STUDY ON ENCAPSULATION (STABILIZATION/SOLIDIFICATION) OF WASTE MERCURY USING SODIUM SULFIDE AND ORDINARY PORTLAND CEMENT

By

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Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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Nik Asmadi Aznan

ABSTRACT

Stabilization/ solidification of mercury-containing wastes have received considerable attention recently, due to concerns about health and environment impact caused by the waste mercury. There are a lot of stabilization/ solidification methods such as Sulfur Polymer Stabilization/Solidification (SPSS), Chemically Bonded Phosphate Ceramics (CBPC), and stabilization/solidification using reactivated carbon and cement. Among these methods, stabilization/solidification of mercury-containing wastes using Ordinary Portland Cement (OPC) is one of the most widely used methods for immobilization of mercury-containing wastes. However, no papers report on the stabilization/solidification of mercury using sodium sulfide and Ordinary Portland Cement (OPC).

Therefore, this paper presents the study on encapsulation of waste mercury by using stabilization/ solidification method. Sulfide induced stabilization is used in this study and the stabilized mercury will be solidified with ordinary Portland cement. Two parameters that affect the stabilization/solidification process were investigated in order to enhance its effectiveness.

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In the name of ALLAH S.W.T, the most merciful and compassionate, praise to ALLAH, he is the almighty, eternal blessing and peace upon the Glory of the Universe, our beloved Prophet Muhammad (S.A.W), and his family and companions.

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CHAPTER 1

INTRODUCTION

1.1 Background

Mercury is a highly toxic element. Both inorganic and organic mercury can cause serious health effects. Department of Environment, Ministry of National Resources and environment Malaysia has identified waste mercury (mercury hazardous waste is defined as any waste that has a Toxicity Characteristic Leaching Procedure (TCLP) value greater than 0.2 mg/L) as a human health and environmental problem that needing additional scientific and technical research. Many reports (e.g., Report on indicators to evaluate and track the health impacts of mercury and identify vulnerable populations) stress the adverse impacts of mercury on both humans and wildlife[1]. Particularly, mercury is receiving the major focus due to its unique characteristics, such as high volatility and bioaccumulation. Because of the unique characteristics of mercury, further research need to be done to develop effective method for treatment of mercury-containing waste.

For the past years, many methods have been developed for mercury-containing waste treatment such as precipitation, adsorption, ion exchange treatment, chemical reduction, biological detoxification and membrane extraction. Among these methods, under the current Land Disposal Restrictions (LDRs) program, U.S. Environmental Protection Agency (EPA) has established only thermal treatment (e.g., roasting/retorting) as the best demonstrated available technology (BDAT) for treatment of waste containing greater than 260 mg/kg of mercury.

However, thermal treatment is not effective method for treatment high-mercury wastes because many subcategories of mercury wastes (e.g., inorganic salts, corrosive wastes, incineration residues, and wastewater

treatment residues) are not directly amenable to roast/retort treatment, and are not accepted by commercial retorting facilities. On the other hand, there is a growing excess of mercury stocks, as uses of mercury decline [2]. For these reasons, new treatment technologies should be investigated to treat high mercury wastes.

One of the most established technology to treat high mercury-containing waste is encapsulation. Encapsulation is a method that converts mercury into less soluble or leachable forms to inhibit migration into environment after disposal. According to (40 Code of Federal Register [CFR] 268.42)[38], Encapsulation technologies are based primarily on solidification processes that act to "substantially reduce surface exposure to potential leaching media."

Encapsulation technologies can also involve a combination of physical entrapment through solidification and chemical stabilization through precipitation, adsorption, or other interactions. This combined treatment approach is sometimes referred to as stabilization/solidification [3] and this report will focus on stabilization/solidification method.

1.2 Problem Statement

Researchers agreed that mercury contained in radioactive or mixed waste is not suitable for thermal recovery and recycling treatment. Thus, the U.S. EPA has recognized that Stabilization/Solidification may be an appropriate treatment option for heavily contaminated mercury mixed wastes or debris [4].

Stabilization/Solidification (S/S) methods have long been applied to immobilize hazardous wastes such as treatment of heavy metal bearing sludges and inorganic wastes [5] and it is also considered to be an effective pathway to immobilize mercury from wastes.

Stabilization involves a chemical immobilization of hazardous element, through chemical bonds to an immobile matrix, or chemical conversion to an immobile species, thereby reducing vaporization or leaching to the environment and solidification involves a physical immobilization of hazardous constituents, producing a final waste form that is consolidated to reduce the surface area of the waste available for vaporization or leaching[6].

There are a lot of stabilization/ solidification methods such as Sulfur Polymer Stabilization/Solidification (SPSS), Chemically Bonded Phosphate Ceramics (CBPC), and stabilization/solidification using reactivated carbon and cement. Among these methods, stabilization/solidification of mercury-containing wastes using Ordinary Portland Cement (OPC) is one of the most widely used methods for immobilization of mercury-containing wastes[5].

Although the method has been widely used in mercury treatment, there are no available data that can be found in literature about stabilization/solidification of mercury-containing wastes using combinations of sodium sulfide and Ordinary Portland Cement (OPC) because the process has not been sufficiently developed due to the complexity of mercury-sulfide chemistry and the high variety of mercury-containing wastes [7]. In addition, until now very little research has attempted to study on the stabilization/solidification

process in stabilize waste containing mercury greater than 260 mg/kg. Therefore, this study is aims to develop new method to treat mercury by using sodium sulfide and Ordinary Portland Cement(OPC).

Stabilization/solidification of mercury-containing wastes using sulfide and Ordinary Portland Cement (OPC) process is dependent on the sulfide dosage and pH [8][9]. Hence, this study is also to investigate the two parameters in enhances the effectiveness of the stabilization/solidification process.

1.3 Objective

The objectives of this research is to investigate the effectiveness of stabilization/solidification of mercury by using sodium sulfide and Ordinary Portland Cement(OPC) and to optimize the parameters that influence the effectiveness of the mercury stabilization/solidification process. The most important factors influencing the effectiveness of the mercury treatment are stabilization/solidification pH and sulfide dosage.

1.4 Scope of study

The scopes of study for this project are as follows:

In this study, the waste mercury surrogates were prepared by using mercuric chloride. The stabilization of mercury-containing wastes was performed using sodium sulfide. Stabilization variables such as total waste Hg^{2+} concentrations, stabilization pH, and sulfide/mercury (S/Hg) molar ratio were investigated. Then the stabilized mercury were subjected to Ordinary Portland cement solidification. Mercury stabilization/ solidification effectiveness was evaluated using the Toxicity Characteristic Leaching Procedure (TCLP) test 1311 EPA [35].

CHAPTER 2

LITERATURE REVIEW

2.1 Health Effects

Mercury is a chemical (element) that occurs naturally in the environment in several forms. Mercury is a shiny, silver-white, odorless liquid with a metallic taste in the metallic or elemental form. Mercury can form mercury compounds by combine with other elements, such as oxygen, carbon or chlorine. These compounds are called "organic mercury" if they contain carbon, and "inorganic mercury" if they do not [10]. All forms of mercury are considered poisonous [11].

