Occurrence and Treatment of Hexavalent Chromium and Arsenic

in Arizona Municipal and Industrial Waters

by

Alexandra Bowen

A Thesis Presented in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Approved April 2014 by the
Graduate Supervisory Committee:

Paul Westerhoff, Chair
Rolf Halden
Kiril Hristovski

ARIZONA STATE UNIVERSITY

May 2014

ABSTRACT

Arsenic (As) and chromium (Cr) occur naturally in AZ surface and groundwaters, pose different health impacts, and exhibit different treatment efficacies. Hexavalent chromium (Cr(VI)) has newly recognized human health concerns, and State and Federal agencies are evaluating a low Cr(VI)-specific maximum contaminant level (MCL) for drinking water. Occurrence of Cr and As in municipal drinking waters and industrial cooling tower waters was quantified by grab samples and compared with sampling results obtained from a new passive sampler developed specifically for Cr(VI). Cr(VI) and As concentrations in groundwater used for cooling tower make-up water concentrations were ~3 ppb and ~4 ppb, respectively, and were concentrated significantly in blowdown water (~20 ppb and ~40 ppb). Based upon pending Cr(VI), As, and other metal regulations, these blowdown waters will need routine monitoring and treatment.

Cr(VI) concentrations in a water treatment plant (WTP) raw and finished water samples varied from 0.5 and 2 ppb for grab samples collected every 4 hours for 7 consecutive days using an ISCO sampler. The development of an ion exchange (IX) based passive sampler was validated in the field at the WTP and yielded an average exposure within 1 standard deviation of ISCO sampler grab data. Sampling at both the WTP and cooling towers suggested sources of Cr(III) from treatment chemicals or wood preservatives may exist. Since both facilities use chlorine oxidants, I quantified the apparent (pH=5) second-order rate constant for aqueous chlorine (HOCl/OCl$^-$) with Cr(III) to form Cr(VI) as 0.7 M^{-1}s^{-1}. Under typical conditions (2 ppb Cr(III) ; 2 mg/L Cl$_2$) the half-life for the conversion of Cr(III) to the more toxic form Cr(VI) is 4.7 hours.

The occurrence studies in AZ and CA show the Cr(VI) and As treatment of groundwaters will be required to meet stringent Cr(VI) regulations. IX technologies, both strong base anion (SBA) and weak base anion (WBA) resin types were screened (and compared) for Cr removal. The SBA IX process for As removal was optimized by utilizing a reactive iron coagulation and filtration (RCF) process to treat spent IX brine, which was then reused to for SBA resin regeneration.

DEDICATION

I dedicate this thesis, and countless hours of research, to all those who have both supported and encouraged me throughout this chapter of my life--especially my loving, and inspiring family. Thank you for instilling in me the desire to learn, and teaching me to become the compassionate (Julia), loyal (Mom), and grateful (Dad) person that I believe I am today. Although hundreds and hundreds of miles away, I have never once felt alone in the desert. For after all, we all know that old Bowen family dictum - "*Reward for Endeavor…*"

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

This thesis describes the occurrence and treatment of chromium (Cr) and arsenic (As) at

Arizona industrial cooling towers and water treatment plants (WTP) using groundwaters, canals,

and surface waters for makeup water. Because of its associated health risks and mobility within

the environment, understanding techniques to physically remove Cr, or transform hexavalent Cr

(Cr(VI)) to the less toxic, trivalent Cr (Cr(III)) are needed to reduce environmental and human

health exposures. Furthermore, because National Pollutant Discharge Elimination Standards

(NPDES) permits are often connected with drinking water MCLs, it is possible that changes to the

MCL will require more extensive treatment of industrial waters (e.g. cooling tower blowdown

water) that are discharged to surface waters. It is important to best understand contaminant

occurrence before effective engineered treatment technologies can be developed and employed.

Figure 1.1 depicts portions of this thesis relating to the occurrence and treatment of Cr and As.
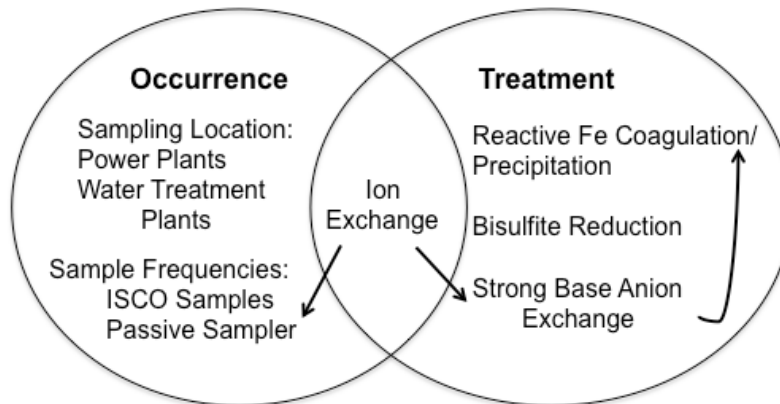
Figure 1.1: Occurrence and Treatment of Chromium and Arsenic

As shown in Figure 1.1, in the "Occurrence" portion of the diagram, occurrence data was obtained

through sample collections of industrial waters (power plants) and municipal waters (WTPs). This

sampling data presented interesting questions about true water quality. Many areas throughout

the country, much like Arizona, draw water from a variety of sources (groundwater, surface water,

etc.), which equates to seasonally dependent water quality. Current sampling procedures

(drinking water) call for routine grab samples, which indicate water quality at the specific time of

sample collection. For many compounds that are of more concern over longer exposures of time (carcinogens, i.e. Cr(VI)), this sample may not be indicative of actual consumer/ecological exposures. For this reason, an inline (passive) sampler was developed capable of representing average time-weighted contaminant concentrations. Although one of the Environmental Protection Agency's (EPA) best available technology (BAT) for Cr(VI) is ion exchange (IX), as shown in the "Treatment" portion of the Figure 1.1, IX was used as a concentrator for the quantification of average time-dependent Cr(VI) levels for the development of this sampler. IX was then utilized as this BAT and tested at the lab scale for As and Cr treatment. Reactive iron coagulation/precipitation was used to further optimize the IX process to minimize waste production. This is the same technology that was investigated for the treatment of industrial cooling tower water blowdown water which contains significant levels of Cr and As. These blowdown waters were also treated through the use of bisulfite which reduced Cr(VI) to Cr(III) which is the less toxic, less persistent form of the pollutant. Dissimilarly to this reduction, some sampling data indicated that Cr(III) was potentially present from treatment chemicals or aging infrastructure (i.e. Cr-treated wood) at these facilities, which utilize chlorine oxidants. Conversion of Cr(III) to Cr(VI) was quantified by the development of a second-order-reaction rate constant for the oxidation reaction.

Specific chapters cover the following topics:

- Chapter 2: Hexavalent Chromium, Selenium and Arsenic Occurrence: Fate and Treatment in Powerplant Discharge, Canals and Potable Water Treatment Plants
    - Samples in AZ were collected and analyzed for metal concentrations throughout a variety of water sources;
    - Metal concentrations across treatment processes in both industrial and municipal waters were used to quantify treatment efficacies;
    - Full-scale treatment processes were reproduced in the lab and compared with field sampling data.
- Chapter 3: Time-Dependent Hexavalent Chromium Monitoring
    - Passive sampling is a fairly novel approach to water quality monitoring;

- A passive sampler was successfully developed and validated at a water treatment facility in parallel to an ISCO autosampler.

- Chapter 4: Evaluation of Reduction Coagulation Filtration and Anion Exchange Brine Optimization for Arsenic Removal
    - Ion Exchange is a widely utilized technology for As and Cr removal from groundwater that still requires process optimization;
    - Bench-scale work was used to represent operating conditions at an existing full-scale IX plant;
    - Brine was treated using the RCF process, and was successfully reused to regenerate spent IX resins.

- Chapter 5: Kinetics of Chromium (III) Oxidation to Chromium (VI) via Hypochlorite Addition
    - An apparent, second-order rate constant was developed for the oxidation of Cr(III) to Cr(VI) by aqueous chlorine at pH=5.

1.1 Background on Chromium in Water

1.1.1 Background Information

Chromium is the 21st most abundant element in the Earth's crust (Sorg, 1979). Chromium (Cr) in water results from a number of both anthropogenic and naturally occurring sources. Cr ion minerals can dissolve and release Cr into groundwater. Cr is also an important industrial metal used in the manufacture of many diverse products including catalysts, pigments and paints, steel alloys, chemicals, and refractories (US Environmental Protection Agency, 2014). Years of use for ore mining, ore processing operations, and improper waste disposal for manufacturing activities have lead to Cr contamination in soil, groundwater, and surface waters. Redox stable forms of chromium exist in water as chromite (Cr(III)), and hexavalent chrome (Cr(VI)). Both the solubility and health risk of Cr(III) are significantly lower than for Cr(VI).

In 1975, the United States Environmental Protection Agency (USEPA) set an interim (enforceable) Maximum Contaminant Level (MCL) standard for total chromium at 50 parts per

billion (ppb) through the National Interim Primary Drinking Water Regulations (NIPDWR). In 1991, the interim MCL was replaced with a final standard of 100 ppb, based on reasoning indicating that Cr(VI) was not carcinogenic via oral ingestions, which is why the MCL was more conservative. The 100 ppb standard is based primarily upon existing studies indicating that those who use water-containing chromium in excess of this level may experience allergic dermatitis (U.S. Department of Health and Human Services, 2008). In 1996, the World Health Organization adopted the stricter recommendation of 50 ppb for total Cr (World Health Organization, 2003). Public concern for Cr(VI) was heightened by the 2000 movie, "Erin Brokovich." The film is an artistic rendering of the groundwater contamination incident in Hinkley, California, and a class-action lawsuit against an electric power company that resulted in a large settlement (AWWA, 2014). In 2008, the EPA began to re-evaluate this standard for total chromium, in order to better address the potential carcinogenic effects caused by the consumption of Cr(VI). The State of California then released a draft MCL for Cr(VI) of 10 ppb.

Cr(III) is much less toxic than Cr(VI), and is an essential element in humans. Cr(VI) is relatively mobile in the environment and is classified as a Class A (known human carcinogen) based on epidemiological studies of workers exposed to Cr(VI) dust (U.S. Environmental Protection Agency, 1999). The carcinogenic hazard of drinking water exposure to Cr(VI) has yet to be definitively established. Recent toxicological and carcinogenic studies of hexavalent chromium ingested orally by mice and rats have shown clear evidence of carcinogenic activity based on increased incidences of neoplasms of the small intestine (Costa, 2003), which further supports the concern that regulatory agencies have relative to the carcinogenic health hazards of widespread human exposure to Cr(VI) in drinking water.

1.1.2 Oxidation and Reduction Chemistry of Chromium

Chromium (atomic number 24, relative atomic mass 51.996) is a member of the group VIB. Chromium has oxidation states ranging from Cr^{2-} to Cr^{6+}, but it most commonly occurs as Cr^0, Cr^{2+}, Cr^{3+}, and Cr^{6+} (Figure 1.1). Cr(II) compounds are basic, Cr(III) compounds are amphoteric, and Cr(VI) compounds are acidic (Katz & Salem, 1994). Divalent chromium is

relatively unstable as it is rapidly oxidized to the trivalent form, thus only two forms—trivalent and hexavalent are found in nature (National Academy of Sciences, 1974). The mobility and toxicity of chromium in the environment largely depends on its oxidation state. The relation between Cr(III) and Cr(VI) is described by Equation 1.1.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr(III) + 7H_2O \quad E_0 = +1.33 \text{ V} \qquad \textbf{(Equation 1.1)}$$
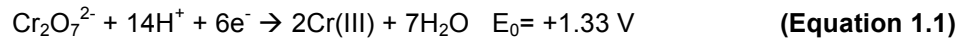
The difference in electric potential between the two oxidation states shows the strong oxidizing properties of Cr(VI) and the energy required to oxidize Cr(III) to Cr(VI), and similarly, the tendency for Cr(VI) to be reduced to Cr(III). In order to accomplish reduction, a source of electrons (reductant) must be provided so that Cr(VI) can be reduced to Cr(III). Naturally occurring reductants such as iron(II) (ferrous iron) compounds, sulfur(II) compounds transform hexavalent chromium compounds to trivalent chromium compounds. Reduction rates are pE and pH dependent (Katz & Salem, 1994) .
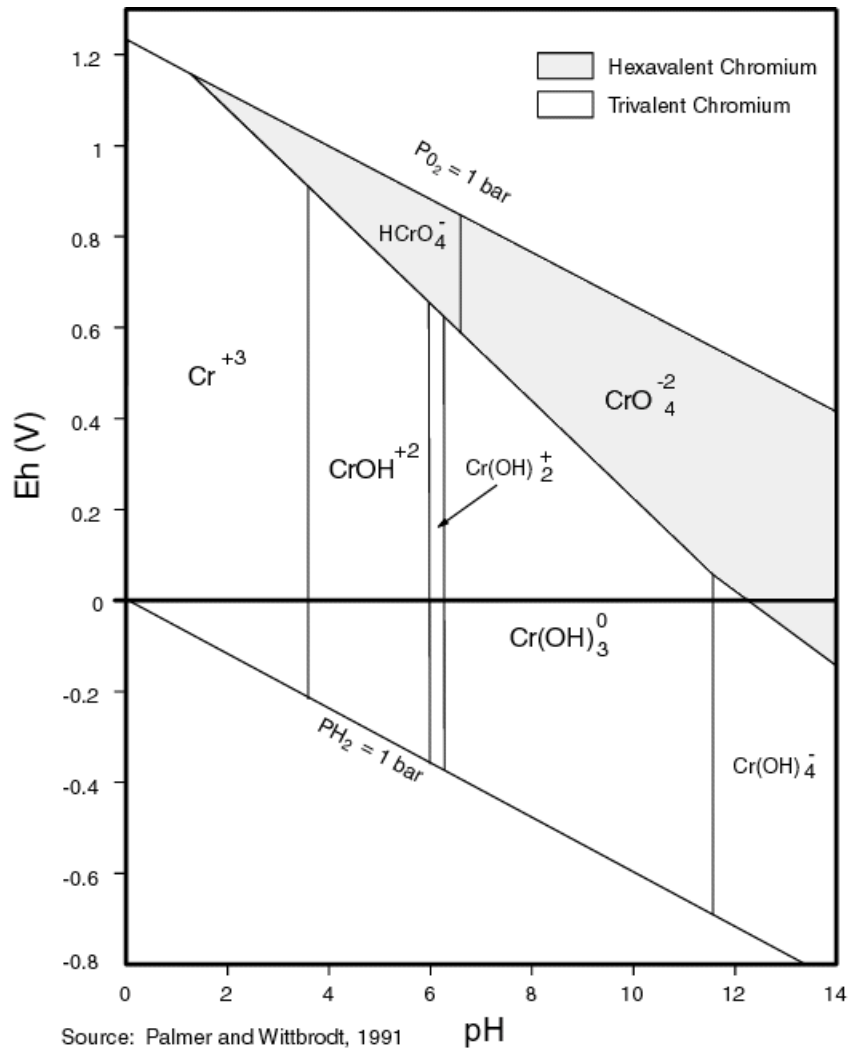
Figure 1.2: Eh-pH Diagram for Chromium

(Center for Environmental Research Information, 2008)

1.1.3 Trivalent Chromium Compounds

Dissolved in water, Cr(III) gives water a green tint. Figure 1.2 shows that under reducing conditions, Cr(III) is the most thermodynamically stable form of chromium. Cr(III) predominates as Cr^{3+} ion at pH<3. At pH>3, Cr(III) hydrolysis in water forms chromium hydroxide species $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$ (amorphous precipitate), and $Cr(OH)_4^-$. Typical groundwaters and surface waters of pH values ranging from 6-8 indicate the predominate aqueous Cr(III) to be $Cr(OH)_3^0$

and $Cr(OH)_4^-$. The solubility of trivalent chromium compounds is limited by the formation of several oxide and hydroxide species (Katz & Salem, 1994).

Precipitation of Cr(III) can be divided into three types: pure solids (amorphous precipitation) of $Cr(OH)_3^0$; coprecipitation of Cr with other heavy metals such as iron; and high molecular weight organic acid complexes such as humic acid polymers. (Center for Environmental Research Information, 2008) Solubility of Cr(III) precipitates resulting from changes in Eh/pH conditions. The solubility of Cr(III) is controlled by amorphous $Cr(OH)_3^0$ solubility with a reported solubility product (K_{sp}) of 6.7E-31 mol^4/L^4 at 25° C.

Figure 1.3 shows the solubility of chromite species with respect to pH. Under slightly acidic pH conditions, pH=5, $Cr(OH)^{2+}$ dominates, at neutral pH=7, $Cr(OH)_2^+$ dominates, and under more basic conditions, pH=9, $Cr(OH)_3$ species dominates.
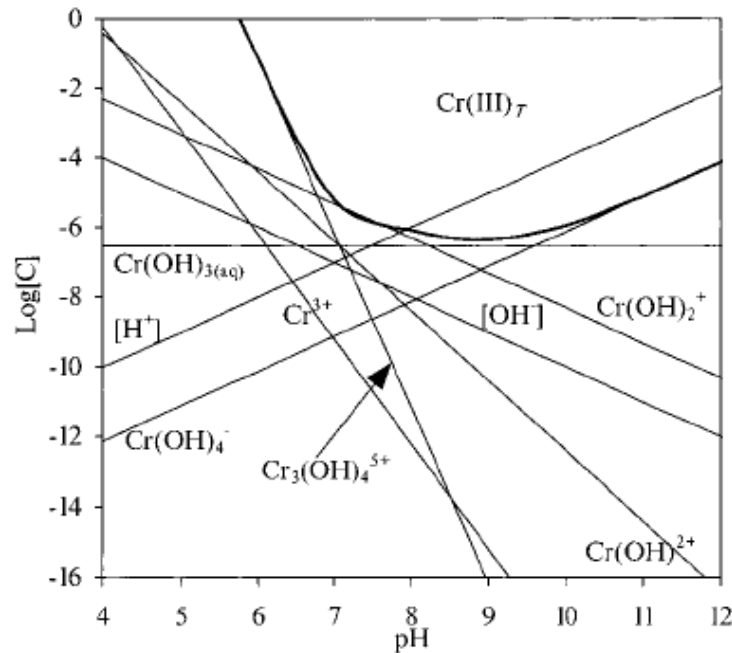
Figure 1.3: Solubility of Chromite with respect to pH (Barber & Stuckey, 2000)

1.1.4 Hexavalent Chromium Compounds

Hexavalent chromium compounds are more soluble than trivalent chromium compounds under most environmental conditions. Examples of water-soluble Cr(VI) compounds include

sodium chromate (873 g/L at 30°C) and potassium chromate (629 g/L at 20°C) (Taylor & Francis Group, 2008). Cr(VI) compounds dissolved in water are dark yellow, in color and Cr(III) compounds are green in color.

1.1.5 Health Effects and Chromium Regulatory Status

Chromium was first regulated in the U.S. Public Health Service's Drinking Water Standards in 1946 because studies showed that it caused lung tumors when inhaled (Brandhuber et al., 2004). The World Health Organization (WHO) has long held that Cr(VI) concentrations in drinking water should be less than 50 ppb (World Health Organization, 2003). The US EPA has set an enforceable drinking water standard of 100 ppb for total chromium, which includes Cr(VI) and Cr(III). This standard was established in 1991 and was based upon studies showing that some people exposed to water with higher Cr levels exhibited allergic dermatitis (skin irritation) (US Environmental Protection Agency, 2014).

A chromium paradox exists, as although Cr(III) is an essential nutrient for human nutrition, specifically in glucose metabolism (Vincent, 2000), most hexavalent chromium compounds are toxic and have been thought to be carcinogenic in nature. Reduction of toxic Cr(VI) to Cr(III) reduces toxicity by a factor of about 100 (Liu, 1997). The original MCL for total chromium was established because the analytical methods of the time could not distinguish between valence states (Sorg, 1979). The state of California set a more stringent MCL for total chromium of 50 ppb, based on health studies showing Cr(VI) toxicity (McGuire et al., 2007). The state of California is mandated to set a MCL specifically for Cr(VI) to low ppb levels.

In 1991 when the US EPA replaced the existing MCL for total Cr (of 500 ppb) with the less strict levels of 100 ppb, the state of California did not follow the change of the federal MCL, rather it stayed with its 50 ppb standard. In 1996, Congress made amendments to the SDWA. In California, this included the development of risk-based drinking water contaminant standards that are protective of human health. These new standards, known as Public Health Goals (PHGs), correspond to a one-in-a-million (10^{-6}) cancer risk. In 1999, California's Office of Environmental Health and Hazard Assessment (OEHHA) published a low PHG of 2.5 ppb for total Cr (OEHHA,

1999). Events between 1999-2001 resulted in a state law that required California Department of Public Health (CPDH) to adopt a Cr(VI) specific MCL. In July of 2011 OEHHA established a Cr(VI)-specific PHG of 0.02 ppb. This established PHG allowed CDPH to continue promulgating a primary MCL for Cr(VI). In August of 2013, CDPH proposed an MCL for Cr(VI) of 10 ug/L. Completion of the rulemaking process may take up to a year after the proposal, so it is thought that an MCL for Cr(VI) may be established in 2014 (California Department of Publich Health, 2014).

1.1.6 Engineered Chromium Removal Technologies

Treatment technologies to remove (or recover) chromium from industrial wastewaters have been well developed and reported (Sorg, 1979). These industrial wastewaters contain ppm levels of chromium, which are not environmentally relevant concentrations that are present in drinking water sources (Patterson, 1985). It is for this reason why more studies are being conducted to better understand the applicability, and optimization, of engineered treatment technologies for low-level Cr(VI) removal.

Ion exchange (IX) has been named a best available technology (BAT) for chromium removal by the EPA. IX is a process used to remove dissolved ionic constituents (metal oxo-anions like arsenate and chromate) from water (Crittenden, et al., 2010). Ion exchange resins are solid phase beads that are initially saturated with noncontaminant ions, i.e. chloride or hydoxide. As water comes into contact with these resins covered in chloride or hydroxide ions, anions with a higher affinity for the charged functional groups on the resin backbone will exchange binding sites, and release the chloride or hydroxide ions into solution (Brandhuber et al., 2004). Based upon the resin-specific ionizable group attached to the resin backbone, anion exchangers can be classified into two categories: strong based anion exchangers and weak base anion exchangers.

Strong base anion (SBA) exchange resins remove the chromate anion according to Equation 1.2

$$-X^+\text{-}Cl^- + HCrO_4^- \rightarrow -X^+\text{-}HCrO_4^- + Cl^- \textbf{ (Equation 1.2)}$$

SBA resins behave similar to strong bases, in that they are not likely to protonate in water. SBA resins have been widely proven for hexavalent chromium removal, as their functional groups remain ionized over a wide range of pH values. (Brandhuber et al., 2004; McGuire et al., 2007) When all ion exchange sites have been filled with anions from solution, the resin is considered to be exhausted. At this time, the resin can be regenerated using a solution of high ionic strength, which will replace anions currently filling IX sites with chloride ions, releasing the anions into the brine solution.

Weak base anion (WBA) exchange resins behave similarly to weak bases, in that they are likely to protonate in water. WBA resins have been used for groundwater remediation of waters containing high hexavalent chromium levels for their relatively high capacity and selectivity towards chromate. Despite their high capacity for chromate, their functional groups can only remain charged below pH 6, making treating pH neutral waters more difficult. Similarly, due to their high selectivity between the WBA exchangers and chromate ion, it becomes more difficult to regenerate WBA resins due to this strong complexation.

The aqueous chemistry of chromium is advantageous, from a treatment (separation) perspective, as specific Cr characteristics can be exploited for other removal purposes:

- Ionic Cr(VI) can be removed by technologies which utilize electrostatic attraction (sorption) or ion replacement (ion exchange);
- Metallic properties of chromium allow chromium complexation with other heavy compounds (precipitation and settling or filtration);
- Low solubility of Cr(III) at pH>7 offer treatment via precipitation;
- High standard electrode potential imply reductants (Fe(III) or Mn(II)) may be used to reduce Cr(VI) to Cr(III);
- The divalent anionic charge of Cr(VI) can be used for attraction to a charged polymeric membrane (Brandhuber et al., 2004).

1.2 Background on Arsenic in Water

1.2.1 Arsenic Background Information

Arsenic (As) occurs in two primary forms; organic and inorganic. Organic (carbon-containing) arsenic is found in food sources, existing as monomethyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA), and arseno-sugars, and is used by pesticides for agricultural applications as monosodium methanearsonate and disodium methanearsonate (National Academy of Sciences, 1974). Inorganic As, considered to be the most toxic form of the element, exists in groundwaters, surface waters, as well as in foods. As has both natural and anthropogenic sources. Naturally occurring arsenic is present in drinking water supplies from erosion of natural earth minerals, e.g. shale in AZ. Other sources of arsenic include agricultural applications, and industrial purposes, which include wood preservations, and semi-conductor applications. Redox stable forms exist primarily in water as trivalent arsenite (As(III)) and pentavalent arsenate (As(V)) (U.S. Environmental Protection Agency, 1999).

The MCL for total As in drinking water is 10 ppb, established under the Safe Drinking Water Act. The MCLG for As is zero. Health effects associated with drinking water contaminated with As include skin damage, circulatory system problems, and increased risk of cancer.

1.2.2 Oxidation and Reduction Chemistry of Arsenic

Arsenic (atomic number 33, relative atomic mass 74.9216 g/mol) is a member of the Pnictogen, "Nitrogen" (US EPA, 2013) group on the periodic table. Arsenic can occur in water as As^{5+}, As^{3+}, As^0, As^{3-} oxidation states. As illustrated in Figure 1.4, most natural As(III) (arsenite) containing waters in pH range of 6.5 to 8.5 will have arsenite in the undissociated form, arsenious acid (H_3AsO_3) at neutral pH. As(III) has a high solubility at neutral pH and is more toxic to many organisms. Natural As(V) (arsenate) containing waters in pH range of 6.5 to 8.5 will have ionic arsenate as $HAsO_4^-$ and $H_2AsO_4^{2-}$. Some phases of As(V) are less soluble within neutral pH range, however because of their ionic nature these compounds are more reactive in solution, making some treatment technologies more effective (i.g. IX, adsorption, membrane filtration). Most natural waters contain the more toxic inorganic form of arsenic, arsenite. Groundwaters,

under reducing conditions, contain As(III), whereas surface waters, under more oxidizing

conditions, contain As(V) species (International Consultants, INC. and Malcom Pirnie, INC.,

2000).
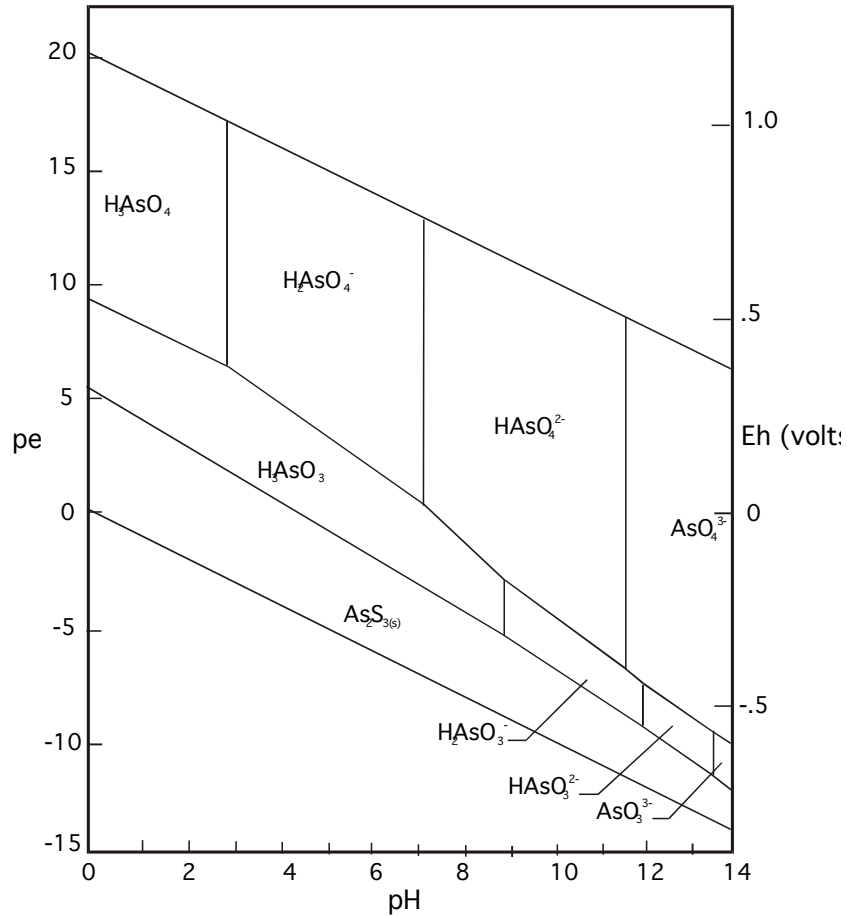
Figure 1.4: Eh-pH diagram for aqueous Arsenic Species

(Panagiotaras & Panagopoulos, 2012)

1.2.3 Arsenic Health Effects and Regulatory Status

In January of 2001, the EPA created a new MCL for arsenic in drinking water at 10 ppb

which replaced with old standard of 50 ppb, known as the Arsenic Rule. The old MCL of 50 ppb

was enforced under the Safe Drinking Water Act, but had originally been established in 1942

based on a Public Health Service standard. The new standard of 10 ppb is based on studies that

have shown long-term exposure risks to drinking As-contaminated waters to increase risk of

cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate. Non-cancer health

effects of ingesting water with arsenic include cardiovascular, pulmonary, immunological, neurological and endocrine effects. (US EPA, 2013)

1.2.4 Engineered Arsenic Removal Technologies

Dissimilar to Cr, the aqueous chemistry of arsenic is advantageous, from a treatment perspective, specific As(V) characteristics can be exploited for removal purposes:

- Ionic As(V) species can be removed by technologies which utilize electrostatic attraction (sorption), ion replacement (ion exchange), or by separation (charged membranes);
- Arsenic can be removed by iron-based adsorbents;
- Coprecipitaiton with iron-hydroxides is a widely proven As removal technique.

