ENGINEERED TREATMENT OF AS-LADEN REGENERATION BRINE FROM ION EXCHANGE PROCESSES

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Thomas Riemann Steinwinder

Certificate of Approval:

____________________________ Mark O. Barnett Associate Professor Civil Engineering	____________________________ Dongye Zhao, Chair Assistant Professor Civil Engineering
____________________________ T. Prabhakar Clement Associate Professor Civil Engineering	____________________________ Stephen L. McFarland Acting Dean Graduate School

ENGINEERED TREATMENT OF AS-LADEN REGENERATION BRINE FROM ION EXCHANGE PROCESSES

Thomas Riemann Steinwinder

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Thomas Riemann Steinwinder

Signature of Author

Date of Graduation

THESIS ABSTRACT

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Thomas Riemann Steinwinder

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Arsenic (*As*) contamination of drinking water sources has been one of the most challenging global environmental issues. In the United States, the newly revised maximum contaminant level (MCL) of 10 µg/L requires thousands of utilities to either modify their existing treatment systems or adopt new *As*-removal technologies. While ion exchange (IX) is one of the EPA approved best available technologies for *As* removal, IX processes generate large volumes of *As*-laden regeneration brine due to lack of *As* selectivity. The resultant liquid process waste residuals require costly additional treatment and disposal.

Addition of ferric chloride has been well-documented and commonly used to remove *As* from aqueous solution via co-precipitation and adsorption. Previous studies have determined the optimal pH and Fe/As molar ratio for treating drinking water. In this study ferric chloride addition was investigated as a cost-effective means to treat *As*-laden spent regeneration brine, where arsenic, sulfate, bicarbonate, and chloride concentrations (300 mg/L, 605 mg/L, 305 mg/L, and 24 g/L, respectively) were orders of magnitude greater than typical drinking water treatment levels. Batch tests revealed that nearly 100% of the *As* in spent brine can be removed with a Fe/As molar ratio of 2 at pH 6 and 7. Furthermore, column tests indicated that treated brine can be reused for regenerating a polymeric ligand exchanger and nearly 100% of the resin's capacity can be recovered.

It has been estimated that millions of tons of *As*-bearing sludge are annually introduced as waste residuals from water treatment processes. This study determined the optimum conditions to yield the most stable process waste residuals. The EPA TCLP and California WET tests were employed to determine the leachable *As* in the brine treatment residuals. When the brine was treated using an Fe/As molar ratio of 5 and 20, the resultant *As*-laden sludge easily passed the TCLP and WET respectively, both with a limit of 5 mg/L *As*. Addition of 90 mM calcium decreased leachable *As* by 80% while adding 210 mM calcium increased *As* leached by 60% suggesting an optimum range of calcium addition for further stabilization of the treatment residuals. Calcium addition to the brine treatment process also decreased the chemical costs by 18% and reduced the mass of sludge produced by 20%. Furthermore, a dry aging period of 98 days had significant effects on extractable *As*, increasing extracted *As* by 54% in residuals formed at a Fe/As ratio of 5 while decreasing extracted *As* by 70% in residuals formed by Fe/As of 10.

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Style manual or journal followed: Auburn University Graduate School: Guide to Preparation and Submission of Theses and Dissertations.

Computer software used: Microsoft Office XP: Excel, PowerPoint, Word, SigmaPlot 8.0, and VisualMINTEQ.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

1.1 Arsenic Chemistry

Arsenic (*As*) is a naturally occurring element present in rocks, soils, water, and biota. Described as a metalloid, *As* is the 33rd element on the periodic table and ranks 52nd in average concentration in the earth's crust (Demayo, 1985). *As* is commonly found in the natural environment in inorganic form as an oxyanion in two valence states, *As*(V) (arsenate) or *As*(III) (arsenite). The ratio of *As*(V) to *As*(III) is a function of the pH and redox conditions of the system (Masscheleyn et al., 1991). Figures 1.1 and 1.2 show the speciation of *As*(V) and *As*(III) respectively as a function of pH.

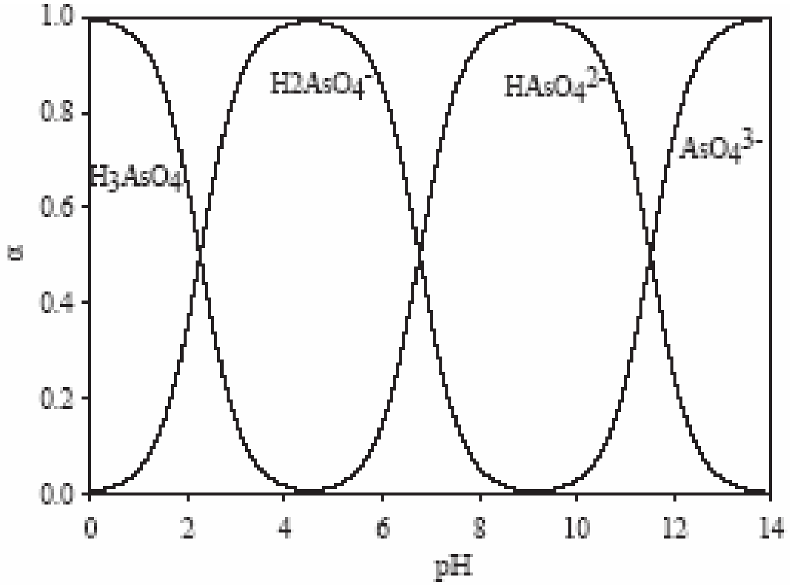

Figure 1.1. Distribution of As(V) as a function of pH. Figure from Ghimire et al. (2003).

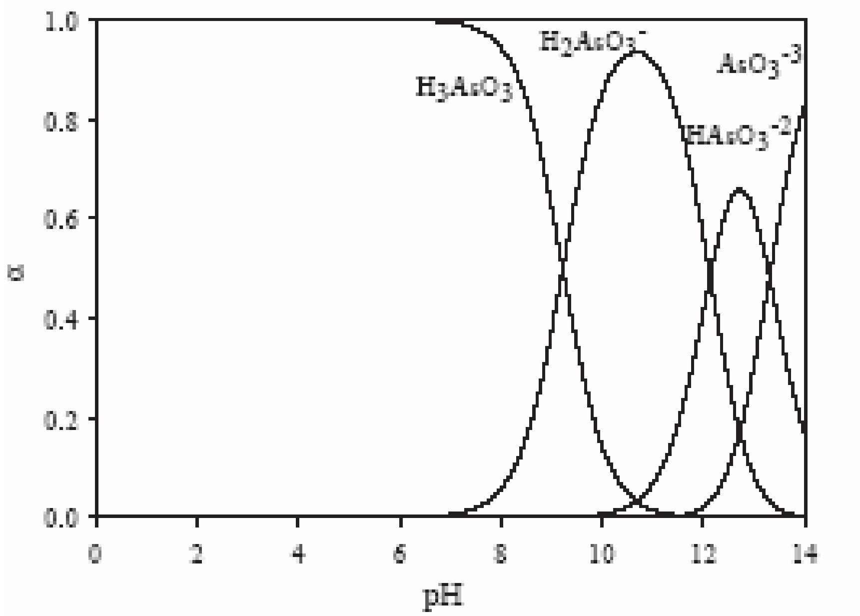

Figure 1.2. Distribution of As(III) as a function of pH. Figure from Ghimire et al. (2003).

The equilibria for both *As*(V) and *As*(III) are given in equations 1.1-1.6 along with their respective acid disassociation constants (O'Neill, 1990).

Arsenic acid, As(V)

$H_3AsO_4 + H_2O \leftrightarrow H_2AsO_4^- + H_3O^+$ pK$_a$=2.20 (1.1)

$H_2AsO_4^- + H_2O \leftrightarrow HAsO_4^{2-} + H_3O^+$ pK$_a$=6.97 (1.2)

$HAsO_4^{2-} + H_2O \leftrightarrow AsO_4^{3-} + H_3O^+$ pK$_a$=11.53 (1.3)

Arsenous Acid, As(III)

$H_3AsO_3 + H_2O \leftrightarrow H_2AsO_3^- + H_3O^+$ pK$_a$=9.22 (1.4)

$H_2AsO_3^- + H_2O \leftrightarrow HAsO_3^{2-} + H_3O^+$ pK$_a$=12.13 (1.5)

$HAsO_3^{2-} + H_2O \leftrightarrow AsO_3^{3-} + H_3O^+$ pK$_a$=13.4 (1.6)

The most thermodynamically stable compounds of *As* in the natural water environment (pH 6~8) are H_3AsO_3 for *As*(III) and $H_2AsO_4^-$ or $HAsO_4^{2-}$ for *As*(V) (Smith et al., 1998). *As*(V) is the more common species under oxidizing conditions (Eh>200mV and pH 5-8) making it the ubiquitous species in surface waters (Smith et al., 1998).

1.2 Origin

Arsenic can be released into the environment through both natural and human activities. The common natural sources of *As* include volcanic activity, erosion of *As*-bearing sediments and rocks, and forest fires (EPA, 2001). The anthropogenic sources of *As* are widespread and can be categorized as: industry, mining, agriculture, and other sources (Smith et al., 1998). Figure 1.3 shows the *As* use in the United States between 1910 and 1997 (Welch et al., 2000). In the past 30 years, lumber treatment has become a major contributor to *As* use.

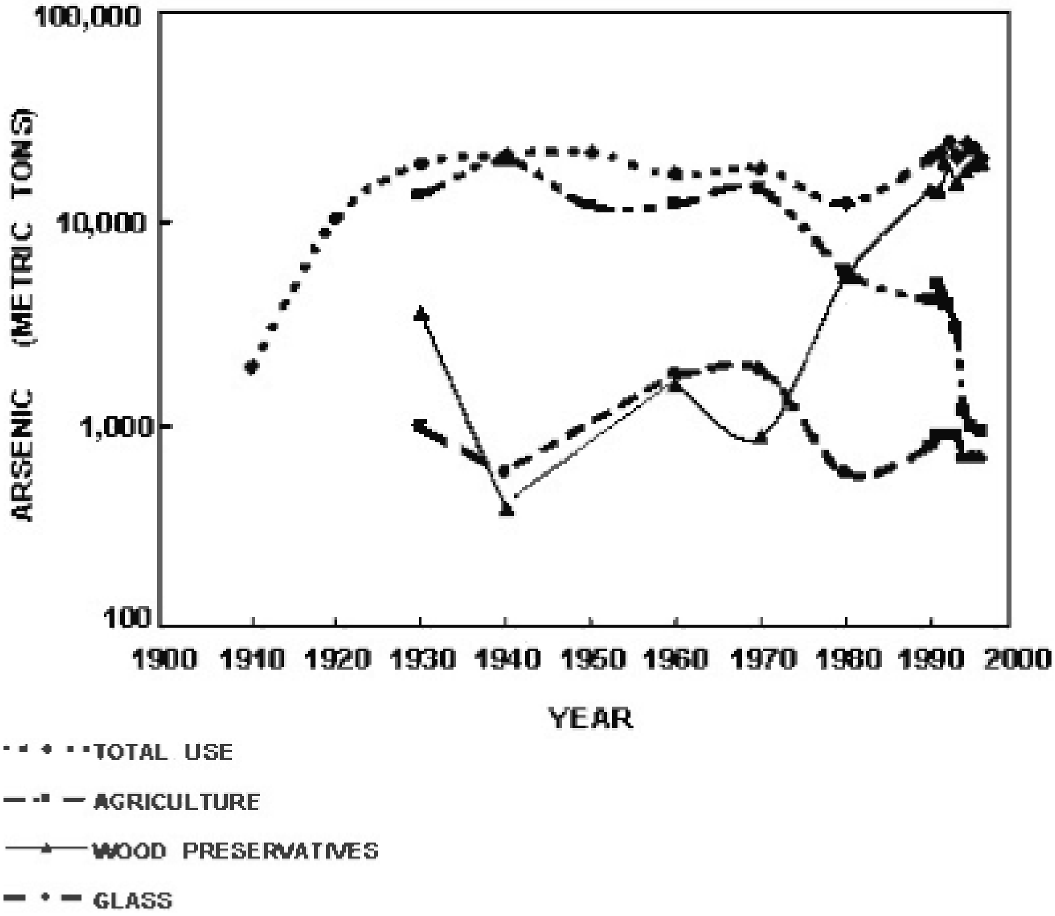

Figure 1.3. Arsenic use in the United States between 1910-1997. Figure from Welch et al. (2000).

Manufacture of ceramics, glass, electronics, pigments, cosmetics, fireworks, and steel are some of the other major industrial users of *As*. Mining and smelting of Pb, Zn, Cu, and Au ores act as a source since *As* is a natural component of these ores. From the 19th century until recently, inorganic arsenic compounds have been a major component of pesticides and herbicides used in agriculture. Other anthropogenic sources include fly ash from coal burning, tannery wastes, and lumber treatment (Smith et al, 1998).

1.3 Risk and Occurrence

As exposure is known to have adverse health effects on humans. Two major exposure pathways are ingestion of *As*-containing food and consumption of *As*-contaminated drinking water (ATSDR, 2000). Cancer of the kidney, lungs, skin, bladder, nasal passages, liver, and prostate has been linked to long-term exposure to arsenic in drinking water (EPA, 2001). In 1999, the National Research Council released a report concluding that consumption drinking water contaminated with *As* (even at low concentrations) has harmful cardiovascular, neurological, reproductive, respiratory, hepatic, hematological, diabetic, and dermal effects (NRC, 2001). Even at *As* levels 10 µg/L the risk of death due to lung and bladder cancer is 12 to 23 deaths per 10,000 people (NRC, 2001).

As contamination of drinking water sources is widespread throughout the world and has been reported to have caused *As* toxicity problems in countries including the United States, Germany, Chile, Argentina, the United Kingdom, Taiwan, India, and Bangladesh (ATSDR, 2000). The United States Geological Survey (USGS) has estimated that 14% of groundwater sources in the United States exceed 5µg/L *As* (Focazio et al., 1999), while the EPA states that approximately 2% of the US population receives drinking water containing >10 μ/L *As* (Holm, 2002). The Natural Resources Defense Council also estimates that 56 million people in the United States are exposed to unsafe levels of *As* in drinking water (Mushak, 2000).

1.4 Legislation and Standards

The first legislative effort to minimize the harmful effects of water pollution occurred in 1972 with the passing of the Federal Water Pollution Control Act Amendments which later became known as the Clean Water Act. Control of arsenic in drinking water began in 1975 when the EPA established the first maximum contamination level (MCL) for *As* at 50 μg/L (EPA, 2000a). The Safe Drinking Water Act as amended in 1996 required the U.S. Environmental Protection Agency to issue a new drinking water standard for *As*. In response to this risk concern, the U.S. Environmental Protection Agency (EPA) adopted a maximum contaminant level (MCL) for arsenic of 10 μg/L (EPA, 2001b). The new MCL became effective January 2006. To meet the more stringent drinking water standards, existing treatment systems will have to be upgraded or new systems installed.

1.5 Removal Technologies

There are numerous *As*-removal technologies that have been developed. Some of the most commonly used methods include coagulation with alum or ferric salts (Chwirka et al., 2004; Ghurye et al., 2004; Clifford et al., 2003; Fan et al., 2003; Brandhuber and Amy, 1998; McNeill and Edwards, 1997; Hering and Elimelech, 1996; Scott et al., 1995), sorption using activated alumina (AA) (Wang et al., 2002), standard ion exchange resins (IX) (Clifford, 1999), and reverse osmosis (RO) (EPA, 2002). Recently, one-time use granular adsorptive media has gained much interest. Granular ferric hydroxide (GFH) (Sperlich et al., 2005; Badruzzaman et al., 2004; Driehaus et al., 1998), granular ferric oxide (GFO) (Westerhoff et al., 2005; Manna et al., 2003), and iron-coated sand (Benjamin et al., 1996) are the common examples of this type of media. The treatment cost of these technologies increases in the following order: coagulation, AA, IX, and RO (Chen et al., 1999). While coagulation is the cheapest technology, it is very difficult to meet the new MCL using this technology alone and thus additional treatment such as microfiltration is often required (Ghurye et al., 2004). Other processes such as IX using strong base anion exchange resins, AA adsorption, or RO are less cost-competitive due to lack of selectivity for *As*, frequent regeneration requirements and production of large volumes of *As*-laden process residuals (EPA, 2000c). GFH and GFO are relatively cheaper sorbents but because they are non-regenerable they may result in large volumes of *As*-laden wastes, which will require additional handling and disposal.

To aid utilities in achieving the new MCL, a number of other technologies have recently been explored, including coagulation with nanocrystalline titanium dioxide (Pena et al., 2005), zero-valent iron (Kober et al., 2005; Leupin and Hug, 2005), polymer-supported iron nanoparticles (Cumbal and Sengupta, 2005), iron oxide impregnated activated carbon (Vaughan Jr. and Reed, 2005) and ferrihydrite crystallization process (Richmond et al., 2004). However, these new techniques are in the developmental stage and have not been tested in a wide range of conditions.

One common method of *As* removal for drinking water systems is standard ion exchange (IX) (Clifford et al, 2003; Clifford, 1999). IX is considered a best available technology (BAT) by the EPA for removal of *As*(V) (EPA, 2000a). While IX exhibits efficient *As* removal in many cases, the elevated occurrence of competing anions such as sulfate will greatly decrease the resin's affinity for arsenate (Clifford et al., 2003), thus increasing the need for regeneration. Regeneration can account for a significant amount of total process costs and results in an *As*-laden waste brine that requires further treatment. Minimizing the need for regeneration is paramount for an efficient IX treatment process design.

1.6 Polymeric Ligand Exchange Technology

Recently, a novel technology for removing *As*(V) from drinking water has been developed at Auburn University. The unique ion exchanger, termed polymeric ligand exchanger (PLE), was prepared by loading Cu^{2+} ions onto a chelating resin, DOW 3N, and it was shown to be highly selective for *As*(V) even in the presence of competing anions such as sulfate, bicarbonate and chloride (An et al., 2005). Figure 1.4 depicts the functionality of the PLE.

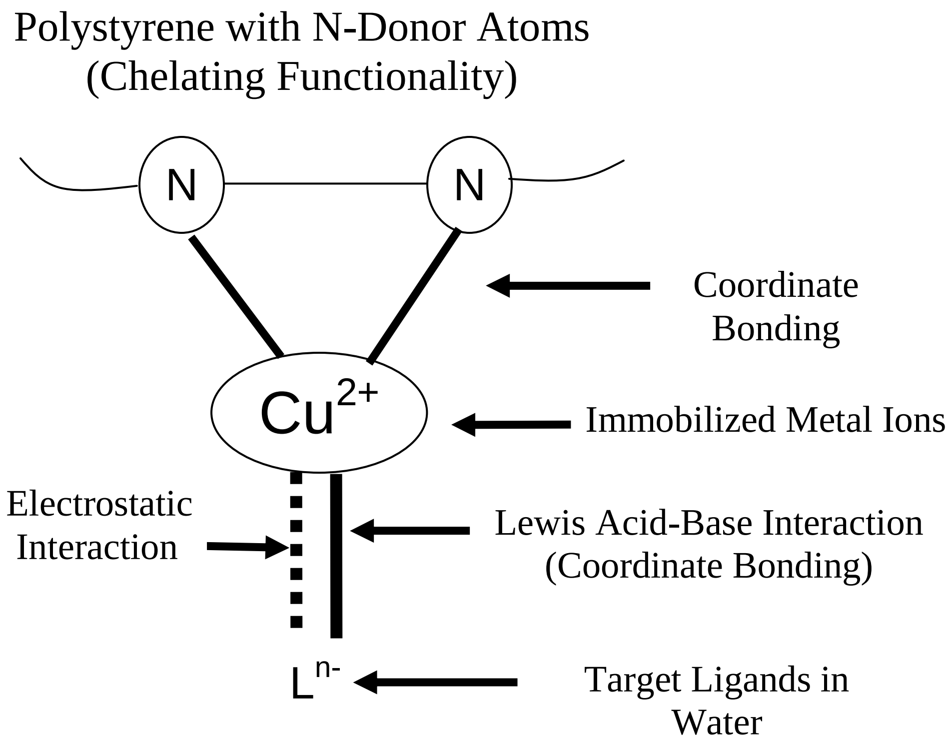

Figure 1.4 Conceptual diagram of a PLE. Figure from An et al. (2005).