Mercury has been recognized as a toxic hazard for centuries. The effects of mercury depend upon the nature of the mercury compounds involved and the route of exposure. Metallic or elemental mercury is easily volatilized at room temperature. The vapor formed during mercury volatilization can be inhaled into the lungs and the vapor will be passed into the blood stream. If contact directly with the elemental mercury it can also pass through the skin and goes into the blood. However, elemental mercury is not absorbed out of the stomach, and if swallowed, it usually passes out of the body without harm [18].

Inorganic mercury compounds are more dangerous than elemental mercury. It is not only can be inhaled and absorbed through the lungs, and may pass through the skin but the compounds can also be absorbed through the stomach if swallowed. Many inorganic mercury compounds are irritating or corrosive to the skin, eyes and mucus membranes as well [18]. The effects of inorganic mercury poisoning on human is it may result in disorders of the

central nervous system and possibly psychoses. According to EPA, the major effect from chronic exposure to inorganic mercury is kidney damage [11].

The most dangerous mercury form is organic mercury because the compounds are more toxic than inorganic forms. Organic mercury compounds can enter the body readily through all three routes-lungs, skin and stomach. 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 [12].

The most famous mercury incident in the world is Minamata Disease or sometimes referred to as Chisso-Minamata disease. Minamata Disease is a neurological syndrome caused by severe mercury poisoning. It was first discovered in Minamata City, Japan in 1956. Chisso Corporation, a chemical factory was discharged methyl mercury compounds with the factory effluent into environment and then polluted the environment. This highly toxic chemical bioaccumulated in shellfish and fish in Minamata Bay and Minamata Disease occurred through the food chain when the inhabitants ate high amount of these seafoods. Symptoms of Minamata Disease include deteriorates nervous system, cause involuntary movement, and damage to hearing, speech and vision. In extreme cases, it can cause death and the disease can also affect fetuses in the womb[36].

2.2 Application 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 the chlorine production has been by far the largest single source of mercury pollution [13]. 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. The uses of mercury and global mercury demand reported by Linda E. Greer are summarized as follow [14]:

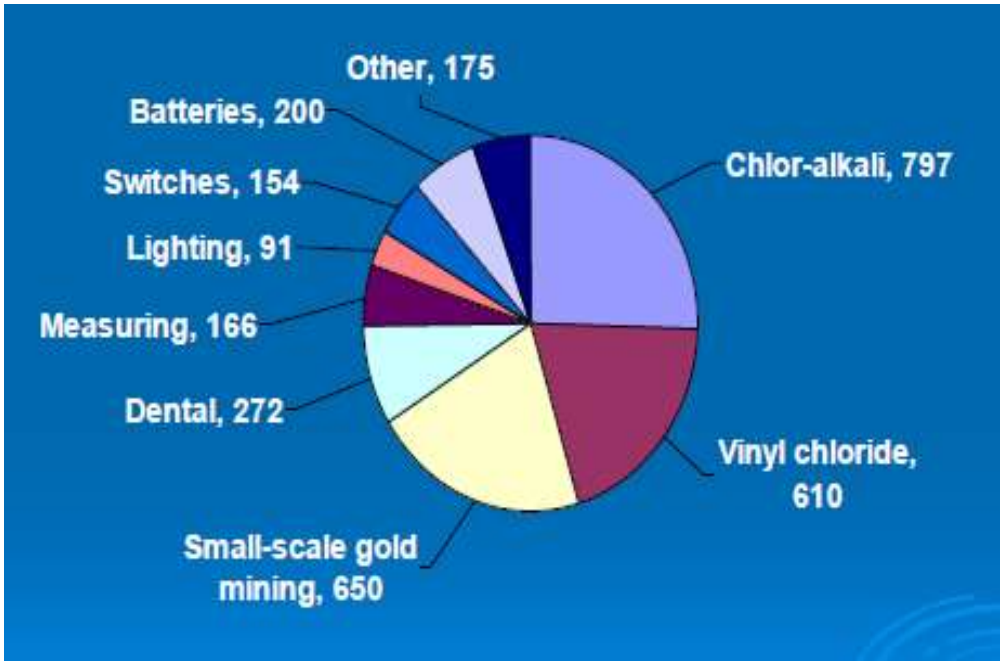

Figure 2.1: Global mercury consumption 2004(tonnes) [14]

Region	Mercury consumption (tonnes)
European Union (15)	302
North America	314
Other OECD	100
Central & Eastern Europe/CIS	530
Arab States	100
East Asia and Pacific	1100
Latin America & Caribbean	450
South Asia	400
Sub-Saharan Africa	90
TOTAL	3386

Table 2.1: Global manufacturing demand for mercury by region, 2000 [14]

2.3 Source of Human Exposure

Mercury is a naturally occurring element (around 80 μg/kg) in the Earth's crust[15]. Over geological time, it has been distributed throughout the environment by natural processes, such as volcanic activity; fires; movement of rivers, lakes, and streams; oceanic upwelling; and biological processes. Since the beginning of humans life, and particularly since the industrial revolution of the late 18th and 19th centuries, anthropogenic sources have become a significant contributor to the environmental distribution of mercury and its compounds [15].

As with other components of the lithosphere, natural global cycling has always been a primary contributor to the presence of chemical elements in water, air, soils, and sediments. This process involves off-gassing of mercury from the lithosphere and hydrosphere to the atmosphere, where it is transported and deposited onto land, surface water, and soil. Major anthropogenic sources of mercury in the environment have been mining operations, industrial processes, combustion of fossil fuels (especially charcoal), production of cement, and incineration of municipal, chemical, and medical wastes. Point sources of anthropogenic mercury release, revolatilization from environmental media, sorption to soil and sediment particles, and bioaccumulation in the food webs contribute to further distribution and subsequent human exposure [15]. Brito EMS et al. added the use of elemental mercury to capture gold particles as an amalgam has also contributed to the environmental burden of mercury and its compounds [16] and according to Skare I, dental amalgam fillings are the primary source of mercury exposure for the general population [17].

2.4 Sulfide Application in Mercury Treatment

Sulfide precipitation is widely use in mercury treatment. The method is one of the most commonly reported precipitation methods for removal of inorganic mercury from wastewater. Sulfide (e.g., as sodium sulfide or another sulfide salt) is used to convert the soluble mercury to the relatively insoluble mercury sulfide form:

$$Hg^{2+} + S^{2-} \longrightarrow HgS\ (S)$$ (US EPA, 1997) [11].

Due to the very low solubility of mercuric sulfide, mercury is effectively removed from aqueous solutions. Googin et al. reported his achievement in removing mercury from water to a level not greater than 2 ppb, 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 [19]. Besides, sulfide is not limited for removing mercury from water but also used to remove mercury from soil and sediment, as well as 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 [20]. 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. invented a method 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 [21]; and Ader et al. invented a process 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 [20]. 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 cement doped with mercuric oxide (HgO) or liquid elemental mercury (Hg^0) [22].

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 [23].

2.5 Ordinary Portland Cement Applications in Mercury Treatment

Mercury is a metal that difficult to treat in solid wastes. So far, no effective technology has been found to effectively immobilize mercury in solid wastes. Stabilization/solidification (S/S) technologies have been proven to be effective in immobilizing other heavy metals, such as Pb, Cd and Cr (immobilization level of the heavy metal (%) for Pb(99.35 %), Cd(99.46 %), and Cr(96.90 %)), but difficulties have been encountered when trying to stabilize/solidify mercury-containing wastes because of mercury is highly volatile element [39].

