MERCURY IMMOBILIZATION BY SUBSURFACE REACTIVE MECHANISMS

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Signature of Author

Date of Graduation

THESIS ABSTRACT

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Mercury contamination is becoming a prevalent problem for environmental engineers. Chlor-alkali plants and coal fire power plants are the main contributors to the spread of this neurotoxin into the environment. Mercury is a unique contaminant because it is volatile at room temperature; it dissolves in water, and is a groundwater and soil contaminant. Conventional means of clean up will spread the contamination further, therefore immobilization of this contaminant in place is an important means by which to prevent mercury contamination of land and aquifers.

In this thesis, mercury immobilization was evaluated using an iron sulfide (FeS (s)) barrier as well as sulfide injections. An FeS (s) barrier was used because previous research has shown that the Fe^{2+} in this mineral will readily exchange with Hg^{2+} to form HgS (s), the least soluble mercury species. Sulfide injections were considered to determine if a HgS monolayer could form around elemental mercury (Hg^0) beads reducing the availability of the mercury to interact with the surrounding groundwater.

Column experiments were conducted to determine the performance of these immobilization methods under flowing conditions. The column tests revealed that FeS (s) is a good barrier for mercury removal under flowing conditions. The FeS (s) significantly adsorbed mercury from flowing groundwater conditions. Additionally, the column tests also showed that sulfide injections may be an effective means to contain mercury contamination and prevent contact between groundwater and Hg^0.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

INTRODUCTION

1.1 Problem Statement

Mercury contamination is an environmental problem that affects virtually everyone. Mercury is a unique contaminant because it is a metal that is liquid at room temperature, volatile at room temperature, and exists in the environment as a dense non-aqueous phase liquid (DNAPL). The EPA acknowledges the prevalence of mercury contamination and has it listed as the third most important contaminant on the CERCLA priority list of hazardous substances (USEPA 2009). Finding an effective means by which to prevent mercury contamination is a pressing environmental problem.

1.2 Objectives

The primary objectives of this research were to gain a better understanding of iron sulfide (FeS (s)) as a subsurface reactive barrier and to find a means by which to prevent mercury contamination through the development of an HgS (s) monolayer around elemental mercury (Hg^0) beads using sulfide (S (-II)) injections. Column tests were conducted to simulate contaminated groundwater flow in order to gather realistic information about the interactions between these two treatment methods and Hg^0 in the field. Results from the barrier tests were used to find a maximum barrier capacity, while the results from the S(-II) injection tests were used to find the amount of Hg^0 that could be prevented from contaminating groundwater. Parameters such as mercury concentration, pH, sulfide concentration, and flow rate were considered in designing these experiments. X-ray Diffraction was used to confirm the presence or absence of mineral compounds in the columns.

1.3 Organization

The organization of this report follows the guidelines for a standard thesis as outlined in the *Guide to Preparation and Submission of Theses and Dissertations* by the Auburn University Graduate School. Chapter 2 contains a literature review, Chapter 3 contains the general methods, and Chapter 4 contains the results for mercury immobilization using an FeS (s) barrier and S (-II) injections.

CHAPTER TWO

LITERATURE REVIEW

2.1 Mercury Health Risks

According to the agency for Toxic Substances and Disease Registry (ASTDR) mercury is a neurotoxin (ASTDR, 2006). The nervous system is highly sensitive to any mercury exposure, which usually leads to brain malfunctions and, in prolonged cases, total brain failure. Exposure can also lead to kidney damage as well as have negative effects on a developing fetus.

2.2 Mercury Exposure Pathways

Mercury is a unique contaminant because it is a multiphase risk. Elemental mercury can dissolve in water and is volatile at room temperature; therefore the most basic forms of mercury contamination are in water and air. Mercury volatilizes from either natural sources, or man-made sources; and also via fluxes from natural water bodies, then enters the atmosphere where a number of mechanisms can cause the mercuric ion to precipitate down back to the earth with rain water (Morel, Kraepiel et al. 1998). Due to the complexity that comes with mercury contamination and its prevalence in the environment it is ranked third on the 2007 CERCLA priority list of hazardous materials (ASTDR, 2006; EPA 2009). The EPA limit for mercury concentrations in drinking water is set at 2 μg/L, and the OSHA regulation for periodic occupational exposure in the atmosphere is 0.05 mg/m^3 for metallic Hg^0 and 0.1 mg/m^3 of organic mercury (ASTDR, 2006).

While contamination in water and air are important, the EPA is mainly concerned with methyl mercury, “the primary pathway of human exposure.”(EPA, 2006) Mercury is methylated by sulfate reducing bacteria, and has been shown to be directly linked to the sulfate concentration in sediments (Morel, Kraepiel et al. 1998; King, Kostka et al. 2000) The bacteria take the different forms of mercuric sulfide complexes and turn them into methyl mercury compounds under anoxic conditions. Once the methyl mercury is formed it can escape into the aerobic, aquatic environment where it is consumed by small bacteria and microorganisms, which are then consumed by different aquatic species, slowly working the mercury up the food chain (Morel, Kraepiel et al. 1998). Figure 2.1 illustrates how methyl mercury is formed in the environment. The biomagnification of mercury in these microorganisms and the subsequent bioaccumulation of mercury into fish species that humans consume is the reason that methyl mercury is the primary concern of the USEPA. Elemental mercury is also a soil and groundwater contaminant because it is found in nature (e.g. around mercury mines) and also due to the man made uses that lead to more widespread contamination.

2.3 Mercury as a Groundwater Contaminant

Elemental mercury is a global contaminant which can contaminate any type of water body including ground water. The contamination could be due to natural occurrences of elemental mercury or from anthropogenic contamination. Elemental

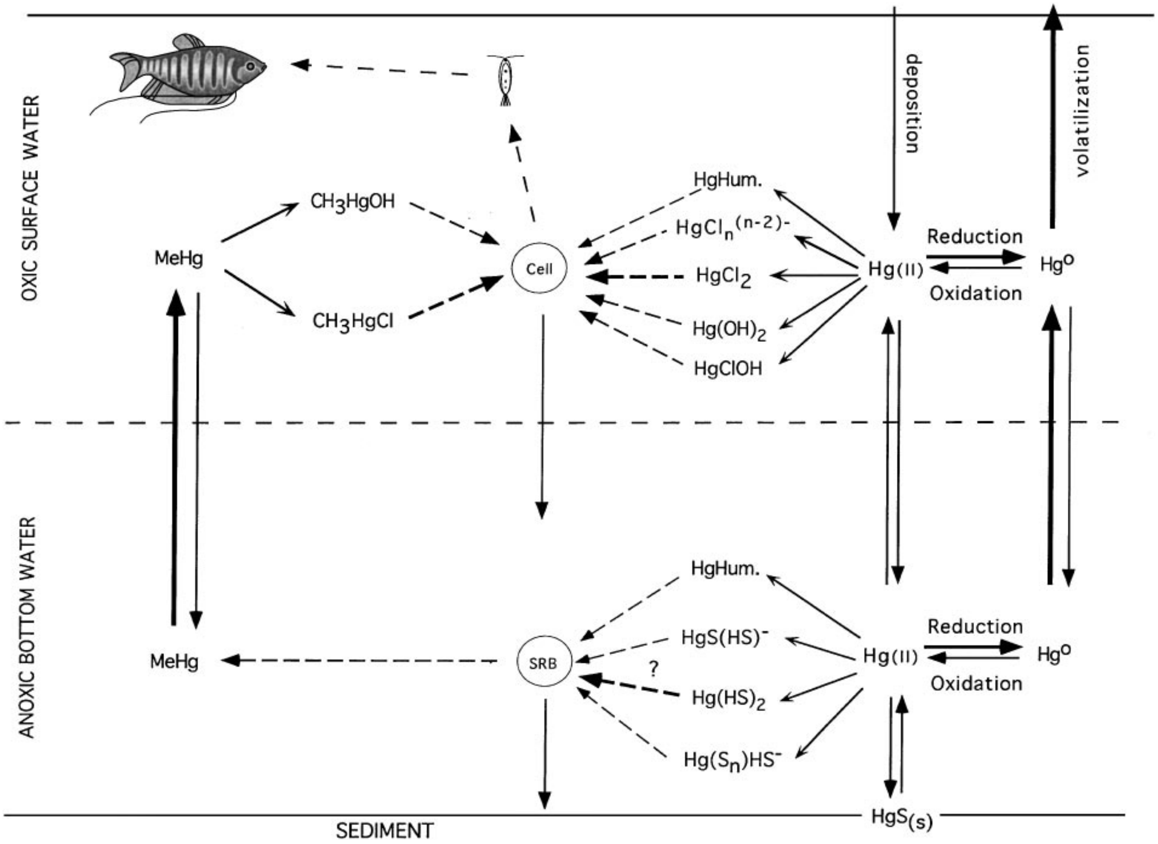

Figure 2.1: Methylation of mercury in the environment. The figure was taken from (Morel, Kraepiel et al. 1998)

mercury is often used in industry and mining, however the most common occurrence of elemental mercury spills have been attributed to schools and universities (Baughman 2006). Elemental mercury acts as a DNAPL naturally, always seeking the lowest point. One remediation method in the past has been excavation of the contaminant to incinerate the surrounding soil, thereby physically removing the contaminant. However, the more disturbed the soil, the deeper the mercury will migrate, spreading the contaminant further. There are also concerns that this type of treatment causes high mercury atmosphere emissions, and also that it is expensive (Piao and Bishop 2006). Once an elemental mercury bead enters a groundwater aquifer it can migrate to the aquitard. Subsurface Hg^0 is not exposed to sunlight. According to Amyot et. al. (2005) elemental mercury that is in the dark can be oxidized to Hg (II) in the presence of chloride or oxygen. Elemental mercury and

Hg (II) in the groundwater poses a serious hazard to individuals who use wells to provide their water. Removing the contaminant before it reaches drinking water wells or gets into surface water is important for successful remediation of mercury.

2.4 Remediation Methods for Mercury

Adsorption, mercury-ligand bonding, ion exchange, and precipitation have all been used to remove mercury from water. Activated carbon has been used as an adsorption mechanism for mercury removal (Ebadian, 2001). Research has shown that greater removal efficiency, with effluent mercury concentrations of 0.2 μg/L, has been achieved if the activated carbon was pretreated or modified to incorporate carbon disulfide. Mercury-ligand bonding is an in-situ treatment where a ligand is introduced to a contaminated site's soil and the ligand binds with the mercury to form a strong precipitate. While many of these ligands have been developed, few seem to maintain their bond when conditions are not ideal (Matlock, Howerton et al. 2003). In an effort to create a ligand that would maintain the metal ligand bond better, Matlock et. al. (2003) found 1,3-benzendiamidoethanethiol ($BDETH_2$). When in solution, $BDETH_2$ can become the $BDET^{2-}$ ligand and bind well with mercury and maintain the bond under high stress environments (Matlock, Howerton et al. 2003). Anion exchange works very well at removing mercury under conditions where mercury is complexed with an anion such as chloride or hydroxide (Ebadian, 2001). Sulfide precipitation is another common method for mercury removal where sulfide is introduced into the wastewater and mercuric sulfide is precipitated out. Research has shown that sulfide precipitation can achieve 99.9% removal of mercury; however, the lowest effluent concentrations achieved were between 10 and 100 µg/L (Ebadian, 2001). The ability of mercury to be bound to prevent leaching has been discussed by Blue et. al. 2007. They found that Mercury will bind to K2BDET and other reagents, including Na2S, and prevent the mercury from leaching(Blue, Van Aelstyn et al. 2008). They did express concern about possible degradation of this binding by soil bacteria(Blue, Van Aelstyn et al. 2008).

2.5 Mercuric Sulfide (HgS) Formation

Mercuric Sulfide (HgS) is important to the remediation of mercury contamination because it is a highly insoluble mercury solid that will precipitate out of solution. The HgS compound is formed by the interaction of a Hg (II) ion and a S(-II) ion (Ebadian, 2001).

$$Hg^{2+} + S^{2-} \rightarrow HgS \qquad (2.1)$$

$$K_{sp} = 10^{-53}$$

The HgS mineral is specifically listed as a non-mobile species of mercury due to its low solubility (Han, Kingston et al. 2003). HgS occurs naturally in two forms, cinnabar which is red, and metacinnabar which is black. Ideal conditions for HgS formation occur in reducing environments where sulfate reduction occurs to produce the sulfide ion (S(-II)); an example of this would be flooded soils (Barnett, Harris et al. 1997). Barnett et. al. (1997) went further by mapping the specific area on the

pe-pH diagram for flooded soil from the East Fork Poplar Creek in Oak Ridge, Tennessee. They found that in the zone on the pe-pH diagram where HgS is stable, sulfate reduction also occurs, which would be ideal for HgS production (Barnett, Harris et al. 1997). Also, when S (–II) is oxidized, creating solid sulfur, it creates an alkaline environment and alkaline environments promote HgS formation because the lack of hydrogen ions allows for Hg(II) and S(-II) to complex readily. (Svensson, Allard et al. 2006).

The pH of the area in which HgS is being formed is important as well. If the pH exceeds 8 then a disulfide mercury complex exists (HgS_2^{2-}), which is a more soluble compound (Charnock, Moyes et al. 2003; Svensson, Allard et al. 2006). Charnock et. al. (2003) found that at pH 11.4 this specific complex forms when the solution is saturated with HgS. Mercury complexation with polysulfides is a natural occurrence, which must be considerd because these polysulfide complexes increase the solubility of HgS (Charnock, Moyes et al. 2003). Jay et. al. (2000) conducted a study to determine the effect polysulfides had on HgS solubility and found that, in the presence of elemental sulfur (S^0), dissolved mercury concentrations rose. When the pH was low, the solubility was minimally affected, however at high pH the solubility of HgS was significantly affected and resulted in very high dissolved mercury measurements (Jay, Morel et al. 2000).

Another means by which HgS formation can be negatively impacted is in the presence of natural organic matter (NOM). The presence of dissolved organic matter (DOC) in an area where HgS formation occurs, enhances the solubility of HgS thereby releasing mercury back into the environment (Waples, Nagy et al. 2005). Waples et. al. (2005) wanted to determine the dissolution rate of HgS in the presence of various forms of dissolved organic matter and determine if sorption of dissolved organic matter on HgS was important in promoting HgS dissolution. The authors found that three principle factors had a significant impact on the dissolution of HgS, ultraviolet light adsorbance, aromaticity, and molecular weight, all having a positive relationship to HgS dissolution rate increase (Waples, Nagy et al. 2005)).

2.6 Iron Sulfide (FeS) as a Remediation Mechanism for Mercury

The interaction between iron sulfide and mercury has been thoroughly studied as a mechanism by which to remediate mercury contamination. FeS (s) is a natural sink for Hg in the environment. It commonly exists naturally in soil and sediment and the reaction will cause surface complexation of the FeS (s), or the Hg may be substituted into the FeS (s) mineral through ion exchange. (Wolfenden, 2005) There are a number of mechanisms by which the interaction between FeS (s) and Hg (II) can produce HgS (s). Morse and Luther (1999) define these interactions (Table 2.1). These reactions were written assuming that they were taking place in an anoxic environment (Morse and Luther 1999). FeS will react with oxygen readily and is therefore useful under anoxic conditions but not very useful when exposed to oxygen (Morse and Arakaki 1993). The strongest inorganic Hg (II) ligand is chloride, and therefore in saline environments these chloride complexes may inhibit HgS (s) formation (Morse and Luther 1999). A study was conducted to determine if chloride

Table 2.1: HgS formation mechanisms as defined by Morse and Luther (1999).

$FeS + Hg^{2+} \rightarrow Fe - S\text{-}Hg^{2+}$	Mercury adsorption onto FeS
$Fe - S\text{-}Hg^{2+} \rightarrow Fe(Hg)S + Fe^{2+}$	Mercury inclusion into FeS
$FeS + Hg^{2+} \rightarrow HgS + Fe^{2+}$	Ion exchange to form HgS

inhibited mercury sorption onto FeS (s). Brown et.al. (1979) found that chloride did not inhibit mercury sorption, and noted that this was contradictory to previous research. Brown et. al. (1979) also found that in batch experiments both Hg (II) and Hg^0 concentrations were reduced by FeS (s).

Jeong et. al. (2007) found that the Hg(II) sorption mechanisms when the ratio between Hg (II) and S (-II) is less than one, depend on the molar ratio between Hg(II) and FeS (s). When the molar ratio is small (< 0.05), adsorption is the important mechanism because reactive surface sites become more available on the FeS mineral surface (Jeong, Klaue et al. 2007). At high ratios (>0.05) HgS precipitation becomes the important means by which Hg(II) reacts with FeS (Jeong, Klaue et al. 2007). However, when the ratio is greater than one Jeong et.al. (2007) report that the chloride relationship with mercury has to be included in the adsorption scheme. Jean and Bancroft (1986) found that the amount of mercury that adsorbed to pyrrhotite ($Fe_{1-x}S$) in their experiment where the Hg/S ratio was 1:1 was directly related to the amount of S (-II) present on the surface of the mineral. They concluded that this relationship, that links the two parameters, means that mercury is adsorbed onto the sulfide group and eliminates the possibility of precipitation as a HgS (s) forming mechanism (Jean and Bancroft 1986). They also found that chloride became a factor during the adsorption of Hg (II) and proposed that after a monolayer of mercury has adsorbed to the sulfide group, a second layer forms consisting of $HgCl_2$ (Jean and Bancroft 1986). Jeong et. al. (2007) also proposed that Hg_2Cl_2 forms as an additional precipitate in conditions where the molar ratio of Hg (II) to S(-II) exceed one. They proved that Hg_2Cl_2 did not exist under very basic conditions.