Many existing conventional drinking water treatments are capable of lowering As concentrations to <10 ug/L, though many of these methods remove As(III) less efficiently than As(VI) (Dodd et al., 2006). Because of it's charge neutrality, arsenite, is usually preoxidized using chlorine, permanganate, or ozone, arsenate in order to achieve ionic charge.

1.3 Thesis Objectives

The goal of this thesis is to understand occurrence of select oxoanions (Cr, As, Se) in AZ waters and assess techniques to remove them from water. Specific objectives of each chapter and portions of presented research will be described as follows:

- Chapter 2: Understand the fate of Cr, Se (selenium) and As in impacted Salt River Project (SRP) waters in order to help municipalities to plan for potential changes in regulatory NPDES or aquifer discharge limits as well as investigate treatment technologies for simultaneous removal of pollutants (Cr, As, and Se).
- Chapter 3: Develop and deploy an in-situ passive sampler for Cr(VI) that is more representative of time-weighted averaged water quality, when compared to traditional grab samples.
- Chapter 4: Develop a reaction-rate describing the oxidation of Cr(III) to the more toxic and persistent form, Cr(VI) by aqueous chlorine.

- Chapter 5: Determine the efficacy of the potential reuse of spent brine for SBA IX help reduce hazardous waste accumulation (and disposal) for an existing SBA facility.

- Chapter 6 summarizes results, draws conclusions, provides recommendations for utilities, and discusses areas for future studies.

CHAPTER 2

HEXAVALENT CHROMIUM, SELENIUM AND ARSENIC OCCURRENCE,

FATE AND TREATMENT IN POWERPLANT DISCHARGE,

CANALS AND POTABLE WATER TREATMENT PLANTS

(This is a report provided to Salt River Project)

Arizona's Salt River Project (SRP) is one of the nation's largest public power utilities, providing electricity and water to more than 2 million people in Central Arizona. (Salt River Project, 1996). Groundwater in SRP service area contains naturally occurring levels of chromium (Cr), arsenic (As) and selenium (Se). Use of these groundwaters directly at SRP power plants or when blended with surface waters from rivers and canals poses a challenge to meet discharge limits. Specifically, concentrations of these heavy metals in cooling tower blowdown water accumulate significantly as water is evaporated, producing waste streams with high metal concentrations. New, lower discharge limits on these metals are being considered which necessitates consideration of how to remove the metals from blowdown water before discharge. Additionally the fate of these metals and their speciation throughout the SRP waters is still not entirely understood. The purpose of this project is to determine the occurrence of Cr, As and Se in SRP waters and identify possible treatment methods for these metals.

The occurrence of total Cr, Se, As, and hexavalent chromium (Cr(VI)) in SRP wells, power plants, and water treatment plants was investigated. Preliminary results indicate that the levels of these metals are close to or surpassing regulatory limits, and there may be processes within the SRP facilities that lead to increased levels of Cr(VI) and As. Evaluation of treatment strategies for removing hexavalent chromium have identified promising results using either bisulfite as a chemical reductant (reducing Cr(VI) to Cr(III)) or reactive iron coagulation for precipitation of metals.

2.1 Contaminant Background

2.1.1 Chromium

Arizona has a regulatory discharge limit determined by the National Pollutant Discharge Elimination System (NPDES) of 11 ppb for Cr(VI) and 230 ppb for trivalent chromium (Cr(III)), but lower levels exist for aquifer protection in some areas. The current Environmental Protection Agency (EPA) maximum contaminant level (MCL) is 0.1 mg/L for total chromium, but in 2010 the EPA decided to conduct additional monitoring of Cr(VI) and consider lower regulations based upon recent health studies. AZ's NPDES discharge limit for Cr(VI) may be lowered, if EPA's MCL is lowered. In groundwater and drinking water, Cr(III) exists predominately as Cr^{3+} ion and as hydroxide complexes $Cr(OH)^{2+}$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ with increasing pH. Under slightly acidic to alkaline conditions, Cr(III) can precipitate as amorphous chromium hydroxide (Fig. 1a). Cr(III) has a lower health risk than Cr(VI), but chlorine and other disinfectants readily oxidize Cr(III) to Cr(VI). Cr(VI) is an anion that is more persistent within water, and is thusly more difficult to remove than Cr(III) which has a lower solubility which can be easily removed through precipitation. Chemical reduction of Cr(VI) to Cr(III) is possible using ferrous compounds (Le 1988), and removal of both forms by commercially available media have been thoroughly investigated already. Among the best technologies for removing Cr(VI) is anion exchange (Adren 1961) for which highly selective resins are available.

2.1.2 Selenium

Selenium is found in the environment in four oxidation states (Fig. 1b): Se(VI), Se(IV), Se(0), Se(-II). It is found as selenate and selenite in oxidized systems, but Se(0) and selenides in anaerobic zones. Both Se(0) and Se(-II) are insoluble. In pH 6-8, only Se(0), selenite, biselenite ($HSeO_3^{-1}$) and selenate are present. SRP has a selenium discharge limit of 2 ppb. Removal strategies for selenium typically involve reduction of selenate, which is not easily adsorbed onto particulates, to selenite, which can be easily immobilized. Biological reduction of Se with anaerobic bacteria or algae has been shown to be very effective, with >95% selenium removal for influent Se of 0.4 mg/L (Hagelstein 2009) and a commercially available bioreactor (ABMet®) from

GE already demonstrated to remove Se < 5 μg/L in pilot and full-scale applications. However, such technologies require substantial real estate and capital/operational costs that may not be feasible for SRP.
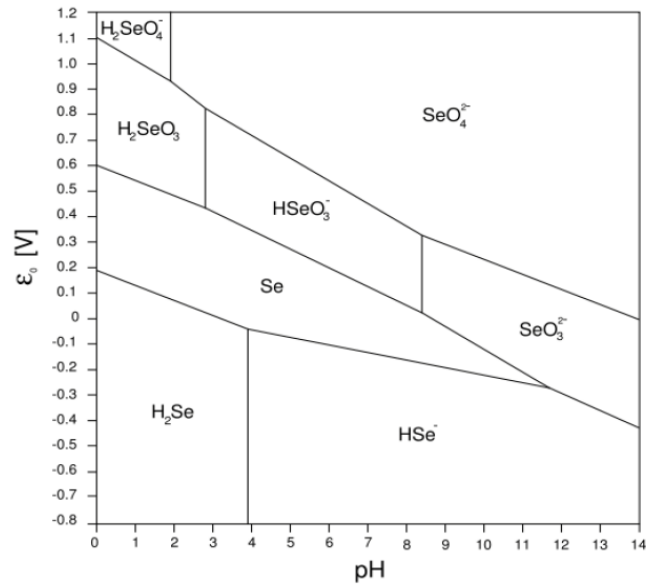
Figure 2.1: Eh-pH Diagram for aqueous selenium species

Chemical reduction technologies for selenate include elemental zinc and iron, in which the metal goes into solution as the cation and forms the hydroxide precipitate to reduce selenate to selenite and elemental selenium. These technologies typically require large amounts of metal in grams-per-liter doses, which are 3-6 orders of magnitude greater than the concentration of selenium being removed (Marchant 1975, Baldwin 1983). Ferrous hydroxide can also be used to reduce selenate to selenite (Murphy 1989). One of the prohibitive features of these technologies is that they produce a significant amount of sludge as product.

2.1.3 Arsenic

Arsenic is also naturally occurring in Arizona, and can occur as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, or AsO_4^{3-} in oxygenated waters. In the case of arsenic, trivalent arsenic (arsenite) is more toxic than the pentavalent form (arsenate). The removal of As(III) is also more difficult than As(V). Dr. Paul

Westerhoff's, Professor at Arizona State University, previous studies on arsenic occurrence and treatment in Arizona (Westerhoff, 2005) showed that As(V) is predominately present in local groundwaters. SRP's previous speciation studies on arsenic occurrence in well waters also show it is in the form of arsenate. Arsenic can be readily removed by iron-based packed bed adsorbents or iron-coagulation/membrane filtration separation for well-head treatment, and is already employed by many local cities. Ferric salts may also adsorb arsenic and require < 10 mg/L ferric ion and can achieve residual As < 10 µg/L.

2.2 Project Objectives

The purpose of this project was to provide SRP with critical information on the occurrence and treatment of trace metals in local waters. This information should lead to better knowledge and approaches for minimizing the amounts of hexavalent chromium, total selenium, and total arsenic in waters and to meet pending regulations. The data collected from the water treatment plants can also be used to determine the possible removal of chromium by the conventional water treatment processes used at the plants and identify possible sources of chromium in the plant.

Another goal of this project was to evaluate several treatment methods for removing hexavalent chromium and selenium. Arsenic removal from water is well studied, and was not a focal point of this project. Both commercially available and proven technologies (e.g. chemical reductant, iron coagulation, titania-based sorbents) and newer, *piloted approaches (photocatalytic reactors) were assessed*[1].

This report describes our findings on the following tasks:

- Task 1 – Fate of Cr, Se and As in SRP impacted waters
- Task 2 – Assessment of treatment technologies for hexavalent chromium

---

[1] Another graduate student was responsible for investigating photocatalytic reduction efficacies for chromate/selenate reduction. Because this is not my work, this work has been omitted from this document.

2.3 Task 1- Fate of Cr, Se and As in SRP impacted Waters

2.3.1 Field Sampling Methods

The main focus for sample collection for this study was the Santan Generating Station. Samples were also collected from the Kyrene Generation Station, the Chandler Water Treatment Plant, and the South Tempe Water Treatment Plant (Figure 2.2). Field samples were collected in 250 mL Nalgene HDPE, sterile, wide mouth bottles.
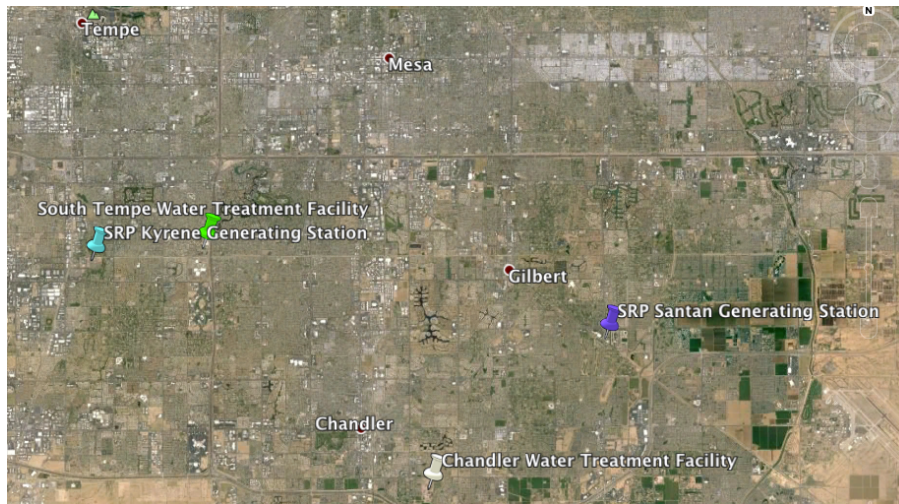
Figure 2.2: Sampling locations

2.3.2 Sampling Locations

Samples from the Santan Generating Station were collected throughout the water treatment process. Samples were collected from the A, B, and C wells which make up the water supplied to the plant during times of canal dryout. When the clarifier was running, clarifier influent and effluent samples were collected. Samples were collected from the makeup water that go directly into Cooling Towers 5 and 6. Blowdown from Cooling Tower 5 and 6 (when operational) were also collected.

The Kyrene Generating Station was only operational for a short period of time during the timeline of this project. Much like the SanTan generating station, samples were collected

throughout the cooling tower water treatment process. Samples were collected from Deep Wells #1 and #2. Cooling Tower makeup water and blowdown were collected.

Representative local water treatment plants, Chandler and South Tempe Water Treatment Plants, were sampled to understand metal occurrence and removal/metal speciation throughout the drinking water treatment processes.

2.3.3 Analytical Methods

Aqueous Cr(VI) concentrations were measured using ion chromatography (IC) followed by post column reaction with 1,5-diphenylcarbohydrazide according to a modified version of the US EPA Method 218.6. This method is based on the anion-exchange chromatography on a Thermo Scientific[TM] Dionex[TM] IonPac[TM] AS7 column and detection after post-column reaction with diphenylcarbazide which yields a compound with visible absorbance at 530 nm. This gives a detection limit for chromate at 0.02 µg/L and can support a reporting limit of 0.06 µg/L. According to EPA Method 218.6, samples were buffered using sodium phosphate buffer. The concentration of total As, Se, and Cr species was determined using As, Se, and Cr using inductively coupled plasma with mass spectrometry (ICP-MS) or optical emission spectroscopy (ICP-OES), following EPA's approved Multi-Analyte Method 200.8. To ensure proper preservation, samples were acidified using UltraPure Nitric Acid (Ultrex). The concentration of Cr(III) was assumed to be the differential between Cr(VI) and total Cr concentrations.

2.3.4 Sampling Results

SanTan Generating Station

Figure 2.3 shows average levels of metals throughout the Santan Generating Station. Samples were collected when the facility was utilizing groundwate, which included the following dates; December 4, 2012, January 7, 2013, and January 17, 2013.
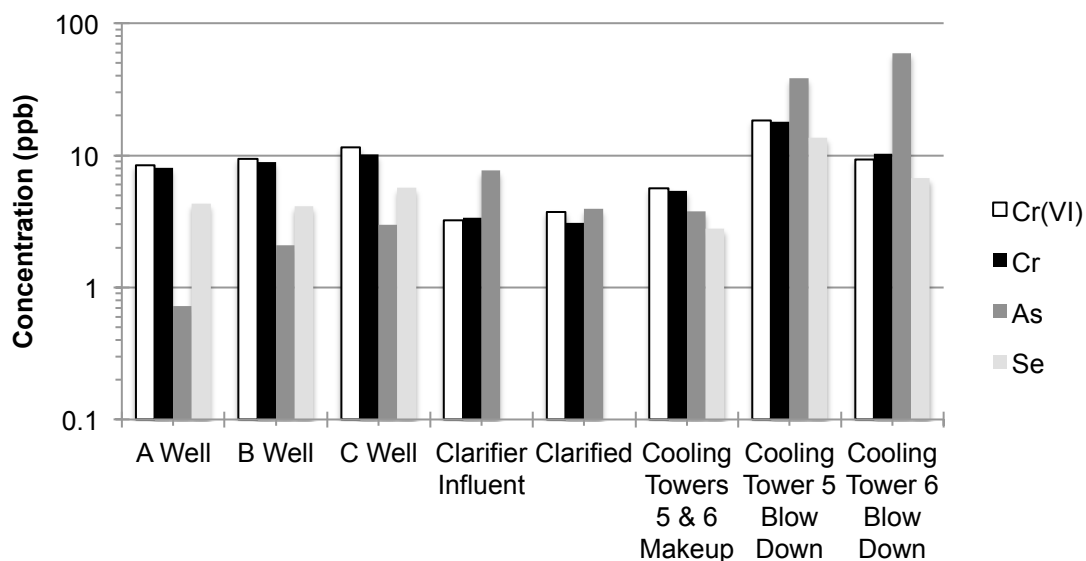
Figure 2.3: Average metal concentrations throughout Santan Generating Station

A trend was observed indicating metal concentration from the cooling tower makeup water to the final blowdown cycle. Metals were concentrated about four times from the influent makeup water (Cr: 5.4 ppb, As: 3.8 ppb, Se: 2.8 ppb) to the cooling tower blowdown water (Cr: 18 ppb, As: 60 ppb, Se: 6.7 ppb). The results in Figure 2.3 also show that all of the chromium within the station is present in the hexavalent oxidation state, indicating oxidative conditions throughout the plant.

Kyrene Generating Station

Figure 2.4 shows metal concentrations throughout the Kyrene Generating Facility from sampling conducted on April 3, 2013. Here metal concentrations were also observed to be concentrated about four times from the cooling tower makeup water (Cr: BRL, As: 2 ppb, Se: 1.6 ppb) to the cooling tower blowdown water (Cr: 5.6 ppb, As: 8.1 ppb, Se: 3 ppb). The low concentration of metals in the cooling tower (CT) makeup water compared to the well water suggests that the process used to treat influent well water removes essentially all chromium from the groundwater. This suggests that chromium is being introduced into the water somewhere

within the cooling towers. Because of the age of the Kyrene plant, it is possible that Cr treated wood slats exist within the cooling tower itself. This could be a potential source of chromium within the plant.
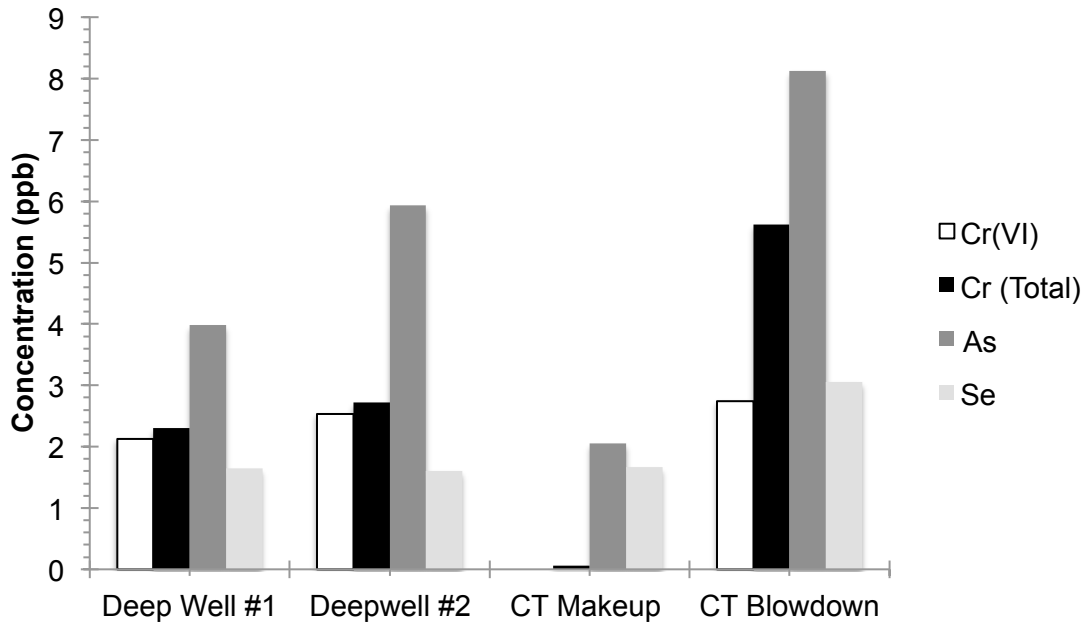
Figure 2.4: Metal concentrations throughout Kyrene Generating Facility

South Tempe Water Treatment Plant

Sampling was conducted at South Tempe Water Treatment Facility on January 17 and March 21 of 2013. Figure 2.5 shows the average metal concentrations at the South Tempe Water Treatment Facility. Influent water comes into the plant from the north (Raw North) and south (Raw South) sides of the plant. Water seems to be of similar quality, with slightly higher arsenic levels from the south side of the plant. This water is then lifted and dosed with coagulant and coagulant aid (polymer). Selenium seems to settle within the sedimentation basin, but reappears in the filter effluent and is then discharged into the reservoir.
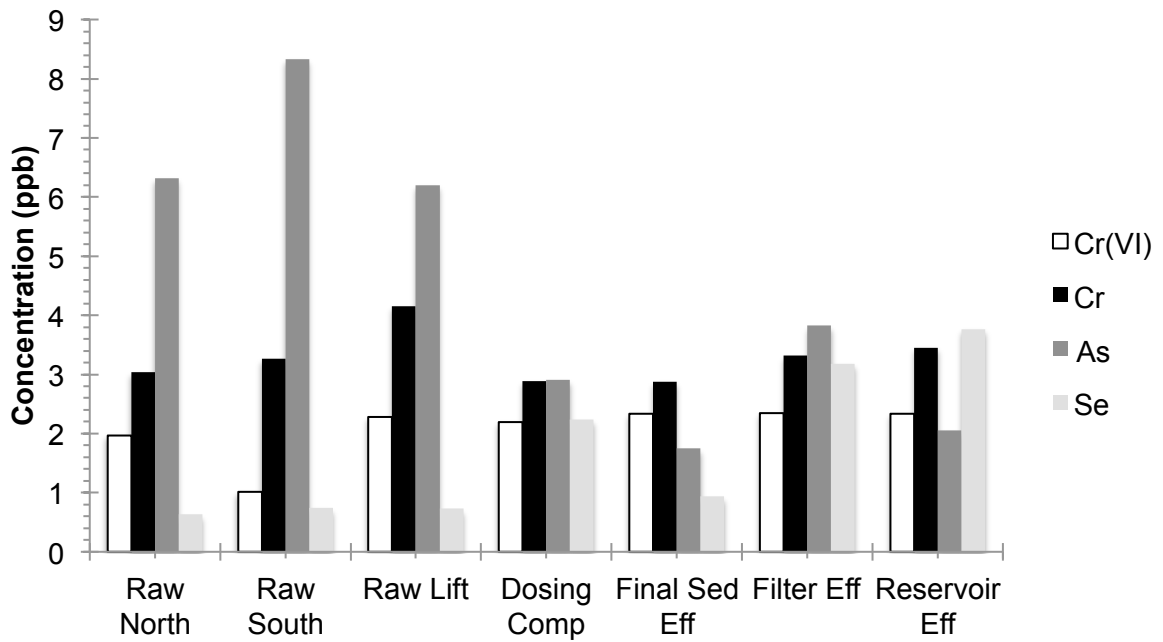
Figure 2.5: Average Metal Concentrations at South Tempe WTP

Chandler Water Treatment Plant

Sampling was performed at the Chandler plant on December 4, 2012, January 17, 2013, and March 21, 2013. Figure 2.6 shows the average metal concentrations at Chandler from the collected grab samples. Interestingly enough, Cr levels within the plant suggest that there is a source of chromium somewhere within the plant, as levels within the plant are substantially higher than those levels that makeup influent water. This was first seen on December 4, 2012; on this day, Chandler's source water contained around 3 ppb of Chromium, and was discharging around 7 ppb of chromium.
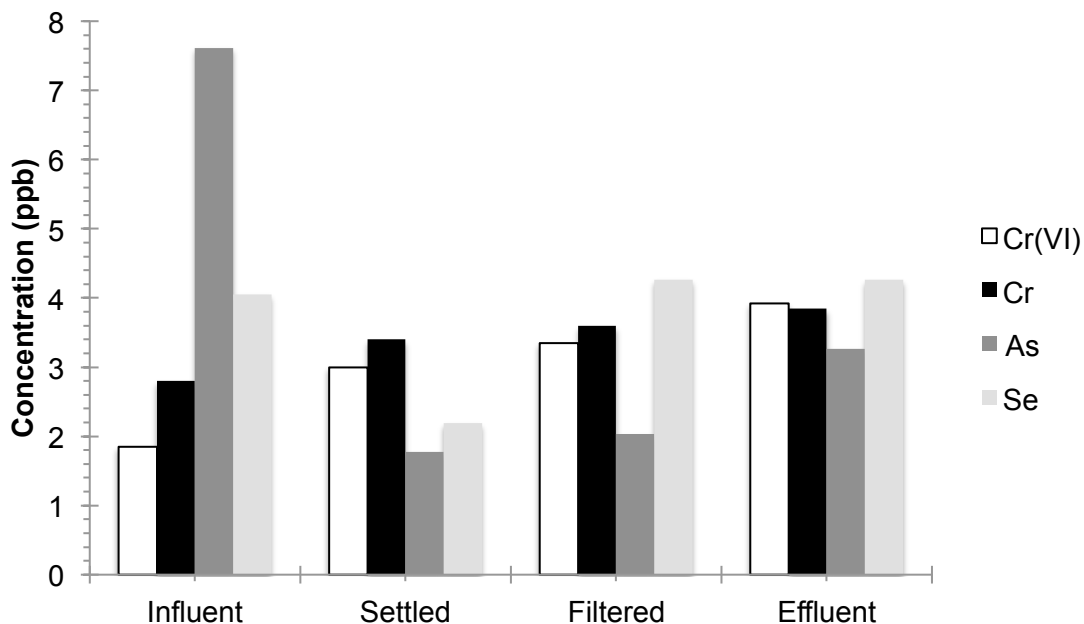
Figure 2.6: Average Metal Concentrations at Chandler WTP

2.4 Task 2- Assessment of Treatment Technologies for Hexavalent Chromium

Our sampling results indicate that chromium and selenium levels within SRP waters are approaching the regulatory limits and may require treatment in the future. Within water treatment facilities, Cr(III) can be precipitated as a hydroxide and removed as a sludge. However, since our sampling results indicate that 1) most of the chromium present in SRP water is in the hexavalent state, and 2) chlorine can easily oxidize Cr(III) to Cr(VI). Therefore, treatment strategies were directed towards hexavalent chromium reduction and removal. In our studies, only total selenium concentrations were analyzed. The reduced form of selenium, selenite, is easier to remove than selenate. Therefore we focused on removal strategies for selenate. Removal of Cr(VI) and Se(VI) using chemical reductants, and sorbents.

2.4.1 Chromium Removal Using Reactive Iron Coagulation

Hexavalent chromium can be reduced to Cr(III) in the presence of ferrous ion in the following reaction:

$$CrO_4^{2-} + 3Fe^{2+} + 8H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \qquad \textbf{Equation 2.1}$$
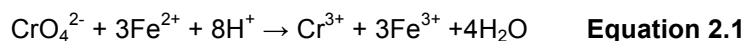
This reaction results in precipitation of $Cr(OH)_3$ by ferric hydroxide due to their low solubility at neutral-range pHs. In this study jar tests were performed to understand the dosing requirements for ferrous iron in order to remove Cr(VI) in SRP waters. The effect of ferrous iron on removal of arsenic and selenium was also investigated.

Jar Test Methods

A series of jar tests were performed at different ratios of ferrous sulfate to chromium. For these jar tests, a mixture of SanTan A and B well water was used to obtain a representative matrix that is present within the SanTan facility. This well water was then spiked with 15 ppb Cr(VI) (0.03 µM). Different molar ratios of Cr(VI) to ferrous iron ranged from 1:10 to 1:75 (of excess iron) to observe Cr(VI) reduction/removal. Ferrous sulfate heptahydrate was used to make stock solutions daily. A jar testing apparatus was used. 2 L of the well water was spiked with 15 ppb Cr(VI) and put into jars. During rapid mixing (300 rpm), ferrous sulfate stock was spiked at desired doses for one minute. After one minute, jars were allowed to flocculate at 50 rpm (slow mix) for two minutes. There were no visible flocs observed since the chromium and iron levels were so low. Chlorine was then added to the jars to ensure that all ferrous iron was oxidized to ferric iron prior to sample filtration in order to protect the analytical equipment from particulate ferric iron. Chlorine was dosed according to stoichiometric demand as described by the equation below.

$$\tfrac{1}{2} HOCl + Fe^{2+} + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2} Cl^- + \tfrac{1}{2} OH^- \qquad \textbf{(Equation 2.2)}$$
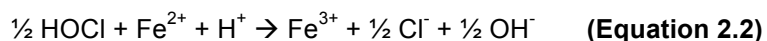
Samples were then filtered with a 0.45 µm cellulose membrane, and analyzed for hexavalent chromium using the IC with post-column reaction, and total chromium using the ICP-MS.

