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Ion-exchange (IX): arsenic and chromium removal from brines and removal of inorganic contaminants by specialty resins

Behrang Pakzadeh
University of Nevada Las Vegas

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ION-EXCHANGE (IX): ARSENIC AND CHROMIUM REMOVAL FROM BRINES AND REMOVAL OF INORGANIC CONTAMINANTS BY SPECIALTY RESINS

by

Behrang Pakzadeh

Bachelor of Science
Sharif University of Technology (SUT), Tehran, Iran
2001

Master of Science
Technical University of Denmark (DTU), Lyngby, Denmark
2006

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of the requirements for the

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Department of Civil and Environmental Engineering
Howard R. Hughes College of Engineering

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Behrang Pakzadeh

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Jacimaria R. Batista, Committee Chair

Thomas C. Piechota, Committee Member

Sajjad Ahmad, Committee Member

Kazem Taghva, Committee Member

Spencer M. Steinberg, Graduate Faculty Representative

Ronald Smith, Ph. D., Vice President for Research and Graduate Studies
and Dean of the Graduate College

May 2010

ABSTRACT

Ion-Exchange (IX): Arsenic and Chromium Removal from Brines and Removal of Inorganic Contaminants by Specialty Resins

by

Behrang Pakzadeh

Dr. Jacimaria R. Batista, Examination Committee Chair
Associate Professor of Civil and Environmental Engineering
University of Nevada, Las Vegas

Although ion exchange is highly efficient in removing inorganic contaminants, similar to other water treatment technologies, ion exchange has some drawbacks that need to be studied further. Three issues related to drawbacks of ion-exchange resins in water treatment were addressed in this research. The first issue was the influence of anionic inorganic co-contaminants including nitrate, Cr(VI), Se(VI), and As(V) on the performances of nitrate and perchlorate specialty (selective) resins in water treatment. It was found that nitrate can be removed from waters using perchlorate specialty resins, but the resin is poorly regenerated. Perchlorate was not easily removed from either nitrate or perchlorate specialty resins. The results showed that simultaneous removal of nitrate and Cr(VI) is optimal when using nitrate specialty resin. Perchlorate/nitrate specialty resins were inefficient in removing As(V), but could exchange Cr(VI) or Se(VI). A major issue realized from this research is the accumulation of co-contaminants in specialty resins and their release during resin regeneration. Such a release may deem waste regenerant brines hazardous, significantly affecting disposal costs. The presence of the co-contaminant ions affected the run length and the brine composition when perchlorate or nitrate specialty resins were used. Brine treatment is a serious challenge for IX water industry when removing arsenic (V) or chromium (VI) from drinking water.

Arsenic (V) removal from brines using ferric chloride was the second issue of this research. The optimum pH range for the process was found to be 4.5-6.5. Higher brine alkalinity affected coagulation because it commands larger amounts of acid to lower the pH to the desired level. Increasing ionic strength slightly enhanced the arsenic (V) removal efficiency. For arsenic (V) concentrations typical in ion exchange brines and to achieve a remaining As (V) concentration of 5 mg/L, Fe/As molar ratios varying from 1.3 to 1.7 are needed at operating pH values of 5.5 to 6.5. The Fe/As ratios needed to treat brines are significantly lower than those used to treat drinking waters. Solids concentration varying from 2 to 18 mg/L were found.

The third issue of this research was chromium removal from IX brines. Optimum pH range for the process was found to be 8-10.3. The chromium removal efficiency improved only slightly when the ionic strength increased from 0.1 M to 1.5 M. For chromium (VI) concentrations typically found in IX brines, a CaS_5/Cr(VI) molar ratio varying from 0.6 to 1.4 was needed to obtain a final chromium concentration below 5 mg/L. The maximum total chromium removal efficiencies were obtained at reducing conditions when oxidation reduction potentials of the brines were between -0.1 to 0 V. Solids concentrations varying from 0.2 to 1.5 g/L were found. The results of this research have direct application to the treatment of residual wastes brines containing chromium.

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CHAPTER 1

INTRODUCTION

1.1. Background

Ion-exchange (IX) is an efficient technology to remove dissolved inorganic contaminants from drinking water, including arsenic, selenium, chromium, nitrate, perchlorate, and uranium. Similar to other water treatment technologies, ion-exchange has some drawbacks that need to be studied further. One deficiency of ion-exchange that needs further consideration is the impact of co-occurring contaminants such as arsenic, chromium, selenium, or uranium when specialty resins are used. The impact of co-occurring contaminants on the performances of perchlorate and nitrate specialty resins has not been evaluated. Because specialty resins are designed to minimize the effect of sulfate, they have very high capacity for ions of interest and consequently operate for a long time before regeneration or disposal is needed. Accordingly, even co-contaminants that are present at very small amounts in the influent water will accumulate at higher levels in the resin and will appear in the regenerant waste brine. The impact of co-contaminants (i.e., chromium(VI), selenium(VI), or arsenic(V)) on the performances of perchlorate and nitrate specialty resins were investigated in this research.

To be economically feasible, spent IX resin beds must be regenerated, generally, using sodium chloride. Regeneration produces waste brines and their disposal is a major challenge to the water industry. These waste brines are generally deemed hazardous because they contain high levels of the contaminant of interest (e.g., arsenic, chromium, or uranium), high alkalinity, and high ionic strength. In this research, treatment of waste

IX brines containing arsenic and chromium, with ferric chloride and calcium polysulfide, respectively, was investigated.

Three specific issues are addressed in this research:

1.2. Issue One: Impact of Co-Contaminants on the Performances of Perchlorate and Nitrate Specialty Resins

Several inorganic contaminants, including arsenic (Ghurye et al., 1999), selenium (Sorg and Logsdon, 1978), chromium (Korngold et al., 2003), nitrate (Tripp and Clifford, 2006), perchlorate (Gu and Brown, 2006), and uranium (Gu et al., 2004) can be removed from waters by ion-exchange. Ion-exchange has caught the attention of water treatment suppliers because it can meet the stringent maximum contaminant levels required by the U.S. EPA.

The presence of co-contaminants in water is a challenge for ion-exchange plant design because the optimal conditions for their removal may differ. Furthermore, co-contaminants can accumulate in resins and waste brines hindering brine disposal and resin reuse. Commonly, conventional strong base anion (SBA) exchange resins have been utilized to remove inorganic contaminants from drinking water (Clifford & Weber, 1986; Ghurye et al., 1999; Sengupta, 1995). These resins are effective in removing inorganic contaminants, however, the volume of water that can be processed before the resin needs regeneration is significantly reduced by the presence of sulfate, which is a divalent anions that occurs in most waters. SBA resins have a high affinity for sulfate and other multivalent ions, as compared to monovalent anionic contaminants. When

SBA resins are used, most of their capacity is captured by sulfate or other multivalent ions, thereby, reducing their capacity to remove the contaminant of interest.

In the last decade, specialty resins, also known as selective resins, have been developed to remove inorganic contaminants from water. These resins are designed to have high affinity for the contaminant and less affinity for sulfate. It has been reported that an important factor affecting the selectivity of ion-exchange resins is the spacing of exchange sites (Clifford & Weber, 1986; Guter, 1984, Liu & Clifford, 1996). The distance between active exchange sites affects the divalent-monovalent selectivity (Guter, 1984). For example, by increasing the length of the trialkyl group from methyl to hexyl, the selectivity of the resin for ClO_4^- is increased, while the selectivity of the resin for SO_4^{2-} or other divalent ions is decreased (Gu & Coates, 2006). The order of the selectivity of the perchlorate selective resins is known to be perchlorate > nitrate > chloride > bicarbonate (Gu & Coates, 2006). Similarly, nitrate specialty resins are produced by increasing the length of the functional group from trimethyl-amines to triethyl-amines or tributyl-amines (Guter, 1984). Divalent ions need to adsorb into two active sites; thus, when the spacing between active sites increases, divalent ions [e.g., sulfate (SO_4^{2-}), hydrogen arsenate ($HAsO_4^{2-}$), chromate (CrO_4^{2-}), or selenate (SeO_4^{2-})] cannot be adsorbed; however, monovalent ions (e.g., nitrate or perchlorate) are still adsorbed by the resin because they need only one active place in which to be adsorbed (MWH, 2005). In most drinking waters, divalent ions [i.e., hydrogen arsenate ($HAsO_4^{2-}$), chromate (CrO_4^{2-}), or selenate (SeO_4^{2-})] are the predominant species of As(V), Cr(VI), or Se(VI). In this research, it was hypothesized that perchlorate specialty resins were highly efficient in removing nitrate. It was also hypothesized that perchlorate and nitrate specialty resins were less efficient in removing divalent co-contaminants, i.e., hydrogen arsenate ($HAsO_4^{2-}$), chromate (CrO_4^{2-}), or selenate (SeO_4^{2-}), than conventional resins.

Because of their higher selectivity, the use of specialty resins to remove nitrate (Rochette, 2006; Tripp & Clifford, 2006; Ghurye et al., 1999; Liu & Clifford, 1996) and perchlorate (Gu & Brown, 2006; Tripp & Clifford, 2000; Batista et al., 2000) from water has increased significantly. Specialty resins are more costly than SBA resins, but larger volumes of water can be processed before the resin capacity is exhausted thereby reducing the overall operational costs (Gu & Coates, 2006). Although perchlorate and nitrate specialty resins have been developed and tested at pilot and full-scale to remove ions of interest (i.e., perchlorate and nitrate) (Ghurye et al., 1999; Liu & Clifford, 1996; Siegel et al., 2006; Gu et al., 2003), the performance of these resins to remove co-occurring contaminants such as As(V), Se(VI), Cr(VI) have not been studied to date. In the case of nitrate and perchlorate, several waters contaminated with perchlorate also contain varying levels of nitrate (U.S. EPA, 1999; Batista et al., 2002). Some perchlorate or nitrate-contaminated waters may also contain lower levels of As(V), Se(VI), Cr(VI), and/or uranium (U.S. EPA, 1999). It was hypothesized that the presence of inorganic co-contaminants negatively affects the amount of water that can be processed as well as the management of the used resin and its regeneration. Co-contaminants can accumulate in the resin to levels that create a hazardous waste. Specialty ion-exchange resins stay in service for a long time before breakthrough occurs because they are unselective for sulfate and highly selective for the anions they are designed to remove. Although co-contaminants may be present in the water at trace levels, the long time the resins stay in service results in the accumulation of a significant amount of contaminants (Ghurye et al., 1999). In California, several wells contaminated with perchlorate and arsenic, for example, contain trace levels of uranium. When treating these waters with specialty resins, the potential accumulation of uranium in the resin must be taken into consideration because of stringent disposal regulations for wastes containing uranium. The same can be said for waters containing trace levels of selenium, arsenic, and chromium. In this research, the removal of the inorganic co-contaminants by perchlorate and nitrate specialty resins is addressed.

Spent IX resin should be regenerated and reused to reduce the operational costs of water treatment (Gu et al., 2003; Batista et al., 2000). Ion-exchange resins are commonly regenerated with an 8 to12 % NaCl brine solution, which is cost effective and widely used. Nitrate can be desorbed from nitrate specialty resins using a NaCl brine. Because of its high selectivity for perchlorate, and the hydrophobic character of both perchlorate ion and the resin, the regeneration of a perchlorate-laden perchlorate specialty resin is ineffective even when excessive volumes of brine solutions are used (Gu & Coates, 2006; Gu et al., 2000; Batista et al., 2000; Tripp & Clifford, 2000). The feasibility of desorbing inorganic co-contaminants such as nitrate, As(V), Se(VI), or Cr(VI) from perchlorate selective specialty resins has not been investigated to date. It was hypothesized that arsenic, chromium, and selenium-laden perchlorate or nitrate specialty resins were regenerable.

1.3. Issue Two: Arsenic Removal from Ion-exchange Brines Using Ferric Chloride

The standard of 10 μg/L was set as the maximum contaminant level (MCL) for arsenic in the United States on January 18, 2001. Water treatment plants have had to comply with the new regulation since January 23, 2006. The current MCL provides protection for more than 13,000,000 Americans (U.S. EPA, 2007). Ion-exchange has been listed as one of the best available technologies to remove arsenic (V) from water (MacPhee et al., 2001). Conventional strong base anion resins or specialty resins are utilized to efficiently remove arsenic from waters (Kim and Benjamin, 2004; Clifford and Ghurye, 2002; Chwirka et al, 2004; Clifford, 1999; McNeill and Edwards, 1995). Arsenic ions move through the bed, exhausting the ion-exchange capacity until arsenic breaks through. The spent IX resin beds must be regenerated, generally, using sodium chloride. The regeneration process produces brine solutions with high concentrations of arsenic and high alkalinity (MacPhee et al., 2001). If the generated brine contains more than 5 mg/L (Toxicity Characteristic (TC)) of arsenic, it is considered hazardous waste according to the Resource Conservation and Recovery Act (RCRA) (U.S. EPA, 2003). Residual wastes generated from arsenic removal ion-exchange plants are usually considered hazardous. The costs of disposal and handling of hazardous wastes are drastically higher than non-hazardous wastes (Meng et al., 2001). The disposal and handling costs account for 12 to 34% of the total costs (Frey et al., 1998). Hazardous brines are banned from disposal in municipal solid or hazardous waste landfills because they are in a liquid form that contains high concentrations of regulated contaminants. Generated solid wastes in the brine treatment process have to pass the EPA Toxicity Characteristic Leaching Procedure (TCLP) test (and Waste Extraction Test (WET) in California) to be considered non-hazardous, and can be disposed of in the municipal solid waste landfills (U.S. EPA, 2003). The TCLP and WET tests limit arsenic to less than 5 mg/L in an extracted fluid for the waste to be considered non-hazardous. Therefore, hazardous brines must be treated or disposed of by another technique. MacPhee et al. (2001) reported that IX brine is difficult to treat for meeting in-stream standards, and arsenic removal from ion-exchange residuals need to be investigated thoroughly. Currently, brine disposal is the main challenge in the ion-exchange process. Therefore, there is a need to remove arsenic from waste brines to produce a waste that is non-hazardous and of low volume. Arsenic can be removed from brines using ferric chloride ($FeCl_3$). Arsenic removal with ferric chloride from drinking waters is a well documented process and has been studied for many years (Lakshmanan, 2008; Ghurye et al., 2004; Davis et al., 2001 and 2002; Meng et al., 2000; Hering et al., 1997; McNeill and Edwards, 1997; Hering et al., 1996a; Cheng et al., 1994; Pierce and Moore, 1982; Shen, 1973). The optimal values of pH and the required ferric chloride dosage are known for arsenic removal from drinking waters. In addition, the effects of co-contaminants on the arsenic removal process have been previously investigated. However, the application of ferric chloride to remove arsenic from brines has not been thoroughly investigated. Arsenic-iron hydroxide sludge passes the TCLP test and is considered non-hazardous (Phenrat et al., 2008; Steinwinder and Zhao, 2007; Clifford et al., 2003; Mercer and Tobiason, 2008). Removal of arsenic from ion-exchange residuals decrease the costs of disposal and may increase the number of feasible alternatives for its reuse and resource recovery (Clifford et al., 2003; MacPhee et al., 2001; An et al., 2005). Arsenic is adsorbed by iron precipitates, and liquid can be separated from solid precipitates by filtration. Ionic strength is an important factor in chemical equilibrium. The kinetics of the reactions varies with ionic concentrations (Mercer and Tobiason, 2008). Due to high ionic strength, high alkalinity, and high arsenic concentrations of ion-exchange brines, the optimum conditions for arsenic removal with ferric chloride are likely to be different from those for drinking water. Clifford and Ghuryre (1999) were the first researchers to address brine treatment with ferric chloride for brine reuse in arsenic removal by the ion-exchange process. Clifford et al. (1999) established an optimum pH of 5.5 and ferric chloride dosage for treatment of a specific brine containing 3.45 mg/L arsenic. MacPhee et al. (2001) investigated treatment of arsenic residuals from ion-exchange, activated alumina, reverse osmosis, nanofiltration, and iron-manganese removal processes using ferric chloride. However, their approach for treatment of ion-exchange residuals was not successful in compared with other residuals. MacPhee et al. (2001) reported that ion-exchange residual treatment requires further investigations. Clifford et al. (2003) completed the work from Clifford et al. (1999) by investigating the effect of Fe/As molar ratios on the arsenic removal efficiency by ferric chloride for specific brine containing 3.45 mg/L arsenic. Steinwinder and Zhao (2007) determined the optimal conditions for treatment of a particular spent regeneration brine containing 300 mg/L arsenic using ferric chloride. They also studied the effects of calcium hydroxide addition in stabilizing the arsenic-laden sludge after brine treatment. Mercer and Tobiason (2008) investigated arsenic removal from membrane concentrate containing up to 0.5 mg/L arsenic. They studied the effects of ionic strength and pH on the arsenic removal efficiency. Mercer and Tobiason (2008) also evaluated the performance of preformed (freshly formed hydrous ferric oxide (HFO)) versus in situ formed HFO. However, this study does not address the removal process at high arsenic concentrations. All the aforementioned studies addressed the arsenic treatment from specific brines. There has not been a comprehensive study conducted to model the IX brine treatment process with ferric chloride that can be applied to many different brine types using their major characteristics (i.e., initial arsenic(V) concentrations, alkalinities, and ionic strengths) to assist the IX water industry in designing brine treatment units.

This research investigated arsenic (V) removal by ferric chloride from ion-exchange brines with high alkalinities, ionic strength, and As(V) concentrations. The goal was to estimate the required ferric chloride dosages using the major characteristics of brines. This study also addressed the effects of ionic strengths, pH, and alkalinity on the removal process.

Mercer and Tobiason (2008) found that increasing the ionic strength of the solution with NaCl increased the adsorption of As(V) onto hydrous ferric oxide precipitates in brines containing 0.5 mg/L As(V). Moreover, Xu et al. (2009) reported that increasing the ionic strength increased the adsorption of As(V) on two variable charge soils, i.e., Haplic Acrisol and Rhodic Ferralsol. Edzwald et al. (1974) and Sato et al. (2005) reported that increasing the ionic strength reduced the electrostatic repulsion between particles and therefore increased particle aggregation in waters. Mercer and Tobiason (2008) reported that increasing the alkalinity from 400 to 1400 mg/L decreased the arsenic removal using hydrous ferric oxide (HFO) in a brine containing 0.5 mg/L As(V).

In this research, it was hypothesized that ionic strength favored the arsenic removal from brines in comparison to drinking waters, while alkalinity depressed the removal process. Experimental laboratory batch experiments were performed to test the hypothesis. MINEQL+, a chemical equilibrium modeling software, was used to model the process. The experimental and modeling results were statistically compared to evaluate the accuracy of modeling.

1.4. Issue Three: Chromium Removal from Ion-Exchange Brines Using Calcium Polysulfide

A maximum contaminant level (MCL) of 0.1 mg/L for total chromium became effective by the U.S. EPA in 1992. Considerable research studies have been conducted on technologies to remove chromium from drinking waters. Chromium removal by ion-exchange from water has been pointed out as an efficient technology (Shi et al., 2009; Gode and Pehlivan, 2005; Atia, 2006; Rengaraj et al., 2003; Alguacil et al., 2004; Sengupta and Clifford, 1986). The ion-exchange treatment process is currently used by many water supply utilities, and is very successful in producing water with chromium levels, which satisfies the EPA's MCL. However, regeneration of the ion-exchange resins leads to the generation of the waste streams that must be managed. Moreover, chromium also occurs as a co-contaminant for the other inorganic contaminants (e.g., arsenic or nitrate). In these cases, chromium will also be exchanged and therefore it may be present at high concentrations in the generated brines. Similar to arsenic, chromium levels greater than 5 mg/L in the brine solutions are considered hazardous. Therefore, the generated waste residual must be treated prior to disposal. The brines generated from chromium removal ion-exchange plants or other ion-exchange plants in which chromium presents as a co-contaminant can be treated utilizing calcium polysulfide.

Calcium polysulfide has been used to reduce and remove Cr(VI) from drinking water, other water and wastewater (Yahikozawa et al., 1978; Freedman et al., 2005; Graham et al., 2006). However, calcium polysulfide has never been used to treat ion-exchange brines containing chromium. Cr(VI) removal from groundwaters (Freedman et al., 2005; Graham et al., 2006) and wastewaters (Yahikozawa et al., 1978) by calcium polysulfide has been investigated, and calcium polysulfide has been utilized for removal of heavy metals for many years (Yahikozawa et al., 1978; Licht and Davis, 1997; Haas and Vamos, 1995; Aratani et al., 1978). To my knowledge, the chromium removal from brines with calcium polysulfide has not been studied. There is a strong need to document the chromium removal process and investigate its optimal parameters. This treatment reduces the volume of the produced hazardous waste, and also diminishes the danger of recontamination of the environment.

Calcium polysulfide quickly reduces the Cr(VI) to Cr(III), and chromium precipitates as $Cr(OH)_3$ (Yahikozawa et al., 1978). Calcium polysulfide has been utilized for geological fixation of groundwaters contaminated by chromium, and the results were promising (Jacobs et al., 2001; Storch et al., 2002; Messer et al., 2003; Yu and Tremaine, 2002). Calcium polysulfide also has been utilized for remediation of Cr(VI) from chromite ore processing residue by Graham et al. (2006), Wazne et al. (2007a and 2007b), and Moon et al. (2008). The parameters that affect the process are alkalinity and pH of the solution (Graham et al., 2006; Wazne et al., 2007b). The chromium removal processes from groundwater and chromite ore processing residue were more efficient at alkaline pH values (Graham et al., 2006; Wazne et al., 2007b). It is hypothesized that high pH of brines favors the Cr(VI) removal from brines using calcium polysulfide. Edzwald et al. (1974) and Sato et al. (2005) reported that increasing the ionic strength favors particle coagulation due to decreasing the electrostatic repulsion between particles. Reduction of Cr(VI) to Cr(III) is the main mechanism of the chromium removal using calcium polysulfide (Yahikozawa et al., 1978). In view of the fact that coagulation is not the main mechanism of chromium removal using calcium polysulfide, it is hypothesized that increasing the ionic strength slightly improves the efficiency of chromium removal.

The goal of this research was to study the removal of chromium using calcium polysulfide from synthetic ion-exchange brines by performing laboratory coagulation batch experiments based on a Central Composite Design, which is a response surface methodology (Zaroual et al., 2009; Ölmez, 2009). This study addressed the effects of ionic strengths, initial Cr(VI) concentration, calcium polysulfide dosage, pH, and alkalinity on the chromium removal process. The response surface methodology was utilized to investigate the main and interaction effects of major influencing parameters, including pH, calcium polysulfide dosage, and initial Cr(VI) concentration.

1.5. Research Objectives and Hypotheses

This research aimed at investigating three issues associated with ion-exchange use to remove inorganic contaminants:

In Issue One, impact of co-contaminants (i.e., As(V), Cr(VI), or Se(VI)) on the performances of perchlorate and nitrate specialty resins was investigated. It was hypothesized that the presence of inorganic co-contaminants negatively affects the amount of water that can be processed as well as the management of the used resin and its regeneration. In addition, it was hypothesized that nitrate, arsenic, chromium, and selenium-laden perchlorate specialty resins were regenerable using NaCl solution.

Issue Two addresses As(V) removal from IX brines using ferric chloride. The modeling and experimental experiments were used to investigate the effects of important parameters, including pH, initial As(V) concentration, ferric chloride dosage, ionic strength, and alkalinity on the As(V) removal process. Hypothesis set forth for Issue Two of this research was that ionic strength enhances As(V) removal while alkalinity depresses As(V) removal from IX brines.

The goal of Issue Three is to evaluate the removal of chromium from synthetic ion-exchange brines using calcium polysulfide and determine the effects of initial Cr(VI) concentration, calcium polysulfide dosage, pH, and ionic strength on the removal process. Hypothesis put forth for Issue Three is that both high alkalinity and high ionic strength of the brines favor chromium removal with calcium polysulfide as compared to drinking waters.

CHAPTER 2

STATE OF KNOWLEDGE

2.1. Occurrence, Health Effects and MCL of Inorganic Contaminants Removed by Ion-Exchange (IX)

Nitrate, perchlorate, arsenic, chromium, uranium and selenium concentrations above their MCL levels in drinking water pose a risk to the public. Ion-exchange has been used to remove nitrate, perchlorate, uranium, arsenic and chromium from contaminated waters.

Nitrate

Nitrate can be found naturally in waters at moderate concentrations, but nitrate contamination of surface and ground waters is caused by human and animal wastes, excessive use of chemical fertilizers, and discharge of municipal and industrial wastewaters (Samatya et al., 2006a). Ingesting nitrate-contaminated (>10 mg NO_3^- - N/L) drinking water can cause death or health risks such as methemoglobinemia, diuresis, increased starchy deposits and hemorrhaging of the spleen (Lehman et al., 2008; Fewtrell, 2004; Kross et al., 1992). The US EPA set the MCL for nitrate at 10 mg NO_3^- - N/L. Figure 2.1 shows the nitrate concentrations found in several groundwater wells in Arizona, California, New Mexico and Nevada. The data indicates that nitrate concentrations in southwest groundwaters can be as high as 138 mg NO_3-N / L.

Perchlorate

Perchlorate (ClO_4^-) is considered to be a drinking water contaminant. Perchlorate reduces iodine uptake in the thyroid gland, causing hypothyroidism, which leads to a general slowing of metabolism in a number of organ systems. Perchlorate is extremely dangerous to fetuses and infants because it causes hormone insufficiencies that affect growth (e.g., development of the brain or central nervous system) (U.S. EPA, 2008).

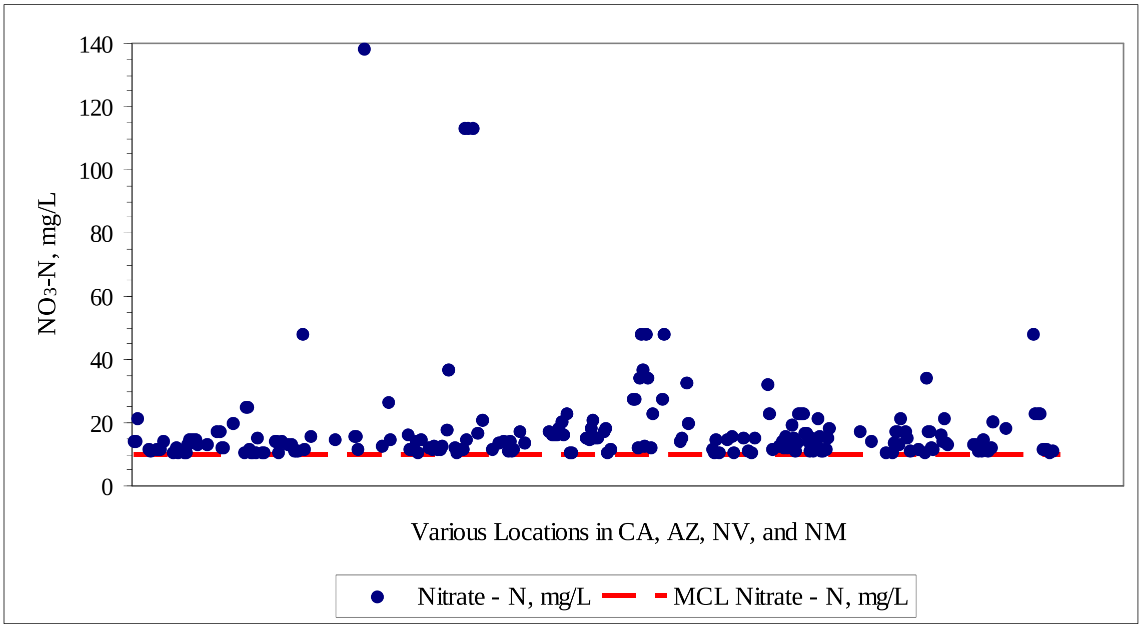


Figure 2.1 Nitrate Concentrations in Contaminated Groundwater Wells in CA, AZ, NV, and NM (Compiled By the Environmental Engineering Laboratory, UNLV)

The most widely used salt of perchlorate is ammonium perchlorate, which is used as an oxidizer in the solid fuels used in rocket motors, explosives, fireworks, and road flares. Perchlorate can occur naturally (e.g. caliche ores from Chile are a natural source of perchlorate) (U.S. EPA, 2008). However, improper disposal of wastewaters containing perchlorate has resulted in groundwater pollution (Gu et al., 2003; Batista et al., 2002). For example, improper discharge of waste containing perchlorate by the chemical industry in Henderson, Nevada has resulted in a significant threat to Lake Las Vegas and Lake Mead (the source of drinking water for Las Vegas), and perchlorate concentrations of 0.5-1 mg/L and 0.005-0.015 μg/L have been detected in Lake Las Vegas and Lake Mead, respectively (Batista et al., 2002). Perchlorate has been detected near perchlorate related industries in Arizona, California, Idaho, Indiana, Kansas, Maryland, New Mexico, New York, Pennsylvania, Texas, Utah, and West Virginia (U.S. EPA, 2008). Typically, perchlorate concentrations detected in groundwaters are less than 100 μg/L, but perchlorate concentrations as high as 1000 μg/L have been observed (Figure 2.2).

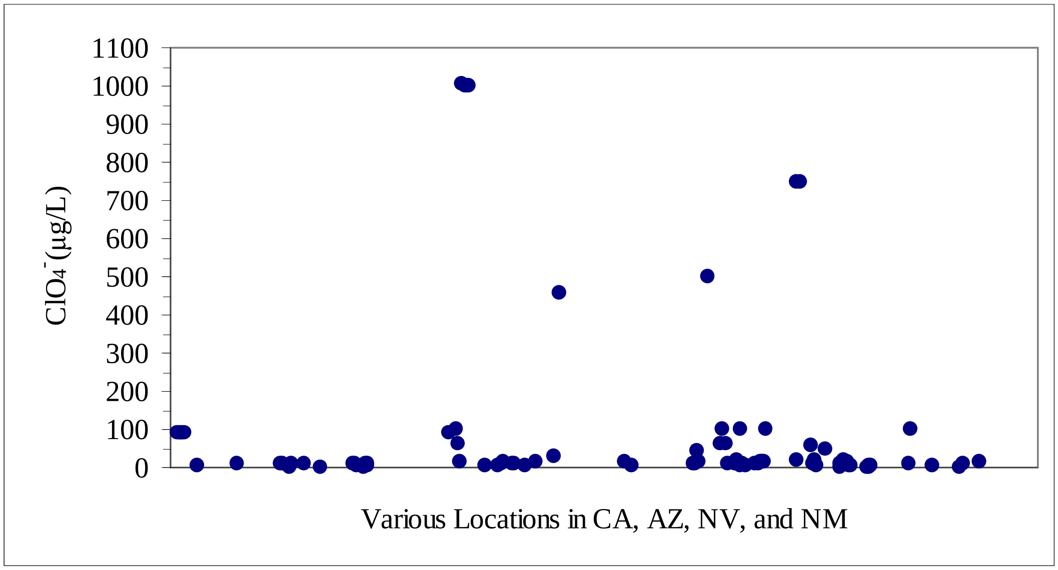


Figure 2.2 Perchlorate Concentrations in Contaminated Groundwater Wells in CA, AZ, NV, and NM (Compiled by the Environmental Engineering Laboratory, UNLV)

There is no federal MCL for perchlorate, but an Interim Drinking Water Health Advisory level of 15 μg/l has been suggested by the US EPA to assist state and local officials in setting regulations to address local drinking water contamination by perchlorate (U.S. EPA, 2008). As such, New Mexico, Texas, New York, California, Arizona and Nevada individually have set maximum perchlorate levels of 1, 4, 5, 6, 14 and 18 μg/L, respectively, in their drinking waters. Concentrations of perchlorate found in various wells in AZ, CA, NV, and NM have been compiled and are presented in Figure 2.2.

Arsenic

Arsenic is a carcinogen connected to cancer of the bladder, lungs, skin, kidney, nasal passages, liver and prostate (U.S. EPA, 2007). Ingestion of arsenic causes adverse effects in humans such as thickening and discoloration of the skin, stomach pain, nausea, vomiting, diarrhea, numbness in hands and feet, partial paralysis and blindness (U.S. EPA, 2007; Chen et al., 1992; Smith et al., 1992). Arsenic concentrations in groundwaters between 10 and 120 μg/L have been reported (Smedley and Kinniburgh, 2002; Chen et al., 2002). Although arsenic occurs naturally, geochemical reactions, industrial waste discharges and agricultural use of arsenic pesticides can also cause elevated arsenic concentrations in groundwater (Wang et al., 2002; Kuhlmeier and Sherwood, 1996; Ferguson and Gavis, 1972).

The U.S. EPA set the MCL for arsenic at a concentration of 10 μg/L on January 18, 2001. Water treatment plants have had to comply with the new regulation since January 23, 2006. The current MCL provides protection for more than 13,000,000 Americans (U.S. EPA, 2007). Figure 2.3 shows arsenic levels in groundwater wells in California, Arizona, and New Mexico. The data shows that arsenic concentrations in contaminated southwest groundwaters can be as high as 274 μg/L.

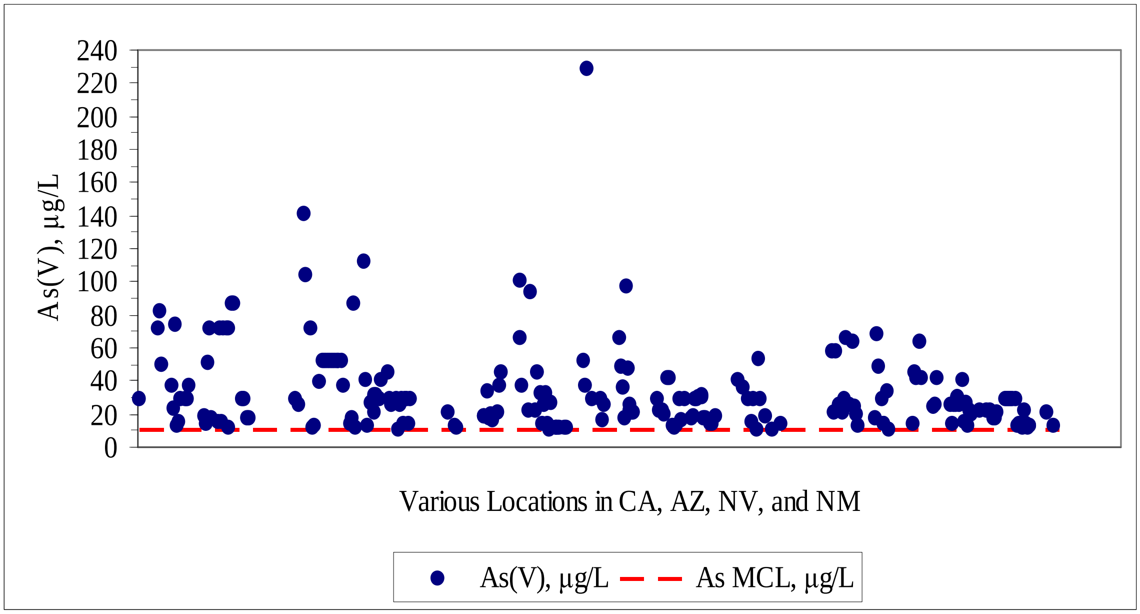


Figure 2.3 Arsenic Concentrations in Contaminated Groundwater Wells in CA, AZ, NV, and NM (Compiled by the Environmental Engineering Laboratory, UNLV)

Chromium

Chromium is a potential carcinogen, and it is toxic (Fendorf and Guangchao, 1996). Excessive intake of chromium by humans leads to skin irritation, liver dysfunction, and damage to circulatory and nerve tissues in the kidney (U.S. EPA, 2006b). The US EPA has enforced a MCL value of 0.1 mg/L for chromium in drinking water since 1992. Chromium is utilized in steel production, corrosion control, leather tanning, oxidation, wood treatment, anodizing, and electroplating (Rengaraj et al., 2003; Sengupta, 1995; Nriagu and Nieboer, 1988; Stephenson, 1987). Chromate concentrations of 0.5 to 2.8 mg/L have been observed in four groundwater wells in California (Environmental Engineering Laboratory, UNLV). In some cases, chromium also presents in groundwater wells as a co-contaminant with arsenic.

Selenium

At high dosages, selenium is a toxic element in drinking water. However, at low levels it is an essential nutrient for animals (U.S. EPA, 2006a). Selenium occurs in water as selenate (SeO_4^{2-}) with oxidation state of +6, or selenite (SeO_3^{2-}) with oxidation state of +4. Selenic acid, H_2SeO_4 (a strong acid), dissociates in water to produce two protons and SeO_4^{2-}. Selenous acid, H_2SeO_3 (a weak acid), produces both $HSeO_3^-$ (hydrogen selenite) and SeO_3^{2-} (selenite) (Kapoor et al., 1995). Selenite is more toxic and less stable than selenate (Brasher and Ogle, 1993; Korpela, 1988). Short-term exposure to high concentrations of selenium causes fatigue and irritability, hair and fingernail changes, and damage to the peripheral nervous system. Chronic (long term) exposure to elevated levels of selenium causes hair and fingernail loss, damage to kidney and liver tissue, and damage to the nervous and circulatory systems (U.S. EPA, 2006se). Selenium's MCL of 0.05 mg/L was set by the US EPA, and water supply utilities have had to comply with this regulation since 1992. Selenium can be found naturally in ores (e.g., chalcopyrite, galena, and pyrite) containing other elements. Selenium compounds are used in many metallurgical processes and in the electronic and copy industries. It is found in petroleum products, pigments, metal alloys, glass, rubber, textiles, medical therapeutic agents, and photographic emulsions (Nishimura et al., 2007; U.S. EPA, 2006se). Typical selenium concentrations of 0.06 to 400 μg/L have been detected in groundwater and surface water; however, the concentration of selenium in groundwater can be as high as 6000 μg/L (WHO, 2003). High concentrations of dissolved selenium (1300 and 4200 μg/L) have been detected in shallow ground and surface waters in the western part of the San Joaquin

Valley in California. Selenium concentrations greater than 10 μg/L have been detected in 3 out of 113 wells in the central San Joaquin Valley in California (USGS, 1995).

Selenium can be removed from drinking water using the following treatment methods: ion-exchange, adsorption with activated alumina, reverse osmosis, and coagulation/filtration (U.S. EPA, 2006a; Kapoor et al., 1995). Reverse osmosis, ion-exchange and activated alumina are effective (99%, 98%, and >90%) in removing selenium from water, but removal efficiencies depend on the selenium speciation. For example, activated alumina is very effective in removing selenite, but limited in removing selenate in the presence of sulfate (Maneval et al., 1985). In view of the fact that selenium occurs as anions, it can be removed by anion-exchange resins. Sorg and Logsdon (1978) reported that anion-exchange is effective in removing selenate and selenite from water and wastewater. However, the removal efficiency depends on the concentrations of competing anions (e.g., sulfate and nitrate) in water (Maneval et al., 1985).

Selenate is more preferred by SBA resins than selenite. The selectivity of selenate, selenite, and competing anions for a SBA resin was reported to be in order of $SO_4^{2-} \sim SeO_4^{2-} > NO_3^- > SeO_3^{2-} > Cl^- > HCO_3^-$ (Maneval et al., 1985). Therefore, selenate removal by ion-exchange is more effective than selenite (Maneval et al., 1985). Nishimura et al. (2007) stated that selenate can be removed by ion-exchange over a pH range of 3 to 12. Selenous acid does not completely dissociate to selenite in acidic pH; therefore, alkaline pH is favorable for selenite removal by ion-exchange (Goodman, 1996).

Uranium is a radioactive element, which occurs naturally in surface water and groundwater, posing a direct threat to water supplies. Uranium removal with ion-exchange and uranyl-carbonate species is discussed in Appendix 1.

2.2. Classification of Ion-Exchange Resins

Although synthetic selective resins are expensive (Gingras and Batista, 2002), they are utilized to remove contaminants from waters due to their high efficiency and capacity. Synthetic resins are composed of three main elements: Styrenic or acrylic polymers, divinylbenzene (DVB), and functional groups. Styrenic or acrylic polymers are the backbone of resins. Divinylbenzene functions to crosslink the vinyl polymers. Functional groups are connected to the resin backbone with covalent bonds. Divinylbenzene (DVB) is formed from a benzene ring attached to two vinyl groups; vinyl is also called ethenyl ($-CH{=}CH_2$). Functional groups are an important part of ion-exchange resins that allow the exchage of ions.

Resins are classified according to their matrix, pore size, functional groups, and selectivity. Vinyl polymers used in a resin matrix are primarily either polystyrene with a structural formula of poly(1-phenylethane-1,2-diyl), or polyacrylic with a structural formula of poly(2-Propenoic Acid) or poly(CH_2=CHCOOH). Therefore, vinyl resins are classified as styrenic or acrylic.

There are two distinct physical forms of resin available in the market: gel (microreticular), and macroporous (macroreticular) (MWH, 2005). Gel type resins are translucent resin beads with high water content, and they lose the pore structure integrity when dry. However, macroporous (macroreticular) resins hold their structural integrity when they are dry. The pore sizes of a resin depend upon the degree of crosslinking of the vinyl polymers in the resin backbone. The degree of DVB crosslinking of geltype resins is between 4 and 12%, usually 8% (MWH, 2005) while the degree of DVB crosslinking of macroporous (macroreticular) resins is in the region of 20 to 25% (MWH, 2005). Geltype resins show a large amount of shrinking or swelling during ion-exchange reactions, but macroporous (macroreticular) resins do not exhibit the same degree of shrinking or swelling. The percentage of swelling is inversely related to the degree of crosslinking within the resin (MWH, 2005). Macroporous resins have larger pores than those found in gel resins, while gel resins have higher capacity and better regeneration efficiency than macroporous resins. However, macroporous resins have higher stability and selectivity than gel resins (DOW, 2009a).

There are four major types of ion-exchange resins available on the market, categorized according to their functional groups: (1) strong acid cation (SAC), (2) weak acid cation (WAC), (3) strong base anion (SBA), and (4) weak base anion (WBA).

The functional group for SAC exchange resins is a charged sulfonate group. SAC resins are able to remove metal ions from water. These resins have pKa values less than zero, which means that they will easily give up a proton and dissociate at any pH (0 to 14). The exchange reaction for an SAC resin in hydrogen form is (MWH, 2005):

$$n[\overline{RSO_3^{-}}]H^{+} + M^{n+} \leftrightarrow [\overline{nRSO_3^{-}}]M^{n+} + nH^{+} \qquad (2.1)$$

SAC exchange resins show 7% shrinkage for gel type, and 3 to 5% for macroporous (macroreticular) resins due to loss of a hydrogen proton, which is relatively larger than other cations. The capacity of SAC resins is between 1700 and 2100 meq/L. SAC exchange resins can be regenerated with HCl. The regeneration reaction for an SAC resin can be written as (MWH, 2005):

$$[n\overline{RSO_3^-}]M^{n+} + HCl \leftrightarrow n[\overline{RSO_3^-}]H^+ + nM^+Cl^- \tag{2.2}$$

The functional group on WAC exchange resins is usually a carboxylate. According to MWH (2005), the exchange reaction for a WAC resin can be written as:

$$n[\overline{RCOO^-}]H^+ + M^{n+} \leftrightarrow [n\overline{RCOO^-}]M^{n+} + nH^+ \tag{2.3}$$

and the regeneration reaction is:

$$[n\overline{RCOO^-}]M^{n+} + HCl \leftrightarrow n[\overline{RCOO^-}]H^+ + M^{n+}(Cl^-)_n \tag{2.4}$$

WAC exchange resins give up a proton when the pH is greater than 6 because the pKa of WAC exchange resins are in the range of 4 to 5. Less acid (HCl or H_2SO_4) is required to regenerate a WAC exchange resin than is required for SAC exchange resins. WAC is used to remove cations from water with high alkalinity (MWH, 2005). Weak acid ion-exchange has been used for water softening (Szlag and Wolf, 1999).

SBA exchange resins can be categorized into two types based on their functional groups. The functional group in a SBA (Type 1) exchange resin is a Type 1 quaternary amine group (R_4N^+) with a fixed positive charge carrying hydroxide or chloride ion, which will be exchanged with anions in water. Type 1 quaternary amine groups have three similar alkyl groups methyl ($-CH_3$), ethyl ($-C_2H_5$), propyl ($-C_3H_7$), butyl ($-C_4H_9$), or pentyl ($-C_5H_{11}$). The exchange reaction for a SBA (Type 1) exchange resin in hydroxide form can be written as (MWH, 2005):

$$n[\overline{R(CH_3)_3N^+}]OH^- + A^{n-} \leftrightarrow [n\overline{R(CH_3)_3N^+}]A^{n-} + nOH^- \tag{2.5}$$

The regeneration reaction for SBA (type 1) is (MWH, 2005):

$$n[\overline{R(CH_3)_3N^+}]A^{n-} + NaOH \leftrightarrow n[\overline{R(CH_3)_3N^+}]OH^- + (Na^+)_n A^{n-} \qquad (2.6)$$

The functional group in a SBA (type 2) exchange resin is a type 2 quaternary group, which consists of an ethanol group. The exchange reaction for a SBA (type 2) is:

$$n[\overline{R(CH_3)_2(CH_3CH_2OH)N^+}]OH^- + A^{n-} \leftrightarrow [\overline{nR(CH_3)_2(CH_3CH_2OH)N^+}]A^{n-} + nOH^-$$

(MWH, 2005) (2.7)

SBA resins have pK_b values of 0 and 1, meaning that the functional group on the resin is completely dissociated when the pH value of the solution is less than 13 (MWH, 2005). SBA (type 1) exchange resin is chemically more stable than SBA (Type 2) resin, while SBA (type 2) exchange resin has higher regeneration efficiency and exchange capacity than SBA (type 1) resin. SBA exchange resin in hydroxide form shrinks when it exchanges hydroxide with other anions because hydroxide is a large ion compared to the other anions in water it is being exchanged for (MWH, 2005).

A tertiary amine group is the functional group and exchange site in WBA exchange resins. The tertiary amine functional group does not possess a fixed positive charge. WBA resins are available in either chloride or freebase forms, which can adsorb ions without the exchange of an ion. According to MWH (2005), the exchange reaction for a freebase form WBA exchange resin is in the following manner:

$$[\overline{R(CH_3)_2N}]HOH + H^+ + A^- \leftrightarrow [\overline{R(CH_3)N}]HA + HOH \qquad (2.8)$$

The regeneration reaction occurs according to the reaction (MWH, 2005):

$$[\overline{R(CH_3)_2N}]HOH + HA \leftrightarrow [\overline{R(CH_3)N}]HA + HOH \qquad (2.9)$$

WBA resin works properly for solutions with the pH between 6.7 and 8.3 at 25°C (5.7< pKb <7.3). Bases (e.g. NaOH, NH_4OH, or Na_2CO_3) can be used to regenerate the WBA resin. The regeneration efficiency for WBA resin is much higher than that of SBA resin. WBA and SBA resins may be used in combination for demineralization of water to reduce the regenerant costs. WBA/SBA resins in combination may also increase the efficiency of the whole system in absorbing organic matter (MWH, 2005).

The total number of exchangeable ions in a resin is the theoretical or total capacity of the resin. The wet volume exchange capacity is the total number of ions that can be adsorbed onto a resin, depending on the moisture content of the resin. The wet volume exchange capacity is usually expressed in terms of milliequivalent per milliliter or liter of resin (meq/mL or meq/L). In this dissertation, ion-exchange resin capacities are expressed in terms of wet volume capacity. The dry weight capacity of a resin can be expressed as milliequivalents per gram of dry resin (meq/g-resin).

2.3. Selectivity in Ion-Exchange

There are two types of resins available in the market: highly selective (specialty) resins and conventional resins. Specialty resins are reported to be more efficient and cost effective in removing contaminants from waters, particularly in the presence of sulfate and other competing ions. Because of their higher selectivity, the use of specialty resins to remove nitrate (Rochette, 2006; Tripp and Clifford, 2006; Ghurye et al., 1999; Liu and Clifford, 1996; van der Hoek and Klapwijk, 1988), arsenic (Greenleaf et al., 2006; An et al., 2005; Clifford et al., 2003; Korngold et al., 2001; Ghurye et al., 1999), chromium (Korngold et al., 2003; Siegel et al, 2007), and perchlorate (Gu and Brown, 2006; Tripp and Clifford, 2000; Batista et al., 2000) from groundwaters is increasing. For example, a nitrate selective resin has low selectivity for sulfate so more of the resin capacity is allocated to the nitrate than the case with a non-selective resin.

Selectivity is the preference of resins for particular ions. Ion-exchange resins usually have more affinity or preference for certain ions. In multi-component systems, the capacity of the resin that can be captured by a certain ion is proportional to the selectivity or preference for that ion by the resin (MWH, 2005). To illustrate selectivity, mass laws can be applied to describe ion-exchange equilibrium, treating ion-exchange as a stochiometric reaction. A generalized form of this stochiometric reaction is (MWH, 2005):

$$n[\overline{R^{\pm}}]A^{\pm} + B^{n\pm} \leftrightarrow [n\overline{R^{\pm}}]B^{n\pm} + nA^{\pm} \qquad (2.10)$$

Where:

- $\overline{R^{\pm}}$ is the ionic group inside the ion-exchange resin
- A and B are exchanging ions
- n is the valence of the exchanging ion.

According to stoichiometry, all binary exchange processes can be represented as:

$$K_B^A = \frac{[A^{\pm}]^n\{\overline{R^{\pm}}B^{n\pm}\}}{\{\overline{R^{\pm}A^{\pm}}\}^n[B^{n\pm}]} \qquad (2.11)$$

Where:

- K_B^A = selectivity coefficient for either cation or anion A exchanging with ion B onto the resin
- $[A^{\pm}]$ = aqueous-phase concentration of presaturant ion, eq/L
- $[B^{\pm}]$ = aqueous-phase concentration of counterion, eq/L
- $\{\overline{R^{\pm}}A^{\pm}\},\{\overline{R^{\pm}}B^{n\pm}\}$ = activities of resin-phase presaturant ion and counter-ion, respectively.

If the resin phase is defined in terms of concentration, the equilibrium stoichiometric equation can be expressed as

$$K_j^i = \frac{C_j^n q_i}{q_j^n C_i} \qquad (2.12)$$

Where:

- Cj = aqueousphase concentration of presaturant ion, eq/L
- q_i = resin-phase concentration of counter-ion, eq/L
- q_j = resin-phase concentration of presaturant ion, eq/L
- C_i = aqueous-phase concentration of counter-ion, eq/L (MWH, 2005).

Anion and cation removal from water can be modeled using software. An example is IX-PRO, which was created by Dr. Gerald A. Guter in 1996. The equilibrium expression for an ion-exchange process can be obtained by applying mass laws. In addition to the equilibrium equations, diffusion kinetic relationships are also considered and used for the calculation of effluent concentrations (Appendix 2). The equilibrium equations are the basis for the modeling of an ion-exchange process (Guter, 1984). The details of equilibrium and kinetic relationships that describe an ion-exchange process are presented in Appendix 2.

The physical and chemical properties of resins, contaminants (counterions) and solutions affect the selectivity of a resin for ions. Resins prefer ions with a smaller hydrated radius (i.e. the extent of surrounding water molecules) because these ions attach to the resins more tightly and reduce the swelling pressure. The surrounding water exerts an osmotic pressure into the resin matrix while exchanging with the resin. This pressure causes the swelling (MWH, 2005). The hydrated radius is inversely proportional to the ionic radius, which increases with increasing atomic number of the ion. The orders of preference for some metals with respect to hydrated radii are (MWH, 2005):

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+,$$

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$$

Similarly, the orders of preference for some anions with respect to their hydrated radii are (MWH, 2005): $ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^-$

Ions with a higher charge and valence are preferred by resins, as shown in the following series (MWH, 2005):

$Th^{4+} > Al^{3+} > Ca^{2+} > Na^+$ (preference order with strong acid cation resins)

$PO_4^{3-} > SO_4^{2-} > Cl^-$ (preference order with strong base anion resins)

However, there are also some exceptions to this rule. H^+ and OH^- are the most preferred ions and chromate (CrO_4^{2-}) is less preferred than nitrate:

$SO_4^{2-} > I^- > NO_3^- > CrO_4^{2-} > Br^-$ (MWH, 2005)

Therefore, the presence of sulfate and nitrate in groundwater along with chromate is a major concern in chromate removal by ion-exchange, because most of the resin capacity may be occupied by sulfate or nitrate instead of chromate.

Sulfate is also a major competitor of nitrate in the ion-exchange process using conventional resins. Sulfate ions capture most of the capacity of the resin, and little capacity remains for nitrate adsorption. Thus, after a few bed volumes of water pass through the ion-exchange column, nitrate can be detected in the effluent (Clifford and Weber, 1986; Guter, 1984, Liu and Clifford, 1996). To overcome this issue, specialty resins have been developed. Specialty resins have high affinity for the ions of interest (e.g., nitrate or perchlorate) while having a low affinity for competing ions, particularly sulfate.

It has been reported that an important factor affecting the selectivity of ion-exchange resins is the spacing of exchange sites (Clifford and Weber, 1986; Guter, 1984, Liu and Clifford, 1996). The distance between active exchange sites affects the divalent-monovalent selectivity. A divalent ion needs two adjacent active sites to adsorb to and to satisfy electroneutrality. Hence, increasing the distance between active sites decreases the selectivity for a divalent ion by the resin (MWH, 2005). Guter (1984) developed a nitrate selective resin in accordance with the spacing concept.

Tripp and Clifford (2000) stated that the selectivity coefficient of a resin for perchlorate increases when the length of the alkyl group on the quaternary amine increases. For example, when the alkyl group on the quaternary amine functional group changes from a methyl to an ethyl and then to a propyl group, the selectivity coefficient for perchlorate increases from 125 to 800 and then to 1300. This is a tremendous change in selectivity and shows the important effect of functional groups on the efficiency of the process.

The higher the concentration of an ion in solution, the higher is the preference of the resin for that ion (MWH, 2005). Removal of nitrate from water with a nitrate-selective resin (A520E) has been evaluated by Samatya et al. (2006a; 20006b). Increasing the sulfate to nitrate ratio in the solution from 1 to 10 decreases the percent capacity of the resin allocated to nitrate adsorption from 98% to 85%.

The TDS or ionic strength of the solution influences the selectivity for a particular ion by resins. At high ionic concentration (TDS > 1000 mg/L), preference for an ion by a resin (selectivity) decreases, but this is the ideal situation for the regeneration of the resin. Moreover, at high ionic strength, the previously cited effects of hydrated radii, and ionic charge, valence and concentration on selectivity for an ion by a resin are not applicable (MWH, 2005). Selectivity coefficients for strong base anion (SBA) exchange resins are presented in Table 2.1. Values shown are approximate selectivity coefficients for 0.005-0.010 N solutions containing 250-500 mg/L TSD as $CaCO_3$.

The matrix structure, type of functional groups, and pore size (i.e., gel or macroporous) of a resin all influence selectivity of the resin. Both perchlorate and styrenic type resins are hydrophobic, which leads to higher affinity of the resin for perchlorate than with less hydrophobic resins (Batista et al., 2002). Tripp and Clifford (2000) reported that polystyrenic resins are more hydrophobic than polyvinylpyridine and polyacrylic type resins; therefore, polystyrenic resins may have higher affinity for perchlorate than polyvinylpyridine and polyacrylic resins with similar structures (e.g., the same functional group and percentage of crosslinking). For example, the selectivity coefficient for perchlorate of a macroporous Type 1 SBA exchange resin with a polystyrene-DVB matrix and quaternary amine functional group for perchlorate is reported to be 145, while a resin with similar specifications but with a polyacrylic matrix has been shown to have a perchlorate selectivity coefficient of 10.4 (Tripp and Clifford, 2006).

Tripp and Clifford (2006) examined fifteen resins to evaluate their exchange capacity and concluded that styrenic macroporous resins with divinylpyridine cross linking and tripropylamine functional groups have the highest selectivity coefficient (1300) for perchlorate ion. They found that increasing the solution temperature reduces the selectivity coefficient by 30% for each 20°C increase in temperature.

Table 2.1 Selectivity Coefficients (Relative to Chloride) for Strong-Base Anion-exchange Resins

Ion	Selectivity Coefficient
Cl^-	1
HCO_3^-	0.2-0.4
NO_3^-	2-12
ClO_4^-	5.5-1500
SO_4^{2-}	0.15-11
SeO_4^{2-}	17
$HAsO_4^{2-}$	0.012
HPO_4^{2-}	0.01
CO_3^{2-}	0.03
OH^-	0.06-.65
F^-	0.07-0.1
CH_3COO^-	0.14-0.2
BrO_3^-	1
CN^-	1.3
NO^-	1.3
HSO_4^-	1.6
Br^-	3
I^-	8-18
CrO_4^{2-}	100
HSO_3^{3-}	1.2
SiO_2	0.76[a]
NO_2^-	1.1-1.3

[a] Weak-base anion-exchange resin in OH^- form (Ben Sik Ali et al., 2004)
(Source: compiled from MWH, 2005; Peterson, 1953; Pontius, 1990; Clifford, 1999; Boodoo, 2003; Gu et al., 2001; Tripp and Clifford, 2000)

Porosity is a physical property of resins that affects their selectivity. According to the data presented by Tripp and Clifford (2006), a macroporous resin may have higher selectivity for perchlorate than a gel-type resin with exactly the same specification. This is due to the large size of the perchlorate ion and the higher porosity of the macroporous resin. For example, Type 1 macroporous and gel type polyacrylic resins with quaternary amine functional groups have been reported to have selectivity coefficients for perchlorate of 10.4 and 5.5, respectively (Tripp and Clifford, 2006).

2.4. Laboratory Ion-Exchange Minicolumn Design

Minicolumns are commonly used to predict the performance of the actual ion-exchange plants. Minicolumns must be designed according to a series of theoretical and practical relationships. The results of the minicolumn experiments can be used for the construction of the pilot- or full-scale ion-exchange plants. The major parameters considered in the design are:

1- Diameter of the column as compared to the diameter of the resin bead

2- Length of the column

3- Aspect ratio of the column (ratio of length to diameter)

4- Required mass transfer zone (MTZ)

5- Empty bed contact time (EBCT)

6- Loading flow rate

7- Regenerant concentration

8- Regenerant contact time

9- Regenerant flow rate.

Typically, ion-exchange systems are operated downflow, in which water flows from the top of the column to the bottom (MWH, 2005). However, upflow fluidized system are also used in some cases. Downflow systems are often preferred because of the low energy consumption and low mechanical stress on pumps and pipes in comparison with upflow systems. The use of upflow system is reported to prevent the formation of a mass of bacteria on top of the bed and clogging. The upflow system results in lower mechanical stress on the resins and supports a longer resin lifetime (MWH, 2005). It is also reported that a smaller volume of the rinse water is required for upflow system than downflow system (MWH, 2005).

Small diameter of an ion-exchange column causes flow maldistribution because of wall effects. Possible irregularities in the packing of the resin inside the column may intensify wall effects and cause channeling. Flow maldistribution, a hydrodynamic process, causes the distortion of the resin bed, and must be avoided by adjusting the column diameter (Helfferich, 1995). The more loosely packed areas (or the void volumes) of the column are less resistant to water flow. The flow rate is higher in these areas, also referred to as "channels" (Helfferich, 1995). The flow is very slow at the walls of the column due to the friction imposed between the walls and the solution. However, maximum flow rate is reported to occur at a distance of almost one particle diameter from the column wall. The maximum flow rate may be more than twice as high as the flow at the center of the column (Helfferich, 1995). This high flow rate may cause relocation of the resins near the column walls and imposes "channeling." "channeling" effects become drastic when the ion-exchange column has a small diameter depending on the size of the resins used in the column. It has been reported that "channeling" effects become insignificant in practice when the ion-exchange column diameter is more than thirty times the particle diameter (Helfferich, 1995).

In ion-exchange, the concentration of an ion in the column’s effluent gradually increases as more water is processed (Figure 2.4). The point at which the concentration of a contaminant ion in the effluent of the column reaches a desired level (e.g., MCL of the ion) is called the breakthrough. The exhaustion point is the point at which the concentration of the contaminant ion in the effluent equals to the concentration of the contaminant ion in the influent. The degree of column utilization is the amount of resin exhausted at the point at which the contaminant ion is detected in the effluent divided by the total resin in the column. Figure 2.4 shows a sample breakthrough curve in which the concentrations of the contaminant ion are graphed against the bed volumes of water treated. The degree of column utilization can be calculated from the breakthrough curve. In Figure 2.4, the degree of column utilization can be calculated by dividing the area of “abcd” by the area of “acde” (Helfferich, 1995).

It has been reported that although ion-exchange kinetics is fast, the contact time is not sufficient for attainment of local equilibrium at each specific part of the resin bed. Therefore, local equilibrium tends to spread its boundary (Figure 2.5) (Helfferich, 1995). This spreading action continues through the entire bed, and it can be observed in a breakthrough curve (Figure 2.5). That is why any breakthrough curve looks like a wave. Figure 2.5 should be viewed as the relative motion of influent feed water through the resin bed.

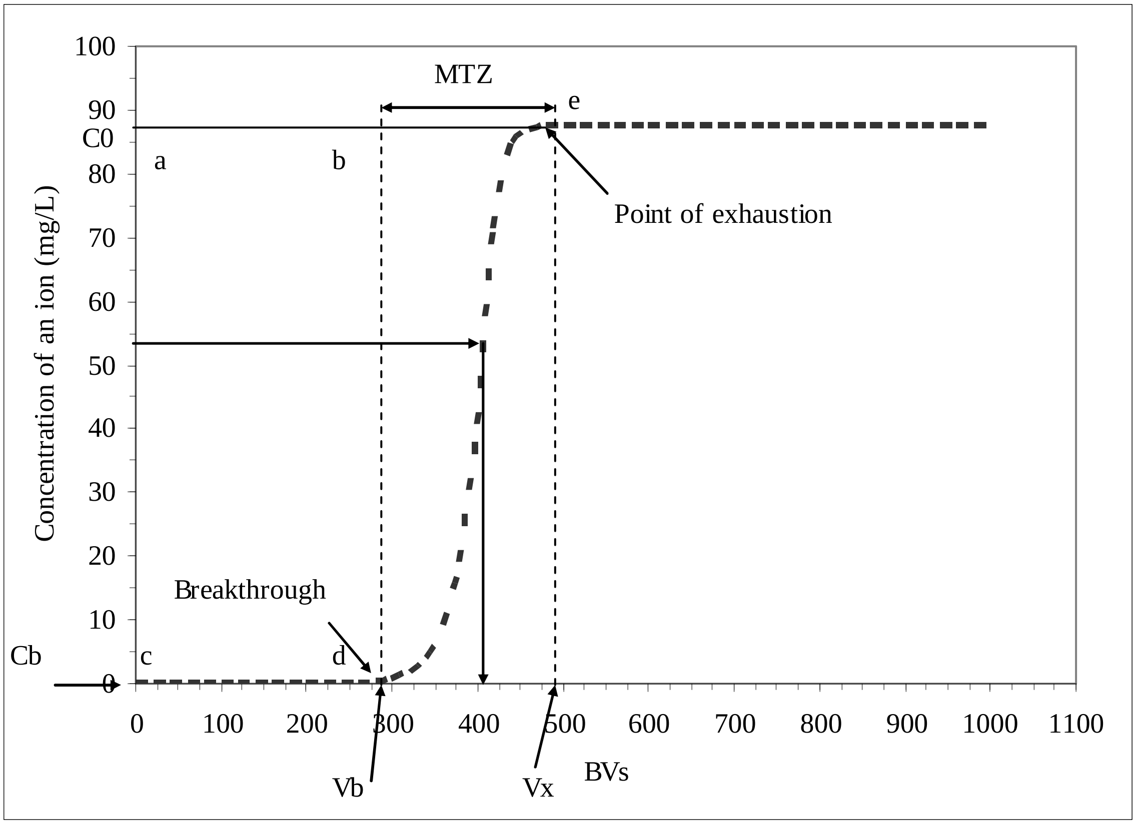


Figure 2.4 An Example of a Breakthrough Curve. The Length of the MTZ and Point of the Breakthrough and Exhaustion Are Presented

The mass transfer zone (MTZ) is part of the length of the ion-exchange column (filled with resin) in which the mass transfer occurs between the aqueous-phase and resin-phase. The goal is to minimize the MTZ, which maximizes the utilization. The preference of the resin for an ion affects the MTZ. The higher the selectivity of the resin for the counter ion, the sharper is the breakthrough curve and the shorter the MTZ. Slower flow rates or smaller beads shorten the MTZ. It has been reported that increasing the length of the ion-exchange bed increases the degree of column utilization and decreases the MTZ. However, increasing the length of the resin column beyond a certain length (the critical length of the MTZ) does not increase the utilization. Moreover, longer columns have higher flow resistance, and obviously more resin is required to fill them (Helfferich, 1995). Therefore, the critical length of the MTZ (a certain length) must be determined, and the resin depth must be equal or more than the MTZ. The theory available for calculation of the MTZ for an activated carbon (Sincero and Sincero, 1996) can be used to determine the MTZ of the ion-exchange bed.

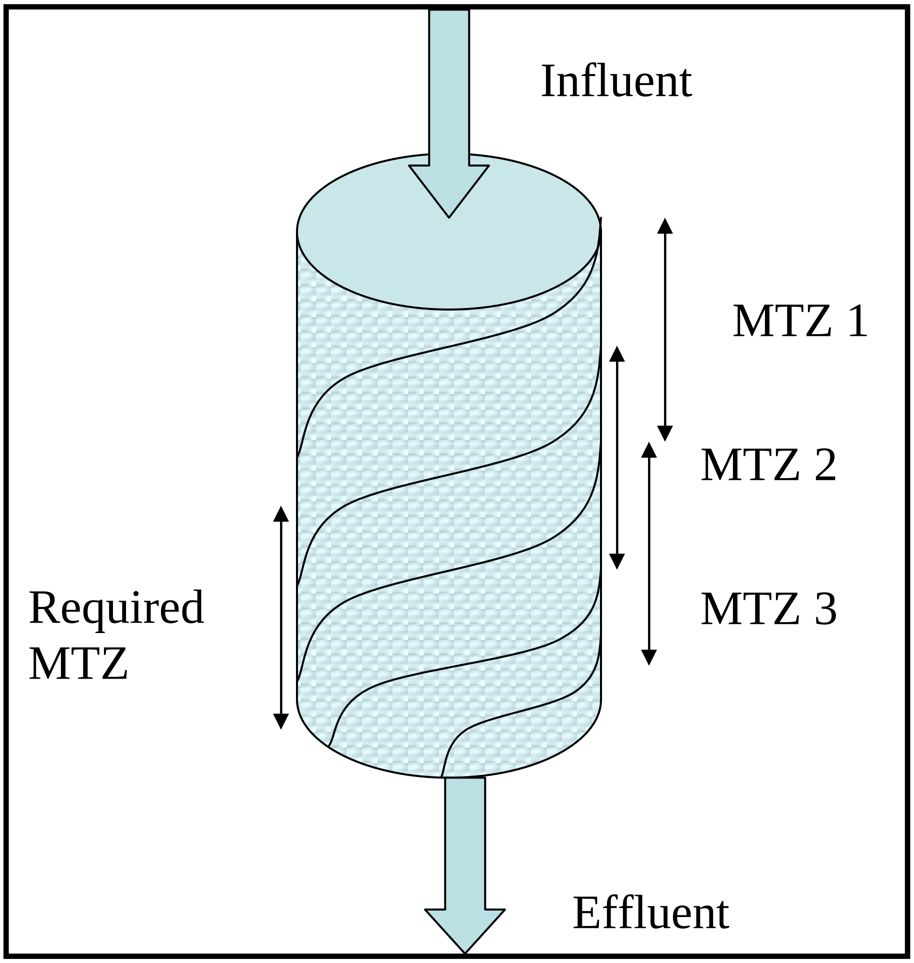


Figure 2.5 Examples of the Mass Transfer Zones along the Ion-Exchange Column

The first step to determine the critical MTZ is to calculate the mass of pollutant retained in the resin from the time that breakthrough has started until the point of the exhaustion. The mass of all the contaminant passed through the column minus the mass of contaminant escaped from the resin bed after the breakthrough gives the mass of the contaminant retained inside the resin (M_r) after the breakthrough of the resin (equation 2.13).

$$M_r = (V_X - V_b)C_0 - \sum (V_{n+1} - V_n)\frac{C_{n+1} + C_n}{2} \qquad (2.13)$$

Where C_0 is the concentration of the contaminant in the influent, mg/L; Vx and Vb are the volumes of the feed water passed through the column at the point of exhaustion and breakthrough; V_n is the volume of feed water passed through the column at point n and C_n is the concentration of the contaminant in the effluent (Figure 2.4) (Sincero and Sincero, 1996). Mr (kg) also can be calculated by the following equation:

$$M_r = A_S \rho_p \delta (X / M)_{ult} \qquad (2.14)$$

where As is the superficial area of the bed, m^2; ρ_P is the packed density of the resin bed, Kg/m^3; δ is the critical MTZ which should be determined in meters; (X/M)ult is the total mass of the adsorbed contaminant per total mass of the resin, kg contaminant / kg resin (Sincero and Sincero, 1996).

The length of the resin column can be determined according to the required aspect ratio of the column. The aspect ratio of the column is the ratio of length and diameter. A high aspect ratio increases the column utilization (Helfferich, 1995). The aspect ratio is usually determined and provided by the manufacturers. It has been suggested that the lab column aspect ratios of greater than 4:1 (length to diameter) are the best, and the appropriate commercial column aspect ratios are between 2:1 and 4:1 (length to diameter)

(DOW website). At a constant diameter (or cross section) of the column, increasing the length of the column increases the breakthrough and the overall capacity of the operation.

The ion-exchange process requires a certain amount of time for the attainment of local equilibriums. Therefore, the flow rate should be adjusted to assure enough time for the exchange process. The empty bed contact time (EBCT) equals the time required for the solution to pass through one bed volume of a resin. The EBCT can be calculated by dividing the volume of the resin in the column (V_r) by the flow rate (Q) (MWH, 2005):

$$\mathrm{EBCT} = V_r / Q \tag{2.15}$$

Typically, the operational service flow rates are provided by the manufacturers. The following equation indicates the relationship between the large-scale EBCT and the small-scale EBCT. It is used for scaling the data obtained from a small column to predict a larger scale column when using the granular activated carbon (GAC) particles.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{SC}}{d_{LC}}\right]^2 \tag{2.16}$$

SC and LC stand for small-scale and large-scale, respectively, and d is the diameter of the GAC particle (Pontius, 1990).

In the ion-exchange column, the resin diameters in the small-scale and large-scale columns are the same ($d_{SC} = d_{LC}$) and therefore the EBTCs are similar. Thus, the service flow rates in the ion-exchange column experiments must follow the recommendations of the manufacturers. The EBCT can be calculated by choosing a volume (based on the required diameter and length) and knowing the service flow rate.

For scale-up of the minicolumn experimental data to full scale, the height of bed in the full scale plant and small scale plant must be the same (MWH, 2005). For the same height of the IX bed, similar brteakthrough curves can be produced from the laboratory experiments and full scale IX plants (MWH, 2005). The recommended height of the resin bed for the operation is between 0.6 m and 1 m (MWH, 2005). Often, performing minicolumn experiments at these heights are impractical, and pilot scale experiments with resin bed height of 0.6-1.0 m are required for the design of full scale plants (Helfferich, 1995; MWH, 2005).

2.5. Highly Selective (Specialty) and Conventional Ion-exchange Resins for Nitrate and Perchlorate Removal

Both highly selective (specialty) and conventional strong base anion (SBA) exchange resins are used to remove perchlorate and nitrate from aqueous solutions. Examples of specialty and conventional resins are given in Table 2.2. Major resin vendors include ResinTech, Purolite, Rohm & Haas, Sybron/Lanxess and Dow Chemical. Table 2.2 shows ion-exchange resins, which are capable of removing nitrate, perchlorate, arsenic and chromium from waters. Specialty resins are more expensive than conventional resins; for example, a conventional resin typically costs $95/cu ft while a specialty resin costs $140 / cu ft. The specific selectivity coefficients of these resins for various contaminants have been obtained from ResinTech, New Jersey, USA (Table 2.3)

Ion-exchange seems to be the most efficient process in removing nitrate from waters (Guter, 1984; Launch and Guter, 1986; Samatya et al., 2006a). Both nitrate selective and conventional resins have been used to remove nitrate from waters. However, nitrate selective resins have been shown to be more effective than conventional resins due to the higher affinities for nitrate (Ghurye et al., 1999; Samatya et al., 2006a; Liu and Clifford, 1996). The performance results from several bench and pilot scale studies using various ion-exchange resins are summarized in Table 2.4. The amount of water treated ranged from 327 to 750 bed volumes (BVs, a volume of solution treated equal to the volume of the resin bed) and from 137 to 610 BVs using nitrate selective and conventional resins, respectively. Typically, the effluent water had less than 10 mgNO_3^-- N/L while the influent water nitrate concentrations were as high as 23 mgNO_3^-- N/L.

The most efficient technology for the removal of perchlorate from drinking water is ion-exchange using resins that are highly selective for perchlorate (Gu et al., 2000; Tripp and Clifford, 2000; Batista et al., 2000; Guter, 1999). The process is fairly simple and does not require a full time operator.

The results of several studies that investigated the efficiency of ion-exchange resins used to remove perchlorate from groundwaters are shown in Table 2.5. The reported range of groundwater volumes treated is from 10,000 to 420,000 BVs, depending on the influent perchlorate concentration. A perchlorate selective resin treated up to 420,000 BVs of groundwater containing 8-11 μg/L perchlorate, and 37,000 BVs of groundwater containing 860 μg/L of perchlorate (Siegel et al., 2007; Carlin et al., 2004; Gu et al., 1999, 2003, 2007b). A nitrate selective resin treats 17,000 to 60,000 BVs of groundwater containing 8 to 450 μg/L of perchlorate. A conventional strong base Type 1 resin treats up to 10,000 BVs of groundwater containing 100 μg/L of perchlorate.

Table 2.2 Specialty (Perchlorate, Nitrate, and Arsenic Selective) and Conventional Strong-Base Anion-exchange Resins Available in the Market

Resin Name/ Manufacturer	Resin Matrix/ Type	Functional Group	Capacity meq/L	Recommended Application	Specialty/ Conventional
SIR-110-HP ResinTech	Styrene-DVB Gel	Tri-n-butyl-amine $R\text{-}N\text{-}(C_4H_9)_3^+\ Cl^-$	600	Perchlorate, Nitrate	Perchlorate Selective
SIR-100-HP ResinTech	Styrene-DVB Macro-porous	Tri-ethyl-amine $R\text{-}N\text{-}(C_2H_5)_3^+\ Cl^-$	850	Nitrate, Perchlorate	Nitrate Selective
SBG1-HP ResinTech	Styrene-DVB Gel	Type I, Tri-methyl-amine $R\text{-}N\text{-}(CH_3)_3^+\ (Cl^-$ or $OH^-)$	1450	Nitrate, Arsenic, Chromium, Perchlorate	Conventional
ASM-10-HP ResinTech	Styrene-DVB Gel	Hybrid adsorbent $R\text{-}N\text{-}R^+Cl^-$	1000	Arsenic Perchlorate, Nitrate, Selenate, Chromium	Arsenic Selective
A530E Purolite	Polystyrene-DVB	Bifunctional Quarternary amine $\text{-}N\text{-}R_4^+Cl^-$	600	Perchlorate	Perchlorate Selective
A532E Purolite	Polystyrene-DVB	Bifunctional Quarternary amine $\text{-}N\text{-}R_4^+Cl^-$	750	Perchlorate	Perchlorate Selective
A520E Purolite	Polystyrene-DVB Macro-porous	Type I, Quaternary-amine $R\text{-}N\text{-}(CH_3)_3^+\ Cl^-$	900	Nitrate	Nitrate Selective
Amberlite PWA2 Rohm and Haas	Polystyrenic Gel	-	600	Perchlorate	Perchlorate Selective
DOWEX 1 DOW	Styrene-DVB Gel	Type I, Tri-methyl-amine $R\text{-}N\text{-}(CH_3)_3^+\ Cl^-$	1400	Perchlorate, Nitrate	Conventional
DOWEX NSR-1 DOW	Styrene-DVB Macro-porous	Tri-ethyl-amine $R\text{-}N\text{-}(C_2H_5)_3^+\ Cl^-$	900	Nitrate	Nitrate Selective
DOWEX PSR-2 DOW	Styrene-DVB Gel	Tri-n-butyl-amine $R\text{-}N\text{-}(C_4H_9)_3^+\ Cl^-$	650	Perchlorate	Perchlorate Selective
DOWEX PSR-3 DOW	Styrene-DVB Macro-porous	Tri-n-butyl-amine $R\text{-}N\text{-}(C_4H_9)_3^+\ Cl^-$	600	Perchlorate	Perchlorate Selective

(Source: Compiled from the websites of the resin manufacturers: ResinTech, Purolite, DOW, Rohm and Haas)

Table 2.3 Selectivity Coefficients (Relative to Chloride) for SBG1, SIR100, and SIR110

Ion	Type 1 Non-selective (SBG1)	Nitrate Selective (SIR100)	Perchlorate Selective (SIR110)
Cl^-	1	1.0	1.0
HCO_3^-	0.25	0.2	0.2
NO_3^-	4.0	6.0	23.0
SO_4^{2-}	0.15	0.03	0.003
$HAsO_4^{2-}$	0.075	0.015	0.0015
CrO_4^{2-}	1.3	0.2	0.03
ClO_4^-	500	500	3500

(Source: ResinTech)

Table 2.4 Comparison of Results for IX Resins in Removing Nitrate from Waters

Resin Name/ Manufacturer	Resin Type	Influent Nitrate (mg/L)	Effluent Nitrate-N (mg/L)	Experiment Scale	BVs	Reference
Amberlite IRA 996 Rohm & Haas	Nitrate selective	10.5	7	Bench	750	Ghurye et al., 1999
Ionac SR6 Syborn	Nitrate selective	10.5	7	Bench	680	Ghurye et al., 1999
Amberlite IRA 458 Rohm & Haas	Conventional	10.5	7	Bench	610	Ghurye et al., 1999
Amberlite IRA 404 Rohm & Haas	Conventional	10.5	7	Bench	560	Ghurye et al., 1999
A520E Purolite	Nitrate selective	22.6	10	Bench	580	Samatya et al., 2006a
Amberlite IRA 996 Rohm & Haas	Nitrate selective	21.8	10	Pilot	450	Liu and Clifford, 1996
Ionac SR6 Syborn	Nitrate selective	21.6	10	Pilot	350	Liu and Clifford, 1996
Amberlite IRA 996 Rohm & Haas	Nitrate selective	14.1	10	Pilot	327	van der Hoek and Klapwijk, 1987
Ionac ASB-1P Syborn	Conventional	21.2	10	Pilot	205	Liu and Clifford, 1996
Duolite A101-D Auchtel	Conventional	16.0	9.53	Pilot	137	Launch and Guter, 1986

Mini-column tests were conducted to treat water containing 8-11 μg ClO_4^- / L, 4-7 mg NO_3^--N/ L, 25-40 mg SO_4^{2-} / L, and 230-240 mg HCO_3^- / L as $CaCO_3$ using Purolite (A530E), ResinTech (SIR-110-HP), Sybron(Ionac SR-7) and Rohm & Haas (PWA2 and PWA555) resins. Perchlorate leakage (> 2 μg/L) in the effluent was detected at 420,000, 220,000, 105,000, 80,000, and 60,000 BVs using the SIR-110-HP, PWA2, A530E, SR-7 and PWA555 resin, respectively (Table 2.5). Pilot scale plant tests were conducted using A530E, SIR-110-HP and PWA2 resins to treat the same water used in the mini-column tests. A530E started to break through at 65,000BVs; however, no perchlorate was detected in the effluent from the resin columns using SIR-110-HP and PWA2 resins until 112,000 BVs of water had been treated (Siegel et al., 2007).

According to the pilot scale tests (Carlin et al., 2004), PWA2, PWA555, and PWA1 resins have perchlorate capacities of 5446, 961 and 160 mg/L, respectively, and are able to treat a groundwater containing 200 μg ClO_4^- /L, 14.7 mg SO_4^{2-} / L, 9.4 mg NO_3^- / L, 129 mg HCO_3^- /L as $CaCO_3$, and 10.1 mg Cl^- / L. PWA2, PWA555, and PWA1 resins treated water bed volumes of 2.21E+05, 8.42E+04, and 2.72E+04, respectively, with 100 μg ClO_4^-/L in the effluent water, respectively.

The bifunctional resin Purolite A-530E was used at the Aerojet site in Rancho Cordova, CA to treat groundwater contaminated with perchlorate at concentrations of 830-890 μgClO_4^- / L (Gu et al., 2007b). The resin treated 37,000 bed volumes of water before breakthrough of perchlorate occurred, with an average influent flow rate of one bed volume per minute (Gu et al., 2007b). The resin has been successfully regenerated four times in two years, and the regenerated resin has retained its original efficiency.

Siegel et al. (2006) have tested ten new-to-market ion-exchange resins from Calgon (CalRes 2101), DOW (DOWEX1, NSR1), Purolite (A530, MCG-P2), ResinTech (SIR-110-HP), Rohm & Haas (PWA1, PWA2, PWA555) and Syborn (Ionac SR-7)) to evaluate the resins' perchlorate removal performance. Bench scale batch experiments were conducted to determine maximum perchlorate capacity; the results showed that Purolite (A530E) had the highest dry capacity (0.0115 mg $ClO4^-$ / mg resin) followed by ResinTech (SIR-110-HP), Rohm & Haas (PWA2), Dow (DOWEX NSR1) and Sybron (Ionac SR-7), with capacities of 11.1, 7.0, 6.5, and 6.2 μg ClO_4^- / mg resin, respectively.

Carlin et al. (2004) have evaluated the perchlorate removal efficiency of PWA2 (perchlorate selective), PWA1 (conventional), and PWA555 (nitrate selective) resins from Purolite. The study reported that the PWA2 resin is more selective for ClO_4^- over NO_3^-, SO_4^{2-}, and Cl^- by 33, 5000 and 30 times, respectively, when compared to a standard Type I strong base resin.

Boodoo (2003) compared the performance of a number of resins from Purolite, and reported the average capacity of acrylic SBA Type I, styrenic SBA Type I, nitrate selective and bifunctional perchlorate selective resins as 300, 4,000, 7,000, and 28,000 bed volumes, with average media life of 1 month, 1 year, 1.8 years, and 7.4 years, respectively.

Gu et al. (2005) have investigated the sorption affinity and capacity of a series of strong base anion-exchange resins for both U(VI) and ClO_4^-, as well as the effect of sulfate on the performance of these resins. The gel type polyacrylic resin (Purolite A850) showed the highest sorption affinity and capacity for U(VI) among a group of polystyrenic resins (Purolite A530, WBR109, Purolite A520E, Purolite A500, and

DOWEX 1-X8). A dilute acid wash (0.01 M of HCl) of the uranium-laden resin led to desorption of 21.4% and 34% of the total sorbed U(VI) and ClO_4^- from the resin, respectively.

Table 2.5 Comparison of Results for IX Resins in Removing Perchlorate (n.d. = non detectable)

Resin Name/ Manufacturer	Resin Type	Influent Perchlorate (μg/L)	Effluent Perchlorate (μg/L)	Experiment Scale	BVs	Reference
SIR-110 ResinTech	Perchlorate selective	8-11	n.d.	Bench Pilot	420,000 > 110,000	Siegel et al., 2006
PWA2 Rohm and Haas	Perchlorate selective	8-11	n.d.	Bench Pilot	220,000 > 110,000	Siegel et al., 2006
A530E Purolite	Perchlorate selective	8-11	n.d.	Bench Pilot	105,000 65,000	Siegel et al., 2006
SR-7 Syborn	Perchlorate selective	8-11	n.d.	Bench	80,000	Siegel et al., 2006
PWA555 Rohm and Haas	Nitrate selective	8-11	n.d.	Bench	60,000	Siegel et al., 2006
A520E Purolite	Nitrate selective	50	n.d.	Bench	20,000	Gu et al., 1999
D3696 Purolite	Perchlorate selective	50	n.d.	Bench	100,000	Gu et al., 1999
SBG1 & SBG2 ResinTech	Conventional	90-100	n.d.	Bench	10,000	Wang et al., 2008
NSR-1 DOW	Nitrate selective	90-100	n.d	Bench	17,000	Wang et al., 2008
PWA1 Rohm and Haas	Conventional	200	100	Pilot	27,173	Carlin et al., 2004
PWA555 Rohm and Haas	Nitrate selective	200	100	Pilot	84,183	Carlin et al., 2004
PWA2 Rohm and Haas	Perchlorate selective	200	100	Pilot	221,206	Carlin et al., 2004
A520E Purolite	Nitrate selective	450	n.d.	Full	17,000	Gu et al., 2003
D3696 Purolite	Perchlorate selective	450	n.d.	Full	19,000	Gu et al., 2003
A530 E Purolite	Perchlorate selective	860	n.d.	Full	37,000	Gu et al., 2003

A series of metal-loaded chelating resins, which were prepared by loading Cu(II), Co(II), Zn(II), Ni(II), Fe(II), and Fe(III) onto DOWEX M4195 (DOW3N), have been utilized to remove perchlorate from a solution containing 3 mg ClO_4^- / L, 110 mg NO_3 /L, and 100 mg SO_4 /L. All of the resins were exhausted after treating approximately 2000 BVs of solution (Dimick et al., 2008). The chelating resin loaded with Cu(II) was reported to have the highest perchlorate capacity among the six chelating resins that were tested, with a perchlorate selectivity coefficient of 15 (Dimick et al., 2008).

It has been reported that styrenic resin with a tripropyl-amine functional group (a nitrate selective resin) can treat about 100,000 bed volumes of water containing 50 μg ClO_4^- /L, 53 mg SO_4^{2-} /L, and 30 mg NO_3^- /L (Tripp and Clifford, 2006). Tripp and Clifford (2006) showed that standard polyacrylic gel resins with low perchlorate selectivity are suitable to remove perchlorate and nitrate from water with less than 250 mg SO_4^{2-} /L, and that the resin should be run to NO_3^- breakthrough with partial exhaustion and countercurrent regeneration. Polystyrenic gel resin with medium-high perchlorate selectivity can be used to treat water with sulfate and nitrate concentrations of 500 and 5 mg/L, respectively, with partial countercurrent regeneration (Tripp and Clifford, 2006). They also recommended treating contaminated water (<500 mg SO_4^{2-} / L and <5 mg NO_3^- / L) with highly perchlorate-selective resins, with resin disposal or regeneration offsite.

Like other treatment processes, ion-exchange has advantages and disadvantages. The ion-exchange reaction is fast; it can therefore be operated at relatively high flow rates in small and medium sized water supply systems. Ion-exchange is known to be simple to operate, effective and relatively low cost (Gu et al., 2007b; Samatya et al., 2006b; Bae et al., 2002; Boumediene and Achour, 2004), and cost effectiveness has been improving rapidly with technical innovation.

Ion-exchange has many disadvantages, such as iron fouling, adsorption of organic matter, bacterial and chlorine contamination (resins act as filters for bacteria and chlorine), and organic contamination from the resin (release of non-ionized organic matter from the resin's structure). High levels of suspended solids in wastewater may cause clogging of non-selective resins. The water chemistry (e.g. presence of competing ions and pH) of drinking water has a great influence on the contaminant removal efficiency of ion-exchange resins. Spent conventional and nitrate selective resins require frequent replacement and disposal, and perchlorate selective resins are not regenerable and must be replaced after perchlorate breaks through. Residual brines need to be treated and managed prior to being disposed of at landfills. Regeneration of resins is discussed next. Treatment and management of brines containing arsenic and chromium will be discussed in sections 2.9.5 and 2.10.2, respectively.

2.6. Regeneration of Conventional, Nitrate Selective and Perchlorate Selective Resins

Three common types of SBA exchange resins are currently used in the ion-exchange water treatment process: (1) highly selective and regenerable, (2) highly selective but non-regenerable, and (3) conventional or low selective (usually regenerable with sodium chloride). Most of the nitrate selective (highly selective) resins are regenerable using sodium chloride. Normally, perchlorate-selective resins are non-regenerable due to their high affinity to perchlorate ions. The spent perchlorate selective resins are traditionally disposed of (Batista et al., 2000; Gu et al., 2001; Tripp and Clifford, 2000) by incineration. Perchlorate and nitrate selective resins are highly preferential to perchlorate and nitrate over other ions in solution, such as sulfate (Urbansky, 1998; Batista et al., 2000; Samatya et al., 2006a; Rochette, 2006; Tanaka, 2006; Ghurye et al., 1999; Jackson and Bolto, 1990). However, conventional resins have very low selectivity for anions of interest such as perchlorate and nitrate; most of their capacity is exhausted capturing sulfate or other competing ions in the water (Urbansky, 1998; Batista et al., 2000; Tripp and Clifford, 2000). Therefore, conventional resins have to be regenerated frequently, resulting in generation of large volumes of regenerate brines. Residual waste (brine) disposal and handling is expensive. Using a conventional resin to remove perchlorate and nitrate from waters with high sulfate concentrations is therefore not cost effective.