Metal-loaded polymers such as the polymeric ligand exchanger have recently gained interest due to their ability to selectively remove *As* and thus improve upon standard IX technology (Dambies, 2004). Due to arsenate selectivity, the PLE was able to treat ~10 times more bed volumes (BVs) of water than commonly used strong base anion exchange (SBA) resins (An et al., 2005). Although the PLE has been shown to be more efficient than common resins for *As* removal, like all IX resins it must be regenerated with a brine solution resulting in an *As*-concentrated waste brine.

1.7 Brine Treatment and Residuals Production

Concentrated spent regeneration brine is commonly treated by precipitation/adsorption using either ferric or aluminum salts (Clifford, 1999). Clifford reported that a metal/As molar ratio of 20 was required to achieve an *As* removal efficiency of 98%. All solid residuals produced from the brine treatment process must undergo leaching tests to determine their suitability for landfill disposal. The two most common leaching tests are the EPA toxicity characteristic leaching procedure (TCLP) (EPA, 1992) and the California waste extraction test (WET) (California Code of Regulations, 1985). Both the TCLP and WET employ extraction solutions of acetic and citric acid respectively to determine the potential leachable *As* in the disposal environment. Failing the TCLP or WET will cause the wastes to be deemed as hazardous and may increase disposal costs up to 3-fold (Meng et al., 2001). The two major factors affecting brine treatment process feasibility are passing the leaching tests and reducing the volume of residuals produced. Frey et al. (1998) estimated that residuals handling in *As*-removal processes account for, on average, 12-34% of the total process costs.

Therefore, producing a relatively small amount of highly stable sludge is extremely desirable.

1.8 Objectives

The objective of this research was to design an efficient and cost effective process for treating the *As*-laden regeneration brine resulting from the polymeric ligand exchange process. Batch tests conducted under different conditions and multiple leaching procedures were employed to: (1) evaluate the optimal conditions for treatment of spent regeneration brine using ferric chloride, (2) investigate the reusability of treated brine, (3) develop a brine treatment process that will maximize the stability of the solid, *As*-laden end product, and (4) increase the understanding of the mechanisms that promote stability in the *As*-laden residual solid.

In order to determine the cost impacts of brine treatment, a full process design was developed. A cost estimate was prepared based on this design scheme. Costs estimates for different brine treatment conditions were compared to determine the most cost efficient treatment conditions.

1.9 Organization

This thesis is organized according to guidelines outlined in the *Guide to Preparation and Submission of Theses and Dissertations* provided by the Auburn University Graduate School. The publication style format was used. The results of this research are presented in chapters II and III. Chapter IV contains a cost estimate for the brine treatment. Finally, chapter V summarizes the conclusions of this research.

II. TREATMENT OF AS-LADEN REGENERATION BRINE

2.1 Introduction

The new maximum contaminant level for *As* in drinking water of 10 µg/L became effective in January 2006 requiring the development of many new and improved technologies to help water utilities meet the new standard. Of the new technologies studied metal-loaded polymers exhibit selective removal of *As* species in drinking water and improve upon many conventional techniques (Dambies, 2004). A novel metal-loaded polymer resin for *As*(V) removal has been developed at Auburn University. The unique ion exchanger, termed polymeric ligand exchanger (PLE), was prepared by loading Cu^{2+} ions onto a chelating resin, DOW 3N, and proved to be highly selective for *As*(V) even in the presence of competing anions such as sulfate, bicarbonate and chloride (An et al., 2005). Despite its obvious advantages, the PLE like other ion exchange processes results in a spent brine solution with high concentrations of *As* and other co-contaminants. Brine solutions used to regenerate the resin column will concentrate contaminants and eventually become useless for regeneration. While studies indicate that direct reuse of regeneration brine increases the efficiency of the IX process, the treatment of the spent brine and reuse of the treated brine has not been thoroughly investigated.

The addition of ferric chloride ($FeCl_3$) is a well documented technique used to remove *As* from solution via co-precipitation/adsorption. Ferric chloride addition has been studied in depth for drinking water treatment (Pierce and Moore, 1982; Cheng et al., 1994; Hering et al., 1996; McNeill and Edwards, 1997; Ghurye et al., 2004), but less so for the high *As* concentrations and ionic strength present in brine treatment. Co-anions such as sulfate, bicarbonate, and chloride may also be highly concentrated in spent regeneration brine. Previous research has investigated the competitive effect of sulfate, chloride, or carbonate in singular competitive studies (Cadena, 1995; Holm, 2002; Radu et al., 2005), but a thorough study of multiple, concentrated co-anions in ultra-saline solution (as with IX brine) is not available. We hypothesize that due to the high ionic strength of the brine solution, optimal conditions determined for drinking water treatment via ferric chloride will differ from those found for brine treatment. Our objective is to determine the optimal conditions for treatment of spent regeneration brine using ferric chloride resulting in reusable brine.

2.2 Materials and Methods

2.2.1 Simulation of Spent Regeneration Brine

To conduct brine treatment experiments, spent regeneration brine (SRB) was simulated based on analysis of the spent brine collected from column tests performed on a PLE resin. The brine was reused for regeneration of the resin multiple times until finally reaching its capacity. The average composition of the spent brine was: As = 300 mg/L, SO_4^{2-} = 600 mg/L, HCO_3^- = 305 mg/L, and NaCl = 4% (w/w) (or 24 g/L as Cl^-). The average pH and ionic strength (I) of the simulated spent brine was 9.3 and 1.8 M respectively. One liter batches of the SRB were prepared by adding analytical grade sodium arsenate ($Na_2HAsO_4{\cdot}7H_2O$), sodium sulfate (Na_2SO_4), sodium bicarbonate

($NaHCO_3$), and sodium chloride (NaCl) to MilliQ deionized water. All compounds were purchased from Fisher Scientific except the sodium arsenate which was purchased from Sigma-Aldrich.

2.2.2 Brine Treatment

Multiple batch experiments were performed to determine the optimal conditions and process for brine treatment. Ferric chloride (Fisher Scientific) was used for arsenic removal from the brine. First, the effect of different ferric chloride ($FeCl_3$) additions was studied. Several 100 mL samples of SRB were separated into 125 mL Nalgene HDPE bottles. $FeCl_3$ was then added to the bottles at the Fe/As molar ratio of 0, 1, 2, 5, 10, 15, 20, 25, 30, and 40. Bottles were placed on gang mixer for ~2 hours at 200 rpm. After the mixing period, the precipitate was allowed to settle for ~1 hour. The pH of the supernatant was determined using an Orion pH meter (model 520A), and the pH was adjusted using 1 M sodium hydroxide (NaOH) or 1 M hydrochloric acid (HCl) (Fisher Scientific). After each addition of acid or base batches were again mixed and allowed to settle. Finally, mixtures were allowed to age for ~24 hours. Samples were centrifuged; supernatant was removed, filtered with 0.45µm syringe filter, and duplicates were analyzed for arsenic using a Perkin-Elmer Graphite Furnace AA.

Literature suggests that calcium addition to the treatment process will reduce the leachability of *As* from the solid residual (Parks, et al., 2003; Bothe and Brown, 1999; Jing et al., 2003). Before considering the effects that calcium had on the stability of the residual we investigated the effects of calcium on *As*(V) removal from SRB. 100 mL batch samples were prepared as in the metal salt addition experiments. Calcium addition experiments were performed with the $FeCl_3$ treatment process. Additions via calcium hydroxide ($Ca(OH)_2$) were made in two different Ca/Fe molar ratios; 1.5 and 0.5. Supernatants were prepared as before and analyzed for *As* content.

The disposal conditions for treatment residuals can vary widely and can change with time. Residuals may be stored in holding ponds for periods of time ranging from days to years before disposal (Meng et al., 2001; Parks et al., 2003). Lagoons and landfills may become anoxic, and the brine contact time with sludge may vary. The effect of pH on the treatment process was studied in the pH range ~3-11. Fe/As molar ratios of 5 and 20 were used. pH was controlled with 1N NaOH and 1N HCl. After a 2 day equilibration period, the final pH was recorded and the supernatants prepared and analyzed for *As* content. 100 mL and 500 mL SRB batches were also treated with a Fe/As ratio of 5 and 10 respectively and allowed to age in contact with the brine for 2, 20, 60, 200, and 300 days. Varying the aging period may reveal if mechanisms with slower kinetics actively affect *As* mobilization.

Batch tests employing adsorption to pre-formed iron hydroxide for arsenate removal were compared to those where coagulation with $FeCl_3$ was employed. Spent regeneration brine was simulated in the same way as previously described except that no arsenate compound was added. The SRB was then separated into 100 mL samples and placed in 125 mL HPDE Nalgene bottles. Ferric Chloride ($FeCl_3$) was then added to each bottle in the Fe/As ratio of 5 (0.326g $FeCl_3$). Bottles were placed on a gang mixer for 2 hours and then the precipitate was allowed to settle for 1 hour. 5N NaOH was used to adjust pH to > 5 allowing for precipitation of ferric species. Bottles were again placed on the mixer at low speed (~100 rpm) and then precipitates allowed to settle. Using a dropper, approximately 2 mL of brine was removed from the batch and placed in a plastic cup containing 0.125 g sodium arsenate. The solution was then added back to the batch. Another slow mixing period ensued followed by a settling period and pH adjustment. 10 batches were used to cover the pH range from 3 to 12. After stable pH was achieved, duplicates of the supernatant were removed and filtered using a 0.45 μm syringe filter. Duplicates were then analyzed for *As* content using a Perkin Elmer Graphite furnace AA.

2.2.3 Brine Reuse

Three 500 mL batches of SRB were treated using a Fe/As ratio of 15 and a pH of 6 for the first two batches and 9 for the last. Treated brine was removed and a 10 mL sample and duplicate were analyzed for *As* content using a Perkin Elmer Graphite Furnace AA. The pH of the treated brine was then adjusted and the brine reused in a column regeneration run of an exhausted PLE resin.

2.3 Results and Discussion

The results of this study are organized into two sections. The first section describes the optimal conditions for arsenic removal from spent regeneration brine using ferric chloride. The final section presents the results from the use of treated brine in regeneration column experiments with an exhausted PLE resin.

2.3.1 Arsenic Removal from Spent Brine

Batch tests exploring the effects of both ferric chloride addition and pH on the treatment process exhibited optimal ranges for the variables tested. Figure 2.1 shows the

% *As* removed as a function of pH and Fe/As molar ratio. At pH 6 and 7, >99% of *As* was removed from the brine at Fe/As molar ratios 2 – 40. At pH 9, > 99% *As* removal was achieved at Fe/As > 10.

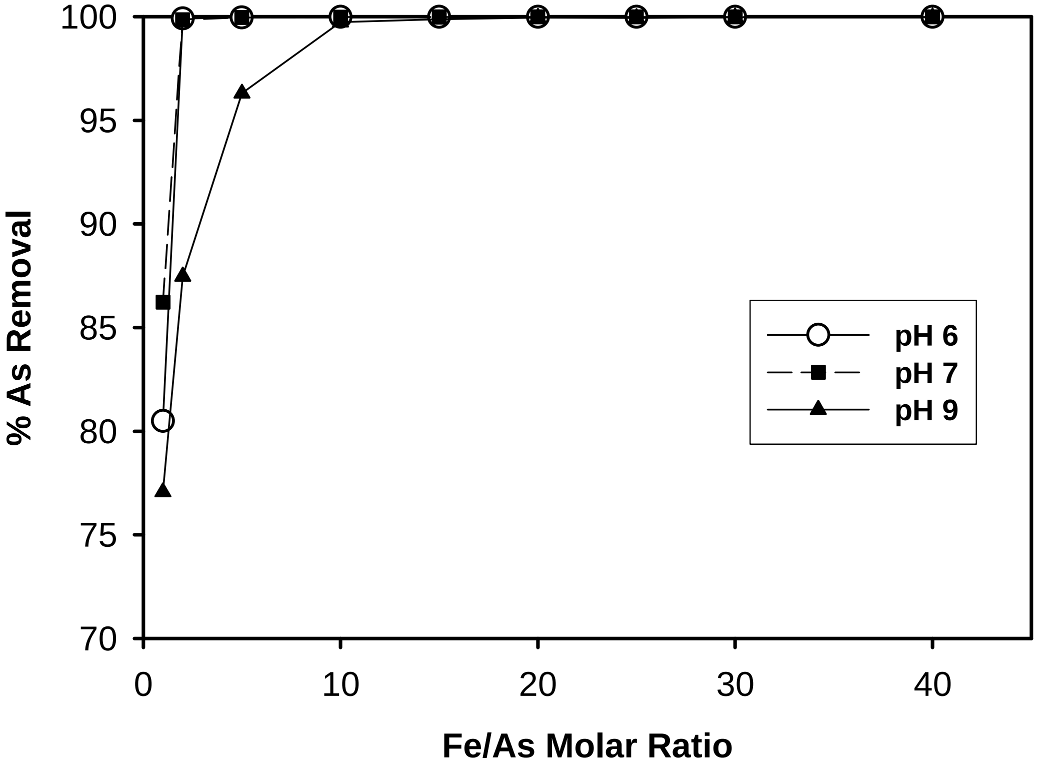

Figure 2.1. *As* removed as a function of Fe addition. A Fe/As molar ratio from 1-40 was used. Experiments were carried out at pH 6, 7, and 9. Initial Arsenate concentration was ~300 mg/L. Initial sulfate, bicarbonate, and chloride concentrations were 600 mg/L, 305 mg/L, and 24 g/L respectively.

Figure 2.1 indicates an increase in removal with an increase in Fe addition at a constant pH. Cheng et al. (1994) observed the same trend in jar tests where $FeCl_3$ was added to raw water containing an influent *As*(V) concentration of 17-20 µg/L. Although the initial concentration of *As*(V) in our batch tests is four orders of magnitude greater (~300,000 µg/L) the same trend is observed. This observation can be attributed to increased availability of Fe for co-precipitation and increased number of surface sites on ferric precipitates facilitating the adsorption of *As*(V).

The decrease in removal efficiency at pH 9 indicates that removal is both a function of available sorbent and pH. The pristine point of zero charge for fresh ferric hydroxide is 7.9 – 8.2 (Dzombak and Morel, 1990). We can expect the isoelectric point in these batch tests to be lower due to aging of the ferric hydroxide and extremely high ionic strength (~2 M). Solution pH will also affect the removal efficiency by changing the electrostatic state of the competing anions such as sulfate and bicarbonate.

Figure 2.2 compares the pH effect in the range 3-11 at Fe/As 5 and 20. Greater than 95% *As* removal was achieved using a Fe/As of 5 within the pH range of 3 – 6.5. In contrast, using a Fe/As ratio of 20, >95% *As* removal was achieved across the entire pH range. These results suggest that there is an optimal pH range (3 ~ 7) for *As* removal from the spent brine, but an increase in $FeCl_3$ addition will allow for effective *As* removal outside of this optimal range. Although removal at pH < 3 was not tested in this research, it has been shown that *As*(V) removal at many Fe/As molar ratios will decrease significantly at pH < 3 (Wang et al., 2003).

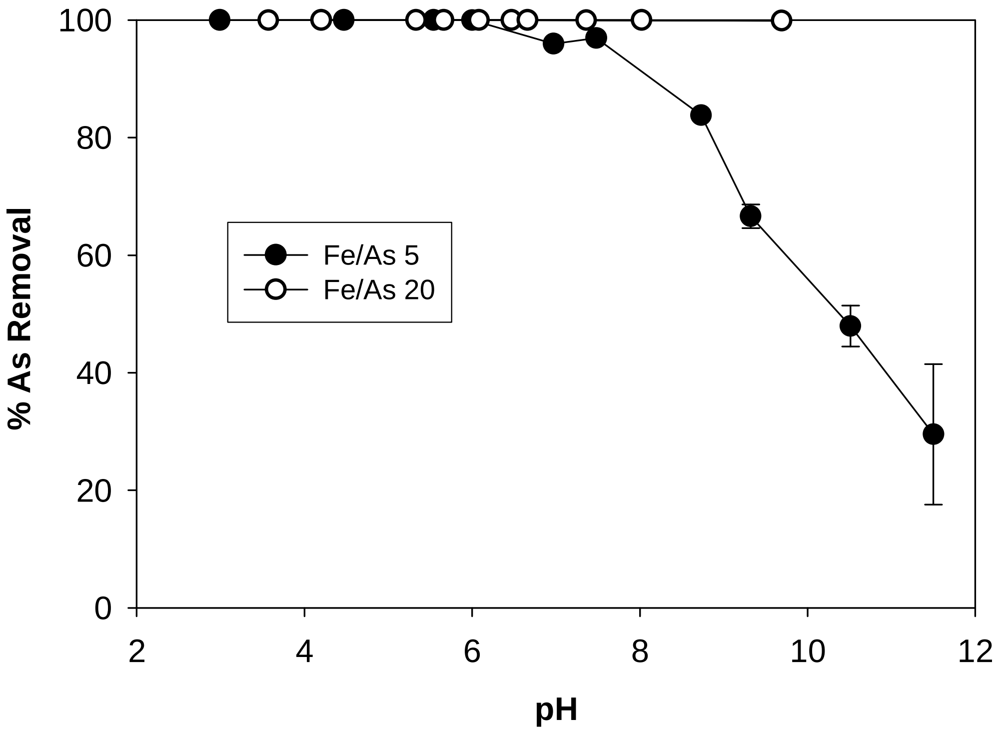

Figure 2.2. Effect of pH on *As* removal. $FeCl_3$ additions were 3.25 g/L (Fe/As 5) and 12.96 g/L (Fe/As 20). pH was adjusted using 1 or 5N NaOH.

The observed optimal pH range in these experiments agrees with those determined by Hering et al. (1996) for *As*(V) removal from drinking using $FeCl_3$ addition. Hering et al. (1996) observed 100% *As*(V) removal between pH 4 ~ 7.5 after which the removal efficiency decreased sharply. This sharp decrease is also observed in figure 2.2 and is attributed to a surface charge reversal on the ferric hydroxide precipitate. As pH increases above the isoelectric point, the surface becomes more negative (Dzombak and Morel, 1990) and electrostatic repulsion of *As* anions begins to ensue. Although the initial conditions differ (*As*(V)=20 μg/L and $FeCl_3$ 4.9 mg/L), the concurring observations between Hering (1996) and this study indicate that the mechanisms that control removal at low *As* concentrations and low ionic strength also prevail in more extreme conditions.