However, they did find $HgCl_2 \bullet 3HgO$ as a salt in samples that had basic pH (Jeong, Klaue et al. 2007).

2.7 Sulfide injections as a Remediation Mechanism for Mercury

Sulfide injection is a newer approach to solving the mercury contamination problem. Sulfide injection may theoretically form HgS (s) around the elemental mercury beads. Creating a monolayer of HgS (s) around the beads would effectively encase the contaminant preventing the contact of elemental mercury with groundwater. These injections depend on the S (-II) ion coming into direct contact with the Hg^0 beads.

McCarthy and Malcolm (1988) tested a number of commercial humic acids to find their elemental makeup. They found that humic acid is primarily composed of carbon and oxygen, with other constituent elements hydrogen, nitrogen, phosphorous, and sulfur (MacCarthy and Malcolm, 1988). The presence of sulfur in humic acid makes it an attractive method for sulfide injection because it is a natural substance that will have minimal impacts on the existing environment. It is important to note that while humic acid can help remediate contaminants, since its chemical makeup is so complex, it should be assessed as a whole rather than by its constituents (McCarthy and Suffet, 1989). A negative impact that humic acid has is that it can discolor drinking water and it also can produce some alternate contaminants through different reactions (McCarthy and Suffet, 1989). Another negative that may result from humic acid exposure would be the presence of natural organic matter. If NOM comes into contact with Hg(II), it increases the mobility of the mercury making the contamination much more widespread (Wernert, 2003). The interaction between heavy metals and humic acid has been studied as a possible means for remediation. Humic acid provides “precipitate-forming” anions, and S (-II) ion that exists is noted to be possibly significant in anoxic conditions, where it normally creates metal precipitates that are very insoluble (Manahan, 1987). Heavy metal complexes with humic acids are easily achieved. However; the specific amount of the contaminant that can be reacted with depends greatly on a variety of conditions such as pH and ionic strength (Perdue, 1988).

The use of NaSH as a remediation technique for heavy metals has not been extensively studied in the same way as humic acid. NaSH is reported to be one of the most stable compounds for sodium(Kagi and Kawaguchi 1997). The NaSH compound dissolves in water following equation 2.2.

$$NaSH \rightarrow Na^{+} + SH^{-} \tag{2.2}$$

Once in solution, the sulfide ion would need to be released to interact with the elemental mercury, and form HgS (s). In order to understand how the injections will react, for both humic acid and NaSH, a pC - pH diagram was constructed (Figure 2.2). The diagram indicates that at higher pH the sulfide ion becomes more prevalent in solution, and at low pH the H_2S compound is the dominant species.

Typically ideal conditions for HgS (s) formation are when pH is low because as pH increases and the sulfide concentration increases, the solubility of HgS increases as well. (Ravichandran, 1999) Exposure of HgS to high sulfide concentrations causes HgS (s) to become more soluble, as well as form more soluble complexes, particularly HgS_2, which is an important parameter in any injection application.

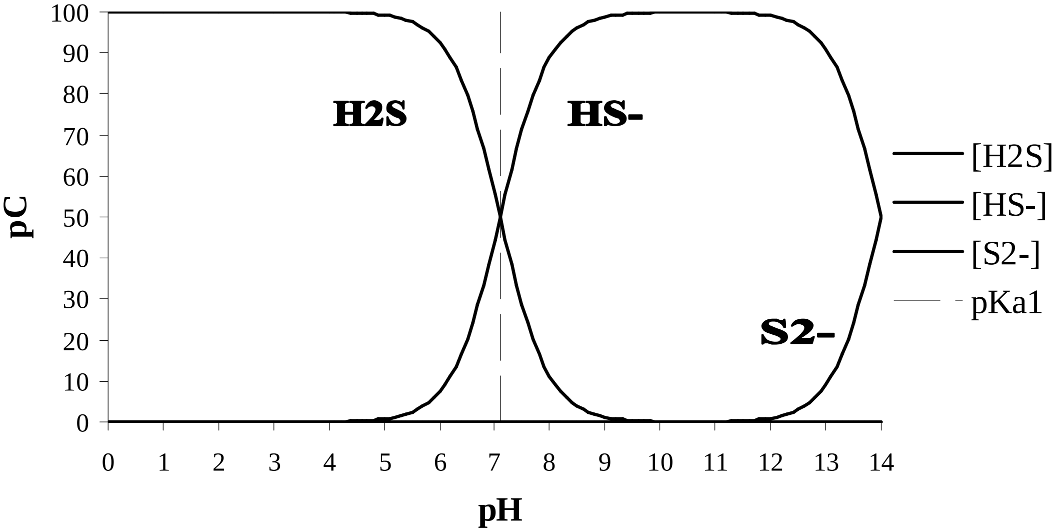

Figure 2.2: pC-pH diagram for the S (-II) system.

CHAPTER THREE

METHODS AND MATERIALS

The experiments that were conducted for this thesis were all column tests. The column tests were used to evaluate both an FeS (s) permeable reactive barrier, and three sulfide injections. All of the control columns and the permeable reactive barrier tests had an influent solution of 0.1 M NaCl for ionic strength stability. The sulfide injections involved three different influents that compared the effect of injecting humic acid, FeS nanoparticles, and NaSH, to a control column. The columns themselves all contained elemental mercury; and Hg-free influent solutions were used. Two types of columns were used in these experiments. The first type of column, used in the first FeS (s) experiments, was 1 cm in diameter, 10 cm long, and made of glass. The second type of column, used for the final FeS (s) experiment as well as all of the injection tests, was 4 cm in diameter, 29.5 cm long, and made of Teflon. The larger diameter columns increased the residence time. There was a problem with getting the effluent mercury concentrations to stabilize at mercury's solubility. The concentrations were much lower; therefore increasing the residence time was determined to be an effective means to bring the mercury concentration up to solubility. Having effluent mercury concentrations at mercury's solubility is important because these will be the concentrations seen in the field. All of the columns for these experiments were prepared in a glove box under N_2 (g) to maintain anaerobic conditions. All of the influents for these experiments were also bubbled with N_2 (g) to remove any dissolved oxygen present in the influent solution.

3.1 Iron Sulfide (FeS (s))

The iron (II) sulfide (99.9% metals basis, < 100 mesh) used in this study was obtained from Alfa Aesar. Previously, Bower (2007) found that XRD results indicated the presence of both triolite (FeS) and pyrrhotite ($Fe_{1-x}S_x$) were present, and that the specific surface area was 0.87 m^2g^{-1} (Kr BET at 77 K) (Bower, 2007). The density of the FeS is 5.01 g/cm^3. The iron sulfide was washed in a 0.1 M HCl solution, to remove as many compounds present in the barrier as possible that are not accounted for, and dried in an anaerobic chamber under N_2 (g). The iron sulfide remained in the anaerobic chamber until use.

3.2 Elemental Mercury (Hg^0)

The Hg^0 used in these experiments was obtained from Fisher Scientific. The Hg^0 beads used in these experiments were washed in a 5% HCl solution, to remove as many compounds present on the Hg^0 surface as possible that are not accounted for, in an anaerobic chamber under N_2 (g) and rinsed with deionized water before being introduced into the columns.

3.3 Quartz Sand

The pure quartz sand used in these experiments was obtained from Sigma-Aldrich. The density of the sand is 2.65 g/cm^3. The pure quartz sand was soaked in a 5%

HCl solution, to remove as many compounds on the sand as possible that were not accounted for; rinsed with deionized water, and dried in an oven before being introduced into the columns.

3.4 Sodium Hydrogen Sulfide (NaSH)

The sodium hydrogen sulfide used in this study was obtained from Fisher Scientific. The NaSH solution was bubbled with N_2 (g) to remove any dissolved oxygen present.

3.5 Artificial Ground Water (AGW)

The artificial ground water influent was prepared for comparison to other influent injections. A one liter influent was prepared that included, 10 mL of artificial ground water stock solution (Table 3.1), 0.05 g of $NaHCO_3$ (50 mg/L), 40 mL of filtered humic acid stock solution resulting in approximately 10 mg/L TOC concentration, and 950 mL of deionized water. The humic acid was obtained from Fisher Scientific. The humic acid stock solution was prepared by adding 1 g of humic acid to a liter of deionized water and then filtered through a 0.45 µm filter. The stock solution was analyzed for TOC and was found to be a 243 mg/L TOC solution. Both the AGW stock solution and the humic acid solution were stored in a refrigerator.

Table 3.1: Artificial Groundwater Stock Solution.

Compound	Concentration (M)
CaCl2	0.1
MgCl2	0.05
NaCl	0.1
KCl	0.0135

3.6 Iron Sulfide (FeS) Nanoparticles

The FeS Nanoparticles were prepared in accordance with a method developed by Xiong and Bower (2005), with the assistance of Qiqi Liang. A 1% (w/v) carboxylmethyl cellulose (CMC) stock solution was prepared by dissolving 4 g of sodium carboxylmethyl cellulose in 400 mL of deionized water. A stir bar was used to ensure that the solution was completely mixed. Once the CMC stock solution was prepared, 10 mL of the stock solution and 90 mL of deionized water were added to a 250 mL volumetric flask to make a 100 mL, 0.1% CMC solution. The solution was purged with N_2 (g) for a half hour to remove any dissolved oxygen. Once the dissolved oxygen was removed 0.0761 g of $FeSO_4$ was added to the CMC solution to form a Fe (II)-CMC complex. The solution was again purged with N_2 (g) for a half hour. After this solution was purged, 0.06158 g of Na_2S•9H2O was added to the

Fe (II)-CMC solution to make 100 mL of a 1 g/L FeS nanonparticle solution. The solution was kept in anaerobic conditions until being introduced into the column. The molar ratio of Fe:S in the solution was approximately 1:1.

3.7 Small Diameter FeS Barrier Column Experiments

The small diameter glass columns were prepared under anaerobic conditions inside a glove box under N_2(g). The FeS barrier was prepared with 0.14 g of washed FeS (s) and 0.28 g of white quartz sand (2:1 sand to FeS ratio). Two columns were required for these tests because in order to see a breakthrough one column has to be a control and one has to have the barrier and the results of each are compared. Once the two effluent concentrations are equal breakthrough has been achieved. Two 1-cm diameter, and 10-cm long, borosilicate glass columns were prepared as illustrated in Figure 3.1. The two columns each contained 5.5 g of white quartz sand with one column containing the FeS barrier. The columns were utilized in this way to compare the break through curves of each column. The columns were packed to a height of 4 cm, resulting in a porosity of 0.33. The iron sulfide barrier was placed 3 cm from the bottom (influent end) of the column. Each of the two columns also contained a one gram Hg^0 mercury bead that was placed in the middle of the columns, 1.5 cm from the influent end.

The influent for both columns was a 0.1 M NaCl solution bubbled continuously with N_2 (g) to remove all of the dissolved oxygen. The columns were run in up flow mode at 0.06 mL/min (ν = 0.076 cm/min, θ = 52.3 min). The diffraction collectors were set to 150 minutes in order to collect 9 mL samples. The effluent mercury samples were preserved by adding 0.5 mL of BrCl to each of the sample vials to

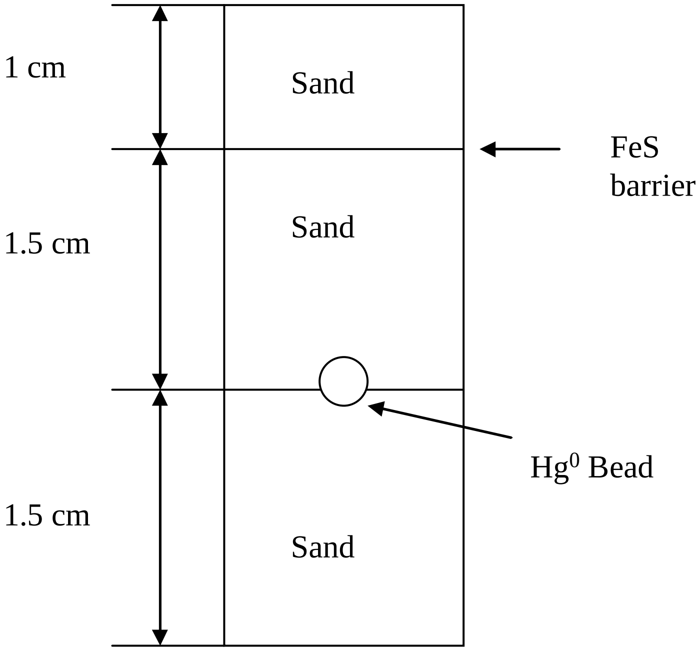

Figure 3.1: Illustration of small diameter glass column setup.

be tested. Any sample that was to be used for pH measurement was not preserved. The pH for these samples was measured using a pH probe and meter.

3.8 Large Diameter FeS Barrier Column Experiments

The large diameter columns were prepared under anaerobic conditions inside an anaerobic chamber under N_2 (g). The FeS (s) barrier, which has a 2:1 sand to FeS (s) ratio, was prepared to contain three times the amount of FeS (s) because it was found that the effluent mercury concentrations from the large diameter columns were three times what they were with the smaller columns. The barrier consisted of 0.42 g of FeS and 0.84 g of pure quartz sand. Two Teflon columns that were 4-cm in diameter and 29.5 cm-long, were used in these experiments.

The column change was due to the effluent mercury concentrations in the control columns. The effluent concentrations needed to be compared to the solubility of mercury because this would be closer to actual conditions that are seen in the field. Sanemasa et. al. (1981) found the solubility of Hg0 to be 63.9 µg/L. Therefore, the target area for where the concentrations of mercury needed to be to be at solubility was said to be between 50 and 70 µg/L. The columns were considered to reach steady-state when the effluent concentrations reached a stability of plus or minus 10%. The effluent mercury concentrations for the initial small-diameter glass columns were much lower than the solubility of mercury (<10 µg/L) and therefore it was subsequently determined that the residence time for the solution in the columns needed to be increased. Increasing residence time increases the amount of time the influent solution would be exposed to the mercury, making the effluent solubility concentrations closer to the actual solubility of mercury. The diameter increase from 1 cm to 4 cm substantially increased the residence time which produced effluent mercury concentrations closer to mercury's solubility.

The highest concentration of mercury possible was desired in these experiments to ensure that an accurate solubility was achieved in the effluent mercury concentrations. Therefore, the columns were packed with mercury to ensure that a large amount of mercury was present, as well as a large surface area of mercury was exposed. The columns each contained six, 0.5 g beads of Hg^0. The first 8 cm of the columns were filled with white quartz sand. On top of this layer, two 0.5 g beads of Hg^0 were placed in the column along a horizontal axis. On top of this elemental mercury layer were placed an additional two centimeters of white quartz sand and then two more 0.5 g Hg^0 beads were placed along a perpendicular axis. On top of this elemental mercury layer were placed an additional two centimeters of white quartz sand and then two more 0.5 g Hg^0 beads were placed along a horizontal axis once again. Finally, the columns were filled to the top with quartz sand, one including a barrier, and kept in the glove box under N_2 (g) until use.

The two columns each contained 565 g of white quartz sand, with one column containing the FeS barrier. The columns were utilized in this way to compare the break through curves of each column. A diagram of this column is shown in Figure 3.2. The columns were packed to a height of 29.5 cm which resulted in a porosity of 0.425. The FeS barrier was placed 25.5 cm from the influent end of the column.

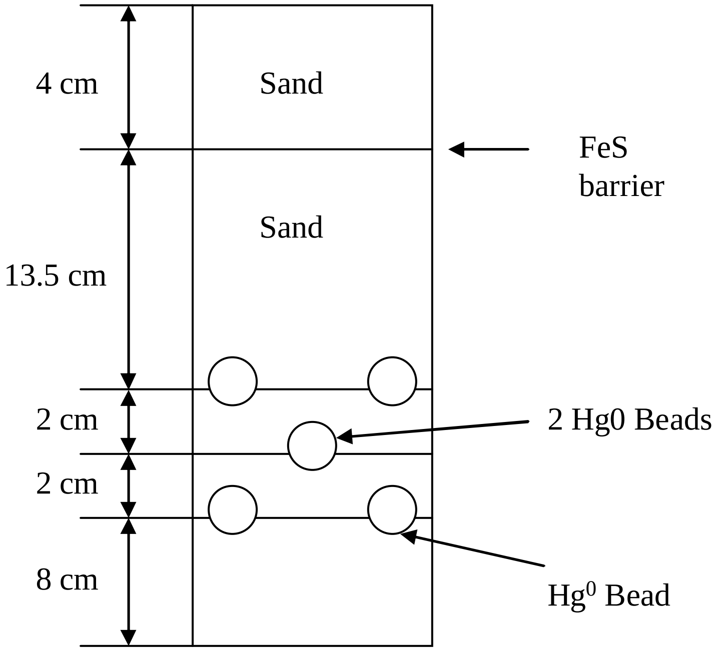

Figure 3.2: Illustration of the large diameter Teflon column setup.

