Report on the Toxicology and Carcinogenesis Studies of Sodium Dichromate Dihydrate in F344/N Rats and B6C3F1 Mice. Draft.

[2] Brandhuber, P.; Frey, M.; McGuire, M.J.; Chao, P.; Seidel, C.; Amy, G.; Yoon, J.; McNeill, L.; Banerjee, K. 2004. Treatment Options for Low-Level Hexavalent Chromium Removal Tested at Bench Scale. Denver, Colo.: AwwaRF.

[3] McGuire Environmental Consultants, Inc. (MEC) 2005. The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale Groundwater Supply: Phase II Demonstration of Pilot-Scale Treatment Technologies. Final report submitted to the City of Glendale. Glendale, CA.

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[4] Qin, G.; McGuire, M.J.; Blute, N.K.; Seidel, C.J.; Fong, L. 2005. Hexavalent Chromium Removal by Reduction with Ferrous Sulfate, Coagulation, and Filtration: A Pilot-Scale Study. *Environ. Sci. Technol.* 39(16):6321-6327.

[5] McGuire, M.J.; Blute, N.K.; Seidel, C.; Qin, G.; Fong, L. 2006. Pilot-Scale Studies of Hexavalent Chromium Removal from Drinking Water. *Jour. AWWA*. 98(2):134-143.

2. Design Parameters

The treatment concept for the Glendale WBA treatment facility is based on retrofitting existing GAC vessels with WBA IX resin for removal of Chromium 6. The facility will consist of the following:

- Existing GAC vessels retrofitted with IX resin
- Bag filters for particulate removal
- Carbonic acid (CO_2) feed facilities for pH adjustment.

IX Vessels

Two existing GAC vessels will be operated in series in a lead and lag configuration. The facility will initially be sized for the design flow with facility storage and pipes sized to accommodate the ultimate design flow. The system is designed as a demonstration scale facility that will have a limited operating period. It is not expected that the facility will need to be in operation for 30 or more years, so the construction material choices are based on a limited life cycle demonstration facility. The design criteria for the IX vessels are based on the criteria in Table 2-1.

Table 2-1.
Design Criteria for Retrofitted IX Vessels

Parameter	IX Vessel (each)
Ultimate Design Flow	600 gpm
Design Flow	425 gpm
IX Loading Rate	2.5 gpm/cf
Required Usable IX Volume at Ultimate Design Flow	240 cf
Required Usable IX Volume at Design Flow	170 cf
Vessel Diameter	8 ft.
Vessel Total Straight Shell Height	7 ft.
Vessel Rounded Bottom Height	2 ft.
Unusable Volume From Bottom of Vessel to Top of Nozzle	1 ft.
Unusable Resin Below Nozzle	15 cf
Total IX Resin Required at Ultimate Design Flow	255 cf
Total IX Resin Required at Design Flow	185 cf

Parameter	IX Vessel (each)
Straight Shell Depth of Resin at Ultimate Design Flow	4.08 ft.
Available Bed Expansion at Ultimate Design Flow	42%
Straight Shell Depth of Resin at Design Flow	2.68 ft.
Available Bed Expansion at Design Flow.	62%
Minimum Required Backwash Rate for 60% Bed Expansion	3.5 gpm/sf (176 gpm)
Backwash Supply	Existing 8” Water Main
IX Resin	Rohm & Haas PWA7 or ResinTech SIR-700[i]
IX Resin Particle Size	0.3 – 1.2 mm
Underdrain Lateral Screen Size	0.25 mm (60 mesh)

The vessels will initially be filled with IX resin based on the design flow. If the output of the facility is increased to the ultimate design flow, additional IX resin will be required.

Backwash Procedures

The size of the vessels will allow for 62% expansion at the design flow and 42% at the ultimate design flow. The backwash water will be provided from the common 8” water transmission line from the other well sites, which will back feed the IX vessels for the washwater supply. The backwash rate will need to be carefully controlled to limit losing any resin during backwashing. It is not anticipated to have to backwash the IX resin often due to particulate accumulation because of the bag filters in front of the vessels. The use of carbon dioxide at concentrations above atmospheric saturation may result in off-gassing within the resin bed when the well is shut down and the vessels de-pressurized. Off-gassing of carbon dioxide in the resin bed could lead to reduced flows in the contactors necessitating an increased backwash frequency. The backwash frequency will be developed based on operational experience. The rate of pressure loss through the IX vessels will be observed and the backwash frequency will be established. It is anticipated that the maximum backwash duration would be 10 minutes. The pressure loss through the vessel will be observed to ensure the backwash duration was sufficient.

Provisions for Backwash Equalization

The backwash water will be discharge directly to a backwash tank located on-site and then discharged at a lower rate from the tank to the existing 6” DIP sewer line. A connection will be provided to connect a hose to the backwash waste line to supply the

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[i] Currently, SIR-700 is not NSF certified. Use of this resin would require that certification. PWA7 is already NSF certified.

containment tank. The use of carbonic acid is anticipated to increase the backwash frequency due to off-gassing of carbon dioxide when the well is shutdown and the potential for air binding the IX media. The partial pressure of Carbon Dioxide at atmospheric pressures is approximately $10^{-3.5}$ atm. After CO_2 addition the partial pressure will increase by 0.2 atmospheres resulting in a 1.2 atm (18 psig) pressure requirement to keep the carbon dioxide in solution. When the well is shutdown and the pipeline and vessel depressurize back to atmospheric pressure there will be the tendency for the carbon dioxide to off-gas and equalize to the atmospheric partial pressure. This may require backwashing after each shutdown of the system. The size of the backwash tank will be 3,000 gallons. This will accommodate a 17 minute backwash. A horizontal Polyethylene Tank will be utilized.

Bag Filters

Prior to the IX vessels, bag filters will be provided for particulate matter removal. The design criteria for the bag filters are provided in Table 2-2.

Table 2-2.
Bag Filter Design Criteria

Parameter	**Design Criteria**
Bag Filter Size	20 micron
Number of Bag Filter Assemblies	2 (1 duty + 1 standby)
Filter Bags per Assembly	6
Design Flow	600 gpm
Maximum Clean Headloss at Design Flow	2 psi
Bag Filter Housing Material	Painted Carbon Steel

Carbonic Acid Feed Facilities

Carbonic acid feed facilities will be provided prior to the IX vessels for pH adjustment to pH 6.0. The design criteria for the Carbonic acid feed facilities are provided in Table 2-3.

Table 2-3.
Carbonic Acid Facilities Design Criteria

Parameter	**Design Criteria**
Ultimate Design Flow	600 gpm
Design Flow	425 gpm
Design Dose	288 mg/L
Maximum Usage at Ultimate Design Flow	2075 ppd
Average Usage at Design Flow	1470 ppd
Total Storage Amount(2)	28,000 lbs.
Days of Storage at Design Flow	19 days

Days of Storage at Ultimate Design Flow	13.5 days
Carrier Water Requirements	65 gpm at 110 psig
Type of Storage Tank	ASME Pressure Vessel
Material	Steel
Pipe and Valve Materials CO^2 Gas	Steel
Pipe and Valve Materials Dissolved CO^2	CPVC
Carrier Water Pipe and Valve Materials	Steel or Copper
Gaskets and Elastomeric Materials	Buna-N

(1) Design dose was determined based on pH and Alkalinity measurements in the field.

(2) Based on site constraints the City of Glendale Water and Power, storage capacity will be limited at the site to 14 tons, requiring more frequent filling of the CO_2 storage tank than a typical 20 to 30 day frequency.

The Carbonic acid facilities consist of the following equipment:

- Skid Mounted 14 ton liquid storage tank assembly. The storage tank is a insulated steel pressure vessel. The assembly includes a weatherproof enclosure at one end to protect the refrigeration unit that is used to maintain the carbon dioxide as a liquid, the electric vaporizer which is used to feed carbon dioxide gas to the solution feeder and the vapor heater which is used to maintain the supplied gas near ambient temperatures.
- Carbonic Acid feed panel. The feed panel includes a flow control valve, flow meter and eductor to control the feed rate of carbon dioxide gas into the carrier water.
- Carrier water pumps. The carrier water pumps are required to boost the pressure of the carrier water through the eductor in the carbonic acid feed panel. Carrier water is provided as a sidestream injection system to improve dissolution of carbon dioxide into solution. A portion of the well flow is diverted for the side stream injection system through the carbonic acid feed panel using a carrier water pump. A duty and standby carrier water pump will be provided.

The equipment will be mounted in a containment area to handle any nuisance spills. The containment area will be utilized for identifying minor pipe leaks and minimizing discharges of the GS-3 well water. The containment area is utilized to alert operators at the remote monitoring location that a spill has occurred, which should initiate a shut-down of the GS-3 well, carrier water pumps and carbon dioxide feed system. The containment area will not be coated with a corrosion resistant coating, since the spill will be addressed immediately and short term exposure will not significantly damage the concrete.

3. Facility Layout

The carbonic acid facilities, backwash tank and the bag filters will be added to the existing GS-3 well site as shown in Appendix 1. The facilities will extend beyond the existing easement. The final configuration of the backwash tank and carbon dioxide storage tank will be modified to improve access to the well. The final layout will be based on discussions with Ralph's on extending the easement area. The site piping will be reconfigured so that the lag IX vessel will discharge into the existing 8" Ductile Iron Pipe (DIP) well effluent as shown in Appendices 2 and 3. The existing 8" connection to the 30" reclaimed water line will be abandoned. Valving will be provided so that the bag filter assembly and the IX vessels can be bypassed. The effluent from the IX vessels will discharge to same location as the existing GS-3 pump, i.e., through the existing 8" well effluent line.

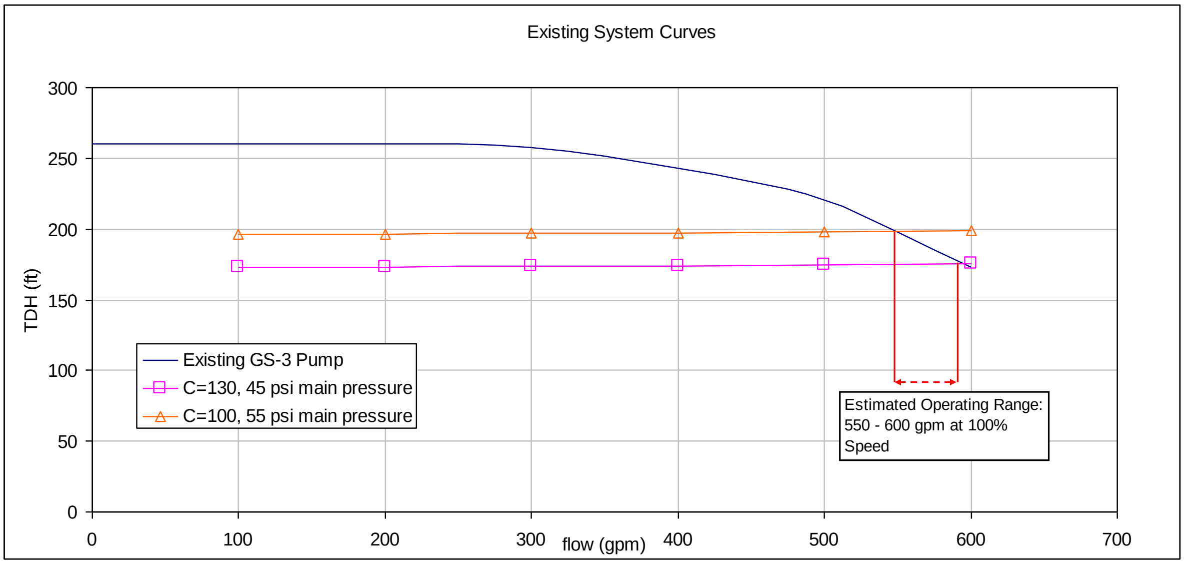
The site piping materials will be Schedule 80 PVC for above grade piping and ductile iron pipe for below grade piping. Exposed PVC will be painted to protect against ultraviolet light. The velocities in the piping will be maintained below 5 ft/s in PVC piping to protect against surge for the PVC. Exposed valves will be PVC Butterfly valves. Buried valves will be ductile iron body resilient wedge gate valves installed in traffic rated valve cans with the valve operators below grade. The piping materials for the carbonic acid system will be Schedule 80 steel for the carbon dioxide gas, and CPVC for the dissolved Carbonic Acid solution after the feed panel. The carrier water piping will be steel or copper instead of PVC due to the higher operating pressure (120 psig) of this piping.

4. Hydraulics

The hydraulics of the current pump in GS-3 and the losses expected from the new facilities were evaluated to determine the projected pumping capacity. Figure 4-1 shows that current GS-3 pump curve from a test performed in June 2007 by CDM (dark blue line). To bracket the range the following assumptions were utilized:

- Best-case C factor: 130
- Worst Case C factor: 100
- Highest Main Pressure: 55 psi
- Lowest Main Pressure: 45 psi

Based on field data from the pump test and the calculated system curves using the assumptions above, the GS-3 pump currently has an estimated operating range of between 550 to 600 gpm at 100% pump speed.



Estimated Operating Range: 550 - 600 gpm at 100% Speed

Figure 4-1: Existing System Curves for the GS-3 Pump without the WBA Facility

The addition of a WBA treatment system between the well and the main will introduce pressure losses due to the bag filters, ion exchange resin beds, and additional piping. For example, the bag filters are estimated to have a 2 psi drop across the filter housing when the filters are clean, and up to a 10 psi drop when dirty (i.e., the point at which filter change-out is recommended by the vendor). The IX system losses were calculated based on pressure loss curves provided by the manufacturers (Appendix 4). Figure 4-2 shows the intersection of the actual GS-3 pump curve (dark blue line) and manufacturer provided pump curve (light blue line) with the upper and lower range for the system curves. The upper range is based on clean bag filters (2 psi differential) and the estimated best-case main pressure (45 psi) and C factor (130). The lower range is based on dirty bag filters (10 psi differential) and the estimated worst case main pressure (55 psi) and C factor (100). The estimated operating range for the pump is between 250 and 480 gpm at 100% pump speed.

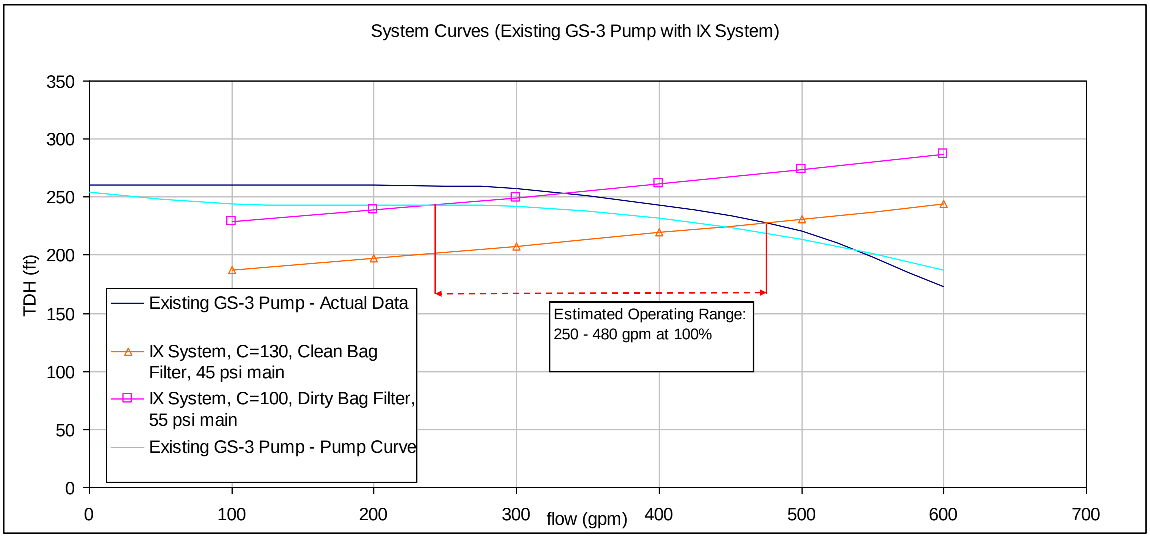


Figure 4-2: Predicted System Curves for the GS-3 Pump with the WBA Facility

Two possibilities exist to achieve an output closer to the desired 425 gpm design capacity for the WBA treatment system. First, the existing GS-3 pump could be used and the bag filters replaced more frequently than when 10 psi pressure loss occurs. Second, the GS-3 pump could be replaced with one capable of achieving a higher operating flow. To achieve the ultimate design flow of 600 gpm, the GS-3 pump will need to be replaced.

Glendale has an unused high head pump that was purchased with the GAC vessels, so the hydraulics were evaluated to determine if the existing high head pump could be used to achieve a higher flow. Figure 4-3 shows the pump curves for 100%, 80%, and 50% pump speeds, along with the system curves for a range of ion exchange system conditions. The analysis indicated that the high head pump could achieve an operating capacity of approximately 410 to 475 gpm at 80% speed. However, operation of the pump at 80% speed would not optimize the capital costs associated with installing a larger 75 HP pump at the facility, and the upper end of the flow operating range would not be improved over the existing GS-3 pump, so the ultimate design flow of 600 gpm would not be met with this pump. Based on this evaluation, it is recommended that Glendale purchase and install a different pump optimized for the ultimate design flow if this expansion in capacity is required.

Other issues that may cause complications with well pump replacement include clearance in the GS-3 vault and the potential costs of a new pump, such as system upgrades to accommodate a larger motor. Exchanging the existing pump with a larger horsepower motor may not be simple due to space constraints. Significant costs may also arise if a new pump is purchased and if modifications to the vault are necessary for the larger motor.

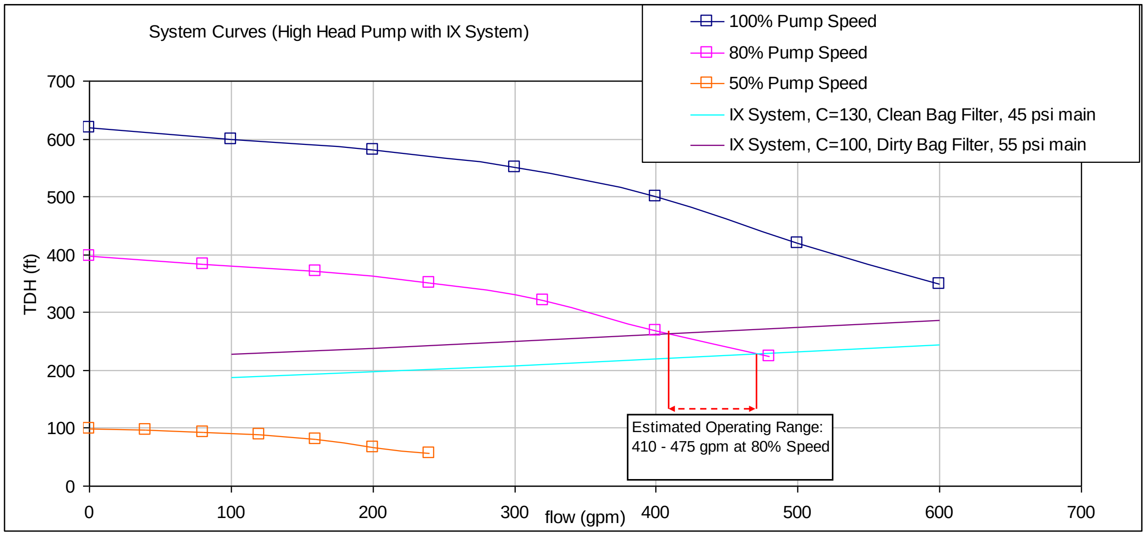


Figure 4-3: High Head Pump Operation with WBA Facility

Based on this hydraulic analysis, Glendale elected to proceed with the design using the existing GS-3 pump with the understanding that pressure losses in the WBA facility will limit the flow compared with the current possible flow capacity of the existing GS-3 pump. The flow output of the demonstration-scale study will be maximized by replacing bag filters on a more frequent basis. If the output of the pump with the new IX system is not sufficient, then the pump will be replaced.

The operation of the demonstration-scale study using the existing pump will also provide useful hydraulic information on head losses through the WBA treatment facility including the rate of pressure loss development through the bag filters. If Glendale decides that the flow is not sufficient with the existing pump, this information will be useful to optimize selection of a more optimal pump based on the actual operating data from the system.

5. Facility Operation

The process schematic for the Chromium 6 removal facilities is shown in Appendix 3. The Chromium 6 treatment facilities for well GS-3 include two bag filters, two IX vessels (existing GAC vessels modified to support WBA IX resin) and a carbonic acid feed system including an liquid carbon dioxide storage tank and dosing system.

The control descriptions for each component are identified below:

- The flow through the IX facilities will be monitored by the existing well effluent meter
- Provisions for local and remote automatic controls are included for the carbonic acid feed system.

5.1. Control Descriptions

IX Vessels

1. Overview:

The two IX vessels will be operated in series in a lead/lag configuration with the effluent from one vessel feeding the inlet of the other. Effluent from the second vessel will be discharged to the existing 8” water transmission main.

2. Monitoring and Control:

The majority of the operational changes for the IX system will be manually initiated. Flow through the IX vessels will be controlled by the well pump speed and losses through the system. It is anticipated that the pump will operate at full speed; thus, no flow control or throttling valves will be used to control flow through the IX vessels.

Backwashing of the IX vessels will be manually initiated. The pump will be shut down and the IX vessel influent and effluent valves will be closed. The common backwash discharge valve will then be opened. The backwash discharge valve on the vessel to be backwashed will be opened and the throttling valve on the backwash effluent will be throttled down to the set position. The effluent valve on this vessel will be opened and the backwash will be initiated. The flow will be monitored on the effluent meter to ensure the backwash rate does not exceed the recommended rate. Once the backwashing period for each vessel is complete, the IX vessels and pump will be placed back in service.

Field instruments used for controlling the IX vessels include:

- Existing flow meter on well pump outlet

- Common flow meter on the IX effluent/backwash supply line

3. Local Display/Control:

The common flow meter will display at the meter and SCADA. The backwash rate will be controlled by manually throttling the valve.

4. Remote Manual Control:

Not applicable (N/A)

5. Remote Auto Control:

N/A

6. Interlocks:

N/A

7. HMI generated alarms and indications:

- High Backwash Flow
- Low Flow

Bag Filters

The control description below is typical for Bag Filter 1 and Bag Filter 2.

1. Overview:

Bag filters will be used to remove particulates from well water prior to ion exchange treatment.

2. Monitoring and Control:

Pressure drops across on the bag filters will be monitored by a differential pressure switch. An alarm will be annunciated remotely on SCADA based on a high differential pressure setpoint. The setpoint will initially be set at 5 psig and will be adjusted based on a evaluation of the rate of particle accumulation and associated impacts on the well pump output during operation.

3. Local Display/Control:

The local display will include a differential pressure reading between bag filters' inlet and outlet at the instrument.

4. Remote Manual Control:

N/A

5. Remote Auto Control:

N/A

6. Interlocks

N/A

7. HMI generated alarms and indications

- High differential pressure

CO_2 Storage Tank

1. Overview:

A 14 ton tank will be provided for liquid carbon dioxide storage. A carbonic acid feed panel will be connected directly to this tank**.** A carrier water pump is required to also feed the carbonic acid feed panel to ensure adequate dissolution of the carbon dioxide. The tank will be equipped with refrigeration system that will automatically maintain the storage tank at 0°F and 300 psig. Automatic control will be provided to start and stop the compressor in refrigerating unit, thereby controlling the temperature of the CO_2 in order to maintain the proper operating pressure.

2. Monitoring and Control:

The refrigerating unit will be equipped with a NEMA 4X control panel for automatic controlling of the compressor. A differential pressure transmitter will be installed on the storage tank to measure the tank level which will be shown locally on the Refrigeration control panel and will be sent to the PLC for remote monitoring by SCADA. High and Low level alarms will be set in SCADA using software switches.
Also high and low pressure switches will be installed on the tank for local alarm on the refrigeration control panel and associated signals will be sent to the PLC for remote alarms in SCADA.

3. Local Display/Control at Refrigeration Control Panel:

Display: Continuous level signal
Alarm: Tank high level alarm
Tank High Pressure
Tank Low Pressure
Tank low level alarm

4. Remote Manual Control:

N/A

5. Remote Auto Control:

N/A

6. Interlocks

- Low-Low level software switch will be used to shutdown the carrier water pumps and CO_2 Feed panel

7. HMI generated alarms and indications

- Storage Tank Level
- Storage Tank Level High
- Storage Tank Level Low
- Storage Tank Level Low Low
- Storage Tank Press High
- Storage Tank Press Low

Carrier Water Pumps

1. Overview:

The carrier water pumps will be used as duty/standby pumps to boost the pressure of the carrier water through the eductor in the carbonic acid feed panel.

2. Monitoring and Control:

New MCC panel will be provided for the carrier water pumps. Duty/standby pump can be started locally from MCC or remotely from PLC.

3. Local Display/Control at MCC:

- Local control:

- HOR switch: When HOR is in Hand mode, operator can start/stop the pump locally, however hardwired high pressure switch will shut down the pump regardless of selected mode (Hand or Remote).

- Local display:
  - On status
  - Overload status
  - Pump outlet pressure high status.

4. Remote Manual Control at SCADA:

When HOR switch at MCC is in Remote position at SCADA, operator can

- Select Duty/standby pump
- Start/stop of the duty pump.

PLC will stop the pump in following situations:

- Pump's outlet pressure high (PSH is hardwired to new MCC and duplicated for PLC for alarm)
- Existing well pump shut down

In this mode, if the duty pump has stopped due to any failure, the Standby pump will be started.

Following signals will be sent from MCC to the PLC:

- Duty/Standby Pump Remote status
- Duty/Standby Pump On status
- Duty/Standby Pump Fault status

Following signals will be sent from PLC to the MCC:

- Duty/Standby Pump On Command

5. Interlocks

Following signals will be used for the pumps' Shutdown command:

- Existing well pump shut down
- Low-low level in storage tank
- Pump's outlet pressure high (hardwired signal in MCC)

6. HMI generated alarms and indications

- Duty/Standby Pump Remote status
- Duty/Standby Pump On status
- Fault (Overload/Outlet Pressure High) status

Carbonic Acid Feed Panel

1. Overview:

Carbonic Acid Feed Panel will be used to feed the carbonic acid to the static mixer. Feed panel will include a CO_2 flow meter, a single PID controller and a gas actuated flow control valve to control the CO_2 feed rate before mixing with carrier water in the inline mixers all inside the panel. The outlet then will be sent to the inlet line of static mixer.

In Hand mode the system will operate based on an operator set local CO_2 feed rate.

When Auto mode is selected at the Feed panel, system feed rate is controlled by the PLC.

In Auto Mode, Run command will be issued by the PLC. The PLC will calculate the required feed rate based on the target applied dose entered by the operator and the flow signal from the existing well pump. CO_2 feed rate is controlled by PID controller based on CO_2 feed setpoint (which is provided by PLC and is flow paced based on main water flow rate) and incoming CO_2 flow rate (from Flow meter inside the Feed panel).

2. Monitoring and Control:

Field instruments used for controlling the CO_2 feed rate will include:

- Existing flow meter on well pump’s outlet
- CO_2 flow meter inside the Feed panel
- pH analyzer on bag filters’ outlet
- Low Pressure switch on the carrier water pump’s outlet

When Auto mode is selected, the CO_2 feed setpoint shall be used by the PID controller to control the CO_2 feed rate by modulating the CO_2 flow control valve.

The pH analyzer will have four separate software switches (Low-Low, Low, High and High-High). The Low and High switches will initiate an alarm at SCADA. The Low setpoint will initially be set at 5.8 and the High will initially be set at 6.2 to ensure the target pH of 6.0 is maintained within a narrow range. The Low-Low and High-High setpoints will stop the well pump, carrier water pumps and the CO_2 feed panel. The Low-Low setpoint will be set at 5.5 and the High-High setpoint will be set at 6.4 to protect the materials of the piping and vessel and to prevent any breakthrough of Chromium 6 through the resin. There will be an adjustable delay on the shutdown from the High-High and Low-Low setpoints to allow for start-up of the carbonic acid feed system.

Also a Low-Low level signal from CO_2 storage tank will stop the Feed panel and carrier water pumps simultaneously.

3. Local Display/Control at CO_2 Feed panel:

- Hand/Off/Auto selector switch
- pH Display

- pH High Alarm
- pH Low Alarm
- Carrier Water Low pressure
- CO_2 Flow rate
- CO_2 Feed setpoint entry (via PID controller keypad)

4. Remote Control:

When CO_2 Feed panel is in Auto mode, PID controller will modulate flow control valve based on CO_2 flow rate (feedback signal from CO^2 flow meter) and remote feed rate setpoint:

In Remote mode, feed rate setpoint will be a flow paced signal based on main water flow rate.

The following signals will be sent from CO_2 Feed Panel To the PLC:

- System ON
- System in Auto
- CO_2 Flow Rate
- pH signal
- Loss of Carrier Water

The following commands will be sent from PLC to the Feed panel:

- Run/Stop command
- CO_2 Feed Setpoint

5. Interlocks

- Shutdown on Low-Low or High-High from the pH analyzer or Low-Low level from the storage tank.

6. HMI generated alarms and indications

- Feed Panel in Auto
- System ON
- CO_2 Flow Rate
- CO_2 Tank Level
- pH value
- pH High-High
- pH High
- pH Low
- pH Low-Low

- Loss of Carrier Water Pressure

6. Electrical and Instrumentation

6.1. I&C Requirement

Existing facilities are controlled by a PLC based control system installed into the CP-3 control panel. The well pump speed is controlled by the VFD installed in the CP-3 VFD panel.

The Chromium 6 treatment facilities will include two bag filters, two IX vessels, a carbonic acid storage tank, and carbonic acid feed panel. The following signals need to be added to the existing control system:

Drives

- Carrier Water Pump No.1
- Carrier Water Pump No.2

Each pump will have following I/O points:

1. Remote selected (Digital Input: DI)
2. On status(DI)
3. Fault status(DI)
4. On Command (DO)

Field Instruments

- DPSH-1: Differential Pressure Switch on Bag Filter No.1 (DI)
- DPSH-2: Differential Pressure Switch on Bag Filter No.2 (DI)
- LSH: Leak Detection Switch in Containment Area: (DI)
- PDIT: Level Transmitter on Carbonic Acid Storage Tank: (AI)
- PSH: High Pressure Switch on Carbonic Acid Storage Tank: (DI)
- PSL: Low Pressure Switch on Carbonic Acid Storage Tank: (DI)
- AIT: pH Analyzer on Bag Filters’ Outlet: AI
- FIT: Flow Meter on IX Vessel Effluent/Backwash Supply: (AI)
- PSH: High Pressure Switch on Carrier Water Pump 1
- PSH: High Pressure Switch on Carrier Water Pump 2

<u>I/O signals from/to CO_2 Feed panel</u>

- “CO_2 Feed Rate” from Flow Meter in Feed panel to the PLC : (AI)
- “CO_2 Feed Setpoint” from PLC to the PSF panel: (AO)
- “ Run command” from PLC to the Feed panel: (DO)
- “Feed panel in Auto ” from Feed panel to the PLC: (DI)
- “System ON” from Feed panel to the PLC: (DI)
- “Loss of Carrier Water” from Feed panel to the PLC: (DI)

Based on above listing, additions to the existing control system will include 14 Digital inputs, 3 Digital Outputs, 4 Analog Inputs and 1 Analog output.

The existing control panel CP-3 includes a Modicon Micro PLC model (110 CPU 612 00), which has 16 Digital Inputs, 12 Digital Outputs, 4 Analog Inputs and 2 Analog Outputs in a single housing. The panel has only one digital input spare, one analog input spare, and one analog output spare. Consequently, I/O expansion is necessary for the new drives and instrumentation.

Expanding the system capacity can be achieved in two ways; by simply linking another Micro PLC, configured as "Child", to the existing Micro PLC as "Parent" over a single cable, high speed I/O Expansion Link, or by utilizing A120 Series I/O. Considering new I/O quantities both solutions are achievable, but to keep 20% spare I/O the latter solution (utilizing A120 series I/O) will be used.

6.2. Electrical Requirements

The primary power supply requirements are for the carbon dioxide feed system. The primary equipment is:

<u>Within the storage tank unit:</u>

Vaporizer: 12 kW

Refrigeration Unit: 1.5 kW

Vapor Heater: 4 kW

<u>Adjacent to the storage tank:</u>

Carrier Water Pump: 3.7 kW

In addition there are some smaller power requirements for controls and instrumentation including: the solution feeder panel, high level switch in containment area, flow meter and pH analyzer.

Coordination between GWP and the Los Angeles Department of Water and Power will be required to upgrade the electrical service at the site. The existing power distribution system will be reconfigured with two combination starters, a four circuit 480 V Panelboard and a sub-feeder circuit breaker. All electrical enclosures with be mounted outdoors and will be NEMA 4X. Limited site lighting will be provided adjacent to the carbon dioxide storage tank. Security and fire alarm system are not required, because the site is within a secured site and carbon dioxide is not flammable. Electrical & control conduits will be both exposed and buried and shall have seal fittings in accordance with the NEC. Drain sealing fittings shall be installed in all vertical conduit runs and at low points in conduit systems to provide continuous, automatic drainage of condensate.

7. Acronym List

AI	analog input
AIT	Analyzer indicating transmitter (pH meter)
AO	analog output
AwwaRF	American Water Works Association Research Foundation
cf	cubic feet
CPVC	chlorinated poly vinyl chloride
CML&C	cement-mortar lined and coated
CO_2	Carbon Dioxide
CPU	central processing unit
Cr(VI)	Chromium 6 or hexavalent chromium
DHS	California Department of Health Services; now Department of Public Health
DPSH	differential pressure switch high
DI	digital input
DIP	ductile iron pipe
DO	digital output
FIT	Flow indicating transmitter (Magnetic Flowmeter)
FRP	fiberglass reinforced plastic
ft	foot
GAC	granular activated carbon
gpd	gallons per day
gpm	gallons per minute
gpm/cf	gallons per minute per cubic feet
gpm/sf	gallons per minute per square feet
GWP	Glendale Water and Power
GWTP	Glendale Water Treatment Plant
HCl	hydrochloric acid
HP	horsepower
I&C	instrumentation and control
I/O	input/output
IX	ion exchange

LIH	level indicator high
LSH	level switch high
MCL	maximum contaminant level
MEC	McGuire Environmental Consultants, Inc.
μg/L	micrograms per liter, or parts per billion (ppb)
mg/L	milligrams per liter, or parts per million (ppm)
mm	millimeter
NEC	National Electric Code
NTP	National Toxicology Program
PCE	perchloroethylene
PI	pressure indicator
PLC	programmable logic controller
PSH	pressure switch high
PVC	poly vinyl chloride
SCADA	supervisory control and data acquisition
TCE	trichloroethylene
TCP	tricholoropropane
VAC	volts alternating current
VFD	variable frequency drive
WBA	weak base anion exchange

8. Appendices

Appendix 1 - Civil Site Plan

Appendix 2 - Mechanical Plan

Appendix 3 - Instrumentation and Control Process Flow Diagram

Appendix 4 - Rohm & Haas PWA7 Product Data Sheet

MINIMUM WATER QUALITY PROTECTION REQUIREMENTS

MINIMUM CONSTRUCTION BEST PRACTICES (BMP's) REQUIREMENTS ARE SPECIFIED IN SECTION 2.16 OF THE PROJECT'S SPECIFICATIONS.

THE CONTRACTOR IS DIRECTED TO IMPLEMENT BMP's IN CONJUNCTION WITH ALL ACTIVITIES AND OPERATIONS. MAINTAIN COPIES OF BMP FACT SHEETS (GUIDANCE PAPERS) AT THE PROJECT SITE AND EMPHASIZE TO WORKER / EMPLOYEES PRACTICES CONTAINED ON EACH FACT SHEETS DURING CONSTRUCTION MEETINGS AND CONSTRUCTION OPERATIONS. THE FOLLOWING BMPs WERE SELECTED FROM THE CALIFORNIA STORM WATER BEST MANAGEMENT PRACTICES HANDBOOK, MUNICIPAL, INDUSTRIAL AND CONSTRUCTION VOLUMES:

1. SITE PLANNING CONSIDERATIONS

PRESERVATION OF EXISTING VEGETATION (ESC02)

2. CONSTRUCTION PRACTICES

DEWATERING OPERATIONS (CA01)
PAVING OPERATIONS (CA02)
STRUCTURE CONSTRUCTION AND PAINTING (CA03)
SPILL PREVENTION AND CONTROL (CA12)
DUST CONTROL (ESG21)
STORM DRAIN INLET PROTECTION (ESC54)

3. VEHICLE & EQUIPMENT MANAGEMENT

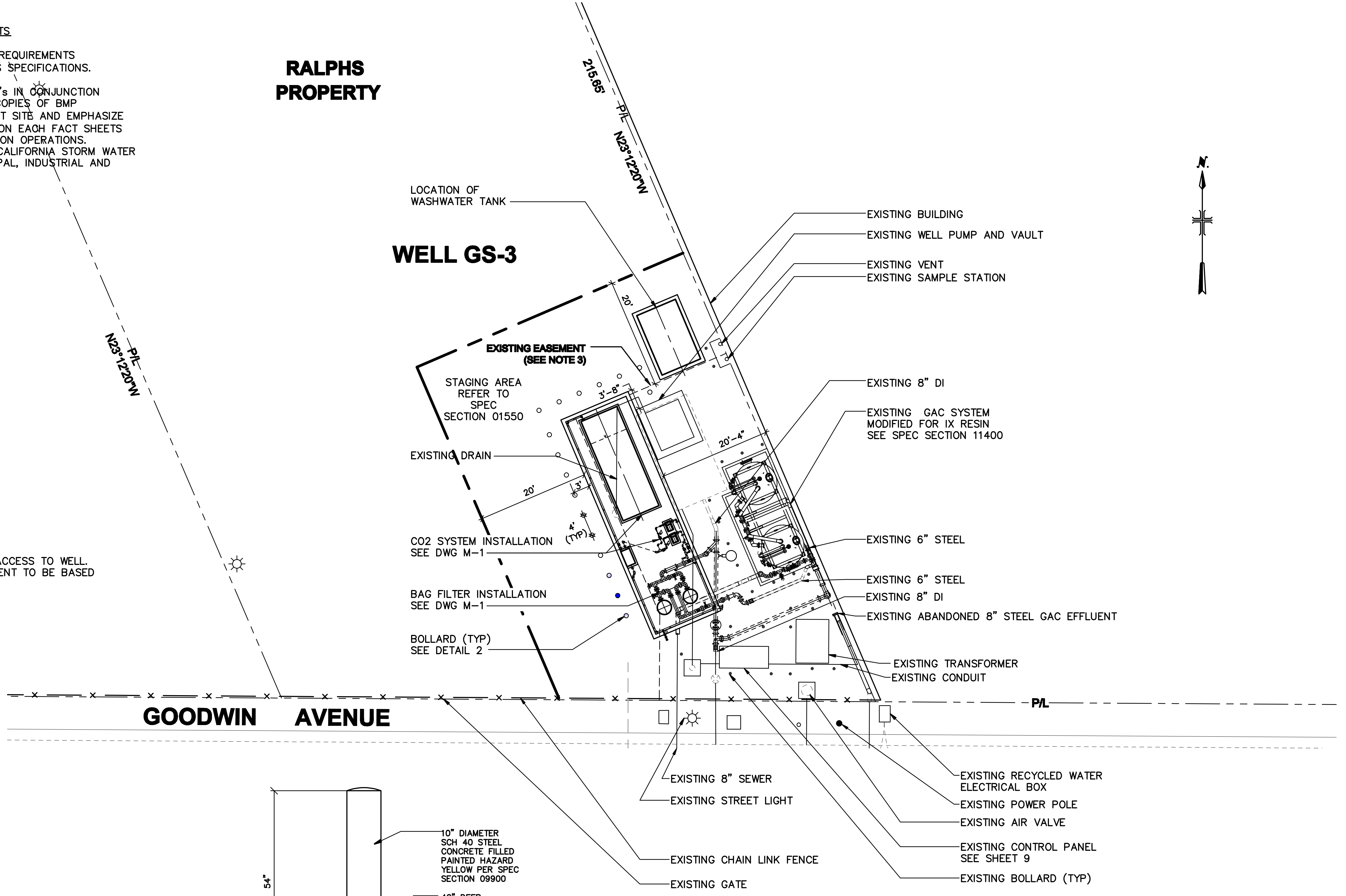
VEHICLE & EQUIPMENT CLEANING (CA30)
VEHICLE & EQUIPMENT FUELING (CA31)
VEHICLE & EQUIPMENT MAINTENANCE (CA32)

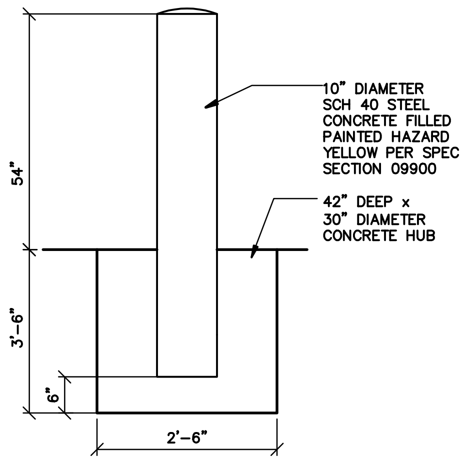
4. MATERIAL MANAGEMENT

MATERIAL DELIVERY AND STORAGE (CA10)
SOLID WASTE MANAGEMENT (CA20)
CONCRETE WASTE MANAGEMENT ((CA23)
SANITARY / SEPTIC WASTE MANAGEMENT (CA24)

NOTES:

1. FINAL LAYOUT TO BE MODIFIED TO IMPROVE ACCESS TO WELL. FINAL LAYOUT AND MODIFICATIONS TO EASEMENT TO BE BASED ON DISCUSSIONS WITH RALPH'S.