Jar Test Results

Jar tests were conducted at pH (initial and final) ranging from 7.6-7.9. Figure 13 shows that substantial Cr(VI) reduction can be achieved using ferrous sulfate doses. At a 75:1 ratio of

ferrous to hexavalent chromium, over 90% reduction is achieved. Total chromium levels were simultaneously reduced, most likely due to trivalent chromium's lower solubility within this pH range.
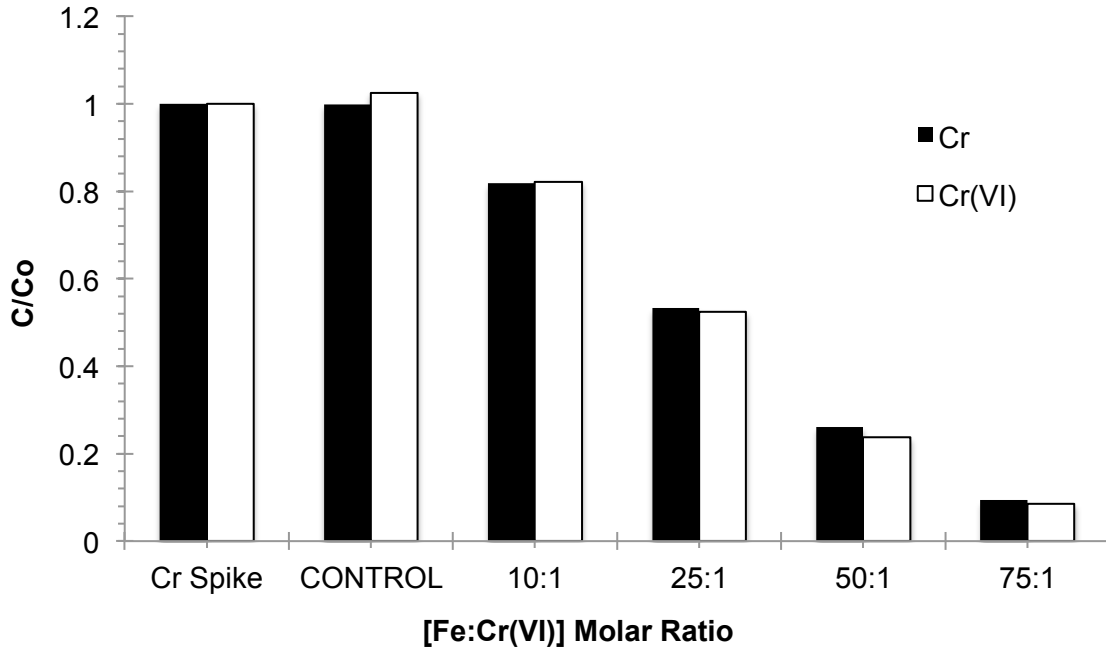
Figure 2.7: Chromium removal in jar tests with ferrous sulfate

Since these results showed that ferrous sulfate could achieve chromium removal, another jar test was performed in SRP well water spiked with 15 ppb of Cr(VI), As, and Se. The jar test pH ranged from 7.7-7.9. The same doses of ferrous sulfate were applied in relation to the Cr(VI) initial concentration. Figure 14 shows the results of the 15 ppb Cr, As, and Se jar test. About 90% of the chromium was still removed at the highest dose of 75:1, and almost 50% of the arsenic was also removed at this dose. These results show that reactive iron coagulation is an effective method for removing both chromium and arsenic from SRP well waters (coprecipitation). However, even with the highest iron dose, selenium levels remained unchanged during the treatment, indicating that this method does not remove selenium.
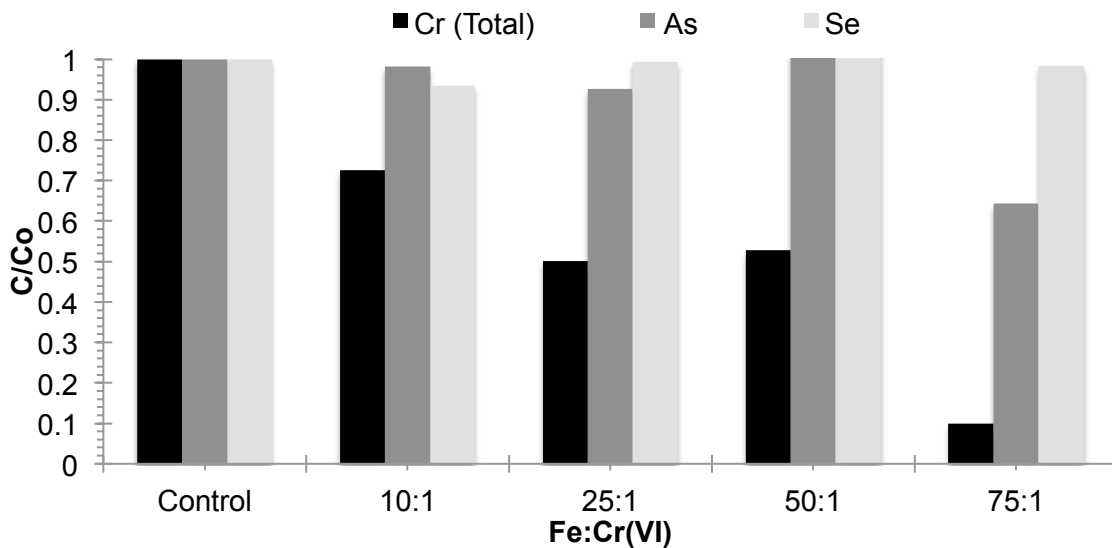
Figure 2.8: 15 ppb Cr, As, Se Jar Test

2.4.2 Chromium Removal using Reduction with Bisulfite

Sodium bisulfite (Na_2SO_3) is used at the SanTan plant by SRP as a de-chlorinating agent with a system concentration of 0.5-3.0 mg/L and discharge concentrations up to 2.2 mg/L as the sulfite ion. It is also often used at 1-1.3 times excess (to chlorine) by SRP. Sodium sulfate, bisulfite, and metabisulfate have been shown to act as very effective chemical reductants of Cr(VI), with fast and complete reduction at pH 2-5 (Beukes 1999, Barrera-Diaz 2012). However, the pH of the SRP waters usually ranges from 7.6-8.6 and it is not clear how effective Na_2SO_3 would be for chemical reduction of Cr(VI) at these pH values.

Plant Tests

To test the effectiveness of sulfite for removal of Cr(VI) in SRP waters, the chromium levels in the cooling tower blowdowns at SanTan and Kyrene plants were monitored when the sodium bisulfite pumps were turned on. The oxidation-reduction potential (ORP) was allowed to reach a stable level before turning on the bisulfite pumps in order to feed the cooling tower blowdown water holding tank. Figure 16a shows the sampling results from the Kyrene plant (sampling date April 3, 2013) before and after the bisulfite was introduced. The Cr(VI)

27

concentration fell from almost 3 ppb to a non-detectable level after the bisulfite was introduced. The levels of arsenic and selenium were not affected. Figure 16b shows the sampling results from the SanTan plant (averaging the results from sample dates Dec. 4, 2012, Jan. 7, 2013, and Jan. 17, 2013). The hexavalent chromium levels were only slightly reduced with the bisulfite treatment. The higher levels of Cr(VI) during this sampling period (almost 20 ppb) may have required a higher concentration of residual bisulfite than was available in the waters at this time. Nonetheless, these results along with the laboratory tests indicate that Cr(VI) can be effectively reduced given the adequate bisulfite dosage.
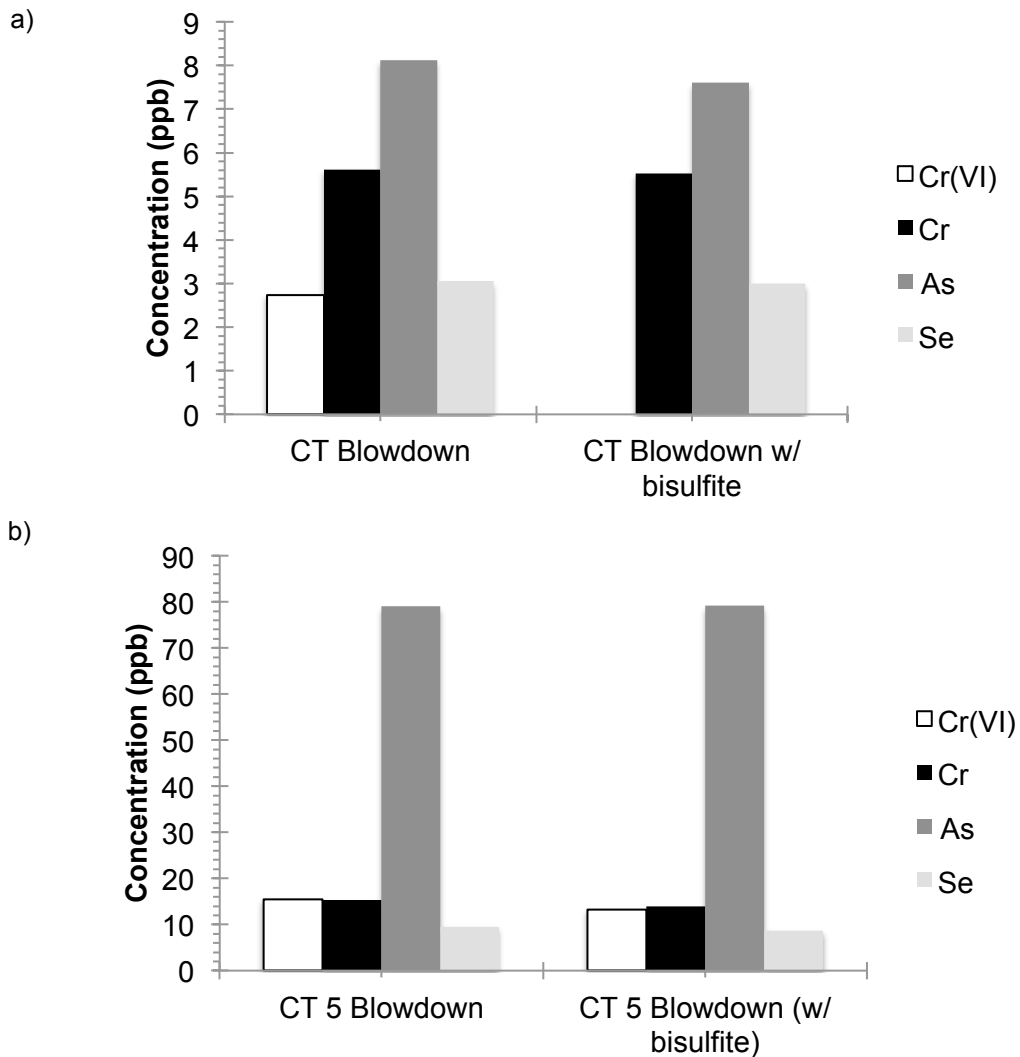
Figure 2.9: Chemical reduction of Cr(VI) with sodium bisulfite in the cooling tower blowdown (a) Kyrene generating facility, (b) SanTan generating facility.

2.5 Conclusions

Important findings from this project include:

- o All metals were observed to be concentrated 4-5 times within the cooling tower blowdown from makeup water; indicating a waste stream requiring treatment prior to discharge into surface waters. These levels are above Arizona discharge limits, and as discharge limits continue to become more stringent, more advanced treatment will be required to comply with permits.

- o It is possible that there are sources of Cr and Se within the water treatment facilities, e.g. potentially within chemical feeds or chromium treated wood. It is thought wooden slats, treated with chromium, are found within the Kyrene Generating Facility's cooling towers. Elevated levels of chromium found within the Chandler Water Treatment Plant suggest certain chemical additions may be introducing unwanted chromium into the system, which could be avoided by choosing an alternative chemical.

- o Chlorine present in water will oxidize remaining Cr(III) to the more toxic and persistent pollutant, Cr(VI). Chlorine is added to cooling tower water to reduce biological growth within the tower. It is evident that the Cr(III) was oxidized by this chlorine because all present Cr within the blowdown water was present as Cr(VI). A potential Cr(VI)-specific regulation of drinking water may result in a Cr(VI)-specific discharge regulation, which would require further treatment.

- o Through utilizing adequate ferrous sulfate doses and mixing, chromium can be successfully removed by ~90% and arsenic by nearly 50% within cooling tower blowdown water via traditional coagulation, precipitation. This process produces solids or precipitated metals, which require proper handling and disposal. Although effective for chromium and arsenic, selenium is not removed via ferrous sulfate, and requires an alternative treatment technology.

- Bisulfite was found to be effective for reducing Cr(VI) to non detect levels at the Kyrene Generating Facility at pH 8.5. This reduction successfully reduced 2.5 ppb of Cr(VI) at the plant, representative of full-scale operating conditions. Should a Cr(VI)-specific discharge limit be enforced within discharge permits, bisulfite may be capable of reducing Cr(VI) to appropriate levels within blowdown waters.

CHAPTER 3

TIME-DEPENDENT HEXAVALENT CHROMIUM MONITORING

Hexavalent chromium (Cr(VI)) and arsenic (As) are of concern to many communities of Arizona. I developed the concept of a Cr(VI) time-integrated passive sampler using an ion exchange (IX) resin, and validation in both the lab and field. Time resolved grab samples and time integrated samples were collected at the Chandler, AZ Water Treatment Plant (WTP) which intake surface water impacted by GW containing Cr(VI) and As. Results show that trace metal concentrations ranged from 0.5 to 2 ppb for Cr(VI) and 3 to 5 ppb for As over a 7-day period, indicating that a single grab samples may not be as representative of water quality as time-integrated samples, which can be obtained using ISCO or passive samplers. ISCO samplers are expensive and accumulate many samples all requiring preservation and quantification, whereas passive samplers are simpler and generate a single sample.

3.1 Methods & Materials

Sampling Location: Chandler Water Treatment Plant

Figure 3.1 shows the location of the Chandler Water Treatment Plant, the locations of its many groundwater wells, and it's proximity to the Consolidated Canal (the plants surface water source). The amount of intake water from groundwater and surface water changes routinely throughout the year to abide by AZ-specific water-right laws. The particular blend of surface and groundwaters changes the plant influent water quality, as will be further discussed within this chapter. The Chandler Water Treatment Plant was selected as the location for these sampling events because of interesting sampling data obtained during the SRP Project (Chapter 2). Results showed that there was a source of Cr somewhere within the plant, as Chandler routinely discharged higher Cr levels than found in plant intake water (Figure 2.6).
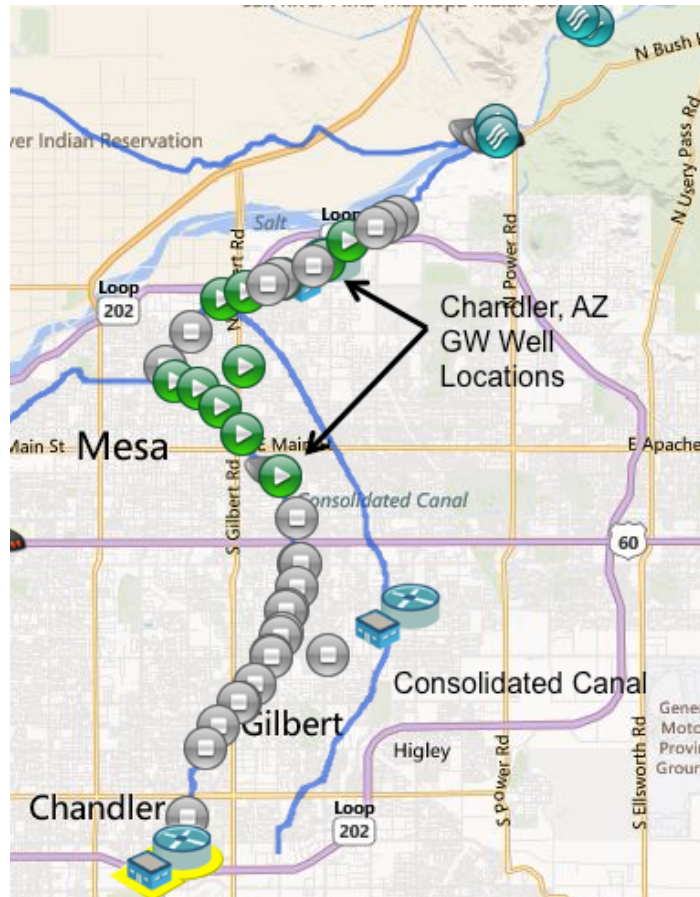
Figure 3.1: Chandler Water Treatment Plant's source water; groundwater well locations, and consolidated canal intake location.

ISCO Sampling

An ISCO sampler (6712 Full-Size Portable Sampler) shown in Figure 3.2, was programmed to collect 800-mL grab samples every 4 hours over the course of 7 days from the Chandler Water Treatment Plant (provided by Arizona State University's CAP LTER). There were two separate sampling events; May 29-June 6 2013 which employed 2 ISCO samplers to collect influent and effluent water samples, and October 15-October 21, 2013 which employed 1 ISCO sampler to collect effluent samples. For influent samples, the ISCO sample collection line was dropped into the treatment plant inlet located on a canal, directly behind the plant's mechanical bar screen (Figure 3.2 (a)). For effluent samples, the intake for the sampler was installed within a finish water (post-chlorination) channel housed inside one of the water testing room at the plant. Over the

course of the 7-days, the ISCO Sampler was connected and powered by a 12 Volt battery and replaced routinely. Nalgene-grade sample bottles were pre-washed with 10% Nitric Acid prior to collection. In the Standard Programming Mode, the sampler was programmed to draw an 800-mL grab sample every 4 hours. Samples were collected over the course of 7 days and analyzed for hexavalent chromium, total chromium, arsenic, and selenium.
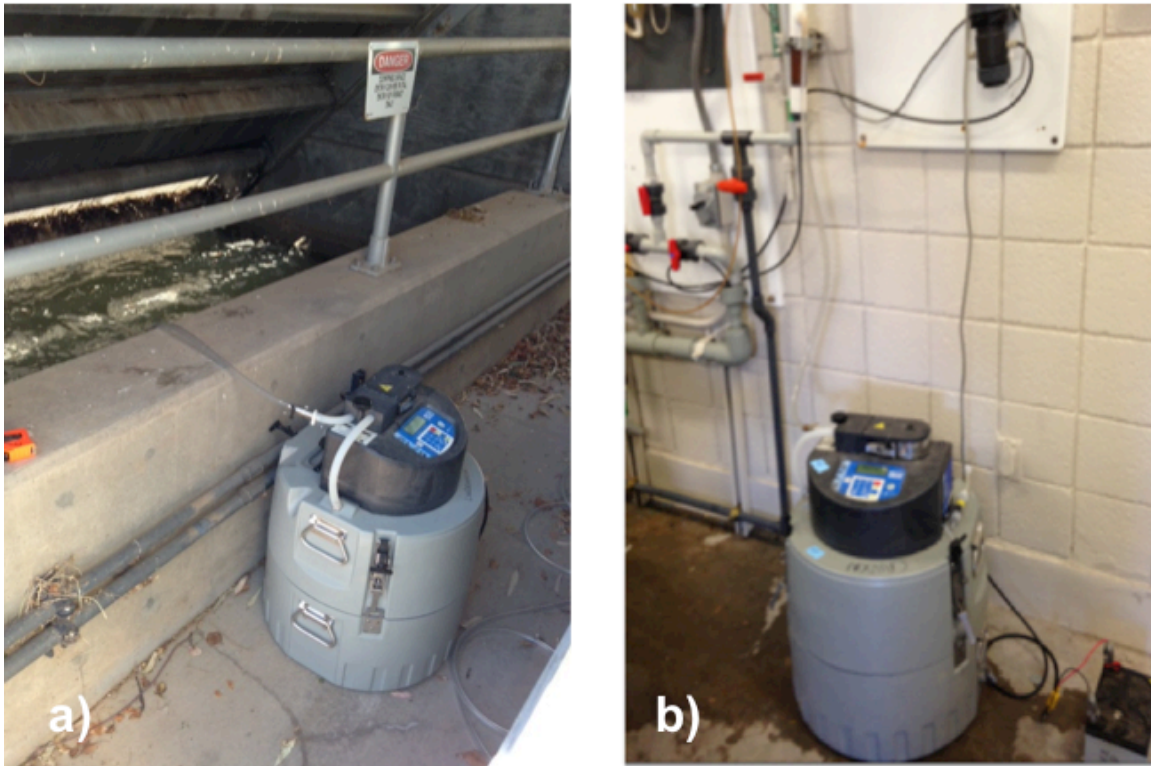
Figure 3.2: ISCO Samplers installed at Chandler WTP at a) plant intake and b) effluent, finish water.

Passive Sampler Design

Two different ResinTech® types of anion exchange media were evaluated for Cr(VI) removal/concentration (Table 3.1). A weak base anion (WBA) exchange resin (SIR-700; ResinTech) has a manufactured screen size distribution of 12 to 50 mesh size. A strong base anion (SBA) exchange resin (SIR-100; ResinTech) has a screen size distribution of 16 to 50, nominal. Both resins were ground, and wet sieved to a sieve size #60-#80 with a mortar and pestle to fit into a glass column (2.5 cm OD, 1.1 cm ID) to maintain $d_{column}/d_{particle} > 75/1$.

Table 3.1: Ion Exchange Resin Screening

Weak/Strong Base	Resin Name	Matrix	Functional group	Selectivity (Reported)
Weak	SIR-700	Epoxy polyamine	*Proprietary amine*	Chromate and dichromate
Strong	SIR-100-HP	Styrene w/DVB	$R\text{-}N\text{-}R_3\text{+}Cl^-$	Nitrate
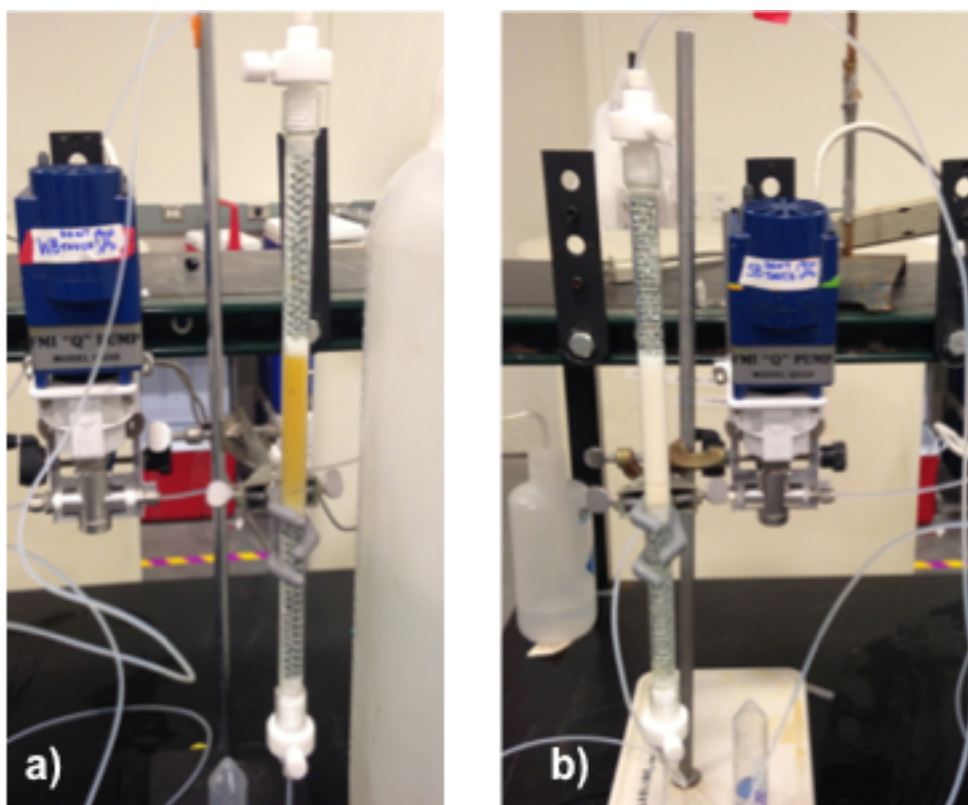
Figure 3.3: Packed glass columns a) WBA (SIR-700) b) SBA (SIR-100)

A lab water matrix was used to validate removal efficiencies for each resin. Deionized water buffered with 2.5 mM sodium bicarbonate (Polystormor Ar (ACS), >99.7%) buffer (to maintain pH=7.8) was spiked with 30 ppb Cr(VI) (Potassium dichromate,>99%, Sigma Aldrich). Spiked water was pumped downward at a flow rate of 15 BV/h (2 mL/min) using a pump (FMI Model QG1150) (Figure 3.3), which corresponds to an empty bed contact time of 4 minutes and

hydraulic loading rate of 0.52 gpm/ft^2 . Each column was loaded for >500 BV.

The SBA resin was rinsed w/5% NaCl to mobilize Cr(VI) from the resin. For a passive sampler to be representative of water quality, it is important that the mass of chromium, which has been concentrated within the column during flow-through to be adequately accounted for. A high ionic strength, 5% NaCl solution was passed through the SIR-100 column at a speed of 5 BV/hr (0.26 mL/min) over 7.5 BV in order to elute off the concentrated chromium, and regenerate the column. The sodium chloride (NaCl, ≥99%, Sigma Aldrich) solution was made in 18MΩ deionized water. A small medical pump was used to achieve this low flow rate.

The collected high ionic strength brine solution was then filtered using a 0.45 um cellulose membrane, and analyzed for total chromium. The brine was diluted 50-times in order to protect the ICP-MS. Based on a mass balance of influent chromium concentrations, the theoretical mass of chromium that should have eluted off into the brine solution was compared with measured chromium concentrations within the brine (Figure 3.4).

Because the SIR-700 (its quaternary amine functional group) has such a high affinity for chromium species, the elution with 5% NaCl used for the SIR-100 would not have been able to displace (recover) the chromium. To analyze the chromium for the SIR-700, the resin was taken out of the column, and Microwave Digested using Nitric Acid. Because resins are polymers, SW 896 EPA Method 3052, Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices, was used. This method is reported to be applicable for the chromium analyte. 100 mg of resin was used to digest (Figure 3.4).