The influent solution, preservation methods, and pH measurement methods were identical in both columns. However, the residence time for these columns was 100 times greater than that of the smaller glass columns at the same flow rate. Due to this, the flow rate could be increased while still maintaining a larger residence time than the smaller columns, which shortened the amount of time needed to run an experiment. The new flow rate used for these experiments was 0.5 mL/min ($\nu = 0.039$ cm/min, $\theta = 741$ min). This flow rate mimics actual groundwater flow rates, which will therefore produce a more accurate estimate of the barrier capacity. The increased flow rate of 0.5 mL/min produced a residence time that was fourteen times greater than the smaller columns.

3.9 Large Diameter Injection Column Experiments

The columns for this experiment were prepared identically to the control columns in the barrier experiments. The influents varied depending on the experiment, and the only reactive material inside the columns was the elemental mercury beads. The columns would begin running with a typical 0.1 M NaCl influent solution and then would have an influent change to the desired solution.

3.10 Analytical Methods

The mercury analysis for these experiments was conducted by cold vapor atomic adsorption spectrophotometry (CVAAS-USEPA Methods 7470A and 7471A). Before the samples were analyzed they were preserved using 0.5 mL of BrCL, and then a 1% hydroxylamine hydrochloride was added to react all of the unused BrCl before the samples were introduced into the atomic adsorption instrument. To ensure data accuracy, spikes and blanks were also run.

X-ray Diffraction (XRD) was performed on the barriers to confirm that HgS was forming. XRD analysis was performed department on a Rigaku Miniflex Diffractometer using Cu-Kα radiation (30 kV, 15 mA). The diffraction data were collected between 3 and 90 degrees at a rate or 0.10° (2θ) per minute.

CHAPTER FOUR

RESULTS AND DISCUSSION

The results for the experiments include data from the barrier and injection tests, as well as column comparisons. The column tests were run with two simultaneous columns, one a variable column, and on a control; this was referred to as running the columns in parallel. The reason for this was that the variable columns needed a means by which to be compared, and so a control column was run to gather data on how a column would react to conditions where the column contained the same amount of mercury but was only exposed to a 0.1 M NaCl influent, which was the standard influent used. Column comparison tests were needed to ensure that when the columns were run in parallel their reactions were similar. Once the validity of the parallel columns was established, each column test involved one or more variable columns and a control column, with the exception of the artificial groundwater test and the injection comparison test. The variable and control column's effluent concentrations were compared, and once the concentrations became the same, breakthrough was assumed to occur. The barrier tests were designed to asses the ability of FeS (s) to effectively remove mercury contamination from groundwater. The injection tests were designed to assess the ability of S (-II) injections to form HgS (s) around the Hg^0 beads in order to effectively contain the contaminants and prevent further exposure of the groundwater to mercury.

4.1 Small Diameter Column Comparison

The small diameter columns were run in parallel as two control columns in order to check for accuracy to ensure that the two columns would react similarly when exposed to the same conditions. This experiment came from previous work conducted by Bower and Xiong in 2006, and the resulting graph is given in Figure 4.1. A column test of theirs was conducted with elemental mercury and taken to equilibrium. A one gram Hg^0 bead washed in a 5% HNO_3 solution, was placed in the middle of a column packed with sand. The influent for the experiment was a 0.1 M NaCl solution that was bubbled with N_2 (g) and had a pH of 6.5 ± 0.5.

The results of the experiment verify that two columns that are set up and run in parallel can be compared to one another; meaning that the control columns for the subsequent experiments will indicate the mercury concentrations that the variable columns are preventing . These columns were prepared under the same conditions, exposed to the same conditions, and reacted in the same way. The two columns deviated from one another by 12% in this experiment. The effluent mercury concentrations for this experiment were slightly higher than the solubility of mercury which was atypical for the remainder of the small diameter glass column experiments.

4.2 Unwashed Hg^0 Small Diameter Glass Column Barrier Experiment

The first barrier column test included two small glass columns each with a one gram unwashed Hg^0 bead. The control column was filled with sand, while the variable column included a 0.1 g washed FeS barrier distributed evenly on the top (effluent side) of the column. The influent solution was a 0.1 M NaCl solution with a

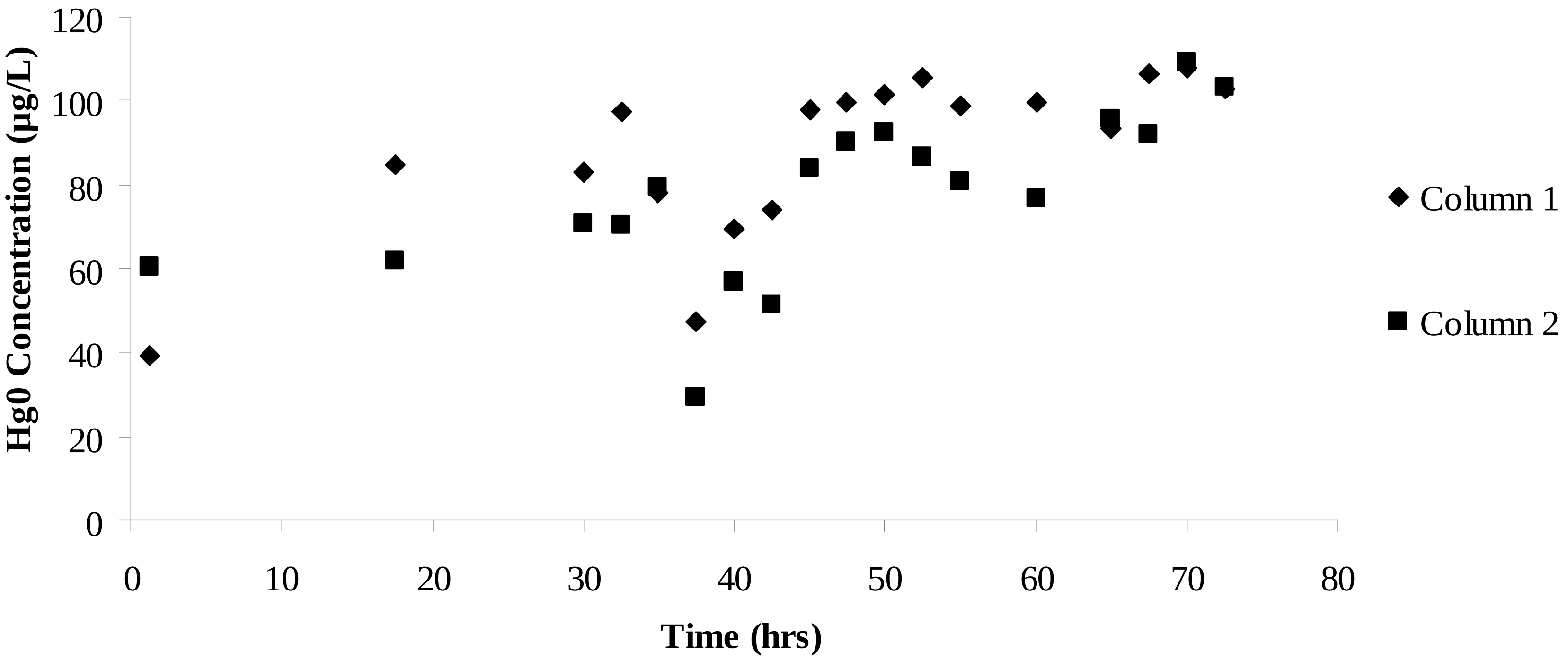

Figure 4.1: Comparison test for small diameter glass columns. Two 1 cm diameter glass elemental mercury columns are shown here. These two columns show that two columns that were run in unison react similarly if the conditions to which each is exposed are the same. The two columns varied from each other by 12% and were thus deemed accurate for comparison. The (■) symbols indicate the effluent mercury concentrations of a column with elemental mercury in it, and the (◆) symbols indicate the effluent mercury concentrations of a column packed identically to the previous one.

pH of 7.11 ± 0.5. The influent solution was bubbled with N_2 (g) to remove any dissolved oxygen. The resulting graph for this experiment is illustrated in Figure 4.2.

The results from this column indicated that two aspects of the experiment needed improvement. First, the elemental mercury beads need to be washed before being introduced into the column. Without washing, the mercury levels are spiked and inaccurate data is reported. Second, the FeS (s) barrier needs to include sand in order to increase the capacity. If the barrier does not include the sand it will foul easily and maximum exposure of FeS (s) to mercury will not be achieved. Due to the inaccuracy of these mercury measurements, an accurate capacity could not be calculated on this experiment; however, the barrier did still perform well and returned a capacity of 9500 µg Hg/g FeS.

4.3 Washed Hg^0 Small Diameter Glass Column Experiment

Applying what was learned from the unwashed Hg^0 experiment a washed Hg^0 experiment was conducted. Two, one gram Hg0 beads were washed in a 5% HCl solution, in a glove box under N_2 (g). The FeS was also washed in a 0.1 M HCl solution in a glove box under N2 (g). The barrier was prepared in the glove box with a 2:1 sand to FeS ratio with 0.28 grams of sand and 0.14 grams of FeS. The influent was a 0.1 M NaCl solution with a pH of 5.6 ± 0.5. The influent solution was bubbled with N_2 (g) to remove any dissolved oxygen. The resulting graph for this experiment is illustrated in Figure 4.3.

The results for this experiment indicated that this method was the best way to run these column tests. The barrier was prepared in a proper manner and all of the

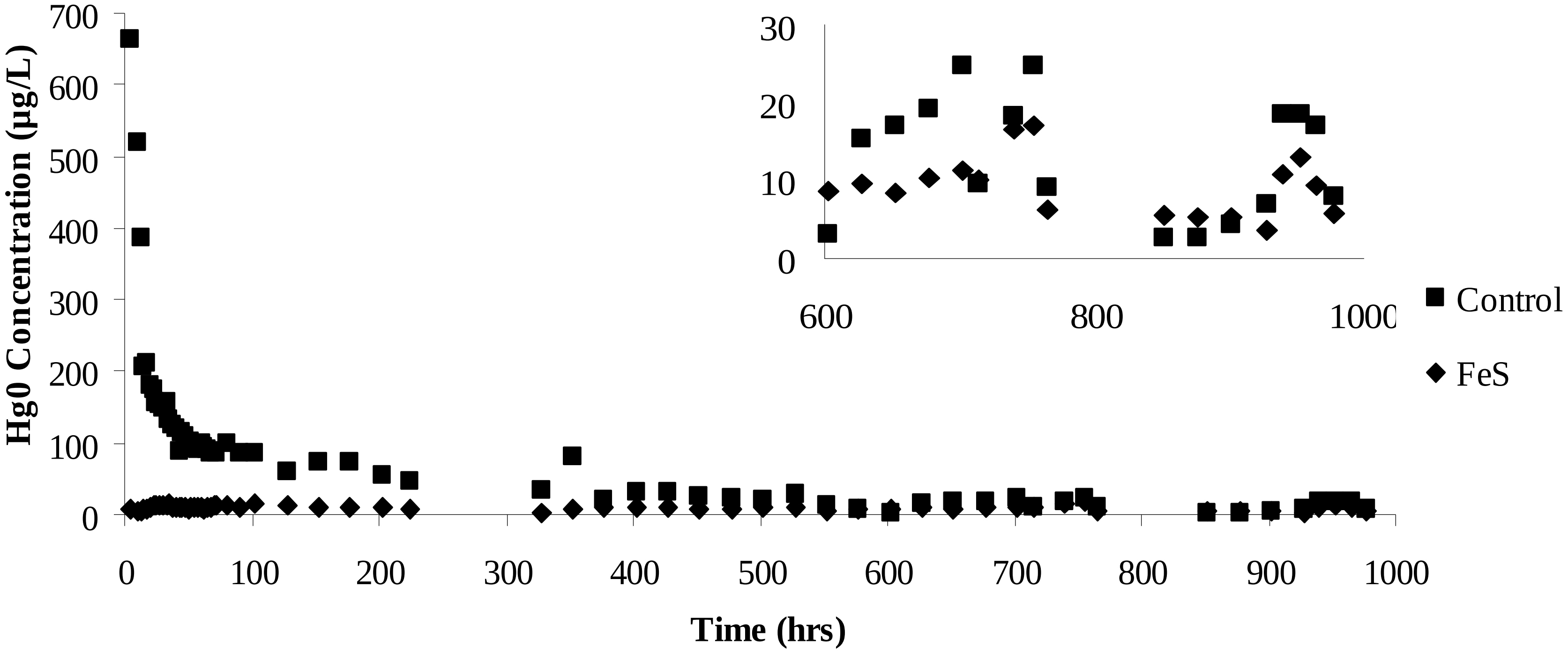

Figure 4.2: Concentration vs. Time for the unwashed mercury columns. Two 1 cm diameter elemental mercury columns are shown here, the (■) symbols indicate the effluent mercury concentrations of the column without the iron sulfide barrier and the (◆) symbols indicate the effluent mercury concentrations of the column with the iron sulfide barrier. The maximum capacity for the barrier was calculated to be 9500 µg Hg/g FeS.

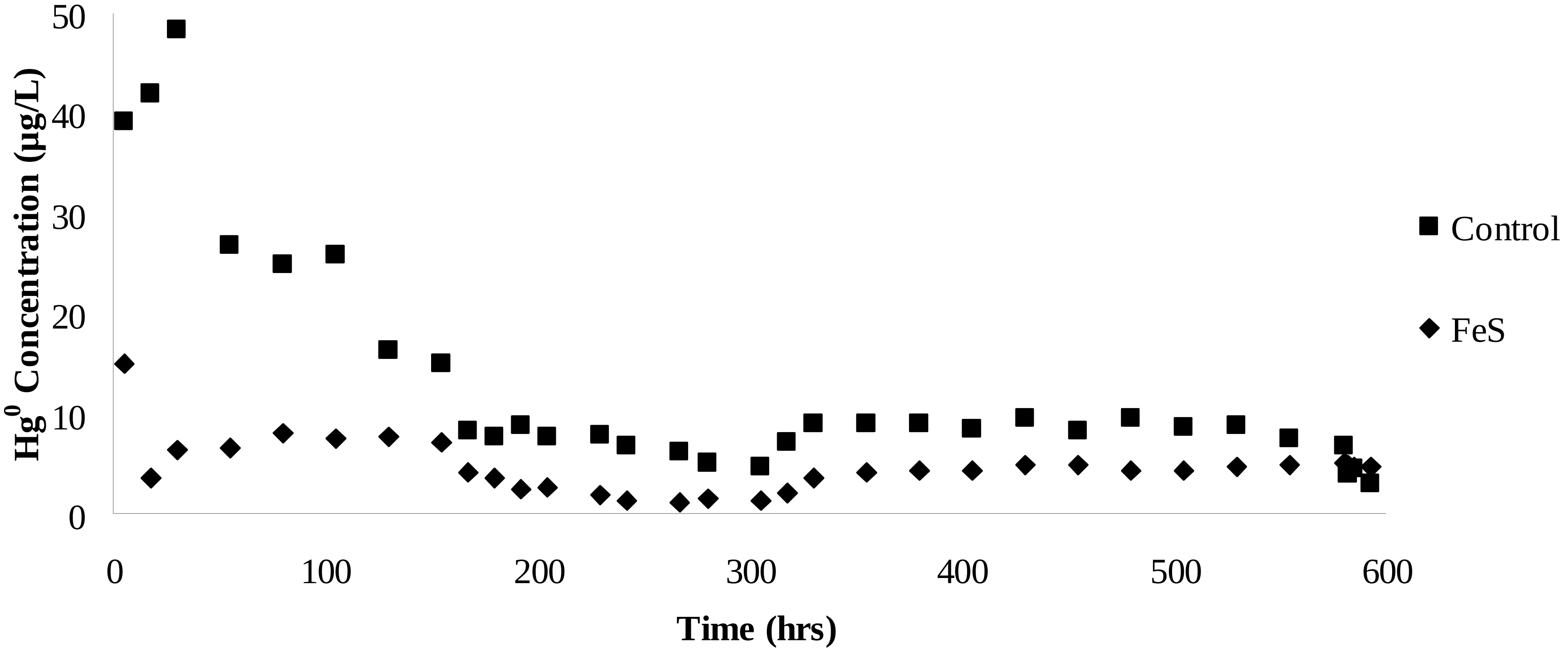

Figure 4.3: Concentration vs. Time for the washed Mercury Columns. Two 1 cm diameter glass elemental mercury columns are shown here, the (■) symbols indicate the effluent mercury concentrations of the column without the iron sulfide barrier and the (◆) symbols indicate the effluent mercury concentrations of the column with the iron sulfide barrier.

components were washed with acid so no other compounds that may have been unaccounted for could contribute to the data gathered. The FeS removed 65% of the total mercury that it was exposed to which resulted in a barrier capacity for the experiment of 980 µg Hg/g FeS. The effluent pH for the FeS barrier column was 5.16 ± 0.5, while the control column had an effluent pH of 5.53 ± 0.5. The break through time for this experiment was 582.5 hours or 24.2 days.