Portland cement has been studied extensively for its reactions causing setting and hardening. Also, its composition is fairly consistent from source to source, which eliminates many variables in studying the process. Therefore, Portland cement has been frequently used to fix heavy metal wastes, such as Pb, Cr and Cd [2].

Studies have shown that heavy metal compounds – oxides and hydroxides, chlorides, sulfates, nitrates – interact in the hydration reactions of cement, both during setting and later during the hardening process. In addition to affecting the setting and hardening rate, these interactions may also function to fix the metals, chemically or physically, in the microstructure [2].

Shively et al. indicated that two types of binding mechanisms might be in effects: first, sorption-precipitation and limited dissolution of the cement matrix limits metal leaching at high pH; second, metal leaching at pH less than 6.0 could be limited by diffusion through the solid matrix or slow dissolution of the silicate matrix [24].

Substantial amounts of heavy metals (Cr, Cd and Pb) remained in the silicon rich solids after the alkalinity had been neutralized during the extractions. Bishop attributed this to chemical complexes formed during interactions with the siliceous cement matrix[25].

Roy et al. used a variety of microscopic and X-ray diffractive techniques to study the microstructure and microchemistry of a mercury containing sludge that had been solidified/stabilized in OPC[9]. They were unable to detect any mercury in their solidified/stabilized samples. Hamilton and Bowers attributed this to the unique potential of mercury to volatilize[22]. They investigated Hg emissions from the finished solidified/stabilized cement monolith and found that HgS showed no tendency to volatilize, while HgO or Hg^0 (liquid) led to the evolution of Hg vapor. On the other hand, the sample headspace vapor results could not be used to predict performance of wastes during leaching tests.

Poon et al. found that the retention potential of the cement matrix for mercury was related to the amount of calcium in the solidified waste[26]. McWhinney et al. also found evidence of close association of calcium rich deposits with mercury, and strongly suggested that physical sorption processes were closely associated with the calcium content and were mainly responsible for mercury containment in the cement matrix[27]. In another paper, Poon and coworkers identified a mechanism that consisted of a combination of chemical fixation and a physical isolation process that was responsible for the containment of mercury in the cement matrix. G.C.C Yang successfully solidified a mercury containing sludge using a commercially available sludge treatment agent, which was a cement-based binder with some proprietary additives[28]. Physical and chemical durability tests were conducted on the solidified monolith. Much more mercury was leached out after physical durability tests, which showed the significance of physical encapsulation. Therefore, it is suggested that cement-based systems alone may not fix mercury in a stable form, due to the complicated chemistry of mercury[13]. Further research is need to be done in order to enhance the effectiveness of OPC in stabilization of mercury.

2.6 Encapsulation of waste mercury

Encapsulation is a method that converts mercury into less soluble or leachable forms to inhibit migration into environment after disposal. According to (40 Code of Federal Register [CFR] 268.42) [38], Encapsulation technologies are based primarily on solidification processes that act to "substantially reduce surface exposure to potential leaching media."

Encapsulation technologies can also involve a combination of physical entrapment through solidification and chemical stabilization through precipitation, adsorption, or other interactions. This combined treatment approach is sometimes referred to as stabilization/solidification[3].

Encapsulation seeks to store waste mercury compounds in a way that stops it from contacting the environment. The compounds are sealed within non-degrading materials, and then stored in a place where they may not be disturbed for extended periods, such as a landfill.

If the waste to be encapsulated contains hazardous or mixed wastes, then the resulting encapsulated product must meet requirement for storage of these substances (Resource Conservation and Recovery Act (RCRA)/ Land Disposal Restrictions US. The limit for mercury is set to 0.2 mg/L.) [11]

Materials used for encapsulation of mercury must be both chemically compatible with the hazardous waste and inert to common environmental conditions that may be encountered in a disposal facility, such as rain infiltration, groundwater flow, and freeze/thaw cycles. Sulfur polymer stabilization/solidification (SPSS), chemically bonded phosphate ceramic (CBPC) encapsulation, and polyethylene encapsulation are three of the techniques that are currently used [3] but the application of the methods are limited due to the several issues such as unknown long-term stability of final wastes form and cost problem.

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

Many sources reported that stabilization/solidification have long been applied to stabilize hazardous waste. Chang reported the methods are especially useful for the treatment of heavy metal bearing sludges and inorganics such as Pb^{+2}, Cu^{+2}, Zn^{+2}, Cr^{+6}, Cd^{+2}, and Mn^{+2}[5]. Some reports suggest that the stabilization/solidification method also can be applied for mercury treatment as discuss below.

2.7.1 Cement-based Stabilization/Solidification(S/S)

The cement-based methods employing Portland cement are the most common ones among the numerous S/S applications [5]. "This process is flexible, effective, accommodates complex mixtures of contaminants and is economical enough to be used for large volumes of wastes" [29]. The process usually involves addition of a heavy metals waste to a cementitious binder, with or without pretreatment with lime (calcium oxide). 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 [9].

Durability testing of a solidified mercury-containing sludge proved that mercury could be processed by S/S [30], 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 [27]. 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 (Hg^0 (l)). Therefore, it is believed that mercury has a strong potential to volatilize from cement-solidified sludge [22].

The other problem associated with Portland cement-based materials is atmospheric carbonation [29]. 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 [31].

2.7.2 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 [9]. 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 [32]. 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 [32]. 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 [5].

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

Chang et al. reported a two-step mercury immobilization process consisting of sulfide pretreatment and cement/fly ash solidification [5]. According to their report, 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 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. They also indicated that mixing ratio of cement/fly ash/sludge, Na_2S/Hg, and FeSO4/Hg affected the leachability and compressive strength of the solid end products [5].

2.7.4 Innovative method- Stabilization/Solidification of waste mercury using sodium sulfide and Ordinary Portland Cement (OPC).

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" [33]. Therefore, more research needs to be performed to investigate new methods or improve available methods to treat mercury-containing wastes. Hence, the objective of this stuy is to investigate new method- Stabilization/Solidification of waste mercury using sodium sulfide and Ordinary Portland Cement (OPC) in immobilize high mercury- containing waste. Optimum paremeters that

CHAPTER 3

METHODOLOGY

3.1 Simulation of Mercury-containing Wastes

In different matrices, mercury exists in both organic and inorganic forms. In this study, the stabilization/solidification process was tested on inorganic mercury wastes (wastes containing 140 mg/kg, 500 mg/kg and 1000 mg/kg total mercury). A lab-simulated mercury surrogate was used in this study and for the preparation of the mercury surrogate waste, Mercury Chloride ($HgCl^2$) was selected. Sand was used as the solid waste matrix because sand is the least adsorptive component in soils and it will minimizes competitive adsorption by substances in real soils. According to Haishan Piao, distilled water was used in all experimental tests [7].

A mercury waste surrogate was prepared using sand spiked with mercury chloride to yield the desired total mercury content. For the preparation of the mercury surrogate, specific procedure is followed as suggested by Jian Zhang [2].