TYPICAL BOLLARD DETAIL

DETAIL NOT USED 1 / –

NOT TO SCALE

DETAIL 2 / –

NOT TO SCALE

MALCOLM PIRNIE

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SCALE: 1" = 10'

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5337003 C-1 2ND PDR-1

CITY OF GLENDALE
WATER AND POWER
GOODWIN WATER TREATMENT PLANT
CIVIL SITE PLAN
SHEET C-1 _OF_ SHEETS

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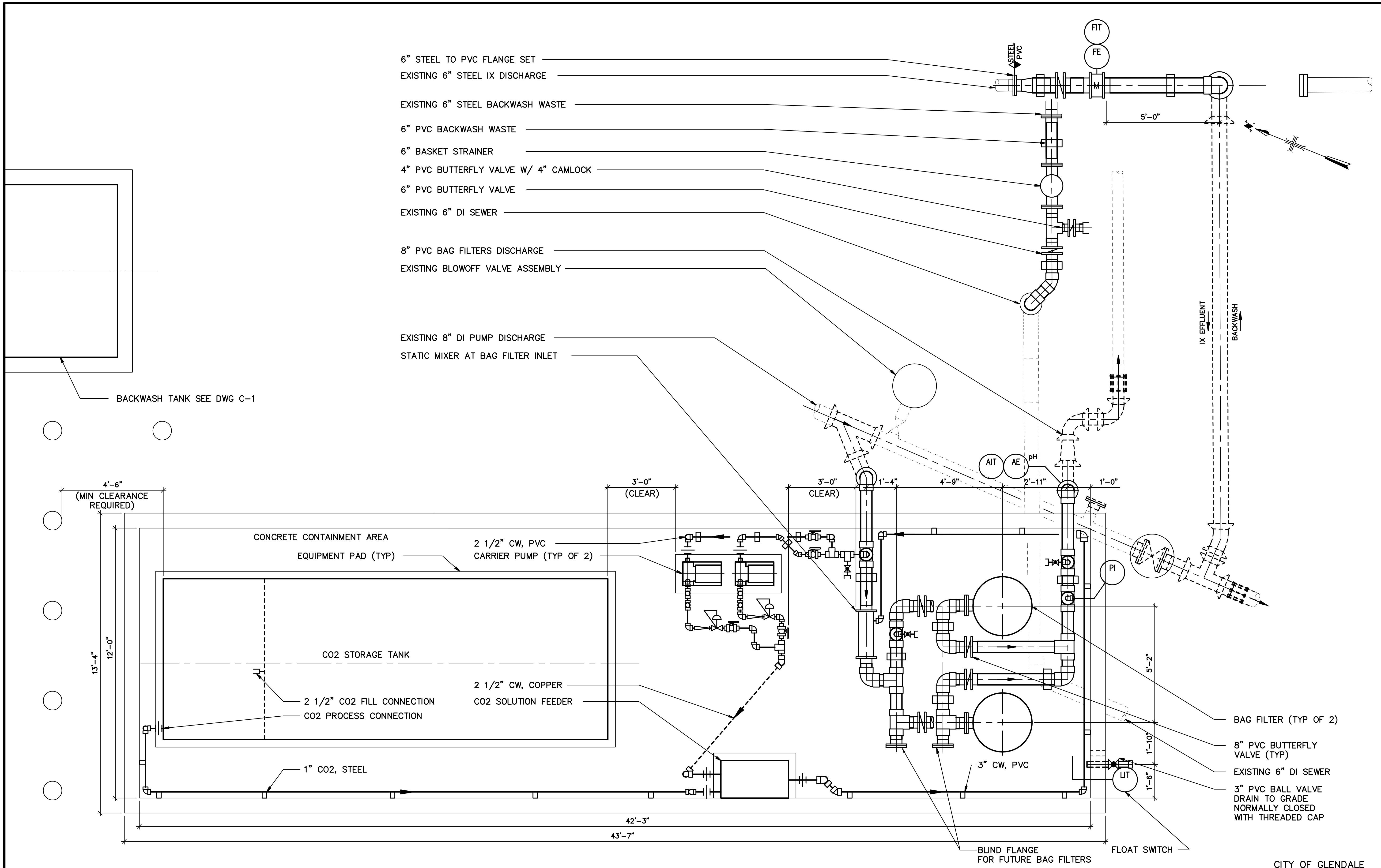

2 0 2
SCALE: 1/2" = 1'-0"

CITY OF GLENDALE
WATER AND POWER
GOODWIN WATER TREATMENT PLANT
MECHANICAL PLAN
SHEET M-1 _OF _SHEETS

5337003 M-1

MALCOLM PIRNIE

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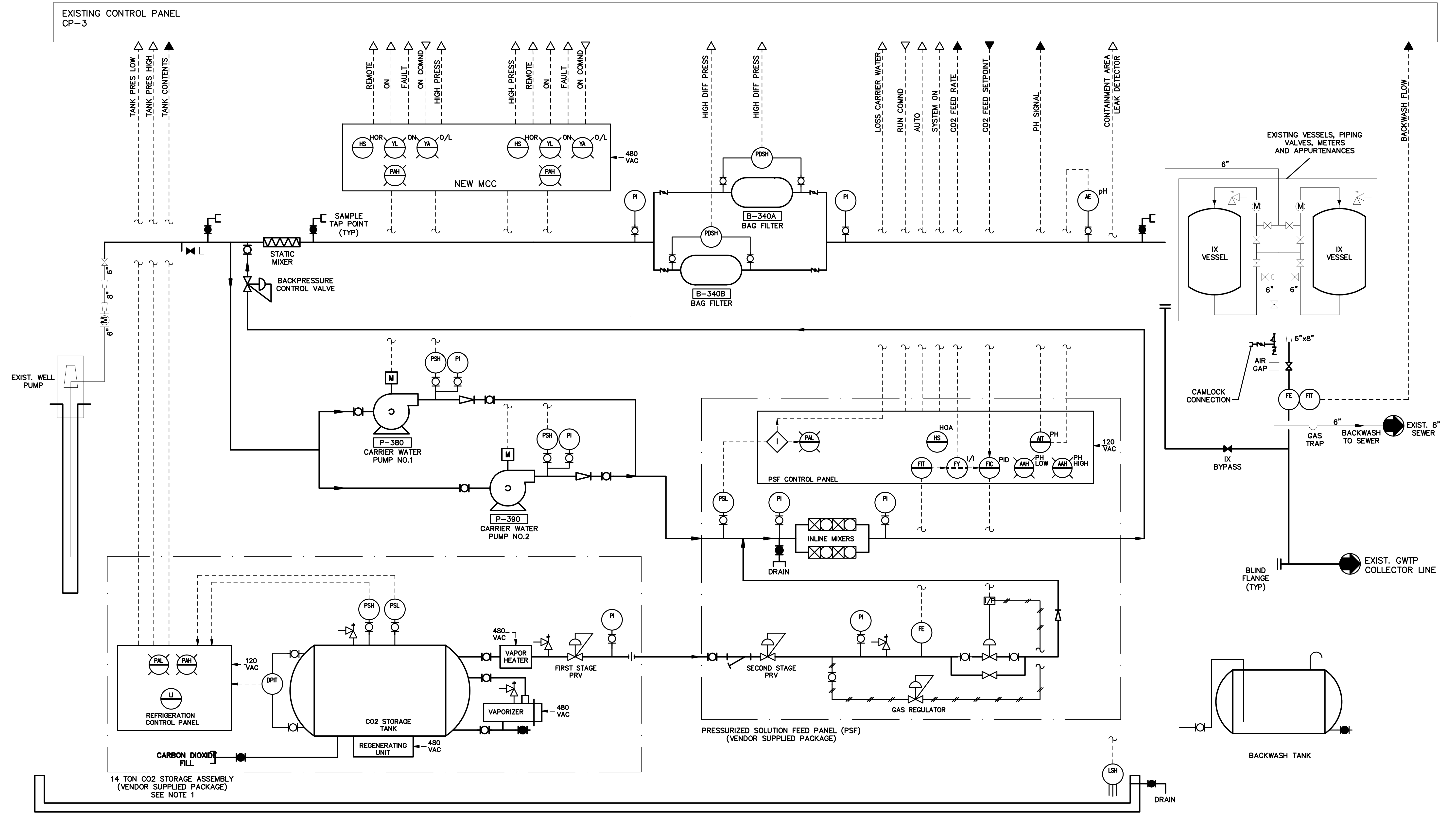

MALCOLM PIRNIE

CITY OF GLENDALE
WATER AND POWER

GOODWIN WATER TREATMENT PLANT

PROCESS AND INSTRUMENTATION DIAGRAM

5337003 I-2 2ND PDR-1

SHEET I-2 12 OF 15 SHEETS

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ROHM
HAAS

AMBERLITE™ PWA7 Resin

Potable Water Grade
Chromate Selective

PRODUCT DATA SHEET

AMBERLITE PWA7 resin is an anion exchange resin designed for the removal of chromate from drinking water. Its high capacity makes AMBERLITE PWA7 resin the perfect choice for a simple, once through chromate removal process for municipal water treatment systems.

PROPERTIES

Physical form	Cream coloured granules	
Matrix	Cross linked polycondensate	
Moisture holding capacity	54 – 64%	
Shipping weight	610 kg/m^3	(38 lb/ft^3)
Particle Size		
Screen grading	0.3 – 1.2 mm	(16 – 50 mesh US Std Screens)
Fines content	<0.300 mm: 3% max	

SUGGESTED OPERATING CONDITIONS

Please contact your Rohm and Haas representative for system design and application testing details.

pH range	< 6.5	
Maximum operating temperature	40 °C	(105 °F)
Minimum bed depth	610 mm	(24 inches)
Typical service flow rate	8 – 40 BV/hr*	(1 – 5 gpm/ft^3)

** 1 BV (Bed Volume) = 1 m^3 solution per m^3 resin*

COMMISSIONING AND LIMITS OF USE

AMBERLITE PWA7 resin is suitable for use in potable water applications after an initial commissioning upflow rinse of 20 bed volumes of water at ambient temperature at service flow rate.

The operating capacity of AMBERLITE PWA7 resin depends on the operating conditions and the feed water conditions.

REGULATORY

AMBERLITE PWA7 resin is certified to ANSI / NSF Standard 61 for drinking water components drinking water components for applications with minimum flow rates greater than or equal to 1.1 gpm/ft^3. Please contact your Rohm and Haas representative for additional certification information.

Resin products are manufactured in ISO 9001 certified facilities.

HYDRAULIC CHARACTERISTICS

Figure 1 and Figure 2 show the pressure drop data for AMBERLITE PWA7 resin as a function of flow rate and water temperature. Pressure drop data are valid at the start of the service run with clean water and a correctly classified bed. Figure 3 and Figure 4 show the bed expansion of AMBERLITE PWA7 resin as a function of backwash flow rate and water temperature.

Figure 1 Pressure Drop (metric)

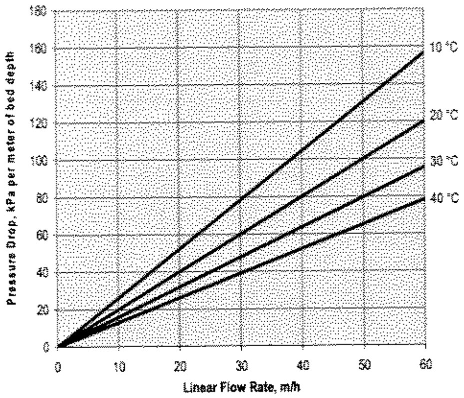


Figure 2 Pressure Drop (US units)

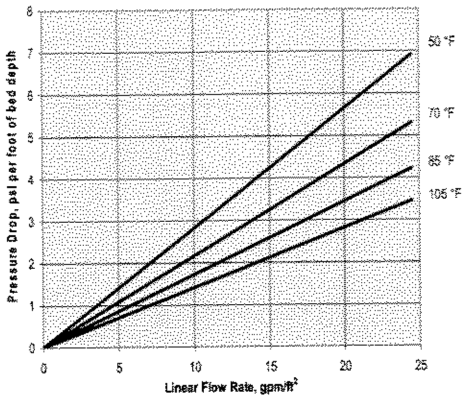


Figure 3 Bed Expansion (metric)

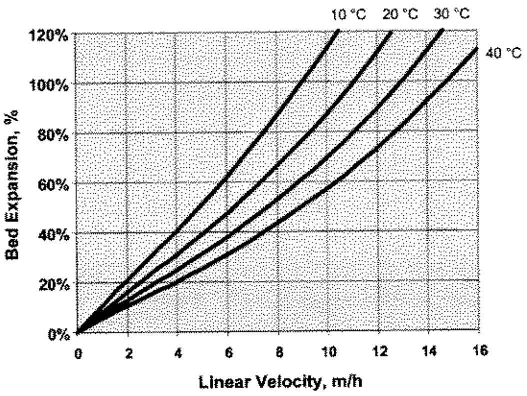
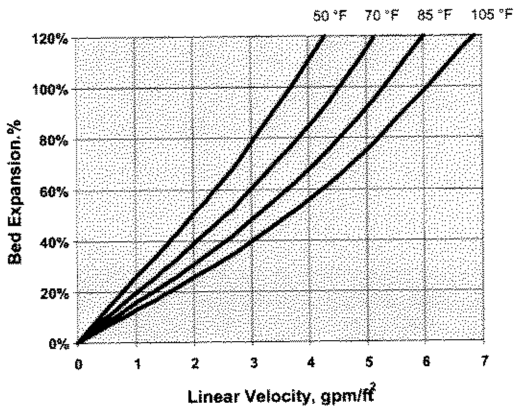


Figure 4 Bed Expansion (US units)



Rohm and Haas/Ion Exchange Resins - Philadelphia, PA - Tel. (800) RH AMBER - Fax: (215) 409-4534
Rohm and Haas/Ion Exchange Resins - 75579 Paris Cedex 12 - Tel. (33) 1 40 02 50 00 - Fax : 1 43 45 28 19

Ion exchange resins and polymeric adsorbents, as produced, contain by-products resulting from the manufacturing process. The user must determine the extent to which organic by-products must be removed for any particular use and establish techniques to assure that the appropriate level of purity is achieved for that use. The user must ensure compliance with all prudent safety standards and regulatory requirements governing the application. Except where specifically otherwise stated, Rohm and Haas does not recommend its ion exchange resins or polymeric adsorbents, as supplied, as being suitable or appropriately pure for any particular use. Consult your Rohm and Haas technical representative for further information. Acidic and basic regenerant solutions are corrosive and should be handled in a manner that will prevent eye and skin contact. Nitric acid and other strong oxidizing agents can cause explosive type reactions when mixed with Ion Exchange resins. Proper design of process equipment to prevent rapid buildup of pressure is necessary if use of an oxidizing agent such as nitric acid is contemplated. Before using strong oxidizing agents in contact with Ion Exchange Resins, consult sources knowledgeable in the handling of these materials.

Appendix B – Quality Assurance Project Plan

Note that the QAPP was updated and re-submitted to the EPA on March 25, 2008. Refer to Section 7 for the updated version.

Appendix C – Pump Curve Evaluation

MALCOLM PIRNIE

Technical Memorandum

Date: July 2, 2007

To: Don Froelich and Peter Kavounas

From: Michael McGuire, Jack Bebee, and Nicole Blute

Subject: Pump Curve Evaluation and Decision

Pump Curve Evaluation

As part of the preliminary design of the GS-3 WBA treatment system, we evaluated the hydraulics of the current pump in GS-3 and the system losses expected from the new facilities to determine the projected pumping capacity. Figure 1 shows that current GS-3 pump curve from a test performed in June 2007 by CDM (dark blue line). To bracket the range, two roughness coefficients (C=130 and 100) and two main pressures (45 and 55 psi) were used in the pump curve evaluation. According to the figure, the GS-3 pump currently has an estimated operating range of between 550 to 600 gpm at 100% pump speed.

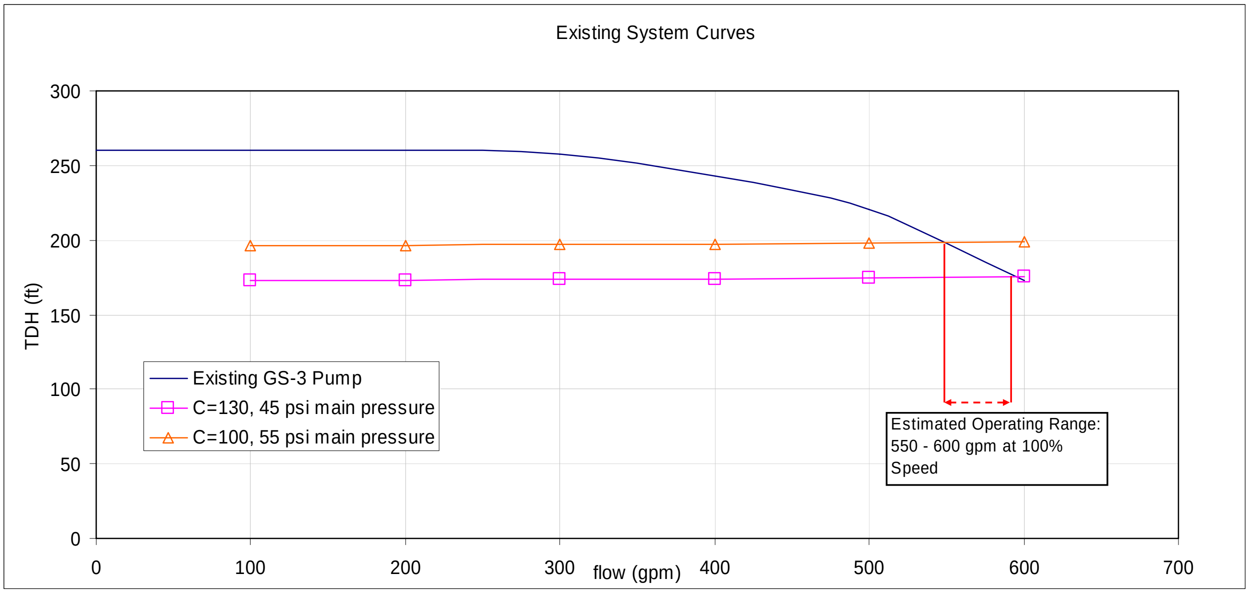


Figure 1. Existing System Curves for the GS-3 Pump without the WBA Facility

The addition of a WBA treatment system between the well and the main will introduce pressure losses, due to the bag filters, ion exchange resin beds, and additional piping. For example, the bag filters are estimated to have a 2 psi drop across the filter housing when the filters are clean, and up to a 10 psi drop for dirty filters (i.e., the point at which filter change-out is recommended by the vendor). Figure 2 shows the intersection of the actual GS-3 pump curve (dark blue line) and manufacturer provided pump curve (light blue line) with the upper and lower range for the system curves. The upper range is based on clean bag filters (2 psi differential) and the estimated best-case main pressure (45 psi) and C factor (130). The lower range is based on dirty bag filters (10 psi differential) and the estimated worst case main pressure (55 psi) and C factor (100). The estimated operating range for the pump is between 250 and 480 gpm at 100% pump speed.

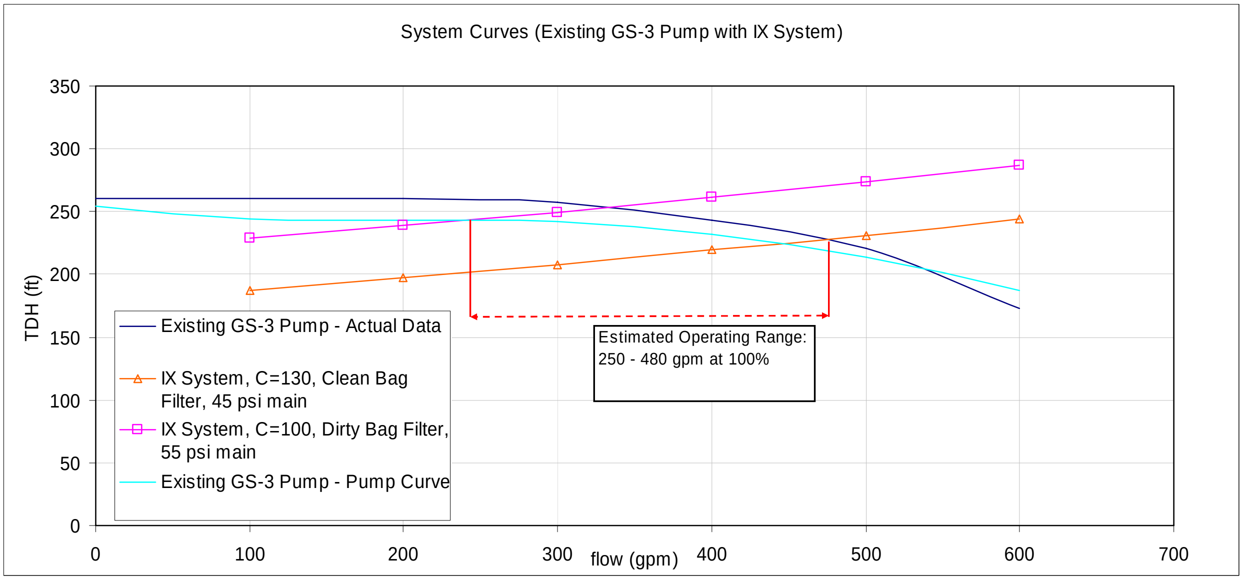


Figure 2. Predicted System Curves for the GS-3 Pump with the WBA Facility

Two possibilities exist to achieve the desired 425 gpm design capacity for the WBA treatment system. First, the existing GS-3 pump could be used and the bag filters replaced on more frequently than when 10 psi pressure loss occurs. Second, the GS-3 pump could be replaced with one capable of achieving a higher operating flow.

Glendale has an unused high head pump purchased with the GAC vessels, so the hydraulics were evaluated to determine if option is possible using the existing equipment. Figure 3 shows the pump curves for 100%, 80%, and 50% pump speeds, along with the system curves for a range of ion exchange system conditions. The analysis indicated that the high head pump could achieve an operating capacity of approximately 410 to 475 gpm at 80% speed. However, operation of the pump at 80% speed would not optimize the capital costs associated with installing a larger 75 HP pump at the facility, and the upper end of the flow operating range would not be improved over the existing GS-3 pump. Based on this evaluation, purchasing and installing a new pump optimized for the system would likely be preferable compared with using the existing high head pump.

Other issues that may cause complications with well pump replacement include clearance in the GS-3 vault and the potential costs of a new pump and system upgrades to accommodate a larger motor. Exchanging the existing pump with a larger horsepower motor may not be simple due to space constraints. Significant costs may also arise if a new pump is purchased and electrical modifications are necessary for the larger motor.

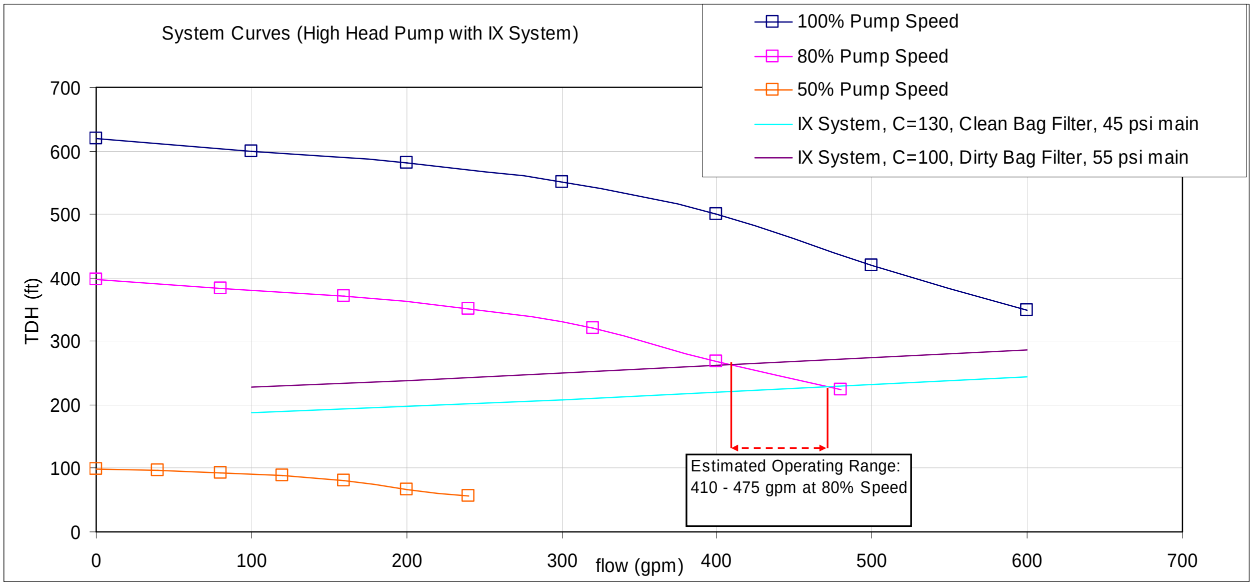


Figure 3. High Head Pump Predicted System Curves with the WBA Facility

Recommendations

Based on this hydraulic analysis, we recommend that Glendale proceed with the preliminary design using the existing GS-3 pump. It should be noted that pressure losses in the WBA facility will limit the flow compared with the current possible flow capacity of the existing GS-3 pump. However, flow limitations might be overcome during the demonstration-scale study by replacing bag filters on a more frequent basis.

Operation of the demonstration-scale study using the existing pump will also provide useful hydraulic information on head losses through the WBA treatment facility including the rate of development of pressure loss through the bag filters. If Glendale decides that the flow is not sufficient with the existing pump, this information will be useful to optimize selection of a more optimal pump based on the actual operating data from the system.

Appendix D – Corrosivity Evaluation of the Treated WBA Water

Technical Memorandum

Date: September 24, 2007

To: Don Froelich

From: Danny Qin, Nicole Blute, and Michael McGuire

Subject: Corrosivity of the proposed WBA resin treated effluent due to acid addition

In an effort to remove hexavalent chromium (Cr(VI)) from its contaminated groundwater supplies, the City of Glendale is proposing to test two Cr(VI) treatment processes at demonstration scale: weak-base anion exchange (WBA) and reduction-coagulation-filtration (RCF). The RCF process was recommended by an Expert Panel that reviewed the pilot testing results in the Phase II Pilot Study[1] and the Phase III Bridge Project[2]. The WBA process is being carried forward to demonstration scale as a result of a decision by Glendale and additional testing at Lehigh University recommended by the Expert Panel. The two demonstration-scale systems (with capacity of 425 gpm for WBA and either 567 or 1,134 gpm for RCF) will be constructed to treat Cr(VI) contaminated water from high-Cr wells of the Glendale Operable Unit. Treated water (i.e., chromium levels less than 5 μg/L) will be used for human consumption after blending with lower chromium wells at the Glendale Water Treatment Plant.

Final design of the WBA system is currently in progress, while pre-design of the RCF system is scheduled in several months. This memorandum is intended to address an outstanding water quality issue for the WBA process: the corrosion potential of the WBA treatment process effluent, which may be of concern due to the pH reduction necessary for WBA resin use. The potential impact of integrating the WBA treated water (with lower pH) into the existing Glendale SOU transmission system is assessed in this technical memo.

Proposed WBA process

Cr(VI) removal using WBA resin is a novel treatment technology application for drinking water. During the Phase II Pilot Study and Phase III Bridge Project, WBA resin (Duolite A7 resin manufactured by Rohm & Haas; since renamed PWA7) consistently demonstrated an exceptional Cr(VI) removal capacity. Another WBA resin, ResinTech SIR-700, showed a high capacity but mixed results in consistently achieving the treatment goal of 5 μg/L. As determined in the Phase III Bridge Project, the mechanism

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[1] McGuire Environmental Consultants, Inc. (MEC) 2005. The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale Groundwater Supply: Phase II Demonstration of Pilot-Scale Treatment Technologies. Final report submitted to the City of Glendale. Glendale, CA.

[2] McGuire, M.J., Blute, N.K., Qin, G., Kavounas, P., Froelich, D., Fong, L. 2007. Hexavalent Chromium Removal from Drinking Water Using Weak- and Strong-Base Ion Exchange and Reduction/Coagulation/Filtration. Denver, Colo.: AwwaRF.

of Cr(VI) removal and/or retention by WBA resin involves a reduction process in which Cr(VI) is reduced to Cr(III).

The WBA demonstration-scale system will be located at Glendale South Operable Unit (SOU) well site GS-3 adjacent to Goodwin Street in the City of Los Angeles. The system will consist of two ion exchange (IX) vessels operated in series (lead-lag) with upstream hydrochloric acid addition for pH depression. Figure 1 provides a process flow schematic for the treatment system. Due to its high capacity and difficulty in regeneration, the WBA will be used as a once-through, disposable media.

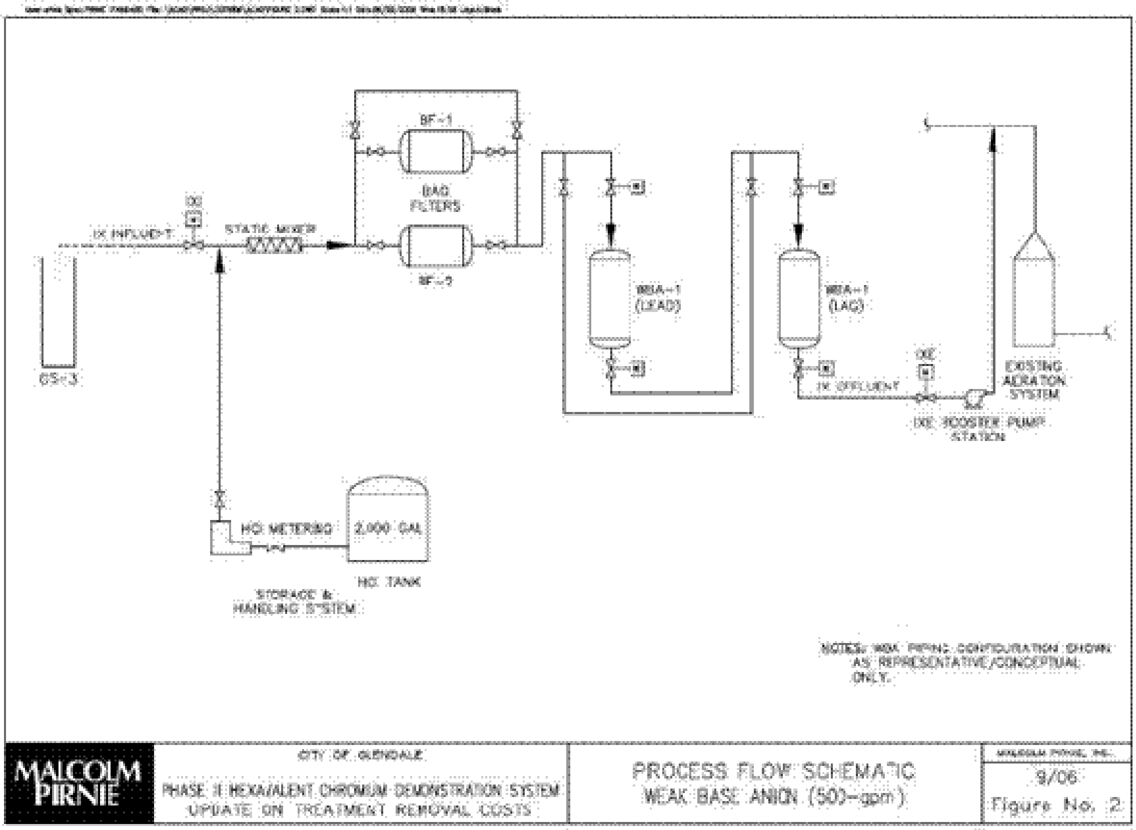

Figure 1: Process flow schematic of the WBA system

The WBA resin was found to require pH reduction for effective use; a pH of 6.0 was shown to both remove Cr(VI) to levels below the treatment goal of 5 µg/L and to maximize Cr(VI) capacity of the resin. Hydrochloric acid will be injected into the GS-3 well water upstream of the IX vessels to maintain a constant pH of 6.0. As shown in pilot testing, the pH does not change significantly as the water passes through the IX beds; consequently, the WBA treated water will have a pH of approximately 6.0. The potential for increased corrosivity of this water was therefore considered in this preliminary design phase technical memo.

Methodology

Water utility operators have relied on precipitation of calcium carbonate ($CaCO_3$) for many years to control corrosion of distribution system materials. Several indices are available to describe the potential for precipitation of $CaCO_3$ including: Langelier Saturation Index (LSI), Aggressiveness Index, Ryznar Index, Driving Force Index and Calcium Carbonate Precipitation Potential (CCPP)[3]. Among them, LSI and CCPP are the most commonly used indices by researchers and utility managers.

In this assessment, LSI and CCPP values were calculated using a model developed by Rothberg, Tamburini, and Winsor (RTW Model for Corrosion Chemistry and Water Process, Version 4.0). Water quality parameters input into the RTW Model included pH, temperature, alkalinity, total dissolved solids (TDS), calcium (Ca^{2+}), chloride (Cl^-), and sulfate (SO_4^{2-}).

Water quality data for pH, temperature, and alkalinity from all four Glendale SOU wells (GS-1, GS-2, GS-3, and GS-4) were obtained from field analysis conducted on June 11, 2007. pH and temperature were measured using a Hach SensION1® meter with a specialized sampling apparatus developed for this testing (see Figure 2 for details). The purpose of the sampling apparatus was to minimize the release of supersaturated carbon dioxide (CO_2) from the groundwater to ensure the accuracy of pH measurement. Previous testing in the Phase III Bridge Project indicated that off gassing of CO_2 led to rapid increases in the Glendale groundwater pH. In addition to pH measurements, alkalinity was determined immediately in the field using Hach Method 8203.

Ca^{2+}, Cl^-, SO_4^{2-} and TDS are monitored approximately every three years in the Glendale GS wells; historical data (up through 2007) provided by CDM were used in the RTW modeling.

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[3] Rossum, J.R., and Merrill, D.T., "An Evaluation of the Calcium Carbonate Saturation Indexes," Jour. AWWA, 75:2, February 1983.

Figure 2: pH and temperature measurement with the specialized sampling apparatus developed to minimize CO_2 off gassing (pH probe shown in the center of the apparatus)

Results

Table 1 lists the field analysis results of pH, temperature, and alkalinity from all four GS wells. The pH values in all GS wells were quite similar – approximately 7.0 using the sampling apparatus. Unfortunately, carbon dioxide degassing was not fully eliminated during pH sampling even with the apparatus, as evidenced by the bubbles inside in the sampling line (Figure 3). The measured pH was expected to be a little higher than the actual groundwater pH due to this off gassing. In Phase III Bridge Project testing, the pH in GS-3 well was determined to be 6.8 using an in-line pH probe under pressure (i.e., without CO_2 degassing). Since all other wells showed similar pH values to the GS-3 well in this testing on June 11th, a pH of 6.8 was found to be a good estimate for all of the GS wells; this value was consequently used in the RTW Model. Field temperature data from each well were also used as the model input.

Table 1: Water quality results from GS wells on June 11, 2007

	Well ID			
Field Measurements	**GS-1**	**GS-2**	**GS-3**	**GS-4**
pH	7.01	7.02	7.05	6.97
Temperature (°C)	21.6	22.1	22.9	23.6
Alkalinity (mg/L as $CaCO_3$)	162	156	154	141

Figure 3: Release of some supersaturated CO_2 in the sampling line

Table 2 lists the historical Ca^{2+}, Cl^-, SO_4^{2-}, TDS, and alkalinity data from the four GS wells from 1998 to 2007. Table 2 shows that water quality in all four GS wells was generally similar and did not change much over a 9 year period.

Table 2: Historical water quality data ranges for the GS wells sampled between 1998 and 2007

	Well ID			
Lab Measurements	**GS-1**	**GS-2**	**GS-3**	**GS-4**
Ca^{2+} (mg/L)	87 - 98	80 - 86	79 - 90	82 - 90
Cl^- (mg/L)	65 - 88	53 - 58	59 – 68	63 – 70
SO_4^{2-} (mg/L)	140 - 160	96 - 110	96 - 110	112 – 130
TDS (mg/L)	540 - 630	440 - 530	450 - 530	480 – 540
Alkalinity (mg/L as $CaCO_3$)	223 - 251	205 - 244	176 - 220	163 – 187

* Note: Ca^{2+}, Cl^-, SO_4^{2-}, and TDS were measured five times between 1998 and 2007.

As seen in Tables 1 and 2, alkalinity measured in the field was lower than the historical data. The reason for this difference is not clear. Consequently, two sets of LSI and CCPP values were determined using both the field data and the historical data.

Table 3 summarizes the ranges in LSI and CCPP of the RTW Model output using datasets from 1998, 1999, 2000, 2002, 2004, and 2007. Regardless of the alkalinity input in the model, all GS well water had negative LSI values between -0.22 and -0.50 and

CCPP values in the -27 to -37 mg/L $CaCO_3$ range, indicating that the water is corrosive in the existing Glendale SOU transmission system.