Studies have shown that the addition of Ca^{2+} into the treatment process will increase the removal efficiency at higher pH by either calcium arsenate formation (Bothe and Brown, 1999) or shielding the more negative surface charge. Parks et al. (2003) concluded that enhanced removal in the presence of Ca^{2+} is a result of Ca neutralizing the more negative surface charge of ferric hydroxide at higher pH and/or adsorption of Ca^{2+} forming a 'bridge' to enhance electrostatic interactions with *As* anions. Dzombak and Morel represent this calcium effect in the following manner (1990).

$$FeOH + Ca^{2+} \leftrightarrow FeOHCa^{2+} \qquad (2.2)$$

At pH > 7, the *As*(V) species present in aqueous solution will be $HAsO_4^{2-}$, thus electrostatic interactions between the ferric hydroxide and arsenate anion will occur due to the Ca intermediary.

While calcium addition aids removal in the upper pH range (Bothe and Brown, 1999; Parks, 2003) it was tested for any adverse effects in the optimal pH range for *As* removal (3 - 7). Figure 2.3 indicates that the addition of Ca to the treatment process will not affect the removal efficiency at pH 6.

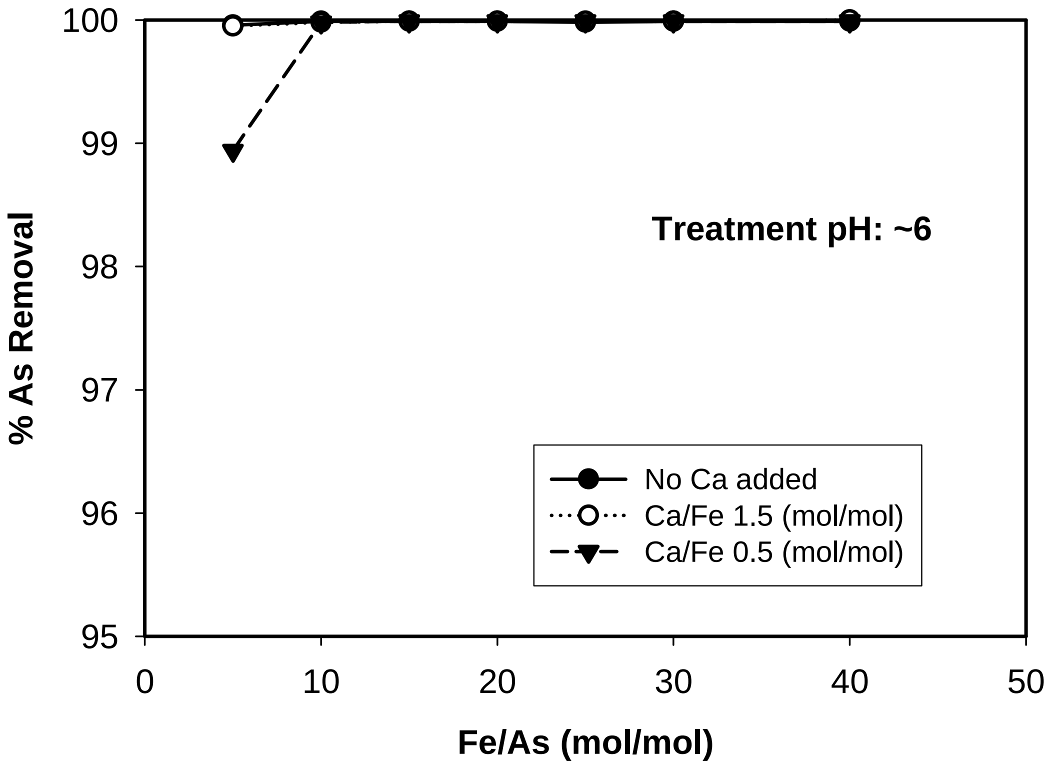

Figure 2.3. Effect of calcium addition on *As* removal. Treatment pH was 6. Fe/As 5-40 was investigated at Ca/Fe molar ratios of 0, 0.5, and 1.5. Notice y-axis scale range is 95 – 100%.

Addition of Ca to the Fe treatment process in the Ca/Fe ratios of 0, 0.5, and 1.5 showed no change in the removal efficiency of *As* from the brine solution. Ca effect on the leachability of process residuals will be discussed later (chapter III).

One very important factor of the treatment process that must be investigated is treatment residence time. What is the optimal period that the treated brine should be left in contact with the ferric precipitates? It has been shown that co-precipitation and adsorption of *As*(V) onto ferric hydroxides is a kinetically fast process (Dzombak and Morel, 1990). However, the kinetically fast equilibrium times for this process have recently been called into question (Zhao and Stanforth, 2001; Zhang and Selim, 2005). Figure 2.4 shows the *As* remaining in the brine after treatment for different periods of time. Both sets of batch tests indicate that aqueous *As* has not stabilized even after 300 days. In both cases, the optimal removal occurs earlier in the treatment process, < 20 days for the 100 mL tests and < 60 days for the 500 mL tests.

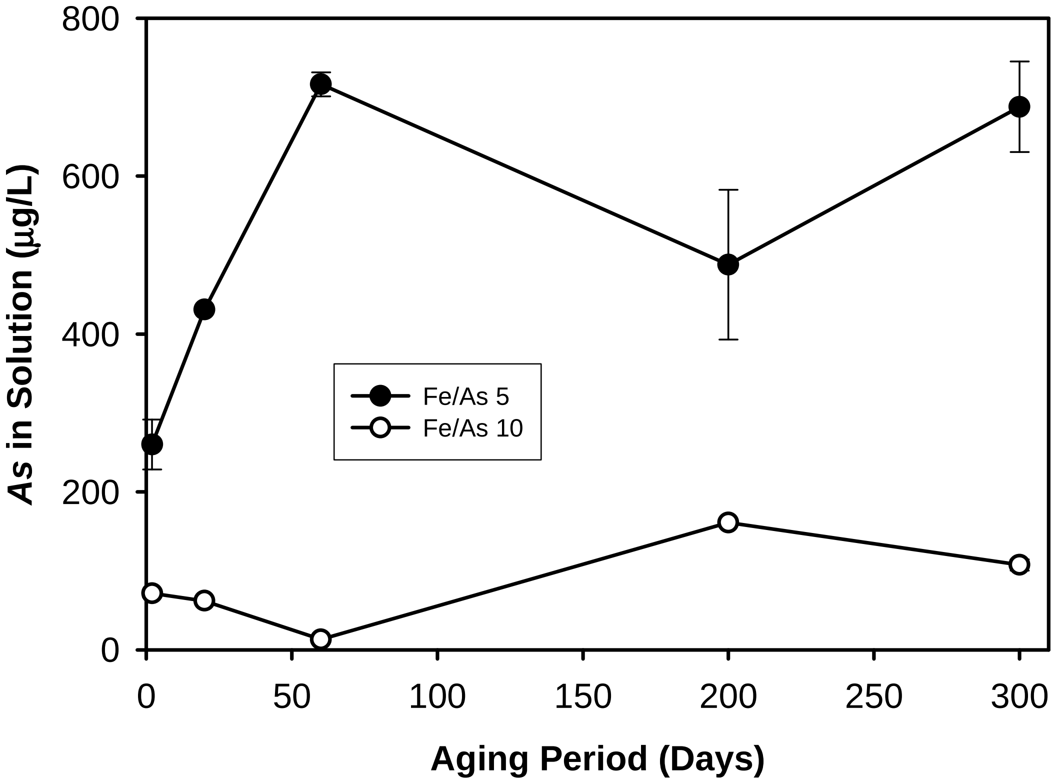

Figure 2.4. *As* removal over time. *As* remaining in solution after 2, 20, 60, 200, and 300 days of aging in treatment batch tests. Filled circles and open circles represent batch tests using Fe/As 5 and 10 respectively. pH ranged from 6 – 7 and 5.5 – 6.3 for Fe/As of 5 and 10 respectively. Note, standard deviation of duplicates for Fe/As of 10 are so small that error bars are not visible.

There were slight variations in pH (5.5~7) in figure 2.4. While pH has been shown to effect removal efficiency, there is no correlation between slight pH variations and changes in *As* removal shown in figure 2.4. Zhao and Stanforth (2001) report similar fluctuations in aqueous *As* and phosphate concentrations. The authors describe a new concept of surface precipitation as a dynamic process. First, non-exchangeable *As* is adsorbed to the ferric hydroxide surface as stable inner-sphere complexes. Next, Fe in solution will adsorb to the newly complexed negatively charged surface of *As* anions. As the soluble Fe drops, equilibrium is lost and more Fe dissolves from ferric hydroxide. This process continues until an amorphous precipitate develops on the ferric hydroxide surface (Zhao and Stanforth, 2001). A dynamic process such as this could potentially account for the results in figure 2.4 but further studies are necessary to determine why equilibrium was not reached after 300 days. These results indicate that the residence time of the brine in the treatment process may be an important factor in achieving optimum removal.

Ferric chloride additions were made to brine containing no *As*, then *As* was added after ferric precipitates had formed allowing surface adsorption to act as the primary removal mechanism. Removal efficiency at different pH was compared to removal profiles for ferric chloride addition to a typical *As*-containing brine at different pH. Both removal profiles were determined using Fe/As molar ratio of 5 (figure 2.5). Greater removal efficiency was observed for ferric chloride addition than adsorption onto pre-formed ferric hydroxide where the Fe/As molar ratios were identical. Figure 2.5 indicates a consistent range difference between adsorption and ferric chloride addition for *As* removed in the pH range 6 ~ 12. This enhanced removal efficiency (up to 40%)

observed for ferric chloride addition to *As*-containing brine suggests that a mechanism supplementing surface adsorption is aiding in *As* removal when ferric chloride is added.

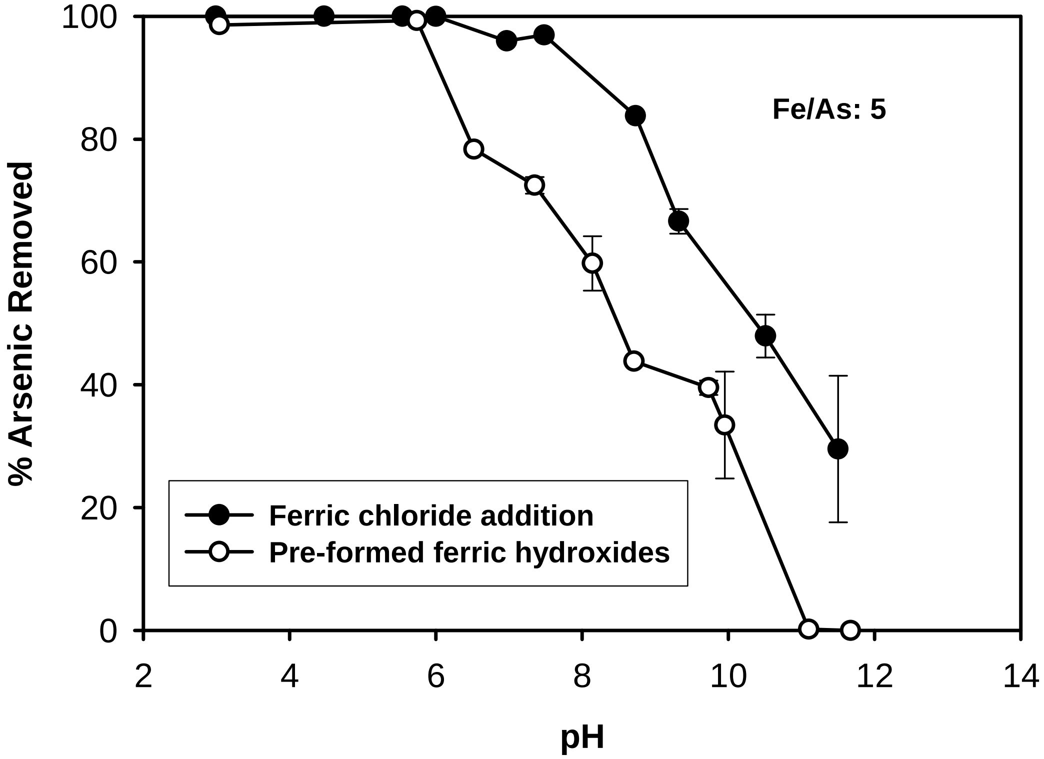

Figure 2.5. Comparing *As* removal by in situ and pre-formed ferric hydroxide. Solution pH is varied from 3 ~ 12. Ferric chloride addition in a Fe/As molar ratio of 5 was used.

These results can be explained by the occurrence of either a supplemental removal mechanism(s) such as precipitation of a Fe-As species or enhanced adsorption. In order to test the first hypothesis x-ray diffraction (XRD) was employed on a powdered sample formed by the addition of $FeCl_3$ in the molar ratio of 15. Figure 2.6 shows the results of the XRD analysis.

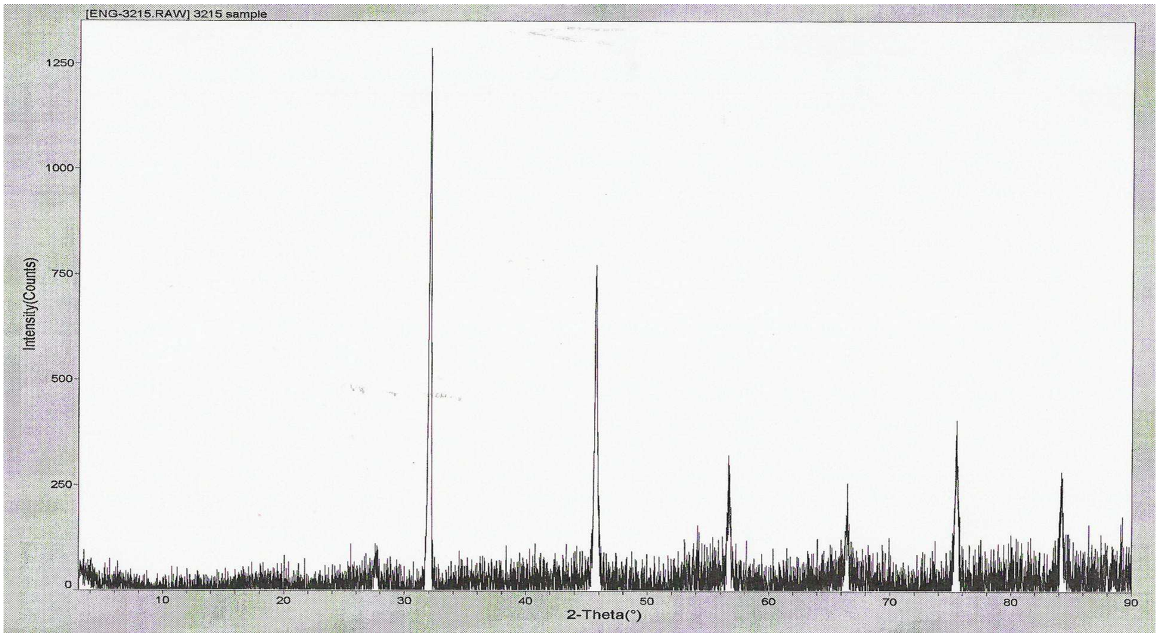

Figure 2.6. XRD analysis of process residuals. Residuals were formed at Fe/As molar ratio of 15 and pH 6.

The peaks observed in figure 2.6 are halite (NaCl) which is a secondary mineral formed during the drying process. No crystalline species are observed other than halite suggesting that the iron precipitates are highly amorphous. Therefore, based on these XRD data, it seems that precipitation of ferric arsenate species is not a mechanism aiding in the removal of *As* from the brine.

The second hypothesis of enhanced adsorption was investigated by Ghurye et al. (2004) when the authors observed a similar trend while studying iron coagulation with drinking water. The authors suggested that during in situ formation of ferric hydroxides, there are more available sites for adsorption as precipitated particles first begin to agglomerate. Pre-formed ferric hydroxide would only have available adsorption sites on the surface of the particles (Ghurye et al., 2004). The primary particles of ferric hydroxide are approximately 5 nm in diameter (Richmond et al., 2004). Arsenate anions in the brine rapidly adsorb to the surface of the ferric hydroxide particles. As a larger precipitate forms the inclusion of *As* and other co-anions within the crystal structure prevent the development of well-ordered crystallization, thus the precipitate remains amorphous as suggested by figure 2.6 (Jessen et al., 2005). Figure 2.7 is a representative diagram of this hypothesis indicating that inclusion of anions into the agglomerating precipitates may account for the enhanced removal efficiency observed in figure 2.5.

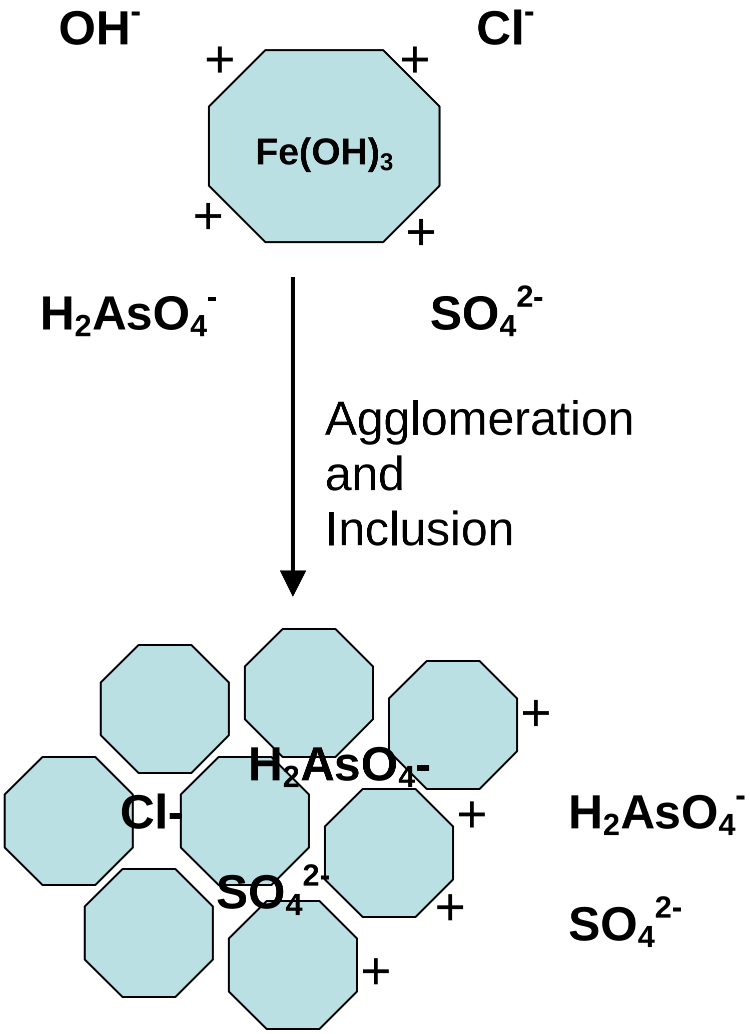

Figure 2.7. Representation of anion inclusion mechanism.

These results and discussion lead to the conclusion that coagulation with $FeCl_3$ is more efficient for removing *As*(V) from brine solution than adsorption onto pre-formed ferric hydroxide as has been previously concluded regarding treatment of drinking water (Cheng et al., 1994; Hering et al., 1999; Ghurye et al., 2004). The optimal pH for the treatment process is 3 – 6.5 and ~100% removal can be achieved using a Fe/As molar ratio as low as 2.

2.3.2 Treated Brine Reuse

Treatment of spent regeneration brine in a cost effective manner that produces a stable *As*-laden residual can become even more efficient if the treated brine can be reused. Upon removal of the *As*-laden precipitate, pH of the three treated brine supernatants were adjusted (table 2.3). The treated brines were then reused for a regeneration run of an exhausted PLE column. Table 2.3 shows the compositions of the three batches of treated brine and the corresponding regeneration efficiency when it was used for regeneration of a PLE resin at pH 9 or 10.

Table 2.1 Properties of three treated brines. pH adjustments were made with NaOH 1N.