2.6.1 Regeneration Principles for Conventional and Nitrate Selective Resins

Regeneration is a key process in water treatment with ion-exchange, and it greatly affects the cost and efficiency of the process (MWH, 2005). Imperfect regeneration due to low regenerant volumes leads to untimely breakthrough and contaminant leakage. However, regeneration with excessive volumes of regenerant (e.g., sodium chloride) results in high operational costs. The complete regeneration of resins is not practical, so compromises have to be made (Guter, 1984). For example, even if two thirds of the capacity of a resin is regenerated, the process will be efficient and economical, and usually one or two bed volumes of sodium chloride are sufficient for effective regeneration.

There are two techniques used to regenerate ion-exchange resins: cocurrent and countercurrent regeneration (MWH, 2005). In cocurrent regeneration, the regenerant is passed through the resin bed in the same direction as the contaminated water being treated (typically downward), while in the countercurrent regeneration process, the regenerant is passed through the spent resin bed in the opposite direction of the water being treated (typically, regenerant passes upward through the bed) (MWH, 2005). Countercurrent regeneration is preferred in most cases due to its higher efficiency and lower regenerant volume requirement. Bed fluidization is the upward expansion of resin beads in the empty headspace of an ion-exchange vessel, and it may occur in the countercurrent regeneration process. Bed fluidization may destroy the resin and must be prevented by using inert granules to fill the headspace or by using air and water blockages. Filling up the ion-exchange vessel completely also prevents bed fluidization in the countercurrent regeneration mode (MWH, 2005).

In the ion-exchange resin regeneration process, the optimum dosage of regenerant is the lowest concentration (typically, 1 or 2 BVs) of regenerant solution required to regenerate a resin as quickly as possible. Optimum regenerant dosage can be obtained by conducting pilot scale experiments with various concentrations of a regenerant at a (low) flow rate of 2-5 BV/h. Usually, 3-14% (w/v) sodium chloride solutions (80-320 kg $NaCl/m^3$ resin) are used to regenerate strong-acid cation-exchange resins, and 1.5-14% NaCl (40-320 kg $NaCl/m^3$ resin) (solutions are used to regenerate SBA exchange resins (MWH, 2005).

After the regeneration process has been completed, regenerant residue inside the resin beads has to be rinsed off before a new run cycle is started. Typically, two to six bed volumes of clean water are required to clean the resin for the next cycle. Insufficient rinsing of the resin beads leads to early leakage of the contaminants during the operation cycle. The main reason for the leakage is the remaining contaminant ions in the resin media at the top or bottom of the column, depending on whether countercurrent or concurrent regeneration is used (MWH, 2005).

Nitrate removal using ion-exchange has been reported as an effective process (Liu and Clifford, 1996). However, the process generates brines with high nitrate concentrations, and those brines need to be managed. van der Hoek and Klapwijk (1988) reported a 90% reduction in brine production using a combined ion-exchange/biological denitrification process with an Amberlite IRA 996 resin and methanol as carbon source for the denitrification process. Clifford and Liu (1993b) reported that denitrification of the generated brine in the nitrate removal process may reduce salt consumption by 50% and salt discharge by 90%. Liu and Clifford's (1996) results agree with their bench scale studies in 1993. Liu and Clifford (1996) demonstrated biological denitrification of a spent ion-exchange brine in a batch reactor using methanol as the denitrification carbon source. Moreover, the denitrified brine is re-usable; therefore, the waste discharge can be reduced up to 90% by the denitrification process compared with conventional ion-exchange regeneration processes.

2.6.2 Regeneration of Perchlorate Selective Resins and Methods to Improve the Process

Resins that are highly selective for perchlorate are mostly treated as non-regenerable (Carlin et al., 2004), i.e., "throw away", or "use and burn." Although regeneration of highly perchlorate selective resins has been reported, large volumes of concentrated sodium chloride solutions (12%) are required for the regeneration process (Tripp and Clifford, 2000; Batista et al., 2000). High selectivity for perchlorate makes the regeneration process difficult and costly because large (58.8 cm^3/g-mole) poorly hydrated (hydrophobic) perchlorate ions (Batista et al., 2002) strongly bond to the resin (Gu et al., 2001). Styrenic type perchlorate-selective resins are also hydrophobic and have high selectivity coefficients for perchlorate, which makes regeneration even more difficult (Batista et al., 2002).

Metal-loaded chelating resins are called polymeric anion-exchangers, and have been utilized for removing anions from solutions (Chanda et al., 1988; Helfferich, 1995; Zhao et al., 1998; Zhu et al., 1992). Polymeric anion-exchangers containing dual functional groups are able to remove anions (Zhao et al., 1998). Dimick et al. (2008) studied whether perchlorate could be removed from a synthetic solution by a series of polymeric anion-exchangers, which were prepared by loading Cu(II), Co(II), Zn(II), Ni(II), Fe(II), and Fe(III) onto Dowex M4195 (DOW3N). The exhausted resins (perchlorate-laden) were regenerated using 4% NaCl solution; the resin loaded with Fe(III) showed the highest regeneration efficiency (Dimick et al., 2008). Most of the resins in this experiment were regenerable if at least five bed volumes of 4% NaCl solution was used as the regenerant; use of those volumes of regenerant leads to the generation of large volumes of brine contaminated with perchlorate.

A conventional polyacrylic Type 2 resin can be used for perchlorate removal and it is easily regenerable. However, frequent regenerations are required, producing a large volume of contaminated brines (Tripp and Clifford, 2000). Similarly, Batista et al. (2000) stated that many bed volumes of 12% sodium chloride brine are required to remove only six percent of the perchlorate accumulated in a relatively selective resin; moreover, increasing the temperature of the perchlorate-laden resins improved the process only minimally (Batista et al., 2002). These issues translate to high operational costs and residual disposal problems.

Utilizing single-use perchlorate-selective resins for water treatment purposes is expensive, and resin incineration contaminates the environment. Therefore, regeneration of selective resins and their final brine disposal problems have to be resolved in order to make the ion-exchange process reasonable and attractive for removal of hazardous contaminants in water (Tripp and Clifford, 2000, Batista et al., 2000). Research efforts have attempted to identify improvements to techniques for the regeneration of perchlorate selective resins such as:

- biological treatment of ion-exchange brine containing perchlorate and nitrate (Batista et al., 2002; Hiremath et al. (2006); Lin et al. (2007), Lehman et al., 2008; Patel et al., 2008)
- bio-regeneration of perchlorate laden resin (Wang et al., 2008; Wang et al., 2009)
- chemical regeneration of bifunctional resins (Gu et al., 2000, 2001, 2003, 2005, 2007).

Batista et al. (2002) stated that combining ion-exchange technology with biological reduction of the ion-exchange residual waste is the most promising technology for the removal of perchlorate from water. Biological perchlorate reduction has been reported in various studies (Batista et al., 2002; Hiremath et al. (2006); Lin et al. (2007); Lehman et al., 2008; Patel et al., 2008; Cang et al., 2004). Perchlorate is utilized as an electron acceptor under anaerobic conditions by bacteria when an electron donor (e.g. carbon source or hydrogen) is present (Batista et al., 2002). Moreover, some microorganisms are able to reduce perchlorate even under extreme conditions (e.g., high salt, ammonium, and sulfate concentrations) in a brine solution (Batista et al., 2002; Gingras and Batista, 2002; Patel et al., 2008; Lin et al., 2007). The idea is to use non-selective re-usable strong base resins to remove perchlorate and nitrate from water; the residual ion-exchange brine containing perchlorate and nitrate is then treated biologically.

Cang et al. (2004) developed two bacterial cultures from marine sediments; these cultures had the ability to decompose perchlorate within 24 hours in 3-6% NaCl solutions. Hiremath et al. (2006) and Lin et al. (2007) have used the cultures developed by Cang et al. (2004) to remove perchlorate and nitrate from ion-exchange spent brine. Hiremath et al. (2006) reported that the perchlorate and nitrate concentrations in the brines being treated were reduced to below detectable limits; the brines being treated had properties of 3-10% NaCl, 400-4000 mg/L nitrate, 600-6000 mg/L sulfate, and 5-9 pH. Lin et al. (2007) stated that the addition of divalent cations (e.g., Mg^{2+} and Ca^{2+}) to the brines being treated improved the biological degradation of perchlorate. After biological treatment of ion-exchange brines, the resin-laden brines may be re-used in the ion-exchange process.

The biological treatment of ion-exchange brines containing perchlorate and nitrate has been investigated with a NP30 bacterial culture (Patel et al., 2008; Lehman et al., 2008; Lin et al., 2007; Hiremath et al., 2006). NP30 is a bacterial culture that is able to degrade perchlorate and nitrate in saline solutions and ion-exchange brines (Lehman et al., 2008; Lin et al., 2007; Hiremath et al., 2006; Patel et al., 2008). Patel et al. (2008) have operated a fluidized bed reactor housing a column of activated carbon that has been inoculated with the NP30 culture, and mixed with fresh granular activated carbon. This system has been used for perchlorate-only and combined nitrate and perchlorate removal from a synthetic brine (6% NaCl). The electron donor in the reactor was acetate; the perchlorate and nitrate feed concentrations were 293-306 mg/L and 193-948 mg/L, respectively, and effluent perchlorate and nitrate feed concentrations were less than 2.3 mg ClO_4^- /L and 10 mg NO_3-N/L, respectively.

The biological treatment of perchlorate and nitrate in ion-exchange spent brine (6% NaCl) has been accomplished in a sequencing batch reactor (SBR) by Lehman et al. (2008). They reported that the addition of nitrate at concentrations up to 800 mg/L did not reduce the perchlorate reduction efficiency of the reactor. Polyacrylic resin (Purolite A-850) was used in 20 cycles of water treatment (loading) and partial regeneration; the effluent water satisfied the MCl for nitrate (10 mgNO_3^{-}—N/L) and the California Department of Health Services notification level for perchlorate (6 μg ClO_4^- /L). However, partial regeneration of the resin resulted in the accumulation of perchlorate in the resin, so the resin eventually needed to be regenerated fully, which then generated an excess volume of brine. The accumulation of non-targeted ions (i.e., uranium, silica, fluoride, barium, and arsenic, etc.) was another disadvantage of the process.

Wang et al. (2008) reported the feasibility and kinetics of a direct bio-regeneration of six different resins (DOWEX1, SBG2, SBG1, NSR-1, A530E, and SIR110), which were directly contacted with a perchlorate reducing bacterial culture. They claimed that the bio-regenerated resins are re-usable; however, they have shown the results of only two run cycles. Moreover, it is not clear from their data whether they observed any perchlorate in the effluent while using the regenerated resins. According to a scanning electron microscopy analysis, the regenerated resin surface was clear without any biofilm formation, which re-affirms that the regenerated resins are re-usable (Wang et al., 2008).

Complete regeneration of perchlorate laden bifunctional anion-exchange resins using a novel tetrachloroferrate ($FeCl_4^-$) displacement technique has been developed at Oak Ridge National Laboratory (Gu et al., 2000, 2001, 2003, 2005, 2007). A field trial of the Oak Ridge technology showed a 30-40% loss of resin capacity after regeneration as the result of the precipitation of iron oxyhydroxides. Application of a 0.5-micron filter prior to the ion-exchange treatment process greatly decreased the resin fouling (Gu et al., 2003). Complete decomposition of perchlorate in ferric chloride and hydrochloric acid under controlled temperature and pressure has been demonstrated by Gu et al. (2003). The complete reduction of perchlorate in brine solution occurred at 195ºC in the $FeCl_3$-HCl solution in less than one hour in both batch and flow through (continuous) reactors (Gu et al., 2003). The process did not alter the chemical properties of the $FeCl_3$-HCl solution , which can therefore be reused, thus offering a cost effective method for perchlorate removal (Gu et al., 2003).

Perchlorate reductions in acidic media have been reported using aluminum, copper, nickel, and iron metal on electrodes constructed of several metals (Gu et al., 2003). Gu et al. (2003) demonstrated that perchlorate in the regenerant solution can be reduced to Cl^- at 190°C in a thermoreactor with a residence time of one hour, while the ferrous ion (Fe^{2+}) oxidized to Fe^{3+} with a destruction efficiency of 92-98%. Kim et al. (2004a) criticized the reduction process developed by Gu et al. (2003) and stated that the process is not applicable for full scale treatment processes due to the high temperature and pressure, low pH, and long residence time required. They supported the process of directly reducing perchlorate in water at ambient temperature and pressure by chemical (Gurol and Kim, 2000) or biological reduction (Logan et al., 2001; Rittman, 2003).

However, Gu et al. (2007) reported a successful field site demonstration of perchlorate contaminated groundwater treatment using highly selective, regenerable ion-exchange resin (Purolite A-530E). The perchlorate laden resin was regenerated using one bed volume of a mixed solution of $FeCl_3$ (1 M) and HCl (4M) (Gu et al., 2001, 2003), and twenty kilograms of perchlorate (almost 100% efficiency) were recovered in the regeneration process. Loading and regeneration have been repeated for four cycles in two years without significant capacity loss or deterioration of the resin.

Gu et al. (2007) suggested options for recovery and/or disposal of the perchlorate in the waste solution generated by ion-exchange resin regeneration. The treated solution can be re-used while the amount of perchlorate remaining in the treated solution will not greatly affect the regeneration process. Perchlorate in the waste residual can be precipitated as $KClO_4$ at 20°C by adding 30 ml of saturated potassium chloride solution to 100 ml of the waste solution, resulting in 94% recovery of perchlorate in its salt form. Although six bed volumes of a mixed solution of $FeCl_3$-HCl are required to completely regenerate a spent A-530E resin bed, most of the perchlorate in the spent resin can be recovered by eluting with as little as 1 BV of regenerant solution. The generated waste, with a volume of only about 0.001% of the treated water, can be neutralized and disposed of as hazardous waste (Gu et al., 2007).

Gutierrez et al. (2008) used 0.1 M NaI in 2 M HCl with 35% methanol solution to regenerate perchlorate-laden Purolite A-530E resin. They believe sodium iodide solution can be used as a replacement to tetrachloroferrate ($FeCl_4^-$) in situations where stainless steel high pressure pumps and columns are required, or in applications where non-acidic conditions are desired. Gutierres et al. (2008) suggested using sodium hydroxide to increase the pH and precipitate iron as ferric hydroxide. Excess sodium in the generated brine solution can be removed using a cation-exchange resin column; KCl or a solution of KCl and 80% methanol can then be added to the brine. Consequently, the perchlorate will precipitate as $KClO_4$, which is 200 times less soluble than $NaClO_4$. Gu et al. (2001) regenerated perchlorate laden resin Purolite A-530E resin completely and partially (Gu et al., 2007) with 6 and 1 bed volume(s) of $FeCl_4^-$, respectively. However, Gutierrez et al. (2008) used 100 and 20 bed volumes of 0.1 M iodide solution to recover perchlorate from the spent resin completely and partially, respectively. Although they suggested that this process be applied only in special conditions of field operation, it is a costly process.

Gu et al. (2005) studied methods for the separation of uranium from perchlorate to avoid production of a mixed residual waste containing both uranium and perchlorate. Uranium occurs as a co-contaminant to perchlorate in groundwater. Naturally occurring uranium also adsorbs to the resins used for perchlorate removal; thus, the waste generated from the regeneration process became hazardous, containing both perchlorate and uranium. Bifunctional resins proved to be effective for removing perchlorate from groundwater (Gu et al., 2007); moreover, they are regenerable using $FeCl_3$-HCl solution. Bifunctional resins (A530A and WBR109) are composed of $(ethyl)_3N/(hexyl)_3N$ and $(ethyl)_3N/(butyl)_3N$ functional groups on a polystyrene backbone, respectively. A dilute acid wash of the spent resins with 0.01 M HCl at pH 2 resulted in almost 75% desorption of total sorbed U(VI) from spent bifunctional resins, but only about 0.1% desorption of total sorbed ClO_4^-. Subsequently, remaining perchlorate in the bifunctional resins can be removed using $FeCl_3$-HCl solution (Gu et al., 2001) while the generated waste containing uranium can be reduced (Lovely et al., 1991; Fredrickson et al., 2000) or disposed of properly. Gu et al. (2005) concluded that bifunctional resins can be used to remove perchlorate and uranium from contaminated groundwaters, and those resins can be regenerated in a two step regeneration process: a dilute acid wash and sequential displacement using a $FeCl_3$-HCl solution.

2.7. Coagulation Principles

Coagulation generally involves the use of hydrolyzed metal salts, pre-hydrolyzed metal salts or organic polymers to remove suspended, colloidal, and/or dissolved organic or inorganic substances from water or wastewater (MWH, 2005). A coagulant is added to water to transform the colloidal, suspended, and dissolved matter to solid form so that it can be removed from the solution with a subsequent process. Addition of high dosages of one or more coagulants to the solution produces precipitation products, which form larger particles called “flocs” that can be removed by gravity sedimentation and/or filtration (Choong et al., 2007; MWH, 2005). This technology can be applied in most water and wastewater treatment processes, including physical, biological and chemical systems.

The most common chemical coagulants are metal salts (e.g., aluminum sulfate, or “Alum” ($Al_2(SO_4)_3.14H_2O$), aluminum chloride ($AlCl_3$), ferric chloride ($FeCl_3$), and ferric sulfate ($Fe_2(SO_4)_3$) (MWH, 2005). Pre-hydrolyzed metal salts are utilized when low dosages of a coagulant are needed because it is hard to control the metal species when metal salts are placed directly in water. Pre-hydrolyzed salts decrease the solution pH less than metal salts. Pre-hydrolyzed metal salts such as polyaluminum chloride ($Al_n(OH)_mCl_{3n-m}$) are produced as the result of the reaction of alum or ferric with different salts (e.g., chloride, sulfate). Organic polymers with high positive charge density are also utilized as coagulants. Polymers are used to promote the formation of larger flocs, or as a filter aid (Choong et al., 2007). Coagulant aids (clay, sodium silicate, calcium carbonate, powdered activated carbon) are typically insoluble substances aiding the coagulation process. Coagulation aids are utilized in waters containing low concentrations of particles to assist in the formation of larger flocs (MWH, 2005).

2.7.1. Properties of Particles and Forces at the Solid-Solution Interface

Particles found in waters can be described as water repelling (hydrophobic), water attracting (hydrophilic), and micelles (hydrophobic-hydrophilic) (MWH, 2005). Hydrophobic particles have a low attraction to water; thus, their interfaces with water are easily identifiable. These particles are unstable thermodynamically and tend to aggregate irreversibly over time. Hydrophilic particles have a high attraction to water. The solid-solution interfaces of hydrophilic particles are not well defined due to the charged surfaces and interaction with water (MWH, 2005). Micelles are approximately spherical in shape, and are aggregates of both hydrophobic and hydrophilic molecules in a colloidal solution (MWH, 2005). Hydrated metal oxides (including iron or aluminum oxides), clays, proteins, humic acids, silica (SiO_2), and asbestos fibers are hydrophilic. These particles are polarized or ionized; therefore, water molecules attach to their surface functional groups (MWH, 2005).

Most particles in natural water have negative charges and are covered with positive counter-ions in bulk solution to assure electroneutrality. The electrical double layer (EDL) theory proposes that positive counter-ions are located at two different layers (regions), covering the core negative particle (MWH, 2005; Stumm and Morgan, 1996).

The first layer is exactly on the surface of negative particulate matter. This layer is formed of cations linked to the negatively charged surface by electrostatic and adsorption forces. This is the layer closest to the surface of particulate matter; it has a thickness of 5 Å and is known as the Stern layer (also as the Helmholtz layer after the Helmholtz-Perrin model). Cations in the Stern layer cannot neutralize the negative charge of the particle, and the remaining negative charge will be in balance with cations in the diffuse layer known as the Gouy-Chapman diffuse layer (MWH, 2005; Stumm and Morgan, 1996). The electrical double layer may extend up to 300 Å in the solution (depending on the solution characteristic) in order to satisfy electroneutrality (MWH, 2005).

There are various attractive and repulsive forces at the solid-solution interface. Particles in natural waters are stable through a balance between the repulsive electrostatic forces and attractive forces such as the van der Waals force (MWH, 2005). Introducing a coagulant into the solution destabilizes the particles by eliminating the balance between attractive and repulsive forces. Furthermore, adsorption occurs when the sum of attractive forces is larger than the sum of negative forces at the solid-solution interface (Stumm and Morgan, 1996).

Generally, there are four main forces present at the solid-solution interface: (1) chemical forces, (2) electric forces (i.e. attractive and repulsive forces, and induction energies), (3) London-van der Waals forces, and (4) hydrogen bonding (Stumm and Morgan, 1996). The covalent bonds or electrostatic forces are the largest forces at solid-solution interfaces, with more than 40 KJ/mol. Van der Waal forces and hydrogen bonds are in the same energy range (between 10-40 KJ/mol), noticeably smaller than chemical reaction energies and electrostatic forces, but larger than induction energies (<10 KJ/mol)

(Stumm and Morgan, 1996). Chemical forces occur at very short distances: covalent bonds, the sharing of electrons between atoms or between atoms and other covalent bonds. Electric forces merge over longer distances than those for chemical reaction. In view of the fact that most waters in solution have negative charges, repulsive electrostatic charge (two negative particles repelling each other) is the principal mechanism controlling the stability of particles in natural waters (MWH, 2005). Coulomb's law describes the attractive and repulsive electric forces (MWH, 2005). Induction energy is also principally electrical in nature. It occurs from molecular interactions between molecules with permanent dipoles (Stumm and Morgan, 1996). Such dipole-dipole interactions are also called orientation energy. Examples of permanent dipole molecules are HCl, H_2O, and NH_3.

Brownian motion is responsible for particle-particle interaction in colloidal solutions. Colloidal particles are in highly random motion due to numerous collisions with molecules of the fluid. These random motions may lead to two particles becoming close enough that van der Waals forces can come into play, and an attachment between two particles develops (MWH, 2005).

Van der Waals forces originate from electric and magnetic resonance induced by oscillating movements of electrons in atoms on the particle surfaces, and they only occur where two particles are very close to each other. Neutral molecules become instantaneously charged as a result of their vicinity to a bipolar molecule or by negatively charged electron clouds in non polar molecules (Stumm and Morgan, 1996). This force is also known as the dispersion force, which was introduced by London in 1930. The

London dispersion force is an explanation for the liquefaction of gases. Both the London dispersion and van der Waals forces are symmetric (Stumm and Morgan, 1996).

It should be noted that van der Waals forces overcome electrostatic forces only if two particles become so close together that electrostatic forces and the EDL would normally force them apart (MWH, 2005). Application of a chemical coagulant neutralizes or reduces the repulsive electrostatic forces; consequently, the electrostatic and EDL energy barriers are removed, van der Waals forces become dominant and aggregation occurs.

Hydrogen bonding is a connection between a hydrogen atom and two polar molecules. Hydrogen acts as a proton donor and the other molecule (for example, water) acts as a proton accepter. Hydrogen bonding occurs at a preferred orientation and is not symmetric (Stumm and Morgan, 1996).

2.7.2. Mechanisms of Coagulation

The mechanisms of coagulation involve (MWH, 2005): (1) charge neutralization, (2) compression of the electrical double layer (EDL), (3) enmeshment in a generated precipitate, or “sweep floc”, (4) polymer bridging, and (5) adsorption. Suspended particles (1-100 μm) are removed during coagulation by charge neutralization and/or precipitate formation (i.e “sweep floc”); however, colloidal particles (0.001-1 μm), natural organic matter (NOM) (< 0.45 μm), and dissolved organic or inorganic substances (< 0.001 μm) are primarily removed via adsorption onto the surface of precipitates formed during coagulation (MWH, 2005).

(1) Negative particles dispersed in water can be neutralized by adsorption of positive ions when they are provided in the solution as chemical coagulants (MWH, 2005). When coagulation is used to remove suspended particles, the positive charge of the coagulant

destabilizes the particles by reducing or removing their electrical surface charges. Inorganic metal coagulants hydrolyze rapidly in the solution and form insoluble precipitates. These precipitates can neutralize the charges on small particles and form bridges between them. For example, when ferric chloride is added to a solution, iron (III) hydrolyzes and produces $FeOH^{2+}$, and $Fe(OH)_2^+$, which can neutralize negative particles. Cationic polymers also provide positive charges resulting in formation of larger particles (MWH, 2005). If the surface charge of the particles in a solution is known, the required dosage of coagulant can be determined (MWH, 2005). Direct measurement of the surface charge is not possible, but the surface charge on a particle can be estimated indirectly utilizing electrokinetic phenomena (MWH, 2005). Electrokinetic phenomena are the combination of several observable facts in a fluid containing particles. Zeta potential is the electrokinetic potential drop across the diffuse layer (i.e. between the Stern layer and the bulk solution) (Stumm and Morgan, 1996). When a particle moves in the bulk solution due to an applied electric field, it drags a cloud of ions, and some of the liquid adheres to the particle and migrates with it. There is a shear plane (slipping plane) (MWH, 2005) between the liquid adhering to the solid and the bulk solution. The zeta potential is the electrokinetic charge on this shear plane (Stumm and Morgan, 1996), and cannot be measured experimentally. However, measurement of electrophoretic mobility is feasible, and the zeta potential can be calculated from the electrophoretic mobility. It has been shown that when the absolute value of the zeta potential is less than 20 mV, rapid flocculation occurs (MWH, 2005).

(2) Compression of the EDL helps the aggregation of particles in solution. The particles come close to each other due to Brownian motion and attract each other because

when the EDL is compressed the van der Waals' forces of attraction are greater than electrostatic repulsive forces (MWH, 2005). Coagulant can be added to the solution to increase the ionic strength of the solution. When the ionic strength of a solution increases, the EDL of particles in the solution becomes thinner and the particles' electrical potential is reduced. The ionic strength is defined as (MWH, 2005):

$$I = \frac{1}{2}\sum Z^2 M \qquad (2.17)$$

Where:

- I = the solution's ionic strength, mole/L
- Z = the magnitude of positive or negative charge on an ion
- M= the molar concentration of cationic or anionic species, mol/L.

The electrical double layer (EDL) thickness is equal to the distance from the particle at which the electrical potential is 37% of the potential at the particle surface. The EDL thickness is average of how far repulsive forces can extend into the solution (MWH, 2005).

Ionic strength is an extremely important factor that affects the EDL thickness. It has been shown that when the ionic strength of a solution increases from 0.001 mol/L to 0.9 mol/L the thickness of the electrical double layer of particles in the solution decreases from 96.2 Å to 3.2 Å. Van der Waals' forces operate at distances less than 10 Å (MWH, 2005). In solutions with ionic strengths above 0.1 mol/L, van der Waals forces can operate because the thickness of the double layer of particles is less than 10 Å. The charge of ions in a solution has an extreme effect on the thickness of the EDL. For the same concentration, a solution containing ions with higher charge will have thinner EDLs. For instance, if a solution with 5000 mg/L of NaCl satisfies the flocculation process for hydrophobic particulates, 80 mg/L of $CaCl_2$ will induce the same flocculation effects.

(3) When high dosages of a chemical coagulant are added to a solution with the proper pH, insoluble metal hydroxide precipitates appear in the solution. These generated precipitates can destabilize the particles in the solution through adsorption or entrapment. Particulate matter can be enmeshed inside the formed precipitates and settle down with them. This process is called "*sweep floc*" or "*precipitation and enmeshment*" (Adamson, 1990; Stumm and Morgan, 1996; MWH, 2005) and only occurs when high dosages of coagulant are added to the solution. When precipitation of coagulant occurs at the edge or surface of particulate matter, the particulate matter is enmeshed in the generated precipitates (MWH, 2005). The required dosages of coagulant are strongly related to the pH of the solution in the presence of NOM, and the optimal pH for application of aluminum or iron salts is reported as 6-8. However, in the absence of NOM, the sweep floc mechanism is independent of the type of particles. This means that the dosages of the coagulant that must be added to the solution can be determined based on the concentration of particulate matter (regardless of its type) in the solution. Moreover, the type and concentration of NOM greatly affect the dosage of the chemical coagulates and must be considered in the coagulation design process (MWH, 2005). The proper dosages of hydrolyzing coagulant and the optimal pH can be determined with jar tests.

(4) Non-ionic polymers with high molecular weight (10^5 to 10^7) have been applied as effective coagulant aids for many years (MWH, 2005), where the dominant mechanism in the process is inter-particle bridging and adsorption (MWH, 2005). When a non-ionic

polymer coagulant is introduced into a solution, the added polymers adsorb to the surface of stable particles (polymer bonding) and destabilize the particles. Polymers are usually longer and larger than the particles in the solution and also have various heads and branches. Therefore, each head or branch of a polymer can adsorb on a particle and inter-particles bridges form, which help the flocculation process (MWH, 2005).

(5) Adsorption is the main mechanism for the removal of dissolved substances (e.g., arsenate and chromate) by coagulation. Adsorption principles are discussed next.

2.8. Adsorption Principles

Adsorption is an important phenomenon used in the water treatment process to remove dissolved contaminant ions. Adsorption is the main mechanism in water treatment by ion-exchange, activated alumina, and granular ferric hydroxide (GFH). Adsorption is also the main mechanism in coagulation, specifically for removing dissolved ions. Adsorption is the mass transfer of ions from a liquid phase to a solid phase. In this process, counter ions are adsorbed or accumulated on a solid-water interface to reach electroneutrality (Stumm and Morgan, 1996, Batista, 1995; Adamson, 1990). Adsorption influences the distribution of substances between the aqueous phase and solid phase, the electrostatic properties of suspended particles and colloids (e.g., in coagulation), and the reactivity of surfaces (Stumm and Morgan, 1996). The four main forces presented in the Coagulation Principles section of this document also govern the adsorption process (see 2.7.2). Adsorption is a competitive process in which OH^- ($10^{-14}/10^{-pH}$) is competing with other ions present in the solution; thus, adsorption is strongly pH dependent (Stumm and Morgan, 1996).

2.8.1. Physiochemical and Electrical Properties of Oxide and hydroxide Surfaces

The surface charge of oxides/hydroxides is an important factor in coagulation/adsorption. These surfaces are usually complex and surface charges may arise from various sources. The electrical charges at the oxide surfaces can be developed in three principal ways: (1) isomorphous replacement (crystal imperfections), (2) preferential adsorption of organic matter, and (3) chemical reactions at the surface (Stumm and Morgan, 1996; MWH, 2005). In addition, most particles in natural waters have negative surface charges (σ_P); however, they are balanced by the charges in bulk solution (σ_D) and the overall charge is zero: $\sigma_P + \sigma_D = 0$.

The crystal structure of metal oxides, including aluminum and silica, develops a negative charge when a central metal ion is replaced by a metal ion with lower valence in the crystal structure (Stumm and Morgan, 1996; MWH, 2005). This process is called isomorophous replacement. Imperfections, which are broken bonds on the crystal edge, occur during the formation of crystals in clay and similar particles. The imperfections can cause surface charges to develop (Stumm and Morgan, 1996; MWH, 2005). Soluble salts also can contain a surface charge due to matrix pattern imperfections (Stumm and Morgan, 1996; MWH, 2005).

Many NOMs and biotic particles including fulvic acid, algae, and sewage treatment effluent are negatively charged in the pH range of natural waters because they contain carboxylic acid groups (Stumm and Morgan, 1996; MWH, 2005). For example, considering organic matter with functional amino and carboxyl groups, the surface charge can result from protolysis:

$NH_3^+–R–COOH \leftrightarrow NH_3^+–R–COO^- \leftrightarrow NH_2–R–COO^-$ (Stumm and Morgan, 1996) (2.18)

The oxide and hydroxide surfaces (e.g., ferric hydroxide) are able to react both as an acid and as a base (MWH, 2005). The hydroxide and oxide surfaces are amphoteric, having the potential to donate either H^+ or OH^- ions (MWH, 2005; Batista, 1995). For example, Fe–OH is able to gain or lose electrons.

$Fe–OH_2^+ \leftrightarrow Fe–OH \leftrightarrow Fe–O^-$ (Stumm and Morgan, 1996) (2.19)

The net surface charge density of an oxide/hydroxide surface is directly related to sorption densities of H^+, OH^-, metal ions, and anions (Stumm and Morgan, 1996). The net surface charge density of a hydrous oxide is given by:

$$\sigma_P = F[\Gamma_H - \Gamma_{OH} + \Sigma(Z_M\Gamma_M) - \Sigma(Z_A\Gamma_A)] \quad (2.20)$$

where:

- σ_P = the net surface charge is in C/m^2
- F = the Faraday constant of 96,490 C/mol
- Z = the valence of sorbing ion
- Γ_H, Γ_{OH}, Γ_A, and Γ_M = the sorption densities of H^+, OH^-, anions and metal ions, respectively, in mol/m^2 (Stumm and Morgan, 1996).

The net proton charge (in C/m^2) is equal to the difference between H^+ and OH^- sorption densities multiplied by Faraday's constant:

$$\sigma_H = F[\Gamma_H - \Gamma_{OH}] \quad (2.21).$$

Moreover, the surface charge in mol/kg, can be calculated as $Q_{H\text{ or }OH} = \Gamma_{H\text{ or }OH}s$ where s is the specific surface area of the solid in m^2/kg. The net surface charge accumulated at the interface (Q_P) in mol/kg can be determined by measuring all the cations, anions, H+ and OH- adsorbed to the surface of the solid (Stumm and Morgan, 1996). The surface charge at hydroxide surfaces can be estimated experimentally by alkali-metric titration of pre-formed solid hydroxide in the presence of a neutral electrolyte. The adsorptions of an anion (A^{2-}) to a solid surface are modeled as:

$$Q_P = \{S–OH_2^+\} – \{S–O^-\} - \{S–A^-\} \qquad (2.22)$$

and the relationship between the surface charge and charge density is:

$$\sigma_P = Q_P F/s \qquad (2.23)$$

pH affects surface charges, and accordingly, the adsorption capacity, because metal speciation on the surface of solids depends strongly on the pH of the solution. The point of zero charge (pzc) is the pH at which the sum of all charges including cations, anions, H^+ and OH^- on the oxide surface is zero (Stumm and Morgan, 1996). At pH values above the pzc the surface charge is positive and at pH values below the pzc the surface charge is negative (Stumm and Morgan, 1996; MWH, 2005). A positive surface charge favors the adsorption of anions. At constant pH, addition of an anion to a solution at equilibrium increases surface protonation, and decreases the pzc value.

The pzc of goethite (FeOOH) at 0.1 M ionic strength is reported to be 7.9 by Sigg and Stumm (1981). The pzc of various inorganic particles are presented in Table 2.6. The pzc of amorphous $Fe(OH)_3$ is reported as 8.5 in low ionic strength waters (Stumm and Morgan, 1981; MWH, 2005). The pzc also depends on the ionic strengths of the aquatic solutions; therefore, the pzc of ferric hydroxide may vary in solutions with different ionic strengths. The pzc of ferric hydroxide has been reported to be between 7.9 and 8.2 by Dzombak and Morel (1990).

The isoelectric point (IEP) of a particle refers to the condition in which the total surface charge density is zero (σ_P = 0) when the particles have anions and cations attached to them (Stumm and Morgan, 1996). It is also defined as the point where particles do not shift/move in an applied electric field (Stumm and Morgan, 1996). A particle at its IEP is neutral, and the electric potential between the particle and the bulk solution is zero.

Table 2.6 Pzc of Inorganic Particulates

Particle	**Pzc**
$Al(OH)_3$ amorphous	7.5-8.5
Al_2O_3	9.1
CuO_3	9.5
$Fe(OH)_3$ amorphous	8.5
MgO	12.4
MnO_2	2-4.5
SiO_2	2-3.5
$CaCO_3$	8-9
$Ca_5(PO_4)_3OH$	6-7
$FePO_4$	3
$AlPO_4$	4

(Source: MWH, 2005)

2.8.2. Mechanisms of Adsorption of Anions on oxide and hydroxide surfaces

There are two theories to explain the adsorption of anions on oxide and hydroxide surfaces: (1) surface complex formation (complexation), and/or (2) surface precipitation (Dzombak and Morel, 1990). Surface precipitation and surface complex formation are different, but it is difficult to distinguish them from each other (Dzombak and Morel, 1990). Surface complex formation occurs at only the first layer of sorbing solids; however, surface precipitation occurs on the second and subsequent layers. The properties of a forming multilayer surface vary continuously from the properties of the original solid to those of a pure precipitate of the sorbing anion. Deprotonation occurs in both surface precipitation and surface complex formation. pH plays a major role in the adsorption process because proton (H^+) and hydroxyl (OH^-) ions are important factors in both mechanisms. Considering XOH as a functional group on the surface, acid-base equilibria are presented as:

$$X\text{–}OH + H^+ \leftrightarrow X\text{–}OH_2^+ \tag{2.24}$$

$$X\text{–}OH + OH^- \leftrightarrow X\text{–}O^- + H_2O \tag{2.25}$$

Where X represents a metal ion (Stumm and Morgan, 1996).

Anion Surface Complex Formation

According to surface complexation theory, the adsorption of anions and cations occurs via two possible mechanisms (Dzombak and Morel, 1990; Stumm and Morgan 1996; Batista, 1995): (a) deprotonation (or protonation) reactions of the surface hydroxyl groups, and (b) complex formation in solution (Stumm et al., 1992; Dzombak and Morel, 1990; Anderson et al., 1985). In the surface complexation model, adsorption is the surface complex formation of an anion (e.g., arsenate) or cation with a Lewis acid site of the central ion of the hydrous oxide (e.g., Fe(III) in ferric hydroxide). Compression of the electrical double layer (EDL) or increasing the ionic strength of a solution by addition of a coagulant, enhances the adsorption. Increasing the ionic strength of a solution decreases the zeta potential of particles and hydroxide(oxide) surfaces. Moreover, at high ionic strength, oxide surfaces have greater surface charges, but compressed EDL (Dzombak and Morel, 1990; Stumm and Morgan, 1996). Therefore, according to the surface complexation model, high ionic strength typically is favorable for adsorption onto oxide/hydroxide surfaces.

Surface complexation reactions include surface hydrolysis and formation of coordinative bonds at the surface with anions. Surface charges develop from the surface complex formation itself (Dzombak and Morel, 1990). It is assumed that all binding sites on the surface of the adsorbent are available and uniform for anion binding (Dzombak and Morel, 1990). Considering A^{3-} (e.g., arsenic) as a trivalent anion, anion surface complex formation can be expressed as:

$$\equiv XOH^o + A^{3-} + H^+ \leftrightarrow \equiv XA^{2-} + H_2O \qquad K_{1A}^{app} \qquad (2.26)$$

and/or

$$\equiv XOH^o + A^{3-} + 2H^+ \leftrightarrow \equiv XHA^- + H_2O \qquad K_{2A}^{app} \qquad (2.27)$$

The intrinsic equilibrium K values, which do not depend on the surface charge, can be corrected by the Coulombic correction factor considering the influence of pH and ionic strength:

$$K_A^{app} = K_A^{\text{int}} \exp(-\Delta ZF\psi / RT) \qquad (2.28)$$

- K_A^{app} = apparent equilibrium constant
- F = the Faraday constant of 96,490 C/mol
- Z = the valence of sorbing ion
- ψ = the potential at the surface in volts
- R = the molar gas constant (8.314 J/mol.K)
- T = the absolute temperature, K

The following species are present in the anion surface complexation: H^+, OH^-, H_3A, H_2A^-, HA^{2-}, A^{3-}, $\equiv XOH^o$, $\equiv XOH^{2+}$, $\equiv XO^-$, $\equiv XA^{2-}$, and $\equiv XHA^-$. Equations (2.26), (2.27) and (2.29) through (2.34) below define the mass laws:

$$\equiv XOH_2^+ \leftrightarrow \equiv XOH^o + H^+ \quad K_{a1}^{app} \qquad (2.29)$$

$$\equiv XOH^o \leftrightarrow \equiv XO^- + H^+ \quad K_{a2}^{app} \qquad (2.30)$$

$$H_2O \leftrightarrow H^+ + OH^- \quad K_W \qquad (2.31)$$

$$H_3A \leftrightarrow H_2A^- + H^+ \quad K_1 \qquad (2.32)$$

$$H_2A^- \leftrightarrow HA^{2-} + H^+ \quad K_2 \qquad (2.33)$$

$$HA^{2-} \leftrightarrow A^{3-} + H^+ \quad K_3 \qquad (2.34)$$

The equations governing the relationship between surface charge and charge potential also must be considered in the adsorption calculations:

$$\sigma = (F / AS)\, f(\psi) \qquad (2.35)$$

$$\sigma = 0.1174 c^{1/2} \sinh(Z\psi \times 19.46) \qquad (2.36)$$

Where:

- A = specific area in m^2/g
- S = solid concentration in g/L or mol/L
- $f(\psi)$ = the total surface charge ($f(\psi) = \exp(-F\psi / RT)$).

Anion Surface Precipitation

Surface precipitation of an anion may occur at the surface of the adsorbent. Surface precipitation was defined by Farley et al. (1985) as a multilayer adsorption process. They stated that surface precipitation occurs on various layers on top of the original adsorbent. An anion or cation added to a sorbing surface forms the first layer and the formed surface properties are completely different than those of the original sorbing surface. Each anion adsorbed on the surface of the solid will be protonated and adsorbs protons from the solution or metal ion from the adsorbing oxide, creating a positively charged layer that can adsorb other anions (Dzombak and Morel, 1990). In surface precipitation, a new solid is produced and precipitates onto the surface of the existing adsorbent solid.

The surface precipitation model can be integrated into any surface complexation model (Dzombak and Morel, 1990) considering the following surface precipitation reactions:

Precipitation of $X(OH)_{3(s)}$:

$$\equiv XOH^o + X^{3+} + 3H_2O \leftrightarrow \equiv X(OH)_{3(s)} + \equiv XOH^o + 3H^+ \qquad 1/K_{spX} \tag{2.37}$$

and/or precipitation of $XA_{(s)}$:

$$\equiv XHA^- + X^{3+} + A^{3-} \leftrightarrow \equiv XA_{(s)} + \equiv XHA^- \qquad 1/K_{spXA} \tag{2.38}$$

Formation of $\equiv X(OH)_{3(s)}$ and $XA_{(s)}$ species should also be considered in the calculations. The solubility products for surface precipitation are the same as solubility products for bulk solution precipitations. Surface precipitation can occur on the total mass of available ferrous hydrous oxide in a solution (Dzombak and Morel, 1990).

2.8.3. Adsorption Isotherms

Adsorption isotherms illustrate the correlation between the concentration of adsorbate (e.g., arsenic) in the solution, the amount of adsorbate adsorbed, and the available adsorption sites in equilibrium at a constant temperature. The most commonly used isotherms are the Langmuir and Freundlich isotherms.

The Langmuir isotherm is a simple assumption that implies 1:1 stoichiometry between adsorption sites and adsorbate on surface sites. The Langmuir adsorption isotherm describes the equilibrium between the surface and the solution assuming all active sites on the adsorbent surface have uniform energies (MWH, 2005). The isotherm is described by the following equation:

$$q_A = \frac{Q_M b C_A}{1 + b C_A} \qquad (2.39)$$

Where:

- Q_M = the maximum adsorbent-phase concentration of the adsorbate when surface sites are saturated with adsorbate, in mg adsorbate/g adsorbent; related to adsorption capacity
- b (or K_{ad}) = the Langmuir adsorption constant of adsorbate in L/mg, related to energy of adsorption; increases with an increase in binding energy.
- C_A and q_A = equilibrium concentrations of adsorbate in the solution and adsorbent-phase, respectively, in mg/L. A linear version of the Langmuir equation is used to plot C_A/q_A versus C_A, which is a straight line with slope of $1/Q_M$ and intercept of $1/(bQ_M)$:

$$\frac{C_A}{q_A} = \frac{1}{b_A Q_M} + \frac{C_A}{Q_M} \qquad (2.40)$$

The Freundlich adsorption isotherm represents the equilibrium concentrations of the adsorbate in solution and a heterogeneous adsorbent-phase (Rengaraj et al., 2003):

$$q_A = K_F C_A^n \qquad (2.41)$$

Where:

- K_F = the Freundlich adsorption capacity parameter, in mg/g; related to the sorption capacity of the heterogeneous adsorbent
- n = the unitless adsorption intensity parameter.

The logarithmic form of the equation for the Freundlich isotherm is used for convenience in equilibrium studies:

$$\log q_A = \log(K_F) + n \log C_A \qquad (2.42)$$

Adsorption can be described as an aqueous system following reversible first order kinetics when only one adsorbate is adsorbed on a heterogeneous surface:

$$A \xrightarrow{k_1} B \qquad A \xleftarrow{k_2} B \qquad (2.43)$$

where k_1 and k_2 are forward and reverse reaction rate constants, respectively. Considering x as the concentration of adsorbate (eg., Cr(VI)) transferred from liquid phase to the resin phase and C_i as the initial adsorbate liquid phase concentration, the transfer rate can be expressed as:

$$\frac{dx}{dt} = k_1(C_i - x) - k_2 x \qquad (2.44)$$

where t = time

At equilibrium, where dx/dt = 0, the equilibrium constant, K_C, can be represented as:

$$K_C = \frac{k_1}{k_2} = x/(C_i - x) \qquad (2.45)$$

and the overall rate constant, k is:

$$k = k_1 + k_2 = k_1 + \frac{k_1}{k_C} \qquad (2.46)$$

2.8.4. Adsorption Models

Double Layer Model: The Diffuse Layer Model

Two terms are considered in a sorption reaction: (1) the chemical free energy of binding to a specific surface site, which is a constant, and (2) Coulombic free energy of binding generated by the electrostatic charge at the surface (Dzombak and Morel, 1990). The product of these two terms is the equilibrium constant of the sorption reaction, which satisfies the mass law equation. This constant coloumbic term is a surface activity coefficient and can be calculated from the Gouy Chapman equation for the electrical double layer (Stumm and Morgan, 1996).

Dzombak and Morel (1990) expanded the basic theory of the electrical double layer and stated that in order to model a hydrous oxide surface, two surface sites with high and low affinities should be considered because of the heterogeneity of the hydrous oxide surfaces. This means that a solution containing hydrous oxide surfaces is a mixture of various components having a mixture of surface sites and affinities to the large anion and cation concentrations in the solution.

The surface charge density, σ_P (C/m^2) is directly dependent on the potential at the surface, Ψ_0 (volt):

$$\sigma = (8RT\varepsilon\varepsilon_0 c \times 10^3)^{1/2} \sinh(Z\psi_0 F / 2RT) \qquad (2.47)$$

Where:

- F = the Faraday constant (96,490 C/mol)
- Z = the valence of sorbing ion
- R = the molar gas constant (8.314 J/mol.K)
- T = the absolute temperature (K) of the solution
- ε = the dielectric constant of water (dimensionless; 78.5 at 25°C)
- ε_0 = the permittivity of free space (8.854×10^{-12} C/V-mor C^2/Jm)
- c = the electrolyte concentration (M).

At low potentials, equation (2.47) can be simplified to:

$$\sigma_P = \varepsilon\varepsilon_0 c k \psi_0 \qquad (2.48)$$

where k (called the Debye parameter) is the double-layer thickness (in meters) which can be calculated as:

$$k = \left(\frac{2F^2 I \times 10^3}{\varepsilon \varepsilon_0 RT} \right)^{1/2} \qquad (2.49)$$

Finally, the surface charge density can be simplified to the following at 25°C:

$$\sigma_P = 2.5 I^{1/2} \psi_0 \qquad (2.50)$$

where I is the ionic strength of the electrolyte (mol/L).

Considering thermodynamic assumptions, the total interaction energy of the solid-liquid interface can be specified as

$$\Delta G_{tot} = \Delta G^o_{chem} + \Delta G^o_{coul} \qquad (2.51)$$

ΔG^o_{chem} is an essential of the chemical reaction while ΔG^o_{coul} is the Coulombic term, which is a electrostatic energy obliged to surface potential. The coulombic energy is responsible for the migration of ions from solution to the solid surface (Dzombak and Morel, 1990; Stumm and Morgan, 1996) and can be calculated as:

$$\Delta G^o_{coul} = \Delta Z F \psi_0 \qquad (2.52)$$

where ΔZ is the change in the charge of the surface species because of the adsorption reaction. Also:

$$\Delta G^o_{tot} = -RT \ln K \qquad (2.53)$$

For example, the proton release of ferric oxide can be written as:

$$\equiv \mathrm{FeOH} \leftrightarrow \equiv \mathrm{FeO} + \mathrm{H}^+ \qquad (2.54)$$

and

$$K^s_{a2}(app) = K^s_{a2}(\mathrm{int}) \exp\left(\frac{F\psi_0}{RT} \right) = \frac{\{\equiv FeO^-\}[H^+]}{\{\equiv FeOH\}} \qquad (2.55)$$

where K(int) and K(app) are the intrinsic and apparent equilibrium constants. It should be noted that the surface potential cannot be measured experimentally; however, the surface charge can be calculated using the ion concentration on the surface. $pK_{a1}^{s}(\text{int})$ and $pK_{a2}^{s}(\text{int})$ for HFO have been reported between 7.29 ± 0.1 and 8.93 ± 0.07 with 95% confidence.

Double Layer Model: Constant Capacitance

The double-layer charge density equation can be reduced to a linear relationship under certain conditions of surface charge (potential) and ionic strength (Stumm and Morgan, 1996).

$$\sigma_P = C\psi_0 \tag{2.56}$$

C is the integral capacitance of the oxide solution interface in Farad/m^2. The integral capacitance is constant and is composed of two parts: (1) a diffuse layer component described by the Gouy-Chapman equation (C_G), and (2) the compact layer component (C_H) described by Helmholtz-Perrin and Stern (Stumm and Morgan, 1996). The equation for the integral capacitance is:

$$C^{-1} = C_G^{-1} + C_H^{-1} \tag{2.57}$$

The capacitance model can be usually applied at high or low ionic strengths in which the charge/potential relationship is approximately linear. At high ionic strength C_G is much greater than C_H so C is approximately equals to C_H. At low ionic strength C_G is much smaller than C_H and C is approximately equal to C_G. Moreover, CG ≈ 2.3 $I^{1/2}$ when the surface potential is smaller than 25 mV (Stumm and Morgan, 1996). This imposes a linear relationship between charge and potential at solid-liquid interfaces.

2.8.5. Properties of Ferric Iron as a Coagulant

Amorphous ferric hydroxide (also called hydrous ferric oxide, HFO, or amorphous iron oxyhydroxide), which is a solid, is formed as a result of the rapid hydrolysis of ferric iron. (Dzombak and Morel, 1990). Schecher and McAvoy (2001) suggested that in addition to ferric hydroxide, ferrihydrite ($Fe_5HO_8 \bullet 4H_2O$), goethite (α-FeOOH), hematite (Fe_2O_3), magnetite ($FeO \bullet Fe_2O_3$) and lepidocrocite (γ-FeOOH) may also form as a result of hydrolysis of ferric iron. Natural iron oxide materials having similar patterns to HFOs and are often called ferrihydrite. The chemical composition of hydrous ferric oxide is reported as $Fe_2O_3.nH_2O$, but its structure is uncertain (Dzombak and Morel, 1990). The "n" value in the chemical formula has been reported to be between 1 and 3, but the chemical composition varies between $Fe_2O_3.nH_2O$ and Fe_2O_3 (Dzombak and Morel, 1990). Density of HFOs has been reported to be between 2.2 and 4.0 g/cm^3 with an average near 3.5 g/ cm^3 (Dzombak and Morel, 1990).

Physical-chemical properties of fresh and aged HFOs are different. Freshly formed HFOs are nearly spherical and particle sizes have been reported between 1 and 10 nm (Dzombak and Morel, 1990). However, aged HFOs look like a swollen gel with high water content. Aged HFOs form aggregates, which are in the micrometer size range and have high porosity (Dzombak and Morel, 1990). The acid-base chemistry of solutions of HFOs varies greatly with time (Swallow et al., 1980). The pH of a solution in which HFO precipitation is occurring varies quickly in the first hour and then stabilizes after three or four hours (Davis, 1977; Dzombak and Morel, 1990). Aged HFOs gradually convert to a crystalline iron oxide often goethite (α-FeOOH). For example, a solution of 2-10% HFO transforms to goethite after 12 to 15 days (Dzombak and Morel, 1990).

Many scientists have found that the surface area of HFO is between 159 and 700 m^2/g (Dzombak and Morel, 1990). Davis (1977) assumed 2 nm diameter spheres of HFOs with 3.57 g/cm^3 (Murphy et al., 1976) density and calculated a theoretical surface area of

840 m^2/g for HFO. BET (Brunauer, Emmett and Teller) measurement is a well known process for the measurement of the specific surface area of a material (Brunauer et al., 1938). Dzombak and Morel (1990) believed that BET (Brunauer et al., 1938) measurements were not accurate and underestimated surface areas. They stated that the actual surface area of HFO was between 300 and 840 m^2/g and they used 600 m^2/g in their modelings, according to the recommendations of Davis (1977), Davis and Leckie (1978), and Luoma and Davis (1983).

Ferric Chloride

Ferric chloride dissociates in water into iron (III) and chloride ions as described in the following equations: (Stumm and Morgan, 1996):

$Fe^{3+} + Cl^- \leftrightarrow FeCl^{2+}$ $\Delta H^o = 5.6$ kcal mol^{-1} log K= 1.48 (2.58)

$Fe^{3+} + 2Cl^- \leftrightarrow FeCl_2^+$ log K= 2.13 (2.59)

$Fe^{3+} + 3Cl^- \leftrightarrow FeCl_3^0$ log K= 1.13 (2.60)

Deprotonation reactions of Fe^{3+} in water are presented below (Stumm and Morgan, 1996):

$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+$ $\Delta H^o = 10.4$ kcal mol^{-1} log K= -2.19 (2.61)

$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+$ $\Delta H^o = 17.1$ kcal mol^{-1} log K= -5.67 (2.62)

$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3^0 + 3H^+$ $\Delta H^o = 24.8$ kcal mol^{-1} log K= -12.56 (2.63)

$Fe^{3+} + 4H_2O \leftrightarrow Fe(OH)_4^- + 4H^+$ $\Delta H^o = 31.9$ kcal mol^{-1} log K= -21.6 (2.64)

$2Fe^{3+} + 2H_2O \leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$ $\Delta H^o = 13.5$ kcal mol^{-1} log K= -2.95 (2.65)

$3Fe^{3+} + 4H_2O \leftrightarrow Fe_3(OH)_4^{5+} + 4H^+$ $\Delta H^o = 14.3$ kcal mol^{-1} log K= -6.3 (2.66)

The $Fe(OH)_3^0$ produced will precipitate as $Fe(OH)_3(s)$, which is an absorbent, and provide surface sites as follows:

$$FeCl_3.6H_2O + 3HCO_3^- \rightarrow Fe(OH)_3(am) \downarrow + 3Cl^- + 3CO_2 + 6H_2O \quad (2.67)$$

Dissolution reactions of ferric hydroxide are (MWH, 2005):

$$Fe(OH)_3(s) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O \qquad \log K_{s0} = 3.2 \text{ to } 4.891 \quad (2.68)$$

$$Fe(OH)_3(s) + 2H^+ \leftrightarrow FeOH^{2+} + 2H_2O \qquad \log K_{s1} = 0.91 \text{ to } 2.701 \quad (2.69)$$

$$Fe(OH)_3(s) + H^+ \leftrightarrow Fe(OH)_2^+ + H_2O \qquad \log K_{s2} = -0.779 \text{ to } -2.5 \quad (2.70)$$

$$Fe(OH)_3(s) \leftrightarrow Fe(OH)_3^0 \qquad \log K_{s0} = -8.709 \text{ to } -12 \quad (2.71)$$

$$Fe(OH)_3(s) + H_2O \leftrightarrow Fe(OH)_4^- + H^+ \qquad \log K_{s0} = -16.709 \text{ to } -19 \quad (2.72)$$

The speciation of Fe(III) is illustrated in Figure 2.6. The thick line located above all other lines shows the solubility of freshly precipitated amorphous hydroxide at various pH values. This line is the sum of all dissolved Fe(III) species in the solution. For conditions above the line, Fe(III) precipitates, and for conditions below the solubility lines, Fe(III) species are in dissolved forms.

Fe(III) is fairly insoluble in the pH range of 5 to 9, with the minimum solubility occurring at a pH of 8.5 (Figure 2.6). Recommended operating pH for coagulation using ferric chloride is between 6 and 8. Accelerated corrosion rates were found to occur at pH values below pH 6. Distribution of dissolved Fe(III) species (hydrolysis of Fe(III)) in a 1 M Fe(III) solution is illustrated in Figure 2.7 as a function of pH. It was assumed that the solution was heterogeneous (i.e. ferric hydroxide would not precipitate).

For pH values less than 3, Fe^{3+} and $FeOH^{2+}$ are the predominant species of Fe(III). According to their dissolution reactions (equations 2.68 and 2.69), Fe^{3+} and $FeOH^{2+}$ do not easily precipitate as ferric hydroxide. $Fe(OH)_2^+$ is the predominant Fe(III) species at pH values between 2.5 and 8, and $Fe(OH)_2^+$ precipitates as ferric hydroxide (equation 2.70). The production of amorphous ferric hydroxide starts to accelerate for pH values above 2.5 (Figure 2.6). $Fe(OH)_3$ (aq) exists at pH values between 6 and 11, with its maximum concentration at pH 8.7 (Figure 2.7). $Fe(OH)_3$ (aq) transforms easily to $Fe(OH)_3$ (s) (equation 2.71), and therefore Fe(III) is fairly insoluble over the pH range of 5 to 9. For pH values above 9, $Fe(OH)_4^-$ becomes the predominant species of Fe(III), and $Fe(OH)_4^-$ does not transform to solid ferric hydroxide. Thus the solubility of Fe(III) increases for pH values above 9 (Figure 2.6).

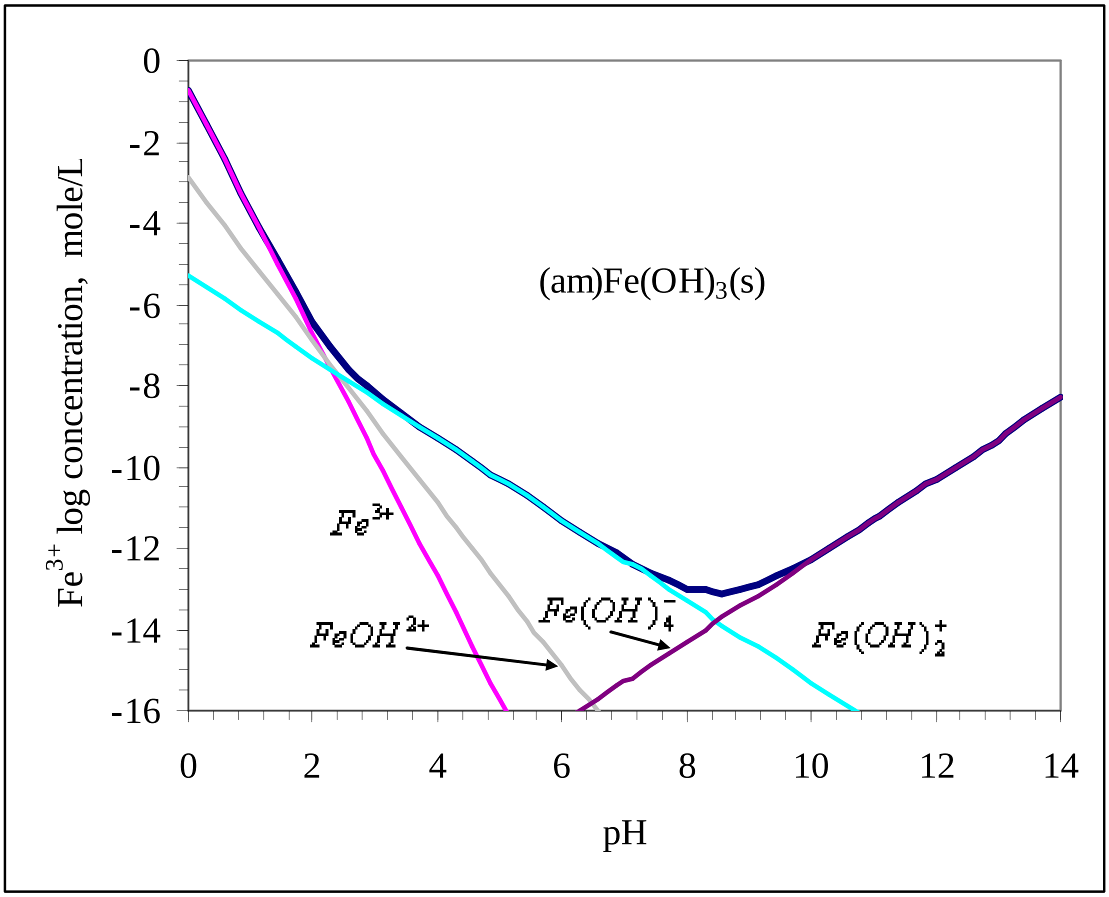


Figure 2.6 Computed Solubility of Precipitated $Fe(OH)_3(S)$ (25°C, Initial Fe(III) = 56 g/L (1 M)) (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001)

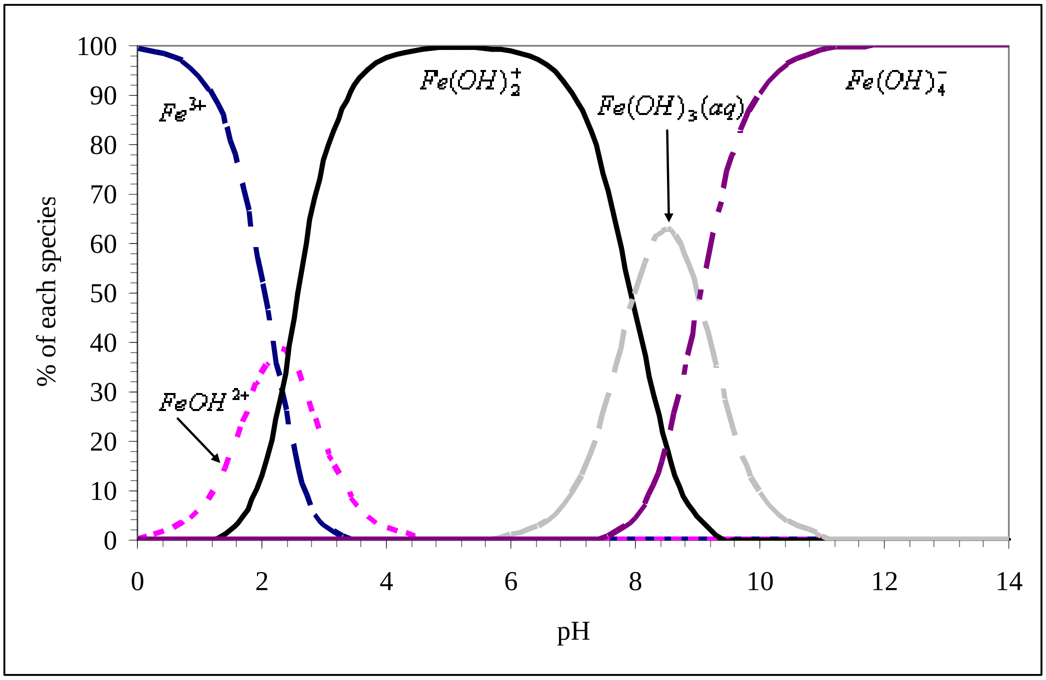


Figure 2.7 Computed Liquid-Phase Distribution of Ionic Species for Fe (III) System, Fe(III) = 100 mg/L (1.8×10^{-3} M) (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001)

2.9. Arsenic Removal from Brines

2.9.1 Arsenic Health Effects and Chemistry

Arsenic poisoning has occurred in nature for centuries. Arsenic is a carcinogenic element and needs to be removed from drinking water, which is the main route of arsenic exposure for the general population. Arsenic causes adverse health effects if ingested, inhaled or absorbed through the skin (U.S. EPA, 2007). Chronic health effects of long term exposure to arsenic at concentrations less than 50 µg/L include skin, bladder, lung, kidney, nasal passage, liver and prostate cancer (U.S. EPA, 2007), and cardiovascular and neurological effects (Le, 2002). Acute health effects that can occur after short lived exposures to high concentrations of arsenic are coughing, chest pains, difficult breathing, headache, nausea, vomiting, diarrhea, and skin irritation and redness (E.E.D., 2004). The maximum contaminant level (MCL) in the United States for arsenic was set by the US EPA at 10 µg/L on January 18, 2001, and water treatment plants in the U.S. have had to comply with the new regulation since January 23, 2006. The MCL provides protection for more than 13,000,000 Americans who live in areas where untreated ground waters contain elevated levels of arsenic (U.S. EPA, 2007). High concentrations of arsenic in surface and groundwater can occur naturally or anthropogenically. More than 99% of the total arsenic in natural reservoirs (rocks, oceans, soils, biota, and atmosphere) originates from minerals and rocks (Francesconi and Kuehnelt, 2002). Arsenic occurs primarily in association with sulfur-containing minerals (Magalhães, 2002). The most abundant mineral containing arsenic is arsenopyrite (FeAsS), and other important arsenic-containing minerals are arsenolite (As_2O_3), olivenite (Cu_2OHAsO_4), cobaltite (CoAsS), proustite (Ag_3AsS_3) (Francesconi and Kuehnelt, 2002), realgar (AsS), and orpiment (As_2S_3) (Magalhães, 2002). Organic arsenic compounds also widely occur in biota, especially in marine life. Arsenic contamination of surface and groundwater can also be associated with the arsenic used in herbicides, insecticides, desiccants, feed additives, wood treatments, chemical warfare agents, and drugs (Nriagu, 2002).

Arsenate (As(V)) and arsenite As((III)) are the major arsenical contaminants in drinking water (Francesconi and Kuehnelt, 2002). Arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) occur together in fresh waters; indeed, arsenate is the predominant species of arsenic because it is thermodynamically more stable than arsenite (Figure 2.10) (Francesconi and Kuehnelt, 2002). Typical arsenic levels in contaminated groundwaters are reported to be between 10 to 120 µg/L (Smedley and Kinniburgh, 2002; Chen et al., 2002). Arsenic contaminations in the range of 10 to 274 µg/L, with an average of 33 µg/L, were detected in groundwaters in the southwest United States (Figure 2.3). Moreover, arsenic concentrations greater than 50 µg/L were found in some groundwaters in parts of Oregon, Nevada, California, Texas, and Montana by the U.S. Geological Survey (USGS) (Ryker, 2001). Arsenic contamination at levels greater than 10 µg/L is very common in groundwaters of Nevada, Southern California, and Arizona (Ryker, 2001).

Arsenate is the product of the third ionization of arsenic acid, a triprotic acid and an oxidizing element. Arsenic acidity is described by three equilibrium (Schecher and McAvoy, 2001):

$$H_3AsO_4 \leftrightarrow H^+ + H_2AsO_4^- \qquad K_1 = 10^{-2.5} \qquad (2.73)$$

$$H_2AsO_4^- \leftrightarrow H^+ + HAsO_4^{2-} \qquad K_2 = 10^{-6.96} \qquad (2.74)$$

$$HAsO_4^{2-} \leftrightarrow H^+ + AsO_4^{2-} \qquad K_3 = 10^{-11.24} \qquad (2.75)$$

The predominance diagram for arsenic acid dissociation products in water versus pH are presented in Figure 2.8. For pH values less than 2.5, arsenic acid (H_3AsO_4) is the major species of As(V). In the pH range of 2.5 to 6.96, dihydrogen arsenate ($H_2AsO_4^-$) is the predominate species. Hydrogen arsenate ($HAsO_4^{2-}$) is the major form of As(V) in the pH range of 6.96 to 11.24. When pH increases above 8.6, hydrogen arsenate transforms to arsenate (AsO_4^{3-}), which becomes the predominate species at pH values greater than 11.24.

Arsenous acid (H_3AsO_3 or $As(OH)_3$), also known as arsenious acid, acts as a weak acid (Francesconi and Kuehnelt, 2002). The dissociation constants for arsenous acid were extracted from MINEQL+ (Schecher and McAvoy, 2001); the dissociation reactions can be written as:

$$H_3AsO_3 \leftrightarrow H^+ + H_2AsO_3^- \qquad K_1 = 10^{-9.29} \tag{2.76}$$

$$H_2AsO_3^- \leftrightarrow H^+ + HAsO_3^{2-} \qquad K_2 = 10^{-12.04} \tag{2.77}$$

$$HAsO_3^{2-} \leftrightarrow H^+ + AsO_3^{2-} \qquad K_3 = 10^{-13.414} \tag{2.78}$$

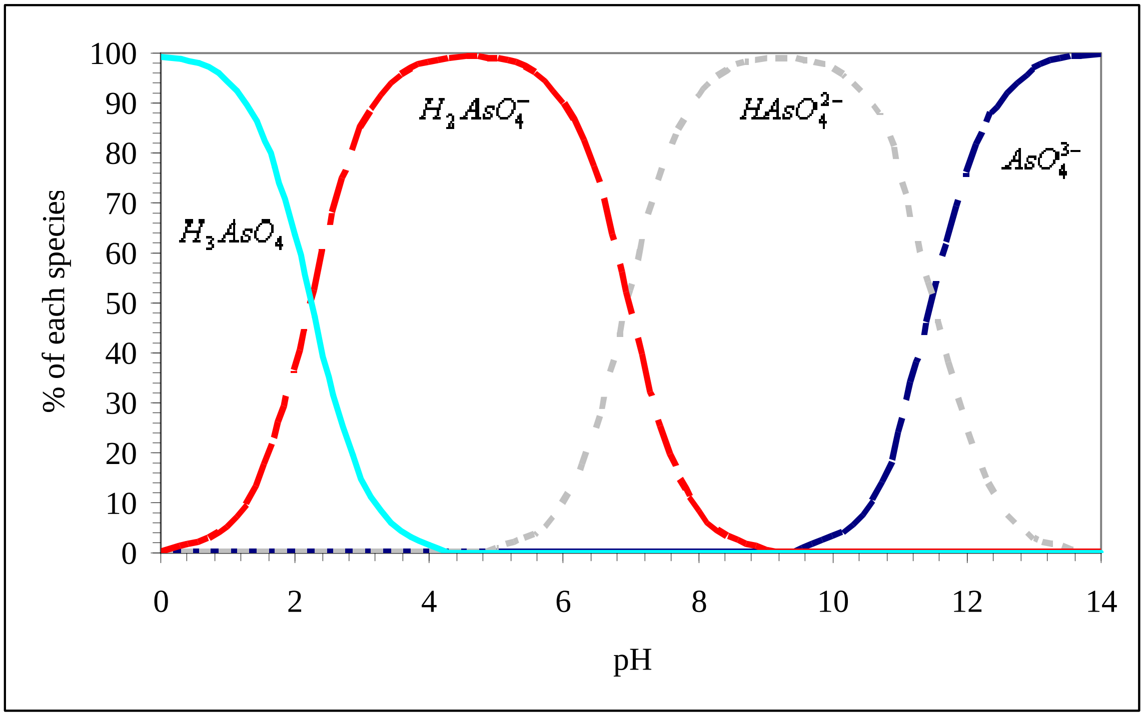


Figure 2.8 Computed Liquid-Phase Distribution of Ionic Species for an As(V) System, As(V) = 200 μg/L (2.7 × 10^{-6} M), I = 0 M (MINEQL+ Was Utilized for the Computation, Schecher And Mcavoy, 2001)

Arsenous acid may also gain a proton (Schecher and McAvoy, 2001) at pH values less than 2 in the reaction:

$$H_3AsO_3 + H^+ \leftrightarrow H_4AsO_3^+ \qquad \beta_1 = 10^{-0.305} \tag{2.79}$$

The distribution diagram for As(III) species versus pH is presented in Figure 2.9. Arsenous acid exists and predominates at pH values less than 9.3. Arsenous acid adsorbs a proton and transforms to $H_4AsO_3^+$ at pH values less than 2. Dihydrogen arsenite ($H_2AsO_3^-$) becomes the predominant species of As(III) in the pH range of 9.3 to 12. Hydrogen arsenite ($HAsO_3^{2-}$) is the primary As(III) species in the pH range of 12 to 13.4. Arsenite (AsO_3^{3-}) exists at pH values greater than 12, and is the major species for pH values above 13.4.

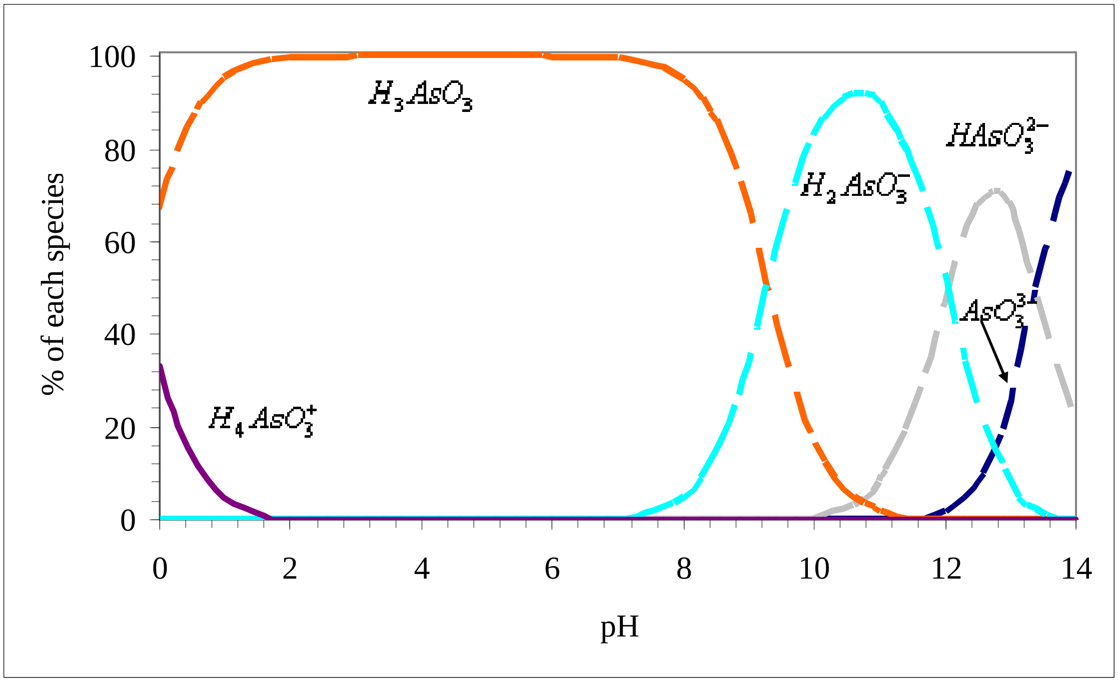


Figure 2.9 Computed Liquid-Phase Distribution of Ionic Species for an As(III) System, As(III) = 200 µg/L (2.7×10^{-6} M), I = 0 M (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001)

As(III) species are more toxic and mobile than As(V) species (Arienzo et al., 2002; Pierce and Moore, 1982; Magalhães, 2002). Arsenic can be oxidized or reduced, and the oxidation/reduction reaction for arsenous acid and hydrogen arsenate is (Inskeep et al., 2002):

$$H_3AsO_3 + H_2O \leftrightarrow HAsO_4^{2-} + 4H^+ + 2e^- \qquad K = 10^{-28.63} \qquad (2.80)$$

The distribution of As(III) and As(V) in water is governed by the redox potential of the aqueous solution (Inskeep et al., 2002; Clifford and Ghurye, 2002). The distribution of As(III) and As(V) can be illustrated using pe-pH (Eh-pH) diagrams. Arsenate species predominate in oxidizing water with moderate and high redox potentials, while the concentration of arsenite species increase in reducing waters (Inskeep et al., 2002; Clifford and Ghurye, 2002; Magalhães, 2002). A simplified pe-pH diagram is constructed using Mathcad software based on equations 2.73-2.78 and the following reduction half reaction (Figure 2.10):

$$2e^- + 2H^+ + AsO_4^{3-} \leftrightarrow AsO_3^{3-} + H_2O \qquad K = 10^{4.845} \qquad (2.81)$$

At pH values between 6 and 8, As(V) is thermodynamically stable at Eh values greater than -0.1 V (Figure 2.10). As(V) species are stable and predominant at oxidizing conditions (Eh > 0) for ph values less than 7.5. As(III) species appear mostly in reducing conditions. For pH values greater than 7, As(III) only exists at reducing conditions (E_h < 0), while at acidic pH (< 7), arsenous acid can be present in both oxidizing and reducing conditions (Figure 2.10). In summary, acidic pH is favorable for reduction of As(V) to As(III) and alkaline pH is suitable for oxidation of As(III) to As(V), because low levels of energy are required for these redox reactions.

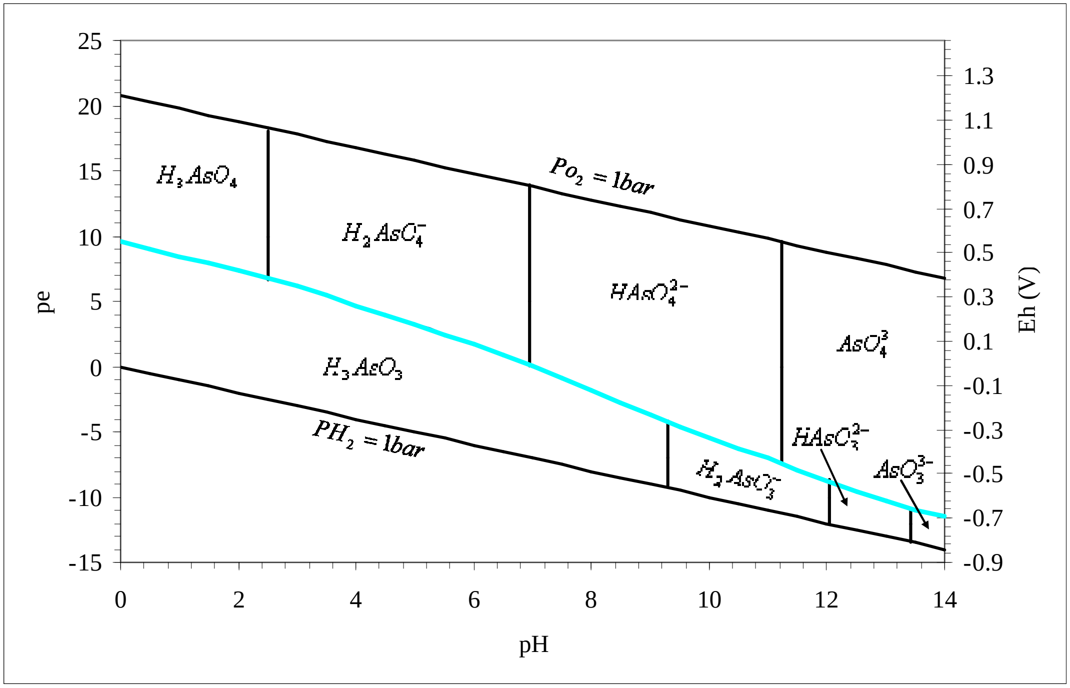


Figure 2.10 Simplified pe-pH (E_h-pH) Diagram for the As-H_2O System (The Diagram Does not Consider the Arsenic-Sulfur Products)

2.9.2 Arsenic Treatment Technologies

Ion-exchange, reverse osmosis, metal oxide adsorption and coagulation/filtration are efficient technologies for the complete removal of arsenic from drinking water (MWH, 2005; Clifford and Ghurye, 2002). In all of these processes, adsorption plays a major role. All of these processes are more efficient in removing As(V) than As(III), primarily because arsenite is adsorbed less by solid phases. Arsenite exists as arsenous acid with a neutral charge, which cannot be adsorbed at pH values less than 9.3 (Figure 2.9). Therefore, As(III) must be oxidized to As(V) prior to treatment to facilitate removal (MWH, 2005; Clifford and Ghurye, 2002; U.S. EPA, 2003). Typically, As(III) is oxidized to As(V) using oxidizing agents such as chlorine, permanganate, ozone, etc.

Ion-Exchange (IX) Technology

Ion-exchange is an important and effective technology to remove As(V) from natural waters (Clifford, 1999; U.S. EPA, 2000; MWH, 2005). The use of ion-exchange for arsenic removal is economically attractive for small water suppliers providing drinking water for less than 10,000 people (U.S. EPA, 2003) and point-of-entry (POE) systems (Wang et al., 2002). Anionic exchange resins are able to adsorb ionic forms of arsenic. In the pH range of natural waters (6 to 9) (MWH, 2005), As(V) exists in the form of $H_2AsO_4^-$ and $HAsO_4^{2-}$ while As(III) presents in its non-ionic form (arsenous acid). Therefore, As(V) can be efficiently removed using ion-exchange (Clifford, 1999; Clifford et al., 1998); however, As(III) removal is inefficient using ion-exchange (Clifford, 1999; Clifford et al., 1998). Thus, preoxidation of As(III) to As(V) is necessary prior to ion-exchange treatment. Arsenic concentrations up to 600 µg/L can be removed efficiently (>99%) by ion-exchange (Korngold et al., 2001). Ion-exchange technology provides consistent effluent water containing less than 0.2 µg/L of arsenic (MWH, 2005). Typically, strong base anion-exchange resins are utilized for arsenic removal from drinking waters because of their efficiency over a larger pH range than weak base anion-exchange resins (Wang et al., 2000). Both SBA type 1 and type 2 can be used for As(V) removal achieving same performance level (MWH, 2005; Clifford, 1999; Kim et al., 2003). SBA resins with polystyrene type matrix may perform slightly better than SBA resins with other matrix types (MWH, 2005). Conventional SBA type 1 and type 2 resins (sulfate selective) are more efficient in removing arsenic than nitrate selective specialty resins (Ghurye et al., 1999). The run length of conventional SBA exchange resin was reported to be (800-900 BV) 3-4 times the specialty nitrate selective resins (200-300 BVs) for treating water containing 11.2 μg/L As and 10 mg/L (NO_3^- - N) (Ghyrye et al., 1999). The reason for this is the poor affinity of monovalent nitrate-selective resin for the divalent As(V) ion (i.e. $HAsO_4^{2-}$). Reducing the pH to transform $HAsO_4^{2-}$ to $H_2AsO_4^-$ does not improve the resin affinity because $H_2AsO_4^-$ has lower affinity than $HAsO_4^{2-}$ by the resin (Clifford, 1999). Some specialty resins are manufactured for enhance arsenic removal to provide high affinity for arsenic (Table 2.7).

Ion-exchange chelating resins also have been utilized for arsenic removal (An et al., 2005). A chelating ion-exchange resin (e.g., DOW 3N) can be used as a host for a metal (e.g., Cu^{2+}) or functional group, which must be loaded into the resin, providing positive charge to adsorb arsenic through surface complexation and/or electrostatic interactions between metal and anionic As(V) species (An et al., 2005). DOW 3N loaded with Cu^{2+} was reported to have a higher affinity to arsenate (arsenate/sulfate separation factor of 12) than commercially available SBA exchange resins (0.1-0.2) (An et al., 2005). This chelating resin treated 10 times more bed volumes of water than SBA exchange resins. However, 22 bed volumes of 4% NaCl were used to recover 95% arsenate capacity in the spent DOW 3N-Cu^{2+} (An et al., 2005). The high regenerant volume requirement for the regeneration process makes the process economically unattractive as compared with conventional SBA exchange resins.

The presence of co-contaminants including SO_4^{2-}, NO_3^-, and Cl^- reduce the efficiency of arsenic removal by ion-exchange resins (Korngold et al., 2001). Ion-exchange is practical and economically attractive for waters containing less than 120 mg/L SO_4^{2-} and 500 mg/L TDS (Clifford et al., 2003, MWH, 2005). Optimal water quality conditions for using ion-exchange to remove arsenic from water in small scale water supply systems are: pH 6.5-9, < 5 mg/L NO_3^-, < 50 mg/L SO_4^{2-}, < 500 mg/L TDS, and < 0.3 NTU turbidity (U.S. EPA, 2003). Presence of sulfate in waters is a major limiting factor for application of ion-exchange for arsenic removal, and it drastically reduces the run length of the process (Clifford, 1999; Ghurye et al., 1999). Increasing sulfate concentration from 40 to 220 mg/L reduced the run length from 1030 BVs to 250 BVs to remove the same concentration of 13 µg/L arsenic (Table 2.8). All the run lengths in the Table 10 are based on 2 µg/L As in the effluent stream.

Table 2.7 Anion-exchange Resins Used or Recommended for As(V) Removal

Resin Name/ Manufacturer	Resin Type	Resin Matrix	Functional Group	Total Capacity (meq/L)
A300E/ Purolite	Type 2 SBA Gel	Polystyrene- DVB	Type 2 Quaternary Ammonium $R(CH_3)_2(CH_3CH_2OH)N^+Cl^-$	1400
ASM-10-HP/ ResinTech	SBA Gel	Styrene- DVB	Hybrid Adsorbent $R\text{-}N\text{-}R^+Cl^-$	1000
Lewatit FO 36/ LANXESS	WBA Macroporous	Polymeric	Hybrid Iron Oxide Adsorbent $-CH_2-N(CH_3)_2/FeOOH$	-

(Source: compiled from Purolite, ResinTech, and LANXESS websites)

Table 2.8 Effects of Sulfate on Ion-Exchange Run Length for Arsenic Removal (Clifford, 1999)

Location	As (µg/L)	TDS (mg/L)	Sulfate (mg/L)	Run length (BV)
Hanford, CA	50	213	5	1500
McFarland, CA	13	170	40	1030
Albuquerque, NM	26	328	82	640
McFarland, CA (SO_4^{2-} spiked)	13	259	100	490
McFarland, CA (SO_4^{2-} spiked)	13	436	220	250

Conventional SBA Type 1 or Type 2 resins are recommended to treat waters containing arsenic and nitrate (Ghurye et al, 1999). The arsenic breakthrough (800-900BVs) occurs after the nitrate breakthrough (560-610 BVs) due to higher selectivity of resin for arsenic than nitrate. Therefore, the spent resin must be regenerated at the nitrate breakthrough to achieve high quality effluent (Clifford, 1999). Some conventional SBA, chelating, and specialty resins, which have been used for arsenic removal from waters are presented in Table 2.9. Styrenic and acrylic matrixes, micro and macroporous, and Type 1 and Type 2 SBA exchange resins have been utilized for arsenic removal from waters. Chelating resins loaded by metals with positive charges also were used to adsorb arsenic ions.

Results of some arsenic treatment studies using ion-exchange resins are presented in Table 2.10. The specification of the resins used in these studies is presented in Table 2.9. Contaminated waters containing between 11 to 90 µg/L As(V) and 40 to 220 mg/L sulfate were treated using ion-exchange technology. Conventional SBA resins are able to treat up to 900 bed volumes of water containing less than 90 µg/L As(V) and 40 mg/L sulfate. Chelating resins or modified resins showed higher capacity (up to 6000 BVs) to remove arsenic.

The arsenic removal efficiencies of the ion-exchange resins depend on the empty bed contact time (EBCT) and concentration of regenerant (MWH, 2005). The EBCTs of 1.5 to 3.0 minutes are recommended for arsenic removal. Arsenic can be easily regenerated using NaCl (MWH, 2005). Clifford (1999) showed that the run length of the ASB-2 type 2 SBA resin decreased by 25% when a regenerant concentration of 10 lbs NaCl/ft^3 was used instead of 20 lbs NaCL/ft^3. Down-flow cocurrent regeneration is more efficient for regenerating arsenic-laden resins than conventional counter current mode (MWH, 2005). A possible explanation for the hihger efficiency is that arsenic is accumulated in the resins on the top part of the ion-exchange vessel near the feed water, and when regenerant solution is applied down-flow, it contacts the highest arsenic concentrations and removes them (MWH, 2005).

Table 2.9 Characteristics of Common Resins Used For Arsenic Removal from Waters.