Weak Base Anion Exchange

2500 BV C_{INF} (Cr)   750 BV

Strong Base Anion Exchange

2_{WBA}) Collect resin & digest with HNO_3^-

2_{SBA}) 5% NaCl @ 5 BV/hr

Microwave Digest (EPA Method 3052)

100 mg SIR-700

SIR-700

SIR-100

7.5 BV NaCl

C_{EFF} (Cr) = 0
(No Breakthrough)

3) Analyze for Cr

Measured Mass$_{Brine}$=
[$C_{Cr,Nitric}$]×[Volume$_{Nitric}$]×[Mass of Resin Bed/100 mg]

Measured Mass$_{Cr, SBA}$=
[$C_{Cr,brine}$]×[7.5 BV]

4) Compare results with Mass Balance Calculation

Theoretical Mass$_{Cr, WBA}$=
[Cr$_{INF}$]×[2500 BV]×[BV]

Theoretical Mass$_{Cr, SBA}$=
[Cr$_{INF}$]×[750 BV]×[BV]

Figure 3.4: Conceptual Operating parameters for WBA and SBA resins

3.2 Results

3.2.1 ISCO Sampling Results

Figures 3.5-3.10 shows results from two, 7-day ISCO sampling event. The first sampling event took place from May 29-June 5 of 2013 (Figures 3.5-3.8). Both influent (Figures 3.5 and 3.6) and effluent (Figures 3.7 and 3.8) samples were taken (2 ISCO samplers). Influent chromium levels fluctuated between 0.5 and 1.6 ppb. Average Cr concentration over the course of 7 days was 1 ppb +/- 0.2. Arsenic levels fluctuated between 4.7 and 7.2 ppb, averaging 6.15 +/- 1.5 ppb. Selenium levels fluctuated by nearly a factor of 4, between 1.4 and 4.7 ppb, averaging 2.3 +/- 0.9 ppb.
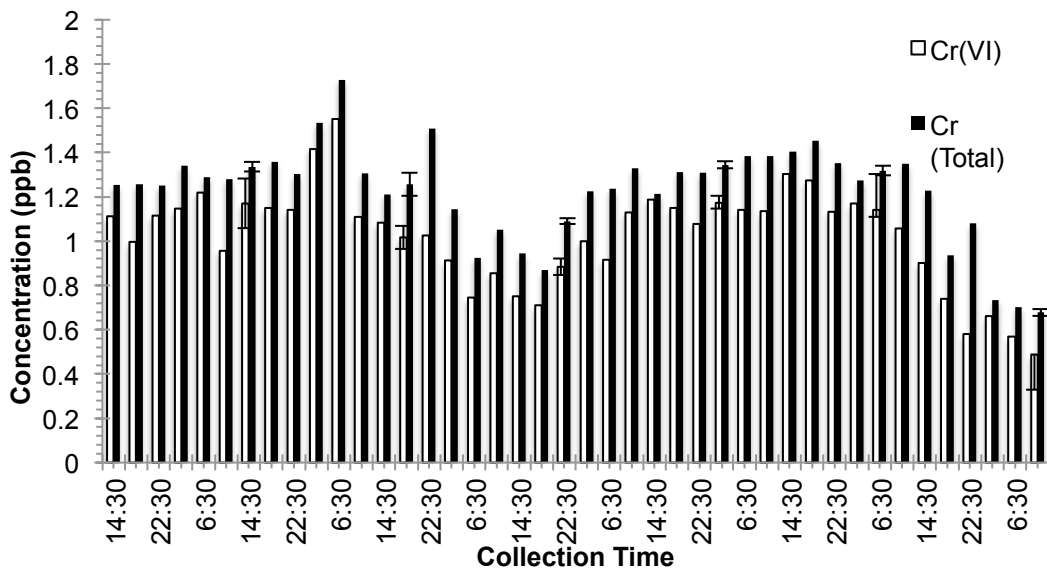
Figure 3.5: Chandler, AZ WTP Influent ISCO Chromium Sampling, May 29-June 6, 2013 (error bars indicate 1 standard deviation of triplicate samples)
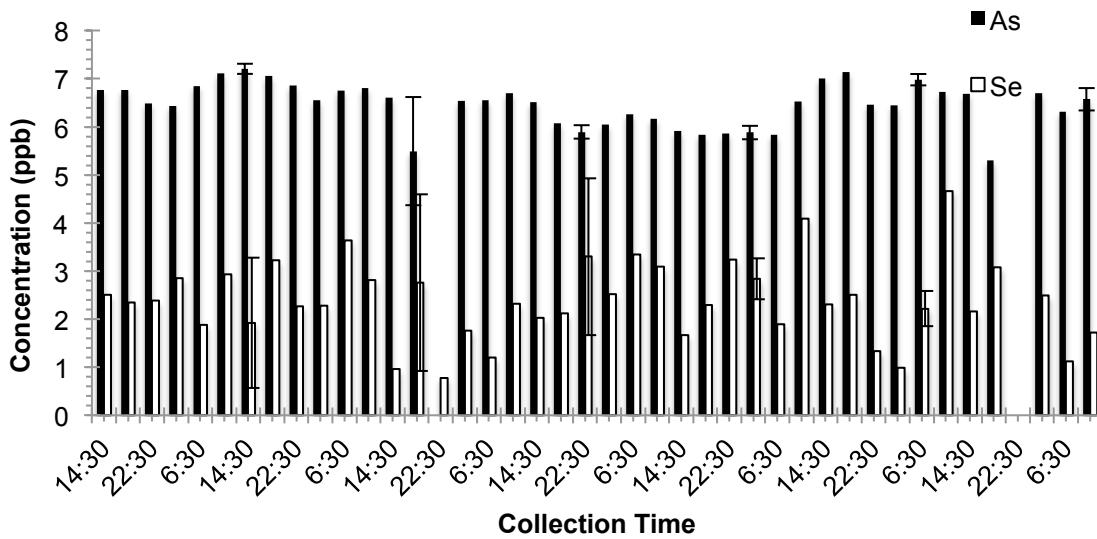
Figure 3.6: Chandler, AZ WTP Influent ISCO Arsenic/Selenium Sampling, May 29-June 6, 2013 (error bars indicate 1 standard deviation of triplicate samples)

Figures 3.7 and 3.8 show effluent metal concentrations. Chromium concentrations varied between 0.82 and 1.6 ppb, averaging 0.9 +/- 0.2 ppb. These effluent chromium concentrations are not very much lower than average influent Cr levels (1 ppb). Arsenic levels varied between 1.9 and 3.2 ppb, averaging 2.6 +/- 0.3 ppb. Arsenic levels in the finish water are substantially

37

lower than average influent concentrations (6.5 ppb), indicating substantial As removal within the plant. Effluent selenium levels ranged from 1.8 to 8.1 ppb, averaging 4.6 +/- 1.5 ppb. This is a wide range for Se in effluent waters. This is actually higher than the influent concentration, 2.3 ppb Se. This shows the potential for sources of Se to be within the plant, e.g. chemical feeds, or specific infrastructure materials within the plant.
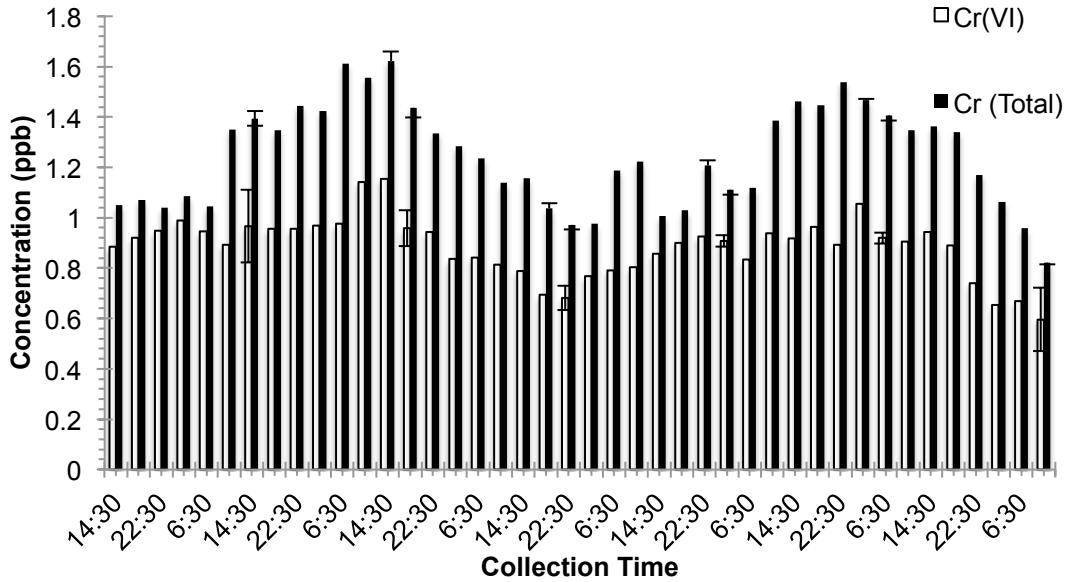
Figure 3.7: Chandler, AZ WTP Effluent ISCO Chromium Sampling, May 29-June 6, 2013 (error bars indicate 1 standard deviation of triplicate samples)
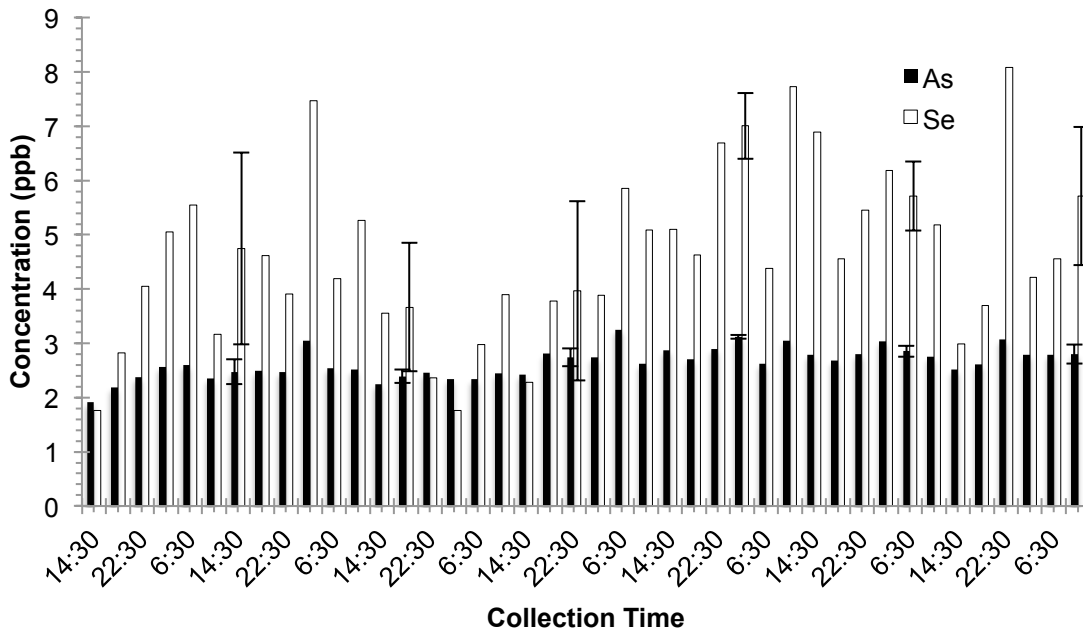
Figure 3.8: Chandler, AZ WTP Effluent ISCO Arsenic and Selenium Sampling, May 29-June 6, 2013 (error bars indicate 1 standard deviation of triplicate samples)

The second ISCO Sampling period occurred from October 15-21, 2013. Only effluent (finish water) samples were collected at this time. As shown in Figure 3.5, all chromium in the Chandler WTP effluent is present as hexavalent chromium. Over 7 days, chromium levels fluctuated by nearly a factor of 4, between ~0.5 ppb and >2 ppb, averaging 1.4 ppb +/- 0.6. Cr(VI) levels are slightly higher than total Cr, because of separate analytical measurements, and standards. This shows that water quality does vary over a 7-day period. This average chromium concentration is slightly higher than the average effluent concentration during the June ISCO sampling event (1 ppb), and is most likely attributed to more groundwater intake in October, compared to June. Considering a potential Cr(VI)-specific MCL for Cr(VI) of 1 ppb, based on this data, the average time integrated sample would be above the MCL while 33% of the grab samples (from ISCO sampling data) would be below the MCL. This illustrates current reliance upon a single grab sample in order to represent human exposure to Cr(VI) in drinking waters.

39
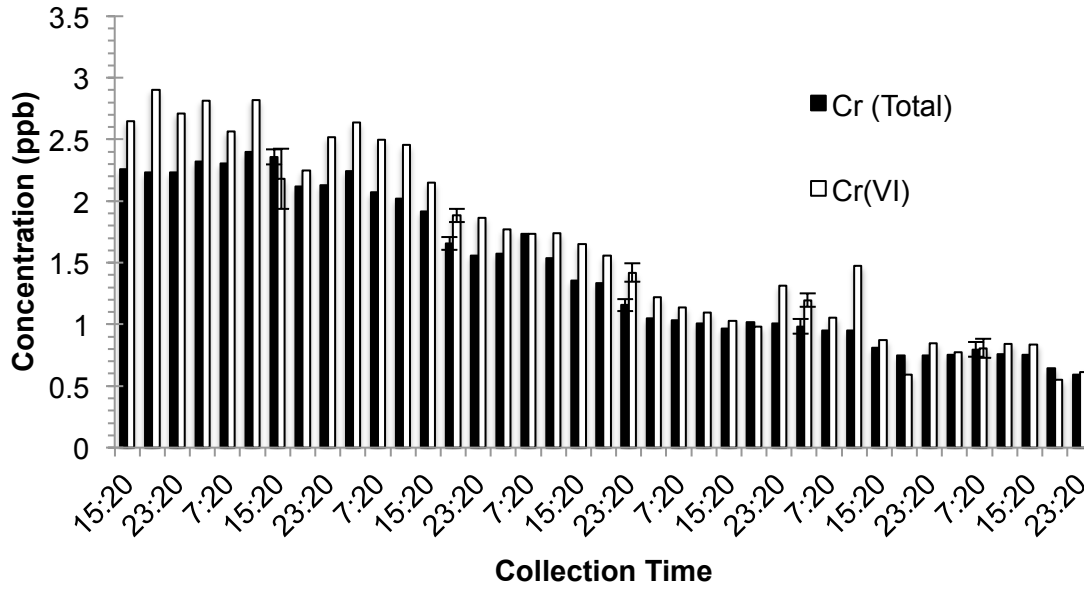
Figure 3.9: Chandler, AZ WTP Effluent ISCO Chromium Sampling, 10/15/13-10/21/13 (error bars indicate 1 standard deviation of triplicate samples)

At the same site, arsenic levels varied from 3.5 to >5 ppb and selenium levels fluctuated from 10 to >19 ppb. Average As concentration over the sampling period was found to be 4.17 +/- 0.65 ppb and average Se concentration was found to be 13.65 +/- 3 ppb. Although not in exceedence of it's MCL (50 ppb), this level of Se is high, especially when compared with influent data from October, showing average Se concentrations to be only ~2.3 ppb. The lowest As concentration was found to be 3.3 ppb and the maximum As was found to be 5.2 ppb. Similar to June's sampling even, As effluent concentrations remain relatively stable indicating the plant's ability to control effluent As.
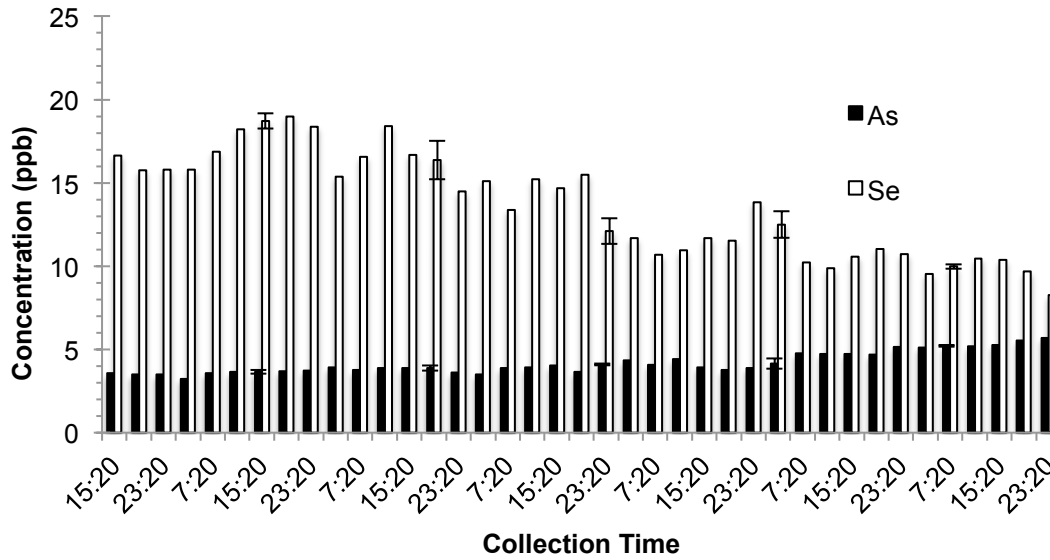
Figure 3.10: Chandler, AZ WTP ISCO Arsenic and Selenium Sampling, 10/15/13-10/21/13 (error bars indicate 1 standard deviation of triplicate samples)

3.2.2 Cr(VI) Passive Sampler Lab Validation

The SBA SIR-100 Column was run for 750 BV using 7 ppb Cr(VI) in 2.5 mM NaHCO$_3$ (pH=7.8). Effluent samples measured for Cr(VI), are shown in Figure 3.11. Less than 5% of the influent Cr(VI) was detected in the column effluent after 750 BV. A total Cr(VI) mass of 43 ug was applied to the column over 750 BV and it is assumed based on no breakthrough of Cr(VI) that all 43 ug was retained on the SBA resin (Figure 3.11). After elution using 7.5 BV of 5% NaCl, this brine solution contained 38.8 ug Cr(VI) (Figure 3.13), or 90.3% of the Cr(VI) was recovered. Achieving only 90% Cr(VI) recovery, rather than 100% recovery, is most likely due to the large (50-times) dilution made on the brine prior to analyzing the sample.
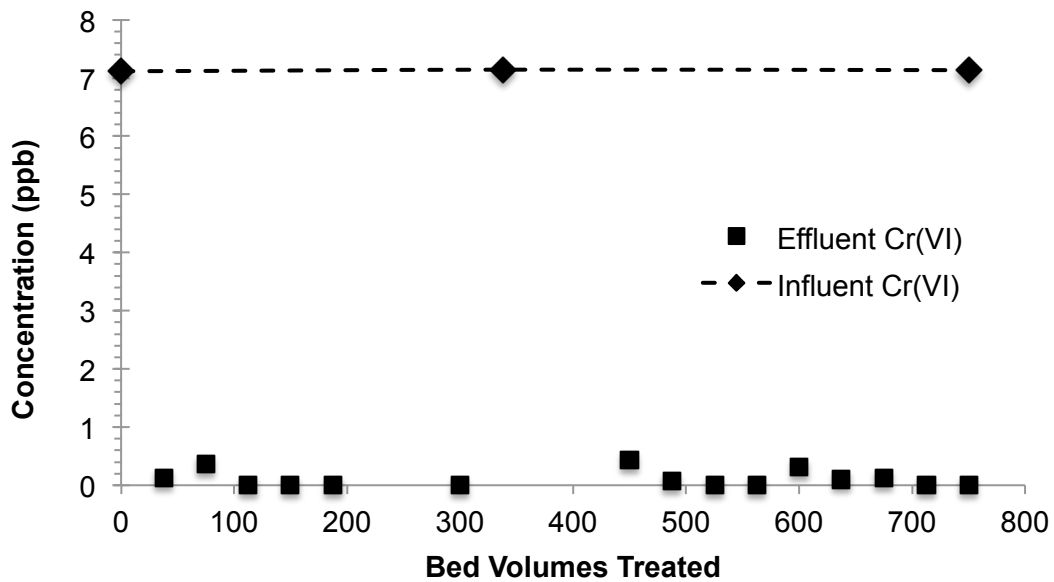
Figure 3.11: SBA Cr(VI) Breakthrough in buffered (2.5 mM sodium bicarbonate) DI water

The WBA SIR-700 column was run for 2500 BV, as it is reported to have a very high

selectivity for Cr(VI). Influent water was similar to that used for the SIR-100 SBA column, which

was DI water buffered with 2.5 mM sodium bicarbonate, and spiked with 12 ppb Cr(VI). Effluent

samples measured Cr(VI), are shown in Figure 3.12. No Cr(VI) breakthrough was observed over

the 2500 BV ran for the SIR-700 resin. A total Cr(VI) mass of 350 ug was applied to the column

over 2500 BV and it is assumed based on no breakthrough of Cr(VI) that all 350 ug was retained

on the WBA resin (Figure 3.12). After digestion with Nitric acid, the acidic solution only contained

101 ug Cr (Figure 3.13), or 29% of the Cr(VI) was recovered. It is possible that only 29% of Cr(VI)

that was recovered from the WBA resin is due to resin that was lost within the glass wool used to

column. Because all of the resin needed to be collected from the packed column, and digested, it

is most likely that a large portion of chromium within the resin bed was lost during the digestion

process.

Due to the high recovery (>90%) of Cr(VI) obtained using the SIR-100 SBA resin, and

due to the ease of elution, compared to a Nitric Acid digestion, the SIR-100 SBA resin was

selected to use for passive sampling of Cr(VI) rather than the SIR-700 and its low recovery (29%).
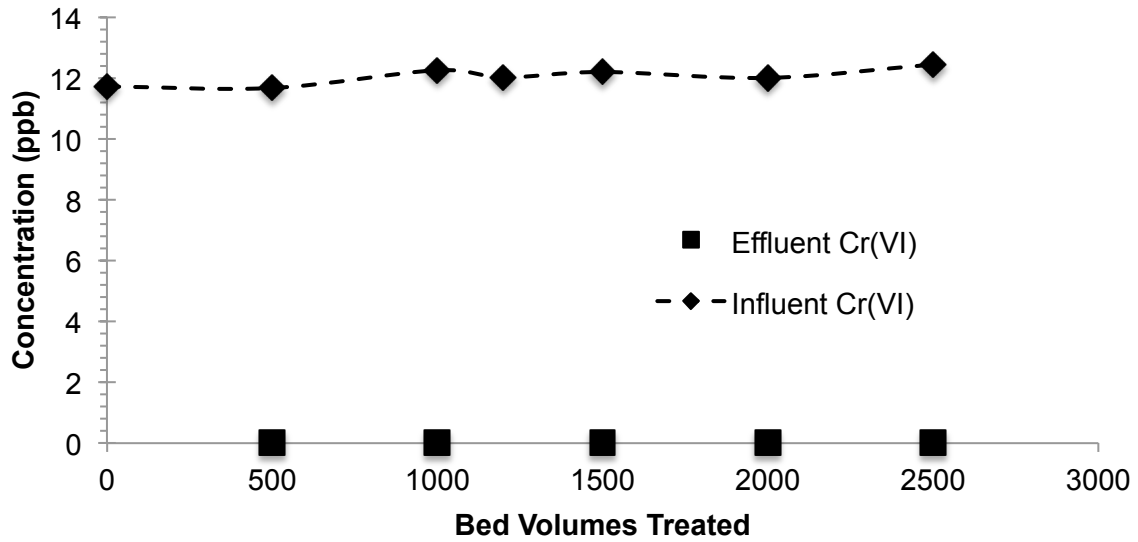
Figure 3.12: WBA Cr(VI) Breakthrough in buffered (2.5 mM sodium bicarbonate) DI water
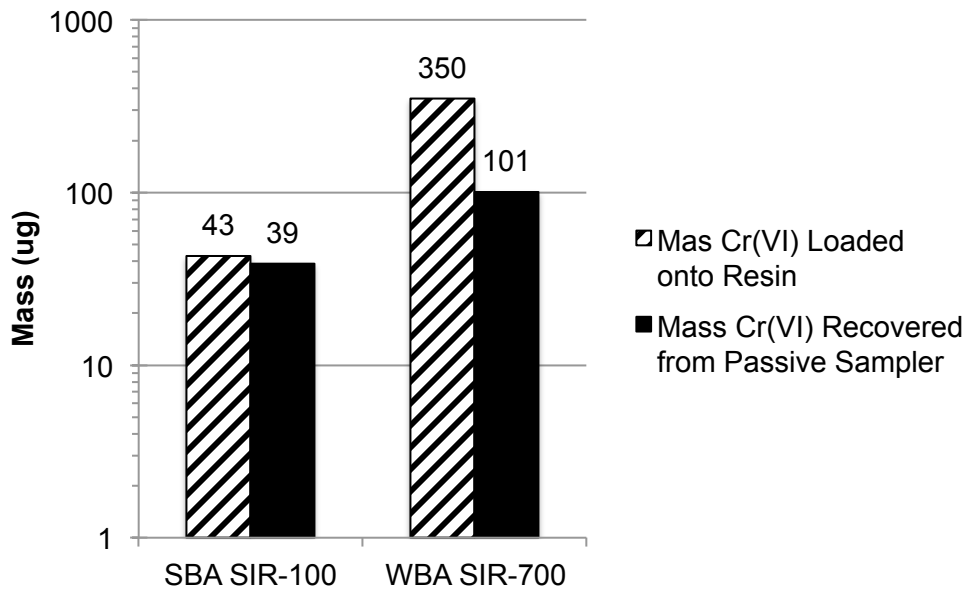
Figure 3.13: Chromium Recoveries for SBA vs. WBA in buffered (2.5 mM sodium bicarbonate) DI water

3.2.3 Passive Sampler Validation at Chandler WTP

Whereas the lab validation used a clear water matrix with constant Cr(VI) influent concentrations, I wanted to validate the system in the field with Chandler WTP water, real water which can have time-variable Cr(VI) concentrations (Figures 3.5, 3.7, and 3.9). To evaluate the performance of the passive samplers at a WTP two new columns were packed with crushed, virgin SIR-100 to the same specifications as the initial resin screening (Figure 3.3 b); The column used previously for initial resin screening (run for 750 BV, and regenerated, as shown in Figure 3.11), was installed and run in parallel with the two newly packed passive samplers. Pictured in Figure 3.14 are the three passive samplers installed at the Chandler WTP, adjacent to another ISCO sampler. Pictured from left to right, are Columns A and B, which are both newly packed with Virgin Resin and are intended to give duplicate results. To the far right is Column C, which is the same column that was run to obtain Figure 3.11 (which has been regenerated one time). The ability of Column C to achieve similar recoveries as Columns A and B would be indicative to whether or not these passive samplers can be used for multiple installments.

Figure 3.14: Passive Samplers Setup at Chandler WTP

Figure3.15: ISCO and Passive Samplers at Chandler WTP

The feed lines for the passive samplers were placed into the same feed used for the ISCO Sampler (A channel containing plant finish water, housed inside of a water quality sampling room). The medical pump was used to draw flow from this feed at a speed of 4.76 BV/hr (0.64 mL/min), which results in 800 BV of water passing through the samplers over the course of the 7-day sampling period (50 more BV than used for lab validation). Flow through the passive samplers began at the same time as the ISCO Sampler drew its first sample (Figure 3.15).

At the end of the sampling event, the passive samplers were brought back to the lab for elution (quantification of Cr over the week's sampling time). Similar to the previous elution scheme, a 5% NaCl solution was passed through each column at a speed of 5 BV/hr (0.67 mL/min) over 5 BV. Samples were then analyzed for total chromium. Figure 3.16 shows the recoveries of the 3 passive samplers. Theoretically, because there was no breakthrough observed during the initial SBA resin screening, it would be assumed that all of the applied Cr(VI) mass on each column would be retained over 800 BV. A total Cr(VI) mass of 9.3 ug was applied to each column, based on average Cr(VI) concentration (1.4 ppb) from ISCO sample results (Figure 3.9). After elution using 5 BV of 5% NaCl, the brine solutions for columns A and B contained 8.6 ug Cr(VI), or 93% of the Cr(VI) was recovered. After elution using 5 BV of 5% NaCl, the brine solution for column C contained 3.9 ug Cr(VI), or only 42% of the Cr(VI) was recovered. These results show that passive samplers made of virgin resin can effectively represent average concentrations of chromium, similar to the performance observed using a clear water matrix in the lab, however they are not as effective during a second cycle of accumulation and regeneration.
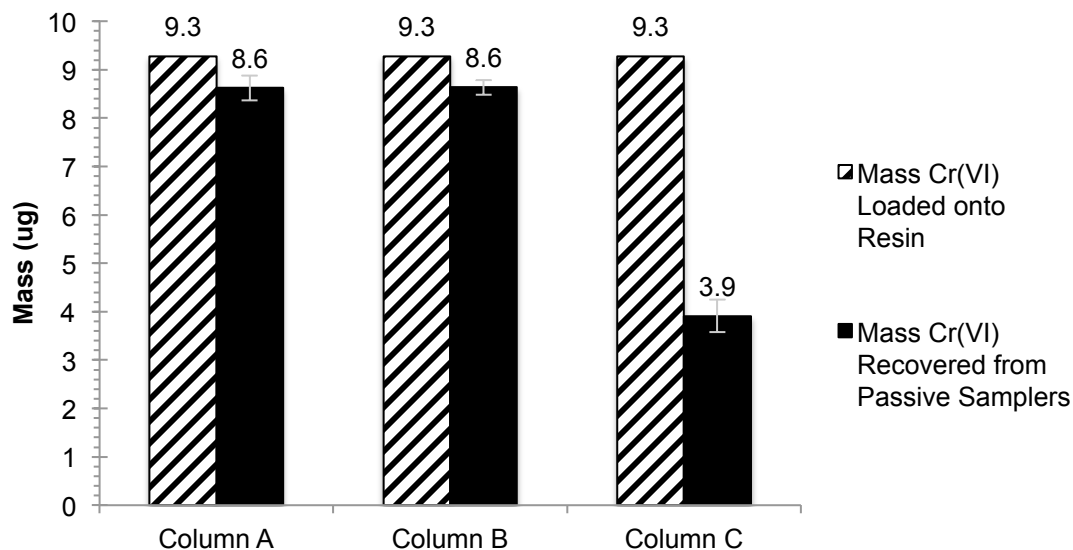
Figure 3.16: Chromium recoveries from passive samplers at Chandler WTP; error bars indicate 1 standard deviation of triplicate samples
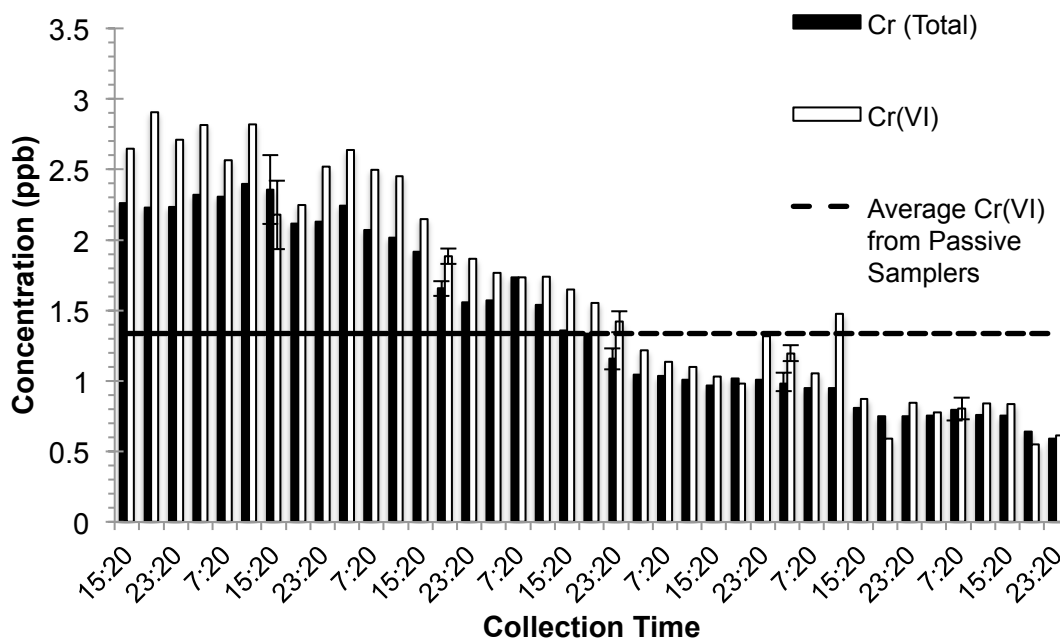
Figure 3.17: Passive vs. ISCO Sampler at Chandler WTP 10/5/13-10/21/13 (error bars indicate 1 standard deviation of triplicate samples)

3.3 Summary and Conclusions

Collecting time resolved grab samples, at the Chandler WTP, using an ISCO sampler indicated that Cr and As can fluctuate significantly over a 7-day period. This indicates that individual grab samples could misrepresent average water quality data. A passive sampler using ion exchange resin was developed and validated against the ISCO sampler at the Chandler WTP. Cr(VI) eluted from the column after the 7-day sampling period and was found to achieve >90% recovery indicating that a passive, inline sampler is capable of representing average, time-dependent water quality data (Figure 3.17).

