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ABSTRACT

Stabilization of mercury-containing wastes has received considerable attention recently, due to concerns about air emissions from typically used thermal treatment technologies. Because of the extremely low solubility of mercuric sulfide, sulfide-induced stabilization is considered to be an effective way to immobilize mercury while minimizing mercury emissions. However, little is known of the mechanisms involved. In addition, the process of sulfide-induced stabilization of mercury-containing wastes has not been sufficiently developed; therefore, further research is needed to optimize the process-controlling parameters.

In this study, the stabilization of mercury-containing wastes was performed using sodium sulfide. Primary stabilization variables such as stabilization pH, sulfide/mercury (S/Hg) molar ratio, and stabilization time were investigated. Mercury stabilization effectiveness was evaluated using the Toxicity Characteristic Leaching Procedure (TCLP) and constant pH leaching tests. The effectiveness of mercury immobilization by sulfide was tested in the presence of various concentrations of interfering ions.

The results demonstrate that stabilization pH and sulfide dosage have significant effects on the stabilization efficacy. It was found that the most effective mercury stabilization occurs at pH 6 combined with a sulfide/mercury molar ratio of 1. The mercury stabilization efficiency reached 99%, even in the presence of interferents. The

constant pH leaching results indicate that sulfide-treated mercury wastes produce significantly higher mercury concentrations in high pH ($\text{pH} > 10$) leachants relative to others. Nevertheless, the mercury stabilization efficiency was still as high as 99%, even with exposure of the wastes to high pH leachants. Therefore, it is concluded that sulfide-induced stabilization is an effective way to stabilize mercury-containing wastes. The treatment optimization study indicates that the combined use of increased dosage of sulfide and ferrous ions ($\text{S/Hg} = 2$ and $\text{Fe/Hg} = 3$ at $\text{pH} = 6$) can significantly reduce the interferences by chloride and/or phosphate during sulfide-induced mercury immobilization.

Visual MINTEQ simulation results indicate that the precipitation of cinnabar is the main mechanism that contributes to the mercury stabilization by sulfide. However, the formation of soluble mercury sulfide species at excess sulfide dosage due to the common ion effect can cause mercury remobilization from sulfide sludge under conditions that can exist in the landfills.

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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Mercury is a highly toxic element. Both inorganic and organic mercury can cause serious health effects. The December 1997 *Mercury Report to Congress* (US EPA, 1997) identified mercury as a human health and environmental problem needing additional scientific and technical research. Other Agency reports (e.g., *Great Waters Second Report to Congress*, 1997; *Utility Air Toxics Report to Congress*, 1998) stress the adverse impacts of mercury on both humans and wildlife (US EPA, 1999). Particularly, mercury is receiving the major focus due to its unique characteristics, such as high volatility and bioaccumulation.

Many studies have reported on mercury-containing waste treatment methods. Conventional mercury treatment methods include incineration, precipitation, coagulation/co-precipitation, adsorption, and ion exchange. New methods, such as biological detoxification and membrane extraction, are now emerging. Among these methods, thermal treatments such as incineration, retorting and roasting are the currently allowable Land Disposal Restriction (LDR) treatment technologies, and are widely used in mercury treatment (US EPA, 1999). Inorganic high concentration-mercury wastes are being treated by retorting or roasting for recovery. However, commenters and petitioners have asserted that many subcategories of mercury wastes (e.g. inorganic salts, corrosive

wastes, incineration residues, wastewater treatment sludges) are not directly amenable to retorting/roasting treatment and are not accepted by commercial retorting facilities. In addition, there are concerns about air emissions from the traditional thermal treatment technologies. Therefore, evaluation of the effectiveness of alternatives to thermal treatments is needed, particularly for the stabilization/solidification process, to meet Resource Conservation and Recovery Act (RCRA) standards while minimizing mercury emission (US EPA, 1999).

Stabilization/Solidification (S/S) methods have long been applied to immobilize hazardous wastes. S/S methods are especially useful for the treatment of heavy metal bearing sludges and inorganic wastes (Chang et al., 1993). Stabilization is also considered to be an effective pathway to immobilize mercury from wastes. The stabilizing agents used for mercury immobilization include clay, cement, fly ash, sulfide, and so on. Among these methods, sulfide immobilization of mercury is one of the most widely used methods for removal of inorganic mercury from wastewater. However, due to the complexity of mercury-sulfide chemistry and the high variety of mercury-containing wastes, the process of sulfide-induced stabilization of mercury-containing wastes has not been sufficiently developed and, therefore, further research is needed to optimize process-controlling parameters. In addition, until now very little research has attempted to investigate the mechanisms of sulfide immobilization. Therefore, this research is also aimed at understanding the mechanisms of sulfide-induced mercury stabilization.

1.2 Research Objectives

The objectives of this research are to characterize the mercury stabilization process by sulfide and provide commercially available optimized sulfide-induced stabilization techniques for mercury-containing wastes. Optimized parameters are developed to improve treatment efficiency. Stabilization, pH, sulfide dosage, reaction time, and complexants are the most important factors influencing the effectiveness of mercury treatment.

The specific objectives for this research are:

- 1) To assemble an inorganic high-mercury surrogate waste, which can be used in the first phase of the stabilization study. The lab-assembled mercury surrogate and a real mercury waste will be characterized both physically and chemically prior to the sulfide treatment.
- 2) To study the kinetics of the mercury-sulfide reaction under different pH and sulfide dosage conditions. An optimum stabilization contact time will be established from this step.
- 3) To investigate the effects of stabilization pH and sulfide dosage on the sulfide-induced mercury stabilization process. This phase is the key step in determination of optimum parameters that control the sulfide treatment process.
- 4) To evaluate the effectiveness of stabilization by conducting several kinds of leaching tests. In this research, the Toxicity Characteristic Leaching Procedure (TCLP),

liquid/solid ratio leaching tests, and constant pH-based leaching test will be performed on both treated and untreated wastes.

5) To examine the influence of interfering ions on the sulfide-induced mercury stabilization process. Some common cations, anions, and organic complexants will be tested for their effects. TCLP is a regulatory benchmark. For the worst-case scenarios, when the TCLP results do not comply with regulatory limits, further treatment will be conducted to increase the effectiveness of treatment.

6) To investigate the performance of the optimized treatment process by applying the optimized parameters on a real mercury waste. Several leaching tests will be conducted to assist with the evaluation of treatment efficacy.

7) To develop a leaching model using the geochemical equilibrium model, MINTEQA2, combined with thermodynamic data. The leaching model will be designed to predict equilibrium distributions and behavior of aqueous species after the leaching process under given initial conditions.

1.3 Significance of the Research

There have recently been concerns about air emissions from traditional thermal treatment technologies for mercury wastes due to the high volatility of mercury. Therefore, investigation of the issues regarding the effectiveness of alternatives to thermal treatment, particularly stabilization/solidification, is necessary to improve mercury treatment while minimizing air emissions. In this research, sulfide-induced mercury stabilization/solidification was investigated. Because of the particularly low solubility of mercuric sulfide (0.017 mg/l at 18 °C), sulfide should be an effective agent to stabilize mercury from wastes. Furthermore, sulfide is a very common ion in nature, and using sulfide to treat mercury-containing wastes is a cost-effective pathway. This research provided a set of optimized design parameters to effectively immobilize mercury in wastes. The parameters include sulfide dosage, stabilization pH, liquid/solid ratio, and reaction time.

The second major purpose of this proposed research was to investigate the mechanisms of sulfide-induced stabilization and of the leaching process. Most studies of sulfide-induced mercury stabilization have concentrated on the leaching behavior of the treated products and the design control of the process. Very few detailed studies of mechanisms on sulfide-induced mercury immobilization in complex wastes exist. This research examined the nature of these wastes and their sulfide stabilization mechanisms, as well as the mechanisms of the leaching process, using a modified MINTEQA2 model.

Thus, this research provides valuable information that will contribute to the improvement of mercury stabilization techniques.

1.4 Organization of the Dissertation

The materials in this dissertation are organized in the following order. Following Chapter 1, which describes the problem statement, research objectives, and the significance of the research, Chapter 2 focuses on a literature review. The material emphasizes background information on health effects, usage, and sources of mercury; stabilization/solidification (S/S) methods used in mercury treatment; sulfide application in mercury treatment; mercury-sulfide chemistry, and variables that affect leaching behavior of heavy metals.

Chapter 3 provides detailed information on various materials and methods applied throughout this study. It describes various procedures involved in the characterization of mercury-containing wastes and determination of mercury and other constituents from the leaching process. The procedures for several leaching tests conducted in this study are also discussed.

Various results obtained from this study are summarized in Chapter 4, which also covers some discussions to give explanations for the observed results. The characteristics of mercury-containing wastes are described, and the mercury-sulfide reaction kinetics is presented. In addition, the effects of stabilization pH and sulfide dosage, and of

interfering ions on the sulfide-induced stabilization process are discussed, followed by the results obtained from different leaching procedures on the sulfide-stabilized mercury wastes. A leaching model was developed in this research. Hence, the last section of this chapter details the results of leaching simulations, and compares them with the observed data.

The last chapter, Chapter 5, presents a summary of this research and provides some recommendations for future work that can be initiated.

Appendices provide detailed procedures for the leaching tests that were used throughout this study, and the raw data obtained from this research study.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 About Mercury

2.1.1 Health Effects

Mercury has been recognized as a toxic hazard for centuries. The effects depend upon the route of exposure and the nature of the mercury compounds involved.

Metallic mercury is slowly volatilized at room temperature, and about 80% of the vapor entering the lungs can be absorbed. It is lipid soluble and can enter the brain, from which it is only slowly eliminated. The symptoms of low-level mercury poisoning are subtle (e.g. headaches, fatigue, nausea, personality changes) and may be difficult to distinguish from other causes. Mercury exposure is particularly hazardous to pregnant women.

Inorganic mercury poisoning may result in disorders of the central nervous system and possibly psychoses. The major effect from chronic exposure to inorganic mercury is kidney damage.

The organic forms of mercury are more toxic than inorganic forms. Acute exposure to high-level methyl mercury in humans results in central nervous system effects such as blindness, deafness, and impaired levels of consciousness. Chronic (long-

term) exposure to methyl mercury in humans also affects the central nervous system. Effects such as paresthesia (a sensation of pricking on the skin), blurred vision, malaise, speech difficulties, and constriction of the visual field result from methyl mercury exposure (Encyclopedia of Chemical Engineering, 1981; Fthenakis et al., 1994).

2.1.2 Usage of Mercury

Mercury has historically been utilized for a number of general purposes. Mercury is widely used in caustic-chlorine production, and the loss of mercury from mercury cell process in chlorine production has been by far the largest single source of mercury pollution (Conner, 1990). Mercury is also widely used in laboratory work for making thermometers, barometers, diffusion pumps, and other instruments. It is useful in electronics for producing mercury-vapor lamps, and mercury-switches in circuits. In agriculture, mercury has been used in fungicides, pesticides, bactericides, and disinfectants; most of the mercury-based pesticides and fungicides have been banned for being hazardous substances. Mercury also has been used as a catalyst for the production of vinyl chloride monomers, urethane foams, anthraquinone derivatives and other products. Mercury is also commonly used in making cells, dental preparations, antifouling paint, and batteries. Compounds containing mercury are used in medicine, as detonators for explosives, and as a pigment. Within the United States alone, manufacturers use 500-600 metric tons of mercury annually (Encyclopedia of Chemical Engineering, 1981; Conner, 1990; US EPA, 2000). The uses of mercury in the United States are summarized in Table 2.1.

Table 2. 1 Uses of Mercury in the United States
(Conner, 1990)

Use	1959	1968	1978
Agriculture	110	118	21
Amalgamation	9	9	<0.5
Catalysis	33	66	29
Dental preparation	95	106	18
Electrical applications	426	677	619
Caustic-chlorine	201	602	385
General laboratory	38	69	14
Industrial and control	351	275	120
Paint			
Antifouling	34	14	
Mildew proofing	87	351	309
Paper and pulp	150	14	
Pharmaceuticals	59	15	15
Others	298	285	216
Total	1892	2600	1681

2.1.3 Sources of Mercury

Mercury is released into the environment from natural and anthropogenic sources. In a recent report, US EPA estimated that mercury emissions produced by human activities rival or exceed natural inputs. Based on emission properties, EPA divided anthropogenic mercury sources into the following four groups: (1) combustion point sources; (2) manufacturing point sources; (3) miscellaneous point sources; and (4) area sources (US EPA, 2000).

It was estimated that the total global anthropogenic emissions of vapor phase mercury in 1988 were about 1,000 to 6,000 tons per year (Nriagu and Pacyna, 1988), and it is reported that in the United States alone anthropogenic sources emit 263 tons of mercury annually to the atmosphere (US EPA, 2000). Of this total, combustion point sources account for 85% of the anthropogenic mercury emissions. Unlike most other trace metals that are emitted in particulate forms, mercury has been reported to be released primarily in the vapor phase in the elemental form. Elemental mercury vapor is not effectively captured in typical air pollution control devices.

2.2 Stabilization/Solidification (S/S) Application in Mercury Treatment

S/S methods have long been applied to stabilize hazardous wastes. The methods are especially useful for the treatment of heavy metal bearing sludges and inorganics, as noted by many investigators (Chang, 1993).

Cement-based S/S

The cement-based methods employing Portland cement are the most common ones among the numerous S/S applications (Chang, 1993). "This process is flexible, effective, accommodates complex mixtures of contaminants and is economical enough to be used for large volumes of wastes" (Lange, 1996). The process usually involves addition of a heavy metals waste to a cementitious binder, with or without pretreatment with lime. At the resulting high pH, heavy metals are expected to precipitate as their respective insoluble hydroxides, since many heavy metals reach their lowest solubility at about pH 10 (Roy, 1992).