Resin Name/ manufacturer	Resin Type	Resin Matrix	Functional Group	Total Capacity	Reference
Ionac ASB-1/ Sybron	SBA Type 1 Gel	Styrene-DVB	Quaternary ammonium $-N-(CH_3)_3^+Cl^-$	1400	Kim and Benjamin, 2004b
Ionac ASB-2/ Sybron	SBA Type 2 Gel	Styrene-DVB	Quaternary ammonium $-N-(CH_3)_2(CH_3CH_2OH)^+Cl^-$	1400	Ghurye et al., 1999
Amberlite IRA 404/ Rohm and Haas	SBA Gel	Polyacrylic	Quaternary ammonium $-N-(CH_3)_3^+Cl^-$	1100	Ghurye et al., 1999
Amberlite IRA 458	SBA Gel	Styrene-DVB	Quaternary ammonium $-N-(CH_3)_3^+Cl^-$	1200	Ghurye et al., 1999
Amberlite IRA 900	SBA Type 1 Macroporous	Styrene-DVB	Quaternary ammonium $-N-(CH_3)_3^+Cl^-$	1000	An et al., 2005
$C-145-Fe^{3+}$	SAC - modified Macroporous	Polystyrene-DVB	Sulphonic acid $R-SO_3^-Na^+$ + HFO	1500	DeMarco et al., 2003
DOW3N-Cu^{2+}	Chelating Macroporous	Styrene-DVB	Bis-Picolylamine $-Cu^{2+}$	-	An et al., 2005
ArseneX	Hybrid Macroporous	Polystyrene	HFO	-	Sarkar et al., 2007

Typically, ion-exchange resins used for arsenic and chromium removal are regenerated with sodium chloride to allow for resin re-uses lowering the cost of the treatment process. In addition to high arsenic and chromium levels, brines have high alkalinities and ionic strengths. The high alkalinity of brines is associated with adsorption of bicarbonate by the resins. The high ionic strength is related to the use of sodium chloride as a resin regenerant (Figure 2.11). The residual ion-exchange brines usually have high concentrations of arsenic and/or chromium. The ion-exchange process residuals (brines) pose a threat to the environment, and brine disposal makes the operation difficult and expensive (Clifford and Ghurye, 1999; Clifford et al., 1998). The generated brine, a liquid waste stream, must contain arsenic and/or chromium concentrations less than the Toxicity Characteristic (TC) of 5 mg/L according to the Resource Conservation and Recovery Act (RCRA) in order for the waste to be considered as non-hazardous (U.S. EPA, 2003). Disposal and handling of hazardous wastes are many times more than non-hazardous wastes (Meng et al., 2001). Hazardous waste handling is very expensive, around $300 per drum (55 US gallons) (US DOE, 2007). Disposal and handling of the generated waste is reported as 12-34% of the total cost (Frey et al., 1998). Hazardous liquid wastes are banned from disposal in municipal solid or hazardous waste landfills and must be treated or disposed of in an another technique. To differentiate between solid or liquid type, a waste must pass the Paint Filter Liquids Test (PFLT) to determine if free liquids are present in the waste. Therefore, there is a demand for technologies to treat chromium and/or arsenic containing wastes. These technologies should produce low volumes and stable solid wastes. Solid wastes must also pass the EPA Toxicity Characteristic Leaching Procedure (TCLP) (and Waste Extraction Test (WET) in California) to be allowed to be disposed of in the municipal solid waste landfills otherwise they have to be disposed of in hazardous waste landfill (U.S. EPA, 2003).

Table 2.10 Run Lengths of Arsenic Removal from Waters Containing Various As(V) Concentrations Using Various Ion-Exchange Resins at Different Sulfate Levels.

Resin	Sulfate (mg/L)	Influent As(V) (μg/L)	Maximum Effluent As(V) (μg/L)	Bed Volumes (BVs)	Reference
Ionac ASB-2	100	11.2	2	490	Ghurye et al., 1999
Ionac ASB-2	220	11.2	2	250	Ghurye et al., 1999
Amberlite IRA 404	40	11.2	2	800	Ghurye et al., 1999
Amberlite IRA 404	100	11.2	2	340	Ghurye et al., 1999
Amberlite IRA 404	220	11.2	2	170	Ghurye et al., 1999
Amberlite IRA 458	40	11.2	2	900	Ghurye et al., 1999
Amberlite IRA 458	100	11.2	2	370	Ghurye et al., 1999
Amberlite IRA 458	220	11.2	2	200	Ghurye et al., 1999
Ionac ASB-2	90.8	24.9	2	400	Clifford et al., 2003
Ionac ASB-2	82	25.9	2	640	Ghurye et al., 1999
Ionac ASB-1	125	42	0	340	Kim and Benjamin, 2004
C-145-Fe^{3+}	120	50	10	4000	DeMarco et al., 2003
Amberlite IRA 900	120	50	10	300	DeMarco et al., 2003
Amberlite IRA 900	183.4	75.3	0	600	An et al., 2005
DOW3N-Cu^{2+}	183.4	75.3	10	6000	An et al., 2005
ArseneX	120	90	10	2000	Sarkar et al., 2007

The TCLP and WET are designed to determine the mobility of both organic and inorganic compounds present in liquid, solid, and multiphase wastes in a landfill condition (U.S. EPA, 2003). Ghosh et al. (2004) reported that the TCLP underestimates leaching of arsenic from solid residuals under land fill conditions and does not simulate the landfill condition properly (Steinwinder and Zhao, 2007). A waste should pass the WET besides the TCLP only in California. The extraction fluid containing acetic acid and sodium hydroxide is utilized in the TCLP test while the citric acid and sodium hydroxide are used to make the extraction fluid in the WET procedure. The time of the WET (48 h) procedure is longer than the TCLP test (18 ± 2 h), and the TCLP specifies the tumbler but the WET specifies the shaker table. The head space of samples in the

TCLP is filled up with the ambient air while in the WET the headspace is purged with N_2 (Ghosh et al., 2004). Both the TCLP and WET limit for the arsenic is 5 mg/L.

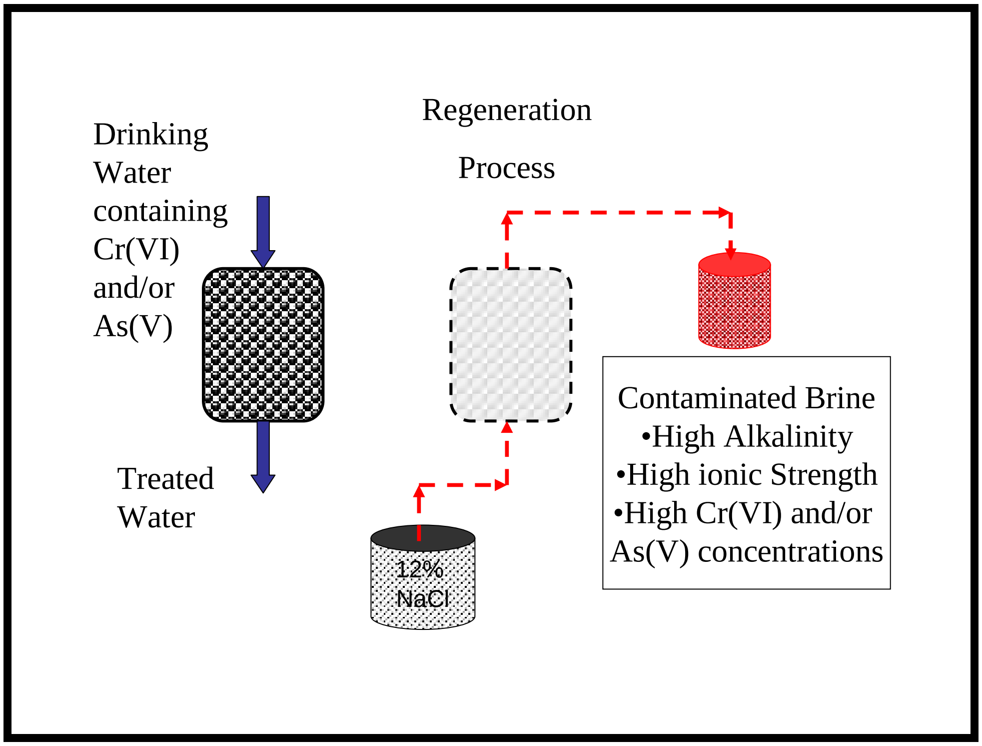


Figure 2.11 Schematic of an Ion-Exchange System to Treat Waters Contaminated with As(V) And/Or Cr(VI)

The generated ion-exchange brine containing high concentration of arsenic can be treated using ferric chloride (see coagulation/filtration technology) (Clifford, 1999; MacPhee, 2001; MWH, 2005). Arsenic adsorbs to the formed hydrous ferric oxides, which can be separated from the liquid through filtration. Ferric chloride is very efficient in removing arsenic and lowers the arsenic level in the liquid part. Therefore, the liquid waste can be conventionally discharged (e.g., to the municipal wastewater) or re-used

(An et al., 2005), which reduces the waste discharge. The solid waste generated in the process contains high concentrations of arsenic; however, it easily passes the TCLP and WET (Steinwinder and Zhao, 2007; Mercer and Tobiason, 2008; Clifford et al., 2003). Thus, the generated precipitates can be disposed of in municipal solid waste landfills. Arsenic removal from brines using ferric chloride will be discussed in section 2.9.5.

Sorption Technologies: Activated Alumina and Granular Ferric Hydroxide

Activated alumina (AA) is an important metal-oxide adsorbent of arsenic (MWH, 2005). Activated alumina has been used in water treatment industry to remove arsenic, selenium, fluoride, silica, and natural organic matter (NOM) from waters. Activated alumina is produced by incomplete drying (activation) of precipitated aluminum hydroxide ($Al(OH)_3$) at temperatures between 300 to 600 °C. Activated alumina is a mixture of highly porous (50-300 m^2/g) amorphous and gamma aluminum oxide (γ-Al_2O_3) granules with diameters of about 0.3-0.6 mm (Clifford and Ghurye, 2002). Activated alumina contains active Al-OH surface sites, which undergo surface complexation by gaining and losing protons. Activated alumina has a pzc of 8-9, and gain a net positive charge at pH values below 8-9. The optimum pH range of 5.5-6.0 is recommended for arsenic removal from water (Kim et al., 2004c; Clifford and Ghurye, 2002).

Activated alumina needs to be protonated prior to adsorption of $H_2AsO_4^-$ or F^- by HCl or H_2SO_4 (Clifford and Ghurye, 2002). The HCl-acidified alumina exchanges its Cl^- by $H_2AsO_4^-$ at pH 5.5-6.0. Spent activated alumina can be regenerated using a 0.25-1.0 N NaOH solution as follow, and the alumina-NaOH must be regenerated with HCl for another arsenic removal run (Clifford and Ghurye, 2002). However, single-use of activated alumina is reported more economical for small systems (MWH, 2005).

Arsenic recovery using activated alumina is reported as up to 75% (MWH, 2005). The activated alumina has a high arsenic removal capacity due to its high porosity, and typically can treat 10,000 BVs of contaminated water before breakthrough. Run lengths of 1000 to 13000 BVs have been reported for arsenic removal by activated alumina (MWH, 2005; Clifford, 1999).

Granular ferric hydroxide (GFH) is an efficient metal-oxide adsorbent with high capacity to remove arsenic (MacPhee et al., 2001). The GFH are iron-based adsorbents, and are described as akaganéite-like mineral, and characterized as β-FeOOH (Badruzzaman et al., 2004). The GFH's grains (0.32-2 mm) are bigger than those of activated alumina (0.6-0.6mm). The GFH has much larger capacity and better performance (32,000-85000 BVs) than the activated alumina (10,000 BVs). The GFH has a very promising performance; however, it is very expensive (MWH, 2005).

Coagulation/Filtration Technology

Coagulation is a physical-chemical treatment process that uses coagulants such as ferric chloride, ferric sulfate, alum, or lime to destabilize colloidal, suspended and dissolved matter, and to allow for the aggregation of particles. The coagulation process results in the formation of flocs, which can be removed by filtration (U.S. EPA, 2003; MWH, 2005). Coagulation/filtration is the most used technology at large plants to remove arsenic. Conventional sand filtration is reported to be efficient for arsenic removal (Yuan et al., 2003); however, traditional sand filtration strictly for arsenic removal for small plant sizes is expensive due to the size and cost of equipment required for the amount of arsenic to be removed (U.S. EPA, 2003). Microfiltration is reported to be efficient in removing arsenic containing precipitates, and is economical for small systems (U.S. EPA, 2003). The membrane used for microfiltration requires frequent backwashing, producing residual waste that need to be managed (U.S. EPA, 2003). In coagulation, arsenic is removed by a combination of precipitation, co-precipitation, and adsorption followed by filtration (MWH, 2005; Phenrat et al., 2008). Arsenic adsorbs to ferric hydroxide precipitates, which are separated from water by filtration (MWH, 2005; Phenrat et al., 2008). Coagulation and adsorption principles are discussed in sections 2.7 and 2.8, respectively. As mentioned earlier, oxidation of contaminated waters is required prior to arsenic removal by coagulation (Lee et al., 2003; Lytle et al., 2005; Hering et al., 1996a). Coagulation/filtration processes must be optimized by adjusting the pH, coagulant dosages, mixing length and intensity (U.S. EPA, 2003).

Iron-based coagulants are more effective (80-100% efficiency) in removing arsenic than alum (20-100%) or lime (60-90%) (Fan et al., 2003; Cheng et al., 1994; McNeill and Edwards, 1997; MWH, 2005). Iron precipitates are more stable than aluminum precipitates in the pH range of 5.5 to 8.5. Aluminum-based coagulants form both precipitates and soluble complexes in water at pH 5.5-8.5, and the soluble fraction cannot adsorb arsenic, therefore reducing overall removal efficiency. At pH values above 7, the overall efficiency of aluminum-based coagulants decreases dramatically, while iron-based coagulants are still efficient at pH values less than 8.5 (U.S. EPA, 2003). Sorg and Logsdon (1978) found that ferric sulfate is very efficient (~100%) in removing 0.05 mg As(V)/L at pH values less than 8.5, while aluminum sulfate removed 90% of As(V) at pH values less than 7. Typical coagulant dosages for ferric salts and alum are 5 to 30 mg/L and 10 to 50 mg/L, respectively (MWH, 2005). Lime softening is used for hardness removal, while addition of lime increases pH, and calcium and magnesium form hydroxide precipitates. Co-precipitation of As(V) at pH values less than 10.5 by magnesium hydroxide and calcium is possible but inefficient (less than 10%) (U.S. EPA, 2003). However, excess lime can be utilized for the purpose of arsenic removal, resulting in 60 to 90% removal efficiency (MWH, 2005). Lime softening solely for the purpose of As(V) removal is expensive and is not recommended (U.S. EPA, 2003).

Ferric chloride and ferric sulfate are reported to have similar efficiencies in arsenic removal during coagulation (Fan et al., 2003). Seith et al. (1999) reported that Fe(II) salts can also be used for arsenic removal from drinking waters because these salts are oxidized to Fe(III) during the water treatment process. Combinations of iron salts are reported effective in removal of arsenic (Guo et al., 2000). Han et al. (2002) reported that a combination of ferric chloride and ferric sulfate increased arsenic removal efficiency during coagulation. The combination of iron salts provides various complexes of adsorbent surfaces that allow for efficient removal of arsenic from contaminated waters.

2.9.3. Mechanisms of Arsenic Removal by Iron Precipitates during Coagulation

Ferric chloride dissolves in solution and forms amorphous hydrous ferric oxide (HFO), which has high porosity and numerous active surfaces for sorption. Mechanisms of arsenic removal during coagulation using Fe(III) salts are: (1) adsorption, and (2) enmeshment in a generated precipitate, or "sweep floc" (Hering et al., 1996a; Benefield and Morgan, 1990).

Adsorption is believed to be the major mechanism for arsenic removal during coagulation with HFOs (Hering et al., 1996a; Dzombak and Morel, 1990; Phenrat et al., 2008; Guo et al., 2007). The main mechanism of anion adsorption is surface complex formation, in which protonated hydroxyls on the adsorbent surface are exchanged for other anions (Stumm and Morgan, 1996; Stumm et al., 1992; Dzombak and Morel, 1990). Surface complex formation (coordination) is a combination of cations with anions containing free pairs of electrons (Stumm and Morgan, 1996). The bond between arsenate and surface protonated hydroxyl functional groups on iron solids may be formed via surface complex formation (Stumm and Morgan, 1996; Sherman and Randall, 2003; Waychunas et al., 1993; Fuller et al., 1993).

Iron (III) ions function as Lewis acid sites, surface sites capable of receiving a pair of electrons (Stumm and Morgan, 1996). pH dependence of anions (extent of acid dissociation) and affinity of the ferric hydroxide surfaces for available anion species (e.g., AsO_4^{3-}) determine the extent of surface coordination (Stumm and Morgan, 1996). There are various theories that attempt to explain the coordination chemistry of ferric hydroxide and arsenate complexes. Generally in iron oxides, Fe^{3+} is octahedrally coordinated to six OH^-, O^{2-}, or H_2O in various combinations, producing different crystal structures or polymorph of iron (Schaetzl and Anderson, 2005). The number of oxygen atoms shared between octahedra affects the crystalline structure of iron oxide (Schaetzl and Anderson, 2005). Inner-sphere and outer-sphere surface complexes can be formed between iron oxide and anions (e.g., arsenate) or cations (Stumm and Morgan, 1996). The inner sphere complex is a covalent chemical bond (i.e. σ-bond), while the outer-sphere complex is an ion pair in which ions of opposite charges come close to each other, and neutralize each other's charges (Stumm and Morgan, 1996). The inner sphere complex is directly formed between an anion (e.g., arsenate) and the metal (e.g., Fe) by sharing electrons, while outer sphere complex form between an anion (e.g., arsenate) and the first coordinated shell around the metal (e.g., H_2O) (Stumm and Morgan, 1996). An anion can bond to a metal (sharing electrons) at its various non-contiguous sites. When an anion shares its electrons through one or two sites, it is classified as monodentate or bidentate, respectively (Housecroft and Constable, 2006). An arsenate, tetrahedral anion, can bond with one or two octahedra shaped iron oxides, and these complexes are called mononuclear and binuclear, respectively (Waychunas et al., 1993). Arsenic-iron inner-sphere surface complexes have been reported as the main form of bonding between arsenic and iron (oxyhydr)oxides using XAFS method (Meng et al., 2000; Sherman and Randall, 2003; Waychunas et al., 1993; Phenrat et al., 2008). However, Phenrat et al. (2008) observed both outer and inner-sphere surface complexes in arsenic-iron hydroxide sludge. Surface complexes are formed via bidentate links between surface oxides (e.g., FeOH) and arsenate (Stumm and Morgan, 1996; Sherman and Randall, 2003; Waychunas et al., 1993; Guo et al., 2007). Bidentate binuclear corner-sharing (Sherman and Randall, 2003; Guo et al., 2007) and bidentate mononuclear edge-sharing links (Sherman and Randall, 2003; Waychunas et al., 1993; Guo et al., 2007) were observed between arsenate and active iron surfaces. Sherman and Randall (2003) found that the bidentate corner-sharing complex is more stable than the bidentate edge-sharing complex. Monodentate bonds also reportedly occur between arsenate and ferrihydrite (Meng et al., 2000; Waychunas et al., 1993) but not crystalline FeOOH polymorphs (Meng et al., 2000; Waychunas et al., 1993; Sherman and Randall, 2003). The higher the ferrihydrite concentration (mol Fe/mol As(V)), the greater the number of monodentate bridges that are formed (Waychunas et al., 1993). Similar to arsenate, arsenite adsorbs to Fe(III) surfaces via inner-sphere surface complexes, and the major complex types are bidentate mononuclear edge sharing and bidentate binuclear corner-sharing (Ona-Nguema et al., 2005).

Dzombak and Morel (1990) suggested that in addition to surface complex formation, surface precipitation of arsenic on a hydrous ferric oxide may occur during adsorption. Langmuir et al. (2006) studied the solubility products of amorphous ferric arsenate and crystalline scorodite ($FeAsO_4$:$2H_2O$). They reported the log solubility product (log Ksp) of amorphous ferric arsenate as -23.0 to -24.45, which is consistent with the results of Lumsdon et al. (2001). However, Waychunas et al. (1993) observed that precipitation of arsenate or scorodite-like phases do not occur at pH 8 on the surface of crystalline polymorphs. In addition, Phenrat et al. (2008) reported that an insoluble iron-arsenic precipitate was not formed in arsenic-iron hydroxide sludge. Similarly, Fuller et al. (1993) showed that neither ferric arsenate nor any other As-bearing surface is formed during arsenic removal by ferrihydride (adsorption or co-precipitation) despite high concentrations of arsenic. Finally, scorodite ($FeAsO_4.2H_2O$) mineral does not form at typical arsenic levels in waters (Edwards, 1994).

Site densities of HFO for arsenate (AsO_4^{3-}) to Fe were reported between 0.1 and 0.13 at pH 4 assuming 89 g HFO/mol Fe (Pierce and Moore, 1982). Surface densities of 0.16 for sorption sites on HFO for arsenite (H_3AsO_3) were reported for pH ranges of 7 to 7.5 by Ferguson and Anderson (1974), and surface densities between 0.05 and 0.18 at pH 7 were found by Pierce and Moore (1982). Sorption ratios of 0.7 mol As/mol Fe for co-precipitation and 0.25 for adsorption of arsenic to pre-formed solids were found by Mercer and Tobiason (2008). Fuller et al (1993) and Mercer and Tobiason (2008) used

0.7 mol site/mol iron in their surface complexation models. Mercer and Tobiason (2008) used 5×10^5 and 2×10^5 m^2/mol Fe to model arsenic removal during co-precipitation at ionic strengths of 0.2 and 0.7 M, respectively. Dzombak and Morel (1990) presented the surface complexation reactions for adsorption of AsO_4^{3-} on HFOs as follows, with their best estimates of K values:

$$\equiv FeOH^{o} + AsO_4^{3-} + 3H^{+} \leftrightarrow \equiv FeH_2AsO_4^{\circ} + H_2O \qquad K_1 = 10^{29.31} \tag{2.82}$$

$$\equiv FeOH^{o} + AsO_4^{3-} + 2H^{+} \leftrightarrow \equiv FeHAsO_2^{-} + H_2O \qquad K_2 = 10^{23.51} \tag{2.83}$$

$$\equiv FeOH^{o} + AsO_4^{3-} + H^{+} \leftrightarrow \equiv FeAsO_4^{2-} + H_2O \qquad K_3 \text{ no value reported} \tag{2.84}$$

$$\equiv FeOH^{o} + AsO_4^{3-} \leftrightarrow \equiv FeOHAsO_4^{3-} + H_2O \qquad K_4 = 10^{10.58} \tag{2.85}$$

Adsorption is strongly pH dependent. At low pH, anion-exchange is favored because the concentration of competing OH^- ions is low. Moreover, release of the OH^- ions by the iron precipitate into solution is favorable at low pH (Stumm and Morgan, 1996). Generally, at high dosages of ferric chloride, higher arsenic removal efficiency can be achieved with lower pH, along with reduction in colors and trihalomethane (Hering et al., 1996a).

2.9.4. Arsenic Removal by Ferric Chloride from Drinking Water

Arsenic can be removed from water using pre-formed ferric hydroxide solids or through direct application of ferric chloride into a solution containing arsenic (co-precipitation). When ferric chloride at a low dosage is added to water, it destabilizes the colloidal particles and results in the formation of aggregates (Hering et al., 1996a). Addition of a high dosage of ferric chloride to the solution causes the formation of the amorphous ferric hydroxide (Sorg and Logsdon, 1978; Edwards, 1994; Hering et al., 1996a), and arsenic will be absorbed onto surfaces of the ferric hydroxide precipitates that are produced (Meng et al., 2000). Arsenic removal during direct application of ferric chloride is reported to be more effective than arsenic adsorption on pre-formed HFO solids (Edwards, 1994; Fuller et al., 1993, Hering et al., 1996a; Meng et al., 2000; Mercer and Tobiason, 2008). Jia and Demopoulos (2005) studied the adsorption of arsenate onto ferrihydrite in solution, and reported that arsenic removal using ferric chloride is three times more effective than with pre-formed ferric hydroxide solids. Similarly, Holm (2002) reported that the sorption capacities of in situ formed solids are approximately 3.8 times the capacities using pre-formed HFOs. Higher adsorption densities can be achieved in co-precipitation because more absorbing surfaces are available in co-precipitation than in the application of pre-formed solids due to the production of fresh ferric hydroxide precipitates during the co-precipitation process (Hering et al., 1996a). Moreover, polymerizing iron oxy-hydroxide (i.e., FeO(OH)) formed during co-precipitation result in an increase in the number of adsorption sites, and consequently, more adsorption of arsenic occurs (Mercer and Tobiason, 2008). In co-precipitation, surfaces adsorb arsenic prior to aggregate formation; however, for adsorptions to preformed solids, the aggregates are already formed and arsenic can only be adsorbed on the surface of the aggregates; therefore, fewer surface sites are available Mercer and Tobiason, 2008). Aging of ferrihydrite decreased the adsorption sites available for As(V) adsorption due to crystallite growth (Fuller et al., 1993).

As(III) removal using ferric chloride during coagulation is less efficient (20 to 30%) than removal of As(V) (>90%) in the pH range of 5 to 8.5 (Shen, 1973; Sorg and Logsdon, 1978; Clifford et al., 1998; Jiang, 2001; Hering et al., 1996a; 1996b; Arienzo et al., 2002; Pierce and Moore, 1982). Therefore, pre-oxidation of As(III) to As(V) is required for efficient arsenic removal using ferric chloride coagulation.

Ferric chloride for use in removal of arsenic from groundwaters is readily available (even in developing countries), cheap, non-hazardous and easy to handle (Khan et al., 2002). When ferric chloride is added to groundwaters, it consumes alkalinity and produces ferric hydroxide. One mole of $FeCl_3$ consumes three moles of bicarbonate, as follows:

$$FeCl_3 + 3HCO_3^- \leftrightarrow Fe(OH)_3(s)\downarrow + 3CO_2 + 3Cl^- \qquad (2.86)$$

Although application of ferric chloride for As(V) removal is possible in the pH range of 3 to 8.5 (Hering et al., 1996a; MWH, 2005), the optimal pH range for As(V) removal with ferric chloride was reported to be between 5.0 and 6.2 (Ghurye et al., 2004; Macphee et al., 2001). The arsenate adsorption on HFO increases with decreasing pH (Pierce and Moore, 1982; Hering et al., 1996), but Wang et al. (2003) stated that arsenic removal efficiency with ferric chloride significantly decreases at pH lower than 3. For very acidic pH, the arsenic acid, non-ionic form of As(V) is the predominant species, which cannot be removed by adsorption (see Figure 2.8). For pH above 8.5, the removal efficiency of As(V) decreases drastically (Sorg and Logsdon, 1978; Edwards, 1994; Jiang, 2001; Böckelen and Niessner, 1992; Cheng et al., 1994; Scott et al., 1995; McNeill and Edwards, 1995; Joshi and Chaudhuri, 1996). The pzc of the fresh ferric hydroxide is between 7.9 and 8.2, and aging of the ferric hydroxide or high ionic strength waters reduce the pzc (Dzombak and Morel, 1990). Ferric hydroxide is positively charged at pH values less than 7.9-8.2, and negatively charge at pH values above its pzc. This explains the decline in As(V) removal efficiency by ferric hydroxide at pH values above 8.5.

Moreover, Gulledge and O’Connor (1973) stated that hydroxyl ions are competing with arsenate for active HFO surfaces. At an acidic pH, there are low concentrations of hydroxyl ions, and there is less competition between those hydroxyl ions and arsenate. Therefore, more active HFO surfaces are available to adsorb arsenate and arsenic removal efficiency increases.

Increasing the pH from 3 to 9 increases the removal efficiency of As(III) by ferric hydroxide from 20% to 75%. Highest As(III) removal efficiency (75%) can be achieved at pH 9 (Meng et al., 2000). Arsenous acid (non-ionic form) is the primary form of As(III) at pH values less than 9.3, and therefore cannot be adsorbed by amorphous ferric hydroxide (Figure 2.9). Simultaneous removal of As(III) and As(V) by ferric hydroxide is not possible (Figure 2.8 & 2.9).

Arsenic removal from drinking water using ferric chloride has been investigated extensively (Hering et al., 1996a; Meng et al., 2000; Hering et al., 1997; Chwirka et al., 2004; Ghurye et al., 2004). The performance results from several As(V) removal experiments (coagulation/microfiltration) are summarized in Table 2.11. At an optimum pH and ferric chloride dosage, arsenic can be completely removed from contaminated drinking waters (pH 6-8) using coagulation/microfiltration process (Table 2.11). Hering et al. (1996) reported that coagulation and sedimentation alone can remove up to 30% of typical As(V) concentrations in drinking waters. However, 96% removal efficiency can be achieved through application of 1.0 micron filters after coagulation, and even higher As(V) removal efficiencies are possible using finer mesh filters (0.1 micron filters). Pilot plant and full scale studies usually show lower removal efficiencies than laboratory studies (50% to 90% removal) (Johnston and Heijnen, 2001). Cheng et al. (1994)

reported less than 1 µg/L arsenic remaining in drinking water treated by ferric chloride under optimal conditions. Typical doses of ferric chloride are 1 to 21 mg Fe(III)/L (i.e., 3 to 61 mg $FeCl_3$/L), and Fe(III)/As(V) molar ratios are 25 to 572 (Table 2.11). Similarly, Edwards (1994) reported that approximately 20 to 2000 mol Fe(III)/mol As(V) were required to remove soluble As(V) at concentrations up to 100 µg/L. Optimal Fe(III):As(V) molar ratios of 20 (Sorg and Logsdon, 1978) and 25 (Meng et al., 2002) were proposed to remove typical concentrations of arsenic in drinking waters without pH adjustment. However, the required ferric chloride doses are pH dependent, and decreasing pH values from 8 to 5 decreases the required doses of ferric chloride (Ghurye et al., 2004). Indeed, the required $FeCl_3$ dosage was reduced by two thirds when pH was lowered from 8.5 to 6.8 by acid addition (Chwirka et al., 2004). Nenov et al. (1992) reported an optimal Fe(III)/As(V) molar ratio of 7 to remove As(V) from groundwater at pH 5. Similarly, Böckelen and Niessner (1992) stated that an iron to arsenic molar ratio of 7 is sufficient to reduce arsenic concentrations in acidic contaminated water (50 and 200 µg/L) to below the maximum allowed contaminant level of 10 µg/L.

The required ferric chloride dosage also depends on the initial concentrations of As(V) in contaminated waters, and increasing the initial concentrations of As(V) contamination decreases the required amount of ferric chloride (Table 2.11). For low concentrations of contaminants (e.g., arsenate), particles are removed by adsorption and sweep flocculation. However, for moderate to high concentrations of particles, charge neutralization and flocculation also play important roles (MWH, 2005). Therefore, for high concentrations of As(V) (100 to 300 µg/L), lower Fe(III)/As(V) molar ratios (15-30) result in the same removal efficiency as higher Fe(III)/As(V) ratios (50-250) for low concentrations of arsenic (20 to 50 µg/L). An adsorption capacity of 26 mg As/gram Fe(III) using $Fe(OH)_3$ at pH 7.9 is reported by Seith et al. (1999) for contaminated water containing 21 µg/L As.

Water co-contaminants including sulfate, silicate, bicarbonate, phosphate and natural organic matter (NOM) affect arsenic removal with ferric chloride (Meng et al., 2004; Hering et al., 1996a, 1997). Meng et al. (2002) found that the affinity of contaminant to ferric hydroxide was in the following order: arsenate > phosphate > arsenite > silicate > bicarbonate. The presence of sulfate slightly (less than 10%) inhibits the adsorption of As(V) and As(III) to ferric hydroxide (Meng et al., 2000; Wilkie and Hering, 1996; and Hering et al., 1996a). Meng et al., (2000, 2002) and Hering et al. (1996a) found that silicate concentrations below 1 mg/L slightly decreased (10%) the removal of As(III) and had no effect on the removal of As(V). However, the removal of As(III) and As(V) with ferric chloride decreased from 90% to 45% when silicate concentration increased from 1 to 10 mg/L (Meng et al., 2000).

If pH of the solution to be treated is adjusted to 6.8 prior to As(V) removal by acid addition, bicarbonate concentrations up to 14 mM (854 mg/L) do not affect the removal of As(V). However, when bicarbonate concentration is increased from 0 to 13 mM, the removal of As(III) decreases from 96% to 64% (Meng et al., 2002). Phosphate also decreases the removal efficiency of arsenic (Meng et al., 2000, 2002; Roberts et al., 2004). Phosphate concentrations up to 80 µM have slight (< 10%) negative effects, but phosphate concentrations of 0.1 mM drastically reduce the removal of As(III) from 95% to 24% (Meng et al., 2002). Meng et al. (2002) reported that arsenic in Bangladesh ground waters has high mobility due to combined effects of co-contaminants (phosphate, silicate, and bicarbonate). Presence of 2.2 mM bicarbonate or 0.062 mM phosphate had negligible (< 5%) negative removal effects, while 0.64 mM Silicate had moderate (<15%) negative effects on the removal of As(V) (Meng et al., 2002). However, simultaneous combination of the identical concentrations of phosphate, bicarbonate, and silicate drastically reduced the removal of As(V) from 99% to 59% (Meng et al., 2002).

Table 2.11 Summary of Studies on Arsenic Removal by Ferric Chloride from Drinking Waters

Study Type	Coagulant dose (mg Fe(III)/L)	pH	Initial As(V) (μg/L)	mol Fe(III) / mol As(V)	% As(V) removal	Reference
Bench scale Synthetic water	1.7	7	20	115	100	Hering et al., 1996a
Pilot Groundwater	2.7	7.9	21	174	98	Jekel and Seith, 2000
Pilot Groundwater	2	6.4	33.7	81	97	Ghurye et al., 2004
Bench scale Groundwater	1.4	7	37.5	51	100	Holm, 2002
Bench scale Synthetic water	7.4	7.1	40	251	95	Chwirka et al., 2004
Bench scale Synthetic water	3	6.5	50	81	98	Lakshmanan et al., 2008
Pilot Groundwater	20.7	7.3	90	312	99	Chwirka et al., 2004
Pilot Groundwater	5.2	6	90	78	96	Chwirka et al., 2004
Bench scale Synthetic water	1.7	7	100	23	100	Hering et al., 1996a
Bench scale Synthetic water	1	6	100	14	95	Meng et al., 2000
Bench scale Groundwater	6.7	6.8	300	30	99.3	Meng et al., 2002

The presence of NOM also reduces the efficiency of arsenic removal with ferric chloride (Hering et al., 1997; Tipping, 1981). NOM in water shields the ferric hydroxide adsorption surfaces available to the arsenic components in the water, thereby reducing removal efficiency. Increasing the NOM concentration from 0 to 4 mg/L considerably decreased (from 98% to 30%) the removal of As(V).

2.9.5. Arsenic Removal by Ferric Chloride from Industrial Water: Ion-Exchange Brines

Water treatment technologies for arsenic removal, including ion-exchange, activated alumina adsorption, reverse osmosis, nanofiltration, and coagulation for arsenic removal produce arsenic-laden residuals, which must be properly disposed of to prevent further contamination of the environment. Brine treatment is the main challenge for ion-exchange arsenic removal plants (MacPhee et al., 2001). Ion-exchange generated brine is difficult to treat in order to meet in-stream standards, and arsenic removal from ion-exchange residuals has not been thoroughly investigated. Arsenic removal from ion-exchange residual brines with ferric chloride may increase the possibilities for the disposal, reuse and resource recovery of the brines (MacPhee et al., 2001). Typically, ion-exchange brines contain high concentrations of arsenic, along with high ionic strengths and alkalinities. Ion-exchange brines may contain up to 300 mg/L of arsenic (Steinwinder and Zhao, 2007). Sample arsenic-laden residuals are presented in Table 2.12, modified from MacPhee et al. (2001). Ion-exchange residuals contain the highest concentration of dissolved arsenic and alkalinity.

Removal of arsenic from brines during coagulation is dependant on the pH, arsenic concentration, alkalinity, and ionic strength of the brine (MWH, 2005; Mercer and Tobiason, 2008). Effects of pH and initial arsenic concentrations have been discussed in previous sections. Arsenic removal is favorable at acidic pH (3-7). The higher the initial concentration of arsenic, the lower the required molar ratio of Fe(III):As(V) (Table 2.11).

Therefore, high initial arsenic concentration is favorable for arsenic removal by ferric chloride.

Table 2.12 Characterizations of Ion-Exchange, Activated Alumina Adsorption, Reverse Osmosis, and Nanofiltration Residuals

Characteristics	Ion-exchange	Activated Alumina	Reverse Osmosis	Nanofiltration
pH	9.0-9.7	7.1	7.3-7.9	6.6-7.1
Total As (mg/L)	10.5-24.8	2.63	0.546-0.663	0.486-0.523
Dissolved As (mg/L)	10.3-24.7	0.12	<0.002	0.007-0.009
Alkalinity (mg/L as $CaCO_3$)	950-7000	268	600-2800	210-325
Total Hardness (mg/L as $CaCO_3$)	86-90	13	460-840	1560-1750
Sulfate (mg/L)	910	16338	544	1075-1190
TDS (mg/L)	4100-6240	10240	11750-14300	1533-1765
Conductivity (µS/cm)	8100-12440	22640	23800-28500	3080-3515
Ionic Strength (M)	0.1-0.16	0.26	0.30-0.36	0.04-0.05
Total Fe (mg/L)	0.01-0.49	0.83	0.65-0.86	0.46-2.16

(Source: modified from MacPhee et al. (2001))

Ionic strength is an important factor in arsenic removal using coagulation with ferric chloride. Increasing ionic strength of the solution favors arsenic removal during co-precipitation (Mercer and Tobiason, 2008). The double layer of particles in solution is more compressed in solutions with high ionic strength. Therefore, when particles come close to each other due to Brownian motion, they adsorb each other due to van der Waals forces, which increase the particle aggregation in solution (MWH, 2005; Letterman, 1999; Edzwald et al., 1974). In addition, Mercer and Tobiason (2008) stated that in high ionic strength solutions, the repulsive electrostatic forces are lower than in low ionic strength solutions. The effect of ionic strength on coagulation was discussed in section 2.7.

Arsenic removal from low ionic strength solutions (0.008 M) was less efficient than in high ionic strength solutions (0.2-1.5 M) (Mercer and Tobiason, 2008). Arsenic coagulation flocs formed in a solution with 0.008 M ionic strength were not large enough to be filtered with microfilteration; thus, ultrafiltration was necessary. However, arsenic coagulation in brines with high ionic strengths produced larger flocs which were removed by microfilitration, and ultrafiltration was unnecessary (Mercer and Tobiason, 2008).

Stumm and Morgan (1996) presented a graph from Dzomback and Morel (1990) illustrating the relationship between ionic strength, surface charge, and pH for coagulation on hydrous ferric oxide. The surface charge of hydrous ferric oxide is zero at its pzc (~ pH 8), and increases (positive charge) when pH decreases from 8 to 4. The surface charge also increases when the ionic strength of the solution increases. Specifically, at a similar pH, hydrous ferric oxide has higher surface charge at higher ionic strengths (Stumm and Morgan, 1996). For example, at pH 5, the surface charge of hydrous ferric oxide was 5, 10, and 20 $\mu C/cm^2$ in solutions with 0.001, 0.01, and 0.1 M ionic strengths, respectively (Stumm and Morgan, 1996). Therefore, high ionic strength of ion-exchange residual brines induces higher charges on hydrous ferric oxide.

Alkalinity has a large effect on arsenic removal during coagulation (Appelo et al., 2002; Holm, 2002; Arai et al., 2004). Although alkalinity favors amorphous ferric hydroxide formation after addition of ferric chloride (Steinwinder and Zhao, 2007) (equation 2.86), it inhibits sorption of heavy metals onto goethite (Lee and Hering, 2003; Van Geen et al., 1994; Villalobos et al., 2001) or hydrous ferric oxide (Zachara et al., 1987; Meng et al. (2000); Wilkie and Hering, 1996). pH is directly related to alkalinity, and high alkalinity produces high pH values. Mercer and Tobiason (2008) showed that increasing alkalinity from 400 to 1400 mg/L as $CaCO_3$ decreased arsenic removal efficiency when final pH of the solution was uncontrolled. It has been reported that removal of 500 ppb As(V) from a solution containing 1400 mg/L as $CaCO_3$ alkalinity requires approximately 30 mols of Fe per mol of As(V); however, at lower pH, a Fe/As molar ratio of 10 was sufficient to achieve >90% removal efficiency (Mercer and Tobiason, 2008). The effect of alkalinity on arsenic removal needs further investigation (MacPhee et al., 2001).

Steinwinder and Zhao (2007) reported that the optimal pH range for arsenic removal from brines using ferric chloride of 3 to 6.5 was similar to the pH range required for arsenic removal from drinking waters (Hering et al., 1996a; MWH, 2005). Steinwinder and Zhao (2007) observed 100% As(V) removal between pH 3 and 6.5 using Fe/As molar ratios of 2 or higher; at pH greater than 6.5, the removal efficiency sharply decreased. Mercer and Tobiason (2008) found that efficiency of arsenic removal from brines was increased when pH was reduced from 8.1 to 6.2. Fe(III)/As(V) molar ratios of 15, 9 and 6 were required to obtain > 90% removal at pH 8.1, 7.3, and 6.2, respectively (Mercer and Tobiason, 2008). Thus lower ferric chloride doses are required at lower pH values. Clifford et al. (2003) reported that final arsenic concentrations of waters initially containing 3450 μg/L As(V) after coagulation at a 20 Fe(III)/As(V) molar ratio decreased from 1443 to 16 μg/L when pH was reduced from 7.9 to 5.5.

Several precipitation results, which achieved the highest removal efficiency in its particular coagulation study, are presented in Table 2.13. Arsenic removal by ferric chloride has resulted in arsenic reductions greater than 99% at optimal conditions of pH and ferric chloride dosages.

Typical ferric chloride dosages (as Fe) of 1.7 to 10.3 mg/L are used in drinking water operations (MWH, 2005) (Table 2.13). Higher coagulant dosages (40 to 1100 mgFe(III)/L, i.e., 116 to 3192 mg $FeCl_3$/L) are required for arsenic removal from brines compared to the dosages required for the treatment of drinking waters (1 to 21 mg Fe(III)/L, i.e., 3 to 61 mg $FeCl_3$/L). Arsenic concentrations in brines (up to 300 mg/L) are an order of magnitude greater than those in drinking water (up to 0.300 mg/L), and therefore more ferric chloride is required for brine treatment (Table 2.11 and 2.13). But the required Fe(III)/As(V) molar ratio varies between 2 and 143 (Table 2.13) for brines, which are less than the molar ratios required (20 to 250) for arsenic treatment of drinking water. The required Fe(III)/As(V) molar ratios are smaller for high concentrations of arsenic. For instance, 300 mg/L of arsenic was removed using 2 mol Fe(III) per mol As(V) while 84 mol Fe(III) per mol As(V) was required to remove 0.5 mg/L of arsenic.

Clifford (1999) stated that adding 12 moles of Fe per one mole of As is sufficient to remove 90% of soluble arsenic from a wastewater containing 90 mg/L arsenic. Arsenic removal from an ion-exchange brine containing 3.45 mg/L As was investigated by Clifford et al. (1998). Clifford et al., (1998) used iron dosages based on 1 to 50 Fe(III)/As(V) molar ratios following filtration through a 0.22 µm filter. At pH 5.5 and 6.2, a molar ratio of 20:1 and 50:1 (150 and 375 mg/L) were required to lower arsenic concentration to 20 µg/L (99.5 % removal efficiency).

Steinwinder and Zhao (2007) investigated arsenic removal with ferric chloride from a brine generated by the ion-exchange process. The brine contained arsenic, chloride, sulfate and bicarbonate concentrations of 300 mg/L, 24 g/L (4 wt%), 605 mg/L and 305 mg/L, respectively. The pH of the brine to be treated was controlled using 1 N NaOH and 1 N HCl; pH was measured after a 2 day equilibration period.

Table 2.13 Summary of Studies on Arsenic Removal by Ferric Chloride from Reverse Osmosis (RO), Nanofiltration (NF), Spent Filter Backwash (SFB), Activated Alumina (AA), And Ion-Exchange (IX) Residuals

Residuals	Coagulant dose (mgFe(III)/L)	pH	Initial As(V) (mg/L)	mol Fe(III) / mol As(V)	% As(V) removal	Reference
RO	4.42	6.2	0.5	12	98	Mercer and Tobiason, 2008
RO	31	6.2-8.1	0.5	84	100	Mercer and Tobiason, 2008
NF	51+ 4 mg/L polymer	6.2	0.486	143	98.9	MacPhee et al., 2001
RO	51+2 mg/L Polymer	6.0	0.546	127	92.5	MacPhee et al., 2001
SFB	17	7.1	1.41	16.4	99.1	MacPhee et al., 2001
SFB	26	6.2	1.74	19.9	96.0	MacPhee et al., 2001
AA	17	7.0	2.63	8.8	94.1	MacPhee et al., 2001
IX	51	5.5	3.45	20	99.5	Clifford et al., 2003
IX	127	5.2	3.45	50	99.7	Clifford et al., 2003
IX	34	6.2	10.5	4.4	87.8	MacPhee et al., 2001
IX	167	5.6	11.3	20	99.7	Clifford et al., 2003
IX	68 + 0.5 mg/L Polymer	6.2	24.8	3.7	29.4	MacPhee et al., 2001
IX	34	8.8	33.2	1.4	86.9	MacPhee et al., 2001
IX	442	6-7	300	2	> 99	Steinwinder and Zhao, 2007
IX	1105	9	300	5	> 99	Steinwinder and Zhao, 2007
IX	1105	3-6.5	300	5	> 99	Steinwinder and Zhao, 2007
IX	4421	3-11	300	20	> 99	Steinwinder and Zhao, 2007

Steinwinder and Zhao (2007) stated that adding ferric chloride at a Fe(III)/As(V) molar ratio of 2 is sufficient to completely remove arsenic from the brine at pHs between 3 and 6.5. At pH 9, arsenic removal efficiency of >99% was only achieved utilizing ferric chloride by increasing the Fe(III)/As(V) molar ratios to more than 10. Adding iron at a 20 Fe(III)/As(V) molar ratio decreased the arsenic concentration in the treated effluent to less than 1.5 mg/L. Fe/As molar ratios of 10 to 15 and more than 20 were reportedly required to remove 500 ppb arsenic (V) from brines with 90 and 95% removal efficiencies, respectively. For Fe/As molar ratios less than 5, the removal process is greatly dependent on the pH, and pH adjustment is required. At Fe/As molar ratio of 20 or higher, 95% arsenic removal efficiency is achieved over a wide range (3 to 11) of pH (Steinwinder and Zhao, 2007).

Mercer and Tobiason (2008) studied arsenic removal from high ionic strength solutions. They investigated the effects of the ionic strength, pH, and preformed versus in situ formed HFO. The arsenic (V) concentration in the solution to be treated was 0.5 mg/L in all experiments. The ionic strengths of the solutions varied from 0.008 to 1.5 M and alkalinity of the solutions were 400 (8 meq/L) or 1400 (28 meq/L) mg/L as CaCO3. Arsenic precipitation was accomplished using ferric chloride and preformed HFO solids. Microfiltration and ultrafiltration resulted in negligible differences in arsenic concentrations in the filtered solution (Mercer and Tobiason, 2008). Ferric chloride in the range of 10^{-6} to 10^{-3} M (0.056 to 168 mg/L as Fe) was added to solutions with ionic strengths varying from 0.2 to 1.5 M and alkalinity of 400 mg/L (8 meq/L) (Mercer and Tobiason, 2008). Fe(III):As(V) molar ratios of 10-15 and > 20 were reportedly capable of removing 500 μg/L arsenic (V) with 90 and 95% removal efficiencies, respectively

(Mercer and Tobiason, 2008). Reducing pH to less than 7 improved the removal efficiency for the solution with 0.2 M ionic strength. The Fe/As molar ratio required to achieve >90% removal efficiencies at pH 7.3 and 6.1 are approximately 9 and 6, respectively. However, arsenic removal from the same solution at high ionic strengths (0.7 M) showed a slight increase in arsenic removal efficiency when pH was lowered from 8.0 to 6.5.

Applying 500 to 1000 mg/L ferric chloride to a solution along with hydrated lime achieved an arsenic removal efficiency of 98 to 99% from water containing 9.8 mg/L arsenic (Harper and Kingham, 1992). Similarly, applying 200 to 1000 mg/L of ferric chloride to water contaminated with 31 mg/L arsenic resulted in 86 to 93% removal efficiency (Harper and Kingham, 1992).

Kinetics of ferric chloride precipitation and arsenic removal by ferric chloride was studied by Rose and Waite (2003) and McNeil and Edwards (1997). Rose and Waite (2003) reported that the hydrolysis and precipitation of ferric iron in seawater followed second order kinetics with a rate constant of 4×10^7 $M^{-1}s^{-1}$ at a pH of 8.1. The presence of colloids and particles may increase the rate of the process because they enhance the polymerization process (Pham et al., 2006). Mercer and Tobiason (2008) used 5×10^5 and 2×10^5 m^2/mol Fe to model arsenic removal during co-precipitation for ionic strengths of 0.2 and 0.7 M, respectively. Adsorption coefficients (K) for the moles of arsenic removed per mole of iron removed in ferric chloride precipitation tests were reported as 80 to 120 mM^{-1} by McNeil and Edwards (1997) and 13 to 105 mM^{-1} by MacPhee et al. (2001).

Residual waste generated in treatment of ion-exchange brine using ferric chloride easily passed the TCLP limit of 5 mg/L. TCLP level of the generated waste reported below 0.5 mg/L (MacPhee et al., 2001). Therefore, the treated brine with ferric chloride is not hazardous by present regulations. Chwirka (1999) reported the arsenic concentration in ion-exchange residuals as 10 mg/L and produced residual volume as 4000 gal/MG. The quantity of solids produced was 2.8 kg/ML with arsenic concentration of 14,250 mg per kg dry weight of solids produced. Steinwinder and Zhao (2007) concluded that the waste residuals from treated brines using ferric chloride easily pass the TCLP at Fe/As molar ratios between 5 and 20 and WET at Fe/As >= 20. After a series of WET and TCLP tests, Steinwinder and Zhao (2007) concluded that the WET test is more stringent and should be considered as a means to compare stability of the produced sludge. For example, sludge produced from arsenic coagulation with ferric chloride at Fe/As molar ratio of 5, resulted in leachable arsenic of 675 mg/L and 0.7 mg/L extracted in WET and TCLP tests at pH 6. It should be noted that citric acid can reduce $Fe(OH)_3$ to Fe^{2+}.

Calcium has the ability to immobilize arsenic at high pH (Parks et al., 2003; Bothe and Brown, 1999). $Ca(OH)_2$ addition to the produced sludge during arsenic treatment with ferric chloride reduces the arsenic leachability of the sludge (Bothe Brown, 1999; Parks et al., 2003; Jing et al., 2003; Jing et al., 2005a and 2005b). When calcium hydroxide ($Ca(OH)_2$) was added at the Ca:Fe molar ratio of 1.5, it caused 80% decrease in leachable As in the WET test, 18% decrease in the cost, and 20% reduction of the mass of sludge produced. Prior to addition of the calcium hydroxide the extracted arsenic in WET for the generated sludge was 21.2 mg/L, while after the addition of calcium hydroxide at Ca/Fe was 1.5, the produced sludge passed the WET test (Steinwinder and Zhao, 2007). This result contradicts the findings by Parks et al. (2003) who stated that addition of lime into a solution containing pre-formed solid decreased arsenic leachability in the WET only at pH>11. It should be considered that Steinwinder and Zhao (2007) added $Ca(OH)_2$ while Parks et al. (2003) used CaO. The reason for the variation could be different procedures of the experiments. Steinwinder and Zhao (2007) conducted a co-precipitation experiment to remove arsenic and they added the calcium in the beginning of mixing along with the ferric chloride. However, Parks et al. (2003) studied adsorption of arsenic to pre-formed solids. It can be concluded that calcium doesn’t help surface adsorption; instead, it helps aggregation of particles during co-precipitation. The arsenic solubility can be reduced from 6430 mg/L from untreated waste to 0.823 mg/L by adding 7 g of cement to every 1 g of arsenic sludge. The treated sludge passed the leachability standards (Palfy, 1999). $FeCl_3$ is more efficient and expensive than lime and cement in stabilizing the waste residuals. Moreover, cement and lime increase the produced sludge volume and disposal cost (Jing et al., 2003; Jing et al., 2005a and 2005b).

2.10. Chromium Removal from Brines

This section presents findings in the literature that support the knowledge gap and hypothesis of the third issue addressed in this research, which is chromium removal from ion-exchange brines with calcium polysulfide. Chromium removal from waters with low ionic strengths using calcium polysulfide has been studied extensively (Aratani et al., 1978; Yahikozawa et al., 1978; Freedman et al., 2005). Several articles have been published regarding in-situ remediation or geofixation of hexavalent chromium (Cr(VI)) in aquifers (Yu and Tremaine, 2002; Storch et al., 2002; Messer et al., 2003). Several studies have addressed calcium polysulfide remediation of Cr(VI) contamination from chromite ore processing residue (Graham et al., 2006; Wazne et al., 2007a, Moon et al., 2008). Ion-exchange brines have much higher ionic strengths, alkalinities, and chromium concentrations than surface and ground waters. Although the mechanisms of chromium removal from brines by calcium polysulfide are likely to be the same as that for waters, the optimum conditions for removal (e.g. pH, dosage, ionic strength) are different. To date, no studies have been found that specifically address chromium removal from brine solutions with high ionic strengths using calcium polysulfide.

2.10.1 Chromium Health Effects and Chemistry

Chromium is toxic to humans and animals and needs to be removed from water to protect consumers of drinking water. The health effects of short term (acute) exposure to chromium in humans are skin irritation or ulceration. Long term (chronic) exposure to chromium results in damage to the liver, kidney, circulatory and nerve tissues, as well as skin irritation (U.S. EPA, 2006). There is a high probability for accumulation of chromium in aquatic life if it is released into the environment (U.S. EPA, 2006). Chromium bio-accumulates in flora and fauna in aquatic environments and causes ecological problems (Rengaraj et al., 2001; Bharti and Saxena, 1979). The National Institute for Occupational Safety and Health (NIOSH) recommends a maximum concentration of 10^{-3} mg Cr/m^3 in water bodies (Rengaraj et al., 2001). The maximum contaminant level (MCL) of 0.1 mg/L chromium in drinking water became effective in 1992 (U.S. EPA, 2006). The California Department of Health Services (DHS) adopted a state MCL for chromium in drinking water of 0.05 mg/L in January 2001 (OEHHA, 2001).

A public health goal (PHG) for chromium in drinking water of 2.5 μg/L was adopted in 1998 by the California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA, 2001). The PHG for chromium in drinking water minimizes the risk that more than one cancer case per one million people will occur in 70 years from daily consumption of the water (OEHHA, 2001). PHGs are health protection goals based solely on public health considerations provided by OEHHA to DHS in California. Only health hazards are considered when setting PHGs; they are therefore often impossible to comply with. When DHS receives a PHG, economic factors and technical feasibility are taken into account in setting the MCLs. Drinking water suppliers face the challenge of dealing with emerging water quality concerns in regards to chromium.

It is known that chromium in groundwater occurs at two oxidation states--chromite (Cr(III)) and chromate (Cr(VI)). Cr(III) is less toxic than Cr(VI); furthermore, Cr(III) is naturally available in foods at low concentrations as an essential human dietary nutrient. However, inhalation of hexavalent chromium causes lung cancer. A recent study of animals confidently concluded that hexavalent chromium is a carcinogenic element in drinking waters (Cone and Environment Health News, 2009). Chromate contamination in groundwaters is the result of improper discharge of wastewater from chromium-related industries. Chromate is utilized in steel production, corrosion control, leather tanning, oxidation, wood treatment, anodizing, and electroplating (Rengaraj et al., 2003; Sengupta, 1995; Nriagu and Nieboer, 1988; Stephenson, 1987). Chromium also occurs naturally, and the existence of 82 different chromium minerals has been reported by the International Mineral Association (IMA). Approximately 30% of those minerals contain Cr(VI) (e.g., chromates, hydroxides, and oxides). The primary chromium ore is chromite, a magnesium-iron-chromium-aluminum oxide, $((Mg,Fe^{2+})(Al,Cr,Fe^{3+})_2O_4)$. Chromium typically constitutes between 15 and 65% (with an average of 46.46%) of chromite ore (Guertin et al., 2004).

Cr(VI) is highly soluble at any pH, and $Cr_2O_7^-$ (dichromate), $HCrO_4^-$ (bichromate), and CrO_4^{2-} (chromate) are common species of hexavalent chromium at pH 6 to 8 (Sengupta and Clifford, 1986). The reaction equations below show the different species of hexavalent chromium in equilibrium with the water phase (Sengupta and Clifford, 1986).

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \qquad \log K\ (25°C)\ -0.8 \qquad (3.87)$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-} \qquad \log K\ (25°C)\ -6.5 \qquad (3.88)$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \qquad \log K\ (25°C)\ 1.52 \qquad (3.89)$$

$$HCr_2O_7^- \leftrightarrow H^+ + Cr_2O_7^{2-} \qquad \log K\ (25°C)\ 0.07 \qquad (3.90)$$

The following equations also describe the formation of higher forms of chromate. Equilibrium constant values for these species have not been determined, though their existence has been reported (Sengupta and Clifford, 1986).

$$Cr_2O_7^{2-} + H^+ + HCrO_4^- \leftrightarrow Cr_3O_{10}^{2-} + H_2O \qquad (3.91)$$

$$Cr_3O_{10}^{2-} + H^+ + HCrO_4^- \leftrightarrow Cr_4O_{13}^{2-} + H_2O \qquad (3.92)$$

Distribution of hexavalent chromium species for a total Cr(VI) concentration of 10^{-4} M at various pHs are calculated using MINEQL+ and presented in Figure 2.12. Chromic acid (H_2CrO_4) only exists at pH less than 2, and bichromate becomes the predominant species of hexavalent chromium in the pH range of 2 to 6.5. When the pH increases above 6.5, bichromate transforms to chromate, and the predominant species of Cr(VI) at pH > 8 is chromate.

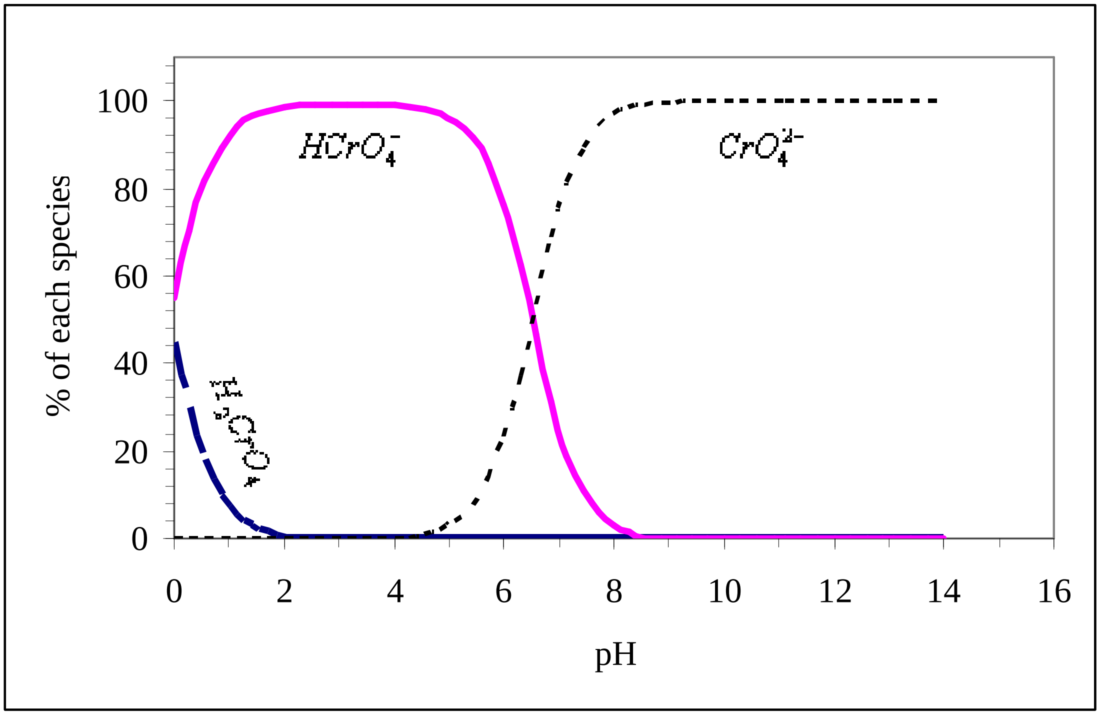


Figure 2.12 Computed Liquid-Phase Distribution of Ionic Species for Cr(VI) System, Cr(VI) = 5.2 mg/L (10^{-4} M) (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001)

Distribution of various species of Cr(VI) for a total concentration of 100 mg/L (1.92 mM) is presented in Figure 2.13. The predominant species of Cr(VI) at pH 6 to 8 are CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$, all of which are soluble and mobile in water. When the pH increases from 2 to 8, $Cr_2O_7^{2-}$ transforms to CrO_4^{2-}. Above pH 8, the predominant species of Cr(VI) is CrO_4^{2-}.

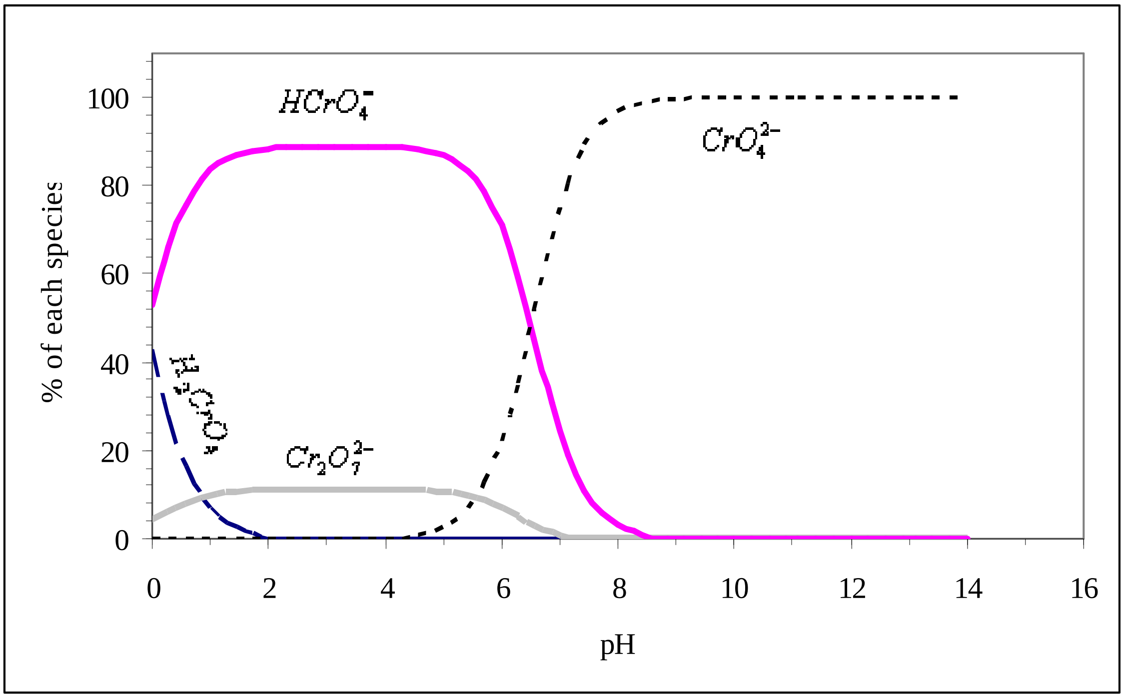


Figure 2.13 Computed Liquid-Phase Distribution of Ionic Species for Cr(VI) System, Cr(VI) = 0.104 g/L (2×10^{-3} M) (MINEQL+ Was Utilized for the Computation, Schecher And Mcavoy, 2001)

In the pH range of approximately 1 to 6.5, the relative distribution of bichromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) depends on the total chromate concentration in the solution (equation 2.89). For example, at high Cr(VI) concentrations (0.104 g/L or 2×10^{-3} M), for pH between 2 and 6, $Cr_2O_7^{2-}$ is the predominant species (89%) along with 11% $HCrO_4^-$. Fractions of dichromate and bichromate versus the total chromium concentrations at pH 4 in solution are presented in Figure 2.14. $Cr_2O_7^{2-}$ dominates when the total Cr(VI) concentrations in solution are greater than 1560 mg/L (30 mM).

A pE-pH diagram for chromium was constructed and is presented in Figure 2.15, considering the four hydrolysis constants of trivalent chromium ($\beta1 = 10^{-4}$, $\beta2 = 10^{-9.7}$, $\beta3 = 10^{-18}$, $\beta4 = 10^{-27.4}$), equation 2.88, and the following reduction equation:

$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4\ H_2O \qquad E0 = 1.195\ V \text{ and } K = 10^{60.64}$ (3.93)

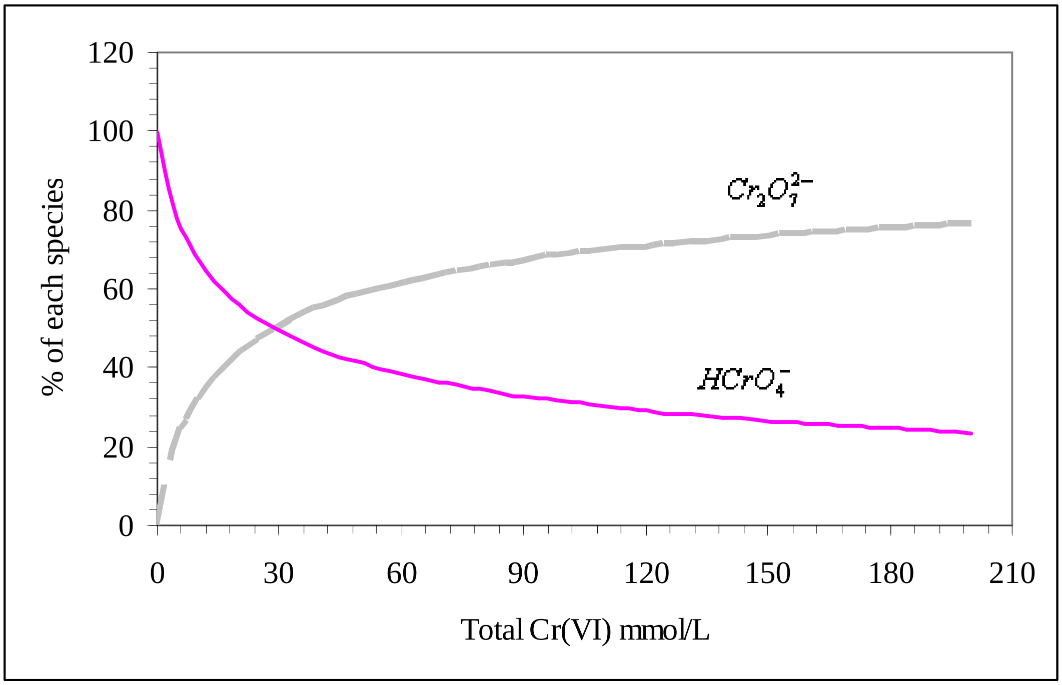


Figure 2.14 Computed Fraction of Bichromate ($HCro_4^-$) and Dichromate ($Cr_2O_7^{2-}$) in the Liquid-Phase at pH 4 as a Function of the Total Cr(VI) Concentration (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001)

Figure 2.15 shows that both Cr(III) and Cr(VI) exist over wide pH ranges. However, Cr(III) only exists under reducing conditions (pe or Eh > 0). The diagram indicates that Cr(VI) occurs naturally in groundwaters under oxidizing conditions. If the oxidation and reduction potential of groundwater is lowered, Cr(VI) is reduced to trivalent chromium and precipitates as chromium hydroxide in favorable alkaline pH ranges.

Cr(III) is less soluble than Cr(VI) in water, and can be precipitated as a hydroxide. Chromium hydroxide ($Cr(OH)_3(s)$) and Cr_2O_3 (eskolaite) are two solid forms of Cr(III).

$Cr(OH)_3$ (s) is formed from reduction of CrO_4^{2-}, and it is more likely to regulate the solubility of trivalent chromium in waters and wastewaters. The solubility of the Cr(III) hydroxide can be estimated as a function of pH. Cr(III) hydrolyzes and forms several species including Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_3$ (aq), $Cr(OH)_4^{-}$, $Cr2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, and $Cr_4(OH)_6^{6+}$ (Rai et al., 1987). The sum of all the soluble species of trivalent chromium, $Cr(III)_T$, can be determined at any pH; this gives the overall solubility as a function of pH (Figure 2.16). The minimum solubility occurs in the pH range of 8.6-8.9, and the optimum pH for Cr(III) precipitation is 8.8.

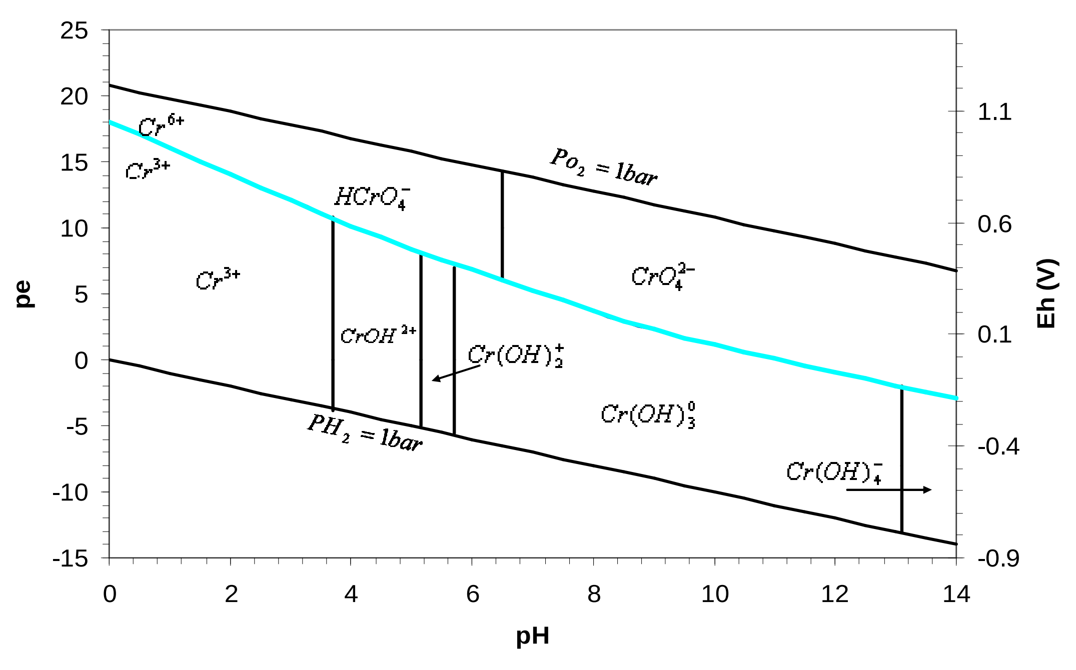


Figure 2.15 Computed pe-pH (Eh-pH) Diagram for Chromium System, Cr = 52 mg/L (10^{-3} M) (Mathcad and MINEQL+ Were Utilized for the Computation, Schecher and Mcavoy, 2001)

Cr(III) easily precipitates as $Cr(OH)_3(s)$ for pH greater than 5.1. Figure 2.17 presents the distribution of Cr(III) species versus pH for a homogenous solution in which $Cr(OH)_3(s)$ is assumed not to precipitate at 0.52 mg/L (10^{-5} M). Cr^{3+} is the predominant species of Cr(III) when the pH of the solution is less than 4; as pH increases above 4, it begins to transform to $Cr(OH)_2^+$, reaching a peak concentration at pH 4.8. $Cr(OH)_2^+$ is the predominant species of Cr(III) at pH values between 6 to 8.5, which is the typical pH range for most waters. $Cr(OH)_3(aq)$ predominates at pH values between 8.5 and 9.5, and for pH values greater than 9.5, $Cr(OH)_4^-$ becomes the predominant species of trivalent chromium.

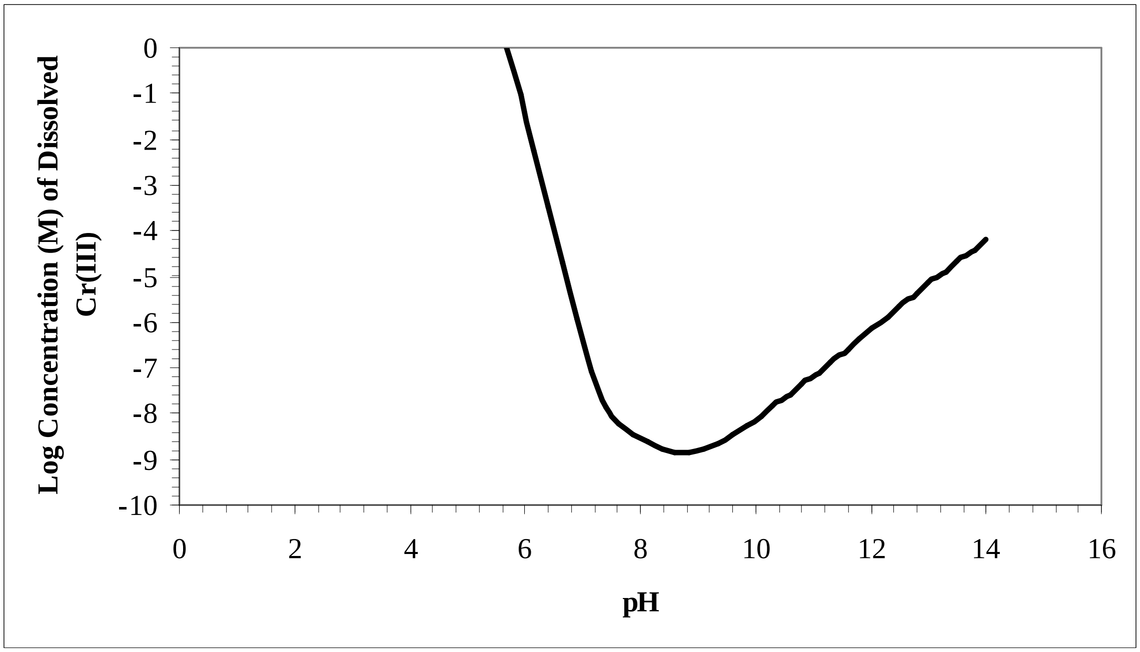


Figure 2.16 Computed Solubility of Precipitated $Cr(OH)_3(S)$ (25°C, I = 10^{-2} M, Initial $Cr(OH)_2^+$ = 86 g/L (1 M)) (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001)

Generally, Cr(III) tends to precipitate shortly after hydrolysis begins unless the concentration of soluble Cr(III) in the solution is reasonably low. The distribution of Cr(III) species is presented in Figure 2.18 for a low concentration (10^{-5} M or 0.52 mg/L) of total Cr(III), assuming that only $Cr(OH)_3(s)$ forms and that Cr_2O_3 will not form in the solution.

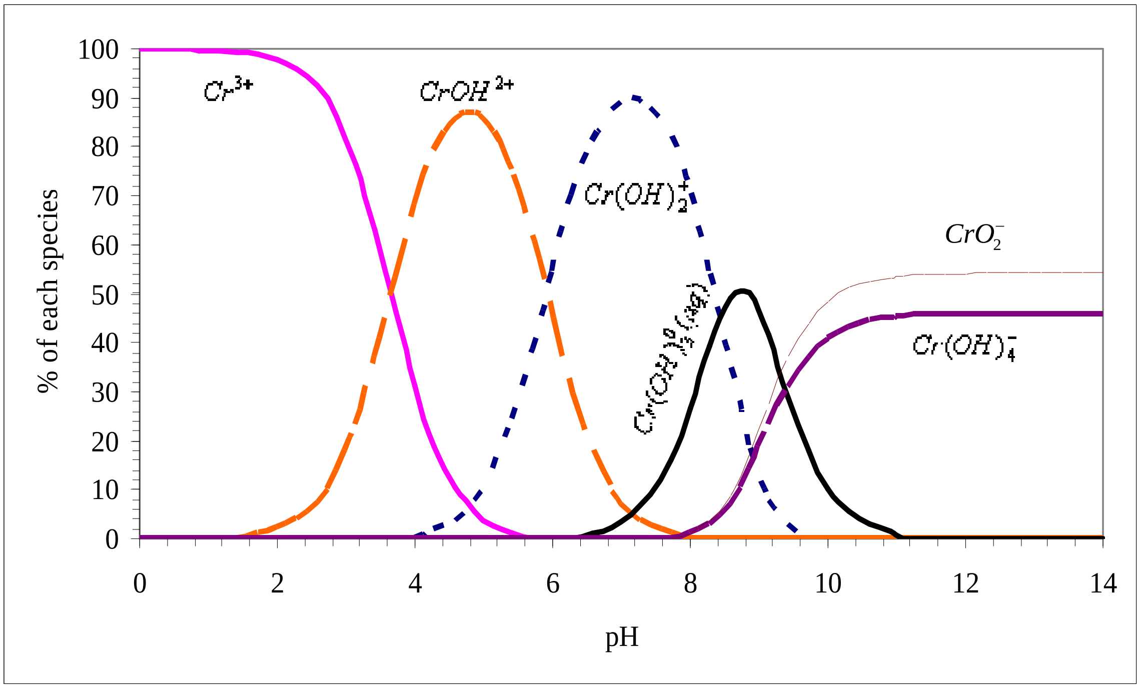


Figure 2.17 Computed Liquid-Phase Distribution of Ionic Species for a Hypothetical Homogenous Trivalent Chromium System, Cr(III) = 0.52 mg/L (10^{-5} M), Assuming No Precipitation Occurs (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001).

Figure 2.18 shows that Cr^{3+} is present at very acidic pH, and its concentration decreases as it hydrolyzes to $CrOH^{2+}$ with increasing pH. At pH 5.2, $CrOH^{2+}$ reaches its maximum concentration, and is the predominant trivalent chromium species. When the pH is greater than 5.1, Cr(III) precipitates as $Cr(OH)_3(s)$; at pH greater than 6, $Cr(OH)_3(s)$ is the predominant species. At very high pH (13.5-14) $Cr(OH)_3(s)$ does not form; instead, $Cr(OH)_4^-$ appears as the predominant species.

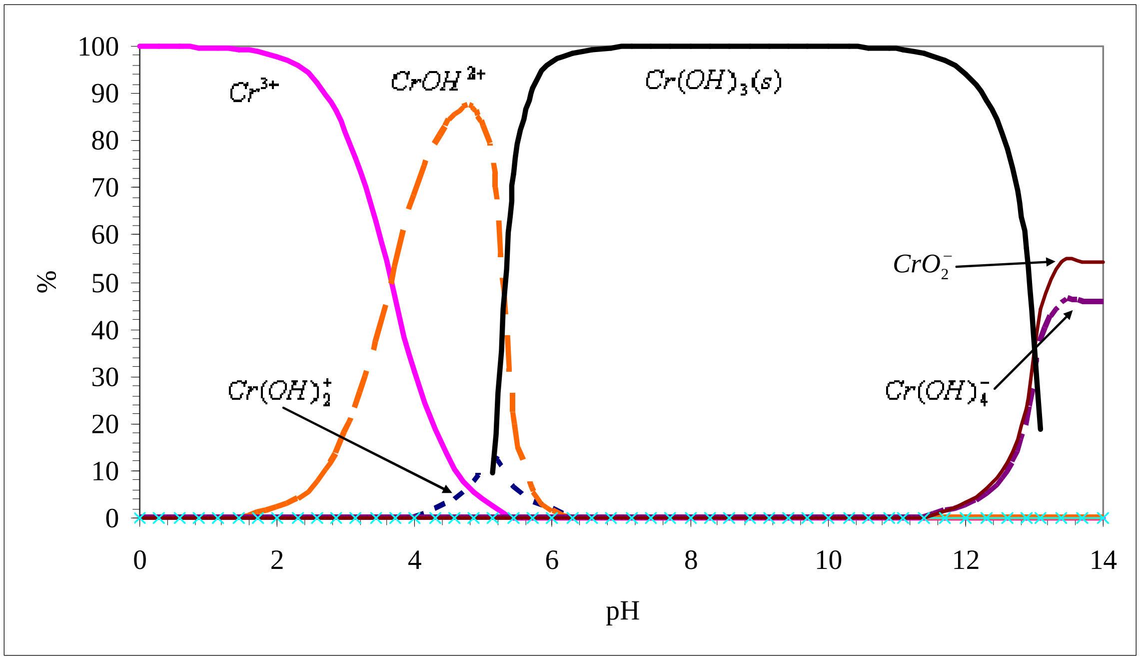


Figure 2.18 Computed Liquid-Phase Distribution of Ionic Species for a Trivalent Chromium System, Cr(III) = 0.52 mg/L (10^{-5} M), Assumed Only $Cr(OH)_3(S)$ Forms (MINEQL+ Utilized for the Computation, Schecher and Mcavoy, 2001)

2.10.2 Chromium Treatment Technologies

Several methods for chromium removal from aqueous solution have been reported, such as ion-exchange, electrocoagulation, coagulation, membrane filtration, adsorption, biosorption, foam flotation, electrolysis and surface adsorption. In this section, the most widely used chromium removal techniques, which have also been suggested by the EPA

(U.S. EPA, 2006), will be reviewed and summarized. These techniques are ion-exchange, electrocoagulation, coagulation, reverse osmosis, lime softening, and activated carbon.

Ion-Exchange Technology

Ion-exchange is a very effective technology for removal of chromium from waters (especially in small systems) and it produces very consistent effluent quality. Anionic ion-exchange resins have been utilized to remove hexavalent chromium (CrO_4^-, $HCrO_4^-$ and $Cr_2O_7^{2-}$) and cationic resins can be used to remove trivalent chromium (Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, and $Cr_4(OH)_6^{6+}$),. Anion-exchange resins have been used to remove Cr(VI) from groundwater, cooling water, and industrial water (Gode and Pehlivan, 2005). Typical groundwater pH ranges from 5 to 8 (Liang et al., 2000) so CrO_4^-, $HCrO_4^-$ and $Cr_2O_7^{2-}$ may be present in groundwater, and all can be removed by anion-exchange resins. Cation-exchange resins have been used to remove Cr(III) from water, wastewater, and industrial wastewater (e.g., tannery and electroplating wastewater). Cr^{3+}, $CrOH^{2+}$, and $Cr(OH)_2^+$ are soluble trivalent chromium species in groundwater and can be removed using cation-exchange resins.

Synthetic IX resins with specific chromium preference allow designers to accurately predict the run length of the resin beds; however, regeneration of IX resins generates brines that need to be treated (U.S. EPA, 1981; Robinson et al., 1974; Rengaraj et al., 2001; Batista, 2006). Moreover, ion-exchange is sometimes not cost effective for chromium removal from waters with high sulfate levels because sulfate is highly preferred by anion-exchange resins (non-selective resins), and sulfate usually occurs in very high concentrations compared to other contaminants in waters. The drawbacks arising from the presence of sulfate in the anion-exchange process have been discussed previously in section 2.3, along with tables showing the selectivity coefficients of various resins (Table 2.1).

In groundwaters, Cr(VI) occurs as the major contaminant above the MCL or as a co-contaminant, below the MCL in waters contaminated with nitrate, arsenic, selenium, and uranium. Therefore, brines from ion-exchange resin systems that remove contaminants other than chromium may also contain high chromium concentrations. Chromium contamination concentrations between 500 and 2810 ug/L that appear in wells in California are depicted in Figure 2.19.

Typically, ion-exchange resins used for arsenic and chromium removal are regenerated with sodium chloride to allow for resin re-use, lowering the cost of the treatment process. In addition to high arsenic and chromium levels, brines have high alkalinities and ionic strengths. The high alkalinity of brines is associated with adsorption of bicarbonate by the resins. The high ionic strength is related to the use of sodium chloride as a resin regenerant (Figure 2.11). The residual ion-exchange brines usually have high concentrations of chromium.

Brine solutions containing more than 5 mg/L of chromium are considered hazardous; the EPA Toxicity Characteristic Leaching Procedure (TCLP) limit is 5 mg/L (Hazardous waste > 5 mg/l Cr). Hazardous waste handling is very expensive, at approximately $300 per drum (55 US gallons) (U.S. DOE, 2007). There is therefore a demand for technologies that can be used to treat chromium and arsenic containing wastes. These technologies should produce low volumes of stable wastes.

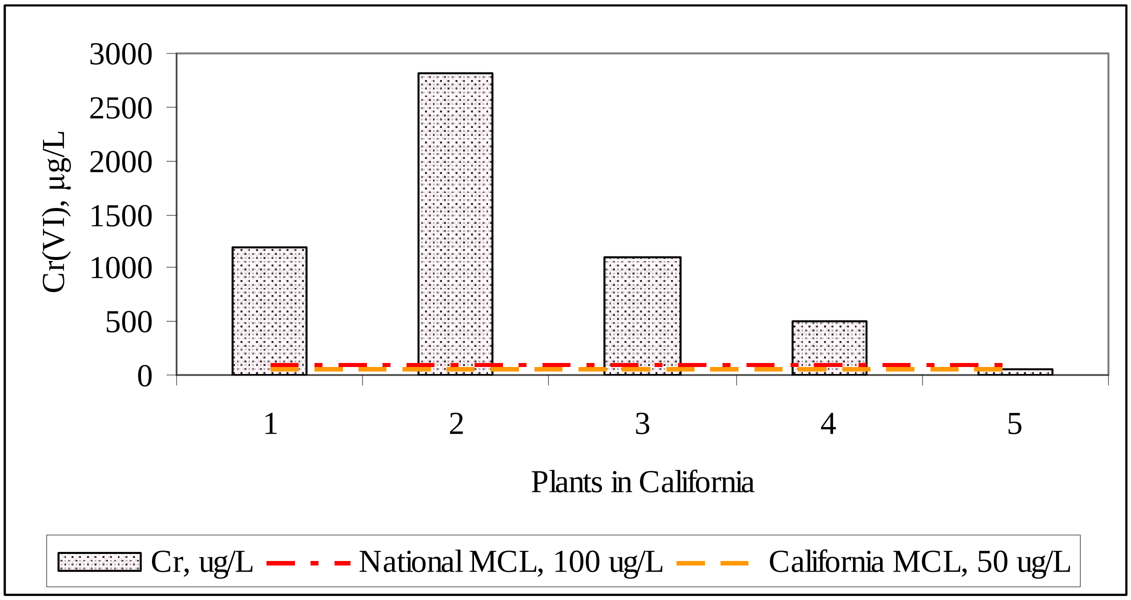


Figure 2.19 Chromate Concentrations in Five Ion-exchange Chromium Removal Units in California.

Removal of Cr(VI) by Ion-Exchange

Some of the anion-exchange resins which have been utilized or recommended for Cr(VI) removal are presented in Table 2.14. Strong or weak base anion-exchange resins can be used for Cr(VI) removal (Table 2.14), but weak base anion-exchange resins are preferred for Cr(VI) removal from industrial wastewaters due to their much greater regeneration efficiencies (MWH, 2005). A Type 2 strong-base anion-exchange resin (e.g., DOWEX SAR) is more easily regenerated than a Type 1 strong-base anion-exchange resin (e.g., DOWEX 1) (DOW, 2009b).

Resins with either tertiary or quaternary amine functional groups can be utilized for Cr(VI) removal (Table 2.14). The removal capacity of resins used for Cr(VI) removal can be increased by decreasing the alkyl group length from butyl to methyl (Ortiz-Palacios et al., 2008). Both macro-porous and gel type resins can be used for Cr(VI) removal (Table 2.14). Gel type resins are known to have higher capacity and better regeneration efficiency than macro-porous resins. However, macro-porous resins are more resistant to osmotic shock (swell less) than gel type resins (Ortiz-Palacios et al., 2008). Moreover, macro-porous resins are more efficient in the presence of organic matter than gel type resins.

The results of batch tests for removal of Cr(VI) from waters contaminated with 12 to 124 mg Cr(VI)/L using ion-exchange resins are summarized in Table 2.15. Up to 99% chromium removal has been achieved in batch experiments using 1 g-resin/L of solution in the pH range of 1-5.

The pH of the solution is an important factor that controls the sorption of Cr(VI) by ion-exchange resins, and the highest sorption of Cr(VI) to strong and weak-base anion-exchange resins occurs in the pH range of 2-4, with maximum sorption occurring at a pH of 3 (Gode and Pehlivan, 2005; Shi et al., 2009; Atia, 2006). Gode and Pehlivan (2005) reported maximum removal of Cr(VI) with anion-exchange resins in the pH range of 2 to 6 for an initial Cr(VI) concentration of 100 mg/L. Under similar conditions but with a different resin type, Shi et al. (2009) found that a pH range of 1-5 was optimum for Cr(VI) removal. Also, Atia (2009) showed that maximum Cr(VI) removal occurs between pH 2 to 4 for an initial 100 mg/L Cr(VI) concentration. Atia et al. (2009) studied RPA, a weak-base anion-exchange resin with a pzc of 6, and RQA, a strong-base anion-exchange resin which is positively charged over the pH range of 2-10. At higher pH values, RQA resins were more efficient than RPA resins in the removal of Cr(VI).