Specific conclusions include:

- Cr and As concentrations can fluctuate significantly over a 7-day period at water treatment plants, especially at a plant that intakes from a number of different groundwater wells and surface water sources. Specifically, Cr(VI) levels ranged from 0.5-2 ppb at the Chandler Water Treatment Plant showing nearly a 4-time variation. This fluctuating water quality indicates that grab samples may not be representative of true water quality, and similarly, ecological and consumer risk over periods of time.

- In the lab a passive sampler, a column packed with SBA (SIR-100) resin, was able to achieve >90% recovery of applied Cr(VI) based on a mass balance, by using an elution scheme with sodium chloride solution. This recovery is most likely not 100% due to the large dilution factor (100x) used to analyze collected eluent. Comparatively, a passive sampler using WBA (SIR-700) resin was only able to achieve >40% recovery through microwave acid digestion of the resin, most likely due to the loss of chromium mass in glass wool used to pack the column. Due to the high recovery, and ease of quantification compared to a microwave acid digestion, utilizing SBA for Cr(VI) passive sampling was selected to be tested in the field.

- Results obtained from the passive (SBA) sampler employed at Chandler WTP complimented the continuous grab samples collected by the ISCO during a 7-day period. This proves that in-situ passive samplers are capable of representing fluctuating water

quality; perhaps more representative of actual exposure levels compared to period grab

samples.

CHAPTER 4

ANION EXCHANGE BRINE TREATMENT FOR ARSENIC AND CHROMIUM

REMOVAL BY REDUCTIVE COAGULATION

Coachella Valley Water District (CVWD) draws its drinking water supply from over 100 groundwater wells to serve is population of 30,000. Hexavalent chromium (Cr(VI)) and arsenic (As) occurs naturally in CVWD groundwaters, and if the California Department of Health (CDPH) promulgates a MCL for Cr(VI), more extensive treatment will likely be required.

CVWD initiated a project for the Water Research Foundation (WRF) and contracted an engineering consulting firm, (Arcadis). Arcadis consulted Arizona State University to lead the bench-scale work for brine optimization of the strong base anion (SBA) exchange treatment scheme. SBA ion exchange (IX) optimization involves the reuse of spent brine to minimize costly disposal volumes of hazardous waste and reduce overall treatment/operational costs. Bench-scale studies were conducted in the ASU labs, focusing on limits of spent brine reuse as well as identifying treatment needs for brine prior to reuse. Specific objectives of the bench-scale testing to optimize SBA brine management for CVWD include:

- Characterizing resin performance with and without direct brine reuse;

- Monitor As and Cr(VI) breakthrough and peaking following regeneration;

- Determining the potential for spent brine recycling with and without treatment to remove As and Cr(VI);

- Optimize As and Cr(VI) removal from recycled spent brine using chemical precipitation with a ferric/ferrous blend.

4.1 CVWD Background Information

CVWD currently treats groundwater at three water treatment facilities (combined capacity of 13 MGD) using SBA technology specifically for arsenic removal. Based on monitoring at the SBA facilities, SBA treatment is also effective for Cr(VI) removal. Two of the largest CVWD SBA treatment facilities have similar design characteristics. As an example, one of the facilities (6806 SBA IXTP) is described below.

Groundwater is pretreated at the facility using a 5-um bag filter system. A 4,000 gpm IXTP consists of two 2,000 gpm treatment trains, each consisting of 16 vessels with a sequential regeneration control system, rinse and waste brine processing. The 16 vessels are operated in parallel and are regenerated automatically based on a time in service that is programmed into the logic controller. Each vessel holds 25 cubic feet of resin, totaling about 185 gallons (Table 4.1). The vessels are operated in down-flow mode. Regeneration typically occurs around 1300 bed volumes (BV) with sodium chloride (NaCl).

Table 4.1: CVWD SBA Vessel Description

Criteria	Treatment
Maximum Flow Rate (Q_{max})	2,000 gpm
Average Fow Rate (Q_{ave})	1,500 gpm
Maximum Operating Pressure	150 psig
Vessel Diameter	3 ft
Empty Bed Contact Time at Q_{max}	2.2 min
Hydraulic Loading Rate	12.5 gpm/ft^2
Estimated Resin Bed Life at Q_{ave}	1,200 BV

The major cost of SBA operation is the disposal of hazardous spent brine, which requires special handling. The brine generated at the CVWD facilities is treated in a brine processing unit (BPU) which allows the liquid brine to be disposed of as non-hazardous waste. The solid waste is considered hazardous, and must be sent to a hazardous waste site many miles offsite.

The current BPU facility utilizes co-precipitation of metals (As and Cr) using a ferric/ferrous iron blend, followed by a decant and filtration process. The treated (liquid) brine passes the California Waste Extraction Test (WET) and federal Toxicity Characteristic Leaching Procedure (TCLP) and is characterized as non-hazardous, but must be trucked over 100 miles to a receiving facility that discharges into an ocean outfall. This shipment occurs 2 to 3 times per

week from each CVWD SBA facility. The sludge generated from this precipitation exceeds the As and Cr threshold for WET and must be treated as non-RCRA hazardous waste. Brine disposal is the most costly element of operating the facilities. If the RCF is successful, there is opportunity for the utility to significantly reduce operating costs.

It is thought that brine produced through the regeneration of the SBA IX vessels can be collected, and reused multiple times, and by doing so reduce the costs associated with the trucking of waste materials (Figure 4.1). This would reduce the volume of hazardous waste and would also reduce salt use and brine production by reusing spent brine prior to treatment and final disposal. In addition, many basins across California are focusing on salt management, so minimization of salty brine waste could be an important step towards achieving statewide salt level control.
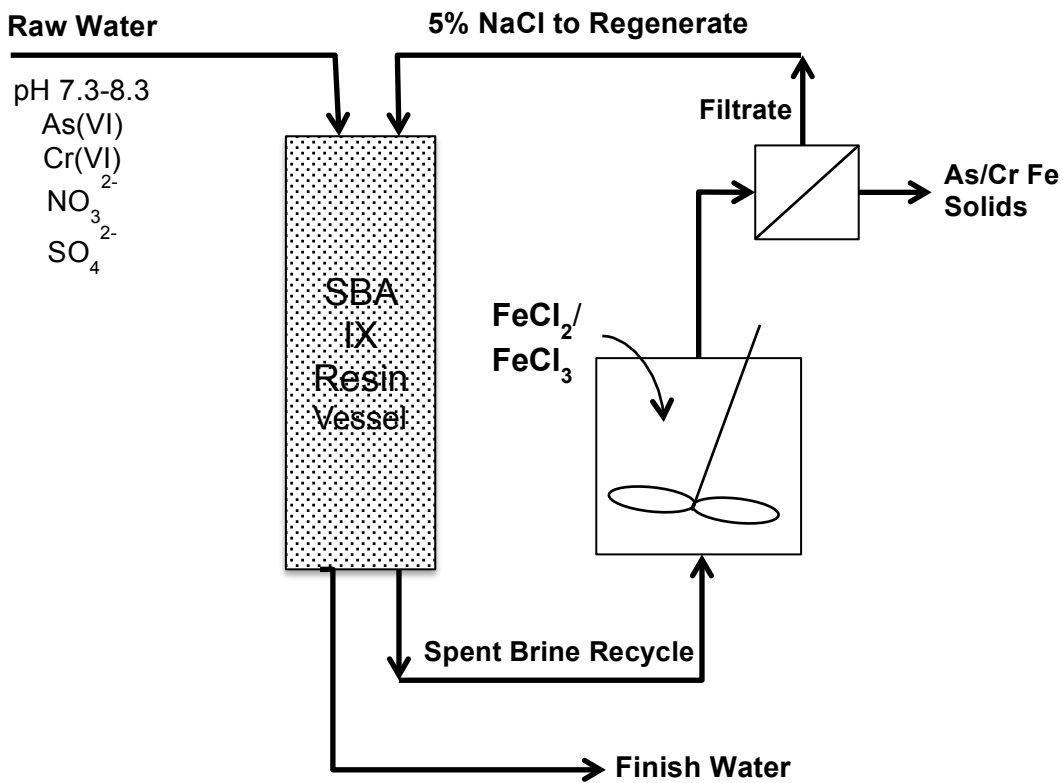
Figure 4.1: Conceptual diagram of brine recycle using reactive iron for SBA IX

4.2 Materials & Methods

4.2.1 Column Operating Procedures

      SBA columns were setup and operated under conditions similar to existing CVWD SBA facilities. The SBG-1 (Resintech) SBA resin was received from the manufacturer with a screen size distribution of 12 to 50 mesh size, and the SIR-100 resin was received with a screen size distribution of 16 to 50, nominal. Both the WBA, SIR-700 and SBA, SIR-100 were ground, and wet sieved to a sieve size #60-#80 (<220 um) with a mortar and pestle. Sieve #200 was used to catch remaining fines. Resins were ground to achieve a 75:1 ratio, of column diameter to resin size, in order to avoid wall effects through the column.

      Columns were operated similar to that used previously (Yang, et al, 2013). Yang, et. al used a commercially available SBA resin, Purolite A-520E, specific towards nitrate removal. A 30-mL BV was used, and packed into glass columns (OD=2.5 cm; ID=1.1 cm) and operated with an EBCT of 2.2 min, equal to the EBCT at the CVWD facilities, at a flowrate of 27 BV/hr. The top and bottom of the glass columns (ACE Glass) were packed with glass beads and glass wool to disperse flow regime from the top of the column and provide a media support layer for the bed.

      Columns were operated with water supplied by a piston pump (FMI Model QG1150) equipped with a ceramic pump head and Teflon tubing. After a certain number of run BVs, the resin was regenerated with 10 BVs of brine solution (5% NaCl) at a flow rate of 12 BV/hour. After regeneration, columns were flushed with 3 BV of nanopure water at 12 BV/hour before feeding columns with synthetic CVWD groundwater at the speed of 27 BV/hour and monitoring anion breakthrough.

      Three types of column regeneration schemes were investigated. Firstly, synthetic groundwater water was passed through two columns (duplicates) until the resin reached exhaustion, then regenerated using virgin (fresh) brine, repeated over 7 cycles. These two columns represent baseline performance for SBA resin life. Secondly, synthetic groundwater was passed through another column until the resin reached exhaustions, and was then regenerated using virgin brine. This brine was then collected, and used to regenerate the column repeatedly after cycles of exhaustion and repeated to reach 7 cycles. This column indicates whether or not

brine can be directly reused for column regeneration (without any treatment). Thirdly, the synthetic groundwater was passed through a third column until the resin reached exhaustion, regenerated with virgin brine, and then treated using a precipitation step (reactive iron), and then used for subsequent regeneration cycles. This was repeated for 7 cycles of exhaustion/regeneration. Contaminant breakthrough and peaking from this column was compared with baseline resin performance (columns regenerated with virgin resin) to determine proof of concept.

Table 4.2: CVWD Groundwater Water Quality Data

Cr(VI) Level	# Wells	Parameter	Alkalinity	As	Cr(VI)	Cr (Total)	Hardness, Total	Fe	NO$_3^-$	pH	κ	SO$_4^{2-}$	TDS	U
Cr(VI) < 2	8	# of Detects	7	2	0	0	7	0	4	8	7	8	8	4
		Average	104	5.8	-	-	146	-	6.4	7.7	1027	122	523	2.6
		Minimum	61	3.7	-	-	16	-	4.7	7.2	240	0	146	1.2
		Maximum	151	7.8	-	-	291	-	9.4	8.4	2100	280	1200	4.2
Cr(VI) 2-5	22	# of Detects	21	0	22	0	21	0	22	22	21	22	22	18
		Average	137	-	3.7	-	183	-	12.2	7.9	490	66	295	6.2
		Minimum	62	-	2.4	-	95	-	2.1	7.3	313	19	180	2
		Maximum	163	-	4.8	-	300	-	35	8.4	740	160	490	12
Cr(VI) 5-10	39	# of Detects	37	3	39	18	34	0	31	39	34	39	39	31
		Average	121	11.5	7.6	12.3	105	-	8.5	7.8	339	29	200	4.3
		Minimum	88	7.9	5.2	10	51	-	2	7.2	250	13	146	1.6
		Maximum	145	15.8	10	16	190	-	38.3	8.2	660	153	414	11
Cr(VI) >10	37	# of Detects	37	3	37	35	36	1	30	37	36	37	37	31
		Average	102	6.7	14	15.3	93	230	3.7	7.8	371	47	222	4.2
		Minimum	68	2.5	11	11	23	230	2	7.3	240	15	142	1.4
		Maximum	150	11.9	21	24	200	230	25	8.3	820	220	540	9.3

The water quality of CVWD wells is summarized in Table 4.2. Having water from CVWD shipped to ASU labs was impractical. Therefore, Tempe Tap water was dechlorinated by passing it across a small GAC column and then spiked with As(V), Cr(VI), nitrate to approximate levels of these ions in CVWD of 23 ppb, 20 ppb, 7 mg-N/L, respectively. Tempe tap water is a similar pH to CVWD groundwater, averaging 7.5-7.8, similarly, sulfate levels similar to CVWD, between 25 and 80 ppm. To simulate CVWD groundwater, Tempe, AZ tap water was spiked with appropriate concentrations of hexavalent chromium, arsenic, and nitrate. For jar testis using reactive iron,

salts used for the brine treatment jar tests included; ferric iron, as ferric chloride ($FeCl_3$, >98%, Sigma-Aldrich) and ferrous iron as ferrous sulfate, heptahydrate ($FeSO_4 \cdot 7H_2O$, >99%, Mallinckrodt Chemicals).

4.2.3 Brine Treatment Jar Test Method

The current treatment plant uses a ferrous/ferric blend coagulant to treat spent brine in order to reduce disposal costs. To further investigate brine treatment, a series of jar tests were conducted using synthetic CVWD brine, and actual brine, shipped from CVWD at varying ferrous/ferric doses.

Synthetic CVWD brine was produced in the lab by creating a 5% NaCl solution in 18MΩ deionized nanopure water. Cr(VI) and As were spiked into the brine solution to simulate levels in CVWD brine, based upon the following assumptions: 1300 BV of CVWD groundwater ran with average Cr(VI) and As concentrations of 10 ppb and 20 ppb, respectively, and then regenerated over 10 BV. This synthetic brine solution was then separated into 2-L aliquots into each jar of the jar tester.

Iron doses were selected based on increasing molar ratios of excess Fe to Cr(VI). Initially, the tests began with a rapid-mix phase with each jar being mixed at a rate of 300 rpm. During this blending phase, appropriate volumes of a ferrous (ferrous sulfate) or ferric (ferric chloride) iron stock solution were dosed into each jar depending on the desired [Fe:Cr(VI)] molar ratio. Jars were allowed to mix at this fast spend for 60 seconds, encouraging particle interactions and coagulation. After 60 seconds, the mixing speed was slowed to 50 rpm to allow for particle flocculation. After another 60 seconds, the mixing was turned off, and flocs were allowed to settle. Samples were collected from the supernatant, filtered, and appropriately analyzed for arsenic and chromium.

Prior to sample collection, jar tests conducted with ferrous were dosed with the stoichiometrically required amount of sodium hypochlorite to oxidize ferrous to ferric iron. This was done in order to avoid ferrous hydroxide formation within analytical equipment. The

stoichiometric, molar, amount of chlorine needed to oxidize any ferrous to ferric iron to be [1:2], based upon the following reaction:

$$\tfrac{1}{2}\ HOCl + Fe^{2+} + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\ Cl^- + \tfrac{1}{2}\ OH^- \qquad \textbf{(Equation 4.1)}$$
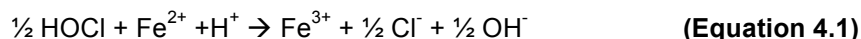
Appropriate amounts of sodium hypochlorite were added to each jar during another rapid-mix (300 rpm) rapid mix stage. Samples were then collected following chlorine addition.

4.2.5 Analytics

Samples were filtered through a 0.45 um cellulose membrane for analysis via ion chromatography or inductively coupled plasma mass spectrometry. Hexavalent chromium concentrations were measured using ion chromatography (Dionex ICS 2000) following a manufacturer recommended modification of EPA Method 218.6 (Basumallick & Rohrer, 2012). The modified method uses Dionex IonPac AG7 guard and Dionex IonPac AS7 analytical columns, an eluent of 250 mM ammonium sulfate/100 mM ammonium hydroxide at a flow rate of 0.36 mL/min, a 1000 uL injection volume, and post-column reaction with 2 mM diphenylcarbazide/10%methanol/1 N sulfuric acid (using a 125 uL reaction coil) followed by visible absorbance detection at 530 nm. This method results in a minimum detection level of 0.001 ug/L, which is suitable for analysis at the proposed California Public Health Goal (PHG) of 0.02 ug/L. Samples to be analyzed for hexavalent chromium were spiked with 1% of ammonium hydroxide buffer.

Total chromium, arsenic, and selenium concentrations were measured using a Thermo Fisher Scientific XSeries 2 quadrapole ICP-MS and Cetac ASX-520 autosampler. Samples were preserved using 2-3% nitric acid (ULTREX, Sigma-Aldrich). Sample introduction consisted of a conical spray chamber with impact bead and concentric nebulizer with a flow of 1 mL/min. The spray chamber was cooled to 3° C by a Peltier cooling system. Collision Cell Technology (CCT) mode was used to reduce interferences by the argon gas used to generate the plasma by using a mixture of 7% hydrogen/93% helium. The differential between total chromium and hexavalent chromium was considered to be trivalent chromium.

Total chlorine levels were measured using HACH Method 8167 DPD Method Powder Pillows (0.02 to 2.00 mg/L as Cl_2). (Hach Company, 2007) This Method uses a DR 2800 Spectrophotometer.

Major anions (nitrate, sulfate, and chloride) were measured using high-pressure ion chromatography (Dionex ICS-5000 HPIC system, following Part A of EPA Method 300.0 (Determination of Inorganic Anions by Ion Chromatography). Sample is introduced into the IC, pass through the capillary guard column (IonPac AG18, Thermo Scientific), are separated within the capillary analytical column (IonPac AS18, Thermo Scientific), through the suppressor and then pass through a conductivity detector. Eluent solution is a mixture of sodium bicarbonate and sodium carbonate. (Pfaff)

4.3 Results and Discussion

4.3.1 Columns Regenerated with Virgin Brine

Two columns (duplicates, Column A and B) were run to exhaustion and regenerated using virgin (fresh) brine. These columns represent current operations at the CVWD facility, and provide information for baseline performance for SBA IX (SBG-1 resin) to remove specific groundwater contaminants (Figures 4.2 and 4.3).

The first cycle of exhaustion for the duplicate columns was run over 2000 BV. At 667 BV, complete arsenic breakthrough occurred. The efficiency of IX process for arsenic is highly sensitive to the presence of competing ions, including sulfate. It has been shown that sulfate has a higher affinity for IX sites than arsenate species (Clifford, 1999). CVWD reported relatively high sulfate levels, ranging from ND-280 mg/L, so it was not surprising to see complete arsenate breakthrough at a relatively small number of treated BVs (667 BV) using Tempe Tap water with sulfate levels of 80 mg/L (Figures 4.2 a and 4.3 b). Competition between anions for IX sites, of specific water matrices greatly determines the applicability of a specific IX process for adequate removals (Wang, et al., 2000).

Because sulfate levels were relatively high in the source water (80 mg/L) both columns show displacement of previously sorbed arsenate from the resin, indicative of higher arsenic

concentrations in the effluent than the influent, at the sample taken at 667 BVs. This phenomenon is called chromatographing peaking, and is an undesirable operating condition for IX technologies. This displacement was most likely caused by sulfate concentrations, as not too long after arsenic chromatographic peaking occurred, complete sulfate breakthrough was observed at the sample taken at 800 BV for Column A, and 1500 BV for Column B.

Figure 4.2 and 4.3 also plot chloride concentrations. The SBG-100 is in the chloride ionic form; so influent anions displaced chloride ions during initial column runtimes.

a)
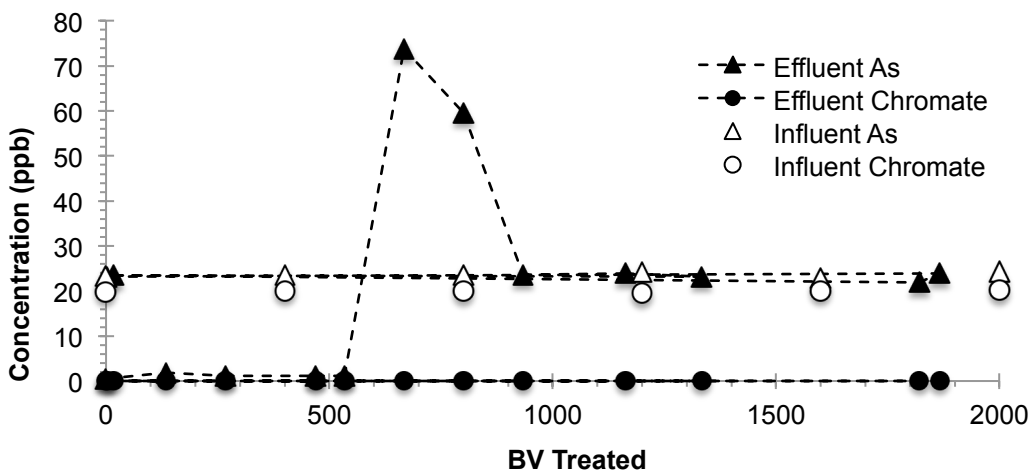
b)

Figure 4.2: Columns to be regenerated with virgin brine: Exhaustion #1 (Column A) Contaminants breakthrough in synthetic CVWD groundwater, pH=7.8-8.7. a) Chromium and Arsenic Breakthrough, b) Sulfate and chloride (major competing anion) breakthrough.

57

a)

b)

Figure 4.3: Columns to be regenerated with virgin brine: Exhaustion #1 (Column B) Contaminants breakthrough in synthetic CVWD groundwater, pH=7.8-8.7. a) Chromium and Arsenic Breakthrough, b) Sulfate and chloride (major competing anions) breakthrough.

After eluting both columns once with virgin brine, the columns were run for a second exhaustion cycle, for 2000 BV (Figures 4.3 and 4.4). Once again, complete arsenic breakthrough occurred at 667 BV. Tempe tap water for this exhaustion cycle contained lower sulfate levels (26 mg/L) than previously used during the first exhaustion cycle (80 mg/L), yet arsenic breakthrough occurred at the same number of BVs treated. Complete sulfate breakthrough occurred simultaneously with arsenic breakthrough.

a)

b)

Figure 4.4: Columns to be regenerated with virgin brine: Exhaustion #2 (Column A) Contaminants breakthrough in synthetic CVWD groundwater, pH=7.8-8.7. a) Chromium and Arsenic Breakthrough, b) Sulfate (major competing anion) breakthrough.
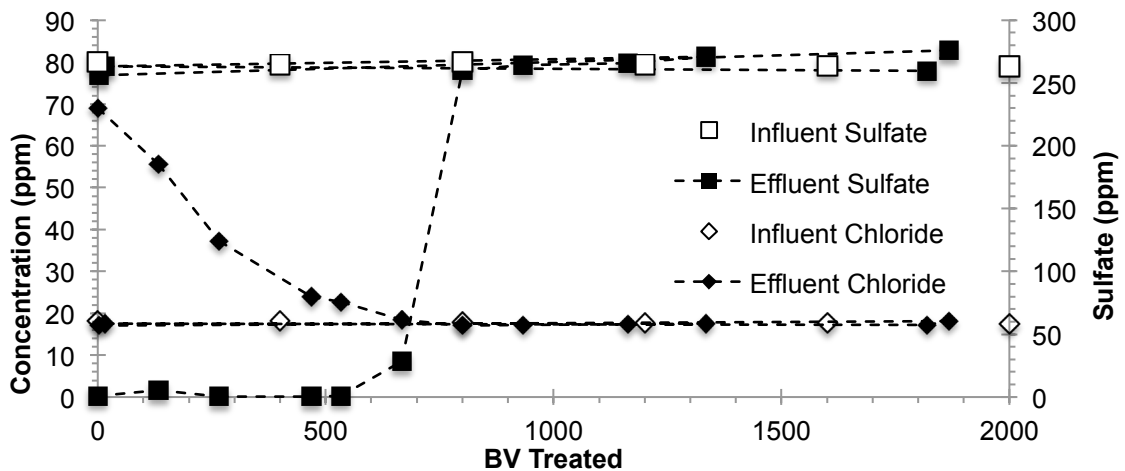
a)

b)

Figure 4.5: Columns to be regenerated with virgin brine: Exhaustion #2 (Column B) Contaminants breakthrough in synthetic CVWD groundwater, pH=7.8-8.7. a) Chromium and Arsenic Breakthrough, b) Sulfate (major competing anion) breakthrough.

For all following cycles, columns were only run to 450 BV, rather than the original 2000 BV, in order to avoid this arsenic chromatographic peaking (Figures 4.6-4.15). Neither Cr nor Cr(VI) breakthrough was observed over 450 BV. Column B (Figure 4.7) showed an initial detection of chromate, suggesting that the column was not properly flushed following the column elution. Low levels (1-2 ppb) of arsenic was detected periodically over 450 BV, suggesting that not all arsenate was adequately exchanging with IX sites within the bed.