Durability testing of a solidified mercury-containing sludge proved that mercury could be processed by S/S (Yang, 1993), and much research has been performed on cement-based S/S of mercury-containing wastes. It is reported that mercury exists partially as an oxide precipitate in Portland cement (McWhinney, 1990). However, some problems are related to cement-based treatment of mercury containing wastes. It is reported that no mercury was detected in Portland cement-stabilized samples after stabilization, while elemental mercury vapor (Hg vapor) was detected in the headspace of batch reactors that contained S/S ordinary Portland cement doped with mercuric oxide (HgO) or liquid elemental mercury (Hg⁰ (l)). Therefore, it is believed that mercury has a strong potential to volatilize from cement-solidified sludge (Hamilton, 1997).

The other problem associated with Portland cement-based materials is atmospheric carbonation (Lange, 1996). Carbon dioxide-bearing water is deleterious

because ordinary Portland cement paste is readily dissolved in an acidic environment, thus affecting the leachability characteristics of cement-based waste over time (Bonen, 1995).

Cement/fly ash S/S

The cement-based methods are indeed very effective for a wide variety of wastes. However, their use may be dependent on the cost of cement. In order to reduce the treatment cost due to the use of cement, various reusable wastes have been used as additives in the cement-based methods. A Portland cement/fly ash binder was used to solidify a heavy-metal sludge containing Cr, Ni, Cd, and Hg (Roy, 1991). The sludge was composed of the hydration products of cement/fly ash mixtures and impure, complex compounds of the waste metals. In fact, because of a good adsorption capacity for Hg (II), fly ash is used in removal of mercury from wastewater (Sen, 1987; Hassett, 1999). Adsorption of mercury on coal fly ash conforms to Freundlich's adsorption model. Mercury capture on fly ash has been attributed to the carbon contained in fly ash (Hassett, 1999).

Nevertheless, the leachability of mercury in the cement/fly ash-treated sludge increased with curing time, and a great amount of fly ash was required for an acceptable treatment result. This would increase the cost of final disposal (Chang, 1993).

Two-step treatment with combined sulfide pretreatment and cement/fly ash solidification

Chang et al. (1993) reported a two-step mercury immobilization process consisting of sulfide pretreatment and cement/fly ash solidification. Sodium sulfide and ferrous sulfate were used in pretreatment, wherein an excess amount of sulfide was used to stabilize mercury while ferrous sulfate was employed to remove excess residual sulfide. Their experimental results indicated that the stabilization efficiency was strongly enhanced by the pretreatment process, and the tendency of total leachate mercury to increase with curing time was greatly reduced within the ranges of experimental conditions. The mixing ratio of cement/fly ash/sludge, $\text{Na}_2\text{S}/\text{Hg}$, and FeSO_4/Hg affected the leachability and compressive strength of the solid end products.

Innovative methods

The conventional cement-based S/S treatments cannot effectively reduce the leachability of mercury "mainly due to the relatively high solubility of mercury hydroxide and the tendency for mercury to form soluble complexes with organic and inorganic ligands" (Meng et al., 1998). Therefore, much research is being performed to investigate new methods to treat mercury-containing wastes.

The application of sulfur polymer

Sulfur polymer cement (SPC) was developed by the U.S. Bureau of Mines as a low-cost, corrosion resistant construction material. It contains 95% elemental sulfur, and 5% organic modifiers to enhance stability. The sulfur polymer S/S process was developed

for mixed waste mercury (Environmental & Waste Management Group et al., 1998). Fuhrmann et al. (2002) developed a new process to immobilize elemental mercury wastes using SPC and sodium sulfide. In this process, elemental mercury was stabilized by excess sodium sulfide additives, and then solidified by SPC. It was reported that the treated mercury waste met US EPA leaching criteria and had low mercury vapor pressure. SPC does not corrode under acidic conditions, and elemental sulfur is able to chemically bind metals, especially as metal sulfides, which are completely immobile. Disadvantages compared with cement are the low heat resistance (115°C) and the higher processing temperature (130°C, as sulfur has its lowest viscosity at this temperature) (Alkemade and Koene, 1996).

The application of used tires

Used tire rubber was evaluated for immobilization of Hg (II) in a contaminated soil using batch extraction and field rainwater leaching tests (Meng et al., 1998). Ground rubber tire particles were utilized for immobilization of Hg (II) in a spiked soil. Results indicated that the rubber had a high adsorption capacity for Hg (II) when pH values were between 2-8.

2.3 Sulfide Application in Mercury Treatment

Sulfide precipitation is one of the most commonly reported precipitation methods for removal of inorganic mercury from wastewater. In this process, sulfide (e.g., as

sodium sulfide or another sulfide salt) is added to the waste stream to convert the soluble mercury to the relatively insoluble mercury sulfide form:

Due to the very low solubility of mercuric sulfide, mercury is effectively removed from aqueous solutions. Googin et al. (1986) reported a process for removing mercury from water to a level not greater than two parts per billion, using an ion exchange material that is contacted first with sulfide-containing compounds and second with a compound containing a bivalent metal ion, forming an insoluble metal sulfide.

Furthermore, sulfide is used to remove mercury from soil and sediment, as well as to stabilize mercury-containing waste. The treatment of mercury in aqueous media by contacting the mercury-containing solution with a sulfide to form insoluble mercury sulfide is disclosed in many US Patents, e.g. numbers 3674428, 4147626, and 4614592 (Ader et al, 1989). Sulfide salt or elementary sulfur is used to produce water-insoluble mercuric sulfide. Usually these sulfide-agents are added in combination with other chemicals or binders to improve the removal or stabilization effectiveness. For example, Fristad et al. (1998) invented a process for removing mercury from soil wherein a mild leachant solution, comprised of an aqueous solution of an acid and a salt, is added to wash the soil before adding sulfide to remove mercury; and Ader et al. (1989) invented a method for stabilization of mercury-containing waste by adding elemental sulfur and cement kiln dust to the waste to reduce the leachable mercury to an environmentally

acceptable level. Mercury stabilized/solidified as mercuric sulfide (HgS , black) emitted no mercury vapor, although mercury vapor was detected in the headspace of batch reactors that contained stabilized/solidified ordinary Portland cement doped with mercuric oxide (HgO) or liquid elemental mercury (Hg^0) (Hamilton, 1997).

Although there is widespread use of sulfide in treating mercury-containing wastes, successful resolutions for the problems associated with this method have rarely been found in literature until now. Problems with sulfide induced S/S treatment of mercury-containing wastes are: (1) the formation of soluble mercury sulfide species at excess dosage of sulfide, due to the common ion effect, and (2) remobilization of mercury at high pH ranges. These drawbacks can cause mercury resolubilization from sulfide sludges under conditions that can be found in landfills (Hansen and Stevens, 1992). Therefore, research for optimization of sulfide-induced stabilization of mercury containing waste is needed, both theoretically and practically.

2.4 Mercury-Sulfide Chemistry

In order to obtain an improved sulfide treatment of mercury-containing wastes, it is important to understand mercury sulfide chemistry that can provide information on the mercury sulfide reaction, speciation, and distribution.

Sulfide can convert soluble mercury to the relatively insoluble mercuric sulfide form (US EPA, 1997):

$$K_{sp} = 10^{-52}$$

HgS has an extremely low solubility and high resistance to oxidative dissolution (Hamilton, 1997). Therefore, sulfide is the most widely used agent in mercury treatment. However, as mentioned previously, mercury can be remobilized in the presence of excess sulfide because the mercury can form various water-soluble mercury-sulfide complexes, as shown in Table 2.2 (Clever et al., 1985):

Table 2. 2 Mercury and Sulfide/Bisulfide Reactions and Constants

(Clever et al., 1985)

Equilibrium Reaction	-logK
$\text{HgS (s)} + 2\text{H}_2\text{S} = \text{HgS}(\text{H}_2\text{S})_2$	4.25
$\text{HgS (s)} + \text{H}_2\text{S} + \text{HS}^- = \text{Hg}(\text{HS})_3^-$	3.50
$\text{HgS (s)} + 2\text{HS}^- = \text{HgS}(\text{HS})_2^-$	3.51
$\text{HgS (s)} + \text{S}^{2-} = \text{HgS}_2^{2-}$	-0.57

Each of these species is dominant at certain pH ranges (Please refer to Figure 2.1), and the most important finding is the tendency of total soluble mercury to increase with pH values (Barnes et al., 1967). Figure 2.2 explains another important relationship between solubility of mercury and sulfide concentration (Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1993). Total soluble mercury increases when the sulfide concentration increases. Therefore, it is very clear that pH and sulfide

concentration will be the most important variables in studying of the mercury-sulfide reaction.

Figure 2. 1 Solubility of Mercury (II) Sulfide vs. pH

(Clever et al., 1985)

Figure 2. 2 Solubility of Mercury (II) Sulfide vs. Sulfide Concentration

(Kirk-Othmer Encyclopedia of Chemical Technology, 1993)

The sorption of mercury (II) onto solid mercury sulfide from acidic solution is another pathway that affects the mercury-sulfide chemistry. Hasany et al. (1999) reported the retention of mercury (II) by mercury sulfide in detail with respect to sorptive medium, agitation time, and sorbent and sorbate concentration. The mercury sorption data followed the Langmuir isotherm over the entire concentration of mercury investigated (Hasany et al., 1999). It is also reported that the sorption of mercury (II) may proceed through a metathetical reaction in which a metal sulfide is displaced by an appropriate ion in the solution:

Or the sorption of a hydrolyzed species:

2.5 Fundamental Concepts of Leaching

Landfills are containment structures used to hold and contain solid wastes, preventing groundwater contamination and thereby protecting human health and the environment. The problem of groundwater contamination arises when water, primarily rainwater, infiltrates and percolates through the waste by gravity. Therefore, leaching is

the primary criterion for determining the efficacy of a S/S process. Assessment of contaminant leaching is a complex task that must address the contaminant release rate and concentration of leaching contaminants. The contaminant leaching behavior can be quantified if the following fundamental properties are determined: the solubility of the contaminants, diffusivity of the contaminant in the matrix, and the site-specific mode of contact between the matrix and any potential leachant. Knowledge of these parameters will allow for development of a systematic leaching behavior profile with predictive ability (Garra-brants et al., 1995).

Several factors influence the release of contaminants from wastes. These factors include, but are not limited to, the major element chemistry, solution pH, redox status of the system, the presence of complexants, and the liquid to solid ratio. Many short-term leaching tests have been developed which seek to estimate the long-term leaching rates of contaminants under controlled conditions that may contribute to the destabilization of the wastes. Current leaching tests can be categorized as two types: equilibrium-aimed and dynamic-aimed leaching tests (Kosson et al., 1991). The Toxicity Characteristic Leaching Procedure (TCLP), the solid stability in water, and a pH-based leaching test will be used in this research to investigate the metal leaching behavior under equilibrium conditions, as well as to obtain dynamic leaching rates of heavy metals from landfill systems.

TCLP is a current standard regulatory test intended to determine the potential mobility of contaminants in a liquid or solid under simulated landfill conditions. However, recently there are some concerns about the TCLP test because of the problems

related to this leaching protocol, such as undefined endpoint pH, unknown release regime (solubility or availability), un-guaranteed equilibrium, and inconsideration of release rate (Garrabrants et al., 1995). As a result, the TCLP has been used in some situations where it is not appropriate, which may over- or under-predict the contaminant's leaching potential. Therefore, in order to understand and predict the quality of leachate that would be generated, it is necessary to obtain more data and information on thermodynamics and kinetics that influence the leaching of various constituents under disposal conditions.

Recently, a variety of leaching tests have been designed to assess leachability trends of contaminants in wastes. In addition to TCLP, liquid/solid ratio leaching tests, constant pH-based leaching tests, column leaching tests, American Nuclear Society 16.1 (ANS), and sequential leaching tests, are the most commonly used leaching tests. However, none of them actually represents the actual leaching behavior of contaminants in the landfill systems.

CHAPTER 3

MATERIALS AND METHODS

3.1 Research Methods Overview

Figure 3.1 presents an overview of the research methods that were applied throughout this study. More detailed information on the materials and methods are covered in the following sections of this chapter.

Figure 3. 1 Overview of the Experimental Design

3.2 Simulation and Characterization of Mercury-containing Wastes

3.2.1 Simulation of Mercury-containing Wastes

Mercury exists in both organic and inorganic forms in different matrices. In this research, the sulfide-induced mercury immobilization process was tested on inorganic high-mercury wastes (wastes containing greater than 260 mg/kg total mercury). Both a lab-simulated mercury surrogate and a real mercury waste were used in this study.

Mercuric nitrate ($\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$) was selected for the preparation of the mercury surrogate waste, which was used both in kinetic and stabilization test studies. Mercuric nitrate and mercuric chloride are the most widely used mercury (II) salts. Due to the severe interference effects of chloride on mercury and sulfide chemistry (Schuter, 1991), mercuric nitrate was chosen in the first phase of the research so that the most simplified mercury-sulfide reaction system could be created. Later, the influence of chloride on the sulfide-induced mercury stabilization process was investigated in the interference effects study.

Pure cube test sand (CT-109A ELE International) was used as the solid waste matrix so as to minimize competitive adsorption by substances in real-world soils. MilliQ water was used in all experimental tests.

A mercury waste surrogate was prepared using sand spiked with mercuric nitrate to yield the desired total mercury content. The specific procedure followed for the preparation of the mercury surrogate is described below:

- 1) Weigh sufficient amount of pure cube test sand for surrogate samples.
- 2) Dry the sand to constant weight at 60 °C. The quantity of sand needed for each surrogate sample is weighed out to the nearest 0.1 grams and stored in a clean glass sample container.
- 3) Weigh out the appropriate weight (to the nearest 0.001 grams) mercury nitrate based on final desired concentration.
- 4) Remove approximately half of the sand from the glass container.
- 5) Add the mercury from step 3) to the half-full glass sample container.
- 6) Add the sand removed in step 4) back to the sand/mercury mixture.
- 7) Add 5% w/w MilliQ water to the sand/mercury mixture.
- 8) Age the surrogates for 2 weeks.