Batch #	**Treatment pH**	**Remaining As in Treated Brine (μg/L)**	**Adjusted pH**	**% PLE Capacity Recovery**
1	9	130	9.0	68
2	6	20	9.0	86
3	6	45	10	100

Table 2.1 indicates that the presence of 130 µg/L *As* remaining in the treated brine inhibits the recovery of the arsenate capacity yielding only 68% recovery capacity after 34 bed volumes (BVs). When the concentration of *As* remaining in the brine is reduced to 20 µg/L, the *As*(V) capacity recovery increases to 86%, also in 34 BVs. When the pH of the treated brine is increased to 10, ~100% of the resin capacity was recovered. Figure 2.13 shows nearly all arsenate capacity was recovered using ~ 18 BVs of the treated spent brine initially containing 45 µg/L *As* (An et al., 2005). The treated brine also contained 30 g/L Cl^-, sulfate, and bicarbonate. Note that due to addition of $FeCl_3$, chloride was increased by ~25%, which favors the subsequent regeneration efficiency.

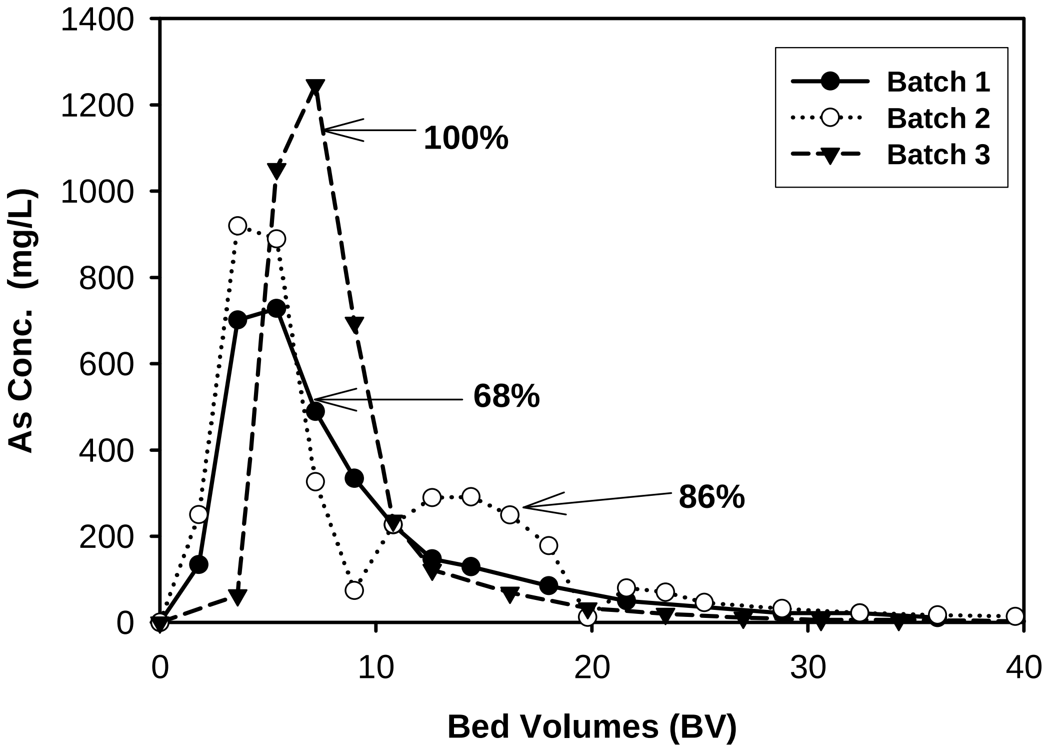

Figure 2.8. Elution histories of regeneration of exhausted PLE using treated brine. Batch 1, 2, and 3, achieved 68%, 86%, and 100% or resin capacity recovery respectively. The specific contents of each batch are available in table 2.3. Note: The sharp dips in batch 3 data have not been repeatable and potentially due to experimental or analytical error.

The ability to reuse the brine had two main advantages: (1) decreased the overall process costs (discussed in chapter IV), and decreased the amount of potentially hazardous treatment waste residuals. Reusing the treated brine reduces the total brine used by 50% on a yearly basis which decreases both the costs of making the brine (NaCl costs) and the costs of treating the brine ($FeCl_3$ and $Ca(OH)_2$ costs).

2.4 Conclusions

The results of this research reveal that multiple parameters affect the optimal conditions for brine treatment. The few available studies regarding brine treatment with ferric chloride seem to overestimate the Fe additions needed efficiently remove brine. Clifford (1999) reported that a Fe/As molar ratio of 13 was needed to reduce an *As* concentration of 90 mg/L to less than 1.5 mg/L. We found that an initial concentration of 300 mg/L *As* could be reduced to <1 mg/L using a Fe/As of 2 at pH 6. Although efficient removal could be achieved at low Fe additions the results were very sensitive to pH at Fe/As < 5. Furthermore, 100% removal was achieved at pH 6, 7, and 9 at Fe/As 10 and greater, making additions in the Fe/As molar ratio greater than 20 costly and inefficient.

An optimal pH of 3 ~ 6.5 was observed for *As* removal from the spent brine. This optimal range is similar to the one determine by Hering et al. (1996) for drinking water treatment. Using a high $FeCl_3$ such as Fe/As 20 allowed for 100% removal across the pH range 3 – 10, indicating that increased Fe addition will decrease the pH sensitivity.

It is clear that ferric chloride addition is a much more efficient means to remove high concentrations of *As* from spent brine. While adsorption onto preformed ferric hydroxide did achieve 100% removal at low pH, the average operating pH of the brine treatment process is circum neutral where adsorption alone was inefficient. For example, at pH ~7 addition of ferric chloride achieved 20% greater removal efficiency than adsorption. We propose that this enhanced removal efficiency is due to increased available surface area as primary precipitates are formed resulting in inclusion the inclusion of anions into the precipitate mass as particles agglomerate. This mechanism was first hypothesized by Ghurye et al. (2004) when similar results were observed during coagulation studies for removing *As*(V) from drinking water.

Finally, treated brine could be reused to recover 100% of resin capacity during regeneration. The most optimal pH for treated brine reuse is 10. Also, the successfully reused treated brine contained 45 µg/L residual *As* indicating that 100% removal of *As* is not entirely necessary for successful reuse. Reuse of treated brine reduces amount of waste produced and reduces costs (chapter IV).

III. MINIMIZING ARSENIC LEACHABILITY FROM TREATMENT PROCESS WASTE RESIDUALS

3.1 Introduction

Arsenic removal technology research recently experienced an increased interest caused by the newly implemented maximum contaminant level (MCL) of 10 µg/L *As*. Studies have indicated that new techniques such as granular ferric adsorptive media (Driehaus, 2004), enhanced coagulation (Ghurye, 2004), and metal-loaded ion exchange resins (Dambies, 2004; An et al., 2005) provide for the removal of aqueous *As* below the new MCL under a variety of initial raw water conditions and co-contaminant concentrations. The focus on Arsenic treatment is now shifting downstream to the waste products such as spent adsorptive media, brine treatment residuals, and *As*-laden residuals from coagulation processes.

Recent literature indicates that there is a need to further study the interactions/reactions that occur with treatment residuals in their disposed environments such as landfills and lagoons. Current methods of testing the leachability of drinking water treatment residuals are in question. Ghosh et al. (2004) argued that the commonly used EPA Toxicity Characteristic Leaching Procedure (TCLP) does not simulate true landfill conditions. Furthermore, the authors suggested that the TCLP underestimates the leachable *As* from solid residuals under certain common landfill conditions such as alkaline pH and low redox potential (Ghosh, 2004). The presence of calcium has been shown to further immobilize *As* at high pH (Parks et al., 2003; Bothe and Brown, 1999). Jing et al. (2005) studied the leachability of treatment adsorbents such as, granular ferric hydroxide (GFH) and granular ferric oxide (GFO), and observed that leaching of *As* was lowest at pH 5-7. Due to the widespread use of IX and the recent successes of metal-loaded polymer technology for *As* removal, we believe that similar stability profiles are necessary for disposal of *As*-laden solids from treatment of spent regeneration brine.

Currently, the waste residuals from water treatment processes are subject to leaching tests such as the EPA toxicity characteristic leaching procedure (TCLP) and waste extraction test (WET) in California. These leaching tests determine if the waste is characterized as non-hazardous. The current limit for both the TCLP and WET is 5 mg/L *As* in the extraction fluid. Historically this limit is set at 100 times the MCL. A subsequent tightening of the TCLP and WET limits in response to the new MCL will cause facilities to consider treatment technology that not only removes *As*, but also results in a low volume and stable waste residual.

Ferric hydroxides are known to undergo significant structural changes over time as the crystal structure releases water in order to achieve a more thermodynamically stable state (Dzombak and Morel, 1990). New ferric hydroxide is amorphous, porous, and has a high surface area (Sorensen et al., 2000). It is metastable in this form and eventually morphs into a more ordered crystalline structure, usually goethite, hematite, or magnetite (Sorensen et al., 2000). The more crystalline forms have a decreased bonding site density and may release sorbed anions (Dixit and Hering, 2003). Understanding how these changes will affect *As* mobility is critical.

Our objectives were to: (1) develop a brine treatment process that will maximize the stability of the solid, *As*-laden waste product; (2) determine the effect of aging on As leachability from waste residuals; and (3) reveal the mechanisms that govern As leachability in the disposal environment.

3.2 Methods

Spent regeneration brine (SRB) was prepared in the same manner discussed in chapter II. Brine was treated using ferric chloride addition under different conditions outlined below. Resulting precipitates were air-dried or oven-dried, crushed with a mortar and pestle, and subjected to either the TCLP or WET leaching procedures.

3.2.1 Leaching Tests

Three tests were used to assess *As* leachability and thus relative stability of the *As*-laden solid residual: The TCLP, TCLP-ext (extended), and WET.

1) TCLP was preformed according to EPA method 1311. In brief, 1 g of solid sample and 20 mL of TCLP fluid #1 were placed into scintillation vials. TCLP fluid #1 was made by adding 5.7 mL glacial CH_3CH_2OOH and 64.3 mL of 1 N NaOH to 500 mL DI water and diluting to 1 L with DI water. The final pH of the solution was 4.93±0.05 (EPA, 1992). The vials were placed on an end-over-end mixer and mixed for 18±1 hours to allow for extraction equilibrium.
2) TCLP-ext was preformed by modifying EPA method 1311. In this case, the extraction period of this procedure was modified from 18±1

hours to 30±1 hours. The extraction period was extended in an effort to reach equilibrium between sample and extraction fluid.

3) WET was performed following the method prescribed by the California Department of Health Services (SOP No. 910). In brief, a citrate buffer extraction solution was prepared and purged with nitrogen gas. The 0.2 M citrate solution was prepared by dissolving 42.0 g monohydrate citric acid in 950 mL of DI water. The solution was titrated to pH 5 with 50% NaOH and diluted to 1 L with DI water (California Code of Regulations, 1985). WET solution was purged with nitrogen gas for 30 minutes to simulate an anoxic environment. Dry *As*-laden sludge samples were placed in 25 mL scintillation vials. The sample to extraction solutions ratio was 1:10 (1 g sample to 10 mL solution). All samples were prepared by the same procedure with duplicates and an extraction period of 48 hours. Some headspace was left in the scintillation vials. The WET is reported to be a more stringent test with ferric hydroxide residuals because the citric acid solution is a stronger complexing agent than the TCLP acetic acid solution and because WET extraction is carried out in an anoxic environment.

The EPA method 3050B was used to determine the total Fe and *As* content of the treatment residuals. The method consists of acid digestion with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Digestates were diluted and analyzed using a Perkin Elmer GF-AA.

3.2.2 Iron and Calcium Effect

The effect of Fe and Ca addition on the leachability of *As* was studied using 500 mL batch tests. Larger batch tests were used in order to produce ample precipitates for multiple leaching tests. Fe was added to SRB in the Fe/As molar ratio of 5, 10, 15, and 20. The resulting precipitates were dried and pulverized with a mortar and pestle. Leaching tests (section 3.2.1) were performed to determine the leachable *As* under each condition. Calcium hydroxide was added to the $FeCl_3$ treatment process, where Fe/As 15 was used, in the amounts of 0, 30, 90, 150, and 210 mM Ca.

The optimal conditions of the treatment (*As* removal) process do not necessarily correspond to the conditions minimizing *As* leaching from the ferric hydroxide precipitate. Using a Fe/As 10, 500 mL batch experiments were performed where the pH of the treatment process was 3.6, 6.3, 9.4, and 12.1. The effect of pH on leachable *As* was determined by the WET.

3.2.3 Wet Aging

500 mL samples of SRB were placed in 1 L Nalgene bottles. $FeCl_3$ in the Fe/As molar ratio of 10 was then added to each bottle. The bottles were placed on a gang mixer for 2 hours and allowed to settle for 1 hour. pH was adjusted to ~6.5 using 5.0 N NaOH. Bottles were mixed again and allowed to settle. Samples were placed in a hood at 25º C and allowed to age for 2, 20, 60, 200, and 300 days. At the end of the aging period the treated brine pH was recorded and ~10 mL (plus duplicate) of treated brine were removed for analysis. The remaining treated brine was removed and the sludge was moved to a

200 mL bottle. The 1 L bottle was washed with about 10 mL of treated brine and the solution added to the new bottle. The samples were then centrifuged at 2000 rpm for 10 minutes. The supernatant was removed and the sludge allowed to air dry for 14 days. After drying period, WET was performed on the residuals to determine relative stability. After a 14 day air-dry period, samples were allowed to continue dry aging in an open-air laboratory environment.

3.2.4 Dry Aging

Batch tests were prepared using Fe/As molar ratios of 5, 10, 15, and 20. Also batches with Fe/As 15 containing 30, 90, 150, and 210 mM Ca^{2+} were prepared. These Ca-addition batches were made using $Ca(OH)_2$. pH was adjusted to ~6 using 5 N NaOH. The mixtures were aged for 5 days. After the 'wet' aging period, two 10 mL samples of the supernatant were removed and analyzed for total *As* using a Perkin Elmer GF-AA. The rest of the supernatant was removed. Remaining precipitates were transferred to 250 mL bottles and centrifuged. Finally, precipitates were placed in a hood at ~25^{o} C and allowed to air dry. It was determined by weighing the samples daily that the Fe-precipitates reached a drying equilibrium after 14 days. Precipitates were then pulverized with a mortar and pestle. Leaching tests were performed to determine the leachable *As* after air drying periods of 14, 42, 70, and 98 days.

3.2.5 Temperature Effects

The affects of oven drying on *As* leaching were investigated. Fe/As molar ratios of 10 and 20 were used to prepare residuals. The pH was adjusted to ~6 and precipitates were allowed to settle and ‘wet’ age for ~5 days. Following the removal of the treated brine, the precipitates were centrifuged, transferred to aluminum foil trays, and dried in an oven at 105º C. After 6 hours the dried precipitates were pulverized with a mortar and pestle and returned to the oven. WET was applied to dried residuals after 1, 20, and 40 days of aging in the oven. In order have a control test from the same batch test, approximately 2 g of wet sludge was removed from the residuals before being placed in the oven. This removed portion was allowed to air dry for 20 days and tested with the WET. Comparing *As* leaching in an air-dried and oven-dried sample after the same amount of time and from the same batch will aid in determining the factors controlling *As* mobility.

3.3 Results and Discussion

3.3.1 Stabilizing Process Waste Residuals

As environmental regulations become increasingly stringent, the cost for handling and disposal of water treatment process waste residuals is becoming an increasingly important issue. For the PLE-based technology to be viable, the volume of the final process waste that leaves the plant must be small and the *As* leachability must be minimal. Determining the proper amount of adsorbent/co-precipitant necessary for removal may be quite different from the amount required to ensure a stable and disposable end product.

Figures 3.1 and 3.2 indicate that as amount of Fe added to the treatment process increases, the stability of the waste residual also increases. In figure 3.1, increasing the Fe/As molar ratio from 5 to 15 results in a 96% decrease in the *As* leached by the WET

(675.2 mg/L and 21.2 mg/L at Fe/As 5 and 15 respectively). Increasing the Fe/As to 20 results in 4.85 mg/L *As* extracted which passes the WET limit of 5 mg/L for *As*. Figure 3.2 shows a similar trend with the TCLP test where residuals formed even at relatively lower Fe additions (Fe/As of 5) easily pass the TCLP limit also 5 mg/L *As*.

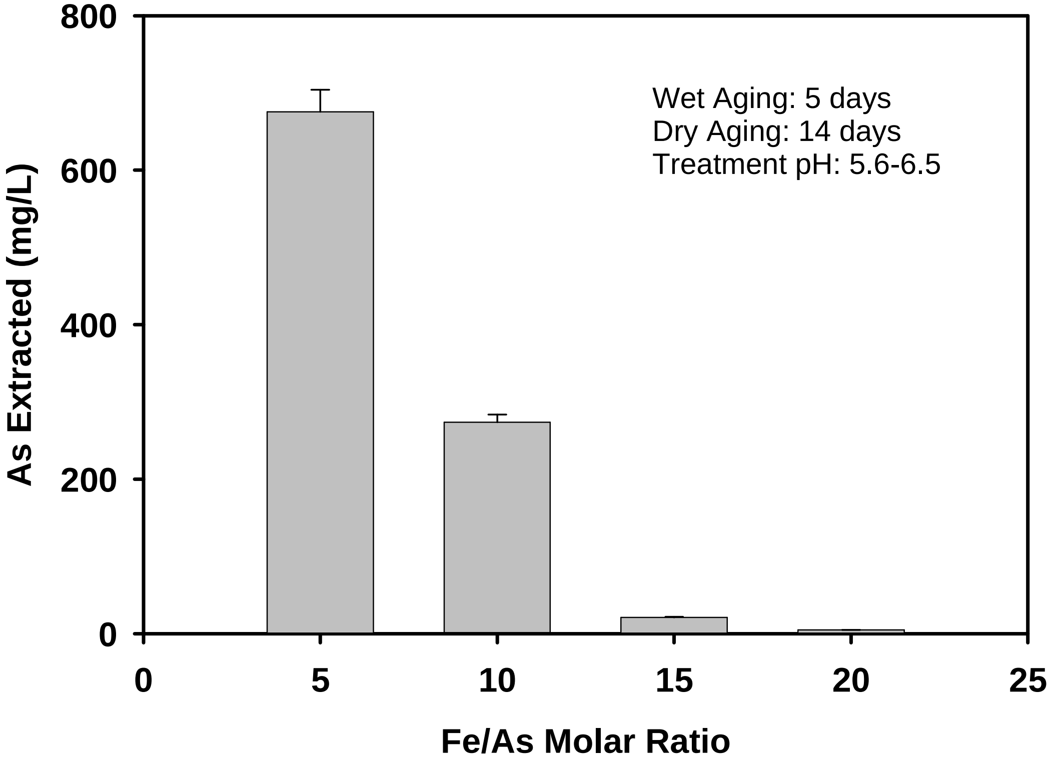

Figure 3.1. Extracted *As* by WET at different Fe/As molar ratio. Bars represent mean of duplicate Waste Extraction Tests indicating As extracted at Fe/As of 5, 10, 15, and 20. Error bars indicate standard deviation of duplicate tests. The sludge was air dried for 14 days before WET was employed.