The barrier was taken to X-ray diffraction after being removed from the column. The column was disassembled in the glove box under N_2 (g) and the barrier was placed in a brown glass vial to ensure that the barrier was exposed to as little oxygen as possible in order to preserve the barrier as it was in the column and prevent oxidation. The results for the XRD analysis indicated that one of the two mercury sulfide complexes was present. HgS has two forms: Cinnabar, and Metacinnabar, and Metacinnabar was indicated to be the compound forming which is shown from the data in Figure 4.4.

Pictures were taken of the columns throughout the experiment. An interesting color change occurred on the effluent side of the FeS (s) barrier column. The area downstream of the barrier turned a rusty color which would indicate that iron was being oxidized, which would be consistent with an ion exchange of iron and mercury on the barrier. This picture is Figure 4.5.

The experiment shows that FeS can effectively remove mercury form groundwater under flowing conditions. However, the steady state effluent control concentration was 9 ± 2 µg/L compared to the equilibrium solubility of mercury that was wanted, between 50 and 70 µg/L. Comparing the barrier to the solubility of

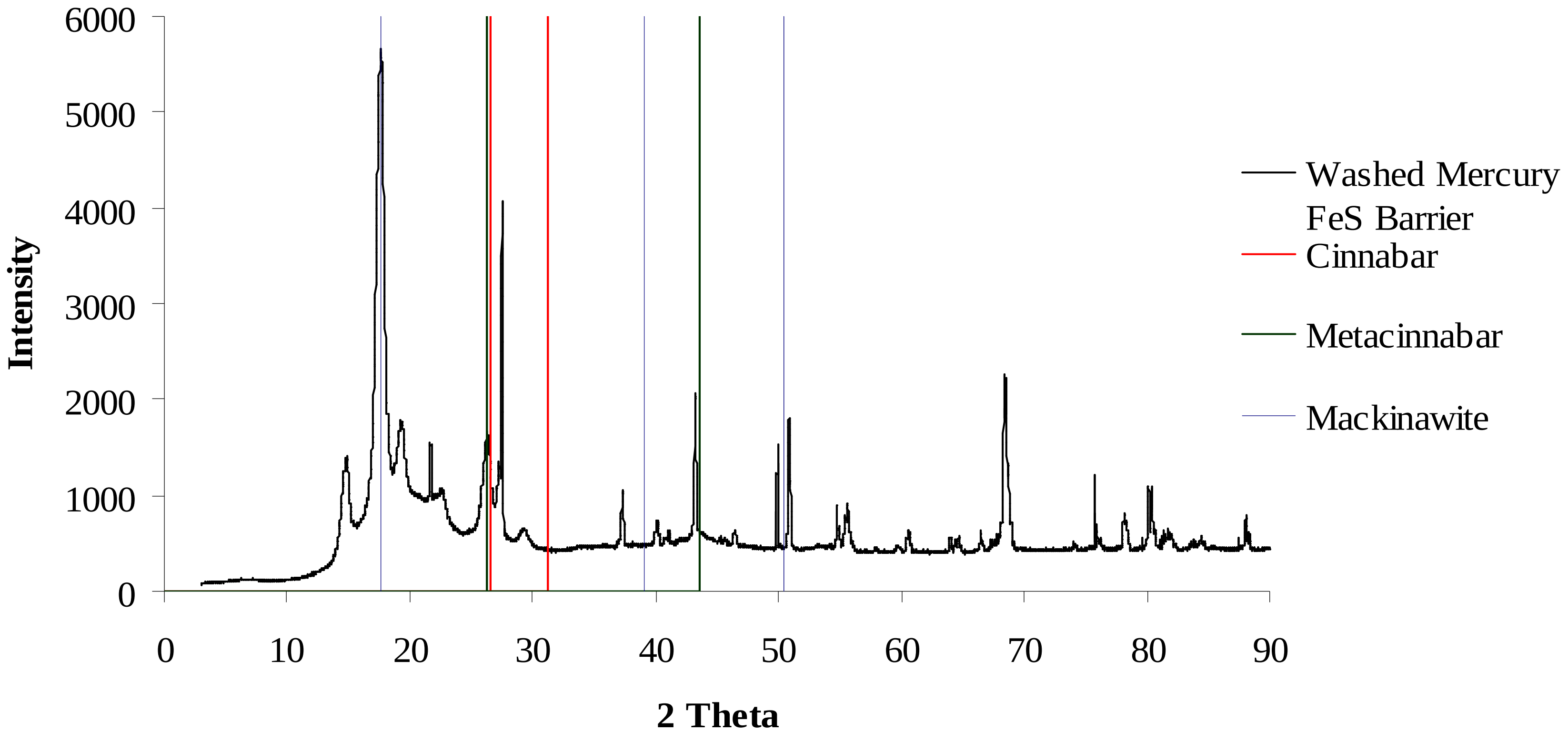

Figure 4.4: XRD data for the washed Mercury Columns. The x-ray diffraction data for the FeS barrier is shown on this graph as the solid black line. The blue vertical lines indicate Mackinawite (FeS), the red vertical lines indicate Cinnabar (HgS), and the green vertical lines indicate Metacinnabar (HgS). The first Metacinnabar peak at 2θ equal to 26.29 seems to indicate that Metacinnabar is forming on the barrier.

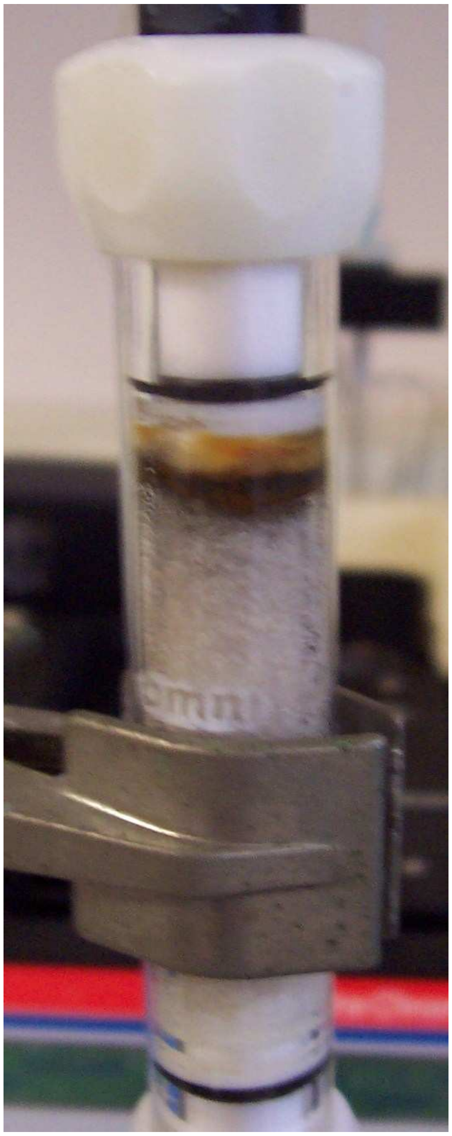

Figure 4.5: Small diameter glass column FeS (s) barrier test picture.

mercury is important because these are the concentrations that would typically be seen in an actual mercury contaminated site. Therefore in order to bring the mercury concentrations up to the solubility of mercury the residence time needs to be increased. If the residence time is increased, the water will have more time to interact with the Hg^0 beads and thus allow more mercury to be released into the water. Having this increase will make the effluent concentrations better mimic actual groundwater contamination where flow rates are generally slow.

4.4 Large Diameter Teflon Column Comparison Experiment

Residence time depends on two parameters, flow rate and total pore volume. The flow rate could not be lowered on the smaller columns because we were running at 0.06 mL/min and the lowest setting on the pump is 0.05 mL/min. Therefore, larger columns were needed to attain a larger residence time. Two 4-cm diameter, 29.5-cm long Teflon columns were obtained to increase the column volume. The large diameter Teflon columns were prepared in the glove box under N2 (g). Six half gram Hg^0 beads were placed in the columns as shown in chapter three in order to contaminate the column as much as possible to achieve the solubility of mercury. The remainders of the columns were filled with pure quartz sand. The influent for this experiment was a 0.1 M NaCl with a pH of 7.4 ± 1; the solution was bubbled continuously with N_2 (g) in order to remove any dissolved oxygen. The column flow rates were set to 0.5 mL/min which, with the much larger diameter and volume, returned a residence time that was 14 times greater than that of the small glass columns. The results for this experiment are illustrated in Figure 4.6.

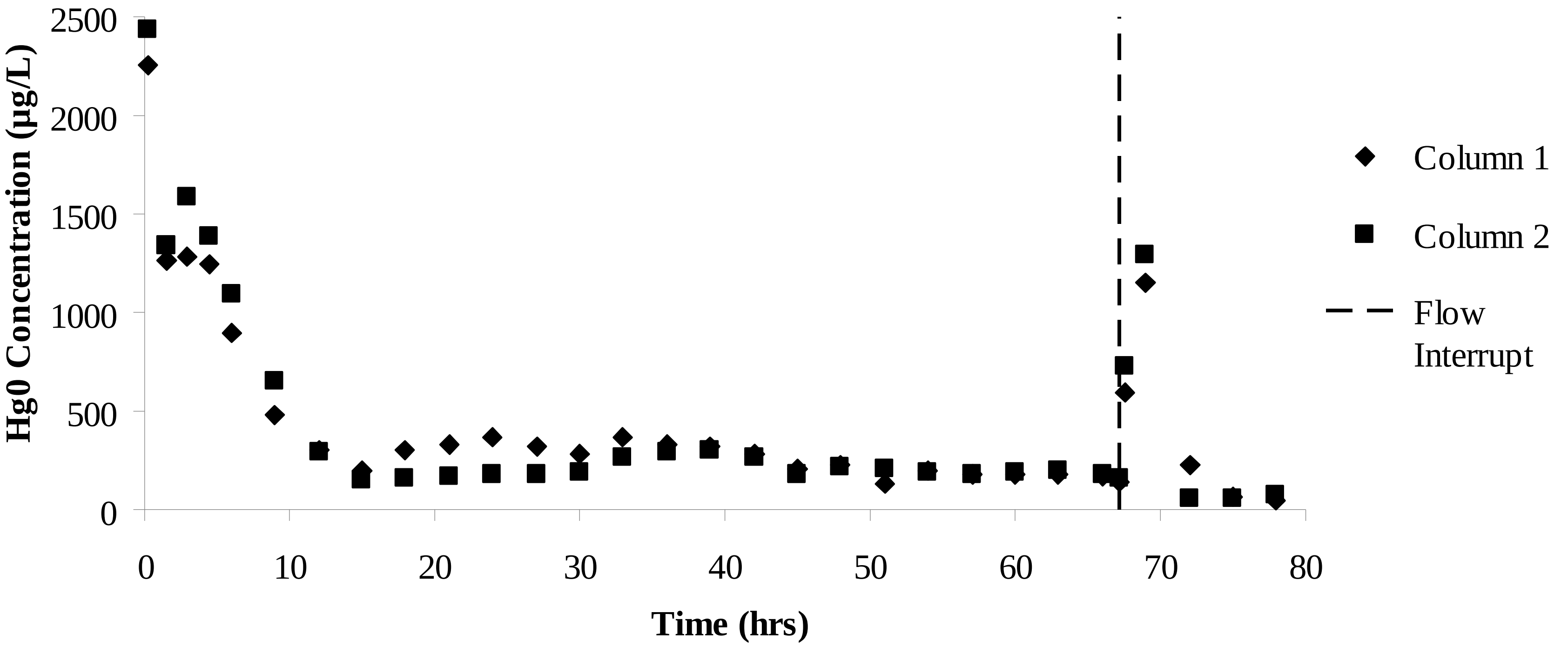

Figure 4.6: Comparison Test for large diameter Teflon columns. Two 4 cm diameter elemental mercury columns are shown here. These two columns show that two columns that are set up and run in unison are representative of one another and can be compared.

The (■) symbols indicate the effluent mercury concentrations of a column with elemental mercury in it, and the (◆) symbols indicate the effluent mercury concentrations of a column packed identically to the previous one. The two columns varied by 2%.

The results for the comparison test indicated that two large diameter Teflon columns can be compared to one another when run in parallel. The two columns were compared by percent variance and deviated from each other by 2%, which was deemed accurate for comparison. While the results for the comparison were satisfactory, the effluent concentrations remained high at ~ 190 ± 40 µg/L, which is twice as high as the reported solubility of mercury. The effluent concentrations were closely monitored for the remainder of these experiments to ensure that comparisons being made did not deviate too far from the solubility of mercury. The effluent pH was monitored and was found to be low during the beginning of the experiment with pH values equal to 3.7, and then slowly returning to the influent pH. The pH data for this experiment is illustrated in Figure 4.7. A 24-hour flow interrupt was also conducted at time equal to 67.2 hours to determine the effect if flow ceased. The two columns both rose in effluent concentration immediately after flow resumed and then came back down to the solubility of mercury ~ 62 ± 9 µg/L.

4.5 Large Diameter Teflon Column Barrier Experiment

The large diameter Teflon columns were prepared as described in section 3.8 of this document, in the glove box under N_2 (g). The influent for this experiment was a 0.1 M NaCl solution that was bubbled with N_2 (g) to remove any dissolved oxygen. The influent pH was 7.48 ± 1.1. The barrier for the test was a 2:1 sand to FeS ratio with 0.42 g FeS and 0.84 g of washed quartz sand. The results for this experiment are illustrated in Figure 4.8.

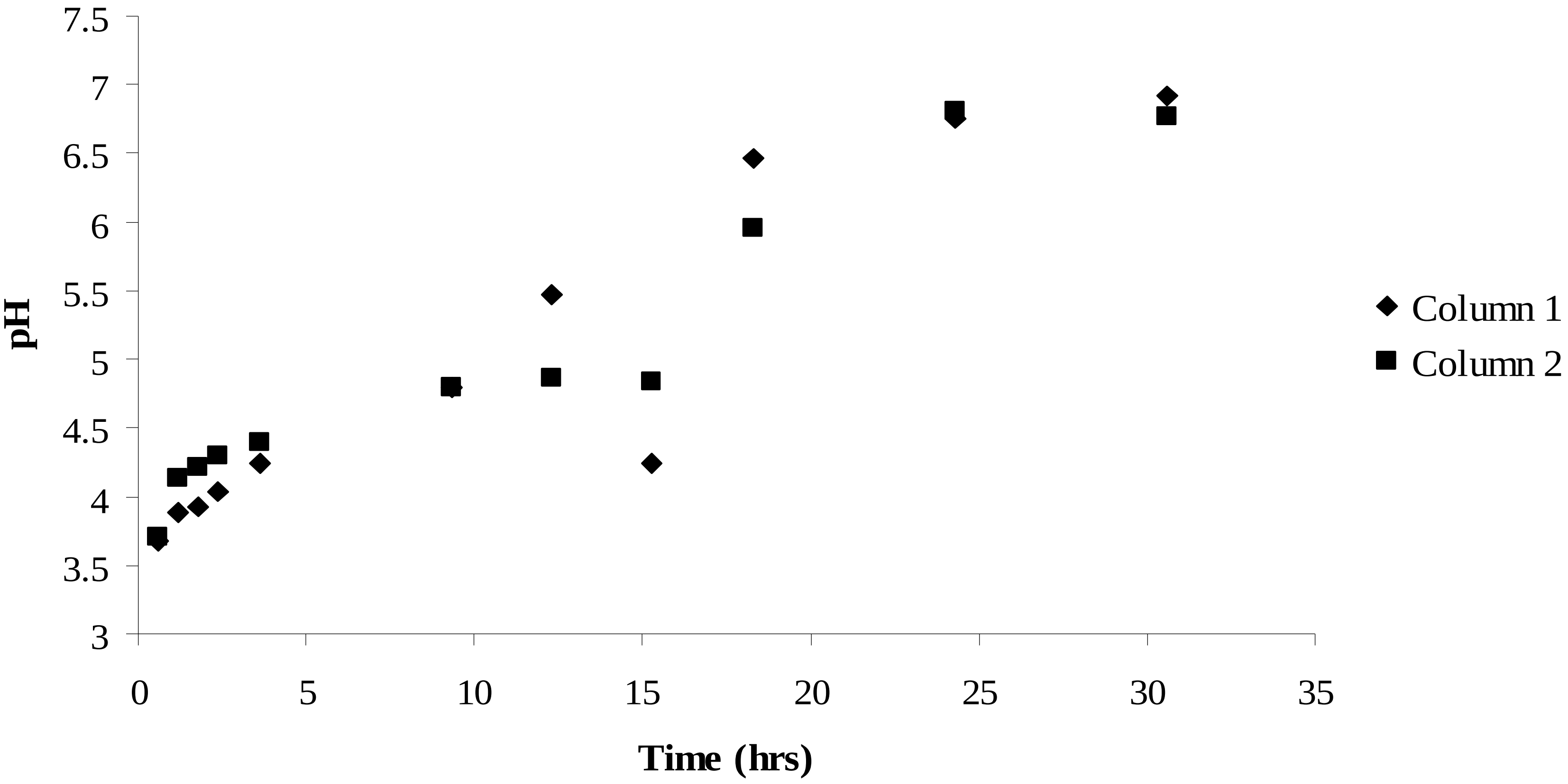

Figure 4.7: pH vs. Time for large diameter comparison test. Two 4 cm diameter elemental mercury columns are shown here, the (■) symbols indicate the effluent pH values for column 1 and the (◆) symbols indicate the effluent pH concentrations for column 2. The pH started out low and then slowly came back up to the influent pH.