The total Hg concentrations of the surrogates used in the study were 140, 500, 1000 g/kg. This range of mercury concentration was determined by what would be generally found in mercury-contaminated soils, and it covers both low ($\leq$ 260 mg/kg total Hg) and high mercury wastes ($>$ 260 mg/kg total Hg) [2].

Desired amounts of $HgCl_2$ and sand were weighed. The sand and the mercuric chloride were alternatively added into a jar. Then the $HgCl_2$ and the sand were manually mixed, with distilled water was added during mixing. The total amount of distilled water added was 5% of the sand on a weight basis.

The surrogates were put in a hood for drying and aging for 3 days. According to Hebatpuria, a longer aging period for the surrogates was found to be unnecessary [34]. The total Hg concentration in each surrogate batch was analyzed using mercury analyzer (NICSP-3D) at Hg Solution Sdn. Bhd Lab, Paka- Malaysia.

3.2 Sulfide dosage

Based on the mercury-sulfide chemistry, one of the most important factors affecting mercury stabilization effectiveness is sulfide dosage. According to Haishan Piao, at high pH values, mercury can be remobilized if there is presence of excess sulfide [7]. Different sulfide dosages were tested in this study 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. In this experiment, two different S/Hg molar ratios, 1 and 3, were investigated at each of several pH values, with more emphasis then given to the S/Hg molar ratio that provided the highest stabilization efficiency [7].

3.3 Stabilization pH

The others important element that affects stabilization/solidification process in mercury treatment is stabilization pH. Theoretically, in the presence of excess sulfide, solubility of mercury will increase when the pH increases due to the formation of water-soluble mercury and sulfide/bisulfide complexes [7]. 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, 6, 8, and 10 for each selected S/Hg molar ratio.

The test procedure applied for the sulfide-induced mercury stabilization is briefly described as following as suggested by Haishan Piao [7]:

10 grams (dry basis) of mercury waste and an amount of sodium sulfide sufficient to meet the indicated S/Hg molar ratio were weighed (see appendix 1) and were placed into 100 mL bottles. Approximately 50 mL of distilled water was added into the bottles and the pH of the above mixtures was adjusted to the initial pH values of 2, 4, 6, 8, and 10, using 1N NaOH and/or 2N HNO_3. The mixtures were tumbled until reach its equilibrium. The pH of the mixtures throughout the stabilization experiment was monitored and if necessary, pH adjustment is repeated. Upon the completion of the reaction, final pH measurement for each mixture was taken. After final pH measurement, leachate samples were collected by filters the mixtures through 0.45 μm glass fiber filters. For the samples storage, the samples was acidified to a pH of less than 2 with HNO3 and store at 4 °C until analyzed for its mercury concentration. The filter cakes are dried and these dried filter cakes are used for Ordinary Portlant Cement solidification. The leachate samples were digested and analyzed for total mercury concentration via mercury analyzer (NICSP-3D) at Hg Solution Sdn. Bhd Lab, Paka- Malaysia.

3.4 Ordinary Portland Cement(OPC) solidification

After sulfide mercury stabilization, the dried filter cakes were mixed with OPC for solidification. ASTM type 1 Ordinary Portland Cement was used in this study. Prior to solidification, pH of the dried filter cakes were measured and adjusted to the desired pH which are 2, 4, 6, 8, and 10. The water/OPC ratio used was 0.5. After setting for 5 days, the cement paste mixture was crushed and subjected to the TCLP test. The particle size of the crushed

samples was < 9.5 mm, according to the requirement of the TCLP procedure. A series of control samples was produced by mixing OPC and un-stabilized surrogates, using the ratios mentioned above.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	$CaSO_4$	Specific Gravity	Specific Surface Area cm^2/g
22	5.1	3.2	65	1.4	1.6	3.1	3.17	3220

Table 3.1: Typical composition of type 1 OPC(%)

3.5 Toxicity Characteristic Leaching Procedure (TCLP)

TCLP is one of the Federal Environmental Protection Agency (EPA) test methods that are used to characterize waste as either hazardous or non-hazardous for the purpose of disposal. According to EPA, the TCLP limit for mercury is 0.2 mg/L. According to Haishan Piao, TCLP can serve as a regulatory benchmark and allow a comparison with a broad database of results obtained from testing of other materials [7].

In this study, TCLP Hg from both treated and untreated wastes was also used to evaluate the stabilization/solidification efficiency. There are two extraction fluid used in TCLP test (extraction fluid #1(pH 4.93) and extraction fluid #2(pH 2.88))[35].

Prior to running the TCLP tests, waste samples should be analyze to determine the appropriate extraction fluid. In this study, extraction fluid #1 is used because mercury is volatile element and based on Toxicity Characteristic Leaching Procedure 1311 EPA[35], stated that "Determination of appropriate extraction fluid: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1)"[35]. In performing TCLP test, for each TCLP test, 5 grams of the crushed waste sample were added to a 125 mL container with 100 mL TCLP extraction fluid #1. The containers were sealed and tumbled for 18 hours. After 18 hours, each leachate sample was

measured for pH value and filtered through 0.7 μmpore size filer, then subjected to the appropriate analytical procedure.

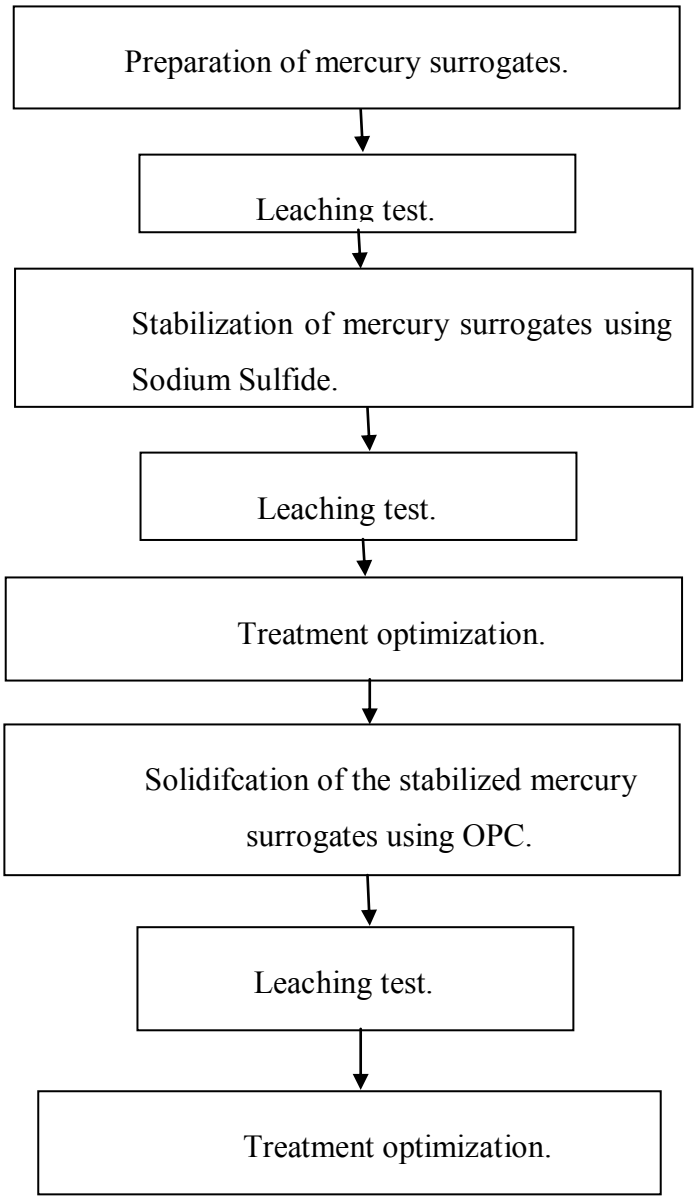

Figure 3.1 Overview of the experimental design.