Figure 4.6: Columns to be regenerated with virgin brine: Exhaustion #3 (Column A) Contaminants breakthrough in synthetic CVWD groundwater

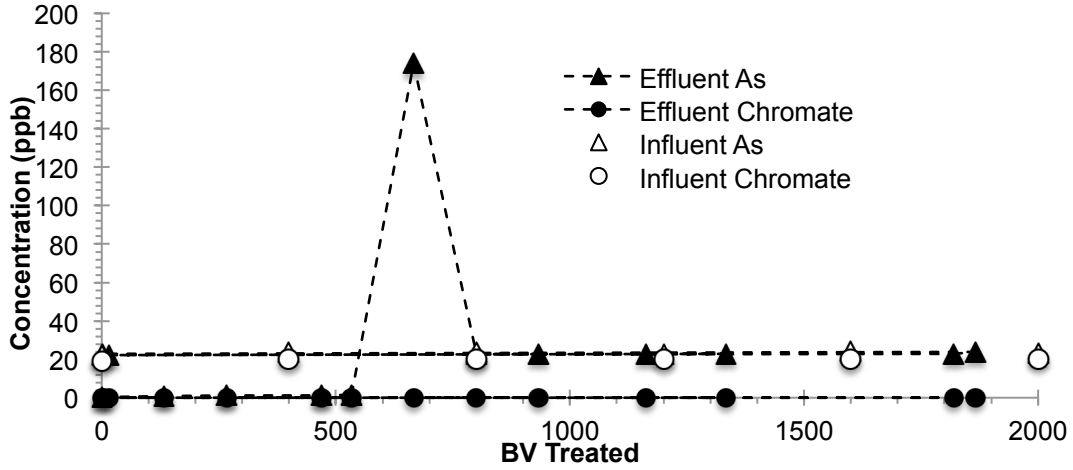**Figure 4.7: Columns to be regenerated with virgin brine: Exhaustion #3 (Column B) Contaminants breakthrough in synthetic CVWD groundwater**

Columns were run for a fourth exhaustion cycle (Figures 4.8 and 4.9). Neither Cr nor Cr(VI) breakthrough was observed over 450 BV. Both columns show higher detections of As in column effluent. Specifically Column B (Figure 4.9) showed effluent As concentration of 4ppb at 45 BV. Chromatographic peaking for As was observed for column A at 450 BV, suggesting that the resin was not completely/adequately regenerated during the previous regeneration cycle. Column B also showed a higher level (11 ppb) of As at 400 BV.
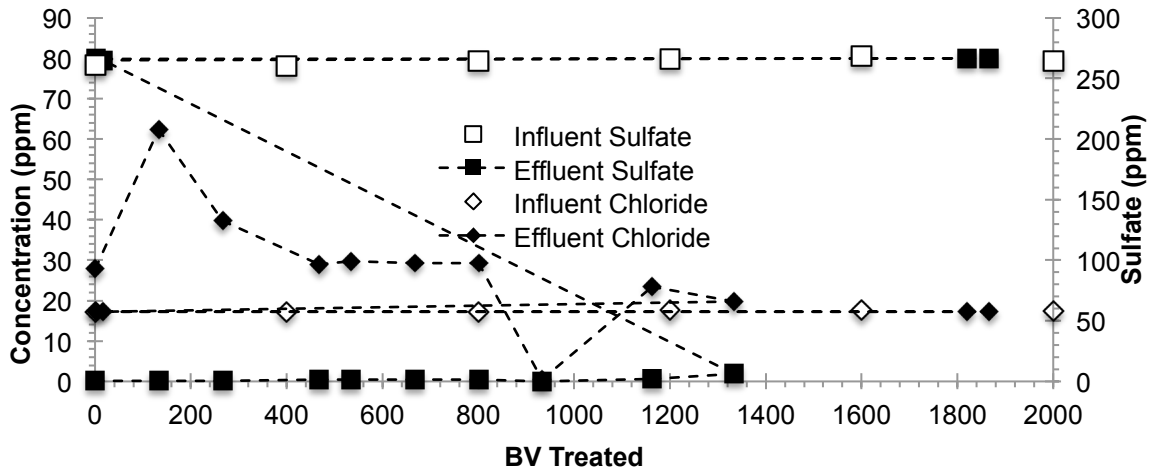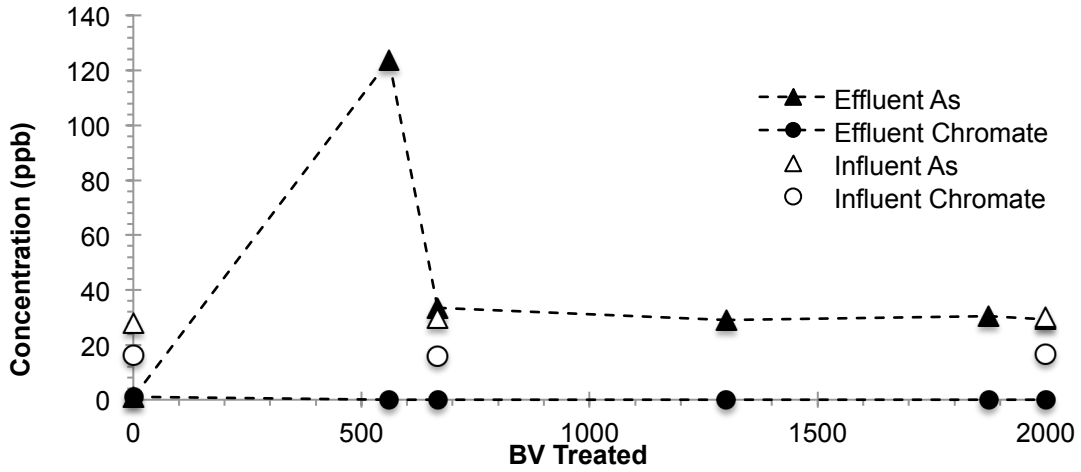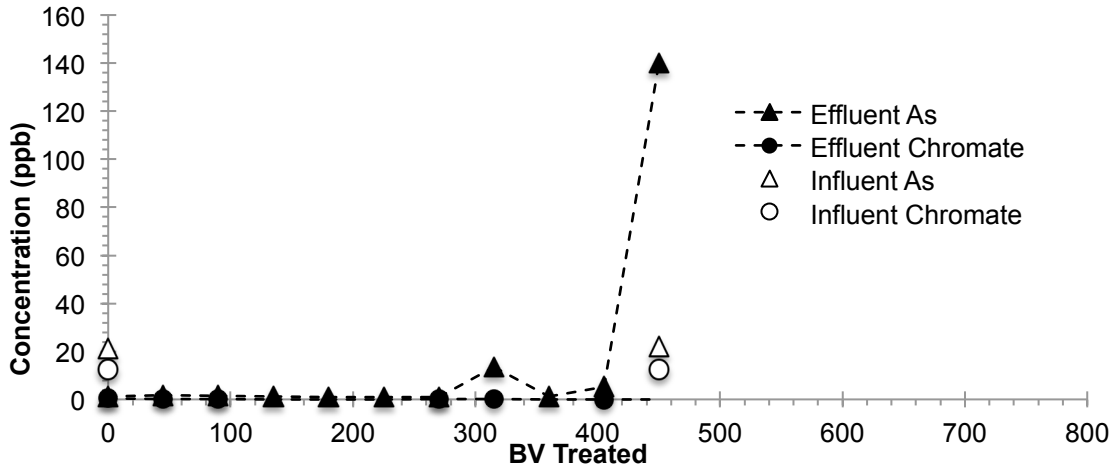
Figure 4.8: Columns to be regenerated with virgin brine: Exhaustion #4 (Column A) Contaminants breakthrough in synthetic CVWD groundwater
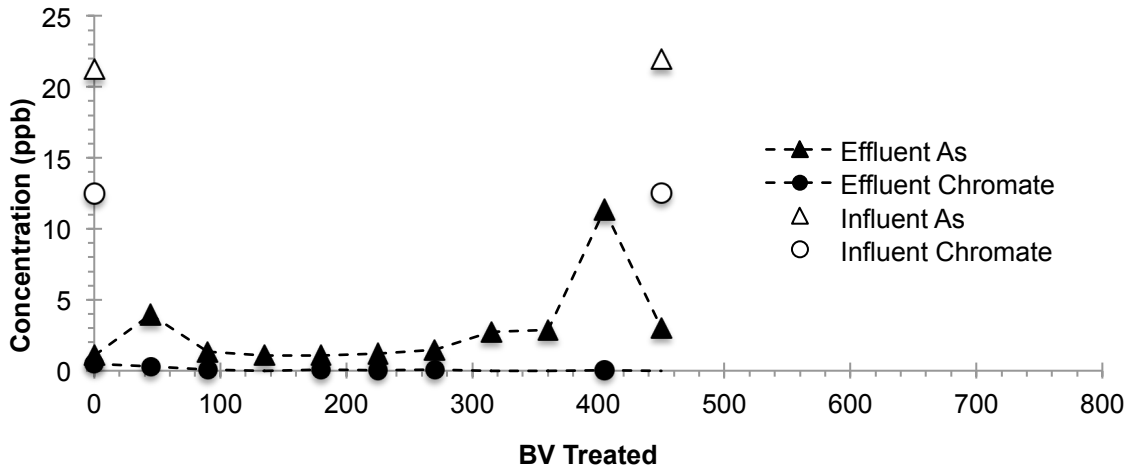
Figure 4.9: Columns to be regenerated with virgin brine: Exhaustion #4 (Column B) Contaminants breakthrough in synthetic CVWD groundwater
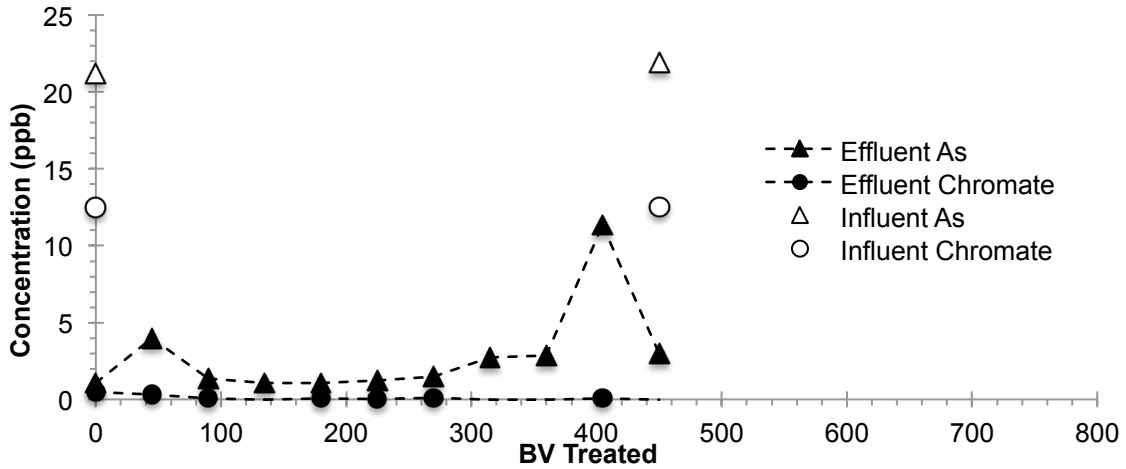
Figure 4.10: Columns to be regenerated with virgin brine: Exhaustion #5 (Column A) Contaminants breakthrough in synthetic CVWD groundwater
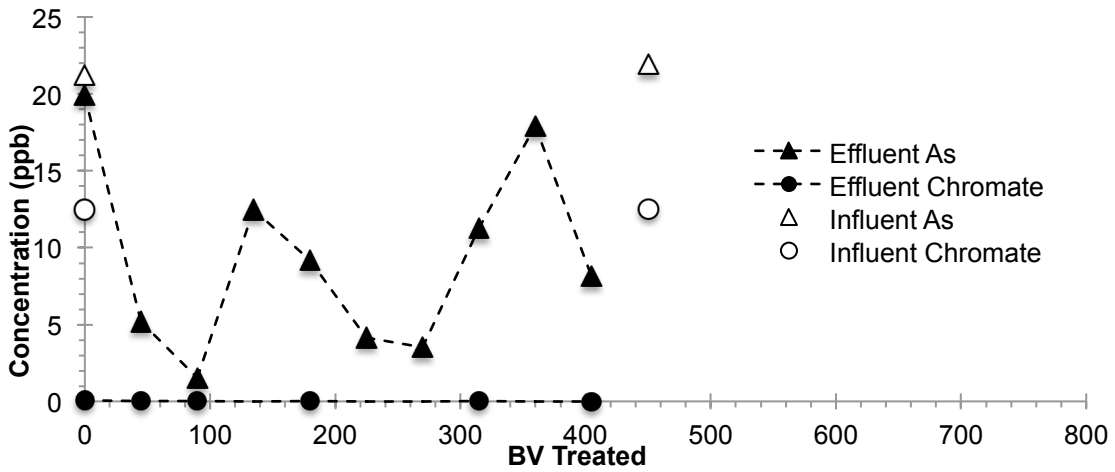
Figure 4.11: Columns to be regenerated with virgin brine: Exhaustion #5 (Column B) Contaminants breakthrough in synthetic CVWD groundwater

Columns were run for a fifth exhaustion cycle (Figures 4.10 and 4.11). Neither Cr nor Cr(VI) breakthrough was observed over 450 BV. Both columns did not necessarily show arsenic peaking, however, there were arsenic detections in each of the effluent samples.
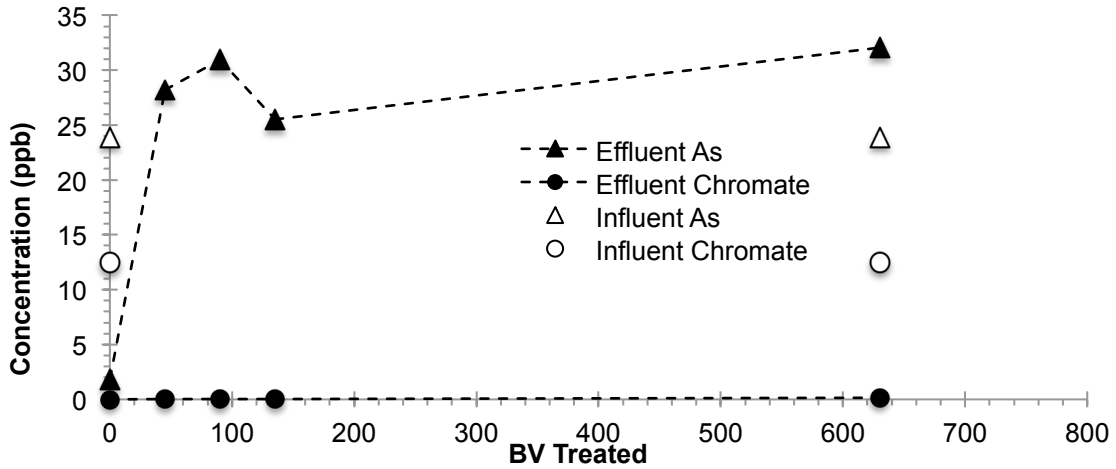
Figure 4.12: Columns to be regenerated with virgin brine: Exhaustion #6 (Column A) Contaminants breakthrough in synthetic CVWD groundwater
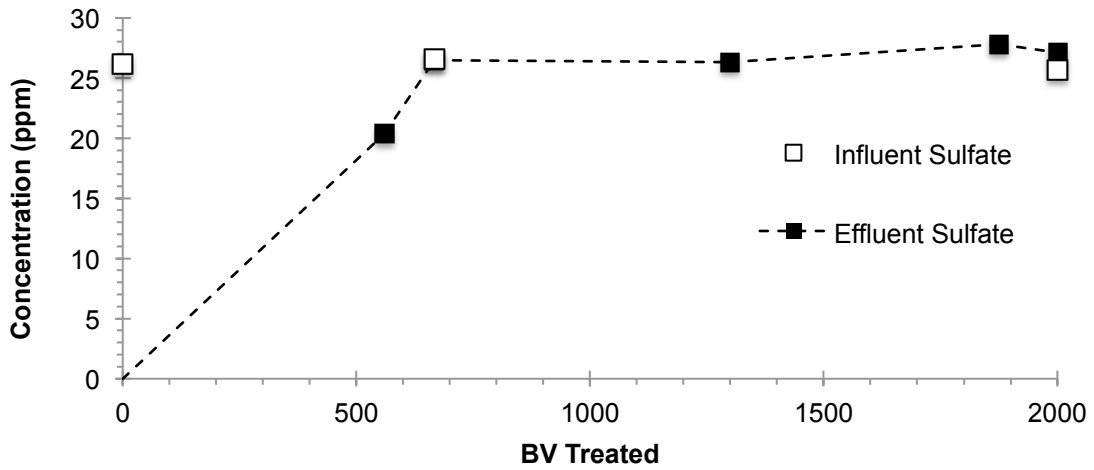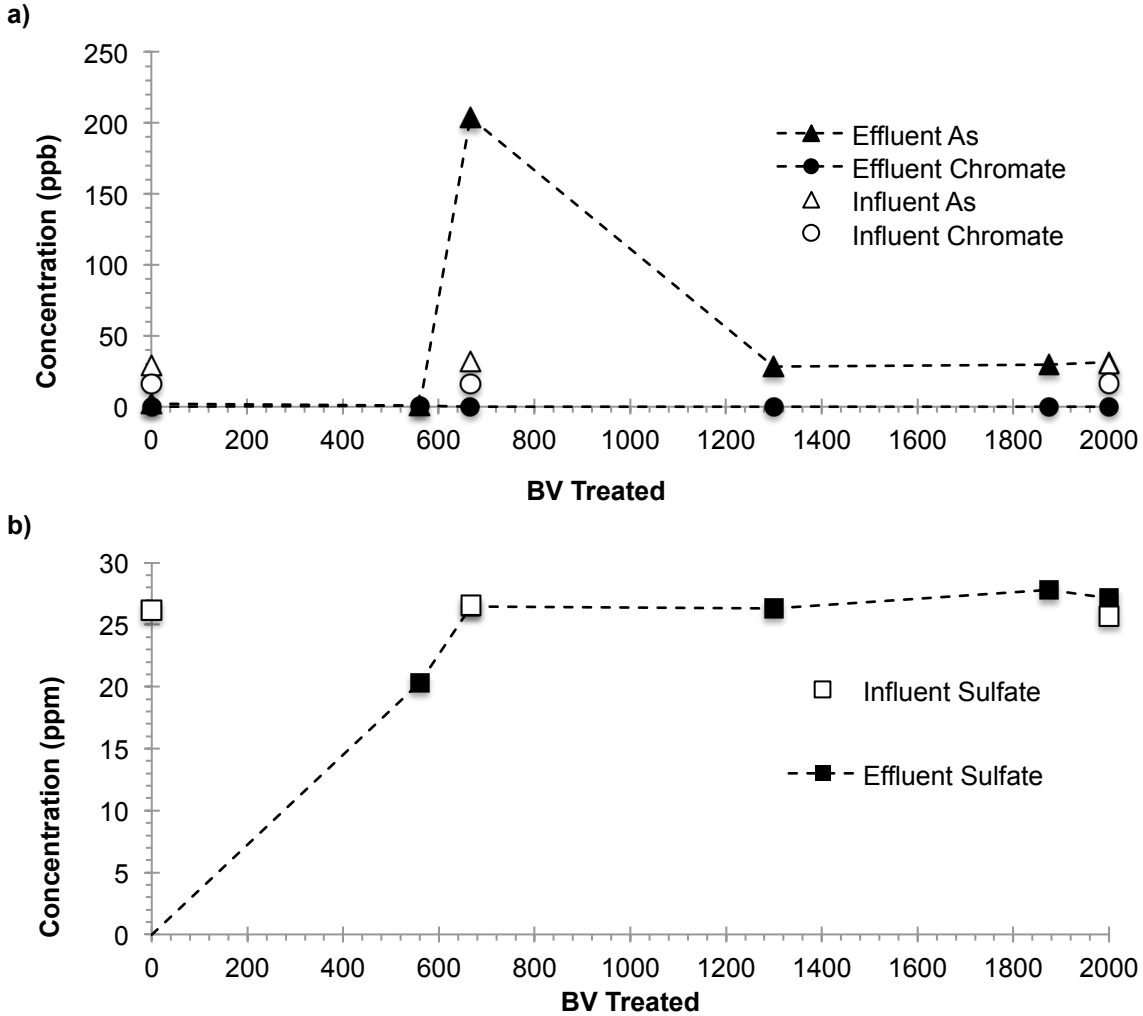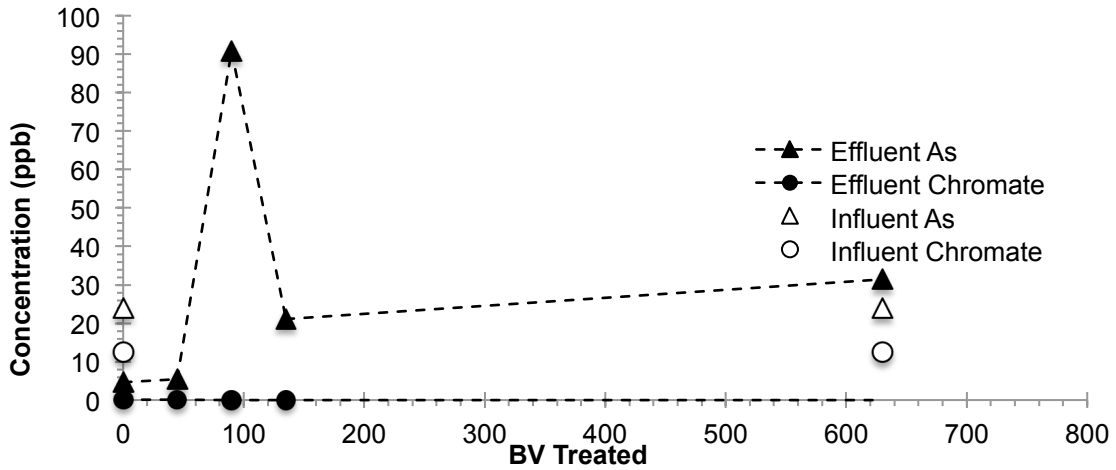

Figure 4.13: Columns to be regenerated with virgin brine: Exhaustion #6 (Column B) Contaminants breakthrough in synthetic CVWD groundwater

Columns were run for a sixth exhaustion cycle (Figures 4.12 and 4.13). Neither Cr nor Cr(VI) breakthrough was observed over 450 BV. Both columns show almost immediate arsenic chromatographic peaking at >100 BV treated. This trend of As breakthrough at lower BV treated indicates deteriorating resin performance, meaning something that is taking up IX sites, is not being regenerated using the 5% NaCl solution.
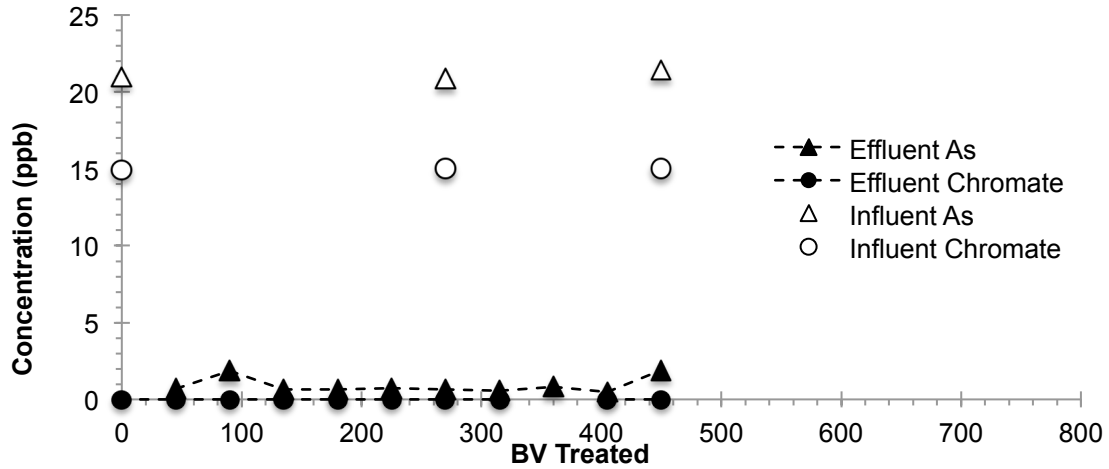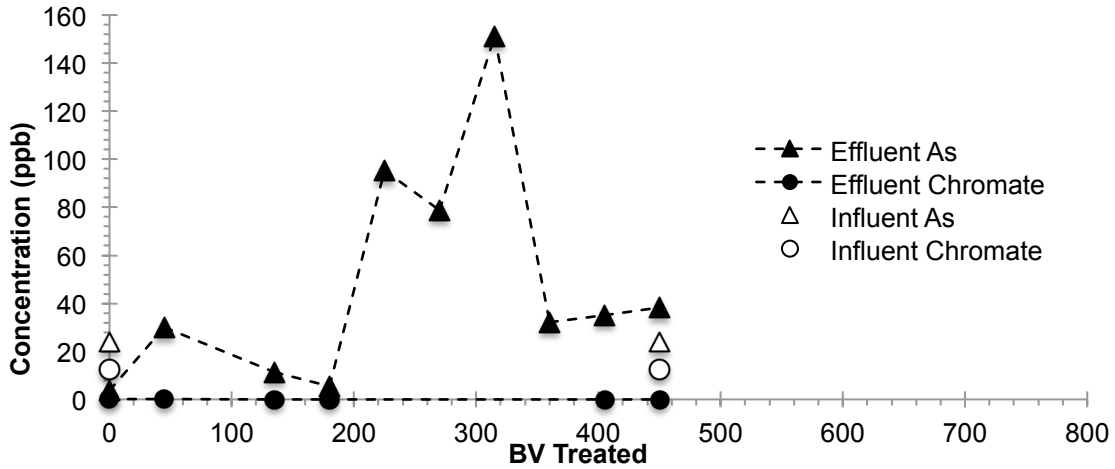
Figure 4.14: Columns to be regenerated with virgin brine: Exhaustion #7 (Column A) Contaminants breakthrough in synthetic CVWD groundwater
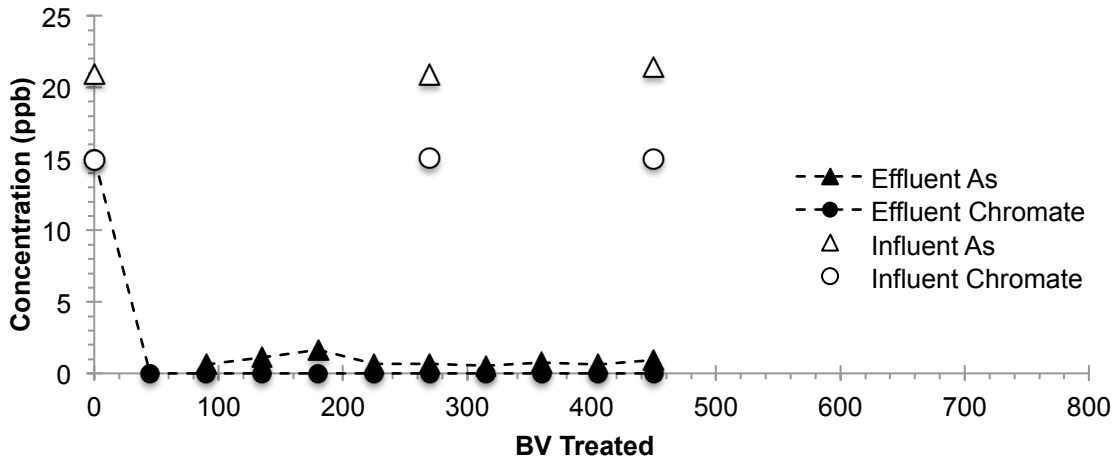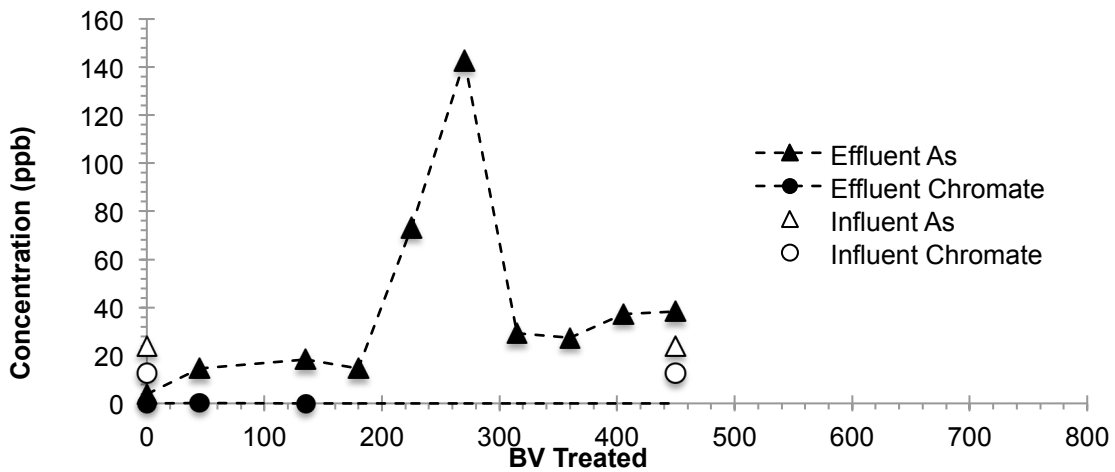

Figure 4.15: Columns to be regenerated with virgin brine: Exhaustion #7 (Column B) Contaminants breakthrough in synthetic CVWD groundwater

Columns were run for a seventh (final) exhaustion cycle (Figures 4.14 and 4.15). Neither Cr nor Cr(VI) breakthrough was observed over 450 BV. Both columns, once again show arsenic breakthrough at just over 200 BV. This further shows the deteriorating resin performance with increasing exhaustion/regeneration cycles.