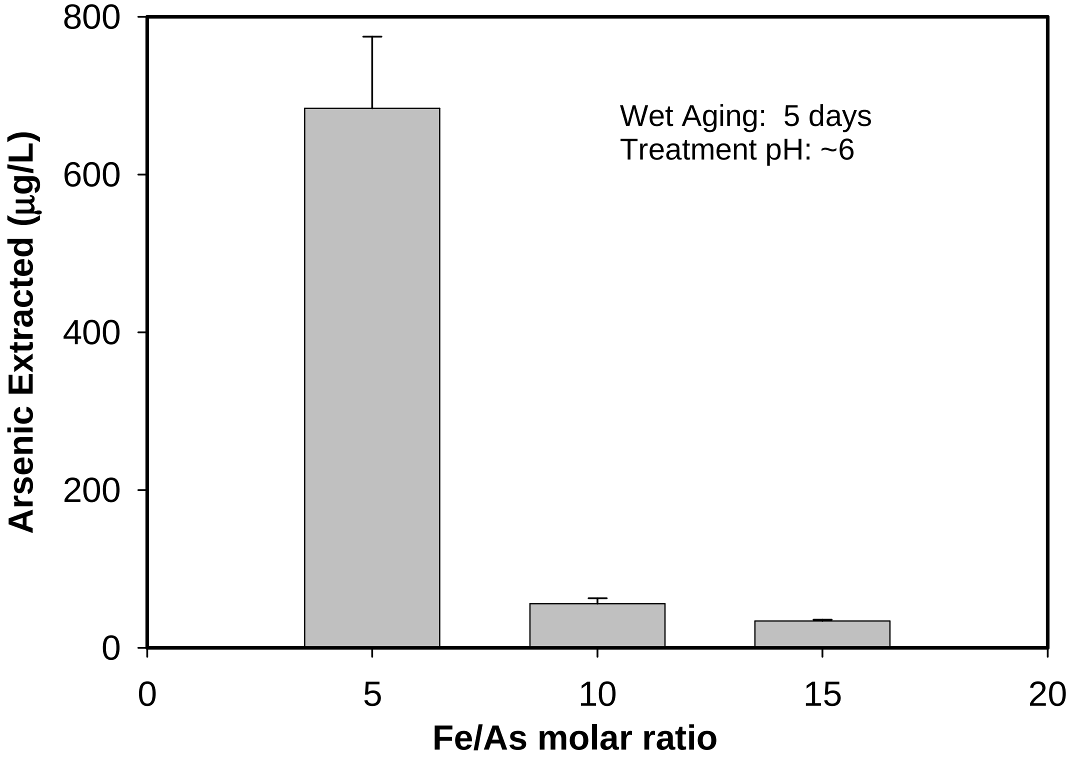

Figure 3.2. Extracted *As* by the TCLP-ext at different Fe/As molar ratio. Error bars indicate standard deviation of duplicate tests.

At a Fe/As of 5 the TCLP-ext resulted in ~0.7 mg/L *As* extracted. When compared to the 675 mg/L *As* extracted with the WET, it is evident that the WET is a much more stringent extraction procedure and therefore is used for the duration of this study as a means to compare the different parameters in sludge stabilization.

As previously mentioned, calcium has been reported to decrease the mobility of *As*(V) from ferric media (Bothe and Brown, 1999; Parks et al., 2003; Jing et al., 2003; Jing et al., 2005). Calcium as $Ca(OH)_2$ was added at 0, 30, 90, 150, and 210 mM Ca to the treatment process where an Fe/As of 15 was used. Figure 3.3 shows that Ca addition of 30 mM decreases leachable *As* by 80 and 41% in the TCLP and TCLP-ext respectively. Figure 3.4 exhibits that the addition of Ca, in a particular range, will further stabilize the ferric residual according to the California WET. Addition of 90 mmol/L Ca (6.66 g/L $Ca(OH)_2$) decreases the leachable Arsenic by 80%. Furthermore, using 90 mmol/L of Ca reduces the leachability so that the solid residual passes the WET test limit of 5 mg/L *As*.

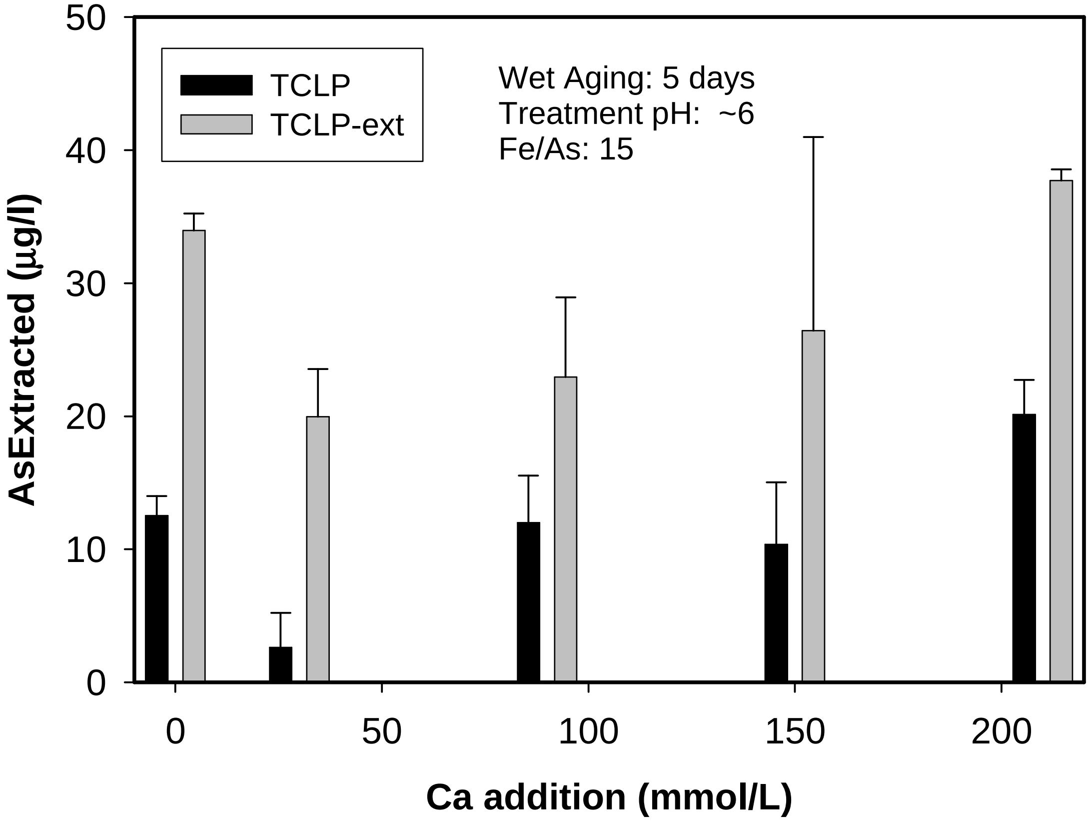

Figure 3.3. Calcium effect on extractable *As* by TCLP and TCLP-ext. Ca additions were 0, 30, 90, 150, and 210 mM. Fe/As was fixed at 15 (9.73 g/L $FeCl_3$).

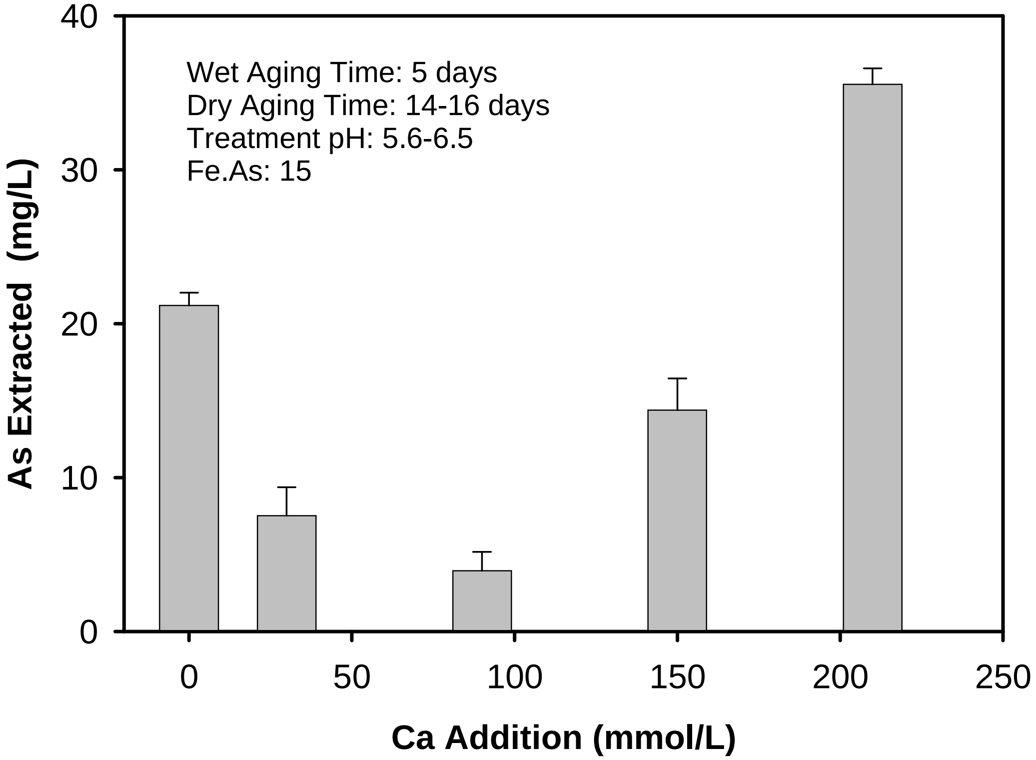

Figure 3.4. Calcium effect on extractable *As* by WET. Calcium was added at 0, 30, 90, 150, and 210 mM via $Ca(OH)_2$. The Fe/As used for treatment was 15.

All calcium addition batch experiments were performed using a treatment pH of 5.6 – 6.5. The previously discussed mechanisms, described by Parks et al. (2003) that increase the removal efficiency at high pH will be inactive at circum neutral pH levels (i.e. neutralizing a more negative surface charge). The pH environment of these tests is slightly acidic, yet decreased leachability is observed with Ca addition in a certain range. This optimal Ca addition is followed by an increase in extractable *As* as Ca addition increases. This further stabilization at sub neutral pH (Ca addition: 30 – 90 mM) may be a function of how the Ca is added to the treatment process. Parks et al. (2003) added Ca via lime to mixtures containing pre-formed ferric hydroxide residuals. It was found that the addition of lime decreased *As* leachability in the WET at pH > 11 (Parks et al., 2003). The authors did not observe a decrease in leachable *As* at circum neutral pH. In contrast, we observed a decrease in leachable *As* (WET) of 80% when Ca was added 90 mM at pH 6.4. However, when 210 mM Ca were added extractable *As* increased by 40% from samples where no Ca was added. The main difference in our procedure and the procedure used by Parks was that $Ca(OH)_2$ was added simultaneously with $FeCl_3$. We propose that the observed optimum range of increased stability of the ferric hydroxide was not a surface mechanism as observed in Parks et al. (2003) but a result of available Ca during primary precipitation of the ferric species during the treatment process. We investigated three hypotheses potentially explaining the observed optimal range of Ca reducing *As* leachability: water content will reduce *As* leached, formation of calcium arsenate or some other new precipitate may increase stability, and calcium may react with citrate in the WET reducing the effective strength of the extraction solution.

If water content retained after air drying increases at Ca addition of 90 mM, the effective amount of residual in the extractions test will be reduced thus reducing the potential *As* leached. Residuals were considered “dry” once no further change in mass was observed during air drying. On average, this point was achieved in 10 – 12 days. In order to determine the water content of these residuals, they were air dried for 14 days, weighed, and then placed in an oven at 105º C and weighed again after 6, 48, and 240 hours. No significant change in mass was observed after the first 6 hours of oven drying. Table 3.1 exhibits the water content (mass basis) of the samples used in the Ca addition experiments. Table 3.1 indicates that water content increases as Ca addition increases and does not correlate to the optimal range in *As* leachability observed in figure 3.4.

Table 3.1 Water content Mass removed after oven drying at 105º C.

Sample	**Fe/As**	**Ca Addition (mM)**	**Water Content (%)**
17-200	15	0	7.52
Ca1	15	30	9.99
Ca2	15	90	12.57
Ca3	15	150	12.59
Ca4	15	210	14.76

XRD was employed on a powdered sample formed by an Fe/As molar ratio of 15 and Ca addition of 90 mM (6.67 g/L $Ca(OH)_2$). In figure 3.5 the distinct peaks are due to halite (NaCl) which was a secondary mineral formed during drying. No peaks above background noise indicate the crystalline structure of ferric or calcium minerals. Therefore, we cannot conclude that the formation of calcium precipitates are decreasing leachable *As* in the observed optimal range.

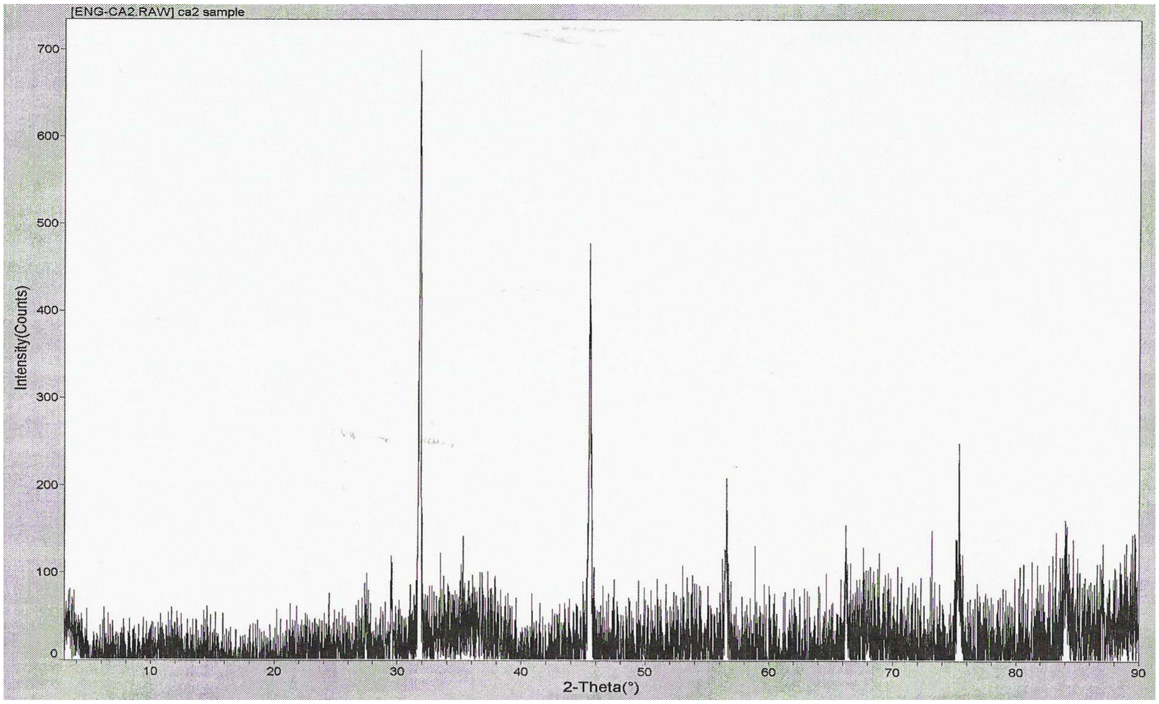

Figure 3.5. XRD results of residuals formed with Fe and Ca addition. Fe/As molar ratio was 15 and Ca addition was 90 mM ($Ca(OH)_2$ = 6.67 g/L).

Our final hypothesis is that Ca enhances stability because of its interactions with the extraction solutions of the TCLP and WET. A white precipitate was formed during the WET for samples treated with Ca additions (figure 3.6). However, no such precipitate was noticed forming in the TCLP test. Spectroscopic studies are necessary to characterize the white precipitate formed during the WET, but preliminary investigations using visualMINTEQ for chemical equilibrium modeling of this situation suggests that both calcium citrate ($CaHC_3H_5O(COO)_3 \cdot 4H_2O$) and calcium arsenate ($Ca_3(AsO_4)_2$) may be forming.

Figure 3.6. Photograph of solid residuals after WET. Sample on left had no Ca addition while calcium was added as 90 mM Ca (6.67 g/L $Ca(OH)_2$) to the sample on right. Note the yellow-white precipitate present in the sample on right but not on left. Most of the extraction solution has been removed for analysis from the two vials.

Citrate is a triprotic acid and its speciation is based on the following pKa values, 3.1, 4.8, and 6.4. (Dean, 1992). The pH of the WET solution is adjusted to 5 therefore we can assume the citrate will be present as $HC_3H_5O(COO)_3^{2-}$. Citrate in this form will complex with Fe^{3+} and Ca^{2+} by the following reactions (Dean, 1992):

$$Fe^{3+} + HC_3H_5O(COO)_3^{2-} \leftrightarrow FeHC_3H_5O(COO)_3^{+} \quad \log K_{sp} = 12.5 \tag{3.1}$$

$$Ca^{2+} + HC_3H_5O(COO)_3^{2-} \leftrightarrow CaHC_3H_5O(COO)_3^{o} \quad \log K_{sp} = 4.68 \tag{3.2}$$

The reaction equilibrium constants (K_{sp} values) indicate that citrate will more readily complex with Fe^{3+}, but this can only occur if Fe^{3+} is available. We propose that the Ca addition to the treatment process forms soluble surface precipitates on the ferric hydroxide allowing it to be more available for dissolution and complexation during the WET. Calcium, in effect, dilutes the extraction power of the WET solution by complexing with the citrate. This mechanism may account for the decrease in *As* leachability at Ca addition 30 – 90 mM.

As Ca addition is increased (150 – 210 mM) more leachable *As* was observed. Using mass balance it was determined that Ca constituted 2 and 8% of the total weight of the solid formed at additions of 90 and 210 mM respectively. In general, Ca precipitates are more soluble than Fe precipitates (Paktunc et al., 2003). It is possible that increasing the total amount of Ca in the solid formed would increase the solubility of the residual thus releasing more *As* during extraction tests. This explanation is strictly hypothesis and more studies of these Ca-supplemented residuals are necessary to understand the true mechanisms governing *As* extractability.

Solution pH greatly affects the *As* solubility in the disposal environment. Both very acidic and alkaline pH tends to decrease the concentration of *As* sorbed to ferric hydroxide and oxide precipitates (Dzombak and Morel, 1990; Hering et al., 1999; Parks et al., 2003; Ghosh et al., 2004; Jing et al., 2005). Previous experiments have indicated that pH 3 ~ 7 is the optimal range for *As*(V) removal from the brine solution (figure 2.2). Here, the effect of treatment pH on *As* leachability was explored. Once *As* removal is achieved, the treated brine is removed from the iron-precipitate and prepared for reuse. The residuals are air-dried in most cases and disposed in landfills barring that they are characterized as non-hazardous. In many cases the dried residuals are reintroduced to an aqueous environment in the landfill as leachate comes into contact with the disposed *As*-laden residuals. The following results describe how the treatment pH of the brine-precipitate mixture will affect the leachability of *As* determined by the WET. Residuals exhibited decreased *As* leachability as the treatment pH was increased. Figure 3.7 shows that increasing the treatment pH will decrease the *As* leached from the air-dried solid residuals during WET. These results are counterintuitive because it has been shown that as pH increases desorption of *As* from ferric hydroxide surface will also increase (Parks et al., 2003; Jing et al., 2005).