3.6 Tools

Chemical parameter	Method of analysis
pH	pH meter
Leachability	TCLP Extractor(1311 method, EPA) Mercury Analyzer NICSP-3D / CVAAS

Table 3.2: Chemical Parameters and Analyses Methods

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Study on stabilization of waste mercury by sodium sulfide at different mercury-containing waste.

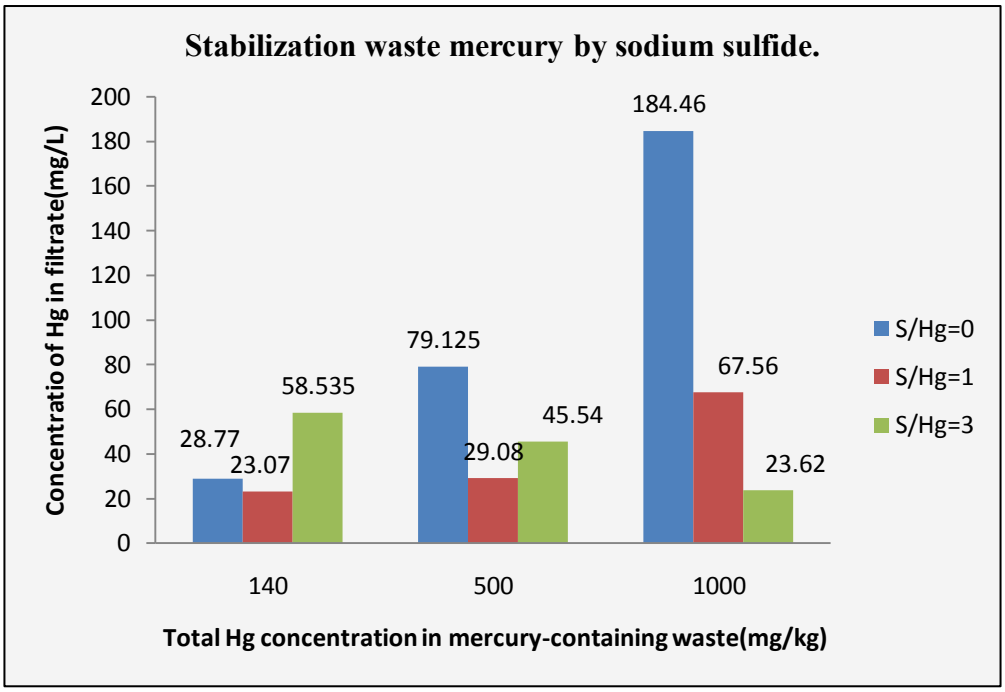

Figure 4.1: Stabilization waste mercury by sodium sulfide.

The objective of the study is to determine the effect of sulfide dosage in stabilization of mercury wastes. Three different total Hg concentrations of the surrogates were used in the study which are 140, 500, 1000 mg/kg. This range of mercury concentration was determined by what would be generally found in mercury-contaminated soils, and it covers both low (≤ 260 mg/kg total Hg) and high mercury wastes (> 260 mg/kg total Hg). All pH were set constant at pH 6 in this study.

Figure 4.1 was shown the results of stabilization of mercury by sodium sulfide. The results were expressed as mercury concentration in the stabilization solution (filtrate). The results have shown the effect of sulfide dosage on mercury stabilization for different total Hg concentration of mercury-containing wastes.

From the figure, for all three different wastes containing of mercury, the treated wastes by sulfide showed the lower mercury concentration in leachate compared to the untreated wastes.

The percentage of mercury stabilizes by sulfide shown in the Figure 4.2. The percentage of mercury stabilizes by sulfide is calculated using formula below:

$$\left(\frac{\text{Filtrate Hg untreated surrogate} - \text{Filtrate Hg treated surrogate}}{\text{Filtrate Hg untreated surrogate}}\right) x\ 100$$

- equation 4.1

From the figure, at lower mercury-containing wastes, mercury not much stabilizes compare to the greater mercury-containing wastes. For S/Hg ratio of 1, the only 19.8% of mercury in 140 mg/kg mercury surrogate sample can be stabilize compare to 500 and 1000 mg/kg mercury surrogate samples which stabilize up to 63.25% and 63.38 % respectively. For S/Hg ratio of 3, at greater mercury- containing waste (waste containing 1000 mg/kg mercury), approximately 87.2 % of mercury stabilized by sulfide. This happen because in the excess of sulfide, the formation of soluble mercury sulfide species occurred due to the common ion effect as presented in the open literature [23].