The composition of the mercury surrogate waste is tabulated in Table 3.1

Table 3. 1 Composition of the Mercury Surrogate Waste

Desired Mercury Content (mg/kg)	Hg (NO₃)₂ · H₂O (g)	Sand (g)	Water (mL)
5,000	8.566	941.4	50.00

Compared with a simple simulated waste, there are wide varieties in composition of a real waste, which may lead to results that deviate from surrogate-based experimental results. Therefore, a real mercury waste was also applied in this study. A real mercury-containing waste, with total mercury content of 2,300 mg/kg, was obtained from contaminated sediment at a Superfund site. In order to minimize the heterogeneous effects of the real waste, particle size reduction was conducted before sulfide stabilization.

3.2.2 Characterization of Mercury-containing Wastes

In order to obtain baseline information on the untreated mercury-containing wastes, physical and chemical characterizations were conducted prior to sulfide stabilization.

Determination of physical parameters

Physical parameters determined in this study were particle size distribution, specific gravity, moisture content, and texture classification.

Particle size is directly associated with the available surface area of the waste, which is the area exposed to stabilizing agents and the leachant. The total available surface area will directly affect the rate of mercury stabilization and the leaching process. The measurements on particle size distribution will aid in understanding the effect

surface area has on stabilization and leaching. Particle size distribution was determined by standard method ASTM D 422-63.

ASTM D 2216-80 is a method for laboratory determination of moisture content of soil and rock. As the waste would weigh differently under different environments, consistency of sampling can be maintained by knowing the moisture content of the waste.

Table 3. 2 Physical Parameters and Analyses Methods

Physical parameter	Method of analysis
Particle size distribution	ASTM D 422-63
% Moisture	ASTM D 2216-80
Specific gravity	ASTM C 642-82
Texture procedure	Pipette method

Determination of chemical parameters

Chemical characterization included total mercury, relevant elemental analyses, pH, and several leaching tests on the original wastes.

Total mercury in mercury-containing wastes is one of the most important parameters. By measuring it prior to treatment, the amount of sulfide needed to treat the waste can be determined. US EPA standard method SW-846-7470A was used to digest solid samples. The total mercury in the waste was then analyzed by Cold Vapor Atomic

Absorption Spectroscopy (CVAA). Total sulfur in the waste was determined thermally using a Leco Sulfur Analyzer.

pH controls speciation and solubility of mercury-contaminated waste; thus it is one of the most important factors in evaluating waste leachability. pH values of solid wastes were measured using a digital Fisher Scientific Accumet pH meter 915 with a gel filled pH/ATC electrode.

TCLP and other leaching tests were carried out on the wastes prior to sulfide treatment to determine the leachability of the original wastes (please refer to the Section 3.4 for more detailed information about leaching tests). Leaching results were also used as a baseline to evaluate the stabilization efficiency.

Table 3. 3 Chemical Parameters and Analyses Methods

Chemical parameter	Method of analysis
Total mercury (mg/kg)	SW-846-7470A and CVAAS
Total sulfur	Leco Sulfur Analyzer
Chloride	Potentiometric known addition method
pH	pH electrode
Leachability	TCLP and constant pH leaching test; Leachate Hg was digested and analyzed by SW-846-7471 and CVAAS, respectively.

3.3 Kinetics Study of Mercury-Sulfide Reaction

Mercury surrogate and sulfide reaction kinetics were investigated to control the treatment time and to obtain the most effective immobilization pathway and corresponding parameters.

Sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) was used in this phase of the study to react with mercury in the simulated wastes. Mercury surrogates were combined with sodium sulfide at three different molar concentrations, i.e. sulfide/mercury (S/Hg) molar ratios of 0.5, 1, and 3. MilliQ water was added to the mixture to obtain a liquid solid ratio of 10, followed by adjustment of pH to desired points, i.e. pH 2, 6, or 10. HNO_3 and/or NaOH were used to adjust the pH. The samples were introduced into a zero headspace batch reactor and then tumbled to provide complete mixing and reaction until equilibrium was achieved. Samples were taken from the batch reactor at 1, 2, 4, 10, 24, 48, 96, 144, and 168 hours. The mercury content was analyzed for each sample to obtain Hg-S reaction kinetics curves for each pH tested. Thus, an optimum reaction time for the sulfide-induced mercury treatment process was determined.

3.4 Stabilization of Mercury Surrogate Using Sulfide

Upon completion of the kinetics study, mercury surrogate wastes were subjected to sulfide stabilization using the determined optimum reaction time. Sulfide dosage and stabilization pH were the two primary variables in this phase of study.

Sulfide dosage:

According to the mercury-sulfide chemistry, sulfide dosage is one of the most important factors affecting mercury stabilization effectiveness. In the presence of excess sulfide, mercury can be remobilized at high pH values. In this study, different sulfide dosages were tested to find the optimum dosage, where the effectiveness of mercury stabilization is highest. Sulfide to total mercury (S/Hg) molar ratio is an appropriate parameter to express sulfide dosage and the relationship between the desired amount of mercury and sulfide. From preliminary studies, it was found that S/Hg of 0.5 is not an effective option for sulfide-induced mercury treatment. Therefore, two different S/Hg molar ratios, 1 and 3, were investigated in this study at each of several pH values, with more emphasis then given to the S/Hg molar ratio that provided the highest stabilization efficiency.

Stabilization pH:

pH is another important element that affects sulfide treatment of mercury. Theoretically, solubility of mercury will increase when the pH increases in the presence of excess sulfide, due to the formation of water-soluble mercury and sulfide/bisulfide

complexes. A wide range of pH values were tested in this experiment to compare experimental results with theoretical conclusions, as well as to find the optimum pH value for stabilization. Applied pH values were 2, 4, 5, 6, 7, 8, and 10 for each selected S/Hg molar ratio. More pH values were evaluated at pH ranges of interest according to the previous study's results to get the optimum pH values combined with S/Hg molar ratios.

The test procedure applied for the sulfide-induced mercury stabilization is briefly described as following:

- 1) Weigh 5 grams (dry basis) of mercury waste and an amount of sodium sulfide sufficient to meet the indicated S/Hg molar ratio (Table 3.4). Place the solids into 125 mL HDPE bottles.
- 2) Add 50 mL of deionized water into the bottles (a liquid/solid mass ratio of approximately 10 was maintained due to the complete dissolution of the sodium sulfide).
- 3) Adjust the pH of the above mixtures to the initial pH values of 2, 4, 5, 6, 7, 8, and 10, using 1N NaOH and/or 2N HNO₃. Run test triplicates for each stabilization formulation.
- 4) Tumble the mixtures until equilibrium is reached. Monitor the pH of the mixtures throughout the stabilization experiment, and repeat step 3) as necessary.
- 5) Upon the completion of the reaction, take a final pH measurement for each mixture.

- 6) Filter the mixtures through 0.45 μm glass fiber filters and collect approximately 50 mL leachate samples.
- 7) Acidify the samples to a pH of less than 2 with HNO_3 and store at 4 $^{\circ}\text{C}$ until analyzed for its mercury concentration.
- 8) Dry the filter cakes (i.e. the stabilized mercury wastes) in an oven at 40 $^{\circ}\text{C}$ until the mass is stable to within $\pm 0.01\text{g}$ (overnight is generally sufficient to obtain the required control). These dried filter cakes are used for further leaching tests.
- 9) Digest and analyze the leachate samples for total mercury concentration via CVAAS.
- 10) Conduct several leaching tests on the sulfide-stabilized mercury wastes (refer to Section 3.4 for the detailed information on the leaching tests).

Table 3. 4 Mercury Surrogate Stabilization Test Matrix

S/Hg molar ratio	pH 2	pH 4	pH 5	pH 6	pH 7	pH 8	pH 10
0	X	X	X	X	X	X	X
1	X	X	X	X	X	X	X
3	X	X	X	X	X	X	X

3.5 Leaching Tests

A variety of leaching tests are designed to assess leachability trends in both treated and untreated wastes under controlled conditions that may contribute to the

destabilization of the wastes. Leaching tests performed include TCLP, liquid/solid ratio leaching, and constant pH leaching tests. Upon completion of each leaching test, the leachable mercury was analyzed by CVAAS.

Toxicity Characteristic Leaching Procedure (TCLP):

TCLP is a standard regulatory test intended to determine the potential mobility of contaminants in a liquid or solid under simulated landfill conditions. The TCLP limit for mercury is 0.2 mg/L. TCLP can serve as a regulatory benchmark and allow a comparison with a broad database of results obtained from testing of other materials. TCLP Hg from both treated and untreated wastes in this study was also used to evaluate the stabilization efficiency.

Prior to performing the TCLP tests, an initial pH measurement of the waste was made to determine the appropriate pH of the extraction fluid (4.93 or 2.88) that must be used in the test. The pH of the untreated mercury surrogate and the real mercury waste were 2.96 and 8.31, respectively. The pH of some sulfide-treated mercury waste was higher than 5.0. However, addition of HCl as specified in the TCLP procedure for wastes with pH above 5.0 could reduce the pH to lower than 5. As a result, the extraction fluid corresponding to a pH of 4.93 was used for untreated and sulfide-treated mercury wastes. This means the TCLP leaching test was performed at the pH value where the lowest mercury solubility was reported.

For each TCLP test, 5 grams of dried waste sample were added to a 125 mL container with 100 mL TCLP extraction fluid. The containers were sealed and tumbled for 18 hours. Each leachate sample was measured for pH value, filtered through 0.7 μm -pore size filter, and then subjected to the appropriate analytical procedure.

Liquid/Solid ratio leaching test:

This non-standard test varied the liquid/solid ratio to study the effect of the leachate concentration on the diffusion of contaminants from the waste form. Four tests were run using 0.5, 1.0, 2.0, and 5.0 grams of sulfide-treated mercury wastes. Each solid sample was placed in a 125 mL Nalgene HDPE bottle and then filled with 100 mL of MilliQ water. The bottles were capped and tumbled for 96 hours, with samples being extracted at 18, 48, and 96 hours. Each leachate sample was measured for pH value, and then filtered through a 0.7 μm -pore size filter. Each filtered leachate sample was acidified to a pH of less than 2 with HNO_3 and stored at 4 °C until analyzed for mercury concentrations via CVAAS.

Constant pH-based leaching:

Constant pH leaching tests are a means to determine the effect pH has on the stability of a waste. The procedure was developed at the University of Cincinnati. The method is based on leaching samples in a constant pH solution, adjusting the sample pH to the set point as necessary. The leaching apparatus is shown in Figure 3.2. In this study, the constant pH leaching test was run at pH values of 2, 4, 6, 8, 10, and 12 using 200 mL of MilliQ water and 10 grams of dried solid samples to produce a liquid/solid mass ratio

of 20:1. Duplicate tests were run at pH values of 2, 6, 8, and 12. The pH was maintained for a 14-day period, with aliquots of the samples and the experimental blank collected for analysis at 2, 10, 24, 96, 168, 240, and 336 hours. The leachate samples were filtered through 0.7 μm -pore size filters, acidified to a pH less than 2, and then subjected to the mercury concentration measurement.

Figure 3. 2 Schematic Diagram of Automated pH Control System

3.6 Interference Study

The best treatment pathways will be selected upon completion of the sulfide-induced treatment and leaching tests. However, a real waste is much more complex in its composition than surrogates. Many organic and inorganic materials may interfere with stabilization as well as with the leaching process. In order to get more applicable treatment methods, effects of some common cations, anions and organic ligands were investigated.

The interference effects experiments were performed under the same conditions as for the previously described stabilization test experiments, except that specified amounts of interferents were added into the solutions. The primary variable in this phase of the study was the concentration of the interferents. Interferents/mercury molar ratios of 0.5, 1, 3, and 5 were tested in this study.

3.6.1 Cations: Fe^{2+} and Pb^{2+}

Iron and lead can also produce low solubility metal sulfides; therefore, the presence of these cations may affect the availability of soluble sulfide ions in solution for the formation of mercury sulfide precipitate. Because of the much lower solubility of mercury sulfide than that of iron and lead, the competition effects of these metals may not be significant. However, these metal ions can capture excess sulfide by forming metal sulfide precipitates, resulting in a different leaching behavior for treated wastes.

3.6.2 Anions: PO_4^{3-} , CO_3^{2-} and Cl^-

The existence of these anions in the sample matrix may affect the speciation of mercury by forming precipitates or complexes between mercury and anions. Mercury phosphates are insoluble salts in water over a wide pH range (Qvarfort-Dahlman, 1975). At high pH values, where mercury sulfide is remobilized, the presence of phosphate may produce a positive effect on the sulfide treatment.

Carbonate is a very common ion in nature. Mercury forms the water-insoluble compound (HgCO_3 (s)) in the presence of carbonate. Therefore, mercury speciation can be changed. Because the solubility of mercury carbonate is a function of pH and carbon dioxide partial pressure (Clever, 1985), the influence of carbonate will vary at a different pH range or carbon dioxide level.

Mercury can form mercury chloride complexes in the presence of excess chloride. Schuster (1991) reported increased solubility of mercuric sulfide in the presence of chloride in the solution. It is also reported that chloride ion concentration has a significant effect on Hg (II) adsorption on and desorption from sediments or their components (Wang et al., 1985). An increase in salinity decreased the affinity of Hg (II) for sediment and kaolinite (Feick, et al., 1972). The reduction of Hg adsorption or the increase of desorption from sediments is attributed to the complex formation of chloride with mercury (Gilmour, 1971; Krenkel, 1974). Mercury can form mercury chloride complexes

in the presence of excess chloride, changing the mercury speciation, and thus the effectiveness of sulfide treatment.

3.6.3 Organic: EDTA

Mercury has high affinity for various organic ligands. Ravichandran et al. (1998) reported enhanced solubility of cinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. Enhanced dissolution of cinnabar, mercuric oxide and chloride has also been observed in the presence of humic acid (Benes and Havlik, 1979). In order to evaluate the effects of organic ligands on sulfide stabilization, a common organic ligand - EDTA- was selected for this study.