Table 2.14 Anion-Exchange Resins Used or Recommended for Cr(VI) Removal

Resin Name/ Manufacturer	Resin Type	Resin Matrix	Functional Group	Total Capacity (meq/L)	Reference
Lewatit MP 62 Sybron	WBA Macro-porous	Styrene-DVB	Tertiary amine Trimethylamine $N(CH_3)_3^+$	1700	Gode and Pehlivan, 2005
Lewatit MP 610 Sybron	SBA Macro-porous	Styrene-DVB	Tertiary amine Dimethylethanolamine $(CH_3)_2(CH_3CH_2OH)N^+$	4144	Gode and Pehlivan, 2005
D301 Guang Zhou Mingju	WBA Macro-porous	Styrene-DVB	Tertiary amine $(R\text{-}N(CH_3)_2)$	5016	Shi et al., 2009
D314 Guang Zhou Mingju	WBA Macro-porous	Acrylic Acid	Tertiary amine $(R\text{-}N(CH_3)_2)$	7560	Shi et al., 2009
D354 Guang Zhou Mingju	WBA Macro-porous	Styrene-DVB	Tertiary amine $(R\text{-}N(CH_3)_2)$	5016	Shi et al., 2009
D252	SBA Macro-porous	-	Quaternary amine $(\text{-}NR_4)$	-	Wang et al., 2000
RPA	WBA Macro-porous	Acrylic	Tertiary amine $(\text{-}NR_3)$	-	Atia, 2006
RQA	SBA Macro-porous	Acrylic	Quaternary amine $(\text{-}NR_4)$	-	Atia, 2006
DOWEX 1 DOW	SBA Gel	Styrene-DVB	Quaternary amine $R\text{-}N\text{-}(CH_3)_3^+$	1400	DOW website
DOWEX SAR DOW	SBA Gel	Styrene-DVB	Dimethylethanol amine $R(CH_3)_2(CH_3CH_2OH)N^+$	1400	DOW website
DOWEX 21 K XLT	SBA Gel	Styrene-DVB	Quaternary amine $R\text{-}N\text{-}(CH_3)_3^+$	1400	DOW website
Amberlite PWA7	WBA	Phenolic	-	1900	Rohm and Haas website
Amberlite PWA8	WBA Gel	Acrylic	-	1600	Rohm and Haas website

The pH of the solution is an important factor that controls the sorption of Cr(VI) by ion-exchange resins, and the highest sorption of Cr(VI) to strong and weak-base anion-exchange resins occurs in the pH range of 2-4, with maximum sorption occurring at a pH of 3 (Gode and Pehlivan, 2005; Shi et al., 2009; Atia, 2006). Gode and Pehlivan (2005) reported maximum removal of Cr(VI) with anion-exchange resins in the pH range of 2 to

6 for an initial Cr(VI) concentration of 100 mg/L. Under similar conditions but with a different resin type, Shi et al. (2009) found that a pH range of 1-5 was optimum for Cr(VI) removal. Also, Atia (2009) showed that maximum Cr(VI) removal occurs between pH 2 to 4 for an initial 100 mg/L Cr(VI) concentration. Atia et al. (2009) studied RPA, a weak-base anion-exchange resin with a pzc of 6, and RQA, a strong-base anion-exchange resin which is positively charged over the pH range of 2-10. At higher pH values, RQA resins were more efficient than RPA resins in the removal of Cr(VI).

There are different explanations for the higher removal efficiency of Cr(VI) at pH 3: (a) the influence of the pH on the functional group of the resin (Gode and Pehlivan, 2005), and (b) preferential adsorption of $HCrO_4^-$ at pH 3 (Atia, 2009). Gode and Pehlivan (2005) believe that the efficiency of functional groups of Lewatit MP 62 (weak base) and MP 610 (strong base) resins is at its maximum at pH 3. This means that the functional group easily exchanges its OH^- or Cl^- with the bichromate or dichromate ions. In the pH range of 1 to 6.5, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are the predominant species of Cr(VI) in aqueous solutions. Both of these species can be adsorbed by ion-exchange resins (Gode and Pehlivan, 2005; Shi et al., 2009; Atia, 2006). Atia (2009) found that bichromate is the predominant Cr(VI) species for total Cr(VI) concentrations less than 30 mmol/L and pH 1-6.5, and therefore the selectivity of the SBA and WBA resins for $HCrO_4^-$ is at its maximum at pH 3.

For pH < 1, chromic acid (H_2CrO_4) is the predominant species of Cr(VI). Chromic acid is not ionized and cannot be adsorbed by resins, which explains the decrease in removal efficiency for pH < 3, when $HCrO_4^-$ and $Cr_2O_7^{2-}$ transform to chromic acid.

Table 2.15 Batch Experiments for Cr(VI) Removal Using Ion-Exchange Resins

Resin Name/ Manufacturer	pH	Initial Cr (mg-Cr(VI)/L-solution)	% Percent removal using 1 g-resin/L-solution	Reference
Lewatit MP 62 or Lewatit MP 610	5 5	12 60	99 95	Gode and Pehlivan, 2005
D252	1 3 5 6	100 100 100 100	84 99 95 92	Wang et al., 2000
RPA	3 8	100 100	80 18	Atia, 2006
RQA	3 8	100 100	99 78	Atia, 2006
D301, D314, or D354 Guang Zhou Mingju	1-5 10	124 124	99.4 4.8	Shi et al., 2009

There are different explanations for the decrease in Cr(VI) removal efficiency at neutral to alkaline pH values. SBA resins are positively charged at any pH, while WBA resins are positively charged at pH values less than their pKa values (8.3 to 6.5) (MWH, 2005). For pH >6.5, CrO_4^{2-} becomes the predominant species of Cr(VI). Gode and Pehlivan (2005) reported that although chromate is preferred by resins, the presence of OH^- ions at pH > 6.5 forms hydroxyl complexes of chromium, which decrease the uptake of Cr(VI) at alkaline pH. However, Atia (2009) agreed with MWH (2005) and stated that at alkaline pH, the resin functional groups become deprotonated; therefore, there are no Cl^- ions available to be exchanged with chromate ions. Untea et al. (2000) reported that the most effective removal of Cr(VI) from solutions with pH > 6 was achieved using anion-exchange resins in OH^- form. Lewatit MP-500A, a macro-porous strong-base anion-exchange, has high selectivity for Cr(VI) even in its CrO_4^{2-} form, and the selectivity for various ions by this resin has been found to be: $CrO_4^{2-} > SO_4^{2-} > Cl^- > OH^-$. Zhao et al. (1998) developed an anion-exchange resin constructed with a polystyrene-DVB matrix and bispicolamine group containing a nitrogen atom coordinated with a Lewis acid-Cu(II) in a covalent way without charge neutralization; thus, positive charge allows trapping of chromate ions in pH ranges from neutral to alkaline.

The percent Cr(VI) removal (percent sorption onto the resin) decreases when the initial chromium concentrations are increased (Gode and Pehlivan, 2005; Shi et al., 2009). Gode and Pehlivan (2005) observed a 4% decrease in Cr(VI) removal efficiency when they increased the initial Cr(VI) concentration from 12 to 60 mg/L. Shi et al. (2009) reported a decrease in Cr(VI) removal efficiency from 99.4% to 52% when the Cr(VI) concentration was increased from 40 to 190 mg/L for a styrenic WBA resin at pH 3. In the same situation, the % Cr(VI) removal was reduced from 95% to 36% for an acrylic WBA resin.

Resins with a styrene matrix are more efficient in removing Cr(VI) from water than resins with an acrylic matrix (Table 2.14). RPA, a WBA acrylic type resin with a tertiary amine functional group, removes only 80% of the chromium from a solution containing 100 mgCr(VI) /L at pH 3, while D301 (a resin similar to RPA except with an acrylic matrix) removes 99.4% of the chromium from a solution with an initial chromium concentration of 124 mg Cr(VI)/L (Table 2.14). Shi et al. (2009) showed that D314, a WBA acrylic type resin, has lower Cr(VI) removal efficiency (72%) than D301 and D354

(WBA styrenic type resins) (90%) when treating contaminated waters with initial chromium concentrations between 40 and 190 mg/L at pH 3.

The Langmuir and Freundlich isotherm constants found in several studies of Cr(VI) removal by ion-exchange is presented in Table 2.16. The adsorption capacity of resin used for Cr(VI) removal varies between 21 and 156 mg Cr(VI)/g-resin (Table 2.16). According to the Langmuir isotherm, adsorption energies for the adsorption of chromium are between 0.40 and 1.56 L/mg. D354 has the highest adsorption n value at 1.56 L/mg. The higher the adsorption energy, the higher is the binding strength, which may result in poor regeneration of the resin. When Cr(VI) is strongly bonded to a resin, high volumes of regenerant solution are required to break the bonds and fully regenerate the resin. According to the Freudlich isotherm constants, adsorption capacities of the resins studied in the tests summarized in Table 2.16 range from 5.8 to 88.3 mg/g, and n values are between 0.1 and 6.6. The trend of increasing the Freudlich isotherm constants matches the trend for the Langmuir constants.

Table 2.17 shows adsorption (forward) and desorption (backward) first order kinetic constant rates for various resins. Adsorption is clearly dominant over desorption. Overall constant rate varies between 0.003 to 0.11 (1/h) with an average of 0.05-0.07 (1/h) for initial Cr(VI) concentrations between 3 to 6 mg/L. Lewatit MP 62 has the highest overall kinetic rate of 0.11 (1/h). This means that Cr(VI) adsorption in Lewatit MP 62 occurs faster than in the other resins presented in Table 2.17; therefore, this resin requires the shortest empty bed contact time when used for Cr(VI) removal.

Table 2.16 Summary of Isotherm Parameters for the Adsorption of Cr(VI) on Ion-Exchange Resins

Resin name	Langmuir isotherm		Freundlich isotherm		References
	Q_M (mg-Cr(VI)/ g-resin)	b (L-solution/ mg-Cr(VI))	K_F (mg-Cr(VI)/ g-resin)	n	
Lewatit MP 62	20.8	0.48	-	-	Gode and Pehlivan, 2005
Lewatit M 610	21.3	0.67	-	-	Gode and Pehlivan, 2005
Amberlite IRA-904	30.58	0.163	5.82	2.3	Demir and Arisoy, 2007
RPA	39	-	-	-	Atia, 2009
RQA	48	-	-	-	Atia, 2009
D252	53.03	0.40	27.4	0.1	Wang et al., 2000
D314	120.5	0.5	58.0	5.9	Shi et al., 2009
D301	151.5	0.92	79.1	6.1	Shi et al., 2009
D354	156.2	1.56	88.3	6.6	Shi et al., 2009

Table 2.17 Summary of Isotherm Parameters and Rate Constants for the Adsorption of Cr(VI) on Ion-Exchange Resins

Resin name	First order rate constants				References
	Initial (mg-Cr(VI)/ L-solution)	Overall rate (1/h)	Forward rate (1/h)	Backward rate (1/h)	
D252	-	0.0027	-	-	Wang et al., 2000
D314	3	0.0490	0.0477	0.00127	Shi et al., 2009
Lewatit M 610	6	0.05	0.049	0.0009	Gode and Pehlivan, 2005
D301	3	0.0604	0.0602	0.00018	Shi et al., 2009
D354	3	0.0670	0.0669	0.00011	Shi et al., 2009
Lewatit MP 62	6	0.11	0.11	0.0005	Gode and Pehlivan, 2005

Removal of Cr(III) by Ion-Exchange

Several anion-exchange resins utilized for Cr(III) removal in different studies are presented in Table 2.18. Macro-porous or gel type resins can be utilized for Cr(III) removal (Table 2.18), and their capacities vary from 400 to 2200 meq/L. Both strong and weak acid cation-exchange resins can be utilized for Cr(III) removal from waters or wastewaters (Table 2.18). The SAC exchange resins used for Cr(III) removal are primarily in H^+ form and have sulfonic acid (or sulfonate) functional groups and styrenic matrices. The WAC exchange resins utilized for Cr(III) removal have iminodiacetic acid or carboxylic acid functional groups and are primarily in Na^+ form. Moreover, these WAC resins have both styrenic and acrylic matrices. Table 2.18 summarizes the characteristics of some of the cation-exchange resins used for Cr(III) removal from aqueous solutions.

Results of several batch experiments for removal of Cr(III) from waters and wastewaters are presented in Table 2.19. The results show that Cr(III) can be completely removed from solutions with initial Cr(III) concentrations of up to 27.3 and 33.3 mg/L when using WAC and SAC exchange resins, respectively, at acidic pH range of 2-4.

pH plays a major role in adsorption of Cr(III) on to cationic exchange resins, and Cr(III) can be removed using both strong and weak-acid cation-exchange resins in the pH range of 2-6 (Table 2.19). At pH > 6, adsorption of Cr(III) onto ion-exchange resins is not possible due to the formation of chromium hydroxide solids. Gode and Pehlivan (2006) reported that the optimum pH for Cr(III) removal was 3.5 when using Amberjet 1200 H, a strong-acid cation-exchange resin. The maximum adsorption of Cr(III) has been reported to occur at pH 4.5 on Lewatit TP 207 and Chelex 100, which are weak-base cation-exchange resins (Gode and Pehlivan, 2003). Cr(III) removal by ion-exchange resins is favorable at acidic pH 2-4 (Rengaraj et al., 2002). Rengaraj et al. (2003) achieved 95% Cr(III) removal at pH 2-6, and reported that the optimum pH for Cr(III) removal is 3.8. Cavaco et al. (2007) determined the optimum pH of 2.6 for Cr(III) removal with the weak-acid cation-exchange resins, Diaion CR11 and Amberlite IRC 86.

Table 2.18 Characteristics of Cation-exchange Resins Used for Cr(III) Removal

Resin Name/ Manufacturer	Resin Type	Resin Matrix	Functional Group	Total Capacity (meq/L)	Reference
SKN1 Mitsubhishi Chemical Co.	SAC	Styrene-DVB	Sulfonic Acid $H\text{-}S(=O)_2\text{-}OH$	1700	Rengaraj et al., 2001
IRN77 Rohm and Haas	SAC Macro-porous	Styrene-DVB	Sulfonic Acid $H\text{-}S(=O)_2\text{-}OH$	1900	Rengaraj et al., 2001
Amberjet 1200 H Rohm and Haas	SAC	Styrene-DVB	Sulfonic Acid $H\text{-}S(=O)_2\text{-}OH$	1800	Rengaraj et al., 2003
Amberlite IR120 Rohm and Haas	SAC Macro-porous	Styrene-DVB	Sulfonic Acid $H\text{-}S(=O)_2\text{-}OH$	1900	Alguacil et al., 2004
Amberjet 1500 H Rohm and Haas	SAC	Styrene-DVB	Sulfonate $R\text{-}S(=O)_2\text{-}O^-$	2000	Rengaraj et al., 2003
Lewatit S 100 Sybron	SAC Gel	Styrene-DVB	Sulfonic Acid $H\text{-}S(=O)_2\text{-}O^-Na^+$	2000	Gode and Pehlivan, 2006
Amberjet IRN 97 Rohm and Haas	SAC Gel	Polystyrene-DVB	Sulfonic Acid $H\text{-}S(=O)_2\text{-}OH$	2150	Rengaraj et al., 2003
Chelex 100 Bio-Rad Lab.	WAC Macro-porous	Polystyrene	Chelating Iminodiacetic acid $NaN(CH_2CO_2H)_2$	400	Gode and Pehlivan, 2003
Diaion CR 11 Mitsubishi Chemical Co.	WAC	Polystyrene	Chelating Iminodiacetic acid $HN(CH_2CO_2H)_2$ or $NaN(CH_2CO_2H)_2$	460	Cavaco et al., 2007
Amberjet IRC86 Rohm and Haas	WAC	Polyacrylic	Carboxylic R-COOH	1191	Cavaco et al., 2007
Lewatit TP 207 Sybron	WAC Macro-porous	Polystyrene	Chelating Iminodiacetic acid $NaN(CH_2CO_2H)_2$	2200	Gode and Pehlivan, 2003

Langmuir and Freundlich isotherm kinetics for Cr(III) removal with strong and weak-acid cation-exchange resins are presented in Table 2.20. These resins have adsorption capacities between 5 and 189 mg/g (Table 2.20); Amberjet 1500 H has the highest adsorption capacity of 189 mg/g. The Cr(III) binding energies are between 0.002 and 0.207 L/mg. Diaion CR11 (Na^+ form) forms the strongest bond with Cr(III) with a b value of 0.207 L/mg. Freundlich isotherm n, the binding strength, indicates the affinity of a resin for Cr(III) (Rengaraj et al., 2001). n values are between 0.23 and 1.48; Chelex

100 has the highest affinity (1.48) for Cr(III) and Amberlite IR120 has the lowest affinity (0.23) among the resins presented in Table 2.20.

Table 2.19 Batch Experiments for Cr(III) Removal Using Ion-Exchange Resins

Resin Name/ Manufacturer	pH	Initial Cr (mg-Cr(III)/ L-soltion)	% Percent removal using 1 g-resin/L-solution	Reference
Amberjet 1200 H Amberjet 1500 H Amberjet IRN97 H	2 to 6	2	95	Rengaraj et al., 2003
Lewatit S 100	3.5	3.11	100	Gode and Pehlivan, 2006
Amberjet IRN97 H	3.8	6.7 to 20	100 to 37	Rengaraj et al., 2003
Amberjet 1500 H	3.8	10 to 20	100 to 92	Rengaraj et al., 2003
Lewatit TP 207 Chelex 100	4.5	15.8	100	Gode and Pehlivan, 2003
Amberjet 1200 H	3.8	20 to 40	100 to 42	Rengaraj et al., 2003
SKN1 IRN77	2 to 4	20	100	Rengaraj et al., 2001
Diaion CR 11 or Amberjet IRC86	2.6	27.3	100	Cavaco et al., 2007
SKN1	6	20	65	Rengaraj et al., 2001
	8	20	90	
	3.5	33.3 to 100	100 to 55	
IRN77	5	20	55	Rengaraj et al., 2001
	8	20	78	
	3.5	33.3 to 100	100 to 61	

First order kinetic rates for the adsorption of Cr(III) on to ion-exchange resins are presented in Table 2.21. The SAC exchange resins often have greater overall kinetics than the WAC exchange resins. Overall kinetic rates of adsorption/desorption for the various resins listed in Table 2.21 are between 0.003 and 1.065 (1/h). Increasing the initial concentrations of Cr(III) in the solutions increases the overall and forward kinetic rate constants. Adsorption kinetic constants (forward) are higher than desorption rate constants (backward); this indicates that the adsorbed Cr(III) is relatively stable on the resins. Amberlite IR120 showed the lowest forward kinetic rate (0.003 1/h) and lowest affinity (0.23); this resin may not be a suitable choice for Cr(III) removal. Chromium removal by ion-exchange follows first order kinetics, and Cr(III) is faster (average overall rate of 0.44 1/h) than Cr(VI) removal via ion-exchange (average overall rate of 0.056 1/h).

Table 2.20 Summary of Isotherm Parameters for the Adsorption of Cr(III) on Cation-Exchange Resins

Resin name	Langmuir isotherm		Freundlich isotherm		References
	Q_M (mg-Cr(VI)/ g-resin)	b (L-solution/ mg-Cr(VI))	K_F (mg-Cr(VI)/ g-resin)	n	
Diaion CR11(H^+)	5.02	0.13	-	-	Cavaco et al., 2007
Lewatit TP 207	15	0.0017	-	-	Gode and Pehlivan, 2003
Chelex 100	17.7	0.004	1.56	1.48	Gode and Pehlivan, 2003
Lewatit S 100	20.3	0.12	-	-	Gode and Pehlivan, 2006
Diaion CR11(Na^+)	24.7	0.207	-	-	Cavaco et al., 2007
Amberlite IRC 86	31.7	0.19	-	-	Cavaco et al., 2007
Amberjet IRN97	58.14	0.16	6.31	1.31	Rengaraj et al., 2003
Amberlite IR120	67.7	0.09	16.3	0.23	Alguacil et al., 2004
Amberjet 1200H	84.04	0.039	3.28	1.04	Rengaraj et al., 2003
Amberjet 1500H	188.67	0.022	4.99	0.89	Rengaraj et al., 2003

Although the removal of both Cr(VI) and Cr(III) via ion-exchange is possible, Cr(VI) removal is more efficient than Cr(III) removal. Cr(VI) selective resins have higher total (1400-7500 meq/L) and chromium (average 71.2 mgCr(VI)/g-resin) capacities than Cr(III) selective resins (400-2100 meq/L and average 51.3 mgCr(III)/g-resin). In addition, Cr(VI) selective resins have greater binding constants than Cr(III) selective resins. Cr(VI) removal by anion-exchange is optimum at pH range from 2 to 4, while Cr(III) removal via cation-exchange is optimum in the pH range of 2-6.

Table 2.21 Summary of First Order Rate Constants for the Adsorption of Cr(III) on Cation-Exchange Resins

Resin name	First order rate constants				References
	Initial (mg-Cr(III)/ L-solution)	Overall rate (1/h)	Forward rate (1/h)	Backward rate (1/h)	
Amberlite IR120	10 40 320	0.003 0.003 0.0025	-	-	Alguacil et al., 2004
Lewatit S 100	3.12	0.03	0.03	0.001	Gode and Pehlivan, 2006
Lewatit TP 207	3.12	0.0344	0.0274	0.0070	Gode and Pehlivan, 2003
Chelex 100	3.12	0.2159	0.2099	0.0065	Gode and Pehlivan, 2003
IRN77	50 100 150	1.0605 0.4862 0.4987	1.0602 0.4857 0.4919	0.0003 0.0005 0.0068	Rengaraj et al., 2001
SKN1	50 100 150	0.5315 0.5387 0.7628	0.5313 0.5375 0.6439	0.0002 0.0012 0.1189	Rengaraj et al., 2001
Amberjet 1200H	10 15 20	0.3914 0.4034 0.4461	0.3518 0.3991 0.4396	0.0396 0.0043 0.0065	Rengaraj et al., 2003
Amberjet 1500H	10 15 20	0.6256 0.6022 0.6723	0.6168 0.5970 0.6676	0.0088 0.0052 0.0047	Rengaraj et al., 2003
Amberjet IRN97	10 15 20	0.6006 0.5955 0.6814	0.5862 0.5872 0.6729	0.0144 0.0083 0.0085	Rengaraj et al., 2003

Electro-Coagulation Technology

In the electrochemical process, reduction of Cr(VI) to Cr(III) can be accomplished using electrochemical units. The process consists of electrolysis using an aluminum or iron anode. Iron electrodes are reported to be more efficient than aluminum electrodes (Mouedhen et al., 2009); however, some studies state that aluminum electrodes are also effective (Zongo et al., 2009; Heidmann and Calmano, 2008). The application of this technology for hexavalent chromium removal requires a reduction step followed by a precipitation step. The main reactions that occur at the anode during electrolysis using Al or Fe electrodes are (Zongo et al., 2009):

$$Al \rightarrow Al^{3+} + 3\,e^{-} \qquad E_0 = -1.662\ V \qquad (2.94)$$

$$Fe \rightarrow Fe^{2+} + 2\,e^{-} \qquad E_0 = -0.447\ V \qquad (2.95)$$

$$H_2O \rightarrow 2H^{+} + ½\,O_2 + 2e^{-} \qquad E_0 = 1.229\ V \qquad (2.96)$$

Mouedhen et al. (2009) believe that the reduction of Cr(VI) occurs by Fe(II) anodically generated. The main reaction occurring at the cathode electrode during Cr(VI) removal by electrocoagulation is (Mouedhen et al., 2009; Zongo et al., 2009):

$$2H_2O + 2e- \rightarrow H_2 + OH^{-} \qquad E_0 = -0.828\ V/NHE \qquad (2.97)$$

At the cathode made of iron, the following reaction may occur at acidic pH conditions.

$$6H^{+} + Cr_2O_7^{2-} + 6\,e^{-} \rightarrow Cr_2O_4^{2-} + 3\,H_2O \quad \text{(at pH < 6.5) (Mouedhen et al., 2009)} \quad (2.98)$$

However, at neutral to alkaline pH, there is no $Cr_2O_7^{2-}$ available to be reduced; the following reactions are thought to occur. There are disagreements among scientists about the reduction mechanisms at neutral to alkaline pH values at Fe cathodes (see equations 2.99-2.105).

$Cr^{6+} + 3Fe^{2+} \rightarrow Cr^{3+} + 3\,Fe^{3+}$ (Mouedhen et al., 2009) (2.99)

$3Fe^{2+} + CrO_4^{2-} + 4H_2O \rightarrow 3\,Fe^{3+} + Cr^{3+} + 8OH^-$ $(6.5 < pH < 7.5)$

(U.S. EPA, 1979; Beszedits, 1988; Mouedhen et al., 2009) (2.100)

$CrO_4^{2-} + 3\,Fe(OH)_2 + 4H_2O \rightarrow 3Fe(OH)_3 + Cr(OH)_3 + 2OH^-$ $(pH > 7.5)$

(Mouedhen et al., 2009) (2.101)

$CrO_4^{2-} + 8H^+ + 3Fe^{2+} \rightarrow Cr^{3+} + 3\,Fe^{3+} + 4H_2O$ $E_0 = 0.760$ V/NHE

(Zongo et al., 2009) (2.102)

$Cr_2O_7^{2-}\,(aq) + 6Fe(OH)_2\,(aq) + 7H_2O \rightarrow 2Cr(OH)_3 + 6Fe(OH)_3 + 2OH^-$ (Mouedhen et al., 2009) (2.103)

$2HCrO_4^- + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6\,Fe^{3+} + 8H_2O$ (Thella et al., 2008) (2.104)

$HCrO_4^- + 7H^+ + 3\,e^- \rightarrow Cr^{3+} + H_2O$ (Zongo et al., 2009) (2.105)

At a cathode made of aluminum, an electrochemical reduction of hexavalent chromium to trivalent chromium occurs according to the following reaction equations:

$Cr_2O_7^{2-} + 6\,e^- + 14H^+ \rightarrow 2Cr^{3+} + 7\,H_2O$ (acidic pH) (2.106)

$CrO_4- + 3e^- + 4H_2O \rightarrow Cr^{3+} + 8OH^-$ (alkaline pH) (2.107)

Most researchers agree that Cr(III) precipitates as $Cr(OH)_3(s)$ (Thella et al., 2008; Mouedhen et al., 2009; Zongo et al., 2009) when using either aluminum or iron cathodes; however, Mouedhen et al. (2009) reported $Cr_2O_4^{2-}$ also precipitates as $FeCr_2O_4$ in the vicinity of Fe cathode.

The electrochemical process occurs quickly (Beszedits, 1988). Typically, the electrochemical reduction process occurs in less than 60 minutes (Mouedhen et al., 2009; Zongo et al., 2009; Thella et al., 2008). However, it requires pH adjustment and produces large amounts of sludge because of co-precipitation of iron hydroxide (U.S. EPA, 1979).

Many studies have investigated the removal of Cr(VI) by electrocoagulation (Table 2.22). Electrocoagulation of Cr(VI) is affected by the type of electrodes and current densities used in the process. Both Fe and Al electrodes have been utilized for Cr(VI) reduction. For the same current densities, Fe electrodes are more efficient than Al electrodes in removing Cr(VI) from waters (Mouedhen et al., 2009; Thella et al., 2008; Zango et al., 2009); however, Al electrodes have been shown to be capable of removing Cr(VI) at high efficiencies (> 92%) if higher current densities are used (Reddithota et al., 2007; Adhoum et al., 2004). For example, at pH 7 in a solution with an initial Cr(VI) concentration of 45 mg/L, an Fe electrode is able to completely remove Cr(VI) at a current density of 100 A/m^2 in 30 minutes, while an Al electrode with the same current density removes only 51% of the Cr(VI) in the solution after 110 minutes (Mouedhen et al., 2009). However, an Al electrode supplied with 480 A/m^2 current density successfully reduced 96% of the chromium in a solution with an initial chromium concentration of 50 mgCr(VI)/L (Adhoum et al., 2004). Al electrodes are efficient at very high current densities (480 A/m^2) while Fe electrodes work perfectly even at very low current densities. The current densities required for Fe and Al electrodes to reduce Cr(VI) are between 50 and 200 A/m^2 and 80 to 480 A/m^2, respectively (Table 2.22). Cr(VI) reduction by electrocoagulation can be completed within 15 to 180 minutes initial Cr(VI) concentrations of the solution and the current density of the process. Fe electrodes are faster than Al electrode in removing Cr(VI) from waters. Initial Cr(VI) concentrations of 15 to 200 mg/L have been completely reduced using electrocoagulation. For Fe electrodes, the higher the current density, the faster is the reduction process. High currents increase the pH more than low currents do, but even though Al electrodes require high current densities, at similar current densities, initial Cr(VI), and pH conditions, Al electrodes increase the pH of the solution less than Fe electrodes do (Table 2.22).

Removal of Cr(VI) from aqueous solutions is favored at acidic pH conditions (Mouedhen et al., 2009; Thella et al., 2008; Zango et al., 2009). Thella et al. (2008) reported a pH of 2 is optimum for Cr(VI) removal with Fe electrodes. The pH ranges of 2-8 (Thella et al., 2008) and 4-8 (Adhoum et al., 2004; Reddithota et al., 2007) have been reported to be favorable for Cr(VI) removal by electrocoagulation with iron and aluminum electrodes, respectively. Mouedhen et al. (2009) achieved 100% Cr(VI) removal efficiency over pH range of 2-7.8 with Fe electrodes. Most groundwaters have pH values greater than 8, and after electro-coagulation of Cr(VI) final pH values could increase to as high as 11.

Adhoum et al. (2004) and Reddithota et al. (2007) reported pH values of less than 4 or greater than 8 reduce the efficiency of Cr(VI) removal by electrocoagulation with Al electrodes. It is reported that the amphoteric behavior of $Al(OH)_3$ explains the decrease in Cr(VI) removal efficiency (Reddithota et al., 2007). At pH > 8, $Al(OH)^-$ becomes the predominant species of Al, and at pH < 4, Al^{3+} is the predominant species. Al^{3+} and $Al(OH)^-$ do not precipitate, while $Al(OH)_3$ forms only between pH 4 and 8, and enhances the Cr(VI) precipitation process (Reddithota et al., 2007).

Table 2.22 Summary of Studies on Cr(VI) Removal with Electrocoagulation Using Al and Fe Electrodes

Electrodes Anode/ cathode	Current density (A/m^2)	Initial pH	Final pH	Initial Cr(VI) (mg/L)	Time (min)	% Cr(VI) removed	Reference
Fe/Fe	25	2	-	15	40	86	Thella et al., 2008
Fe/Fe	50	2	2.5	15	30	100	Thella et al., 2008
Fe/Fe	75	2	-	15	20	100	Thella et al., 2008
Fe/Fe	80	4-8	> 8	-	15	99.6	Reddithota et al., 2007
Fe/Fe	100	7	11	45	30	100	Mouedhen et al.., 2009
Fe/Fe	50	2	-	10-100	20	100	Thella et al., 2008
Fe/Fe	50	2-8	-	100	50	100-88	Thella et al., 2008
Fe/Fe	100	2	3	180	45	100	Mouedhen et al.., 2009
Fe/Fe	50	7.8	11	180	180	100	Mouedhen et al.., 2009
Fe/Fe	100	7.8	11	180	75	100	Mouedhen et al.., 2009
Fe/Fe	200	7.8	11	180	40	100	Mouedhen et al.., 2009
Fe/Fe	50	7.5	9.2	200	60	75	Zongo et al., 2009
Fe/Fe	100	7.5	9.8	200	60	98	Zongo et al., 2009
Fe/Fe	150	7.5	10.1	200	40	98	Zongo et al., 2009
Fe/Fe	200	7.5	10.1	200	30	100	Zongo et al., 2009
Al/Al	80	4-8	> 8	-	15	94	Reddithota et al., 2007
Al/Al	480	-	-	24	20	91.6	Adhoum et al., 2004
Al/Al	480	6.8	7.3	26	20	99	Reddithota et al., 2007
Al/Al	100	7	9.3	45	110	51	Mouedhen et al.., 2009
Al/Al	160	2-4	5-8.9	50	20	55-82	Adhoum et al., 2004
Al/Al	160	4-8	9	50	20	82	Adhoum et al., 2004
Al/Al	160	8-8.5	9-9.2	50	20	82-57	Adhoum et al., 2004
Al/Al	480	6	-	50	10	96	Adhoum et al., 2004
Al/Al	50	7.5	8.5	200	60	31	Zongo et al., 2009
Al/Al	100	7.5	9.1	200	60	51	Zongo et al., 2009
Al/Al	150	7.5	9.3	200	60	55	Zongo et al., 2009
Al/Al	200	7.5	9.4	200	60	85	Zongo et al., 2009

Coagulation Technology

Chromium coagulation is a two step removal process that involves reduction and precipitation. For high flow rates coagulation/filtration is the most common and low cost process for chromium removal (Beszedits, 1988). High capital cost makes coagulation/filtration less applicable for low flow rates; the process is also slow, and requires highly trained operators (Beszedits, 1988). Cr(VI) is highly soluble and cannot be precipitated at any pH. Therefore, in the first step, Cr(VI) needs to be reduced to Cr(III), and in the second step, trivalent chromium precipitates as chromium hydroxide.

Traditionally, gaseous sulfur dioxide (SO_2), sodium bisulfite ($NaHSO_3$), or sodium sulfite (Na_2SO_3) have been utilized to reduce Cr(VI) to Cr(III) in water and wastewater. The reduction process occurs rapidly at low pHs. The reduction of Cr(VI) to Cr(III) occurs spontaneously at pH 2, and takes 30 minutes to complete at pH 3 (Beszedits, 1988). Therefore, pH adjustments are required in the coagulation process for reduction of Cr(VI) to Cr(III) using gaseous sulfur dioxide (SO_2), sodium bisulfite ($NaHSO_3$) or sodium sulfite (Na_2SO_3). The pH of the solution must be lowered to values between 2 and 3 by adding acid (e.g. sulfuric acid) (Forbes, 1979; Erdem, 2004). It also can be observed from the pe-pH chromium diagram (Figure 2.15) that the reduction of Cr(VI) to Cr(III) is favorable at pH < 3 under reducing conditions (Figure 2.15) because lower reducing potentials are required at pH < 3 compared to those required at pH >3.

After reduction of Cr(VI) to Cr(III), the optimum pH for Cr(III) precipitation has been reported to be between pH 8.5 and 9.0 (Erdem, 2004; Beszedits, 1988). Solution pH therefore needs to be adjusted to high values using a base (e.g lime or caustic soda). pH adjustments result in high operational costs and a need for highly trained operators for chromium removal. There is a need for more effective coagulants that are more flexible in the operation.

Since 1980, more attention has been spent on the reduction of Cr(VI) to Cr(III) by two important reductants: iron (Lee and Hering, 2003; Sedlak and Chan, 1997; Fendrof and Guangchao, 1996; Qin et al., 2005), and sulfide (U.S. EPA, 1981; Messer et al., 2003; Graham et al., 2006; Wazne et al., 2007a).

Cr(VI) Removal by Coagulation Using Iron

Hexavalent chromium reduction and chromium hydroxide formation are reported as the main mechanisms for Cr(VI) removal from waters and wastewaters using Fe^{2+} (Fendorf and Li, 1996; Lee and Hering, 2003; Eary, 1988; Eary and Rai, 1988; Sedlak and Chan, 1997); however, sorption of Cr(VI) onto freshly precipitated $Fe(OH)_3(am)$ is also reported by Lee and Hering (2003). Reduction of Cr(VI) by Fe^{2+} can be represented by one of the following reactions:

$$Cr(VI)(aq) + 3Fe(II)(aq) \rightarrow Cr(III)(aq) + 3Fe(III)(aq) \qquad 3 < pH < 10$$

(Eary and Rai, 1988) (2.108)

$$H_xCrO_4^{x-2}(aq) + 3Fe^{2+}(aq) + iH_2O \leftrightarrow Cr(OH)_y^{3-y}(aq) + 3Fe(OH)_z^{3-z}(aq) + jH^+$$

(pH < 10; where i = (y + 3z) and j = (x + y + 3z)) (Fendorf and Li, 1996) (2.109)

or

$$CrO_4^{2-} + 3Fe^{2+}(aq) + 8H_2O \rightarrow 4Fe_{3/4}Cr_{1/4}(OH)_3(s) \qquad (pH \geq 6.5)$$ (Lee and Hering, 2003) (2.110)

In addition, hexavalent chromium reduction using ferrous sulfate is described as:

$Cr_2O_7^{2-} + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O + SO_4^{2-}$ (Batista, 2006) (2.111).

In water with high dissolved oxygen concentrations, Fe(II) may be oxidized by O_2 as well:

$4Fe^{2+} + O_2(aq) + 4\,H_2O \rightarrow 4\,Fe(OH)_3(s) + 8\,H^+$ (Lee and Hering, 2003) (2.112)

This process may decrease the overall reduction efficiency of Cr(VI) by Fe(II).

It has been shown that Cr(III) should be sorbed and/or co-precipitated with the ferric hydroxide, or precipitated as chromium hydroxide (Lee and Hering, 2003; Eary and Rai, 1988; Fendorf and Li, 1996; Rai et al., 1989). The following reactions have been used to represent the precipitation process of trivalent chromium.

$xCr^{3+} + (1-x)Fe^{3+} + 3\ H_2O \leftrightarrow (Cr_xFe_{1-x})(OH)_3(s) + 3\ H^+$ (Eary and Rai, 1988; Fendorf and Li, 1996) (2.113)

$Cr(OH)_3(s) \leftrightarrow Cr^{3+} + 3OH^-$ log K = -30 (Stumm and Morgan, 1995) (2.114)

$Fe(OH)_3(s) \leftrightarrow Fe^{3+} + 3OH^-$ (Stumm and Morgan, 1995) (2.115)

$Cr^{3+} + 3\ FeSO_4 + 6\ NaOH + 0.5\ O_2 \rightarrow Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 7\ H_2O + SO_4^{2-}$

(Batista, 2006) (2.116),

A summary of coagulation studies using ferrous sulfate for chromium removal are presented in Table 2.23. Cr(VI) concentrations up to 17 mg/L can be completely removed (>99%) from waters and wastewaters using Fe^{2+}, which can be provided using ferrous sulfate or ferrous ammonium sulfate. The coagulant dosages needed (0.1 to 81 mg Fe^{2+} /L) depends on the pH and the initial concentrations of Cr(VI).

pH is an important parameter in Cr(VI) reduction by Fe^{2+} (Table 2.23). There are different opinions regarding the optimum pH for Cr(VI) reduction by Fe^{2+}. The Cr(VI) reduction rate was found to be minimum at pH 4 and increases at lower and higher pH values (Lee and Hering, 2003; Sedlak and Chan, 1997). Fendrof and Li (1996) measured Cr(VI) reduction rates by Fe(II) and reported minimum and maximum reduction rates at pH 4 and pH 9, respectively. However, Eary and Rai (1988) showed that chromium (VI) reduction is possible in the pH range of 2.0-11.5. Initial Cr(VI) concentrations of 4 to 25 mg/L) were reduced to below 100 μg/L in pH ranges of 5.5-7.2 and 10-11 using $FeSO_4.7H_2O$ (Zotter and Licskó, 1992). An excellent Cr(VI) removal efficiency was reported in a pilot scale plant when the solution pH was maintained in the range of 6.5 to 7.3 for initial Cr(VI) concentrations of 100 μg/L.

Different Fe(II)/Cr(VI) molar ratios have been utilized to reduce and remove Cr(VI) from waters and wastewaters (Table 2.23). A 10:1 Fe(II)/Cr(VI) molar ratio is reported to be sufficient to remove 98.5% of 100 μg/L Cr(VI) in a pilot scale study. Increasing the molar ratio from 10 to 50 decreases the reaction time from 46 to 6 hours (Qin et al., 2005). Eary and Rai (1988) found that 3 mols of Fe(II) are required to reduce 1 mol of Cr(VI) in the pH range of 2.0 to 10.0 for initial concentration of 5 mgCr(VI)/L.

Although Cr(VI) can be reduced by Fe^{2+}, and precipitated as chromium hydroxide, Cr(VI) can also be adsorbed onto ferric hydroxide that is generated by the addition of ferrous sulfate (Lee and Hering, 2003), or other iron minerals (e.g. $Fe_2O_3.H_2O$(am), Fe_2O_3, α-FeOOH) (Rai et al., 1989).

Iron oxides have been shown to have higher adsorptivity for chromate than alum does (Rai et al., 1989). Cr(VI) sorption onto freshly precipitated $Fe(OH)_3$(am) accounts for only 25% of the Cr(VI) removal from aqueous solutions at optimum conditions (e.g., pH 5.2) (Rai et al., 1989). Usually, Cr(VI) removal due to sorption to iron hydroxide is poor and accounts for less than 10% of the initial Cr(VI) removal for pH above 6 (Lee and Hering, 2003). Similarly, alum can adsorb up to 11% of the chromium from a solution containing 0.45 mgCr(VI)/L (Sorg, 1979). The highest Cr(VI) adsorption efficiency has been obtained in the pH range of 4-6 for $Fe_2O_3.H_2O$(am), Fe_2O_3, and α-FeOOH. Increasing the pH from 6 to 8 dramatically decreases the adsorption efficiency (Rai et al., 1989; Lee and Hering, 2003).

Table 2.23 Summary of Studies on Cr(VI) Reduction by Coagulation

Study Type	Coagulation Process	Coagulant dose Fe^{2+} (mg/L)	pH	Initial Cr (mg Cr(VI)/L)	Mol Fe(II) /Cr(VI)	% Cr(VI) removal	Refrence
Synthetic water	$(Fe(NH_4)_2(SO_4)_2 .6H_2O)$ as Fe^{2+} 0.2 µm filter or ultrafilter	0.109-0.652	8.2	0.050	2-12	100	Lee and Hering, 2003
Synthetic water	$(Fe(NH_4)_2(SO_4)_2 .6H_2O)$ as Fe^{2+} 0.2 µm filter or ultrafilter	0.163-0.543	8.2	0.050	3-10	35-95	Lee and Hering, 2003
Synthetic water	$(Fe(NH_4)_2(SO_4)_2 .6H_2O)$ as Fe^{2+} 0.2 µm filter or ultrafilter	0.65	8.2	0.056	12.5	>99	Lee and Hering, 2003
Synthetic water	$(Fe(NH_4)_2(SO_4)_2 .6H_2O)$ as Fe^{2+} 0.2 µm filter or ultrafilter	0.280	6.5-7	0.058	4.5	51-92	Lee and Hering, 2003
Pilot scale study (23-46 hours)	$FeSO_4$ as Fe^{2+} and filtration	1-5	6.5-7.1	0.1	10-50	>95	Qin et al., 2005
Ohio river	$FeSO_4$ as Fe^{2+}	10.7	8.5	0.12	89	76	Sorg, 1979
Ohio river	$FeSO_4$ as Fe^{2+}	10.3	8.5	0.13	79	73	Sorg, 1979
Ohio river	$FeSO_4$ as Fe^{2+}	8.8	7.0	0.14	63	15	Sorg, 1979
Ohio river	$FeSO_4$ as Fe^{2+}	12.8	7	0.16	80	55	Sorg, 1979
Ohio river	$FeSO_4$ as Fe^{2+}	11.8	8.3	0.31	38	78	Sorg, 1979
Ohio river	$FeSO_4$ as Fe^{2+}	11.1	8.6	1.29	8.6	71	Sorg, 1979
Groundwater	$FeSO_4$ as Fe^{2+}	30.2	7.2	3.6	8.4	94.4	Zotter and Licsko, 1992
Groundwater	$FeSO_4$ as Fe^{2+}	30.4	7.2	4.6	6.6	95.6	Zotter and Licsko, 1992
Groundwater	$FeSO_4$ as Fe^{2+}	80.6	7.5	16.8	4.8	99.4	Zotter and Licsko, 1992
Wastewater 40-95°C	$(Fe(NH_4)_2(SO_4)_2 .6H_2O)$ as Fe^{2+}	15	2-10	5	3	100	Eary and Rai, 1988

At alkaline pH, Cr(III) can be adsorbed to ferric hydroxide, precipitated as $Cr(OH)_3(s)$, and/or co-precipitated as $(Cr,Fe)(OH)_3$. As shown in Figure 2.18 (speciation of Cr(III)), $Cr(OH)_3(s)$ forms in solution at pH 6-12. Cr(III) precipitates out of the solution as chromium hydroxide at alkaline pH > 8.8. Therefore, for Cr(III) precipitation, solution pH needs to be adjusted to ~ 8.8 using lime or caustic soda.

Cr(III) Removal by Coagulation Using Ferric Chloride, Ferric Sulfate and Alum

Ferric chloride, ferric sulfate, and alum have been utilized as coagulants to precipitate Cr(III) out of solution. Ferric chloride is more efficient than alum in removal of Cr(III) from waters and wastewaters, and alum is more efficient than ferric sulfate (Table 2.24). Ferric chloride, alum, and ferric sulfate have shown up to 99%, 96%, and 90% Cr(III) removal efficiencies, respectively (Table 2.24). Adding 800 mg/L ferric chloride to a solution containing 20 mgCr(III)/L removes 99% of the Cr(III), while addition of the same amount of alum removed 83% of Cr(III) from the solution. Adding 34 mg/L of alum into a solution containing 0.12mg/L removed 96% of the Cr(III) in the solution, while 37 mg/L of ferric sulfate removed 83% of Cr(III) from the same water (Table 2.24). Efficient Cr(III) precipitations occur at pH > 7 (Table 2.24).

pH 10 has been reported as the optimum pH for chromium removal using ferric chloride and aluminum sulfate from tannery wastewater containing 16.8 mg/L Cr(III) (Song et al., 2004). At pH 10, 400 to 800 mg/L ferric chloride or aluminum sulfate were required to remove 16.8 mg/L of chromium from tannery wastewater with 90-95% removal efficiency (Song et al., 2004).

Table 2.24 Summary of Studies on Cr(III) Precipitation Using Ferric Chloride, Ferric Sulfate, or Alum

Study Type	Coagulation Process	Coagulant dose (mg/L)	pH	Initial Cr(III) (mg/L)	% Cr(III) removal	Refrence
Wastewater	$FeCl_3$ and 0.5 mg/L polymer	40	6.8-7.0	0.076	92	Johnson et al., 2008
Wastewater	$FeCl_3$	600	7.5	2-150	99.2-21.8	Song et al., 2004
Tannery Wastewater	$FeCl_3$	800	7.5	20	99	Song et al., 2001
Ohio river	Alum	29	8.1-8.3	0.12	69-73	Sorg, 1979
Ohio river	Alum	34	7.1	0.12	>96	Sorg, 1979
Well water	Alum	30-27	6.5-6.9	0.12	49-77	Sorg, 1979
Wastewater	Alum	700	7.5	2-150	83-50.6	Song et al., 2004
Tannery Wastewater	Alum	800	7.5	20	83	Song et al., 2001
Ohio river	$Fe_2(SO_4)_3$	37	7.2-8.2	0.12	84-90	Sorg, 1979
Well water	$Fe_2(SO_4)_3$	33	7.5	0.12	87	Sorg, 1979
Well water	$Fe_2(SO_4)_3$	30	6.5	0.12	83	Sorg, 1979

Cr(VI) Removal by Coagulation Using Sulfides: H_2S, Na_2S, and Na_2SO_3

Sulfides such as calcium polysulfide (CaS_x), hydrogen sulfide (H_2S), sodium sulfide (Na_2S), and iron sulfide (FeS) have been utilized to reduce Cr(VI) to Cr(III). The vast majority of metals form hydroxides at alkaline pH values. Some heavy metals also form stable sulfides; the product of metal precipitation by sulfide or polysulfide is a fairly insoluble metal sulfide that precipitates out of the solution. The reaction chemistry is assumed to be:

$$M^{2+} + S^{2-} \rightarrow MS \qquad (2.117)$$

Connor (1990) reported that sulfide alone is not effective in precipitating trivalent chromium. The kinetics of the reaction between Cr(VI) and sulfides are very slow (Lee and Hering, 2003). Most studies reported that Cr(VI) reduction with sulfides is possible and that the process is fairly efficient (Table 2.25) (Kim et al., 2001; Lai and McNeill, 2006; Connor, 1990). Addition of sodium sulfide to obtain 43 mol S^{2-}/Cr(VI) in solution leads to 80 and 20% Cr(VI) removal efficiencies at pH 5 and 9, respectively (Lai and MacNeill, 2006). The efficiency of Cr(VI) reduction by sodium sulfide improves when pH of the solution decreases.

The reason sulfide alone is not effective for chromium removal is that most waters have pH values less than 14; thus, all of the sulfur added to the solution is not available in the ionic form of S^{2-}. Therefore, more sulfide than the stoichiometric requirement must be added to the solution to provide sufficient ionic S^{2-} for the reduction process. The speciation of sulfide is described below.

Three species of sulfide (H_2S, HS^-, and S^{2-}) exist in aqueous solutions depending on the pH of the solution. The distribution of S species ($H_2S/HS^-/S^{2-}$) versus the pH of solution is calculated from the following equations and using MINEQL+ computer code (Schecher and McAvoy, 2001) (Figure 2.20):

$$H_2S \leftrightarrow H^+ + HS^- \qquad K_1 = 10^{-7.02} \qquad (2.118)$$

$$HS^- \leftrightarrow H^+ + S^{2-} \qquad K_2 = 10^{-17.3} \qquad (2.119)$$

The K_2 value is high and reported to be approximately 17 by Stumm and Morgan (1996).

Hydrogen sulfide (H_2S) is the predominant sulfur species below pH 7, hydrosulfide (HS^-) becomes predominant between pH 7 to 14, and S^{2-} becomes the predominant species of S at a pH of approximately 14. Therefore, the extent of trivalent chromium precipitation is directly related to the pH of the solution.

Table 2.25 shows applications of H_2S, FeS, Na_2S, Na_2SO_3 and Na_2S as reductants to remove Cr(VI) from solutions. These reductants have removal efficiencies between 20 and 80%. An acidic pH value of 5 is favorable for Cr(VI) reduction by Na_2SO_3 and Na_2S. However, Na_2SO_3 and Na_2S are not efficient coagulants for Cr(VI) reduction.

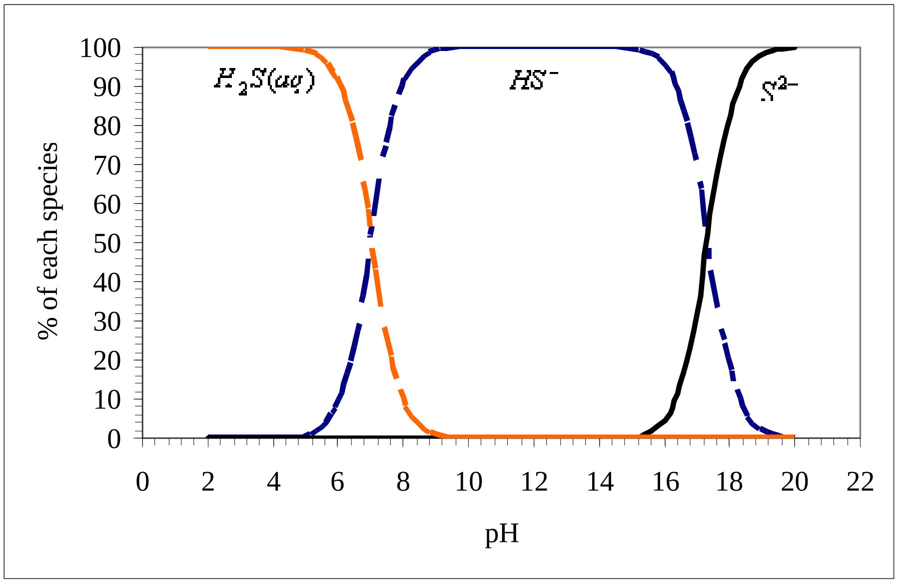


Figure 2.20 Computed Liquid-Phase Distributions of Ionic Species for $H_2S/HS^-/S^{2-}$ System (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001)

Table 2.25 Summary of Batch Studies on Cr(VI) Reduction in Synthetic Waters by Various Sulfide Containing Reductants

Reductant	RM Mol S^{2-}/mol Cr(VI)	Initial Cr(VI) (mg/L)	% Cr(VI) removal	pH	Reference
H_2S	1.5	0.2	36	7.8	Kim et al., 2001
FeS and Na_2S	2	3.3	100	-	Anon, 1998
Na_2SO_3	4.3	0.1	30	5-9	Lai and MacNeill, 2006
Na_2SO_3	43	0.1	50	5-9	Lai and MacNeill, 2006
Na_2S	43	0.1	80-20	5-9	Lai and MacNeill, 2006

Sodium sulfide has is not recommended as a reductant for Cr(VI) due to its long reaction time (120 h) (Lai and MacNeill, 2006). Calcium polysulfide shows the highest reduction efficiency in comparison with ferrous ammonium sulfate, sodium metabisulfate, and zero valent iron (Leoper et al., 2002).

Cr(VI) Removal by Coagulation Using Calcium PolySulfide

Calcium polysulfide as a reductant provides extra S^{2-} in the solution. Large excesses of calcium polysulfide therefore may not be required to remove heavy metals. The chemistry of metal precipitation with calcium polysulfide is similar to that for sulfide (Aratani et al., 1978):

$$MCl_2 + CaS_x \rightarrow MS_x + CaCl_2 + S_{x-1} \qquad (2.120)$$

Furthermore, decomposition of the metal polysulfide formed may result in production of insoluble metal sulfide and more sulfide ions (Aratani et al., 1978):

$$MS_x \rightarrow MS + S_{x-1} \qquad (2.121)$$

Calcium polysulfide decomposition is highly pH dependant and isaffected by the relative proportions of polysulfide, hydrosulfide, and hydroxide in the solution (Licht and Davis, 1997). However, chromate reduction does not depend on the S^{2-} concentrations in the solution, though it depends on the H_2S and CaS_2O_3 concentrations in the solution (Yahikozawa et al., 1978).

Calcium polysulfide is applicable to hexavalent chromium removal from waters and wastewaters at typical pH values without any pH adjustment. This product is highly alkaline ($pH > 11$) (Jacobs, 2001). Calcium polysulfide is relatively inexpensive at $1/gallon; it has good pH buffering capacity; it is stable and persistent (Storch, 2003). Calcium polysulfide (CaS_x) is commercially available as Cascade^{TM} (CaS_5) from Best

Sulfur Products, and comes as 29% of the active ingredient in the solution (Jacobs, 2001). Calcium polysulfide was formerly used as an insecticide or a disinfectant in agriculture (Yahikozawa et al., 1978). CaS_x is manufactured as a byproduct of the reaction of lime with sulfur, and it has a deep orange-red color with a sharp odor of rotten eggs. Hexavalent chromium can be reduced to Cr(III) and precipitated as chromium hydroxide using calcium polysulfide (Haas and Vamos, 1995; Yahikozawa et al., 1978).

In the presence of oxygen, calcium polysulfide rapidly decomposes to calcium thiosulfate (CaS_2O_3), hydrogen sulfide (H_2S), and solid sulfur in solution (Yahikozawa et al., 1978; Aratani et al., 1978). The equations for the decomposition of calcium polysulfide into thiosulfate (CaS_2O_3) and hydrogen sulfide (H_2S) can be represented as:

$$CaS_x + 1.5\ O_2 \rightarrow CaS_2O_3 + (x\text{-}2)S, \qquad (2.122)$$

$$CaS_x + CO_2 + H_2O \rightarrow CaCO_3 + H_2S + (x\text{-}1)S \qquad (2.123)$$

Chromium does not precipitate as chromium sulfide, but as chromium hydroxide (Yahikozawa et al., 1978). At acidic pH, dichromate dissociates to chromate, and chromate is subsequently reduced to Cr(III) by CaS_2O_3 and H_2S; the related equations are presented below (Aratani et al., 1978; Yahikozawa et al., 1978):

$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O,\ \text{and} \qquad (2.124)$$

$$2CrO_4^{2-} + 3S_2O_3^{2-} + 10\ H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 3S + 5H_2O, \qquad (2.125)$$

$$2CrO_4^{2-} + 3H_2S + 10\ H^+ \rightarrow 2Cr^{3+} + 3S + 8H_2O, \qquad (2.126)$$

Kim et al. (2001) studied the stoichiometry and kinetics of Cr(VI) reduction using hydrogen sulfide, and suggested the following stoichiometric reaction:

$$2CrO_4^{2-} + 3\ H_2S + 4H^+ \rightarrow 2\ Cr(OH)_3(s) + 3\ S(s) + 2H_2O \qquad (2.127)$$

Kim et al. (2001) reported a theoretical stoichiometry of 1.5 mol S^{2-} per mol Cr(VI) at pH 8.2 assuming that elemental sulfur and chromium hydroxide are the products of the process. A similar equation has been reported by Storch et al (2002), Messer et al. (2003), Graham et al. (2006), and Wazne et al. (2007a):

$$2CrO_4^{2-} + 3CaS_5 + 10H^+ \rightarrow 2\ Cr(OH)_3(s) + 15\ S(s) + 3\ Ca^{2+} + H_2O \qquad (2.128)$$

Yahikozawa et al. (1978) stated that the color change in the first 10 minutes of the coagulation process indicates the reduction of Cr(VI) according to equations (2.124-2.126). The initial color of the solution in their experiment was brown (dichromate); the color of the solution changed to yellow (chromate), and finally turned to light green ($Cr(OH)_3$). Another example of the overall reduction of Cr(VI) by calcium polysulfide is presented below.

Reduction of Cr(VI) by calcium polysulfide produces stable sludge that passes the TCLP test (Graham et al., 2006; Wazne et al., 2007a, Moon et al., 2008). The final sludge volume produced in the chromium removal process using calcium polysulfide is likely to be less than those produced in two step removal technologies using iron. However, the calcium polysulfide operation requires stringent safety precautions (Batista, 2006). The excess hydrogen sulfide in the process can be recycled to the aeration system and re-used (Yahikozawa et al., 1978).

A summary of studies of Cr(VI) reduction using calcium polysulfide is presented in Table 2.26. Addition of calcium polysulfide to the solution has been shown to rapidly reduce Cr(VI) to Cr(III) over the pH range of 8 to 12.5 (Graham et al., 2006). The process of removal of Cr(VI) using calcium polysulfide was more effective at pH 12 than at pH 9.5 (Wazne et al., 2007). By contrast, Graham et al. (2006) found decreasing the pH of the solution from 12 to 9.3 had a slightly negative effect on the efficiency of Cr(VI) removal from contaminated groundwater and chromite ore processing residue for a starting Sx:Cr(VI) ratio of ~1:1. The process was performed at lower pHs while higher volumes of calcium polysulfide were added to increase the pH (Licht and Davis, 1997). As such, Cr(VI) reduction was very efficient (> 99%) in the pH range of 5 to 12.8 (Yahikozawa et al., 1978). In view of the fact that calcium polysulfide is less expensive than acids, it is appropriate for the removal of Cr(VI) from waters and wastewaters at any pH values.

The CaS_x/Cr(VI) molar ratios required to remove 2.7 to 200 mgCr(VI)/L from waters were found to be between 8.3 to 0.88 (Table 2.26). The CaS_x/Cr(VI) molar ratios required to remove low concentrations of Cr(VI) from water are higher than those for high concentrations (> 30 mg/L) of Cr(VI) (Graham et al., 2006). The stoichiometric relationship (CaSx/Cr(VI)) for reduction of high concentrations of Cr(VI) (>30 mg/L) has been reported to be 1.66 and 1.5 by Graham et al. (2006) and Messer et al. (2004), respectively. This ratio is applicable when the contaminated water has low ionic strength, low alkalinity and no impurities (e.g. organic matter).

A calcium polysulfide dosage of 3 mol CaS_5 per 1 mol Cr(VI) was reported as effective in removing Cr(VI) from chromite ore processing residue (COPR); thus, the residue passed the EPA Toxicity Characteristic Leaching Procedure (TCLP) test with a maximum limit of 5 mg/L in a bench scale study (Wazne et al., 2007a). An ex-situ 1000-lb pilot scale batch test was conducted using a calcium polysulfide dosage of 3 mol CaS_5 per mol Cr(VI) over a period of 15 months. Results obtained 10 months after the experiment started showed that only 62% of the Cr(VI) was reduced by calcium polysulfide (Wazne et al., 2007a). Bench experiments showed that contaminated groundwater containing 24 mg Cr(VI)/L can be treated by adding calcium polysulfide, yielding 99% reduction; the amount of calcium polysulfide used yielded a CaS_x:Cr(VI) molar ratio of 5 to 7.5 (Leoper et al., 2002).

Table 2.26 Summary of Studies on Cr(VI) Reduction by Calcium Polysulfide

Type of Study	RM mol-CaS_x/ mol Cr(VI)	Initial Cr(VI) (mg/L)	% Cr(VI) removal	Initial pH	Final pH	Reference
Bench Scale Synthetic water (4 hours)	8.3 to 3.33	2.7 to 13.4	100	-	-	Graham et al., 2006
Bench Scale Synthetic water (4 hours)	1.67	26.8	98	-	-	Graham et al., 2006
Groundwater	1.8	45	100	7.7	9.1	Freedman et al., 2005
Bench Scale Synthetic water (4 hours)	1.66	67 to 134	100 to 50	-	-	Graham et al., 2006
CORP (TCLP)						
1 hour	2	103	70.6	9	9.59	Moon et al., 2008
1 month	2	103	99.9	9	10.24	
18 months	2	103	95.7	9	10.82	
CORP (TCLP)	3	103	100	9.7	10.20	Wazne et al., 2007b
1 month	3	165	100	9.5	10.16	
CORP (TCLP)						
1 hour	2	165	87.3	9	9.99	Moon et al., 2008
1 month	2	165	99.99	9	10.28	
18 months	2	165	97.1	9	10.22	
CORP Solution (1 mM NaCl)	2.3	180 to 220	100 to 77	10.7 to 9.4	between (8-12.5)	Graham et al., 2006
	2.3	30 to 180	100	12.1 to 10.7		
	0.88	20 to 200	100	12.0 to 10.9		
	1.4	30 to 200	100	12.8 to 11		
Groundwater Total Cr = 3550	1.31	3425	100	9.91	-	Graham et al., 2006

Cr(VI) reduction by calcium polysulfide is a quick process. It has been reported that 25 mg/L Cr(VI) has been removed within 30 minutes at pH 5 using calcium polysulfide with aeration (Yahikozawa et al., 1978). Graham et al. (2006) reported that 26.8 mg Cr(VI) / L was completely removed in 50 minutes using 0.1% (i.e. 2.15 mM) calcium polysulfide, and that the reaction followed pseudo-first-order kinetics (with a rate constant of 0.077 (1/min).

Calcium polysulfide has been utilized in geological fixation of aquifers contaminated with Cr(VI). Typically, calcium polysulfide has been applied at high CaSx:Cr(VI) molar ratios (> 10). The Cr(VI) in the aquifers was reduced when the oxidation-reduction potential of the aquifers became negative (reducing).

Calcium polysulfide was utilized for in-situ geological fixation of a contaminated groundwater containing 200 mg Cr(VI)/L at a depth of 165. Approximately 9,000 gallons of calcium polysulfide, along with 79,000 gallons of water was introduced into the aquifer. When the oxidation-reduction potential of the groundwater became negative, Cr(VI) levels dropped rapidly to less than 1 mg/L (Messer et al., 2003).

Calcium polysulfide was used to treat a contaminated (up to 150 mg Cr(VI)/L) carbonate aquifer in the southwest United States by Yu and Tremaine (2002). The aquifer was contaminated by an active chromate processing plant adjacent to a river. The calcium polysulfide (CASCADE^{TM}) was obtained from the Best Sulfur Products, and contained 14 moles of reactive sulfur per gallon of CASCADE^{TM}. The calcium polysulfide was applied to the aquifer per the manufacturer’s recommendation of 10 mole sulfur per mol Cr(VI). Efficiency of the process was evaluated by monitoring the Cr(VI) concentrations in the aquifer in samples obtained from various observation wells in the area. At the majority of the sampling areas, Cr(VI) was removed to below the standard. At those places where calcium polysufide was injected, up to 99% of the Cr(VI) was removed from the groundwater. However, in points further down-gradient from the injection wells, only 30% Cr(VI) removal was obtained (Yu and Tremaine, 2002). The geochemical environment in the aquifer was predominantly oxidizing. After injection of calcium polysulfide to the aquifer, the oxidation-reduction potential (E_h) of the aquifer at most of the observing locations were lowered (as expected) to negative values between -412mV and -503 mV, which are reducing geochemical conditions (Yu and Tremaine, 2002).

Reverse Osmosis

Chromium can be removed using reverse osmosis to very low levels (Hafez and El-Manharawy, 2004; Scholz and Lucas, 2003; Bilstad and Madland, 1992). Reverse osmosis plants require small installation space (Beszedits, 1988; Scholz and Lucas, 2003). No chemical addition is required for the process (Scholz and Lucas, 2003). However, high flow rates result in high cost; a major drawback of the process. Moreover, reverse osmosis generates large side stream brine concentrate (8-40% rejection depending on pretreatment and water quality) (REMCO, 2006; Scholz and Lucas, 2003; Beszedits, 1988). This means that part of the water being treated is wasted as concentrate in the process. Membrane fouling often occurs, which necessitates careful operation and maintenance.

Lime Softening

Lime can be used to increase the pH of a solution and to remove Cr(III). Typically, lime softening is a process used to remove hardness (i.e. Ca^{2+} and Mg^{2+}) from waters using lime (CaO) or soda ash (Na_2CO_3). The use of lime softening can also remove Cr(III) and other heavy metals (e.g. arsenic, mercury, lead) (MWH, 2005). For Cr(III) precipitation, pH adjustment to > 8.8 is required using lime or caustic soda. Good or excellent Cr(III) removal can, therefore, be achieved by lime softening, however, lime softening is not effective in removing Cr(VI) because Cr(VI) is soluble at all pH values (see Table 2.27).

Activated Carbon

Both Cr(VI) and Cr(III) can be removed by activated carbon. Like ion-exchange resins, there are two types of activated carbon, which exist in acidic and basic forms (Mohan and Pittman, 2006). Acidic activated carbons (L carbons) are prepared at 200-400°C; this develops acidic surface oxides that can adsorb bases (e.g. positively charged heavy metals in solution, such as Cr^{3+}). These activated carbons exhibit a negative zeta potential at favorable pH values, and are hydrophilic. They reduce the solution pH. Basic activated carbons (H carbons) are activated at 800-1000°C, possess basic surface oxides, and increase solution pH. Basic activated carbon has a positive zeta potential and adsorbs negative ions (e.g. CrO_4^{2-}) (Mohan and Pittman, 2006).

Advantages of activated carbon for chromium removal are: high surface area, high porosity, high capacity, high rate of adsorption and fast kinetics. However, activated carbon is expensive (depending on the type of carbon), has problems with hydrophilic substances, and has high reactivation costs. Moreover, the reactivation results in a loss of carbon (Mohan and Pittman, 2006).

The removal efficiency of activated carbon greatly depends on the type of activated carbon used in the treatment process. Granular Activated Carbon (GAC) has been shown to have Cr(III) or Cr(VI) removal efficiencies of up to 90%, while Powdered Activated Carbon (PAC) can remove up to 60% of Cr(III) or Cr(VI) from water (MWH, 2005). Modified activated carbon has been used to remove chromium, copper, zinc, and cyanide from an electroplating wastewater, and the efficiency of modified activated carbon was compared to that of plain activated carbon. The modified activated carbon showed a 6.84 mg Cr per g-carbon capacity. Both Cr(III) and Cr(VI) removal are favored at acidic pH $<$ 6 (Mohan and Pittman, 2006). Maximum adsorptions of Cr(III) and Cr(VI) have been shown to occur at pH 5 and 4, respectively (Mohan and Pittman, 2006). Cr(III) and Cr(VI) concentrations of 20 to 1000 mg/L can be removed from solutions using activated carbons (Aggarwal et al., 1999).

Effectiveness of various treatment technologies (i.e. ion-exchange, reverse osmosis, coagulation, lime softening, and activated carbon) for chromium removal are compared in Table 2.27.

Ion-exchange and reverse osmosis have been shown to be excellent technologies for Cr(III) and Cr(VI) removal. Both technologies are able to remove chromium completely from waters. However, both technologies generate residual wastes having high ion strengths, high alkalinities, and high concentrations of chromium. There is little knowledge available to address chromium removal from brines and there is a high demand to document and optimize the process. Conventional coagulation is only efficient in Cr(III) removal, and requires pH adjustments. Cr(VI) can be reduced and removed from waters and wastewaters by redox-assisted coagulation. Activated carbon is not as efficient as ion-exchange and has similar disadvantages to ion-exchange such as high cost and the requirement to reactivate the carbon used in the process.

Table 2.27 Overall Effectiveness of Water Treatment Process for Cr(III) and Cr(VI) (MCL 0.1 Mg/L) (MWH, 2005).

Water treatment processes	% Cr(III) removal	% Cr(VI) removal
Ion-exchange (anion)	0	90-100
Ion-exchange (cation)	90-100	0
Reverse Osmosis	90-100	90-100
Coagulation	60-100	0
Coagulation/reduction: Ferrous	80-90	15-100
Coagulation: Alum and Ferric Chloride	20-99	0-10
Coagulation/reduction: H_2S, Na_2S, and Na_2SO_3	0	20-80
Coagulation/reduction: CaS_x	90-100	95-100
Lime Softening	60-100	0
Activated Carbon	20-90	20-90

CHAPTER 3

METHODOLOGY

3.1. Work Plan to Address Issue One

Issue One of this research focused on the use of perchlorate and nitrate specialty resins in removing inorganic contaminants, other than those for which the resin was designed. The hypotheses put forth for Issue One of this research were:

Hyothesis a) Perchlorate and nitrate selective specialty resins were expected to be more efficient in removing nitrate, and less efficient in removing arsenic, selenium, and chromium than conventional resins. The reason for this was that the active sites in perchlorate and nitrate specialty resins were spaced farther apart due to larger alkyl functional groups than those in conventional resins. Although perchlorate and nitrate specialty resins might exchange divalent ions (i.e., sulfate (SO_4^{2-}), hydrogen arsenate ($HAsO_4^{2-}$), chromate (CrO_4^{2-}), or selenate (SeO_4^{2-})), resulting in the formation of weak bonds, it was expected that the removal of divalent ions was not as effective as the removal of monovalent ions (i.e., perchlorate or nitrate).

Hypothesis b) Nitrate-laden, arsenic-laden, chromium-laden, and selenium-laden perchlorate specialty resins were expected to be regenerable using a 8-12% NaCl solution because of the selectivity of perchlorate specialty resin for arsenic, chromium, selenium, and nitrate species were expected to be less than this resin's selectivity for perchlorate.

3.1.1. Experimental Approach

To test hypotheses a and b, a series of breakthrough curves were generated by performing a series of laboratory minicolumn tests. The breakthrough curves for perchlorate and nitrate specialty resins were compared with the conventional resin's breakthrough. Furthermore, the possibility of the regeneration of the spent resins was evaluated using an 8 to 12% NaCl solution.

3.1.2. Experimental Procedure for Laboratory Breakthrough Curves Generation

Three perchlorate specialty resins (SIR 111, SIR 110 HP and PWA2) and one nitrate specialty resin (SIR 100, ResinTech) were examined for nitrate removal from synthetic waters using minicolumns, and their performances were compared with each other and to a conventional Type 1 resin (SBG1, ResinTech). A perchlorate specialty resin (SIR110 HP), a nitrate specialty resin (SIR100), and a concentional resin (SBG1) were examined for chromium (VI), selenium (VI), and arsenic (V) removal from drinking water. Their performances were compared with each other.

Characteristic of Resins Selected for the Study

Perchlorate specialty resins that were evaluated include SIR110 and SIR111 from ResinTech and PWA2 from Rohm and Haas. SIR 100 and SBG1 are a nitrate specialty resin and a conventional resin, respectively, from ResinTech (Table 3.1). Selectivity coefficients reported by the manufacturer are presented in Table 3.2.

Laboratory Ion-Exchange Minicolumn Design

The design of minicolumns must follow a series of relationships, taking into consideration the fact that data obtained from the small-scale laboratory columns are usually used for the construction of the large-scale columns, and for predicting the performance of the large-scale columns. The major parameters for which the laboratory ion-exchange experiments must be designed are: diameter of the column, length of the column, the aspect ratio of the column (ratio of length and diameter), required mass transfer zone (MTZ), empty bed contact time (EBCT), service flow rate, regenerant concentration, regenerant contact time, and regenerant flow rate. The theories behind the minicolumn design have been previously discussed in section 2.4.

Table 3.1 Characteristic of SBG1, SIR100, SIR111, PWA2, and SIR110

Resin	Manufacturer	Capacity meq/l	Polymer structure	Functional Group
SBG1 (conventional or non-selective)	ResinTech	1300	Styrene-DVB	$R\text{-}N\text{-}(CH_3)_3^+Cl^-$
SIR100 (nitrate selective)	ResinTech	960	Styrene-DVB	$R\text{-}N\text{-}R_3^+Cl^-$
SIR111-Macroporous (perchlorate selective)	ResinTech	560	Styrene-DVB	$R\text{-}N\text{-}(C4H_9)_3^+Cl^-$
PWA2 (perchlorate selective)	Rohm and Haas	600	-	N.A.
SIR110-HP (perchlorate selective)	ResinTech	600	Styrene-DVB	$R\text{-}N\text{-}(C4H_9)_3^+Cl^-$

Column diameters of one to five centimeter are recommended for the small-scale column experiments (MWH, 2005). In this research, the minicolumn diameter was considered to be at least thirty times greater than the average resins bead's diameter.

To determine the required MTZ for the resins used in this research, a series of laboratory experiments were performed for nitrate removal using SBG1, SIR100, SIR110, SIR111, and PWA2. The SIR100 showed the largest MTZ length among all the breakthrough curves obtained for the resins used. Therefore, the SIR100 breakthrough curve was selected for the MTZ calculations. The results of the calculation are summarized in Table 3.3. The detailed calculations are presented in Appendix 3.

Table 3.2 Selectivity Coefficients Reported by the Manufacturer for SIR110, SIR111, PWA2, SIR100, and SBG1

Ions	SBG1 selectivity coefficient	SIR100 Selectivity coefficient	SIR 110 Selectivity coefficient	SIR 111 Selectivity coefficient	PWA2 Selectivity coefficient
Cl^-	1.00	1	1	1	1
HCO_3^-	0.25	0.2	0.2	0.2	0.2
NO_3^-	4	6	23	23	23
SO_4^{2-}	0.15	0.03	0.003	0.003	0.003
ClO_4^-	500	500	3500	3500	3500
$HAsO_4^{2-}$	0.075	0.015	0.0015	0.0015	0.0015
CrO_4^{2-}	1.3	0.2	0.03	0.03	0.03

The critical MTZ for an ion-exchange column with a four centimeter diameter was 0.7 to 0.8 cm, which showed that the MTZ was not a determining factor for the selection of the length of the resin bed.

The length of the resin column can be determined according to the required aspect ratio of the column. The aspect ratio of the column is the ratio of length and diameter. A high aspect ratio increases the column utilization (Helfferich, 1995). The aspect ratio is usually determined and provided by the manufacturers. It has been suggested that the lab column aspect ratios of greater than 4:1 (length to diameter) are the best, and the appropriate commercial column aspect ratios are between 2:1 and 4:1 (length to diameter) (DOW website). At a constant diameter (or cross section) of the column, increasing the length of the column increases the breakthrough and the overall capacity of the operation. In this research, the aspect ratio of 5:1 (length to diameter) was used. The process of sizing the columns is presented in Table 3.4.

The service flow rates in the ion-exchange column experiments must follow the recommendations of the manufacturers. The EBTC was calculated by choosing a volume (based on the required diameter and length) and knowing the service flow rate.

Table 3.3 Summary of the Results of the MTZ Calculations

Parameter	Value
mL of resin	10
Density, kg/m^3	673
Resin, Kg	0.006735
Surface Area, m^2	0.001256
Total mass passed after breakthrough, kg	0.000600
Total mass retained, kg	0.000330
Mass escaped after breakthrough, kg	0.000303
Mr, kg	0.000297
$(X/M)_{ult}$	0.048999
MTZ, m	0.007
MTZ, cm	0.72

In this research, the length of 10 cm and the diameter of 2.54 centimeter were selected for the ion-exchange process. Therefore, the volume of the resin was 50 ml. The suggested volumetric flow rates by the manufacturers were used to determine the required empty bed contact time and the service flow of the column experiments. The volumetric flow rates are shown in Table 3.5. The volumetric flow rate of 3.00 gpm /cu.ft. was selected for the resin loading process. In all the experiments that were conducted, the resin volume was 50 milliliters and the flow rate was 25 ml/minutes. This flow rate equals two minutes of empty bed contact time for the resin. The experiments were performed with an empty bed contact time (EBCT) of two minutes.

Table 3.4 Sizing the Ion-Exchange Minicolumns

Resin name	Diameter (mm)		Required Diameter 30 ×Resin diameter (cm)		Selected diameter (cm)	Selected aspect ratio (length to diameter)	Column length (cm)
	Min.	Max.	Min.	Max.			
SBG1	0.297	1.2	0.891	3.6	2.5	4	10
SIR100	0.297	1.2	0.891	3.6	2.5	4	10
SIR110 HP	0.297	1.2	0.891	3.6	2.5	4	10
SIR111	0.297	1.2	0.891	3.6	2.5	4	10
PWA2	0.297	1.2	0.891	3.6	2.5	4	10

Glass beads and wool were placed at the bottom of the column to assist with flow distribution. Fifty milliliters of each dry resin were respectively placed in a 2.54 centimeter glass column. The feed water was pumped through the columns. The pump had an adjustable speed, and was adjusted to pump 25 ml of the feed water into the columns. Samples were collected using a Foxy 200 autosampler. The schematic drawing of the equipment for the treatment of the feed water is presented in Figure 3.1.

The required volume of the feed water also was calculated based on the influent concentrations and the equilibrium equations, which are similar to those presented in Appendix 1. This calculation was required to assure the complete exhaustion of the resin to generate complete breakthrough curves. A sample of calculations to find the required volumes of feed water for the SIR100 resin is presented in Table 3.6. One hundred and ninety one liters of feed water is required for the nitrate removal column experiment using SIR100.

The volume of the resin was known and the liters of feed water required was calculated as the volume of the resin multiplied by the number of BVs required for the complete exhaustion.

Table 3.5 Suggested and Selected Feed Rate Velocities for the Ion-exchange Full-Scale and Mini-Column Experiments Using Five Selected Resins

Resin name	Suggested vol. flow rates by manufacturer		Selected Vol. flow rate(gpm / cu.ft.)	Selected flow rate(ml per min. / ml of resin)	Resin volume (ml)	Service Flow of the column (ml per min. per 50 ml of resin)	EBCT (min)
	Min.	Max.					
SBG1	2	4	3	0.401	50	25	2.0
SIR100	2	4	3	0.401	50	25	2.0
SIR110 HP	n.a.	n.a	3	0.401	50	25	2.0
SIR111	n.a.	n.a	3	0.401	50	25	2.0
PWA2	n.a.	10	3	0.401	50	25	2.0

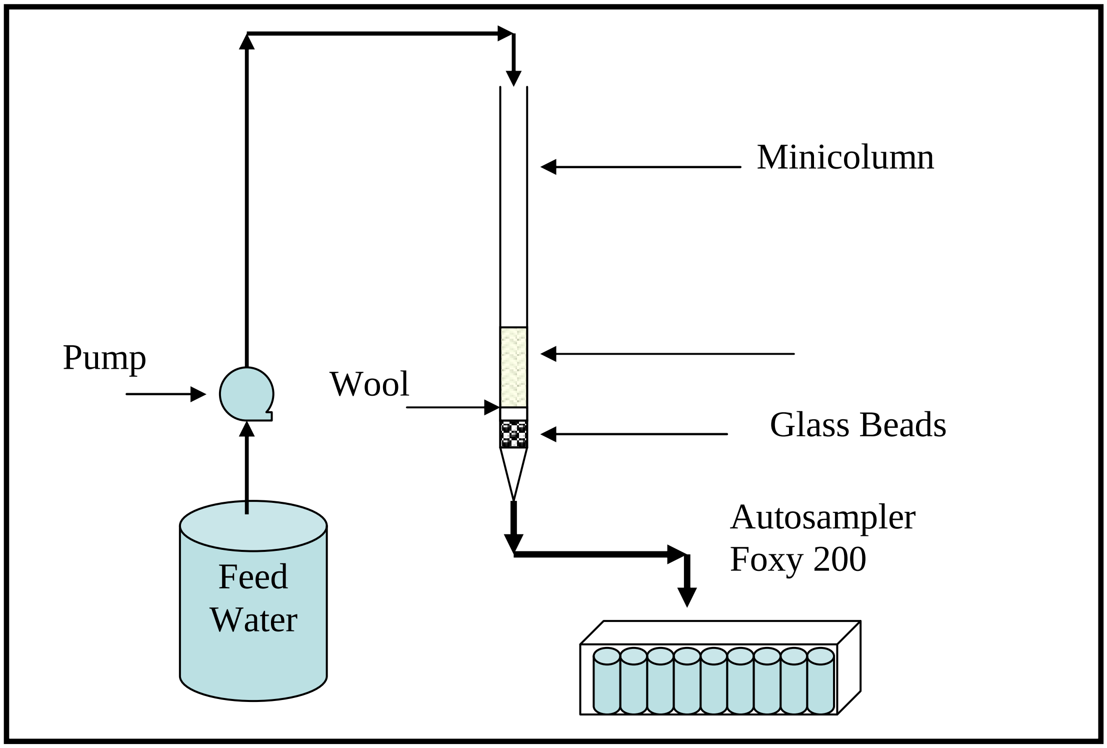


Figure 3.1 Laboratory Ion-Exchange Minicolumn Loading Process

Sodium chloride is typically used for the regeneration of resins. The regeneration process prepares the resin for the next loading cycle by replacing the contaminant ions accumulated inside the resin with chloride. The regeneration process is more effective when sodium chloride solution is more concentrated. Sodium chloride has high solubility in water, and almost 359 grams of sodium chloride can be dissolved in one liter of water (35% NaCl) at 25ºC (Feldman, 2005). However, typically, 4% to 12% NaCl (0.68 to 2.05 eq/L NaCl) solutions are used for the regeneration of the strong base anion-exchange resins because of the limited capacity of the SBA resins. The maximum capacity of the SBA resins is up to 1.5 eq/L. Therefore, one to two BVs of 4% to 12% sodium chloride solution is sufficient to regenerate an exhausted resin. In this research, a 8% NaCl solution was used for the regeneration processes.

Table 3.6 Calculations to Determine the Required Feed Water for Exhaustion of SIR100 When Removing Nitrate from Synthetic Water Using a Minicolumn

Resin Name	SIR 100
Volume (ml)	252
Density (kg/m^3)	673
Resin, kg	0.169596
Nitrate for exhaustion, kg	0.015
Influent nitrate, mg/L	80
L of feed water required	191
BVs of feed water	757

The regeneration flow rate was slower than the service flow rate. In the regeneration process, a certain regenerant contact time is required for attainment of equilibrium between the sodium chloride solution and the resin. This time allows for the transfer of the chloride ion from the solution to the resin-phase. This time must also allow the accumulated ions to transfer from the resin-phase to the solution. In view of the fact that the exhausted resin is saturated with various ions, more time is required for the regeneration process in comparison with the ion-exchange treatment process (MWH, 2005). The recommended flow rates for the regeneration of the selected resins are presented in Table 3.7. An empty bed contact time of 40 minutes was used for the regeneration of the resins. One bed volume (50 mL) of 8 % NaCl was pumped into the column up-flow at the speed of 40 minutes per BV. The regeneration process was continued for 10 BVs.

The regeneration process is presented in Figure 3.2. The regenerant solution was pumped up-flow to the column and samples were collected from the top. For sample collection purposes, a Foxy 200 autosampler was used.

Table 3.7 Calculations of the Required Regeneration Flow Rate Based on the Manufacturers' Recommendations

Resin name	Suggested regenerant contact time (min)	Selected regenerant contact time (min)	Resin Volume (ml)	Regeneration Flow rate, ml/min/50 ml resin	Regeneration Flow rate, gpm/ cu. ft.
SBG1	40	40	50	0.8	0.2
SIR100	30	40	50	0.8	0.2
SIR110	n.a.	40	50	0.8	0.2
SIR111	n.a.	40	50	0.8	0.2
PWA2	n.a.	40	50	0.8	0.2

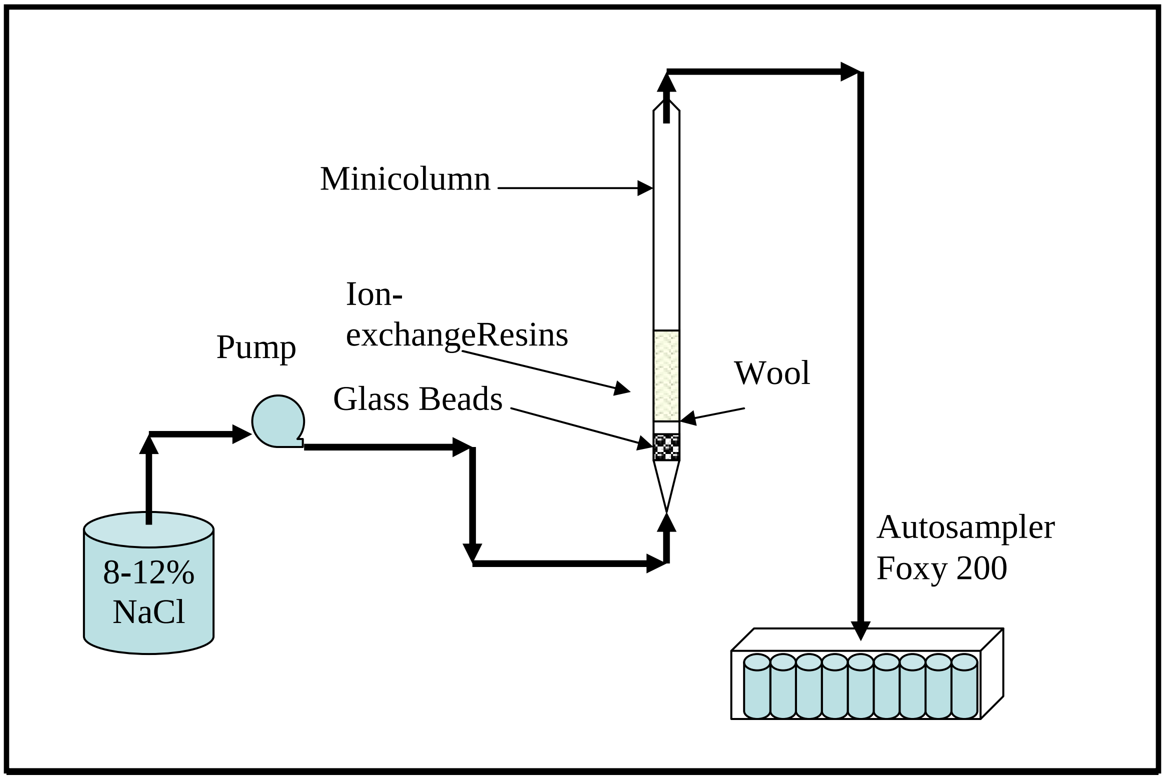


Figure 3.2 Regeneration Process for a Laboratory Ion-Exchange Column

Experimental Set-Up for Nitrate Removal Using Perchlorate and Nitrate Selective Specialty Resins

Perchlorate selective resins have very high selective coefficients for nitrate (e.g., 23 as compared to 6 for nitrate selective specialty resins as outlined in Table 3.2). Some waters are contaminated with both perchlorate and nitrate, and it is therefore of value to examine how perchlorate selective specialty resins performing with nitrate removal. For each resin, a column run experiment was performed according to the set up presented in Table 3.8. This water composition is a typical composition of the contaminated (by nitrate) groundwaters that are being treated by the ion-exchange process in California. Compositions of a series of groundwaters were collected, and the average concentrations of each constituent were used. The effluent of the ion-exchange column was monitored for nitrate concentration at equal time intervals until the breakthrough of the column occurs. The effluent water was sampled with a Foxy 2000 auto-sampler. The breakthrough curves were constructed using Microsoft Excel in which contaminant concentrations versus the bed volumes of water passed through the column are presented. In total, five column runs (considering 5 resins) were conducted to study the nitrate removal by the specialty resins.