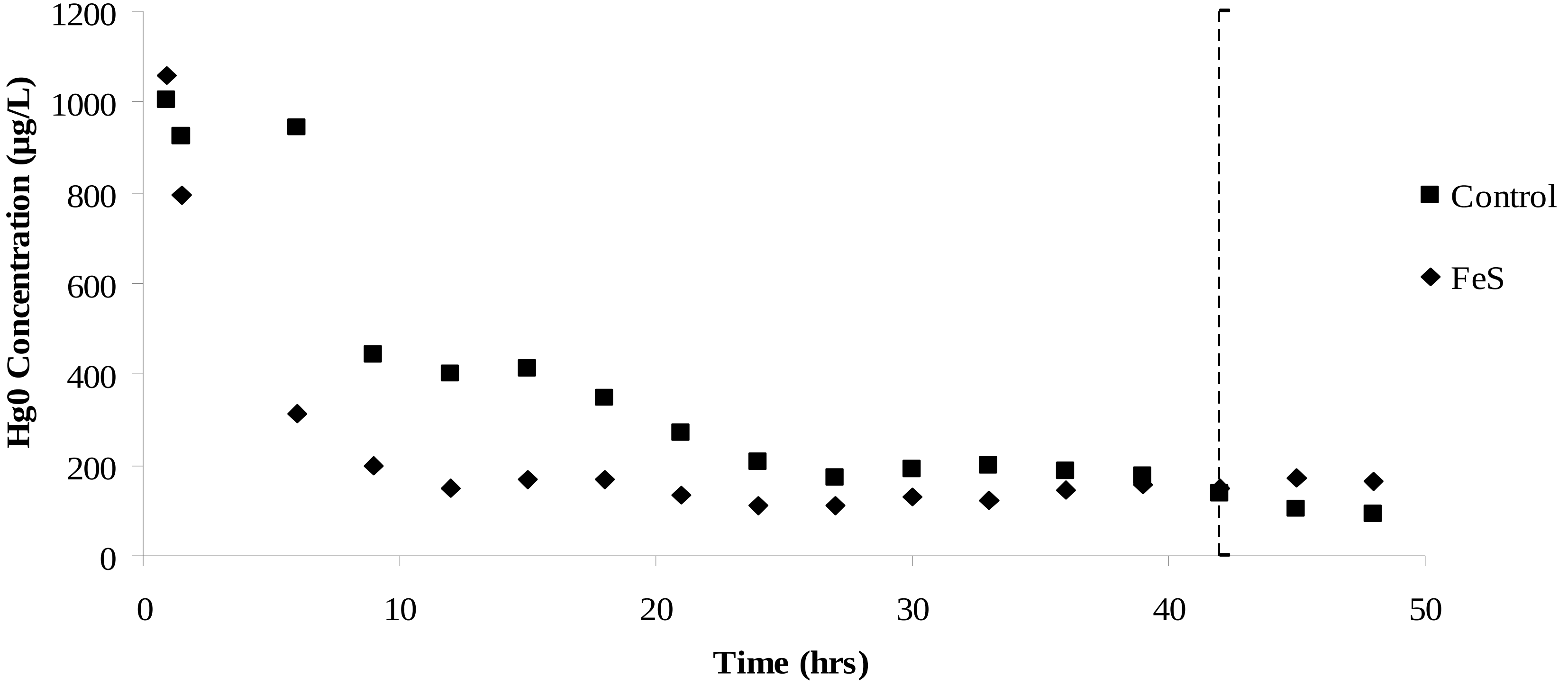

Figure 4.8: Concentration vs. Time for large diameter FeS barrier test. Two 4 cm diameter elemental mercury columns are shown here, the (■) symbols indicate the effluent mercury concentrations of the column without the iron sulfide barrier and the (◆) symbols indicate the effluent mercury concentrations of the column with the iron sulfide barrier.

The experiment indicates that FeS is a good means by which to remove mercury from groundwater using a subsurface permeable reactive barrier. The FeS barrier removed 45% of the mercury that it was exposed to returning a capacity of 2066 µg Hg/g FeS. The effluent mercury concentrations did not come down to the solubility of mercury before the barrier reached capacity, at capacity the effluent concentrations were ~140 µg/L, they were intended to be closer to between 50 and 70 µg/L. The effluent mercury concentrations for the column with the barrier, under these conditions, took two days to break through. . The effluent pH was monitored and was found to be low during the beginning of the experiment with pH values equal to 3.9, and then slowly returning to the influent pH. The pH data for this experiment is illustrated in Figure 4.9.

Once the experiment was over the barrier was analyzed via X-ray Diffraction. The XRD results are illustrated in Figure 4.10. The column was disassembled in the glove box under N_2 (g) and the barrier was placed in a brown glass vial to ensure that the barrier was exposed to as little oxygen as possible in order to preserve the barrier as it was in the column and prevent oxidation. The XRD data for the large column barrier do not conclusively indicate that either cinnabar or metacinnabar, the two forms of HgS, are present.

4.6 Artificial Groundwater Experiment

The artificial groundwater test was designed to test the reaction of mercury from exposure to an influent composed of typical constituents of groundwater as opposed to the typical 0.1 M NaCl influent that has been used in the previous

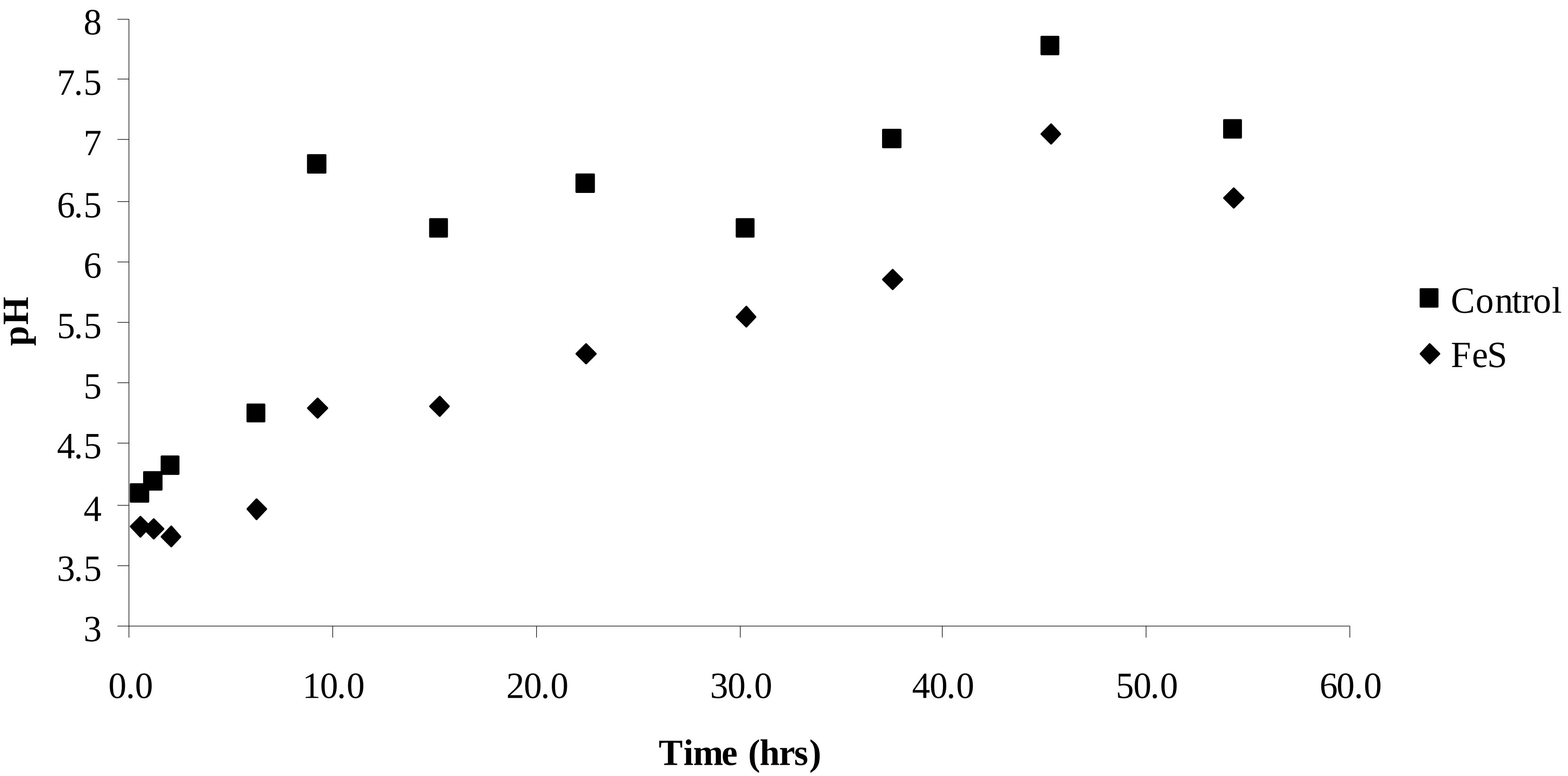

Figure 4.9: pH Data for Large Diameter Teflon Column Barrier test. The effluent pH for this experiment started out low and slowly came back up to the influent pH. The (■) symbols indicate the effluent pH values for column 1 and the (◆) symbols indicate the effluent pH concentrations for column 2.

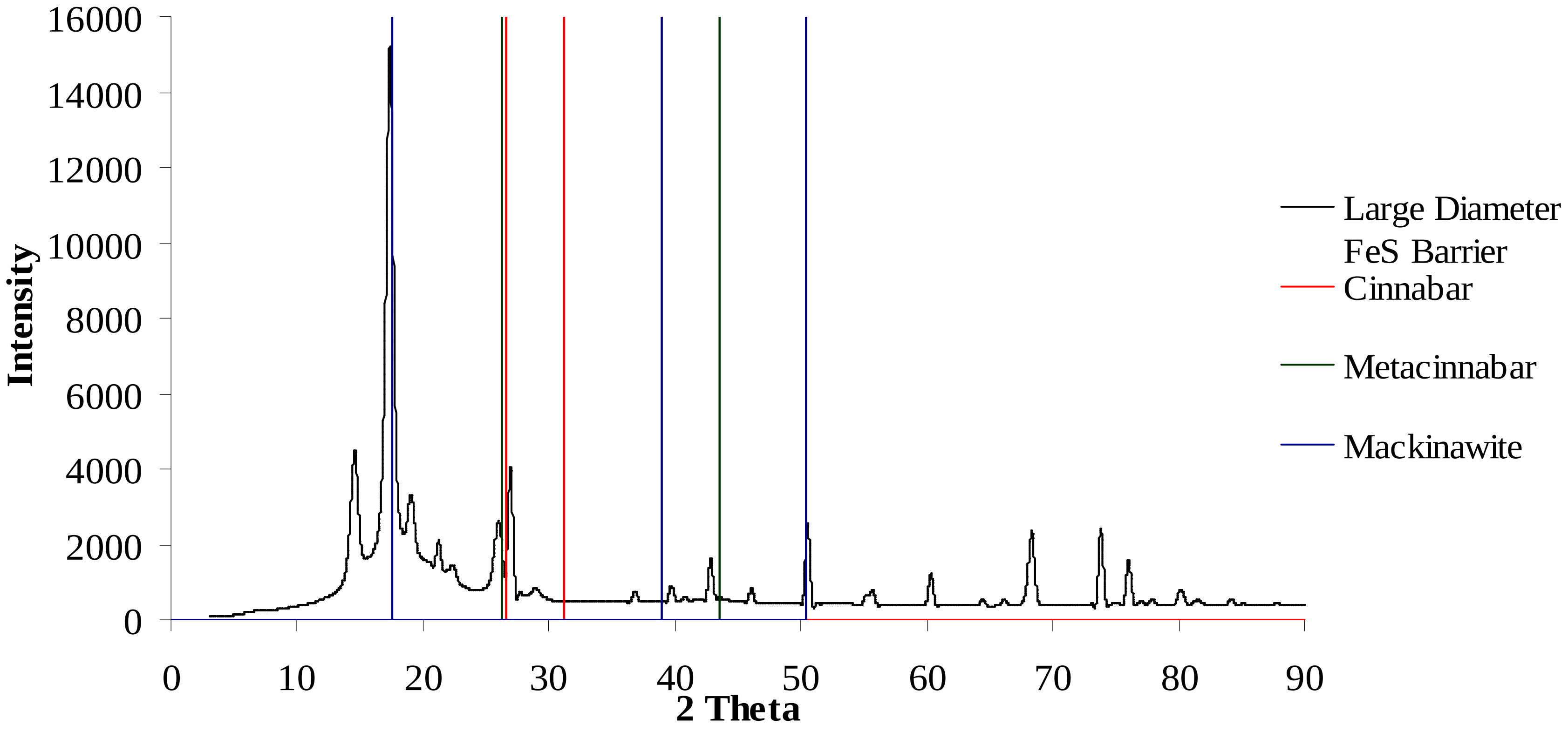

Figure 4.10: XRD Data for Large Diameter Teflon Column Barrier. The x-ray diffraction data for the FeS (s) barrier is shown on this graph as the solid black line. The blue vertical lines indicate Mackinawite (FeS), the red vertical lines indicate Cinnabar (HgS), and the green vertical lines indicate Metacinnabar (HgS). The XRD data does not indicate that either form of HgS (s) is present.

experiments. The only other influent that was used in this experiment was a TOC influent which had a concentration of 100 mg/L TOC. The artificial groundwater test involved two columns that were prepared as if they were control columns with the only reactive substance in the column being the Hg^0 beads. The artificial groundwater influent was prepared as described in section 3.5 of this document. The pH of the artificial groundwater influent was 7.6 ± 0.1 and the influent was left open to the air rather than bubbled with N_2 (g). Both of the columns that were prepared for this experiment were exposed to the artificial groundwater because the goal of the experiment was to observe whether or not HgS (s) was forming around the Hg^0 beads. The two columns for this experiment were prepared in the glove box under N_2 (g). Each contained six, washed, 0.5 g Hg^0 beads that were included in the columns as they were in the FeS (s) barrier test. The columns were filled with washed quartz sand and remained in the glove box until use. The flow rate for this experiment was 0.5 mL/min (ν = 0.039 cm/min, θ = 741 min). The results for this experiment are illustrated in Figures 4.11a and 4.11b.

The artificial groundwater influent test was designed to observe the reaction of an Hg^0 column exposed to artificial groundwater influent, observe how the columns would react to TOC exposure, observe how the columns reacted to a flow interrupt after exposure to both AGW and TOC, and finally, to observe if HgS (s) will form around the Hg0 beads. The experiment began with the artificial groundwater influent. The effluent mercury concentrations fell to below 20 μg/L and stayed under 20 μg/L for the remainder of the exposure time. Conditions remained this way for three days to establish that the results were consistent. After the three day period the

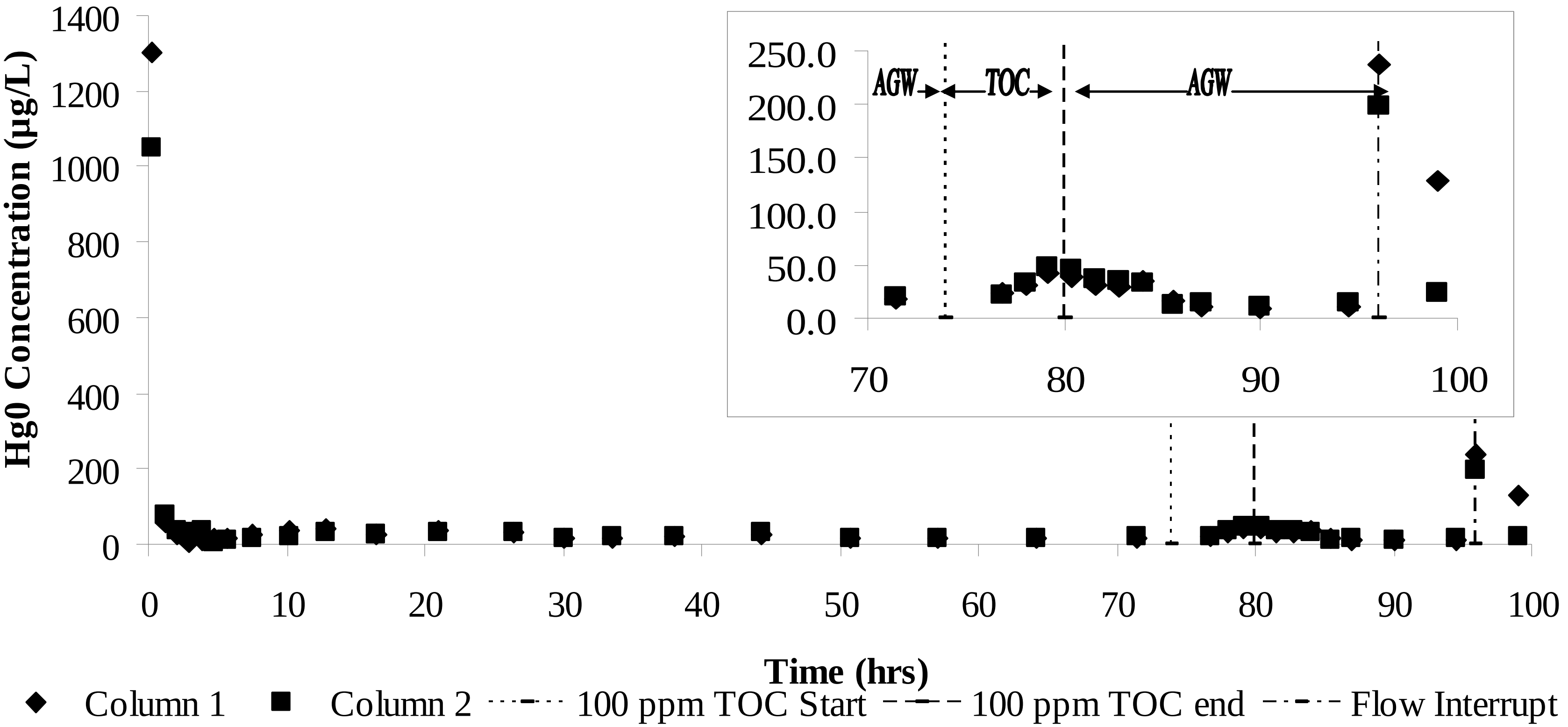

Figure 4.11a: Concentration vs. Time for the Artificial Groundwater Test. Two 4 cm diameter elemental mercury columns were both exposed to the artificial groundwater influent, the (◆) symbols indicate column 1, and the (■) symbols indicate the effluent mercury concentrations for column 2. The two columns were also exposed to a high TOC injection.