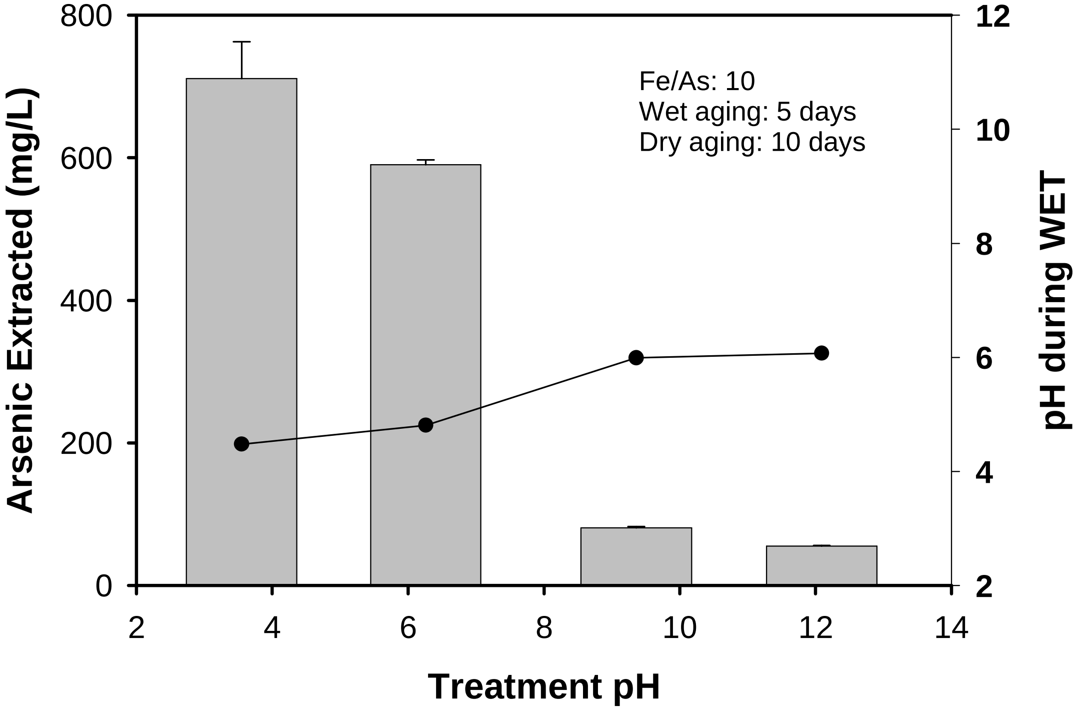

Figure 3.7. As extracted by WET at different treatment pH. pH 3.6, 6.3, 9.4, and 12.1 were used during brine treatment with a Fe/As of 10. Right-hand y-axis shows pH measured at the completion of WET.

It should be noted that treatment pH will be quite different from the pH of the mixture during the WET extraction procedure. The pH of the WET extraction fluid is set at 5. The right-hand y-axis in figure 3.7 shows the pH at the end of the WET. This pH will control sorption and dissolution during the extraction process. Table 3.2 shows the pH of the batch mixture during treatment with $FeCl_3$ and the final pH of the mixture after the WET fluid was mixed with the dried sludge for 48 hours. Clarifying the relationship between the treatment pH and pH during leaching tests will aid utilities in determining the optimal pH for their processes promoting the most stable residual.

Acid digestion of the residuals using the EPA method 3050B revealed that the total *As* present in the residuals formed at four different pH was about the same for each dried sample, ~30 mg/g (28-33 mg/g). The four samples were formed using the same Fe/As molar ratio of 10. Measuring the total *As* and Fe as well as the WET extracted *As* and Fe concentrations revealed that increasing the pH of the treatment mixture before drying the residual decreased both the extractable *As* and Fe. This positive correlation between increased *As* and Fe at lower pH suggests that the *As* leachability in this pH range (4.5 ~ 6.0) was controlled by Fe oxyhydroxide dissolution (complexing with citric acid) rather than desorption. Furthermore, the final pH of WET procedures never increased above the isoelectric point for ferric hydroxide which also indicates that desorption may not be a major factor. Figure 3.8 indicates that the extracted fraction of both *As* and Fe decrease with increasing pH. The extracted *As* fraction shows an 85% decrease when the treatment pH is increased from 6.3 to 9.4 (WET pH 4.8 to 6.0) while extracted Fe fraction shows a 35% decrease.

Table 3.2. Comparison of Extracted As and Fe at different pH. Note the low mass balance for residual treated at pH 12.1.

Treatment pH	**Dry Aging (days)**	**Final WET pH**	**WET Extracted *As*/ Total *As* (3050B)**	**WET Extracted Fe/ Total Fe (3050B)**	**Mass Balance on *As* (%)**
3.6	10	4.48	0.25	0.73	96.6
6.3	10	4.81	0.21	0.63	95.0
9.4	10	5.99	0.03	0.41	99.7
12.1	10	6.07	0.02	0.25	51.0

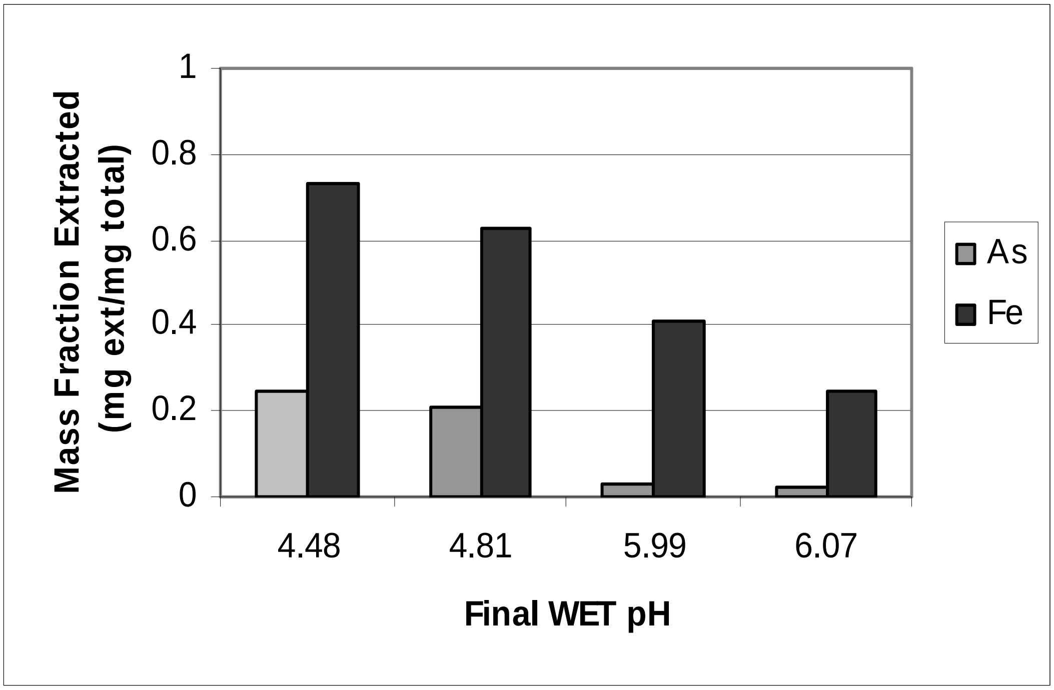

Figure 3.8. Comparing extracted fraction of *As* and Fe. Mass extracted is shown as mass (mg) *As* or Fe extracted during WET divided by mass (mg) *As* or Fe measured after acid digestion.

These results suggest that the iron precipitates are more stable during the WET when treated at a higher pH. This is a product of the pH changes that occur during the WET. Although the final pH of the WET procedures were close in range (4.48-6.07; table 3.2) we observe that the two samples with pH > 5 have decreased leachability. These results coincide with observations of Jing et al. (2005) who concluded, after examining *As* desorption from five different adsorbents, that *As* desorption is a minimum at pH 5 to 7.

3.3.2 Aging Effect

Many drinking water treatment facilities use ferric chloride ($FeCl_3$) coagulation to remove (or reduce) *As* from source water. It is estimated that these utilities will produce millions of tons of *As*-bearing residuals annually (Frey, 1998). These residuals are commonly placed in large holding ponds for accumulation and dewatering, and often reside for multiple years before being disposed (Meng et al., 2001). Investigating how *As* will behave while these slurries age is important from both an environmental health and process design standpoint. If aging increases *As* mobility then the sludge may be characterized as a hazardous waste, greatly increasing transport and disposal costs.

Understanding aging effect on brine treatment residuals is even more important because the residuals are commonly more concentrated than drinking water treatment residuals. Meng et al. (2001) reported *As* concentrations in sludge from drinking water treatment plants 0.6 to 1.5 mg/g. Brine treatment commonly produces residuals containing 25-35 mg/g *As* concentrations. Figure 3.9 indicates that *As* leaching as measured by the WET decreases with increased aging. A 60% decrease in extracted *As* was observed between 2 and 300 days of aging.

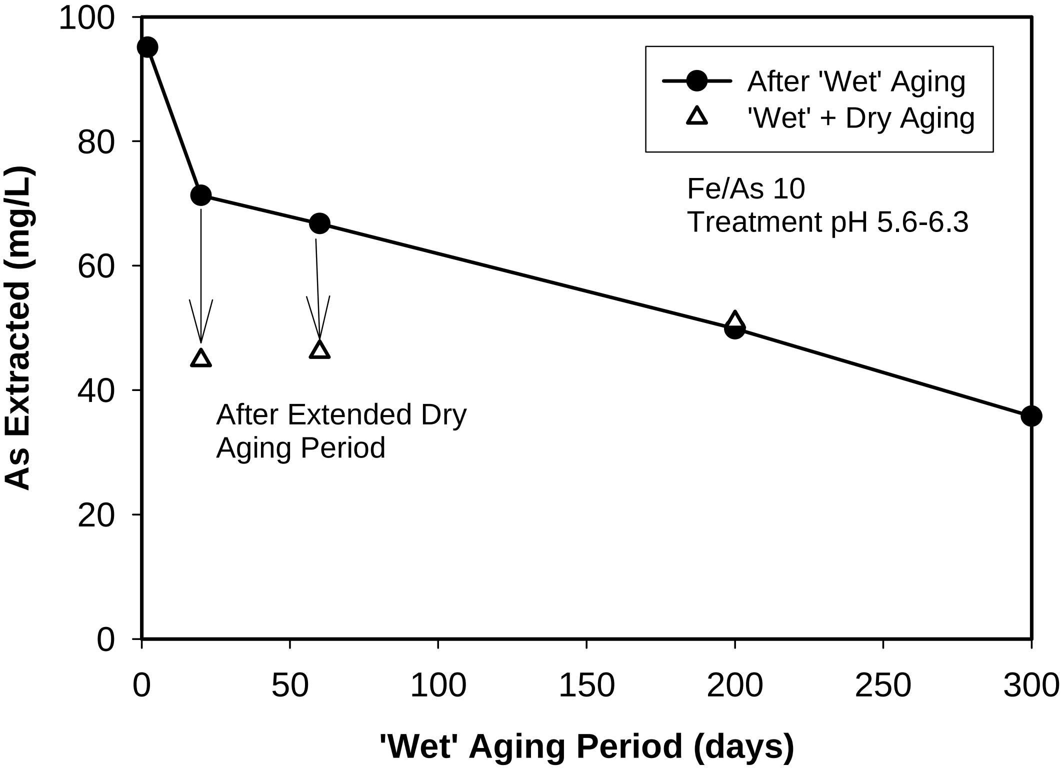

Figure 3.9. Effect of batch aging on extractable *As*. Note that all unfilled triangles denote the extracted *As* after a total of 300 days. Samples aged for different times in situ (as specified on x-axis) but were allowed to continue aging in open air conditions (triangles).

In order to determine if there is a difference between aging in situ (‘wet’ aging) and dry aging in an open air environment, the residuals were kept in open plastic trays after their initial WET. Therefore, at then end of 300 days, all residuals had aged for approximately 300 days (i.e. wet aging + dry aging = 300 days). The WET was again employed on the samples at this point and the results are shown as the unfilled triangles in figure 3.9. We observed a flattening of the slope indicating that all samples have approximately the same *As* leachability after 300 days regardless of fraction of wet to dry aging. These results suggest that aging in general is an important factor in *As* leaching, but the relative wet and/or dry aging is less significant.

It is well documented in literature that the increased aging time increases *As* adsorption onto iron containing soils and media (O’Reilly et al., 2001; Zhang and Selim, 2005) and decreases *As* desorption (Lin and Puls, 2000). Over time *As* anions must develop more stable complexes with the ferric hydroxide particle. Zhao and Stanforth (2001) studied arsenate and phosphate competitive adsorption and concluded that primary adsorbed *As* is non-exchangeable while exchangeable *As* resides in an amorphous surface precipitate. It is probable that over time *As* diffuses from this surface precipitate to internal bonding sites forming more stable inner sphere complexes that decrease desorption as well as extractable *As*.

Figure 3.10 shows changes in extractable *As* with respect to dry aging period. Samples at Fe/As of 10, 15, and 20 all exhibit decreased extractable *As* with time as described in figure 3.1. In contrast, residuals formed with a Fe/As of 5 exhibit the extractable *As* increasing by approximately 30% between 14 and 98 days aging.

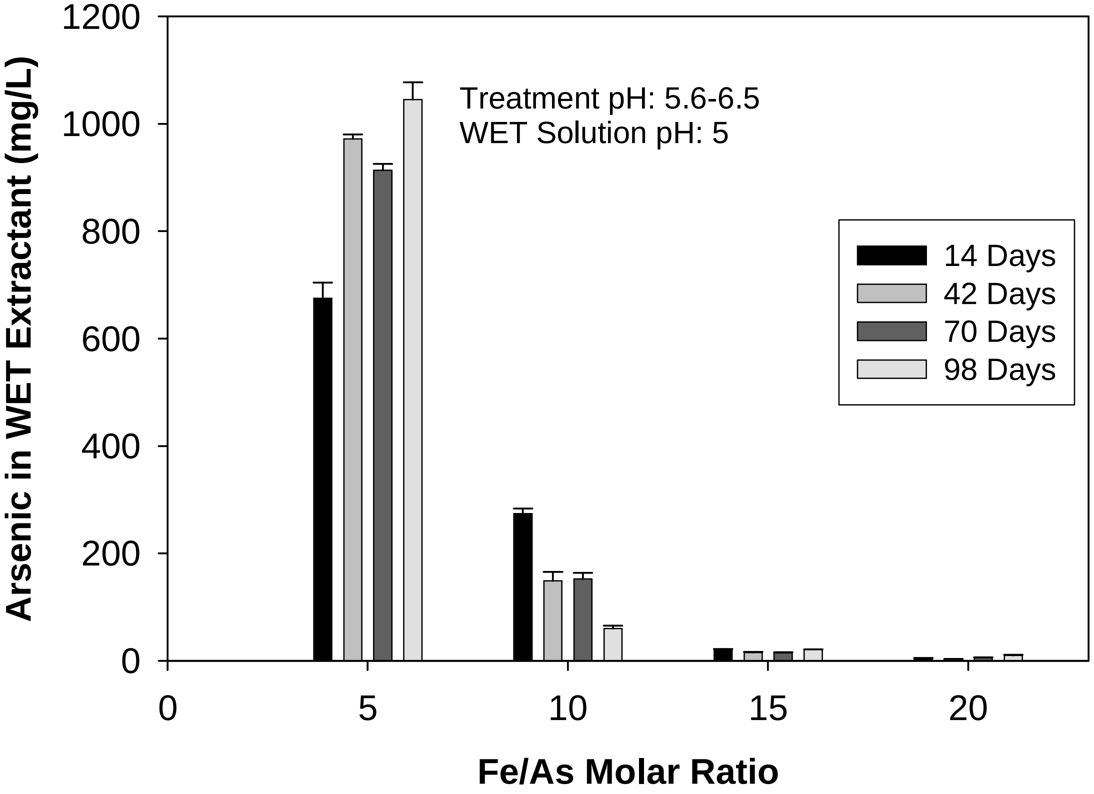

Figure 3.10. Extractable *As* at different dry aging periods and Fe/As. Fe/As of 5, 10, 15, and 20 were used.

All conditions were controlled where the only difference was Fe addition. Richmond et al. (2004) reported a novel idea of considering supersaturation ratios (S) along with pH and Fe/As for observing *As* removal. Supersaturation is described by the following equation (Richmond et al. (2004):

$$S = \frac{c}{c^*} \tag{3.1}$$

Where, c is the concentration of the solute and c* is the equilibrium solubility of the solute. The authors reported that decreasing the supersaturation ratio will increase the order of crystallinity in the ferric hydroxide or ferrihydrite (Richmond et a., 2004). Many researchers have determined that increased order of crystallinity in ferric hydroxides results in more mobile *As* (Dixit and Hering, 2003; Jessen et al., 2005). It is probable that due to the lower Fe addition in the sample with a Fe/As 5, the supersaturation ratio was lower than the samples with higher Fe additions. Thus, a more ordered ferric hydroxide may have been formed, as suggested by Richmond, and continued to crystallize with time, resulting in the increase extractable *As* (figure 3.10).

In contrast to residuals formed with different Fe addition, residuals formed with Ca additions exhibit no consistent relationship between aging time and *As* extracted by the WET (figure 3.11).

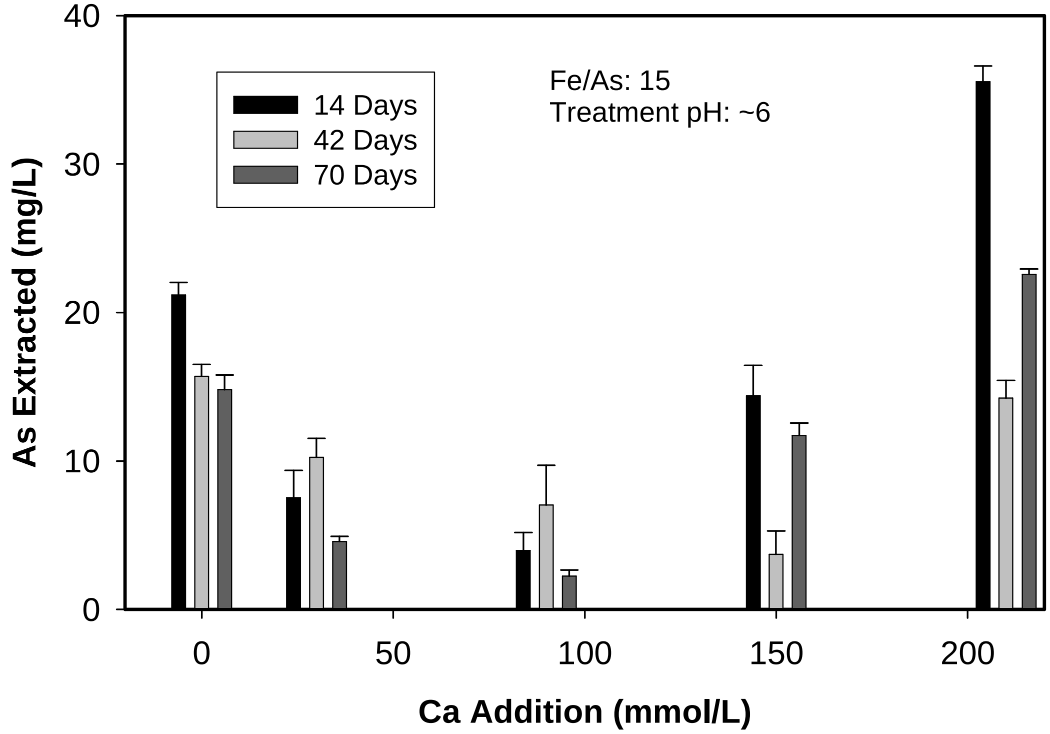

Figure 3.11. Effect of Dry Aging on residuals treated with calcium.