Table 3: Summary of RTW Model output

	Well ID			
	GS-1	**GS-2**	**GS-3**	**GS-4**
LSI				
Field alkalinity data[a]	-0.40 to -0.45	-0.46 to -0.48	-0.43 to -0.48	-0.46 to -0.50
Historical alkalinity data[b]	-0.22 to -0.31	-0.27 to -0.36	-0.28 to -0.42	-0.35 to -0.43
CCPP (mg/L as $CaCO_3$)				
Field alkalinity data[a]	-33 to -37	-36 to -37	-34 to -37	-33 to -35
Historical alkalinity data[b]	-27 to -34	-31 to -36	-30 to -37	-32 to -35

Note:

a. Calculated with field alkalinity data as shown in Table 1
b. Calculated with historical alkalinity data as shown in Table 2

According to RTW modeling, the planned change in pH for using the WBA resins (from the ambient groundwater pH of 6.8 to pH 6.0) will reduce the LSI Index and CCPP corrosion indices as shown in Table 4. The LSI and CCPP values of WBA treated water were calculated as -1.51 and -162 mg/L, respectively, indicating the water would be more aggressive than the raw GS-3 water (LSI of -0.43 and CCPP of -34 mg/L).

Table 4: Summary of water quality and RTW Model output data for raw GS-3 water and the WBA treated water

	Raw GS-3 water	**WBA treated GS-3 water (pH 6.0)**
Water Characteristics		
pH	6.8	6.0
Temperature (ºC)	22.9	22.9
Alkalinity (mg/L as $CaCO_3$)	154[a]	82[b]
Ca^{2+} (mg/L)	89[c]	89[d]
Cl^- (mg/L)	68[c]	128[e]
SO_4^{2-} (mg/L)	110[c]	110[d]
TDS (mg/L)	466[c]	526[e]
Calculated Values		
LSI	-0.43	-1.51
CCPP (mg/L)	-34	-162

Notes:

a. Field alkalinity data as shown in Table 1
b. Average alkalinity of WBA resin (PWA7) treated effluent as measured during Phase III Bridge Project
c. Data from 5/16/2007
d. Assumed to be equivalent to raw GS-3 water
e. HCl addition is expected to increase the Cl^- and TDS concentrations in WBA treated water by approximately 60 mg/L

Under normal operation (i.e., all GS wells operating), the WBA treated water will first blended with GS-4 well water in the transmission pipeline. Assuming both GS-3 and GS-4 wells were running at design capacity (425 gpm), LSI and CCPP values were determined using the RTW Model (Table 5).

Table 5: Summary of water quality and RTW Model output data of blending the WBA treated water (pH 6.0) and raw GS-4 well water

	WBA treated GS-3 water (pH 6.0)	Raw GS-4 water
Water Characteristics		
pH	6.0	6.8
Temperature (ºC)	22.9	23.6
Alkalinity (mg/L as $CaCO_3$)	82	141[a]
Ca^{2+} (mg/L)	89	90[b]
Cl^- (mg/L)	128	70[b]
SO_4^{2-} (mg/L)	110	130[b]
TDS (mg/L)	526	510[b]
Design flow rate (gpm)	425	425
Calculated Values	**Blended water**	
pH	6.33	
Temperature (ºC)	23.3	
Alkalinity (mg/L as $CaCO_3$)	112	
Ca^{2+} (mg/L)	90	
Cl^- (mg/L)	99	
SO_4^{2-} (mg/L)	120	
TDS (mg/L)	520	
LSI	**-1.04**	
CCPP (mg/L)	**-101**	

Note:

a. Field alkalinity data as shown in Table 1
b. Data from 5/16/2007

Summary and Recommendations

The results of this investigation indicated that the well water was already corrosive with respect to calcium carbonate under ambient groundwater conditions. The addition of WBA treatment, including pH adjustment to 6.0, will increase the magnitude of the negative LSI and CCPP values. However, the impact of this change (i.e., from -0.44 to -1.05 for LI and -34 to -101 for CCPP) on corrosivity of the cement-mortar lined piping is uncertain since the water is corrosive to begin with. Visual inspection of the pipeline condition before and after the demonstration-scale study is strongly recommended to evaluate the impact of WBA treated effluent on the pipeline and the necessity of pH adjustment after treatment.

10. WBA Demonstration-Scale QAPP

Phase III Demonstration-Scale WBA Resin Treatment Technology Evaluation

The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale, California Ground Water Supply:

Phase III
Demonstration-Scale
WBA Resin
Treatment Technology Evaluation

QUALITY ASSURANCE PROJECT PLAN

Draft Submitted to the USEPA Region 9 on
September 18, 2007

Updated March 25, 2008

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Appendix B. ELAP Certifications

0. Approval by Project Participants

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Eugenia McNaughton, Ph.D, USEPA	Date
Peter Kavounas, City of Glendale	Date
Michael McGuire, Ph.D., P.E., MMP	Date
Michael MacPhee, Ph.D., MMP	Date
Laurie McNeill, Ph.D., Utah State University	Date
Gary Amy, Ph.D., UNESCO	Date
Mel Suffet, Ph.D., UCLA	Date

Distribution List of Principal Project Participants

Each organization included in this project is to receive and retain a copy of this QAPP.

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1 Project Description and Objectives

The City of Glendale's groundwater supply in the San Fernando Valley has been contaminated with a wide variety of chemicals, including hexavalent chromium [Cr(VI)], trichloroethylene (TCE), perchloroethylene (PCE), 1,2,3-trichloropropane (TCP), and others, mainly as a result of the improper disposal of industrial waste products. Extraction and treatment of volatile organic compounds (VOCs) is underway in the San Fernando Valley using air stripping and granular activated carbon (GAC), and the treated water is served to customers. Although Cr(VI) was also found in the groundwater supplies, levels were below the total Cr maximum contaminant level (MCL) of 50 μg/L in California. No Cr(VI) treatment was included with the VOC facilities at the time they were constructed.

Until June 2007, the health effects of Cr(VI) in drinking water were uncertain; Cr(VI) was a proven carcinogen by inhalation but little evidence existed to demonstrate the impact of Cr(VI) ingestion. However, a recent study conducted by the National Toxicology Program (NTP) showed that Cr(VI) is a carcinogen by ingestion in animal studies (NTP 2007). Even prior to this study, the Legislature of California mandated that the California Department of Public Health (DPH) establish a Cr(VI) MCL. First, the Office of Environmental Health Hazard Assessment (OEHHA) must set a public health goal (PHG), which will likely be based on the new NTP findings. In Glendale, public concern about Cr(VI) in the groundwater supply led the city to embark on a multi-phase study to identify and install Cr(VI) treatment in anticipation of a Cr(VI) MCL lower than the current total Cr MCL in California.

In the year 2000, the City of Glendale, along with the Cities of Los Angeles, Burbank, and San Fernando, initiated a testing program to develop a full-scale Cr(VI) treatment system capable of removing Cr(VI) to low parts-per-billion levels. The **Phase I Bench-scale study** was conducted to improve the understanding of fundamental chromium chemistry and to screen promising technologies for their ability to treat and remove Cr(VI) to very low levels. The Phase I study is complete and the final report was published by AwwaRF (Brandhuber et al. 2004). The **Phase II Pilot-scale study** was initiated in the summer of 2003 to further test the promising Cr(VI) removal technologies at the pilot scale (i.e., several gallons-per-minute flows) using Glendale groundwater. A final report on the Phase II pilot-scale study was completed in 2005 (MEC 2005). Selected results were also published in peer-reviewed scientific journals (Qin et al. 2005, McGuire et al. 2006).

The **Phase III Demonstration-scale study** will finalize the treatment evaluation, residuals assessment, and cost estimate development by implementing one or more Cr(VI) removal technologies. The initial part of the Phase III effort was designated as the Phase III Bridge Project, which included additional studies to finalize testing of weak-base anion exchange resins for Cr(VI) treatment, refinement of treatment technology cost estimates based on Phase III Bridge Project results, and assembly of an expert panel to recommend one or more treatment processes for demonstration-scale testing. The Phase III Bridge Project was completed in early 2007.

The Phase III Demonstration-scale study will test weak-base anion (WBA) exchange using a 425 gpm well. Depending on additional funding availability, the City of Glendale may also construct a reduction-coagulation-filtration (RCF) treatment system on one or more other wells. This QAPP covers only the WBA treatment system, which is funded in part by the USEPA State and Tribal Assistance Grant (STAG).

The purpose of this project is to demonstrate the effectiveness of WBA resin in removing Cr(VI) to low part-per-billion levels. The system will be operated for one year under the STAG grant, and treated water will be put to beneficial use by serving Glendale's consumers. Treatment cost information developed in the Phase II Pilot-scale and Phase III Bridge studies will be updated as a result of this effort. This information is intended to be of use to other utilities requiring Cr(VI) treatment and to the state of California in setting a Cr(VI) MCL.

1.1 Treatment System Description

Cr(VI) removal by WBA resin is a novel application of ion exchange for drinking water treatment. Originally, WBA resin was believed to behave similarly to strong-base anion exchange (SBA) resins in terms of removal mechanism, except that the WBA resins are only useful in the acidic pH range where the functional groups are protonated and thus have positively charged exchange sites to attract Cr(VI) as chromate or bichromate ion. However, the WBA resin tested in the Phase II pilot study (Duolite A7, now called PWA7, resin provided by Rohm & Haas) showed a 20 times higher Cr(VI) removal capacity compared with five SBA resins tested. Other observations, such as leakage of Cr(III) during periods in which pH values were lower than 5.5, indicated that an ion exchange mechanism alone was not likely responsible for all of the Cr(VI) removal by WBA resin.

As part of the Phase III Bridge study, five other WBA resins were tested to evaluate Cr(VI) removal. In addition, the impact of pH on the performance of the top resins was assessed to minimize acid addition requirements. PWA7 resin again showed a high Cr(VI) capacity along with another WBA resin (ResinTech SIR-700, which did not perform as well as the PWA7 initially but improved over time). Testing confirmed that more than 95% of the Cr(VI) retained on both resins was in the form of Cr(III), as observed directly by x-ray absorption spectroscopy. The true mechanism of Cr(VI) removal and retention by the WBA resins is hypothesized to first involve adsorption followed by reduction and retention perhaps by the resin backbone (SenGupta and Sarkar, 2007).

To date, WBA has only been tested in bench- and pilot-scale studies. The proposed demonstration-scale WBA system will be the first installation of this technology in a drinking water treatment application.

The WBA system that will be constructed and tested in the Phase III Demonstration-scale study will consist of the following major components:

- Ion exchange vessels (two 8-ft. diameter vessels each containing 185 cubic feet of WBA resin)
- Bag filters (two parallel filter housings containing 10-micron filters),

- Carbon dioxide (CO_2) storage tank (14 tons), and
- CO_2 feed and control system.

Figure 1-1 provides a process flow schematic for the WBA system. The system will consist of a pair of lead/lag vessels with upstream CO_2 addition for pH depression. Due to the resin's high capacity and difficulty in regeneration, WBA resin will be used as a once-through, non-regenerable media.

The WBA system will be located at the GS-3 well site adjacent to Goodwin Street in the City of Los Angeles. The GS-3 well was selected for testing the WBA demonstration-scale system for two primary reasons: (1) GS-3 is one of the high Cr(VI) wells, with a current Cr(VI) concentration of approximately 50 μg/L (historical peak of 69 μg/L); and (2) a pair of unused GAC vessels exist at the GS-3 well site and can be retrofitted for WBA resin, thus minimizing capital costs for ion exchange vessels.

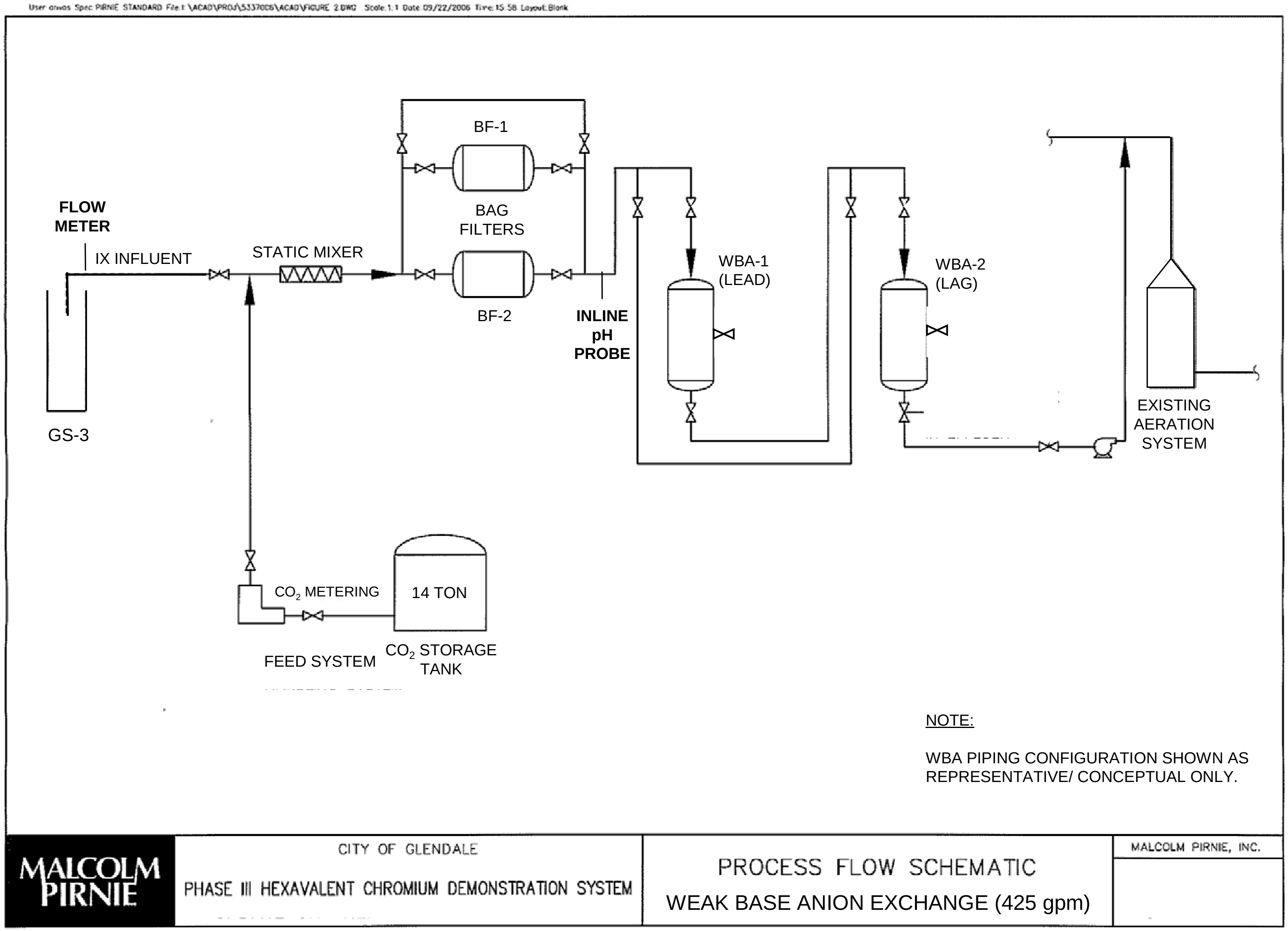


Figure 1-1. Process Flow Schematic of the WBA Exchange System

1.2 Project Objectives

The objectives of the Phase III Demonstration-scale study include the following:

- Evaluate Cr(VI) removal capacity of WBA resin at the demonstration-scale (approximately 425 gpm) and the ability to scale-up bench and pilot results;
- Quantify demonstration treatment performance with respect to Cr(VI) removal over extended periods of time (i.e., at least one year);
- Assess the impact of WBA resin treatment on finished water quality, including any leaching of nitrosamines, and develop mitigation strategies;
- Optimize day-to-day operations of the WBA treatment system and develop a comprehensive operations and maintenance manual;
- Assess the reliability of the demonstration-scale WBA technology during a year of operations and identify necessary backwashing or fluffing frequency;
- Confirm residuals optimization and disposal strategies identified in the Phase III Bridge project;
- Verify unit cost information developed in the pilot study with actual treatment costs; and
- Publicly disseminate project plans and findings to a wide audience, including water agencies also concerned with Cr(VI) in water supplies, California DPH, the USEPA, and consumers.

Glendale's goal of the WBA treatment system is to reduce Cr(VI) concentrations to less than 5 ppb using the WBA resin. Since a Cr(VI)-specific MCL does not currently exist and the total Cr concentrations in the blended water are below the total Cr MCL, the success or failure of the project cannot be defined as a specific concentration. Nevertheless, the change-out criteria for the WBA resin will be when Cr(VI) or total Cr exceeds 5 ppb in the lag bed effluent or 50% in the lead bed effluent (whichever occurs first).

For residuals disposal, critical values that may trigger hazardous waste restrictions in this treatment system include:

- total chromium (5 mg/L by California Waste Extraction Test, or CWET, and 5 mg/L by the Toxicity Leaching Characteristic Procedure, TCLP)
- uranium (total by kinetic phosphorescence analysis, KPA).

The WBA resin may initially leach N-Nitrosodimethylamine (NDMA), as shown in the Phase III Bridge Project. Each bed of resin will be rinsed during the initial backwash for approximately 9-10 minutes. Subsequently, the vessels will be put into normal operation, which includes dilution with approximately 4,575 gpm of water from the other wells at the GWTP, followed by an approximately 50% dilution with MWD water at the Grandview Pumping Station. Overall, the GS-3 water will be diluted to approximately 5% of the total flow before the water is served to customers, providing sufficient mitigation of nitrosamines leached from the resin upon startup to yield a finished water level below the Notification Level of 10 ppt.

2 Project Organization

2.1 Key Points of Contact

Refer to the above Distribution List of Principal Project Participants for the key points of contact at each organization.

2.2 QA Managers

The QAPP dictates procedures that will be used by two primary organizations: McGuire Malcolm Pirnie and the ELAP-certified laboratories (Montgomery Watson Harza (MWH) Laboratories and Test America). With respect to data quality assurance, Malcolm Pirnie is charged with the tasks of sample collection, handling, field analysis of selected parameters, data management, data reduction, and data validation. McGuire Malcolm Pirnie's QA Manager will be Dr. Michael MacPhee. He is independent of Project Management and his only role in the project is as QA Manager. The QA Manager at MWH Labs will be Ms. Linda Geddes, Quality Assurance Officer. The QA Manager at Test America will be Marti Ward.

2.3 Responsibilities of Project Participants

Each project participant responsible for critical components in this project is listed in Table 2-1. Team members' affiliations and overall project involvement roles are also listed. Project involvement roles specified here include: Planning, Coordination, Sample Collection, Sample Custody, Measurements (Analytical, Physical, and Process), Data Reduction, Data Validation, and Report Preparation. The project team organization is illustrated in Figure 2-1.

The majority of the project team was significantly involved in Phase II testing, which was covered by the QAPP entitled *The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale Ground Water Supply: Phase II Demonstration of Pilot Scale Treatment Technologies* (dated July 31, 2003). Dr. Bruce Macler has been the EPA Project Manager of the Phase II and Phase III efforts and is up-to-date on the historical study progress. Peter Kavounas and Don Froelich have also been key participants in the previous projects representing the City of Glendale. Dr. Michael J. McGuire, currently the Project Manager, was the Principal-in-Charge of the last study. Dr. Michael J. MacPhee will serve in the same role as in Phase II, as Technical Advisor and Quality Assurance Manager. Dr. Nicole Blute will plan, coordinate, oversee the field operations, and prepare reports. In the Phase II effort, Dr. Blute conducted the pilot-scale operations along with Dr. Danny Qin, who will conduct the field testing in the demonstration study. Dr. Qin is highly experienced in field sampling and analysis, having worked on the Phase II Pilot Study and Phase III Bridge Study and Additional RCF Testing, among other compliance testing and pilot testing efforts for other clients. The three university technical advisors, Dr. Mel Suffet, Dr. Laurie McNeill, and Dr. Gary Amy, have all been part of the Phase I and Phase II efforts. The two laboratories selected for this effort have been used in the prior work or in other projects with the City of Glendale.

Table 2-1.
Project Participant Roles

Team Member	Title and Organization	Overall Project Involvement	Specific Involvement
Bruce Macler, Ph.D.	USEPA, Project Manager	Project Manager	Project Management
Peter Kavounas, PE	City of Glendale	Glendale Principal Investigator	Planning Coordination
Don Froelich, PE	City of Glendale	Glendale Project Management	Planning Coordination
Leighton Fong, PE	City of Glendale	Glendale Project Management	Coordination
Michael McGuire, Ph.D., PE	Vice President, MMP	MMP Project Manager	Experimental Design Report Preparation
Michael MacPhee, Ph.D.	Vice President, MMP	MMP Technical Advisor	MMP Quality Assurance Manager
Nicole Blute, Ph.D.	Project Engineer, MMP	MMP Deputy Project Manager	Planning Coordination Data Reduction and Validation Report Preparation
Danny Qin, D.Env.	Engineer, MMP	Study Field Testing	Study Operations Sample Collection Sample Custody Field Measurements (analytical, physical, process) Data Management
Yolanda Martin	Project Manager, MWH Labs	Analytical Support	Coordination of Analytical Laboratory Measurements
Linda Geddes	QA Officer, MWH Labs	Laboratory Quality Assurance	Laboratory Quality Assurance
Kay Clay	Project Manager, Test America Labs	Analytical Support	Coordination of Analytical Laboratory Measurements
Marti Ward	QA Officer, Test America Labs	Laboratory Quality Assurance	Laboratory Quality Assurance
Gary Amy, Ph.D.	Professor, UNESCO	Technical Advisor	Experimental Design
Laurie McNeill, Ph.D.	Associate Professor, USU	Technical Advisor	Experimental Design

Mel Suffet, Ph.D.	Professor, UCLA	Technical Advisor	Experimental Design
To Be Determined	To Be Determined	To Be Determined	Construction

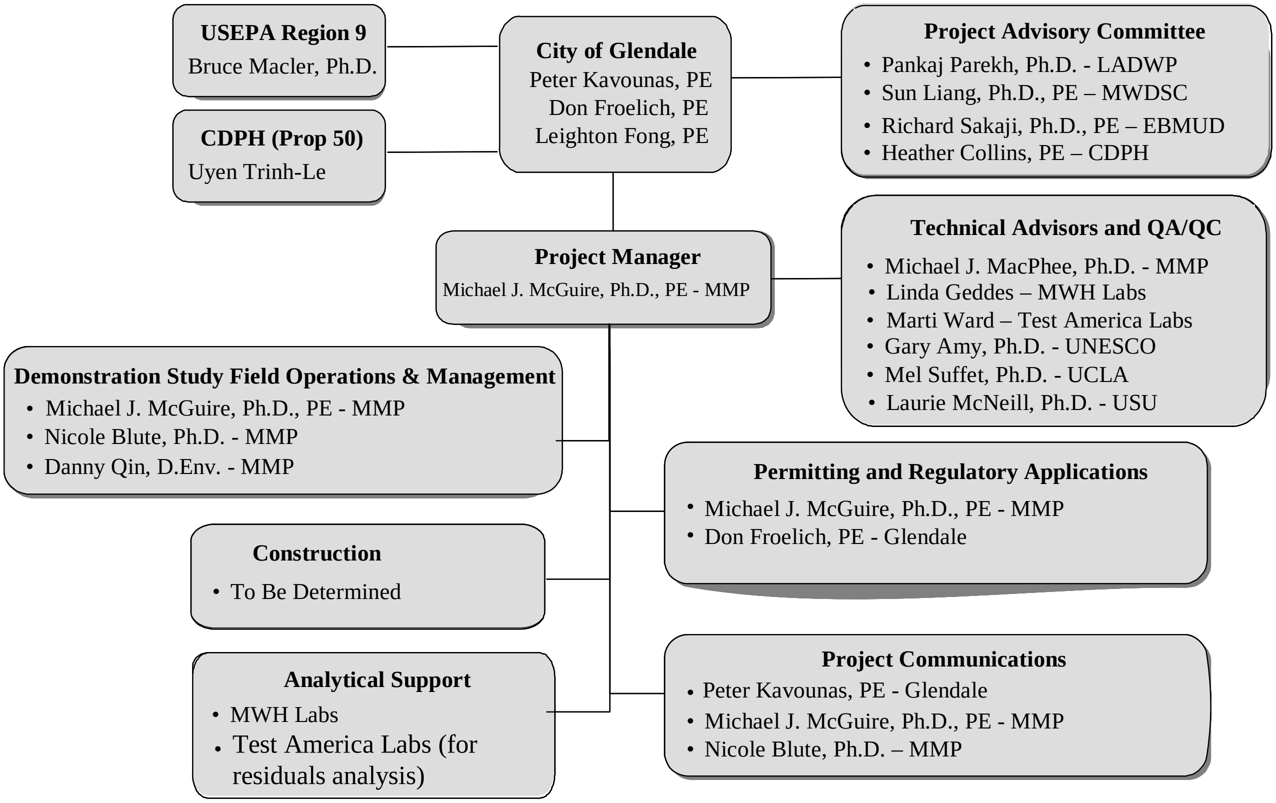


Figure 2-1. Demonstration Study Team Organization and Lines of Communication

2.4 Laboratory Certification Requirements

Each of the laboratories that will be used is certified by the California Department of Public Health under the State's Environmental Laboratory Accreditation Program (ELAP; certifications in Appendix B). Each laboratory's QA and Project Managers will be responsible for ensuring that the laboratory staff are appropriately trained and qualified to conduct the analyses.

3 Experimental Approach

3.1 General Approach and Test Conditions

Evaluation of WBA resin for Cr(VI) removal at the demonstration scale will focus on the measurement of key chemical and process parameters described in this section. Of critical importance, the project team will closely monitor Cr(VI) and total Cr concentrations in influent, mid-treatment train, and effluent water samples. In addition, other process-related parameters and water quality constituents described below will be measured to assess operational effectiveness and the impact of the WBA technology on water quality.

3.2 Sampling Strategy

Table 3-1 lists the proposed sampling parameters for the WBA demonstration-scale testing. In addition to chemical and physical analytical measurements, process-related parameters listed in Table 3-2 will be assessed.

3.2.1 Aqueous Samples

Critical sampling parameters in the demonstration study include Cr(VI), total Cr [ie., Cr(VI) plus Cr(III)], and pH. Other chemical and physical parameters, including temperature, conductivity, turbidity, and alkalinity will be routinely measured. Anions such as sulfate, nitrate, phosphate, and silicate may impact ion exchange treatment; consequently periodic measurements of these parameters will also be obtained. Nitrosamines, which have been found to leach from ion exchange resins, will be monitored in the start-up period of the demonstration-scale study to identify strategies to mitigate initial releases (e.g., flushing the resin for a specified period of time).

3.2.2 Residuals

Treatment residuals, including exhausted ion exchange resin and backwash water, will also be assessed to confirm disposal options using the Toxicity Characteristic Leaching Procedure (TCLP, EPA Method 1311 as mandated by 40 CFR 261) and the California Waste Extraction Test (CWET). Pilot-scale testing indicated that the spent WBA resins would be classified a hazardous waste in the State of California based on total chromium concentrations leached during the California WET test. Uranium accumulated on the spent WBA resin will also be determined throughout the testing; PWA7 resin may need to be replaced prior to 50% resin breakthrough to avoid uranium concentrations exceeding 500 mg/kg (i.e., the threshold above which the waste could be classified a low-level radioactive waste).

During the demonstration study, a vendor will be contracted to provide resin delivery and disposal services. Since the spent resin will likely be a hazardous waste according to CWET, the vendor will be required to appropriately dispose of the resin in accordance with the prevailing hazardous waste restrictions in California.

3.3 Sampling/Monitoring Locations

All of the samples collected for analysis will be obtained from the demonstration-scale study site at GS-3. Samples will be collected from sample ports shown in Figure 3-1. Sample types collected at each of these locations are highlighted in Table 3-1.

For the WBA treatment systems, sampling locations include the raw GS-3 well water (pre-CO_2 addition), influent water to the lead ion exchange vessel (post-CO_2 addition and bag filtration), lead vessel midpoint (50% depth), lead vessel effluent, lag vessel midpoint (50% depth), and lag vessel effluent.

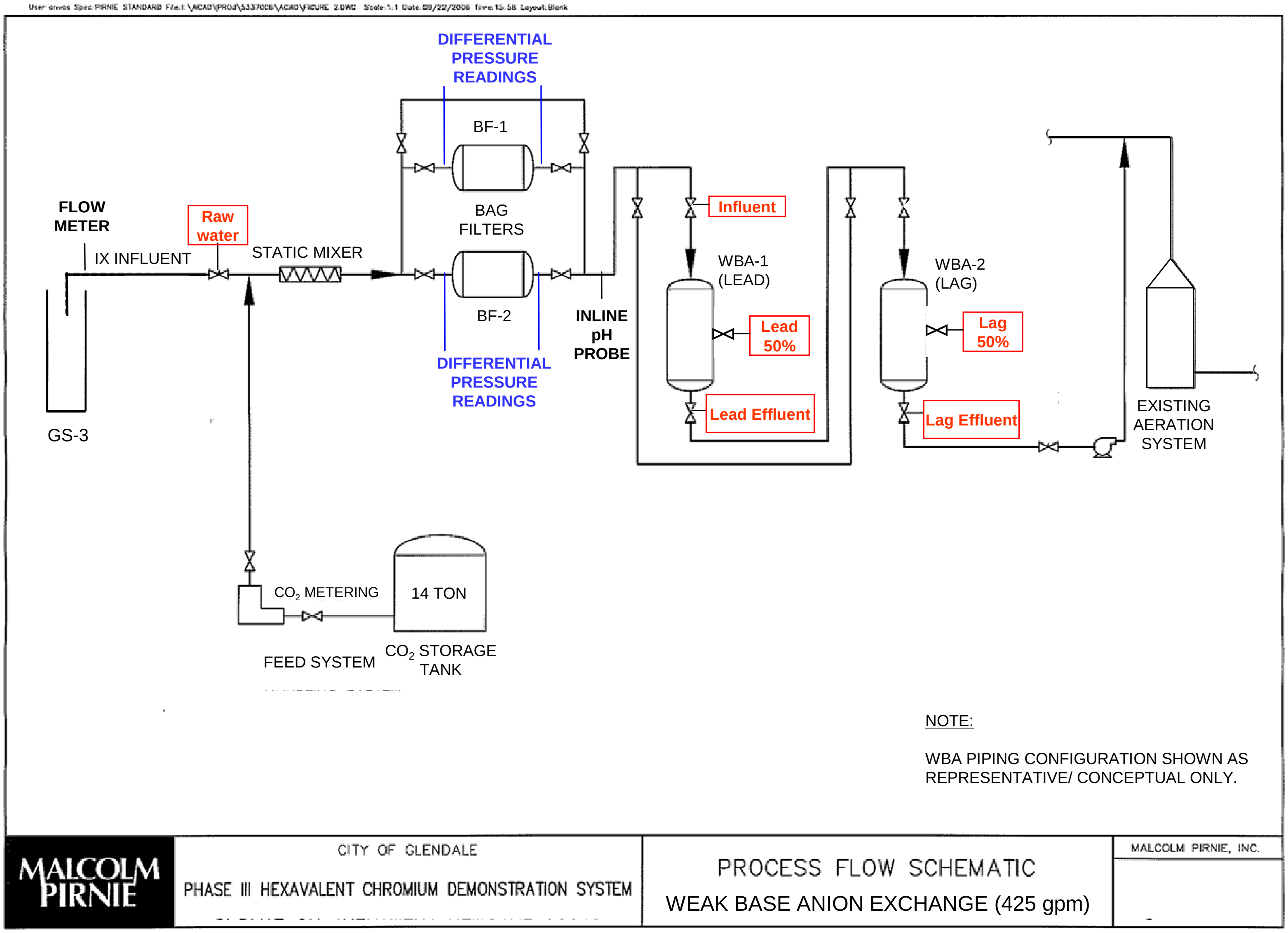


Figure 3-1. Sampling Locations for Chemical and Process Parameters (highlighted in red)

Table 3-1. Analytical Measurements for the WBA Demonstration-Scale Study, Identified as Critical (C) and Non-Critical (N/C) Measurements

Sampling Types and Locations	**Cr(VI)**	**Total Cr**	**pH**	**Temp.**	**SO_4^{2-}**	**NO_3^-**	**PO_4^{3-}**	**SiO_2**	**Alk-alinity**	**Cond-uctivity**	**Turb-idity**	**Nitros-amines**	**TCLP, WET tests**	**Ura-nium**
Raw water (before pH adjustment)			N/C											
Influent (after pH adjustment)	C	C	C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	C		
Lead Vessel 50% bed depth	N/C	N/C												
Lead Vessel Effluent	C	C	C	N/C										
Lag Vessel 50% bed depth	N/C	N/C												
Lag Vessel Effluent	C	C	C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	C		
Residuals (spent resin)													C	C
Backwash Water		C												

Table 3-2. Process-Related Measurements

	Flow rates	**Pressure loss through BF-1**	**Pressure loss through BF-2**	**Backwash frequency**	**EBCT**	**# Bed volumes to breakthrough (> 5 μg/L)**	**# Bed volumes to 50% saturation of the lead vessel**	**CO_2 feed rate and volume use rate**
WBA	C	C	C	C	C	C	C	C

3.4 Sampling/Monitoring Frequency

The planned sampling frequency for chemical and physical parameters, shown in Table 4-1, is based on treatment process design and the expected one year duration of testing. Samples will be collected at a sufficient frequency to provide enough information to achieve the project's stated objectives. For a predicted bed life of 207 days (based on maximum uranium accumulation), the weekly chromium sampling frequency will capture an approximately 29-point breakthrough curve. Process-related parameters, such as flow rate and pressure loss, will be taken on a daily basis to determine when bag filters should be changed and backwash initiated. Other chemical and physical analyses of influent and treated water will be collected at least monthly or more frequently as deemed necessary.

A weekly Cr(VI) and total Cr sampling frequency will be established for the following key sampling points:

- Influent
- Lead vessel 50% depth
- Lead vessel effluent
- Lag vessel effluent

Once breakthrough occurs such that the lead bed effluent Cr concentration exceeds 5 μg/L, the lag vessel 50% depth location will be added to the list of sampling points monitored weekly and the lead vessel 50% depth sampling curtailed (until the next bed is installed and the lead and lag vessel order is changed).

pH, which is a critical parameter due to its impact on WBA resin treatment, will be measured continuously at a point near the influent sampling point to the vessels. Note that sufficient mixing is necessary to enable capture of stable pH values representative of the influent to the WBA resin; thus, CO_2 will be added upstream of the bag filters and samples collected after the bag filters and before the lead vessel inlet.

Nitrosamines will be measured during the first day of startup according to California DPH permit requirements.

Non-critical parameters, including temperature, sulfate, nitrate, phosphate, silicate, alkalinity, conductivity, and turbidity, will be measured monthly at the following sampling points:

- Influent
- Lag vessel effluent.

Bag filter changes will be triggered by a drop in the treatment system flow rate below 425 gpm or differential pressure greater than 10 psi, whichever occurs first. Besides the initial bed washing, vessel backwashing will be conducted when the flow rate drops below 425 gpm, if the system has been recently shutdown, and the bag filters have a low differential pressure (level to be determined based on operational experience gained during the initial weeks of testing).

3.5 Identification of Measurements

Tables 3-1 and 3-2 identify analytical and process-related measurements and specify whether they are critical (C) or non-critical (N/C) analytes.

3.6 Evaluation of Project Objectives

Treatment technology success will primarily be judged by the effectiveness of the process for removing Cr(VI) and total Cr from the water supply. This objective will be assessed by calculating the difference between influent and effluent chromium concentrations during the demonstration-scale study. Efficiency of removal will be calculated as follows:

$$\text{Removal (\%)} = (1- [\text{Cr}_{\text{effluent}}]/[\text{Cr}_{\text{influent}}])*100\%.$$

Effluent Cr(VI) and total Cr will be measured and plotted as a function of time to determine when breakthrough occurs. Number of bed volumes (i.e., volume of water treated per volume of the resin bed) of water treated will be calculated at breakthrough of the lead vessel (i.e., defined as Cr concentrations of greater than 5 μg/L) and also 50% saturation.

Operations and maintenance (O&M) issues associated with the WBA resin will be assessed, as listed in Table 3-2. For example, pressure drop through the beds and resultant backwashing frequency for the resin will be determined in the demonstration-scale study.

The Phase III Bridge study indicated that the spent WBA resin was classified as hazardous in the state of California due to the California Waste Extraction test (WET -- CCR Title 22 §66261.24) but not in states governed only by the federal Toxicity Characteristic Leaching Procedure (TCLP – EPA Method 1311 as mandated by 40 CFR 261). Subsamples of disposable spent media from the demonstration test will be analyzed to verify the hazardous nature of the residuals and, subsequently, the disposal options.

A broader purpose of the demonstration testing is to develop a technology that can be applied in other water utilities needing Cr(VI) treatment. Glendale's demonstration study will therefore foster a better understanding of the WBA treatment technology for Cr(VI) removal from groundwater.

4 Sampling Procedures

4.1 Methods to Establish Steady-State Conditions

Achievement of steady-state conditions will be determined on the basis of process operating parameters rather than water quality. For WBA resin, dynamic water quality conditions will occur during operation, whereby the treated water quality will change over time as the media becomes exhausted. Therefore, sampling conditions that reflect steady-state operations will be based on the consistency of flows and chemical feed conditions (in particular, a stable pH within plus or minus 0.2 pH units).

4.2 Known Site-Specific Factors Affecting Sampling and Monitoring Procedures

The GS-3 well site will have dedicated space, power, and water from the GS-3 well. The effluent will be pumped into the transmission line leading to the GWTP for VOC treatment. The ion exchange vessels and piping will be designed with sampling ports to enable appropriate sampling for technology performance assessment as detailed in Section 3.

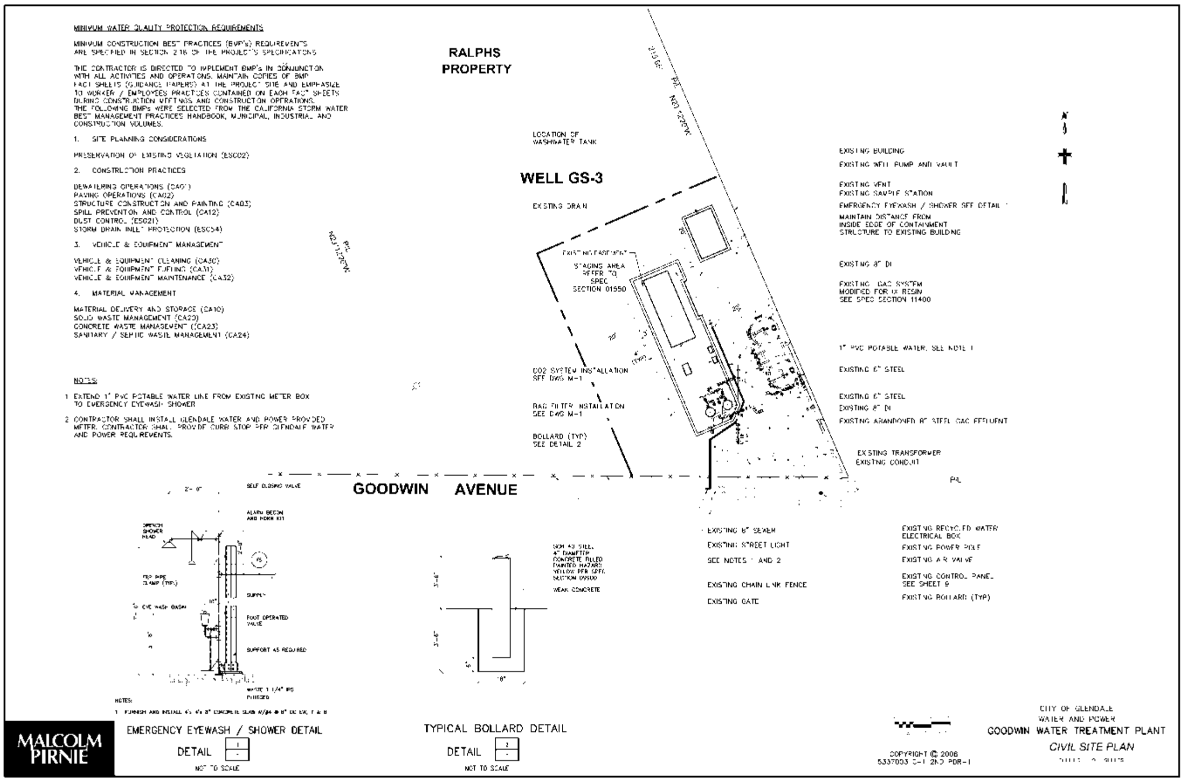
Limited hours of site accessibility (approximately 8 hours per day) will affect the possible time on site. However, the system will be tied into the existing SCADA system and will be alarmed. Operators are available around the clock in case the system experiences problems. The WBA resin is expected to last for at least 6 months prior to reaching 50% breakthrough on the lead vessel, which supports a weekly sampling periodicity.