3.7 Stabilization of Real Mercury Waste Using Sulfide

Upon completion of the mercury surrogate stabilization and interference study, the optimized treatment parameters were selected, including optimum stabilization pH, sulfide dosage, reaction time and liquid to solid ratio. In order to assess the applicability of these optimum process control parameters on real mercury wastes, a real mercury sediment waste from a Superfund site was introduced in this phase of the study. This real mercury waste was subjected to the treatment by sulfide under the optimized treatment conditions. Several leaching tests, including TCLP, liquid/solid ratio leaching, and constant pH-based leaching test, were conducted on the stabilized real mercury waste to evaluate the efficacy of the treatment.

3.8 Treatment optimization

TCLP serves as a standard regulatory test. As mentioned previously, if the TCLP results do not comply with regulatory limits when applying a set of optimum parameters into worst-case scenarios, treatment optimization would be necessary. In this research, we tested a two-stage pretreatment procedure that would be employed followed by cement solidification. At the first stage of pretreatment, the optimized parameters that have been determined from previous research would be applied to stabilize mercury, while at the second step, ferrous sulfate would be added to precipitate excess sulfide. Because cement based stabilization will tremendously increase the pH of the sample matrix, excess sulfide should be removed to prevent mercury remobilization. As described in the literature review, two-stage pretreatment prior to cement-fly ash solidification may be an effective method to stabilize mercury. Therefore, the cement solidification combined with the optimized sulfide treatment parameters, as well as ferrous sulfate, will effectively stabilize mercury-containing wastes.

3.9 Analytical Methods

All samples were weighed using a Mettler PM 4600 balance or Mettler B303 balance. A Fisher Scientific Isotemp Oven (Model 615G) was used to dry solid samples. An end-over-end 30 ± 2 rpm tumbler was used to tumble samples.

Upon completion of each leaching test cycle, pH and mercury concentration were measured on the leachates. The pH was measured using a digital Fisher Scientific Accumet pH meter 915 with a gel filled pH/ATC electrode. The pH meter was calibrated with standard buffer solutions at pH 4.0, 7.0, and 10.0 before each use or not less than twice per day.

MilliQ water was used in all tests and reagents. All reagents used were of analytical standard quality. All experiments in this study were run in triplicate and were conducted in acid-washed (50%(v/v) HNO₃) HDPE lab ware.

The concentrations of total mercury, both in solid and liquid samples, were measured via CVAAS. A Perkin-Elmer Analyst 300 atomic absorption spectrophotometer equipped with a FIAS 100 cold vapor analyzer was used to analyze the total mercury concentrations. Before the analysis, each sample was subjected to digestion. Liquid and solid samples were digested for total mercury analysis according to U.S. EPA SW846 methods 7470A and 7471, respectively. The liquid samples were digested by concentrated sulfuric acid and nitric acid, 5% potassium permanganate, and potassium persulfate; while the solid samples were digested using aqua regia (three parts of concentrated hydrochloric acid and one part of concentrated nitric acid), and 5% potassium permanganate. A 1,000 mg/kg mercury standard was purchased from Fisher. Five mercury standard solutions (1, 5, 10, 20, and 40 µg/L mercury) were used in the calibration of the FIAS 100 cold vapor analyzer, as well as in the quality assurance and quality control tests.

3.10 Leaching Model

A leaching model was developed using MINTEQA2, a geochemical equilibrium speciation model capable of calculating equilibrium speciation of metals in complicated environmental settings where metals are distributed in aqueous, solid, and gaseous phases (US EPA, 1991). For various leaching tests, this model was used to predict the equilibrium behavior of mercury under different leaching conditions. Initial concentrations of various dissolved constituents, such as Hg^{2+} , Fe^{2+} , Pb^{2+} , S^{2-} , Cl^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} ; pH values; and the solid phases of mercury-containing wastes are input to the MINTEQA2 model. This model includes an extensive database of reliable thermodynamic data with which the model calculations are processed. However, the existing thermodynamic database of mercury and sulfide species was not big enough to complete the proposed modeling process. Therefore, some thermodynamic data were collected or calculated from other sources, such as published literature (Clever et al., 1985; Helper and Olofesson, 1975), encyclopedias of chemical engineering, and handbooks of chemistry and physics. Eighmy et al. (1995, 1997, 1998) reported the results of MINTEQA2 were in reasonably high agreement with the analytical data for both aqueous and solid phases when using the small mineral database available in MINTEQA2 model.

A leaching model will provide useful information for the study of the leaching mechanisms. For instance, for the constant pH leaching tests, the solid phase that controls the leachate composition as a function of pH were determined and the speciation of

mercury in the leachate were predicted using this model. Therefore, by combining the results of the MINTEQA2 model and that of microstructural examination of the waste surface, mechanisms of the leaching process can be determined.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Outline of the Chapter

The various results obtained from this study are described in this chapter. Following section 4.1, which provides a brief introduction to the organization of this chapter, section 4.2 presents the physical and chemical characteristics, as well as the leaching behavior of the untreated mercury surrogate and the real mercury waste used in this research. Section 4.3 discusses the kinetics of the mercury surrogate and sulfide reaction. Kinetic curves obtained from different stabilization pH and sulfide dosage experiments are presented, and an optimized reaction time is determined. Various results of the sulfide-induced mercury surrogate stabilization tests are summarized in section 4.4. The effects of stabilization pH and sulfide dosage on the mercury stabilization process are discussed, and a set of optimized stabilization control parameters are determined. Section 4.5 describes the influences of interfering materials on the sulfide-induced mercury treatment process. The effects of some common cations, anions, and EDTA are discussed. The treatment parameters optimized for some scenarios where the influences of the interfering materials are severe are also described. The results of the sulfide-induced real mercury waste stabilization are summarized in section 4.6. Results of several leaching tests, as well as the stabilization efficiencies calculated from the leaching results, are presented. The last section, section 4.7, deals with the development of a leaching

model. Leaching simulation results obtained from the modified MINTEQA2 model are presented, and are also compared with the observed results.

4.2 Characteristics of Mercury-containing Wastes

4.2.1 Characteristics of the Mercury Surrogate Wastes

A mercury surrogate was created using Cube Test Sand (CT-190A, ELE International) spiked by mercuric nitrate, as described in the section 3.1.1. In order to obtain background information before stabilization, the prepared surrogate was characterized and subjected to chemical and physical analyses. The results are listed in Table 4.1.

Table 4. 1 Characteristics of Mercury Surrogate Waste

Total Mercury (mg/kg)	5,262
TCLP Hg (mg/L)	238.0
Specific Gravity	2.65
Bulk Density (g/cm³)	1.497
Grading	Sieve No. 16 retains 0 % Sieve No. 30 retains 2 % Sieve No. 40 retains 30 % Sieve No. 50 retains 75 % Sieve No. 100 retains 98 %

The physical characteristics, such as specific gravity, bulk density, and grading, of the mercury surrogate were the same as that of Cube Test Sand.

The measured total mercury content of the surrogate was 5,262 mg/kg. The TCLP Hg concentration for the untreated surrogate was found to be 238.0 mg/L, which is well above the TCLP limit (0.2 mg/L); therefore, the mercury surrogate would be categorized as a hazardous waste needing treatment before disposal.

In addition to the TCLP test, the constant pH leaching procedure was performed on the untreated mercury surrogate. The purpose of this test was to provide a baseline comparison with the treated wastes. Results of the constant pH leaching test for the untreated mercury surrogate are summarized in Table 4.2 and plotted in Figure 4.1. It was found that the amount of mercury leached from the sample decreased as pH increased through pH 5, and then rose as the pH increased to 12. All of the samples failed the TCLP limit through the entire pH range tested, as expected for the untreated waste form. The lowest leachate mercury concentration of 147.7 mg/L was found at pH 5, while the maximum value of 455.6 mg/L was reached at pH 2.

Table 4. 2 Constant pH Leaching Results for Untreated Surrogate

pH	Leachate Hg Concentration (mg/L)
2	455.6
4	235.3
5	147.7
6	239.8
7	253.6
8	272.2
10	306.5
12	347.9

Figure 4. 1 Constant pH Leaching Results for Untreated Surrogate

4.2.2 Characteristics of Real Mercury Wastes

To assist in evaluating sulfide-induced mercury treatment technologies, a real mercury waste was introduced. The real waste, with a total mercury content of 2,300 mg/kg, was obtained from contaminated sediment at a Superfund site. The sample was collected during a sampling event from September 4 through September 7, 2001. A crop protection chemicals (CPC) plant and a mercury cell chlor-alkali plant were operated on a portion of the site for 30 years; they have been shut down for the past 20 years.

Table 4.3 summarizes the characteristics of the mercury sediment waste. The texture of the sediment was classified as sandy loam, and the sediments had a very low bulk density, in the range of 1.12 to 1.44 g/cm³ (specific gravity of 1.1 to 1.4).

The content of some common cations and anions were also analyzed for the mercury sediment waste. From the total mercury and chloride content, as well as the background information on the sediment site, it was suggested that mercury was mainly present as chloride salts in the waste.

As can be seen, the real mercury waste would also be categorized as a hazardous waste, because it failed the TCLP test (TCLP Hg of 1.862 mg/L > 0.2 mg/L).

Table 4. 3 Characteristics of Mercury Sediment Waste

Total Hg (mg/kg)	2,300
TCLP Hg (mg/L)	1.862
Organic Matter (%)	2.08
K⁺ (mg/kg)	253
Ca²⁺ (mg/kg)	3,450
Mg²⁺ (mg/kg)	425
Na⁺ (mg/kg)	7,828
CEC	55.5
Redox Potential (mv)	168.2
Cl⁻ (mg/kg)	5,940
Textural Classification	Sandy Loam
Specific Gravity	1.1 – 1.4
Bulk Density (g/cm³)	1.12 – 1.44

The leaching behavior of the real mercury waste over a wide range of pH is tabulated in Table 4.4 and also presented in Figure 4.2. As can be seen, the measured mercury concentration in the leachate decreased as the pH increased through pH 6, reaching a minimum mercury concentration of 0.858 mg/L at pH 6. Then the mercury concentration rose as the pH increased to 12, reaching a maximum concentration of 17.45 mg/L at pH 12. There was little change in the mercury concentration over the pH interval of 10 through 12. In general, significantly more mercury was released at the extreme pH conditions compared to that at moderate pH conditions. Again, all of the untreated samples failed the TCLP limit over the whole pH range tested.

Table 4. 4 Constant pH Leaching Results for Untreated Real Mercury Waste

pH	Leachate Hg Concentration (mg/L)
2	16.04
4	3.022
6	0.8580
8	1.532
10	15.05
12	17.45

Figure 4. 2 Constant pH Leaching Results for Untreated Real Mercury Waste

4.3 Results of Mercury Surrogate - Sulfide Kinetics

To obtain the optimum treatment time and possible immobilization pathways, the kinetics of the mercury surrogate-sulfide reaction were investigated in the preliminary stage of this study. Kinetics experiments were carried out at three different pH values: 2, 6, and 10, combined with three different S/Hg molar ratios: 0.5, 1, and 3. The kinetics results for each tested pH are presented in Figure 4.3, 4.4, and 4.5, respectively.

Figure 4.3 shows the kinetics results obtained at the stabilization pH of 2. Results are expressed as measured mercury concentration in the stabilization solution as a function of reaction time. It can be seen that the leachate mercury concentration at 2 or 4-hour time points are higher than that at 1-hour time points, then it gradually reduces until it reaches equilibrium. This possibly means that 1 or 2 hours' time is needed for mercury to be completely released from the solid matrix (sand in this case).

pH values were monitored through the experiment. In this experiment, pH was controlled between 1.8 and 2.4 over the whole process. But, it was also observed from the experiment that pH of the system showed strong tendency of increase until it reached the equilibrium. This is probably due to the strong alkalinity of sulfide in solution. There was concern about the sulfide oxidation in the system; however, sulfide oxidation should result in pH dropping. Therefore, it can be concluded that sulfide oxidation is not a very significant pathway in this process. But, it should be kept in mind that if we consider very

low-level concentration of mercury in solution, a small fraction of sulfide oxidation could still affect the final results.

It is also evident from Figure 4.3 that equilibrium was essentially reached within 10 hours for all three S/Hg molar ratios. Also, it was found that, the lower the S/Hg molar ratio, the higher the mercury concentration in the filtrate, meaning the lower sulfide dosage resulted in lower stabilization efficiency at this pH.

Figure 4. 3 Mercury-Sulfide Kinetics at pH 2

The kinetics results for a stabilization pH of 6 are plotted in Figure 4.4. Apparently, the kinetics curves for pH 6 are more complicated than those for pH 2. At a S/Hg molar ratio of 0.5, the reaction reached equilibrium within 10 hours. However, at S/Hg molar ratios of 1 and 3, the experimental results indicate that the mercury-sulfide reaction is a relatively slow process that takes more than 100 hours to reach equilibrium. In addition, it was found that the filtrate mercury concentration was reduced significantly from 3.469 mg/L and 6.202 mg/L at the beginning of the reaction to 0.0045 mg/L and 0.573 mg/L at equilibrium at S/Hg ratios of 1 and 3, respectively. Therefore, it was concluded that providing a sufficient reaction time is very important to obtain high stabilization efficiencies at this stabilization pH. In this set of experiments, the lowest equilibrium mercury concentration was obtained at a S/Hg molar ratio of 1, while the highest one was observed at a S/Hg molar ratio of 0.5.

Figure 4. 4 Mercury-Sulfide Kinetics at pH 6

Figure 4.5 presents the kinetics results for pH 10 at three S/Hg molar ratios. Again, the reaction equilibrium was reached within 10 hours at the S/Hg molar ratio of 0.5. However, it took around 48 hours to reach equilibrium when S/Hg molar ratios of 1 and 3 were applied. In these reaction scenarios, the S/Hg molar ratio of 0.5 resulted in the maximum equilibrium mercury concentration in the filtrate, while the minimum mercury concentration was reached at the S/Hg molar ratio of 1.