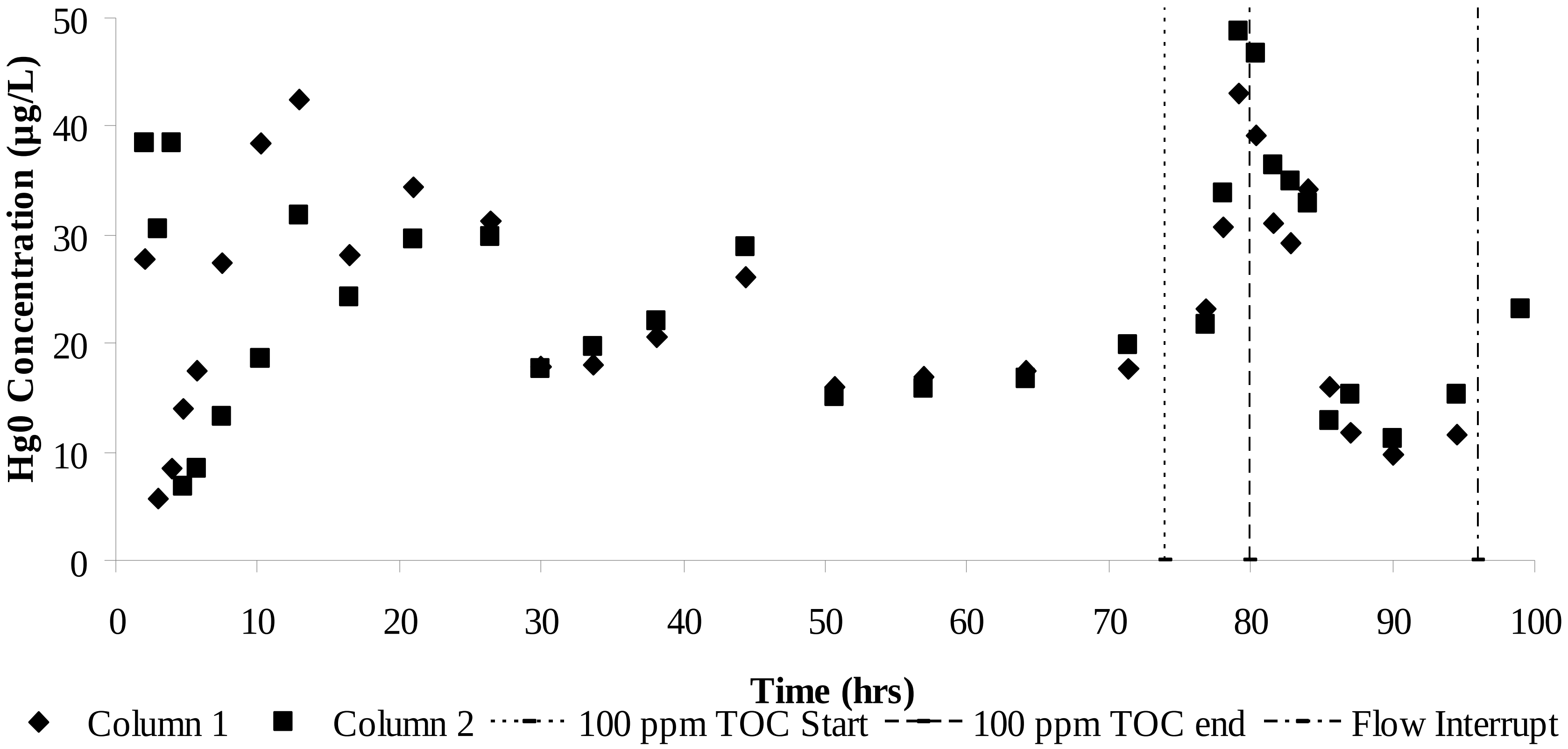

Figure 4.11b: Concentration vs. Time for the Artificial Groundwater Test. Two 4 cm diameter elemental mercury columns were both exposed to the artificial groundwater influent, the (◆) symbols indicate column 1, and the (■) symbols indicate the effluent mercury concentrations for column 2. The two columns were also exposed to a high TOC injection.

influent was changed in order to expose the Hg^0 to a higher concentration of TOC, to observe the reaction of the columns to a higher TOC concentration. The TOC concentration for the artificial groundwater was ~ 10 mg/L. The new influent was made by diluting the stock humic acid solution to ~100 mg/L TOC and had a pH of 7.31 ± 0.02. The columns reacted to the higher TOC concentration with an increase in effluent mercury concentration to between 20 and 50 µg/L. The mercury concentrations remained elevated until the influent was changed back to the artificial groundwater. Once the influent was changed back, the effluent mercury concentrations returned to below 20 µg/L as seen before the influent change. A flow interrupt was conducted after the effluent mercury concentrations stabilized. Once the columns restarted, the effluent mercury concentrations began high at ~ 200 µg/L and then began to return to the typical effluent concentration for the artificial groundwater influent, below 20 µg/L. The effluent mercury concentrations were not consistent with HgS (s) forming around the Hg^0 beads. The sand that was in the column was stained from the artificial groundwater influent; however, the Hg^0 beads appeared to be clean. The effluent pH was monitored and was found to be low during the beginning of the experiment with pH values equal to 4.41, and then slowly returning to the influent pH. The pH data for this experiment is illustrated in Figure 4.12.

4.7 Influent Sulfide Injection Comparison

The objective of this experiment was to compare three influent injections, TOC, FeS nanoparticles, and NaSH, to determine which injection returned the best

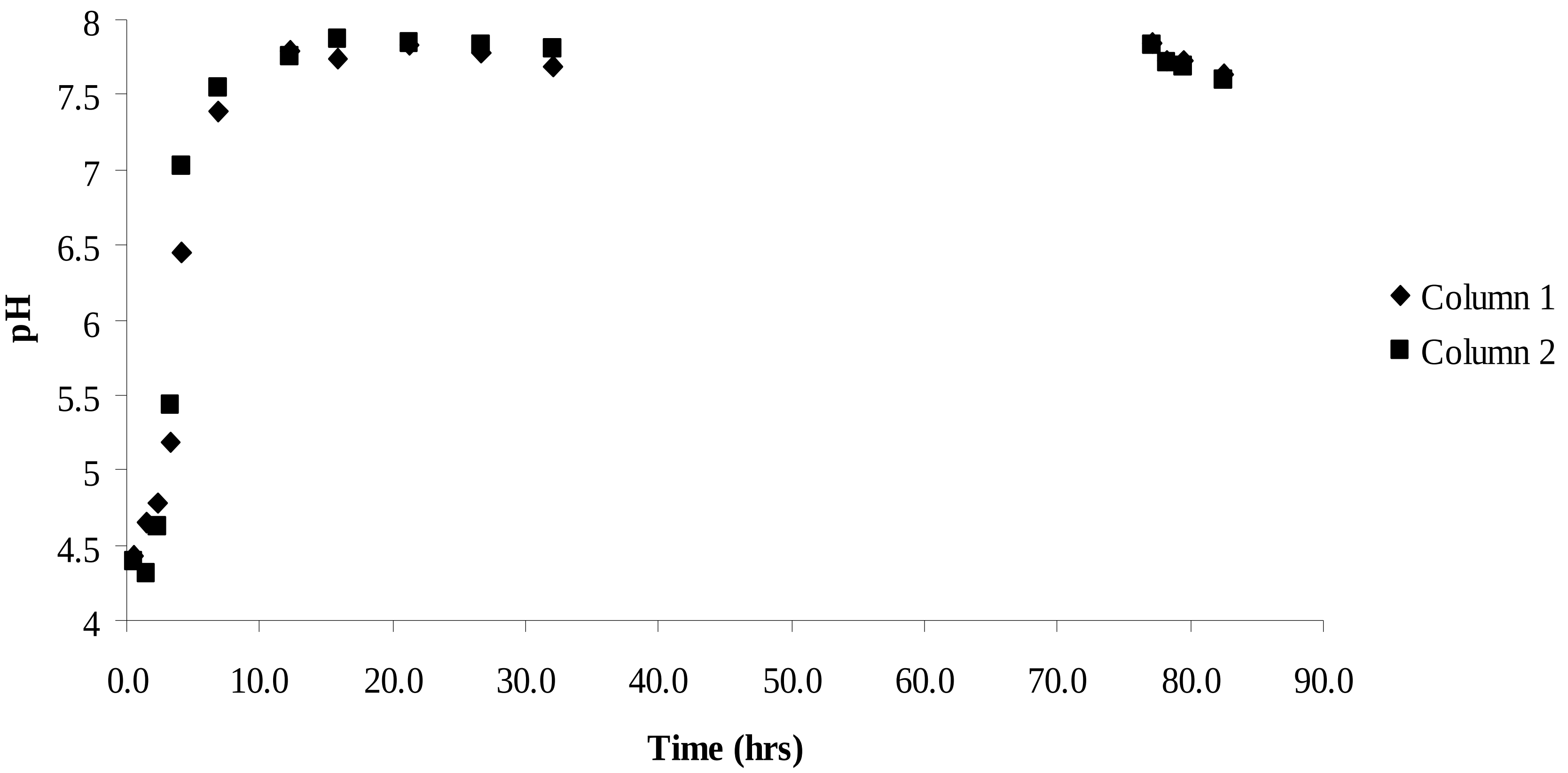

Figure 4.12: pH Data for Large Diameter Teflon Column Barrier test. The effluent pH for this experiment started out low and slowly came back up to the influent pH. The (■) symbols indicate the effluent pH values for column 1 and the (◆) symbols indicate the effluent pH concentrations for column 2. The effluent pH started out low and slowly came up to the influent pH.

response from the Hg^0 columns. The columns were prepared identically to the artificial groundwater test. The initial influent for each of the columns was a 0.1 M NaCl solution that was bubbled continuously with N_2 (g) to remove any dissolved oxygen. The flow rate for this experiment was 0.5 mL/min ($\nu = 0.039$ cm/min, $\theta = 741$ min).

. Three columns with three different injections were run for this test. The first two columns were exposed to the FeS nanoparticles and the NaSH injection respectively. The FeS nanoparticles were prepared as outlined in section 3.6, all 100 mL were used for the injection. The NaSH injection was 100 mL of a 1000 mg/L NaSH solution. After twenty five hours the influents were changed from a 0.1 M NaCl influent to the injection influents. The 100 mL injections were injected into 900 mL of 0.1 M NaCl deionized water under N_2 (g) making a one liter influent. After the entire liter of injection influent was used, the influent was changed back to a 0.1 M NaCl solution. The 0.1 M NaCl influent solution was run for 12 hours. The third column, the TOC column, had to be run separately because only two Teflon columns were available. The stock humic acid from the artificial groundwater test was used to make the TOC injection; the injection was 40 mL of stock humic acid into. The 40 mL injection influent was added to 960 mL of 0.1 M NaCl solution that was continuously bubbled with N_2 (g). The influent was changed from the 0.1 M NaCl solution to the injection influent at time equal to 35.5 hours. The entire liter of injection influent was used and then the influent was returned to a 0.1 M NaCl influent. The 0.1 M NaCl influent was allowed to run for 12 hours before the experiment was stopped. The results for this experiment are illustrated in Figures 4.13 a, b, and c.

The results for this experiment compared the reactions of Hg0 under flowing conditions to three different sulfide injections. All of the columns reached the solubility of mercury, 81 ± 8 µg/L, after 24 hours. The FeS nanoparticles column, during exposure, saw an increase in the effluent mercury concentration to a maximum of 250 µg/L and steadily descending to 100 µg/L. After the influent was changed back to a 0.1 M NaCl solution, the effluent concentrations dropped to below 5 µg/L indicating that HgS (s) may have been forming around the outside of the Hg^0 beads. The TOC column reacted to exposure by dropping in effluent mercury concentration to between 40 and 15 µg/L. When the influent was changed back the effluent concentrations remained in the same range between 40 and 15 µg/L, indicating that HgS (s) may not have formed around these Hg^0 beads. The NaSH column, during exposure, dropped in effluent mercury concentration to between 30 and 50 µg/L. Once the influent was returned to a 0.1 M NaCl solution the effluent mercury concentrations dropped to below 5 µg/L and remained below 5 µg/L for the remainder of the experiment which is consistent with HgS (s) forming around the Hg^0 beads. The HgS (s) formation was not confirmed with X-ray Diffraction, only observations of how the effluent concentrations responded to the injections were noted because the objective of the experiment was to determine which injection performed the best. The HgS (s) formation that is referred to is only noted because it is the explanation that the author thought best described the reaction. Due to the NaSH injection’s low concentrations during exposure, the NaSH injection was

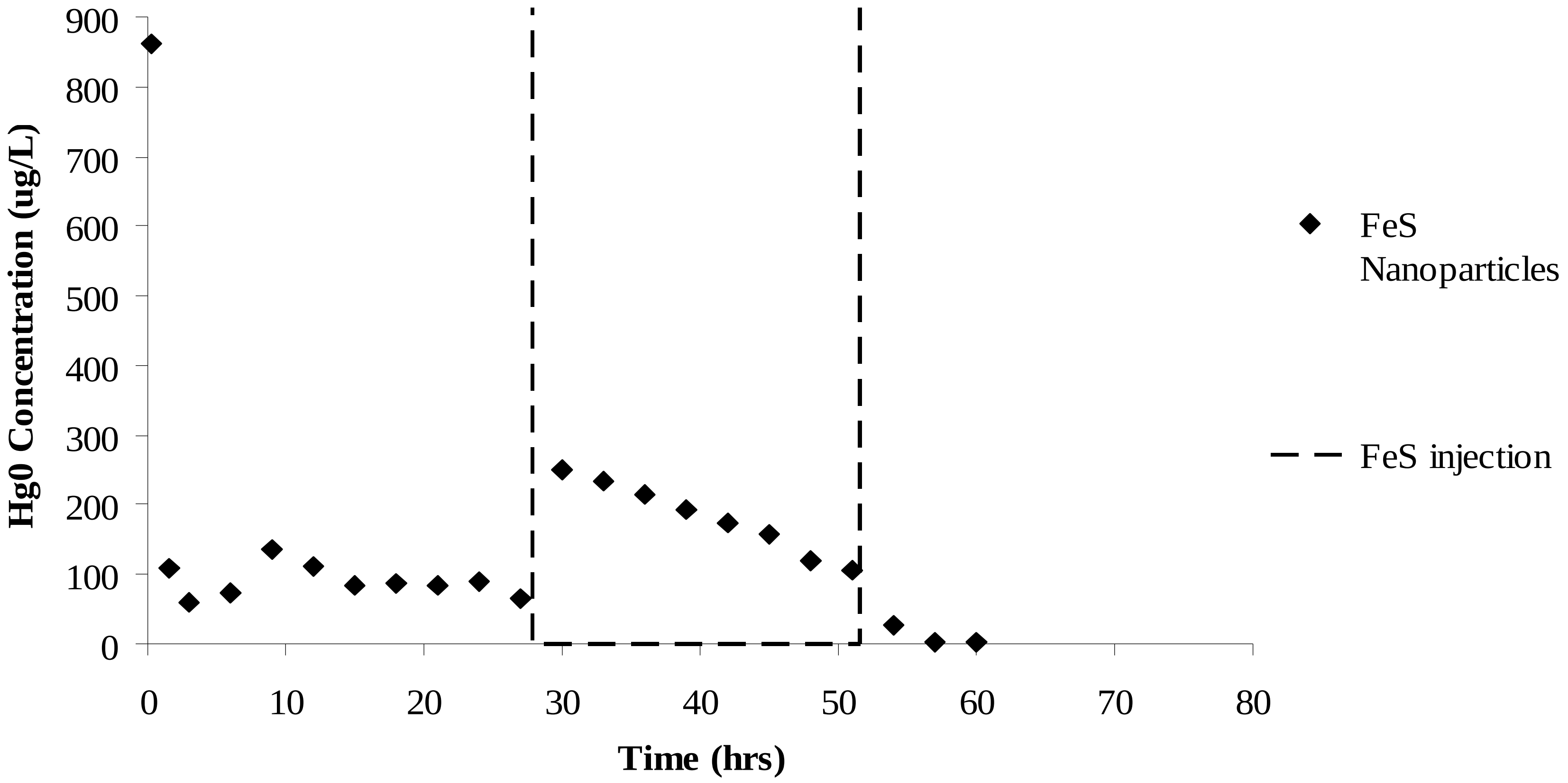

Figure 4.13a: Concentration vs. Time for the Sulfide Injection Test. Three columns were set up to compare the effluent mercury concentrations of three different sulfide injections. The (◆) symbols represent the effluent mercury concentrations for the column exposed to FeS nanoparticles.