4.3 Site Preparation Prior to Sampling

The demonstration-scale facility will be located at the GS-3 well site, as shown in Figure 4-1. The City of Glendale has an easement within the Ralph’s Grocery warehouse property located in the City of Los Angeles. The GS-3 well site is located on the Ralph’s property just off of Goodwin Street.

Site preparations that will be conducted before the demonstration-scale study commences include the following tasks:

- retrofitting the existing GAC vessels with different screens to support ion exchange media,
- construction of a concrete pad and installation of a CO_2 feed system,
- preparation of necessary electrical power supplies,
- integration of the treatment system with the existing Supervisory Control And Data Acquisition (SCADA),
- piping of the raw GS-3 well water to the treatment system, and
- piping of the ion exchange treated water to the transmission pipeline serving the GWTP.



MINIMUM WATER QUALITY PROTECTION REQUIREMENTS

MINIMUM CONSTRUCTION BEST PRACTICES (BMP's) REQUIREMENTS ARE SPECIFIED IN SECTION 2.16 OF THE PROJECT'S SPECIFICATIONS

THE CONTRACTOR IS DIRECTED TO IMPLEMENT BMP's IN CONJUNCTION WITH ALL ACTIVITIES AND OPERATIONS. MAINTAIN COPIES OF BMP FACT SHEETS (GUIDANCE PAPERS) AT THE PROJECT SITE AND EMPHASIZE TO WORKER / EMPLOYEES PRACTICES CONTAINED ON EACH FACT SHEETS DURING CONSTRUCTION MEETINGS AND CONSTRUCTION OPERATIONS. THE FOLLOWING BMPs WERE SELECTED FROM THE CALIFORNIA STORM WATER BEST MANAGEMENT PRACTICES HANDBOOK, MUNICIPAL, INDUSTRIAL AND CONSTRUCTION VOLUMES.

1. SITE PLANNING CONSIDERATIONS

PRESERVATION OF EXISTING VEGETATION (ESC02)

2. CONSTRUCTION PRACTICES

DEWATERING OPERATIONS (CA01)
PAVING OPERATIONS (CA02)
STRUCTURE CONSTRUCTION AND PAINTING (CA03)
SPILL PREVENTION AND CONTROL (CA12)
DUST CONTROL (ESC21)
STORM DRAIN INLET PROTECTION (ESC54)

3. VEHICLE & EQUIPMENT MANAGEMENT

VEHICLE & EQUIPMENT CLEANING (CA30)
VEHICLE & EQUIPMENT FUELING (CA31)
VEHICLE & EQUIPMENT MAINTENANCE (CA32)

4. MATERIAL MANAGEMENT

MATERIAL DELIVERY AND STORAGE (CA10)
SOLID WASTE MANAGEMENT (CA20)
CONCRETE WASTE MANAGEMENT (CA23)
SANITARY / SEPTIC WASTE MANAGEMENT (CA24)

NOTES:

1. EXTEND 1" PVC POTABLE WATER LINE FROM EXISTING METER BOX TO EMERGENCY EYEWASH SHOWER
2. CONTRACTOR SHALL INSTALL GLENDALE WATER AND POWER PROVIDED METER. CONTRACTOR SHALL PROVIDE CURB STOP PER GLENDALE WATER AND POWER REQUIREMENTS.

Figure 4-1. GS-3 Well Site and Property Easement Boundaries

4.4 Sampling/Monitoring Methods

Chemical and physical analytes will be measured in this demonstration-scale study either in the field or in a laboratory. The analytical methods and locations of analyses are shown in Table 4-1.

Laboratory analytical measurements will be sent to one of two labs:

- MWH Labs for Cr(VI), total Cr, nitrate, and nitrosamines
- Test America Labs – for TCLP, CWET, and uranium in residuals

The laboratory analyses of total chromium (a California DPH regulated constituent) will be performed by ICP-MS using EPA Method 200.8. Cr(VI) will be analyzed using EPA Method 218.6, which is an ion chromatography method. Nitrate will be analyzed using Method 300.0. Nitrosamines will be measured with EPA Method 521. Treatment residuals from the WBA treatment process will be analyzed for TCLP (metals – specifically, chromium levels will be of concern), CWET (metals – specifically, chromium levels will be of concern), and uranium analyses prior to disposal. All other parameters will be analyzed using the methods shown in Table 4-1.

Quality assurance field sampling includes field-collected duplicate samples and field blanks (refer to Section 6.1 for full details). Generally, field-collected duplicate samples will be collected for at least 10% of all samples. These duplicates will not be identified as QA samples when sent to the laboratory.

Field-collected blanks will include metal-free deionized water added to a sample bottle in the field and shipped to the laboratory for analysis (testing field sample handling, transport, and storage, including preservative reagents). Blanks submitted to the laboratory for analysis will not be identified as QA samples.

Samples will not be composited to amplify sample volume or average samples over time. Sufficient sample volume will be available for the required analyses. To achieve the project objective of evaluating Cr(VI) removal efficiency as a function of time, sample compositing is not desirable.

In addition to chemical and physical analytical measurements, process measurements listed in Table 3-2 will be recorded daily. Flow rate and pressure drop across the vessels will be monitored throughout the demonstration-scale testing to determine when backwashing is needed. Empty bed contact time (EBCT) will be calculated by dividing the media volume in a vessel by the flow rate. The number of bed volumes of water treated will then be calculated as the volume of treated water divided by the resin bed volume.

Table 4-1.

Sampling Frequency, Analytical Methods, & Analytical Location

Sample Analysis	Analytical Method	Analysis Location	Sampling Frequency
Cr(VI)	EPA 218.6 (IC)	MWH Labs	Weekly
Total Cr	EPA 200.8 (ICP-MS)	MWH Labs	Weekly
Sulfate	Hach 8051 (Turbidimetric)	Field	Monthly
Nitrate	EPA 300.0 (IC)	MWH Labs	Monthly
Phosphate	Hach 8048 (Colorimetric)	Field	Monthly
Silicate	Hach 8185 (Colorimetric)	Field	Monthly
Alkalinity	Hach 8203 (Titration)	Field	Weekly
Conductivity	SM 2510B (Conductance)	Field	Weekly
pH	SM 4500H+ B (Electrometric)	Field	Continuous online monitoring
Temperature	SM 2550 (Thermometric)	Field	Weekly
Turbidity	SM 2130 B	Field	Weekly
Nitrosamines	EPA 521	MWH Labs	Start of test[a]
Residuals – TCLP	EPA 1311 – Extraction EPA 6010B – Total Cr	Test America Labs	End of lead vessel life
Residuals – CWET	CWET Test (Title 22) – Extraction EPA 6010B – Total Cr EPA 7196A – Cr(VI)	Test America Labs	End of lead vessel life
Residuals: Uranium	ASTM5174-91 (KPA method)	Test America Labs	Monthly on lead vessel

[a] Nitrosamines will be analyzed at a frequency required by the DPH permit

4.5 Calibration of Sampling/Monitoring Equipment

Field equipment calibration will be performed in accordance with manufacturer specifications for each instrument. Calibration procedures for field equipment will be included in the Operations Manual developed for this project. Certified standard solutions will be used to test the functionality and accuracy of each piece of analytical instrument within the range of measurements and at a frequency specified by the manufacturer, or at least once per month.

Process instruments, such as flow meters and pumps, will be calibrated before the demonstration-scale treatment unit is brought online, at one intermediate time during operations (minimally), and at the conclusion of the test. Calibration procedures for process instruments will be included in the Operations Manual developed for this project. Calibration results and date and time of calibration will be recorded in the Field Sampling Log Book.

Trained operators will determine whether the calibrations are acceptable based on the allowed drift specified by the manufacturer. If an instrument is not functioning properly (e.g. calibration attempts are unsuccessful or the standard curve is unacceptable), the operator will obtain a calibrated back-up instrument for interim use and will send the malfunctioning instrument for repair.

4.6 Avoidance of Cross-Contamination

Sample contamination will be avoided by practicing clean sampling techniques. Water samples will be collected from dedicated sampling ports by directly filling pre-cleaned sample bottles Sample collections staff will avoid contact with the interior surfaces of the bottles. Hosing from the sampling ports will initially be acid-cleaned to remove any contaminants. Between collected samples, the ends of the hoses will be covered with clean polyethylene coverings to prevent contamination. Prior to sample collection, the sampling port and hose will be flushed for at least 1 minute to clean out the lines.

California DPH recommends *not* filtering drinking water samples to avoid potential sorption of Cr(VI) on the filter membranes and cross-contamination (CA DHS, 2001). Cr(VI) samples will therefore remain unfiltered in the field.

4.7 Selection of Representative Samples

Samples collected in this demonstration-scale study will be representative of the whole study based on consistent sampling at established sampling locations indicated in Table 3-1 and sampling frequencies shown Table 4-1.

Solid resin samples for TCLP, WET, and uranium analyses will be collected during a fluidized backwashing of the resin to obtain a representative sample of the bed.

4.8 Sample Amounts Required for Analysis

Table 4-2 lists the sample analysis methods, sample amounts required for analysis according to each method (including QA aliquots except field-collected duplicates), preservatives, and maximum holding times. The same amounts will be required for each analysis at each sampling location. Field-collected duplicate sample quantities discussed in Section 4.4 will be in addition to the bottles below.

To determine if spent media will be classified as a hazardous waste, TCLP and WET tests will be performed on the media. The Federal TCLP test requires a minimum of two 100-gram samples: one sample to determine percent solids, and one sample on which the extractions will be performed. California WET mandates a 50 gram sample for analysis.

4.9 Sample Containers

All samples will be collected using containers pre-cleaned and approved by the USEPA for the analytes of interest. Samples for the critical Cr(VI) and total Cr analyses will be collected in pre-cleaned plastic bottles provided by the laboratory or, for field testing, those shown to be clean of contamination in the Phase II testing. Bottle types for other analyses of interest may be plastic or glass (EPA 1997), although plastic will be used to eliminate breakage during shipping (refer to Table 4-2). Empty containers will be stored in the original packaging until use. Once collected, samples will be shipped to the laboratories for analysis according to the protocol for sample custody.

4.10 Sample Identification

Samples will be identified using a standardized code that imparts sampling information to each party. Each sample location will be assigned an ID as follows (referring to Figure 3-1):

- Raw water: SP-1
- Influent: SP-2
- Lead Bed 50%: SP-3
- Lead Bed Effluent: SP-4
- Lag Bed 50%: SP-5
- Lag Bed Effluent: SP-6

Next, the appropriate sample type (e.g. raw water, lead bed effluent) will be recorded. The date and time will then be recorded using the convention of military time. The analyte(s) to be measured in that sample will be recorded on the label, as will the preservative used. Finally, the field sample collector’s initials will be added.

An example identification label is as follows:

Sample Location ID ___________________
Sample Type ___________________
Date and Time ___________________
Analyte(s) ___________________
Preservative, if any ___________________
Field Sampler Initials ___________________

Table 4-2.

Sample Handling Requirements

Sample Analysis	Sample Size Required, including QC Aliquots	Container Material	Preservative	Maximum Holding Time
Cr(VI)	250 mL	P[1]	$(NH_4)_2SO_4$/ NH_4OH to pH 9-9.5	24 hours[4]
Total Cr	250 mL	P	HNO_3 to pH <2	6 months
Sulfate	60 mL	P, G[2]	4ºC	28 days
Nitrate	50 mL	P	4ºC	48 hours
Phosphate	60 mL	P	4ºC	48 hours
Silicate	60 mL	P	4ºC	28 days
Alkalinity	200 mL	P, G	4ºC	14 days
Conductivity	500 mL[3]	P, G	4ºC	28 days
pH	500 mL[3]	P, G	None	Analyze Immediately
Temperature	500 mL[3]	P, G	None	Analyze Immediately
Turbidity	500 mL[3]	P, G	None	Analyze Immediately
Nitrosamines	2 L	Amber glass	At or below 10ºC[5]	14 days until extraction; 28 days after extraction
Residuals: TCLP	200 g	P	4ºC	180 days (metals)
Residuals: CWET test	50 g	P	4ºC	180 days (metals)
Residuals: Uranium	100 g	P	4ºC	28 days

[1] P = Plastic. [2] G = Glass. [3] Combined 500 mL bottle for conductivity, pH, temperature, and turbidity.

[4] Although samples preserved with ammonium sulfate/ammonium hydroxide buffer (pH 9 to 9.5) can be held for 28 days, analyses will be conducted within 24 hours..

[5] Chill nitrosamine samples prior to shipment if they are greater than 10ºC at the time of collection.

4.11 Sample Preservation Methods

Table 4-2 lists the preservation requirements for each of the methods that will be used in the demonstration study. Details of sample preservation include whether the sample needs to be chilled, if an acid, base, or buffer is required, the type of container required for sample collection and storage, and the maximum holding time.

As the critical analytes, more details for Cr(VI) and total Cr are provided here. Samples for total Cr will be preserved with 2% nitric acid (HNO_3). It is intended that Cr(VI) samples will be analyzed within 24 hours of sample collection, thereby avoiding the need for preservative. However, samples will be preserved with ammonium sulfate/ ammonium hydroxide buffer (extending the hold time to 28 days) in case the samples cannot be measured within 24 hours. During each weekly sampling event, the pH of one sample for Cr(VI) analysis and one for total Cr after preservative addition will be verified by pouring out a small amount of the preserved sample onto pH paper. This approach to testing pH will reduce the volume removed from the sampling bottles.

4.12 Sample Holding Time Requirements

Maximum holding times for each of the analytes are shown in Table 4-2.

4.13 Sample Shipment

Samples will be shipped by courier from the site of collection (GS-3) to the appropriate contract laboratory using a reputable shipping company or lab courier. Shipping containers will consist of coolers with ice packs to chill samples and bubble wrap to protect the bottles during transit.

4.14 Sample Chain-of-Custody

Samples will be considered “in custody” when they are in someone’s physical possession or view, locked up, or stored in a secure area accessible only by authorized personnel. A minimal number of persons participating in sample handling and custody is desirable.

Samples collected for analyses will be recorded in a Field Sampling Log Book using waterproof, permanent ink. The log will contain the following information: Sample ID (as described in Section 4.11), results of field measurements, and descriptions of incidents that may have affected operations.

After samples have been collected for laboratory measurements, the field staff person will complete the Sample Chain-of-Custody form in ink, affix and sign Custody Seals, place the completed Chain-of-Custody in a sealed plastic bag affixed to the inside lid of the cooler, and surrender the samples to the ELAP-certified lab courier or authorized shipper for shipment. Upon arrival at the contract laboratory, laboratory personnel will immediately log the samples in on the Chain-of-Custody form, inspect for damage and sample integrity, and store the samples as appropriate until analysis. Problems encountered during sample shipping will be reported to the analytical manager.

4.15 Sample Archives

Samples will be stored at 4°C after analysis until personnel at the laboratory and McGuire Malcolm Pirnie review sample data and associated quality control analyses. In general, samples are kept by MWH or Test America Laboratories for two years. Unless directed otherwise, samples will then be disposed of in accordance with appropriate environmental health and safety regulations for hazardous chemical waste.

5 Testing and Measurement Protocols

5.1 Measurement Methods

The analytical methods for the water quality parameters and treatment residuals will conform to EPA guidelines and recommended test methods, including those in *Standard Methods for the Examination of Water and Wastewater* (APHA 1999). Standard Operating Procedures (SOPs) to be used for all measurements are included in Appendix A.

At MWH Laboratories, total chromium analyses will be performed using the ICP-MS method (EPA Method 200.8). Ion chromatography (EPA Method 218.6) will be used to analyze Cr(VI). Nitrate will be measured using EPA Method 300.0 (IC). Nitrosamines will be measured using EPA Method 521. Treatment residuals from each process will be shipped to a certified laboratory (Test America Labs) for TCLP, California WET, and uranium analyses prior to disposal.

Other water quality parameters will be measured in the field by trained operators (as discussed in Section 4.6) using SOPs provided in Appendix A.

5.2 Verification of Unproven Methods

No unproven laboratory methods will be used in this project.

5.3 Calibration Procedures

For Cr(VI) analysis, the ion chromatograph at MWH Labs will be calibrated each analysis day using a 6-point calibration curve ranging from 0.1 to 50.0 μg/L. Acceptance criteria include a correlation coefficient for the linear calibration curve of greater than 0.999. The method detection limit (MDL) at the laboratory is reported to be 0.015 μg/L. However, the method reporting limit (MRL) is 0.1 μg/L. Samples falling within the range of the MDL and MRL will be flagged as “J values”. An external laboratory control sample (LCS) at 2 μg/Lwill be analyzed for every batch of 20 samples or less. The acceptance percent recovery range for the LCS sample is within 90-110%. A 20 ppb instrument performance check (IPC) sample will be run after the initial calibration and subsequently after every 10 samples, with an acceptable percent recovery range of 95 to 105%. A laboratory reagent blank (LRB) will also be measured after every 10 samples and should be below the MRL of 0.1 μg/Leach time.

Total Cr samples will be analyzed by ICP-MS, which includes daily calibration using a 3-point calibration curve (plus a blank) ranging from 1 to 250 μg/L. Acceptance criteria include a correlation coefficient for the linear calibration curve of greater than 0.999. The laboratory-reported MDL for total Cr is 0.192 μg/L, and the MRL is 1 μg/L. An initial calibration verification standard (ICV) will be analyzed immediately after the calibration curve with an acceptance percent recovery range of 95 to 105%. A continuing calibration verification standard (CCV) will be run subsequently after every 10 samples, with an acceptable percent recovery range of 90 to 11%. A continuing calibration blank (CCB) will also be measured after every 10 samples and should be below one-half of the MRL of 1.0 μg/Leach time.

If the laboratory calibration check criteria are not met, the analysis run will be stopped and the instrument recalibrated. Additional details are available in the Appendix A SOPs.

Nitrosamine analysis will be conducted by capillary column gas chromatograph with large volume injection and chemical ionization trap mass spectrometry. The daily calibration curve will consist of 6 samples ranging from 2 to 100 ng/L, and acceptance criteria for each calibration standard will be within 70-130% (or 50-150% for the lowest standard). A continuing calibration check (CCC) sample will be run after the initial calibration curve and after every 10 samples, with acceptance criteria of between 70-130% of the true value.

Leachate metal concentrations using the TCLP and CWET methods will be measured using ICP-AES. Details of the standards used to calibrate the ICP-AES for the various metals are shown in Appendix A. In general, at least 3 standards and a blank are used to calibrate the instrument daily, with acceptance criteria of greater than 0.995 for the correlation coefficient. Following the calibration, an initial calibration verification (ICV) sample will be run, with acceptance criteria of 95-105%. An initial calibration blank (ICB) will subsequently be run and should fall within +/- of the MRL from zero. CCV and CCB samples will then be run every 10 samples with acceptance levels of 90-110% and +/- the MRL from zero, respectively.

Total uranium concentrations accumulated on the resin will be tested using kinetic phosphorescence analysis (KPA). Solid samples will be digested during sample preparation. Seven standards ranging from 1 to 300 μg/Lare used in the instrument calibration procedure, with acceptance criteria of a correlation coefficient greater than 0.995. After the calibration curve, ICV and ICB samples will be run, with acceptance criteria of 90-110% for the ICV. CCV and CCB samples will then be analyzed after every 10 samples and must fall within 90-110% for the CCV sample and within +/- the MRL from zero for the CCB sample.

Other analyses run at the ELAP-certified laboratories (e.g., nitrate) will conform to the calibration procedures described in the SOPs (Appendix A). Standard calibration curves run on the field instrument will be sufficient to ensure that the instrument is operational and large deviations in concentrations are real phenomena.

6 QA/QC Checks

6.1 Quantitative Acceptance Criteria for Data

QA/QC sampling, which includes field-collected duplicate samples and blanks, as well as laboratory, split samples (i.e., replicate analyses) and matrix spikes will be used to verify consistency in sample collection and handling and analytical accuracy.

6.1.1 Field QA/QC Samples

Field-collected duplicate samples will be obtained for at least 10% of all samples collected and will be co-located samples taken one right after the other. Duplicates will not be identified as QA/QC samples when sent to the laboratory. Field-collected duplicates will serve to ensure acquisition of representative samples, consistency of sampling, and precision of the analytical methods. Acceptance criteria for the field-collected duplicate samples will be within the analytical acceptance criteria for the specific analytical method (Appendix A).

Field blank samples will be prepared by filling metal-free distilled water in the sample bottles provided by the lab (with added preservatives, if necessary); these samples will be sent for analysis to test any possible contamination during sample handling, transport, and storage. At least one field blank sample per method will be prepared for each shipment. The routine frequency for the field blanks will be approximately one in ten samples to be shipped (i.e., 10% field blanks). Field blanks submitted to the laboratory for analysis will not be identified as QA/QC samples. The proposed QA/QC sampling and analysis frequency is listed in Table 6-1. Acceptance criteria for the field blanks will be +/- the MRL from zero.

For field-measured chemical parameters (sulfate, phosphate, silicate), accuracy and precision acceptance criteria will be based on manufacturer specifications, which will be tested using standards prepared in the water matrices. In general, acceptance criteria for these analytes will be less than 20% for field-collected duplicate samples. For the field methods, precision will be analyzed every 20 samples from repeat analyses on known-concentration accuracy check standards, with an acceptance criteria of 80 to 120%.

6.1.2 Laboratory QA/QC Samples

Calibration curve development and CCV samples were discussed in Section 5.3. Additional QA/QC samples to test for accuracy and precision are described below.

Accuracy (a combination of random and systematic error) in Cr(VI) and total Cr analyses will be evaluated by determining percent recoveries in samples spiked in the laboratory. A matrix spike (MS) will be performed on 10% of samples (or at least one sample per run), chosen at random. MS recoveries should be between 90 and 110% of the expected value for Cr(VI) and between 70 to 130% for total Cr. National Institute of Standards and Technology (NIST) traceable Cr(VI) solutions and ICS total Cr standard solutions will be used for matrix spikes. Accuracy will also be tested throughout the runs and after every 10 samples by analyzing a mid-range IPC sample and a laboratory reagent blank (LRB). The acceptance criteria for the IPC sample is between 95 and 105%. The LRB should be below ½ the MRL. If concentrations are outside of these ranges, corrective actions will be performed as detailed in the SOPs for Method 218.6 or 200.6 (Appendix A).

Precision (random error) will be investigated by performing repeat analyses on the same analytical instruments. For every batch of twenty samples, a LCS and a MS will be run. The acceptable ranges for these sample results are between 90 and 110% for Method 218.6 and 70 to 130% for Method 200.8. Laboratory replicates and matrix spike duplicates (MSD) will be analyzed for every batch of twenty samples with an acceptance criteria of < 20% relative percent difference (RPD).

Table 6-1.
Quality Assurance Sampling and Measurement Frequency

Sample Analysis	**Sampling QA/QC Frequency**			
	Sample Frequency	**Field-Collected Duplicates**	**Laboratory Matrix Spikes**	**Field Blanks**
Cr(VI)	Weekly	10% of samples	5% of samples	1/week
Total Cr	Weekly	10% of samples	5% of samples	1/week
Sulfate	Monthly	10% of samples	None	1/month
Nitrate	Monthly	10% of samples	None	1/month
Phosphate	Monthly	10% of samples	None	1/month
Silicate	Monthly	10% of samples	None	1/month
Alkalinity	Weekly	10% of samples	None	None
Conductivity	Weekly	10% of samples	None	None
pH	Continuous online monitoring	Weekly	None	None
Temperature	Weekly	10% of samples	None	None
Turbidity	Weekly	10% of samples	None	None
Nitrosamines	Start of test[a]	10% of samples	5% of samples	1/sample shipment
Residuals: TCLP	End of resin bed life	10% of samples	5% of samples	None

Sample Analysis	Sampling QA/QC Frequency			
	Sample Frequency	Field-Collected Duplicates	Laboratory Matrix Spikes	Field Blanks
Residuals: CWET	End of resin bed life	10% of samples	5% of samples	None
Residuals: Uranium	Monthly on lead vessel	10% of samples	5% of samples	None

[a] Nitrosamines will be analyzed at a frequency required by the DPH permit

As the critical parameters in evaluating the success of the project, total Cr and Cr(VI) concentration data quality will also be subjected to paired sample analyses (i.e., Cr(VI) and total Cr samples collected at the same time). Paired samples will be used to assess the chromium speciation and verify that the two concentrations are similar, as observed in the Phase III Bridge Project. Discrepancies between the total Cr and Cr(VI) values will be investigated more closely to ensure that no bias exists for the total Cr analyses (as was observed in the Phase III Additional RCF Testing project).

6.2 Additional Project-Specific Quality Assurance Objectives

In addition to the primary objective of evaluating the effectiveness of Cr(VI) removal from water using the WBA resin, this demonstration-scale study will test the operations and maintenance (O&M) requirements for this technology. Table 3-2 highlights the critical process-related measurements that will be obtained during testing. To ensure quality data are collected to evaluate these objectives, flow rates and pressures will be measured and assessed within the acceptance criteria set forth by manufacturer specifications for the instrumentation.

6.3 Procedures to Assess QA Objectives

Quality assurance objectives will be assessed as detailed throughout this QAPP. Field measurements will be tested for accuracy by frequent calibration of equipment, for precision by obtaining replicate analyses of parameters, and for any contamination that may occur during sample handling and transfer by analyzing blanks.

Laboratory analyses, including critical chromium measurements, will be subjected to numerous procedures to assess quality assurance objectives. Sample accuracy will be tested by comparing sample concentrations to matrix spike concentrations and laboratory control samples. Relative percent differences on replicate samples will be used to determine instrumental precision. The examination of QA parameters including accuracy, precision, and sample contamination will enable us to have confidence in data and trends observed throughout the demonstration-scale study.

7 Data Reporting, Data Reduction, & Data Validation

7.1 Data Reporting Requirements

Table 7-1 details the reporting requirements (units, MDL, and MRL) for each of the analyses to be performed. All of the analyses in Table 7-1 for water samples are expressed in mg/L or μg/L. Data reporting requirements for residuals analyses are also listed in Table 7-1.

7.2 Field and Data Deliverables

Field data to be collected includes pH, temperature, conductivity, turbidity, alkalinity, sulfate, phosphate, and silicate. Measurements will be recorded in the Field Sampling Log Book and entered into Microsoft Excel.

Laboratory data for Cr(VI), total Cr, nitrate, and nitrosamines will be reported to McGuire Malcolm Pirnie by the contract laboratories. The data will be stored in the project data management system as well as at the contract laboratory. Routine analytical QC data will also be stored electronically.

McGuire Malcolm Pirnie will gather all data and prepare summary tables and graphics to characterize the findings from the demonstration-scale study. Quality assurance procedures (refer to Section 7.4) will be used to validate and confirm the data.

7.3 Data Reduction Procedures

In the laboratory and in the field, analytical measurements will be converted to concentrations by running appropriate calibration curves on the same instrument and interpolating the sample values.

Sample and QC concentrations received from the labs will be entered manually into a Microsoft Excel spreadsheet, from which efficiencies of Cr(VI) removal will be calculated. A minimum of 10% of data entered will be checked by the Malcolm Pirnie Quality Assurance Manager or Deputy Project Manager to ensure that transcription errors have not occurred.

Table 7-1.
Measurement Data Reporting

Sample Analysis	Analytical Method	Units	Method Detection Level (MDL)	Method Reporting Level (MRL)
Cr(VI)	EPA 218.6	µg/L	0.015	0.1
Total Cr	EPA 200.8 (ICP-MS)	µg/L	0.192	1
Nitrate	300.0 (IC)	mg/L	0.009	0.100
Sulfate	Hach 8051 (Turbidimetric)	mg/L	5	5
Phosphate	Hach 8048 (Colorimetric)	mg/L	0.5	0.5
Silicate	Hach 8185 (Colorimetric)	mg/L	1	1
Alkalinity	Hach 8203 (Titration)	mg/L (as $CaCO_3$)	10	10
Conductivity	SM 2510B (Conductance)	µmho/cm	TBD	TBD
pH	SM 4500H+ B (Electrometric)	pH units	N/A	N/A
Temperature	SM 2550 (Thermometric)	ºC	N/A	N/A
Turbidity	SM 2130 B	NTU	0.02	0.02
Nitrosamines	EPA 521	ng/L	NDMA – 0.476 NMEA – 0.393 NDEA – 0.758 NDPA – 0.785 NDBA – 0.719 NPYR – 0.361	NDMA – 2 NMEA – 3 NDEA – 5 NDPA - 7 NDBA – 4 NPYR – 2
Residuals: TCLP	EPA 1311 (TCLP) EPA 6010B (ICP): Total Cr	µg/L	2.466	10
Residuals: STLC	CA WET Test (Title 22:§66261.126) EPA 7196A: Cr(VI) EPA 6010B (ICP): Total Cr	mg/L mg/L	2.985 2.466	10 10
Residuals: TTLC	CA WET Test (Title 22:§66261.126) EPA 7196A: Cr(VI) EPA 200.7 (ICP-MS): Total Cr	mg/kg mg/kg	2.985 2.466	10 10
Residuals: Uranium	ASTM 5174-91 (KPA method)	mg/kg	0.00403	0.010

N/A = Not Applicable; TBD = To Be Determined.

7.4 Data Validation Procedures

Depending on the analytical measurement, the types of QA/QC samples may include the following:

- Laboratory matrix spike samples that are used to assess the accuracy of laboratory procedures in at least 5% of the samples;
- Laboratory blank samples that are used to determine the MDL of the analytical procedure and to detect potential laboratory contamination;
- Laboratory control samples that are subjected to multiple analyses to determine laboratory precision in at least 5% of the samples;
- Field-collected duplicate samples to assess how representative samples are and the degree to which the samples reflect actual field conditions; and
- Field-collected blank samples to detect potential problems in the sample collection, handling, and preservation methods.

Operational data will be routinely collected onsite using standardized log sheets. Log sheets will contain information about operational conditions and will be transferred into Microsoft Excel each week.

At the contract laboratory, a person other than the analyst will compare ten percent of all spreadsheet data to original hard-copy printouts. The analyst will ensure that all QC criteria are met, and the analysis manager will review all QC data monthly. The contract labs also conducts an annual performance evaluation for all methods.

Field data entered manually will be validated internally by qualified MMP personnel. Calculations performed in a spreadsheet will be carefully examined to ensure the accuracy of the formulas, data input, and results. After data have been validated and reduced, the MMP QA Manager will review the files to ensure that the data are not suspicious. Any quality control data that do not meet the acceptance criteria, either in the field or in the laboratory, will be flagged and either reported with an explanatory note or excluded from the data reduction.

7.5 Data Storage Requirements

Project data will be generated and duplicated in several locations. Operational data and water quality data generated on site will be recorded on standardized sheets in the Field Sampling Log Book. Water quality samples collected will be labeled to ensure correct identification of sample results returned from off-site laboratories. Information collected on water quality samples will include: sample identification number, name of person who collected the sample, date, time, sample volume, and sample preservation method.

Electronic and hard copies of data will be sent to McGuire Malcolm Pirnie by the contract labs. Project data in the Field Sampling Log Book and off-site laboratory reports will be entered into and will reside in the main project data files. The project data files will serve many purposes, including validation of data entry, central storage of all project data, and routine reduction and reporting of operational and water quality data. In addition, the contract labs will keep the electronic data for at least 5 years.

The main project data files will be hosted on the data server at the McGuire Malcolm Pirnie-Santa Monica office. This data server is routinely backed up on daily, weekly, and monthly schedules, with weekly off-site backups. The server is protected with hardware firewall, and the data files are protected from viruses with reputable anti-virus software.

7.6 Project Documentation

The product documents from this project include an operations and maintenance manual and a final report. However, monthly reports will also be produced for this project to provide updates, including discussion of any QA/QC issues and any necessary resolutions.

8 Assessments

8.1 Audit Schedule

Internal audits are not scheduled for this project. However, the Quality Assurance managers at McGuire Malcolm Pirnie and the contract laboratories will review all QC data monthly to ensure that QC objectives are being met.

8.2 Corrective Action Procedures

The need for corrective action may be identified by assessing standard QC procedures. The essential steps in the corrective action system are detailed below.

Identification and definition of the problem
Corrective action will be required if analytical data are determined to be out-of-control. An analytical batch will be considered to be out-of-control when replicate samples, matrix spiked samples, calibration blanks, the standard curve, calibration check samples, or external reference samples fail to meet the QC criteria.

Investigation and determination of the cause of the problem
When an analysis is determined to be out-of-control, steps will be taken to determine the cause. First, it must be determined whether a calculation error has occurred. Then the instrument used in the analysis will be checked against performance specifications. The indicators of being out-of-control will be a clue to the problem. For example, wrong readings of laboratory control samples may indicate the instrument is not properly set-up or standards are bad; if replicates are not within precision limits, contamination may be a problem; if spike recovery is outside acceptable limits, matrix interferences may have occurred; or if blanks are too high, contamination has probably occurred.

Determination of a corrective action to eliminate the problem

- Calibration check samples
  If results of the daily calibration sample check are out-of-control, as indicated by flagged values, causes may include instrument malfunction or improper set-up, bad standards, or operator error. The first step will be to check instrument performance. The instrument will be restarted. If this does not bring the system back into control, then standards will be re-made and analyzed. If the problem is operator error, the analyst will be re-trained and put through a rigorous QC check before he/she can continue with the sample analyses.

- Accuracy

  When a result is out-of-control as indicated by flagged values for spiked samples, the following steps will be taken to determine the cause. First, calculations will be checked. Then the instrument will be checked for proper set-up. The sample(s) will be reanalyzed. If these steps do not bring the analysis under control, then the spiked sample will be prepared again and analyzed. It may be necessary at this time to prepare fresh standards. If all of the above procedures do not bring the analysis into control, analysis will be performed by standard addition. All samples analyzed in the batch containing the out-of-control sample will be re-analyzed by the procedure used to bring the analysis back into control.

- Precision

  When a result for replicate analysis is out-of-control as indicated by flagged values, steps will be taken to determine the cause. First calculations will be checked. Then instrument performance will be evaluated. The sample(s) will be reanalyzed. If these procedures do not bring the samples back into control, then all samples in the analytical batch will be prepared again and analyzed.

- Blank contamination

  If the laboratory control blank shows contamination (i.e. concentrations greater than ½ the MRL during analysis, materials and reagents used to make that blank will be replaced before additional samples are prepared. Also, glassware and sample preparation will be re-evaluated to ensure that contamination is not occurring during these processes. Standards prepared with contaminated reagents will be discarded, and samples will be reprocessed.

- External reference sample analysis

  The inability of the laboratory to accurately analyze an external reference sample is indicative of analytical problems related to sample preparation procedures, instrument operation, or calibration. If the calibration check sample within the same analytical batch analysis is also out-of-control, a problem with the instrument or operator performance is indicated. Corrective action will be taken as described earlier. If the calibration check sample is within the control limits, the problem may be with the sample preparation procedure. At this point the calibration standards will be prepared again and analyzed. If this fails to bring the measurement back into control, the procedure will be reevaluated to determine if there are points within the procedure likely to be the source of contamination or the cause of a loss of the analyte. All samples analyzed in the batch with the out-of-control sample will be re-analyzed by the procedure used to bring the check samples back into control.

8.3 Implementation of Corrective Action

Analysts at the contract laboratories will have the authority to implement corrective action (described in Section 8.2 Investigation and Determination of the Cause of the Problem) during an analysis run if quality control samples are determined to be out-of-control. The Quality Assurance managers and Project Managers at McGuire Malcolm Pirnie and the contract laboratories will review QC logs monthly and will consult with the analyst if further corrective action is identified as necessary. Following any corrective action, the primary investigators will ensure that the analysis is truly back in control, as indicated by consistently meeting quality control criteria.

9 References

APHA, AWWA, and WEF. 1995. Standard methods for the examination of water and wastewater, 19th ed. American Public Health Association, Washington, DC, 1995.

Brandhuber, P.; Frey, M.; McGuire, M.J.; Chao, P.; Seidel, C.; Amy, G.; Yoon, J.; McNeill, L.; Banerjee, K. 2004. Treatment Options for Low-Level Hexavalent Chromium Removal Tested at Bench Scale. Denver, Colo.: AwwaRF.

California DHS, 2001, Chromium-6 (Hexavalent Chromium) in Drinking Water: Sampling and Analysis. http://www.dhs.ca.gov/ps/ddwem/chemicals/Chromium6/Cr+6labs.htm# Recommendations for Sample Collection

EPA. 1993. Method 300: Determination of Inorganic Anions in Drinking Water by Ion Chromatography. 600/R-93-100.

EPA. 1994. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry. EPA-600/R-94/111.

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

EPA. 1997. Manual for the Certification of Laboratories Analyzing Drinking Water: Criteria and Procedures Quality Assurance. EPA-815/B-97/001.

Lee, G.; Hering, J.G. 2003. Removal of chromium(VI) from drinking water by redox-assisted coagulation with iron(II). *J. Wat. Supply: Res. & Technol. – Aqua*, *52*, 319-332.

McGuire, M.J.; Blute, N.K.; Seidel, C.; Qin, G.; Fong, L. 2006. Pilot-Scale Studies of Hexavalent Chromium Removal from Drinking Water. *Jour. AWWA.* 98(2):134-143.

McGuire Environmental Consultants, Inc. (MEC) 2005. The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale Groundwater Supply: Phase II Demonstration of Pilot-Scale Treatment Technologies. Final report submitted to the City of Glendale. Glendale, CA.

National Toxicology Program (NTP), 2007. Technical Report on the Toxicology and Carcinogenesis Studies of Sodium Dichromate Dihydrate in F344/N Rats and B6C3F1 Mice. Draft.

Qin, G.; McGuire, M.J.; Blute, N.K.; Seidel, C.J.; Fong, L. 2005. Hexavalent Chromium Removal by Reduction with Ferrous Sulfate, Coagulation, and Filtration: A Pilot-Scale Study. *Environ. Sci. Technol.* 39(16):6321-6327.