Figure 4. 5 Mercury-Sulfide Kinetics at pH 10

By summarizing the results observed in the kinetics study, it was found that it took a much shorter time to reach equilibrium at a S/Hg molar ratio of 0.5 compared to the other sulfide dosages used in the experiments. The faster rate of reaction is possibly due to the relatively simple reaction pathways involved in the low-sulfide dosage systems. As described in section 2.4, mercury (II) and sulfide simply produce a mercuric sulfide precipitant in the absence of excess sulfide. However, in the presence of the excess sulfide, such as S/Hg =1 and 3, the mercuric sulfide can be resolubilized by forming mercury (II) sulfide/bisulfide complexes, which may take more time to reach equilibrium.

It was also found through comparison of the kinetics curves for the S/Hg molar ratio of 1 and 3 at each pH tested, that the reaction reached equilibrium within 10 hours at pH 2, while much longer times were needed at pH 6 and 10. The reason is possibly because of the simpler sulfide species at pH 2 compared to that at a higher pH. At the low pH range, sulfide mainly exists as H_2S , while at the higher pH range, H_2S and HS^- , and even S^{2-} , will be present, which may involve more complicated reaction pathways. Thus, the reaction time needed for equilibrium may be increased.

Although a faster reaction rate was observed at a S/Hg molar ratio of 0.5, much higher equilibrium mercury concentrations were obtained at each stabilization pH compared to those observed at other sulfide dosages used in this study. This is an expected result that can be explained as following: when S/Hg = 0.5, only half the required mercury concentration on a molar basis of sulfide was provided for mercury in

the wastes to produce mercuric sulfide precipitants. From the HgS molecular formula, the stoichiometric ratio between sulfide and mercury is 1, to form mercuric sulfide precipitant. Therefore, in the case of $S/Hg = 0.5$, some of the mercury had no chance to combine with sulfide, resulting in a high equilibrium mercury concentration in the stabilization solution. For this reason, only S/Hg molar ratios of 1 and 3 were investigated in further tests. In addition, in order to guarantee achieving reaction equilibrium at every stabilized pH to be tested, a reaction time of 168 hours was used in all of the following experiments.

4.4 Results of Mercury Surrogate Stabilization by Sulfide

4.4.1 Equilibrium Mercury Results

As discussed in section 2.4, pH and sulfide dosage are the most important variables that affect sulfide-induced mercury stabilization efficacy. Therefore, in order to obtain optimum treatment parameters, the mercury surrogate was stabilized using sodium sulfide at six stabilization pH conditions, combined with two S/Hg molar ratios for each pH.

Figure 4.6 shows the sulfide-induced mercury surrogate stabilization test results. Results are expressed as equilibrium mercury concentration in the aqueous phase as a function of stabilization pH and sulfide dosage. Mercury concentrations in the filtered leachate obtained from the treated surrogate were well below those obtained from the untreated surrogate. It was found that equilibrium mercury concentrations were much lower in the low pH range (pH 2-6) than those at the higher pH range (pH 7-10). The lowest equilibrium Hg concentration was found at pH 6 with S/Hg = 1; the average filtrate Hg concentration under these conditions was only 2.8 µg/L. The effects of sulfide dosage on Hg stabilization are much more complicated. It was found that, in the very low pH range (pH 2 and 4), the filtrate Hg concentration decreased with an increase of sulfide dosage; while at higher pH ranges (pH 5 - 10), the opposite results were observed. For example, at a stabilization pH of 2, the filtrate Hg concentration decreased from 38.9 µg/L to 3.7 µg/L, while at pH 10 it increased from 2,365 µg/L to 76,750 µg/L, respectively, when the S/Hg molar ratio increased from 1 to 3.

Figure 4. 6 Equilibrium Hg Results for Mercury Surrogate

Figure 4.7 presents the percentages of total Hg released from the mercury stabilization process. As can be seen, the untreated waste released 30 - 91 % of the total mercury into the aqueous phase under different pH conditions; while only 0.0007 – 11 % of the total mercury was released from the sulfide-stabilized mercury wastes.

Table 4.5 shows the efficiencies of the sulfide-stabilization process based on the percentage of total mercury released from the untreated and treated wastes. The stabilization efficiency is defined as:

$$(\text{Filtrate Hg}_{\text{untreated surrogate}} - \text{Filtrate Hg}_{\text{treated surrogate}}) / (\text{Filtrate Hg}_{\text{untreated surrogate}}) * 100\%$$

- Equation 4.1

The efficiency calculations indicate that treatment of the mercury surrogate with sodium sulfide is very effective in lowering equilibrium mercury concentrations in the filtrate. In general, most of the treated samples retained over 99 percent of the mercury that was released from the untreated waste.

Table 4. 5 Stabilization Efficiency (%) Calculated from Equilibrium Mercury

Results

Stabilization pH	S/Hg = 1	S/Hg = 3
2	99.99	99.99
4	99.98	99.98
5	99.99	99.98
6	99.99	99.99
7	99.99	99.95
8	99.96	92.81
10	99.52	80.80

Figure 4. 7 Percentage Hg Released from Stabilization Process

4.4.2 Results of Leaching Tests

Leaching tests are the most important procedures indicating the efficacy of mercury immobilization by sulfide. In this study, TCLP, the liquid/solid ratio leaching test, and the constant pH leaching test were conducted on sulfide-stabilized mercury surrogates.

4.4.2.1 TCLP Results

TCLP tests were performed to evaluate mercury stabilization effectiveness and to determine optimized process parameters. TCLP results for the stabilized mercury surrogate are summarized in Table 4.6 and are also plotted in Figure 4.8. It was found that sulfide treatment substantially lowered the TCLP mercury concentrations relative to untreated samples. As can be seen, except for the stabilization scenarios at pH 2 and 4 with a S/Hg molar ratio of 1, TCLP Hg results passed the TCLP limit for all scenarios. The lowest TCLP Hg concentration was again found at the stabilization combination of pH 6 and S/Hg molar ratio of 1, where only 4.3 $\mu\text{g/L}$ of mercury was detected in the TCLP leachate.

Table 4. 6 TCLP Hg (mg/L) Results for Mercury Surrogate

Stabilization pH	S/Hg = 0	S/Hg = 1	S/Hg = 3
2	10.85	7.239	0.0094
4	86.63	4.077	0.0101
5	58.97	0.0104	0.0516
6	66.70	0.0043	0.0352
7	73.62	0.0089	0.0792
8	83.83	0.0053	0.0408
10	52.32	0.0970	0.1676

The percentages of total mercury leached from the TCLP leaching tests are presented in Figure 4.9. As can be seen, the untreated mercury surrogate leached 4-34 % of the total mercury from the TCLP leaching test; while the sulfide-treated mercury surrogate leached much less (only 0.002 – 3 %) mercury into the leachant.

Stabilization efficiencies for the TCLP results are shown in Table 4.7. Here the efficiency was calculated as noted below:

$$(\text{TCLP Hg}_{\text{untreated surrogate}} - \text{TCLP Hg}_{\text{treated surrogate}}) / (\text{TCLP Hg}_{\text{untreated surrogate}}) * 100\%$$

- Equation 4.2

The calculation results show that the stabilization efficiencies were higher than 99 % for most of the treatment scenarios, indicating sulfide is an effective reagent for reducing the mobility of mercury into the aqueous phase.

From the evaluation of equilibrium mercury and TCLP mercury results for the mercury surrogate, it was concluded that a stabilization pH of 6 combined with S/Hg = 1 was the most effective scenario for which both the minimum equilibrium mercury and TCLP mercury concentrations were observed. Therefore, the following experiments were aimed at further evaluating this treatment scenario.

Table 4. 7 Stabilization Efficiency (%) Calculated From TCLP Mercury Results

Stabilization pH	S/Hg = 1	S/Hg = 3
2	33.28	99.91
4	95.29	99.99
5	99.98	99.91
6	99.99	99.95
7	99.99	99.89
8	99.99	99.95
10	99.81	99.68

Figure 4. 8 TCLP Results for Mercury Surrogate

Figure 4. 9 Percentage Hg Leached from the TCLP Leaching Tests

4.4.2.2 Results of Liquid/solid Ratio Leaching

The leaching behavior of stabilized mercury surrogates at different liquid/solid ratios was observed using the liquid/solid ratio leaching procedure. The mercury surrogates stabilized by sulfide at pH 6 with S/Hg = 1 were subjected to this leaching test.

Figure 4.10 shows the sulfide-treated mercury surrogate leaching performance observed at four different liquid/solid leaching ratios. As can be seen, at the beginning (18 hour tumbling period), the leachate mercury concentration varied with the L/S ratio variation. However, after the reaction reached equilibrium (after 48 hour tumbling period), fluctuations of leachate mercury concentration reduced significantly. The order-of-magnitude similarity in observed leachate mercury concentrations through different levels of L/S ratio suggests a solubility limit might control the observed concentrations. Also, it was found that the leachate mercury concentration did not increase with greater volumes of leachant. Consequently, it can be concluded that the release of mercury from the tested wastes is not a diffusion-controlled process.

Figure 4. 10 Liquid/solid Ratio Leaching Results for Stabilized Mercury Surrogate

4.4.2.3 Results of Constant pH Leaching Test

From the previous results and discussion, it was found that pH is one of the most important factors that control mercury solubility in water; therefore, the effect pH has on mercury leachability was evaluated using constant pH leaching tests.

Prior to the leaching test, the mercury surrogate samples were treated by sulfide at pH 6 combined with $S/Hg = 1$. In this study, the constant pH leaching test was run on pH values of 2, 4, 6, 8, 10, and 12 using a liquid/solid mass ratio of 20:1. Leachate samples (approximately 10 mL) were drawn using a 0.45 μm syringe filter at periodic intervals. The first samples of leachate were taken at contact time of 2 hours. Subsequent samples were obtained at the reaction time periods of 10, 24, 96, 168, 240, and 336 hours.

Figure 4.11 illustrates the constant pH-based leaching results as a function of leachant pH and contact time. From the graph, it was found that the leachate mercury concentration gradually increased with the contact time at each pH tested. At the beginning of leaching, i.e. contact times of 2 and 10 hours, the mercury concentrations in leachate were all below 10 $\mu g/L$; while after a contact time of 10 hours, the amount of mercury in the leachate increased measurably with the contact time, finally reaching the highest leachate concentration of 145.7 $\mu g/L$ at 336 hours with exposure of the sample to pH 12. However, all the leachate results passed the TCLP limit, even at the worst-case scenarios.

The effects of pH on the leaching behavior of the sulfide-stabilized mercury surrogate are also illustrated in Figure 4.11. The amount of mercury leached from the sample decreased as pH increased through 4, and then rose as pH increased to 8. After that, it decreased again through pH 10, and then increased as pH increased to 12, finally reaching the highest value at pH 12. The leachate mercury concentrations showed two local minimum values at pH 4 and 10. It was noticed that, although the amount of leached mercury increased with the contact time, no significant change in the leaching trends occurred over the wide pH range with the contact time.

Figure 4.12 compares the leaching performance of the sulfide-stabilized mercury surrogate with that of the untreated mercury surrogate. From the constant pH leaching results, it was found that the soluble mercury concentration dramatically increased at pH values above 6, reaching a maximum mercury concentration at pH 12. This indicates the possible formation of soluble mercury sulfide/bisulfide species at high pH conditions.

The percentages of total mercury leached at different pH of leachant are shown in Figure 4.13. As can be seen, compared with the high percentage of leaching for the untreated surrogate, mercury leached from the sulfide-stabilized surrogate decreased significantly.

Stabilization efficiencies were calculated using Equation 4.2 stated in the previous section; the calculated results are shown in Table 4.8. It is evident that compared with the

high soluble mercury concentrations of the unstabilized materials, all of the stabilization efficiencies are over 99 %, even with exposure of the wastes to high pH leachants.

Table 4. 8 Stabilization Efficiency (%) Calculated from the Constant pH Leaching Results for the Mercury Surrogate

pH of Leachant	Efficiency (%)
2	99.99
4	99.99
6	99.98
8	99.95
10	99.98
12	99.96

**Figure 4. 11 Constant pH Leaching Results for Stabilized Mercury Surrogate –
Effects of Contact Time**

Figure 4. 12 Constant pH Leaching Results for Stabilized Mercury Surrogate

Figure 4. 13 Percentage Hg Leached from Constant pH Leaching Tests for Stabilized Mercury Surrogate

4.5 Interference Study

From the previous study, it was found that sulfide is an effective reagent to stabilize the mercury surrogate. However, before sulfide can be successfully used as a mercury-immobilizing material, one factor needs to be considered: sulfide has to be able to immobilize Hg in the presence of interfering cations, anions and organic ligands. Therefore, in this study, interferences by some common cations, anions and organic ligands were also investigated.

Mercury surrogates were reacted with sulfide in the presence of varying levels of interfering cations, anions and organic ligands to test the effects of these materials on Hg immobilization by sulfide. The interference study experiments were performed under the optimal stabilization conditions. Four different concentrations of interferents were used: 0.5, 1, 3, and 5 times the total Hg concentration on a molar basis.

4.5.1 Effects of Cations: Fe^{2+} and Pb^{2+}

Figure 4.14 illustrates the equilibrium mercury concentrations measured in stabilization solutions in the presence of Fe^{2+} and Pb^{2+} . The dissolved mercury concentration ranged from 3.5 to 55.7 $\mu\text{g/L}$ and from 9.0 to 83.0 $\mu\text{g/L}$ after sodium sulfide reacted with the mercury surrogate in the presence of Fe^{2+} and Pb^{2+} , respectively. As can be seen, the equilibrium mercury concentration increased in the presence of Fe^{2+}

and Pb^{2+} , compared to that obtained from the controls (samples in which no interfering materials were added). This is especially evident at the cation/Hg molar ratio of 3.