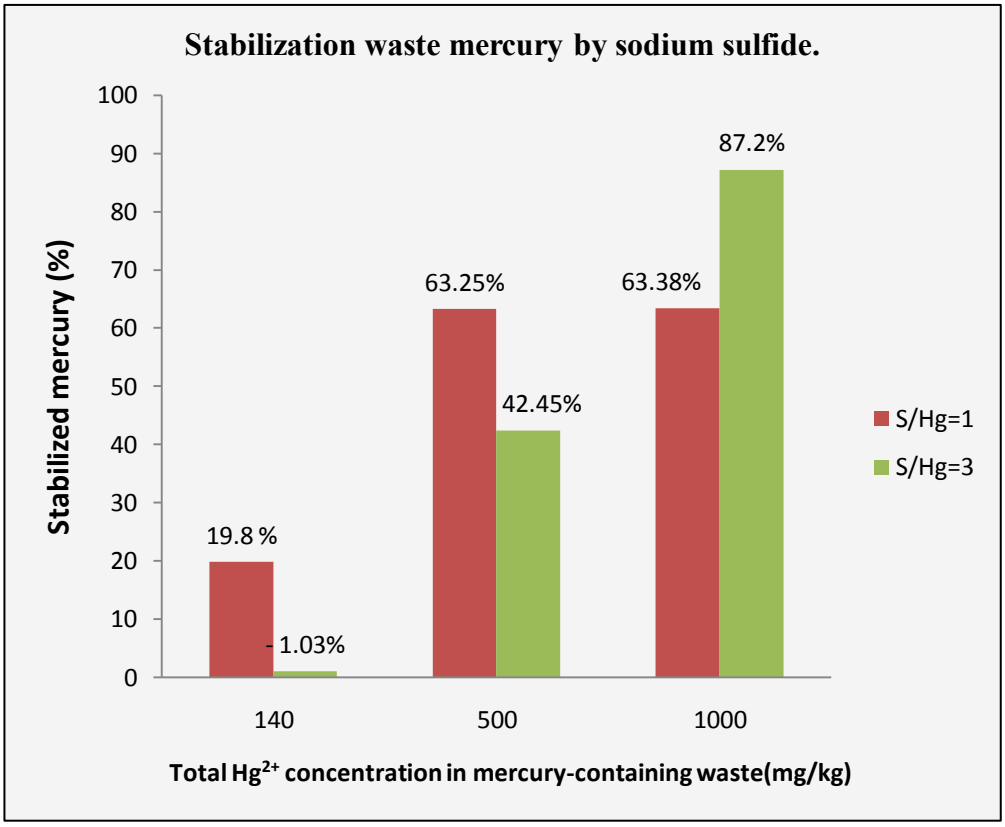

Figure 4.2: Percentage of stabilize mercury

4.2 Study on solidification of stabilized mercury by Ordinary Portland Cement at different mercury-containing waste.

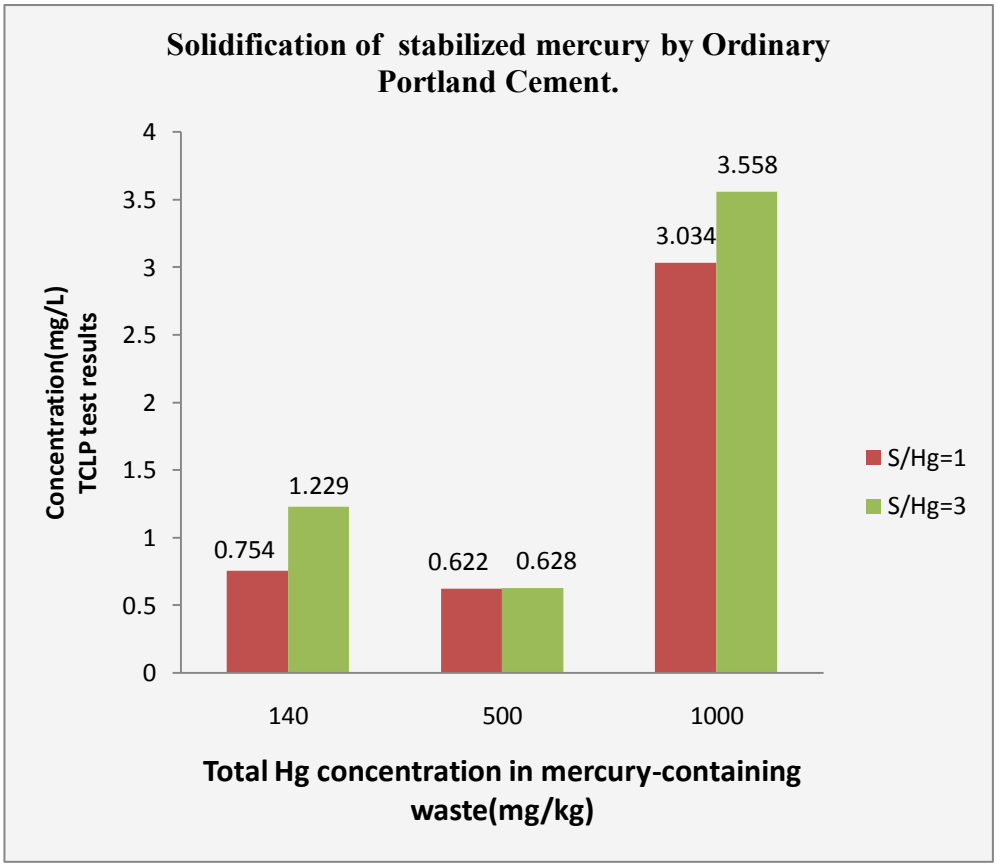

Figure 4.3: Solidification of stabilized mercury by Ordinary Portland Cement.

The objective of this study is to enhance the effectiveness of stabilization mercury process by solidified the stabilized mercury with Ordinary Portland Cement. The process is called stabilization/solidification of mercury using sulfide and Ordinary Portland Cement. TCLP tests were performed in this study to evaluate mercury stabilization/solidification effectiveness and to determine optimized process parameter. TCLP results for the stabilized/solidified mercury surrogate are summarized in Figure 4.3. It was

found that stabilization/solidification treatment using sulfide and OPC significantly lowered the TCLP mercury concentrations relative to untreated samples. As can be seen, not more than 4 mg/L of mercury was detected in the TCLP leachate. Based on the figure, the lowest TCLP Hg concentration found at the stabilization/solidification of waste contains 500 mg/kg of mercury.

Stabilization/solidification efficiencies for the TCLP results are shown in Figure 4.4. Here the efficiency was calculated as noted below:

$$\frac{(\text{TCLP Hg untreated surrogate} - \text{TCLP Hg treated surrogate})}{(\text{TCLP Hg untreated surrogate})} x\ 100$$

Equation 4.2

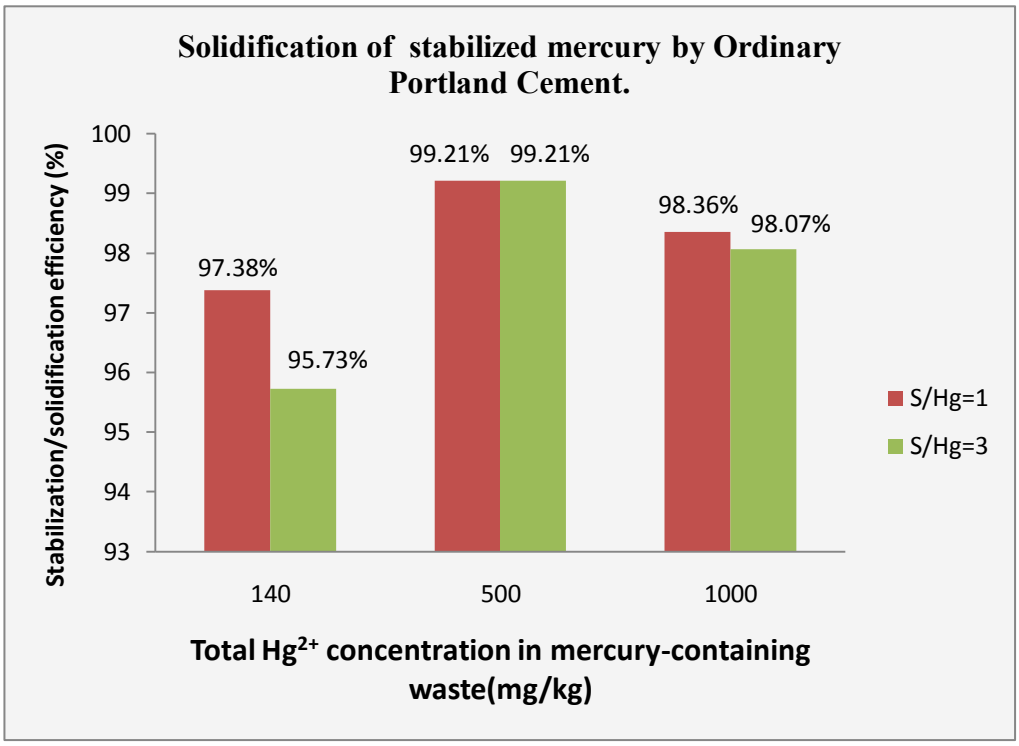

Figure 4.4: Stabilization/ Solidification efficiency

The figure shown that up to 99% mercury can be stabilized by solidified the stabilized mercury with ordinary Portland cement. It shown that all mercury-

containing waste can be treated by the stabilization/solidification method. Sulfide dosage have not much affect on the solidification process as shown in the result. Unfortunately, the results obtained were not pass TCLP limit (0.2 mg/L). This is due to the present of the other ions in cement matrix such as Cl^- and PO_4^{3-} that react with mercury to form soluble mercury compounds [8].