Sengupta, A.; Sarkar, S. 2007. Trace Cr(VI) Removal by Weak Base Duolite A-7 and SIR-700 from Groundwater in Glendale, CA: Underlying Mechanism. *Report to the City of Glendale, CA.*

10 Appendices

Appendix A – SOPs

Appendix B – ELAP Certifications

Appendix A - SOPs

1. Cr(VI)– EPA Method 218.6

2. Total Cr– EPA Method 200.8

3. Nitrate – EPA Method 300.1

4. Sulfate – Hach Method 8051

5. Phosphate – Hach Method 8048

6. Silicate – Hach Method 8185

7. Alkalinity – Hach Method 8203

8. Conductivity – Standard Method 2510B

9. pH – Standard Method 4500H+ B

10. Temperature – Standard Method 2550

11. Turbidity – Standard Method 2130B

12. Nitrosamines – Standard Method 521

13. TCLP – EPA Methods 1311 (leaching), SW-846 6010C (and EPA Method 200.7) for metals, and SW-846 7470A (mercury)

14. California WET – CWET (Title 22)

15. Uranium – ASTM5174-9

Appendix B – ELAP Certifications

1. MWH Labs
2. Test America Labs

11. RCF Pilot Testing

Report on Additional RCF Pilot Testing to Optimize Design

Glendale Water and Power
141 North Glendale Ave, 4th Floor • Glendale, CA 91206

Report on Additional RCF Pilot Testing to Optimize Design

Task 19

May 8, 2008
Final

Report Prepared By:

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B. As-Built (Final) Process and Instrumentation Diagram and Photos
C. Data Summary Sheets

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1. Executive Summary

The City of Glendale, in partnership with McGuire Malcolm Pirnie, tested six treatment technologies for hexavalent chromium, Cr(VI), in the 2003-2004 Phase II Pilot-scale study. One of the pilot-tested technologies – reduction with ferrous sulfate, coagulation/aeration, and filtration (RCF) – successfully removed Cr(VI) from 100 μg/L to less than 5 μg/L (and to less than 1 μg/L under some conditions). The purpose of the initial Phase II pilot testing was to demonstrate if the various technologies were effective at all. Essentially, Phase II was designed to test the proofs of the overall treatment concepts. Optimization of the process design for scale-up was not possible given the scope and budget of the Phase II project.

Further optimization was recommended as part of the Phase III demonstration effort to identify the most effective, and least costly, design of an RCF system. The key objectives of the additional RCF pilot testing were to determine the reduction time necessary, aeration time necessary, and the possibility of passive backwash water treatment and recycle.

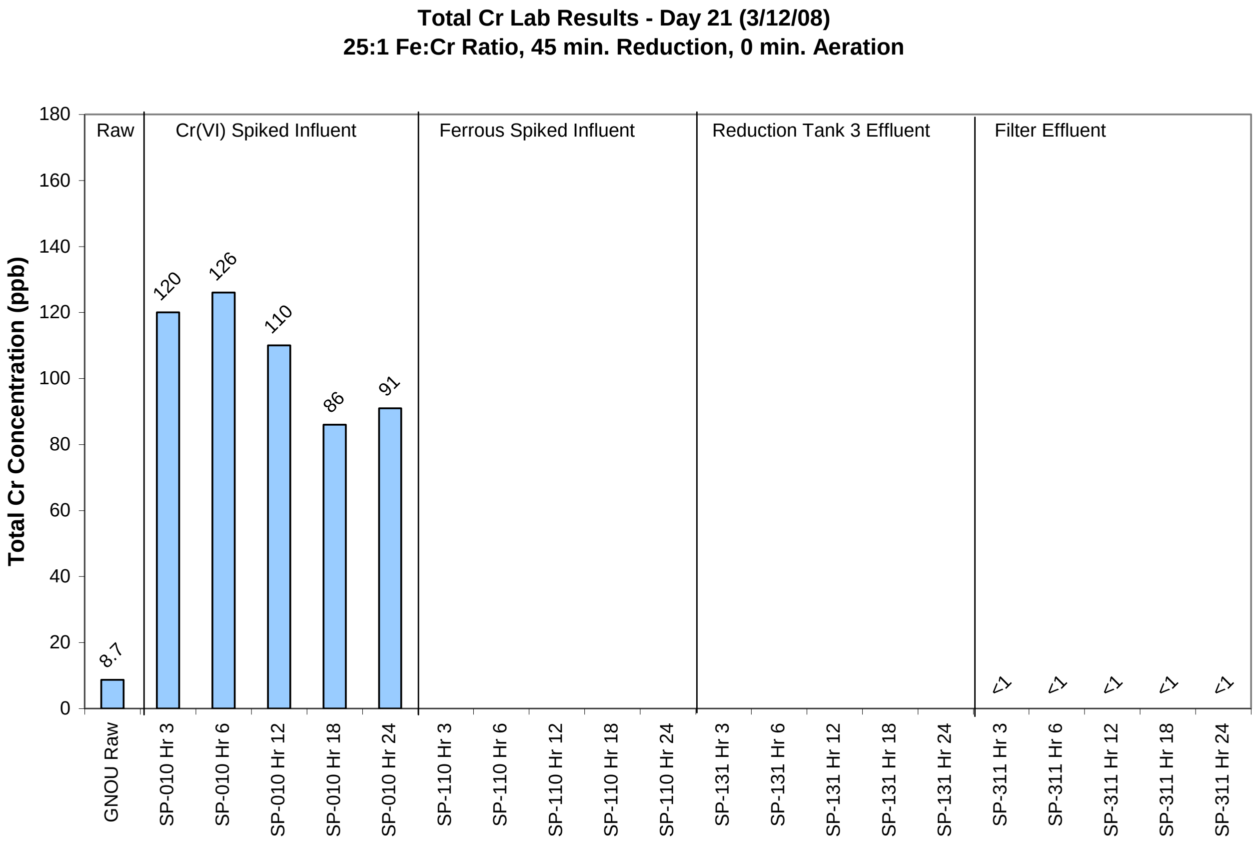
The additional RCF pilot testing included verification of system effectiveness (i.e., using conditions found to yield favorable results in Phase II pilot testing), longer time periods to test 24-hour filter runs, shorter reduction times (30 or 15 minutes compared with 45 minutes), shorter aeration times (12, 6, or 0 minutes compared to 18 minutes), and optimized combinations of effective reduction and aeration times. A modular approach was used in constructing the pilot testing system to allow for testing these multiple variables.

The removal of total Cr (and, thus, Cr(III)), rather than Cr(VI) alone, was critical to evaluate the success of the RCF drinking water treatment process. Cr(III) can be reoxidized to Cr(VI) in distribution systems by typical concentrations of free chlorine and chloramine secondary disinfectants. Therefore, reduction of Cr(VI) without removal of the total Cr was not a feasible treatment alternative for Glendale.

Phase III additional pilot testing results revealed that 45 minutes of reduction time (followed by filtration) was successful in consistently reducing Cr(VI) and removing total Cr to concentrations below 1 μg/L (i.e., the method reporting level) without the need for an aeration step (Figure 1-1). In addition, little pressure drop across the filters was observed during this 24-hour run, indicating that longer runs might be possible, further reducing the frequency of backwashing and the quantity of washwater produced.

Closer investigation of the RCF process provided evidence that full Cr(VI) reduction occurred within 15 to 30 minutes. Ferrous iron, Fe(II), oxidation required a detention time longer than 15 to 30 minutes or the presence of an aeration step. However, without aeration, ferrous iron was completely converted to ferric iron, Fe(III), and removed by the time the water reached the filter effluent, indicating that either additional contact time in the pilot plant piping between the ferrous iron and dissolved oxygen or air entrainment during the rapid mix/polymer addition step oxidized the remaining ferrous iron to ferric iron. With efficient particle removal in the granular media filters, total chromium concentrations less than 1 μg/L can be anticipated in the demonstration treatment facility.

Figure 1-1: Total Cr Concentrations Measured During the Optimized 24-Hour Run



Pilot testing revealed that clarified backwash water could be recycled to the treatment process influent without negatively impacting Cr(VI) treatment. Thus, backwash water recycle should be included in the design of the demonstration-scale facility to minimize water losses and reduce wastewater quantities. A passive means of filtration to dewater the backwash solids should also be included in the demonstration study design because it offers great cost savings over a filter belt press and was found to yield high quality filtrate in the pilot testing. Other design recommendations are included in Appendix A.

Based on these pilot test findings, we recommend that Glendale design an RCF system with 45 minutes of reduction time, polymer addition in a rapid mix tank after the reduction tanks, and dual-media granular filtration. No pH adjustment and no additional aeration (beyond that provided by the dissolved oxygen concentrations in the water) were necessary in the pilot testing, which will result in significant capital cost savings in the RCF system construction. However, during the design process physical space and hydraulic capacity should be included in the demonstration-scale plant design in case pH adjustment and aeration are needed at a later time.

2. Introduction and Objectives

In 2003-2004, the City of Glendale, in partnership with McGuire Malcolm Pirnie, conducted the Phase II Pilot-scale study of six treatment technologies for removing hexavalent chromium [Cr(VI)] from groundwater. One of the pilot-tested technologies – reduction with ferrous sulfate, coagulation/aeration, and filtration (RCF) – successfully removed Cr(VI) from 100 μg/L to less than 5 μg/L (and to less than 1 μg/L in under some conditions). The purpose of the initial Phase II pilot testing was to demonstrate if the various technologies were effective at all. Essentially, Phase II was designed to test the proofs of the overall treatment concepts. Optimization of the process design for scale-up was not possible given the scope and budget of the Phase II project.

In October 2007, an expert panel workshop was convened by Glendale to identify cost-effective Cr(VI) treatment technologies that were appropriate for further testing at demonstration scale. The expert panel members, including Bruce Macler, Pankaj Parekh, Sun Liang, Richard Sakaji, Mel Suffet, Laurie McNeill, Arup SenGupta, and Gary Amy, unanimously recommended the RCF process for demonstration-scale testing. Primary considerations for their recommendation included process effectiveness, a thorough understanding of the technology, and ease of permitting. Consequently, the City of Glendale intends to design and build a demonstration-scale RCF treatment facility to treat part or all of the water from two high-chromium wells from the North Operable Unit (GN-2 and GN-3).

As Glendale moves into the design phase for the RCF system, further optimization of the RCF system was required as part of the Phase III demonstration effort to identify the most effective, and least costly, design. Consequently, optimization pilot testing was conducted and is described in this report. Outstanding design issues considered included:

- **Reduction time needed for Cr(VI) reduction by ferrous sulfate.** Bench-testing literature[1] reported that as much as 45 minutes was needed to remove Cr(VI) from 55 to 5 μg/L using ferrous sulfate; consequently, the Phase II pilot test relied upon this information and found that 45 minutes was sufficient for Cr(VI) reduction. However, it has come to our attention that an operational RCF treatment system for a confidential client found that 10 minutes of in-pipe mixing followed by approximately 15 minutes of batch mixing (for a total of 25 minutes of reduction time) was sufficient. For a 1,000 gpm treatment system, the difference between 30 and 45 minutes of reduction time is approximately 20,000 gallons of tankage. Consequently, a modular approach for additional pilot-scale testing (i.e., 3 reactors in series, each providing 15 minutes of reaction time) was evaluated to determine how much reduction time should be built into the demonstration study design.

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[1] Lee, G. and Hering, J. 2003. Removal of Chromium(VI) from Drinking Water by Redox-Assisted Coagulation with Iron(II). *Journal of Water Supply: Research and Technology – AQUA.* 52:5:319-332.

- **Need for aeration to accomplish coagulation.** To maximize the chances of removing particulate iron and chromium during pilot testing filtration, the Phase II pilot design included multiple aeration columns fitted with coarse bubble diffusers fed by an air compressor. However, the need for this step and the duration of aeration necessary had not been evaluated in any detail. This additional pilot testing evaluated the need for aeration and how much time would be required.

- **Filtration approach.** Granular media (anthracite and sand) filters were used in the Phase II pilot testing and proved to be highly effective at removing iron and chromium particles from the process water. However, extensive studies of filter performance over time were not conducted. Tests of different iron doses indicated that bed depth penetration of the particles may be linked to dosage. During the Expert Panel, Dr. Gary Amy recommended the possible use of microfiltration (MF) membranes to achieve consistent, effective particle removal. However, the MF option is considerably more costly than dual media filtration. The existing Cr(VI) RCF treatment facility for the confidential client mentioned previously is reported to have tubular Pall MF treatment. Due to budgetary restraints, Glendale decided to test dual-media filtration in this pilot test optimization but may consider MF for the demonstration-scale study.

- **Sludge dewatering.** Initial cost estimates for sludge dewatering included a filter belt press, which added significant capital costs to the design and complexity to the operations. Due to the small quantities of sludge produced by RCF, a more passive means of sludge dewatering (similar to the Flo Trend Systems, Inc. approach) may be an option for Glendale and was tested in this pilot test optimization.

- **Backwash water recycle.** In the Phase II pilot testing, backwash water was shown to be effectively settled using a relatively small dose of polymer 1.0 ppm). If settled backwash water is recycled to the head of the plant, possible impacts of this polymer on the process train may occur. This possibility was tested to determine any potential impacts on the process.

Due to the number and substance of outstanding design issues as well as the fact that this is a new treatment technology for Cr(VI) removal to low levels for drinking water applications (the operational RCF installation for the confidential client notwithstanding, since full design details are not available for that installation), this additional optimization pilot testing of the RCF system was necessary. **The key objectives of the pilot testing were to determine the reduction time necessary, aeration time necessary, and the possibility of passive backwash water treatment and recycle.**

3. RCF Process Description

3.1. General Conceptual Design for Demonstration-Scale Testing

In the RCF process, Cr(VI) is first reduced to Cr(III) with the addition of excess ferrous iron (Fe^{2+}), which is oxidized to ferric iron (Fe^{3+}) by the electron transfer during the reduction of Cr(VI) and by dissolved oxygen present in the water. Ferrous iron doses found to be acceptable in Phase II testing ranged from 1.5 to 2.5 mg/L for treating 100 μg/L of Cr(VI) to less than 5 μg/L. Cr(III) either precipitates, forms a co-precipitate with the ferric iron, or adsorbs onto the ferric floc. The ferric iron/Cr(III) particles form larger floc during the aeration and coagulation (with the use of a polymer) stages. Particles are then removed by filtration.

RCF is a mature treatment process for removing high concentrations of Cr(VI) from industrial wastewaters. RCF minus the reduction step (i.e., just coagulation/filtration) is an accepted technology for arsenic removal in drinking water treatment. Unfortunately, only limited studies have been conducted to examine the possibility of achieving low chromium treatment goals using the RCF process for drinking water. Some studies have demonstrated that ferrous sulfate effectively reduces Cr(VI), but that subsequent Cr(III) removal by filtration is not effective under all conditions. In Phase II testing, a pilot-scale RCF unit (approx. 2-gpm capacity) successfully removed total chromium to below detectable levels for an extended period (23 to 46 hrs).[1]

Based on the Phase II pilot test, a demonstration-scale RCF system was conceptually designed with a treatment capacity of 500 gpm (one of the likely configurations to treat a single well). According to a recent cost estimate by Malcolm Pirnie, the total capital cost for the 500-gpm RCF system was $3.05 million and the annual operations and maintenance (O&M) cost was estimated at $164,000. Due to limited funding availability, the treatment capacity for the demonstration-scale treatment unit may have to be reduced to 100 gpm.

The RCF demonstration-scale system will be located adjacent to the Glendale Water Treatment Plant (GWTP) to treat groundwater from Well Sites GN-2 and/or GN-3. These two wells have high levels of Cr(VI), which make them good candidates for the demonstration study.

3.2. Phase III RCF Pilot Testing

Phase III additional RCF pilot testing was conducted at the Glendale Water Treatment Plant on an empty concrete pad located within a containment area. Figure 3-1 shows a simplified schematic of the pilot-scale treatment process. Appendix B provides the final as-built process flow schematic for the RCF pilot testing system by AVANTech, the vendor who supplied the system. Appendix B also contains photos of the final as-built pilot plant.

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[1] Qin, G.; McGuire, M.J.; Blute, N.K.; Seidel, C.J.; Fong, L. 2005. Hexavalent Chromium Removal by Reduction with Ferrous Sulfate, Coagulation, and Filtration: A Pilot-Scale Study. *Environ. Sci. Technol.* 39(16):6321-6327.

Raw water from the North Operable Unit was fed at a rate of 2 gpm to the pilot plant with in-line spiking of Cr(VI) to achieve a target concentration of 100 µg/L. Chromic acid (10% weight to volume--w/v) was diluted to 0.1% in the chemical day tank, which was used for spiking. The Cr(VI)-spiked water then entered an influent holding tank and was pumped out to the reduction tanks. Ferrous sulfate addition occurred in the pipeline from the influent holding tank to the first reduction tank. Ferrous sulfate was added to the spiked influent water at a dose of either 1.5 or 2.5 mg/L (as Fe) using ferrous sulfate solution (5% w/v) diluted to approximately 3% with distilled water. The diluted ferrous sulfate solution pH was still very low (approximately 2.96--compared with 2.57 in the 5% solution), which minimized any ferrous sulfate oxidation during each day's run.

Three reduction tanks with detention times of approximately 15 minutes each were piped in series, with the ability to bypass one or two tanks. Effluent from the final reduction tank flowed into a small tank where the water was pumped into three aeration columns in series. Water flowed into the tops of the aeration columns and a 10 Standard Cubic Feet per Minute (SCFM) countercurrent of air bubbles was provided using coarse bubble diffusers (connected to an air compressor) at the bottoms of each column. The pilot plant could be operated with aeration tanks either as 0, 1, 2, or 3 in series.

Sodium hydroxide chemical feed was built into the design of the pilot system between the final reduction tank and the first aeration column but was not used. This capacity was built into full-scale testing elsewhere for a confidential client to adjust the pH to greater than 7.7. As discussed in the Results section, pH adjustment was not necessary for complete ferrous iron oxidation in the water matrix tested during this pilot study.

Downstream of the aeration columns, polymer was added into a rapid mix tank for enhanced floc formation. Three different polymers were used during this testing. In Phase II pilot testing, Magnafloc Ciba E40 anionic polymer was used. Discussions with the Ciba vendor during this pilot testing revealed that the E40 product is not yet NSF-certified; consequently, a similar product (Magnafloc Ciba E38) was substituted and yielded similar floc formation. Experience at a full-scale treatment facility for a confidential client determined that Nalco 9901 anionic polymer formed a good floc to coagulate ferric iron in a Cr(VI) removal facility, so Nalco 9901 was also used in some pilot runs.

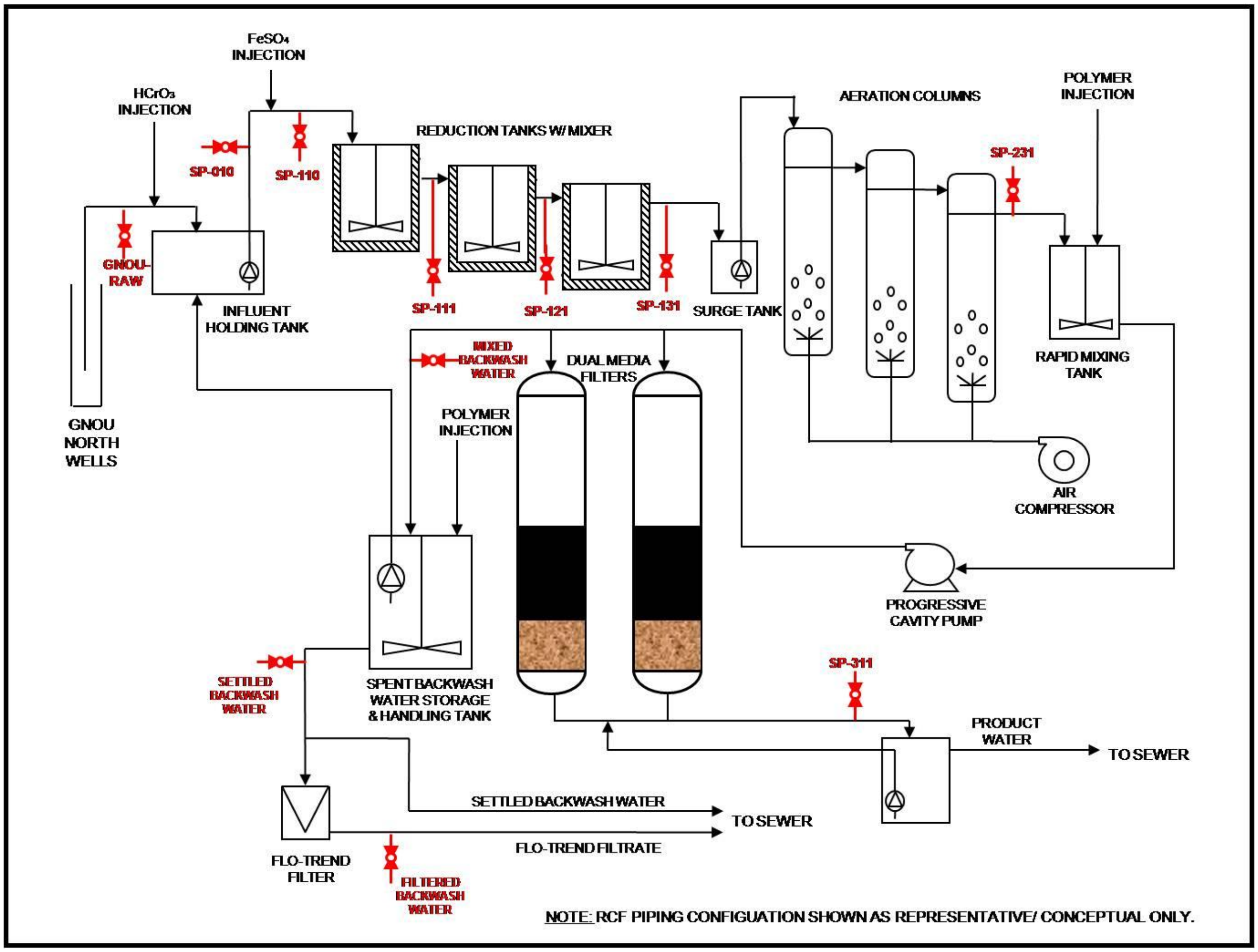
Early testing (February 4-7, 2008) included the use of a surge tank and sump pump after the rapid mix tank and before the filter columns, but this configuration caused dramatic break-up of the floc that had already formed. Starting on February 11th, the system was reconfigured to place the surge tank and sump pump upstream of the rapid mix tank, and the rapid mix tank was elevated to provide gravity flow to the filters. However, the additional head was not sufficient to allow for a run longer than 6 to 8 hours. In addition, more free board above the filter beds was found to be necessary to allow for better backwashing (incorporating air scour, which was not originally planned by AVANTech). Consequently, system modifications were made on February

17th and 18th to add a progressive cavity pump between the rapid mix and filter columns to permit pressurized filter column operation. Modifications also included the addition of five feet of free board above the filter beds to allow for more vigorous and efficient backwashing. Operations on and after February 19th represent the final system configuration.

The filtration media consisted of 26 inches of anthracite (1.0 to 1.25 mm diameter, uniformity of <1.5) and 14 inches of sand (0.5 to 0.6 mm silica sand), with a gravel (3/8 to 3/4 inch) support underdrain. Both anthracite and sand were purchased from an established supplier with AWWA certification. The parallel, dual media filters were operated at a hydraulic loading rate of approximately 3 gpm/sf throughout the testing period,

Filtered water was sent to an effluent tank prior to discharge to the sewer. This clean effluent was also used to backwash the filters at a rate of approximately 7.5 gpm per column (21 gpm/sf) for 5 minutes. Spent backwash water was piped to a separate holding tank for discharge to the sanitary sewer. A sample of the settled backwash solids was collected for processing through the Flo Trend Systems, Inc. material.

Figure 3-1: Simplified schematic of the RCF pilot system



4. Testing Periods and Methods

RCF treatment process optimization included testing periods to change single variables associated with the treatment process components and optimized process train testing. The sections below provide an overview of the data collection and study protocol used in the RCF pilot testing, including monitoring parameters, locations, frequency, and analytical approach. Results are provided in Section 5.

4.1. Testing Periods

The RCF pilot testing periods included verification of system effectiveness (i.e., using conditions found to yield favorable results in Phase II pilot testing), longer time periods to test 24-hour filter run times, shorter reduction times (30 or 15 minutes compared with 45 minutes), shorter aeration times (12, 6, or 0 minutes compared to 18 minutes), and other combinations of effective reduction and aeration times. Table 4-1 shows the breakdown of the testing periods during Phase III piloting.

Table 4-1.
Phase III RCF Testing Periods

	Date	Reduction time	Aeration time	Filter run time	Target Fe:Cr dose	Polymer
Day 1	4-Feb-08	45 min	18 min	6-8 hrs	15:1	Nalco 9901 - 0.2 ppm
Day 2	5-Feb-08	45 min	18 min	6-8 hrs	25:1	Nalco 9901 - 0.2 ppm
Day 3	6-Feb-08	45 min	18 min	6-8 hrs	25:1	Nalco 9901 - 0.2 ppm then Ciba E40 - 0.38 ppm
Day 4	7-Feb-08	-	-	-	-	-
Day 5	8-Feb-08	-	-	-	-	-
Day 6	11-Feb-08	45 min	18 min	6-8 hrs	25:1	Nalco 9901 - 0.2 ppm
Day 7	12-Feb-08	45 min	18 min	6-8 hrs	25:1	Ciba E40 - 0.28 ppm
Day 8	13-Feb-08	45 min	18 min	6-8 hrs	25:1	Ciba E40 - 0.28 ppm
Day 9	14-Feb-08	30 min	18 min	6-8 hrs	25:1	Ciba E40 - 0.26 ppm
Day 10	15-Feb-08	15 min	18 min	6-8 hrs	25:1	Ciba E40 - 0.26 ppm (a.m.), 0.1 ppm (p.m.)
Day 11	18-Feb-08	-	-	-	-	-
Day 12	19-Feb-08	45 min	12 min	6-8 hrs	25:1	Ciba E40 - 0.092 ppm
Day 13	20-Feb-08	45 min	6 min	6-8 hrs	25:1	Ciba E40 - 0.085 ppm
Day 14	21-Feb-08	30 min	6 min	6-8 hrs	25:1	Ciba E40 - 0.085 ppm
Day 15	22-Feb-08	15 min	12 min	6-8 hrs	25:1	Ciba E40 - 0.095 ppm
Day 16	25-Feb-08	45 min	0 min	6-8 hrs	25:1	Ciba E40 - 0.094 ppm
Day 17	26-Feb-08	45 min	18 min	6-8 hrs	25:1	Ciba E38 - 0.1 ppm
Day 18	27-Feb-08	45 min	18 min	24 hrs	25:1	Ciba E38 - 0.093 ppm
Day 19	28-Feb-08	45 min	18 min	24 hrs	25:1	Ciba E38 - 0.1 ppm
Day 20	29-Feb-08	45 min	No air	6-8 hrs	25:1	Ciba E38 - 0.1 ppm
Day 21	12-Mar-08	45 min	No air	24 hrs	25:1	Ciba E38 - 0.1 ppm

4.2. Monitoring Parameters

4.2.1. Water Quality Parameters

Table 4-2 shows the laboratory analyses that were conducted during the pilot testing. Cr(VI), total Cr [Cr(VI) plus Cr(III)], and total suspended solids (TSS) were measured by Montgomery Watson Harza (MWH) Laboratories at seven sampling points. Table 4-2 also contains the sampling point IDs corresponding to the locations shown in the P&ID drawing in Appendix B.

Table 4-3 lists the field analyses, including Cr(VI), total iron, ferrous iron, pH, temperature, turbidity, dissolved oxygen (DO), and oxidation reduction potential (ORP). Selected effluent samples were also filtered through a 0.2 micron filter to compare the total Cr results of membrane filtered and membrane unfiltered effluent.

In general, each day consisted of three sampling events timed to correspond with the beginning, middle, and end of the run. The first sampling event confirmed dosing and occurred approximately one to two hours into the run. The middle and end of the run samples were used to assess process efficiency. The middle samples were collected after approximately 3 to 4 hours of operation. End of the run samples were collected approximately 6 hours into operation. For 24-hour runs, total Cr and iron samples were collected after 3 hours, 6 hours, 12 hours, 18 hours, and 24 hours. Effluent turbidity samples were measured hourly during all sample runs as a proxy for iron and chromium breakthrough.

Supernatant from the settled backwash water was monitored twice after two 24-hour runs for Cr(VI), total Cr, total iron, pH, and turbidity. Filtrate water quality from the Flo Trend system was also measured for Cr(VI), total Cr, and total Fe.

The volume of solids generated during backwashing was estimated following the 24-hour runs. The backwash tank was first flushed and vacuumed to remove any water and solids before beginning the test. Water from a single backwash (both columns) was captured in the backwash tank, mixed, and two samples were collected. A 500 mL sample was analyzed for total suspended solids. A 1,000 mL sample was analyzed for settleable solids according to Standard Methods 2540F using an Imhoff cone.

Table 4-2.
Laboratory Analyses and Sample Locations for RCF Pilot Testing

	Lab Analyses		
Sampling Location	**Cr(VI)***	**Total Cr^**	**TSS**
SP-010 - Cr(VI) Spiked Influent	2 /day: • middle of run • end of run	2 /day: • middle of run • end of run	-
SP-131 - After Reduction Tank #3	1 /day: • middle of run	-	-
SP-231 - Aeration Process Effluent	1 /day: • middle of run	-	-
SP-311 - Filter Effluent	2 /day: • middle of run • end of run	2 /day: • middle of run • end of run	-
BW Tank - Settled Backwash Water	1 /week	1 /week	-
BW Tank - Mixed Backwash Water	1 /week	1 /week	1 / iron dose
Flo Trend Filtrate - Filtered Backwash Water	1 /pilot testing	1 / pilot testing	-

* Turnaround time of 5-days
^ Turnaround time of 24-hours

Table 4-3.
Field Analyses and Sample Locations for RCF Pilot Testing

	Field Analyses							
Sampling Location	**Cr(VI)**	**Total Iron**	**Ferrous Iron**	**pH/Temp**	**ORP**	**Turbidity**	**Dissolved Oxygen**	**Settleable Solids**
GNOU Raw Water (at sample tap)	1 / week	1/ week	1/ week	1/ week	1/ week	1/ week	1 / week	-
SP-010 - Cr(VI) Spiked Influent	2 /day: • beginning of run • middle of run	-	-	2 /day: • middle of run • end of run	1 /day: • middle of run	1/day: • end of run	2 /day: • middle of run • end of run	-
SP-110 - Fe-Spiked Influent	-	2 /day: • beginning of run • middle of run	2 /day: • beginning of run • middle of run	2 /day: • middle of run • end of run	1 /day: • middle of run	1/day: • end of run	-	-
SP-111 - After Reduction Tank #1	1 /day: • middle of run	-	-	-	-	-	-	-
SP-121 - After Reduction Tank #2	1 /day: • middle of run	-	-	-	-	-	-	-
SP-131 - After Reduction Tank #3	1 /day: • middle of run	2 /day: • middle of run • end of run	2 /day: • middle of run • end of run	2 /day: • middle of run • end of run	1 /day: • middle of run	-	2 /day: • middle of run • end of run	-
SP-231 - Aeration Process Effluent	-	2 /day: • middle of run • end of run	2 /day: • middle of run • end of run	2 /day: • middle of run • end of run	1 /day: • middle of run	-	2 /day: • middle of run • end of run	-
SP-311 - Filter Effluent	-	2 /day: • middle of run • end of run	2 /day: • middle of run • end of run	2 /day: • middle of run • end of run	-	8 /day: • hourly	-	-
BW Tank - Settled Backwash Water	-	1 /week	-	1 /week	-	1 /week	-	-
BW Tank - Mixed Backwash Water	-	-	-	-	-	-	-	1 / iron dose
Flo Trend Filtrate - Filtered Backwash Water	-	1 / pilot testing	-	-	-	-	-	-

4.2.2. Process Parameters

In addition to chemical and physical water quality analyses, process-related parameters were recorded to evaluate the operations of the RCF pilot system. The process-related parameters included flow rate and pressure buildup through the filter columns.

Backwash sediment samples were collected from the bottom of the backwash tank once during the pilot runs and filtered using material supplied by Flo Trend Systems, Inc. Filtrate quality was determined by monitoring for iron and chromium concentrations. In addition, the floc toughness after dewatering with the Flo Trend material was assessed by mixing the floc in a jar tester at 300 RPM to visually assess whether the floc stayed together or broke apart. The sludge was also visually inspected to determine the dryness (e.g., whether the sludge was wet and slimy or dry and matte in appearance).

Following testing, the piping and tanks were inspected to assess any scale formation from the ferric iron precipitates. The occurrence of scale on RCF process components has been reported for another full-scale RCF installation.

4.3. Monitoring Locations

Samples were collected from sample ports identified in Appendix B. Sample locations for the RCF pilot testing are highlighted in Table 4-2 and Table 4-3. For the pilot system, sampling locations included the raw Glendale North Operable Unit (GNOU) water (obtained from the combined transmission main from the North Operable Unit); Cr(VI) spiked influent water; ferrous sulfate-spiked influent water; after each of the three reduction tanks; the effluent from the aeration column(s); filter effluent from the granular media filters; settled backwash water from the backwash tank; and mixed water from the backwash tank. In addition, one sample was collected from the bottom of the backwash tank to test Flo Trend solids separation on a small scale.

4.4. Monitoring Frequency

4.4.1. Water Quality Parameters

The sampling frequency followed for chemical parameters are shown in Table 4-2 and Table 4-3. The selected frequency was based on treatment process design and the duration of pilot testing (four 5-day weeks).

4.4.2. Process Parameters

Flow rates were measured on a daily basis, and pressure buildup was recorded each hour through the 24-hour filter runs.

4.5. Analytical Approach

Analytical methods for the water quality parameters and treatment residuals conformed to EPA guidelines and recommended test methods for Cr(VI) and total Cr. Standard-tested Hach methods were used for field monitoring.

Total Cr and Cr(VI) were measured by ELAP-certified MWH Laboratories. The laboratory analyses of total chromium were performed by ICP-MS (EPA Method 200.8). Cr(VI) was analyzed using IC (EPA Method 218.6). TSS was measured gravimetrically using EPA Method 160.2. All other parameters were analyzed in the field using the methods shown in Table 4-4.

The Method Reporting Levels (MRLs) at MWH Labs for Cr(VI) and total Cr are 0.1 µg/L and 1 µg/L, respectively. Samples found to be less than these values were reported as "<MRL."

Table 4-4.
Analytical Methods, Locations of Analyses, and Detection Limits

Sample Analysis	Analytical Method	Analysis Location	Method Detection Level (MDL)	Method Reporting Level (MRL)
Cr(VI) – Lab	EPA 218.6 (IC)	MWH Labs	0.015 µg/L	0.1 µg/L
Total Cr	EPA 200.8 (ICP-MS)	MWH Labs	0.192 µg/L	1.0 µg/L
TSS	EPA 160.2 (Gravimetric)	MWH Labs	4 mg/L	4 mg/L
Cr(VI) – Field	Hach Method 8023 (Diphenylcarbohydrazide)	Field	10 µg/L	10 µg/L
Total Iron	Hach Method 8147 (FerroVer)	Field	0.02 mg/L	0.02 mg/L
Ferrous Iron	Hach Method 8146 (1,20-Phenanthroline)	Field	0.02 mg/L	0.02 mg/L
pH	SM 4500H+ B (Electrometric)	Field	N/A	N/A
Temperature	SM 2550 (Thermometric)	Field	N/A	N/A
ORP	Ag/AgCl Combination Electrode	Field	N/A	N/A
Turbidity	SM 2130 B	Field	0.02 NTU	0.02 NTU
Dissolved Oxygen	Hach Method 8166 (HRDO)	Field	0.3 mg/L	0.3 mg/L
Settleable Solids	SM 2540F (Volumetric)	MWH Labs	0.5 mL/L	0.5 mL/L

4.6. Quality Assurance/Quality Control Checks

QA/QC sampling in the field included duplicate samples and blanks. Field-collected duplicate samples were obtained for 10% of lab samples by collecting one sample after the other. Field-collected blanks were also collected using distilled water. Duplicates and blanks were not identified as QA/QC samples when sent to the laboratory.

Laboratory analyses were subjected to numerous procedures to assess QA/QC objectives. A combination of matrix spikes (MS), matrix spike duplicates (MSD), laboratory reagent blanks (LRB), instrument performance check samples (IPC) for Method 218.6 and continuing calibration verification (CCV) samples for Method 200.8, and laboratory control samples (LCS) were analyzed.

Accuracy (a combination of random and systematic error) in Cr(VI) and total Cr analyses was evaluated by determining percent recoveries in matrix spike samples. A matrix spike was performed on 10% of samples (or at least one sample per run; spike added in the laboratory), chosen at random. Spike recoveries between 90 and 110% of the expected value for Cr(VI) and between 70 to 130% for total Cr were acceptable. Accuracy was also tested at the beginning of the runs and after every 10 samples by sampling a mid-range IPC sample and a LRB. The acceptance criterion for the IPC sample was between 95 and 105%.

Precision (random error) was investigated by performing repeat analyses on the same analytical instruments. For every batch of twenty samples, LCS and MS samples were run. The acceptable ranges for these sample results were between 90 and 110% for Method 218.6 and 70 to 130% for Method 200.8. Laboratory duplicates or MSD samples were analyzed for every batch of twenty samples with an acceptance criteria of <20% Relative Percent Difference (RPD).

5. Results and Discussion

Due to the large amount of data collected during pilot testing, only the key findings are summarized and discussed in this report. All data are available in Appendix C.

5.1. Cr(VI) Reduction

In the RCF process, Fe(II) promotes the reduction of Cr(VI) to Cr(III). Pilot testing investigated the time required to accomplish full Cr(VI) reduction by sampling the end of the reduction process using 15, 30, or 45 minutes of reduction tank detention time. Figure 5-1 shows that Cr(VI) was significantly converted to Cr(III) after the first 15 minutes of reduction time. Two runs using 15 minutes of reduction time revealed Cr(VI) concentrations at the 15-minute reduction tank sampling point of 1.5 and 0.3 μg/L. After 30 minutes of reduction time in two other runs, the Cr(VI) concentrations remaining were 0.37 and 0.11 μg/L. Forty-five minutes of reduction time typically yielded Cr(VI) values of less than the MRL (0.1 μg/L). No reoxidation of Cr(VI) occurred in the aeration columns or filters.