Table 3.8 Column Run Set-Up to Evaluate the Results Generated for Nitrate Removal

Column Run No.	1	2	3	4	5
Resin	SBG1	SIR100	SIR110	SIR111	PWA2
Cl^- (mg/L)	60	60	60	60	60
HCO_3^- (mg/L)	180	180	180	180	180
NO_3^- (mg/L)	80	80	80	80	80
SO_4^{2-} (mg/L)	100	100	100	100	100
ClO_4^- (mg/L)	0.02	0.02	0.02	0.02	0.02

The spent resins were regenerated, and the regeneration (elution) curves were produced showing the contaminant concentrations versus the bed volumes of the regenerant used for the process. A twelve percent NaCl solution was used at a slow flow rate to regenerate the spent resins. The set up for the regeneration processes for the five spent resins used are presented in Table 3.9.

Experimental Set-Up for Arsenic, Selenium, and Chromium Removal Using Perchlorate and Nitrate Selective Specialty Resins

To study arsenic (V), chromium (VI), and selenium (VI) removal, column experiments were conducted for three ion-exchange resins, which are SIR 110 (perchlorate selective), SIR 100 (nitrate selective), and SBG1 (conventional) from ResinTech. To obtain a typical water quality composition, the water compositions of various wells of the Southwestern regions of the United States were obtained. Table 3.10 outlines the typical concentration ranges of major water constituents in parts of the Southwestern regions of the United States. The average of each constituent was selected as typical water quality.

Table 3.9 Regeneration Set-Up to Evaluate the Results Generated for Nitrate Removal

Regeneration Run No.	1	2	3	4	5
Resin	SBG1	SIR100	SIR110	SIR111	PWA2
Regenerant	NaCl	NaCl	NaCl	NaCl	NaCl
Regenrant dose	12%	12%	12%	12%	12%
Regenerant volume (BV)	5	5	5	5	5

Nine column runs were performed in duplicate to evaluate arsenic (V), selenium (VI), or chromium (VI) removal by perchlorate and nitrate specialty resins. The experimental set up for column runs is presented in Table 3.11. The total feed water required, the frequency of sample collection, and the total number of samples was determined.

Table 3.10 Common Water Constituents in the Contaminated Wells in the Southwestern Regions of the United States (Compiled from the Water Quality Database of Basin Water Inc., Rancho Cucamonga, CA)

Constituent	Concentration Range	Average	Median	Unit
Chloride	2-100	71	37	mg/L
Bicarbonate	12-500	192	180	meq/L
Sulfate	1-500	168	96	mg/L
Nitrate	10-140	18	14	mg/L
Arsenic	10-100	33	26	µg/L
Selenium	0.06-400	200	-	µg/L
Chromium	5-3000	627	9	µg/L

The spent resins were regenerated using a 12% NaCl solution. The regeneration set-up is presented in Table 3.12. Nine elution curves were produced from the laboratory experiments and then compared with each other.

3.2. Work Plan to Address Issue Two

Issue Two of this research deals with arsenic removal from ion-exchange brines using ferric chloride. The coagulation batch precipitation tests were performed to investigate the effects of pH, ionic strength, ferric chloride dosage, initial As(V) concentration, and alkalinity on As(V) removal from brines using ferric chloride. Adsorption modeling based on the chemical equilibrium using MINEQL+ was also performed to evaluate potential removals of arsenic (V) with ferric chloride and to support the experimental data. MINEQL+ is a chemical equilibrium modeling system, and the surface adsorption can be modeled by this software. As(V) removal from drinking waters using ferric chloride is a well documented process, and it is widely accepted that the main mechanism of As(V) removal using ferric chloride is adsorption. As(V) is adsorbed into the hydrous ferric oxide (HFO) precipitates. The effects of pH and co-contaminants on arsenic removal from drinking water are also known. However, there has not been a research effort published to directly address arsenic removal from ion-exchange brines using ferric chloride. In this research, the required ferric chloride dosages intended for the treatment of various arsenic concentrations were determined for various major characteristics of brines. In addition, the effects of ionic strength, alkalinity, and pH on arsenic removal by ferric chloride were investigated. Hypotheses set forth for Issue Two of this research were:

a) Compared to As(V) removal from drinking waters using ferric chloride, As(V) removal from brines was expected to be more efficient because high ionic strength reduced the electrostatic repulsion forces and therefore facilitated particle aggregation in waters.

b) High alkalinity depressed arsenic removal.

3.2.1. Experimental Approach

To test the hypotheses a and b for Issue Two, a series of coagulation batch experiments were performed. The effects of pH, ionic strength, and alkalinity on the adsorption of arsenic onto HFO precipitates were investigated when removing various concentrations of arsenic.

The first objective was to determine the optimum pH for As(V) removal from brines using ferric chloride. To study the effects of pH, As(V) adsorption were investigated when using ferric chloride at a constant Fe/As molar ratio of 4 for various synthetic brines (various ionic strengths and alkalinities) at different pH values (ranging from 1-14). Similar condition was modeled using MINEQL+. The description of MINEQL+ is presented in the next section. Experimental data and the results of adsorption modeling were presented in graphs showing the percent of arsenic removed versus pH, and therefore optimum pH of the process was determined.

Table 3.11 Column Run Set-Up for Arsenic, Selenium, or Chromium Removal

Column Run No.	6	7	8	9	10	11	12	13	14
Resin	SBG1	SIR100	SIR110	SBG1	SIR100	SIR110	SBG1	SIR100	SIR110
Chloride (mg/L)	50	50	50	50	50	50	50	50	50
Bicarbonate (mg/L)	250	250	250	250	250	250	250	250	250
Sulfate (mg/L)	250	250	250	250	250	250	250	250	250
Arsenic (µg/L)	50	50	50	-	-	-	-	-	-
Selenium (µg/L)	-	-	-	200	200	200	-	-	-
Chromium (µg/L)	-	-	-	-	-	-	1000	1000	1000
Resin volume (ml)	10	10	10	10	10	10	10	10	10
Column diameter (cm)	1	1	1	1	1	1	1	1	1
Flow rate (ml/min)	5	5	5	5	5	5	5	5	5

Required ferric dosages at optimum pH were found by conducting 12 coagulation batch tests (9 different ferric chloride dosages and 3 replicas) for each initial As(V) concentration. These experiments were performed at a constant optimum pH of 5.5 or 6.5 for various As(V) concentrations while increasing ferric chloride concentration to achieve the desired removal efficiency. For each concentration of arsenic, a graph was made showing the percent of arsenic removal efficiencies at a constant optimum pH of

5.5 or 6.5 versus ferric chloride dosages applied in different batches. Similar conditions were modeled using MINEQL+ to support the experimental data.

Table 3.12 Regeneration Set-Up for Arsenic, Selenium, or Chromium Removal

Regeneration Run No.	6	7	8	9	10	11	12	13	14
Resin	SBG1	SIR100	SIR110	SBG1	SIR100	SIR110	SBG1	SIR100	SIR110
Regenerant	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl
Regenrant dose	12%	12%	12%	12%	12%	12%	12%	12%	12%
Resin volume (ml)	10	10	10	10	10	10	10	10	10
Column diameter (cm)	1	1	1	1	1	1	1	1	1
Regeneration rate (ml/min)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Regenerant volume (BV)	5	5	5	5	5	5	5	5	5
Frequency of sample collection (BV)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Total Number of samples	25	25	25	25	25	25	25	25	25

To study the effect of ionic strength and alkalinity, three As(V) concentrations (low, medium, and high) were chosen for adsorption modeling at different ionic strengths and alkalinities. For each arsenic concentration, a series of adsorption batch experiments were performed by increasing ferric chloride dosages at various ionic strengths or alkalinities. For each concentration, a graph was made showing the percent of As(V) removed versus the ferric chloride dosages for different ionic strengths or alkalinities. These data were also modeled using MINEQL+.

The concentration of dissolved arsenic before and after the batch experiments was measured. To measure arsenic concentration after coagulation, solids were separated from the liquid by gravity sedimentation. The pH of each batch was measured before and after the experiment.

Modeling was performed to replicate the experimental results. The results of modeling and experiments were compared and discussed. The modeling supported the experimental data and also can be used as a tool for the design purposes of ion-exchange brine treatment units.

Typical Brine Composition

Ion-exchange residual waste qualities from various plants in Arizona and California were evaluated (Basin Water Inc., Rancho Cucamonga, CA). Ion-exchange residual waste usually had high concentrations of soluble As(V). Data obtained for brine quality from ion-exchange As(V) removal plants in Arizona and California are presented in Table 3.13. Modeling simulations and coagulation experiments were designed according to these data.

Table 3.13 Typical Brine Quality

Constituent	Concentration
Arsenic	5-100 mg/L
Chromium	5-100 mg/L
Alkalinities	20-200 meq/L
Sulfate	100-1000 meq/L
pH	8-10
NaCl	6% - 12%

3.2.2. Modeling of Arsenic Removal Using Ferric Chloride by MINEQL+

Software Description

MINEQL+ is a chemical equilibrium software that has the ability to model the surface adsorption of arsenic into ferric hydroxide precipitates. MINEQL+ has a two-layer adsorption model, which can be used to predict arsenic removal from brines during coagulation. Adsorption of arsenic from drinking waters has been previously modeled with physicochemical models (Holm, 2002; Hering et al., 1997; Hering et al., 1996a; Wilkie and Hering, 1996).

Adsorption is assumed as the only mechanism for arsenic removal and therefore co-precipitation of arsenic by ferric hydroxie/oxide precipitates is not considered in MINEQL+. In view of the fact that adsorption is the main mechanism of arsenic removal using ferric chloride, not including the co-precipitation in the modeling should have a little impact on the results. The general reaction when ferric chloride is added to a solution is:

$$FeCl_3.6H_2O + 3HCO_3^- \rightarrow Fe(OH)_3(am) \downarrow + 3Cl^- + 3CO_2 + 6H_2O \quad (3.1)$$

The reactions—2.58 to 2.66 and 2.73 to 2.75—plus the following reactions and their equilibrium constants are assumed to occur in the arsenic removal process by ferric chloride:

$$H_2O \leftrightarrow H^+ + OH^- \qquad K_W \qquad (3.2)$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad K_1 \qquad (3.3)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \qquad K_2 \qquad (3.4)$$

$$\equiv FeOH_2^+ \leftrightarrow \equiv FeOH^o + H^+ \qquad K_{a1}^{app} \qquad (3.5)$$

$$\equiv FeOH^o \leftrightarrow \equiv FeO^- + H^+ \qquad K_{a2}^{app} \qquad (3.6)$$

$$\equiv FeOH^o + AsO_4^{3-} + 2H^+ \leftrightarrow \equiv FeHAsO_4^- + H_2O \qquad K_{2A}^{app} \qquad (3.7)$$

The Coulombic correction factor was used for the correction of the intrinsic equilibrium K values based upon the influence of pH and ionic strength. The following species are present in the anion surface complexation: H^+, OH^-, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}, $\equiv FeOH^o$, $\equiv FeOH^{2+}$, $\equiv FeO^-$, $\equiv FeAsO_4^{2-}$, and $\equiv FeHAsO_4^-$.

The following components were selected and considered in adsorption calculations: H2O, H^+, AsO_4^{3-}, CO_3^{2-}, Cl^-, Fe^{3+}, coul., Fe(st)OH, and Fe(wk)OH. When $FeCl_3$ is added to water, $Fe(OH)_3$ solids are formed and pH decreases. These solids contain active adsorbing surfaces to which arsenic is adsorbed. The initial conditions of the brine were established as the first step by entering the concentrations of all elements in the brine, except the ferric chloride concentration. The condition of the system is assumed to be closed to the atmosphere; therefore, total carbonate concentration can be calculated automatically by entering the pH and total alkalinity by MINEQL+. Ionic strengths were also automatically calculated by MINEQL+. The ion balance report was evaluated and the amount of charge discrepancy in the system was corrected by adding Na^+ to the system. The pH of the system was calculated by MINEQL+ to satisfy the electroneutrality of the system. The initial pH was the optimum pH or the experiment pH. At this point, the program was ready for an adsorption multiple titration modeling. The two-layer FeOH was chosen from available adsorption models. The two-layer FeOH model in MINEQL+ is designed according to the findings of Dzomback and Morel (1990).

The adsorption model in MINEQL+ requires the surface area of ferric chloride precipitates for the adsorption calculations. The surface area of HFO was considered 600 m^2/g in MINEQL+ (Dzomback and Morel, 1990).

3.2.3. Laboratory Experiments Procedure

To test the arsenic removal from brines using ferric chloride, a series of batch experiments were conducted at the Environmental Lab, Department of Civil Engineering, UNLV. Coagulation batch experiments were conducted on synthetic brine solutions using a PB-700 standard JarTester from Phipps & Bird. The JarTester has six 1” × 3” stainless steel paddles, spaced six inches apart (Figure 3.3). The JarTester mixing speed is adjustable.

The batch experiments were performed in one liter beakers utilizing 250 ml of the synthetic brine solution. pH and arsenic concentration of the synthetic solution were measured prior to adding ferric chloride. pH measurement in brines must follow specific procedure. pH must be corrected considered the effect of ionic strength on the activity of hydrogen ion. Pitzer equations can be used for thie pupose. The pH measurement in brines is addressed in Appendix 4. The final pH in the coagulation test is a very important parameter. Adding ferric chloride to the brine decreases the pH. A titration curve was constructed showing the concentrations of ferric chloride added to the solution versus the pH decrease. Therefore, the pH decrease for a known concentration of ferric chloride can be anticipated. The pH of each solution was adjusted to the desired value using sulfuric acid. Coagulation treatment experiments were performed for two minutes rapid mix at 120 rpm right after ferric chloride addition, followed by a thirty minutes slow mix at 30 rpm for flocculation. After the mixing process is completed, the beakers were stayed in place for thirty minutes allowing the suspended precipitates to settle down and the solution to reach equilibrium. The pH of the solution was recorded. To measure the remaining soluble arsenic, the liquid and solids must be separated prior to the measurements. Twenty milliliters of the treated brine solution were collected for arsenic measurement, and the sample was centrifuged at 3500 rpm for thirty minutes using a Sorvall Legend RT centrifuge to separate the liquid from the solids (Figure 3.4).

The arsenic concentration of centrifuged samples was measured using an AA 5300 spectrometer. The volumes of sludge produced were also measured using a 500 mL measuring cylinder. The solutions were homogenously mixed and 25 mL of the mixed solution was transferred to glass vials for turbidity measurements using a 2100N Hach turbidity meter (Figure 3.5).

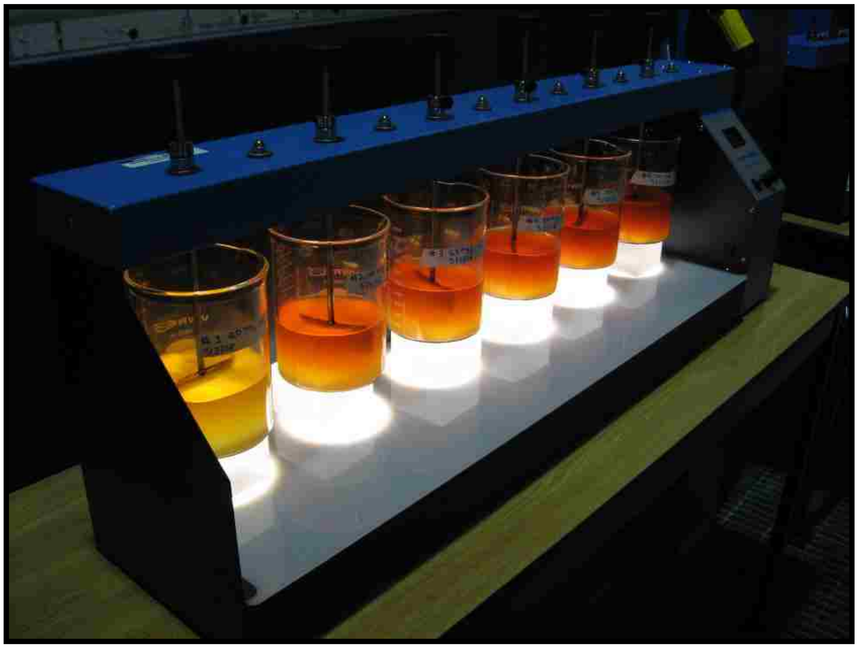


Figure 3.3 Batch Experiments Using JarTester

Figure 3.4 20 mL of Solutions Were Centrifuged for the Solid/Liquid Separation Using Sorvall Legend RT

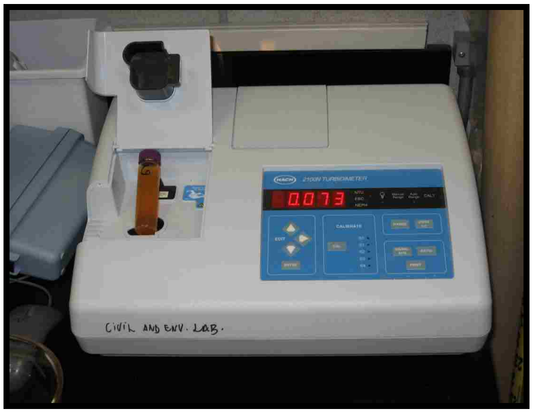


Figure 3.5 Turbidity Was Measured Using a 2100N Hach Turbidity Meter

All solutions were prepared using deionized (DI) water. The source of DI water was tap water, which was pretreated by the activated carbon and reverse osmosis columns from the Culligan Company, and deionized by a Barnstead Nanopure system. The glassware was soaked in an acidic solution for 24 hours and completely washed with Microclean and was rinsed three times by deionized water. Primary stock solution (1000 mg/L) for arsenic was prepared by sodium hydrogen arsenate granules ($Na_2HAsO_4.7H_2O$) from the Alfa Aesar Company. The 1000 mg/L arsenic stock solution was utilized to prepare the synthetic brine solutions. A ferric chloride stock solution (100 g/L) was prepared from the 540 g/L of $FeCl_3$ from the Fisher Scientific Company. To make the synthetic brines, 99.9% NaCl granules from EMD Chemicals was added to deionized water. Sodium bicarbonate ($NaHCO_3$) from the EMD Chemicals Inc. was used to provide alkalinity in brines. A 2N sulfuric acid solution was prepared using a stock solution of 99% sulfuric acid from the VWR Company. The 2N sulfuric acid solution was used to adjust the pH.

3.2.4. Experimental Design

Effects of pH

To study the effects of pH on the As(V) removal efficiency, a series of batch experiments were conducted according to the following Table 3.14. As(V) concentration and alkalinity in all batches were 50 mg/L and 50 meq/L, respectively. In this research, the ferric and As(V) ratio of 4 was used to study the effects of pH on As(V) removal from brines using ferric chloride. The optimum Fe/As molar ratio was constant, while the pH increases from 1 to 12.5 at three sodium chloride percentages of 0, 4, and 8. In total, eigtheen treatment experiments were performed to investigate the effects of pH on the As(V) removal efficiency.

Table 3.14 Numbers of the Batch Experiments to Study the Effects of pH on Arsenic Removal by Ferric Chloride at the Determined Optimum Fe/As Molar Ratio for an Initial Arsenic Concentration of 50 mg/L and 100 meq/L Alkalinity

% NaCl	0, 4, and 8
Batch No.	pH
1, 2, 3	2
4, 5, 6	4
7, 8, 9	5.5
10, 11, 12	8.5
13, 14, 15	10.5
16, 17, 18	12.5

These experimental data were modeled using MINEQL+. To model the effects of pH on the removal process, an average concentration of arsenic (50 mg/L) in brines was considered; and concentration of ferric chloride was entered as 4 Fe/As molar ratio. An average alkalinity of brines was entered as 50 meq/L. pH was entered as a multiple variable, which was increased from 1 to 14. The number of calculations was 20. The typical concentrations of sodium chloride for regeneration of ion-exchange brines are between 4% and 12% (MWH, 2005). Therefore, usually, the salt content of ion-exchange brines varies between 4% and 12% NaCl. The modeling was performed at different ionic strengths by adding 0 %, 4 %, and 8 % NaCl. The number of simulations and input data are presented in Table 3.15.

In sum, three multivariable simulations were performed using MINEQL+ to determine the optimum pH for arsenic removal process using ferric chloride at various ionic strengths.

Table 3.15 Numbers of the Simulations and Input Data to Study the Effects of pH on Arsenic Removal by Ferric Chloride at 4 Fe/As Molar Ratio for an Initial As(V) Concentration of 50 mg/L and 100 meq/L Alkalinity

Simulation No.	pH	% NaCl
1	1-14	0
2	1-14	4
3	1-14	8

Optimum Ferric Chloride Dosages

A series of batch experiments were conducted to remove As(V) from synthetic brine solutions containing 6% NaCl and 50 meq/L alkalinity by addition of various dosages of ferric chloride followed by solid /liquid separation. All parameters were fixed but total concentrations of Fe^{3+} and Cl^- were increased from zero to a desired value, which resulted in the complete removal of arsenic. For this purpose, the results of adsorption modeling were used to determine the range of ferric required for the complete arsenic removal in the batch experiments. Twelve batch experiments were performed using various ferric chloride dosages. Six percent NaCl and fifty meq/L alkalinity were fixed in the batches while the arsenate concentrations were varied between 10 to 120 mg/L. pH was adjusted to the optimum pH. Concentrations of ferric chloride and the Fe/As molar ratios are presented in Table 3.16. Six initial arsenic concentrations, 12, 21, 39, 57, 79, and 109 mg/L were considered for the batch experiments. Twelve batch experiments, nine different Fe^{3+} concentrations and three replicas, were performed for each As(V) concentration. In total, 72 batch experiments were performed to obtain optimum dosages of ferric chloride for an initial arsenic concentration at pH 6.5 and 1.2 M ionic strength.

Table 3.16 Batch Experiment Settings: Iron/Arsenic Molar Ratios and Ferric Chloride Dosages for Each Batch. pH of Solution was Adjusted to pH 6.5. 6% NaCl and 100 meq/L were Constant in All Batch Experiments.

As(V) mg/L	Batch No.	1	2	3	4	5	6	7	7	9	10	11	12
12	Fe/As	1.5	3.1	4.6	6.1	7.7	11.5	15.4	19.2	23.1	3.1	11.5	23.1
	Fe(III) (M)	0.2	0.5	0.7	1.0	1.2	1.8	2.5	3.1	3.7	0.5	1.8	3.7
21	Fe/As	0.9	1.8	2.6	3.5	4.4	6.6	8.8	11.0	13.2	1.8	6.6	13.2
	Fe(III) (M)	0.2	0.5	0.7	1.0	1.2	1.8	2.5	3.1	3.7	0.5	1.8	3.7
39	Fe/As	0.5	0.9	1.4	1.9	2.4	3.5	4.7	5.9	7.1	0.9	3.5	7.1
	Fe(III) (M)	0.2	0.5	0.7	1.0	1.2	1.8	2.5	3.1	3.7	0.5	1.8	3.7
57	Fe/As	0.3	0.6	1.0	1.3	1.6	2.4	3.2	5.7	6.1	0.3	1.6	6.1
	Fe(III) (M)	0.2	0.5	0.7	1.0	1.2	1.8	2.5	4.3	4.6	0.2	1.2	4.6
79	Fe/As	0.2	0.5	0.7	0.9	1.2	1.8	2.3	4.1	4.4	0.5	1.8	4.4
	Fe(III) (M)	0.2	0.5	0.7	1.0	1.2	1.8	2.5	4.3	4.6	0.5	1.9	4.6
109	Fe/As	0.2	0.3	0.5	0.6	0.8	1.2	1.5	2.7	2.9	0.3	0.8	2.9
	Fe(III) (M)	0.2	0.5	0.7	1.0	1.2	1.8	2.5	4.3	4.6	0.5	1.3	4.6

Finally, the laboratory results were compared to the results of the simulations to demonstrate the ability of MINEQL+ to predict the required ferric chloride dosages. A series of adsorption models were conducted to simulate removal of arsenic from the synthetic brine solutions containing 6% NaCl and 50 meq/L alkalinity by addition of various dosages of ferric chloride. pH was adjusted to 6.5 which was determined in the tests that were investigate the effects of pH. Concentrations of the arsenate in the brine solution were varied between 10 to 120 mg/L while 6% NaCl and 50 meq/L alkalinity were fixed in the process. For each initial concentration of arsenic, a multirun titration modeling was performed using different ferric chloride dosages (Table 3.17). In each simulation, concentrations of ferric chloride were increased until the remaining soluble arsenic concentration was zero. Six initial arsenic concentrations, 12, 21, 39, 57, 79, and 109 mg/L were considered for the simulations of the treatment experiments. In total, six multirun titration simulations were performed to obtain optimum dosages of ferric chloride for an initial arsenic concentration. To obtain the optimum ferric chloride dosages, parameters was entered in MINEQL+ according to Table 3.17.

Table 3.17 Simulations Settings: Ranges of Iron/Arsenic Molar Ratios and Ferric Chloride Dosages for Each Batch. pH of Solution was Adjusted to 6.5. 6% NaCl and 50 meq/L were Constant in All Batch Experiments

Simulation No.	Initial As(V) (mg/L)	Range of $FeCl_3$ (Fe) (M)	Fe/As molar Ratio
1	12	0.2-3.7	1.5-23.1
2	21	0.2-3.7	0.9-13.2
3	39	0.2-3.7	0.5-7.1
4	57	0.2-4.6	0.3-6.1
5	79	0.2-4.6	0.2-4.4
6	109	0.2-4.6	0.2-2.9

Ionic Strength Effects

The sodium chloride concentrations of ion-exchange brines can be as high as 12% (MWH, 2005). To investigate the effect of ionic strength, sodium chloride concentrations in brines were varied between 0 to 12%. Three series of coagulation batch experiments were performed for initial arsenic concentrations of 9.7, 42.3, and 98 mg/L at 0.1, 0.8, and 1.5 M ionic strengths (Table 3.18). The final pH of all coagulation batch experiments was 5.5.

The results were compared for a better understanding of the effects of ionic strength on the arsenic removal efficiency. Finally, the results of batch experiments were compared to the results of the simulations to evaluate how well the MINEQL+ simulations fit the experimental results. In total, fifty four batch experiments were performed to study the effects of the ionic strength. In total, nine multirun titration simulations were performed to study the effects of the ionic strength.

Table 3.18 Batch Experiment Settings: Iron/Arsenic Molar Ratios and Ferric Chloride Dosages for Each Batch. pH of Solution was Adjusted to pH 5.5. Alkalinity 100 meq/L was Constant in All Batch Experiments.

		Ionic strength					
Batch No.	As(V) (mM)	0.1 M		0.8 M		1.5 M	
		Fe (mM)	Fe/As	Fe (mM)	Fe/As	Fe (mM)	Fe/As
1	0.1	0.2	1.9	0.2	1.9	0.2	1.9
2	0.1	0.4	2.8	0.4	2.8	0.4	2.8
3	0.1	0.5	3.8	0.5	3.8	0.5	3.8
4	0.1	0.7	5.7	0.7	5.7	0.7	5.7
5	0.1	1.0	7.6	1.0	7.6	1.0	7.6
6	0.1	1.1	8.5	1.1	8.5	1.1	8.5
7	0.6	0.5	0.9	0.5	0.9	0.5	0.9
8	0.6	1.2	2.2	1.2	2.2	1.2	2.2
9	0.6	1.8	3.3	1.8	3.3	1.8	3.3
10	0.6	2.2	3.8	2.2	3.8	2.2	3.8
11	0.6	2.5	4.4	2.5	4.4	2.5	4.4
12	0.6	3.1	5.5	3.1	5.5	3.1	5.5
13	1.3	1.0	0.8	1.0	0.8	1.0	0.8
14	1.3	1.8	1.4	1.8	1.4	1.8	1.4
15	1.3	2.5	1.9	2.5	1.9	2.5	1.9
16	1.3	3.1	2.3	3.1	2.3	3.1	2.3
17	1.3	3.7	2.8	3.7	2.8	3.7	2.8
18	1.3	4.3	3.3	4.3	3.3	4.3	3.3

Alkalinity Effects

To study the effect of alkalinity, the alkalinity of the solution were varied between 50 and 300 meq/L. The coagulation batch experiments were performed for initial arsenic concentrations of 48 mg/L and 0.8 M ionic strength. The final pH was uncontrolled to simulate the fullscale procedure. Six coagulation batch experiments were performed for brines containig initial alkalinities of 50, 100, or 200 meq/L. The batch experiment settings are presented in Table 3.19. In sum, eigtheen coagulation batch experiments were performed.

Table 3.19 Batch Experiment Settings: Iron/Arsenic Molar Ratios and Ferric Chloride Dosages for Each Batch. pH of Solution was uncontrolled. Initial As(V) = 48 mg/L (0.64 mM)

Batch No.	Fe (mM)	Fe/As molar ratio	Initial Alkalinity g-HCO_3^- /L	Final pH	Initial Alkalinity g-HCO_3^- /L	Final pH	Initial Alkalinity g-HCO_3^- /L	Final pH
1	0.6	1.0	3.1	8.3	6.1	8.5	12.2	8.5
2	1.2	1.9	3.1	8.1	6.1	8.2	12.2	8.4
3	1.8	2.9	3.1	7.8	6.1	8.1	12.2	8.3
4	2.5	3.9	3.1	7.6	6.1	8.0	12.2	8.2
5	3.1	4.8	3.1	7.4	6.1	7.8	12.2	8.1
6	3.7	5.8	3.1	7.3	6.1	7.6	12.2	7.8

3.3 Work Plan to Address Issue Three

Many small scale ion-exchange treatment plants around the United States, especially in the Southwest (Arizona, California, and New Mexico), have been utilizing calcium polysulfide to treat their generated brines. These plants have used batch tests for each individual brine waste to determine the chemical consumption. However, to date there is no systematic method published to predict the optimal condition for the operators. Therefore, plants wishing to treat their brine by this technology have to conduct a series of trial and error batch experiments to obtain the optimal operation conditions, including the pH of the solution and the required dosages of calcium polysulfide. The results of this research can be used for design of the brine treatment units.

3.3.1. Experimental Approach

Preliminary batch experiment results for Cr(VI) removal with CaS_5 indicated that pH, CaS_5 dosage, and initial Cr(VI) concentration were the major parameters influencing Cr(VI) removal from IX brines. Alkalinity and pH are dependent variables. CaS_5 and pe are also dependent variables. Ionic strength was found to be a unimportant parameter, and the effects of ionic strength were investigated separately. A Central Composite Design (CCD), which is a widely used type of response surface methodology (Zaroual et al., 2009; Ölmez, 2009), was used to evaluate the effects of the three major parameters on the chromium removal efficiency. Surface response methodology has been successfully used by various authors to quantify the effects of initial concentration, pH, and coagulant dosage during coagulation of heavy metals (Baskan and Pala, 2009; Zaroual et al., 2009; Ölmez, 2009). The goal of this design was to provide a quadratic equation that predicts the chromium removal efficiency based on the major parameters.

A multiple-regression analysis was used for fitting the quadratic prediction equation to the experimental data. MINITAB, version 15, a statistical software (Minitab Inc., State College, Pennsylvania), was used to make the required adjustments, calculate the coefficients, and perform analysis of variance (ANOVA) and lack-of-fit. In this study, a three-factorial and a three-level central composite design with two replicas experiments for non-center points and six replicas for the center point were used leading to a total number of 34 coagulation batch experiments. The purpose of the design was to gain an overall vision on the effects of interactions between the major parameters on chromium removal efficiency. This prediction equation was used in interpreting the experimental data.

In addition, two series of laboratory batch experiments were performed to investigate the effects of ionic strength and alkalinity on the removal process. Hypothesis put forth for Issue Three was that both high alkalinity and high ionic strength of brines favor chromium removal by calcium polysulfide. The reason was that high pH was favorable for the chromium hydroxide precipitation. In addition, increasing the ionic strength of the solution decreases the electrostatic repulsive forces between particles by compressing the double layer, and, therefore, increased particle aggregations.

3.3.2. Laboratory Set Up and Operation of Batch Tests

Coagulation procedure for chromium removal from brines is similar to arsenic removal, which was explained in section 3.2.3. Calcium polysulfide was used for chromium removal from the ion-exchange brines. The synthetic brine was prepared and used in all chromium removal experiments. Calcium polysulfide solution from Best Sulfur Products has 14 mols-S/gal, which is equal to 3.6988 mols-S/L.

Two hundred and fifty milliliter of synthetic brine was added to 1000 ml beakers of a jar tester. For each initial concentration of chromium (5, 10, 20, 40, 60, 80, and, 100 mg/L), nine batch tests were conducted adding various volumes of calcium polysulfide. Jar test apparatus was used to run batch experiments for a thirty two minutes continuous mixing (two minutes at 120 rpm and thirty minutes at 30 rpm) to allow for floc growth. pH of solutions was measured after and before adding the CaS_5 to the solution. Chromium was measured by atomic adsorption spectrometry (PerkinElmer AAnalyst 100) or DR 5000 (Spectrophotometer) before and after the thirty two minutes continuous mixing. Forty milliliters of solutions were centrifuged for thirty minutes at 4500 rpm after continuous mixing and the chromium concentration of supernatant solution was measured.

3.3.3. Batch Experiments Procedure

Effects of pH

To evaluate the effect of pH, a series of coagulation batch experiments were performed for brines with an initial Cr(VI) concentration of 47.5 mg/L, 1.16 mM of CaS_5, varying pH values from 2.2 to 12.4, and ionic strengths of 0.1, 0.4, 0.8, or 1.5 M. The pH was adjusted using either hydrochloric acid or sodium hydroxide. For each ionic strength level, nine experiments were performed at nine different pH values; four of these experiments were performed in duplicate. The coagulation batch experiment settings are presented in Table 3.20. In sum, fifty two batch experiments were conducted to study the effects of pH. The Cr(VI) concentration, total chromium concentration, pH, and oxidation reduction potential of brines were measured before and after cogulation.

Optimum Calcium Polysulfide Dosages

In order to determine the required amount of calcium polysulfide (CaS_5) for each initial concentration of chromium varying from 9 to 93.2 mg/L, nine batch experiments (three in duplicate) were conducted for each initial concentration of chromium by adding various dosages of calcium polysulfide to brines with 1.2 M ionic strength.

Chromium levels of 5 to 100 mg/L were found in brines generated from the ion-exchange chromium removal plants in Arizona and California. Chromium concentrations of 9, 25.4, 35.2, 46.3, 74.2, and 93.2 were selected to cover the chromium range of 5 to 100 mg/L.

Calcium polysulfide is commercially available as Cascade. This product is highly alkaline (pH > 11) and is manufactured by reacting lime with sulfur solutions.

Table 3.20 Batch Experiment Settings: Initial Cr(VI) Concentration of 47.5 mg/L and 1.16 mM of CaS_5 Were Constant

Batch No.	I = 0.1 M Final pH	I = 0.4 M Final pH	I = 0.8 M Final pH	I = 1.5 M Final pH
1	2.2	2.0	1.7	1.6
2	5.1	4.9	4.7	4.5
3	5.5	5.3	5.1	5.6
4	6.0	5.9	6.1	6.1
5	6.5	6.7	6.5	6.2
6	7.6	7.4	7.3	7.2
7	9.0	8.8	8.6	8.4
8	10.5	10.3	10.2	10.3
9	12.4	12.4	12.3	12.3
10	6.0	5.9	4.7	6.1
11	9.0	8.8	6.5	7.2
12	10.5	10.3	8.6	8.4
13	12.4	12.4	12.3	12.3

Graphs depicting the percent of chromium removed against calcium polysulfide dosages added to the brine were generated for each initial chromium concentration separately. Finally, optimum calcium polysulfide dosages, which resulted in the complete chromium removal, were plotted against initial chromium concentrations. For each initial chromium concentration, twelve different batches (nine different CaS_5 dosages and three replicas) were performed, while various dosages of calcium polysulfide was used in each batch according to Table 3.21. In total, seventy two (12×6) coagulation batch experiments were performed.

Table 3.21 Chromium Removal with CaS_5 - Batch Experiments Matrix for Various Cr(VI) Concentrations at 100 meq/L Alk, pH 8.4 and 1.2 M Ionic strength.

Ionic strength (M)	1.2	1.2	1.2	1.2	1.2	1.2
Alkalinity, meq/L	100	100	100	100	100	100
Cr(VI), mg/L	9	25.4	35.2	46.3	74.2	93.2
Batch No.	CaS_5 (mM)	CaS_5 (mM)	CaS_5 (mM)	CaS_5 (mM)	CaS_5 (mM)	CaS_5 (mM)
1	0.10	0.12	0.12	0.14	0.29	0.14
2	0.14	0.17	0.17	0.29	0.58	0.29
3	0.29	0.23	0.23	0.58	1.16	0.58
4	0.43	0.29	0.44	1.16	1.45	1.16
5	0.58	0.43	0.53	1.45	2.03	1.45
6	0.87	0.58	0.58	1.74	2.32	2.32
7	1.16	0.87	0.87	2.32	4.63	4.63
8	2.32	2.32	1.16	2.89	5.79	5.79
9	2.89	5.79	2.32	5.79	8.68	8.68
10	0.43	0.29	0.44	1.16	1.45	1.16
11	1.16	0.87	0.87	2.32	4.63	4.63
12	2.89	5.79	2.32	5.79	8.68	8.68

Ionic Strength Effects

In order to determine the required amount of calcium polysulfide (CaS_5) for each initial concentration of chromium varying from 9 to 93.2 mg/L, eleven batch experiments (nine different CaS_5 and three replicas) were conducted for each initial concentration of chromium by adding various dosages of calcium polysulfide to brines with 1.2 M ionic strength. The batch experiment settings are presented in Table 3.22. In total, forty four (4×11) batch experiments were performed to study the effects of ionic strength on chromium removal.

Table 3.22 Chromium Removal with CaS_5 - Batch Experiments Matrix for Various Ionic Strengths at 100 meq/L Alkalinity, pH 8.5 and 46 mg/L Initial Cr(VI) Concentration

Ionic strength (M)	0.1	0.8	1.5	2.1
Alkalinity, meq/L	100	100	100	100
Cr(VI), mg/L	46	46	46	46
Batch No.	CaS_5 (mM)	CaS_5 (mM)	CaS_5 (mM)	CaS_5 (mM)
1	0.1	0.1	0.1	0.1
2	0.3	0.3	0.3	0.3
3	0.6	0.6	0.6	0.6
4	1.2	1.2	1.2	1.2
5	1.4	1.4	1.4	1.4
6	2.3	2.3	2.3	2.3
7	2.9	2.9	2.9	2.9
8	5.8	5.8	5.8	5.8
9	0.1	0.1	0.1	0.1
10	1.2	1.2	1.2	1.2
11	5.8	5.8	5.8	5.8

Alkalinity Effects

The final step of the simulations was to evaluate the effects of initial carbonate alkalinity on chromium removal efficiency by calcium polysulfide. The effect of alkalinity was evaluated through executing a series of batch experiments for brines containing four levels of alkalinity 0.01, 0.5, 2.5, and 5.0 g/L as $CaCO_3$, ionic strength of 0.8 M, and Cr(VI) concentration of 48.2 mg/L by adding varying dosages of CaS_5. The batch experiment matrix to evaluate the effect of alkalinity on removal efficiency is reported in Table 3.23. In total, forty eight (4×12) coagulation batch experiments were performed to study the effects of ionic strength on the chromium removal.

Table 3.23 Chromium Removal with CaS_5 - Batch Experiments Matrix for Various Alkalinities at 0.8 M ionic strength and 48 mg/L Initial Cr(VI) concentration.

Ionic strength (M)	0.8	0.8	0.8	0.8
Alkalinity (g/L as $CaCO_3$)	0.01	0.5	2.5	5.0
Cr(VI), mg/L	48	48	48	48
Batch No.	CaS_5 (mM)	CaS_5 (mM)	CaS_5 (mM)	CaS_5 (mM)
1	0.1	0.3	0.3	0.3
2	0.3	0.6	0.6	0.6
3	0.6	0.9	1.2	1.2
4	0.9	1.2	1.4	1.4
5	1.2	1.4	1.7	1.7
6	1.4	1.7	2.0	2.0
7	1.7	2.0	2.3	2.3
8	2.0	2.3	2.9	2.9
9	2.3	5.8	5.8	5.8
10	0.6	0.9	0.6	0.6
11	1.2	1.7	2.9	2.9
12	2.0	5.8	5.8	5.8

3.4. Analytical Methods

Sample Collection, Preservation, and Analysis of Ion-Exchange Minicolumn Experiments

Ten milliliters of the aqueous solution were collected from the feed water of each ion-exchange column experiment. For the loading or regeneration process, the samples were collected at the planned intervals for each process using a Foxy 200 autosampler. Preferably, samples were measured on the same day of sample collection. Otherwise, samples containing arsenic, selenium, or chromium were acidified with nitric acid to lower the pH of the sample to equal or less than two, and all samples were transferred to high density polyethylene (HDPE) plastic containers (Standard Methods, 1989). The HDPE plastic containers were stored in a refrigerator at 4°C prior to the measurements for a maximum of 6 months as per Standard Methods recommendations. Samples containing nitrate were acidified with sulfuric acid (pH <= 2) and were stored in the refrigerator at 4°C for a maximum of 28 days. In the nitrate removal ion-exchange column experiment, the nitrate concentration in the samples was measured using an ion chromatograph (Dionex, ICS-2000) as per Standard Methods. In the arsenic, selenium, or chromium removal column experiments, arsenic, selenium, or chromium were measured using an AA 100.

Sample Collection, Preservation, Analysis of Batch Experiments, and Hazardous Waste Management

The pH of the solutions was measured before and after adding ferric chloride or calcium polysulfide with an Accumet Research AR25 pH meter from Fisher Scientific. The pH meter was calibrated using three buffers (4, 7, and 10). Twenty five milliliters of the untreated brine solution were collected to determine the arsenic or chromium concentrations before each treatment process. After the treatment process, twenty five milliliter homogenous samples were collected for post treatment measurements. Preferably, samples were measured on the same day of the batch experiments to determine the arsenic and chromium concentrations; otherwise, samples were acidified with nitric acid (pH < 2) and stored in a refrigerator at 4°C for a maximum duration of 6 months. Homogenous twenty five milliliter samples were shaken and transferred to a 2100N turbidity meter from Hach to determine the turbidity. In view of the fact that sample preservation is not recommended for turbidity measurements, the measurements were performed promptly after the batch tests. After the turbidity measurement, the samples were transferred to a Sorvall Legend RT Bechtop centrifuge for solid-liquid separation. Arsenic or chromium concentrations in the cleared liquid part of the samples were measured by atomic adsorption spectrometry using an AA 5300 spectrometer from Perkin Elmer. The total volume of precipitates generated in the batch experiments were also measured using a graduated cylinder.

The generated waste from the batch experiments usually have high concentrations of arsenic or chromium (5 > mg/L). These wastes are considered hazardous and must be handled carefully. For this purpose, two ten gallon HDPE plastic containers are marked for the contaminated waste with arsenic or chromium. The generated wastes from arsenic or chromium batch experiments were transferred to the respective plastic container. The HDPE plastic containers were stored in a hazardous waste storage cabinet. The hazardous waste containers were collected weekly by a branch of the Environmental Protection Agency located at UNLV.

Methods

The analytical methods that were used to analyze the samples for turbidity, nitrate, arsenate, chromate, and selenate are presented below.

Turbidity measurement (Nephelometric Method (2130 B))

Turbidity was measured according to Nephelometric Method (2130 B) using a Hach 2100 N turbidity meter. The turbidity is defined as the intensity of light scattered by the sample compared to the intensity of light scattered by a standard reference made from formazin. The turbidity is reported in nephelometric turbidity units (NTU). The turbidity meter was calibrated using five formazin standard references provided by the manufacturer. The turbidity of the standard references are <0.1, 20, 200, 1000, and 4000 NTU. Twenty milliliters of each sample were transferred to a special twenty milliliter vial, and the vial was vigorously shaken for the precipitates to become suspended. The vial was placed in the turbidity meter and the turbidity was read and recorded in NTU.

Nitrate measurement (NO_3) (Ion Chromatographic (IC) Method (4500 B and 4110))

Nitrate was measured based on the 4110 C method, determination of anions by ion chromatography using a Dionex ICS-2000 ion chromatograph. Samples did not contain particles larger than 0.45 μm and were filtered prior to the measurements. Five milliliters of an aqueous sample were placed in the 5-ml Eppendorf vials. Aqueous samples were injected into the analytical columns. Ions were separated based on their affinity for the strongly basic anion-exchanger located inside the column. The detection limit of nitrate for the Dionex ICS-2000 at the environmental laboratory was chosen as 0.01 mg/L. Concentrations of 0.01 to 10 mg/L of nitrate can be measured by the IC, and concentrations above this limit were diluted accordingly. The ion chromatograph was calibrated using six standards with concentrations of 0.1, 1, 2, 5, 8, and 10 mg/L. The standard solutions were prepared from a 1000 mg/L standard stock solution purchased from VWR. The standards were prepared by diluting volumes of the standard stock solution into deionized water (DI). The concentrations of nitrate were automatically calculated by the software provided by Dionex.

Arsenic, Selenium, and Chromium (Atomic Absorption Spectrometric Method (3113))

An aqueous sample is aspirated into a flame and atomized in a spectrometer. The elements inside the solution are atomized in front of a beam of light which is directed through the flame. The amount of light absorbed by the element is measured by a detector inside the spectrometer. Each metal has its own outstanding characteristic absorption wavelength and requires a particular lamp that provides the respective wavelength that can be absorbed by the metal. The amount of energy that is absorbed by the atomized metal inside the flame is proportional to the concentration of the metal in the solution over a specified concentration range (Standard Methods, 1989). The wavelengths required for arsenic, selenium, and chromium detections are presented in Table 3.24.

Table 3.24 Matrix Modifiers, Wavelengths, Detection Limits and Optimum Concentration Ranges for Electrothermal Spectrometry Measurement of Arsenic, Selenium, and Chromium

Element	Matrix Modifier for Interference Removal (10 μL modifier/10 μL sample)	Wavelength, nm	Estimated Detection Limit, μg/L	Optimum Concentrations Range, μg/L
As	1500 mg Pd/L + 1000 mg $Mg(NO_3)_2$/L	193.7	1	5-100
Cr	500-2000 mg Pd/L + citric acid (1-2%)	357.9	2	5-100
Se	1500 mg Pd/L + 1000 mg $Mg(NO_3)_2$/L	196.0	2	5-100

Brines can be analyzed by direct aspiration; however, dilution of the sample is strongly recommended before the aspiration to prevent solids buildup on the burner head or graphite furnace. Solids buildup decreases the accuracy of light detection and requires frequent cleaning of the graphite furnace or the burner head. Measuring brines also requires frequent recovery checks using a series of standards. It is recommended that the background correction be used when measuring the concentration of metals in brines

(Standard Methods, 1989). The estimated detection limits and optimum concentrations ranges for arsenic, selenium, and chromium are presented in Table 3.24.

The graphite furnace was used for the low level arsenic, selenium, or chromium. The flame was used for the high concentration samples. In electrothermal atomic absorption spectrometry, a graphite furnace was used and a sample volume was dispensed into the graphite sample tube (or cup) for measurement. There were three steps of heating for the measurement of the sample. A low current was applied to the tube to dry the sample. Then, a medium current heats the tube to destroy any organic matter in the sample. Finally, a high current heated the tube to atomize the remaining inert elements. Normally, after the measurement, the tube was flushed and cleaned for enhancing the accuracy of the measurements (Standard Methods, 1989).

The measurement of metals using electrothermal atomic absorption spectrometry is subject to significant interferences; however, matrix modification can be used to minimize some interference. Matrix modifiers were directly added to the graphite sample tube to increase the metal's atomization efficiency.

The recommended matrix modifiers (Standard Methods, 2005) are presented in Table 3.24.

3.5. Analysis of Data

3.5.1 Introduction

In this study, three series of experiments were performed to address the issues related to selective ion-exchange resins and the removal of arsenic and chromium from ion-exchange brines.

3.5.2. Data Analysis for Issue One

To assure the accuracy of the experimental data, the average of the values from the duplicate sample measurements and mean deviation was calculated. Up to 5% deviation per the average of the measured values was acceptable; otherwise, the measurements were repeated (Table 3.25). This provided a 95% confidence level for the measurements.

Table 3.25 Data Outputs from Experiments.

Number of Distinct Sampling Points	BVs	Experiment Run 1	Experiment Run 1 Average Conc[a].
1	20	C11, C12	E1C1ave
2	40	C21, C22	E1C2ave
:	:	:	:
n	BVn	Cn1, Cn2	E1Cnave

[a] E and C Stand for Experiment and Concentration, Respectively.

Data Analysis for Nitrate Removal

The one-factor-at-a-time approach was utilized to design nitrate removal experiments using one of the five different resins (SBG1, SIR100, SIR110, SIR111, PWA2). One typical water quality was selected for the experiments. This water was used to test the five different resins. Therefore, all parameters were fixed except the type of the resins tested. The results of the laboratory experiments were presented as graphs showing concentrations of nitrate in the effluent of the ion-exchange column against the bed volumes of water passed through. The volume of water and the interval of sampling required for the laboratory ion-exchange experiments was caculated. Duplicate measurements were conducted for each individual sample (Table 3.25). Five breakthrough curves were combined in one graph. The results were compared based on the following criteria:

1- The breakthrough point at which nitrate was detected in the effluent.

2- The point at which nitrate concentration reached the nitrate's MCL.

3- Exhaustion point

4- Total nitrate adsorbed into the resin

Data Analysis for Arsenic, Selenium, and Chromium Removal

The one-factor-at-a-time approach was utilized to design arsenic, selenium, or chromium removal experiments. Ion-exchange column experiments were performed for a water contaminated with arsenic, selenium, or chromium using one of the three ion-exchange resins (SBG1, SIR100, SIR110) at a time. Experimental data were compared with each other and literature. In total, nine breakthrough curves were generated to evaluate the effects of the contaminants on the removal process. The results were compared based on the following criteria:

1- The breakthrough point at which arsenic, selenium, or chromium was detected in the effluent.

2- The point at which arsenic, selenium, or chromium concentration reached their MCL.

3- Exhaustion point

4- Total arsenic, selenium, or chromium adsorbed into the resin

3.5.3. Data Analysis for Issue Two

Many coagulation batch experiments were performed to investigate As(V) removal from ion-exchange brines using ferric chloride. The arsenic removal coagulation process was also modeled using the MINEQL+ computer program. For the model validation, a regression analysis was applied using the Minitab statistical software. In this research, the level of significance was set to 0.05 (5%) to assure a 95% confidence interval. In Issue Two, the residual for the arsenic removal was the difference between the remaining arsenic concentration from the modeling and the average result of the experiments. The null hypothesis was that there was no evidence of lack of fit. The model fitted the experimental data when the residuals were equal to random errors of the measurements (less than 5% difference). The alternative hypothesis was that there was evidence of lack of fit (> 5%). If the residuals appeared not to behave randomly, the model was not valid.

In addition, available data in the published literature (i.e., Hering et al., 1996 and Mercer and Tobiason, 2008) for arsenic removal using ferric chloride were modeled by MINEQL+, and the model was also validated using the published data.

Five major parameters that affect arsenic removal using ferric chloride are: initial As(V) concentration, ferric chloride dosage (Fe/As molar ratio), pH, ionic strength, and alkalinity. In this research, the full factorial (balance) design and one-factor-at-a-time approach were used to design the experiments and determine the required statistical analysis for evaluating the generated data.

A full factorial design (5×2) for five viariables and two levels was selected to be used as a tool to perform the modeling and the laboratory experiments. Thirty-two experiments and modeling (2^5) were required for the full factorial design. The experiments were repeated to produce duplicate results for evaluating the interaction effects. In total, sixty-four expeiments were performed according to Table 3.26.

A full factorial design was selected to quantify the main and interaction effects of ionic strength, pH, alkalinity, initial arsenic concentration, and Fe/As molar ratio on arsenic removal. The statistical analysis determined how significant these parameters were in the arsenic removal process. The results of the experiments and modeling were evaluated based on a regression model (or factorial analysis of variance (ANOVA)) for the factorial design using the Minitab statistical software.

The one-factor-at-a-time approach was also used to design the experiments and determine the required statistical analysis for evaluating the generated data. In all the one-factor-at-a-time designs, for the model validation, a regression model was applied using the Minitab statistical software. According to the statistical analysis, it was determined how well the model predicts the arsenic removal process using ferric chloride.

Data Analysis for the Effects of pH and Ionic Strength

For this part, pH or ionic strength was separately considered variables (the major parameters) while the initial arsenic concentration, Fe/As molar ratio, and alkalinity were fixed values. The initial arsenic concentration and alkalinity were the median concentrations for typical ion-exchange brine, 50 mg/L and 50 meq/L, respectively. The Fe/As molar ratio of 4 was selected. The one-factor-at-a-time approach was also used to determine the optimum pH at various ionic strengths when arsenic and alkalinity levels were fixed to 50 mg/L and 50 meq/L, respectively.

In the modeling, pH varied between 1 and 14 for different solutions with sodium chloride concentrations of 0, 2, 4, 6, 8, 10, and 12%. The results were presented in one graph. The experiments were also performed for NaCl concentrations of 0, 4, 8, and 12%.

Table 3.26 Full Factorial Design (5×2) for Arsenic Removal Using Ferric Chloride for Five Variavles: pH, Ionic Strength, Ferric Chloride Dosage , Alkalinity, and Initial Arsenic Concentration

Run	pH (A)	Ionic strength (B)	Fe/As molar ratio (C)	Initial As concentration (D)	Alkalinity (E)	Function (%As removal, Y)
1	+1	+1	+1	+1	+1	Y1-1, Y1-2
2	-1	+1	+1	+1	+1	Y2-1, Y2-2
3	+1	-1	+1	+1	+1	Y3-1, Y3-2
4	-1	-1	+1	+1	+1	Y4-1, Y4-2
5	+1	+1	-1	+1	+1	Y5-1, Y5-2
6	-1	+1	-1	+1	+1	Y6-1, Y6-2
7	+1	-1	-1	+1	+1	Y7-1, Y7-2
8	-1	-1	-1	+1	+1	Y8-1, Y8-2
9	+1	+1	+1	-1	+1	Y9-1, Y9-2
10	-1	+1	+1	-1	+1	Y10-1, Y10-2
11	+1	-1	+1	-1	+1	Y11-1, Y11-2
12	-1	-1	+1	-1	+1	Y12-1, Y12-2
13	+1	+1	-1	-1	+1	Y13-1, Y13-2
14	-1	+1	-1	-1	+1	Y14-1, Y14-2
15	+1	-1	-1	-1	+1	Y15-1, Y15-2
16	-1	-1	-1	-1	+1	Y16-1, Y16-2
17	+1	+1	+1	+1	-1	Y17-1, Y17-2
18	-1	+1	+1	+1	-1	Y18-1, Y18-2
19	+1	-1	+1	+1	-1	Y19-1, Y19-2
20	-1	-1	+1	+1	-1	Y20-1, Y20-2
21	+1	+1	-1	+1	-1	Y21-1, Y21-2
22	-1	+1	-1	+1	-1	Y22-1, Y22-2
23	+1	-1	-1	+1	-1	Y23-1, Y23-2
24	-1	-1	-1	+1	-1	Y24-1, Y24-2
25	+1	+1	+1	-1	-1	Y25-1, Y25-2
26	-1	+1	+1	-1	-1	Y26-1, Y26-2
27	+1	-1	+1	-1	-1	Y27-1, Y27-2
28	-1	-1	+1	-1	-1	Y28-1, Y28-2
29	+1	+1	-1	-1	-1	Y29-1, Y29-2
30	-1	+1	-1	-1	-1	Y30-1, Y30-2
31	+1	-1	-1	-1	-1	Y31-1, Y31-2
32	-1	-1	-1	-1	-1	Y32-1, Y32-2

Data Analysis for the Optimum Ferric Chloride Dosages

The one-factor-at-a-time approach was used to design the experiments and determine the optimum ferric chloride dosages for various initial arsenic concentrations. Each arsenic concentration was modeled separetely. For each initial arsenic concentration, pH, alkalinity, and ionic strength were fixed to 6.5, 50 meq/L, and 6%, respectively. The ferric chloride dosages were increased until 100% arsenic removal is achieved. Batch experiments were also conducted to determine the optimum ferric chloride dosages. The results of the experiments were combined with the modeling results in one graph.

A concentration of ferric chloride at which arsenic was non-detectable in the solution was pointed out as an optimum ferric chloride dosage. Finally, optimum ferric chloride concentrations were graphed against initial arsenic concentrations in the solution. For the design purposes, this was an important graph to determine the optimum (and required) ferric chloride dosages for a known initial arsenic concentration.

Data Analysis for Ionic Strength Effects

The one-factor-at-a-time approach was also used to determine the effects of ionic strength on the arsenic removal process. The modeling performed for three arsenic concentrations in a brine solution containing 6% NaCl were repeated for brines containing 0, 8, and 12% NaCl. The alkalinity was fixed at 50 meq/L. The ferric chloride concentrations were increased until the remaining soluble arsenic is zero.

Data Analysis for Alkalinity Effects

For the modeling, one arsenic concentration was used. The ferric chloride concentration was increased to achieve the complete arsenic removal at alkalinities of 0, 10, 50, and 100 meqL and 6% NaCl without pH adjustment. The model validation was conducted based on the F test lack of fit and the analysis of residuals.

3.5.4 Data Analysis for Issue Three

The major independent variables (i.e., pH, initial Cr(VI) concentration, and CaS_5 dosage) were designated as X_1, X_2, and X_3, respectively.

The coded and uncoded values of each variable for the Central Composite design is presented in Table 3.27.

Table 3.27 Coded and Uncoded Levels of Each Factor for the Central Composite Design. Coded Levels Were -1, 0, and +1.

Independent variables (uncoded)	Unit	Symbol	Coded Level		
			-1	0	+1
pH	Value	X_1	4.7	8.6	12.5
Initial Cr(VI) concentration	mg/L	X_2	9	46	93
CaS_5 dosage	mM	X_3	0.58	1.16	2.32

Experimental data points that were used for the Central Composite design are presented in Table 3.28. The goal of these designs was to predict the response surface function (Y), which is the total chromium removal efficiency in this research, based on the independent variables (X_1, X_2, and X_3) according to equation 3.8.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (3.8)$$

Where b_0 is the model constant coefficient; $b_1 \ldots b_3$ are the linear coefficients; $b_{12} \ldots b_{23}$ are the cross product coefficients; $b_{11} \ldots b_{33}$ are the quadratic coefficients (Mathews, 2005). The prediction limits were chosen as 0 % and 100 %. These coefficients were calculated using MINITAB, version 15. Surface plots of the chromium removal efficiency as a function of pH and initial Cr(VI) concentration or CaS_5 dosage and initial Cr(VI) concentration were plotted using equation 3.8.

Table 3.28 Experimental Data Points and Responses Used in Central Composite Design and Predicted Chromium Removal Efficiencies.

Run[a]	pH	Initial Cr (mg/L)	CaS_5 dose (mM)	Experimental Response[b]	Predicted Response
1	-1 (4.7)	-1 (9)	-1 (0.58)	19.2	23.1
2	+1 (12.5)	-1 (9)	-1 (0.58)	68.4	65.1
3	-1 (4.7)	+1 (93.2)	-1 (0.58)	1.0	0.0
4	+1 (12.5)	+1 (93.2)	-1 (0.58)	17.7	17.3
5	-1 (4.7)	-1 (9)	+1 (2.32)	11.9	9.6
6	+1 (12.5)	-1 (9)	+1 (2.32)	60.0	67.3
7	-1 (4.7)	+1 (93.2)	+1 (2.32)	19.3	19.9
8	+1 (12.5)	+1 (93.2)	+1 (2.32)	68.5	61.9
9	-1 (4.7)	0 (46)	0 (1.16)	15.8	23.8
10	+1 (12.5)	0 (46)	0 (1.16)	62.6	65.8
11	0 (8.6)	-1 (9)	0 (1.16)	94.0	88.5
12	0 (8.6)	+1 (93.2)	0 (1.16)	53.2	69.8
13	0 (8.6)	0 (46)	-1 (0.58)	74.7	84.5
14	0 (8.6)	0 (46)	+1 (2.32)	98.7	100.0
15	0 (8.6)	0 (46)	0 (1.16)	95.0	92.1
16	0 (8.6)	0 (46)	0 (1.16)	96.0	92.1
17	0 (8.6)	0 (46)	0 (1.16)	96.0	92.1
18	0 (8.6)	0 (46)	0 (1.16)	97.0	92.1
19	0 (8.6)	0 (46)	0 (1.16)	92.0	92.1
20	0 (8.6)	0 (46)	0 (1.16)	99.0	92.1

[a] Two replicas were performed for run 1-14

[b] Average of two replicas are presented for run 1-14

Table 3.29 shows coefficients of the second-order polynomial equation (equation 3.8). These coefficients were calculated using the MINITAB (ver. 15) based on the experimental data for the chromium removal efficiency.

Table 3.30 shows the result of the analysis of variance (ANOVA) and lack-of-fit between the experimental and predicted responses.

Data Analysis of Effects of pH

The effects of pH on chromium removal was evaluated in brines containing 50 meq/L alkalinity and 50 mg/L Cr(VI). Calcium polysulfide at the determined optimum value was applied to brines containing 0, 6, 8, or 12% NaCl. The results of experiments were combined in one graph.

Table 3.29 Estimated Regression Coefficients of the Quadratic Model for the Central Composite Design for Chromium Removal Efficiency from Brines Using CaS_5. $R^2 = 0.9655$, adjusted $R^2 = 0.9344$

Source	Coefficient	Value
Constant	b_0	92.1399
X_1	b1	21.0007
X_2	b2	-9.3756
X_3	b3	7.7603
X_1X_1	b11	-47.3858
X_2X_2	b22	-12.977
X_3X_3	b33	0.0953
X_1X_2	b12	-3.9211
X_1X_3	b13	3.9211
X_2X_3	b23	10.5997

Table 3.30 Analysis of Variance (ANOVA) of Response Surface Quadratic Model for Central Composite Design.

Source	Df[a]	Seq. SS[b]	Adj. SS[c]	Adj. MS[d]	F[e]	P
Regression	9	22760.5	22760.5	2528.94	31.07	< 0.001
Linear	3	5891.6	5891.6	1963.85	24.13	< 0.001
Square	3	15724.1	15724.1	5241.37	64.4	< 0.001
Interaction	3	1144.8	1144.8	381.61	4.69	0.027
Residual Error	10	813.9	813.9	81.39		
Lack-of-Fit	5	787.1	787.1	157.42	29.33	0.001
Pure Error	5	26.8	26.8	5.37		
Total	19	23574.4				

[a] Degree of freedom; [b] Sequential sum of squares; [c]Adjusted sum of squares; [d]Adjusted mean of squares; [e] $F_{critical} = < 0.0001$

Data Analysis of Optimum Calcium Polysulfide Dosages

The one-factor-at-a-time approach was utilized to determine the optimum calcium polysulfide dosages for chromium removal from brines containing various initial Cr(VI) concentrations. In all brines that were treated, the alkalinity and sodium chloride were fixed at 50 meq/L and 6 % NaCl. The calcium polysulfide dosages were different according to the initial chromium concentration in brines. Finally, the optimum dosages of calcium polysulfide were graphed against the initial hexavalent chromium concentrations. This graph is an important tool for design the brine treatment units.

Data Analysis for Ionic Strength Effects

Ionic strength effects on chromium removal were investigated in brines containing 50 mg/L Cr(VI) with 0, 6, 8, or 12% NaCl (50 meq/L alkalinity). The experimental results were combined in one graph.

Data Analysis for Alkalinity Effects

The one-factor-at-a-time approach was utilized to determine the effects of alkalinity on chromium removal using calcium polysulfide for brines containing 50 mg/L Cr(VI). The sodium chloride concentration was fixed at 8%. Alkalinity of brines was increased from 0 to 140 meq/L. The results of the experiments were presented in one graph.

3.6. Quality Assurance/Quality Control (QA/QC)

The QA/QC evaluation is an essential part of this research to guarantee the quality of the results obtained from various experiments and computer modeling. The QA/QC outcomes contribute to improve consistency, comparability, and confidence of the results of the research. Quality assurance in this research is a planned system of review procedures to prevent systematic errors (i.e., instrumental and human errors). Quality control is a system of routine checks on data acquisition and estimating uncertainties (Avenhaus et al., 2006).

Quality Assurance

The parameters being measured in this research were pH, waste volume, and concentrations of arsenic, selenium, chromium, and nitrate. Concentrations of arsenic, selenium, and chromium in water or brines were measured before and after the treatment process using an atomic absorption (AA) 5300 spectrometer. pH, and waste volume were measured in the brine treatment experiments. pH as a master variable played an important role in coagulation experiments in this research, so it was measured accurately. Nitrate concentration was measured in the ion-exchange minicolumn run experiments using an ion chromatograph (IC) (Dionex ICS-2000). Although the goal of the quality assurance process was to measure all parameters accurately, some instrumental and human errors might occur during the process. Therefore, a series of precautions were considered and applied to maintain accuracy in obtaining results:

1. An analytical balance (CP1245 Sartorius) was used for weighing chemicals and was calibrated daily using standard weights (5 and 50 g). In addition, outside contractors have inspected and calibrated the balances located in the UNLV Environmental Engineering Lab every six month.
2. The micropipettes were calibrated each time that they were used. The accuracy of micropipettes was checked by weighing known volumes of water aspirated by pipette on an analytical balance. The DI water was used for this purpose. A certain volume of water was taken out by the pipette and was weighed by the analytical balance. If the weight and volume were equal, then the pipette was accurate. If not, then it was sent to an independent contractor for calibration.

3. The pH meter was calibrated using 4, 7, and 10 pH standard solutions following the standard procedure provided by the manufacturer. The slope of the calibration curve was more than 95%. Special buffers were made for pH measurements in brines. The NaCl was added to these buffers to adjust the effects of ionic strength of the acitivity of hydrogen ion.
4. All glassware was soaked in a weak acid (Micro 90) for at least one day. After that, the glassware was washed with tap water and soap. Finally, the glassware was rinsed off at least three times with DI water.
5. All the samples obtained were measured in the same day of acquisition; otherwise, they were acidified (pH <= 2) by nitric acid and were stored in a refrigerator at 4°C. Sample preservations were previously described in the analytical methods.
6. During ion-exchange column experiments, the flow rate was adjusted using a 25 ml graduated cylinder and a stop watch. During the run, it was constant at all times. For this purpose, after adjusting the flow rate in the beginning of the run process, it was measured repeatedly many times.
7. A piece of wool was placed at the tope and bottom of the ion-exchange column for a better distribution of water inside the column.
8. Nitrate concentrations in the samples obtained from the minicolumn experiments were measured using a Dionex ICS-2000. The IC was calibrated before each measurement using five standard samples of nitrate providing the required measurement range. The R-squared value of the calibration curve

was more than 0.999. The nitrate standards were selected to provide a required range for nitrate measurements.

9. The AA 5300 spectrometer was used for arsenic, selenium, and chromium measurements in brines before and after the treatment. The AA 5300 was calibrated before each measurement using at least three arsenic or chromium standards. The R-squared value of the calibration curve was more than 0.99. The standards used for calibration procedure covered the required range for sample measurements.

Quality Control

The quality control process was conducted to diminish the uncertainties of all analysis. To reduce the uncertainties in the measurements, replicates of the measurements were conducted followed by a statistical analysis to control the quality of measurements. Arsenic, selenium, chromium, and nitrate concentrations in a sample were measured two times.

CHAPTER 4

IMPACT OF INORGANIC ANIONIC CO-CONTAMINANTS ON PERFORMANCES OF PERCHLORATE AND NITRATE SPECIALTY ION-EXCHANGE RESINS

4.1. Abstract

The influence of anionic inorganic co-contaminants including nitrate, Cr(VI), Se(VI), and As(V) on the application of nitrate and perchlorate specialty (selective) resins in water treatment was investigated. Mini-column tests were performed using a synthetic wastewater that simulates typical groundwaters contaminated with inorganic contaminants. One issue investigated was the removal of nitrate with specialty resins. It was found that nitrate can be removed from waters using perchlorate specialty resins, but the resin is poorly regenerated. A second issue was desorption of perchlorate accumulated in specialty resins; perchlorate is not easily removed from either nitrate or perchlorate specialty resins. A third issue evaluated was concurrent removal of perchlorate and nitrate with specialty resins. The results revealed that nitrate can be desorbed, but perchlorate accumulates in both resins. A fourth issue addressed concurrent removal of nitrate and Cr(VI), Se(VI), or As(V) using specialty resins. The results showed that simultaneous removal of nitrate and Cr(VI) is optimal when using nitrate specialty resin. Perchlorate/nitrate specialty resins are inefficient in removing As(V), but can exchange Cr(VI) or Se(VI). A major concern is the presence of high levels of Cr(VI), As(V), or Se(VI) in the waste brine, which affects the brines disposal. The fifth issue was concurrent removal of perchlorate and Cr(VI), Se(VI), or As(V). Perchlorate specialty resins have very low run length for these divalent contaminants. This research revealed that nitrate specialty resins are very efficient in removing Cr(VI),

and they can be easily regenerated. Perchlorate specialty resins exchange Cr(VI) and Se(VI), but not As(V). The presence of the co-contaminant ions affects the run length and the brine composition when perchlorate or nitrate specialty resins are used.

4.2. Introduction

Ion-exchange (IX) is an efficient technology to remove inorganic ionic contaminants from drinking water, including pentavalent arsenic [As(V)] (Ghurye et al., 1999), hexavalent selenium [Se(VI)] (Sorg & Logsdon, 1978), hexavalent chromium [Cr(VI)] (Korngold et al., 2003), nitrate (Tripp & Clifford, 2006), and perchlorate (Gu & Brown, 2006, Batista et al, 2000). Drinking waters may contain more than one inorganic contaminant at different concentrations. The presence of inorganic contaminants in waters is associated with serious health risks. Consuming nitrate-contaminated drinking water can cause health risks such as methemoglobinemia, diuresis, increased starchy deposits, and hemorrhaging of the spleen (Lehman et al., 2008; Fewtrell, 2004; Kross et al., 1992). The U.S. EPA set the MCL for nitrate at 10 mg/L (as N). Perchlorate reduces iodine uptake in the thyroid gland, causing hypothyroidism, which leads to a general slowing of metabolism in a number of organ systems. There is no federal MCL for perchlorate, but an interim drinking water health advisory level of 15 μg/L has been suggested by the U.S. EPA (U.S. EPA, 2008). Arsenic is a carcinogenic element connected to cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate (Smedley & Kinniburgh, 2002). The U.S. EPA set the MCL for arsenic at a concentration of 10 μg/L on January 18, 2001 (Smedley & Kinniburgh, 2002; Chen et al., 2002). Chromium is a potential carcinogen (Fendorf & Guangchao, 1996). The U.S.

EPA has enforced a MCL value of 0.1 mg/L for chromium in drinking water since 1992. Long term exposure to elevated levels of selenium causes hair and fingernail loss, damage to kidney and liver tissue, and damage to the nervous and circulatory systems (Fan & Kizer, 1990). Selenium's MCL of 0.05 mg/L was set by the U.S. EPA, and water supply utilities have had to comply with this regulation since 1992.

The presence of co-contaminants is a challenge for ion-exchange plant design because the optimal conditions for their removal may differ. Furthermore, co-contaminants can accumulate in resins and waste brines hindering brine disposal and resin reuse. Commonly, strong base anion (SBA) exchange resins have been utilized to remove inorganic contaminants from drinking water (Clifford & Weber, 1986; Ghurye et al., 1999; Sengupta, 1995). These resins are effective in removing inorganic contaminants, however, the volume of water that can be processed before the resin needs regeneration is significantly reduced by the presence of sulfate, which is a divalent anions that occurs in most waters. SBA resins have a high affinity for sulfate and other multivalent ions, as compared to monovalent anionic contaminants. When SBA resins are used, most of their capacity is exhausted by sulfate or other multivalent ions, thereby, reducing their capacity to remove the target anion.

In the last decade, specialty resins, also known as selective resins, have been developed to remove inorganic contaminants from water. These resins are designed to have high affinity for the contaminant and less affinity for sulfate. It has been reported that an important factor affecting the selectivity of ion-exchange resins is the spacing of exchange sites on the quaternary ammonium functional group (Clifford & Weber, 1986; Guter, 1984, Liu & Clifford, 1996). The distance between active exchange sites on the quaternary amine functional group affects the divalent-monovalent selectivity (Guter, 1984). For example, by increasing the length of the trialkyl group from methyl to hexyl, the selectivity of the resin for ClO_4^- is increased, while the selectivity of the resin for SO_4^{2-} or other divalent ions is decreased (Gu & Coates, 2006). The order of the selectivity of the perchlorate selective resins is known to be perchlorate > nitrate > chloride > bicarbonate (Gu & Coates, 2006). Similarly, nitrate specialty resins are produced by increasing the length of the functional group from trimethyl-amines to triethyl-amines or tributyl-amines (Guter, 1984). Divalent ions need to adsorb into two active sites; thus, when the spacing between active sites increases, divalent ions [e.g., sulfate (SO_4^{2-}), hydrogen arsenate ($HAsO_4^{2-}$), chromate (CrO_4^{2-}), or selenate (SeO_4^{2-})] cannot be adsorbed; however, monovalent ions (e.g., nitrate or perchlorate) are still adsorbed by the resin because they need only one active place in which to be adsorbed (MWH, 2005). In most drinking waters, divalent ions [i.e., hydrogen arsenate ($HAsO_4^{2-}$), chromate (CrO_4^{2-}), or selenate (SeO_4^{2-})] are the predominant species of As(V), Cr(VI), or Se(VI).

Because of their higher selectivity, the use of specialty resins to remove nitrate (Rochette, 2006; Tripp & Clifford, 2006; Ghurye et al., 1999; Liu & Clifford, 1996) and perchlorate (Gu & Brown, 2006; Tripp & Clifford, 2000; Batista et al., 2000) from water has increased significantly. Specialty resins are more costly than SBA resins, but larger volumes of water can be processed before the resin capacity is exhausted thereby reducing the overall operational costs (Gu & Coates, 2006). Although perchlorate and nitrate specialty resins have been developed and tested at pilot and full-scale to remove ions of interest (i.e., perchlorate and nitrate) (Ghurye et al., 1999; Liu & Clifford, 1996;

Siegel et al., 2006; Gu et al., 2003), the performance of these resins to remove co-occurring contaminants such as As(V), Se(VI), Cr(VI) have not been studied to date. In the case of nitrate and perchlorate, several waters contaminated with perchlorate also contain varying levels of nitrate (U.S. EPA, 1999; Batista et al., 2002). Some perchlorate or nitrate-contaminated waters may also contain lower levels of As(V), Se(VI), Cr(VI), and/or uranium (U.S. EPA, 1999). Co-inorganic anion contaminants negatively affect the amount of water that can be processed as well as the management of the used resin and its regeneration (Ghurye et al., 1999). Co-contaminants can accumulate in the resin to levels that create a hazardous waste. Specialty ion-exchange resins stay in service for a long time before breakthrough occurs because of they are unselective for sulfate and highly selective for the anions they are designed to remove. Although co-contaminants may be present in the water at trace levels, the long time the resins stay in service results in the accumulation of a significant amount of contaminants (Ghurye et al., 1999). In California, several wells contaminated with perchlorate and arsenic, for example, contain trace levels of uranium. When treating these waters with specialty resins, the potential accumulation of uranium in the resin must be taken into consideration because of stringent disposal regulations for wastes containing uranium. The same can be said for waters containing trace levels of selenium, arsenic, and chromium. In this research, the removal of the inorganic co-contaminants by perchlorate and nitrate specialty resins is investigated.

Spent IX resin should be regenerated and reused to reduce the operational costs of water treatment (Gu et al., 2003; Batista et al., 2000). Ion-exchange resins are commonly regenerated with an 8 to12 % NaCl brine solution, which is cost effective and widely used. Nitrate specialty resins are typically regenerable. Because of high selectivity for perchlorate, and the hydrophobic character of both perchlorate ion and the resin, the regeneration of a perchlorate-laden perchlorate specialty resin is ineffective even when excessive volumes of brine solutions are used (Gu & Coates, 2006; Gu et al., 2000; Batista et al., 2000; Tripp & Clifford, 2000). The feasibility of desorbing inorganic co-contaminants such as nitrate, As(V), Se(VI), or Cr(VI) from perchlorate selective specialty resins has not been investigated to date.

Commercially available perchlorate selective resins have a higher affinity for nitrate than nitrate specialty or conventional SBA resins. For example, according to ResinTech (West Berlin, NJ), relative to Cl^-, selectivity coefficients of SIR 110 (perchlorate specialty resin, SIR 100 (nitrate specialty resin), and SBG1 (conventional resin) for nitrate are 23, 6, and 4, respectively.

In this research, performances of perchlorate and nitrate specialty resins in removing and desorbing inorganic co-contaminants (nitrate, As(V), Se(VI), and Cr(VI)) are investigated and compared with a conventional SBA resin, using bench-scale column testing.

4.3. Experimental

Laboratory-scale mini-columns were used to generate breakthrough curves for conventional, nitrate, and perchlorate selective resins in the presence of individual inorganic co-contaminants. Subsequently, the spent resins were regenerated using a NaCl brine solution and regeneration curves were produced. The breakthrough and regeneration curves along with resin cost comparison and waste disposal considerations were used for the performance evaluation.

4.3.1. Materials

Feed water for ion-exchange column experiments was prepared with DI water and spiked with different ions from stock solutions. Reagent-grade (99.9%) NaCl granules (EMD Chemicals Inc., USA) were added to deionized water to obtain a primary stock solution of 50 g/L Cl^-. Sodium bicarbonate ($NaHCO_3$, EMD Chemicals Inc., USA) was used to prepare a 61 g/L of HCO_3^- stock solution. A primary stock solution (1000 mg/L) for As(V) was prepared using sodium hydrogen arsenate granules ($Na_2HAsO_4.7H_2O$, Alfa Aesar, Ward Hill, MA, USA). A primary stock solution (1000 mg/L) for Cr(VI) was prepared using potassium chromate crystals (K_2CrO_4, J.T. Baker Reagent Chemicals). Nitrate stock solution (1000 mg/L) was prepared using sodium nitrate ($NaNO_3$, EMD Chemicals Inc., USA). A concentrated (10^5 mg/L) stock solution of SO_4^{2-} was prepared using (Na_2SO_4, EMD Chemicals Inc., USA). Perchlorate stock solution of 1000 mg/L was prepared using $NaClO_4$ (EMD Chemicals Inc., USA).

All glassware was soaked in an acidic solution (2% Micro-90, International Products Corp., Burlington, New Jersey) for at least 24 hours and completely rinsed with DI water before use.

Five types of resin [SBG1, SIR100, SIR111, SIR110 (ResinTech, West Berlin, NJ), and PWA2 (Rohm and Haas, Philadelphia, PA) were examined for their performances to remove inorganic that occurs as co-contaminants. SIR 111 is not commercially available, and it was produced by the ResinTech for this research. The structure of SIR111 is similar to SIR110, but SIR111 is macroporous and SIR110 is a gel type resin. The characteristics of the resins investigated are presented in Table 4.1.

Table 4.1 Characteristics of SBG1, SIR100, SIR110, SIR111, and PWA2

Resin	Application	Capacity (meq/L)	Structure	Type	Functional Group
SBG1[a]	Conventional (Type 1)	1300	Styrene-DVB	Gel	Trimethylamine
SIR100[a]	Nitrate Specialty	960	Styrene-DVB	Macroporous	Triethylamine
SIR110[a]	Perchlorate Specialty	780	Styrene-DVB	Gel	Tributylamine
SIR111[a,c]	Perchlorate Specialty	560	Styrene-DVB	Macroporous	Tributylamine
PWA2[b]	Perchlorate Specialty	600	Styrene-DVB	Gel	N.A.

[a] ResinTech
[b] Rohm and Haas
[c] SIR111 is not commercially available, and produced only for research purposes by ResinTech.

4.3.2. Experimental Procedure

The efficiency of perchlorate/nitrate specialty (selective) resins to remove co-contaminants (e.g., nitrate, arsenic, selenium, and chromium) was evaluated by generating breakthrough curves in the laboratory using column loading. Furthermore, regeneration feasibility for all resins was considered. Three perchlorate specialty resins (SIR 111, SIR 110 HP and PWA2) and one nitrate specialty resin (SIR 100) were examined for nitrate removal from synthetic waters using mini-columns, and their performance were compared with each other and to a conventional Type 1 resin (SBG1m ResinTech, West Berlin, NJ).

Column Specifications

The design of minicolumns took into consideration the fact that data obtained from the small-scale laboratory columns are usually used for the construction of the large-scale columns, and therefore the hydraulic retention time in the lab mini-columns was the same as used in full-scale operations. Other parameters considered include diameter of the column as related to the size of the ion-exchange bead, length of the column, the aspect ratio of the column (ratio of length and diameter), required mass transfer zone (MTZ), empty bed contact time (EBCT), service flow rate, regenerant concentration, regenerant contact time, and regenerant flow rate.

Minicolumn diameters of one to five centimeters are recommended for the small-scale column experiments (MWH, 2005). In this research, the minicolumn diameter of 2.54 cm was used. The critical MTZ for an ion-exchange column with a 2.54 centimeter diameter was calculated (MWH, 2005; Helfferich, 1995) as 0.7 to 0.8 cm, which showed the MTZ is not a determining factor for the selection of the length of the resin bed.

The length of the resin column was determined according to the required aspect ratio. The aspect ratio of the column is the ratio of length to diameter. A high aspect ratio increases the column utilization (Helfferich, 1995). Typically, the aspect ratio is determined and provided by the manufacturers. It has been suggested that the lab column aspect ratios of greater than 4:1 (length to diameter) are the best, and the appropriate commercial column aspect ratios are between 2:1 and 4:1 (length to diameter) (DOW website; Helfferich, 1995). At a constant diameter (or cross section) of the column, increasing the length of the column increases the breakthrough and the overall capacity of the operation. In this research, the aspect ratio of 3.9:1 (length to diameter) was used, which resulted in a length of 9.9 cm and volume of 50 mL for the resin used. The experimental Plexiglas mini-column was fabricated in the UNLV Mechanical shop.

Empty bed contact times of 2 to 4 minutes were suggested by the manufacturers (i.e., ResinTech, and Rohm and Haas). In this research, empty bed contact time of 2.5 minutes was selected for the loading process. Therefore, the loading was performed at a service flow rate of 20 mL/min. This flow rate was in the range of the suggested volumetric flow rates of 13-27 mL/min./50 mL-resin by the manufacturers.

In the resin loading tests, glass beads and wool were placed at the bottom of the column to assist with flow distribution. The feed water was pumped through the column downwards using a Masterflex 7553-70 pump (Cole-Parmer Instrument Co., Vernon Hills, IL). The pump had an adjustable speed, and was adjusted to pump 20 mL/min of the feed water into the column. Samples were collected at evenly distributed intervals using a Foxy 200 Autosampler (Teledyne Isco, Inc., Lincoln, NE). Samples containing chromium, nitrate, or perchlorate were analyzed on the same day of sample collection. Samples containing arsenic or selenium were acidified with nitric acid to lower the pH of the sample to equal or less than two, and samples were transferred to high density polyethylene (HDPE) plastic containers (Standard Methods, 2005). The HDPE plastic containers were stored in a refrigerator at 4°C prior to the measurements, and were analyzed within 2 weeks of sample collection date.

The required volume of feed water was calculated based on the influent concentrations (MWH, 2005). This calculation was required to assure the complete exhaustion and regeneration of the resin. The concentrations of contaminant in feed water as well as pH were measured prior to column experiments.

Sodium chloride was used for the regeneration of resins. The regeneration process prepares the resin for the next loading cycle by replacing the contaminant ions accumulated inside the resin with chloride. The regeneration process is more efficient when sodium chloride solution is more concentrated. However, typically, 4% to 12% NaCl (0.68 to 2.05 eq/L NaCl) solutions are used for the regeneration of the strong base anion-exchange resins because of the limited capacity of the SBA resins. The maximum capacity of the SBA resins is to 1.5 eq/L. Therefore, one to two BVs of 4% to 12% sodium chloride solution is sufficient to regenerate an exhausted resin. In this research, an 8% or 12% NaCl solution was used for the regeneration processes.

The regeneration flow rate is slower than the service flow rate. In the regeneration process, a certain regenerant contact time is required for attainment of equilibrium between the sodium chloride solution and the resin. This time allows for the transfer of the chloride ion from the solution to the resin-phase. This time must also allow the accumulated ions to transfer from the resin-phase to the solution. In view of the fact that the exhausted resin is saturated with various ions, more time is required for the regeneration process in comparison with the ion-exchange loading process (MWH, 2005). The recommended flow rates for the regeneration of the selected resins are 30 to 40 minutes. In this research, an empty bed contact time of 40 minutes was used for the regeneration of the resins. Countercurrent regeneration was performed. In counter current regeneration, the flow of NaCl solution is in the opposite direction from exhaustion flow. Ten bed volumes of NaCl were pumped into the column up-flow at the speed of 40 minutes per BV at a flow rate of 1.3 mL per minute. The samples were collected at every 0.5 BV using a Foxy 200 Autosampler (Teledyne Isco, Inc., Lincoln, NE).

Composition of Water Used in the Minicolumn Experiments

To obtain a typical water quality composition, the water compositions of various wells of the Southwestern regions of the United States were obtained from Basin Water Inc., Rancho Cucamonga, California. Table 4.2 outlines the typical concentration ranges of major water constituents in parts of the Southwestern regions of the United States. These data were used for selection of water compositions for the column runs.

Table 4.2 Typical Water Constituents in Wells Containing Inorganic Contaminants in the Southwestern Regions of the United States (Obtained from the Database of Basin Water Inc., Rancho Cucamonga, CA)

Constituent	Concentration Range	Average	Median	Unit
Chloride	2-100	75	60	mg/L
Bicarbonate	12-500	192	180	mg/L
Sulfate	1-500	168	96	mg/L
Nitrate	10-140	90	85	mg/L
Arsenic	10-200	33	26	µg/L
Selenium	0.06-400	207	200	µg/L
Chromium	5-3000	627	9	µg/L

Five ion-exchange column experiments were performed for the purpose of removing nitrate from water. The feed water composition for each test is presented in Table 4.3. The median concentrations of bicarbonate, sulfate, nitrate, and chloride were used for the experiments. A typical concentration of perchlorate (0.025 µg/L) was used to investigate whether perchlorate can be released from nitrate selective resins. The mini-columns for the experiments of SIR110 and PWA2 were run in duplicate. Each of the spent resins was regenerated using a twelve percent sodium chloride solution.

Table 4.3 Feed Water Composition of IX Column Experiments to Remove Nitrate

Feed Water Composition	Unit	Utilized Resin				
		SBG1	SIR100	SIR111	PWA2	SIR110
pH	Value	8.41	8.50	8.41	8.44	8.53
Cl^-	mg/L	60.0	60.1	60.0	60.1	64.6
HCO_3^-	mg/L	180.0	180.0	180.0	180.0	181.3
NO_3^-	mg/L	94.3	85.7	91.2	87.5	72.7
SO_4^{2-}	mg/L	100.0	100.0	100.0	100.0	100.1
ClO_4^-	μg/L	0.024	0.024	0.024	0.021	0.027

To evaluate the performance of perchlorate and nitrate specialty resins in removing and desorbing each contaminate of interest (i.e., Cr(VI), Se(VI), or As(V)), three IX column experiments were executed in duplicate using SBG1 (conventional), SIR100 (nitrate specialty), and SIR110 (perchlorate specialty) resins (Table 4.4).

Breakthrough curves were produced from the experimental results, showing concentrations of contaminant versus bed volumes of water passed through the resin column. The feed water composition is presented in Table 4.4. Typical concentrations of chloride, bicarbonate, and sulfate were selected for the column experiments. The concentration of 0.2 mg/L was selected for Cr(VI), As(V), and Se(VI); thus, the comparison between the resin capacities for Cr(VI), As(V), and Se(VI) became possible.

The spent resins were regenerated (countercurrent) using eight percent sodium chloride solutions, and regeneration curves were produced.