In many instances contaminant-laden residuals are heat treated to dry sludge and reduce volume for disposal. It has been widely reported that transformations in ferric hydroxides and oxides occur under increased temperature (Sorensen et al, 2000; Martinez et al., 2001). In order to test these effects in residuals formed during brine treatment samples formed at Fe/As 10 and 20 were placed in an oven to dry age at 105º C. WET was applied to the samples after 1 and 20 days. Figure 3.12 indicates that at both Fe/As 10 and 20, there is significant increase in extractable *As* when the sample is aged at 105º C. Residuals formed at both molar ratios exhibited twice as much extractable *As* after aging for 20 days. The is the complete opposite observation from figure 3.9 where extractable *As* decreases with time at Fe/As 10.

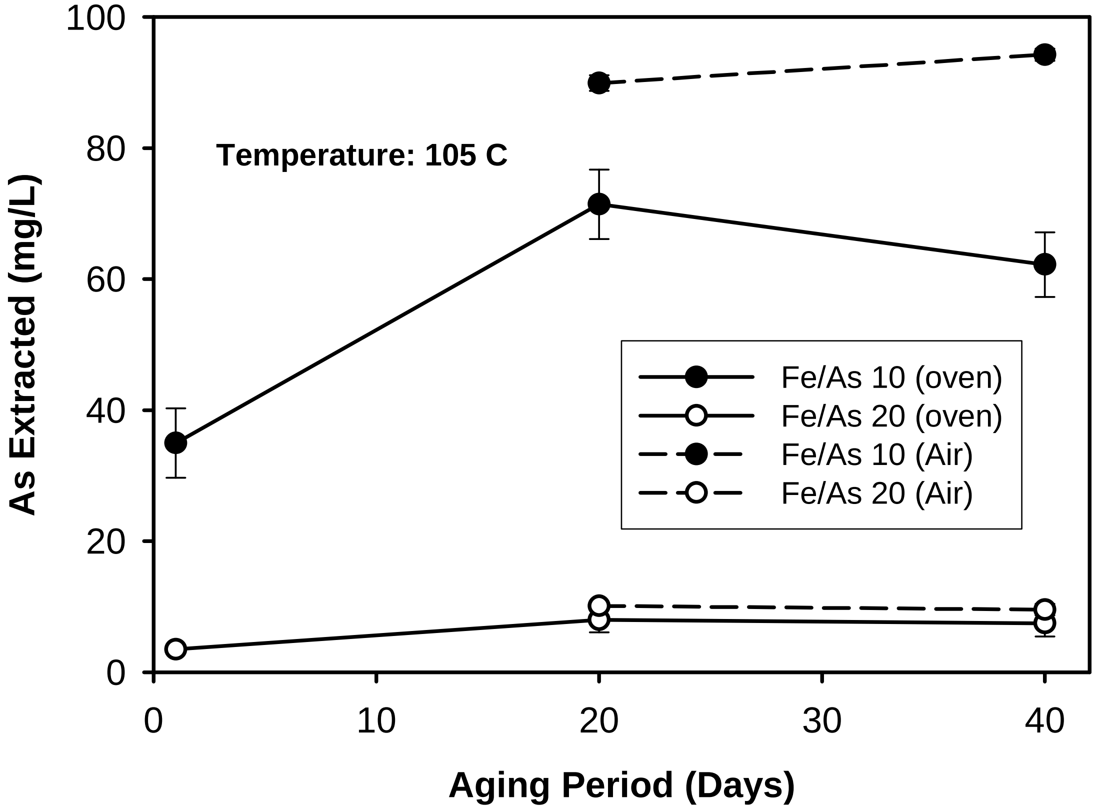

Figure 3.12. Effect of Aging at 105º C.

Sorensen et al. (2000) studied changes in ferric hydroxides induced by heat and aging. Increased temperature causes the transformation of ferric hydroxide to an ordered structure to occur more rapidly. This transformation may take years to occur in strong salt matrices such as IX brine and at room temperature (Sorensen et al., 2000). The conflicting results in figure 3.9 and 3.12 indicate that crystal transformations are occurring in the heated samples thus decreasing surface site densities for bonding and increasing the *As* extractable by the WET. Samples aged at room temperature are not undergoing such changes (or changes are much slower) and extractable *As* is decreasing with time as *As* diffuses into the more porous, amorphous precipitate.

3.4 Conclusions and Implications

Increasing Fe addition resulted in decreased *As* leachability in both the TCLP and WET. All samples tested passed the TCLP while it required treatment with a Fe/As of 20 to pass the WET. However, addition of 90 mM Ca further decreased the extractable *As* and allowed for the passing of the WET. It was confirmed that addition of Ca to the treatment process increased the residual stability while having nearly no added effect on removal efficiency.

Optimal pH range for decreasing *As* leachability is a function of the procedure being used to determine leachability (California WET, TCLP, etc.). For instance, while literature indicates that desorption is minimum at pH 5 – 7 (Jing et al., 2005), we observe an extraction minimum when treatment is performed at pH 9 – 12. This is because of the buffering capacity of citrate. A treatment pH of 9 – 12 correlates to a pH of 5 – 6 during the WET. Hence, understanding pH changes during leaching procedures is paramount in determining the process design resulting in non-hazardous residuals.

In general the results of the aging experiments indicate that changes occurring within the crystal structure of ferric hydroxides have a major impact on the extractable *As* as determined by the WET. If the change to a more ordered structure can be impeded or slowed then *As* extractability (leachability) will continue to decrease as *As* in the transient surface coatings diffuse to a more internal and stable bonding site over time. High concentration of anions as with IX brine and foreign cation inclusion will impede the recrystallization process providing an amorphous ferric hydroxide with higher surface area and higher reactivity (Jessen et al., 2005). Samples in figure 3.9 and 3.10 (Fe/As 10 – 20) indicate that this can be achieved with residuals formed from brine treatment. Increased stability was observed for up to 98 days (figure 3.10). However, heat and low supersaturation will increase the rate of recrystallization causing *As* to become more mobile (Sorensen et al., 2000; Richmond et al., 2004). Residuals formed at Fe/As 5 in figure 3.10 and samples in 3.12 exhibit this occurrence.

These results suggest that while heat treating may be beneficial in reducing volume for disposal, the residuals are likely to exhibit decreased performance in leaching tests such as the TCLP and WET over time. Also, while using a Fe/As of 5 for treatment of the simulated regeneration brine can be used to pass the TCLP, *As* leaching will increase over time due to internal changes of the residuals. Therefore, Fe/As ratios increasing the supersaturation ratio should be considered to impede recrystallization of ferric hydroxides. Lastly, while the addition of Ca in a certain range significantly increased the stability of the residuals, no definite conclusions can be made regarding the effect aging on these Ca-bearing residuals.

In order for this research to benefit the drinking water industry it is necessary to organize these results into a metric integrating the optimal conditions for brine treatment, brine reuse (chapter II), and stabilizing residuals (chapter III). Table 3.3 denotes the optimal pH and Fe dose for each part of the treatment process.

Table 3.3. Optimal pH and Fe/As. Note that optimal ranges will vary when calcium is added to the treatment process.

As Removal	Residual Stability	Brine Resuse
Optimal Treatment pH		
• 3-7 • >7 (with calcium) (Parks et al, 2004)	9-12 (for WET)	10
Optimal Fe/As molar ratio		
>2	• 20 (no calcium) • 15 (calcium) • <15 (calcium + increased pH)	Function of As removal

Along with the optimal conditions (table 3.3), three main relationships were expounded upon for brine treatment. Many of these relationships have been previously observed for treatment of drinking water (Cheng et al., 1994; Hering et al., 1996; Parks et al., 2003). The three important relationships are as follows:

1. Fe/As increase = Removal increase = process cost increase
2. Calcium increase = removal pH increase = stability increase = Fe/As decrease = cost decrease
3. Treating at a pH ≠ 10 will require pH adjustment for brine reuse = cost increase

These three relationships, in addition to the optimal conditions in table 3.3, are organized into the options diagram below. Each option is supplemented by the results from the specific test (WET or TCLP) to indicate the non-hazardous nature of the residuals developed in each set of conditions. It should be noted that 'Option 3' does not have supplemental WET results. This option is based on the observation that increasing the treatment pH will further increase stability (according to WET). Also, the results for the TCLP option were 0.7 mg/L *As*, while the limit for the TCLP is 5 mg/L *As*. It is probable that using a much lower Fe/As will suffice to pass the TCLP, especially under the optimal conditions previously discussed.

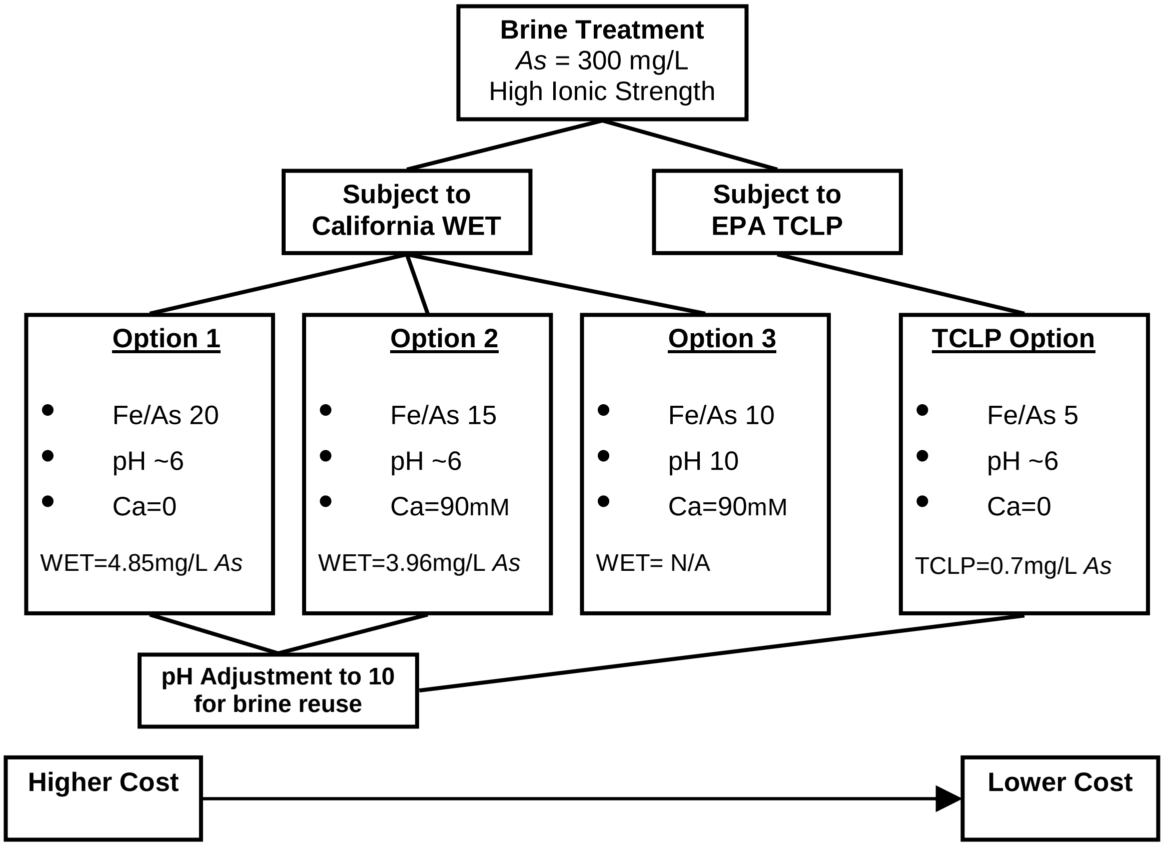

Figure 3.13. Schematic diagram for optimizing brine treatment. Diagram indicates the different treatment options for passing the WET and TCLP along with their relative costs relationship. As removal from the brine in each option was >99%.

IV. COST IMPLICATIONS OF BRINE TREATMENT

4.1 Introduction

The waste streams associated with different *As*-removal techniques may be very expensive to handle, transport, and dispose. Frey et al. (1998) reported that handling and disposal of process wastes on average makes up 12 – 34% of the total process costs. The toxicity of the waste will also affect the disposal costs. Treatment residuals failing the TCLP or WET (both with a limit of 5 mg/L *As*) will be deemed a hazardous waste and may increase the disposal cost up to four times (Meng et al., 2001). Spent regeneration brine from IX processes is considered a hazardous waste and must be further treated. Chemical additives such as $FeCl_3$ can be added to remove *As* from the brine via precipitation/adsorption (Clifford, 1999). $FeCl_3$ in the proper concentration can form *As*-laden precipitates that will pass the leaching tests but these additives can also be expensive and greatly increase process costs. Many utilities may add cheap stabilizers to the residuals such as lime or cement to decrease *As* leaching (Jing et al., 2003; Jing et al., 2005), but this will greatly increase the amount of sludge produced thus increasing disposal costs. Palfy et al. (1999) had to add 7 g of cement to every 1 g of *As*-laden sludge in order to meet leachability standards. Disposal costs are determined on a ‘per ton’ basis so reducing the mass produced is desirable. It is evident that determining the conditions balancing the costs of chemical additives, *As* leachability in residuals, and volume of sludge produced is paramount for an efficient brine treatment process.

The objectives of this study were to determine the most cost efficient conditions of brine treatment for passing both the WET and TCLP. Previous results (chapter III) revealed that simultaneous addition of $FeCl_3$ and $Ca(OH)_2$ will decrease leachable *As* in both the WET and TCLP. Cost effects of adding calcium to the treatment process will also be determined.

4.2 Methods

The volume of brine produced from a polymeric ligand exchange process using a 5-year design and design flow of 0.1 MGD was determined. Resin properties, influent water conditions, *As* breakthrough behavior, and regeneration conditions were all based on experimental conditions used in An et al. (2005). Specific description of parameters used is provided in appendix A. Brine was assumed to be reused five times before becoming spent. $FeCl_3$ additions of Fe/As 5 and 20 were used to pass the TCLP and WET respectively. As concluded in chapter III, $Ca(OH)_2$ in the amount of 6.67 g/L added with $FeCl_3$ in the Fe/As of 15 will also pass the WET. The cost effects of this scenario were also determined. The amount of NaOH was used to adjust treatment process to a pH of 6 for all Fe and Ca additions. All pricing for industrial quantity chemicals came from Spectrum Chemical Company (www.spectrumchemical.com).

Sludge production was determined based on 500 and 100 mL batch tests. The amount of sludge produced (g/L) was extrapolated for a 0.1 MGD process with a 5-year design plan.

4.3 Results

The costs of the main brine treatment compounds used were: $FeCl_3$ – 16.62 $/kg; NaOH – 5.41 $/kg; $Ca(OH)_2$ – 3.91 $/kg. Calcium hydroxide addition will result in a basic solution and require an addition of HCl (30% by weight) to adjust pH to 6. Costs for technical grade HCl are 1.51 $/L. Table 4.1 indicates the quantity of additives needed to pass the TCLP and the WET. Table 4.2 indicates the cost of the chemical additions used for each situation. It costs about 75% less to pass the TCLP than the WET based on the chemical additives used. The addition of calcium hydroxide (6.67 g/L) to the treatment process reduces the costs of passing the WET by 18%. Adding Ca in the optimal amount allowed for the reduction of $FeCl_3$, which is the most costly chemical additive, by 25%.

Table 4.1. Quantity of chemical additives for brine treatment.

Leaching Test	**Fe/As**	**Volume Brine Treated (L) (5-year design)**	**$FeCl_3$ (kg/yr)**	**NaOH (kg/yr) *HCl (L/yr)**	**$Ca(OH)_2$ (kg/yr)**
TCLP	5	177,490.4	772.8	120.7	0
WET	20	177,490.4	3091.2	482.8	0
WET (Ca)	15	177,490.4	2318.4	*3106.1	236.8

Table 4.2. Estimated yearly costs of chemical additives. 5-year design was used.

Leaching Test	**$FeCl_3$ ($/yr)**	**NaOH ($/yr) *HCl (L/yr)**	**$Ca(OH)_2$ ($/yr)**	**Total ($/yr)**
TCLP	12843.94	653.00	0.00	13496.93
WET	51375.74	2611.95	0.00	53987.69
WET (Ca)	38531.81	*4690.18	925.89	44147.89

Chemical addition is not the only factor contributing to the cost of brine treatment. Disposal of the waste residuals produced can potentially be the most costly part of the whole water treatment process (Frey et al., 1998). Disposal costs are based on the mass of waste produced, therefore the total sludge (air-dry weight, kg) to be disposed in a year were calculated in table 4.3. As expected, with increasing Fe addition the amount of sludge produced also increased. In contrast, it was observed that the addition of Ca (at constant Fe/As) decreased the mass of sludge produced. Addition of 90 mM Ca reduced the final mass of sludge produced by ~20%. These results are counterintuitive since the mass of total additions (Fe + Ca) increased. In order to investigate these results a total analysis was performed on all contaminants and additions made for a 100 mL batch treated with no Ca and one with 90 mM Ca (6.67 g/L $Ca(OH)_2$). Fe/As molar ratio was kept constant at 15. Figure 4.1 exhibits the contribution each component made to the dried residual.

Table 4.3. Sludge production from brine treatment. Sludge disposed column is an estimate based on 0.1 MGD design flow and 5-year design plan.

Sample	Fe/As (molar ratio)	Ca (mM)	Sludge produced (g/L)	Sludge disposed (kg/yr)
5	5	0	6.6	234.4
10	10	0	11.2	397.7
15	15	0	15.2	539.8
20	20	0	18.6	660.5
Ca1	15	30	13.8	490.1
Ca2	15	90	12.0	427.6

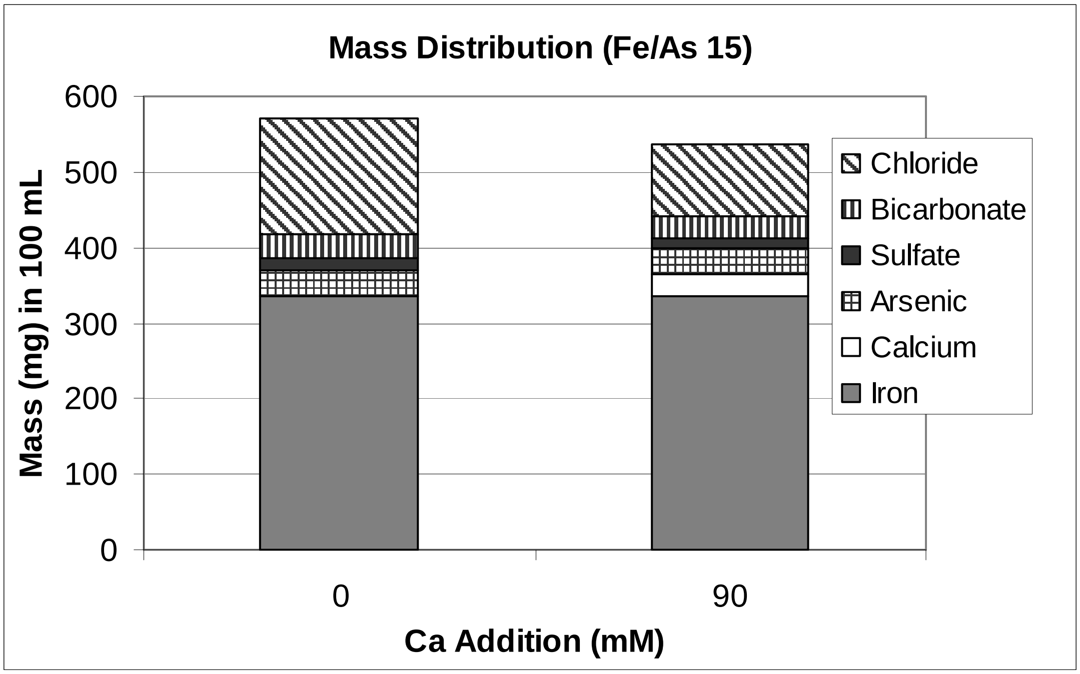

Figure 4.1. Mass distribution of components in solid residuals. Ca additions were 0 and 90 mM by $Ca(OH)_2$. Fe addition in both batches was 3.35 g/L via $FeCl_3$. Contaminant initial concentrations were: Cl^- - 30.38 g/L, SO_4^{2-} - 600 mg/L, HCO_3^- - 305 mg/L.