Figure 5-1: Hexavalent Chromium Reduction

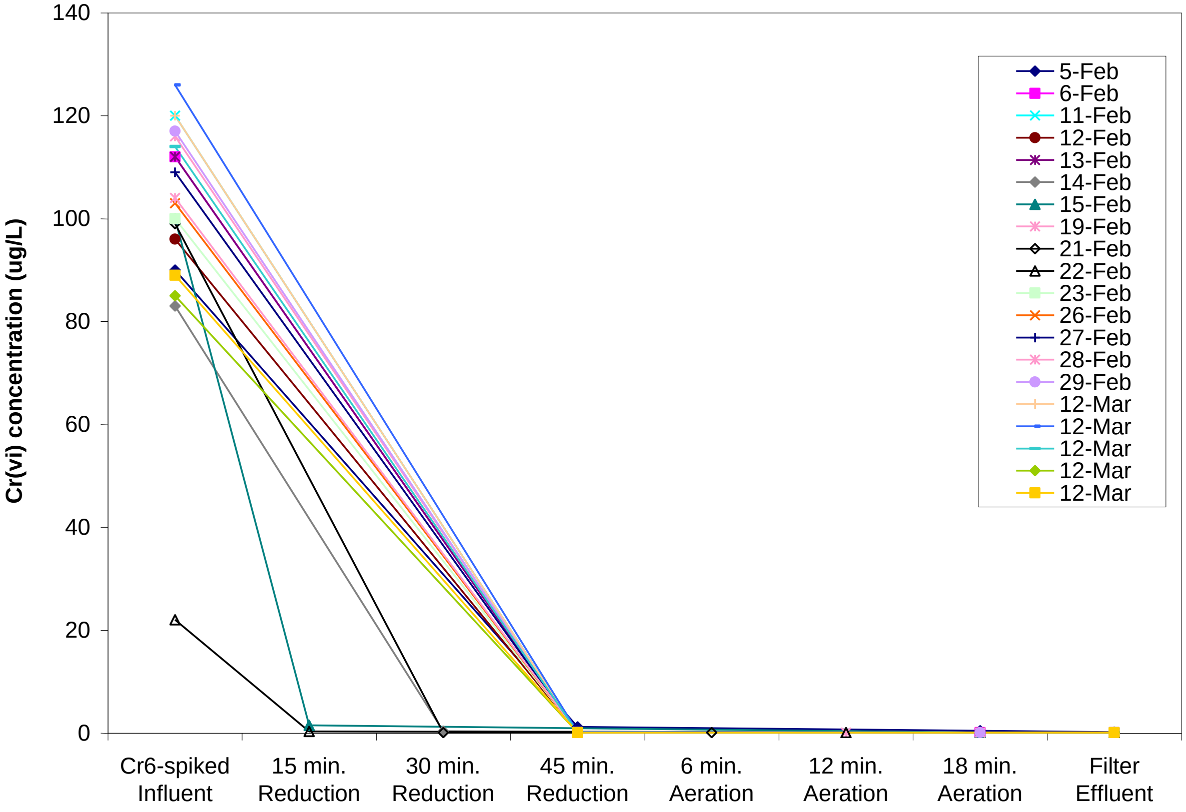
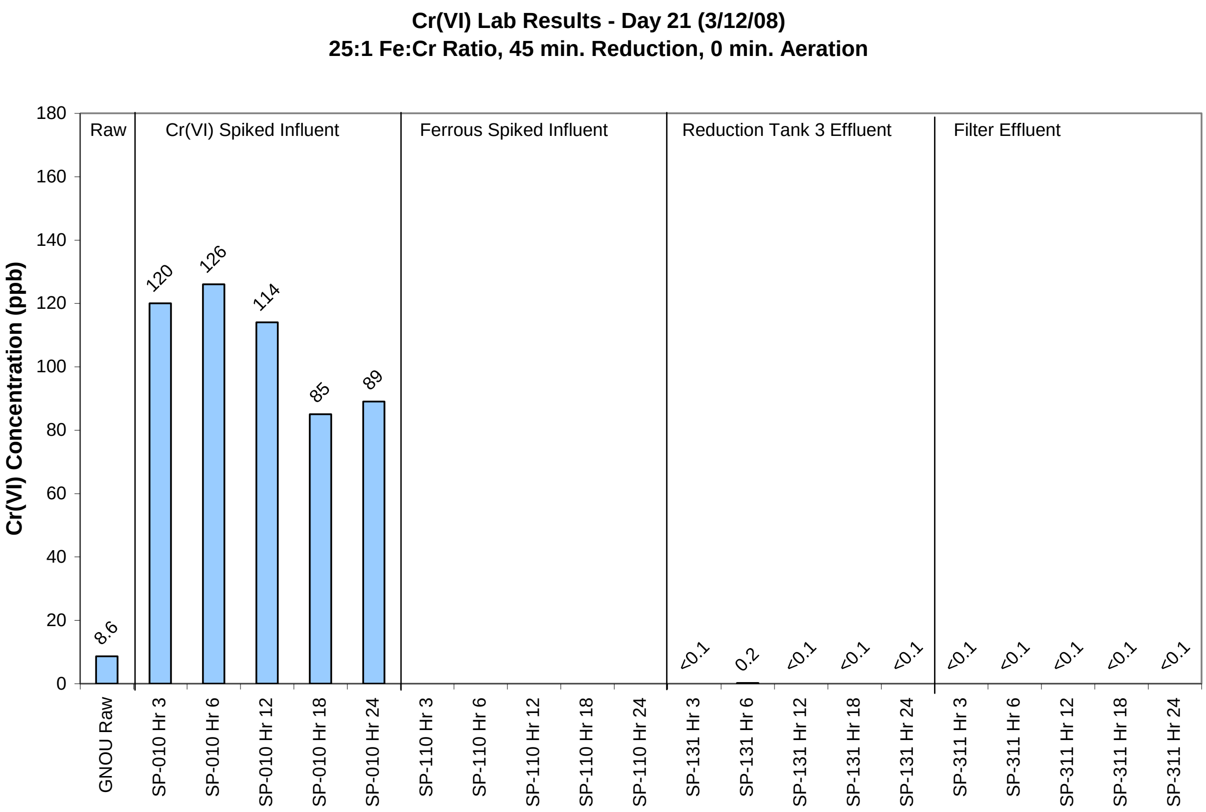


Figure 5-2 highlights the Cr(VI) reduction for the optimized case of 45-minutes reduction and 0 minutes of aeration on March 12th. As shown in this figure, all of the sampling times exhibited

Cr(VI) less than 0.2 µg/L after 45 minutes of reduction time. Filter effluent Cr(VI) concentrations were all less than 0.1 µg/L.

Figure 5-2: Hexavalent Chromium Reduction in the Optimized 24-Hour Run



5.2. Ferrous Iron Oxidation

Ferrous-spiked influent water was analyzed for both total iron and ferrous iron throughout pilot testing. According to the Hach field methods used for these analyses, ferrous iron comprised approximately 44% ± 12% of the total iron concentration in the spiked influent water. However, the total iron concentration was used to set the iron dose based on the desired iron-to-chromium ratio, since the successful Phase II testing also relied upon total iron rather than ferrous. The reason for the low percent ferrous concentration in the ferrous sulfate solution was unknown and occurred in spite of precautions taken to minimize ferrous oxidation (e.g., ensuring a low pH was maintained in the diluted stock solution and using distilled water as the diluent).

For the ferrous iron observed in the iron-spiked influent water, oxidation to ferric iron in the reduction tanks required at least 45 minutes. Figure 5-3 shows that runs testing 15 minutes or 30 minutes of reduction time resulted in measurably higher ferrous iron concentrations, in most cases, in water exiting the reduction tanks. On average, 15 minutes of reduction time resulted in 60±16% ferrous remaining in solution, 30 minutes of reduction time resulted in 26±12% ferrous remaining in solution, and 45 minutes of reduction time resulted in 21±10% ferrous remaining in solution.

Figure 5-3: Ferrous Iron Oxidation in the Reduction Tanks

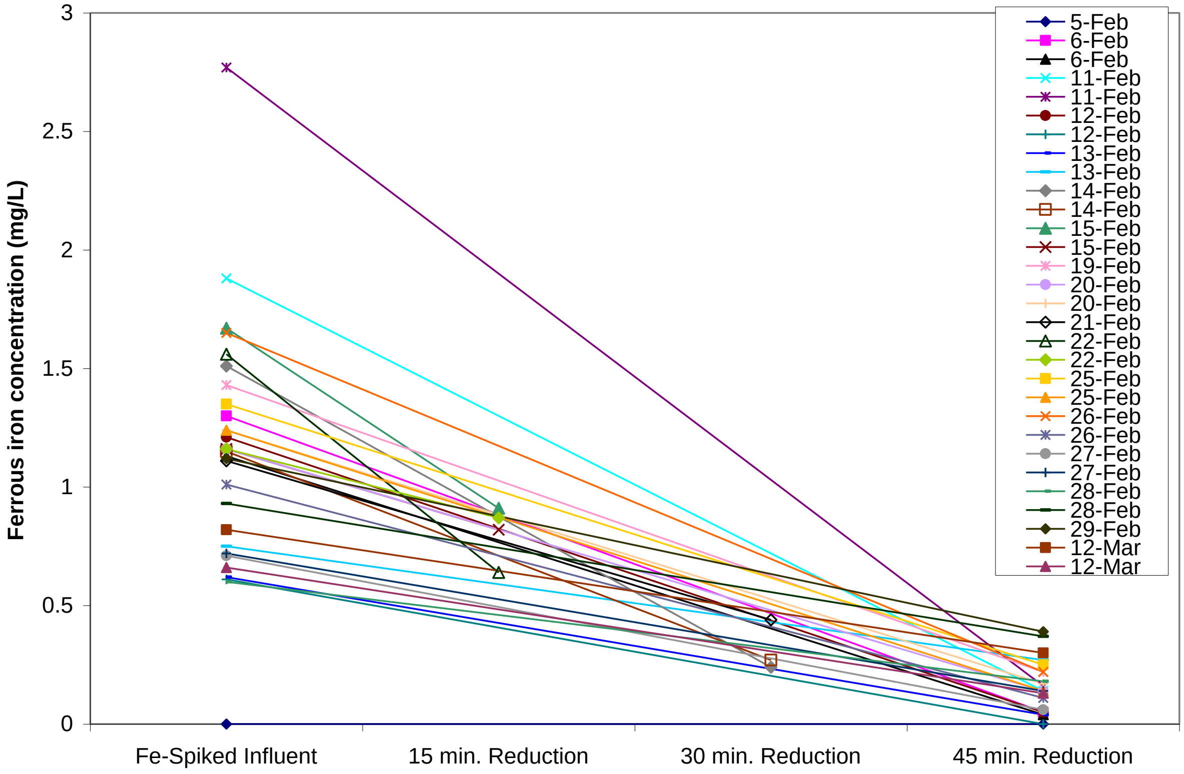


Figure 5-4 confirms that the remaining ferrous iron after the reduction step was oxidized to less than 0.1 mg/L in solution by the aeration step. Even the cases in which lower reduction times were used (Figure 5-5) and all of the ferrous iron was not oxidized in the reduction tanks, it was effectively oxidized during the aeration step.

Figure 5-4: Ferrous Iron Oxidation Through the RCF Process

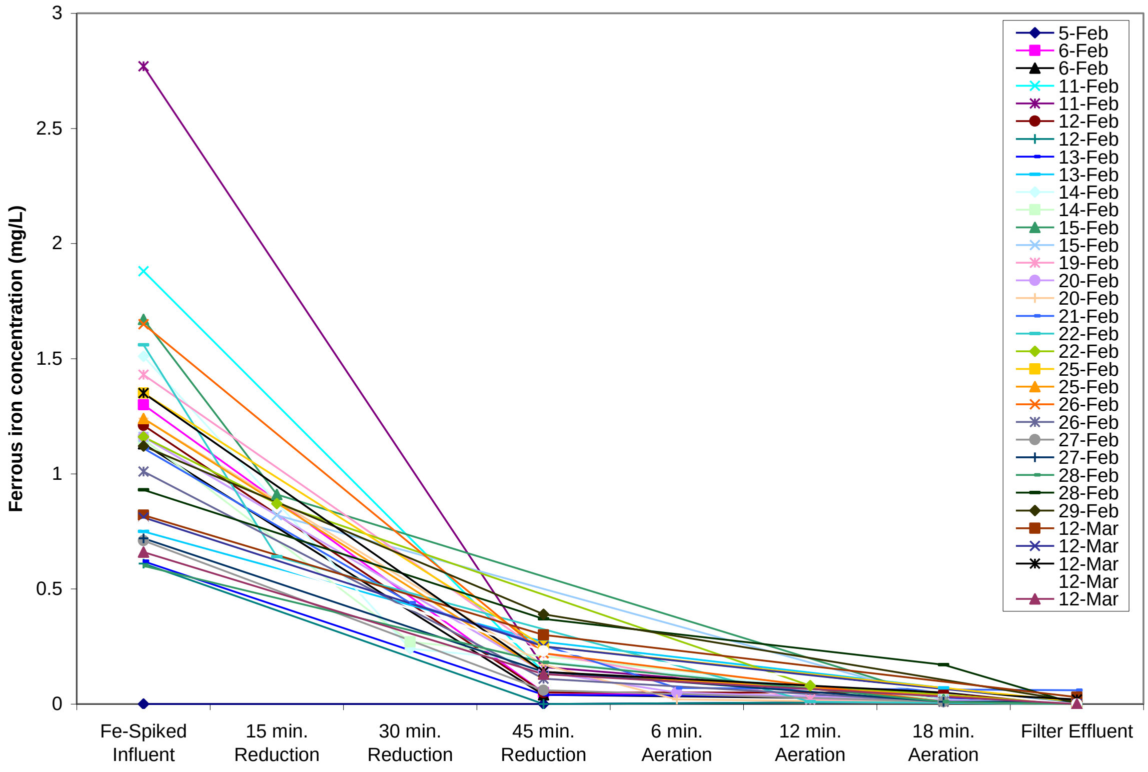
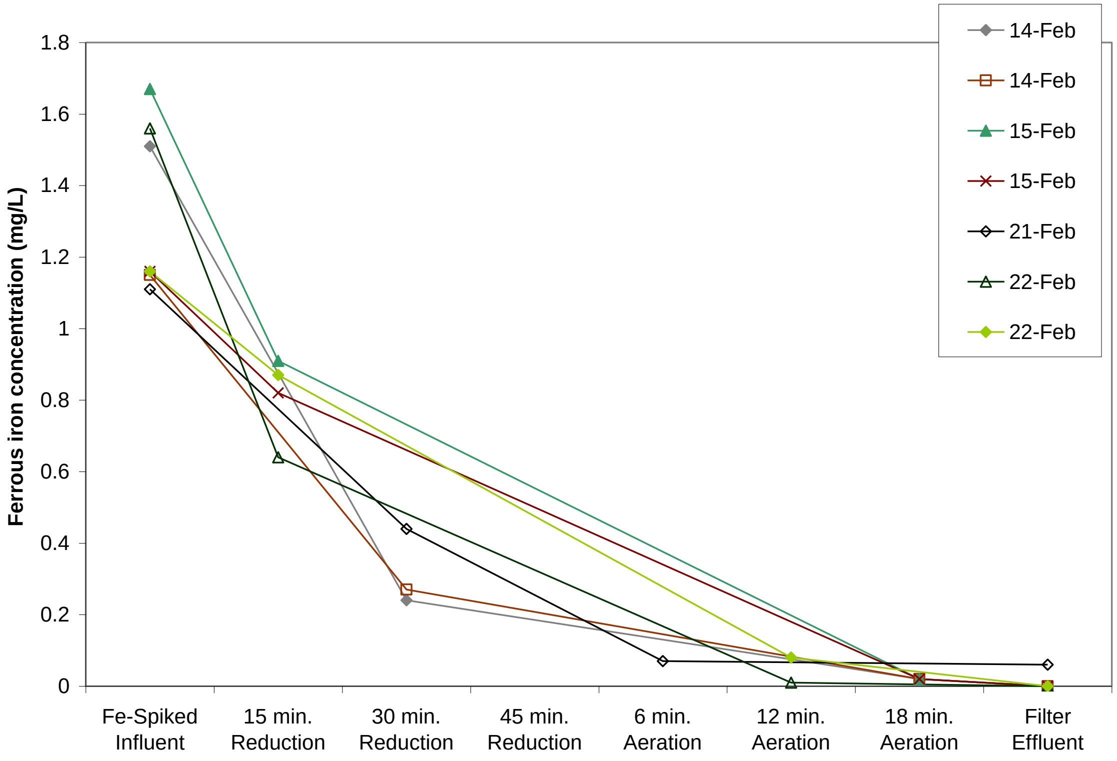


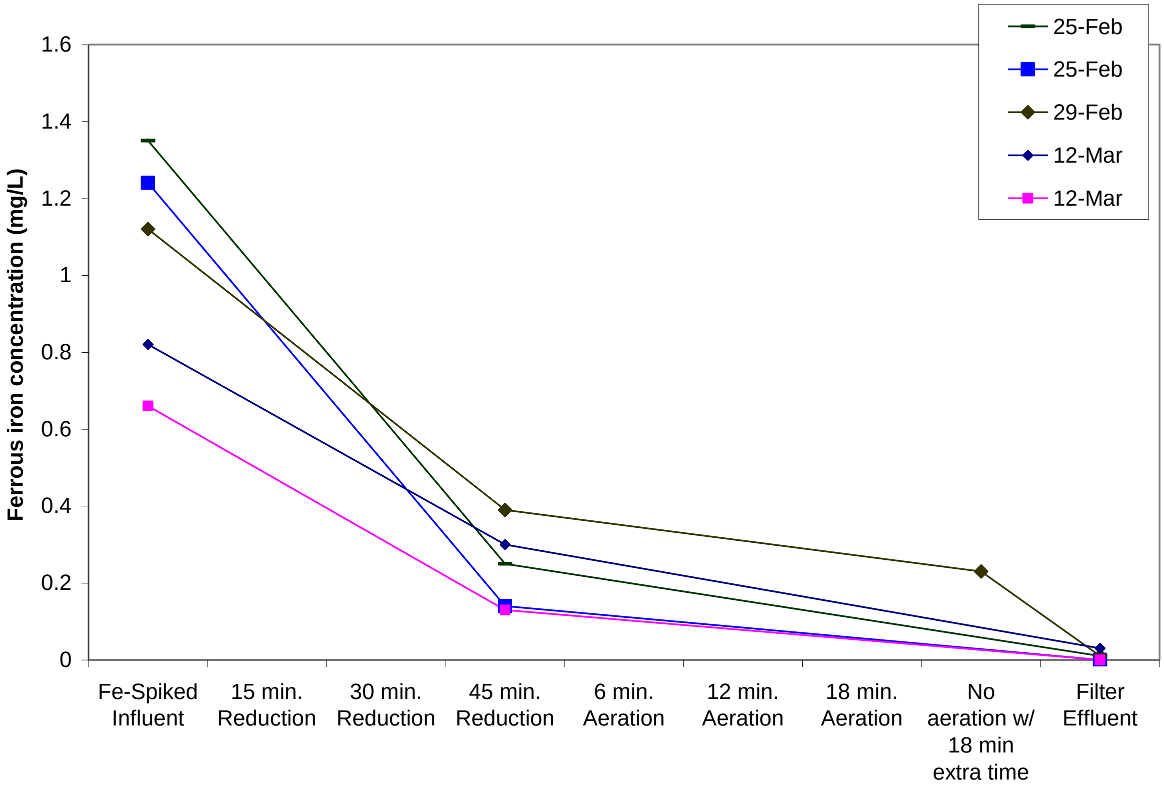
Figure 5-5: Ferrous Iron Oxidation by Aeration in Lower Reduction Time Runs



Three runs were conducted to determine if additional detention time without aeration could provide the conditions necessary to oxidize remaining ferrous iron (Figure 5-6). On February 25th and March 12th, the aeration columns were bypassed, resulting in only 5 minutes' detention time in the rapid mix plus 8 minutes' time in the filtration columns above the media (a total of 13 minutes after the last reduction tank). All samples collected on those days showed ferrous iron levels near the MRL after the water exited the filters, indicating that the remaining 0.13 to 0.30 mg/L ferrous iron present after the reduction tanks was oxidized and removed to achieve an effluent ferrous iron concentration of less than 0.03 mg/L. Without sufficient oxidation, the ferrous iron would not have been removed by the filters because ferrous iron is soluble in water.

On February 29th, water was routed through the aeration columns without the air compressor in use to provide additional detention time without active oxygen addition. Similar ferrous oxidation and removal by the filter effluent was observed in this run compared with the runs on February 25th and March 12th. These results indicated that additional detention time without active aeration oxidized all of the ferrous iron to ferric iron, likely due to the plentiful dissolved oxygen concentrations in the water or air entrainment during the rapid mix step.

Figure 5-6: Ferrous Iron Oxidation without Aeration

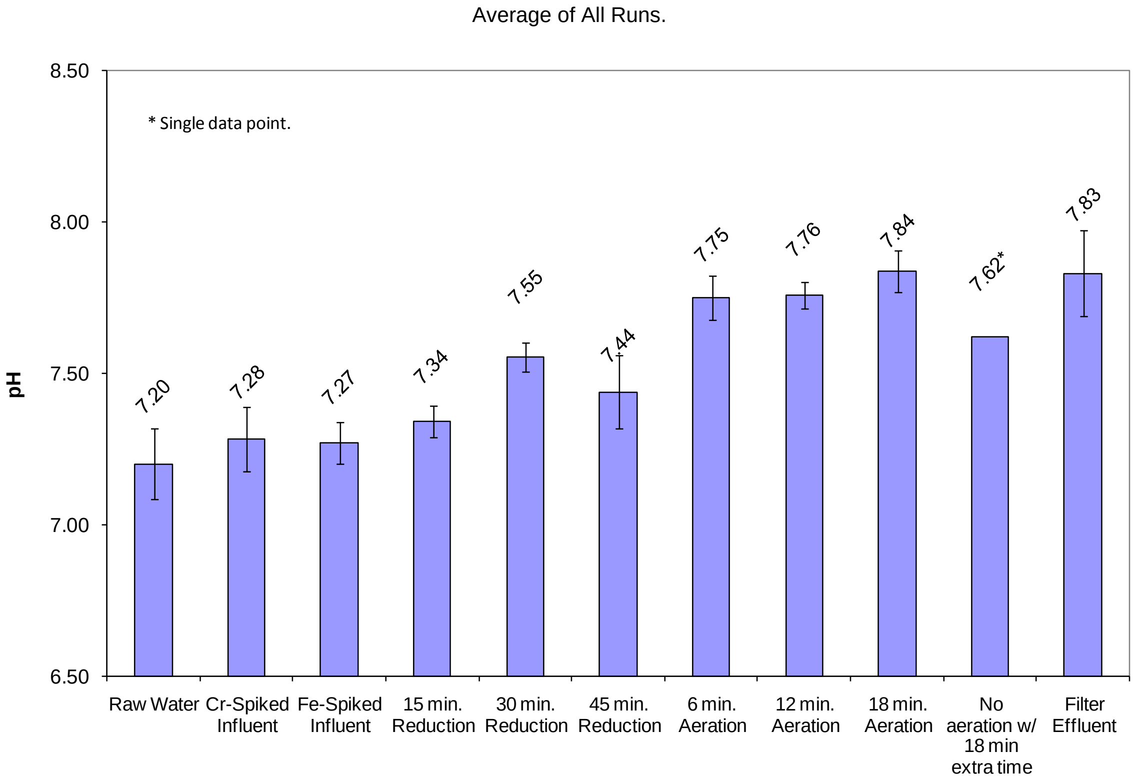


5.3. pH Changes

Figure 5-7 shows the increase in pH observed through the RCF process. No discernable difference from the ambient pH was observed after ferrous injection, while a slight increase in pH occurred with the reduction step. Aeration, however, caused a slightly greater pH due to stripping of carbon dioxide from the water. The ambient pH of approximately 7.3 to 7.5 in the reduction tanks increased to approximately 7.8 after aeration. Six, 12, and 18 minutes of aeration all showed a similar resultant pH. By comparison, lack of aeration resulted in pH levels that were 0.1 to 0.2 units lower than with aeration. Runs with and without aeration were both effective in achieving the total Cr goals, indicating that ambient pH values were sufficient for ferrous oxidation, floc formation, and particle removal.

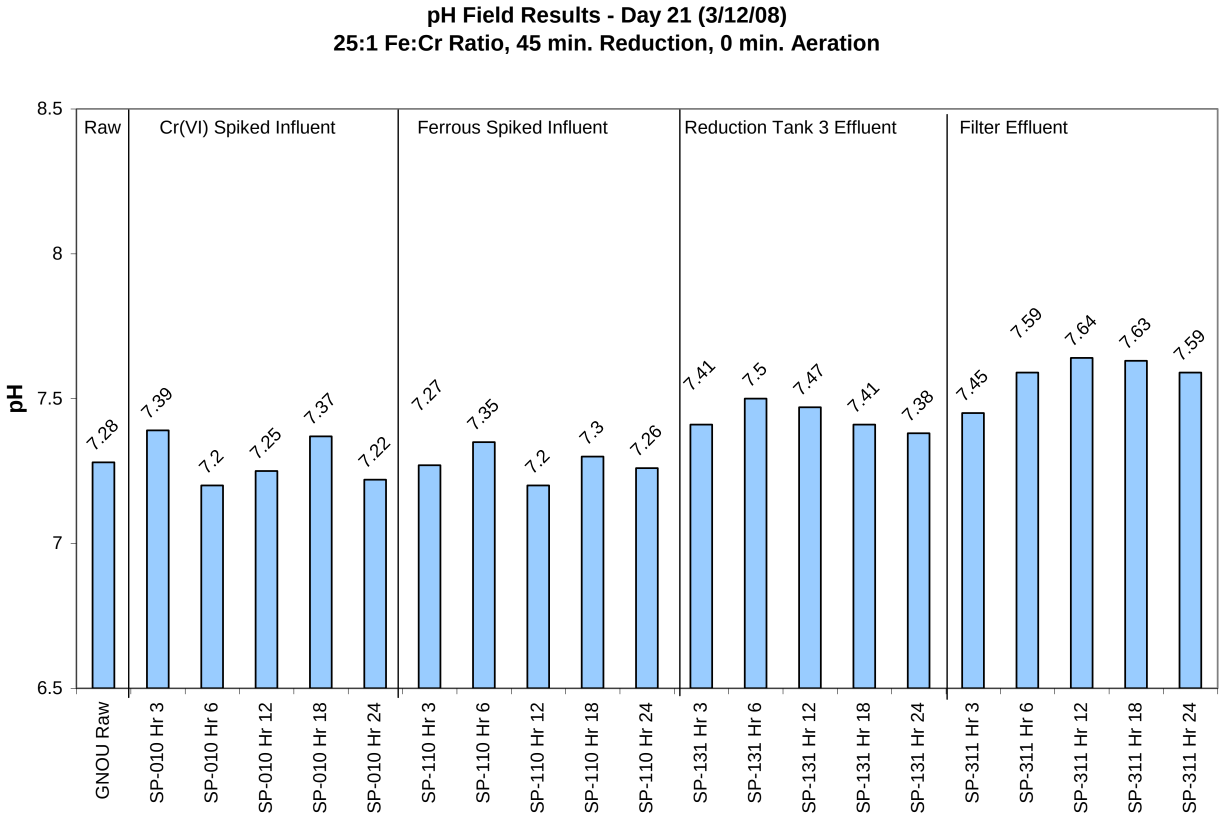
Although the ability to feed sodium hydroxide before the aeration columns was available in the pilot test, an increase in pH beyond ambient levels was not necessary for effective removal of the iron hydroxide particles. Similar findings were observed in the Phase II pilot testing.

Figure 5-7: pH Change Observed Through the RCF Process



For the optimized 24-hour run (45 min. reduction, 0 min. aeration), the pH change observed was less significant than for the average of all runs (Figure 5-8). The lack of aeration (and lower removals of CO_2) was responsible for the smaller change in pH. However, total Cr and total Fe results shown in Figure 5-13 indicate that the ambient pH conditions tested in this pilot were able to achieve target removal goals.

Figure 5-8: pH Change During the 24-Hour Optimized Run



5.4. Dissolved Oxygen and Oxidation-Reduction Potential

The average of dissolved oxygen measurements collected during RCF pilot testing are shown in Figure 5-9. The groundwater contained an average of 5.7 mg/L dissolved oxygen. Mixing/air equalization during the influent spiking and reduction process increased the DO by between 1 to 2.2 mg/L, and aeration increased the DO by an additional 0.7 to 1.7 mg/L. DO concentrations were approximately at the oxygen saturation limit at the measured temperatures (8.2 to 9.1 mg/L for temperatures ranging from 25 to 20°C) after the aeration step.

Figure 5-10 highlights the relatively constant DO values observed during the 24-hour run without aeration. DO measurements even without the aeration step were high throughout the RCF process, and accounted for the additional ferrous iron oxidation observed after the reduction tanks.

Figure 5-9: Dissolved Oxygen Concentrations in the RCF Process

Average of All Runs.

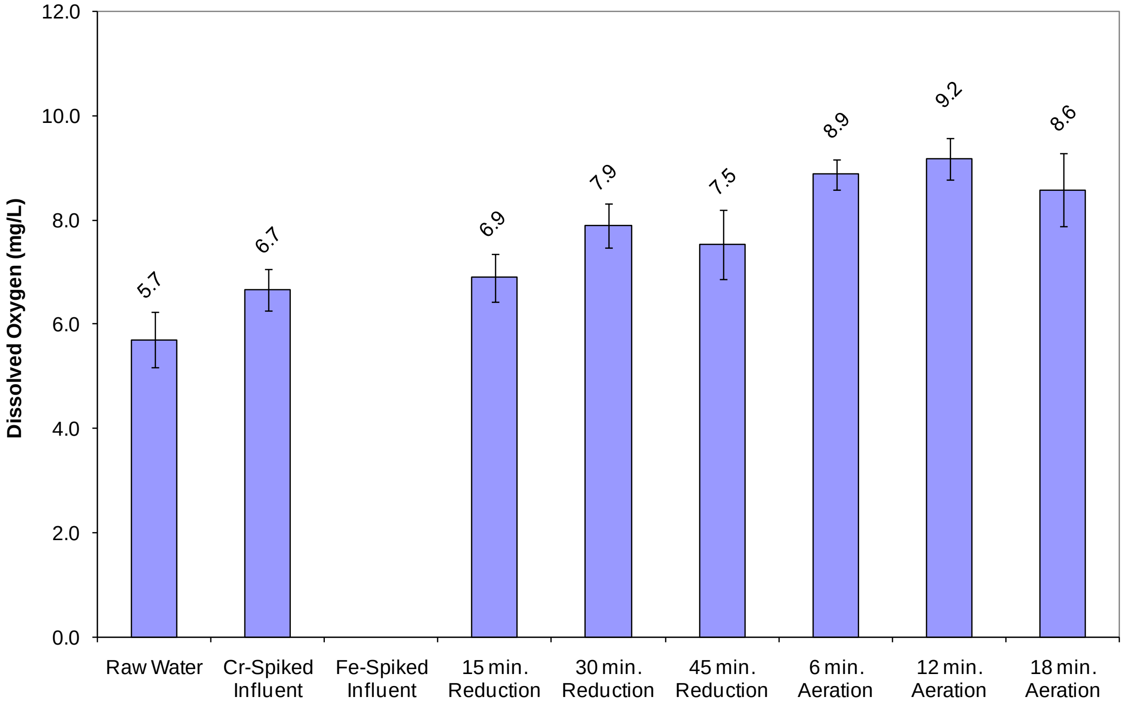
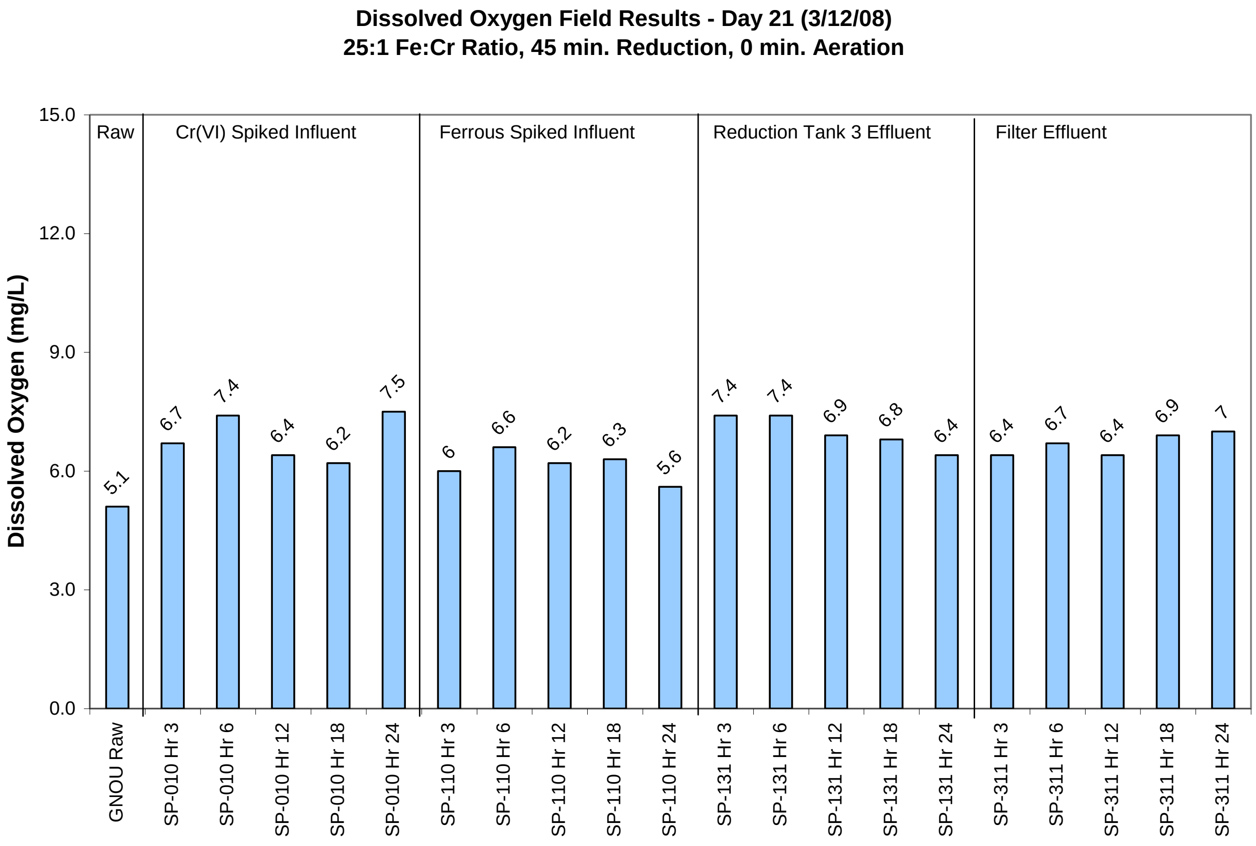


Figure 5-10: DO Concentrations in the RCF Process During the 24-Hour Optimized Run



Average ORP values through the RCF process are shown in Figure 5-11. The GNOU raw water was characterized by a relatively high ORP value, which decreased to a negative value with the addition of ferrous sulfate. ORP remained low in the three reduction tanks then increased with aeration. No discernable difference was observed between ORP values for the 6-, 12-, and 18-minute aeration steps, and no further increase in DO was apparent after 6 minutes of aeration (Figure 5-9).

Figure 5-12 provides the ORP values for the 24-hour optimized case run. Compared with the average of all runs, the final ORP (filter effluent) was lower for than the average ORP values leaving the aeration columns. The ORP increase between the final reduction tank and the filter effluent may have been due to air entrainment in the rapid mix/polymer addition tank.

Figure 5-11: ORP Values Through the RCF Process

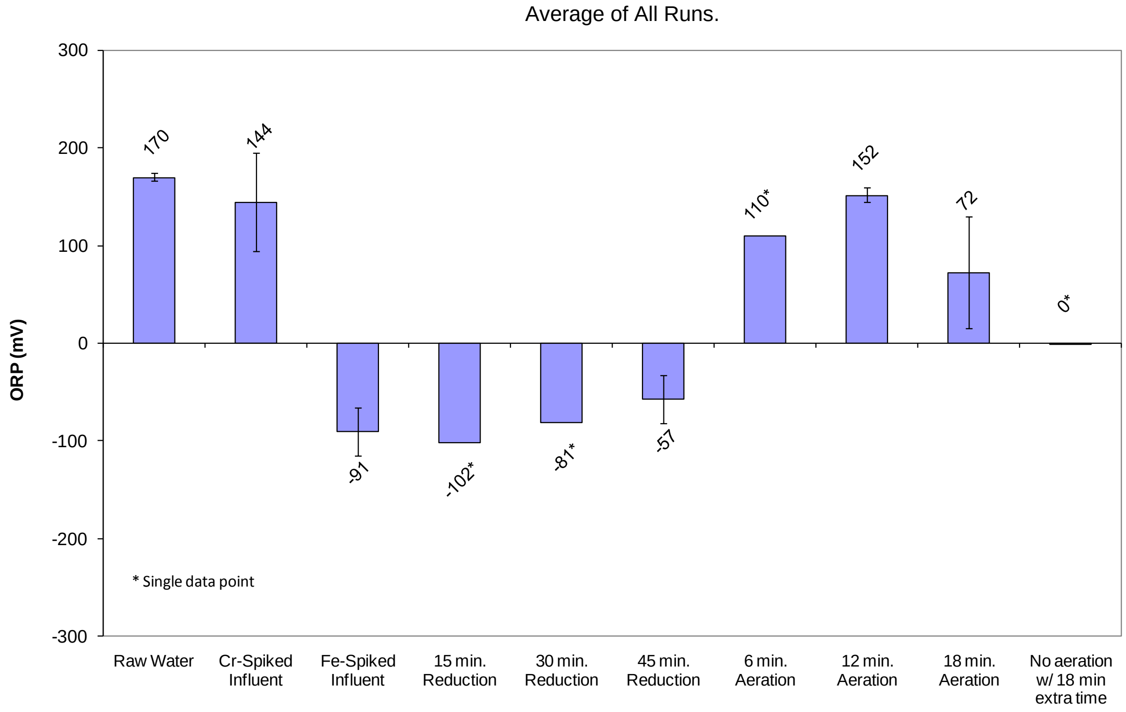
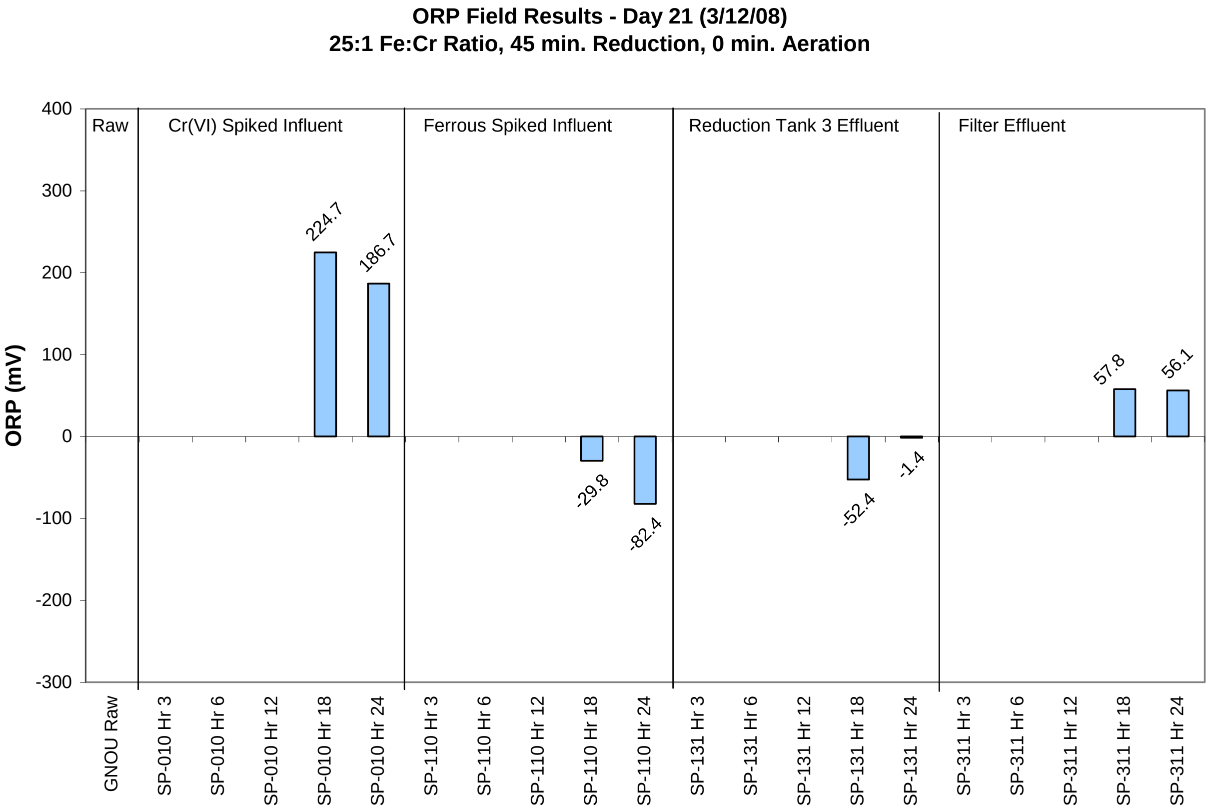


Figure 5-12: ORP Changes During the 24-Hour Optimized Run



5.5. Particle Removal

As discussed in Section 2.2, several modifications were made to the pilot unit to improve floc formation and filtration during testing. Figure 5-13 shows the improvement in effluent total iron and turbidities after removing the sump pump from between the rapid mix tank and the filters. Visible floc breakup after rapid mix/polymer addition was observed in the initial operation due to the sump pump. Both the gravity feed and progressive cavity pump filter operation yielded lower total iron effluent concentrations and turbidities compared with the original configuration. The pilot study demonstrated the importance of using progressive cavity pumps to lift water containing iron floc so that the floc structure would not be compromised. In general, total iron concentrations and turbidities were lower than 0.05 mg/L and 0.3 NTU, respectively, after the modifications.