Table 4.4 Feed Water Composition of IX Column Experiments to Remove Cr(VI), Se(VI), or As(V)

Feed Water Composition	Unit	Utilized Resin SBG1	 SIR100	 SIR110
pH	Value	8.25	8.25	8.25
Cl^-	mg/L	70	70	70
HCO_3^-	mg/L	190	190	190
SO_4^{2-}	mg/L	170	170	170
Cr(VI)	mg/L	0.2	0.2	0.2
Se(VI)	mg/L	0.2	0.2	0.2
As(V)	mg/L	0.2	0.2	0.2

4.3.3. Analytical Methods

Nitrate (NO_3^-) and perchlorate (ClO_4^-) were measured by ion-chromatography using Standard Method 4110 (Standard Methods, 2005) on a DIONEX ICS-2000 ion chromatograph. The ion chromatograph was calibrated using six standards, covering the required measurement ranges for high (i.e., 10 to 100 mg/L) or low (i.e., 0.1 to 10 mg/L) concentrations. The calibration curves has R^2 values greater than 0.9990. An Ionpac AS 20 Analytical column (DIONEX Co., Sunnyvale, CA) or Ionpac AS16 Analytical column (DIONEX Co., Sunnyvale, CA) were used for nitrate or perchlorate measurements, respectively. An eluent solution of 8 mM KOH was used. A high performance conductivity detection cell, ASRS Ultra II (4 mm), along with a DS6 heated conductivity cell was used as a detector. The injection volume for the detection process was 1000 μL.

The detection limits of nitrate and perchlorate for the Dionex ICS-2000 were chosen as 0.01 and 0.001 mg/L. Cr(VI) concentration was measured by a DR 5000 spectrophotometer (Hach, Loveland, Colorado, USA) with a detection limit of 0.001 mg/L following the standard procedures (Method No. 3500 Cr) (Standard Methods, 2005).

Arsenic and selenium concentrations in the samples were measured with an ICP (Inductively-coupled plasma Spectrophotometer) (Thermo Electron Iris Advantage, USA) according to Method 3125 (standard methods, 2005). The pH values of the solutions were measured with an Orion 920A+ pH meter equipped with an Orion 8102BNUWP probe (Thermo Electron Corporation, USA). The pH meter was calibrated with four standardbuffers (2, 4, 7, and 10). For the loading or regeneration process, 25-mL samples were collected at planned intervals for each ion-exchange mini-column experiment using a Foxy 200 Autosampler (Teledyne Isco, Inc., Lincoln, NE). The perchlorate, nitrate, and Cr(VI) measurements were performed on the same day of the sample collection. Arsenic and selenium measurements were performed within two weeks of the sample collection date. Samples containing arsenic or selenium were acidified using nitric acid (pH < 2), and stored in a refrigerator at 4°C prior to the measurements (standard methods, 2005).

4.3.4. Cost Analysis

A cost comparison was performed to evaluate the implications of the presence of co-contaminants on the cost of water treatment and waste disposal. The data obtained for breakthrough and regeneration were used to determine the operating and capital costs of different resins considering an 8 year life time of the resins. The operating and capital costs of perchlorate/nitrate specialty and conventional resins were calculated and compared with each other.

Operating cost comparison of resins has to take into consideration the cost of salt for regeneration, and the cost of waste disposal. Resin costs were 3355 US$/m^3 for type 1 resin, 3885 US$/m^3 for nitrate specialty resin, and 6110 US$/m^3 for perchlorate specialty resin. These costs were obtained from manufacturers. The cost of salt used in the calculations was 0.120 US$/kg of salt and constitute the current market price for bulk salt certified for use in water treatment. The waste disposal cost used was 53 US$/m^3 of brine (an estimate by Basin Water Inc.). Cost estimate was performed using the laboratory column results for BVs needed for breakthrough and regeneration efficiency. Independent of the data set used, the costs presented give an assessment of the operating costs involved in using a resin for the desired contaminant.

The flow rate of 0.0505 m^3/s (200 gpm) used in the cost estimate corresponds to a small size ion-exchange system. It was assumed that a twelve-bed ion-exchange system was used, nine of the beds were in-use at all times, and three beds were in regeneration and rinse processes. The ion-exchange column bed size was 708 L, and operation days and hours in a month were 30 and 720, respectively. The empty bed contact time was 2 minutes, and 55 % resin capacity recovery was the goal of the regeneration process.

4.4. Results and Discussion

4.4.1. Loading and Regeneration for Nitrate Removal

The breakthrough curves (i.e., bed volumes of influent water processed versus effluent concentration) obtained from the laboratory minicolumn experiments for the conventional, nitrate specialty, and perchlorate specialty resins are shown in Figure 4.1. The MCL of nitrate (44 mg/L) in the effluent is shown by the dashed horizontal line in the graph. The MCL of 44 mg/L for the conventional, nitrate, and perchlorate specialty resins was reached at bed volumes of 340, 358, 422, 468, and 565, respectively. It took approximately 393, 428, 541, 643, and 720 BVs for SBG1, SIR111, SIR100, PWA2, and SIR110, respectively, to reach complete resin saturation. The feed concentration was between 85 and 90 mg/L of nitrate.

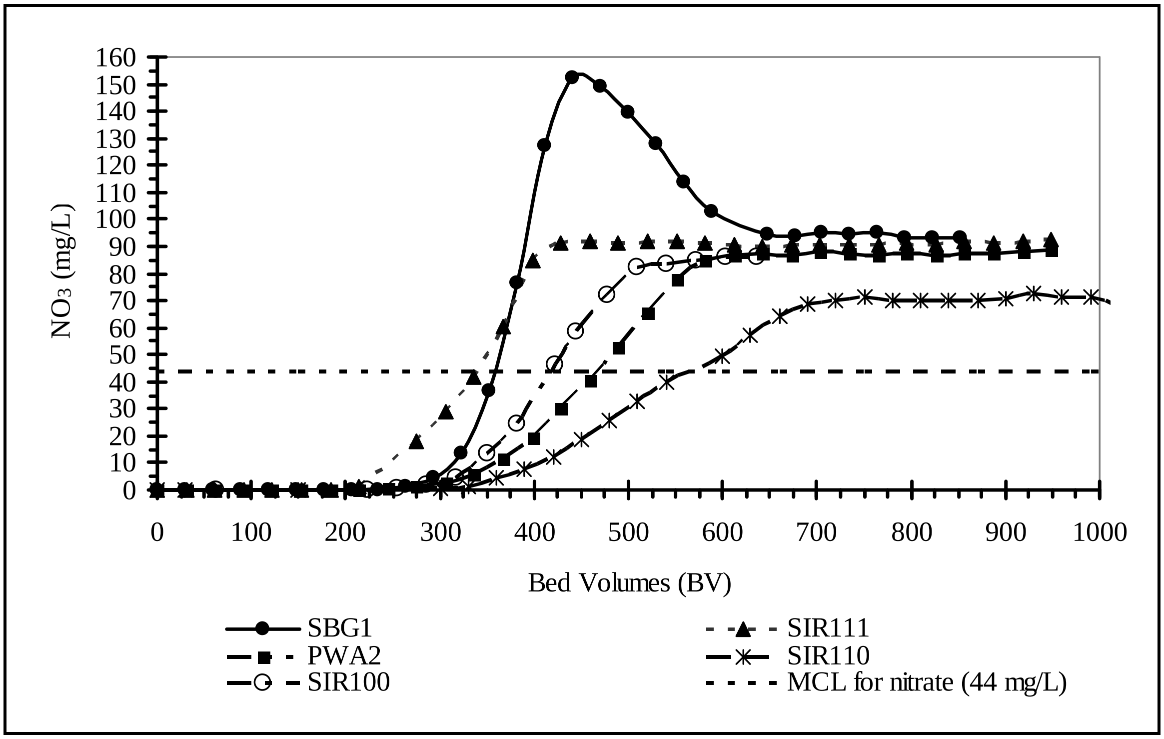


Figure 4.1 Breakthrough Curves for SBG1, SIR100, SIR111, PWA2, and SIR110 for NO_3

The bed volumes and percent differences to reach nitrate's MCL, compared to the standard Type 1 resin SBG1, for all resins examined are presented in Table 4.5. The perchlorate specialty resins, SIR110 and PWA2, showed the highest BVs and 30 to 58% more BVs before breakthrough. The nitrate specialty resin processed about 18% more BVs than the conventional resin. These results show that perchlorate specialty resins can also exchange nitrate. This finding is significant since many waters contaminated with perchlorate also contain nitrate at varying concentrations (U.S. EPA, 1999). SIR111 resin showed lower run length for nitrate removal in comparison with SBG1. The SBG1 breakthrough curve in Figure 4.1 reveals some nitrate "dumping" (i.e., concentrations higher than feed concentrations) promoted most likely by sulfate present in the feed water. SBG1 is a conventional resin where sulfate competes strongly for exchange sites.

Table 4.5 Comparison of BVs at Which the Nitrate Effluent Concentration Reached the MCL of 44 mg/L and Percent Difference in BVs in Comparison with SBG1 Resin

Column test	BVs to Breakthrough at (44 mg/L)	% difference in BVs compared to SBG1
SBG1	358	0
SIR100	422	17.9
SIR111	340	-5.0
PWA2	468	30.7
SIR110	565	57.8

Figure 4.2 shows the regeneration of the resins tested for nitrate removal utilizing 12% NaCl as the regenerant.

The amount of nitrate exchanged with the resin was calculated using the breakthrough and regeneration curves by integration of the area under the curves (Table 4.6). High nitrate capacities of 89% and 98% were found for perchlorate specialty resins, SIR 111 and PWA2. Perchlorate specialty resins SIR110 had a lower capacity of 77%. The nitrate specialty resin had a nitrate capacity of 59% while the conventional resin had a capacity of only 46%. Therefore, Perchlorate specialty resins have higher capacity to nitrate than nitrate specialty or conventional resins. The reason is that perchlorate specialty resins have higher selectivity coefficient for nitrate (i.e., 23) than nitrate specialty (i.e., 6) or conventional (i.e., 4) resin. This higher selectivity is achieved in resin manufacturing by increasing the size of the amino functional group attached to the resin (Guter, 1984). The larger the amino-group the harder it is for divalent ions, such as sulfate, to attach to the resin (Gu and Coates, 2006; Liu and Clifford, 1996; Guter, 1984).

Total nitrate recovered in the regeneration was calculated by integration of the area under the curves (Table 4.6). The nitrate specialty resin, SIR 100, was fully regenerable (i.e., 99.96%) and about 30% more efficiently regenerated than the conventional resin. Perchlorate specialty resins PWA2 and SIR 110, both gel-types, regenerated very poorly and only approximately 60% of the nitrate could be detached from the resin. However, SIR111, a perchlorate specialty macroporous regenerated with 87% efficiency. Interesting, this resin had the lowest number of BVs processed until breakthrough. These results indicate that nitrate is more easily detached from macroporous than gel perchlorate specialty resins. The specialty resins PWA2 and SIR 110 were very effective in removing nitrate from waters, but they regenerated poorly. To obtain the same level of regeneration in perchlorate specialty resins, greater amounts of regenerant would be needed (Figure 4.2) and greater amounts of brine would be generated.

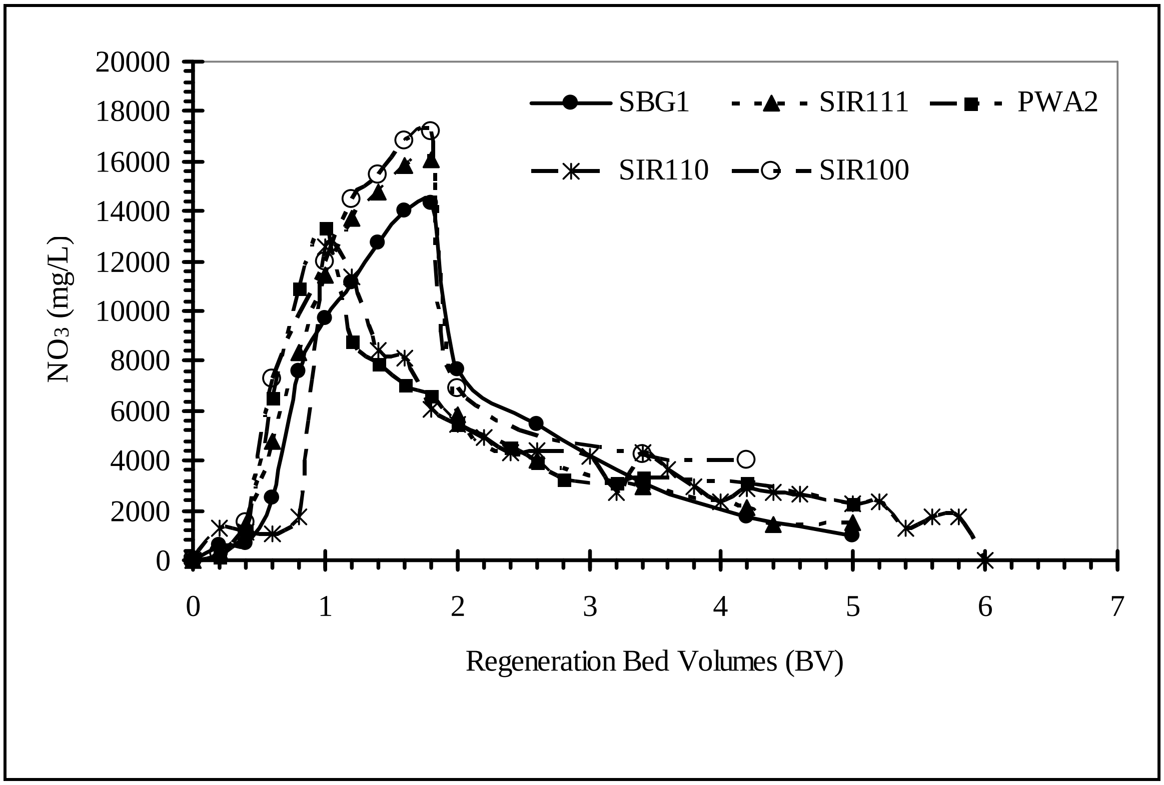


Figure 4.2 Regeneration Curve for SBG1, SIR100, SIR111, PWA2, and SIR110 with 12% NaCl after Nitrate Removal

The implications of the findings described below are significant to the treatment of waters containing both perchlorate and nitrate. If the water is treated for perchlorate and nitrate is a co-anion, then some of the resin capacity will be used up by nitrate. Because most perchlorate specialty resins are not regenerated, then the final effect is that some resin capacity will be lost to nitrate. However, the use of macroporous resin for these cases may be a feasible choice. SIR111 is not commercially available and was developed for this research. If macroporous perchlorate specialty resins were used in waters that are contaminated with perchlorate and has low levels of nitrate, the resin could be periodically regenerated to remove nitrate and free the capacity for perchlorate.

In waters where both nitrate and perchlorate are above the MCLs, one has to consider the best treatment process sequence. Treating for nitrate first with a nitrate specialty resins followed by perchlorate removal with a perchlorate specialty resin would be a feasible choice because the water exiting the nitrate system would then be treated for perchlorate with no detriment to the resin capacity from nitrate. However, one has to consider the accumulation of perchlorate in nitrate specialty resins as well. This will be discussed later in this document.

Table 4.6 Regeneration Efficiencies of Nitrate-Laden Resins – SBG1, SIR100, SIR110, SIR111, and PWA2

Resin	NO_3 captured (g-NO_3/L-resin)	NO_3 captured (meq/L)	Resin capacity (meq/L)	NO_3 capacity (%)	Selectivity Coefficients for nitrate	NO_3 in brine (g-NO_3/L-resin)	% Regeneration efficiency
SBG1	37.1	598	1300	46	4	25.8	69.6
SIR100	35.4	571	960	59	6	35.4	99.96
SIR111	31.0	500	560	89	23	26.9	86.9
PWA2	36.5	589	600	98	23	23.2	62.0
SIR110	37.4	603	780	77	23	23.1	61.7

Table 4.7 shows operating cost calculations when considering the breakthrough BVs and regeneration BVs obtained in the laboratory experiments. The results show that

nitrate specialty resin is the least costly resin for removing nitrate from drinking water. Using a conventional resin for nitrate removal increased the operating cost by 70.7 % in comparison with a nitrate specialty resin. Although some perchlorate specialty resins showed higher capacity for nitrate, their overall operating costs were higher (29.1 % to 117.8 %) than a nitrate specialty resin.

Table 4.7 Operating Cost Estimate for Nitrate Removal by Various Resin Types

Resin	BVs of Salt used for 55 % NO_3 removal	BVs of brine used in a month	Salt + waste disposal cost, US$ per month	% Difference with SIR100
SIR100	1.4	178.8	8,692.1	0.0
SBG1	2.9	305.2	14,834.3	70.7
SIR111	1.9	230.9	11,222.5	29.1
PWA2	3.6	402.3	19,558.2	125.0
SIR110	4.7	389.5	18,934.7	117.8

Using perchlorate specialty resins to remove nitrate is not recommended. Although these resins showed higher capacities and bed volumes to treat nitrate, they required higher volumes of sodium chloride brine to regenerate, resulting in higher operational costs.

Perchlorate specialty resins are more expensive than nitrate specialty resins. Therefore, if perchlorate specialty resins are used for the removal of nitrate, one has to weigh the larger capacity of nitrate against higher salt costs and waste disposal.

The performance from several bench and pilot scale studies using various ion-exchange resins are summarized in Table 4.8.

Table 4.8 Comparison of Results for IX Resins in Removing Nitrate from Waters

Resin Name/ Manufacturer	Resin Type	Influent Nitrate (mg/L)	Effluent Nitrate (mg/L)	Experiment Scale	BVs	Reference
Amberlite IRA 996 Rohm & Haas	Nitrate specialty	46.5	31	Bench	750	Ghurye et al., 1999
Ionac SR6 Syborn	Nitrate specialty	46.5	31	Bench	680	Ghurye et al., 1999
Amberlite IRA 458 Rohm & Haas	Conventional	46.5	31	Bench	610	Ghurye et al., 1999
Amberlite IRA 404 Rohm & Haas	Conventional	46.5	31	Bench	560	Ghurye et al., 1999
Duolite A101-D Auchtel	Conventional	70.9	42	Pilot	137	Lauch & Guter, 1986
SIR 110	Perchlorate specialty	72.7	44	Bench	565	This research
SIR 100 ResinTech	Nitrate specialty	85.7	44	Bench	422	This research
PWA2 Rohm & Haas	Perchlorate specialty	87.5	44	Bench	460	This research
SIR111 ResinTech	Perchlorate specialty	91.2	44	Bench	340	This research
SBG1 ResinTech	Conventional	94.3	44	Bench	358	This research
Amberlite IRA 996 Rohm & Haas	Nitrate specialty	96.5	44	Pilot	450	Liu & Clifford, 1996
Ionac SR6 Syborn	Nitrate specialty	96.5	44	Pilot	350	Liu & Clifford, 1996
Ionac ASB-1P Syborn	Conventional	96.5	44	Pilot	205	Liu & Clifford, 1996
A520E Purolite	Nitrate specialty	100.1	44	Bench	580	Samatya et al., 2006

The amount of water treated ranged from 327 to 750 BVs and from 137 to 610 BVs using nitrate selective and conventional resins, respectively. Typically, the effluent water had less than 44 mg/L nitrate while the influent water nitrate concentrations were as high as 100.1 mg/L of nitrate. In this research, the influent nitrate concentration of 90 mg/L was used, and the conventional resin treated 358 BVs of water while nitrate or perchlorate specialty resins treated 422 or 565 BVs of water, respectively. Both nitrate specialty and conventional resins have been used to remove nitrate from waters.

However, nitrate specialty resins can achieve higher number of BVs than conventional resin, and nitrate specialty resins can be regenerated easier than conventional resins. Liu and Clifford (1996) reported that Amberlite IRA 996, a nitrate specialty resin, treated 450 BVs of water containing 96.5 mg/L nitrate. In this research, SIR 100, a nitrate specialty resin, treated 422 BVs of water containing 85.7 mg/L nitrate. A conventional resin, Ionac ASB-1P, treated 205 BV of water containing 96.5 mg/L, while in this research, a conventional resin, SBG1, treated 358 BV of water containing 94.3 mg/L nitrate.

Investigation of the Presence of Perchlorate in Regenerant Brines

In this research, the water fed to the ion-exchange columns contained 24-27 µg/L of perchlorate. The goal was to investigate whether perchlorate would accumulate in the resins for waters that must be treated for nitrate, but yet contain small concentrations of perchlorate. Table 4.9 shows the concentrations of perchlorate in the feed water of the IX column experiments and the brines which were generated in those experiments. Perchlorate was not detected in the brines of the IX column experiments, even for the SBG 1 resin that was a conventional resin. The detection limits of perchlorate in drinking water and brines were 1 and 20 µg/L.

Considering, for example, the SIR 100 resin that processed 422 BVs of water containing 24.2 µg/L of perchlorate for nitrate to breakthrough, this corresponded to a loading of 84.4 µg/L of perchlorate. If all perchlorate was removed into 3 BVs (30 mL) of brine, 2800 µg/L of perchlorate was expected to be present in the brine. However, perchlorate was not detected. It indicates that perchlorate was exchanged and accumulated in all types of resin used, but it was not removed at significant levels from the resins during regeneration. Concurrent removal of perchlorate and nitrate will be discussed next.

Table 4.9 Perchlorate Concentrations in the Feed Waters and the Brines of IX Column Experiments

Resin name	Perchlorate (μg/L) Feed water	Perchlorate (μg/L) in Brine First 3 BVs of regeneration	Perchlorate (μg/L) in Brine BVs 4-5 of regeneration
SBG1	24.1	Non detect	Non detect
SIR100	24.2	Non detect	Non detect
PWA2	20.6	Non detect	Non detect
SIR110	26.6	Non detect	Non detect
SIR111	24.2	Non detect	Non detect

The results of several studies that investigated the efficiency of ion-exchange resins used to remove perchlorate from groundwaters are shown in Table 4.10. The reported range of groundwater volumes treated is from 10,000 to 420,000 BVs, depending on the influent perchlorate concentration. A perchlorate selective resin treated up to 420,000 BVs of groundwater containing 8-11 μg/L perchlorate, and 37,000 BVs of groundwater containing 860 μg/L of perchlorate (Siegel et al., 2007; Carlin et al., 2004; Gu et al., 2007). A nitrate selective resin treats 17,000 to 60,000 BVs of groundwater containing 8 to 450 μg/L of perchlorate. A conventional strong base Type 1 resin treats up to 10,000 BVs of groundwater containing 100 μg/L of perchlorate. Conventional resins can treat 2000-3760 BVs of water contaminated with high initial concentration of 40 mg/L perchlorate (Batista et al., 2002).

Table 4.10 Comparison of Results for IX Resins in Removing Perchlorate

Resin Name/ Manufacturer	Resin Type	Influent Perchlorate (μg/L)	Effluent Perchlorate (μg/L)	Experiment Scale	BVs	Reference
SIR 110 ResinTech	Perchlorate selective	8-11	n.d.	Bench Pilot	420,000 > 110,000	Siegel et al., 2006
PWA2 Rohm and Haas	Perchlorate selective	8-11	n.d.	Bench Pilot	220,000 > 110,000	Siegel et al., 2006
A530E Purolite	Perchlorate selective	8-11	n.d.	Bench Pilot	105,000 65,000	Siegel et al., 2006
SR-7 Syborn	Perchlorate selective	8-11	n.d.	Bench	80,000	Siegel et al., 2006
PWA555 Rohm and Haas	Nitrate selective	8-11	n.d.	Bench	60,000	Siegel et al., 2006
A520E Purolite	Nitrate selective	50	n.d.	Bench	20,000	Gu et al., 1999
D3696 Purolite	Perchlorate selective	50	n.d.	Bench	100,000	Gu et al., 1999
SBG1 & SBG2 ResinTech	Conventional	90-100	n.d.	Bench	10,000	Wang et al., 2008
NSR-1 DOW	Nitrate selective	90-100	n.d	Bench	17,000	Wang et al., 2008
PWA1 Rohm and Haas	Conventional	200	100	Pilot	27,173	Carlin et al., 2004
PWA555 Rohm and Haas	Nitrate selective	200	100	Pilot	84,183	Carlin et al., 2004
PWA2 Rohm and Haas	Perchlorate selective	200	100	Pilot	221,206	Carlin et al., 2004
A520E Purolite	Nitrate selective	450	n.d.	Full	17,000	Gu et al., 2003
D3696 Purolite	Perchlorate selective	450	n.d.	Full	19,000	Gu et al., 2003
A530 E Purolite	Perchlorate selective	860	n.d.	Full	37,000	Gu et al., 2003
ASB1 Ionac	Conventional	40 mg/L	n.d.	Bench	3,760	Batista et al., 2002
Macro T Sybron	Conventional	40 mg/L	n.d.	Bench	2,000	Batista et al., 2002

(n.d. = non detectable)

Concurrent Removal of Nitrate and Perchlorate

If perchlorate and nitrate simultaneously occur in water at higher concentrations than their MCL, both nitrate and perchlorate specialty resins can be used. The resin must be regenerated when nitrate breaks through while perchlorate accumulates in the resin and is not released by the regeneration. Therefore, when perchlorate breaks through, the resin must be replaced. With the current market prices, utilizing a nitrate specialty resin is less costly than using a perchlorate specialty resin.

Table 4.11 shows the total cost estimate for simultaneous removal of 11 μg/L perchlorate and 87.5 mg/L nitrate from drinking water using either a perchlorate specialty resin or a nitrate specialty resin. The BVs for perchlorate breakthrough were selected from Table 4.10. The BVs for the nitrate breakthrough were obtained from the current study. These values were used for the cost analysis shown in Table 4.11. Even though the perchlorate specialty resin lasted longer, its operating cost was more than the nitrate specialty resin, which resulted in 1.2 times more in the total cost.

Table 4.11 Total Cost Estimate for Simultaneous Perchlorate and Nitrate Removal by a Perchlorate or Nitrate Specialty Resin

Resin	Perchlorate breakthrough	Nitrate breakthrough	Operating cost US$/month	Resin cost US$/month	Total Cost US$/month
Perchlorate specialty	220,000	468	19,558	5,096	24,654
Nitrate specialty	60000	422	8,692	11,880	20,572

When treating water that contains nitrate (concentrations higher than MCL) and low levels of perchlorate, one has to consider the impact of accumulated perchlorate on the life of the resin. Table 4.12 shows the approximate run time of a nitrate specialty resin when treating waters with very low levels of perchlorate (1 μg/L to 9 μg/L). The amount of perchlorate captured by the resin corresponds to 6.6 meq/L. The nitrate specialty resin had a total capacity of 960 meq/L. The accumulated perchlorate in the resin accounts for approximately 1 % of the total resin capacity. Notice that it would 3 to 31 months for perchlorate to break through. Considering resin field lives of 8-12 years, the impact of perchlorate accumulation when treating nitrate-contaminated is negligible. However, when high concentrations of perchlorate are present in water, the design of IX treatment systems for nitrate removal should take into consideration the capacity loss that occurs with time due to the accumulation of perchlorate in the resin.

Table 4.12 Estimation of Perchlorate Accumulation into a Nitrate Specialty Resins

Influent Perchlorate (μg/L)	Run time (month)	Perchlorate captured (meq/L-resin)	BVs of water treated
1	31	6.6	660,000
2	15	6.6	330,000
3	10	6.6	220,000
4	8	6.6	165,000
5	6	6.6	132,000
6	5	6.6	110,000
7	4	6.6	94,286
8	4	6.6	82,500
9	3	6.6	73,333

4.4.2. Loading and Regeneration for Cr(VI) Removal

Figure 4.3 shows the Cr(VI) concentrations in the effluent of IX columns with SBG1 (a conventional resin), SIR100 (a nitrate specialty resin), or SIR110 (a perchlorate specialty resin). The graph presents the Cr(VI) concentration in effluent versus bed volumes of feed water processed. The MCL of the Cr(VI) (0.1 mg/L) in the effluent is shown by the dashed horizontal line in the graphs. The feed water for all experiments had Cr(VI) concentration of 0.2 mg/L. The Cr(VI) concentration in the effluent of the columns reached the chromium MCL of 0.1 mg/L in the order of SIR110, SIR100, and SBG1. The bed volumes at which the SIR110, SIR100, and SBG1 resins passed the 0.1 mg/L of Cr(VI) in their effluent were 1176, 1935, and 2015, respectively. The complete breakthrough of Cr(VI) for SIR110, SIR100, and SBG1 occurred at 1848, 3016, and 3472 BVs, respectively.

The bed volumes to achieve breakthrough at 0.1 mg/L MCL and the percent difference in the performances for the three resins examined are presented in Table 4.13. SBG1, a Type I conventional strong base resin, showed the highest run length for Cr(VI) removal. SIR100, a nitrate specialty resin, which has a higher selectivity for nitrate than SBG1 and lower selectivity for sulfate than SBG1, showed approximately similar run length with only a -4 % difference in run length. Therefore, low chromium concentrations present in waters being treated for nitrate or perchlorate with specialty resin, will accumulate in the resin. This is particularly important in the case of nitrate and perchlorate specialty resins because they have long run times before regeneration takes place.

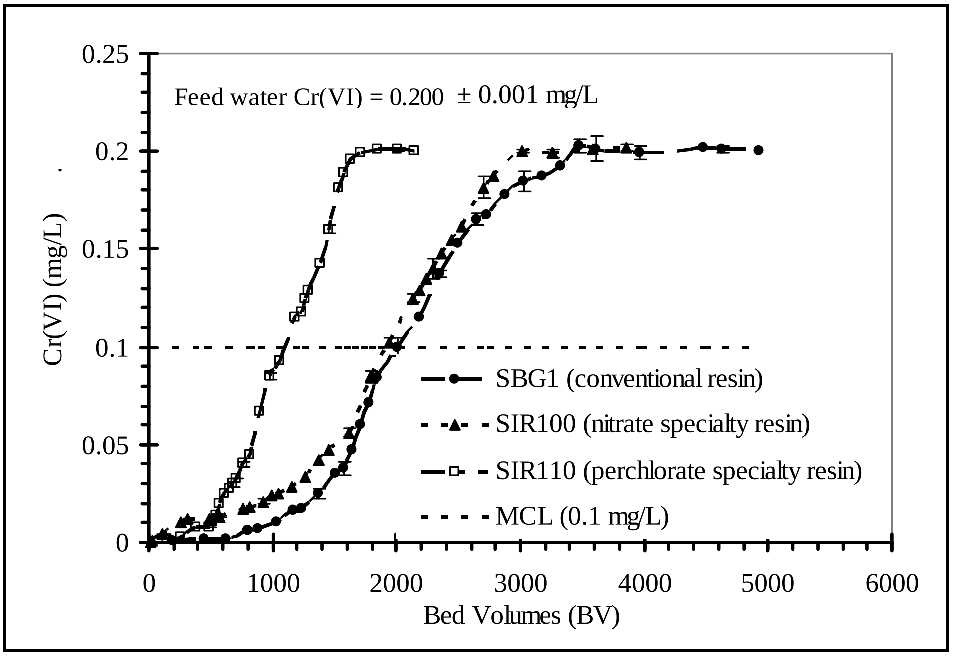


Figure 4.3 Breakthrough Curves for SBG1, SIR100, and SIR110 for Cr(VI)

Table 4.13 Comparison of BVs at Which the Cr(VI) Effluent Concentration Reached the MCL of 0.1 mg/L and Percent Difference in BVs in Comparison with SBG1 Resin

Column test	BVs to Breakthrough at (0.1 mg/L)	% difference in BVs compared to SBG1
SBG1	2015	0
SIR100	1935	-4
SIR110	1176	-42

Figure 4.4 depicts the regeneration curves, using 8% NaCl, for SBG1, SIR100, and SIR110. The Cr(VI) concentration in the generated brine was below 5 mg/L after 2.5, 3.5, and 5.5 for SIR110, SIR100, and SBG1, respectively. The lowest volume of brine was used for the regeneration of SIR110, and the highest volume of brine was utilized for the regeneration of SBG1. A lower volume of brine for regeneration translates to a lower

operational cost. The reason for this is the lowest selectivity of SIR110 for Cr(VI) and highest selectivity of SBG1 for Cr(VI). The selectivity of SIR 100 for Cr(VI) is between that of SIR110 and SBG1 (ResinTech).

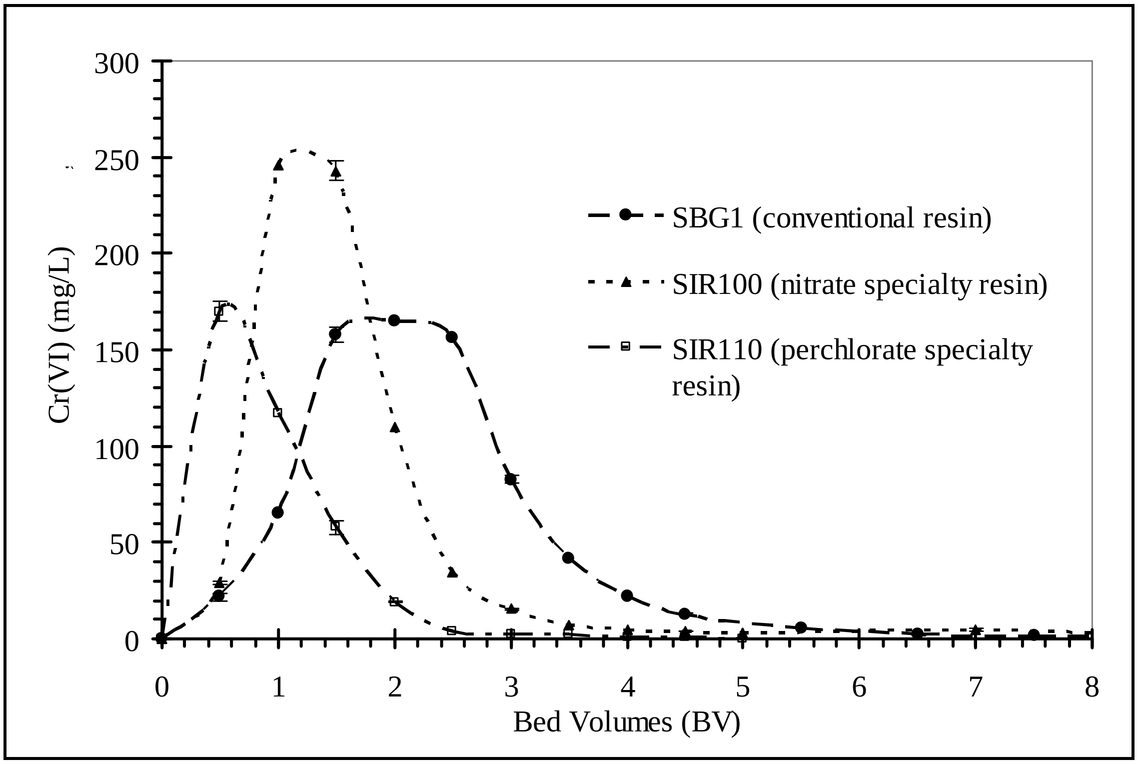


Figure 4.4 Regeneration Curves for SBG1, SIR100, and SIR110 with 8% NaCl for Cr(VI) Removal

The total Cr(VI) exchanged in the loading and total Cr(VI) recovered in the regeneration process are presented in Table 4.14. The amount of Cr(VI) exchanged with the resin and recovered in the regeneration was calculated by integration of the area under the regeneration curves. SBG1, SIR100, and SIR110 had the total Cr(VI) removal capacity of 15.8, 13.9, and 8.3 meq/L-resin. Therefore, the Type I conventional resin

(SBG1) had a greater capacity for Cr(VI) than the nitrate and perchlorate specialty resins. However, The perchlorate specialty resin, SIR 110, had the lowest capacity for Cr(VI). The reason for this can be explained by the higher selectivity of SBG1 for Cr(VI) (1.3) than SIR100 (0.2) or SIR110 (0.03).

Table 4.14 Regeneration Efficiencies of Cr(VI)-Laden Resins – SBG1, SIR100, and SIR110

Resin	Cr(VI) captured (mg-Cr(VI)/L-resin)	Cr(VI) captured (meq/L)	Resin capacity (meq/L)	Cr(VI) Capacity %	Selectivity coefficients[a] (Relative to Cl^-)	Cr(VI) in brine (mg-Cr(VI)/L-resin)	% Regeneration efficiency
SBG1	411	15.8	1300	1.2	1.3	376	91.5
SIR100	362	13.9	960	1.5	0.2	362	100
SIR110	217	8.3	780	1.1	0.03	187	86.2

[a] Obtained from ResinTech Inc., NJ

Although SBG1 showed the highest capacity for Cr(VI), SIR100 (nitrate specialty resin) showed excellent regeneration efficiency. The higher regeneration efficiency and lower salt requirement of SIR100 when compared to SBG1 indicates that SIR100 is more cost effective in removing Cr(VI) from high sulfate water. The implication of these findings is that plants treating for inorganic contaminants using specialty resins should be aware of the capacity loss due to the constant accumulation of other anions (e.g., chromium) in the resin. This is important because run times for specialty resins are very long. In the case of chromium, regeneration is able to remove most of the accumulated metal and resin capacity can be restored. However, the accumulated chromium will end up in the brine solution. If chromium concentrations are above the TCLP limit of 5mg/L the brine will be classified as a hazardous waste, significantly affecting the cost of brine disposal

4.4.3. Loading and Regeneration for Se(VI) Removal

Figure 4.5 shows the Se(VI) concentrations in the effluent of IX columns with SBG1 (a conventional resin), SIR100 (a nitrate specialty resin), or SIR110 (a perchlorate specialty resin) versus bed volumes when treating a water containing 0.21 mg/L of Se(VI). The MCL of the Se(VI) (0.05 mg/L) is shown by the dashed horizontal line in the graphs. The perchlorate selective, nitrate selective, and the conventional resins reached the selenium MCL of 0.05 mg/L at 145, 274, and 355 bed volumes, respectively. The SIR110 breakthrough curve in Figure 4.5 shows that there was some Se(VI) “dumping” (i.e., concentrations higher than feed concentrations) promoted most likely by sulfate present in the feed water. This happened with SIR110 because it had the lowest affinity for Se(VI). Selenate is more preferred by SBA resins than selenite (Maneval et al., 1985, Clifford, 1999). The selectivity of selenate, selenite, and competing anions for a SBA resin was reported to be in order of $SeO_4^{2-} > NO_3^- > SeO_3^{2-} > Cl^- > HCO_3^-$ (Maneval et al., 1985, Clifford, 1999).

Table 4.15 presents the bed volumes at which the concentrations of selenium reached the Se(VI) MCL (0.05 mg/L) and the percent difference between the bed volumes for all the resins investigated. SBG1, the conventional strong base resin, showed the highest run length for Se(VI) removal, followed by SIR100 and finally SIR110. The results showed that the nitrate and perchlorate specialty resins, SIR100 and SIR 110 have significantly lower efficiencies than SBG1.

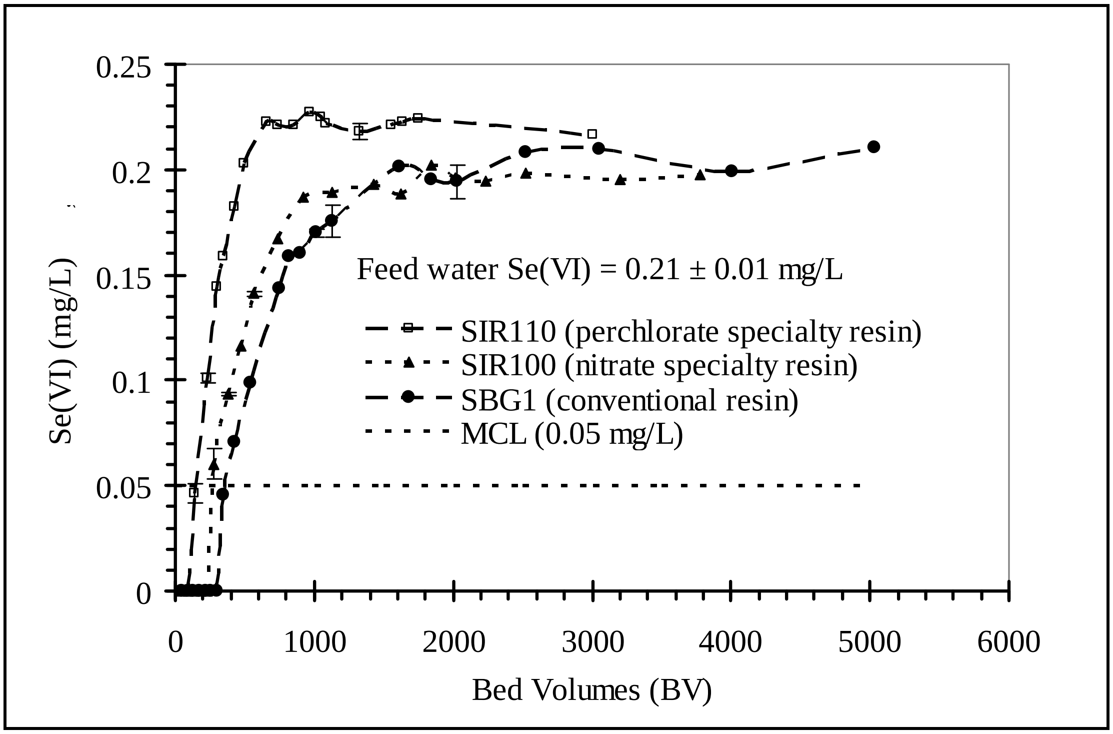


Figure 4.5 Breakthrough Curves for SBG1, SIR100, SIR111, PWA2, and SIR110 for Se(VI)

Table 4.15 Comparison of BVs at Which the Se(VI) Effluent Concentration Reached the MCL of 0.05 mg/L and Percent Difference in BVs in Comparison with SBG1 Resin

Column test	BVs to Breakthrough at (0.05 mg/L)	% difference in BVs compared to SBG1
SBG1	145	0
SIR100	274	-23
SIR110	355	-59

Figure 4.6 shows the regeneration curves, using 8% NaCl, for Se(VI)-laden SBG1, SIR100, and SIR110 resins. SBG1 required the highest bed volumes of NaCl for releasing the Se(VI), followed by SIR100 and SIR110. For instance, the concentrations of Se(VI) in the brine were below 5 mg/L after 2.5, 3.0, and 3.5 bed volumes of brine for SIR110, SIR100, and SBG1, respectively.

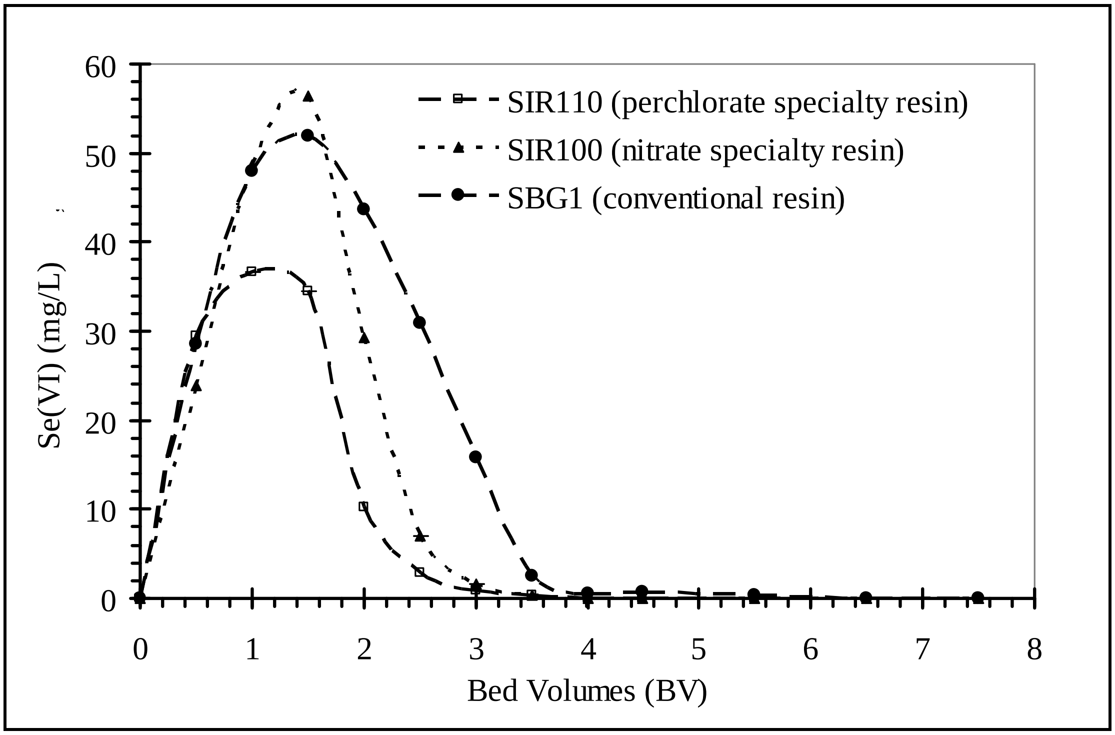


Figure 4.6 Regeneration Curves for SBG1, SIR100, and SIR110 with 8% NaCl

The total Se(VI) accumulated in the resins during the loading and total Se(VI) recovered in the regeneration process are presented in Table 4.16. SBG1, SIR100, and SIR110 had total Se(VI) removal capacities of 3.7, 2.7, and 1.6 meq/L-resin, respectively.

The Se(VI) capacity was the same for the perchlorate and nitrate selective resins and about 30% lower for the conventional resin. SBG1 had the highest capacity for Se(VI); however, SIR110 was the easiest to regenerate. The conventional and nitrate selective resins could be regenerated at 78% level. Therefore, selenium present as a co-contaminant in waters will accumulate in nitrate and perchlorate specialty resins. The accumulated selenium can be removed during regeneration. However, depending on the amount of brine used and the concentration of selenium in waters, waste brines generated in these processes may be deemed hazardous if high selenium concentrations are present. This is specially the case if the resins are used for a long time before breakthrough occurs. In this case significant amount of selenium will accumulate before regeneration.

Table 4.16 Regeneration Efficiencies of Se(VI)-Laden Resins – SBG1, SIR100, and SIR110

Resin	Se(VI) captured (mg-Se(VI)/L-resin)	Se(VI) captured (meq/L)	Resin capacity (meq/L)	Se(VI) capacity %	Selectivity coefficients (Relative to Cl^-)	Se(VI) in brine (mg-Se(VI)/L-resin)	% Regeneration efficiency
SBG1	144.5	3.7	1300	0.2	0.1	111.8	77.4
SIR100	106.1	2.7	960	0.3	0.02	83.6	78.8
SIR110	62.4	1.6	780	0.3	0.002	92.1	92.1

4.4.4. Loading and Regeneration for As(V) Removal

The breakthrough curves of As(V) for SIR110, SIR100, and SBG1 are presented in Figure 4.7 when feed water contained 0.2 mg/L of As(V).

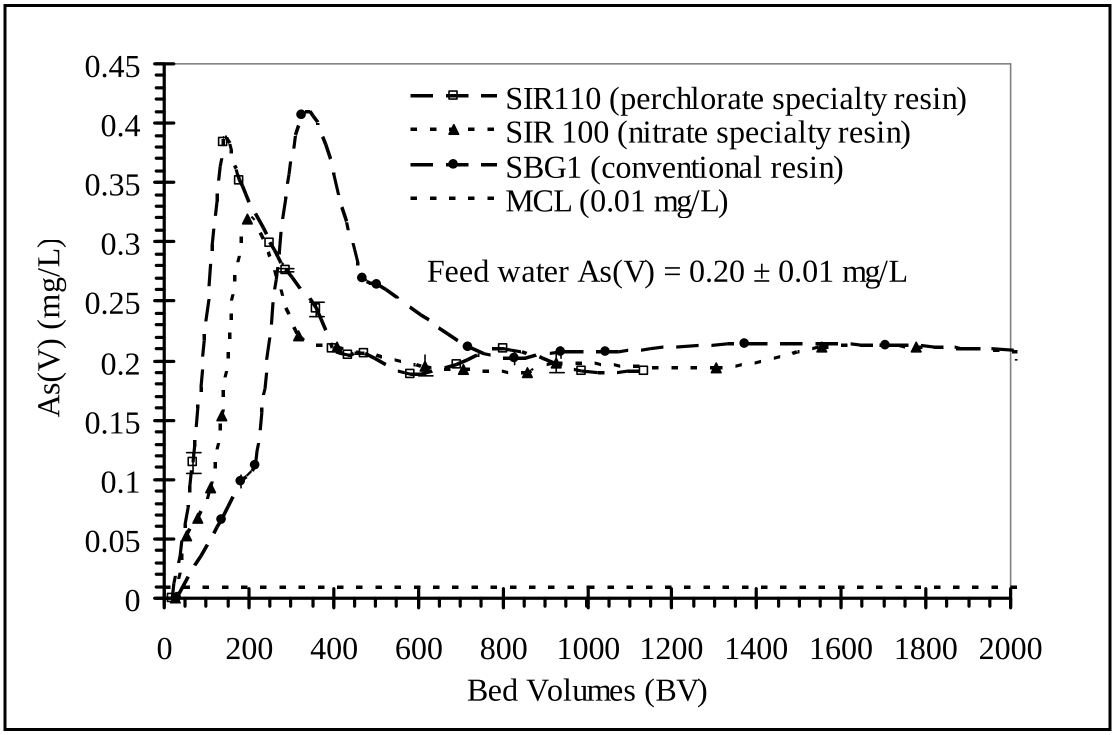


Figure 4.7 Breakthrough Curves for SBG1, SIR100, SIR111, PWA2, and SIR110 for As(V)

The concentrations of As(V) reached the As(V) MCL of 0.01 mg/L at 24, 32, and 46 bed volumes when utilizing SIR110, SIR100, and SBG1 resins, respectively. The SIR110, SIR100, and SBG1 resins were completely exhausted of As(V) at 91, 154, and 249 bed volumes, respectively. After the exhaustion point, all the resins started to release As(V) into the effluent; thus, the As(V) concentrations in the effluents increased. The reason for releasing As(V) is the very low affinity of these resins for As(V) in comparison with their affinity for Cr(VI). Immediate breakthrough of the resins occurred due to the high concentration of As(V) in the feed water. Typically, drinking water As(V) concentrations are lower and more bed volumes of water can be treated prior to the breakthrough. However, this As(V) concentration has satisfied the purpose of this research. The results indicate that arsenic does not exchange well with perchlorate and nitrate selective resins. Therefore, if this resins are used in waters where As(V) is a co-contaminant, only an insignificant amount of arsenic would accumulate in the resin.

The bed volumes at which each resin reached the As(V) MCL of 0.01 mg/L and their respective percent differences in As(V) removal in comparison with SBG1 are shown in Table 4.17. SBG1 lasted the longest and the As(V) removal efficiency decreased by 30 % and 48 % when SIR100 or SIR110 was utilized, respectively. Therefore, perchlorate and nitrate specialty resins do not exchange arsenic. The reason is that the predominant species of arsenic at this pH range is divalent and specialty resins are designed to exclude sulfate and other divalent anions.

Table 4.17 Comparison of BVs at Which the As(V) Effluent Concentration Reached the MCL of 0.01 Mg/L and Percentage Differences in BVs in Comparison with SBG1 Resin

Column test	BVs to Breakthrough at (0.01 mg/L)	% difference in BVs compared to SBG1
SBG1	46	0
SIR100	32	-30
SIR110	24	-48

Figure 4.8 exhibits the regeneration curves, using 8% NaCl, for As(V)-laden SBG1, SIR100, and SIR110 resins. The lowest volumes of NaCl brine was needed for regenerating the As(V)-laden SIR110 in comparison with SIR100 and SBG1. Almost similar volumes of NaCl brine were needed to recover the same amount of As(V) from SIR100 and SBG1. For instance, the concentrations of As(V) in the brine were below 0.1

mg/L after 3.0, 3.5, and 4.5 bed volumes were utilized for SIR110, SIR100, and SBG1, respectively. Nonetheless nitrate and perchlorate specialty resins accumulate a very small amount of arsenic and the small amount accumulated is not easily removed with NaCl brine.

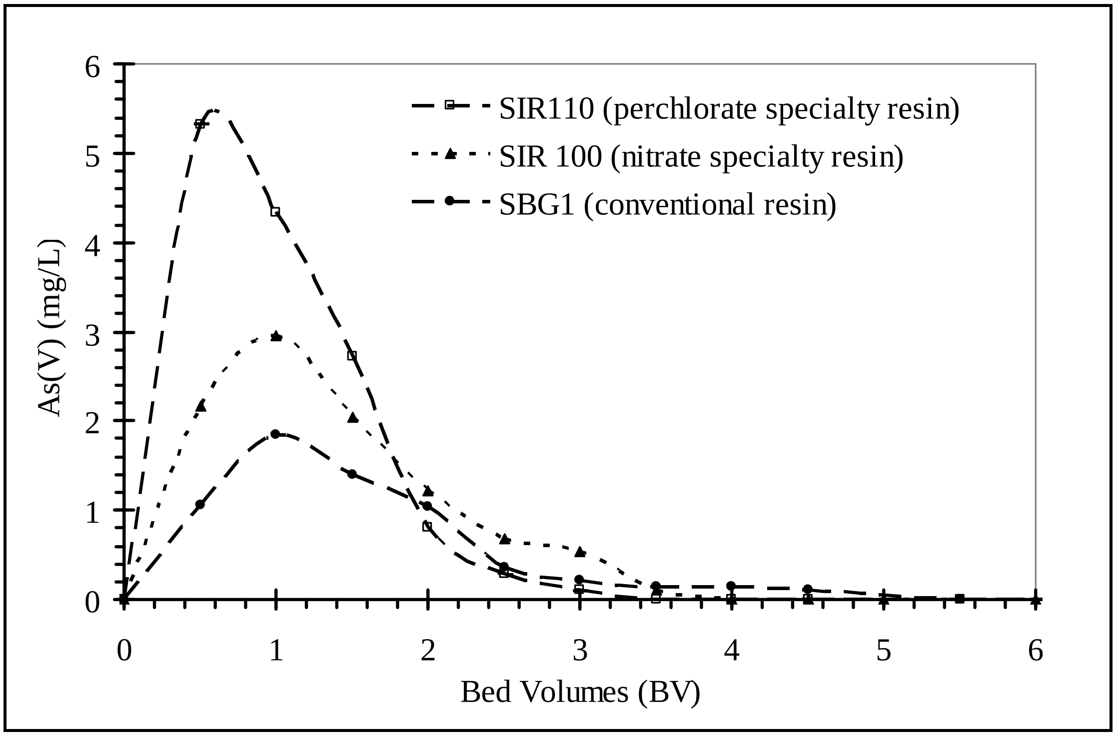


Figure 4.8 Regeneration Curves for SBG1, SIR100, and SIR110 with 8% NaCl for As(V)

The total As(V) exchanged and accumulated in the resins during the As(V) removal process, and total As(V) released in the regeneration process are presented in Table 4.18. SBG1, SIR100, and SIR110 had the total As(V) removal capacities of 0.65, 0.38, and 0.32 meq/L-resin. It can be concluded that SBG1 is the best to use when removing As(V) from water. Similarly, Ghurye et al. (1999) reported that conventional resins were more efficient for combined arsenic and nitrate removal, showing longer run lengths and less arsenic and nitrate leakage into the effluent.

Table 4.18 Regeneration Efficiencies of As(V)-Laden Resins – SBG1, SIR100, and SIR110

Resin	As(V) removed (mg-As(V)/L-resin)	As(V) captured (meq/L)	Resin capacity (meq/L)	As(V) capacity %	Selectivity coefficients (Relative to Cl^-)	As(V) in brine (mg-As(V)/L-resin)	% Regeneration efficiency
SBG1	24.4	0.65	1300	0.05	0.075	3.2	13.1
SIR100	14.3	0.38	960	0.04	0.015	4.8	33.6
SIR110	12.1	0.32	780	0.04	0.0015	6.8	56.2

4.5. Implication of the Findings Regarding The Use of Perchlorate and Nitrate Specialty Resins in Waters with Other Co-Contaminants

This research is the first attempt, to the best of my knowledge, to address the impact of co-contaminants in ion-exchange systems that use perchlorate and nitrate specialty resins. The use of specialty IX resins has become more prevalent in the last decade because of new regulations regarding the presence of perchlorate and arsenic in waters.

One issue addressed in this research was whether perchlorate selective resins could be used for nitrate removal. It was found that nitrate can be removed from waters using perchlorate specialty resins. Perchlorate specialty resins can support 1.7 to 3.2 times more BVs processed before breakthrough than nitrate specialty resins. Despite their higher capacity for nitrate, perchlorate specialty resins do not regenerate well. They require more brine to achieve the same regeneration efficiency of a nitrate specialty resin. The low regeneration efficiency of perchlorate specialty resins, when used for nitrate removal, results in higher salt cost and higher brine disposal cost as compared to nitrate specialty resins. Operating costs for SIR 100, a nitrate specialty resin, are 2.3 times less than those for the perchlorate specialty resins SIR 110 and PWA2. The operating cost for SIR 111, a macroporous perchlorate specialty resin, is about 1.3 times more than that of the nitrate specialty resin, SIR 100. Therefore, using perchlorate specialty resins solely for the purpose of nitrate removal is not recommended. However, this research also found that generation of a macroporous perchlorate specialty resins (SIR 111), loaded with nitrate, was very effective. This resin was specially made for this research and it is not available commercially at large amounts. However, this type of resin may find applications in waters contaminated with both nitrate and perchlorate.

A second issue investigated was whether perchlorate accumulated in nitrate selective resin could be desorbed during the regeneration cycle. Significant amounts of perchlorate were not found in the regeneration brines of nitrate and perchlorate specialty resins. This confirms that perchlorate is not easily removed from either nitrate or perchlorate specialty resins. Therefore, in nitrate removal systems, where perchlorate occurs as a co-contaminant, part of the capacity of the resin will be lost with time because of perchlorate accumulation. Such accumulation may result in earlier replacement of resin beds, which constitute a major cost.

A third issue evaluated was the concurrent removal of perchlorate and nitrate in waters where both contaminants occur at levels higher than the permissible level. When this occurs, nitrate breaks through first as compared to perchlorate, because nitrate in waters occurs at the mg/L level while perchlorate contamination is generally at the ppb level. If one ion-exchange system is used to remove both, the resin will be regenerated for nitrate and perchlorate accumulates. Once the capacity for perchlorate is exhausted then resin of the entire system must be disposed off. This occurs because perchlorate-selective resins generate very poorly. An option is to use two ion-exchange systems in series. In this case, perchlorate will always be removed in the first system because both nitrate and perchlorate selective resins exchange perchlorate. The second system can then be used, and generated, for nitrate removal. That system will not accumulate perchlorate, because it has been removed in the first system. Perchlorate usually occurs at very low concentrations in water (at μg/L level), and, therefore, it captures very small part of the resin capacity (about 1%-3%). Considering resin field lives of 8-12 years, the impact on resin capacity from very low perchlorate concentrations, when treating nitrate-contaminated waters, is very small.

A fourth issue addressed was con-current removal of nitrate and Cr(VI), Se(VI), or As(V). It was found that simultaneous removal of nitrate and Cr(VI) is optimal when using nitrate specialty resin. Chromium occurs naturally in groundwaters in the range of 0.0005-0.21 mg/L in the United States (U.S. EPA, 2002; Guertin et al., 2004). The results of this research showed that 1176 to 2015 BVs of water that contain 0.2 mg/L of Cr(VI) can be treated by IX resins. Typically, 327 to 750 BVs of water can be treated when removing nitrate from water (Table 4.8). Therefore, when treating waters that contain high concentrations of nitrate and Cr(VI), nitrate breaks through sooner than Cr(VI) without regard the type of the resin. From the cost analysis and the results of IX column experiments, it can be concluded that for removing nitrate and Cr(VI) from water, nitrate specialty resins are less costly and more efficient than conventional resins. However, a major concern of the presence of chromium as a co-contaminant is its impact on brine disposal. Depending on the concentration of Cr(VI) in the influent water and the number of BVs run to breakthrough, the waste regenerant brine could contain concentrations high enough to deem the waste hazardous. Waste brines that contain nitrate only are not considered hazardous and are easy to dispose off because nitrate is highly biodegradable. However, if chromium is present at concentrations above the TCLP limit, the waste will be hazardous.

In view of the fact that Se(VI) and As(V) are poorly removed with nitrate specialty resins, a conventional resin is more efficient and economical for concurrent removal of nitrate and Se(VI) or As(V).

Cr(VI), A(V), or Se(VI)-laden nitrate resins were regenerable using a NaCl solution, and their regeneration processes were more efficient than those for the conventional resins. The order of the capacity of ion-exchange resins for Cr(VI), Se(VI), and As(V) is Cr(VI) > Se(VI) > As(V). Similar to Cr(VI) removal, Depending on the concentration of As(V) or Se(VI) in the influent water and the number of BVs run to breakthrough, the waste regenerant brine could contain concentrations high enough to deem the waste hazardous.

The last issue was concurrent removal of perchlorate and Cr(VI), Se(VI), or As(V). In this research, it was found that Cr(VI), A(V), or Se(VI)-laden perchlorate specialty resins are regenerable using a NaCl solution. Nonetheless, Cr(VI), A(V), or Se(VI)-laden perchlorate or nitrate resins were easier to regenerate than spent conventional resins.

However, perchlorate specialty resins showed very low run length for these divalent contaminants. Therefore, if Cr(VI), Se(VI), or As(V) occur as a co-contaminant for perchlorate, the logical option is using two separate columns for the removal. The first IX column can remove perchlorate using a perchlorate specialty resin from water while Cr(VI), As(V) or Se(VI) breaks through the first column instantly. The first column containing perchlorate specialty resin has a very long run length, and it should be replaced after perchlorate breaks through. The second column must operate to remove As(V) or Se(VI). This column has shorter run lengths and must regenerate frequently, and a conventional resin or arsenic/selenium specialty resin could be used for this purpose.

CHAPTER 5

REMOVAL OF ARSENIC FROM ION-EXCHANGE WASTE BRINES WITH FERRIC CHLORIDE

5.1. Abstract

Brine treatment is a serious challenge for arsenic (V) removal from drinking water using ion-exchange. Although arsenic removal with ferric chloride from drinking waters is a well documented process, the application of ferric chloride to remove arsenic (V) from brines has not been thoroughly investigated. In this research, surface complexation modeling and experimental coagulation tests were performed to investigate the influence of ionic strength, pH, Fe/As molar ratios, and alkalinity in the removal of arsenic from IX brines. Surface complexation modeling predicted removal of As(V) was in good agreement with the experimental data. Optimum pH range for the process was found to be 4.5-6.5. Higher brine alkalinity affects coagulation because it commands larger amounts of acid to lower the pH to the desired level. The arsenic removal efficiency slightly improved when the ionic strength was increased from 0.1 M to 0.8 M while no significant difference was observed for ionic strength change from 0.8 to 1.5 M. For arsenic (V) concentrations typical in ion-exchange brines and to achieve a remaining As (V) concentration of 5 mg/L, Fe/As molar ratios varying from 1.3 to 1.7 are needed at operating pH values of 5.5 to 6.5. The Fe/As ratios needed to treat brines are significantly lower than those used to treat drinking waters. The amount of sludge solids generated in the coagulation process was found to increase with Fe/As molar ratios. However, the amount of sludge produce reaches a stable value for higher Fe/As molar ratios. Solids concentration varying from 2 to 18 mg/Lwere found. The results of this

research have direct application to the treatment of residual wastes brines containing arsenic.

5.2. Introduction

Arsenic removal from high ionic strength solutions (~0.1-2 M) is a major challenge for various water treatment technologies, including ion-exchange (IX), activated alumina adsorption, reverse osmosis, and nanofiltration (MacPhee et al., 2001). These treatment processes, when used for arsenic removal, produce arsenic-laden residual wastes, which must be properly disposed of to prevent further contamination of the environment (MacPhee et al., 2001). Because of its high toxicity (Wang et al., 2001; Francesconi & Kuehnelt, 2002; Smedley & Kinniburgh, 2002), the maximum contaminant level (MCL) in the U.S. for arsenic in drinking water was set by the U.S. Environmental Protection Agency (EPA) at 10 µg/L on January 18, 2001, and water treatment plants in the U.S. have had to comply with this new regulation since January 23, 2006 (Wang et al., 2001). Pentavalent arsenic [As(V)] and trivalent arsenic [As(III)] are the major forms of arsenic in drinking water (Francesconi & Kuehnelt, 2002; Smedley & Kinniburgh, 2002). Ion-exchange (IX) has been pointed out as one of the best available technologies to remove As(V) from water due to its excellent efficiency and flexible application to small size treatment plants (MacPhee et al., 2001 ; Clifford, 1999; U.S. EPA, 2000; MWH, 2005).

Conventional strong base anion (SBA) exchange resins and specialty resins have been utilized to efficiently remove As(V) (i.e., $HAsO_4^{2-}$ and $H_2AsO_4^-$ species) from waters (Clifford, 1999; Kim & Benjamin, 2004; Clifford & Ghurye, 2002; Chwirka et al., 2004; McNeill & Edwards, 1995). SBA exchange resin is only efficient in removing As(V), primarily because As(III) exists as arsenous acid with a neutral charge, which cannot be exchanged at pH values less than 9.3 in the IX process. Therefore, As(III) must be oxidized to As(V) prior to ion-exchange treatment (MWH, 2005; Clifford & Ghurye, 2002; U.S. EPA, 2003).

The spent IX resin beds must be regenerated, generally, using sodium chloride for the process to be economically viable. The regeneration process produces brine solutions with high concentrations of As(V), alkalinity, and ionic strength (MacPhee et al., 2001). The high ionic strength is associated with the use of NaCl brine for resin regeneration. The waste brines have high alkalinities because ion-exchange resins exchange bicarbonate present in the water. During regeneration bicarbonate is then released to the waste brine. Brines generated from arsenic removal ion-exchange plants are usually considered hazardous. If the generated brine contains more than 5 mg/L of arsenic, it will be considered a hazardous waste according to the Resource Conservation and Recovery Act (RCRA) of the United States (U.S. EPA, 2003). The costs of disposal and handling of hazardous wastes are drastically higher than that for non-hazardous wastes (Meng et al., 2001).

As(V) can be removed from waters and brines using ferric chloride ($FeCl_3$) coagulation, which produces arsenic-iron hydroxide sludge that generally passes the Toxicity Characteristic Leaching Procedure (TCLP), a test that determines whether a waste is hazardous (Phenrat et al., 2008; Steinwinder & Zhao, 2007; Clifford et al., 2003; Mercer & Tobiason, 2008). As(V) removal with ferric chloride from drinking water is a well documented process and has been studied for many years (Lakshmanan et al., 2008; Ghurye et al., 2004; Davis et al., 2001; Davis et al., 2002; Meng et al., 2000; Hering et al., 1997; McNeil & Edwards, 1997; Hering et al., 1996). However, very few studies have addressed the removal of arsenic from ion-exchange brines.

Ferric chloride dissolves in solution and forms amorphous hydrous ferric oxide (HFO), which has high porosity and numerous active sites for sorption (Hering et al., 1996; Dzombak & Morel, 1990). Adsorption is believed to be the major mechanism for As(V) removal by coagulation with HFOs (Phenrat et al., 2008; Hering et al., 1996; Dzombak & Morel, 1990; Guo et al., 2007). The main mechanism of anion adsorption is surface complex formation, in which available hydroxyl ions on the adsorbent surface are exchanged for other anions (Dzombak & Morel, 1990; Stumm & Morgan, 1996). Arsenic-iron inner-sphere surface complexes have been reported as the main form of bonding between As(V) and iron-oxides and hydroxides (Phenrat et al., 2008; Meng et al., 2000; Sherman & Randall, 2003; Waychunas et al., 1993). However, Phenrat et al. (2008) observed both outer and inner-sphere surface complexes in arsenic-iron hydroxide sludge. Bidentate binuclear corner-sharing (Guo et al., 2007; Zachara et al., 1987) and bidentate mononuclear edge-sharing links were observed between A(V) and active iron surfaces (Guo et al., 2007; Sherman & Randall, 2003; Waychunas et al., 1993).

Steinwinder and Zhao (2005 & 2007) have recently studied the removal of As(V) from a synthetic IX brine using ferric chloride. The brine contained 300 mg/L of As(V) to simulate a waste brine that is reused several times before disposal. The arsenic concentrations in waste brines from typical IX plants in the US will have As(V) concentrations in the mg/L range (Table 5.1), which are several orders of magnitude greater that those found in drinking waters. Therefore, there is a need to evaluate how As(V) removal from brines with ferric chloride is affected by initial As(V) concentration.

The point of zero charge (pzc) of the HFO has been reported to be between 7.9 and 8.2 by Dzombak and Morel (1990). HFO is positively charged at pH values less than 7.9-8.2, and negatively charged at pH values above its pzc. For pH values less than 2.5, arsenic acid (H_3AsO_4) is the major species of As(V). In the pH range of 2.5 to 6.96, dihydrogen arsenate ($H_2AsO_4^-$) is the predominate species. Hydrogen arsenate ($HAsO_4^{2-}$) is the major form of As(V) in the pH range of 6.96 to 11.24. When pH increases above 8.6, hydrogen arsenate transforms to arsenate (AsO_4^{3-}), which becomes the predominate species at pH values greater than 11.24.

Mercer and Tobiason (2008) have studied the removal of As(V) from membrane concentrates. These concentrates may contain ionic strengths similar to those found in IX brines. However, the As(V) concentrations in membrane concentrates (0.5 mg/L) are much lower than IX brines (10-120 mg/L). Therefore, removal of high concentrations of As(V) from IX brines requires further attention. Mercer and Tobiason (2008) stated that increasing the ionic strengths from 0.2 to 1.5 M did not affect the removal efficiency of As(V) from concentrates, and increasing the ionic strength from 0.008 to 1.5 M caused a slight increase in the removal efficiency. Xu et al. (2009) reported that increasing the ionic strength increased the adsorption of As(V) on two types of soil. One reason for the increase in the adsorption efficiency with increased ionic strength is that the electric double layer of particles is more compressed in solutions with high ionic strength. Therefore, when particles come close to each other due to Brownian motion, they adsorb to each other due to van der Waals forces, which increase the particle aggregation in solution (MWH, 2005; Mercer and Tobiason, 2008; Edzwald et al., 1974; Sato et al., 2005; Letterman, 1999). The surface charge also increases when the ionic strength of the solution increases. At a similar pH, hydrous ferric oxide has higher surface charge at higher ionic strengths (Stumm & Morgan, 1996). In addition, Zhang et al. (2009) reported that As(V)-anions may form inner-sphere surface complexes at the solution/solid interface, and therefore the adsorption increases in response to the higher ionic strengths.

Although alkalinity favors HFO formation after addition of ferric chloride (Steinwinder & Zhao, 2007), it inhibits sorption of heavy metals onto goethite (Lee & Hering, 2003; Van Geen et al., 1994; Villalobos et al., 2001) or HFO (Meng et al., 2000; Zachara et al., 1987; Wilkie & Hering, 1996). pH is related to alkalinity, and high alkalinity tend to produce high pH values. Mercer and Tobiason (2008) reported that increasing the alkalinity from 400 to 1400 mg/L as $CaCO_3$ slightly decreased arsenic adsorption onto HFO for a brine containing 0.5 mg/L As(V).

This research addresses As(V) removal from IX brines using ferric chloride. A two-layer surface complexation model was used to predict As(V) removal under various scenarios. Laboratory coagulation experiments were performed to evaluate how accurately the model can predict As(V) removal from ion-exchange brines. The modeling and experimental results were used to investigate the effects of important parameters, including pH, initial As(V) concentration, ferric chloride dosage, ionic strength, and alkalinity on the As(V) removal process. In addition, the quantity of sludge generated in the treatment process was determined for varying ferric chloride dosages and initial As(V) concentrations.

5.3. Experimental

5.3.1. Synthetic Brine Preparation and Reagents

To determine the range of major parameters to be evaluated, the composition of several brines from operating ion-exchange plants in Arizona and California were evaluated, and are presented in Table 5.1. Ion-exchange brines usually have high concentrations of soluble arsenic. Brines generated in IX regeneration process are typically very concentrated, and contain NaCl used to regenerate the resin, plus one to three bed volumes of rinse water. Even diluted brines are hazardous and require further treatments. The brine characteristics presented in Table 5.1 were used in this research to guide appropriate concentration ranges to be used in modeling and in the coagulation experiments.

Table 5.1 Typical Composition of Ion-Exchange Brine Computed from Data on Operating Ion-Exchange Arsenic Removal Plants of California and Arizona

Constituent	Unit	Concentration
As(V)	mg/L	5-120
Alkalinities as $CaCO_3$	g/L	1-10
Sulfate	g/L	4.8-48
pH	-	8-10
NaCl	g/L	40 – 120
Ionic Strength	M	0.6-2.1

All solutions were prepared using high grade deionized (DI) water. The glassware used in the coagulation experiments was soaked in an acidic solution (2% Micro-90; International Products) for at least 24 hours and completely rinsed with DI water. To prepare the synthetic brines, reagent-grade 99.9% NaCl granules (EMD Chemicals) was added to deionized water to obtain a primary stock solution of 120 g/L (2.05 M) NaCl, which was diluted as needed to prepare brines containing 40, 60, and 80 g/L NaCl. Sodium bicarbonate ($NaHCO_3$, EMD Chemicals) was used to prepare a 61 g/L (1 M) HCO_3^- stock solution, which was used to provide the alkalinity in the brines solutions. A primary stock solution (1000 mg/L) for As(V) was prepared using sodium hydrogen arsenate granules ($Na_2HAsO_4.7H_2O$, Alfa Aesar, Ward Hill, MA). The 1000 mg/L As(V) stock solution was utilized to prepare the synthetic brine solutions. A fresh ferric chloride stock solution (100 g/L) was prepared the day of the experiments from a drinking water-grade ferric chloride (536 g/L (3.3 M) of $FeCl_3$ from Kemira Water Solutions).

5.3.2. Experimental Procedure

A series of coagulation batch experiments were conducted on synthetic brine solutions using a PB-700 standard JarTester from Phipps & Bird. The JarTester had six 2.54 cm × 7.62 cm stainless steel blades. The batch experiments were performed in one liter beakers utilizing 250 mL of the synthetic brine solution. Coagulation was performed with two minutes rapid mix of ferric chloride at 12 rad s^{-1} (G = 158 s^{-1}) followed by a thirty minutes slow mix at 3 rad s^{-1} (G=20 s^{-1}) for flocculation. The Jartester was then turned off, and hundred milliliters of the homogenously mixed brine was collected for solid measurements. Next, the remaining solution was allowed to settle for 30 minutes before sample acquisition for arsenic measurement.

Forty-five milliliters of the untreated brine solution were collected to determine the arsenic concentration before each coagulation treatment. To measure the remaining soluble arsenic after the treatment process, Forty-five milliliters of the treated brine solution were collected for arsenic measurement, and the samples were centrifuged at 367 rad s^{-1} for one hour using a Sorvall Legend RT Bechtop centrifuge to separate the liquid from the solids. Next, samples were acidified with nitric acid ($pH < 2$) and stored in the refrigerator at 4°C.

The pH of the solutions was measured before adding ferric chloride, and after the coagulation process, exactly at the time of the sampling for the arsenic measurements. Adding ferric chloride to the brine decreases the pH. Therefore, to achieve the desired pH values, a series of titration curves were constructed for brine solutions with the initial pH values of 5, 5.5, 6, 6.5, 7, 7.5, 8, and 8.5. The curves show the decrease in pH versus the concentrations of ferric chloride added. Therefore, the pH reduction for a known concentration of ferric chloride was anticipated for brines with varying initial pH values. The pH of each solution was adjusted to the desired values using either sulfuric acid or NaOH, while allowing for the anticipated pH decrease caused by ferric chloride addition. Sulfuric acid was used to simulate the real situation in the field. Sulfuric acid is preferred by the IX water industry, because sulfuric acid is a stronger acid than HCl, and lower volumes of sulfuric acid is required for the operation, reducing the risk of storage and handling of the acid.

Coagulation Batch Experiments to Investigate the Effects of pH

To study the effects of pH on the arsenic removal efficiency, eighteen coagulation experiments were performed at six different final pH values (ranging from 1.5 to 12.5) at three levels of ionic strengths (0.1, 0.8, and 1.5 M). Initial arsenic concentration and alkalinity in all batches were 49.2 mg/L (0.66 mM) and 5 g/L as $CaCO_3$, respectively, which are the mean values found in typical IX brines (Table 5.1). Ferric chloride was applied at a constant dosage of 140 mg/L (2.5 mM) $FeCl_3$ (as Fe), corresponding to the Fe/As molar ration of 3.8.

Coagulation Batch Experiments to Validate the Modeling of As(V) Removal

Eighteen coagulation batch experiments were performed for each initial As(V) concentration of 10, 42, or 92 mg/L, including six batch experiments at three levels of ionic strength (0.1, 0.8, and 1.5 M). Ferric chloride dosages in the range of 8-62 mg/L, 27-173 mg/L, and 55-242 mg/L (as Fe) were added to brines containing initial As(V) concentration of 10, 42, or 92 mg/L, respectively. The pH of all solutions was adjusted to a constant pH of 5.5 ± 0.1.

In addition, forty-two batch experiments were conducted to remove varying concentrations of As(V) from the synthetic brine solutions containing 60 g/L NaCl (1.2 M ionic strength) and 2.5 g/L as $CaCO_3$ initial alkalinity by addition of various dosages of ferric chloride. Seven batch experiments were carried out for each initial As(V) concentrations of 12, 21, 39, 57, 79, and 119 mg/L by adding ferric chloride dosages in the range of 12-41 mg/L, 12-68 mg/L, 15-160 mg/L, 15-190 mg/L, 20-190 mg/L, 25-190 mg/L, respectively. Several replicate experiments were performed to assure the quality of data. The pH of brines was adjusted to 6.5 ± 0.1.

Coagulation Batch Experiments to Evaluate the Effects of Alkalinity

To investigate the effects of alkalinity, eighteen coagulation batch experiments were performed for an initial arsenic concentration of 47.7 mg/L and 0.8 M ionic strength for 2.5, 5, and 10 g/L as $CaCO_3$ alkalinities without pH adjustments. These coagulation batch experiments were performed similar to the IX brine treatment in the field because final pH was not controlled during the coagulation process. Therefore, pH decreases by increasing the ferric chloride dosage.

5.3.3. Analytical Methods

Arsenic measurements were conducted within two weeks of sample collection. Samples were diluted for the measurements and the diluted samples contained 40 or 80 g-NaCl/L. Arsenic concentrations in the supernatant were measured by a ICP (Inductively-coupled plasma Spectrophotometer) (Thermo Electron Iris Advantage) according to Standard Methods 3125 (Standard Methods, 2005).

The concentration of total iron in the prepared stock solution was measured by flame atomic absorbance spectrometry (AAnalyst 100 from PerkinElmer) following standard procedures (Method No. 3111 B) (Standard Methods, 2005) prior its use. Three calibration standards and the wave length of 248.3 nm were used for the measurements.

The pH of the solutions was measured by an Orion 920A+ pH meter equipped with an Orion 8102BNUWP probe from Thermo Electron Corporation. The pH meter was calibrated with four buffers (2, 4, 7, and 10). The final pH in the coagulation test is a very important parameter. The total suspended solids (TSS) in the samples were determined according to method 2540 D of the Standard Methods (Standard Methods, 2005) using 0.45 μm filters. The pH values for the brines were corrected considering the effects of high ionic strength induced by NaCl using Pitzer equations.

5.3.4. Surface Complexation Modeling

The two-layer surface complexation model incorporated into MINEQL+, v. 4.6 (Schecher & McAvoy, 2001), was utilized in this research to model As(V) removal from brines. The results of the laboratory coagulation batch experiments were compared to the results of the simulations to evaluate how well the MINEQL+ simulations fit the experimental results. MINEQL+ is a chemical equilibrium software and has the ability to model surface adsorption of arsenic into ferric hydroxide precipitates by using equilibrium and mass balance equations (Schecher & McAvoy, 2001). The two-layer surface complexation model and the database of Dzombak and Morel (1990) were utilized by Hering et al. (1996) to predict arsenic removal by ferric chloride from drinking water. Hering et al. (1996) used the MINEQL+ to predict the arsenic adsorption process in drinking water with very low ionic strengths. Adsorption is assumed as the only mechanism for arsenic removal and therefore co-precipitation of arsenic by iron precipitates is not considered in MINEQL+. In view of the fact that adsorption is the main mechanism of arsenic removal using ferric chloride, not including the co-precipitation in the modeling may have little impact on the results. The solution and surface reactions, and respective equilibrium constants for arsenate, iron, carbonate, and water are presented in Schecher and Mcavoy (2001), Boccelli et al. (2006), and Hering et al. (1996). In the model, the Coulombic correction factor is used for the correction of the intrinsic equilibrium K values based upon the influence of pH and ionic strength (Dzombak & Morel, 1990; Schecher & McAvoy, 2001).

MINEQL+ utilizes the Davis equation to calculate the activity coefficients for various components. The Davis works well for ionic strength values less than 0.5 M, and usually, Pitzer equations are recommended to calculate the activity coefficients in high ionic strength solutions (Xu, 2008). However, Xu (2008) reported that a conventional extended Debye-Huckel equation (similar to Davis equation) was adequate to model ion-interactions in NaCl-dominanted brines with ionic strengths of up to 1.5 M. The ion-exchange brines in this research are NaCl-dominant with ionic strengths of less than (or equal to) 1.5 M. Therefore, the incorporated Davis equation in MINEQL+ is likely to be adequate to calculate the activity coefficients of the adsorption process.

The surface complexation modeling was performed according to Schecher and Mcavoy (2001). In the model, a mole of ferric chloride added to the solution yields 0.55 mg/L hydrous ferric oxide (HFO) or 89 g-HFO per mol-Fe (Hering et al., 1996; Dzombak & Morel, 1990). A surface area of 600 m^2 $g\text{-}HFO^{-1}$ (Dzombak & Morel, 1990; Schecher & McAvoy, 2001) was used in the surface complexation model. Mercer and Tobiason (2008) used a surface area of 562 m^2 g^{-1} to model arsenic removal during co-precipitation at an ionic strength of 0.7 M.

5.3.5. <u>Statistical Analysis</u>

The As(V) removal efficiencies of the model and the experimental data were compared using analysis of variance (ANOVA) and regression analysis at different ionic strengths of 0.1, 0.8, 1.2, and 1.5 M (separately). The null hypothesis was that the modeling fits the experimental data when the coefficient (β) of the linear regression line ($Y = \beta X$) equals to 1. A t-test analysis (paired two-sample) was performed for means of the removal efficiencies among brines with 0.1, 0.8, and 1.5 M ionic strengths. The goal was to evaluate whether an increase in ionic strength resulted in higher As(V) removal efficiencies.

5.4. Results and Discussion

5.4.1. Effect of pH on As(V) Removal from Brines with Ferric Chloride

Figure 5.1 shows the percent arsenic removal from the synthetic ion-exchange brine as a function of pH at ionic strength levels of 0.1, 0.8, and 1.5 M for As(V) and $FeCl_3$ (as Fe) dosages of 0.66 mM and 2.5 mM (Fe/As molar ratio of 3.8), respectively. The lines in the graph represent surface complexation modeling and it will be discussed later. The symbols are experimental data. Hundred percent As(V) removal from the brine was achieved at the pH range of 4.5-6.5. An interesting feature of Figure 5.1 is that it forms a plateau at the optimal pH removal range. It follows that the same percent removal can be achieved at the lower pH range (i.e., pH 4.5) and the upper range (i.e., pH 6.5). Since IX brines have high pH values (i.e.,8-10) and there is a cost associated with acid use to lower the pH, in practice, operating at higher pH values is desirable.

Very poor As(V) removals are achieved at pH < 3.8 and at pH > 7.8. The reason for the drastic decrease in the removal efficiency when pH increased from 7.8 to 12.5 is the HFO surface charge reversal at pH values higher than the pzc of HFO (7.9). At pH values above the pzc, a negative surface charge hinders the adsorption of dihydrogen arsenate ($H_2AsO_4^-$) and hydrogen arsenate ($HAsO_4^{2-}$), because hydroxyl ions are competing with arsenate for active HFO surface sites at high pH values (Gulledge & O’Connor, 1973). Steinwinder and Zhao (2007) showed that As(V) removal efficiency with $FeCl_3$ from an ion-exchange brine containing 300 mg/L As(V) at Fe/As molar ratio of 5 decreased from 100% to 30% when pH increased from 6 to 11.5. Clifford et al. (2003) showed that As(V) removal efficiency with $FeCl_3$ from a brine containing 3.45 mg/L As(V) at Fe/As molar ratio of 20 decreased from 99.7 % to 71.8 % when pH increased from 6.2 to 8.5. In this study, at an ionic strength of 0.8 M, the As(V) removal efficiency decreased from 99.6 % at pH 5.5 to 57.5 % or 12.3 % when the pH was increased to 10 and 12.2, respectively.

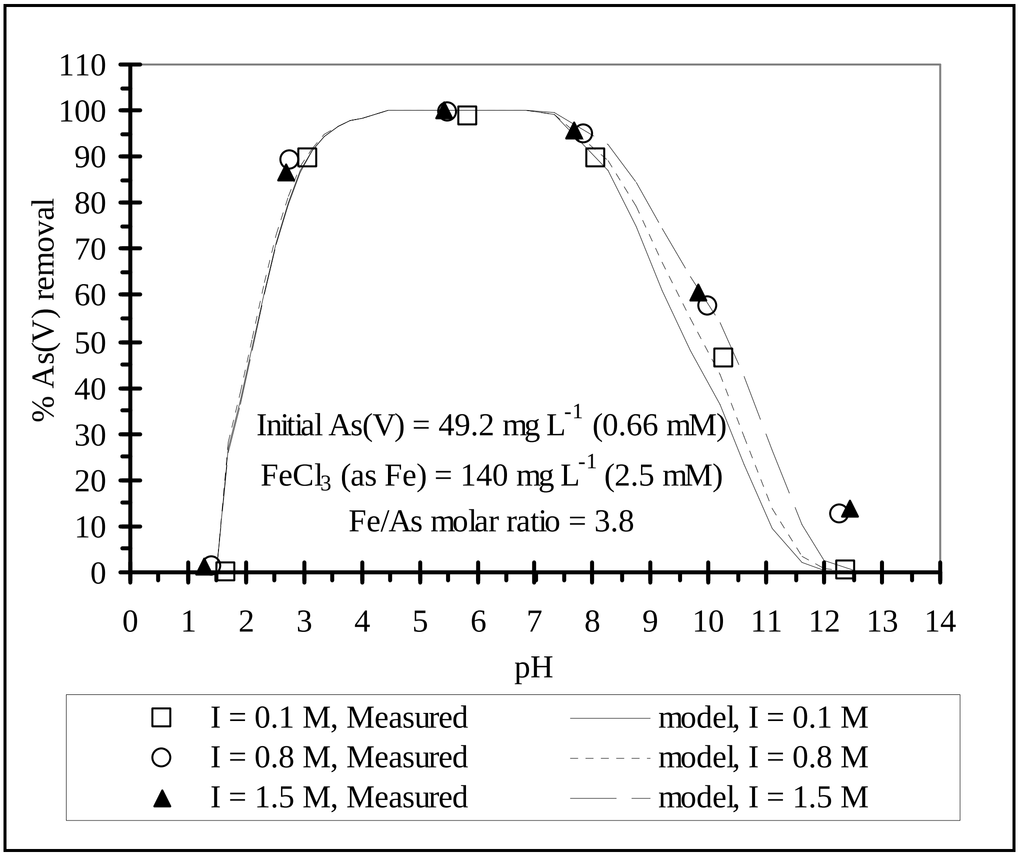


Figure 5.1 Effect of pH and Ionic Strength on the Adsorption of As(V) onto Ferric Hydroxide Precipitates for an Initial As(V) Concentration of 49.2 mg/L and $FeCl_3$ (as Fe) Dosage of 2.4 mM

The data in this study revealed that when the pH decreased from 3.5 to 1.5, the As(V) removal efficiency reduced drastically from 95% to 0 %. Although decreasing the pH of IX brines to such low levels would not be economically feasible or desired, two factors explain the lower to null removal of As(V) at these low pH values. Firstly, at pH < 4, the dihydrogen arsenate species transforms to the non-ionic and non-adsorbable species of As(V), arsenic acid (H_3AsO_4), which predominates at pH < 2.5. Secondly, at pH < 1.5, HFO does not form, that is there is no surface for As(V) to be adsorbed to and iron from $FeCl_3$ is present as the dissolved species (Fe^{3+} and $FeOH^{2+}$). Reduced removal of As(V) by $FeCl_3$ at very acidic pH values has been reported by others (Baskan & pala, 2009; Wang et al., 2003). Baskan and Pala (2009) reported that As(V) removal efficiency decreased from 100% to 10% when pH decreased from 7 to 4 when removing 0.5 mg/L As(V) from drinking with 60 mg/L $FeCl_3$. For an initial As(V) concentration of 8 to 60 mg/L and a constant $FeCl_3$ dosage of 300 mg/L, Wang et al. (2003) found that the As(V) removal efficiency decreased from 100% to 0% when the pH decreased from 4 to 1.8. In this study, As(V) removal efficiency decreased from 100% at pH 5.4 to 0 % at pH 1.4 when removing 50 mg/L As(V) with 140 mg/L $FeCl_3$ (as Fe).