Upon completion of the reaction with sulfide in the presence of cations, the stabilized surrogates were subjected to TCLP testing. The TCLP Hg results are shown in Figure 4.15. The dissolved Hg^{2+} concentration in the TCLP leachate ranged from 5.717 to 73.7 $\mu\text{g/L}$ and from 12.5 $\mu\text{g/L}$ to 95.1 $\mu\text{g/L}$ in the presence of Fe^{2+} and Pb^{2+} , respectively. It was found that the added metals reduced the effectiveness of Hg immobilization by sulfide, as shown by higher TCLP Hg concentrations compared to those of the controls. However, even in the presence of these cations, TCLP Hg concentrations for the stabilized surrogates were still lower than the TCLP limit.

To gain more specific information on the effects cations have on the TCLP tests, the percentages of total mercury leached and the stabilization efficiencies were calculated; the results are presented in Figure 4.16 and Table 4.9, respectively. It was found that the stabilization efficiencies were all higher than 99 %, even though the addition of these cations reduced the stabilization efficiencies. Therefore, sulfide was shown to be an effective Hg stabilizing reagent, even in the presence of the interfering cations.

Table 4. 9 Stabilization Efficiency (%) Calculated from TCLP Mercury

Results in the Presence of Cations

Cation/Hg Molar Ratio	Fe²⁺	Pb²⁺
0.5	99.89	99.86
1	99.99	99.89
3	99.98	99.89
5	99.99	99.98

Figure 4. 14 Equilibrium Hg Results in the Presence of Cations

Figure 4. 15 TCLP Hg Results in the Presence of Cations

Figure 4. 16 Percentage Hg Leached from TCLP Leaching Tests in the Presence of Cations

4.5.2 Effects of Anions: PO_4^{3-} , CO_3^{2-} and Cl^-

The effects of interfering anions on the equilibrium Hg concentration are shown in Figure 4.17. Equilibrium mercury concentrations ranged from 147.1 to 278.6 $\mu\text{g/L}$, from 1.4 to 4.7 $\mu\text{g/L}$, and from 13.5 to 88.6 $\mu\text{g/L}$ after the mercury surrogate reacted with sodium sulfide in the presence of different levels of Cl^- , CO_3^{2-} and PO_4^{3-} , respectively. As can be seen, the equilibrium mercury concentration increased in the presence of Cl^- and PO_4^{3-} , while it decreased in the presence of CO_3^{2-} , compared to that obtained from the controls. The interferences due to Cl^- and PO_4^{3-} increased with an increase in the anion/Hg molar ratios.

Figure 4.18 illustrates the TCLP test results in the presence of interfering anions. Hg concentrations in TCLP leachate increased in the presence of the interfering anions compared to those of controls. Cl^- , CO_3^{2-} and PO_4^{3-} inhibited Hg stabilization by sulfide in the order: $\text{Cl}^- > \text{PO}_4^{3-} > \text{CO}_3^{2-}$ and $\text{PO}_4^{3-} > \text{Cl}^- > \text{CO}_3^{2-}$ at low and high levels of the anion concentrations, respectively.

TCLP Hg concentrations for the sulfide-stabilized mercury surrogates ranged from 452.8 to 512.3 $\mu\text{g/L}$, from 5.2 to 332.6 $\mu\text{g/L}$, and from 21.4 to 756.0 $\mu\text{g/L}$ in the presence of Cl^- , CO_3^{2-} and PO_4^{3-} , which meant that for some scenarios the stabilized mercury surrogates failed the TCLP test.

It can be seen that the effect of Cl^- is significant. Regardless of the concentration, Cl^- increased the TCLP Hg concentration for the stabilized surrogate to a level higher than the TCLP limit. This is probably due to the formation of water-soluble mercury chloride complexes in the presence of chloride (Schuster, 1991). The influence of PO_4^{3-} is more evident at higher PO_4^{3-} concentrations compared to that at lower concentrations. The stabilized surrogates passed the TCLP test in the presence of PO_4^{3-} with $\text{PO}_4^{3-}/\text{Hg}$ molar ratios of 0.5 and 1, while they failed TCLP tests when the $\text{PO}_4^{3-}/\text{Hg}$ molar ratio increased to 3 and 5. Carbonate had little effect on Hg stabilization by sulfide at most $\text{CO}_3^{2-}/\text{Hg}$ ratios. Only at a carbonate/Hg molar ratio of 3, did it cause an increase in TCLP Hg concentration.

The percentages of total mercury leached from the TCLP leaching tests in the presence of anions are presented in Figure 4.19. As shown in the figure, compared to the untreated surrogate, the percentage mercury leached decreased significantly for the sulfide-treated surrogate, even in the presence of interfering anions.

Stabilization efficiencies were calculated using Equation 4.2, and the results are tabulated in Table 4.10. It is clear that compared with the high initial TCLP Hg concentration, the stabilization efficiencies were over 98 % for all scenarios, even in the case where TCLP test failed the TCLP limit, indicating that sulfide is still very effective in stabilizing mercury in the presence of interfering anions.

**Table 4. 10 Stabilization Efficiency (%) Calculated from TCLP Mercury Results in
the Presence of Anions**

Anion/Hg Molar Ratio	Cl⁻	CO₃²⁻	PO₄³⁻
0.5	99.32	99.96	99.97
1	99.31	99.99	99.84
3	99.23	99.50	99.32
5	99.28	99.98	98.87

Figure 4. 17 Equilibrium Hg Results in the Presence of Anions

Figure 4. 18 TCLP Hg Results in the Presence of Anions

Figure 4. 19 Percentage Hg Leached from TCLP Leaching Tests in the Presence of Anions

4.5.3 Effects of Organic Ligand: EDTA

EDTA was selected to examine the influence an organic ligand might have on Hg stabilization by sulfide. As can be seen in Figure 4.20, EDTA caused an increase in the equilibrium Hg concentration compared to that of the controls. Dissolved mercury concentrations ranged from 226.0 to 652.0 µg/L after the reaction of the mercury surrogate with sodium sulfide in the presence of different levels of EDTA. These interferences are especially severe in the presence of EDTA at 0.5 times the total Hg concentration on a molar basis. This is possibly due to the self-combination of EDTA molecular rings at the high EDTA concentration condition, thus reducing the effects EDTA has on mercury stabilization by sulfide. In addition, some of the interferences EDTA has on the mercury stabilization results can be explained as below: as Ravichandran et al. (1998) pointed out the formation of mercuric sulfide follows three steps- nucleation, growth of primary crystallites (~ ten nanometer in size), and aggregation of these micro crystals (micro-sized). He found that EDTA inhibits the aggregation of mercuric sulfide; therefore, some of the “dissolved” Hg measured in the samples might actually be “colloidal” HgS that passed through the 0.45- µm filters.

The stabilized surrogate was subjected to TCLP testing upon completion of the reaction with sulfide in the presence of EDTA. The TCLP Hg results are shown in Figure 4.21. The dissolved Hg^{2+} concentrations in the TCLP leachate ranged from 25.0 to 170.6 µg/L in the presence of different levels of EDTA. It is seen that EDTA caused decreases in efficacy of Hg stabilization by sulfide, as shown by higher TCLP Hg concentrations

compared to those of the controls. However, even in the presence of EDTA, TCLP Hg concentrations for the stabilized surrogates were still lower than the TCLP limit.

Figure 4.22 and Table 4.11 show the percentages of total mercury leached and the stabilization efficiencies calculated from the TCLP Hg concentration obtained from the leaching tests in the presence of EDTA, respectively. As can be seen, the stabilization efficiencies are all higher than 99 %, even in the presence of EDTA. Therefore, it is concluded that sulfide can successfully stabilize mercury in the presence of EDTA.

Table 4. 11 Stabilization Efficiency (%) Calculated from TCLP Mercury Results in the Presence of EDTA

EDTA/Hg Molar Ratio	EDTA
0.5	99.74
1	99.96
3	99.88
5	99.88

Figure 4. 20 Equilibrium Hg Results in the Presence of EDTA

Figure 4. 21 TCLP Hg Results in the Presence of EDTA

Figure 4. 22 Percentage Hg Leached from TCLP Leaching Tests in the Presence of EDTA

4.5.4 Treatment Optimization

As discussed in the previous section, the interferences with mercury immobilization by chloride and phosphate are very evident. The interference with mercury immobilization by phosphate is significant at a high phosphate/mercury molar ratio. The reason for this is possibly that Hg-phosphate precipitants can be formed at a low level of phosphate, while these precipitants can be remobilized at high phosphate concentrations by forming water-soluble mercury-phosphate complexes. Therefore, it was speculated that additional sulfide in the treatment system might act as a competitor of phosphate to capture mercury from the aqueous phase, thus reducing the influence of phosphate. However, as pointed out previously, an excessive amount of sulfide may enhance the solubility of mercury by forming water-soluble mercury sulfide/bisulfide complexes. Therefore, the salt FeSO_4 was added to consume excess sulfide by forming solid FeS(s) . Since the affinity of Fe^{2+} to S^{2-} is lower than that of Hg^{2+} to S^{2-} , the addition of Fe should not affect the Hg immobilization by sulfide (Chang et al., 1993). Consequently, S/Hg (molar ratio) = 2 and Fe/Hg (molar ratio) = 3 were tested to investigate the possibility of our hypothesis. The experimental results confirmed this hypothesis. As can be seen in Figure 4.23, the TCLP mercury concentrations decreased significantly when the sulfide/mercury molar ratio increased from 1 to 2, and they also all passed the TCLP limit.

The same treatment optimization parameters were applied to the mercury-chloride scenarios. As can be seen in Figure 4.24, the interference by chloride was reduced

significantly with $S/Hg = 2$ combined with $Fe/Hg = 3$, shown by the significantly decreased TCLP Hg results, which are all well below the TCLP limits.

The stabilized mercury surrogate was also solidified using Portland cement and fly ash. The weight ratio of cement/fly ash/waste = 3/3/4 was applied. As shown in Figure 4.24, the solidifying the waste further lowered the TCLP Hg results to the level of 2 – 3 $\mu g/L$, indicating that the cement/fly ash solidification is a very effective way to further improve the sulfide-induced mercury stabilization process.

Figure 4. 23 Phosphate Interference Study – TCLP Hg Results

Figure 4. 24 Chloride Interference Study – TCLP Hg Results

4.6 Results of Real Mercury Waste Stabilization

From the previous experimental results, it was concluded that sulfide-induced stabilization is an effective technique to immobilize mercury in a lab-assembled mercury surrogate, even in the presence of interfering materials. To further evaluate this technique, a real mercury waste was introduced in this phase of the study. The characteristics of the real waste were described in section 4.2.2.

The real mercury waste was stabilized by sodium sulfide using optimal stabilization control parameters, i.e. stabilization pH of 6, S/Hg = 1, liquid/solid ratio of 10, and contact time of 168 hours. Upon completion of treatment, the stabilized real wastes were subjected to several leaching procedures to evaluate the stabilization efficacy.

4.6.1 Results of Leaching Tests

4.6.1.1 TCLP Results

TCLP extraction fluid #1, with a leachant pH of 4.93, was used to run TCLP tests on the sulfide-stabilized real mercury waste. As indicated in Table 4.12, after treatment using sulfide, the TCLP Hg was dramatically reduced from 1862 µg/L for the untreated waste to 34.5 µg/L for the treated waste.

Stabilization efficiency was calculated using the following equation:

$$(\text{TCLP Hg}_{\text{untreated waste}} - \text{TCLP Hg}_{\text{treated waste}}) / (\text{TCLP Hg}_{\text{untreated waste}}) * 100\%$$

- Equation 4.3

The calculated stabilization efficiency of 98.15% indicates that the treated mercury waste retained 98.15 % of mercury that was released from the untreated form into the TCLP leachant.

Table 4. 12 TCLP Results for Real Mercury Waste

TCLP Hg for Untreated Waste (µg/L)	1,862
TCLP Hg for Treated Waste (µg/L)	34.5
Stabilization Efficiency (%)	98.15

4.6.1.2 Liquid/solid Ratio Leaching Results

Figure 4.25 shows the results of liquid/solid leaching tests for the stabilized real mercury waste. The leachate mercury concentrations ranged from 13.9 to 66.2 $\mu\text{g/L}$ at different levels of liquid/solid ratio. Increased leachate mercury concentrations were observed at the 96-hour contact time compared to the other two contact time periods selected in this experiment. As can be seen, more measurable fluctuation of leachate mercury concentration was obtained at the 18-hour tumbling period compared to that at the 48 and 96 hour tumbling periods. However, the order-of-magnitude similarity in observed leachate mercury concentrations suggests a solubility limit might control the observed concentrations. In addition, the leachate mercury concentration did not increase with greater volumes of leachant. Consequently, it can be concluded that the release of mercury from the tested wastes is not a diffusion-controlled process.

Figure 4. 25 Liquid/solid Ratio Leaching Results for Real Mercury Waste

4.6.1.3 Constant pH Leaching Results

The constant pH leaching tests were conducted by exposing the sulfide-stabilized real mercury waste to six different pH leachants in the pH range from 2 to 12. The samples were taken by the same procedure that was applied to the constant pH leaching testing of the stabilized surrogate, as described in section 4.4.2.

Figure 4.26 illustrates the leaching performance of the sulfide-stabilized real mercury waste at different levels of leachant pH and contact time. In general, the leachate mercury concentration increased with an increase in the contact time at each pH tested. However, all the leachate results passed the TCLP limit, even at the worst-case scenarios. The effects of pH on the leaching behavior of the sulfide-stabilized mercury surrogate are also indicated in this figure. The amount of mercury leached from the sample decreased as pH increased through pH 6, and then rose slightly as pH increased to 8. After that, it increased significantly through pH 10, and then decreased slightly as pH increased to 12. There was little change in the mercury concentration over the pH interval of 6 through 8, and 10 through 12. Measurably high amounts of mercury were released into the aqueous phase under the three extreme pH conditions, i.e. pH 2, 10, and 12, compared to those in the more moderate pH ranges, i.e. pH 4, 6, and 8. The maximum concentration of 145.7 $\mu\text{g/L}$ was reached at pH 2. It was found that the leaching trend over the wide pH range did not change much with the contact time, although the amount of leached mercury increased with the contact time.