Figure 5-13 shows evidence that particle removal was the key variable resulting in low total Cr effluent concentrations, as was observed in the Phase II RCF pilot testing. Although all three periods exhibited runs with total Cr concentrations less than 5 μg/L, all runs in the third period had effluent total Cr concentrations at or below 1 μg/L. The third period represents the optimum pilot filter configuration and use of the progressive cavity pump.

Figure 5-14 shows the results of two correlations: total Cr vs. turbidities and total Cr vs. total iron. While most results for total Cr were less than detectable, the detectable total Cr concentrations were generally observed when turbidities and/or iron concentrations were relatively high. There is much scatter in both correlations but it appears clear that removal of total Cr was strongly associated with these parameters. We know from previous work that the reduced Cr is attached to iron hydroxide particles that are removed by the granular media filters. There was no indication from any of the data that soluble Cr was breaking through the pilot filters.

Figure 5-13: Effluent Total Cr, Total Fe, and Turbidities After System Modifications

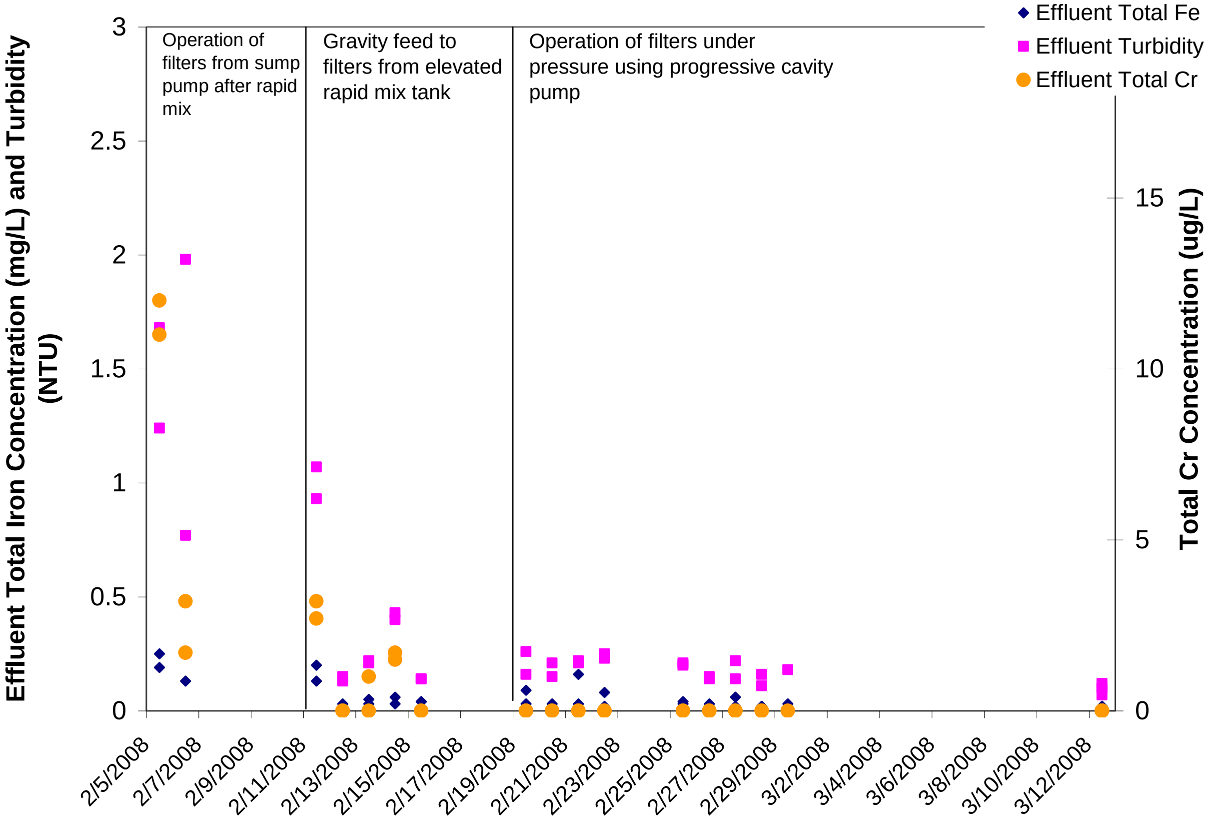
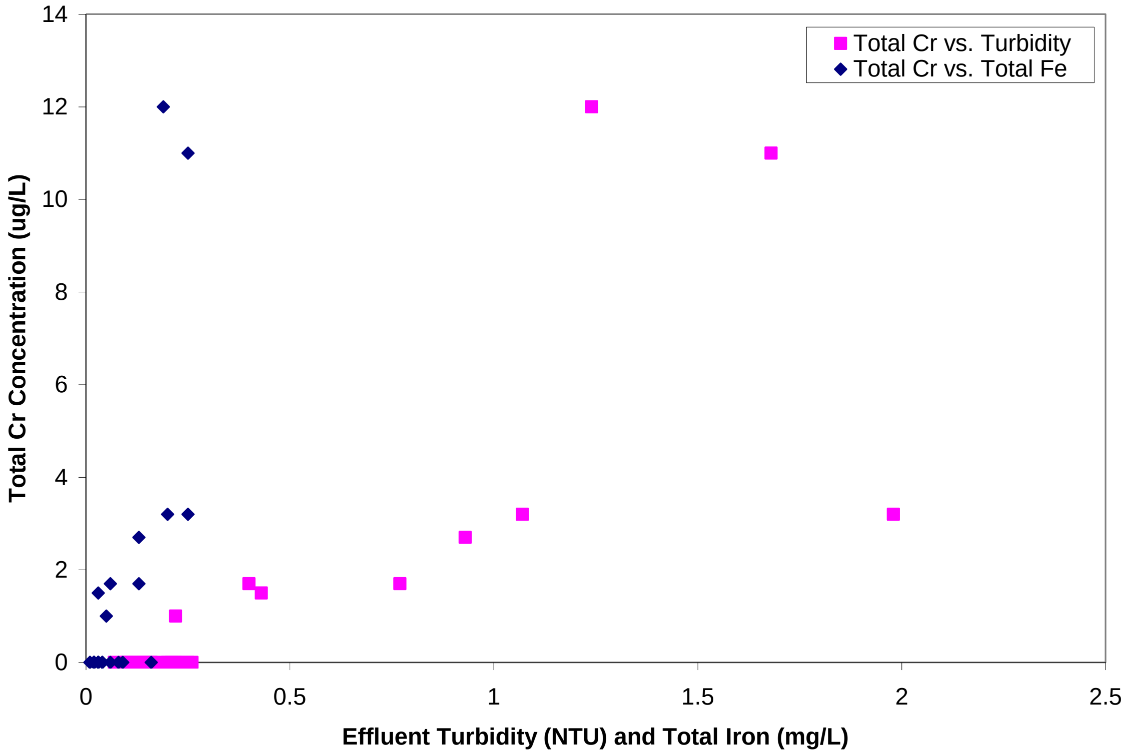


Figure 5-14: Effluent Total Cr Concentrations Compared with Total Iron and Turbidities



5.6. Total Cr Removal

The removal of total Cr, rather than Cr(VI) alone, is critical in evaluating the success of an RCF drinking water treatment process. Previous studies[1] demonstrated that Cr(III) can be reoxidized to Cr(VI) in distribution systems by typical concentrations of free chlorine and chloramine secondary disinfectants. Consequently, total Cr was closely measured in this RCF pilot testing to assess system performance.

Table 5-1 provides a summary of RCF pilot testing results. All except the first two runs achieved the total Cr effluent goal of less than 5 µg/L. Initial runs revealed that the Nalco 9901 polymer tended to form much larger floc than the Ciba polymer, which visually appeared to blind the filters and yield higher total Cr filter effluent concentrations. In addition, floc breakup may have occurred prior to February 19th due to use of a centrifugal pump after the rapid mix, rather than a progressive cavity pump.

After February 19th, all runs exhibited total Cr filter effluent concentrations of less than 1 µg/L with the exception of one sample collected on February 19th (effluent concentration of 1.4 µg/L). As shown in Table 5-1, 45 minutes of reduction time coupled with no aeration was effective in short 6 to 8 hour runs (Days 16 and 20) and also a 24-hour run (Day 21). Figure 5-15 provides

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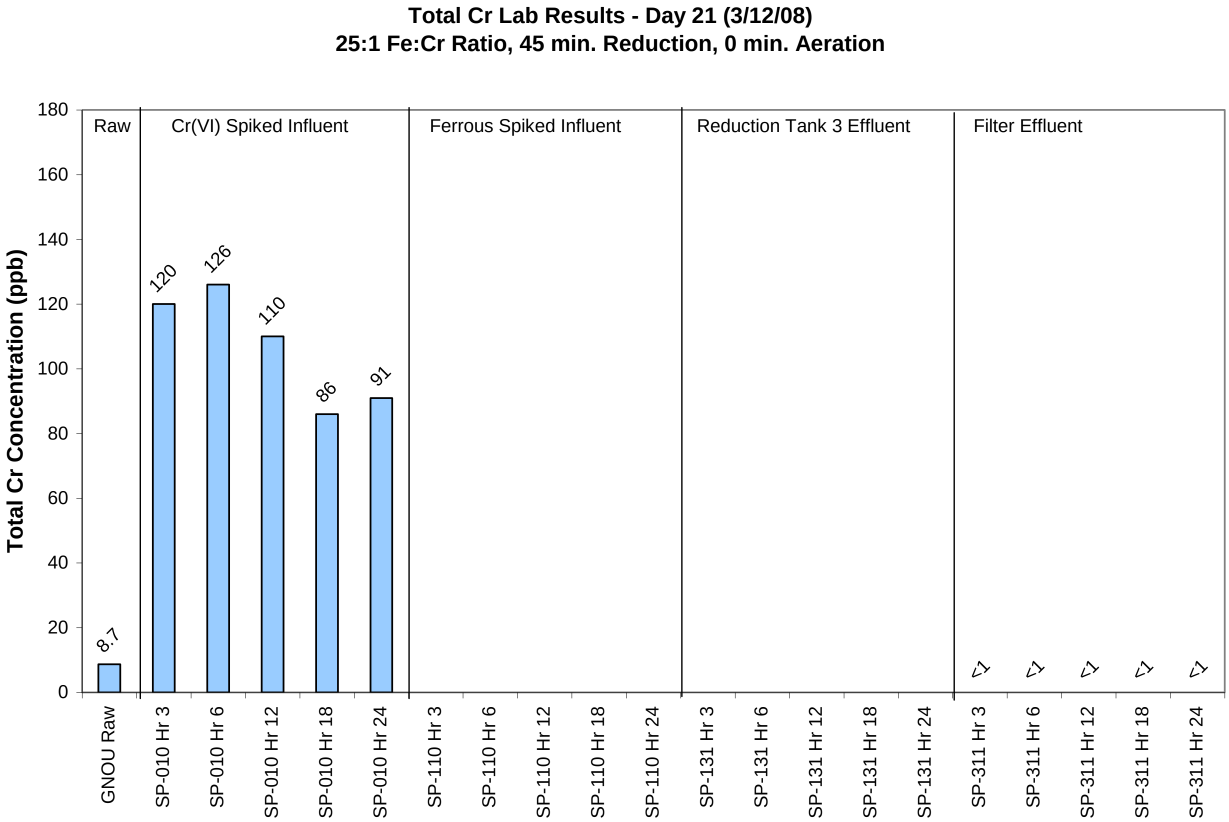
[1] Brandhuber, P. et al. 2005. Low-Level Hexavalent Chromium Treatment Options: Bench-Scale Evaluation. AwwaRF, Denver, CO.

the total Cr laboratory results throughout the 24-hour run, showing influent total Cr concentrations ranging from 86 to 126 μg/L and effluent total Cr concentrations below 1 μg/L. During this 24-hour run, only 0.5 psi of pressure buildup (14 inches of water) was observed in the filters, indicating that even longer runs may be achieved from a head loss perspective. Visible floc penetration and capture in the bed, however, extended to approximately 20-21 inches into the anthracite (out of 24 inches). No breakthrough of iron or turbidity was observed in the 24-hour run without aeration, indicating that the filter bed had sufficient capacity to remove the iron/chromium floc for at least 24 hours. Note, however, that the floc penetration in the 45-minute reduction/0 min aeration runs differed somewhat from the runs using 18 minutes of aeration time in which larger floc was sometimes formed and strained in the first few inches of the anthracite, resulting (in two instances) in pressure buildups of 4.9 to 5.1 psi (approximately 139 inches of water). Floc penetration into the filter beds was more a function of the polymer dose and flocculation of the particles in the rapid mix tank.

Table 5-1.
Summary Table of Results

	Date	Reduction time	Aeration time	Filter run time	Polymer	Total Cr Filter Effluent Results
Day 1	4-Feb-08	45 min	18 min	6-8 hrs	Nalco 9901 - 0.2 ppm	6.6 μg/L
Day 2	5-Feb-08	45 min	18 min	6-8 hrs	Nalco 9901 - 0.2 ppm	11 to 12 μg/L
Day 3	6-Feb-08	45 min	18 min	6-8 hrs	Nalco 9901 - 0.2 ppm then Ciba E40 - 0.38 ppm	3.2 μg/L (Nalco), <1 μg/L (Ciba)
Day 4	7-Feb-08	-	-	-	-	-
Day 5	8-Feb-08	-	-	-	-	-
Day 6	11-Feb-08	45 min	18 min	6-8 hrs	Nalco 9901 - 0.2 ppm	2.7 to 3.2 μg/L
Day 7	12-Feb-08	45 min	18 min	6-8 hrs	Ciba E40 - 0.28 ppm	< 1 μg/L
Day 8	13-Feb-08	45 min	18 min	6-8 hrs	Ciba E40 - 0.28 ppm	< 1 μg/L, 1 μg/L
Day 9	14-Feb-08	30 min	18 min	6-8 hrs	Ciba E40 - 0.26 ppm	1.5 to 1.7 μg/L
Day 10	15-Feb-08	15 min	18 min	6-8 hrs	Ciba E40 - 0.26 ppm (a.m.), 0.1 ppm (p.m.)	< 1 μg/L
Day 11	18-Feb-08	-	-	-	-	-
Day 12	19-Feb-08	45 min	12 min	6-8 hrs	Ciba E40 - 0.092 ppm	< 1 μg/L to 1.4 μg/L
Day 13	20-Feb-08	45 min	6 min	6-8 hrs	Ciba E40 - 0.085 ppm	< 1 μg/L
Day 14	21-Feb-08	30 min	6 min	6-8 hrs	Ciba E40 - 0.085 ppm	< 1 μg/L
Day 15	22-Feb-08	15 min	12 min	6-8 hrs	Ciba E40 - 0.095 ppm	< 1 μg/L
Day 16	25-Feb-08	45 min	0 min (Aeration columns bypassed)	6-8 hrs	Ciba E40 - 0.094 ppm	< 1 μg/L
Day 17	26-Feb-08	45 min	18 min	6-8 hrs	Ciba E38 - 0.1 ppm	< 1 μg/L
Day 18	27-Feb-08	45 min	18 min	24 hrs	Ciba E38 - 0.093 ppm	< 1 μg/L
Day 19	28-Feb-08	45 min	18 min	24 hrs	Ciba E38 - 0.1 ppm	< 1 μg/L
Day 20	29-Feb-08	45 min	0 min (but extra 18 min detention time in aeration columns)	6-8 hrs	Ciba E38 - 0.1 ppm	< 1 μg/L
Day 21	12-Mar-08	45 min	0 min (Aeration columns bypassed)	24 hrs	Ciba E38 - 0.1 ppm	< 1 μg/L

Figure 5-15: Total Cr Results Through the Process Treatment Train on the March 12th Run



5.7. Backwash Water and Solids Recovery

The initial setup for this RCF testing relied upon a backwash flow rate of approximately 7.5 gpm (21 gpm/sf, without air scour) to remove the iron particles captured on the granular media filters. However, increasingly larger iron particles agglomerated with anthracite media began to appear in the filters and were not removed by the backwash water flow alone. On February 19th, an air scour was instituted along with the backwash flow rate (and more filter freeboard to enable effective use of an air scour), which resulted in significantly improved breakup and removal of iron clumps in the filters.

The quantity of backwash water necessary to clean the filters was approximately 38 gallons per column (i.e., 7.5 gpm for 5 minutes). In order to collect enough backwash water for the RCF run incorporating backwash water recycle, the filters were backwashed for a few additional minutes to fill the 100-gallon backwash water holding tank.

As also observed in Phase II testing, an initial polymer dose of 0.2 mg/L did not rapidly clarify the backwash water (i.e., within 20 minutes, corresponding to an overflow rate of 0.125 gpm/sf). Instead, backwash water was effectively settled using a polymer dose of 1.0 mg/L (Magnafloc

Ciba E38). Based on recycle to the head of the plant comprising 4% of the influent flow, a backwash polymer dosage of 1.0 mg/L plus the 0.2 mg/L in the process flow would contribute a maximum of approximately 0.048 mg/L polymer to the influent (assuming none of the polymer is incorporated in the precipitates, which would be unlikely).

Total suspended solids and settleable solids were analyzed for two batches of collected backwash water following the 24-hour runs (February 27th and 28th). Following backwash, the backwash water in the holding tank was mixed using a portable mixer and TSS and settleable solids samples were collected. Physical-chemical results for the backwash water are shown in Table 5-2. The quantities of backwash water for February 27th and 28th runs were 90 and 100 gallons, respectively. After adding 1.0 mg/L of polymer to the tank and mixing for approximately 5 minutes, the backwash water was settled for 32 minutes on February 27th and 1 hour on February 28th. Total Cr and Cr(VI) samples were collected from the settled backwash water.

Table 5-2.
Backwash Water Characterization

Run Start Date	Backwash Water Qty. (gallons)	Mixed BW Water TSS (mg/L)	Settleable Solids (mL/L)	Total Cr (µg/L)	Cr(VI) (µg/L)	Total Iron (mg/L)
Feb. 27, 2008	90	124	3.5	23	<0.1	NA
Feb. 28, 2008	100	70	2.5	30	0.98	1.06

NA = Not analyzed.

During the 24-hour run on February 28th, clarified backwash water was recycled to the influent tank. Solids (and remaining liquid) from the bottom of the backwash tank were removed from the tank and sent through Flo-Trend filter material (Figure 5-16). Particles were captured in the Flo-Trend filter, and the resultant filtrate water had metal concentrations of 0.3 µg/L Cr(VI), 24 µg/L total Cr, and 0.06 mg/L total iron.

De-watered solids captured on the Flo-Trend filter (within an hour after solids separation) were generally characterized as wet and slimy in appearance rather than dry and matted, although solids retained in the upper part of the cone-shaped filter (i.e., given more time to dry) were more dry and matte in appearance. A subsample of the solids was tested for floc “toughness” by mixing the floc in a jar tester at 300 RPM for 5 minutes; the floc broke apart during the mixing and did not resettle within a 30-minute time period.

The volume of backwash water generated for 24-hour filter runs in this pilot testing was approximately 95 gallons (combined quantity arising from two parallel filter backwashes). The 24-hour run time at 2 gpm corresponds to 2,880 gallons of water treated; therefore, the backwash water volume was approximately 3.3% of the flow. Previous estimates of 4% backwash water volume[1] were considered similar, since longer backwashing periods than used in pilot testing may be desired to more thoroughly clean the filters in continuous operation.

Figure 5-16: Flo-Trend Solids Separation of Backwash Water Solids

Settleable solids generated in this testing revealed that approximately 3 mL/L were generated, representing 0.3% of the backwash water as settled sludge. By comparison, cost estimates were calculated using 0.58% as the percentage of backwash water as settled sludge, which provided a more conservative estimate of waste generated by the RCF process.

Solids production was estimated using the following equation[2]:

$$S = 8.34\ Q\ (2.9\ Fe)$$

where, S is the sludge produced (lb dry sludge per day), Q is the plant flow (mgd), and Fe is the iron concentration introduced (mg/L as Fe). This equation is used for the production of $Fe(OH)_3 \cdot 3H_2O$ solids. A 534 gpm RCF system, for example, would generate 47 lbs/day of dry sludge.

Previously[1], assumptions of 3% solids in (thickened) settled sludge and 80% filter press dewatering efficiency estimated the tonnage of solids produced (51 tons per year). Flo-Trend could not provide a dewatering efficiency[3], but indicated that filter presses generate a 2 to 5% drier cake compared with the Flo-Trend units. Assuming that the dewatering efficiency of 3% solid sludge by the Flo-Trend unit is 75%, the tonnage of solids produced will be approximately 64 tons per year.

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[1] Used in O&M cost estimates for the RCF technology.
[2] Cornwell, D.A. 1999. Water Treatment Plant Residuals Management. In: *Water Quality and Treatment*, 5th ed.
[3] Conversation with Russ Caughman of Flo-Trend, March 10, 2008.

Alternately, if the Flo-Trend system generates a residual stream that is 8% solids without thickening (as is occurring in some of their arsenic treatment systems), the quantity of wet solids produced would be approximately 106 tons per year.

After the pilot study was terminated, inspection of the tanks and pipes showed only a moderate staining of the materials caused by ferric iron. No significant buildup of any scale was noted.

5.8. QA/QC Data

QA/QC samples for Cr(VI) and total Cr analyses included the following:

- Field-collected duplicate samples were collected to determine the representative nature of the samples and the degree to which the samples reflect actual field conditions
- Matrix spike samples that were used to assess the accuracy of measurements in the laboratory
- Matrix spike duplicates to ensure precision of laboratory measurements
- Laboratory reagent blank samples that are used to determine the PQL of the analytical procedure and to detect potential problems in the sample collection and preservation methods
- Laboratory control samples or continuing calibration verification samples to determine analytical precision and check for continuing instrument calibration

Table 5-3 shows the results of the field-collected duplicate samples for both total Cr and Cr(VI) with relative percent difference (RPD) values. Excellent agreement between the samples was observed in all cases. In summary, all other QA/QC results provided by the laboratory, including matrix spike duplicates, laboratory reagent blanks, and laboratory control samples or continuing calibration verification samples, were within acceptable ranges as noted in the laboratory reports.

Table 5-3.
Quality Control Sample Results During RCF Pilot Testing

Date	Sample ID	QC Sample ID	Total Cr			Cr(VI)		
			Sample Result	QC Sample Result	RPD (%)	Sample Result	QC Sample Result	RPD (%)
2/5/2008	SP-311-E01	A1	12	12	0	0.72	0.69	4.3
2/6/2008	SP-311-M02	A2	3.2	3.2	0	<0.1	<0.1	NA
2/11/2008	SP-311-E04	A3	2.7	2.7	0	<0.1	<0.1	NA
2/12/2008	SP-311-M05	A4	<1	<1	NA	<0.1	<0.1	NA
2/13/2008	Blank	A5	-	<1	NA	-	<0.1	NA
2/14/2008	SP-010-M07	A6	77	77	0	83	83	0
2/15/2008	SP-311-E08	A7	<1	<1	NA	<0.1	<0.1	NA
2/22/2008	SP-010-E12	A8	98	98	0	103	104	1.0
2/25/2008	Blank	A9		<1	NA		<0.1	NA
2/26/2008	SP-311-M14	A10	<1	<1	NA	<0.1	<0.1	NA
2/27/2008	SP-010-E15	A11	113	110	2.7	114	114	0
2/29/2008	SP-010-M17	A12	-	-	NA	117	115	1.7
3/12/2008	SP-311-6HR	A13	<1	<1	NA	<0.1	<0.1	NA
3/12/2008	Blank	A14	-	<1	NA	-	<0.1	NA

NA = Not applicable.

During the pilot study, unexplained high total Cr values in the filter effluents were reported by the contract laboratory. An investigation of potential sources of high total Cr led to the discovery that all of the high total Cr filter effluent values were spurious. MWH Labs determined that the water matrix being analyzed on one of their instruments resulted in a positive interference with total Cr analysis. Although the analytical issues were resolved in this study, researchers and system operators for the demonstration-scale study should be aware of the potential false positive total Cr results in this water matrix.

6. Summary and Recommendations

Additional RCF pilot testing was intended to determine if the RCF demonstration design could be modified to reduce or eliminate unnecessary process components. In fact, the pilot testing revealed that 45 minutes of reduction time (followed by filtration) was successful in reducing Cr(VI) and removing total Cr without the need for an aeration step. The elimination of the aeration process offers a significant cost savings for the RCF demonstration-scale design.

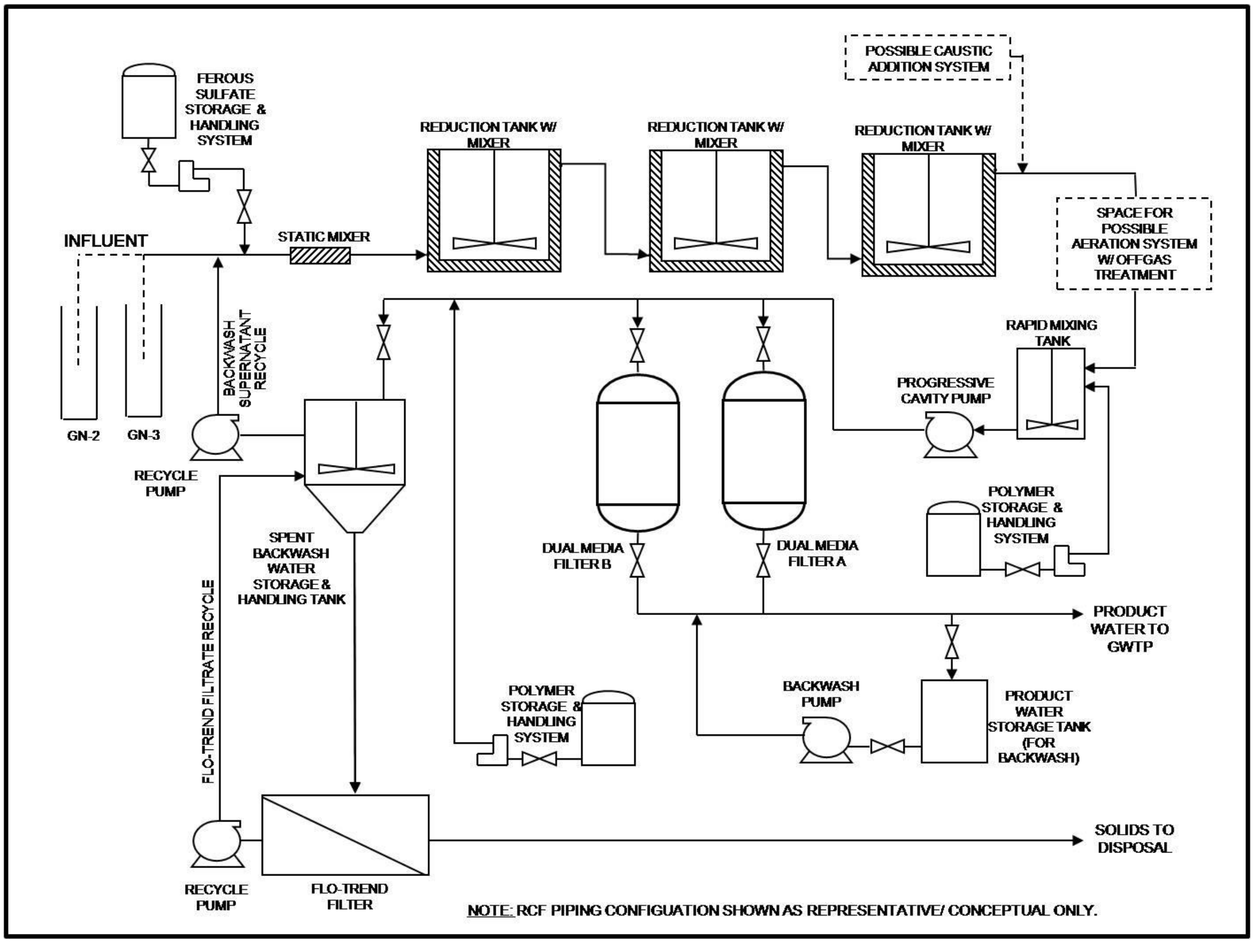
Pilot testing results also provided the following findings with respect to process performance:

- Ferrous sulfate reduced Cr(VI) concentrations from 100 μg/L to less than 1 μg/L within 15 to 30 minutes.
- In the reduction tanks, approximately 21±10% of the ferrous iron remained after 45 minutes of reduction time, whereas 60±16% of the ferrous iron was present after only 15 minutes of reduction time.
- Aeration effectively oxidized the majority of the ferrous iron; even 6 minutes of aeration lowered ferrous concentrations to less than 0.08 mg/L.
- Runs conducted without aeration resulted in filter effluent ferrous iron concentrations of less than 0.03 mg/L, indicating that either additional contact time of the ferrous iron with dissolved oxygen or air entrainment during the rapid mix/polymer addition step oxidized the remaining ferrous iron to ferric iron.
- Total Cr filter effluent concentrations greater than 5 μg/L were coupled with relatively high filter effluent turbidity values (greater than 1 NTU) and high total iron concentrations (greater than 0.19 mg/L).
- Filter run times of 24 hours resulted in a increase across the filter beds of only 0.5 psi (14 inches of water) through the optimized run (45 min. reduction time/0 min. aeration). Based on these results, filter run time to breakthrough for this optimized case would be more dependent on turbidity/iron (and hence, Cr) breakthrough rather than pressure buildup. By comparison, 24-hour runs with 18 minutes of aeration resulted in a much larger pressure increase of 4.9 to 5.1 psi (139 inches of water).
- Magnafloc Ciba E38 anionic polymer was effective in process floc formation (at a concentration of 0.1 ppm) as well as backwash water settling (at a dose of 1 mg/L). Nalco 9901 polymer formed a larger floc and did not effectively remove total Cr by the filters.
- Backwash water settling and recycle of the clarified water (corresponding to 4% of the flow) did not negatively impact the RCF process performance and offers a means of reducing water losses in the treatment process.
- Passive filtration using a technology akin to the Flo-Trend system was effective in dewatering the sludge and producing filtrate water quality low in total Cr and iron.
- No significant scale buildup in the pilot filter tanks and pipes was noted.

Based on these pilot test findings, we recommend that Glendale design an RCF system with 45 minutes of reduction time, polymer addition in a rapid mix tank after the reduction tanks, and dual-media granular filtration. Figure 6-1 shows a schematic of the proposed demonstration-scale

RCF treatment plant (at approximately 100 gpm). No pH adjustment and no additional aeration (beyond that provided by the dissolved oxygen concentrations in the water) were necessary in the pilot testing, which will result in significant capital cost savings in the RCF system construction. However, during the design process physical space and hydraulic capacity should be included in the demonstration-scale plant design in case pH adjustment and aeration are needed at a later time. Backwash water recycle should be included in the design to minimize water losses and wastewater quantities. A passive means of filtration should be included in the demonstration study since it offers great cost savings over a filter belt press and was found to yield high quality filtrate in the pilot testing. In addition, some specific design considerations for the demonstration-scale RCF system are recommended based on pilot plant operation and listed in Appendix A.

Figure 6-1: Flow schematic of the proposed demonstration-scale RCF treatment plant



7. Acknowledgments

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AVANTech Incorporated, Tracy Barker

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8. Appendices

Appendix A: Design Suggestions Based on Pilot Plant Operations
Appendix B: As-Built (Final) Process and Instrumentation Diagram and Photos
Appendix C: Data Summary Sheets

Appendix A: Design Suggestion Based on Pilot Plant Operation

Appendix A: Design Suggestions Based on Pilot Plant Operations

The following is a list of suggestions that design engineers may want to consider for the demonstration-scale RCF system. This list is based on the additional RCF pilot testing findings and review comments received for the "Report on Additional RCF Pilot Testing to Optimize Design."

- Physical space and hydraulic capacity for caustic injection and aeration (with off-gas treatment) should be included in the design
- The design should consider if VOC treatment is necessary. If so, a passive vapor collection system should be designed to collect incidental VOC-bearing air streams from relevant RCF equipments
- The reduction step should take place in three completely stirred reactors (t_D = 15 minutes each) operated in series that are open to the atmosphere.
- Polymer addition should take place in a completely stirred tank open to the atmosphere (t_D = 5 minutes)
- All transfer pumps after the reduction step are recommended to be positive displacement type to help maintain integrity of Fe/Cr floc through the filtration process
- The construction material of the equipment and/or piping in contact with process liquids and/or sludge should be smooth to minimize precipitate build-up. PVC could be the material of choice due to its low surface roughness
- Iron precipitates are anticipated to accumulate throughout the treatment process. Consequently, each of the process equipment should plan for periodic precipitate removal. Cone-bottom reaction/reduction tanks are recommended for the precipitate removal activities
- The GAC effluent from GWTP (upstream of chlorination) might be used for backwashing the filters, thus eliminating backwash water storage tank and pump
- Filter design should include a vigorous backwash system (including air and water) with sufficient freeboard to expand and thoroughly clean the media. Periodic inspection of the media and sampling to detect "mudball" formation which means that access, observation and sampling ports should be included in the filter design.
- Hydraulic loading rate for the dual media filters should be 3 gpm/sf. A sufficient number of filters should be included in the final design so that the hydraulic rate for the filters does not exceed 3 gpm/sf when one of the filters is being backwashed.
- Backwash water recycle should be included in the design to minimize water losses and wastewater quantities.
- A passive means of filtration should be included in the demonstration study since it offers great cost savings over a filter belt press and was found to yield high quality filtrate in the pilot testing. In the preliminary design step, equipment manufactured by Flow Trend should be considered (http://www.flotrend.com/).

Appendix B: As-Built (Final) Process and Instrumentation Diagram and Photos

PIPING AND INSTRUMENTATION DIAGRAM

PILOT SCALE SYSTEM FOR REDUCTION COAGULATION FILTRATION TESTING

GLENDALE, CA

REV	DATE	DESCRIPTION	DRAWN BY	CHECKED BY	APPROVED BY
2	02/29/08	TEST CONFIGURATION	DL	TB	N/A
1	01/25/08	AS BUILT	DL	TB	N/A
0	12/07/07	INITIAL RELEASE	DL	TB	N/A

CUSTOMER / PROJECT
PILOT SCALE R.C.F. SYSTEM
GLENDALE, CA

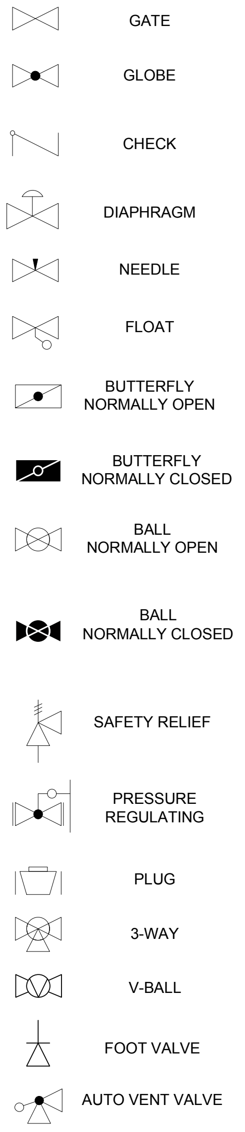
JOB NO. 07-12
FILE ID. 0G2000201-0712-D.VSD
DIMENSIONS IN INCHES UNLESS SPECIFIED

AVANTech INCORPORATED

PROCESS AND INSTRUMENTATION
DIAGRAM
COVER PAGE

SIZE: D
DRAWING NUMBER: 0G200-0712-D
REV.: 2
SCALE:
WT.:
SHEET 1 OF 3

VALVES



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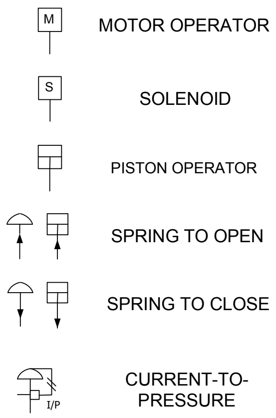
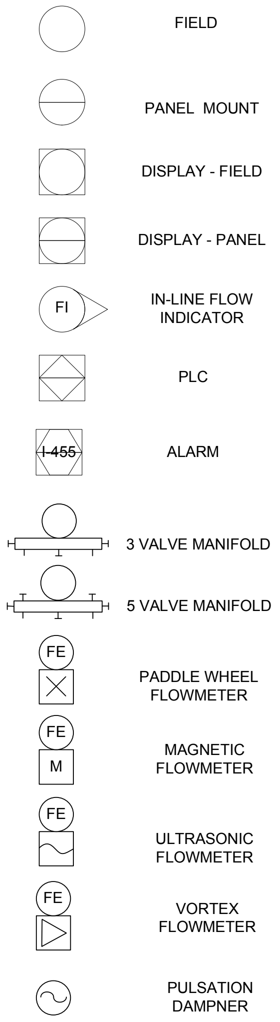
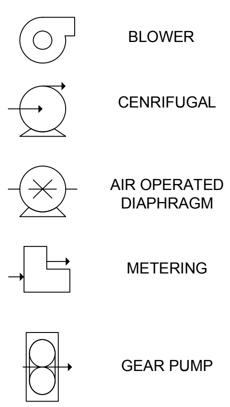


INSTRUMENTS



PUMPS



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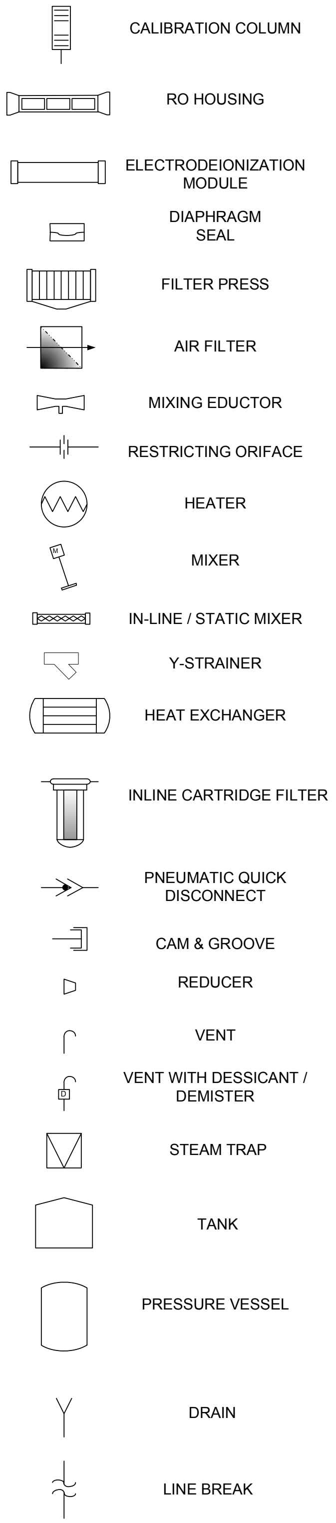

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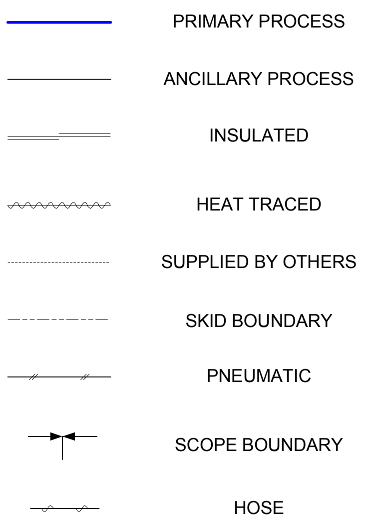
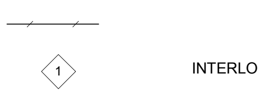


SIGNAL



INSTRUMENT LETTER CODES

A	ANALYZER, ALARM, ANALOG
C	CONDUCTIVITY, CONTROL, CLOSED
D	CONCENTRATION, DENSITY, TURBIDITY, DIFFERENTIAL, DIGITAL, DISCRETE, FAULT, DRIVE
E	PRIMARY ELEMENT, VOLTAGE
F	FLOW, FLOW RATE
G	GAUGE, SITE GLASS
H	HAND SWITCH, HIGH, HIGH-HIGH
I	INDICATOR, ELECTRIC CURRENT, INPUT
L	LEVEL, PILOT LAMP, LOW, LOW-LOW
O	ORIFACE PLATE, OUTPUT, OPEN
P	PRESSURE / VACUUM
Q	QUANTITY, INTEGRATE, TOTALIZE
R	RESISTIVITY, RECORDER
S	SWITCH, SPEED, SOLENOID
T	TEMPERATURE, TRANSMIT, TEE
V	CONTROL DEVICE OR VALVE, VALVE, VIBRATION, VARIABLE
W	WEIGHT OR FORCE, WELL
Y	RELAY, EVENT
Z	ACTUATOR, POSITION, DIMENSION

EQUIPMENT ABBREVIATIONS

A	ACTUATOR
AC	AIR COMPRESSOR
AV	ACTUATED VALVE
AVV	AUTOMATIC VENT VALVE
CF	COALESCING FILTER
M	MOTOR
MC	MOTOR CONTROL
PF	PARTICULATE FILTER
P	PUMP
PV	PRESSURE VESSEL
MV	MANUAL VALVE
PRV	PRESSURE REGULATING VALVE
SP	SAMPLE POINT
SRV	SAFETY RELIEF VALVE
TK	TANK
TS	TRAVEL STOP
VC	VARIABLE SPEED CONTROLLER

NOTE: Except as noted, all automatic valves fail in their normal operating position.