The finding presented herein indicates that to treat ion-exchange brines, the pH, which are typically between 8 and 10, must be lowered. In view of the fact that acids used to lower pH are costly, a pH of 6.5 would be desirable for 100% removal. In this study, the TCLP limit of 5 mg/L of As(V) was achieved at pH of 7.8, indicating that IX brine treatment to reach TCLP limits is efficient at pH below 7.8. It should be noted that As(V) removal from IX brines is possible at pH 8 to 10 at a lower efficiency.

5.4.2. Effects of Ionic Strength, Initial As(V) Concentration, and Ferric Chloride Dosage on Removal

Figures 5.2, 5.3, and 5.4 depict arsenic removal from the synthetic brine with increasing $FeCl_3$ addition for a fixed pH of 5.5, three initial arsenic concentrations (i.e., 9.7 mg/L, 42.3 mg/L, 97.9 mg/L), and ionic strengths of 0.1, 0.8, and 1.5 M. In the Figures, symbols represent experimental data and the lines are surface complexation modeling prediction. As it will be discussed later in section 5.4.3, the model fits the experimental data very well.

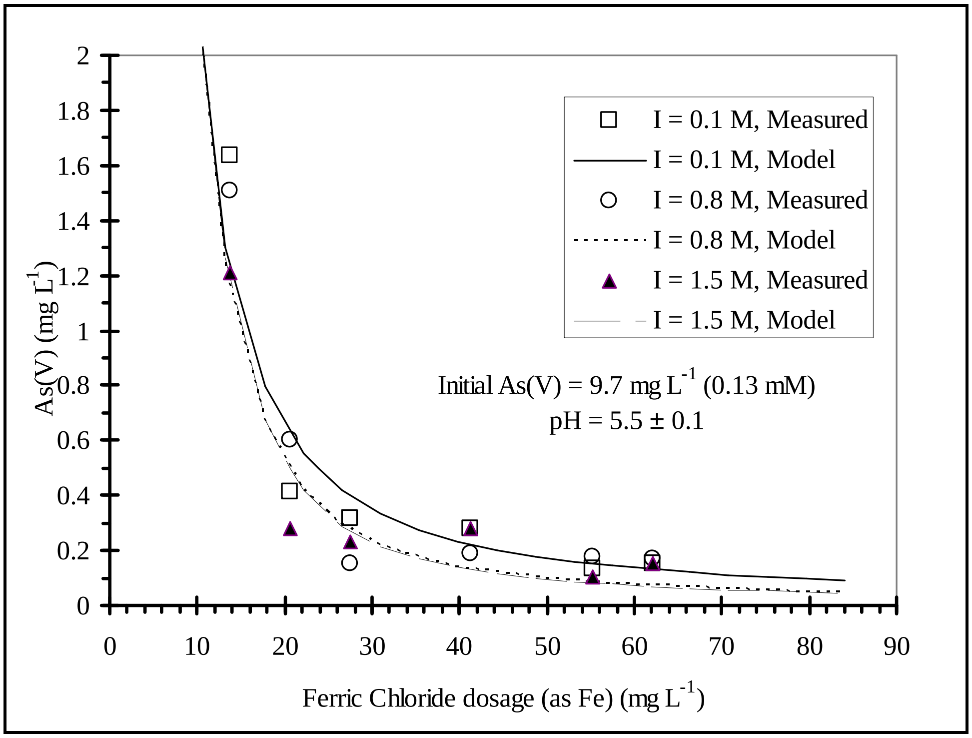


Figure 5.2 Remaining Arsenic(V) Concentrations as a Function of Ferric Chloride and Ionic Strength for an Initial As(V) Concentration of 9.7 mg/L, Initial Alkalinity of 5 g/L as $CaCO_3$, and pH of 5.5

As(V) removal for brines with 0.1, 0.8, and 1.5 M ionic strengths were compared by paired t-test analysis (Table 5.2). The small P values of 0.0158 and 0.0224 (<0.05) indicate that increasing the ionic strength of brines from 0.1 M to 0.8 or 1.5 M promoted a statistical difference in the As(V) removal efficiencies. Notwithstanding its statistical significance, the arsenic removal efficiency increased only slightly (1.6 % and 1.7 %) when the ionic strength was increased from 0.1 to 0.8 M and 1.5, respectively. There is not a statistically significant difference (P value = 0.3945 > 0.05) found between the As(V) removal efficiency for brines with 0.8 to 1.5 M ionic strength. The reason for the increase in As(V) removal efficiency at higher ionic strength can be explained by the higher surface charges on the surface of HFO and by the compression of the electrical double layer, which results in higher particle aggregation (Mercer & Tobiason, 2008; Edzwald et al., 1974; Letterman, 1999; Sato et al., 2005).

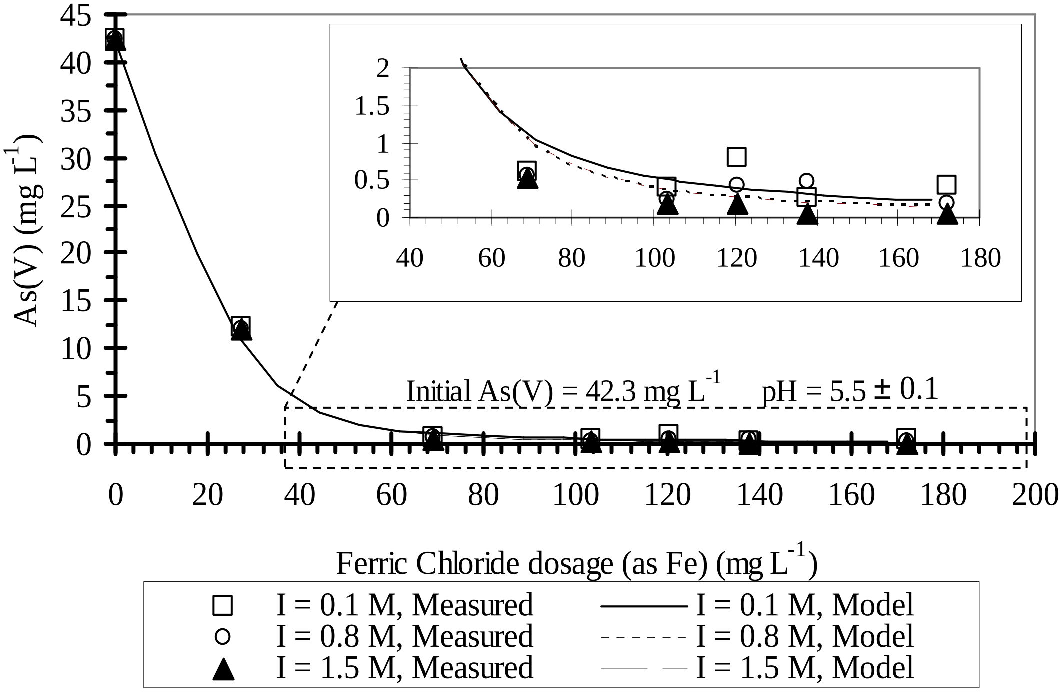


Figure 5.3 Remaining Arsenic(V) Concentrations as a Function of Ferric Chloride and Ionic Strength for an Initial As(V) Concentration of 42.2 mg/L, Initial Alkalinity of 5 g/L as $CaCO_3$, and pH of 5.5

The results show that the amount of dissolved As(V) remaining in the brines decreased with increasing ferric chloride dosages for three initial As(V) concentrations (Figures 5.2, 5.3, and 5.4). The $FeCl_3$ dosages which were used in this study aim at removing arsenic to levels that meet the TCLP standard and to levels below the TCLP standard that would allow for alternative ways to dispose of the brine.

Table 5.2 Results of Paired T-Test for As(V) Removal Efficiencies for Brines with Ionic Strengths of 0.1, 0.8, And 1.5 M

Parameter	T-Test Analysis between		
	0.1 M and 0.8 M	0.1 M and 1.5 M	0.8 M and 1.5 M
Observations	27	27	27
t-stat	-2.2711	-2.1088	-0.2704
P one-tail	0.0158	0.0224	0.3945
t critical one-tail	1.7056	1.7056	1.7056
P two-tail	0.0317	0.0448	0.7890
t critical two-tail	2.0555	2.0555	2.0555

Table 5.3 shows Fe/As ratios to achieve remaining As(V) concentrations of 5 mg/L and 0.5 mg/L for pH = 5.5, different ionic strengths, and different initial As(V) concentrations. For initial As(V) concentrations of 9.7 mg/L, 42.3 mg/L, and 97.9 mg/L, the average Fe/As ratios were 1.1, 1.7, and 1.4 to achieve 5 mg/L remaining As(V) while they were 3.3, 2.4, and 2.3 to obtain 0.5 mg/L remaining As(V). Therefore, for brines with lower arsenic concentration (i.e. 9.7 mg/L), approximately three times more $FeCl_3$ is needed to achieve 0.5 mg/L remaining As(V) as compared to 5 mg/L, the TCLP limit. For initial As(V) concentrations between 42.3 mg/L and 97.9 mg/L, which are typical of

most ion-exchange brines, only about 1.5 times more $FeCl_3$ is needed to achieve 0.5 mg/L remaining As(V) as compared to 5 mg/L. It has been reported that addition of $FeCl_3$ at a Fe/As molar ratio of 2 to a recycled IX brine with initial As(V) concentrations of 300 mg/L resulted in remaining As(V) concentration of < 3 mg/L (Steinwinder & Zhao, 2007). This result is consistent with previous findings (Wilkie & Hering, 1996; Fuller et al., 1993; Pierce & Moore, 1982) that lower Fe/As ratios are needed to remove higher concentrations of arsenic from waters as compared to arsenic removal from drinking waters (Table 5.7).

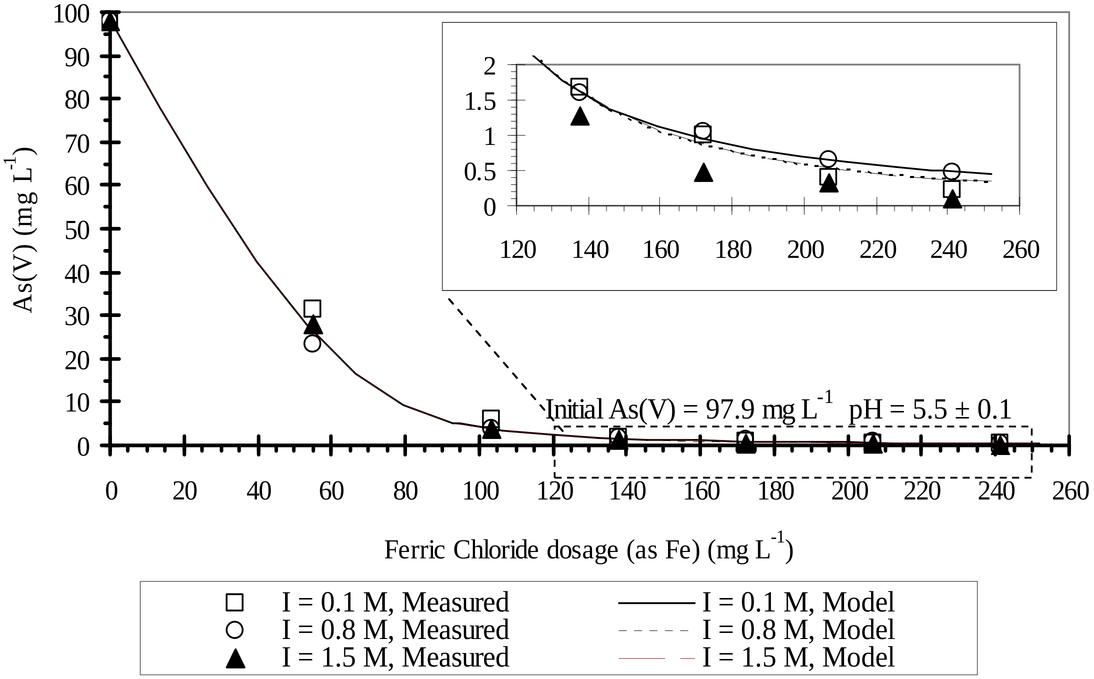


Figure 5.4 Remaining Arsenic(V) Concentrations as a Function of Ferric Chloride and Ionic Strength for an Initial As(V) Concentration of 97.9 mg/L, Initial Alkalinity of 5 g/L as $CaCO_3$, and pH of 5.5

The final desired level of arsenic in a brine treated with ferric chloride will depend on approved disposal methods available in individual municipalities. Brines with remaining arsenic concentrations of 0.5 mg/L are not considered hazardous and could be disposed of by alternative means. In states where wastes with arsenic concentrations with lower arsenic concentration can be discharged by alternative means (e.g. discharged into sewer lines) water utilities may consider applying higher Fe/As ratios to obtain wastes with much lower As(V) concentration, without increasing their $FeCl_3$ consumption much.

Table 5.3 Ferric Chloride Dosages for Brines with pH of 5.5 and Different Ionic Strength Needed to Lower As(V) to 5 mg/L or 0.5 mg/L

As(V) (mg/L)	pH	I (M)	Remaining As(V) = 5 (mg/L)		Remaining As(V) = 0.5 (mg/L)	
			$FeCl_3$ as Fe (mg/L)	Fe /As	$FeCl_3$ as Fe (mg/L)	Fe /As
9.7	5.5	0.1	8.1	1.1	25.6	3.5
		0.8-1.5	7.8	1.1	23.9	3.3
42.3	5.5	0.1	53.3	1.7	86.9	2.8
		0.8-1.5	53.0	1.7	75.3	2.4
97.9	5.5	0.1	108.8	1.5	201.0	2.7
		0.8-1.5	100.9	1.4	171.2	2.3

It has been observed in this study that a larger amount of HFO (i.e. sludge) and larger floc sizes were formed for higher $FeCl_3$ dosages applied compared to smaller dosages. Although several mechanisms including, adsorption, co-precipitation, occlusion, and solid-solution formation have been proposed to explain As(V) removal by $FeCl_3$, adsorption onto HFO in the predominant mechanism (Hering et al., 1996). Adsorption densities of 0.16 to 0.25 mol As(V) per mol Fe have been reported for HFO when treating drinking water with low concentrations of As(V) (Waychunas et al., 1993; Wilkie & Hering, 1996). In addition, very high adsorption densities, ~ 1 mol As(V) per mol Fe, were reported when very high concentrations of As(V) were present (Wilkie & Hering, 1996). At higher $FeCl_3$ (as Fe) dosages (10 to 100 mg/L), the solubility diagram for iron species shows the formation of the large amount of $Fe(OH)_3$-"sweep flocculation." (MWH, 2005). Therefore, at higher $FeCl_3$ dosages, more HFO surfaces are available for As(V) adsorption. In this research, adsorption densities to attain 0.5 mg/L As(V) were 0.29 mol As(V) per mol Fe and 0.43 mol As(V) per mol Fe when initial As(V) concentrations were 9.7 mg/L and 97.9 mg/L, respectively. The higher adsorption densities achieved for higher ferric chloride dosages explain the larger removal efficiencies obtained by Fe/As ratios that are not directly proportional to the concentration of arsenic present in the brine.

5.4.3. Two-Layer Surface Complexation Modeling

The results of coagulation batch experiments were used to validate the surface complexation model utilized in this research. Predicted and experimental values of As(V) removal efficiency were statistically compared (Table 5.4). Analysis shows that the surface complexation model used in this research is in good agreement with the experimentally determined data points. The coefficient of determination (R^2) value between the predicted and observation values was 0.9920. This indicates the model fits the experimental data. Statistical F tests revealed that F values are greater than F_{crit} values. There was no evidence of lack of fit. The determined P values are less than 0.05, specifying that the model is significant at 95% confidence level.

Table 5.4 Statistical Evaluation for Fitness of the Surface Complexation Model to Experimental Data

Source	Df[a]	SS[b]	MS[c]	F[d]	P
Regression[e]	1	129220	129220	14507.19	< 0.0001
Residual Error	121	1078	9	-	
Lack-of-Fit	108	1062	10	8.08	< 0.0001
Pure Error	13	16	1	-	
Total	122	130298	-	-	

[a] Degree of freedom; [b] Sum of squares; [c] Mean of squares; [d] $F_{critical}$ = < 0.0001
[e] $R^2 = 0.9920$; R^2 (adjusted) = 0.9920

Figure 5.5 is a surface plot of As(V) removal efficiency predicted by the surface complexation model at pH 6.5 and ionic strength of 1.2 M for different initial As(V) concentrations and varying $FeCl_3$ (as Fe) dosages from 0 to 200 mg/L.

To achieve 5 mg/L remaining As(V) concentration in brines containing 12 to 112 mg/L As(V), Fe/As molar ratios of 0.9 to 1.3 are required. It means that for approximately 10 times increase in initial As(V) concentration, the Fe/As molar ratio needed is only about 1.4 times higher. To achieve a remaining As(V) concentration of 0.5 mg/L the Fe/As molar ratios are approximately 3 to 4 times those needed for a remaining concentration of 5 mg/L. The lower the desired remaining As(V) concentration, the greater the $FeCl_3$ consumption. Table 5.5 also shows that the lower the remaining As(V) concentration desired, the greater the Fe/As molar ratio needed.

For a remaining As(V) concentration of 0.01 mg/L and an initial As (V) concentration of 12 mg/L, the Fe/As molar ratio needed is 75.6 which is 5 times greater than that (15.0) needed for initial As(V) concentration of 119 mg/L. As it previously discussed, higher surface sites densities available for As(V) adsorption when higher

$FeCl_3$ was added which resulted in a greater removal for high As(V) concentrations in comparison with low As(V) concentrations.

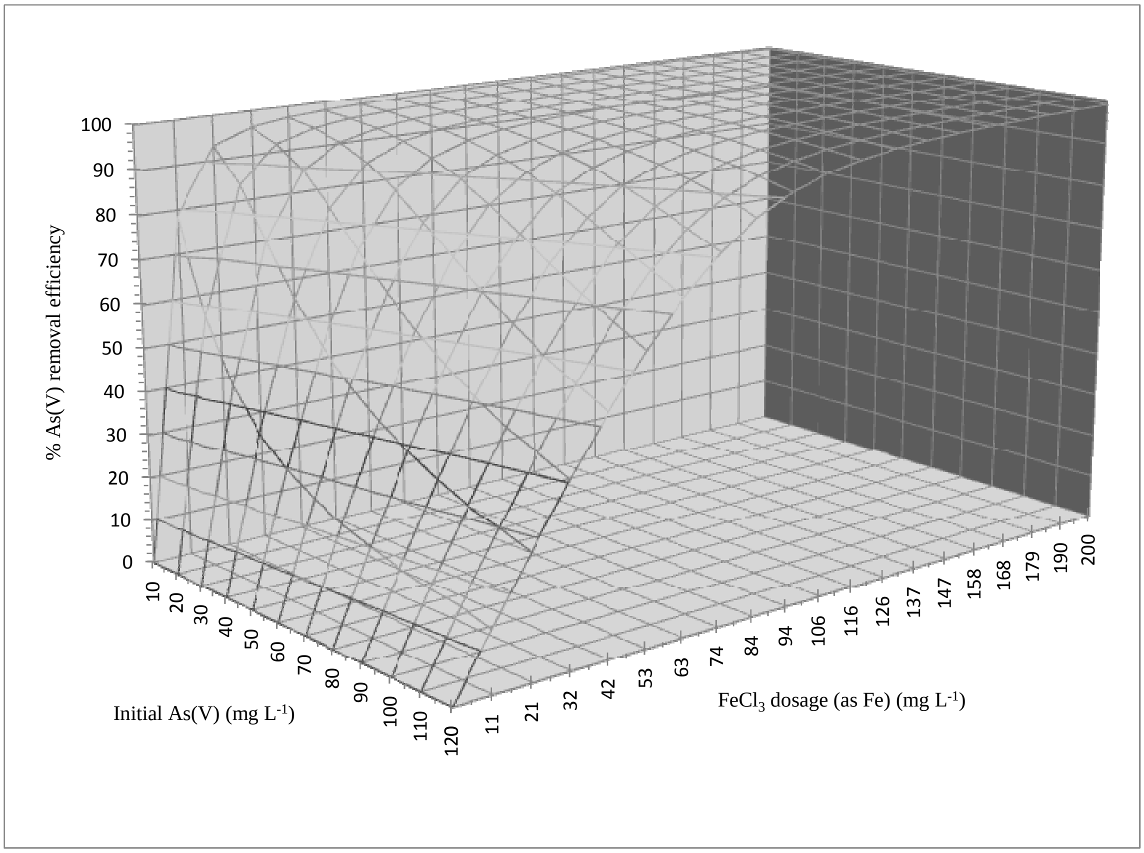


Figure 5.5 Percent Arsenic(V) Removal as a Function of Ferric Chloride Dosage and Initial As(V) Concentration at a Constant Ionic Strengths of 1.2 M, Initial Alkalinity of 5 g/L as $CaCO_3$, and pH of 6.5

By comparing the data presented in Tables 5.3 and 5.5, it can be seen that As(V) removal was slightly more effective at pH 5.5 than 6.5. For brines with initial As(V) concentrations of 9.7 to 97.9 mg/L, to obtain a remaining As(V) concentration of 5 mg/L, 1.1 to 1.4 Fe/As was required at pH 5.5 while 0.9 to 1.3 Fe/As was needed at pH 6.5.

Clifford et al. (2003) reported that for a brine containing 3.45 mg/L As(V) and 20 Fe/As, As(V) removal efficiency was 98.0 % and the As(V) removal efficiency increased to 99.5 % when pH decreased to 5.5.

Table 5.5 Predicted Fe/As Molar Ratios to Lower As(V) in Brines with Ionic Strength of 1.2 M to 5, 0.5, and 0.01 mg/L for Varying Initial As(V) Concentrations and a pH of 6.5

Initial As(V) (mg/L)	Remaining As(V) = 5 (mg/L)	Remaining As(V) = 0.5 (mg/L)	Remaining As(V) = 0.01 (mg/L)
	Fe /As	Fe /As	Fe /As
12	0.9	3.5	75.6
21	1.1	3.5	52.8
39	1.2	4.1	34.0
57	1.3	3.8	25.7
79	1.3	3.6	20.3
119	1.3	3.7	15.0

The highest removal efficiencies from several published studies on arsenic removal from residual wastes and their associated data are shown in Table 5.6. As(V) removal by ferric chloride has resulted in arsenic reductions greater than 99 % at varying pH and ferric chloride dosages. As(V) concentrations in IX brines (up to 120 mg/L) are three orders of magnitude greater than those found in drinking water (up to 120 µg/L (Smedley & kinniburgh, 2002)), and more ferric chloride is required for brine treatment. However, the Fe/As ratios found for residual wastes is much lower than those needed to remove arsenic from drinking waters. Typical ferric chloride dosages of 5 to 30 mg/L are used in drinking water operations (MWH, 2005). Higher coagulant dosages [116 to 3192 mg/L

$FeCl_3$ (as Fe)] are required for arsenic removal from brines compared to reported dosages required for the treatment of drinking waters [3 to 61 mg/L $FeCl_3$ (as Fe)]. Arsenic concentrations in brines are three orders of magnitude greater than those in drinking water. However, the required Fe/As molar ratios vary between 2 and 143 (Table 5.6) for brines, which are less than the molar ratios required (20 to 250) (Table 5.7) for arsenic treatment of drinking water. The required Fe/As molar ratios are smaller for high concentrations of arsenic. For instance, 300 mg/L of arsenic was removed using 2 moles of Fe per mol As(V) while 84 moles of Fe per mol As(V) was required to remove 0.5 mg/L of arsenic. In this research, the Fe/As molar ratios of 14 to 76 required to remove arsenic are smaller than the required Fe/As molar ratios of 20 to 250, which have been found in previous studies for achieving the MCL of 0.010 mg/L in drinking water. As mentioned previously, the amounts required are not directly proportional to the higher As(V) concentration found in brines.

Experimental results of several studies on the removal of As(V) from drinking waters are summarized in Table 5.7. At the optimal pH range (pH 6-8) and ferric chloride dosage, As(V) can be completely removed from contaminated drinking waters using coagulation/filtration process. Typical dosages of $FeCl_3$ (as Fe) are 1 to 21 mg/L, and Fe/As molar ratios are 25 to 572 (Table 5.7). Similarly, Edwards (1994) reported that approximately 20 to 2000 Fe/As molar ratios were required to remove soluble As(V) at concentrations up to 100 µg/L. Optimal Fe/As molar ratios of 20 (Sorg & Logsdon, 1978) and 25 (Meng et al., 2002) were proposed to remove typical concentrations of arsenic in drinking waters without pH adjustment. However, the required ferric chloride doses are pH dependent, and decreasing pH values from 8 to 5 decreases the required doses of ferric chloride (Ghurye et al., 2004). Indeed, the required $FeCl_3$ dosage was reduced by two thirds when pH was lowered from 8.5 to 6.8 (Chwirka et al., 2004).

Table 5.6 Summary of Studies on Arsenic Removal by Ferric Chloride for Reverse Osmosis (RO) and Ion-Exchange (IX) Waste Residuals

Residuals	$FeCl_3$ (as Fe) (mg/L)	pH	Initial As(V) (mg/L)	Fe/As molar ratio	% As(V) removal efficiency	Reference
RO	4.42	6.2	0.5	12	98	(Mercer & Tobiason, 2008)
RO	31	6.2-8.1	0.5	84	100	(Mercer & Tobiason, 2008)
IX	51	5.5	3.45	20	99.5	(Clifford et al., 2003)
IX	127	5.2	3.45	50	99.7	(Clifford et al., 2003)
IX	34	6.2	10.5	4.4	87.8	(MacPhee et al., 2001)
IX	167	5.6	11.3	20	99.7	(Clifford et al., 2003)
IX	62	5.5	9.7	8.5	98.5	This study
IX	32	6.5	12	3.5	95.8	This study
IX	34	8.8	33.2	1.4	86.9	(MacPhee et al., 2001)
IX	172	5.5	42.3	5.5	99.8	This Study
IX	241	5.5	97.9	3.3	99.9	This Study
IX	442	6-7	300	2	> 99	(Steinwinder & Zhao, 2007)
IX	1105	9	300	5	> 99	(Steinwinder & Zhao, 2007)
IX	1105	3-6.5	300	5	> 99	(Steinwinder & Zhao, 2007)
IX	4421	3-11	300	20	> 99	(Steinwinder & Zhao, 2007)

Table 5.7 Summary of Studies on Arsenic Removal by Ferric Chloride for Drinking Waters

Study Type	$FeCl_3$ (as Fe) (mg/L)	pH	Initial As(V) (mg/L)	Fe/As molar ratio	% As(V) removal efficiency	Reference
Bench scale Synthetic water	1.7	7	20	115	100	(Hering et al., 1996)
Pilot Groundwater	2.7	7.9	21	174	98	(Jekel & Seith, 2000)
Pilot Groundwater	2	6.4	33.7	81	97	(Ghurye et al., 2004)
Bench scale Groundwater	1.4	7	37.5	51	100	(Holm, 2002)
Bench scale Synthetic water	7.4	7.1	40	251	95	(Chwirka et al., 2004)
Bench scale Synthetic water	3	6.5	50	81	98	(Lakshmanan et al., 2008)
Pilot Groundwater	20.7	7.3	90	312	99	(Chwirka et al., 2004)
Pilot Groundwater	5.2	6	90	78	96	(Chwirka et al., 2004)
Bench scale Synthetic water	1.7	7	100	23	100	(Hering et al., 1996)
Bench scale Synthetic water	1	6	100	14	95	(Meng et al., 2000)
Bench scale Groundwater	6.7	6.8	300	30	99.3	(Meng et al., 2002)

5.4.4. Effects of Initial Alkalinity

Table 5.8 shows the percent As(V) removal efficiency as a function of $FeCl_3$ (as Fe) added to the solution for alkalinities of 1, 5, and 10 g/L as $CaCO_3$, initial As(V) concentration of 48 mg/L, and ionic strength of 0.8 M. . It was found that increasing alkalinity from 1 to 5 or 10 g/L as $CaCO_3$ resulted in decreased arsenic removal efficiency. As(V) removal efficiency decreased from 99.1 % to 97.8 % when the alkalinity increased from 2.5 to 10 g/L as $CaCO_3$. The reason for the decrease in efficiency with increased alkalinity is the higher final pH values would result from higher alkalinity. High alkalinity tends to produce high pH values, which are not favorable for the adsorption of arsenic onto HFO (Meng et al., 2000; Zachara et al., 1987; Wilkie & Hering, 1996). This implies that IX brines with higher alkalinities require higher dosage of ferric chloride (or acid) than IX brines with low alkalinities.

Table 5.8 Percent As(V) Removal Efficiency and Respective Final pH Values as a Function of $FeCl_3$ (as Fe) Dosage Added to Brines with 48 mg/L As(V), 0.8 M Ionic Strength and Varying Initial Alkalinities

Fe (M)	Fe/As	Init. Alk. 2.5 g/L as $CaCO_3$		Init. Alk. 5 g/L as $CaCO_3$		Init. Alk. 10 g/L as $CaCO_3$	
		% As(V) removal	Final pH	% As(V) removal	Final pH	% As(V) removal	Final pH
0	0	0.0	8.5	0.0	8.5	0.0	8.5
0.6	1.0	27.0	8.3	31.5	8.5	53.7	8.5
1.2	1.9	66.1	8.1	80.8	8.2	71.4	8.4
1.9	2.9	90.1	7.8	91.1	8.1	83.0	8.3
2.5	3.9	97.6	7.6	95.8	8.0	90.9	8.2
3.1	4.8	98.5	7.4	96.8	7.8	93.2	8.1
3.7	5.8	99.1	7.3	99.0	7.6	97.8	7.8

In arsenic removal by ferric chloride coagulation, the pH of the waste brine can be lowered by acid addition or by addition of higher concentrations of $FeCl_3$. This is the case because ferric chloride has an acidic character and its addition result in pH reduction. Therefore, water plants treating IX brines for As(V) removal may lower the pH of the brine with an acid or with excessive $FeCl_3$ dosages. Each of these choices has advantages. Because ferric chloride is relatively inexpensive, acid use is associated with higher operating cost. Using excessive dosages of $FeCl_3$ results in the generation of larger amounts of sludge that has to be disposed off. Depending on the brine characteristics, an economic evaluation is needed to determine the best alternative to lower the pH of the brine.

5.4.5. Sludge Solids Generated from the Coagulation Treatment

The total suspended solids for the coagulation batch experiments shown in Figures 5.1, 5.2, 5.3, and 5.4 and Table 5.8 were measured, it was observed that flocs formed in the brine with 0.1 M ionic strength were smaller than those formed in solutions with 0.8 and 1.5 M ionic strength. Furthermore, it was observed that the flocs formed in low ionic strength brines were very small and passed through a 0.45 μm filter. In addition, it was observed that, for the brine with 0.1 M ionic strength, flocs were formed several hours later in the filtrate from the solution. This observation suggests that in lower ionic strength brine longer flocculation times should be provided for floc growth to assure more efficient solid/liquid separation. Coagulation in brines with high ionic strengths produced larger flocs, which could be removed by the 0.45 μm filter. Mercer and Tobiason (2008) also reported that higher ionic strengths lend themselves to better aggregation of particles allowing formation of larger floc sizes and subsequent more efficient solid/liquid separation.

Figure 5.6 shows the total suspended solids generated for a brine with 1.5 M ionic strength, varying initial As (V) concentrations, and varying Fe/As molar ratios. The amount of sludge produced increased significantly with increasing Fe/As ratios and initial arsenic concentration. A t-test analysis comparing the brines with initial As(V) concentrations of 42.3 mg/L and 97.3 mg/L revealed, at the 95% confidence level (P = 0.015), that the amounts of solid generated are statistically different. The solids formed for initial As(V) concentration of 9.7 mg/L was not included in the analysis because more solids, not included in the data shown, were formed later in the filtrate of these tests.

In Figure 5.6 it can be observed that the amount of solids produced tends to a stable constant value as the Fe/As molar ratios increase. For the brines with initial As (V) concentration of 42.2, and 97.9 mg/L, the solids concentration stabilizes after Fe/As ratios of 2.5 and 4.2, respectively. The amounts of sludge produced in the removal of 9.7, 42.2, and 97.9 mg/L As(V) with 1.5 M ionic strength were 1.3, 15.5, and 17.3 mg/L, respectively. The results also shown that the residual waste brine generated in the treatment of ion-exchange brine contained As (V) concentrations lower than the required TCLP limit. MacPhee et al. (MacPhee et al., 2001) reported that approximately 9 mg/L of sludge produced when 17 to 69 mg/L of $FeCl_3$ (as Fe) was used to treat IX brines containing initial As(V) concentrations of 10.5 to 24.8 mg/L and pH of 9.0 to 9.7.

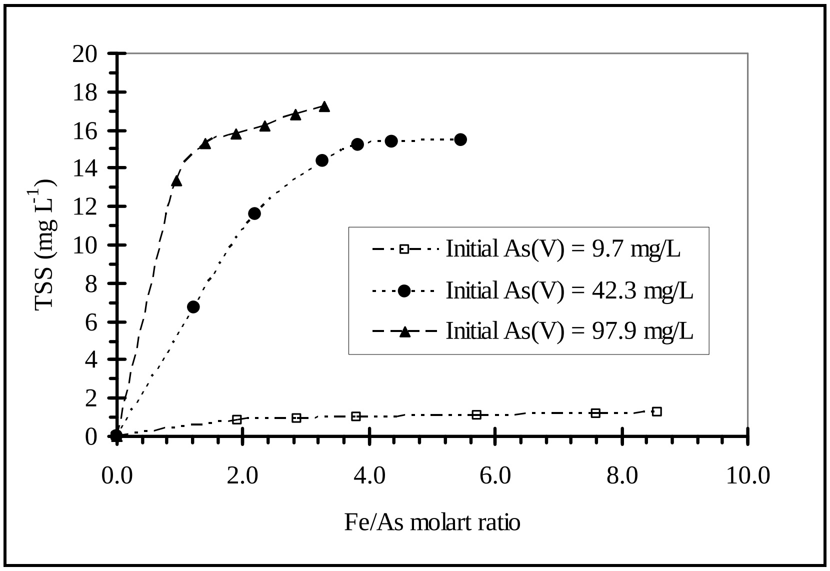


Figure 5.6 Total Suspended Solids Concentration (TSS) as a Function of Fe/As Molar Ratio and Initial As(V) Concentration at I = 1.5 M and pH = 5.5

5.6. Conclusions

The following are the conclusions of this research:

1. Similar to that reported for arsenic removal from drinking waters, As(V) removal from IX brines is a pH dependent process. The optimum pH range (maximum removal) of the adsorption process was found to be 4.5 to 6.5. However, the process was also found to be efficient at higher pH (< 8.5) values when higher dosages of ferric chloride were applied. Because IX brines typically have pH values between 8 and 10, lowering the pH is needed for effective arsenic removal. pH reduction can be accomplished by either adding acid or higher dosages of ferric chloride. Addition of higher $FeCl_3$ dosages results in the generation of larger quantity of sludge. Acid addition involves higher operating costs because acids are relatively more expensive than $FeCl_3$. An economic evaluation is needed to evaluate the best alternative for specific brine characteristics.
2. The surface complexation model used to model adsorption of As (V) onto HFO was in good agreement with the results of the experimental results from batch coagulation tests. Therefore, the modeling can be used to assist the water industry in determined $FeCl_3$ dosages and pH values needed to achieve desired arsenic removals from ion-exchange brines.
3. The removal efficiency of As (V) by ferric chloride coagulation slightly increased when ionic strength of the brine was increased from 0.1 M to 0.8 M or 1.5 M, respectively. No significant improvement in removal efficiency was observed for ionic-strength increase above 0.8 M.

4. Increasing alkalinity from 5 to 10 g/L as $CaCO_3$ slightly decreased the removal efficiency of As (V) with ferric chloride coagulation. The reason for the decrease is the higher pH may be induced by the higher alkalinity.
5. In IX brines, to achieve a remaining As (V) concentration that meets the TCLP limit, the Fe/As molar ratios increase slightly (e.g., 0.9 to 1.3) with a significant increase (e.g., 12 mg/L to 119 mg/L) in initial As (V) concentration. The reason is that the amount of solids generated, for higher initial As(V) concentrations typically found in IX brines, stabilizes for Fe/As molar ratios > 2.4.
6. However, if IX brines were to be treated to achieve the MCL for drinking waters, lower Fe/As molar ratios would be required for higher arsenic levels. This is the case because smaller amounts of solids are formed for lower initial arsenic concentration, and, therefore, more $FeCl_3$ is needed to achieve a desired final As (V) concentration.
7. The amount of sludge solids generated in the coagulation process was found to increase with initial arsenic concentration and with Fe/As molar ratios. However, the amount of sludge produce reaches a stable value for higher Fe/As molar ratios. For brines with initial As (V) concentration of 42.2, and 97.9 mg/L, the solids concentration stabilizes after Fe/As ratios of 2.5 and 4.2, respectively. Solid concentrations varying from 2 to 18 mg/L were found.
8. This research has demonstrated that the higher ionic strength found in IX brines have only a slight effect on the coagulation process. It also demonstrated that the higher alkalinity of the brines affect coagulation because larger amounts of acid are needed to lower the pH to levels that are conducive to adsorption. This

research also revealed that the ferric chloride dosages needed to remove arsenic to TCLP limits is not directly proportional to the higher As (V) concentrations found in brines. For arsenic concentrations typical of ion-exchange brines, Fe/As ratios of about 1.2 to 4 are sufficient to achieve remaining As concentrations that meets or exceeds the required TCLP limit.

CHAPTER 6

REMOVAL OF CHROMIUM FROM ION-EXCHANGE WASTE BRINES WITH CALCIUM POLYSULFIDE

6.1. Abstract

Chromium removal from ion-exchange (IX) brines is a serious challenge for the water industry. Although chromium removal with calcium polysulfide from drinking waters has been investigated, its removal from ion-exchange brines has not been evaluated to date. In this research, a Central Composite Design and experimental coagulation tests were performed to investigate the influence of pH, CaS_5/Cr(VI) molar ratio, alkalinity, and ionic strength in the removal of chromium from IX brines. Optimum pH range for the process was found to be 8-10.3. Increasing brine alkalinity did not affect coagulation. The chromium removal efficiency improved only slightly when the ionic strength increased from 0.1 M to 1.5 M while no significant difference was observed for an ionic strength change from 1.5 to 2.1 M. For chromium (VI) concentrations typically found in ion-exchange brines, a CaS_5/Cr(VI) molar ratio varying from 0.6 to 1.4 was needed to obtain a final Cr concentration < 5 mg/L. The maximum total chromium removal efficiencies were obtained at reducing conditions when oxidation reduction potentials of the brines were between -0.1 to 0 V. The amount of sludge solids generated in the coagulation process was found to proportionally increase with CaS_5 dosage. Solids concentrations varying from 0.2 to 1.5 g/L were found. The results of this research have direct application to the treatment of residual wastes brines containing chromium.

6.2. Introduction

Chromium occurs naturally in groundwaters in the range of 0.0005-0.21 mg/L in the United States (U.S. EPA, 2002; Guertin et al., 2004). However, chromium contamination in waters is generally the result of improper discharge of wastewater from chromium-related industries (Rengaraj et al., 2003; Shi *et al*., 2009; Zaroual et al., 2009; Mouedhen et al., 2009), and Cr(VI) concentrations of up to 3.3 mg/L have been detected in waters near industrial areas (NCASI, 1998). Chromium in groundwater occurs at two oxidation states-- Cr(III) (chromite) and Cr(VI) (chromate) (Sengupta & Clifford, 1986). Cr(VI) is highly soluble and toxic at any pH, and its speciation is pH dependent (Ölmez, 2009; Kim et al., 2009; Gode & Pehlivan, 2005; Ajouyed et al., 2009). Cr(III) is less soluble and toxic than Cr(VI) in water, and can be precipitated as chromium hydroxide, $Cr(OH)_{3,}$ at pH > 5.5 (Ölmez, 2009; Zaroul et al., 2009; Mouedhen et al., 2009).

Commonly, Cr(VI) is removed from wastewater utilizing chemical reduction-precipitation (Mouedhen et al., 2009). Conventionally, this is a two-step process in which Cr(VI) is reduced to Cr(III) at an acidic pH, which favors the reduction process, in the presence of a reducing agent such as sulfide or Fe(II) (Pettine et al., 2006; Pettine et al., 1994; Kim et al., 2001); subsequently, Cr(III) precipitates as $Cr(OH)_3$ at pH values above 5.1. The minimum solubility of Cr(III) occurs in the pH range of 8.6-8.9, and the optimum pH for Cr(III) precipitation is 8.8 (U.S. EPA, 2002). In drinking water applications, chromium occurs as a single contaminant or as a co-contaminant associated with arsenic, selenium, or nitrate (U.S. EPA, 1999).

Cr(VI) can be removed from waters using ion-exchange (Rengaraj et al., 2003; Shi et al., 2009; Gode & Pehlivan, 2005; Atia, 2006). Cr(VI) removal by ion-exchange from water has been identified as an efficient technology, recommended by the United States Environmental Protection Agency (U.S. EPA), and successfully used by many water supply utilities to produce drinking water with chromium levels less than the U.S. EPA's Maximum Contaminant Level (MCL) of 0.1 mg/L (Shi et al., 2009; Gode & Pehlivan, 2005; Atia, 2006; Rengaraj et al., 2003; Alguacil et al., 2004; Sengupta & Clifford, 1986). In the ion-exchange process, Cr(VI) ions move through the bed, exhausting the ion-exchange capacity until Cr(VI) breaks through. The spent IX resin beds must be regenerated using NaCl brine for the process to be economically viable. Regeneration of the ion-exchange resins leads to the generation of chromium-containing IX brines that must be managed. The generated waste brine solutions contain high pH values, alkalinity, initial Cr(VI) concentration, and ionic strength (Siegel & Clifford, 1988). Furthermore, chromium is also found in waste brines of IX plants removing arsenic, selenium, or nitrate where chromium occurs as a co-contaminant and is exchanged by the resin and removed during regeneration. Chromium levels greater than 5 mg/L in the waste brine solutions are considered hazardous according to the U.S. EPA Federal Regulations, 20 CFR & 60, 1 July 1996 (Vijay & Sihorwala, 2003). Hence, the brine must be treated prior to disposal.

Calcium polysulfide, which is a reducing agent, has been used in recent years to reduce and remove Cr(VI) from groundwater (Freedman et al., 2005; Graham et al., 2006; Jacobs et al., 2001; Storch et al., 2002; Messer et al., 2003; Yu & Tremaine, 2002), wastewater (Yahikozawa et al., 1978), and chromite ore processing residue (Graham et al., 2006; Wazne et al., 2007a and 2007b, and Moon et al., 2008). Calcium polysulfide has been reported to provide higher chromium reduction efficiency in comparison with ferrous ammonium sulfate, sodium metabisulfate, and zero valent iron (Leoper et al., 2002). Previous studies have shown that the parameters that affect the process include initial Cr(VI) concentration, calcium polysulfide dosage, and pH (Graham et al., 2006; Wazne et al., 2007b). Calcium polysulfide reduces Cr(VI) to Cr(III) within 30 minutes (Yahikozawa et al., 1978), and Cr(III) precipitates as $Cr(OH)_3$ at alkaline pH (Graham et al., 2006). In mixtures of calcium polysulfide many species are present including polysulfide species (S_5^{2-} and S_4^{2-}), hydrosulfide (HS^-), thiosulfate ($S_2O_3^{2-}$), dithionate ($S_2O_6^{2-}$), and hydrogen sulfide (H_2S) (Yahikozawa et al., 1978; Aratani et al., 1978; Kelsall and Thompson, 1993). The equations for the decomposition of calcium polysulfide into thiosulfate (CaS_2O_3) and hydrogen sulfide (H_2S) can be represented as (Yahikozawa et al., 1978; Aratani et al., 1978):

$$CaS_5 + 1.5\ O_2 \rightarrow CaS_2O_3 + 3S, \qquad (6.1)$$

$$CaS_5 + CO_2 + H_2O \rightarrow CaCO_3 + H_2S + 4\ S \qquad (6.2)$$

The result of an ion chromatography study showed that polysulfide species (S_5^{2-} and S_4^{2-}) and hydrosulfide (HS^-) are the main species in the polysulfide mixture with concentrations approximately 10 times more than that of thiosulfate ($S_2O_3^{2-}$) or dithionate ($S_2O_6^{2-}$) (Kelsall & Thompson, 1993). Therefore, hydrosulfide (HS^-) is suspected to be the main reducing agent in a polysulfide mixture. However, Cr(VI) can be reduced to Cr(III) by HS^-, $S_2O_3^{2-}$, or H_2S; Cr (III) precipitates as chromium hydroxide (Yahikozawa et al., 1978). The reduction equations are presented below (Aratani et al., 1978; Yahikozawa et al., 1978):

$$2CrO_4^{2-} + 3S_2O_3^{2-} + 10\ H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 3S + 5H_2O, \qquad (6.3)$$

$$2CrO_4^{2-} + 3H_2S + 10\ H^+ \rightarrow 2Cr^{3+} + 3S + 8H_2O, \qquad (6.4)$$

$$2CrO_4^{2-} + 3HS^- + 13\ H^+ \rightarrow 2Cr^{3+} + 3S + 8\ H_2O, \qquad (6.5)$$

The standard reduction potential for reducing Cr(VI) to Cr(III) is reported 1.33 V. Half cell voltages for oxidation of hydrosulfide (HS^-) or thiosulfate ($S_2O_3^{2-}$) to elemental sulfur are -0.06 or -0.75 V, respectively (Barrett, 2003).

Kim et al. (2001) reported a stoichiometry of 1.5 mol CaS_5 per mol Cr(VI) at pH 8.2 assuming that elemental sulfur and chromium hydroxide are the products of Cr(VI) reduction using hydrogen sulfide. Equation (6.6) was reported for chromium removal process using CaS_5 (Storch et al., 2002; Messer et al., 2003; Graham et al., 2006; Wazne et al., 2007a):

$$2CrO_4^{2-} + 3CaS_5 + 10H^+ \rightarrow 2\ Cr(OH)_3(s) + 15\ S(s) + 3\ Ca^{2+} + H_2O \qquad (6.6)$$

However, other scientists have also reported that the oxidation of polysulfides results in the formation of S_8 species instead of S species (Kamyshny et al., 2004; Petre et al., 2006). In this research, it is assumed that reaction 6 applies for chromium reduction with calcium polysulfide.

Equation 6.6 corresponds to 1.5 mol CaS_5 per mol Cr(VI). The CaS_5/Cr(VI) molar ratio for reduction of high concentrations of Cr(VI) (>30 mg/L) has been reported to be 1.66 or 1.5 by Graham et al. (2006) or Messer et al. (2004), respectively. Reduction of Cr(VI) by calcium polysulfide produces stable sludge that passes the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) test with a maximum limit of 5 mg/L (Graham et al., 2006; Wazne et al., 2007a, Moon et al., 2008).

Based on previous reports of chromium removal from wastewater, it is hypothesized in this research, that calcium polysulfide can also be utilized to treat ion-exchange brines containing high levels of chromium. Chromium removal from IX brines is a major concern of many ion-exchange treatment plants around the United States, especially in the Southwest. These plants treat water for chromium, arsenic, selenium, or nitrate. Unlike drinking water, the IX brines contain high ionic strength due to use of NaCl as a regenerant, high alkalinity, and initial Cr(VI) concentration. To date, no study has been published to address chromium removal from high ionic strength IX brines. The increased use of ion-exchange and membrane technology, in the last decade, to remove inorganic contaminants from waters has resulted in the generation of contaminated brines, for which treatment technologies are non-existent. Therefore, there is a strong need to investigate this process to develop treatment for this highly toxic waste.

The goal of this research is to evaluate the removal of chromium from synthetic ion-exchange brines using calcium polysulfide and determine the effects of initial Cr(VI) concentration, calcium polysulfide dosage, pH, and ionic strength on the removal process. A Central Composite Design (CCD) was utilized to investigate the interaction effects of pH, initial Cr(VI), and CaS_5 dosage, and to plan the experimental set up. In addition, two series of batch experiments were performed to address the effects of ionic strength and alkalinity on the removal process.

6.3. Experimental

6.3.1. Typical Composition of Actual IX Waste Brine

The typical composition of brines from IX plants treating chromium was determined by collecting data from operating IX plants in the southwest of the United States (Basin Water Inc., Rancho Cucamonga, California). The residual ion-exchange brines usually have high concentrations of chromium (10 to 100 mg/L). In addition to high chromium levels, brines have high alkalinities (0.5 to 10 g/L as $CaCO_3$), sulfate (4.8-48 g/L) and ionic strengths (0.8-2.1 M). The high alkalinity of brines is associated with adsorption of bicarbonate by the IX resins. The high ionic strength is related to the use of sodium chloride as a resin regenerant. The experiments were designed based on the aforementioned data on the brine composition. Synthetic brine was prepared with DI water and varying concentrations of sodium chloride, sodium bicarbonate, and potassium chromate, which were provided from the respective stock solutions. The concentrations of chromium in brines were between 10 to 100 mg/L. Alkalinity and ionic strength of brines were 0.5-5 g/L as $CaCO_3$ and 0.8-2.1 M, respectively.

6.3.2. Central Composite Experimental Design

Preliminary batch experiments results for Cr(VI) removal with CaS_5 indicated that pH, CaS_5 dosage, and initial Cr(VI) concentration were the major parameters influencing Cr(VI) removal from IX brines. The Central Composite Design (CCD), which is a widely used type of response surface methodology (Zaroual et al., 2009; Ölmez, 2009), was used to evaluate the effects of the three parameters on the chromium removal efficiency. Surface response methodology has been successfully used by various authors to quantify the effects of initial concentration, pH, and coagulant dosage during coagulation of heavy metals (Baskan & Pala, 2009; Zaroual et al., 2009; Ölmez, 2009). The goal of CCD was to obtain a quadratic equation that predicts the chromium removal efficiency based on the major parameters. A multiple-regression was the method for fitting the quadratic prediction equation to the experimental data. The statistical software, MINITAB, version 15, (Minitab Inc., State College, Philadelphia, USA) was used to perform the required adjustments, calculate the coefficients, and perform analysis of variance (ANOVA) and lack-of-fit. In this study, a three-factorial and a three-level Central Composite Design with two replica experiments for non-center points and six replicas for the center point were used, leading to a total number of 34 coagulation batch experiments. The purpose of the design was to gain an overall picture on the effects of interactions between the major parameters on the chromium removal efficiency. The quadratic equation obtained was used in interpreting the experimental data. The major independent variables (i.e., pH, initial Cr(VI) concentration, and CaS_5 dosage) were designated as X_1, X_2, and X_3, respectively. The coded and uncoded values of each variable for the Central Composite design are presented in Table 6.1. The coded values were -1, 0, and +1.

Table 6.1 Coded and Uncoded Levels of Each Factor for the Central Composite Design

Independent variables (uncoded)	Unit	Symbol	Coded Level		
			-1	0	+1
pH	Value	X_1	4.7	8.6	12.5
Initial Cr(VI) concentration	mg/L	X_2	9	46	93
CaS_5 dosage	mM	X_3	0.58	1.16	2.32

Experimental data points that were used for the Central Composite design are presented in Table 6.2 The goal of the design was to predict the response surface function (Y), which is the total chromium removal efficiency, based on the independent variables (X_1, X_2, and X_3) according to equation (6.7).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (6.7)$$

where b_0 is the model constant coefficient; $b_1 \ldots b_3$ are the linear coefficients; $b_{12} \ldots b_{23}$ are the cross product coefficients; $b_{11} \ldots b_{33}$ are the quadratic coefficients (Mathews, 2005). The prediction limits were chosen as 0 % and 100 %. These coefficients were calculated using MINITAB, version 15. Surface plots of the chromium removal efficiency as a function of pH and initial Cr(VI) concentration or CaS_5 dosage and initial Cr(VI) concentration were plotted using equation 6.7.

Table 6.2 Experimental Data Points and Responses Used in Central Composite Design and Predicted Chromium Removal Efficiencies

Run[a]	pH	Initial Cr(VI) (mg/L)	CaS_5 dose (mM)	CaS_5/Cr(VI) molar ratio	Experimental Response[b]	Predicted Response
1	-1 (4.7)	-1 (9)	-1 (0.74)	4.3	19.2	23.1
2	+1 (12.5)	-1 (9)	-1 (0.74)	4.3	68.4	65.1
3	-1 (4.7)	+1 (93.2)	-1 (0.74)	0.4	1.0	0.0
4	+1 (12.5)	+1 (93.2)	-1 (0.74)	0.4	17.7	17.3
5	-1 (4.7)	-1 (9)	+1 (2.97)	17.2	11.9	9.6
6	+1 (12.5)	-1 (9)	+1 (2.97)	17.2	60.0	67.3
7	-1 (4.7)	+1 (93.2)	+1 (2.97)	1.7	19.3	19.9
8	+1 (12.5)	+1 (93.2)	+1 (2.97)	1.7	68.5	61.9
9	-1 (4.7)	0 (46)	0 (1.48)	1.7	15.8	23.8
10	+1 (12.5)	0 (46)	0 (1.48)	1.7	62.6	65.8
11	0 (8.6)	-1 (9)	0 (1.48)	8.6	94.0	88.5
12	0 (8.6)	+1 (93.2)	0 (1.48)	0.8	53.2	69.8
13	0 (8.6)	0 (46)	-1 (0.74)	0.8	74.7	84.5
14	0 (8.6)	0 (46)	+1 (2.97)	3.4	98.7	100.0
15	0 (8.6)	0 (46)	0 (1.48)	1.7	95.0	92.1
16	0 (8.6)	0 (46)	0 (1.48)	1.7	96.0	92.1
17	0 (8.6)	0 (46)	0 (1.48)	1.7	96.0	92.1
18	0 (8.6)	0 (46)	0 (1.48)	1.7	97.0	92.1
19	0 (8.6)	0 (46)	0 (1.48)	1.7	92.0	92.1
20	0 (8.6)	0 (46)	0 (1.48)	1.7	99.0	92.1

[a] Two replicas were performed for run 1-14

[b] Average of two replicas are presented for run 1-14

6.3.3. Statistical Analysis

Table 6.3 shows coefficients of the second-order polynomial equation (equation 6.7). These coefficients were calculated using the MINITAB (ver. 15) based on the experimental data shown in Table 6.2 for the chromium removal efficiency. The coefficients of determination values (R^2) and adjusted R^2 are 96.55 % and 93.44% for the model that was developed from the Central Composite Design, respectively. This indicates that only 7% of the total variation could not be explained by the quadratic model, and shows the agreement between the experimental and predicted data.

Table 6.3 Estimated Regression Coefficients of the Quadratic Model for the Central Composite Design for Total Chromium Removal from Brines Using CaS_5. X_1 = pH, X_2 = Initial Cr(VI) Concentration, And X_3 = CaS_5 Dosage

Source	Coefficient	Value
Constant	b_0	92.1399
X_1	b1	21.0007
X_2	b2	-9.3756
X_3	b3	7.7603
X_1X_1	b11	-47.3858
X_2X_2	b22	-12.977
X_3X_3	b33	0.0953
X_1X_2	b12	-3.9211
X_1X_3	b13	3.9211
X_2X_3	b23	10.5997

R^2 = 0.9655, adjusted R^2 = 0.9344

Table 6.4 shows the result of the analysis of variance (ANOVA) and lack-of-fit between the experimental and predicted responses. The calculated F-values of the model were greater than the critical F-value. The higher F-value indicates that the model is more accurate in predicting the variation with the regression equation. Therefore, the square variables were the most significant and the interactions of the variables were the least significant in the model. There was no evidence of lack of fit ($P = 0.001 < 0.05$). All the P values were below 0.05, which assured that the statistical model was significant. Overall, by comparing the F, P, and the coefficient of determination values, it was concluded that the model is statistically significant. This quadratic model along with the results of the coagulation batch experiments was utilized to predict the effects of pH, CaS_5 dosage, and initial Cr(VI) concentration.

Table 6.4 Analysis of Variance (ANOVA) of Response Surface Quadratic Model for Central Composite Design

Source	F^a	P^b
Regression	31.07	< 0.001
Linear	24.13	< 0.001
Square	64.4	< 0.001
Interaction	4.69	0.027
Lack-of-Fit	29.33	0.001

[a] $F_{critical} = < 0.0001$
[b] $P_{critical} = > 0.05$

6.3.4. Reagents

All solutions were prepared using high-grade deionized (DI) water produced by a Thermo Scientific Barnstead Nanopure system. The glassware was soaked in an acidic solution (2% Micro-90, International Products Corp., Burlington, New Jersey) for at least 24 hours and completely rinsed with DI water. Reagent-grade (99.9%) NaCl crystals

(EMD Chemicals Inc., USA) were added to deionized water to make a primary stock solution of 120 g/L NaCl. Sodium bicarbonate ($NaHCO_3$) powder (EMD Chemicals Inc., USA) was used to make a 61 g/L HCO_3^- stock solution. A primary stock solution (1000 mg/L) for Cr(VI) was prepared using potassium chromate crystals (K_2CrO_4, J.T. Baker Reagent Chemicals). A 1.85 M (29% by wt.; 371.2 gCaS_5/L) calcium polysulfide (CaS_5) solution (Best Sulfur Products, Fresno, California) was used for the coagulation processes. Other researchers (Moon et al., 2008; Wazne et al., 2007a and 2007b) have used the same calcium polysulfide product (Best Sulfur Products, Fresno, California) and reported that the calcium polysulfide is in the form of CaS_5. It has also been reported that polysulfide usually occurs as pentasulfide in water (Kamyshny et al., 2004; Licht et al., 1986). Chromium standard solution of 1000 mg/L (RICCA Chemicals Company, Texas) was used for equipment calibrations.

6.3.5. Coagulation Batch Experiments and Analytical Methods

Coagulation batch experiments were performed using a PB-700 standard JarTester (Phipps & Bird, Richmond, Virginia), which had six 2.54 cm × 7.62 cm stainless steel blades, spaced 15.24 cm apart. Two hundred and fifty milliliters of synthetic brine was added to 1 L glass beakers, and placed into the jar tester. The batch experiments were performed by rapidly mixing for two minutes at 12 rad/s ($G = 158\ s^{-1}$) followed by thirty minutes of slow mixing at 3 rad/s ($G=20\ s^{-1}$) for flocculation. The pH and oxidation-reduction potential (ORP or E_h) of solutions were measured after and before adding CaS_5 using an Orion 920A+ pH meter equipped with an Orion 8102BNUWP and Orion Ionalyzer 96-78-000 probes (Thermo Electron Corporation, USA), respectively. In this research, the E_h values are in volts as compared to the standard hydrogen electrode

(SHE). The ORP meter was calibrated using a potassium iodide (KI) ORP standard, Orion 967961 (Thermo Electron Corporation, USA), prior to each use, according to the manufacturer instruction. pE values corresponding to Eh values were calculated from the following equation: $pE = (F \times E_h) / (2.303 \times R \times T)$; where F is Faraday constant (96.42 kJ/V.eq), R is ideal gas constant (8.314 J/k.mol), and T is temperature (°K).

The coagulation batch experiments were performed in beakers opened to the air. No effort was spent to minimize the oxidation of CaS_5 by air, because in the field, CaS5 would be used in the presence of air. It is likely the oxidation-reduction potential measured was affected by the presence of air. However, it has been reported that CaS_5 decomposes slowly (i.e., 60 minutes) by aeration (Yahikozawa et al., 1978). In this experiment the mixing time for coagulation was 32 minutes.

After coagulation, forty-five milliliters of the solution was collected and centrifuged for one hour at 367 rad/s using a Sorvall Legend RT Bechtop centrifuge (Thermo Scientific Co., USA) to separate the liquid from the solids. Total chromium concentration was measured in the separated liquid using a DR 5000 spectrophotometer (Hach, Loveland, Colorado) following the standard procedures (Method No. 3500 Cr) before and after the thirty-two minutes of continuous mixing. The total chromium concentrations of > 10 mg/L were also measured utilizing an atomic adsorption spectrometer (PerkinElmer AAnalyst 100, USA) according to method no. 3111 (standard methods, 2005) to assure the quality of the measurements. Three calibration standards and the wave length of 357.9 nm were used for the measurements. Cr(VI) concentration was measured by a DR 5000 spectrophotometer following the standard procedures (Method No. 3500 Cr) (standard methods, 2005). The chromium in the brine before coagulation is in the form of Cr(VI) (chromate), and, therefore, the Cr(VI) concentration is equal to the total chromium concentration. However, the soluble chromium after coagulation can be in the forms of Cr(VI) or Cr(III); thus, the total chromium concentration is equal to the concentrations of Cr(VI), Cr(III), Cr(II), and Cr(0). In this research, the "total chromium removal" stands for the total chromium concentration, which is Cr(VI) concentration plus Cr(III) concentration. Cr(VI) stands for hexavalent chromium concentration. After coagulation process, the total solids generated in the reduction and precipitation process were measured according to method no. 2540 B (Standard Methods, 2005) using a 0.45 μm GF/C glass-fiber filter (Whatman Inc, Piscataway, NJ).

6.3.6. Batch Experiments to Evaluate the Effects of pH, CaS_5 Dosage, and Initial Cr(VI) Concentration

Three series of batch experiments were performed to evaluate the effects of pH, CaS_5 dosage, and initial Cr(VI) concentration. These experiments were planned after statistical analysis of CCD. The results of CCD provided an overall insight on interactions between variables and assisted the planning of the experiments.

To evaluate the effect of pH, a series of coagulation batch experiments were performed for brines with an initial Cr(VI) concentration of 47 mg/L, 1.5 mM of CaS_5, varying pH values from 2.2 to 12.4, and ionic strengths of 0.1, 0.8, or 1.5 M. The initial pH was adjusted using either hydrochloric acid or sodium hydroxide. For each ionic strength level, nine experiments were performed at nine different pH values; three of these experiments were performed in duplicate.

In order to determine the required amount of calcium polysulfide (CaS_5), for six initial concentration of Cr(VI) varying from 9 to 93.2 mg/L, nine batch experiments (three in duplicate) were conducted for each initial concentration of chromium by adding various dosages of calcium polysulfide to brines with 1.2 M ionic strength.

6.3.7. Batch Experiments to Evaluate the Effects of Ionic Strength and Alkalinity

Two series of coagulation batch experiments were performed to investigate the effects of ionic strength and alkalinity. The effect of ionic strength on the removal process was investigated by conducting a series of batch coagulation experiments for brines at ionic strength levels of 0.1, 0.8, 1.5, or 2.2 M to remove an initial Cr(VI) concentration of 46.0 mg/L using varying dosages of CaS_5. At each ionic strength level, nine batch experiments were performed at different CaS_5 dosages three of which were performed in duplicate.

The effect of alkalinity was evaluated through executing a series of batch experiments for brines containing four levels of alkalinity 0.0024, 0.5, 2.5, and 5.0 g/L as $CaCO_3$, ionic strength of 0.8 M, and Cr(VI) concentration of 48.2 mg/L by adding varying dosages of CaS_5. For each alkalinity level, nine batches were executed; three of these experiments were performed in duplicate.

6.4. Results and Discussion

6.4.1. Effect of Ionic Strength

Figure 6.1a presents total chromium removal from the synthetic brine with increasing CaS_5 addition for a fixed pH of 8.5, initial Cr(VI) concentration of 46 mg/L, and ionic strengths of 0.1, 0.8, 1.5, and 2.1 M. Figure 6.1b depicts the respective oxidation/reduction potentials and pE values for the results of the experiments shown in Figure 6.1a. Both graphs show the error bars for those experiments that were replicated. The standard errors were between 0.1 and 2.1. Chromium removal increased with increasing CaS_5 dosage up to 1.5 mM (1.7 CaS_5/Cr(VI)), then it stayed constant with the addition of up to 3 mM (3.4 CaS_5/Cr(VI)). After 3 mM CaS_5 addition, chromium removal decrease slightly and this trend was observed for all ionic strengths investigated. This trend is consistent with the reduction in potential depicted in Figure 6.1b. The positive brine E_h of 0.44 V was reduced sharply with the addition of CaS_5 and then it stabilized at approximately -0.20 V. The CaS_5 dosages which were used in this study aim at removing Cr(VI) to levels that meet the drinking water MCL (0.1 mg/L) and the TCLP limit of 5 mg/L that would support optional disposal methods for the brine. In addition, maximum chromium removal efficiency that can be achieved using CaS_5 was sought. The effects of calcium polysulfide dosages, E_h values, and initial Cr(VI) will be discussed further in section 6.4.3.

Total chromium removal for brines with 0.1, 0.8, 1.5, and 2.1 M ionic strengths were compared by paired t-test analysis (Table 6.5). The small P values of 0.0099, 0.0016, and 0.0012 (<0.05) indicate that increasing the ionic strength of brines from 0.1 M to 0.8, 1.5, or 2.1 M promoted a statistical significant difference in the total chromium removal efficiencies. Similarly, the small P values of 0.0070 and 0.0026 imply that increasing the ionic strength of brines from 0.8 M to 1.5 M or 2.1 M caused a statistical difference in total chromium removal. Notwithstanding its statistical significance, the total chromium removal increased only slightly (1.4 % to 4.4 %) when the ionic strength was increased from 0.1 M to 0.8 M, 1.5 M or 2.1 M (Table 6.5).

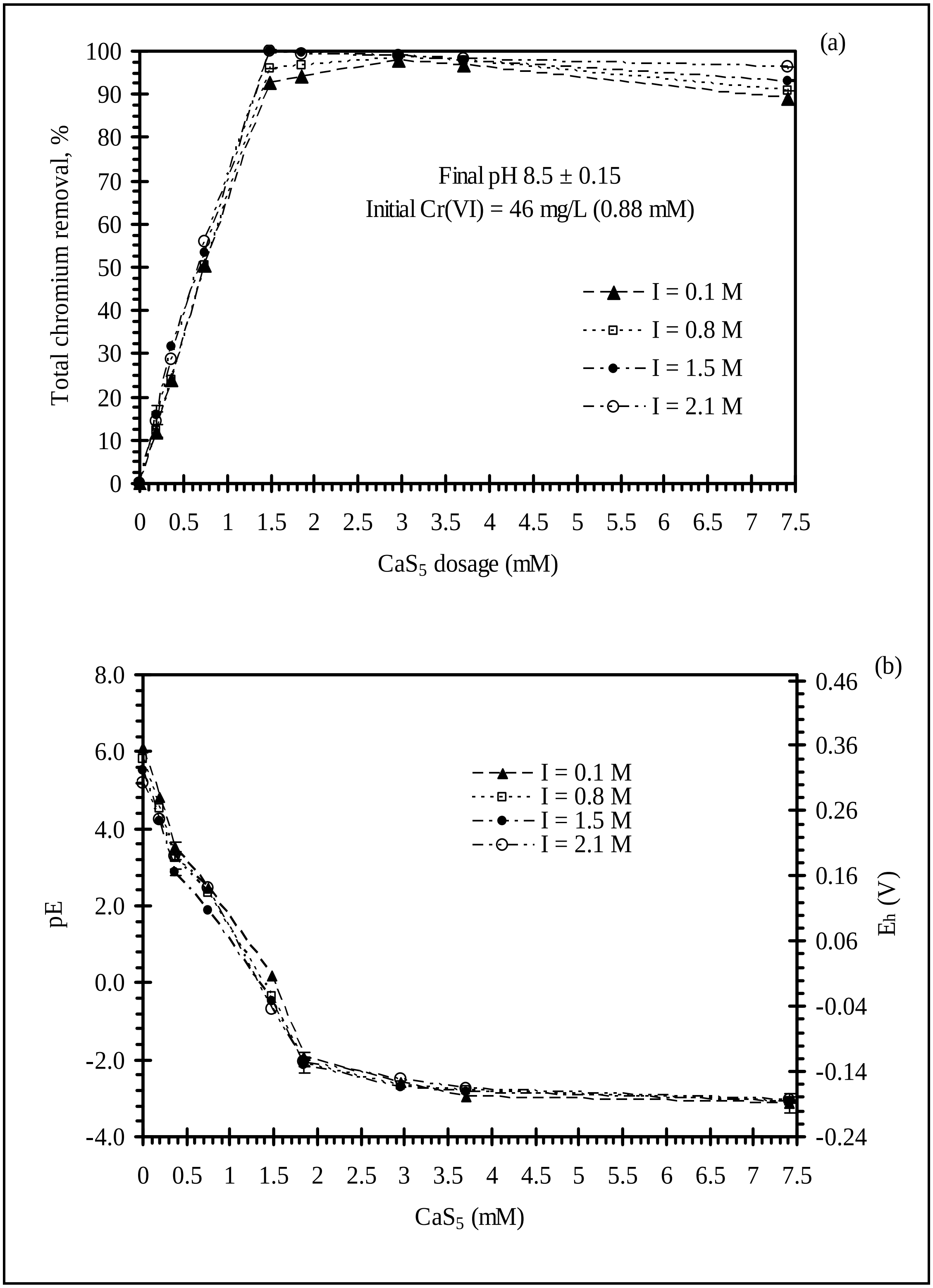


Figure 6.1a Chromium Removal Efficiency as a Function of CaS_5 Dosage and Different Ionic Strength Levels at a Constant Initial Cr(VI) Concentration of 46 mg/L (0.88 mM), pH of 8.5 ± 0.15, and Alkalinity of 5 g/L of $CaCO_3$. Figure 6.1b Oxidation/Reduction Potential (E_h) and pE for Experimental Points Shown in Figure 6.1a

There is no statistically significant difference (P value = 0.4100 > 0.05) found between the total chromium removal for brines with 1.5 to 2.1 M ionic strength.

A separate statistical analysis was run for the data shown in Figure 6.1a. The statistical analysis for data obtained with CaS_5 below 3 mM showed no significant difference (P = 0.15 > 0.05), while for CaS_5 above 3 mM CaS_5 showed a significant difference (P = 0.04 < 0.05). This implies that ionic strength had no effects on the Cr(VI) reduction process when CaS_5 was below 3 mM. Therefore, ionic strength seems to favor only the precipitation of chromium hydroxide causing a slight enhancement in chromium removal. Pettine et al. (1994) reported that the rate constant of Cr(VI) reduction in NaCl media using hydrogen sulfide was insensitive to the change in ionic strength levels from 0.1 M to 1.42 M.

Table 6.5 Results of Paired T-Test for Total Chromium Removal for Brines with Ionic Strengths of 0.1, 0.8, 1.5, and 2.1 M

t-Test Analysis between	P value	Average Difference
0.1 M and 0.8 M	0.0099	1.4 %
0.1 M and 1.5 M	0.0016	4.3 %
0.1 M and 2.1 M	0.0012	4.4 %
0.8 M and 1.5 M	0.0070	2.9 %
0.8 M and 2.1 M	0.0026	3.1 %
1.5 M and 2.1 M	0.4100	0.2 %

6.4.2. Center Composite Design(CCD) Prediction of the Effects of pH and Initial Cr(VI) Concentration on Total Chromium Removal

Figure 6.2 shows a contour plot of combined effects of initial Cr(VI) concentration and pH on total chromium removal (i.e., combination of reduction of Cr(VI) to Cr(III) and precipitation of $Cr(OH)_3$) as predicted by the CCD quadratic model developed. The maximum removal (95%) was obtained at pH values between 8.8 and 10.5 for initial Cr(VI) concentrations of 20-42 mg/L. The chromium removal decreased when pH was increased above 10.5 or decreased below 8.8. Similar plots for various initial Cr(VI) concentration (i.e., 9, 46, and 93.2) and CaS_5 dosages were developed, and it was found that the optimum pH for chromium removal from IX brines is between 8.0 and 10.5.

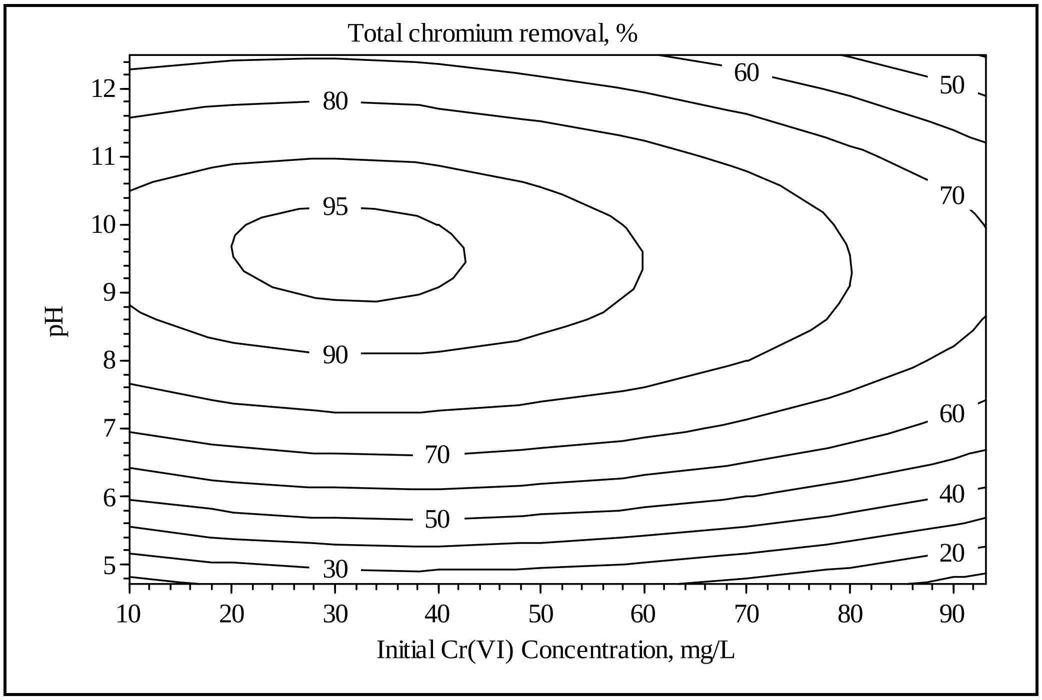


Figure 6.2 Contour Plot of Predicted Total Chromium Removal as a Function of Initial Cr(VI) Concentration and pH at a Constant CaS_5 dosage of 1.5 mM and Ionic Strength of 1.1 M

6.4.3. Effects of pH

The removal of chromium by calcium polysulfide addition occurs in two steps (Yahikozawa *et al*., 1978; Storch *et al*., 2002). In the first step Cr(VI) reduces to Cr(III), and subsequently Cr(III) precipitates as chromium hydroxide ($Cr(OH)_3$) (Yahikozawa *et al*., 1978; Storch *et al*., 2002). Figures 6.3a and 6.3b reveals the two different steps of chromium removal by CaS_5. Figure 6.3a depicts the efficiency of Cr(VI) reduction to Cr(III), based on the remaining Cr(VI) measurements, as a function of pH, ionic strength, a constant CaS_5 dosage of 1.5 mM, and an initial Cr(VI) concentration of 47 mg/L (0.9 mM) obtained for coagulation batch experiments. The graph shows the error bars for the replicated experiments. The standard errors in these experiments were between 0.1 and 1.8. The CaS_5/Cr(VI) ratio was 1.7. One hundred percent Cr(VI) reduction from the brine was achieved at the pH range of 1.6-6.4. Cr(VI) reduction efficiency decreased from 100% to 96% when pH increased from 6.4 to 10.3, respectively (Figure 6.3a). Li et al. (2009) and Kim *et al.* (2001) also reported a decrease in reaction rate constant of Cr(VI) reduction using S^{2-} when pH was increased from 7.5 to 9.3. In this research, the Cr(VI) reduction efficiency strongly decreased from 96 % to 72 % when pH increased from 10.3 to 12.4. When calcium polysulfide was applied to brines with a pH 12.4, the color of the brine became greenish. This is an indication of the presence of soluble species of Cr(VI) or Cr(III) in the brine at this high pH level.

Figure 6.3b shows the total chromium removal for the same experiments presented in Figure 6.3a, as a function of pH, ionic strength, a constant CaS_5 dosage of 1.5 mM, and an initial Cr(VI) concentration of 47 mg/L (0.9 mM). At pH range of 6.5 to 10.3, the highest total chromium removal of approximately 94% was achieved. Therefore, the same percent removal of chromium can be achieved at the lower pH range (i.e., pH 6.5) and the upper range (i.e., pH 10.3). Beszedits (1988) also reported that the optimal pH for Cr(III) precipitation was between pH 8.5 and 9.0 after the reduction of Cr(VI) to Cr(III) in industrial wastewaters. This is consistent with the finding of this research and with the fact that lower solubility of chromium hydroxide occurs at pH values between 8.6 and 8.9.

Figure 6.3b shows that very poor total chromium removal is achieved at $pH < 6.5$ and at $pH > 10.3$. Decreasing pH from 6.5 to 4.5 drastically decreased the removal efficiency from 94% to 15%, and total chromium removal efficiency (15 %) stayed constant for pH values between 1.5 and 4.5. The reason for the decrease is that chromium hydroxide does not form at acidic pH values less than 5.1. Instead, soluble forms of Cr(III) [Cr^{3+}, $CrOH^{2+}$, and $Cr(OH)_2^+$] are present at acidic pHs, and do not precipitate (Lai & MacNeill, 2006). Increasing pH values from 10.3 to 12.4 drastically decreased the total chromium efficiency from 94% to 71 %, because Cr(VI) reduction efficiency decreased at pH values above 10.3 (Figure 6.3a). Another reason is that chromium hydroxide transforms to soluble $Cr(OH)_4^-$ at pH above 10.6. At very high pH (13.5-14) $Cr(OH)_3(s)$ does not form at all; instead, $Cr(OH)_4^-$ appears as the predominant species.

Because the regulations for the disposal of chromium-containing wastes are typically based on total chromium the effect of pH on total chromium removal (Figure 6.3b) should be taken into consideration when treating these wastes. Thus, although Cr(VI) reduction efficiency was found to be at its maximum at $pH < 6.5$ (Figure 6.3a), the overall total chromium removal (Figure 6.3b) was poor at $pH < 6.5$ because the Cr(III) does not precipitate as $Cr(OH)_3$. For pH values similar to those typically found in IX brines (i.e., pH = 8-10), over 94% of Cr(VI) can be reduced to Cr(III) and precipitated as $Cr(OH)_3$ at the brine's pH range. Therefore, no pH change is needed because the high pH of IX brines does not hinder their removal by CaS_5; Indeed, the high typical pH of IX brines facilitate optimal precipitation of $Cr(OH)_3$ and only slightly affects reduction of Cr(VI) to Cr(III). This is a significant advantage of calcium polysulfide as compared to other treatment methods that needed two pH adjustments for chromium removal. The first adjustment is to lower the pH to levels < 6.5 for Cr (VI) reduction followed by a pH increase to above 8 to precipitate Cr (III) (Beszedits, 1988).

Figure 6.3c presents the oxidation/reduction potential (E_h) of the treated brine after coagulation versus the pH for the same experiments shown in Figures 6.3a and 6.3b. Figure 6.3c shows that the higher the pH, the lower the potential E_h, as expected from the Nernst equation (Barrett, 2003). The more positive the reduction potential, the greater the tendency of Cr(VI) to gain electron and be reduced to Cr(III), which is the case at low pH values (Figure 6.3a).

The optimal pH range of 8-10.5 for chromium removal from brines with 1 M ionic strength and 10 to 93 mg/L of initial Cr(VI) concentration was estimated using response surface model (Section 6.4.2). Experimentally, a pH range of 6.5 to 10.3 was found for brines with 47 mg/L initial Cr(VI) concentration and 0.8-1.5 M ionic strength. Therefore, the upper pH values found experimentally closely matches the value found with the model. However, for the lower pH range (i.e., 6.5 to 8), the model predicts a lower removal efficiencies than that experimentally found. Therefore, it is anticipated that the optimal pH range of 8-10.3 for chromium removal with CaS_5 is valid for other brines with initial Cr(VI) concentrations between 9-94 mg/L.

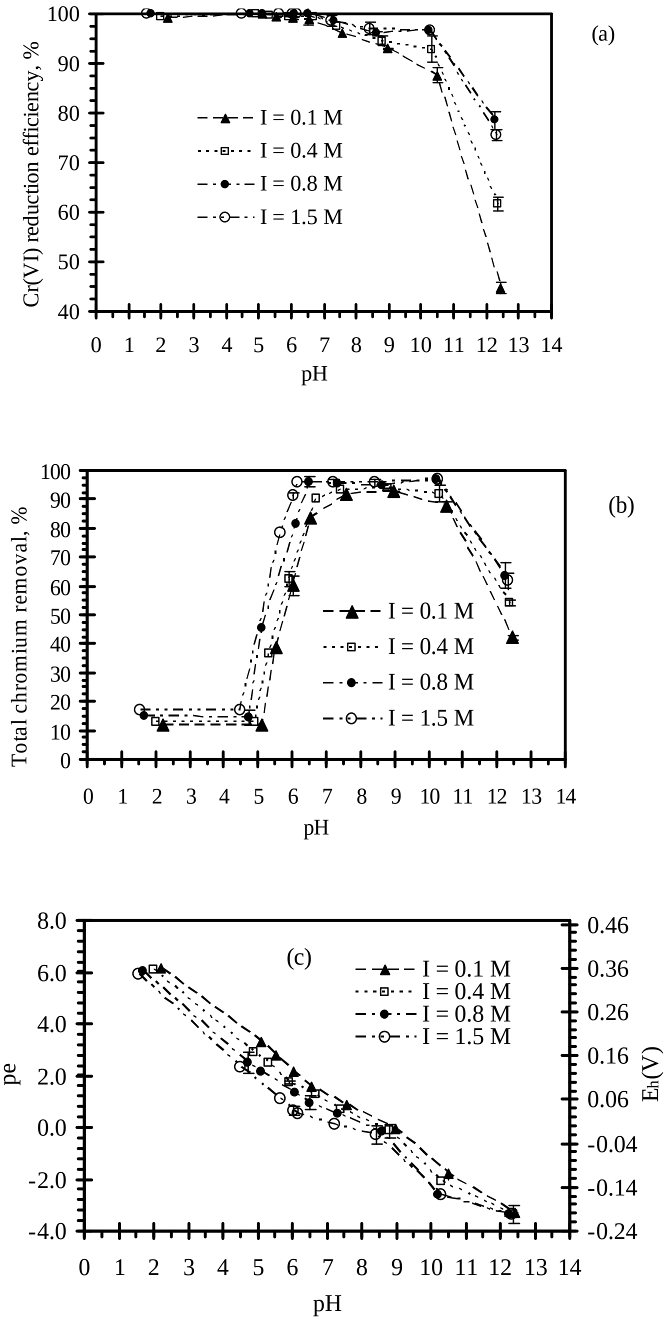


Figure 6.3a Cr(VI) Reduction Efficiency and Figure 6.3b Total Chromium Removal Efficiency as a Function of pH and Different Ionic Strength Levels at a Constant Initial Cr(VI) Concentration of 47 mg/L (0.9 mM) and CaS_5 Dosage of 1.5 mM. Figure 6.3c Oxidation/Reduction Potential (E_h) and pE of the Treated Brines for Points Shown in Parts (a) and (b)

The CCD developed can then be applied to the treatment of IX brines contaminated with chromium.

6.4.4. CCD Prediction for the Effects of CaS_5 Dosage and Initial Cr(VI) Concentration on Total Chromium Removal

Figure 6.4 shows the predicted total chromium removal using the CCD model as a function of Cr(VI) concentration and CaS_5 dosage. The total chromium removal for brines with initial Cr(VI) concentrations of 0.2 to 1.8 mM (10 to 94 mg/L) increased when the CaS_5 dosage varied from 0.8 to 2.9 mM. For brines containing 0.2-0.3 mM chromium (9.3 to 15.6 mg/L), the removal efficiency was at its maximum (91.9 %) when 0.6 mM of CaS_5 (2-3 CaS_5/Cr(VI)) was added, and the total chromium removal decreased to 87.8 % by increasing the CaS_5 dosages from 0.8 mM to 3.1 mM (10-15 CaS_5/Cr(VI)). This result implies that although the removal efficiency increases by increasing CaS_5 dosage, addition of CaS_5 at CaS_5/Cr(VI) molar ratios greater than 3 slightly reduces efficiency for brines containing 0.2-0.3 mM chromium. The CCD model developed in this research provides a reasonable approximation to predict the performance of chromium removal using CaS_5. It is a useful tool to support a technology for which very little is known.

6.4.5. Effects of Calcium Polysulfide Dosage and Initial Chromium Concentration

Figure 6.4 was used to plan a series of coagulation experiments for investigating the effects of CaS_5 dosage and initial Cr(VI) concentration. Figure 6.5a presents the results of batch experiments conducted to determine the total chromium removal as a function of CaS_5 dosages for six different initial Cr(V) concentrations. The standard errors were between 0.2 and 2.3. As expected, the oxidation/reduction potential (ORP) of the brines decreased when CaS_5 dosages increased (Figure 6.5b). The initial ORP of IX brines was between 0.2 and 0.6 V, which was an oxidizing condition, and adding CaS_5 decreased the ORP levels near zero. Figure 6.5 shows that CaS_5/Cr(VI) ratios of 1.7-2.0 were needed for optimal removal of chromium from IX brines. Only a slight benefit in removal was achieved at CaS_5/Cr(VI) ratios between 2 and 4. No benefit can be observed for addition of CaS_5 at a CaS_5/Cr(VI) ratio greater than 4.

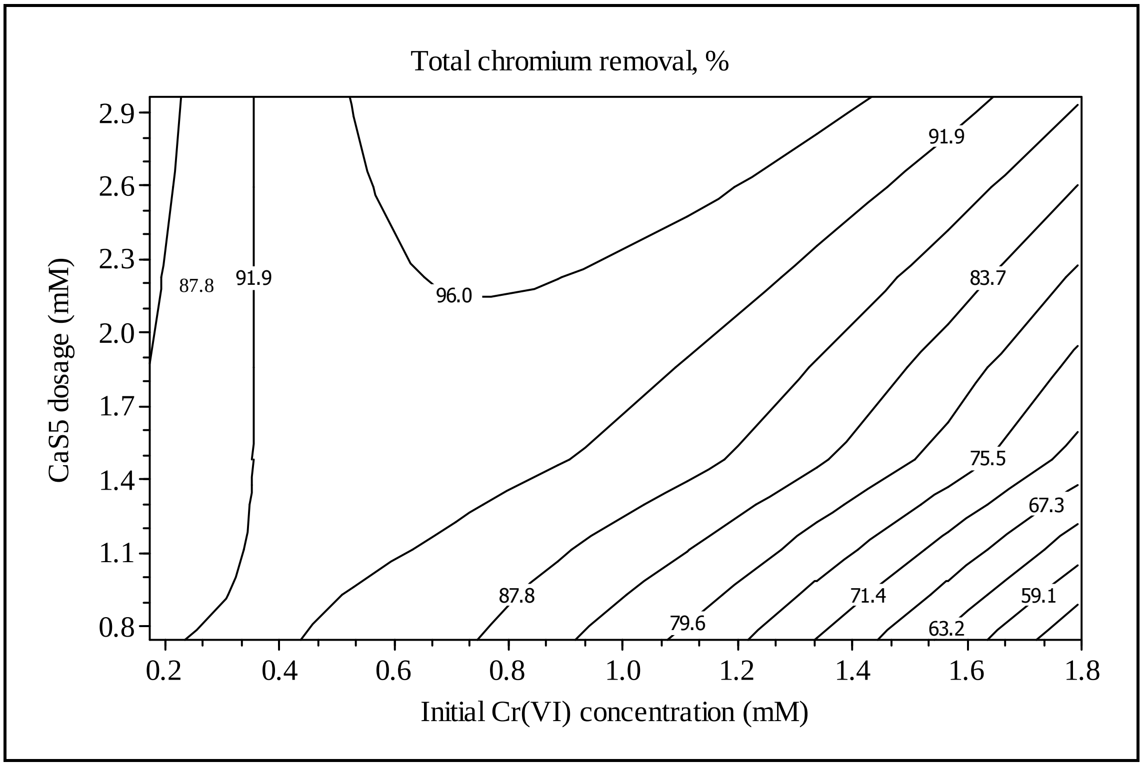


Figure 6.4 Contour Plot of Predicted Total Chromium Removal as a Function of Initial Cr(VI) Concentration and CaS_5 Dosage for Brines with Ionic Strength of 1.1 M and Alkalinity of 5 g/L of $CaCO_3$ at Final pH Values of 8.6

Table 6.6 shows CaS_5/Cr(VI) ratios, which were experimentally found, to achieve remaining chromium concentrations of 5 mg/L, 0.1 mg/L, and < 0.05 mg/L for pH = 8.4, ionic strength of 0.8 M, and different initial Cr(VI) concentrations. To achieve 5 mg/L remaining chromium concentration in brines containing 9 to 93.2 mg/L Cr(VI), CaS_5/Cr(VI) molar ratios of 0.6 to 1.4 was required. It means that for approximately 10 times increase in initial Cr(VI) concentration, the CaS_5/Cr(VI) molar ratio needed is only about 2.3 times higher. To achieve a remaining Cr(VI) concentration of 0.1 mg/L the CaS_5/Cr(VI) molar ratios are approximately 1.2 to 6.2 times those needed for a remaining concentration of 5 mg/L. As such, for brines with lower Cr(VI) concentration (i.e., 9 mg/L), approximately six times higher CaS_5/Cr(VI) is needed to achieve 0.1 mg/L remaining chromium as compared to 5 mg/L, the TCLP limit. For initial Cr(VI) concentrations between 46.3 mg/L and 93..2 mg/L, which are typical of most ion-exchange brines, only about 1.25 times more CaS_5 is needed to achieve 0.1 mg/L remaining Cr(V) as compared to 5 mg/L. The lower the desired remaining Cr(VI) concentration, the more the CaS_5 consumption.