At the end of each cycle, columns were regenerated using the regeneration scheme described previously. Table 4.3 below summarizes recoveries of total Cr, Cr(VI), and As for each regeneration cycle from the analyzed brine (Recoveries average measured masses from Columns A and B). Chromium percent recoveries were obtained by conducting a simple mass balance on contaminant mass that passed through each resin bed. Metals within the brine

65

solution were analyzed, and based on the collected 10 BV (300 mL) of brine collected, the mass

of contaminant that eluted off of the bed, and into the brine was calculated. This "measured

mass" was then compared with the "theoretical mass", representing the total mass that

theoretically should have been collected within the resin bed assuming no breakthrough.

Table 4.3: Recoveries for Columns Regenerated with Virgin Brine:
a) Column A b) Column B

a)

Column A	Regeneration Cycle						
Analyte	1	2	3	4	5	6	7
Cr (Total)	67.6%	92.3%	105%	221%	96.7%	299%	236%
Arsenic	*5.06%**	*3.89%**	81.9%	105%	*53.1%**	*32.2%**	*24.6%**

b)

Column B	Regeneration Cycle						
Analyte	1	2	3	4	5	6	7
Cr (Total)	53.1%	80.7%	114%	215%	147%	223%	167%
Arsenic	*7.37%**	*4.27%**	96.7%	184%	*155%**	*19.7%**	*21.8%**

* indicate complete breakthrough of arsenic during column exhaustion

        Poor As recovery was observed for the first two regeneration cycles because complete

breakthrough was observed during each of the exhaustion runs (Figures 4.2-4.5). However once

only 450 BV were run, as shown in regeneration cycle #3 (Figures 4.6-4.9), As recovery

increased to 81.9% and 96.7% for Columns A and B, respectively. As recovery from regeneration

cycle #4 was >100%, because some of the mass from regeneration cycle #3 that did not properly

elute off, was released during this following regeneration cycle. Arsenic from previous

regenerating cycles continued to elute off during the fourth and fifth regeneration cycles for both

Columns A and B, but as As breakthrough began to occur at lower BV treated, recoveries drop

below 25% for both columns at the sixth regeneration.

After observing no detectable Cr breakthrough during each column exhaustion, the first regeneration showed >50% recovery of chromium, which increased to >80% recovery by the second cycle. It was predicted that some of the mass from the first column exhaustion was eluting off the column in the second column regeneration, which is why there was an increased recovery. This was further validated during the fourth regeneration as Cr recovery was found to be >100%. With each subsequent regeneration, Cr recovery increased with more Cr sorbed from previous exhaustion cycles.

4.3.2 Brine Treatment

Figure 4.2 shows normalized removal of Cr and As based on increasing ratios of excess Fe to Cr. At an excess mass ratio of 5:1, Fe:Cr, there is over a 90% removal of total Cr and As, as well as complete reduction (no detection) of Cr(VI). This shows that Cr and As are easily removed using reactive ferrous sulfate at iron doses (1.3 mg/L-97 mg/L Fe).
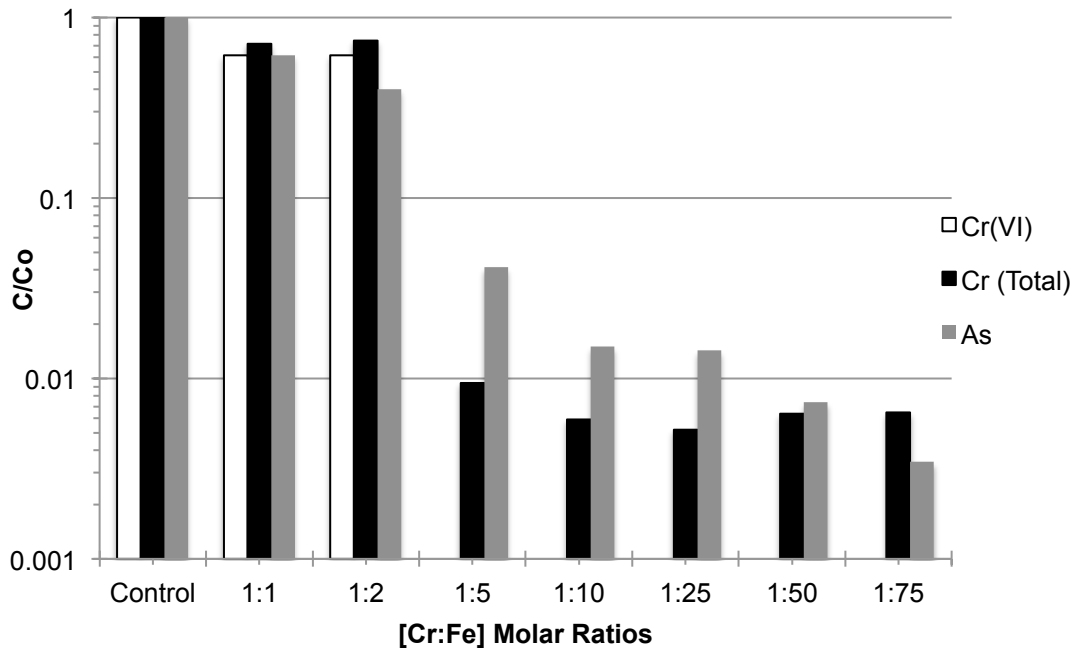
Figure 4.16: Cr, Cr(VI), and As removals using Ferrous Sulfate in synthetic CVWD brine, 1.3 mg/L Cr(VI), 2.6 mg/L As

High sulfate levels severely impact arsenic removal via SBA IX. The sulfate added using the ferrous sulfate salt for the reported molar ratios of [Cr:Fe] range from 2.2-167.7 mg/L. For this reason, using ferrous sulfate to treat spent brine, with intent to reuse, may introduce even more unwanted sulfate into the IX bed, furthering interfering with IX selectivity towards arsenate species. This phenomena could be avoided by using ferric chloride. Ferric chloride is typically used for As removal from water as it precipitates out, and allows for the formation of floc, with which As readily coprecipitates with in solution. A sample of CVWD spent brine was received at ASU, and used for another jar test using ferric chloride. Figure 5.3 below shows the results of the jar test utilizing actual CVWD brine. More ferric salt is required to remove the same amount of Cr and As when compared with ferrous salt. However, there is still observed Cr removal. An excess of 500:1 ferric to Cr(VI) achieves <99% removal of As.
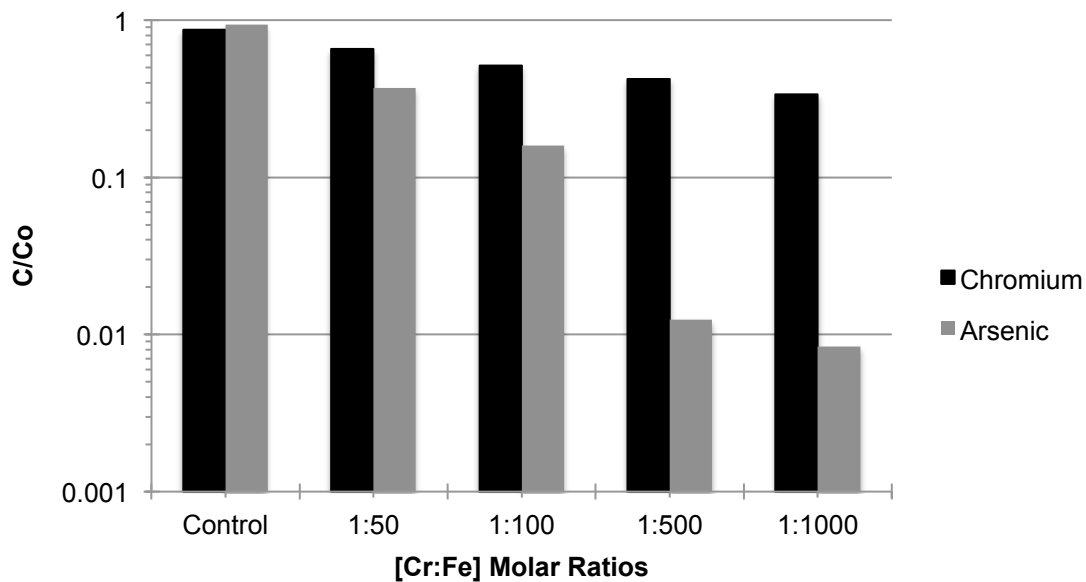
Figure 4.17: Cr and As removals using Ferric Chloride in actual CVWD spent brine

4.4 Summary and Conclusions

A series of column and batch tests were performed to determine how to optimize SBA brine management for CVWD.

Specific conclusions include:

- Sulfate levels (>80 mg/L) can significantly impact SBA's ability to remove As, as demonstrated by the chromatographic peaking of As occurring at >667 BV in column tests. This chromatographic peaking of As occurs because the sulfate anion has a higher affinity for specific IX exchange sites of the SBG-1 resin. As sulfate continues to pass through the resin bed, the sulfate anion essentially elutes off any previously exchanged As from those sites.

- Sulfate levels (>80 mg/L) did not impact SBA's ability to remove Cr nor Cr(VI) from influent water. This was determined based on no detection of Cr in effluent from the columns, after seven cycles of resin exhaustion and regeneration. High Cr recovery indicates that 5% NaCl solution adequately regenerates SBA resins for Cr treatment.

- Brine collected from the regeneration of IX resins can be treated for Cr and As; removing over 90% using ferrous sulfate doses of 6 mg/L Fe_2SO_4. The ferrous sulfate reduces Cr(VI) within the brine. The addition of chlorine oxidizes the ferrous iron to ferric, which coprecipitated with As in solution, removing both As and Cr from the brine. Using ferric chloride was shows to exhibit much lower Cr and As removal at much higher iron doses, indication ferrous sulfate to be the more effective treatment for spent brine.

CHAPTER 5
KINETICS OF CHROMIUM (III) OXIDATION TO CHROMIUM (VI)

VIA HYPOCHLORITE ADDITION

Chemical oxidants (i.e., ozone, chlorine, chloramines, etc.) are commonly used during both drinking and industrial water treatment to disinfect water and eliminate micropollutants. Inorganic chemicals can also be oxidized (e.g. Br^- to BrO^{3-} or Cr(III) to Cr(VI)). Likewise, reductants are often used more in industrial treatments for dechlorination (bisulfate) but can influence chromium speciation in water discharged to the environment. There have been few studies examining Cr (III) oxidation by chlorine. A Water Research Foundation study (Lindsay, Farley, & Carbonaro, 2012) evaluated the effects of a few chemical oxidants for the oxidation of Cr(III) to Cr(VI). The study showed that chlorine could oxidize 50 to 65 percent of Cr(III) to Cr(VI) (Brandhuber et al., 2004).There have been no detailed evaluations of kinetic reaction rates for Cr(III) oxidation to Cr(VI) using chlorine, chloramines, and ozone, nor reduction using bisulfite and stannous chloride. This chapter develops a strategy to investigate Cr(III) oxidation kinetics to Cr(VI) in light of low solubility of Cr(III) at pH levels above 7.

5.1 Chromium and Chlorine Chemistry and Experimental Design

Cr (III) oxidation by hypochlorous acid (HOCl) has a $E^o>0$:

$CrO_4^{2-} + 6H^+ +3e^- \rightarrow Cr(OH)_2^+ + 2H_2O$ $\qquad\qquad$ E^o=1.14 V

Chlorine Reduction Half Reaction:

$HOCl (aq) + H^+ 2e^- \rightarrow Cl^- +H_2O$ $\qquad\qquad$ E^o=1.48 V

$Cr(OH)_2^+ + 1.5HOCl (aq) + 0.5H_2O = CrO_4^{2-} + 1.5Cl^- + 4.5H_2O$ $\qquad$ **E^o=0.34 V**
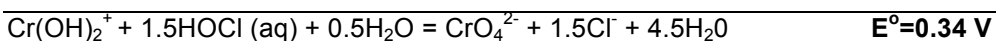
The redox reaction above shows that the oxidation of Cr(III) to Cr(VI) via hypochlorous acid (HOCl) is favorable under standard conditions and stoichiometric relation shows 1.5 to 1 ratio of HOCl to Cr(III). This ratio is not dissimilar to typical free chlorine levels in finished drinking waters are 1 to 5 mg/L (0.03-0.14 mM HOCl) relative to typical

occurrences of chromium in groundwater, which are 1-1000 ppb (0.02-1.9 uM). Reduction of

toxic Cr(VI) to Cr(III) reduces toxicity by a factor of about 100 (Liu, 1997). In groundwater and

drinking water, Cr(III) exists predominately as Cr^{3+} ion, and as pH increases, hydroxide

complexes: $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$ (s), and $Cr(OH)_4^-$. Within water treatment facilities,

Cr(III) is often precipitated as a hydroxide and removed as a sludge.

Table 5.1: Solubilities of Cr(III) at different pH values

pH	Cr(III) Solubility (log(M))
6	-10.5
6.5	-10
7	-9
7.5	-11
8	-12

After conducting a thorough literature review, it has become evident that oxidation

and reduction rate constants are not reported due to issues associated with $Cr(OH)_{3\ (s)}$

precipitation and the accompanying low solubility of Cr(III) at relatively neutral pH levels

(Table 5.1 and Figure 5.1). A typical experimental approach whould have been to measure

oxidant (chlorine) consumption in the presence of excess Cr(III), to maintain pseudo-first-

order conditions with respect to chlorine, but the limited solubility of Cr(III) made this

experimental procedure impractical. However, the experimental approach (excess chlorine,

pH=5) developed has overcome this challenge and allowed the rate constants to be

determined at environmentally relevant chromium concentrations (ppb levels).
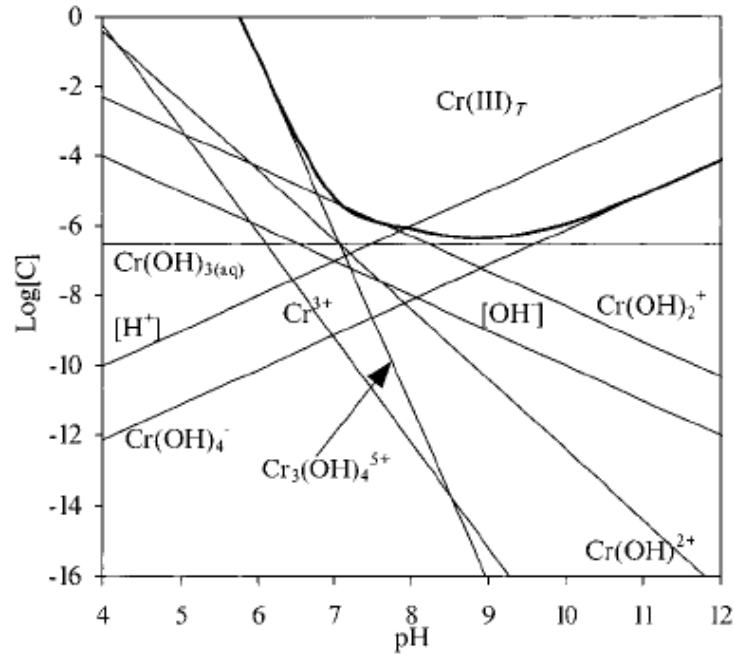
Figure 5.1: Solubility of Chromite with respect to pH (Barber & Stuckey, 2000)

Experiments were conducted under pseudo second order conditions (e.g., [HOCl]>>[Cr(III)]). The evolution of Cr(VI) from Cr(III) in the presence of free chlorine (e.g., HOCl) was measured. Most chlorine reactions with inorganic and organic compounds are oxidation reactions with second-order reaction rates, or first-order with respect to chlorine concentration ([HOCl]), and first order with respect with respect to chromite concentration ([Cr(III)]) (Deborde & von Gunten, 2008):

$$-\frac{d[Cr(III)]}{dt} = k_{app}[HOCl]_{\mathrm{T}}[Cr(III)]$$

(Equation 5.1)

where k_{app} is the apparent second-order rate constant, [Cr(III)] is the total concentration of chromite and $[HOCl]_{\mathrm{T}}$ is the sum of various species of chlorine ([HOCl]+[OCl$^-$]). Hypochlorous acid (HOCl) (Equation 4.2), is a weak acid and dissociates in solution:

$$HOCl \leftrightarrow ClO^- + H^+ \quad \text{pKa=7.5}$$

(Equation 5.2)

72
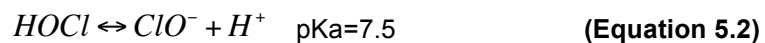
The relative distribution of chlorine species in solution (Figure 5.2) indicates that at pH 5, the predominant species of aqueous chlorine is present as hypochlorous acid (HOCl).
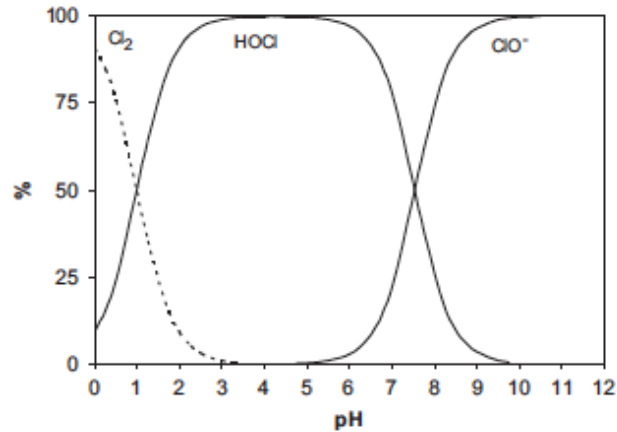
Figure 5.2: Distribution of main chlorine species relative to pH at 25 degrees Celsius, for chloride concentration of 5E10(-3) (Deborde & von Gunten, 2008)

5.2 Methods & Materials

Cr(III) oxidation to Cr(VI) by aqueous chlorine was studied at pH 5 (a pH with higher Cr(III) Solubilities compared with more neutral pH) using batch reactors (amber glass 500 mL) equipped with repipetters (Figure 5.4). Initial Cr(III) solutions contained 1.92 uM Cr(III) (100 ppb). Chlorine concentrations of 96 to 480 uM were added, such that the $Cr(III)/HOCl_T$ ratios ranged from 50/1 to 250/1. These ratios can be used to assume a pseudo first order reaction which should occur such that;

$$\frac{d[HOCl_T]}{dt} = -k'[HOCl_T] \qquad \textbf{(Equation 5.3)}$$

$$k' = k_{app}[Cr(III)] \qquad \textbf{(Equation 5.4)}$$

Samples collected using the repipetter over 7 hours were immediately quenched using DPD (N,N-diethyl-p-phenylenediamine),indicator solution (Figure 5.5). Formation of Cr(VI) was then observed over time by analyzing samples for Cr(VI). This is the same reagent commonly used during the colorimetric method to measure free chlorine. When DPD is added to the sample, chlorine oxidizes the DPD, which forms a magenta-colored byproduct

(Figure 5.3). The intensity of the magenta color is directly related to the amount of free chlorine in solution.
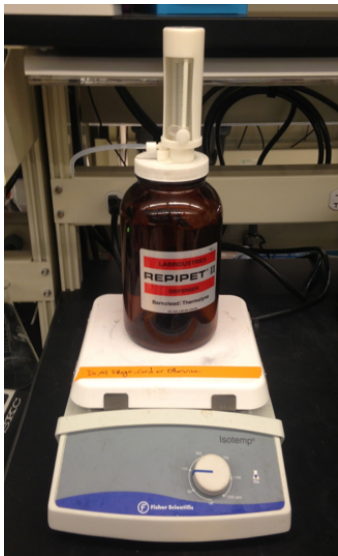
Figure 5.3: 500-mL, amber glass batch reactor, equipped with repipetter

(Colorless)   Würster Dye (Red)
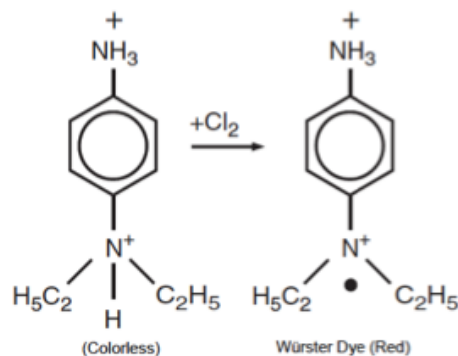
Figure 5.4: Hypochlorous acid and hypochlorite ion oxidize DPD causing a magenta color (HACH)

5.3 Results and Discussion

Figure 5.5 is plotted based on formation of Cr(VI), analyzed using IC with post column reaction. In the presence of free chlorine, at pH 5, the appearance of Cr(VI) is attributed to the disappearance of Cr(III). It can be seen that the oxidation of Cr(III) to Cr(VI) happens faster with increasing excess chlorine dose. It is not evident that any threshold was reached for the formation of Cr(VI) suggesting that any residual chlorine may actually oxidize all chromite, given enough contact time. Because this is not a first order reaction, the disappearance of Cr(III), similarly the oxidation of Cr(VI) over 7 hours is not linear. However, the oxidation reaction is linear over the first 15-30 minutes (Figure 5.6).
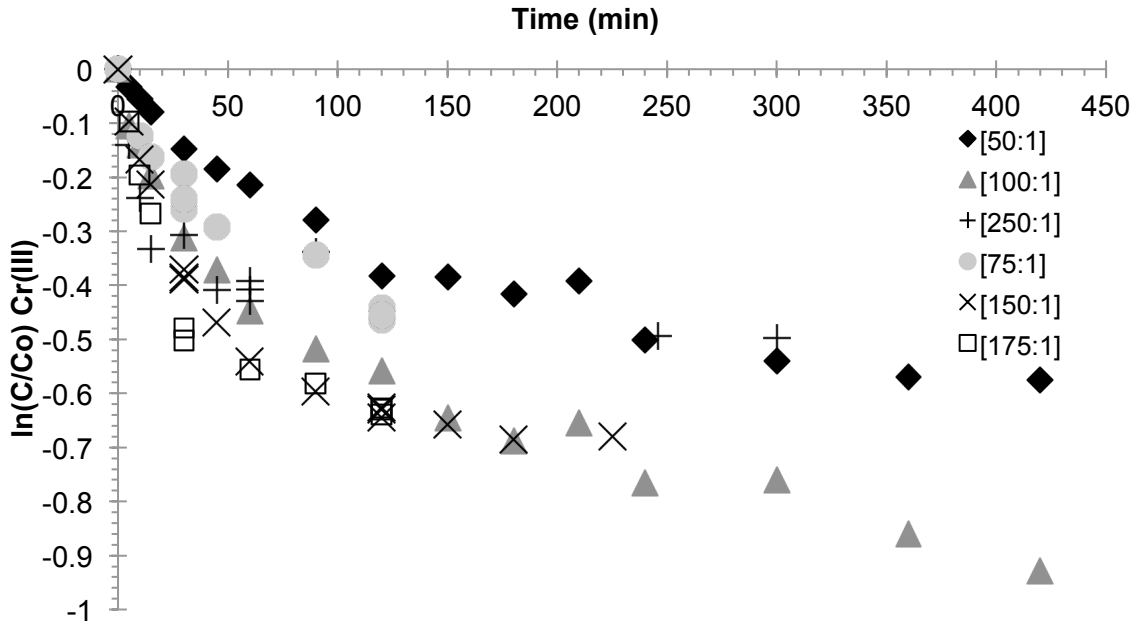
Figure 5.5: Cr(III) (100ppb) oxidation by HOCl, in buffered (5mM phosphate buffer) DI water, at pH=5, for different ratios of Cr(III)/HOCl$_T$

Figure 5.6 shows the linear portion of the initial oxidation of chromite to chromate. Trend lines were intended to include as many points as possible, without allowing associated $R^2 < 0.95$. Each trend line indicates the linear fits associated with different excess chorine doses. These linear (trend) lines represent pseudo-first order reaction constants, which are dependent upon each chlorine dose. The slope of each line can be described by:

$$\ln\left(\frac{C}{C_0}\right)_{Cr(III)} = -k_{app} \cdot t$$

(Equation 5.5)

Where k (t^{-1}) represents a first-order reaction for each specific chlorine dose. Although each of the lines does not pass directly through zero, each y-interception are so small, it was neglected. These linear fits over the shorter durations of time make the kinetics of the oxidation of Cr(III) via HOCl apparent. The fastest oxidation (line with the greatest slope) occurs with the highest level of excess chlorine ([250:1]), similarly, the slowest oxidation (line with the least slope) occurs with the least amount of chlorine ([50:1]).

75
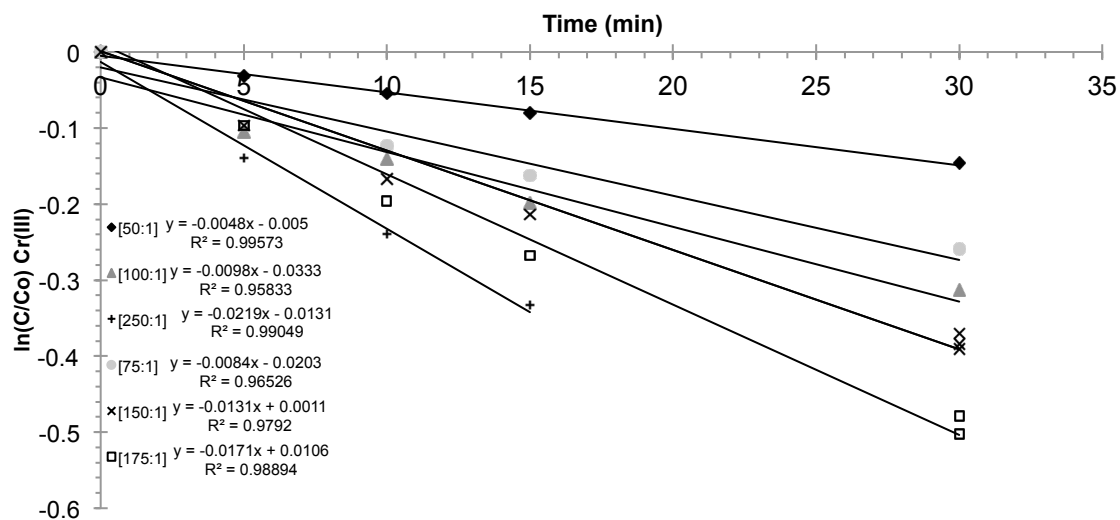
Figure 5.6: Linear Fits of the oxidation of Cr(III) (100 ppb) in the presence of HOCl in DI water (5 mM phosphate buffer, pH=5)

These pseudo-first order reaction rates (Figure 5.6) were plotted against chlorine dose (Figure 5.7). The trend line plotted through the 6 data points indicates a good linear fit with an R^2 value of >0.98. The trend lines shows that the apparent second-order rate constant for the oxidation of Cr(III) via hypochlorous acid, at pH 5, to be 0.7 $M^{-1}s^{-1}$.
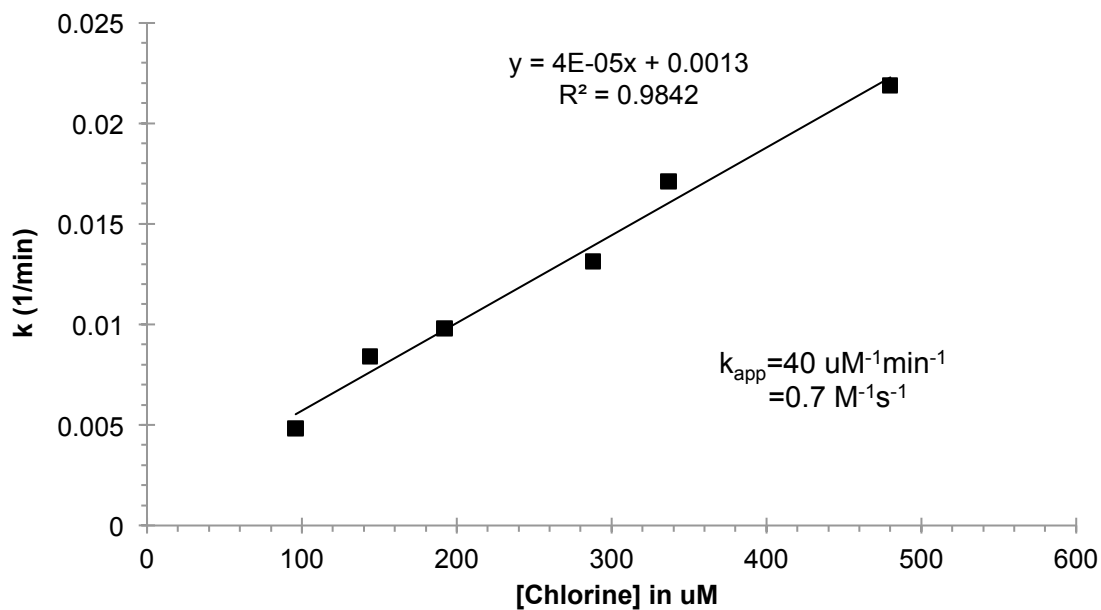
Figure 5.7: Determining apparent second-order-rate constant for oxidation of Cr(III) by HOCl using pseudo-first-order-reaction rate constants

This oxidation reaction occurs much slower (5-6 orders of magnitude slower) than other reported kinetic expressions of oxidation of inorganic compounds with chlorine. At pH of 7, the oxidation of sulfite was reported at $2.3 \times 10^5 \, M^{-1}s^{-1}$, arsenous acid at $2.9 \times 10^5 \, M^{-1}s^{-1}$, and at pH 4, the oxidation of iron(II) was reported at $1.7 \times 10^4 \, M^{-1}s^{-1}$ (Deborde & von Gunten, 2008).