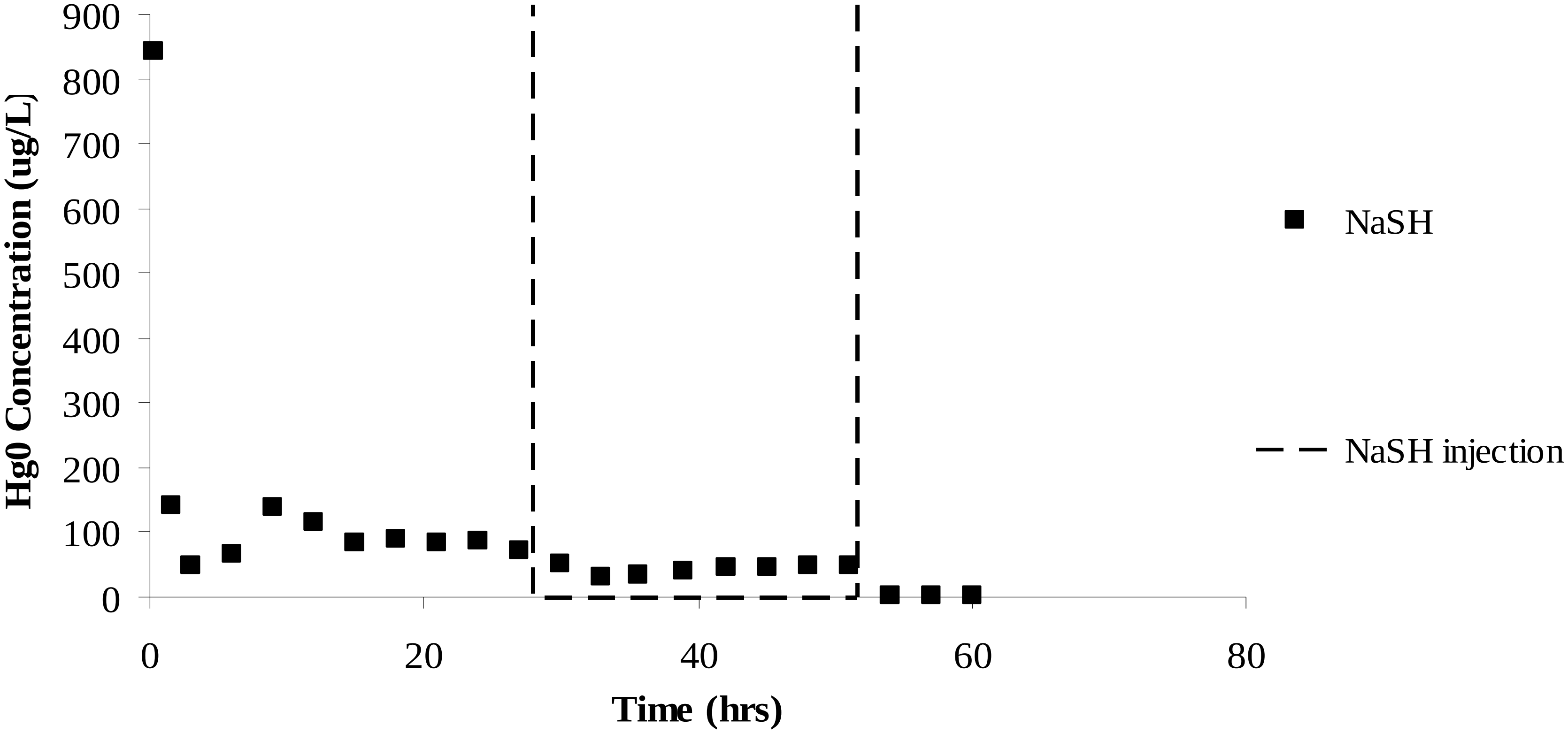

Figure 4.13b: Concentration vs. Time for the Sulfide Injection Test. Three columns were set up to compare the effluent mercury concentrations of three different sulfide injections. The (■) symbols represent the effluent mercury concentrations for the column exposed to NaSH.

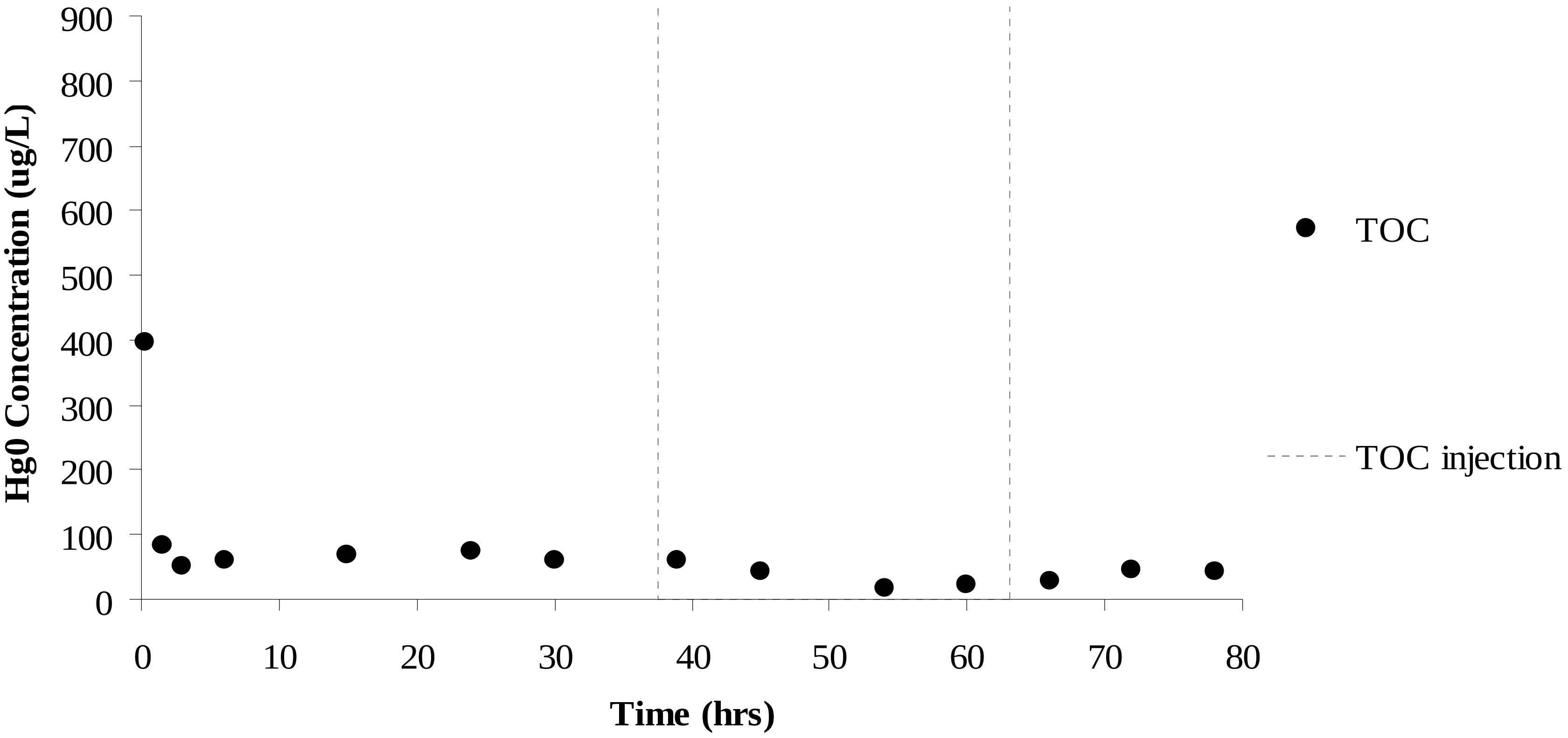

Figure 4.13c: Concentration vs. Time for the Sulfide Injection Test. Three columns were set up to compare the effluent mercury concentrations of three different sulfide injections. The (●) symbols represent the effluent mercury concentrations for the column exposed to the TOC solution.

deemed the best injection for this application.

Pictures were taken throughout the duration of this experiment. Once the experiment was concluded the columns were broken down and inspected to observe if HgS (s) could be visible in the column. Two figures taken when the NaSH column was broken down show that HgS (s) is possibly forming. The Hg^0 in these columns do have a dark residue around them. The presence of HgS (s) were not confirmed with x-ray diffraction. These observations are recorded in Figures 4.14 and 4.15.

4.8 Large Diameter Teflon Column NaSH – Flow Interrupt Test

The NaSH injection test was designed to observe how the Hg^0 column will react to a 0.1 M NaCl, 100 mg/L NaSH influent as well as what the response would be if flow interrupts were included in the experiment. The columns were prepared as before with washed Hg^0 and quartz sand only. The initial influent was a 0.1 M NaCl solution with a pH of 7.88 ± 0.5 and was bubbled continuously with N_2 (g) to remove any dissolved oxygen. The control column was constantly exposed to the 0.1 M NaCl solution. Once the effluent mercury concentrations stabilized at the solubility of mercury, the influent for the variable column was changed to the 0.1 M NaCl, 100 mg/L NaSH influent with a pH of 10.43 ± 0.5, which was bubbled with N_2 (g) to remove any dissolved oxygen. The influent was pumped through for ~ 1.3 pore volumes ($\nu = 0.039$ cm/min, $\theta = 741$ min). After the NaSH influent solution was pumped through, a flow interrupt was conducted where flow was stopped and the NaSH and Hg^0 were allowed to react for four hours. The columns were restarted and pumped through for a second ~ 1.3 pore volumes and then stopped to allow the NaSH

Figure 4.14: Dark residue observed after the NaSH column was broken down.

Figure 4.14: Dark residue observed after the NaSH column was broken down.

and Hg^0 to react again for four hours. The columns were restarted again and pumped through for a third ~ 1.3 pore volumes and then stopped to change the influent back to a 0.1 M NaCl solution, bubbled continuously with N_2 (g). The effluent mercury concentrations were allowed to stabilize, and then the columns were shut down. After ten days the columns were restarted again to take measurements of the effluent mercury concentrations to see if the layer of HgS (s) that may be forming can be maintained over time. The results for this data are illustrated in Figure 4.16.

The results for this experiment indicated reduced effluent mercury concentrations which would be consistent with the HgS (s) layer forming around the Hg0 beads. The effluent concentrations for the control column remained slightly lower than the solubility of mercury, 46 ± 14 µg/L for the duration of the experiment. The effluent concentrations for the column exposed to NaSH behave differently in different situations. While exposed to the NaSH and the flow interrupts during this time the effluent mercury concentrations are between 30 and 50 µg/L. The high mercury concentrations may be due to the fact that the environment during this time is highly concentrated with sulfide, because the column is saturated with the NaSH influent. It has been documented that in environments with high sulfide concentrations the solubility of HgS (s) increases, which may be the cause of the increase in the effluent mercury concentration in this situation. Once the influent was changed back to the 0.1 M NaCl solution, the effluent mercury concentrations dropped to below 10 µg/L, which is consistent with the HgS (s) layer forming around the Hg^0 beads. A ten day flow interrupt was conducted once the effluent mercury concentrations stabilized. The effluent concentrations were taken after the flow

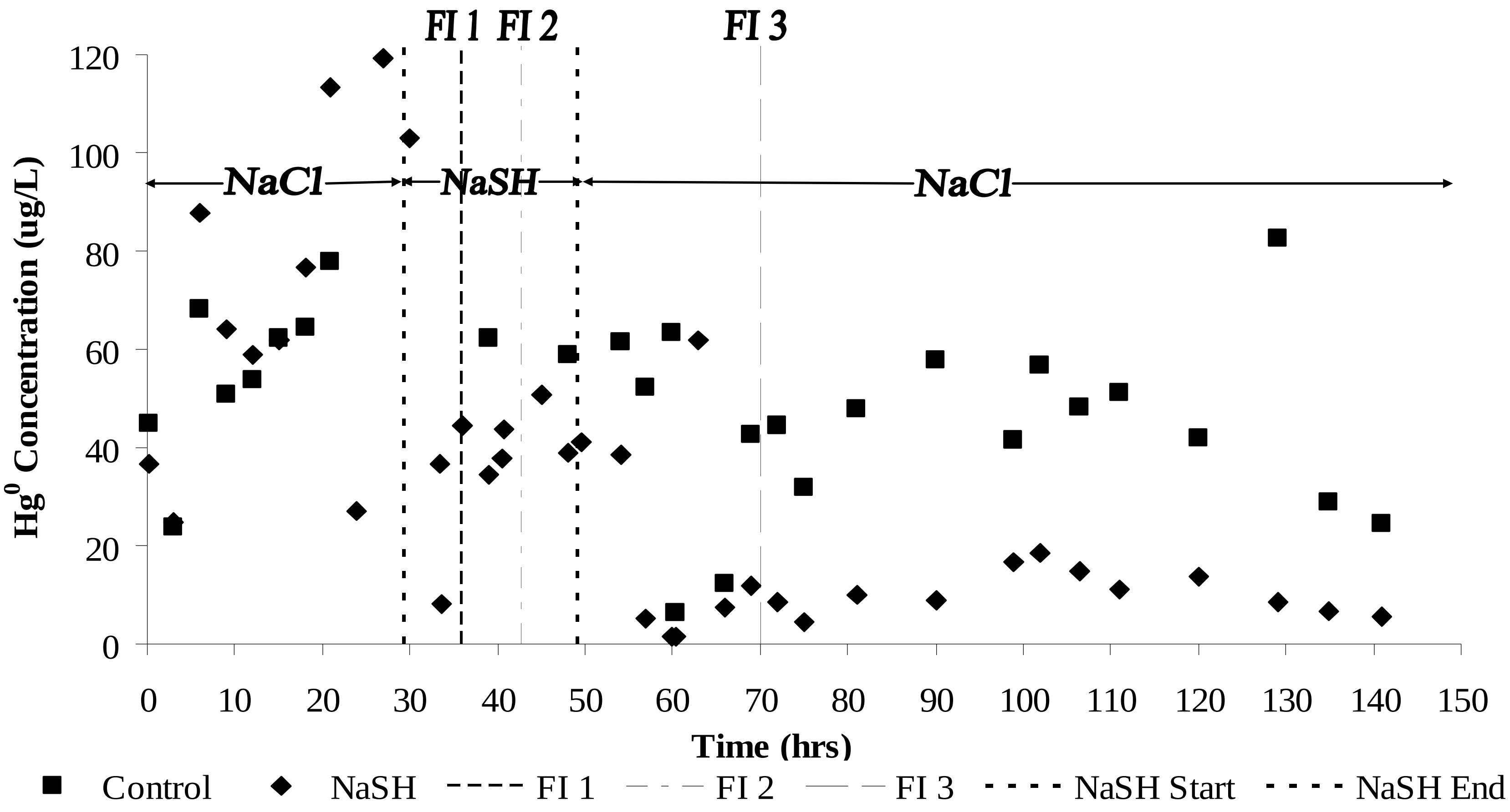

Figure 4.16: Concentration vs. Time for the NaSH – Flow Interrupt test. Two 4 cm diameter elemental mercury columns are shown here, the (■) symbols indicate the effluent mercury concentrations of the column that was not exposed to the NaSH injection and the (◆) symbols indicate the effluent mercury concentrations of the column that was exposed to the NaSH injection. The "FI" stands for flow interrupt, and indicates each of the three that were conducted during the course of this experiment.

interrupt to observe the ability of the layer to be maintained over time. The effluent mercury concentrations after the flow interrupt remained less than 20 µg/L. The low effluent mercury concentrations indicate that if the HgS (s) layer is forming, it can be maintained under ideal conditions for an extended amount of time. The effluent pH was monitored and was found to be low at the beginning of the experiment and then slowly rose to the influent pH. The pH data for this experiment is illustrated in Figure 4.17.