The final desired level of chromium in a brine treated with CaS_5 will depend on approved disposal methods available in individual municipalities. Brines with remaining chromium concentrations of 5 mg/L are not considered hazardous and could be disposed of as a non-hazardous waste, reducing the cost of disposal. In states where wastes with chromium concentrations lower than 0.1 mg/L can be discharged by alternative means (e.g., discharged into sewer lines), water utilities may consider applying higher CaS_5/Cr(VI) ratios to obtain liquid wastes with much lower chromium concentration, without increasing their CaS_5 consumption much.

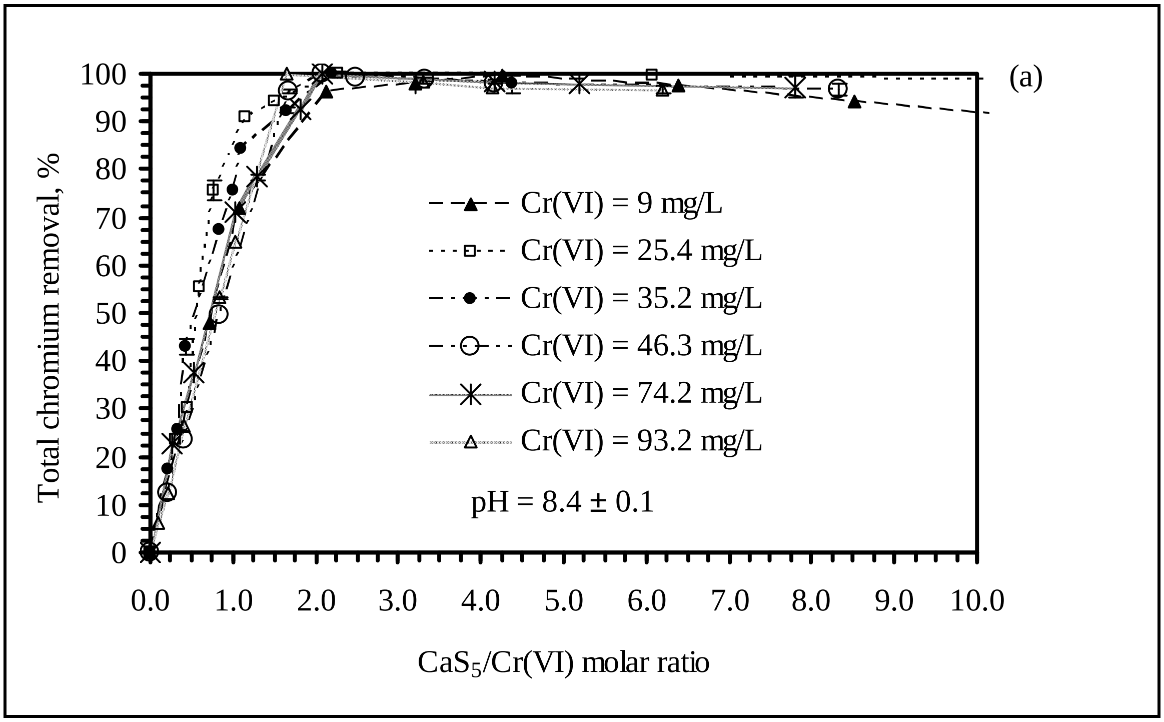


Figure 6.5 Total Chromium Removal as a Function of CaS_5/Cr(VI) Molar Ratio and Different Initial Cr(VI) Concentrations for Brines with Ionic Strength of 0.8 M, Alkalinity of 5 g/L of $CaCO_3$, and a Constant pH of 8.4 ± 0.1

Table 6.6 also shows that the lower the remaining Cr(VI) concentration desired, the greater the CaS_5/Cr(VI) molar ratio needed. For a remaining Cr(VI) concentration of $<$ 0.05 mg/L and an initial Cr(VI) concentration of 9 mg/L, the CaS_5/Cr(VI) molar ratio needed is 4.2 which is 2.5 times greater than that needed for initial Cr(VI) concentration of 93.2 mg/L. The reason for this can be explained with the oxidation reduction potential of brines. A CaS_5 dosage that lowers the oxidation reduction potential to near zero results in a maximum removal (Figure 6. 6).

Figure 6.6 depicts the chromium removal efficiency versus the ORP of the treated brines in this research. It was found that the total chromium removal efficiency correlates strongly with the final ORP of the brines. Lowering the ORP from positive values to between -0.1 and 0 greatly improved the removal efficiency, for brines containing 9-93 mg/L of Cr(VI). Storch et al. (2002) also reported that about 200 mg/L of Cr(VI) reduced to Cr(III) when the ORP of groundwater decreased from +0.2 V to near 0 V when adding CaS_5, during geological fixation of groundwater.

Table 6.6 CaS_5 Dosages for Brines with pH of 8.4 and Ionic Strength of 0.8 M Needed to Lower Chromium to 5 mg/L, 0.1 mg/L, or < 0.05 mg/L

Initial Cr(VI)	Remaining Cr = 5 (mg/L)	Remaining Cr = 0.1 (mg/L)	Remaining Cr < 0.05 (mg/L)
	CaS_5/Cr(VI)	CaS_5/Cr(VI)	CaS_5/Cr(VI)
9 mg/L (0.2 mM)	0.6	3.7	4.2
25.4 mg/L (0.5 mM)	0.8	2.2	2.3
35.2 mg/L (0.7 mM)	1.2	2.2	2.2
46.3 mg/L (0.9 mM)	1.5	2.0	2.0
74.2 mg/L (1.4 mM)	1.9	2.0	2.0
93.2 mg/L (1.8 mM)	1.4	1.7	1.7

Previous studies have found that the CaS_5/Cr(VI) molar ratios required to remove 2.7 to 3425 mg/L of Cr(VI) from waters were found to be between 8.3 to 1.3, respectively (Table 6.7). In this research, the CaS_5/Cr(VI) molar ratios of 4.2 to 1.7 were needed for removal of 9 to 93.2 mg/L of Cr(VI) from IX brines. The CaS_5/Cr(VI) molar ratios required to remove low concentrations of Cr(VI) from water (< 13 mg/L) are higher than those for high concentrations (> 30 mg/L) of Cr(VI). The stoichiometric relationship (CaS_5/Cr(VI)) for reduction of high concentrations of Cr(VI) (>30 mg/L) has been reported to be 1.66 and 1.5 by Graham et al. (2006) and Messer et al. (2004), respectively. This ratio is applicable when the contaminated water has no organic matter (Graham et al., 2006). The CaS_5/Cr(VI) ratio found to be optimal in this research for Cr(VI) concentrations of 9 (4.2) and 93.2 mg/L (1.7) are 2.8 and 1.1 times higher than the stoichiometric ratio of 1.5 found by Kim et al. (2001) for Cr(VI) reduction with hydrogen sulfide, respectively. The CaS_5/Cr(VI) ratio of 8.3 found for removal of 2.7 mg/L Cr(VI) from water (Graham et al., 2006) is 5.5 times higher than the stoichiometric ratio of 1.5 while the CaS_5/Cr(VI) ratio of 1.31 found for removal of 3425 mg/L Cr(VI) from groundwater is 0.87 times less than the stoichiometric ratio of 1.5.

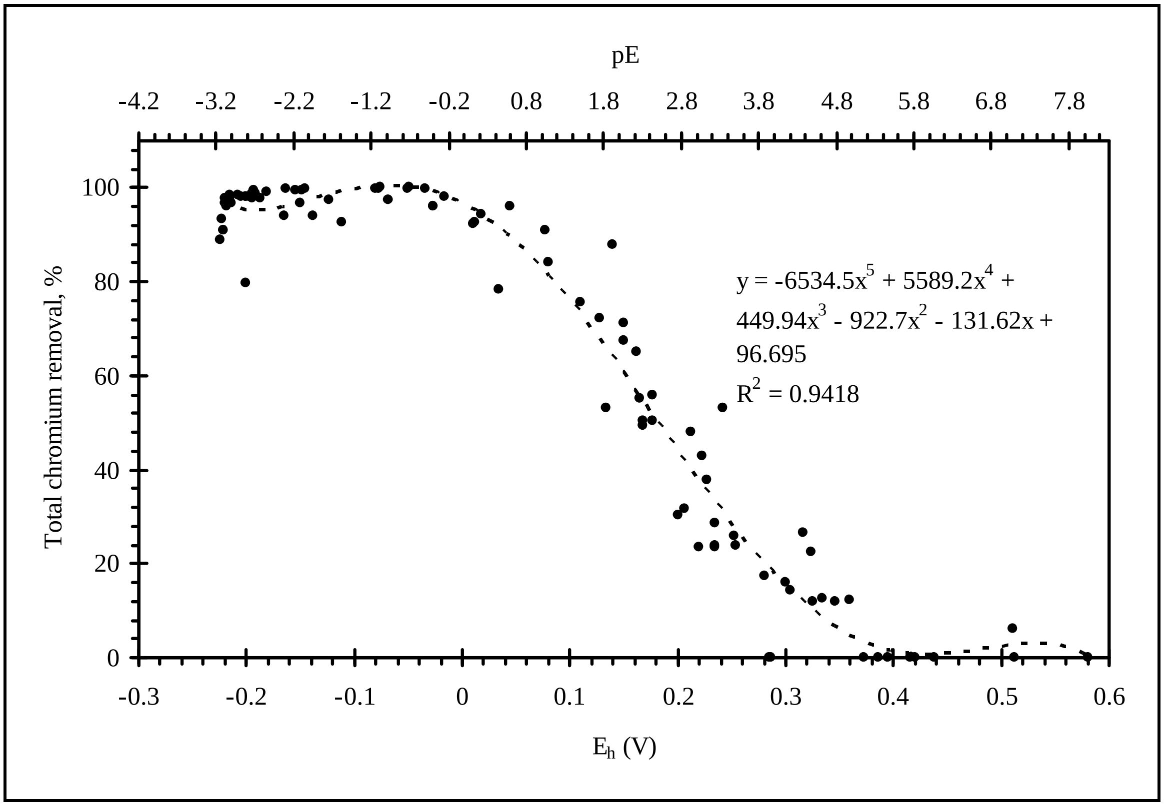


Figure 6.6 Total Chromium Removal as a Function of Oxidation/Reduction Potential (E_h or pE)

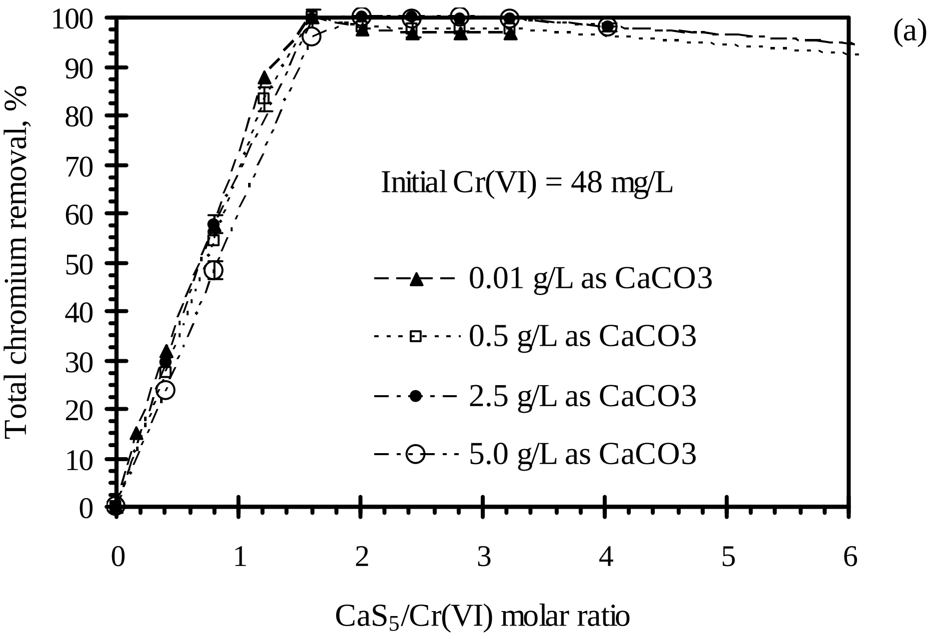
Table 6.7 Summary of Studies on Cr(VI) Reduction by Calcium Polysulfide

Type of Study	CaS_5/Cr(VI)	Initial Cr(VI) (mg/L)	% Cr(VI) removal	Final pH	Reference
Bench Scale Synthetic water	8.3 to 3.33	2.7 to 13.4	100	9.9	Graham et al., 2006
Bench Scale Synthetic water	1.66	26.8-67	98	9.9	Graham et al., 2006
IX Brine	4.2-1.7	9-93.2	> 99.95	8.4	This study
Groundwater	1.31	3425	100	9.9	Graham et al., 2006

6.4.6. Effect of Alkalinity

Figure 6.7a shows the total chromium removal as a function of alkalinity and CaS_5/Cr(VI) molar ratio. The standard errors were between 0.3 and 2.5. Cr(VI) removal for brines with 0.01, 0.5, 2.5, and 5.0 g/L (as $CaCO_3$) alkalinities were compared by paired t-test analysis. The high P values of 0.13 and 0.50 (> 0.05) indicate that increasing the alkalinity of brines from 0.01 to 5 g/L as $CaCO_3$ promoted no statistical difference in the chromium removal efficiencies. Therefore, for IX brines with typical alkalinities of 0.5 to 10 g/L as $CaCO_3$, increasing alkalinity had no major effects on the removal efficiency. In IX brines, high alkalinities are related to high pH values. The effects of pH on total chromium removal by CaS_5 have been discussed in section 6.4.3.

Figure 6.7b shows the final pH versus CaS_5/Cr(VI) molar ratio for the same experiments presented in Figure 6.7a. For brines with 2.5 and 5 g/L of $CaCO_3$, the final pH slightly increased from 8.2 to 8.7 when CaS_5/Cr(VI) molar ratio increased from 0 to 6. For brines with lower alkalinity (< 0.5 g/L of $CaCO_3$), the final pH increased more than the final pH of brines with high alkalinities (2.5 and 5 g/L of $CaCO_3$).



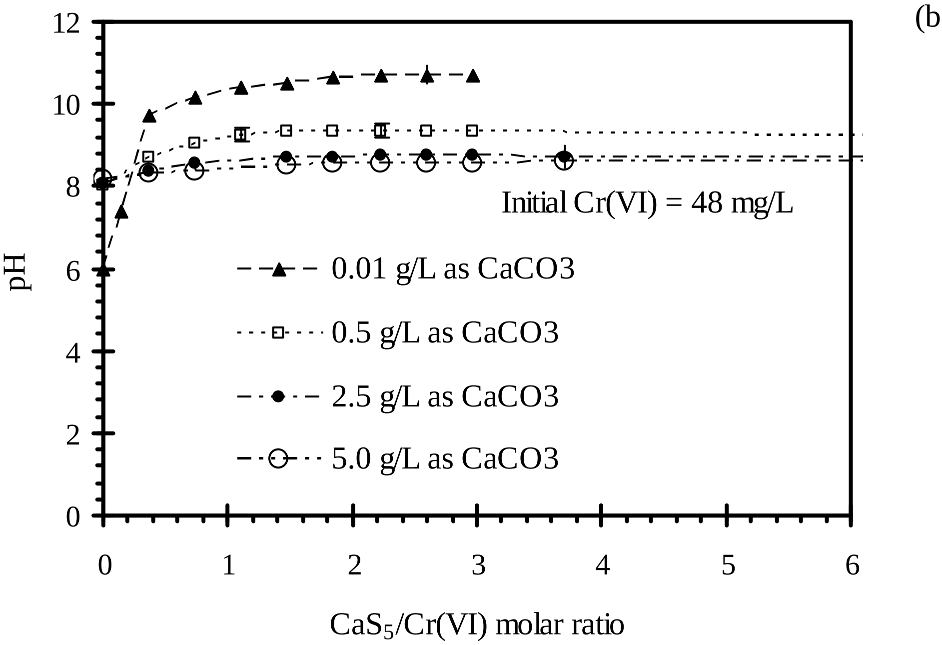


Figure 6.7a Total Chromium Removal as a Function of CaS_5/Cr(VI) Molar Ratio and Different Initial Alkalinities for Brines with Ionic Strength of 0.8 M and Initial Cr(VI) of 48 mg/L. Figure 6.7b The Final pH Values as a Function of CaS_5/Cr(VI) and Different Initial Alkalinities for Points Presented in Figure 6.7a

Interestingly, a brine with a low alkalinity (e.g. 0.01 g/L as $CaCO_3$) would have a low pH of 6.0 that favors reduction of Cr(VI) to Cr(III) and therefore Cr(VI) reduction would be better than it the brine pH were low. But chromium precipitation would not be optimal at this low pH. However, because CaS_5 itself is an alkaline solution and contribute to alkalinity, its addition results in an increase of pH that favors $Cr(OH)_3$ precipitation. Therefore, calcium polysulfide can be successful used even in low alkalinity slightly acidic brines.

6.4.7. Solids Generated in the Removal of Cr by Calcium polysulfide.

Figure 6.8a shows the generated suspended solids with increasing CaS_5 addition for brines with different initial Cr(VI) concentrations. Figure 6.8b presents the generated suspended solid as a function of CaS_5/Cr(VI) molar ratio and different initial Cr(VI) concentrations. The standard errors were between 0.06 and 0.3. TSS linearly increased with increasing CaS_5 independent on the initial chromium concentration. According to equation (6.6) the sludge formed from the removal of chromium by calcium polysulfide contains is a combination of $CaCO_3$, S(s), and $Cr(OH)_3$ (Storch et al., 2002; Messer et al., 2003; Graham et al., 2006; Wazne et al., 2007; Kelsall & Thompson, 1993). Addition of one mol CaS_5 results in generation of five mol S(s), one mol $CaCO_3$(s), and 0.7 mol $Cr(OH)_3$(s) (equation 6.6).

Considering those batch experiments that resulted in the maximum total chromium removal, chromium removal from brines with 9 to 93.2 mg/L of initial chromium resulted in 0.2 to 1.5 g/L of sludge produced when CaS_5 dosage increased from 0.8 mM (4.7 CaS_5/Cr(VI)) to 2.7 mM (1.6 CaS_5/Cr(VI)), respectively. Using higher dosages of CaS_5 results in the generation of larger amounts of sludge that has to be disposed of.

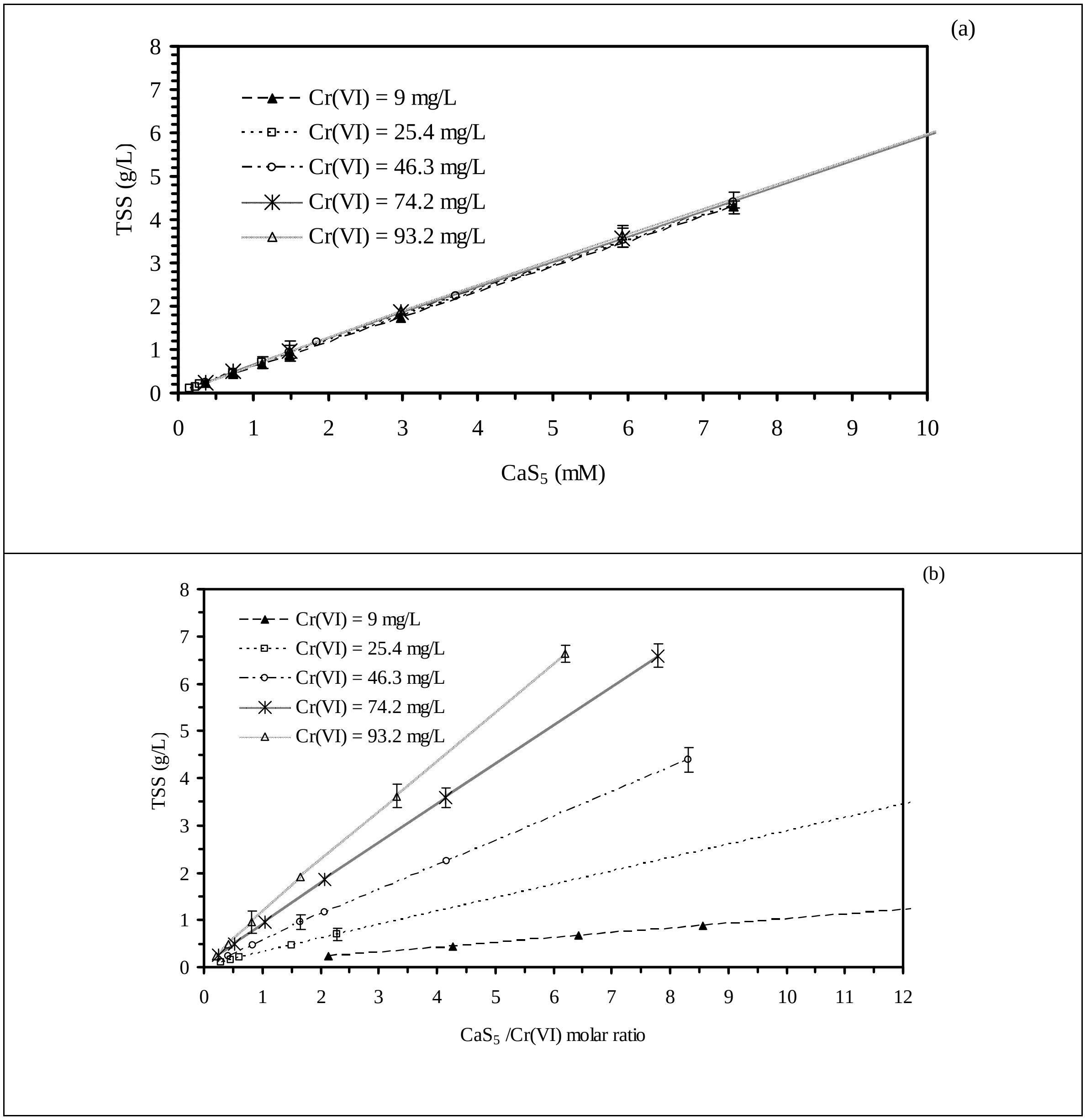


Figure 6.8a Total Suspended Solids Generated After Coagulation as a Function of CaS_5 Dosage and Different Initial Cr(VI) Concentrations. Figure 6.8b Total Suspended Solids as a Function of CaS_5/Cr(VI) Molar Ratio

There is a cost associated with sludge disposal. Depending on the brine characteristics, an economic evaluation is needed to determine the best remaining chromium concentration. In the batch experiments performed for this research, it was observed that a significant amount of $CaCO_3$ scale was formed. IX brines contain high alkalinities, which along with Ca^{2+}, present in CaS_5, produce $CaCO_3$. Scale formation can cause problems for full scale brine treatment units, because scale precipitates in tanks and blades, and may clog pipes. The pipes and mixing blades in the full scale plants must be monitored frequently where CaS_5 is used. The scale formed can be removed using an acid.

6.5. Conclusions

Calcium polysulfide was successfully utilized for Cr(VI) removal from IX brines. A Central Composite design and response surface methodology, along with a series of coagulation experiments, were utilized to investigate the effects of the major parameters, including initial Cr(VI) concentration, pH, and CaS_5 dosages on the removal efficiency. In addition, two series of coagulation experiments were executed to investigate the effects of ionic strength and alkalinity on the removal process. The following are the conclusions of this research:

1. Cr(VI) reduction to Cr (III) was found to be 100% to 93.5 % for pH value of 1.6 to 10.3, respectively. However, the optimum pH range for maximum chromium removal (combined reduction/precipitation) was found to be 8 to 10.3. IX brines typically have pH values between 8 and 10. Because both Cr(VI) reduction and Cr(III) precipitation with calcium polysulfide can also be achieved at the pH range of IX brines, this technology does not require pH adjustment. That constitutes a significant advantage in terms of cost and straightforward operation.

2. The CCD model used to model chromium removal is a fairly simple but useful tool to predict the process. Therefore, the modeling can be used to assist the water industry in determining CaS_5 dosages needed to achieve desired chromium removals from ion-exchange brines.
3. The removal efficiency of chromium by CaS_5 coagulation slightly increased when ionic strength of the brine was increased from 0.1 M to 0.8 M, 1.5 M or 2.1 M. No significant improvement in removal efficiency was observed for ionic strength increase above 1.5 M. Therefore, the high ionic strength of brines does not influence the process.
4. Increasing alkalinity from 0.01 to 5 g/L as $CaCO_3$ had no effect on the removal efficiency of chromium from IX brines. Even brines with low alkalinity which would have pH values slightly below the neutral range can effectively be treated by calcium polysulfide. The reason is Cr(VI) reduction is 100% effective at pH below 6.5, and the addition of calcium polysulfide, which is a basic solution with pH above 11, promotes an increase in pH. This pH increase is sufficient to promote effective precipitation of Cr(III).
5. To achieve the TCLP limit of 5 mg/L chromium in the treated IX brines, the CaS_5/Cr(VI) molar ratios needed increases slightly (i.e., 0.6 to 1.4) with a significant increase (e.g., 9 mg/L to 93.2 mg/L) in initial Cr(VI) concentration. If IX brines were to be treated to achieve the MCL of 0.1 mg/L for drinking waters, higher CaS_5/Cr(VI) molar ratios (i.e., 3.7 to 1.7) would be required for brines containing 9 to 93.3 mg/L of higher chromium levels, respectively. The higher the initial Cr(VI) concentration, the lower is the CaS_5/Cr(VI) molar ratio. The CaS_5/Cr(VI) molar ratio

(3.7) needed to remove 9 mg/L Cr(VI) is 2.2 times higher than the ratio (1.7) required to remove 93.2 Cr(VI).

6. The oxidation/reduction potential of brines was strongly correlated with total chromium removal. The IX brines had positive E_h values (+0.35 to +0.55 V), indicating oxidizing conditions. When the E_h values (ORP) were lowered to between -0.1 and 0 volts, the brines were under reducing conditions, and maximum total chromium removal occurred. Addition of CaS_5 at CaS_5/Cr(VI) ratio of above 4 decreased the ORP to the lowest value of -0.32 V, while causing a slight decrease in total chromium removal. It is thought that this decrease in removal is due to a decrease in the reduction efficiency. Therefore, addition of excessive dosages of CaS_5 is not recommended, because it generates more sludge and lowers the reduction efficiency.
7. The amount of sludge solids generated in the coagulation process was directly proportional to the amount of CaS_5 added. Solid concentrations varying from 0.2 to 1.5 g/L were found for experiments at which maximum total chromium removal was achieved.

CHAPTER 7

CONCLUSIONS, IMPLICATIONS, AND RECOMMENDATION

7.1. Objectives of the Research

Ion-exchange (IX) is an efficient technology to remove dissolved inorganic ionic contaminants from drinking water, including arsenic, selenium, chromium, nitrate, perchlorate, and uranium. Although ion-exchange is highly efficient in removing inorganic contaminants, similar to other water treatment technologies, ion-exchange has some drawbacks that need to be studied further. To be economically feasible, spent IX resin beds must be regenerated, generally, using sodium chloride. Regeneration generates waste brines and their disposal is a major challenge to the water industry. These waste brines are generally deemed hazardous because they contain high concentrations of the contaminants being removed (e.g., arsenic, chromium, or uranium), high alkalinity, and high ionic strength. In this research, treatment of waste IX brines containing arsenic and chromium, with ferric chloride and calcium polysulfide, respectively, was investigated.

Another deficiency of ion-exchange that needs further consideration is the impact of co-occurring contaminants on the process when specialty resins are used. Although specialty resins for nitrate and perchlorate removal have been designed and tested to remove ions of interest (i.e., perchlorate and nitrate), their performance in removing co-contaminants has not been evaluated. Waters contaminated with nitrate and perchlorate may contain other anion such as arsenic, uranium, chromium, and selenium at levels below or above their MCL. Because specialty resins are designed to minimize the effect of sulfate, they have very high capacity for the ion of interest. Consequently, they operate for a long time before regeneration or disposal is needed. Accordingly, even co-contaminants that are present at very small amounts in the influent water will accumulate at higher levels in the resin or in the regeneration waste brine. The performances of perchlorate and nitrate specialty resins in removing nitrate, arsenic, selenium, and chromium were investigated in this research. A summary of the major findings of this research, implications of the findings to the removal of inorganic contaminants from drinking water, and recommendations for further research are presented below.

7.2. Removal of Arsenic from Ion-Exchange Waste Brines with Ferric Chloride

In this research, coagulation batch precipitation tests were performed to investigate the effects of pH, ionic strength, ferric chloride dosage, initial As(V) concentration, and alkalinity on As(V) removal from brines using ferric chloride. A surface complexation modeling based on the chemical equilibrium using MINEQL+ was also performed to evaluate potential removals of arsenic (V) with ferric chloride and to support the experimental data. The following conclusions can be drawn regarding the removal of arsenic from IX brines using ferric chloride:

1. Similar to that reported for arsenic removal from drinking waters, As(V) removal from IX brines is a pH dependent process. The optimum pH range (maximum removal) of the adsorption process was found to be 4.5 to 6.5. However, the process was also found to be efficient at higher pH (< 8.5) values when higher dosages of ferric chloride were applied. Because IX brines typically have pH values between 8 and 10, lowering the pH is needed for effective arsenic removal. pH reduction can be accomplished by either adding acid or higher dosages of ferric chloride. Addition of

higher $FeCl_3$ dosages results in the generation of larger quantity of sludge. Acid addition involves higher operating costs because acids are relatively more expensive than $FeCl_3$. An economic evaluation is needed to evaluate the best alternative for specific brine characteristics.

2. The surface complexation model used to model adsorption of As (V) onto HFO was in good agreement with the results of the experimental results from batch coagulation tests. Therefore, the modeling can be used to assist the water industry in determined $FeCl_3$ dosages and pH values needed to achieve desired arsenic removals from ion-exchange brines.
3. The removal efficiency of As (V) by ferric chloride coagulation slightly increased when ionic strength of the brine was increased from 0.1 M to 0.8 M or 1.5 M, respectively. No significant improvement in removal efficiency was observed for ionic-strength increase above 0.8 M.
4. Increasing alkalinity from 5 to 10 g/L as $CaCO_3$ slightly decreased the removal efficiency of As (V) with ferric chloride coagulation. The reason for the decrease is the higher pH induced by the higher alkalinity.
5. In IX brines, to achieve a remaining As (V) concentration that meets the TCLP limit, the Fe/As molar ratios increase slightly (e.g., 0.9 to 1.3) with a significant increase (e.g., 12 mg/L to 119 mg/L) in initial As (V) concentration. The reason is that the amount of solids generated, for higher initial As(V) concentrations typically found in IX brines, stabilizes for Fe/As molar ratios > 2.4.
6. However, if IX brines were to be treated to achieve the MCL for drinking waters, lower Fe/As molar ratios would be required for higher arsenic levels. This is the case

because smaller amounts of solids are formed for lower initial arsenic concentration, and, therefore, more $FeCl_3$ is needed to achieve a desired final As (V) concentration.

7. The amount of sludge solids generated in the coagulation process was found to increase with initial arsenic concentration and with Fe/As molar ratios. However, the amount of sludge produce reaches a stable value for higher Fe/As molar ratios. For brines with initial As (V) concentration of 42.2, and 97.9 mg/L, the solids concentration stabilizes after Fe/As ratios of 2.5 and 4.2, respectively. Solid concentrations varying from 2 to 18 mg/L were found.
8. This research has demonstrated that the higher ionic strength found in IX brines have only a slight effect on the coagulation process. It also demonstrated that the higher alkalinity of the brines affect coagulation because larger amounts of acid are needed to lower the pH to levels that are conducive to adsorption. This research also revealed that the ferric chloride dosages needed to remove arsenic to TCLP limits is not directly proportional to the higher As (V) concentrations found in brines. For arsenic concentrations typical of ion-exchange brines, Fe/As ratios of about 1.2 to 4 are sufficient to achieve remaining As concentrations that meets or exceeds the required TCLP limit.

The additional work described below could be performed to provide broader insight on the removal of arsenic from brine:

1. Investigating the possibile formation of $FeAsO_4$ precipitates in high ionic strength brines containing high As(V) concentrations and high ferric chloride dosages.

2. Using response surface methodology to investigate the most influential parameters in the arsenic (V) removal process using ferric chloride.
3. Assessing the relationship between the Fe/As molar ratio and results of the TCLP and California WET tests for the waste sludge generated.
4. Investigate the possibility of recycling the brine, once the solids are separated from the liquid.

7.3. Removal of Chromium from Ion-Exchange Waste Brines with Calcium Polysulfide

Calcium polysulfide has been used to reduce and remove Cr(VI) from drinking water, other water and wastewater. However, calcium polysulfide has never been used to treat ion-exchange brines containing chromium. In this research, a Central Composite Design (CCD), which is a widely used type of response surface methodology, was used to evaluate the effects of the three major parameters on the chromium removal efficiency. The goal of this design was to provide a quadratic equation that predicts the chromium removal efficiency based on the major parameters. The following conclusions and implications can be drawn from the results obtained in this research:

1. Cr(VI) reduction to Cr (III) was found to be 100% to 93.5 % for pH value of 1.6 to 10.3, respectively. However, the optimum pH range for maximum chromium removal (combined reduction/precipitation) was found to be 8 to 10.3. IX brines typically have pH values between 8 and 10. Because both Cr(VI) reduction and Cr(III) precipitation with calcium polysulfide can also be achieved at the pH range of IX brines, this technology does not require pH adjustment. That constitutes a significant advantage in terms of cost and straightforward operation.

2. The CCD model used to model chromium removal is a fairly simple but useful tool to predict the process. Therefore, the modeling can be used to assist the water industry in determining CaS_5 dosages needed to achieve desired chromium removals from ion-exchange brines.
3. The removal efficiency of chromium by CaS_5 coagulation slightly increased when ionic strength of the brine was increased from 0.1 M to 0.8 M, 1.5 M or 2.1 M. No significant improvement in removal efficiency was observed for ionic strength increase above 1.5 M. Therefore, the high ionic strength of brines does not influence the process.
4. Increasing alkalinity from 0.01 to 5 g/L as $CaCO_3$ had no effect on the removal efficiency of chromium from IX brines. Even brines with low alkalinity which would have pH values slightly below the neutral range can effectively be treated by calcium polysulfide. The reason is Cr(VI) reduction is 100% effective at pH below 6.5, and the addition of calcium polysulfide, which is a basic solution with pH above 11, promotes an increase in pH. This pH increase is sufficient to promote effective precipitation of Cr(III).
5. To achieve the TCLP limit of 5 mg/L chromium in the treated IX brines, the CaS_5/Cr(VI) molar ratios needed increases slightly (i.e., 0.6 to 1.4) with a significant increase (e.g., 9 mg/L to 93.2 mg/L) in initial Cr(VI) concentration. If IX brines were to be treated to achieve the MCL of 0.1 mg/L for drinking waters, higher CaS_5/Cr(VI) molar ratios (i.e., 3.7 to 1.7) would be required for brines containing 9 to 93.3 mg/L of higher chromium levels, respectively. The higher the initial Cr(VI) concentration, the lower is the CaS_5/Cr(VI) molar ratio.

The CaS_5/Cr(VI) molar ratio (3.7) needed to remove 9 mg/L Cr(VI) is 2.2 times higher than the ratio (1.7) required to remove 93.2 Cr(VI).

6. The oxidation/reduction potential of brines was strongly correlated with total chromium removal. The IX brines had positive E_h values (+0.35 to +0.55 V), indicating oxidizing conditions. When the E_h values (ORP) were lowered to between -0.1 and 0 volts, the brines were under reducing conditions, and maximum total chromium removal occurred. Addition of CaS_5 at CaS_5/Cr(VI) ratio of above 4 decreased the ORP to the lowest value of -0.32 V, while causing a slight decrease in total chromium removal. It is thought that this decrease in removal is due to a decrease in the reduction efficiency. Therefore, addition of excessive dosages of CaS_5 is not recommended, because it generates more sludge and lowers the reduction efficiency.
7. The amount of sludge solids generated in the coagulation process was directly proportional to the amount of CaS_5 added. Solid concentrations varying from 0.2 to 1.5 g/L were found for experiments at which maximum total chromium removal was achieved.

This research could be followed with additional work that would contribute to further understanding of the removal of chromium using calcium polysulfide:

1. Developing a chemical equilibrium model to predict chromium removal with calcium polysulfide.
2. Assessing the relationship between the CaS_5/Cr(VI) molar ratio and results of the TCLP and California WET tests for solids generated, and investigating alternatives for recycle/reuse of the generated sludge.

7.4. Impact of Inorganic Anionic Co-Contaminants on Performances of Perchlorate and Nitrate Specialty Ion-Exchange Resins

Several waters contaminated with perchlorate also contain varying levels of nitrate. Some perchlorate or nitrate-contaminated waters may also contain lower levels of As(V), Se(VI), Cr(VI), and/or uranium. The presence of co-contaminants is a challenge for ion-exchange plant design because the optimal conditions for their removal may differ. Furthermore, co-contaminants can accumulate in resins and waste brines hindering brine disposal and resin reuse. Therefore, it is of value to investigate how perchlorate and nitrate specialty resins perform in the removal of other inorganic contaminants. In this research, performances of perchlorate and nitrate specialty resins in removing nitrate, As(V), Se(VI), and Cr(VI) are investigated and compared with a conventional resin. Several laboratory column experiments were performed for removing nitrate, As(V), Se(VI), or Cr(VI) from drinking water using perchlorate and nitrate specialty and conventional resins. Subsequently, the spent resins were regenerated using a NaCl brine solution. The following conclusions and implications can be drawn from the experimental data:

One issue addressed in this research was whether perchlorate selective resins could be used for nitrate removal. It was found that nitrate can be removed from waters using perchlorate specialty resins. Perchlorate specialty resins can support 1.7 to 3.2 times more BVs processed before breakthrough than nitrate specialty resins. Despite their higher capacity for nitrate, perchlorate specialty resins do not regenerate well. They require more brine to achieve the same regeneration efficiency of a nitrate specialty resin. The low regeneration efficiency of perchlorate specialty resins, when used for nitrate removal, results in higher salt cost and higher brine disposal cost as compared to nitrate specialty resins. Operating costs for SIR 100, a nitrate specialty resin, are 2.3 times less than those for the perchlorate specialty resins SIR 110 and PWA2. The operating cost for SIR 111, a macroporous perchlorate specialty resin, is about 1.3 times more than that of the nitrate specialty resin, SIR 100. Therefore, using perchlorate specialty resins solely for the purpose of nitrate removal is not recommended. However, this research also found that generation of a macroporous perchlorate specialty resins (SIR 111), loaded with nitrate, was very effective. This resin was specially made for this research and it is not available commercially at large amounts. However, this type of resin may find applications in waters contaminated with both nitrate and perchlorate.

A second issue investigated was whether perchlorate accumulated in nitrate selective resin could be desorbed during the regeneration cycle. Significant amounts of perchlorate were not found in the regeneration brines of nitrate and perchlorate specialty resins. This confirms that perchlorate is not easily removed from either nitrate or perchlorate specialty resins. Therefore, in nitrate removal systems, where perchlorate occurs as a co-contaminant, part of the capacity of the resin will be lost with time because of perchlorate accumulation. Such accumulation may result in earlier replacement of resin beds, which constitute a major cost.

A third issue evaluated was the concurrent removal of perchlorate and nitrate in waters where both contaminants occur at levels higher than the permissible level. When this occurs, nitrate breaks through first as compared to perchlorate, because nitrate in waters occurs at the mg/L level while perchlorate contamination is generally at the ppb level. If one ion-exchange system is used to remove both, the resin will be regenerated for nitrate and perchlorate accumulates. Once the capacity for perchlorate is exhausted then resin of the entire system must be disposed off. This occurs because perchlorate-selective resins generate very poorly. An option is to use two ion-exchange systems in series. In this case, perchlorate will always be removed in the first system because both nitrate and perchlorate selective resins exchange perchlorate. The second system can then be used, and generated, for nitrate removal. That system will not accumulate perchlorate, because it has been removed in the first system. Perchlorate usually occurs at very low concentrations in water (at μg/L level), and, therefore, it captures very small part of the resin capacity (about 1%-3%). Considering resin field lives of 8-12 years, the impact on resin capacity from very low perchlorate concentrations, when treating nitrate-contaminated waters, is very small.

A fourth issue addressed was con-current removal of nitrate and Cr(VI), Se(VI), or As(V). It was found that simultaneous removal of nitrate and Cr(VI) is optimal when using nitrate specialty resin. Chromium occurs naturally in groundwaters in the range of 0.0005-0.21 mg/L in the United States (U.S. EPA, 2002; Guertin *et al.*, 2004). The results of this research showed that 1176 to 2015 BVs of water that contain 0.2 mg/L of Cr(VI) can be treated by IX resins. Typically, 327 to 750 BVs of water can be treated when removing nitrate from water (Table 4.8). Therefore, when treating waters that contain high concentrations of nitrate and Cr(VI), nitrate breaks through sooner than Cr(VI) without regard the type of the resin. From the cost analysis and the results of IX column experiments, it can be concluded that for removing nitrate and Cr(VI) from water, nitrate specialty resins are less costly and more efficient than conventional resins.

However, a major concern of the presence of chromium as a co-contaminant is its impact on brine disposal. Depending on the concentration of Cr(VI) in the influent water and the number of BVs run to breakthrough, the waste regenerant brine could contain concentrations high enough to deem the waste hazardous. Waste brines that contain nitrate only are not considered hazardous and are easy to dispose off because nitrate is highly biodegradable. However, if chromium is present at concentrations above the TCLP limit, the waste will be hazardous.

In view of the fact that Se(VI) and As(V) are poorly removed with nitrate specialty resins, a conventional resin is more efficient and economical for concurrent removal of nitrate and Se(VI) or As(V).

Cr(VI), A(V), or Se(VI)-laden nitrate resins were regenerable using a NaCl solution, and their regeneration processes were more efficient than those for the conventional resins. The order of the capacity of ion-exchange resins for Cr(VI), Se(VI), and As(V) is Cr(VI) > Se(VI) > As(V). Similar to Cr(VI) removal, Depending on the concentration of As(V) or Se(VI) in the influent water and the number of BVs run to breakthrough, the waste regenerant brine could contain concentrations high enough to deem the waste hazardous.

The last issue was concurrent removal of perchlorate and Cr(VI), Se(VI), or As(V). In this research, it was found that Cr(VI), A(V), or Se(VI)-laden perchlorate specialty resins are regenerable using a NaCl solution. Nonetheless, Cr(VI), A(V), or Se(VI)-laden perchlorate or nitrate resins were easier to regenerate than spent conventional resins. However, perchlorate specialty resins showed very low run length for these divalent contaminants. Therefore, if Cr(VI), Se(VI), or As(V) occur as a co-contaminant for perchlorate, the logical option is using two separate columns for the removal. The first IX column can remove perchlorate using a perchlorate specialty resin from water while Cr(VI), As(V) or Se(VI) breaks through the first column instantly. The first column containing perchlorate specialty resin has a very long run length, and it should be replaced after perchlorate breaks through. The second column must operate to remove As(V) or Se(VI). This column has shorter run lengths and must regenerate frequently, and a conventional resin or arsenic/selenium specialty resin could be used for this purpose.

Additional work may follow the work presented herein. The following are recommendations for future research:

1. Evaluating uranium removal using perchlorate and nitrate specialty resins.
2. Compare laboratory breakthrough curves with curves generated by ion-echange modeling software.
3. Investigating the effects of sulfate on the performances of perchlorate and nitrate specialty resins when co-contaminants (i.e., As(V), Cr(VI), or Se(VI)) are also present in the influent.

7.5. Contributions of This Research to the Ion-Exchange Field

Due to population growth and water scarcity throughout the world, it is anticipated that the application of ion-exchange specialty resins in removing inorganic contaminants from water will increase. Many waters contaminated with perchlorate and nitrate also contain other inorganic contaminants, and their effect on performances of specialty resins have not been studied to date. In this research, the impact of As(V), Cr(VI), and Se(VI) on the performances of perchlorate and nitrate specialty resins was investigated. In addition, simultaneous removal of nitrate and perchlorate using specialty resins was examined. The results of this research provide insight into how plant designers should sequence IX units when specialty resins are used in the presence of co-contaminants. Furthermore, the research results provide guidance on the potential for hazardous waste brine generation when specialty resins are used. Therefore, this research has direct value to real world applications of IX technology to treat waters contaminated with inorganic contaminants. The water industry can use the results of this research to design IX systems and forecast the quality of the brine.

Ion-exchange (IX) has been pointed out as one of the best available technologies to remove As(V) or Cr(VI) from water due to its excellent efficiency and flexible application to small size treatment plants. However, treatment and disposal of the brines generated is a challenge to the water industry. In this research, optimal parameters for As(V) removal with ferric chloride and Cr(VI) removal with calcium polysulfide from IX brines were determined. The IX industry can utilize the results presented herein to design the brine treatment units, which are the vital part of the IX process. Not only does treatment of brines reduce the operating cost, but it also prevents the contamination of environment with these highly toxic elements (i.e., arsenic and chromium).

APPENDIX 1

URANIUM REMOVAL WITH ION-EXCHANGE: URANYL-CARBONATE SPECIES

Uranium is a radioactive element, which occurs naturally in surface water and groundwater, posing a direct threat to water supplies. Uranium exists in nature primarily as uranium 238 (99.27%) with trace amounts of 0.72 % uranium 235 and 0.0055% uranium 234. Uranium decays slowly over time by emitting an alpha particle; however, the half life of uranium 238 is 4.5 billion years, so it will continue to be a source of water contamination for eons. Ingestion of uranium causes health effects such as bone cancer and kidney dysfunction. If inhaled, uranium penetrates the lung's alveolar region, then to the blood stream (EVS, 2005; U.S. EPA, 2008ur; Giammar, 2001). The U.S. EPA established a national MCL for uranium in drinking water of 0.030 mg/L in 2000 (U.S. EPA, 2008ur). California water supplies have to comply with a more stringent state MCL of 0.025 mg/L for uranium in drinking water (Giammar, 2001). The U.S. nuclear industry has caused uranium contamination of soil and/or groundwater. Several uranium contaminated sites in the United States have been identified, including Hanford, WA, Idaho Falls, ID, Yucca Mountain, NV, San Joaquin Valley, CA, Rocky Flats, CO, Fernald, OH and Savannah River, SC (Giammar, 2001). Uranium concentrations up-to 20 μg/L have been found in groundwater in New Mexico. Uranium has been detected at 978 sites in the U.S., at an average concentration of 2.55 μg/L. Furthermore, a uranium concentration of 700 μg/L has been detected in a small water supply in Canada (WHO, 2004). Uranium occurs at its +6 oxidation state in water. In acidic solutions (pH < 5), uranium presents as a cation (UO_2^{2+}), and therefore it can be removed by strong acid cation-exchange resins. In addition, lime softening, reverse osmosis, and precipitation with $BaSO_4$ (by adding $BaCl_2$) are reported to be effective in removing UO_2^{2+} at pH values less than 5 (Clifford, 2001; Clifford and Zhang, 1994). For pH values between 5 and 6.5, U(VI) exists in the neutral form of UO_2CO_3; thus, it cannot be removed at this pH, and pH should be adjusted to a lower or a higher value depending on the available removal technology. For pH values between 6.5 and 7.6, U(VI) exists as an anion $UO_2(CO_3)_2^{2-}$, and at higher pH values, $UO_2(CO_3)_3^{4-}$ is the predominant form of the U(VI). For pH > 6.5, U(VI) can be removed by anion-exchange, reverse osmosis, and activated alumina adsorption. Strong base anion-exchange resins can be utilized for the removal of U(VI) from water at alkaline pH values (pH > 6.5) (Clifford, 2001; Zhang and Clifford, 1994).

Uranium is the heaviest radioactive element that naturally occurs in the environment. Uranium oxidation states are: III, IV, V, and VI. U(III) transforms to U(IV), and U(V) reduces and oxidizes disproportionately to U(IV) and U(VI), which are stable forms of uranium (Clifford and Zhang, 1995). U(VI) readily combines with oxygen and forms an uranyl ion (UO_2^{2+}), which is the most stable form of U(VI) in the acidic (pH < 5) aqueous solutions. The uranyl ion combines (without losing oxygen, except when combining with F^-) with anions available in water (i.e., CO_3^{2-}, F^-, Cl^-, NO_3^-, SO_4^{2-}, and HPO_4^{2-}) and forms various complexes (Clifford and Zhang, 1995). Among the anions available in water, carbonate and bicarbonate are significant anions that combine with uranyl to form various uranyl carbonate complexes (charged, uncharged, or neutral).

The distribution of various uranyl–carbonate species are presented in Figure A1-1. Uranium exists as an uranyl ion (UO_2^{2+}) at acidic pH (pH < 5.0). Uranyl starts to combine with carbonate at around pH 4, and $UO_2CO_3^0$ becomes the predominant species of U(VI) at pH 5-6.5. When pH increases, more carbonate ions combine with uranyl carbonate. At neutral pH 6.5-7.5, $UO_2(CO_3)_2^{2-}$ is the major species of U(VI); and at an alkaline solution (pH > 8), $UO_2(CO_3)_3^{4-}$ become the predominant species. Uranyl hydroxyl complexes (UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$), and $(UO_2)_3(OH)_5^+$) are also formed in smaller percentages in comparison with carbonate complexes.

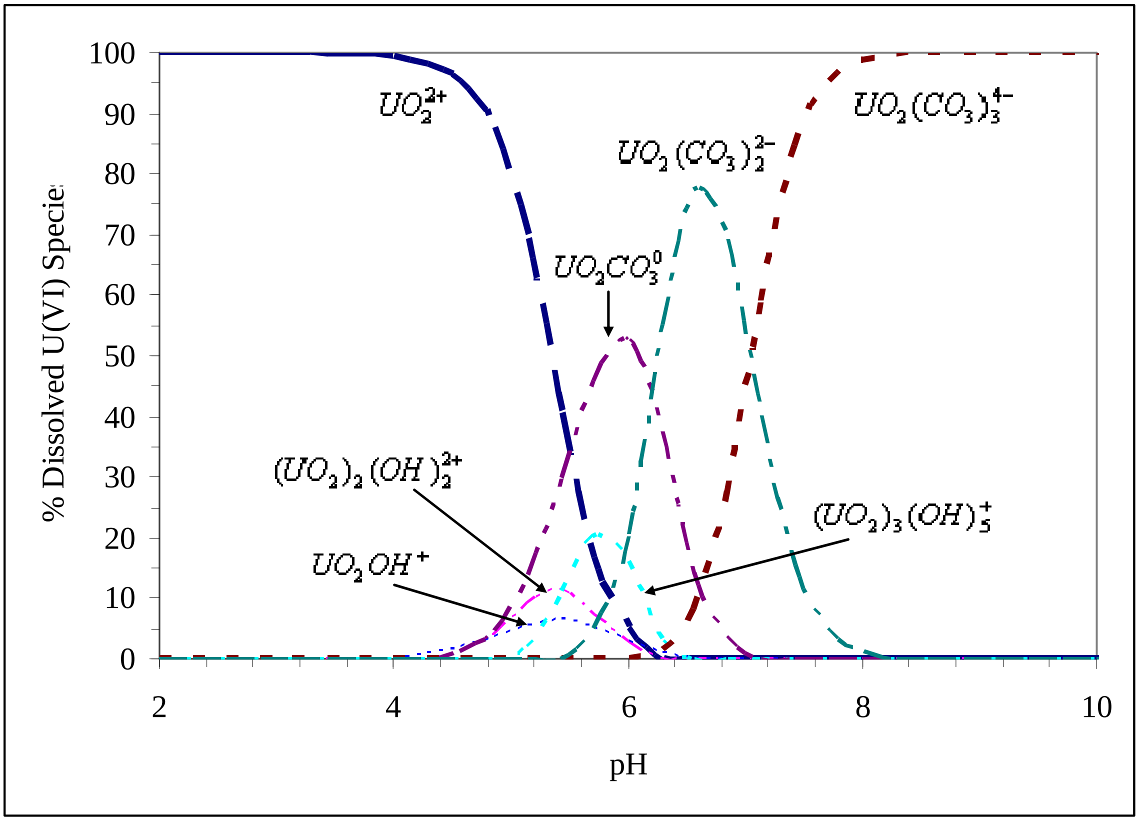


Figure A1-1 Computed Liquid-Phase Distribution of Ionic Species for U(VI) System, $UO_2^{2+} = 5 \times 10^{-6}$ M, I = 0.1 M (MINEQL+ Was Utilized for the Computation, Schecher and Mcavoy, 2001)

The reactions (with related stability constants), which result in the formation of various complexes are presented below (Clifford and Zhang, 1995).

$$\mathrm{UO_2OH^+ + OH^- \leftrightarrow UO_2(OH)_2} \qquad K = 10^{12} \tag{A1-1}$$

$$\mathrm{UO_2^{2+} + OH^- \leftrightarrow UO_2OH^+} \qquad K = 10^{9.8} \tag{A1-2}$$

$$\mathrm{UO_2^{2+} + 2CO_3^{2-} \leftrightarrow UO_2(CO_3)_2^{2-}} \qquad K = 1.67 \times 10^{16} \tag{A1-3}$$

$$\mathrm{UO_2(CO_3)_2^{2-} + CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{4-}} \qquad K = 3.01 \times 10^{5} \tag{A1-4}$$

$$\mathrm{UO_2^{2+} + 3CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{4-}} \qquad K = 5.03 \times 10^{21} \tag{A1-5}$$

$$\mathrm{UO_2^{2+} + Cl^- \leftrightarrow UO_2Cl^+} \qquad K = 10^{0.39} \tag{A1-6}$$

$$\mathrm{UO_2^{2+} + SO_4^{2-} \leftrightarrow UO_2SO_4} \qquad K = 10^{1.7} \tag{A1-7}$$

$$\mathrm{UO_2^{2+} + 2SO_4^{2-} \leftrightarrow UO_2(SO_4)_2^{2-}} \qquad K = 10^{2.55} \tag{A1-8}$$

$$\mathrm{UO_2^{2+} + 3SO_4^{2-} \leftrightarrow UO_2(SO_4)_3^{4-}} \qquad K = 10^{3.4} \tag{A1-9}$$

Although uranyl ions form various complexes with chloride and sulfate, uranyl tricarbonate is the most stable and abundant uranium containing complex in water, with a high stability constant. The tricarbonate complex forms in two steps, which are presented in equations A1-3 and A1-4. Equation A1-3 is a rate limiting step, while equation A1-4 is believed to occur very fast (Clifford and Zhang, 1995). The high stability constant of 5.03×10^{21} and the availability of carbonate in most waters are the reasons for the abundance of uranyl tricarbonate in the aqueous solutions. The uniform distribution of uranium in seawater and oceans is believed to be due to the formation of uranyl tricarbonate (Clifford and Zhang, 1995; Langmuir, 1988; Rogers and Adams, 1970).

A pe-pH (Pourbaix) diagram for uranium in a carbonate system clearly shows that the predominant species of uranium at oxidizing conditions and pH greater than 4.5 are uranyl-carbonates. At pH < 4.5 and oxidizing conditions, uranyl ion is the predominant species of uranium.

Anionic and cationic forms of U(VI) can be removed by utilizing anion or cation-exchange resins. It has been reported that cation-exchange resins started to remove the cationic form of uranium at pH 5.6, and the removal efficiency increased when pH was decreased. Cation resin in H^+ form showed its maximum efficiency (93-97%) at pH equal to 3.5 (Clifford and Zhang, 1995). The uranium removal using cation-exchange resins is strongly pH dependent, and is not as efficient as uranium removal utilizing anion-exchange resins. The anion-exchange resins have high capacity and selectivity for anionic uranyl carbonate complexes-- $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Clifford and Zhang, 1995).

The strong base anion (SBA) exchange resins are commonly used to remove the anionic forms of uranium. Where R is an anion-exchange site on the resin, the exchange reactions between the resin and uranyl-carbonate complexes can be expressed as (Clifford and Zhang, 1995):

$$2\text{-R-Cl} + UO_2(CO_3)_2^{2-} \leftrightarrow R_2UO_2(CO_3)_2 + 2Cl^- \qquad \text{(A1-10)}$$

$$4\text{-R-Cl} + UO_2(CO_3)_3^{4-} \leftrightarrow R_4UO_2(CO_3)_3 + 4Cl^- \qquad \text{(A1-11)}$$

The exhausted resin is regenerated using a conventional NaCl solution. The selectivity coefficients of the resin for the $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ are calculated from the following equations, in which $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ are named K_{UC2} and K_{UC3}, respectively:

$$K_{UC2} = \frac{q_{UC2}C_{Cl}^2}{C_{UC2}q_{Cl}^2} \qquad \text{(A1-12)}$$

$$K_{UC3} = \frac{q_{UC3} C_{Cl}^4}{C_{UC3} q_{Cl}^4} \tag{A1-13}$$

where q and C are resin and aqueous-phase concentrations of UC2, UC3, or Cl$^-$, respectively. The separation factor, which is the distribution of UC2 or UC3 between phases divided by the distribution of Cl$^-$ between phases, can be calculated as:

$$\alpha_{Cl}^{U} = K_{Cl}^{U} (\frac{q_{Cl}}{C_{Cl}})^{|Z|-1} \tag{A1-14}$$

where z is the charge on the ion (MWH, 2005).

Selectivity Coefficients of Uranyl-Carbonate Species

The separation factors for UC2 and UC3 can be calculated as follows:

$$\alpha_{Cl}^{UC2} = K_{Cl}^{UC2} (\frac{q_{Cl}}{C_{Cl}}) \tag{A1-15}$$

$$\alpha_{Cl}^{UC3} = K_{Cl}^{UC3} (\frac{q_{Cl}}{C_{Cl}})^3 \tag{A1-16}$$

Similarly, the separation factor for a sulfate ion can be calculated:

$$\alpha_{Cl}^{SO_4} = K_{Cl}^{SO_4} (\frac{q_{Cl}}{C_{Cl}}) \tag{A1-17}$$

The separation factors for sulfate and uranium are reported to be 9.1 and 3200, respectively, in 0.005-0.010 N solutions (Clifford, 1999). The selectivity coefficient of sulfate was reported as 0.15. Therefore, the distribution of chloride ion between phases for a binary sulfate-chloride system in a 0.005-0.010 N can be calculated as:

$$9.1 = 0.15(\frac{q_{Cl}}{C_{Cl}})^{|2|-1} \rightarrow (\frac{q_{Cl}}{C_{Cl}}) = 60.67 \tag{A1-18}$$

The q_{Cl}/C_{Cl} is known; therefore, the selectivity coefficient for uranyl dicarbonate and tricarbonate can be calculated in a similar system:

$$3200 = K_{Cl}^{UC2}(60.67) \quad \rightarrow \quad K_{Cl}^{UC2} = 52.7 \tag{A1-19}$$

$$3200 = K_{Cl}^{UC3}(60.67)^{|4|-1} \quad \rightarrow \quad K_{Cl}^{UC3} = 0.0143 \tag{A1-20}$$

APPENDIX 2

IX-PRO ION-EXCHANGE MODELING SOFTWARE

Anion and cation removal from water can be modeled using IX-PRO, which was created by Dr. Gerald A. Guter in 1996. This software was copyrighted by Cathedral Peak Software in 1999. This program utilizes both equilibrium and kinetic relationships of the ion-exchange process. IX-PRO follows a practical approach by breaking the process down into several equilibrium steps at which it computes the effluent's water quality for certain bed volumes of water that were passed through the column.

Equilibrium Equation Used in IX-PRO

The equilibrium expression for an ion-exchange process can be obtained by applying mass laws. A generalized form of the stochiometric ion-exchange reaction is (MWH, 2005):

$$n[\overline{R^{\pm}}]A^{\pm} + B^{n\pm} \leftrightarrow [n\overline{R^{\pm}}]B^{n\pm} + nA^{\pm} \qquad \text{(A2-1)}$$

Where:

- $\overline{R^{\pm}}$ is the ionic group inside the ion-exchange resin
- A and B are exchanging ions
- n is the valence of the exchanging ion.

According to stoichiometry, all binary exchange processes can be represented as:

$$K_B^A = \frac{[A^{\pm}]^n\{\overline{R^{\pm}}B^{n\pm}\}}{\{\overline{R^{\pm}A^{\pm}}\}^n[B^{n\pm}]} \qquad \text{(A2-2)}$$

Where:

- K_B^A = selectivity coefficient for either cation or anion A exchanging with ion B onto the resin
- $[A^{\pm}]$ = aqueous-phase concentration of presaturant ion, eq/L
- $[B^{\pm}]$ = aqueous-phase concentration of counterion, eq/L
- $\{\overline{R^{\pm}A^{\pm}}\},\{\overline{R^{\pm}B^{n\pm}}\} =$ activities of resin-phase presaturant ion and counter-ion, respectively.

If the resin-phase is defined in terms of concentration, then the equilibrium stoichiometric equation can be expressed as

$$K_j^i = \frac{C_j^n q_i}{q_j^n C_i} \qquad \text{(A2-3)}$$

Where:

- C_j = aqueous-phase concentration of presaturant ion, eq/L
- q_i = resin-phase concentration of counter-ion, eq/L
- q_j = resin-phase concentration of presaturant ion, eq/L
- C_i = aqueous-phase concentration of counter-ion, eq/L (MWH, 2005).

The separation factor is also a measure of the resin preference for one ion over another ion in the ion-exchange process, and is calculated by applying the following equation:

$$\alpha_j^i = K_j^i \left(\frac{q_j}{C_j}\right)^{|\pm Z|-1} \qquad \text{(A2-4)}$$

The separation factors can be converted among various ions using the following equation:

$$\alpha_k^i = \alpha_j^i \times \alpha_k^j \qquad \text{(A2-5)}$$

The software is able to receive concentrations of up to five ions (three monovalent ions and two divalent ions) simultaneously as the influent water quality. The selectivity coefficients have to be entered to IX-PRO by the user. For a multivariable system with three monovalent ions and two divalent ions, the total concentrations of total resin-phase and aqueous-phase ions are:

$$q_T = q_{m1} + q_{m2} + q_{m3} + q_{d1} + q_{d2} \qquad \text{(A2-6)}$$

$$C_T = C_{m1} + C_{m2} + C_{m3} + C_{d1} + C_{d2} \qquad \text{(A2-7)}$$

The concentrations of various ions (C_{m1},C_{m2}, C_{m3}, C_{d1}, and C_{d2}) and the total resin concentration (q_T) are known and have to be provided to the program by the user. The goal is to calculate resin-phase concentrations of each ion at the equilibrium. The resin-phase ion concentrations can be calculated by applying the following equations:

$$q_{m1} = \frac{q_T C_{m1}}{\alpha_{m1}^{m1} \times C_{m1} + \alpha_{m2}^{m1} \times C_{m2} + \alpha_{m3}^{m1} \times C_{m3} + \alpha_{d1}^{m1} \times C_{d1} + \alpha_{d2}^{m1} \times C_{d2}} \qquad \text{(A2-8)}$$

$$q_{m2} = \frac{q_T C_{m2}}{\alpha_{m1}^{m2} \times C_{m1} + \alpha_{m2}^{m2} \times C_{m2} + \alpha_{m3}^{m2} \times C_{m3} + \alpha_{d1}^{m2} \times C_{d1} + \alpha_{d2}^{m2} \times C_{d2}} \qquad \text{(A2-9)}$$

$$q_{m3} = \frac{q_T C_{m3}}{\alpha_{m1}^{m3} \times C_{m1} + \alpha_{m2}^{m3} \times C_{m2} + \alpha_{m3}^{m3} \times C_{m3} + \alpha_{d1}^{m3} \times C_{d1} + \alpha_{d2}^{m3} \times C_{d2}} \qquad \text{(A2-10)}$$

$$q_{d1} = \frac{q_T C_{d1}}{\alpha_{m1}^{d1} \times C_{m1} + \alpha_{m2}^{d1} \times C_{m2} + \alpha_{m3}^{d1} \times C_{m3} + \alpha_{d1}^{d1} \times C_{d1} + \alpha_{d2}^{d1} \times C_{d2}} \qquad \text{(A2-11)}$$

$$q_{d2} = \frac{q_T C_{d2}}{\alpha_{m1}^{d2} \times C_{m1} + \alpha_{m2}^{d2} \times C_{m2} + \alpha_{m3}^{d2} \times C_{m3} + \alpha_{d1}^{d2} \times C_{d1} + \alpha_{d2}^{d2} \times C_{d2}} \qquad \text{(A2-12)}$$

IX-PRO finds the resin-phase concentration of ions using numerical iterations at various bed volumes of water passed through the column. The separation factors can be calculated using the known selectivity coefficients: K_{m1}^{m1}, K_{m2}^{m1}, K_{m3}^{m1}, K_{d1}^{m1}, and K_{d2}^{m1}.

$$\alpha_{m1}^{m1} = 1,\ \alpha_{m2}^{m1} = K_{m2}^{m1},\ \alpha_{m3}^{m1} = K_{m3}^{m1},\ \alpha_{md1}^{m1} = K_{d1}^{m1}(\frac{q_{d1}}{C_{d1}}), \text{ and } \alpha_{md2}^{m1} = K_{d2}^{m1}(\frac{q_{d2}}{C_{d2}}) \qquad \text{(A2-13)}$$

$$\alpha_{m1}^{m2} = \frac{1}{\alpha_{m2}^{m1}},\ \alpha_{m2}^{m2} = 1,\ \alpha_{m3}^{m2} = \alpha_{m1}^{m2} \times \alpha_{m3}^{m1},\ \alpha_{d1}^{m2} = \alpha_{m1}^{m2} \times \alpha_{d1}^{m1}, \text{ and } \alpha_{d2}^{m2} = \alpha_{m1}^{m2} \times \alpha_{d2}^{m1} \ \text{(A2-14)}$$

$$\alpha_{m1}^{m3} = \frac{1}{\alpha_{m3}^{m1}},\ \alpha_{m2}^{m3} = \alpha_{m1}^{m3} \times \alpha_{m2}^{m1},\ \alpha_{m3}^{m3} = 1,\ \alpha_{d1}^{m3} = \alpha_{m1}^{m3} \times \alpha_{d1}^{m1}, \text{ and } \alpha_{d2}^{m3} = \alpha_{m1}^{m3} \times \alpha_{d2}^{m1} \ \text{(A2-15)}$$

$$\alpha_{m1}^{d1} = \frac{1}{\alpha_{d1}^{m1}},\ \alpha_{m2}^{d1} = \alpha_{m1}^{d1} \times \alpha_{m2}^{m1},\ \alpha_{m3}^{d1} = \alpha_{m1}^{d1} \times \alpha_{m3}^{m1},\ \alpha_{d1}^{d1} = 1, \text{ and } \alpha_{d2}^{d1} = \alpha_{m1}^{d1} \times \alpha_{d1}^{m1} \qquad \text{(A2-16)}$$

$$\alpha_{m1}^{d2} = \frac{1}{\alpha_{d2}^{m1}},\ \alpha_{m2}^{d2} = \alpha_{m1}^{d2} \times \alpha_{m2}^{m1},\ \alpha_{m3}^{d2} = \alpha_{m1}^{d2} \times \alpha_{m3}^{m1},\ \alpha_{d1}^{d2} = \alpha_{m1}^{d2} \times \alpha_{d2}^{m1}, \text{ and } \alpha_{d2}^{d2} = 1 \ \text{(A2-17)}$$

Adolf Fick developed the fundamental equations describing the “phenomenon” of diffusion on the basis of intuition and experiments in 1885. Diffusion occurs in liquids, solids, and gases. For the liquids, having dissolved a contaminant in a solution, Fick stated that diffusion occurs to reduce the concentration gradient that produces a flux. The produced flux will become zero when the concentration gradient is removed, which means that the contaminant is evenly distributed throughout the solution (Wilkinson, 2000). Fick’s first law describes the relationship between the flux and the concentration gradient of a contaminant (or solute):

$$J = -D\frac{\partial C}{\partial y} \qquad \text{(A2-18)}$$

Fick’s first law is a one dimensional equation, and can be extended to three dimensions as follows:

$$J = -D\nabla C = -D\left(\frac{\partial C}{\partial x}, \frac{\partial C}{\partial y}, \frac{\partial C}{\partial z}\right) \qquad \text{(A2-19)} \quad \text{(Wilkinson, 2000)}$$

In these equations, J (mol/m^2) is the flux of the contaminant in the solution, and C (mol/m^3) is the concentration of the contaminant. The ∂ symbol is a partial derivative. Fick's first law has only one dimension, along the y axis, while the extended version has three dimensions (along the x, y, or z axes) (Wilkinson, 2000). D is the diffusion coefficient and is expressed as m^2/s.

Diffusion is believed to occur due to a random exchange of positions of neighbor atoms or molecules because of the random thermal fluctuations in a solution. Therefore, the kinetics of diffusion are temperature dependent and follow this equation:

$$\text{rate} \sim \exp(-Q/RT) \qquad \text{(A2-20)}$$

where Q (J/mol) is the activation energy, which is required for an atom or molecule to start moving from a stable position to another one; R is the gas constant (8.314 J/ mol.K) and T is the temperature in Kelvin.

Diffusion in liquids can be expressed as a function of the viscosity of a liquid (Wilkinson, 2000). Einstein proposed a relationship between the diffusivity and the viscosity for spherical molecules moving through a viscous liquid as follows:

$$D = \frac{k \times T}{4 \times \pi \times r \times \eta} \qquad \text{(A2-21)}$$

Where D is diffusivity; r, T, and k are the molecular radius, temperature, and rate of reaction, respectively. Viscosity is related to the temperature (T) and the free activation energy (ΔG_{vis}) required for the rearrangement of molecules in the liquid (Wilkinson, 2000).

$$\eta = \eta_0 \exp(+\frac{\Delta G_{vis}}{kT}) \qquad \text{(A2-22)}$$

η_0 is approximately equal to (N_0h/V), where N_0, h, and V is Avogadro's number, Planck's constant, and the molar volume, respectively.

Fick's first law is convenient to apply to the steady-state situations. However, applying Fick's first law to cases in which concentration depends on the time and the position is not convenient. Fick's second law is an alternative form of the first law, but it considers the effects of concentration and time for the transient diffusion problems. The generalized form of Fick's second law is:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C) \qquad \text{(A2-23)}$$

where ∇ is the del operator, and dot is the dot product of the del operator and the result of the parenthesis. In the case of ion-exchange, all the resins have a spherical shape and therefore the relationship can be simplified to equation A2-26.

In addition to the equilibrium equations, diffusion kinetic relationships are also considered and used for the calculation of effluent concentrations. There are two rate-limiting steps in the ion-exchange process: (a) particle diffusion, interdifussion of counter ions within the resin, and (b) film diffusion, interdiffusion of counter ions in the adherent film (Helfferich, 1995). To determine if the particle or film diffusion is a rate-determining step, the following criterion must be checked (Helfferich, 1995):

$$\frac{X\bar{D}\delta}{CDr_0}(5 + 2\alpha_j^i) << 1 \text{ particle diffusion control} \qquad \text{(A2-24)}$$

$$\frac{X\bar{D}\delta}{CDr_0}(5 + 2\alpha_j^i) >> 1 \text{ film diffusion control} \qquad \text{(A2-25)}$$

Where X = concentration of fixed ionic groups, eq/L

C = concentration of solution, eq/L

$\overline{D}$ = interdiffusion coefficient in the resin

D = interdiffusion coefficient in the film

r_0 = bead radius

δ = film thickness

The particle diffusion for a particle with spherical geometry and a constant diffusion coefficient for ions A can be expressed as:

$$\frac{\partial \overline{C}_A}{\partial t} = \overline{D}\left(\frac{\partial^2 \overline{C_A}}{\partial r^2} + \frac{2}{r}\frac{\partial \overline{C_A}}{\partial r}\right) \qquad \text{(Helfferich, 1995)} \quad \text{(A2-26).}$$

$\overline{C_A}$ = resin-phase concentration of ion A

t = time

$\overline{D}$ = interdiffusion coefficient in the resin

r = distance of ion from the resin bead center

This equation is solved to obtain concentration of ion A inside the resin at any time by IX-PRO based on the proper initial and boundary conditions. The film diffusion can be expressed as the combination of the two following equations:

$$J_A = D\frac{\Delta C_A}{\delta}\text{, and} \qquad \text{(A2-27)}$$

$$-\frac{dC'_A}{dt} = \frac{3C}{r_0\overline{C}}J_A \qquad \text{(A2-28)}$$

C_A = concentration of ion A outside the film

C'_A = concentration of ion A passed through the film

$\Delta C_A = C'_A - C_A$ = concentration difference between the two boundaries of the film

D = interdiffusion coefficient in the film

δ = film thickness

r_0 = resin bead radius

IX-PRO solves the abovementioned equations to control the film diffusion process in the system. The rate of ion-exchange is the slowest rate caused by particle or film diffusion. Both particle and film diffusions are employed in IX-PRO. Dr. G. A. Guter, the creator of the software, obtained the diffusion coefficients values for aqueous ions from published literature, mainly Helfferich (1995). For example, diffusion coefficients of Na^+ and Zn^{2+} are reported to be 10^{-6}-10^{-8}, and 10^{-7}-10^{-10}, respectively, depending on the degree of crosslinking of the resin. The diffusion coefficient of bromide in an anion-exchanger resin was reported to be between 10^{-7} and 10^{-8} (Helfferich, 1995). The values of resin diffusion coefficients of various ions are not easily available; however, according to the Helfferich (1995) one-half to one-fifth of the aqueous diffusion coefficients can be used as the resin diffusion coefficients. The user has a choice of including the calculations for the particle and/or film diffusions. The kinetics calculations can also be disabled in the program. Diffusion coefficients of 10^{-7} were utilized in the software. Diffusion coefficients can also be entered if the data are available. It has been stated that the effects of diffusion kinetics on the ion-exchange process are far less than the chemical equilibrium. In this research, diffusion coefficients employed by the software (10^{-7}) will be used.

Resin Plate

A resin plate is an imaginary part of a resin column in which equilibrium among all species is achieved before the aqueous phase advances to the next plate. It is assumed that the whole column of the resin does not reach the equilibrium, but the resin column will be divided to horizontal levels forming resin plates. The number of plates for a long column with narrow diameter differs (is more than) from a short column with larger diameter. Usually, ion-exchange columns have high flow rates and large diameter to depth ratios; therefore, the number of possible formed resin plates will be small. According to the instructions manual, at typical flow rates of 1-2 BV/min, regardless of the column diameter, anion-exchange reactions occur in approximately three to four inches of the resin column. Therefore, a four ft deep bed has ten reaction zones or resin plates. However, cation-exchange reactions occur in a 15 inches thick reaction zone that is translated to approximately three resin plates. According to the software manual, five to ten resin plates are sufficient for simulations of the normal ion-exchange column processes. The number of resin plates can be supplied by the user and applied for the calculations in IX-PRO.

Regeneration Process

The regeneration process is also simulated by IX-PRO. IX-PRO records the concentrations of ions accumulated in the resins. After exhaustion, there is a possibility to simulate the regeneration process. To do so, concentration of the regenerant (2000 meq/L NaCL) and number of desired bed volumes of the regenrant for the regeneration process must be entered. IX-PRO uses the same selectivity coefficients that are entered for the loading. However, there is a possibility to change the selectivity coefficients for the regeneration process. IX-PRO also has the ability to perform re-runs for the cycles of continuous loading and regeneration. IX-PRO records the concentrations of ions accumulated at the end of the loading process. The software performs the calculations for the regeneration process using the regenrant dosages and the selectivity coefficients. At the end of the regeneration process, the remaining concentrations of ions will be recorded as the initial condition for the next loading cycle.

IX-PRO Outputs

IX-PRO produces two output files. One of them is a word document file containing:

1. the name of the plant, and date and time of the simulation
2. untreated water quality (five ions) entered by the user
3. average treated water quality for five ions
4. average brine quality
5. useful conversion factors
6. selectivity coefficients
7. concentrations of ions at each resin's plate
8. concentrations of ions in the effluent during the loading process at every BV
9. concentrations of ions in the effluent during the regeneration process at every BV

The second output file is a comma delimited text file containing concentrations of ions in the effluent during the loading and the regeneration processes at every BV.

The output files generated by IX-PRO are hard to analyze and require improvements. Two computer codes will be made using visual basic editor in Microsoft excel. These codes will ease the generation of breakthrough curves in Microsoft excel and the calculations for the design of the brine treatment unit.

APPENDIX 3

MTZ CALCULATIONS

Table A3.1 MTZ Calculations: IX-Pro for Fresh Resin with 6 as Selectivity Coefficient

BV	Volume (L)	NO3 (mg/L) -	(Cn+1 + Cn)/2 (mg/L)	(Vn+1 - Vn) (L)	Cave*Vave /1000000 (kg)
0	0.0	0			
20	0.2	0			
40	0.4	0	Breakthrough		
60	0.6	0.00248			
80	0.8	0.0093	0.01	0.20	1.17918E-09
100	1.0	0.03038	0.02	0.20	3.97197E-09
120	1.2	0.08308	0.06	0.20	1.13574E-08
140	1.4	0.21018	0.15	0.20	2.93554E-08
160	1.6	0.50282	0.36	0.20	7.13714E-08
180	1.8	1.15072	0.83	0.20	1.6552E-07
200	2.0	2.4428	1.80	0.20	3.59712E-07
220	2.2	4.6841	3.56	0.20	7.13403E-07
240	2.4	7.78782	6.24	0.20	1.24844E-06
260	2.6	11.48426	9.64	0.20	1.92914E-06
280	2.8	15.56634	13.53	0.20	2.70777E-06
300	3.0	19.74948	17.66	0.20	3.53512E-06
320	3.2	24.6016	22.18	0.20	4.43955E-06
340	3.4	29.5864	27.09	0.20	5.42422E-06
360	3.6	34.38396	31.99	0.20	6.40344E-06
380	3.8	39.8257	37.10	0.20	7.42839E-06
400	4.0	45.03866	42.43	0.20	8.49493E-06
420	4.2	49.85544	47.45	0.20	9.49891E-06
440	4.4	55.14466	52.50	0.20	1.05105E-05
460	4.6	59.32594	57.24	0.20	1.14585E-05
480	4.8	63.18296	61.25	0.20	1.22632E-05
500	5.0	66.98294	65.08	0.20	1.30296E-05
520	5.2	70.17594	68.58	0.20	1.37296E-05
540	5.4	72.29944	71.24	0.20	1.42618E-05
560	5.6	74.96854	73.63	0.20	1.47415E-05
580	5.8	76.95316	75.96	0.20	1.52074E-05
600	6.0	78.31654	77.63	0.20	1.55425E-05
620	6.2	79.27444	78.80	0.20	1.57749E-05
640	6.4	80.54544	79.91	0.20	1.5998E-05
660	6.6	81.17226	80.86	0.20	1.6188E-05
680	6.8	81.5238	81.35	0.20	1.62859E-05
700	7.0	82.50588	82.01	0.20	1.64194E-05
720	7.2	82.36762	82.44	0.20	1.65039E-05
740	7.4	82.55858	82.46	0.20	1.65091E-05
760	7.6	83.2722	82.92	0.20	1.65997E-05

APPENDIX 4

pH MEASUREMENTS IN BRINES

pH is the cologarithm of the activity of the hydrogen ion in a solution, and defines the acidity or basicity of the solution (Bates, 1964). The pH definition was first introduced by a Danish chemist (Sørensen) at the Carlsberg Laboratory in 1909.

$$pH = -\log(a_H) = \log\frac{1}{a_H} \qquad \text{(A4-1)}$$

where a_H is the hydrogen ion activity in a solution.

The activity of hydrogen can be determined by using the Nernst equation and a hydrogen ion-selective electrode, which measures the electromotive force (or the potential difference) between a hydrogen sensitive electrode (typically a glass electrode) and a reference electrode (typically silver chloride or calomel) (Bates, 1964).

$$E = E^0 + \frac{RT}{nF}\ln(a_H) \qquad \text{(A4-2)}$$

where T, R, and F are the temperature, gas constant, and Farady constant, respectively. n is one (the number of electrons). Therefore, RT/nF equals 59.16. E is the measured potential, and E^0 is the reference electrode potential at the standard state at unity proton activity.

According to May et al. (1982), the combination of the external and internal reference potentials (E_r) and the liquid junction potential (E_l) are also cause the electromotive force, and must be included into the equation.

$$E = E_r + E_l + E^0 + \frac{RT}{nF}\ln(\gamma_{H^+} C_{H^+}) \qquad \text{(A4-3)}$$

E_r is independent of the ionic strength of the solution, but E_l is dependent to the ionic strength of the solution (May et al., 1982). Hydrogen ion activity equals the activity coefficient multiplied by the hydrogen ion concentration (on the molal scale) (Bates, 1964). The activity coefficient can be calculated using the Debye-Hückle equation for solutions with less than 0.1 M ionic strength:

$$-\log \gamma_{H^+} = \frac{Az_i^2\sqrt{I}}{I + Ba\sqrt{I}} \qquad \text{(A4-4)}$$

where I is the ionic strength of the solution, a is the radius of the hydrogen ion and its closely bound water molecules (~ 3 Å), z is the charge of the ion (one in the hydrogen case) (Bates, 1964). A and B are the equation constants and their values are 0.5085 and 0.3281, respectively.

Activity coefficient in high ionic strength solutions (0.1-6 M) can be calculated utilizing Pitzer equations (Pitzer, 1973; Pitzer et al., 1973). Brandariz et al. (1998) calculated the logarithm of the activity coefficient for the hydrogen ion at various ionic strengths produced by various saline media. A modified form of Pitzer's equations was presented by Brandariz et al. (1998) and the equation constants are provided for various saline media.

$$\ln \gamma_{H^+} = f^{\gamma} + PI + QI^2 + RI\exp(-2\sqrt{I}) + T\left[1 - (1 + 1.2\sqrt{I})\exp(-2\sqrt{I})\right] \qquad \text{(A4-5)}$$

$$f^{\gamma} = -A_{\phi}\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2}\ln(1 + 1.2\sqrt{I})\right] \qquad \text{(A4-6)}$$

$$A_{\phi} = \frac{1}{3}A_{\gamma} = \frac{1}{3}(2\pi N_0 d_w / 1000) \qquad \text{(A4-7)}$$

where A_{ϕ} is the Debye-Hückle constant for the osmotic coefficient (1.172 $kg^{0.5}/mol^{0.5}$ for water), N_0 and d_w are the Avogadro's number and the density of the solvent, respectively.

Brandariz et al. (1998) calculated the P, Q, R, and T constants for five inert electrolytes (NaCl, KCl, KBr, KNO_3, and $NaClO_4$) from the Pitzer parameters (Pitzer et al., 1973, Pitzer, 1991). P, Q, R, and T constants for NaCl solutions (0-1.5 M) are 0.4270, -0.0026, 0.2664, and 0.1613, respectively.

The liquid junction potential (E_l) between the filling solution around the electrode and the test solution varies at different ionic strengths (Baumann, 1972). Therefore, the glass electrode response may be affected by the high ionic strength and likely poses an inherent error for during the pH measurement (Baumann, 1972). Baumann (1972) used the following Nernst equations to study the effects of liquid junction potential in high ionic strength solutions:

$$E = \varepsilon + 59.16 \log c_H = \varepsilon - 59.16 \text{ pH} \qquad \text{(A4-8)}$$

where E is the measured potential in millivolts (mV), ε is the sum of the standard potentials of the glass and reference electrodes and the liquid junction potentials. Similarly, the equation between pOH and the measured potential is:

$$E = \acute{\varepsilon} - 59.16 \log c_{OH} = \acute{\varepsilon} + 59.16 \text{ pOH} \qquad \text{(A4-9)}$$

It has been reported that the abovementioned equations show non-Nernstian behavior and the slope of these equations are not 59.16 for high ionic strength solutions (Baumann, 1972; Wiesner et al., 2006). The following equations describe the relationship between the measured potential and the pH or pOH at acidic or alkaline solutions.

$$E = \varepsilon - s \text{ pH}, \qquad \text{(A4-10)}$$

$$E = \acute{\varepsilon} + s' \text{ pOH} \qquad \text{(A4-11)}$$

Wiesner et al. (2006) modified the pH buffer standards according to the following procedure. A known volume of an acidic or alkaline electrolyte was titrated by an acid (e.g., 0.1 M HCl, HNO_3, or $HClO_4$) or a base (e.g., 0.1 NaOH) and the potential of the electrolyte was measured each increment of the titration. The concentrations of H^+ or OH^- at each increment of the titration were known and the pH and pOH values were calculated using Pitzer approximate method (Pitzer et al., 1973). Titration graphs were made for the potentials versus the calculated pH or pOH values. From the titration graphs, ε or έ and s or s’ were determined. For example, the slope and potential for the 0.5 M and 1.0 M NaCl in acidic region were reported as 47.1 and 350.8, and 41.4 and 336.3, respectively, and for the alkaline region, they reported as 72.0 and 466.4, and 71.9 and 463.1, respectively. The ionic strength of the standard pH buffers were adjusted to the ionic strength of the test solution by adding the appropriate salts. After that, the potential of the modified buffers were measured, and pH and pOH values of the modified pH buffers were calculated using equations A4-10 and A4-11 with the respective determined parameters (i.e., s and ε or έ and s’). Finally, the pH meter was calibrated with the salted buffers and determined pH values for the sample measurements.

The difference between the pH measurements using the salted and unsalted buffers were between 0.2 to 0.5 units of pH (Baumann, 1972; Wiesner et al., 2006). The pH difference for 0.5 or 1 M NaCl solutions were 0.25 and 0.5 units of pH (Wiesner et al., 2006).

The partial pressures of CO2 and O2 content have great effects on the pH of brines. When the pCO_2 in brines increases, pH decreases. Moreover, pH directly proportional to dissolved oxygen in the brines (Rieke, 1961). By increasing the salt concentrations in brines, pH decreases (Rieke, 1961).

Hawley and Pytkowicz (1973) stated that the liquid junction potential in brines is different than the one for waters. Therefore, the activity of hydrogen ion measured by an electrode must be corrected using a k constant to correct the salt error potentials.

$$X = k\,(a_H) \text{ and } pX = -\log X \qquad \text{(A4-12)}$$

where pX is the adjusted pH according to the salt concentration.

The k constants for 0.46 M and 0.6 NaCl solutions were reported as 0.96 and 1.01, respectively (Culberson et al., 1970). The k constant for a 0.68 NaCl solution was determined as 0.98 (Hawley and Pytkowicz, 1973).

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VITA

Graduate College
University of Nevada, LasVegas

Behrang Pakzadeh

Degrees:
Bachelor of Science, Civil Engineering, 2001
Sharif University of Technology, Tehran, Iran

Master of Science, Engineering (Environmental Management), 2006
Technical University of Denmark, Lyngby, Denmark

Dissertation Title: Ion-Exchange (IX): Arsenic and Chromium Removal from Brines and Removal of Inorganic Contaminants by Specialty Resins

Dissertation Examination Committee:
Chairperson, Jacimaria R. Batista, Ph.D.
Committee member, Thomas C. Piechota, Ph.D.
Committee member, Sajjad Ahmad, Ph.D.
Committee member, Kazem Taghva, Ph.D.
Graduate Faculty Representetive, Spencer M. Steinberg, Ph.D.