5.4 Kinetic Cr(VI) Formation Potential Applications

To further investigate how this rate constant applies to water in a distribution system in the presence of residual chlorine, this determined apparent second-order reaction rate was used to determine the time would take for a specific chromium concentration, in the presence of a range of chlorine levels to exceed California Public Health Department (CPDP) proposed MCL for Cr(VI) of 10 ppt (Figure 5.8)

Time (hours) for Cr(III) Levels to Exceed Proposed MCL

of **0.01 ppm** as Cr(VI) in the Presence of Chlorine (pH=5)

Residual Chlorine Concentration (mg/L)

Chromium Concentration (ug/L)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
100	1.1	0.9	0.8	0.7	0.6	0.6	0.5	0.5	0.5	0.4
75	1.5	1.3	1.1	1.0	0.9	0.8	0.7	0.7	0.6	0.6
50	2.4	2.0	1.7	1.5	1.4	1.2	1.1	1.0	1.0	0.9
40	3.0	2.6	2.2	2.0	1.8	1.6	1.5	1.3	1.2	1.2
30	4.3	3.6	3.1	2.8	2.5	2.3	2.1	1.9	1.8	1.6
25	5.4	4.6	4.0	3.5	3.1	2.8	2.6	2.4	2.2	2.1
20	7.3	6.2	5.4	4.8	4.3	3.9	3.5	3.2	3.0	2.8
15	11.6	9.8	8.5	7.5	6.8	6.1	5.6	5.1	4.8	4.4
10.5	32.1	27.2	23.6	20.9	18.7	17.0	15.5	14.3	13.2	12.3

Figure 5.8: Time for Cr(III) levels to exceed CDPH proposed MCL for Cr(VI) of 10 ppb in the presence of chlorine

Figure 5.8 shows the tabulated times to exceed CA's PHG. For example- within Santan typical levels of Cr(III) are above 25 ppb in cooling tower makeup water. As the plant chlorinates to reduce biological buildup within the cooling tower, the plant is generating more Cr(VI) if it was not already present as Cr(VI). At this point, if the plant was dosing at 2 mg/L, it would take approximately 3.5 hours to exceed the CA PHG. Another application is at the finish water from a WTP. Currently the US EPA regulates total Cr at 100 ppb. If a plant was treating Cr to a discharge level of 50 ppb, and if the plant were dosing 2 mg/L for residual chlorine and feeding directly into the distribution system, it would only take 1.5 hours to oxidize any existing Cr(III) to Cr(VI), to exceed the proposed MCL.

Within drinking water systems, as defined in 40 CFR 141.2, the product of "residual disinfectant concentration" (C) in mg/L is determined before, or at the first consumer, and the corresponding "disinfectant contact time" (t) in minutes, hence "C" x "t". This CT value can be

considered chlorine exposure. Cr(VI) formation was plotted according to increasing Cr(III) concentrations, with respect to increasing chlorine exposure values (Figure 4.9).
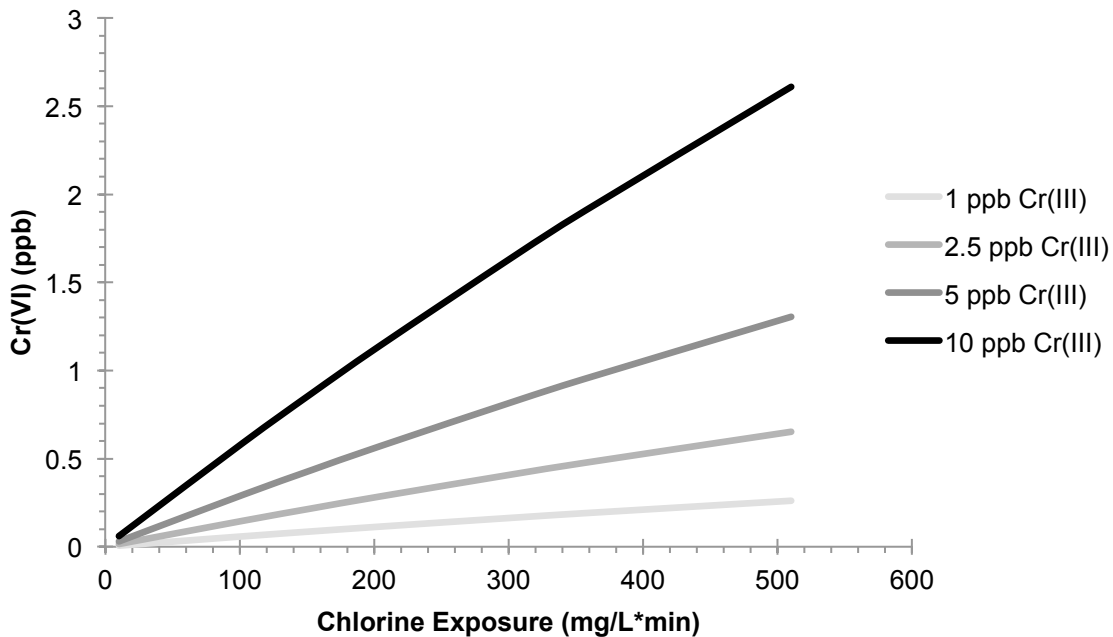
Figure 5.9: Cr(VI) Formation in response to various Ct values, with a residual Chlorine Concentration of 2 mg/L, at pH=5

Figure 5.9 above shows that with increasing Cr(III) concentrations, more Cr(VI) forms at higher Ct values. Oxidants are widely used for disinfection, and Ct values are used to relate disinfection capabilities of different oxidant types. This kinetic rate constant was determined for chlorine, specifically, HOCl, however these Ct values should be compared with oxidation potentials of Cr(III) by different types of oxidants.

5.5 Summary & Conclusions

A rate constant for the oxidation of Cr(III) to Cr(VI) via chlorine was successfully determined to be 0.7 $M^{-1}s^{-1}$. Although there have been many reported rate constants describing the oxidation of specific metals by chlorine, there has been no published rate constant for the oxidation of Cr(III), most likely due to problems with its low solubility at neutral pH levels. Key findings and conclusions of this oxidation work include:

- The precipitation of Cr(OH)$_x$ complexes was avoided by conducting batch experiments at pH = 5, and using environmental relevant Cr(III) concentrations (ppb range), compared with many published metal oxidation via chlorine studies which are done at higher metal concentrations (ppm range).

- An apparent second-order reaction rate constant for the oxidation of Cr(III) to Cr(VI) via HOCl was found to be 0.7 M^{-1}s^{-1}. Although this rate constant is slower than other metal oxidation rate constants (e.g. Arsenite, Bromide), this oxidation occurs at time-scales dissimilar to water age within a distribution system.

- The presence of excess oxidant (chlorine) with respect to μM concentrations of Cr, found in drinking waters suggests that most Cr species will be present as Cr(VI) in the presence of any residual chlorine. This means that samples taken from water treatment plant effluent used to comply with MCL's may not be indicative of Cr(VI) levels at consumers tap. It is possible that Cr species will become oxidized to the more harmful Cr(VI) within the distribution system, with elevated levels of Cr(VI) present at further reaches of distribution system.

CHAPTER 6

SUMMARY & CONCLUSIONS

This chapter presents a summary of observations from each chapter. Subsequent sections integrate these observations into a set of conclusions for my thesis, followed by recommendations for utilities and future work.

6.1 Summary

The objective of Chapter 2 was to both provide SRP with critical information on the occurrence and treatment of trace metals in local waters, as well as to evaluate several treatment methods for removing hexavalent chromium and selenium. Key findings of Chapter 2 include:

- All metals were observed to be concentrated 4-5 times within the cooling tower blowdown from makeup water; indicating a waste stream requiring treatment prior to discharge into surface waters. These levels are above Arizona discharge limits, and as discharge limits continue to become more stringent, more advanced treatment will be required to comply with permits.

- It is possible that there are sources of Cr and Se within the water treatment facilities, e.g. potentially within chemical feeds or chromium treated wood. It is thought wooden slats, treated with chromium, are found within the Kyrene Generating Facility's cooling towers. Elevated levels of chromium found within the Chandler Water Treatment Plant suggest certain chemical additions may be introducing unwanted chromium into the system, which could be avoided by choosing an alternative chemical.

- Chlorine present in water will oxidize remaining Cr(III) to the more toxic and persistent pollutant, Cr(VI). Chlorine is added to cooling tower water to reduce biological growth within the tower. It is evident that the Cr(III) was oxidized by this chlorine because all present Cr within the blowdown water was present as Cr(VI). A potential Cr(VI)-specific regulation of drinking water may result in a Cr(VI)-specific discharge regulation, which would require further treatment.

- Through utilizing adequate ferrous sulfate doses and mixing, chromium can be successfully removed by ~90% and arsenic by nearly 50% within cooling tower blowdown water via traditional coagulation, precipitation. This process produces solids or precipitated metals, which require proper handling and disposal. Although effective for chromium and arsenic, selenium is not removed via ferrous sulfate, and requires an alternative treatment technology.

- Bisulfite was found to be effective for reducing Cr(VI) to non detect levels at the Kyrene Generating Facility at pH 8.5. This reduction successfully reduced 2.5 ppb of Cr(VI) at the plant, representative of full-scale operating conditions. Should a Cr(VI)-specific discharge limit be enforced within discharge permits, bisulfite may be capable of reducing Cr(VI) to appropriate levels within blowdown waters.

The objective of Chapter 3 was to develop, and employ a passive sampler at Chandler WTP, which would prove to be more representative of true water quality when compared to period grab samples obtained from an ISCO sampler. The following observations and conclusions were made:

- Cr and As concentrations can fluctuate significantly over a 7-day period at water treatment plants, especially at a plant that intakes from a number of different groundwater wells and surface water sources. Specifically, Cr(VI) levels ranged from 0.5-2 ppb at the Chandler Water Treatment Plant showing nearly a 4-time variation. This fluctuating water quality indicates that grab samples may not be representative of true water quality, and similarly, ecological and consumer risk over periods of time.

- In the lab a passive sampler, a column packed with SBA (SIR-100) resin, was able to achieve >90% recovery of applied Cr(VI) based on a mass balance, by using an elution scheme with sodium chloride solution. Comparatively, a passive sampler using WBA (SIR-700) resin was only able to achieve >40% recovery through microwave acid digestion of the resin, most likely due to the loss of chromium mass in glass wool used to pack the column. Due to the high recovery, and ease of quantification compared to a

microwave acid digestion, utilizing SBA for Cr(VI) passive sampling was selected to be tested in the field.

- Results obtained from the passive (SBA) sampler employed at Chandler WTP complimented the continuous grab samples collected by the ISCO during a 7-day period. This proves that in-situ passive samplers are capable of representing fluctuating water quality; perhaps more representative of actual exposure levels compared to period grab samples.

The objective of Chapter 4 was to perform a number of bench and batch tests to better optimize SBA brine management for CVWD. Specific conclusions include

- Sulfate levels (>80 mg/L) can significantly impact SBA's ability to remove As, as demonstrated by the chromatographic peaking of As occurring at >667 BV in column tests. This chromatographic peaking of As occurs because the sulfate anion has a higher affinity for specific IX exchange sites of the SBG-1 resin. As sulfate continues to pass through the resin bed, the sulfate anion essentially elutes off any previously exchanged As from those sites.

- Sulfate levels (>80 mg/L) did not impact SBA's ability to remove Cr nor Cr(VI) from influent water. This was determined based on no detection of Cr in effluent from the columns, after seven cycles of resin exhaustion and regeneration. High Cr recovery indicates that 5% NaCl solution adequately regenerates SBA resins for Cr treatment.

- Brine collected from the regeneration of IX resins can be treated for Cr and As; removing over 90% using ferrous sulfate doses of 6 mg/L Fe2SO4. The ferrous sulfate reduces Cr(VI) within the brine. The addition of chlorine oxidizes the ferrous iron to ferric, which coprecipitated with As in solution, removing both As and Cr from the brine. Using ferric chloride was shows to exhibit much lower Cr and As removal at much higher iron doses, indication ferrous sulfate to be the more effective treatment for spent brine.

The objective of Chapter 5 was to develop a rate constant surrounding the oxidation of Cr(III) to Cr(VI) via chlorine, under pseudo-first order reaction conditions. Specific conclusions include

- The precipitation of Cr(OH)$_x$ complexes was avoided by conducting batch experiments at pH = 5, and using environmental relevant Cr(III) concentrations (ppb range), compared with many published metal oxidation via chlorine studies which are done at higher metal concentrations (ppm range).

- An apparent second-order reaction rate constant for the oxidation of Cr(III) to Cr(VI) via HOCl was found to be 0.7 M^{-1}s^{-1}. Although this rate constant is slower than other metal oxidation rate constants (e.g. Arsenite, Bromide), this oxidation occurs at time-scales dissimilar to water age within a distribution system.

- The presence of excess oxidant (chlorine) with respect to µM concentrations of Cr, found in drinking waters suggests that most Cr species will be present as Cr(VI) in the presence of any residual chlorine. This means that samples taken from water treatment plant effluent used to comply with MCL's may not be indicative of Cr(VI) levels at consumers tap. It is possible that Cr species will become oxidized to the more harmful Cr(VI) within the distribution system, with elevated levels of Cr(VI) present at further reaches of distribution system.

6.2 Conclusions

Major conclusions presented throughout this thesis include:

- Local AZ canal, groundwaters, and surface waters are impacted by Cr(VI), As, and Se, but can successfully be treated using reactive iron coagulation and other reductive treatment technologies, i.e. bisulfite.

- Time-integrated Cr(VI) sampling was validated using a SBA IX resin-based passive sampler from which Cr(VI) could be easily recovered and analyzed. This Cr(VI)-passive sampler has novel water quality sampling applications which prove capable of providing more time-dependent representative water quality data, when compared to traditional, periodic grab samples.

- The oxidation of Cr(III) to Cr(VI) via chlorine follows second-order-reaction rate kinetics at a time-scale found within treatment facilities and water distribution systems. Residual

chlorine often added to water treatment plant finish water has the potential to oxidize any Cr species to them more toxic Cr(VI) form within distribution systems before reaching consumer's taps. If a Cr(VI)-specific MCL is developed, and enforced, understanding this conversion of Cr(III) to Cr(VI) both within treatment plants, and within distribution systems is necessary for utilities to comply with the regulation.

- Strong base anion exchange is not effective for As removal in waters with moderate (>80 ppm) sulfate levels, due to sulfate's higher affinity for IX sites compared to arsenate species. However despite moderate sulfate levels, SBA was found to be effective for Cr(VI) removal over seven cycles of resin exhaustion and regeneration. Brine used for the regeneration of SBA resins containing high levels of Cr and As can be treated (>90% of both As and Cr) using relatively low (6 mg/L) ferrous sulfate doses.

6.3 Recommendations to Utilities

If a Cr(VI)-specific MCL is put into place, utilities must have the infrastructure (both monitoring and treatment infrastructure) necessary to comply with discharge levels. To do so, it is important for utilities to monitor Cr(VI) levels, both in influent and effluent streams to understand possible seasonal fluctuating Cr(VI) concentrations. Over a 7-day period, Cr(VI) levels were found to fluctuate significantly (4x), indicating that a better understanding of each WTP's specific water quality should help to determine specific treatment doses, i.e. reactive iron for coagulation, or bisulfite for Cr(VI) reduction. It is evident that SBA IX is a proven technology for Cr/Cr(VI) removal, however, it may not be appropriate for waters with higher (80 mg/L) sulfate levels if treatment of As is also required. Brine produced from SBA IX technologies can be treated to remove excess metals, and reused for resin regeneration in order to reduce overall waste volume, and associated disposal and handling costs. It is also possible that through the use of barium salts, sulfate can simultaneously be removed from these brines along with As and Cr to in order to reduce the number of competing anions within the brine that clearly inhibit the resins' ability to remove specific contaminants.

6.4 Recommendations for Future Research

More work should be done to further develop the passive sampler. The passive samplers developed within this work required a pump, to draw water through the column. Perhaps a column could be installed in true flow-through mode, which would eliminate the need for an external power supply. This could be done by installing a passive sampler connected to the side of a channel within the treatment plant. Water would flow through the passive sampler, through an outlet which could drain to waste. A flow totalizer installed at this point would determine the volume of water passing through the column, which could then be used in mass balance calculations.

Cr(VI) recovery should also be further investigated for WBA resins. Due to their higher capacity for Cr(VI), these resins have the ability to be installed for longer durations of time, without potential Cr(VI) breakthrough. It is possible to recover all of the resin within the column by digesting all resin within the glass wool. It is possible that through this process, higher recoveries could be achieved, and a passive sampler could be used for longer durations of time.

The potential application for other metal oxo-anions, other than chromate, should also be investigated using the sampler (e.g. arsenate). The resin selected for the passive samplers developed in this work did not show the ability to be reused, there are other resins available that may exhibit the ability for sampler reuse. For this reason, other resins should be screened for passive sampling applications.

The apparent second-order-rate constant for the oxidation of Cr(III) to Cr(VI) that was developed should be tested; both at lab scale, and within treatment plants and distribution systems. If Cr(III) really does oxidize to Cr(VI) at a significant rate, consumers at far reaches of distribution systems will be at higher risk for unwanted health impacts associated with chromate in their tap waters. Work should also be done to determine the oxidation of Cr(III) to Cr(VI) via other oxidants, i.e. ozone and chloramines. Since chlorine has been proven to produce many undesirable disinfection byproducts, many plants have switched to other oxidants for oxidation/disinfection purposes. For these reasons, the oxidation of Cr(III) to Cr(VI) by these alternative disinfectants/oxidants would be applicable for other WTPs.

The findings presented within this thesis present many areas for future research opportunities. With California's MCL for Cr(VI) of 20 ppt, being reviewed by August of this year, there is definitive need for further investigations of the behavior and treatment efficacies of aqueous chromate species within industrial and municipal waters.

REFERENCES

Arden, T.V.; Giddings, M. Anion exchange in chromate solution. J. Applied Chem. 11, 229-253 (1961).

AWWA. (2014). Hexavalent Chromium. Retrieved March 24, 2014, from DrinkTap.org: http://www.drinktap.org/home/water-information/water-quality/hexavalent-chromium.aspx?ct=a5648aa9de24032dd446f70d62233aa5ab8b340d0c61f5a8a749f8082 e65dc79eb64791e43c38c2fc264bf4abd9b5ff7a17fd19f7cd571368371b4182ee91968

Baldwin, R.; Stauter, J.; Terrell, D. Process for the removal of selenium from aqueous systems. United States Patent 4,405,464, (1983).

Barber, B. W. P., & Stuckey, D. C. (2000). Metal Bioavailability and Trivalent Chromium Removal in ABR, (July), 649–656.

Barrera-Diaz, C.E., et. al. A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction, Journal of Hazardous Materials, 223-224, 1-12 (2012).

Basumallick, L., & Rohrer, J. (2012). Sensitive Determination of Hexavalent Chromium in Drinking Water. Dionex. Sunnyvale: Thermo Fisher Scientific Inc.

Beukes, J.P., et. al. The reduction of hexavalent chromium by sulphite in wastewater, Water SA, 25, 363-370 (1999).

Brandhuber, P., Frey, M., McGuire, M., Chao, P. F., Seidel, C., Amy, G., … Banerjee, K. (2004). Low-Level Hexavalent Chromium Treatment Options: Bench-Scale Evaluation. Water Research Foundation Report.

California Department of Publich Health. (2014, January 30). Chromum-6 in Drinking Water: MCL Update. Retrieved February 1, 2014, from http://www.cdph.ca.gov/certlic/drinkingwater/Pages/Chromium6.aspx

Center for Environmental Research Information. (2008). In Situ Treatment of Soil and Groundwater Contaminated with Chromium . US Enviornmental Protection Agency, Office of Research and Development. Washington DC: US EPA.

Clifford, D. (1999). Ion Exchange and Inorganic Adsorption. In Water Quality and Treatment: A Handbook of Community Water Supplies (5th ed. ed.). New York: McGraw-Hill.

Costa, M. (2003). Potential hazards of hexavalent chromate in our drinking water. Toxicology and Applied Pharmacology, 188(1), 1–5. doi:10.1016/S0041-008X(03)00011-5

Deborde, M., & von Gunten, U. (2008). Reactions of chlorine with inorganic and organic compounds during water treatment-Kinetics and mechanisms: a critical review. Water research, 42(1-2), 13–51. doi:10.1016/j.watres.2007.07.025

Dodd, M. C., Vu, N. D., Ammann, A., Le, V. C., Kissner, R., Pham, H. V., … Von Gunten, U. (2006). Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: relevance to drinking water treatment. Environmental science & technology, 40(10), 3285–92. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/16749695

HACH. Chlorine, Free and Total. HACH.

Hagelstein, K.; Mudder, T. Selenium treatment technologies and case studies, TMS 138th Annual Meeting & Exhibition: Supplemental Proceedings, (2009).

Hach Company. (2007). DR 2800 Spectrophotometer. Germany: Hach Company.

International Consultants, INC. and Malcom Pirnie, INC. (2000). Technologies and Costs for Removal of Arsenic from Drinking Water. EPA.

Katz, S. A., & Salem, H. (1994). The Biological and Environmental Chemistry of Chromium. New York, NY: VCH Publishers, Inc.

Le, E.; Rai, D. Chromate removal from aqueous waste by reduction with ferrous iron. Environ. Sci. Technol. 22, 972-977 (1988).

Lindsay, D. R., Farley, K. J., & Carbonaro, R. F. (2012). Oxidation of CrIIIto CrVI during chlorination of drinking water.pdf, 1789–1797.

Marchant, W. Method for removing soluble selenium from acidic waste water. United States Patent 3,933,635, (1975).

McGuire, M. J., Blute, N. K., Qin, G., Kavounas, P., Froelich, D., & Fong, L. (2007). Hexavalent Chromium Removal Using Anion Exchange and Reduction With Coagulation and Filtration. AWWA Research Foundation.

National Academy of Sciences. (1974). Medical and Biologic Effects of Environmental Pollutants: Chromium. Washington, D.C.: Printing and Publishing Office, National Acadejmy of Sciences.

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

Panagiotaras, D., & Panagopoulos, G. (n.d.). Arsenic Geochemistry in Groundwater System.

Patterson, J. (1985). Industrial Wastewater Treatment Technology (2nd Edition ed.). Boston, MA: Butterworth.

Pfaff, J. D. Method 300.00 Determination of Inorganic Anions by Ion Chromatography. Environmental Monitoring Systems Laboratory, Office of Research and Development. Cincinnati: Environmental Protection Agency.

Salt River Project. (1996). Retrieved 2014, from srp.net

Sorg, T. J. (1979). Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Organics: Part 4. Journal (American Water Works Association) , 71 (8), 454-466.

Taylor & Francis Group. (2008). CRC Handbook of Chemistry and Physics (88th Edition ed.). (L. DR, Ed.) New York, NY: CRC Press.

U.S. Department of Health and Human Services. (2008). Agency for Toxic Substances and Disease Registry, Public Health Service. Atlanta: U.S. Department of Health and Human Services.

U.S. Environmental Protection Agency. (1999). Integrated Risk Information System (IRIS) on Chromium VI. National Center for Environmental Assessment, Office of Research and Development, Washington, DC.

US Environmental Protection Agency. (2014). Basic Information about Chromium in Drinking Water. Washington D.C.

Westerhoff, P.; Highfield, D.; Badruzzman, M.; Yoon, Y. Rapid small-scale column tests for arsenate removal in iron oxide packed bed columns. J. Environmental Engineering, 131, 1574 (2005).

Westerhoff, P.; Moon, H.; Minakata, D.; Crittenden, J. Oxidation of organics in retentates from reverse osmosis wastewater reuse facilities. Water. Res., 43, 3992-3998 (2009).

Vincent, J. B. (2000). The biochemistry of chromium. The Journal of nutrition, 130(4), 715–8. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/10736319

World Health Organization. (2004). Chemistry of Disinfectants and Disinfectant By-Products. WHO.

World Health Organization. (2003). Guidelines for drinking-water quality (2nd edition ed., Vol. 2). Geneva, Switzerland: World Health Organization.

Yang, T., Doudrick, K., & Westerhoff, P. (2013, March 1). Photocatalytic reduction of nitrate using titanium dioxide for regeneration of ion exchange brine. Water research. doi:10.1016/j.watres.2012.11.047

APPENDIX A

ANALYTICAL METHODS

Aqueous Concentrations and Analysis

All aqueous concentrations were collected, and filtered through a 0.45 um cellulose membrane for analysis via ion chromatography or inductively coupled plasma mass spectrometry, as described further, below.

Hexavalent chromium concentrations were measured using ion chromatography (Dionex ICS 2000) following a manufacturer recommended modification of EPA Method 218.6 (Basumallick & Rohrer, 2012). The modified method uses Dionex IonPac AG7 guard and Dionex IonPac AS7 analytical columns, an eluent of 250 mM ammonium sulfate/100 mM ammonium hydroxide at a flow rate of 0.36 mL/min, a 1000 uL injection volume, and postcolumn reaction with 2 mM diphenylcarbazide/10%methanol/1 N sulfuric acid (using a 125 uL reaction coil) followed by visible absorbance detection at 530 nm. This method results in a minimum detection level of 0.001 ug/L, which is suitable for analysis at the proposed California Publich Health Goal (PHG) of 0.02 ug/L. Samples to be analyzed for hexavalent chromium were spiked with 1% of ammonium hydroxide buffer.

Total chromium, arsenic, and selenium concentrations were measured using a Thermo Fisher Scientific XSeries 2 quadrapole ICP-MS and Cetac ASX-520 autosampler. Samples were preserved using 2-3% nitric acid (ULTREX, Sigma-Aldrich). Sample introduction consisted of a conical spray chamber with impact bead and concentric nebulizer with a flow of 1 mL/min. The spray chamber was cooled to 3° C by a Peltier cooling system. Collision Cell Technology (CCT) mode was used to reduce interferences by the argon gas used to generate the plasma by using a mixture of 7% hydrogen/93% helium. The differential between total chromium and hexavalent chromium was considered to be trivalent chromium.

Total chlorine levels were measured using HACH Method 8167 DPD Method Powder Pillows (0.02 to 2.00 mg/L as Cl_2). (Hach Company, 2007) This Method uses a DR 2800 Spectrophotometer.

Major anions (nitrate, sulfate, and chloride) were measured using high-pressure ion chromatography (Dionex ICS-5000 HPIC system, following Part A of EPA Method 300.0 (Determination of Inorganic Anions by Ion Chromatography). Sample is introduced into the IC,

pass through the capillary guard column (IonPac AG18, Thermo Scientific), are separated within the capillary analytical column (IonPac AS18, Thermo Scientific), through the suppressor and then pass through a conductivity detector. Eluent solution is a mixture of sodium bicarbonate and sodium carbonate. (Pfaff)

BIOGRAPHICAL SKETCH

Alexandra (Allie) Bowen graduated with a B.S. in Environmental Engineering from the University of New Hampshire in Durham, NH. Allie was a proud member of UNH's Environmental Research Group, specifically working under Dr. James Malley, Jr., as one of the original "Malley Cats". Her involvement in undergraduate drinking water research lead her to countless research papers written by Dr. Paul Westerhoff, at Arizona State University. It was at Arizona State University, under Dr. Paul Westerhoff, that she was given an opportunity to peruse, and defend her masters in environmental engineering. With her maters degree, Allie is going on to gain experience in the engineering consulting world by accepting an engineering position with CDM Smith in Cambridge, MA.