Figure 4.1 indicates that in both batches equal Fe, HCO_3^- and *As* were retained in the precipitates. The residuals formed with the calcium addition contained less Cl^- and SO_4^{2-} which contributed to the reduction in mass produced. It should be noted that only about 8% of the total Ca added to the treatment batch was included in the solid precipitate. These results do not consider water mass, sodium, or secondary minerals produced during drying and therefore do not account for the total 20% difference in mass.

4.4 Conclusion

The costs of chemical additives to pass the TCLP are 75% less than those required to pass the WET. The addition of 90 mM Ca decreases the chemical costs of passing the WET by 18%. This cost decrease is due to the reduction of $FeCl_3$ necessary for achieving a leachable *As* level of 5 mg/L. Furthermore, calcium addition decreases the mass of sludge produced 20% thereby reducing disposal costs by an equal amount. One component contributing to the decrease in mass produced with Ca addition was less removal of sulfate and chloride from the brine. This research reveals that careful control of treatment process conditions and the addition of $Ca(OH)_2$ to the process will increase the efficiency of brine treatment, stability of the treatment residuals, and decrease the overall process costs for utilities.

V. CONCLUSIONS

5.1 Summary of Conclusions

The treatment of spent regeneration brine by ferric chloride was optimized at pH and Fe additions similar to drinking water treatment. The most efficient removal was achieved in the pH range 3 – 6.5. *As* removal increased with Fe addition and nearly 100% removal was observed using a Fe/As molar ratio of 2. For Fe/As of 5 and pH > 6, it appears *As* was removed by both direct precipitation via reacting $FeCl_3$ with arsenate and by adsorption to the ferric hydroxide particles. The dual mechanisms resulted in significantly increased removal efficiency (up to 40%) over adsorption onto pre-formed ferric hydroxide. Calcium addition to the treatment process at pH 6 had nearly no effect on *As* removal.

When reused for regenerating an *As*-selective resin, the treated brine (at pH 10) was able to recover nearly 100% of the resin's capacity. While our results indicated the important role of pH in brine reuse, more column experiments should be performed with treated brine to further elucidate the range of conditions where successful reuse of treated brine is possible.

Both TCLP and WET indicated that increased Fe addition greatly decreased leachable *As*. The resultant waste sludge can easily pass the TCLP when brine was treated at a Fe/As molar ratio of 5, and can pass the WET when treated at an Fe/As of 20 both at a treatment pH of 6. Adjusting the treatment batches to alkaline pH shifted the pH of the WET extraction solution to 5 – 7 where leachable *As* was found to be at a minimum. Furthermore, the addition of calcium as $Ca(OH)_2$ in the range of 30 – 90 mM Ca consistently decreased *As* leachability based on the WET, but this effect was less conspicuous with the TCLP test. Increasing the calcium addition to 150 – 210 mM resulted in an increase in leachable *As* indicating an optimal calcium addition of 90 mM. We propose that available calcium in smaller quantities (1-2% of sludge mass) will reduce *As* leaching by complexing with citrate. On the other hand, continuing to increase calcium addition will result in a more soluble sludge increasing the leachable *As*. Spectroscopic studies should be employed to test this hypothesis hopefully revealing the mechanisms governing the observed calcium effect.

Increased dry aging of 98 days resulted in decreased leachable *As* by 78% when the brine was treated with an Fe/As of 10. The opposite effect was observed at a Fe/As of 5, where leachable *As* was increased by 54% after 98 days dry aging. The opposite trends are potentially due to the degree of crystallinity in the ferric hydroxide and its susceptibility to dehydration over time. While the effect of crystallinity on *As* mobility has been documented in previous studies, further spectroscopic analysis is necessary to confirm its effect in our research. No distinct effect of aging was observed in residuals containing calcium additions. Oven drying at 105º C was shown to double *As* leachability in residuals formed at both Fe/As of 10 and 20 as aging time was increased from 1 to 20 days. However, even after 20 days of aging at 105º C, residuals aged for 20 days at 25º C exhibited 25% more extractable *As* at both Fe/As 10 and 20.

This study reveals that the optimal conditions to treat spent brine for reuse and for the TCLP compliance are a Fe/As of 5 and pH of 6. The WET indicated that the lowest leachable *As* was found in residuals formed with an Fe/As of 15, $Ca(OH)_2$ additions of 90 mM as Ca, and a treatment pH of 6 – 10. Also, increasing dry aging period for residuals formed at Fe/As 10 will also enhance the stability of the residuals.

It was found that using a $Ca(OH)_2$ addition of 90 mM as Ca not only decreased leachable *As* in the WET but also decreased overall process costs. Employing calcium addition with ferric chloride to pass the WET decrease the costs of chemical additives by 18%. Furthermore, the mass of sludge produced is 20% less when calcium hydroxide is used in the process.

5.2 Recommendations

This research has shown that the brine treatment process can be controlled to enhance both treatment and cost efficiency. Our findings potentially benefit utilities around the country that employ IX for *As*-removal, handle *As*-bearing residuals, or use the WET to characterize their waste residuals. It is recommended for utilities treating *As*-laden brines to include simultaneous addition of $Ca(OH)_2$ and $FeCl_3$ in the concentrations of 90 mM Ca and a Fe/As molar ratio of 15. Treating the brines in this manner will allow for the successful reuse of treated brines, increased stability of waste residuals, decreased mass of sludge produced, and decreased process costs of brine treatment.

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APPENDIX

COST ESTIMATE OF DOW 3N-CU TREATMENT PROCESS

Introduction

Polymeric ligand exchange (PLE) is a new ion exchange technology allowing for the selective removal of arsenate from drinking water in the presence of high sulfate concentrations (An et al., 2005). As with any new technology, capital and operating costs will ultimately determine the PLE feasibility. A basic cost estimate was prepared at three different design flow rates of 0.1, 1.0, and 5.0 mgd where the As/sulfate aqueous phase concentrations ratio remained the same.

Methods

Resin Properties

Before attempting to quantify the amount of materials used in the treatment process it was first necessary to obtain intrinsic properties of the PLE resin such as total removal capacity, regeneration capacity and optimal working conditions. These properties were determined by experimental column tests (An et al., 2005). Using an estimated bed contact time (EBCT) of 4.1 minutes, 5500 BV of influent water could be treated. The influent contaminant concentrations were: As = 94 µg/L, SO42- = 40 mg/L, HCO3- = 30.5 mg/L, and Cl- = 46.1 mg/L. 100% recovery of the resin capacity could be achieved using ~20 BVs of 4% NaCl brine (40 g/L NaCl). The EBCT for the regeneration was 22.2 minutes. The expected shelf-life according to DOW Chemical for DOW 3N and XUS resins is 8-10 years. Using these conditions a process design was completed.

Design

The volume of resin required was determined using the design flowrate and EBCT. 50% of the total volume was added to account for the lifespan in a 5-year design plan. Once the volume of resin needed for a specific flow rate was determined the column was determined based on the following design parameters (Clifford, 1999): column height must be double resin bed-height to account for 100% potential expansion of resin, diameter-to-height ratio must stay within the range 0.2:1 – 2:1. Process designs for all flow rates were based on a 2 column design.

Using the experimentally determined flow rate, the time per exhaustion cycle was calculated which allowed for the determination of the exhaustion cycles needed per year (and 5-year) period. Also, assuming that the regeneration brine can be reused 5 times before treatment process, the number of brine treatment cycles was also calculated for 1-year and 5-year periods. The number of brine cycles needed per 5-year period allowed for the calculation of total brine volume required.

Using the total water volume treated, resin volume used, and brine volume used in a 5-year period; the amount of additives (NaOH, NaCl and $FeCl_3$) were calculated. Batch tests provided the concentrations of additives necessary for optimal pH, salinity, and coagulant addition (for brine treatment).

Cost data

Column costs were calculated using the equation: $63.288*(\text{volume resin (gal)}^{0.679})$ (EPA, 2000b). Resin costs were based on quotes from the DOW chemical company for DOW 3N resin. 10% was added to the costs accounting for copper loading. Costs for a brine treatment tank (non-corrosive), brine storage tank, pipes, and valves were based on quotes from ModuTank, Inc. Labor hours were calculated using the following equation (EPA, 2000b): Labor (hrs) = #weeks*(3*#exhaustion cycles). #weeks and #exhaustion cycles are on a per 1-year of 5-year period. $28/hr was used for labor costs (EPA, 2000b). All costs given in non-2005 dollars were converted to 2005 dollars using conversion factors (Sahr, 2005). All chemical additive costs were obtained from Spectrum Chemical Company.

Results and Conclusions

The results of the cost estimate and design schemes are presented primarily in tabulated form. A cost summary is provided for each design scenario as well as a breakdown of individual components used in the calculations. The summary reveals that influent *As* concentrations will greatly affect costs. Costs per 1000 gallons treated are $0.82 and $0.51 for 0.1 mgd systems with influent *As* of 94 and 30 μg/L respectively.

The ability to reuse the treated brine greatly decreased brine treatment costs by reducing the amount of NaCl needed on a yearly basis by ~50%. In an effort to make this cost estimate applicable, the design schemes were developed to pass the TCLP.

Therefore a Fe/As molar ratio of 5 was used. The reasons for choosing this ratio are explained in chapter III.

Table A.1. Cost estimate summary. Costs are given for different flow rates in dollars per 1000 gallons treated. These data are based on a 5-year design.

Flow rate (mgd)	**Influent As (μg/L)**	**Influent SO_4^{2-} (mg/L)**	**Cost per 1000 gal ($/1000 gal treated)**
0.1	94	40	0.82
0.1	30	13	0.51
1.0	30	13	0.34
5.0	47	20	0.67

Table A.2. Resin base costs.

Resin	Cost ($/ft^3)
Standard SBA Resin	140
DOW 3N	175
DOW 3N-Cu	193

Design Scenarios

100,000 gpd

Influent:
As = 94 µg/L
SO_4^{2-} = 40 mg/L
HCO_3^- = 30.5 mg/L
Cl^- = 46.1 mg/L

Treatment Capacity (experimental) = 5500 BV
Flowrate = 100,000 gpd

Table A.3. Cost summary and annual requirements at 100,000 gpd.

Cost per 1000 gal treated	$0.83 per 1000 gallons treated
Annual Cost Total (5-year Design)	$30176.59
Total Capital Costs	$37204.95
1st year Operational Costs	$30883.59

	Annual Requirement	**5-year Design Period**
Exhaustion Cycles	24	117
Volume of Resin (gallons / ft3)	313.2 gal / 38.06 ft^3	427.08 gal / 57.09 ft^3
Brine Treatment Cycles	5	23
Volume Water Treated (gal)	36500000	182500000
Volume Brine Used (gal)	21404	46888
NaCl (kg)	3240.6	7098.8
NaOH (kg)	131	603.5
FeCl3 (kg)	840	3864
Labor (hours)*	124	611

* Determined using formula: Labor Hrs = #Weeks + (3*#exhaustion cycles).
Reference: EPA, 2000

Table A.4. Component summary for 100,000 gpd.

Component	Cost	Per unit	Reference	Costs (Capital=total) (Op=annual)	Annual Cost (5-year Design)
Capital Costs					
DOW 3N	175	ft^3	DOW Chemical		
DOW 3N Cu	192.5	ft^3	Add 10%	10989.83	2198.35
XUS	300	ft^3	DOW Chemical		
Columns	3864.56	column	EPA, 2000 *2-column Design	7735.12	1547.03
Brine Treatment Tank	11590		ModuTank Inc.	11590	2318
Brine Tank	6000			6000	1200
Pipes and Valves	890		ModuTank Inc.	890	178
Operational Costs					
FeCl3	16.62	kg	spectrumchemical.com	13960.8	12843.94
NaOH	5.41	kg	spectrumchemical.com	708.71	653.00
Ca(OH)2	3.91	kg	spectrumchemical.com		
NaCl	3.8	kg	spectrumchemical.com	12314.28	5395.10
Labor	31.45#	hour	EPA, 2000	3899.8	3843.19

EPA, 2000 gives $28/hr for small systems. Conversion to 2005 dollars using conversion factor 1.123.
Reference: Sahr, 2005.

100,000 gpd (As = 30µg/L)

Influent:
As = 30 µg/L
SO_4^{2-} = 13 mg/L
HCO_3^- = 10.2 mg/L
Cl^- = 15.4 mg/L

Treatment Capacity (estimation based on exp. capacity) = 16500 BV
Flowrate = 100,000 gpd

Table A.5. Cost summary and annual requirements for 100,000 gpd with low As.

Cost per 1000 gal treated	$0.51 per 1000 gallons treated
Annual Cost Total (5-year Design)	$18450.29
Total Capital Costs	$37204.95
1st year Operational Costs	$13187.62

	Annual Requirement	**5-year Design Period**
Exhaustion Cycles	8	39
Volume of Resin (gallons / ft3)	313.2 gal / 38.06 ft^3	427.08 gal / 57.09 ft^3
Brine Treatment Cycles	2	8
Volume Water Treated (gal)	36500000	182500000
Volume Brine Used (gal)	13666.7	54666.7
NaCl (kg)	2069.2	8276.6
NaOH (kg)	26.3	105
FeCl3 (kg)	168.0	672.0
Labor (hours)*	76	377

* Determined using formula: Labor Hrs = #Weeks + (3*#exhaustion cycles).
Reference: EPA, 2000

Table A.6. Component summary for 100,000 gpd with low As.

Component	**Cost**	**Per unit**	**Reference**	**Costs (Capital=total) (Op=annual)**	**Annual Cost (5-year Design)**
Capital Costs					
DOW 3N	175	ft^3	DOW Chemical		
DOW 3N Cu	192.5	ft^3	Add 10%	10989.83	2198.35
XUS	300	ft^3	DOW Chemical		
Columns	3864.56	column	EPA, 2000 *2-column Design	7735.12	1547.03
Brine Treatment Tank	11590		ModuTank Inc.	11590	2318
Brine Tank	6000			6000	1200
Pipes and Valves	890		ModuTank Inc.	890	178
Operational Costs					
$FeCl_3$	16.62	kg	spectrumchemical.com	2792.16	2233.75
NaOH	5.41	kg	spectrumchemical.com	142.30	113.61
$Ca(OH)_2$	3.91	kg	spectrumchemical.com		
NaCl	3.8	kg	spectrumchemical.com	7862.96	6290.22
Labor	31.45	hour	EPA, 2000	2390.2	2371.33

1 mgd (As=30µg/L)

Influent:
As = 30 µg/L
SO_4^{2-} = 13 mg/L
HCO_3^- = 10.2 mg/L
Cl^- = 15.4 mg/L

Treatment Capacity (estimation based on exp. capacity) = 16500 BV
Flowrate = 1.0 million gallons per day (1 mgd)

Table A.7. Cost summary and annual requirements for 1 mgd at low As.

Cost per 100 gal treated	\$0.34 per 1000 gallons treated
Annual Cost Total (5-year Design)	\$121807.44
Total Capital Costs	\$165315.92
1st year Operational Costs	\$112018.67

	Annual Requirement	**5-year Design Period**
Exhaustion Cycles	8	39
Volume of Resin (gallons / ft^3)	2847.22 / 380.6	4270.83 / 570.9
Brine Treatment Cycles	2	8
Volume Water Treated (gal)	365000000 (365 million)	1825000000 (1.8 billion)
Volume Brine Used (gal)	136666.7	546666.7
NaCl (kg)	20691.3	82765.3
NaOH (kg)	262.4	1049.6
$FeCl_3$ (kg)	1779.9	6719.5
Labor (hours)*	76	377

* Determined using formula: Labor Hrs = #Weeks + (3*#exhaustion cycles).
Reference: EPA, 2000

Table A.8. Component summary for 1 mgd low As.

Component	Cost	Per unit	Reference	Costs (Capital=total) (Op=annual)	Annual Cost (5-year Design)
Capital Costs					
DOW 3N	175	ft^3	DOW Chemical		
DOW 3N Cu	192.5	ft^3	Add 10%	109898.25	21979.65
XUS	300	ft^3	DOW Chemical		
Columns	3864.56	column	EPA, 2000 *2-column Design	36937.67	7387.54
Brine Treatment Tank	11590		ModuTank Inc.	11590	2318
Brine Tank	6000			6000	1200
Pipes and Valves	890		ModuTank Inc.	890	178
Operational Costs					
$FeCl_3$	16.62	kg	spectrumchemical.com	29581.94	22335.618
NaOH	5.41	kg	spectrumchemical.com	1419.59	1135.67
$Ca(OH)_2$	3.91	kg	spectrumchemical.com		
NaCl	3.8	kg	spectrumchemical.com	78626.94	62901.63
Labor	31.45	hour	EPA, 2000	2390.2	2371.33

5 mgd (As = 47µg/L)

Influent:
As = 47 µg/L
SO_4^{2-} = 20 mg/L
HCO_3^- = 15.3 mg/L
Cl^- = 23.1 mg/L

Treatment Capacity (estimation based on exp. capacity) = 16500 BV
Flowrate = 5.0 million gallons per day (5 mgd)

Table A.9. Cost summary and annual requirements for 5 mgd.

Cost per 1000 gal treated	\$0.67 per 1000 gallons treated
Annual Cost total (5-year) Design	\$1,227,165.58
Total Capital Costs	\$502,083.44
1st year Operational Costs	\$812,480.41

	Annual Requirement	**5-year Design Period**
Exhaustion Cycles	12	59
Volume of Resin (gallons / ft^3)	14236.11 / 1902.97	21354.2 / 2854.45
Brine Treatment Cycles	3	12
Volume Water Treated (gal)	1825000000 (1.83 billion)	9125000000 (9.13 billion)
Volume Brine Used (gal)	1025000	4100000
NaCl (kg)	155185	620740
NaOH (kg)	1968	7872
$FeCl_3$ (kg)	12598.94	50395.77
Labor (hours)*	87	435

* Determined using formula: Labor Hrs = #Weeks + (3*#exhaustion cycles).
Reference: EPA, 2000

Table A.10. Component summary for 5 mgd.

Component	Cost	Per unit	Reference	Costs (Capital=total) (Op=annual)	Annual Cost (5-year Design)
Capital Costs					
DOW 3N	175	ft^3	DOW Chemical		
DOW 3N Cu	192.5	ft^3	Add 10%	366321.73	549481.63
XUS	300	ft^3	DOW Chemical		
Columns	3864.56	column	EPA, 2000 *2-column Design	110171.71	22034.35
Brine Treatment Tank	13000		ModuTank Inc. **estimate	13000	2600
Brine Tank	11590			11590	2318
Pipes and Valves	1000		ModuTank Inc.**	1000	200
Operational Costs					
FeCl$_3$	16.62	kg	spectrumchemical.com	209394.38	167515.54
NaOH	5.41	kg	spectrumchemical.com	10646.88	8517.51
Ca(OH)$_2$	3.91	kg	spectrumchemical.com		
NaCl	3.8	kg	spectrumchemical.com	589703	471762.4
Labor	31.45	hour	EPA, 2000	2736.15	2736.15