REV	DATE	DESCRIPTION	DRAWN BY	CHECKED BY	APPROVED BY
2	02/29/08	TEST CONFIGURATION	DL	TB	N/A
1	01/25/08	AS BUILT	DL	TB	N/A
0	12/07/07	INITIAL RELEASE	DL	TB	N/A

CUSTOMER / PROJECT
PILOT SCALE R.C.F. SYSTEM
GLENDALE, CA

AVANTech
INCORPORATED

WATER TREATMENT SYSTEM
LEGEND

JOB NO.	07-12		
FILE ID.	0G2000202-0712-D.VSD		
DIMENSIONS IN INCHES UNLESS SPECIFIED			
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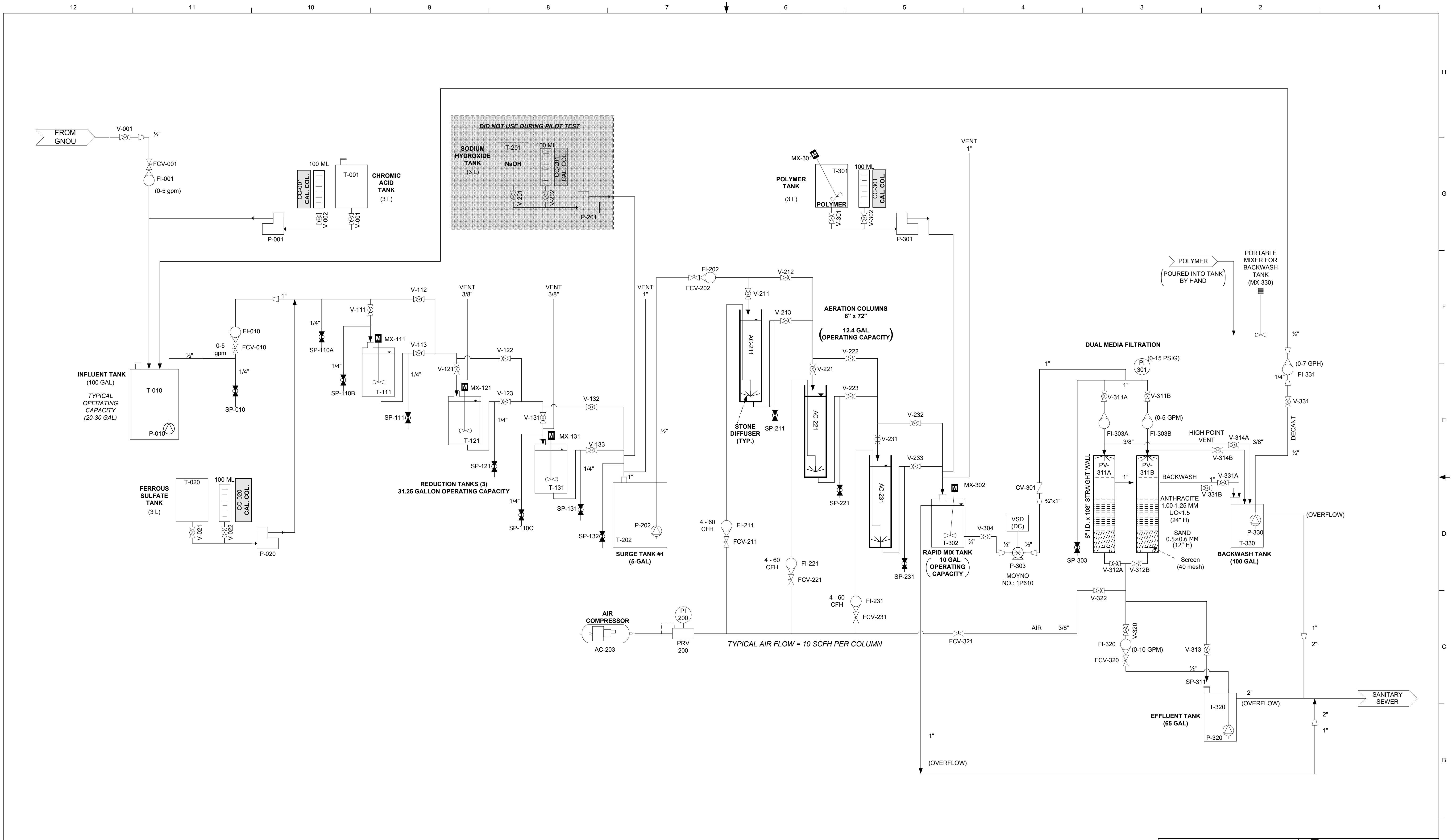
SCALE:	WT.:	SHEET	2 OF 3



REV	DATE	DESCRIPTION	DRAWN BY	CHECKED BY	APPROVED BY
2	02/29/08	TEST CONFIGURATION	DL	TB	N/A
1	01/25/08	AS BUILT	DL	TB	N/A
0	12/07/07	INITIAL RELEASE	DL	TB	N/A

CUSTOMER / PROJECT

PILOT SCALE R.C.F. SYSTEM
GLENDALE, CA

JOB NO. 07-12
FILE ID. 0G2000203-0712-D.VSD
DIMENSIONS IN INCHES UNLESS SPECIFIED

AVANTech INCORPORATED

PROCESS AND INSTRUMENTATION DIAGRAM
WELL WATER TREATMENT SYSTEM

SIZE D
DRAWING NUMBER 0G200-0712-D
REV. 2
SCALE:
WT.:
SHEET 3 OF 3

Photos of the RCF Pilot Testing Equipment

Figure B-1. Chemical Feed Pumps

Figure B-2. Chemical Feed Day Tanks (White PVC columns)

Figure B-3. Cr(VI)-Spiked Influent Tank and Three Reduction Tanks in Series

Figure B-4. Three Aeration Columns in Series and Rapid Mix Tank

Figure B-5. Progressive Cavity Pump Between the Rapid Mix and Filter Columns

Figure B-6. Parallel Filtration Columns and Effluent Tank

Figure B-7. Floc Retention in the Granular Media Filter (24-hour run on 2/28/08)

Figure B-8. Start of Filter Backwashing (Overflow of backwash water)

Figure B-9. End of Filter Backwashing (Overflow of backwash water)

Figure B-10. Backwash Water Holding Tank

Appendix C: Data Summary Sheets

Date:	2/4/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	15:1
Reduction Time	45 min
Aeration Time	18 min
Polymer and Dose	Nalco 9901 - 0.2 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	N/A

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI) (ppb)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning												
		SP-010 Middle												
		SP-010 End	104	98										
SP-110	Fe-spiked Influent	SP-110 Beginning												
		SP-110 Middle				0.001	1.15	0.49						
		SP-110 End					0.96	0.63						
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	0.23											
		SP-131 End												
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1											
		SP-231 End												
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle												
		SP-311 End	<0.1	6.6										
		SP-311 Hr 1												
		SP-311 Hr 2												
		SP-311 Hr 3												
		SP-311 Hr 4												
		SP-311 Hr 5												
		SP-311 Hr 6												
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	BW Beginning												
		BW Middle												
		BW End												
BW Tank	Mixed BW Water	BW End												
Flo Trend Filtrate														

Date:	2/5/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1
Reduction Time	45 min.
Aeration Time	18 min.
Polymer and Dose	Nalco 9901 - 0.2 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	N/A

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI) (ppb)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				100								
		SP-010 Middle	90	110					7.20	21.4			6.5	
		SP-010 End	94	89					7.09	21.9		0.11	6.6	
SP-110	Fe-spiked Influent	SP-110 Beginning					2.24	1.52						
		SP-110 Middle					2.68		7.35	21.0				
		SP-110 End					1.80	0.96	7.15	21.9		2.27		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle				11								
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle				7								
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	1.2			0			7.32	21.2			7.8	
		SP-131 End					1.17	0.00	7.29	22.2			7.6	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	0.42						7.84	20.8			9.4	
		SP-231 End					1.23	0.01	7.80	22.6			8.7	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	0.18	11			0.25	0.00	7.92	20.3				
		SP-311 End	0.72	12			0.19	0.01	7.89	22.8				
		SP-311 Hr 1										2.59		
		SP-311 Hr 2 (M)										1.94		
		SP-311 Hr 3										1.68		
		SP-311 Hr 4										1.24		
		SP-311 Hr 5 (E)										1.20		
		SP-311 Hr 6												
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	BW Beginning												
		BW Middle												
		BW End												
BW Tank	Mixed BW Water	BW End												
Flo Trend Filtrate														

Date:	2/6/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1
Reduction Time	45 min.
Aeration Time	18 min.
Polymer and Dose	Nalco 9901- 0.2 ppm (7:30-9:45am), Ciba E40 - 0.38 ppm (9:45am to end)

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	N/A

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				109								
		SP-010 Middle	112	100		117			7.38	20.8			7.4	
		SP-010 End	106	98					7.19	21.7		0.13	6.7	
SP-110	Fe-spiked Influent	SP-110 Beginning					2.81	1.30						
		SP-110 Middle					2.07	1.13	7.19	20.6				
		SP-110 End							7.23	21.5		3.07		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle				3								
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle				4								
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	<0.1			4	4.11	0.05	7.31	21.2			8.2	
		SP-131 End					3.34	0.04					7.7	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				4.05	0.02	7.77	20.7			9.7	
		SP-231 End					3.31	0.02	7.82	22.1			8.6	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	3.2			0.25	0.00	7.84	20.5				
		SP-311 End	<0.1	<1			0.13	0.01	7.95	23.1				
		SP-311 Hr 1										2.28		
		SP-311 Hr 2 (M)										1.98		
		SP-311 Hr 3										0.51		
		SP-311 Hr 4										0.51		
		SP-311 Hr 5										0.95		
		SP-311 Hr 6 (E)										0.77		
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/7/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1
Reduction Time	45 min.
Aeration Time	18 min.
Polymer and Dose	Nalco 9901 - 0.2 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	N/A

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning				11	0.01	0.00	7.09	20.8	194.6	0.13	6.1	
		GNOU Raw Middle				118								
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning												
		SP-010 Middle												
		SP-010 End												
SP-110	Fe-spiked Influent	SP-110 Beginning					2.16	1.04						
		SP-110 Middle					3.03	1.45						
		SP-110 End												
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle												
		SP-131 End												
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle												
		SP-231 End												
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle												
		SP-311 End												
		SP-311 Hr 1										1.20		
		SP-311 Hr 2										0.77		
		SP-311 Hr 3										0.83		
		SP-311 Hr 4										0.80		
		SP-311 Hr 5												
		SP-311 Hr 6												
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/11/2008	
Experimental Conditions:		
Fe:Cr Dose Ratio Target	25:1	ferrous target rather than usual total iron target
Reduction Time	45 min.	
Aeration Time	18 min.	
Polymer and Dose	Nalco 9901 - 0.2 ppm	

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	2 (after 2.5 hrs); backwashed then

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				118								
		SP-010 Middle	120	117		130			7.32	21.5			6.5	
		SP-010 End							7.36	22.4		0.20	6.7	
SP-110	Fe-spiked Influent	SP-110 Beginning					3.45	1.88						
		SP-110 Middle					4.93	2.77	7.27	22.1				
		SP-110 End							7.23	22.4		4.39		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle				0								
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle				0								
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	<0.1			0	4.48	0.14	7.34	21.8			8.5	
		SP-131 End					3.94	0.16					7.8	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				4.40	0.03	7.80	21.4			9.1	
		SP-231 End					3.88	0.02	7.84	23.5			9.1	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	3.2			0.20	0.01	7.88	21.1				
		SP-311 End	<0.1	2.7			0.13	0.00	7.92	24.2				
		SP-311 Hr 1										1.23		
		SP-311 Hr 2										0.99		
		SP-311 Hr 2.5(M)										1.07		
		SP-311 Hr 3.5										2.26		
		SP-311 Hr 4										1.37		
		SP-311 Hr 5										1.09		
		SP-311 Hr 6 (E)										0.93		
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/12/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	45 min.
Aeration Time	18 min.
Polymer and Dose	Magnafloc Ciba E40 - 0.28ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	0.5

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				127								
		SP-010 Middle	96	95		109			7.32	24.4			6.7	
		SP-010 End	94	93					7.31	24.4		0.07	5.9	
SP-110	Fe-spiked Influent	SP-110 Beginning					2.99	1.45						
		SP-110 Middle					2.73	1.21	7.39	24.9				
		SP-110 End					2.20	0.61	7.36	24.8		8.25		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	<0.1				2.82	0.05	7.48	24.9			7.4	
		SP-131 End					2.52	0.00					8.0	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				2.72	0.05	7.83	24.4			8.8	
		SP-231 End					2.69	0.01	7.93	24.5			8.7	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	<1			0.03	0.00	7.97	24.4				
		SP-311 End	<0.1	<1			0.02	0.00	8.03	25.0				
		SP-311 Hr 1										0.32		
		SP-311 Hr 2										0.21		
		SP-311 Hr 3 (M)										0.16		
		SP-311 Hr 4										0.15		
		SP-311 Hr 5 (E)										0.13		
		SP-311 Hr 6												
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/13/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	45 min.
Aeration Time	18 min.
Polymer and Dose	Magnafloc Ciba E40 - 0.26 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				119								
		SP-010 Middle	112	105		101			7.34	22.5			6.6	
		SP-010 End	122	120					7.49	21.8		0.08	6.6	
SP-110	Fe-spiked Influent	SP-110 Beginning												
		SP-110 Middle					2.42	0.62	7.30	22.1				
		SP-110 End					2.28	0.75	7.30	21.9		12.3		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	0.13				2.45	0.04	7.48	22.3			7.9	
		SP-131 End					2.35	0.27					7.6	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				2.65	0.03	7.86	22.3			8.9	
		SP-231 End					2.30	0.07	7.84	21.8			8.9	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	<1			0.03	0.00	7.93	22.5				
		SP-311 End	<0.1	1			0.05	0.00	7.93	22				
		SP-311 Hr 1										0.53		
		SP-311 Hr 2										0.49		
		SP-311 Hr 3										0.28		
		SP-311 Hr 4										0.22		
		SP-311 Hr 5										0.22		
		SP-311 Hr 6 (M)										0.21		
		SP-311 Hr 7 (E)										0.22		
		SP-311 Hr 8												
BW Tank	Settled BW Water	ettled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/14/2008	
Experimental Conditions:		
Fe:Cr Dose Ratio Target	25:1	total iron
Reduction Time	30 min.	
Aeration Time	18 min.	
Polymer and Dose	Magnafloc Ciba E40 - 0.26 ppm	

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				123								
		SP-010 Middle	83	77		95			7.45	22.8	165.9		6.5	
		SP-010 End	85	79					7.25	23.0		0.11	6.3	
SP-110	Fe-spiked Influent	SP-110 Beginning												
		SP-110 Middle					2.33	1.51	7.32	23.3	-89.6			
		SP-110 End					2.52	1.15	7.18	23.1		7.82		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle	0.37				2.23	0.24	7.58	23.4	-49.7		7.6	
		SP-121 End					2.47	0.27					7.5	
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle												
		SP-131 End												
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				2.25	0.02	7.94	22.8	151.1		8.8	
		SP-231 End					2.25	0.02	7.79	23.8			9.7	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	1.7			0.06	0.00	7.96	21.9				
		SP-311 End	<0.1	1.5			0.05	0.00	7.88	23.8				
		SP-311 Hr 1										0.65		
		SP-311 Hr 2										0.49		
		SP-311 Hr 3										0.39		
		SP-311 Hr 4 (M)										0.40		
		SP-311 Hr 5										0.37		
		SP-311 Hr 6 (E)										0.43		
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/15/2008	
Experimental Conditions:		
Fe:Cr Dose Ratio Target	25:1	total iron
Reduction Time	15 min.	
Aeration Time	18 min.	
Polymer and Dose	Magnafloc Ciba E40 - 0.26 ppm until 8:15; resumed at 1:30 pm - 0.1 ppm dose	

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning	94	89		100								
		SP-010 Middle	100	96		106			7.2	23.8			6.8	
		SP-010 End	104	98										
SP-110	Fe-spiked Influent	SP-110 Beginning					2.85	1.67						
		SP-110 Middle					2.70	1.16	7.24	24.2				
		SP-110 End												
SP-111	After Red. Tank 1	SP-111 Beginning					2.65	0.91						
		SP-111 Middle	1.5				2.67	0.82	7.32	24.2			7.0	
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle												
		SP-131 End												
SP-231	Aeration Effluent	SP-231 Beginning					2.49	0.02						
		SP-231 Middle	<0.1				2.65	0.02	7.75	24.2			8.4	
		SP-231 End												
SP-311	Filter Effluent	SP-311 Beginning	<0.1	<1		7	0.03	0.00						
		SP-311 Middle	<0.1	<1			0.04	0.00	7.84	24.3				
		SP-311 End	<0.1	<1										
		SP-311 Hr 1										1.09		
		SP-311 Hr 2										0.19		
		SP-311 Hr 3										0.17		
		SP-311 Hr 4										0.15		
		SP-311 Hr 5 (M)										0.14		
		SP-311 Hr 6.5 (E)										0.11		
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/19/2008	
Experimental Conditions:		
Fe:Cr Dose Ratio Target	25:1	total iron
Reduction Time	45 min.	
Aeration Time	12 min.	
Polymer and Dose	Magnafloc Ciba E40 - 0.092 ppm	

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	0

			Lab Results			Field results								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				116								
		SP-010 Middle	116	110		125			7.28	22.5	155.6		6.9	
		SP-010 End	127	120					7.20	21.6			7.0	
SP-110	Fe-spiked Influent	SP-110 Beginning					2.24	0.97						
		SP-110 Middle					2.35	1.43	7.23	22.2	-84.2			
		SP-110 End					2.21	1.03	7.34	20.7				
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	0.21				2.10	0.22	7.46	23.3	-58		7.9	
		SP-131 End					2.16	0.24					7.7	
SP-231	Aeration Effluent	SP-231 Beginning					2.23	0.02						
		SP-231 Middle	<0.1				1.99	0.02	7.79	22.6	145.1		9.3	
		SP-231 End					2.17	0.03	7.79	21.9			9.5	
SP-311	Filter Effluent	SP-311 Beginning					0.07							
		SP-311 Middle	0.12	1.4			0.09	0.00	7.89	22.0				
		SP-311 End	<0.1	<1			0.03	0.00	7.85	20.2				
		SP-311 Hr 1										0.30		
		SP-311 Hr 2										0.26		
		SP-311 Hr 3										0.19		
		SP-311 Hr 4 (M)										0.26		
		SP-311 Hr 5										0.22		
		SP-311 Hr 6										0.24		
		SP-311 Hr 7 (E)										0.16		
		SP-311 Hr 8										0.27		
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/20/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	45 min.
Aeration Time	6 min.
Polymer and Dose	Magnafloc Ciba E40 - 0.085 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	1

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning	115	100		136			7.37	23.1	155.1		7.0	
		SP-010 Middle				123								
		SP-010 End	109	96					7.18	22.1		0.11	6.8	
SP-110	Fe-spiked Influent	SP-110 Beginning					2.29	1.16	7.25	21.4	-77.1			
		SP-110 Middle												
		SP-110 End					1.88	1.24	7.27	22.3		5.63		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning	0.28				2.04	0.14	7.57	22.8	-65.8		8.2	
		SP-131 Middle												
		SP-131 End					1.72	0.17					8.0	
SP-231	Aeration Effluent	SP-231 Beginning	0.21				2.01	0.05	7.86	23.1	150.4		8.8	
		SP-231 Middle					1.99							
		SP-231 End					1.72	0.02	7.73	23.1			8.7	
SP-311	Filter Effluent	SP-311 Beginning	<0.1	<1			0.09	0.00	7.90	21.5				
		SP-311 Middle					0.03							
		SP-311 End	0.21	<1			0.02	0.00	7.79	23.3				
		SP-311 Hr 1										0.35		
		SP-311 Hr 2										0.23		
		SP-311 Hr 3 (B)										0.19		
		SP-311 Hr 4												
		SP-311 Hr 5 (M)										0.21		
		SP-311 Hr 6										0.20		
		SP-311 Hr 7 (E)										0.15		
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	2/21/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	30 min.
Aeration Time	6 min.
Polymer and Dose	Magnafloc Ciba E40 - 0.085 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	<1

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				118								
		SP-010 Middle	99	115		120			7.19	22.1	118.8		6.6	
		SP-010 End	89	87					7.40	21.3		0.08	6.9	
SP-110	Fe-spiked Influent	SP-110 Beginning												
		SP-110 Middle					2.97	1.11	7.17	23.4	-98.9			
		SP-110 End					3.32	1.15	7.36	21.6		9.61		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	0.11				2.75	0.44	7.50	23.6	-81		8.1	
		SP-131 End					2.90	0.22	7.58	22.1			8.4	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				2.86	0.07	7.71	24.0	110.2		8.7	
		SP-231 End					2.84	0.06	7.7	22.2			9.3	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	<1			0.03	0.06	7.81	23.5				
		SP-311 End	<0.1	<1			0.16	0.00	7.79	22.6				
		SP-311 Hr 1										0.45		
		SP-311 Hr 2										0.31		
		SP-311 Hr 3										0.30		
		SP-311 Hr 4												
		SP-311 Hr 5										0.21		
		SP-311 Hr 6 (M)										0.21		
		SP-311 Hr 7 (E)										0.22		
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														
0.2 filtered SP-31	Filter Effluent	SP-311 End		<1										

Date:	2/22/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	15 min.
Aeration Time	12 min.
Polymer and Dose	Magnafloc Ciba E40 - 0.095 ppb

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	0

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning				16	0.01	0	7.11	22.3	173.1	0.10	6.2	
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				115								
		SP-010 Middle	22	21		20			7.31	22.9	165		6.4	
		SP-010 End	103	98		116			7.21	22.4		0.12	7.0	
SP-110	Fe-spiked Influent	SP-110 Beginning					3.21	1.56						
		SP-110 Middle					2.99	1.16	7.24	22.4	-121.9			
		SP-110 End					3.07	1.6	7.20	23.1		9.87		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	0.3				2.72	0.64	7.40	23.2	-102.2		6.4	
		SP-131 End					2.86	0.87	7.30	23.1			7.3	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				2.54	0.01	7.75	23.3	159.5		8.6	
		SP-231 End					2.88	0.08	7.70	22.9			9.3	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	<1			0.08	0.00	7.85	23.3				
		SP-311 End	<0.1	<1			0.02	0.00	7.78	23.0				
		SP-311 Hr 1										0.46		
		SP-311 Hr 2										0.29		
		SP-311 Hr 3										0.26		
		SP-311 Hr 4 (M)										0.25		
		SP-311 Hr 5										0.24		
		SP-311 Hr 6										0.22		
		SP-311 Hr 7 (E)										0.23		
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														
0.2 filtered SP-31	Filter Effluent	SP-311 End		<1										

Date:	2/25/2008	
Experimental Conditions:		
Fe:Cr Dose Ratio Target	25:1	total iron
Reduction Time	45 min.	
Aeration Time	0 min. (columns bypassed)	
Polymer and Dose	Magnafloc Ciba E40 - 0.094 ppm	

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	0.5

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				102								
		SP-010 Middle	100	96		117			7.36	22.6	160.8		7.5	
		SP-010 End	107	100					7.22	23.8		0.14	6.6	
SP-110	Fe-spiked Influent	SP-110 Beginning					2.97	1.07						
		SP-110 Middle					2.87	1.35	7.26	22.3	-108.6			
		SP-110 End					3.05	1.24	7.16	23.7		10.4		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	<0.1				2.70	0.25	7.48	23.0	-80.2		8.2	
		SP-131 End					2.87	0.14	7.42	23.5			8.0	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle												
		SP-231 End												
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	<1			0.04	0.01	7.61	22.4				
		SP-311 End	<0.1	<1			0.03	0.00	7.55	23.3				
		SP-311 Hr 1										0.39		
		SP-311 Hr 2										0.27		
		SP-311 Hr 3 (M)										0.20		
		SP-311 Hr 4										0.19		
		SP-311 Hr 5										0.18		
		SP-311 Hr 6 (E)										0.21		
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														
0.2 filtered SP-31	Filter Effluent	SP-311 End		<1										

Date:	2/26/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	45 min.
Aeration Time	18 min.
Polymer and Dose	Magnafloc Ciba E38 (first day) - 0.1 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	1.1

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning				110								
		SP-010 Middle	103	100		110			7.24	20.4	154.4		6.7	
		SP-010 End	110	104					7.26	23.5		0.10	6.5	
SP-110	Fe-spiked Influent	SP-110 Beginning					2.96	1.07						
		SP-110 Middle					2.66	1.65	7.19	24.5	-108.2			
		SP-110 End					2.66	1.01	7.25	24.3		8.94		
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	<0.1				2.59	0.22	7.42	23.9	-84.7		7.7	
		SP-131 End					2.54	0.11	7.51	23.7			7.4	
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				2.60	0.01	7.85	23.8	137.9		8.6	
		SP-231 End					2.50	0.01	7.90	24.3			8.3	
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	<1			0.02	0.00	7.90	23.8				
		SP-311 End	<0.1	<1			0.03	0.00	7.95	24.2				
		SP-311 Hr 1										0.25		
		SP-311 Hr 2										0.22		
		SP-311 Hr 3										0.17		
		SP-311 Hr 4 (M)										0.14		
		SP-311 Hr 5										0.13		
		SP-311 Hr 6 (E)										0.15		
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														
0.2 filtered SP-31	Filter Effluent	SP-311 Middle		<1										

Date:	2/27/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	45 min.
Aeration Time	18 min.
Polymer and Dose	Magnafloc Ciba E38 (first day) - 0.1 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	5.1

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Hr 2				98								
		SP-010 Hr 3	109	104		81			7.45	22.8	154.8		6.2	
		SP-010 Hr 6	114	113		128			7.34	23.2			6.5	
		SP-010 Hr 12		110		133								
		SP-010 Hr 18		110		93								
		SP-010 Hr 24		100		124								
SP-110	Fe-spiked Influent	SP-110 Hr 2					2.81	0.79						
		SP-110 Hr 3					2.83	0.71	7.37	24.1	-91.8	0.16		
		SP-110 Hr 6					2.91	0.72	7.27	24.0		6.61		
		SP-110 Hr 12					2.92							
		SP-110 Hr 18					2.25							
		SP-110 Hr 24					2.46							
SP-131	After Red. Tank 3	SP-131 Hr 2												
		SP-131 Hr 3	<0.1				2.83	0.06	7.45	23.4	-43.8		7.5	
		SP-131 Hr 6					2.85	0.14	7.39	23.7			6.1	
		SP-131 Hr 12					2.93							
		SP-131 Hr 18					1.98							
		SP-131 Hr 24					2.38							
SP-231	Aeration Effluent	SP-231 Hr 2												
		SP-231 Hr 3	<0.1				2.57	0.01	7.85	23.2	36.7		8.1	
		SP-231 Hr 6					2.71	0.01	7.93	23.6			7.3	
		SP-231 Hr 12					2.73							
		SP-231 Hr 18					1.94							
		SP-231 Hr 24					2.38							
SP-311	Filter Effluent	SP-311 Hr 1										0.28		
		SP-311 Hr 2										0.22		
		SP-311 Hr 3	<0.1	<1			0.06	0.00	7.90	23.7		0.19		
		SP-311 Hr 4										0.18		
		SP-311 Hr 5										0.14		
		SP-311 Hr 6	<0.1	<1			0.02	0.01	7.99	23.9		0.13		
		SP-311 Hr 7										0.12		
		SP-311 Hr 8										0.11		
		SP-311 Hr 9										0.09		
		SP-311 Hr 10										0.11		
		SP-311 Hr 11										0.15		
		SP-311 Hr 12		<1			0.01			21.6		0.08		
		SP-311 Hr 13										0.09		
		SP-311 Hr 14										0.09		
		SP-311 Hr 15										0.11		
		SP-311 Hr 16										0.2		
		SP-311 Hr 17										0.23		
		SP-311 Hr 18		<1			0.01			20.4		0.16		
		SP-311 Hr 19										0.18		
		SP-311 Hr 20										0.21		
		SP-311 Hr 21										0.21		
		SP-311 Hr 22										0.18		
		SP-311 Hr 23										0.16		
		SP-311 Hr 24		<1			0.01					0.07		
BW Tank	Settled BW Water	Settled BW water		23										
BW Tank	Mixed BW Water	Mixed BW water			124									3.5
Flo Trend Filtrate		Flo Trend Filtrate												
0.2 filtered SP-31	Filter Effluent	SP-311 Hr 6		<1										

Date:	2/28/2008
Experimental Conditions:	Backwash water recycle
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	45 min.
Aeration Time	18 min.
Polymer and Dose	Magnafloc Ciba E38 - 0.1 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	4.9

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle												
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Hr 2				126								
		SP-010 Hr 3	104	100		91			7.31	23.9	67.7		5.8	
		SP-010 Hr 6	101	103		117			7.06	22.3	68.3			
		SP-010 Hr 12		71		83								
		SP-010 Hr 18		67		80								
		SP-010 Hr 24	103	99		112								
SP-110	Fe-spiked Influent	SP-110 Hr 2					2.12	0.98						
		SP-110 Hr 3					2.29	0.60	7.40	24.5	-99.7			
		SP-110 Hr 6					2.72	0.93	7.30	22.6	-100.9			
		SP-110 Hr 12					1.77							
		SP-110 Hr 18					2.14							
		SP-110 Hr 24					2.78							
SP-131	After Red. Tank 3	SP-131 Hr 2												
		SP-131 Hr 3	0.13				2.26	0.18	7.51	24.6	-69.2		6.4	
		SP-131 Hr 6					2.65	0.37	7.27	22.8	-73			
		SP-131 Hr 12					2.43							
		SP-131 Hr 18					2.33							
		SP-131 Hr 24					2.68							
SP-231	Aeration Effluent	SP-231 Hr 2												
		SP-231 Hr 3	<0.1				2.15	0.01	7.91	24.6	41.6		7.0	
		SP-231 Hr 6					2.50	0.17	7.67	23.0	16.9			
		SP-231 Hr 12					2.36							
		SP-231 Hr 18					2.33							
		SP-231 Hr 24					2.55							
SP-311	Filter Effluent	SP-311 Hr 1										0.26		
		SP-311 Hr 2										0.16		
		SP-311 Hr 3	<0.1	<1			0.04	0.00	7.91	24.3		0.12		
		SP-311 Hr 4										0.12		
		SP-311 Hr 5										0.11		
		SP-311 Hr 6	<0.1	<1			0.02	0.00	8.00	23.6	35.6	0.14		
		SP-311 Hr 7										0.12		
		SP-311 Hr 8										0.1		
		SP-311 Hr 9										0.12		
		SP-311 Hr 10										0.15		
		SP-311 Hr 11										0.16		
		SP-311 Hr 12		<1			0.02					0.14		
		SP-311 Hr 13										0.12		
		SP-311 Hr 14										0.16		
		SP-311 Hr 15										0.15		
		SP-311 Hr 16										0.16		
		SP-311 Hr 17										0.18		
		SP-311 Hr 18		<1			0.00					0.19		
		SP-311 Hr 19										0.21		
		SP-311 Hr 20										0.19		
		SP-311 Hr 21												
		SP-311 Hr 22										0.11		
		SP-311 Hr 23										0.07		
		SP-311 Hr 24		<1			0.02					0.10		
BW Tank	Settled BW Water	Settled BW water	0.98	30			1.02							
BW Tank	Mixed BW Water	Mixed BW water			70									2.5
Flo Trend Filtrate		Flo Trend Filtrate	0.3	2.4			0.06							
0.2 filtered SP-31	Filter Effluent	SP-311 Hr 3		<1										

Date:	2/29/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	45 min.
Aeration Time	18 min.detention time but no air
Polymer and Dose	Magnafloc Ciba E38 - 0.1 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	0

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning	5	4.9										
		GNOU Raw Middle	9.3	9.1		12	0.01	0.00	7.32	21.7	166.9	0.09	5.4	
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Beginning												
		SP-010 Middle	117	112		130			7.03	22.7	45		6.3	
		SP-010 End												
SP-110	Fe-spiked Influent	SP-110 Beginning												
		SP-110 Middle					2.96	1.12	7.30	22.5	-96.5	9.15		
		SP-110 End												
SP-111	After Red. Tank 1	SP-111 Beginning												
		SP-111 Middle												
		SP-111 End												
SP-121	After Red. Tank 2	SP-121 Beginning												
		SP-121 Middle												
		SP-121 End												
SP-131	After Red. Tank 3	SP-131 Beginning												
		SP-131 Middle	<0.1				2.92	0.39	7.41	22.5	-61	16.7	6.5	
		SP-131 End												
SP-231	Aeration Effluent	SP-231 Beginning												
		SP-231 Middle	<0.1				2.83	0.23	7.62	22.9	0.4	16.1	6.7	
		SP-231 End												
SP-311	Filter Effluent	SP-311 Beginning												
		SP-311 Middle	<0.1	<1			0.03	0.01	7.79	23.0	10.1			
		SP-311 End												
		SP-311 Hr 1												
		SP-311 Hr 2										0.32		
		SP-311 Hr 3										0.18		
		SP-311 Hr 4 (M)										0.18		
		SP-311 Hr 5												
		SP-311 Hr 6												
		SP-311 Hr 7												
		SP-311 Hr 8												
BW Tank	Settled BW Water	Settled BW Beginning												
		Settled BW Middle												
		Settled BW End												
BW Tank	Mixed BW Water	Mixed BW End												
Flo Trend Filtrate														

Date:	3/12/2008
Experimental Conditions:	
Fe:Cr Dose Ratio Target	25:1 total iron
Reduction Time	45 min.
Aeration Time	0 min (columns bypassed)
Polymer and Dose	Magnafloc Ciba E38 - 0.1 ppm

Flow Rate (gpm):	2
Change in Pressure Over Run (psi):	0.5

			Lab Results			**Field results**								
Sample Location		**Sample Time**	Cr(VI)	Total Cr	TSS	Cr(VI)	Total Fe	Ferrous Iron	pH	Temp	ORP	Turbidity	Dissolved Oxygen	Settleable Solids
GNOU Raw Water		GNOU Raw Beginning												
		GNOU Raw Middle	8.6	8.7			0.00	0.01	7.28	22.4		0.06	5.1	
		GNOU End												
SP-010	Cr(VI) Spiked Influent	SP-010 Hr 1				128								
		SP-010 Hr 3	120	120		132	0.04	0.02	7.39	22.2		0.07	6.7	
		SP-010 Hr 6	126	126		143			7.20	21.1		0.08	7.4	
		SP-010 Hr 12	114	110		131			7.25	22.0		0.08	6.4	
		SP-010 Hr 18	85	86		80			7.37	22.1	224.7	0.10	6.2	
		SP-010 Hr 24	89	91		100			7.22	23.7	186.7	0.08	7.5	
SP-110	Fe-spiked Influent	SP-110 Hr 1					2.76							
		SP-110 Hr 3					3.20	0.82	7.27	22.5		9.76	6.0	
		SP-110 Hr 6					2.53	0.81	7.35	21.8		6.94	6.6	
		SP-110 Hr 12					2.62	1.35	7.20	22.0		8.08	6.2	
		SP-110 Hr 18					2.44	0.78	7.30	22.8	-29.8	0.91	6.3	
		SP-110 Hr 24					2.65	0.66	7.26	24.0	-82.4	6.75	5.6	
SP-131	After Red. Tank 3	SP-131 Hr 1												
		SP-131 Hr 3	<0.1				3.44	0.30	7.41	22.4		17.9	7.4	
		SP-131 Hr 6	0.2				2.60	0.25	7.50	21.9		13.1	7.4	
		SP-131 Hr 12	<0.1				2.49	0.14	7.47	21.8		14.5	6.9	
		SP-131 Hr 18	<0.1				2.62	0.23	7.41	22.7	-52.4	11.8	6.8	
		SP-131 Hr 24	<0.1				2.47	0.13	7.38	23.8	-1.4	15.1	6.4	
SP-231	Aeration Effluent	SP-231 Hr 1												
		SP-231 Hr 3												
		SP-231 Hr 6												
		SP-231 Hr 12												
		SP-231 Hr 18												
		SP-231 Hr 24												
SP-311	Filter Effluent	SP-311 Hr 1										0.28		
		SP-311 Hr 2										0.15		
		SP-311 Hr 3	<0.1	<1			0.02	0.03	7.45	23.3		0.12	6.4	
		SP-311 Hr 4										0.11		
		SP-311 Hr 5										0.15		
		SP-311 Hr 6	<0.1	<1			0.02	0.00	7.59	21.9		0.10	6.7	
		SP-311 Hr 7										0.08		
		SP-311 Hr 8										0.08		
		SP-311 Hr 9										0.08		
		SP-311 Hr 10										0.08		
		SP-311 Hr 11										0.09		
		SP-311 Hr 12	<0.1	<1			0.02	0.02	7.64	21.9		0.10	6.4	
		SP-311 Hr 13										0.12		
		SP-311 Hr 14										0.22		
		SP-311 Hr 15										0.19		
		SP-311 Hr 16										0.08		
		SP-311 Hr 17										0.07		
		SP-311 Hr 18	<0.1	<1			0.01	0.00	7.63	22.9	57.8	0.07	6.9	
		SP-311 Hr 19										0.08		
		SP-311 Hr 20										0.07		
		SP-311 Hr 21										0.07		
		SP-311 Hr 22										0.08		
		SP-311 Hr 23										0.08		
		SP-311 Hr 24	<0.1	<1			0.01	0.00	7.59	24.1	56.1	0.10	7.0	
BW Tank	Settled BW Water	Settled BW water												
BW Tank	Mixed BW Water	Mixed BW water												
Flo Trend Filtrate		Flo Trend Filtrate												