Figure 4.27 compares the leaching performance of sulfide-stabilized mercury waste with that of untreated mercury waste. The two curves follow the same leaching trend over the entire pH range, i.e. the soluble mercury concentration dramatically increased at pH values of 2, 10, and 12, while reduced values were observed at moderate pH conditions. However, dissolved mercury concentrations showed a 1-2 log unit reduction in leaching after sulfide stabilization.

Figure 4.28 shows the percentages of total mercury leached using the constant pH leaching tests on the real mercury wastes. As can be seen, the percentages of mercury leached from the sulfide-treated mercury wastes decreased two orders of magnitude compared to that from the untreated mercury wastes.

Stabilization efficiencies were also calculated using Equation 4.3, stated earlier, and the calculated results are tabulated in Table 4.13. It is evident that compared with the high soluble mercury concentrations of the unstabilized materials, all of the stabilization efficiencies are over 95 %, even with exposure of the wastes to extreme pH leachants.

Table 4. 13 Stabilization Efficiencies (%) Calculated from Constant pH Leaching**Results for Real Mercury Waste**

pH of Leachant	Efficiency, %
2	99.09
4	98.64
6	98.65
8	99.25
10	99.27
12	99.44

From the constant pH leaching results for the surrogate and real waste, it was found that the leachability of the sulfide-treated mercury wastes, over a wide pH range, is a waste-specific characteristic. For example, for the stabilized mercury surrogate, the soluble mercury concentration dramatically increased at pH values above 6, reaching a maximum mercury concentration at pH 8; while for the stabilized sediment mercury waste, the mercury concentration significantly increased at three extreme pH conditions (pH 2, 10, and 12), reaching the highest mercury concentration at pH 2 (refer to Figure 4.29). However, it is common that sulfide treated mercury wastes produce significantly high mercury concentrations at extremely high pH ($\text{pH} > 10$) leachants, indicating the formation of soluble mercury bisulfide species in the presence of excess sulfide at high pH conditions (Clever et al., 1985). Nevertheless, compared with the high soluble mercury concentrations of the unstabilized materials, the soluble mercury showed a clear reduction in leaching over the entire pH range after treatment.

**Figure 4. 26 Constant pH Leaching Results for Real Mercury Waste –
Effect of Contact Time**

Figure 4. 27 Constant pH Leaching Results for Real Mercury Waste

Figure 4. 28 Percentage Hg Leached from Constant pH Leaching Tests for Real Mercury Waste

Figure 4. 29 Comparison of Constant pH Leaching Results for Mercury Wastes

4.7 Leaching Modeling

Visual MINTEQ was used to simulate the mercury speciation, solubility, and equilibria in the leachate produced from the leaching tests on the mercury wastes.

Visual MINTEQ is a Windows version of MINTEQA2 version 4.0, which was released by the USEPA in 1999. MINTEQA2 is a chemical equilibrium model for the calculation of metal speciation for natural waters. It is probably the most widespread model for these purposes in use today, and it is renowned for its stability.

Visual MINTEQ has been developed by the Department of Land and Water Resources Engineering at Kungl Tekniska Högskolan (KTH) Royal Institute of Technology (KTH, 2002), to make the powerful features of MINTEQA2 more easily accessible for users. The program has the potential of speeding up the management of input and output data, and it has also been modernised to include new options for adsorption modelling.

The formation constants for Hg-S complexes that were used in this modeling study are tabulated in Table 4.14. Hg-S complexes listed in the MINTEQ database include HgS_2^{2-} , $\text{Hg}(\text{HS})_2$, and HgHS_2^- . Based on our literature review, it was found that $\text{HgS}(\text{H}_2\text{S})_2$, $\text{HgS}(\text{HS})_2^-$, and $\text{Hg}(\text{HS})_3^-$ are another three complexes that should be considered in this modelling. The solubility product for $\text{HgS}(\text{s})$ was obtained from the MINTEQA2 database, and logK values of the formation of $\text{HgS}(\text{H}_2\text{S})_2$, $\text{HgS}(\text{HS})_2^-$, and $\text{Hg}(\text{HS})_3^-$ in this table were calculated from the constants reported by Clever, 1985.

**Table 4.14 Mercury-Sulfide Complexes and Equilibrium Constants Used in the
Speciation Models for Dissolved Hg**

Equilibrium Reaction	logK	Source
Aqueous Species		
$\text{Hg}(\text{OH})_2 + 2\text{HS}^- = \text{HgS}_2^{2-} + 2\text{H}_2\text{O}$	29.414	MINTEQA2 database
$\text{Hg}(\text{OH})_2 + 2\text{H}^+ + 2\text{HS}^- = \text{Hg}(\text{HS})_2 + 2\text{H}_2\text{O}$	44.516	MINTEQA2 database
$\text{Hg}(\text{OH})_2 + \text{H}^+ + 2\text{HS}^- = \text{HgHS}_2^- + 2\text{H}_2\text{O}$	38.122	MINTEQA2 database
$\text{Hg}(\text{OH})_2 + 3\text{H}^+ + 3\text{HS}^- = \text{HgS}(\text{H}_2\text{S})_2^- + 2\text{H}_2\text{O}$	54.880	Clever, 1985 and MINTEQA2 database
$\text{Hg}(\text{OH})_2 + 2\text{H}^+ + 3\text{HS}^- = \text{Hg}(\text{HS})_3^- + 2\text{H}_2\text{O}$	48.610	Clever, 1985 and MINTEQA2 database
$\text{Hg}(\text{OH})_2 + \text{H}^+ + 3\text{HS}^- = \text{HgS}(\text{HS})_2^- + 2\text{H}_2\text{O}$	41.980	Clever, 1985 and MINTEQA2 database
Possible Solid Species		
Cinnabar (HgS)	45.694	MINTEQA2 database
Metacinnabar (HgS)	45.094	MINTEQA2 database
$\text{Hg}(\text{OH})_2$	3.4963	MINTEQA2 database
Montroydite (HgO)	3.64	MINTEQA2 database
Possible Gaseous Species		
$\text{H}_2\text{S} (\text{g})$	8.01	MINTEQA2 database

4.7.1 Mercury Speciation in the Mercury Surrogate Solution

Figure 4.30 shows the MINTEQ-computed mercury speciation in the solution containing 500 mg/L Hg (II) as a function of pH. As can be seen, Hg^{2+} , $\text{Hg}(\text{OH})^+$, and $\text{Hg}(\text{OH})_2^0$ are the major species that exist in a Hg (II) solution in the pH range 2-10. Hg^{2+} is the dominant species at the pH range 2-3. At pH 2, Hg (II) is distributed as 97% Hg^{2+} and 3% $\text{Hg}(\text{OH})^+$; while at pH 3, it is distributed as 57% Hg^{2+} , 25% $\text{Hg}(\text{OH})^+$, $\text{Hg}(\text{OH})_2^0$, and 18% $\text{Hg}(\text{OH})^+$. At pH 4, $\text{Hg}(\text{OH})_2^0$ becomes the predominant Hg (II) complex in solution, and from pH 5 on over 99% of total soluble Hg (II) exists as $\text{Hg}(\text{OH})_2^0$.

Due to the formation of insoluble HgO , the amount of total dissolved mercury decreases significantly from pH 2 through pH 4. The total solubility of mercury decreases from 600 mg/L at pH 2 to 80 mg/L at pH 3, then to 45 mg/L at pH 4. It is seen that there is little change in the total soluble mercury concentration in the pH interval from pH 4 through pH 12.

Figure 4. 30 Mercury Speciation in the Mercury Surrogate Solution (S/Hg = 0)

4.7.2 Mercury Solubility Simulation in the Stabilization Solution of the Mercury

Surrogate

To investigate the mechanisms involved in the sulfide-induced mercury stabilization, mercury speciation distributions over wide pH range were simulated by MINTEQA2; the simulation results are shown in Figure 4.30, 4.31, and 4.32 for S/Hg = 0, 1, and 3, respectively. As can be seen, for the system of S/Hg = 0, Hg^{2+} , $\text{Hg}(\text{OH})^+$, and $\text{Hg}(\text{OH})_2^0$ are the major species that exist in a Hg (II) solution in the pH range 2-10. Due to the precipitation of HgO, the concentration of total dissolved mercury decreases significantly from pH 2 through pH 4. And there is little change in the total soluble mercury concentration in the pH interval from pH 4 through pH 12. In the case of S/Hg = 1, the dominant mercury species in the solution are still Hg^{2+} , $\text{Hg}(\text{OH})^+$, and $\text{Hg}(\text{OH})_2^0$. However, most of mercury is combined with sulfide to produce mercuric sulfide (cinnabar); therefore, the total dissolved mercury concentration is extremely low. It is also found that the total mercury concentration is a function of pH: under the acidic or basic condition, more mercury is leached out in solution. From Figure 4.32 it can be seen that the total dissolved mercury increases significantly in the case of S/Hg = 3 compared to the scenario of S/Hg = 1. It is also found that the mercury concentration increases when pH increases due to the formation of soluble mercury and sulfide/bisulfide complexes. It can also be noticed that mercury and sulfide/bisulfide complexes are the dominant species in this scenario, other than free mercury (II) ion or mercury hydroxyl complexes.

The MINTEQ-simulated mercury results are shown in Figures 4.33, 4.34, and 4.35 for S/Hg = 0, 1, and 3, respectively. The results are expressed as total dissolved mercury concentration under different leaching conditions. The observed results are also shown in the same figure, so that these results can be compared with the simulated results. In this research, the mercury leaching behaviour was simulated using Visual MINTEQ as a function of pH, sulfide dosage, and/or interferent concentrations. It should be pointed out that, in this MINTEQ simulation study, the focus of concern was the trends of mercury leaching behaviour rather than the exact amount of mercury leached. Since the leached mercury concentrations are in very low ranges (the level of $\mu\text{g/L}$ or less), the differences between the observed and simulated values are actually very small for most scenarios, even if an order of magnitude or more difference is shown.

It can be seen that the predicted trends of mercury leaching behavior as a function of pH match very well with the trends of the experimentally observed results. It was also found from the mercury speciation that cinnabar is the only solid produced in all the scenarios tested, meaning the predominant mechanism involved in the sulfide-induced stabilization is precipitation. In addition, from the excellent match between the observed and calculated mercury concentrations and the mercury speciation indicated by MINTEQ for the S/Hg = 3 scenarios, it was also found, as expected, that the formation of mercury-sulfide/bisulfide complexes is the reason why increased amounts of mercury were observed at high sulfide-conditions.

However, it is also noticed that the predicted values of total leachate mercury deviated significantly from the observed values in the order: S/Hg = 0 < S/Hg = 3 < S/Hg

= 1. As can be seen in Figure 4.36, the values of $\log (H_{gcal}/H_{gobs})$ were around -0.7, -12, and -2 at S/Hg = 0, 1, and 3, respectively. One factor that possibly contributes to these differences is the very fine particle size of mercuric sulfide. Some of the “dissolved” Hg measured in the samples may actually be “colloidal” HgS that passed through the 0.45- μm filters (Ravichandran et al., 1998). Some of the deviations are probably due to the presence of the sand in the system, and the pore size of filter used in this experiment. Silica, as the primary component of the sand, may adsorb mercury to some extent. In addition, it is reported that mercuric sulfide (HgS) itself can also adsorb Hg (II). Unfortunately, the influences that these adsorption reactions may have on the mercury stabilization could not be included in the simulation process, due to the lack of information on these reactions. They may have led to the noticeable deviations between the predicted and observed values. The other possible reason is due to the pore size of the filter. As stated previously, a large portion of mercury could attach to the fine particles. Therefore, the application of much smaller pore size filters may have led to a decreased mercury concentration in the leachate, thus reducing the difference between the predicted and observed values.

However, the measurably large differences observed for S/Hg = 1 scenario cannot be simply explained by the above reasons. Paquette and Helz (1997) reported the importance of zero-valent sulfur in the inorganic speciation of mercury in sulfidic waters. They observed an enhanced inorganic mercury solubility in water in the presence of S^0 . Since our stabilization experiments were operated under aerobic conditions, sulfide could be converted to zero-valent sulfur, or sulfate, thus increasing the amount of mercury in

the solution. Therefore, the following redox reactions were introduced into the modeling (Pankow, 1991).

In order to allow the redox reactions to take place in the system, Eh values should be input into the MINTEQA program. In this study, the Eh values were input in this way so that the $\log(\text{Hg}_{\text{cal}}/\text{Hg}_{\text{obs}}) \approx -2.0$ (the same level as those observed for the S/Hg = 3 scenarios), and the same trends were kept as for the calculated results without redox reactions (Figure 4.34). Through the simulations, the following Eh values were obtained (Table 4.15).

Table 4. 15 Simulated Results of Eh and $\log \log(\text{Hg}_{\text{cal}}/\text{Hg}_{\text{obs}})$ for S/Hg = 1 Scenario

pH	2	4	5	6	7	8	10
Eh, mV	580	520	400	350	330	300	200
pe	9. 83	8. 81	6. 78	5. 93	5. 59	5. 08	3. 39
$\log(\text{Hg}_{\text{cal}}/\text{Hg}_{\text{obs}})$	-2. 14	-2. 35	-2. 37	-1. 97	-2. 18	-2. 03	-2. 39

As can be seen, through the simulation, the difference between the observed and calculated Hg decreased from 10 log units to 2 log units. Although a manual method was used to obtain the target values, the simulated Eh values were still in a reasonable range, implying that these values may be close to a real situation. It was also found that the simulated pe values had a linear relationship, as follows (Figure 4.37):

$$\text{pe} = -0.819 \cdot \text{pH} + 11.404 \quad R^2 = 0.96$$

The slope -0.819 is close to -1, which is the slope obtained from S^0/HS^- redox reaction. This result indicates that S^0/HS^- is the main redox couple that controls the sulfide oxidation in the system, thus affecting the sulfide and mercury chemistry. This is a tentative conclusion. However, if this is true, then sulfide oxidation is another important pathway that affects the sulfide-induced mercury stabilization for the $S/Hg = 1$ scenarios.