4.3 Study on stabilization waste mercury by sodium sulfide at different pH.

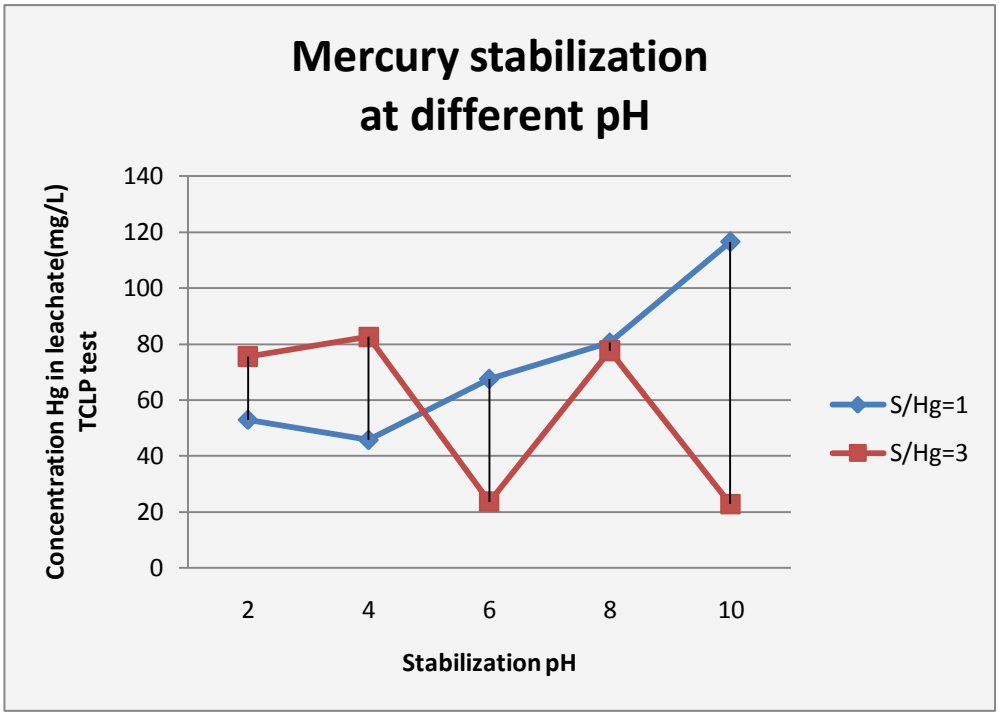

Figure 4.5: Mercury stabilization at different pH

The effect of sulfide stabilization pH on the stabilization of mercury surrogate was shown in Figure 4.5. The results were expressed as mercury concentration in the stabilization solution (leachate). In this study, 8 different pH values were used (pH 2.0, 4.0, 6.0, 8.0, and 10.0) to investigate the influence of stabilization pH on mercury stabilization process. Surrogate containing 1000mg Hg/kg was used in this study.

From the figure, it was shown that stabilization pH affects the stabilization of mercury. For S/Hg molar ratio of 1, the presents of Hg in leachate is small at lower pH but when goes to higher pH, it increase drastically. At pH range 2 and 4, it not much increases but at pH range 4-10, it increased drastically.

The effect of S/Hg molar ratio of 3 is more complicated. At low pH range (pH 2-6) it decreases but at the pH range (pH 6-8), it increase drastically and at pH range (pH 8-10), it decrease again same pattern with pH range (4-6). From the results, it seems that the most effective condition to stabilize mercury is at pH 10 combine with S/Hg molar ratio of 3. However, Clever et al. indicated that in the presence of excess sulfide at high pH conditions, formation of soluble mercury bisulfide species will happen [37]. Therefore, the actual effective condition to stabilize mercury is at pH 6 combine with S/Hg molar ratio of 3.

4.4 Study on solidification of stabilized mercury by Ordinary Portland Cement at different pH.

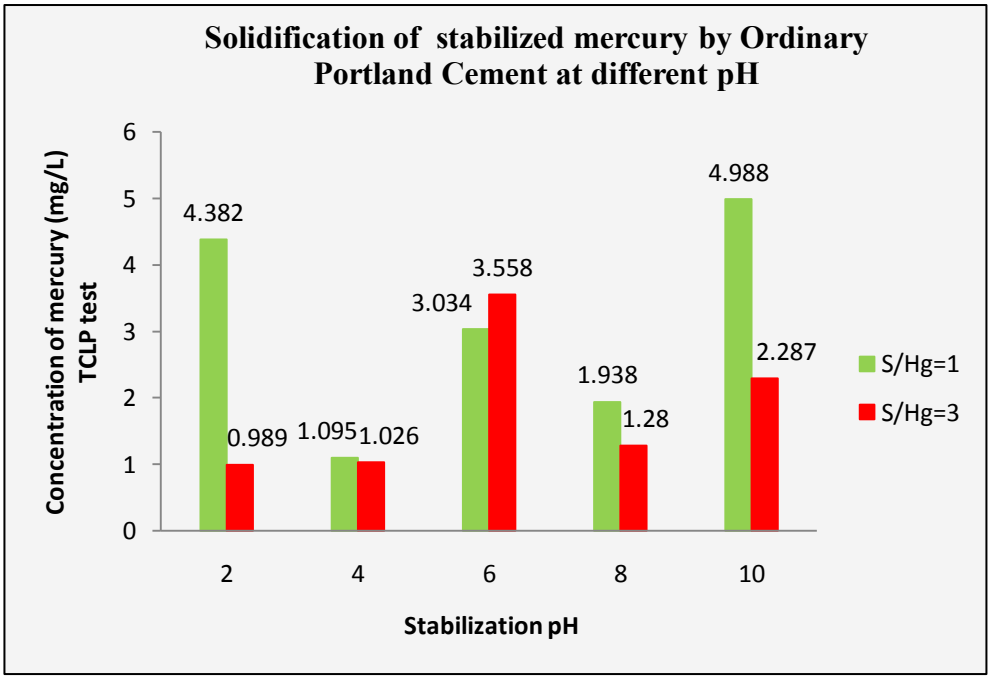

Figure 4.6: Solidification of stabilized mercury by Ordinary Portland Cement at different pH.

After stabilized with sulfide, the surrogates were solidified with Ordinary Portland Cement (OPC). Then, the stabilized/solidified surrogates were subjected to TCLP test. The results of the stabilization/solidification of waste mercury were shown in Figure 4.6. The results were expressed in concentration of mercury (mg/L).