Samples from around the Hg^0 beads were X-ray Diffracted. The XRD data for this experiment is illustrated in Figure 4.18. The column was disassembled in the glove box under N_2 (g) and the barrier was placed in a brown glass vial to ensure that the barrier was exposed to as little oxygen as possible in order to preserve the barrier as it was in the column and prevent oxidation. The results reveal that metacinnabar may be present in the samples provided.

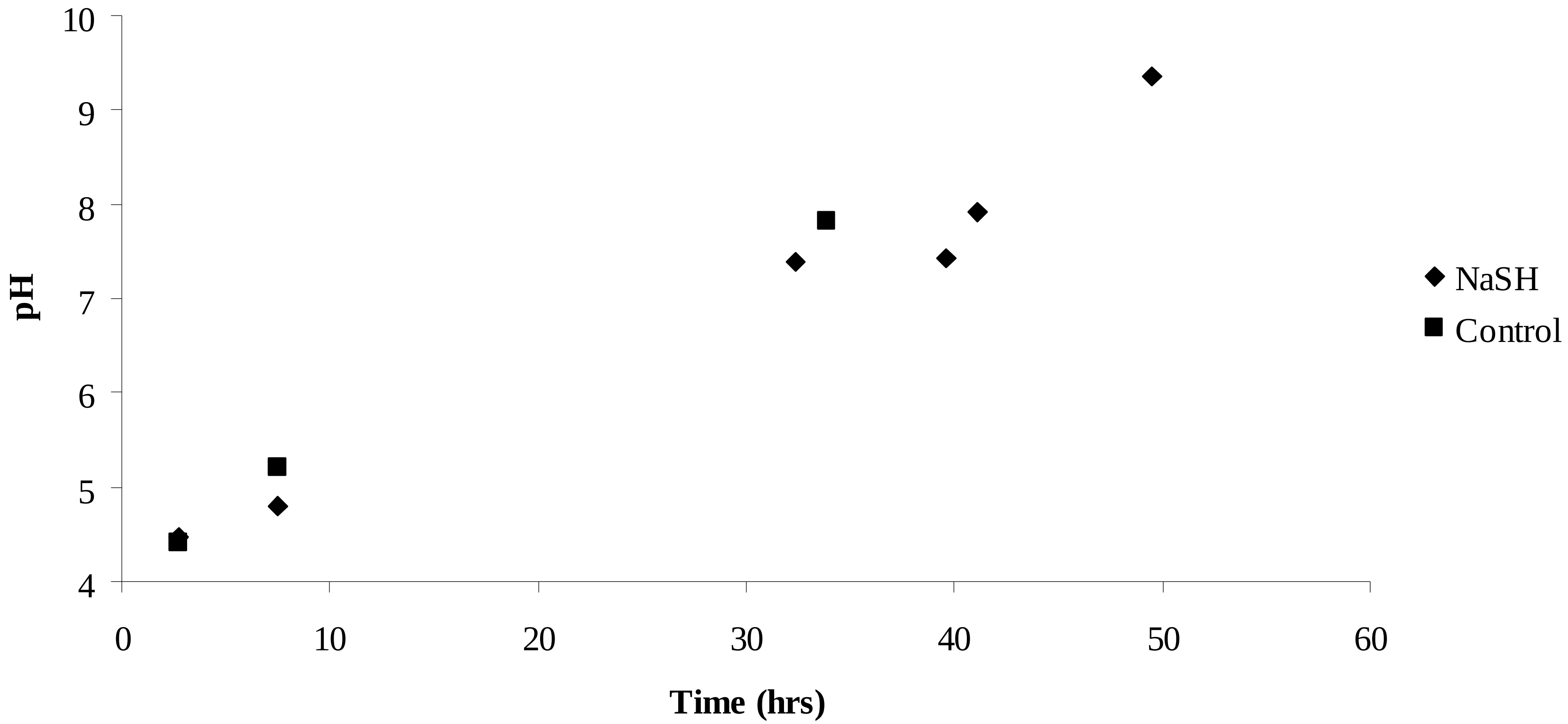

Figure 4.17: pH Data for Large Diameter Teflon Column NaSH test. The effluent pH for this experiment started out low and slowly came back up to the influent pH. The (■) symbols indicate the effluent pH values of the control column and the (◆) symbols indicate the effluent pH concentrations for the NaSH column. The effluent pH started out low and slowly came up to the influent pH.

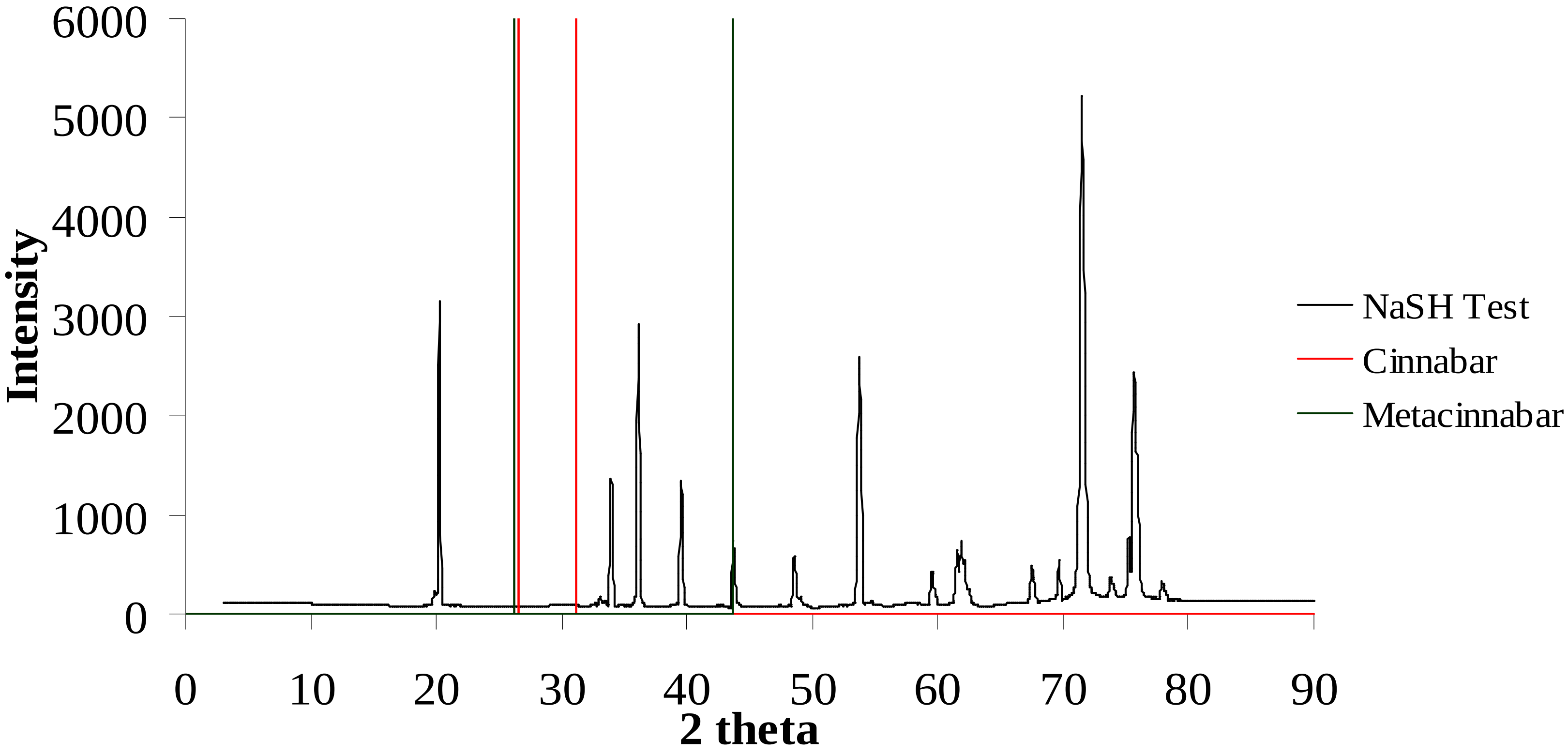

Figure 4.18: XRD Data for the Large Column NaSH – Flow Interrupt Test. The x-ray diffraction data for the NaSH injection is shown on this graph as the solid black line. The green vertical lines indicate Metacinnabar (HgS), and the red vertical lines indicate Cinnabar (HgS)

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions for the FeS (s) Permeable Reactive Barrier

1. The FeS barrier successfully removed mercury contamination in the column studies under flowing conditions. The maximum capacity that was found was 2066 µg Hg/g FeS.
2. The advantage of the barrier is that the capacity is known and that information can be accurately applied to contamination in the field.
3. The disadvantage of the barrier is that it has a capacity and in field applications the barrier would have to be removed through excavation and then replaced every time that the capacity for the column was reached. The replacement of the barrier would be costly and it might have to be replaced a number of times to success fully remove all of the mercury from the groundwater.

5.2 Conclusions for the Sulfide Injections

1. Three sulfide injections, TOC, FeS nanoparticles, and NaSH, were compared to discover which injection immobilized mercury the best. The NaSH was found to perform the best both during exposure and after and was then explored in more depth.
2. The NaSH was found to be a good immobilizer of mercury under flowing conditions. The NaSH influent created a HgS (s) layer around the mercury beads

and successfully prevented 1751 µg of mercury from exiting the column after the influent was changed back to the 0.1 M NaCl solution that was bubbled with N_2 gas.

3. The advantage to the NaSH injection is that the layer of HgS (s) that theoretically could be made would encase the contaminant which would effectively immobilize the Hg^0 permanently.
4. The disadvantage to the NaSH injection is that we do not have a good means to make a calculation on the ability of HgS (s) to form, and we also have no way of confirming that this phenomena would be occurring in the field.

5.3 Recommendations for Further Study

1. The low limit for the concentration of NaSH required that prevents the mercury from coming out of the column is an important parameter to find.
2. The experiments in this thesis all are conducted under ideal conditions; it would be interesting to see the response to a NaSH column if the conditions were changed to reflect high sulfide concentrations and high pH, which are conditions where it would be less ideal for the HgS (s) layer to form.
3. The ability of the HgS (s) layer to stand up in ideal conditions for a long time would be interesting to explore. The layer may break down over time or it may remain and be a good solution to the problem.
4. An effective means by which to measure sulfide concentration would be good for these results. The author tried a number of means by which to measure sulfide: Ion Chromatograph, Chem-Ets Color test, and an Ion Specific Electrode. All of

these did not consistently report an accurate sulfide concentration. If an accurate S (-II) measurement were accessible, then a capacity calculation for S (-II) adsorption onto Hg^0 could be calculated which would be a useful parameter for this application.

5. These NaSH experiments were not conducted under aerobic conditions. The response to the Hg0 column under aerobic conditions would be interesting to see.
6. A good means by which to conduct a batch test with Hg0 would be useful for this treatment method. The author did not find a way to use a DNAPL like Hg^0 in a batch experiment, however, if this type of experiment could be conducted, a better understanding of the adsorption of S(-II) onto Hg^0 could be found.

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APPENDICES

Appendix A: Extra results from the research

One of the results was not included in the thesis but is included here for review. This experiment needs to be redone with an NaSH influent that includes 0.1 M NaCl as well.

4.9 Large Diameter Teflon Column NaSH Influent Test

The NaSH influent experiment was designed to compare a control column with a column that is exposed to NaSH. The control influent was a 0.1 M NaCl solution that was bubbled continuously with N_2 (g). The variable solution for the NaSH exposure was a 0.01 M NaSH solution. The effluent mercury concentrations were lower than the solubility of mercury when the NaSH exposure began and remained low throughout the experiment. The NaSH exposure lasted for one day, after which the influent returned to a 0.1 M NaCl solution. Effluent mercury measurements were made using Atomic Adsorption Spectrophotometry. The results for this experiment are illustrated in Figure 4.12.

The results for this experiment indicate again that the HgS layer may be forming around the Hg0 beads. The effluent concentrations remained low after the influent was changed back to a 0.1 M NaCl solution. After the influent was changed back to the 0.1 M NaCl solution, the HgS layer prevented 92 % of the mercury from coming out of the column. A problem with the data was that the ionic strength needs to be monitored because the samples exit the columns with a residue in them to that makes them murky and unable to be measured for mercury content. The ionic

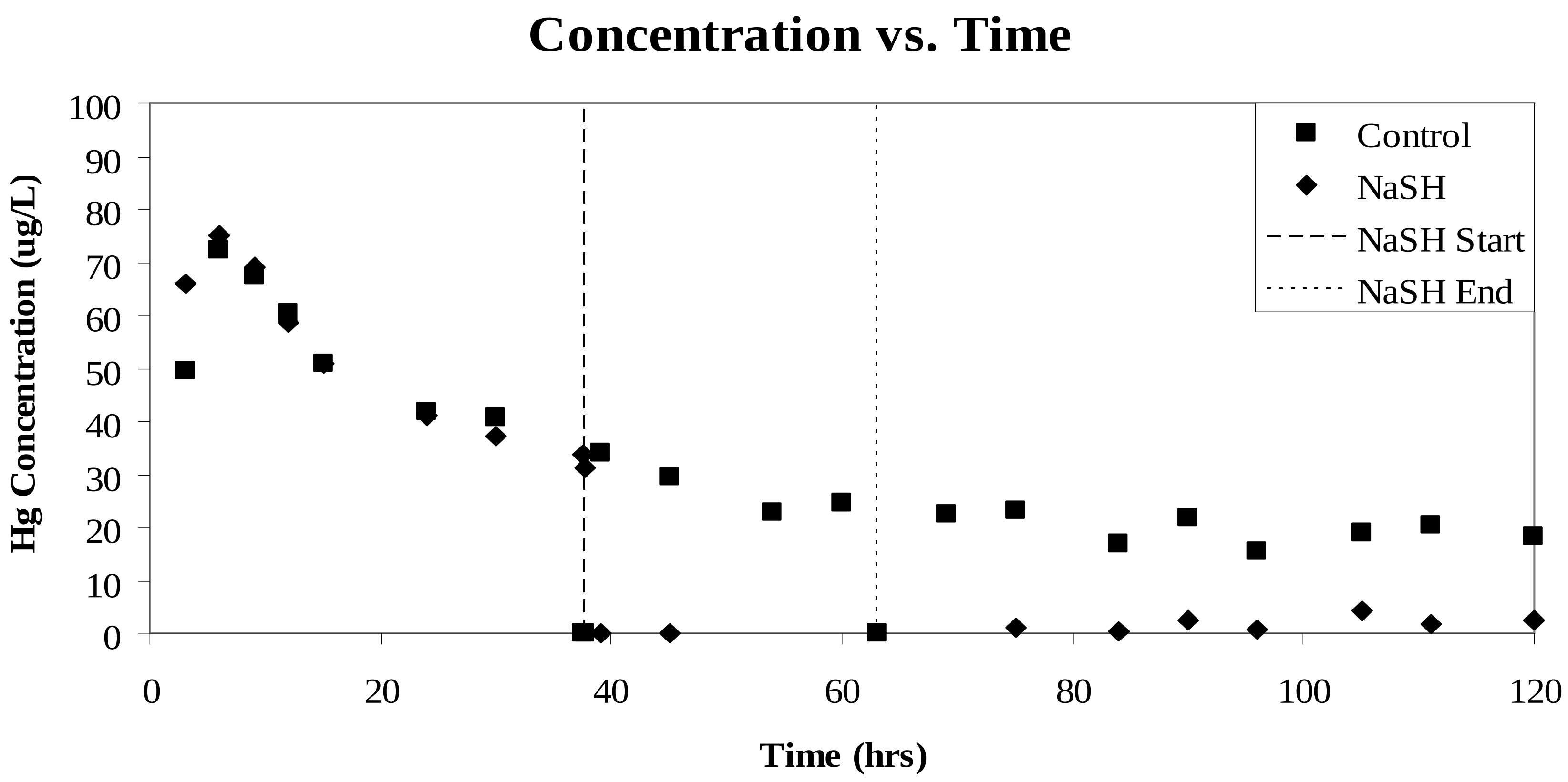

Figure 4.19: Concentration vs. Time for Column Test 14. Two 4 cm diameter elemental mercury columns are shown here, the (■) symbols indicate the effluent mercury concentrations of the column that was not exposed to the NaSH injection and the (◆) symbols indicate the effluent mercury concentrations of the column that was exposed to the NaSH injection. The lines indicate when the effluent mercury concentrations reflect the beginning and end of the NaSH injection.

strength should be able to be adjusted using a 0.1 M NaCl solution with the 0.01 M NaSH solution like the influent for the NaSH – Flow Interrupt test.

Appendix B: Sample calculations.

Example 1:
Example calculation to determine maximum capacity for the FeS barrier.

Given: Effluent mercury concentration data from the control column (Co)
Effluent mercury concentration data from the column with the barrier (Ce)
Amount of FeS in the barrier = 0.14 g
Volume of each sample was 9 mL

$Q_{max} = (\Sigma(C_o * V_i) - \Sigma(C_e * V_i)) / 0.14 \text{ g FeS} = 980\ \mu\text{g/L}$