The same methods were applied to the $S/Hg = 3$ scenario. However, no significant improvement was obtained to reduce the difference between the observed and calculated values, indicating that in a high sulfide system, the conversion of sulfide to its oxidized form is not an important pathway controlling the mercury speciation.

Figure 4. 31 Mercury Speciation Distribution over pH for S/Hg = 1

Figure 4. 32 Mercury Speciation Distribution over pH for S/Hg = 3

Figure 4. 33 Comparison of Observed and Calculated Hg for S/Hg = 0

Figure 4. 34 Comparison of Observed and Calculated Hg for S/Hg = 1

Figure 4. 35 Comparison of Observed and Calculated Hg for S/Hg = 3

**Figure 4. 36 Deviation Plots Showing the Mercury Stabilization Fits to the
Calculated Data**

Figure 4. 37 Deviation Plots Showing the Fits to the Calculated Data for S/Hg = 1

4.7.3 Mercury Surrogate Stabilization Simulation in the Presence of Interferents

As mentioned previously, sodium hydroxide and nitric acid were used in the experiments of sulfide stabilization of mercury. To investigate the possible interference Na^+ and NO_3^- may have on the stabilization results, the effects of these two ions are examined by MINTEQ, and the simulation results are shown in Figure 4.38. As can be seen, the leachate mercury concentration increased slightly in the presence of the various concentration of $\text{Na}^+/\text{NO}_3^-$ compared to that without any interferents. However, since the leached mercury concentrations are in very low ranges (the level below $\mu\text{g/L}$), the differences between the results with and without acid/base are actually very small; therefore, the effects of acid/base can be neglected in this study.

Predicted dissolved mercury concentration curves, in the presence of common cations, anions, and EDTA, respectively, generated by visual MINTEQ are presented in Figure 4.39 through Figure 4.43. These predicted results are also compared with the observed mercury concentration results to evaluate the applicability of the modeling.

Figure 4.39 shows the results of dissolved mercury in the leachate in the presence of cations. In the simulation, initial Fe and Pb were input at concentrations of 1.5, 3, 9, and 15 mM to achieve cation/Hg molar ratios of 0.5, 1, 3, and 5, respectively. The pH was fixed at 6 and initial Hg and sulfide concentrations were input as 3 mM. As can be seen, the predicted curves have the similar trend as the observed curves, i.e. at cation/Hg molar ratios of 0.5, 1, 3, and 5, the mercury concentrations don't change measurably. Because of the lower formation constants for FeS(s) and PbS(s) than that of cinnabar,

iron and lead had little chance to combine with the sulfide, thus causing no apparent effects on the mercury concentration in the leachate.

Mercury solubility was also simulated using MINTEQ in the presence of Cl^- , PO_4^{3-} , and CO_3^{2-} ; results are presented in Figure 4.40, 4.41, and 4.42. It was found that the dissolved mercury concentration increased with increasing chloride concentration (Figure 4.40). The simulation results showed the formation of mercury and chloride complexes as the forms HgCl^+ , $\text{HgCl}_2(\text{aq})$, HgCl_3^- , HgCl_4^{2-} , and HgClOH . The measured mercury in the leachate increased significantly as the concentration of phosphate increased in the solution (Figure 4.41). However, only a slight increase was predicted by the MINTEQ-calculated results. The increased dissolved mercury in the solution is probably due to the formation of mercuric phosphate complexes, such as HgHPO_4 and HgPO_4^- , in the presence of excess phosphate in the system. The increased concentrations of carbonate caused a slight decrease in mercury solubility in water (Figure 4.42), because the more carbonate there is in the system, the more mercuric carbonate precipitates could be produced. This fact was also shown by the observed results.

The total soluble mercury in the solution was also predicted in the presence of EDTA (Figure 4.43). As can be seen, the predicted curve matches well with the observed curve for EDTA/Hg molar ratios of 1, 3, and 5. However, noticeable difference exists for the EDTA/Hg ratio 0.5. It was found from the observed values, that the effect of EDTA on mercury solubility in water was most severe at $\text{EDTA/Hg} = 0.5$ among the various EDTA concentrations tested, although the least effect was indicated for this ratio from the

calculated values. This is possibly due to the self-combination of EDTA molecular rings at the high EDTA concentration conditions, i.e. EDTA/Hg ratios of 1, 3, and 5, thus reducing the effects EDTA has on mercury solubility in the real situation. However, these effects had not been considered in the simulation, thus causing the deviation between the predicted and observed trends.

Figure 4. 38 MINTEQ Calculated Leachate Hg in the Presence of Acid/Base

Figure 4. 39 Comparison of Observed and Calculated Hg in the Presence of Cations

Figure 4. 40 Comparison of Observed and Calculated Hg in the Presence of Chloride

Figure 4. 41 Comparison of Observed and Calculated Hg in the Presence of Phosphate

Figure 4. 42 Comparison of Observed and Calculated Hg in the Presence of Carbonate

Figure 4. 43 Comparison of Observed and Calculated Hg in the Presence of EDTA

4.7.4 Constant pH Leaching Simulation

The leaching behavior of the sulfide-stabilized mercury wastes over the pH range 2-12 was also simulated using MINTEQA. The following assumptions were made prior to the simulations.

Assumption 1) All the mercury in the waste was converted to cinnabar through the sulfide stabilization. Therefore, cinnabar was input as the only finite solid in the leaching model as an initial condition.

Assumption 2) It is assumed that a very small amount of sulfide still remained in the wastes through the adsorption of sulfide into the waste matrix. Thus, sulfide is also input in the leaching system.

Assumption 3) A high content of chloride was observed for the original real mercury waste. An assumption was made that a small amount of chloride was still left in the stabilized mercury waste, thus affecting the mercury leachability.

The leaching simulation results are shown in Figures 4.44 and 4.45 for the stabilized mercury surrogate and the real mercury waste, respectively. For the stabilized mercury surrogate, at some pH range, the trends of simulated results match well with the observed results. For example, the mercury concentration showed a slight decrease from pH 2 to pH 4, and then it increased with the increasing pH through pH 8. However, at the pH range 8-12, the two curves showed a big difference, i.e. the calculated Hg still increased with the increasing pH, while the observed results indicated a decrease at pH 10, and then an increase at pH 12. However, both the observed curve and the calculated

curve reached the maximum at pH 12. The reasons why the amounts of leached mercury decreased at pH 10 are still unclear, and further research regarding the leaching mechanism is needed.

Figure 4.45 tells another story of leaching for the stabilized mercury waste. As can be seen, the trends of two curves match amazingly well, i.e. the Log number of leachate mercury concentration decreased almost linearly from pH 2 to pH 6, and then increased almost linearly from pH 8 to 12, with a slight change between pH 6 and 8. From the MINTEQ mercury speciation simulation (Figure 4.46), it was found that mercury and chloride complexes predominate at pH 2-6, while after pH 8, mercury hydroxides are the dominant species. These results verified that our assumption 3 is true in this case, i.e. chloride does affect the leachability of sulfide stabilized mercury waste.

**Figure 4. 44 Comparison of Observed and Calculated Hg from the Constant pH
Leaching Test for the Mercury Surrogate**

**Figure 4. 45 Comparison of Observed and Calculated Hg from the Constant pH
Leaching Test for the Real Mercury Waste**

Figure 4. 46 Mercury Speciation in the Leachate from the Constant pH Leaching Test for the Real Mercury Waste

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Stabilization/Solidification is an alternative technology to the typical thermal treatments of the mercury-containing solid wastes. The sulfide-induced stabilization process was investigated in this research for immobilizing mercury-containing wastes. The effects of stabilization pH, sulfide dosage, reaction time, and complexants on the sulfide-induced mercury stabilization process were examined. This study determined a set of optimized stabilization parameters to control the treatment process, and an improved understanding of the leaching behavior of mercury-containing wastes. Mechanisms involved in the treatment process, as well as the leaching process, were discussed using the geochemical equilibrium speciation model.

5.1 Conclusions

The following conclusions have been drawn from this study:

- 1) The kinetics of the mercury-sulfide reaction is a function of the pH and sulfide concentration. The reaction time needed to reach equilibrium showed the following order: $\text{pH } 2 < \text{pH } 10 < \text{pH } 6$; while at each pH, $\text{S/Hg} = 0.5 < \text{S/Hg} = 3 < \text{S/Hg} = 1$. The slowest reaction rate was observed at pH 6 with $\text{S/Hg} = 1$. It is also concluded that providing a sufficient reaction time is very important to obtain high stabilization efficiencies; therefore, a reaction time of 168 hours was recommended for sulfide-induced mercury stabilization.

- 2) The study of the effects of stabilization pH and sulfide dosage on mercury stabilization indicated that the equilibrium Hg concentrations in the stabilization solutions were much lower at the low pH range (pH 2-6) than at the higher pH range (pH 7-10). The lowest filtrate Hg concentration was found at pH 6 with $S/Hg = 1$. The effects of sulfide dosage are much more complicated. It was found that in the very low pH range (pH 2 and 4), the equilibrium Hg concentrations decreased with an increase of sulfide dosage; while at higher pH ranges (pH 5 - 10), the opposite results were observed. This is due to Hg resolubilization at the high pH range in the presence of excess sulfide. The water solubility of HgS increases measurably at high pH by forming various water-soluble mercuric bisulfide complexes (Clever et al., 1985).
- 3) TCLP test results indicate that sulfide-induced stabilization is a very effective technique for stabilizing mercury-containing wastes. The mercury stabilization efficiency reached as high as 99% and passed the TCLP limit (0.2 mg/L). From the stabilization scenarios investigated, it is concluded that the most effective stabilization occurred at pH 6 combined with a sulfide/mercury molar ratio of 1.
- 4) The study on interferences due to cations showed that the added cations slightly reduced the effectiveness of Hg immobilization, as shown by higher TCLP Hg concentrations compared to those of the controls (samples in which no interfering materials were added). However, even in the presence of these cations, TCLP Hg concentrations for the stabilized surrogates were still lower than the TCLP limit.

- 5) From the study on the effects of interfering anions on mercury stabilization by sulfide, it was found that TCLP Hg concentrations increased in the presence of the interfering anions compared to those from the controls. The anions Cl^- , CO_3^{2-} and PO_4^{3-} slightly inhibited Hg stabilization by sulfide in the order: $\text{Cl}^- > \text{PO}_4^{3-} > \text{CO}_3^{2-}$ and $\text{PO}_4^{3-} > \text{Cl}^- > \text{CO}_3^{2-}$ at low and high levels of the anion concentrations, respectively. For some scenarios, the stabilized surrogates failed the TCLP test. Nevertheless, comparing with the high initial TCLP Hg concentration (238 mg/L) of the unstabilized material, the Hg stabilization efficiency was still as high as 99%, even in the presence of interfering anions.
- 6) From the treatment optimization study, it is found that the combined use of increased dosage of sulfide and ferrous ions ($\text{S}/\text{Hg} = 2$ and $\text{Fe}/\text{Hg} = 3$ at $\text{pH} = 6$) can significantly reduce the interferences by chloride and/or phosphate during sulfide-induced mercury immobilization. In addition, the solidification of sulfide-stabilized mercury waste by cement and fly ash can further improve the mercury immobilization efficiency.
- 7) EDTA was selected to examine the influence an organic ligand may have on Hg stabilization by sulfide. Although the presence of EDTA caused decreases in the effectiveness of Hg stabilization by sulfide, the stabilized surrogates still all passed the TCLP test.

- 8) The liquid/solid leaching tests on the sulfide-stabilized mercury wastes showed that the leachate mercury concentration did not increase with greater volumes of leachant. Consequently, it can be concluded that the release of mercury from the tested wastes is not a diffusion-controlled process.
- 9) From the constant pH leaching results, it was found that the leachability of sulfide-treated mercury wastes, over a wide pH range, is a waste-specific characteristic shown by two different leaching trends for the stabilized mercury surrogate and the stabilized sediment mercury waste. However, it is common that sulfide treated mercury wastes produce significantly high mercury concentrations at extremely high pH ($\text{pH} > 10$) leachants, indicating the formation of soluble mercury bisulfide species in the presence of excess sulfide at high pH conditions. Nevertheless, comparing with the high soluble mercury concentrations of the unstabilized materials, the mercury stabilization efficiency was still as high as 99%, even with exposure of the wastes to high pH leachants. Therefore, it is concluded that sulfide-induced stabilization is a very effective technique for stabilizing mercury-containing wastes.
- 10) From the experimental results and MINTEQ simulation results, it was concluded that the formation of cinnabar is the main mechanism that contributes to the stabilization of mercury by sulfide. It was also verified that the remobilization of mercury into the aqueous phase from the stabilized form at high sulfide dosage condition is due to the formation of mercury sulfide/bisulfide complexes. Sulfide

oxidation is another important pathway that affects the sulfide-induced mercury stabilization; although it's effects need further investigation.

5.2 Recommendations for Future Study

From our study on the mercury-sulfide stabilization mechanism, it was found that Eh is another important variable that affects the sulfide chemistry, thus affecting the sulfide-induced mercury stabilization process. To better understand the mechanisms involved in the mercury-sulfide chemistry, Eh-dependent stabilization and leaching test are recommended.

Further research regarding the mechanisms for sulfide-induced mercury stabilization is needed. Microstructure examination of the mercury waste before and after treatment, and before and after leaching tests, by using SEM, EDS and XRD, will help to better understand the mechanisms of mercury immobilization by sulfide and of the leaching process.

The experimental results indicated that cement/fly ash-induced solidification could improve the immobilization efficiencies of sulfide-stabilized mercury wastes. Further investigation on the solidification process is needed to evaluate the long-term efficacy of physical encapsulation after sulfide stabilization.

Further investigation of sulfide-induced stabilization on other mercury species, such as elemental mercury, is recommended.

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