From figure, different stabilization pH has significant affect on the mercury stabilization by using Ordinary Portland Cement. For all stabilization pH except pH 6, the concentration of mercury in the leachate that treat with S/Hg=1 is lower compare to the concentration of mercury in the leachate that treat with S/Hg=3. As can be seen in the figure, the lowest TCLP Hg

concentration was found at the stabilization/solidification combination of pH 2 and S/Hg molar ratio of 3, where only 0.989 mg/L of mercury was detected in the TCLP leachate.

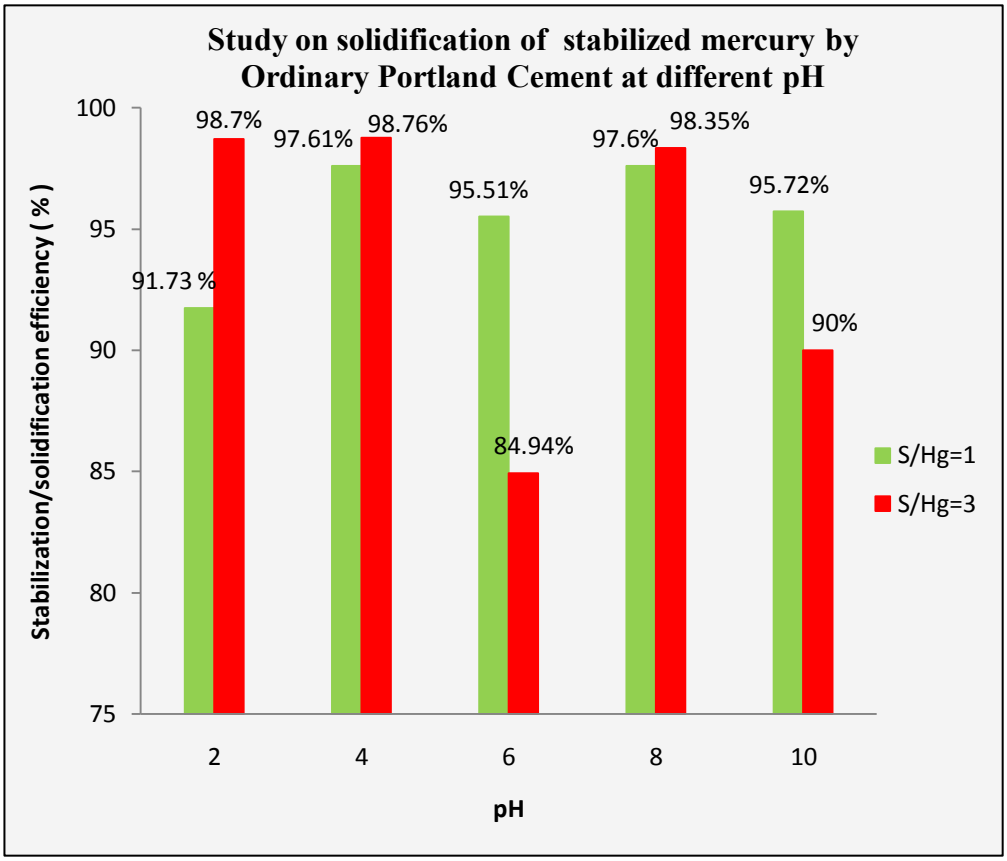

Figure 4.7: Stabilization/solidification efficiency at different pH

Although shown the lowest TCLP Hg concentration, stabilization/solidification combination of pH 2 and S/Hg molar ratio of 3 is still not effective in immobilize waste mercury. Based on figure, the most effective to immobilize waste mercury is at pH 4 and S/Hg molar ratio of 3. The efficiency is 98.76 % which the highest efficiency compares to other condition. As known, none of the results obtained from this experiment pass the TCLP limit which is 0.2 mg /L. the failure is due to the formation of soluble mercury compounds in excess of sulfide and in the presents of ion such as ion chloride and ion phosphate.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

From the results presented, stabilization/solidification of mercury using sodium sulfide and Ordinary Portland Cement has potential to immobilize mercury-containing wastes greater than 260 mg/kg. The higher efficiency of the treatment method is 98.76%. From the experiment, stabilization pH has significantly affected the stabilization/solidification of mercury. It has been found that the effective condition to stabilize/solidify waste mercury is at pH 4.

The sulfide dosage also plays important roles in stabilization/solidification process. The optimum S/Hg molar ratio is 3. However, there are no results obtained in this experiment pass the TCLP limit (0.2 mg/L). This is due to several factors that affecting the stabilization/ solidification process such as formation of soluble mercury compounds in presents of chloride ions or phosphate ions in the process and remobilization of mercury due to excess sulfide at high pH.

5.3 Recommendations for Future Study

From the study on the stabilization/solidification of waste mercury using sodium sulfide and Ordinary Portland Cement, it was found that anions such as chloride and phosphate is important variable that affects the sulfide chemistry, thus affecting the mercury stabilization/solidification process. To better understand the mechanisms involved in the the stabilization/solidification process, anions-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 Ordinary Portlant Cement solidification could improve the immobilization efficiencies of sulfide-stabilized mercury wastes. Further investigation on the solidification process such as hardening time, cement/water ratio and more is needed to evaluate the long-term efficiency of physical encapsulation after sulfide stabilization.

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

CHAPTER 6

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CHAPTER 7

APPENDICES

APPENDIX 1

Total Hg concentration in mercury-containing wastes desired in waste (mg/kg)	$HgCl_2$ (g)	Sand (g)	H_2O (ml)	Na_2S (g) S/Hg=1	Na_2S (g) S/Hg=3
140	0.2	949.8	50	0.34	1.02
500	0.71	949.29	50	1.2	3.6
1000	1.42	948.58	50	2.43	7.29

Calculation the amount of sodium sulfide for S/Hg=1

(0.14 g/kg / 32.07 g/mol of Sulfide)* 78 g/mol of Na_2S = 0.34 g of Na_2S

APPENDIX 2

Result for study of stabilization/solidification of mercury by sodium sulfide and OPC at different mercury-containing wastes.

Untreated S/Hg=0

Hg2+ mg/kg	pH	Hg Concentrationin in leachate(mg/L)
140	6	28.77
500	6	79.125
1000	6	184.46

Treated S/Hg=1

Hg2+ mg/kg	pH	Hg Concentrationin in leachate(mg/L)	TCLP(mg/L)
140	6	23.07	0.754
500	6	29.08	0.622
1000	6	67.56	3.034

Treated S/Hg=3

Hg2+ mg/kg	pH	Hg Concentrationin in leachate(mg/L)	TCLP(mg/L)
140	6	58.535	1.229
500	6	45.54	0.628
1000	6	23.62	3.558

Result for study of stabilization/solidification of mercury by sodium sulfide and OPC at different stabilization pH.

Result of stabilization of mercury using sodium sulfide (TCLP mg/L)

S/Hg	pH 2	pH 4	pH 6	pH 8	pH 10
1	52.965	45.738	67.56	80.52	116.575
3	75.53	82.61	23.62	77.61	22.865

Result of stabilization/solidification of mercury using sodium sulfide and OPC (TCLP mg/L)

S/Hg	pH 2	pH 4	pH 6	pH 8	pH 10
1	4.382	1.095	3.034	1.938	4.988
3	0.989	1.026	3.558	1.28	2.287